Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase

Report 2023

Last update December 2022
Editing by Filippo Baldereschi
Printed in October 2023 by Tipolitografia Contini S.r.l.

Summary

Research Projects

1A: Hard Matter (Nanomaterials and Solid Interfaces)

1B: Soft Matter (Nanomaterials and Liquid Interfaces)

1C: Theory and Modelling

2A: Art Restoration and Environmental Remediation

2B: Metals and Ceramics

2C: Biotechnology

CSGI Research Activity

Outline

CSGI's mission is to promote and coordinate scientific activities in the field of large interface systems, in agreement with national and international research programs for the benefit of companies and private/public research institutions.

The CSGI (Center for Colloid and Surface Science) was established in Florence in December 1993. It was officially recognized by the Italian government in 1994 and is under the supervision and control of the Ministry of University and Scientific Research (MUR). CSGI began its scientific activity in 1995, dedicated to basic research and to the development of new high-tech processes. CSGI, also, contributes to the activities of small and medium-sized enterprises that cannot afford the financial burden of independent research activities.

The mission and strategic functions of CSGI have always been focused, since its foundation, on basic and applied scientific research, with particular attention to the dissemination of the results achieved and to the technology transfer, both nationally and internationally. In this context, among the activities of the CSGI, training plays a role of primary importance.

CSGI research is mainly centered on the field of chemistry and physical chemistry of dispersed systems with a high surface area such as hard and soft nanomaterials, colloids of various kinds, functionalized surfaces, and thin films. In these areas, CSGI organizes, coordinates, and implements specific actions aimed at promoting both basic and applied research, promoting the technology transfer of the results achieved to businessand industry. The CSGI consortium gathers research units belonging to several Italian universities (http://www.csgi.unifi.it) working in the field of physical chemistry of colloids, nanomaterials, and functionalized surfaces. The excellence of the CSGI network is validated by the assessment of the Italian research system (VQR relating to the period 2015-19 and earlier), which testifies that CSGI, in the field of chemistry, is among the best Italian consortia per scientific production level, always positioning in the very high ranking for scientific quality and for the third mission activities. In particular, to achieve these results, the financial support that the Ministry of University and Research (MUR) provides annually represents a driving force of primary importance allowing for the attraction of further fundings, both from the industrial world and through the participation in competitive national and/or European tenders. In practice, this financial support has the fundamental function of "multiplier" for attractingfunds on a competitive basis. In fact, the average budget available on an annual basis, for about 95%, refers to collaborations with organizations as industry and, above, all with international organizations and the European Union.

Scientific research

CSGI gathers the most important Italian research groups in the field of chemistry and physical chemistry of Soft Matter, nanomaterials, surfaces and thin films CSGI’s laboratories represent a fundamental reference for both Italian and foreign scientists operating in the overmentioned research fields. CSGI has been and still is pioneer of the application of nanotechnologies in the field of conservation of the world's cultural and artistic heritage.

- CSGI's activity is focused on promoting technology transfer with numerous production companies, both Italian, European and non-EU. Third mission activity of CSGI has had a significant development over the years through the involvement of numerous companies, with particular reference to multinationals active on the global market in strategic sectors such as: ENI, Procter & Gamble, Biomeuriex, L'Oreal, IDI pharmaceutical companies, Dompé, Rottapharm, Ecocem and Solvay.

- CSGI supports conservation of cultural heritage through "Solutions for Conservation", products for the conservation of the world's artistic heritage. In particular, the Nanorestore formulations have obtained the Solar Impulse Efficient Solution Label from the SOLAR IMPULSE FOUNDATION in Lausanne as materials that respond 100% to the EU Green Deal. The certificate was obtained after a rigorous evaluation process, which identifies efficient and economically profitable solutions that respond to environmental challenges on a global level.

- CSGI coordinates the European Union CLUSTER ECHOES - Enabling Cultural Heritage-Oriented European Strategies. It is a European cluster created on the initiative of the European Commission, which involves the main stakeholders in the field of cultural heritage conservation (universities, research centres, small and medium-sized enterprises, museums, and restorers). With more than 350 members, ECHOES is an important platform available to the scientific community with the aim of sharing, on behalf of the EU, results obtained within the funded projects and proposing to the European Commission strategies and policies for the conservation and enhancement of cultural heritage. ECHOES also contributes to the definition of research guidelines regarding innovative materials applied to the conservation of objects of historical-artistic and architectural interest.

- CSGI has been selected by the European Commission to participate in the Common Exploitation Booster Support Services initiative to support the dissemination activities of the results obtained in the best projects funded by the European research program Horizon 2020. The services offered included meetings and collaborative workshops with external consultants with the aim of developing an effective entrepreneurial strategy for the exploitation of the results obtained within the Nanorestart project (Nanomaterials for the Restoration of Works of Art) coordinated by CSGI. At the end of the process, CSGI was selected to share its successful experience at the conference organized in May 2022 (Info Session on the Horizon Results Booster – NANORESTART best practices – online, 25 May 2022) in order to sponsor these services at European level.

- The Nanorestore products (Advanced solutions for the conservation of Cultural Heritage) developed within the H2020 Nanorestart project have been recognized by the European Commission as Key Exploitable Results ‐ and, therefore, published in the Horizon Results Platform, the European platform that connects the main Europe-wide innovations with potential investors.

- CSGI has been recognized as a Key Innovator at European level by the European Commission's Innovation Radar Committee regarding 11 innovations generated within projects funded by the H2020 Program (Nanorestart, Apache, EvFoundry, Bow).

- CSGI is a member, together with the National Research Council, of BRCHGA – Belt and Road Cultural Heritage Alliance – an alliance sponsored by the People's Republic of China which supports scientific research and protection of cultural heritage of countries and regions located along the New Silk Road (Belt and Road).

Several start-ups have been generated by CSGI researchers: LifeCARES (Life Cycle Assessment, Renewable Energy and Sustainability), which was born as a spin-off of the University of Siena; a mixed CSGI-INSTM work team is active at the Florence operative units, called WeGoNANO (Working Group on carbon-based and Glycan-based NANOstructured materials), coordinated by CSGI, devoted to the development of biocompatible nanomaterials based on carbon and carbohydrates that can be functionalized on-demand according to the requestes of public institutions and/orprivate companies.

Since February 2018, CSGI is member of the National Energy Technology Cluster (CTNE) with the aim of developing strategic plans aimed at aligning and integrating national scenarios and actions with European (SET-Plan, Energy Union) and global (COP 21, Mission Innovation) ones in the energy sector. CSGI thus contributes to strengthening Italy's role in the future EU SET-Plan and contributes to the development of the Integrated National Plan for Energy and Climate (PNIEC).

CSGI obtained funding by EU in different actions within the Marie Curie H2020 program. Many European projects are currently ongoing. As an example: BOW, "Biogenic Organotropic Wetsuits" (FETPROACT-EIC-05-2019, CSGI coordinator), GREENART, "GREen ENdeavor in Art ResToration" (HORIZON-CL2-2021-HERITAGE-01-01, CSGI coordinator), IMPACTIVE, "Innovative Mechanochemical Processes to synthesize green ACTIVE pharmaceutical ingredients" (HORIZON-HLTH-2021-IND-07, CSGI partner), AURORA “Artwork Unique RecognitiOn and tRacking through chemicAl encoded data, miniaturized devices and blockchain alliance” (HORIZON-CL2-2022-HERITAGE-01, CSGI partner) and OTTERS - Social Transformation for Water Stewardship through Scaling Up Citizen Science (Grant Agreement 101094041, Call Horizon-Miss-2021-Ocean-05, CSGI partner).

Educational Activity, Dissemination and Technology Transfer

The training activity, dissemination and technological transfer are a significant part of both intellectual and economic resources of CSGI and take concrete form in: the provision of research grants, post-doc positions, research doctorates and research grants; the organization of workshops, schools, conferences; the training finalized and aimed at the needs of production activities.

- During 2022, CSGI members supervised over 150 bachelor/master theses and about 20 doctoral theses (co-founded by CSGI).

- CSGI actively collaborates with the associated universities by making the research infrastructure available both for the training and for scientific research.

- CSGI actively promotes the constitution of the hybrid Italian multidisciplinary Research Infrastructure for Complex Materials and Interfaces ISIS@MACH ITALIA (IM@IT), hub of ISIS neutron and muon source (UK). IM@IT responds to the growing need of the Italian academia and production system, of SMEs. Unlike large corporations, SMEs usually have limited resources and skills to access and exploit the most advanced tools, which are nonetheless essential for understanding, developing and improving their “productive fabric”.

Structure and Organization of CSGI

Management Offices
President, Council, Director, Audit Council, Technical-Scientific Board.

Director of CSGI
Prof. Emiliano Fratini, Department of Chemistry, University of Florence.

President of CSGI
Prof. Piero Baglioni, Department of Chemistry, University of Florence.

Audit
3 members: 1 member, the president, nominated by the MEF (Ministry of Economy and Finance); 2 members nominated by MUR (Ministry of University and Research).

Website
http://www.csgi.unifi.it/

Foundation
December 21st, 1993

Official recognition by the Italian Government
November 15th, 1994 (G.U. Nr. 267)

Academic and Associated Members

Academic

- University of Florence (headquarter)
- Scuola Normale Superiore in Pisa
- University of Bari “Aldo Moro”
- University of Bergamo
- University of Catania
- University of Cagliari
- University of Molise (Campobasso)
- University of Naples “Federico II”
- University of Pavia
- University of Siena
- University of Perugia

Associated

- Brera Accademia di Belle Arti
- CGA Palermo
- CNR-ISMN Bologna
- Department of Sciences Malpighi, Messina
- Opificio delle Pietre Dure
- Polytechnic Institute of Milan
- STEBICEF Palermo
- University of Bologna
- University of Brescia
- University of Milan, Bicocca
- University of Palermo
- University of Rome, La Sapienza
- University of Rome, Tor Vergata
- University of Rome - TRE
- University of Venice

Personnel

CSGI gathers about 400 researchers including Full Professors, Associate Professors, University Researchers.

Moreover, CSGI employs 28 researchers and 5 administration employees on its own. Several PhD and post-doc students are financially supported through CSGI fellowships. CSGI hosts researchers hired by industrial companies for training and specific research activities, in the framework of various European projects.

CSGI Patents

1) Bottiroli Giovanni, Croce Anna Cleta, Baglioni Piero, Monici Monica – “Macroemulsioni acqua-in-olio a lunga stabilità, loro preparazione ed uso”. Italian Patent PCT/EP96/03201, deposit date 19/07/1996.

2) Baglioni Piero, Dei Luigi, Ferroni Enzo, Giorgi Rodorico – “Sospensioni stabili di idrossido di calcio”. Italian Patent FI/96/A000255, deposit date 31/10/1996.

3) Matteazzi Paolo, Baglioni Piero, Basset Diego – “Process for Recycling, by Milling, Solid Industrial Waste and Materials at the end of their Service Life”. European Patent Application 97203735.2, Priority IT96 FI96A000280.

4) Grassi Giuliano, Chiaramonti David, Baglioni Piero – “Apparato a combustione di etanolo o miscele etanolo per cucine, stufe e illuminazione a uso domestico”. Italian Patent FI/98/A42, deposit date 24/ 02/ 1998.

5) Ambrosone Luigi, Ceglie Andrea – “Software per l’analisi grafica e numerica di dati di Risonanza Magnetica Nucleare per la determinazione della polidispersità di emulsioni”. Italian Patent FI99A000044, deposit date 09/03/1999.

6) Baglioni Piero, Carretti Emiliano, Dei Luigi – “Microemulsioni ed emulsioni di olio in acqua, loro uso per la solubilizzazione di resine polimeriche e impacchi contenenti detti microemulsioni o emulsioni”. Italian Patent FI99A000071, deposit date 02/ 04/1999.

7) Baglioni Piero, Fratini Emiliano, Ricceri Riccardo, Sarti Giuseppe, Chiaramonti David – “Engine fuels consisting of an emulsion comprising mineral and/or natural oils, their preparation and use in internal combustion engine”. PCT International Application WO n. 99936473.0 del 02/07/1999.

8) Baglioni Piero, Bardi Ugo, Bonini Massimo – New method for the production of solid powder and films by compartimentalised solution thermal spraying (CSTS). European Patent Application EP 00-105673.8, deposit date 17/03/2000.

9) Angelico Ruggero, Ceglie Andrea, Hochoeppler Alejandro, Palazzo Gerardo, Stefan Alessandra – “Macroemulsioni acqua-in olio a lunga stabilità, loro preparazione ed uso”. Patent Query N. FI2001A000016, Italian Patent N. 0001328470, deposit date 29/01/2001.

10) Baglioni Piero, Dei Luigi, Fratoni Laura, Lo Nostro Pierandrea, Moroni Michelangelo – “Processo per la preparazione di nano e microparticelle di ossidi e idrossidi di metalli del secondo gruppo e di transizione, nano e microparticelle così ottenute e loro impiego in campo ceramico, tessile e cartario”. Patent Query N. FI2002A000052, deposit date 28/03/2002 – EP 03745367.7.

11) Baglioni Piero, Dei Luigi, Giorgi Rodorigo, Claudio Vinicius Schettino – “Basic Suspensions their Preparation and Use in Processes for Paper Deacidification”. European Patent Application EP 02714088.8, deposit date 15/01/2002.

12) Ambrosone Luigi, Ceglie Andrea – “Materiale assorbente e suoi usi nei processi di bonifica di falde acquifere inquinate da prodotti chimici”. Patent Query FI2003A000236, deposit date 11/09/2003.

13) Ambrosone Luigi, Ceglie Andrea – “Gel stabili contenenti gelatina”. Patent Query N. FI2003A000237, deposit date 11/09/2003.

14) Baglioni Piero, Dei Luigi, Fratoni Laura, Lo Nostro Pierandrea, Moroni Michelangelo – “Preparation of nano and micro-particles of group II and transition metals oxides and hydroxides and their use in the ceramic, textile and paper industries”. PCT Int. Appl. (2003), 10 pp. CODEN: PIXXD2 WO 2003082742 A2 20031009 CAN 139:278604 AN 2003:796605.

15) Fratoni Laura, Lo Nostro Pierandrea – “Composizione detergente a base di un estere dell’acido L-ascorbico”. Patent Query N. TO2003A001032, deposit date 22/12/2003.

16) Baglioni Piero, Dei Luigi, Giorgi Rodorico, Ninham Barry W. – “Process for preparing nano- and micro-sized particles of inorganic compounds”. European Patent Application EP 04101822.7, deposit date 29/04/2004.

17) Ambrosi Moira, Baglioni Piero, Bonini Massimo, Fratini Emiliano – “Nanoparticelle monodisperse di ossidi ed idrossidi metallici e loro applicazione nei settori tessile, cartario e ceramico”. Patent Query FI 2006A000313 – RIF. 7845 PTIT, deposit date 11/12/2006.

18) Baglioni Piero, Ambrosi Moira, Dei Luigi, Faneschi Mauro, Mancioli Luciano, Santoni Sergio – “Ceramic products comprising nanoparticles of zirconium hydroxide and/or glass frits”. Patent Query 7303 PTEP/2006 EP06112439.2, deposit date 10/04/2006.

19) Ceglie Andrea, Venditti Francesco, Lopez Francesco, Palazzo Gerardo, Colafemmina Giuseppe, Angelico Ruggero, Ambrosone Luigi – “Materiale adsorbente contenente tensioattivo cationico, sua preparazione ed uso per la rimozione di metalli da soluzioni acquose”. Patent Query N. FI 2006 A000113 – RIF. 7490 PTIT, Italian Patent N. 0001368154/2009, deposit date 10/05/2006.

20) Ballistreri Alberto, Cambria Maria Grazia, Carnemolla Giovanni Marco, Guglielmino Salvatore Pietro Paolo, Impallomeni Giuseppe, Nicolo Marco Sebastiano – “Production of biodegradable plastics from Brassica carinata oil with high content of erucic acid and from very long chain fatty acids”. Italian Patent IT 1392236, deposit date 13/10/2008.

21) Ballistreri Alberto, Cambria Maria Grazia, Carnemolla Giovanni Marco, Guglielmino Salvatore Pietro Paolo, Impallomeni Giuseppe, Nicolo Marco Sebastiano – “Production of biodegradable plastics from Brassica carinata oil with high content of erucic acid and from very long chain fatty acids”. World Organization Patent WO 2010044118 Priority IT 2008-RM545.

22) Hochkoeppler Alejandro, Baglioni Piero, Stefan Alessandra – "Espressione batterica di un gene artificiale per la produzione di CRM 197 e derivati". Patent Query FI 2009A000137 – RIF. 9741 PTIT, deposit date 25/06/2009.

23) Primiceri Giuseppe, Roda Elena, Stefan Alessandra, Panizza Lucio, Hochkoeppler Alejandro – "Enzyme composition for reducing the release of pharmaceutical active ingredients into the environment". WO/2009/138455A1.

24) Hochkoeppler Alejandro, Roda Elena, Panizza Lucio, Stefan Alessandra – "Method for preventing and controlling biofouling on marine objects". WO/2010/145905A.

25) Panizza Lucio, Roda Elena, Stefan Alessandra, Hochkoeppler Alejandro – "Method for preventing and controlling organisms that infest aqueous systems." WO/2010/145988A1.

26) Smets Johan, Pintens An, Keijzer Olav Pieter Dora Tony, Bodet Jean-Francois, Lebron Ariel, Fratini Emiliano, Vannucci Chiara, Ambrosi Moira, Baglioni Piero, Guinebretiere Sandra Jaqueline, Yan Nianxi, Liu Hongwei – "Encapsulates". Attorney's Docket No. 11547P, 21/04/2010.

27) Fernandez Prieto Susana, Smets Johan, Aouad Yousef Georges, Wevers Jean, Baglioni Piero, Ambrosi Moira, Vannucci Chiara – "Particles". Attorney's Docket No. 11812P2, 15/04/2011.

28) Angelico Ruggero, Lampis Sandrina, Monduzzi Maura, Ceglie Andrea – "Metodo innovativo per la "plastificazione" di grassi vegetali". Italian Patent FI2012A000186, deposit date 19/09/2012.

29) Paduano Luigi, D'Errico Gerardino, Montesarchio Daniela, Vitiello Giuseppe, Mangiapia Gaetano, Luchini Alessandra, Irace Carlo, Colonna Alfredo, Santamaria Rita – "Nanoparticelle ibride magnetite-oro funzionalizzate con struttura nucleo-guscio". Italian patent, deposit date 19/10/2012.

30) Rossi Ranieri, Giustarini Daniela – "Metodo per la misura del glutatione su sangue prelevato tramite digitopuntura" Italian Patent N. 0001420029, deposit date 18/06/2013.

31) Baglioni Piero, Del Buffa Stefano, Ridi Francesca, Bonini Massimo – "Materiale per la rigenerazione dei tessuti ossei contenente minerali argillosi aventi morfologia nanotubolare e stronzio". Italian Patent FI2013A000240, deposit date 15/10/2013.

32) Bettini Ruggero, Hochkoeppler Alejandro, Melegari Cecilia, Primiceri Giuseppe, Stefan Alessandra – "Composizioni farmaceutiche con ridotto impatto ambientale." Italian patent IT 0001415653, deposit date 12/05/2015.

33) Rosace Giuseppe, Colleoni Claudio – "Prodotto antibatterico stabile ai cicli di manutenzione". Italian Patent 102017000138046, deposit date 30/ 11/ 2017.

34) Torsi, Luisa; Palazzo, Gerardo; Cioffi, Nicola; Angione, Maria Daniela; Magliulo, Maria; Cotrone, Serafina; Scamarcio, Gaetano; Sabbatini, Luigia; Mallardi, Antonia "Organic field-effect transistor sensor" International Application PCT/IT2011/000364, US9575029(B2) (WO2013065073-A1; WO2013065073-A8), deposit date 10/10/2011. Published on 21/02/2017.

35) Torsi Luisa, Scamarcio Gaetano, Macchia Eleonora, Manoli Kyriaki, Palazzo Gerardo, Cioffi Nicola, Picca Rosaria Anna – "A field effect transistor sensor and a corresponding array device" PCT International Application PCT/IB2018/050491, deposit date 26/01/2018. Application status: pending.

36) Aouad Yousef Georges, Smets Johan, Zannoni Luke Andrew, Baglioni Piero, Tempesti Paolo, Bartolini Arianna – "Benefit agent containing delivery particle". Patent N. US10538631B2, publication date 21/01/2020.

37) Aouad Yousef Georges, Smets Johan, Zannoni Luke Andrew, Baglioni Piero, Tempesti Paolo, Bartolini Arianna – "Process for making a composition comprising benefit agent delivery particles". Patent N. US10556995B2, publication date 02/11/2020.

38) Hulskotter Frank, Smets Johan, Tahon M. Cedric, Fernandez Prieto Susana, Bodet Jean-Francois, Mamusa Marianna, Baglioni Piero – "Liquid compositions that include delivery particles". European Patent Office S. N. 19175821.8.

39) Baglioni Piero, Zuliani Alessio, Giorgi Rodorico, Chelazzi David – "Materiale composito organico-inorganico a base di olio di ricino per la rimozione di COV (VOC adsorbing component made of castor oil-based organic-inorganic composite material)". Application n. PCT/EP2022/060963.

40) Fratini Emiliano, Baglioni Piero, Ferraro Giovanni (Notari M., Rausa R., G. Assanelli) – "Method for the assessment of the dispersing capacity of new or used lubricating compositionsand of additives for lubricating compositions". Application n. 17/917,758 dated 07/10/2022

CSGI Registered Trade Marks

1) Nanorestore® International Class 01,37,40 FI2008C00067527508 RIF. 19558

2) Nanorestore Paper® International Class 01, 16, 40 FI2011C0009935263 RIF. 27175

3) Nanorestore Gel® International Class 01, 03, 37 Registration n. 12696308 del 12/08/2014 RIF. 30346

4) Nanorestore Cleaning® International Class 01, 03, 37 Registration n. 013603006 del 07/05/2015 RIF. 30836

5) Nanorestore Plus® International Class 01, 37, 40 Registration n. 014414262 del 30/11/2015 RIF. 30836

6) Nanorestore Graffiti® International Class 1, 3, 37 Registration n. 018474575 del 19/05/2021 RIF. T021622EM-01

7) Nanorestore 11/01/2022 RIF. T021773EM-T021773UK

Prospective CSGI Activity

CSGI is involved in several European projects (H2020), in several international and national projects, and in collaborations with industries and SME (small and medium enterprises).

CSGI is developing its own research activity to optimize the application of research projects inspired by the urging demands of small and medium size companies.

CSGI is actively working to offer a valid support to the Italian industrial system to set and develop projects and pre-industrial process.

List of Publications

In the 2020-2022 period, CSGI researchers published more than 2300 articles in international scientific Journals indexed on WOS/Scopus databases.

The updated list of all the publications of CSGI members can be accessed using the QR code or link reported below:

The complete list of publications is on CSGI website: https://www.csgi.unifi.it/publications.php

Conferences

1. Baglioni, P. “Research and Applications on Cultural Heritage”, Napoli 21/01/2020. Invited lecture.
2. Baglioni, P. “Science ABC” c/o Università La Sapienza, Roma 19/02/2020. Invited plenary lecture.
3. Baglioni, P. Corso su conservazione con prodotti Nanorestore e presentazione del progetto EU Apache, New York (USA) 13-18/01/2020. Invited lecture.
4. Baglioni, P. Corso teorico-pratico su nanomateriali per la conservazione, Parigi (Francia) 12-14/02/2020. Invited lecture.
5. Cabrini, M. Giornata di studio AIM, NACE Milano Italia Section, Politecnico Milano: Corrosione sotto sforzo e infragilimento da idrogeno nelle applicazioni petrolchimiche, online conference, 26/06/2020. “Effetto della pressione sulla corrosione SCC in ambiente sour”. Oral presentation.
6. Cardellini, J. Italian Soft Days 2020 - Fourth online Edition, Bari, Italy, 21-25/09/2020. “Gold nanoparticles as a nanoprobe of the viscoelastic properties of lipid vesicles: a “bending ruler” based on nanoplasmonics”. Oral presentation.
7. Caselli, L. ACIS ECR Online Conference, 22/05/2020. “Understanding nano-bio interactions: lamellar and cubic lipid assemblies as synthetic mimics for biological interfaces”. Oral presentation.
8. Caselli, L. awarded as “Soft Matter Best Talk”, Italian Soft Days 2020 - Fourth online Edition, Bari, Italy, 21-25/09/2020. “Understanding nano-bio interactions: lamellar and cubic mesophases as synthetic mimics of biological interfaces”. Oral presentation.
9. Caselli, L.; Montis, C.; Ridolfi, A.; Mangiapia, G.; Moulin, J.F.; Steinke, N.J.; Nylander, T.; Berti, D. Invited Lecture, User Meeting and German Neutron Scattering Conference, online conference, 8-10/12/2020. “Inorganic nanoparticles challenging lamellar and non-lamellar lipid membranes: the role of curvature in nano-bio interactions”. Oral presentation.
10. Caselli, L.; Montis, C.; Ridolfi, A.; Steinke, N.J.; Nylander, T.; Berti, D. 10th International Colloids Conference, online conference, 07-09/12/2020. “Understanding nano-bio interactions: lamellar and non-lamellar lipid assemblies as synthetic mimics for biological interfaces”. Oral presentation.
11. Caselli, L.; Montis, C.; Ridolfi, A.; Steinke, N.J.; Nylander, T.; Berti, D. 94th Virtual ACS Colloid & Surface Science Symposium, 08-12/06/2020. “Understanding nano-bio interactions: lamellar and non-lamellar lipid mesophases as synthetic mimics for biological interfaces”. Oral presentation.
12. Chelazzi, D.; Badillo-Sanchez, D.; Giorgi, R.; Cincinelli, A.; Baglioni, P. ACS FALL 2021 Resilience of Chemistry, American Chemical Society. Congresso tenuto in modalità mista a causa dell’emergenza sanitaria Covid-19, Georgia World Congress Center (GWCC), Atlanta, USA, 22-26/08/2021. “Colloidal fibroin dispersions for the reinforcement of aged silk”. Oral presentation.
13. Clemente, I.; Bonechi, C.; Bacia-Verloop, M.; Rossi, C.; Ristori, S. Italian Soft Days 2020, online conference, 24-25/09/2020. “Green nonlamellar lipid phases as nanovectors for biomolecule delivery”. Poster.
14. Clemente, I.; Bonechi, C.; Bacia-Verloop, M.; Rossi, C.; Ristori, S. ACS Spring 2021, Online conference, 05-16/04/2020. “Lipids from algal biomass provide mesophases with varied symmetry as high-potentiality carriers”. Oral presentation.
15. Conti, D.; Quinzeni, I.; Puscalau, C.; Sturini, M.; Guerra G.; Bruni, G.; Monteforte, F.; Capsoni, D. European School on Ceramics for Energy Conversion and Storage (EnergyCeram), Juelich (Germany), 25-27/11/2020. “High voltage cathode for Sodium-ion batteries: undoped and Mn-doped Na0.7Ni0.35Sn0.65O2”. Poster.
16. Coppola, C.; Muñoz-García, A.B.; Basosi, R.; Infantino, R.; Reginato, G.; Sinicropi, A.; Pavone, M. EnerCHEM 2-Congresso Nazionale del Gruppo Interdivisionale di Chimica per le Energie Rinnovabili, Padova (PD), 12-14/02/2020. “Understanding the interfacial charge transfer between the lead halide perovskite and novel phenothiazine-based organic hole transport materials”. Poster.
17. Fratini, E. MLZ User Meeting & German NEutron SCAttering Conference, Munich (Germany), virtual event, December 2020. “Structure and relaxation dynamics in porous systems: A neutron scattering view” Oral presentation.
18. Giatti, A.; Chelazzi, D.; Mirabile, A. Convegno ANMS 2020, Associazione Nazionale Musei Scientifici, ANMS, 27-28-29/10/2020. I Musei Scientifici Italiani nel 2020. “Elementi di conservazione preventiva alla fondazione Scienza e Tecnica all’interno del progetto europeo APACHE. Invited speaker.
19. Ielo, I.; Galletta, M.; Rando, G.; Rosace, G.; Plutino, M.R. IOP Conference Series: Materials Science and Engineering, 2020, 777(1), 012003. “Design, synthesis and characterization of hybrid coatings

suitable for geopolymeric-based supports for the restoration of cultural heritage". Oral presentation.

20. Lucchesi, G.; Cicchi, S.; Caminati, G. Nanoinnovation 2020, Rome (Italy), 15-18/09/2020. "Microwave-assisted synthesis of anisotropic silver nanoparticles". Poster.
21. Lucchesi, G.; Medda, L.; Banchelli, M.; Matteini, P.; Caminati, G. Italian Soft Days 2020, Bari (Italy), 21-25/09/2020. "New SERS substrate for the detection of Amyloid β oligomer". Poster.
22. Meklesh, V.; Gentile, L.; Olsson, U.; Tunlid, A.; Persson, P. EGU General Assembly 2020, online event, 04-08/05/2020. "Chemical composition and colloidal properties of dissolved organic matter in Norway spruce forest stands of different ages", EGU2020-15883, https://doi.org/10.5194/egusphere-egu2020-15883. Oral presentation.
23. Messina, G.M.L.; Di Napoli, B.; De Zotti, M.; Mazzuca, C.; Formaggio, F.; Palleschi, A.; Marletta, G. Insplorion workshop, Paris, France, 13-14/01/2020. "pH-driven reversible structure of stimuli-sensitive peptide: a molecular sponge". Oral presentation.
24. Milanese C. Seminari del Collegio Borromeo, Pavia, 23/04/2020. "Idrogeno: energia del futuro?". Invited Zoom webinar.
25. Milanese, C. Materials Chemistry 2020, webinar, 11-12/09/2020. "Innovative Carbon-Based Materials for Solid State Hydrogen Storage and Energy Storage". Invited oral presentation.
26. Montis, C. Italian Soft Days 2020 - Fourth online Edition, Bari, Italy, 21-25/009/2020. "Inorganic nanoparticles challenging synthetic and biogenic lipid interfaces: fundamental understanding and biomedical applications". Oral presentation.
27. Parisi, M.L.; Fiaschi, D.; Manfrida, G. Workshop sui risultati del Progetto H2020 GEOENVI Tackling the environmental concerns for deploying geothermal energy in Europe", online event, 29/04/2020. "How to simplify Life Cycle Assessment in deep geothermal projects with the novel GEOENVI tool". Oral presentation.
28. Parisi, M.L.; Fiaschi, D.; Manfrida, G. Workshop sui risultati del Progetto H2020 GEOENVI Tackling the environmental concerns for deploying geothermal energy in Europe", Bruxelles, 04-05/02/2020. "How to simplify Life Cycle Assessment in deep geothermal projects with the novel GEOENVI tool". Oral presentation.
29. Radeghieri, A. IV Congresso Scientifico Nazionale "Sindrome di Down, dalla diagnosi alla terapia", virtual meeting, 16-17/10/2020. "Isolamento di nanoparticelle biogeniche plasmatiche: un promettente approccio nanotecnologico allo studio della sindrome di Down". Oral presentation.
30. Radeghieri, A.; Alacqua, S.; Zendrini, A.; Martini, G.; Bergese, P. 52° Congresso Nazionale Sibioc - Medicina di Laboratorio, virtual meeting, 06-08/10/2020. Oral presentation.
31. Romani, M.; Pronti, L.; Damiani, A.; Severini, L.; Mazzuca, C.; Ruberto, C.; Castelli, L.; Mazzinghi, A.; Cestelli-Guidi, M. XI AIAr National Congress, Naples, 04-06/03/2020. "A multi analytical approach for the characterization of ancient photographic prints before and after chemical cleaning". Oral presentation.
32. Rossi, F.; Parisi, M.L.; Maranghi, S.; Basosi, R.; Sinicropi, A. XIV Convegno della Rete Italiana di LCA, Cortina d'Ampezzo (BL), 09-11/12/2020. "LCA- and LCC-based Solar Home Systems ecodesign". Oral presentation (online).
33. Stella.,L. 7th European Joint Theoretical/Experimental Meeting on Membranes (EJTEMM 2020), Graz, Austria, 07-09/04/2021. "A journey in the complex world of host defense peptides: from in silico to cellular studies" (virtual meeting). Invited lecture.
34. Tartaro, G.; Gentile, L.; Palazzo, G. Italian Soft Days 2020 – Fourth online Edition, Bari, 21-25/09/2020. "Rationalization of microemulsion properties through the HLD-NAC model. Poter.
35. Titubante, M.; Severini, L.; Citiulo, M.L.; Mazzuca, C.; Micheli, L. First Electronic Conference on Biosensors, 02-17/11/2020. "Hydrogels coupled with monitoring electrochemical tool for a cleaning of graphic artworks". Poster.
36. Torsi, L. The 1st International Electronic Conference on Biosensors, online event, 02-17/11/2020. "Ultimately sensitive potentiometric organic bioelectronic sensors". Invited Plenary Presentation.
37. Trovato, V.; Rosace, G.; Colleoni, C.; Sfameni, S.; Migani, V.; Plutino, M.R. IOP Conference Series: Materials Science and Engineering, 2020, 777 (1), 012007. "Sol-gel based coatings for the protection of cultural heritage textiles". Oral presentation
38. Tuccitto, N.; Fichera, L.; Li-Destri, G.; Marletta, G. Workshop Divisionale SCI sezione Chimica Fisica, online, 2020. "Nanoparticles as Suitable Messengers for Next-Generation Molecular Communication". Oral presentation.
39. Zendrini, A.; Paolini, L.; Busatto, S.; Radeghieri, A.; Romano, M.; Ridolfi, A.; Montis, C.; Bergese, P. ISEV Meeting 2020, virtual meeting, 20-22/07/2020. "The CONAN assay: purity grade and concentration of EV microliter formulations by colloidal nanoplasmonics". Oral presentation.

40. Andreassi, M.; Tamasi, G.; Bonechi, C.; Bisozzi, F.; Cangeloni, L.; Salvini, C.; Consumi, M.; Rossi, C. Interfaces. International Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity, Pula (CA), 21-25/09/2021. "Formulation of enriched topical skin products from Vitis vinifera L. grape marc". Poster.
41. Antonaros, F.; Zenatelli, R.; Guerri, G.; Bertelli, M.; Locatelli, C.; Vione, B.; Catapano, F.; Gori, A.; Vitale, L.; Pelleri, M.; Ramacieri, G.; Cocchi, G.; Strippoli, P.; Caracausi, M.; Piovesan A. V Congresso Scientifico Nazionale "Sindrome di Down: dalla Diagnosi alla Terapia", Bologna, Italy, 15-16/10/2021. "Analisi del trascrittoma di cellule umane del sangue con trisomia 21". Poster.
42. Baglioni, P. 35° congresso ECIS, Atene (Grecia), 05-09/09/2021. Invited lecture.
43. Baglioni, P.; Chelazzi, D. First Public Training of the APACHE H2020 Project (Active & Intelligent Packaging materials and display cases as a tool for preventive conservation of Cultural Heritage), Musée du quai Branly Jacques Chirac, Paris (France), 02-03/09/2021. "Innovative "green" gels as new pollutant absorbers in Preventive Conservation". Invited speaker.
44. Balestri, A.; Chiappisi, L.; Montis, C.; Micciulla, S.; Lonetti, B.; Berti, D. European Colloid & Interface Society (ECIS) 2021 – 35th Conference, Athens, 05-10/09/2021. "Hybrid molecular films from natural phospholipids and synthetic block copolymers: a physicochemical investigation". Oral presentation.
45. Bassu, G.; Laurati, M.; Fratini, E. Interfaces conference Pula (CA), 21-25/09/2021. "Transparent porous hydrogel for characterization of micro-particle diffusion". Poster.
46. Bisozzi, F.; Tamasi, G.; Baratto, M.C.; Cangeloni, L.; Bonechi, C.; Consumi, M.; Rossi, C. Interfaces. International Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity, Pula (CA), 21-25/09/2021. "Determination of conversion factors between five antioxidant standards, through the DPPH assay carried out with UV-Vis spectroscopy and EPR". Poster.
47. Bonechi, C.; Donati, A.; Tamasi, G.; Leone, G.; Consumi, M.; Magnani, A.; Rossi, C. Interfaces. International Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity, Pula (CA), 21-25/09/2021. "Solution dynamics of the natural bioactive molecule capsaicin: a relaxation study". Poster.
48. Cabrini, M.; Lorenzi, S.; Pastore, T. AIM – Giornate Nazionali sulla Corrosione e Protezione, virtual edition, 29/06-02/07/2021. "Effetto della temperatura di piastra sulla corrosione localizzata della lega AlSi10Mg ottenuta per Laser Powder Bed Fusion". Oral presentation.
49. Cabrini, M.; Lorenzi, S.; Pastore, T. Convegno AIMAT 2021, Cagliari 15-18/09/2021. "Material's challenges for hydrogen green economy". Oral presentation.
50. Cabrini, M.; Lorenzi, S.; Testa, C.; Galizzi, N.; Carugo, F.; Bocchi, S.; D'Urso, G.; Giardini, C.; Pastore, T. 38° Convegno Nazionale AIM, Virtual Edition, 18-26/01/2021. "Corrosione sotto sforzo di leghe di alluminio indurenti per precipitazione saldate tramite friction stir welding". Oral presentation.
51. Cangeloni, L.; Bonechi, C.; Tamasi, G.; Donati, A.; Leone, G.; Consumi, M.; Magnani, A.; Cappelli, A.; Rossi, C. Interfaces. International Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity. Pula (CA), 21-25/09/2021. "Physichemical characterization of hyaluronic acid and chitosan coating liposomes". Poster.
52. Capsoni, D.; Guerra, G.; Puscalau, C.; Maraschi, F.; Bruni, G.; Monteforte, F.; Profumo, A.; Sturini, M. XXVII Congresso Nazionale della Società Chimica Italiana, virtual event, 14-23/09/2021. "Zinc and Iron based Metal-Organic Frameworks as Ofloxacin adsorbents in polluted waters". Oral presentation.
53. Caputo, D.; Fusco, C.; Nacci, A.; Palazzo, G.; Murgia, S.; D'Accolti, L.; Gentile, L. XXVII Congresso Nazionale della Società Chimica Italiana, Milan (Italy), 14-23/09/2021. "Ecofriendly Isolation of Cellulose from buckwheat chaff". Keynote lecture.
54. Cardellini, J.; Rossi, J.; Lavagna, E.; Berti, D. European Colloid & Interface Society (ECIS) 2021 – 35th Conference, Athens, 05-10/09/2021. "Controlling the self-assembly of inorganic nanoparticles onto lipid vesicles: towards functional hybrid composites". Oral presentation.
55. Carucci, C.; Scalas, N.; Sechi, G.; Piludu, M.; Porcheddu, A.; Cosentino, S.; Monduzzi, M.; Salis, A. XXXV Conference of the European Colloid & Interface Society, ECIS 2021, 05-10/09/2021. "Mesoporous silica nanoparticles as possible drug delivery systems to contrast antibiotic resistance". Oral presentation
56. Carucci, C.; Sechi, G.; Piludu, M.; Cosentino, S.; Monduzzi, M.; Salis, A. Interfaces 2021, Pula (CA) Italy, 16-19/06/2021. "Quercetin loaded polymer coated MSNs as drug delivery strategy against bacteria". Oral presentation.
57. Carucci, C.; Sechi, G.; Piludu, M.; Monduzzi, M.; Salis, A. XXVII Congresso Nazionale Chimica Italiana, online conference, Roma (RM) Italy, 14-23/09/2021. "Drug loaded polymer coated silica

nanoparticles as drug delivery route against bacteria". Oral Presentation.

58. Carucci, C.; Tocco, D.; Sanjust, E.; Magner, E.; Salis, A. Biocatalysis in Non-conventional Media, BNCM 2021, online conference, Milano (MI) Italy, 06-08/05/2021. "Immobilization of Aspergillus sp. Laccase on Fe-BTC and ZIF-zni metal organic frameworks". Oral presentation.
59. Carugo, F.; Barbieri, G.; Cabrini, M.; Cognini, F.; Lorenzi, S.; Pastore, T. Convegno AIMAT 2021, Cagliari, 15-18/09/2021. "Effect of different additive manufacturing tecniques on microstructure and corrosion behavior of alloy 625". Poster.
60. Caselli, L.; Montis, C.; Berti, D. 35th Conference of the European Colloid and Interface Society (ECIS), Athens (Greece), 05-10/09/2021. "Hybrid Soft Assemblies Built from Lipids and Inorganic Nanoparticles: from Interaction to Design of Nanostructured Devices". Oral presentation.
61. Caselli, L.; Ridolfi, A.; Cardellini, J.; Sharpnack, L.; Paolini, L.; Brucale, M.; Valle, F.; Montis, C.; Bergese, P.; Berti, D. ACS Fall 2022, 21-26/08/2021. "Probing the mechanical properties of synthetic and biogenic nanosized lipid vesicles with a plasmon-based nanoruler". Oral presentation.
62. Caselli, L.; Valle, F.; Brucale, M.; Paolini, L.; Bergese, P.; Berti, D. Keynote Lecture, 35th ECIS 2021 Conference of the European Colloid & Interface Society, Athens, 5-10/09/2021. "Assessing the stiffness of synthetic and natural nanovesicles by a "plasmon-based nanoruler". Oral presentation.
63. Chelazzi, D. Symposium of the H2020 APACHE project (Active & intelligent PAckaging materials and display cases as a tool for preventive conservation of Cultural Heritage, H2020 Grant agreement ID: 814496), Federal University of Rio Grande do Sul (Porto Alegre, Brazil). Congresso tenuto online a causa dell'emergenza sanitaria Covid-19, 09/12/2021. "New materials and methods for the preventive conservation of art". Invited speaker.
64. Chelazzi, D.; Badillo-Sanchez, D.; Giorgi, R.; Cincinelli, A.; Baglioni, P. ACS FALL 2021 Resilience of Chemistry, American Chemical Society. Congresso tenuto in modalità mista a causa dell'emergenza sanitaria Covid-19, Georgia World Congress Center (GWCC), Atlanta, USA, 22-26/08/2021. "Colloidal fibroin dispersions for the reinforcement of aged silk". Oral presentation.
65. Chelazzi, D.; Badillo-Sanchez, D.; Giorgi, R.; Cincinelli, A.; Baglioni, P. 35th Conference of the European Colloid & Interface Society (ECIS). Congresso tenuto in modalità mista a causa dell'emergenza sanitaria Covid-19, 05-10/09/2021, Crowne Plaza, Athens (Greece). "Colloidal self-regenerated fibroin for the strengthening of aged silk". Oral presentation.
66. Chiessi, E. Virtual Conference Osmolyte and cosolvent effects in stimuli-responsive soft matter systems, Technischen Universität Darmstadt (Germany), 25-26/02/2021. "Insights on Poly(N-isopropylacrylamide) Coil-to-Globule Transition in Aqueous Environments by Atomistic Molecular Dynamics Simulation". Invited oral presentation.
67. Cinelli, G.; Cuomo F.; Ceglie, A., Lopez, F. XXVII Congresso della Società Chimica Italiana, 14-23/09/2021. "Oxidative stability and polyphenols role in red wine-enriched olive oil emulsions". Poster.
68. Clemente, I.; Bonechi, C.; Bacia-Verloop, M.; Rossi, C.; Ristori, S. ACS Spring 2021, Online conference, 05-16/04/2020. "Lipids from algal biomass provide mesophases with varied symmetry as high-potentiality carriers". Oral presentation.
69. Clemente, I.; Bonechi, C.; Rodolfi, L.; Bacia-Verloop, M.; Rossi, C.; Ristori, S. Interfaces. International Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity, Pula (CA), 21-25/09/2021. "Lipids from algal biomass provide new (nonlamellar) nanovectors with high carrier potentiality for natural antioxidants" Poster.
70. Clemente, I.; Bonechi, C.; Tamasi, G.; Rossi, C.; Ristori S. XXVII Congresso Nazionale della Società Chimica Italiana, online conference, 15-23/09/2021. "Cubic and lamellar mesophases obtained from algal biomass as drug carriers with high potentiality". Oral presentation.
71. Clemente, I.; Bonechi, C.; Tamasi, G.; Rossi, C.; Ristori, S. 35th Conference of the European Colloid and Interface Society 2021, Athens (Greece), 05-10/09/2021. "Using lipids from algal biomass to obtain multicompartment nanocarriers for curcumin delivery" Oral presentation.
72. Clemente, I.; Lamponi, S.; Bonechi, C.; Tamasi, G.; Rossi, C.; Ristori S. Interfaces 2021, Cagliari, 21-25/09/2021. "Cubic and lamellar mesophases obtained from algal biomass as drug carriers with high potentiality". Oral presentation.
73. Clemente, I.; Lamponi, S.; Tamasi, G.; Bonechi, C.; Rossi, C.; Ristori, S. Interfaces. International Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity, Pula (CA), 21-25/09/2021. "Using lipids from algal biomass to obtain multicompartment nanocarriers for curcumin delivery". Poster.
74. Cofelice, M.; Cuomo, F.; Ceglie, A.; Lopez, F. XXVII Congresso della Società Chimica Italiana, 14-23/09/2021. "Rheological Characterization of Hydrogels of Alginate-Based Nanodispersion".

Poster.

75. Consumi, M.; Talarico, L.; Leone, G.; Magnani, A. Congresso internazionale SENSORS 2021 Milano, 20-22/10/2021. “Quartz crystal microbalance-based sensor for accurate quantification and administration of drug loaded solid lipid nanoparticles for drug release in-vitro study". Oral presentation.
76. Consumi, M.; Tamasi, G.; Bonechi, C.; Bisozzi, F.; Cangeloni, L.; Rossi, C. Interfaces. International Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity, Pula (CA), 21-25/09/2021. “Determination of glucosinolate content and myrosinase activity in Brassica oleracea var. italica and Brassica oleracea var. botrytis”. Poster.
77. Consumi, M.; Tamasi, G.; Bonechi, C.; Rossi, C. XXVII Congresso Nazionale della Società Chimica Italiana (SCI), Divisione di Chimica Analitica, 20/09/2021. “Glucosinolate hydrolysis by myrosinase in Brassicaceae tissues: a chromatographic approach”. Oral presentation.
78. Consumi, M.; Tamasi, G.; Rossi, C. Congresso internazionale Waste2Value, 17/11/2021. “Add value to tomato and potato by-products”. Oral presentation.
79. Coppola, C.; D’Ettorre, A.; Parisi, M.L.; Zani, L.; Reginato, G.; Calamante, M.; Mordini, A.; Taddei, M.; Basosi, R.; Sinicropi, A. XXVII Congresso Nazionale della Società Chimica Italiana, Modalità telematica, 14-23/09/2021. “DFT and TDDFT investigation of novel organic catechol-based sensitizers for type II Dye Sensitized Solar Cells (DSSCs)”. Poster.
80. Coppola, C.; Pecoraro, A.; Muñoz-García, A.B.; Infantino, R.; Basosi, R.; Sinicropi, A.; Pavone, M. Merck Young Chemist’s Symposium 2021, Rimini (RN), 22-24/11/2021. “Interfacial charge transfer process between lead halide perovskite and a novel triphenylamine/phenothiazine-based hole transport material: a first- principles study”. Oral presentation.
81. Cuomo, F.; Iacovino, S.; Lopez, F.; Messia, M.C.; Marconi, E. 7th International Conference on Food Chemistry and Technology, virtual event, 08-10/11/2021. “Rheological assessment of the effect of additives on the stability of chia (Salvia hispanica L.) mucilage suspensions”. Oral presentation.
82. De Nigris, A.; Minò, A.; Ambrosone, L. 21th Congresso Nazionale @ITIM2021, Campobasso (Italy), 29-30/11/2021. “Nuovo metodo per la preparazione di nanoparticelle di HfO2 come sensibilizzatori nel trattamento radioterapico dei sarcomi”. Oral presentation.
83. Di Tinno, A.; Cataldo, A.; Ferrigno, L.; Maffucci, A.; Bellucci, S.; Micheli, L. Nano-modified Screen-Printed Electrodes for the Determination of Organic Pollutants, IEEE International Conference on Communications, Montreal, 14-23/06/2021. Virtual oral presentation.
84. Ferraro, G.; Fratini, E.; Rossi, V.L.; Sanesi, A.; Baglioni, P. Interfaces - International conference. Pula (CA), 21-25/09/2021. “Controlled decoration of plastic surfaces with metal nanostructures” Oral presentation.
85. Ferraro, G.; Fratini, E.; Rossi, V.L.; Sanesi, A.; Baglioni, P. XXVII Congresso nazionale della Società Chimica Italiana, virtual conference, 14-23/09/2021. “Controlled decoration of plastic surfaces with metal nanostructures” Oral presentation.
86. Ferron, L.; Milanese, C.; Colombo, R.; Papetti. A. Recent Developments in Pharmaceutical Analysis, virtual edition (RDPA), Modena, 06-08/09/2021. “Evaluation of Rice (Oryza sativa L.) by-products as natural sources of bioactive compounds and energy storage materials”. Poster.
87. Frosi, I.; Milanese, C.; Papetti, A. Waste2Value International Congress, virtual event, 17/11/2021. “Corn cob (Zea mays L.) as a potential source of bioactive compounds: comparison of different extraction methods”. Poster.
88. Frosi, I.; Montagna, I.; Milanese, C.; Papetti, A. Recent Developments in Pharmaceutical Analysis, virtual edition (RDPA), Modena, 06-08/09/2021. “Development of an accelerated stability model to estimate purple corn cob extract (Moradyn) shelf-life”. Oral presentation.
89. Frosi, I.; Montagna, I.; Milanese, C.; Papetti, A. XXVII Congresso Nazionale della Società Chimica Italiana, virtual event, 14-23/09/2021. “Comparison of different extraction methods to recover bioactive compounds from corn waste (Zea mays L.)”. Oral presentation.
90. Gentile, L. Webinar on Material Science, Marzo 2021 “Temperature effect on cationic-based multilamellar vesicles in a cosmetic cream”. Oral presentation.
91. Gentile, L.; Persson, P.; Olsson, U. Congresso Internationale “European Colloid and Interface Society conference”, Athens (Greece), 05-10/09/2021. “Minerals-soil organic matter colloidal aggregates” Oral presentation.
92. Glahn-Martinez, B.; Lucchesi, G.; Benito-Peña, E.; Caminati, G.; Moreno-Bondi, M.C. XIX ISLS & 21th ISBC, Gijon (Spain), 15-18/06/2021. “Biosensing of Tacrolimus in Blood Samples with a Drug Receptor Fused to a Green Fluorescent Protein”. Poster.
93. Guaragnone, T.; Rossi, M.; Chelazzi, D.; Mastrangelo, R.; Severi, M.; Fratini, E.; Baglioni, P. XVII Congresso Nazionale della Società Chimica Italiana, Divisione di Chimica Fisica, Roma, 14-

23/09/2021. “pHEMA/PAA and pHEMA/PVP semi-IPNs: physico-chemical characterization and use for bronze cleaning”. Oral presentation.

94. Leone, G.; Consumi, M.; Pepi, S.; Bonechi, C., Tamasi, G.; Donati, A.; Rossi, C.; Magnani, A. Interfaces. International Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity, Pula (CA), 21-25/09/2021. “Enriched Gellan Gum hydrogel as visco-supplement. Interfaces”. Poster.
95. Li Destri, G.; Ruffino, R.; Tuccitto, N.; Marletta, G. 35th Conference of the European Colloid and Interface Society (ECIS), Athens (Greece), 05-10/09/2021. “Quantitative measurements of nanoscale inter-particle forces at the air/water interface: the role of the ligand chain length”. Oral presentation.
96. Li Destri, G.; Ruffino, R.; Tuccitto, N.; Marletta, G. XXVII Congresso della Società Chimica Italiana, congresso online, 14-23/09/2021. “Forces between nanoparticles at the air/water interface: the role of the ligand chain length”. Oral presentation.
97. Lopez, F.; Iacovino, S.; Sacco, P.; Cuomo, F.; Ceglie, A. Interface International Conference Pula (CA) Sardinia, Italy, 22-24/09/2021. “Essential oils for preserving mucilage from chia seeds”. Poster.
98. Lorenzi, S.; Cabrini, M.; Carugo, F.; Pastore, T. AIM – Giornate Nazionali sulla Corrosione e Protezione, virtual edition, 29/06-02/07/2021. “Studio della corrosion in condense sature di CO2”. Oral presentation.
99. Lorenzi, S.; Cabrini, M.; Coffetti, D.; Coppola, L.; Pastore, T. Convegno AIMAT 2021, Cagliari 15-18/09/2021. “Innovative approach for the study of stress corrosion cracking susceptibility of FSWed aluminum alloys”. Poster.
100. Lorenzi, S.; Cabrini, M.; Coppola, L.; Ferrari, R.; Pastore T.; Lizzori, E.; Lonsi, E.; Tognetti, N.; Scatena, A. AIM – Giornate Nazionali sulla Corrosione e Protezione, virtual edition, 29/06-02/07/2021. “Fenomeni di corrosion in fessura di elementi strutturali”. Oral presentation.
101. Lorenzi, S.; Cabrini, M.; Coppola, L.; Pastore T. AIM – Giornate Nazionali sulla Corrosione e Protezione, virtual edition, 29/06-02/07/2021. “Caratterizzazione dei fenomeni di corrosione nei macrodifetti delle strutture in calcestruzzo armato e precompresso”. Oral presentation.
102. Lorenzi, S.; Galizzi, N.; Cabrini, M.; Carugo, F.; Bocchi, S.; D’Urso, G.; Giardini, C.; Testa, C.; Pastore, T. AIM – Giornate Nazionali sulla Corrosione e Protezione, virtual edition, 29/06-02/07/2021. “Effetto della velocità di deformazione sulla corrosione sotto sforzo di leghe di alluminio saldate tramite friction stir welding”. Oral presentation.
103. Lucchesi, G.; Barletti, B.; Errico, S.; Chiti, F.; Zasloff, M.; Caminati, G. Pula (Italy), 21-25/09/2021. “Interfaces International Conference-From new materials to life science – Structure, Interactions, Dynamics and Activity”. Oral presentation.
104. Lucchesi, G.; Errico, S.; Chiti, F.; Caminati, G. 35th ECIS 2021, Athens (Greece), 05-10/09/2021. “Chemico-physical interaction between phospholipid membrane models and trodusquemine”. Oral presentation.
105. Lucchesi, G.; Errico, S.; Zasloff, M.; Chiti, F.; Caminati, G. Geneva Colloids, Geneva (Switzerland), 08-09/04/2021. “Aggregation behaviour of trodusquemine and its interaction with biomimetic membranes”. Oral presentation.
106. Lucchesi, G.; Medda, L.; Banchelli, M.; Caminati, G. 35th ECIS 2021, Athens (Greece), 05-10/09/2021. “SERS and QCM detection of amyloid β oligomers on Ag modified ITO substrate”. Poster.
107. Marino, S.; Ahmad, U.; Alvino, A. 13th European Conference on Precision Agriculture, ECPA 2021. Precision agriculture ’21, Wageningen Academic Publishers. 1485: 2021. “VIs-image segmentation method for the estimation of agronomic traits in durum and winter-wheat cultivars”. Oral presentation.
108. Messina, G.M.L.; Oikonomou, E.; Heux, L.; Berret, J.F.; Marletta, G. XXVII Congresso Nazionale della Società Chimica Italiana, online, 14-23/09/2021. “Surfactant vesicles and polysaccharides interactions with cellulose nanocrystals”. Oral presentation.
109. Milanese, C.; Frosi, I.; Girella, A.; Puoti, S.; Magnani, G.; Pontiroli, D.; Riccò, M.; Papetti, A. XXVII Congresso Nazionale della Società Chimica Italiana, virtual event, 14-23/09/2021. “Super activated biochar for solid state hydrogen storage and supercapacitors preparation”. Oral presentation.
110. Milanese, C.; Frosi, I.; Papetti, A.; Girella, A.; Berbenni, V.; Magnani, G.; Pontiroli, D.; Riccò, M. Waste2Value International Congress, virtual event, 17/11/2021. “Energy storage in superactivated biochar from rice wastes”. Oral presentation.
111. Milanese, C.; Frosi, I.; Papetti, A.; Girella, A.; Puoti, S.; Magnani, G.; Pontiroli, D.; Riccò, M. European Materials Research Society 2021 Fall Meeting, virtual event, 20-23/09/2021. “Biochar

from vegetal and animal wastes for solid state hydrogen storage and applications as supercapacitors". Oral presentation.

112. Milanese, C.; Frosi, I.; Papetti, A.; Girella, A.; Puoti, S.; Magnani, G.; Pontiroli, D.; Riccò, M. The International Chemical Congress of Pacific Basin Societies Pacifichem 2021, virtual event, 16-21/12/2021. "Innovative carbon-based nanostructures for solid state hydrogen storage and energy storage". Invited oral presentation.
113. Minò, A.; Ambrosone, L. Congresso Nazionale @ITIM 2021, Campobasso (Italy), 29-30/11/2021. "Liposomi come nanocarrier di NAADP nella vasculogenesi". Oral presentation.
114. Minò, A.; Testa, G.; Ambrosone, L. Nanomedicine International Conference and Exhibition, Milano (Italy), 20-22/10/2021. "Nanosystems as enhancements of cell regeneration". Oral presentation.
115. Monduzzi, M.; Carucci, C.; Pivetta, T.; Parsons, D.F.; Salis, A. XXXV Conference of the European Colloid & Interface Society, ECIS 2021, 05-10/09/2021. "Specifc ion effects on Hemoglobin and Bovine Serum Albumin evidentiated in denaturing conditions through ESI-MS investigation". Oral presentation.
116. Montis, C.; Caselli, L.; Ridolfi, A.; Berti, D.; Nylander, T. ACS Fall 2022, 21-26/08/2021. "Lamellar and non-lamellar lipid films as synthetic models of biological membranes: the role of symmetry at nano-bio interfaces". Oral presentation.
117. Montis, C.; Mangiapia, G.; Steinke, N.J.; Nylander, T. 35th Conference of the European Colloid and Interface Society (ECIS), Athens (Greece), 05-10/09/2021. "Challenging lamellar and non-lamellar lipid assemblies with nanoparticles: the role of symmetry at nano-bio interfaces". Oral presentation.
118. Mura, M.; Gonzalez, B.; Izquierdo-Barba, I.; Salis, A.; Vallet-Regi, M. XXVII Congresso Nazionale Chimica Italiana, Modalità telematica, Roma (RM) Italy, 14-23/09/2021. "Nanoantibiotics: design of multifunctional MSN nanosystems containing both antibiotic and copper ions to combat bone infection". Oral presentation.
119. Murgia, S.; Fornasier, M.; Biffi, S.; Bortot, B.; Macor, P.; Manhart, A.; Wurm, F. Interfaces, Pula (CA), 21-25/10/2021. "Cubosomes stabilized by a polyphosphoester-analogue of Pluronic F127 with reduced cytotoxicity". Oral presentation.
120. Op De Beeck, M.; Troein, C.; Siregar, S.; Gentile, L.; Abbondanza, G.; Peterson, C.; Persson, P.; Tunlid, A. EGU General Assembly 2021, online event, 19-30/04/2021. "Regulation of fungal decomposition at single-cell level", EGU21-8198, https://doi.org/10.5194/egusphere-egu21-8198. Oral presentation.
121. Palchetti, I.; Tadini-Buoninsegni, F. 72nd Annual Meeting of the International Society of Electrochemistry, Jeju Island (Korea), hybrid conference, 29/08-03/09/2021. "A bioelectrochemical approach for monitoring drug interactions with membrane transporters". Poster.
122. Paolini, L. Showcase of International collaborative projects and networks on Extracellular Vesicles. 2nd EVIta Symposium, Lucca, Italy, 20-22/09/2021. "The evFOUNDRY project". Oral presentation.
123. Paolini, L.; Federici, S.; Radeghieri, A.; Bergese, P.; 2nd EVIta Symposium, Lucca, Italy, 20-22/09/2021. "Fourier-transform infrared spectroscopy (FT-IR) to characterize EV subpopulations from plasma of subjects with Parkinson's disease and healthy controls". Poster.
124. Parisi, M.L. Convegno dell'Associazione Italiana Chimici del Cuoio sezione Toscana "Green Deal: strategia per lo sviluppo sostenibile", online event, 01/07/2021. "LCA nell'industria del cuoio: stato dell'arte e prospettive". Oral presentation.
125. Parisi, M.L. First International Conference Solar Power Technology– SPTech2021 (online), 08/07/2021. Invited speaker per la tavola rotonda "Solar Energy Policy". Oral presentation
126. Parsons, D.F. 72nd Divisional Meeting of Division of Colloid and Surface Chemistry, The Chemical Society of Japan, Japan, online event, 21/09/2021. "Beyond the Hofmeister series: a theory of buffer specific effects". Invited speaker.
127. Parsons, D.F.; Tadesse, D. XXXV Conference of the European Colloid & Interface Society, ECIS 2021, 05-10/09/2021. "Ion-specific peaks in electrode capacitance and electrode energy determined by ionic steric interactions". Poster.
128. Pomarico, G.; Mandoj, F.; Paolesse, R. 11th International Conference on Porphyrins and Phthalocyanines, Virtual Meeting, 28/06-03/07/2021. "Early Transition Metals Corroles: Titanium and Vanadium Complexes". Oral presentation.
129. Restivo, E.; Pugliese, D.; Gallichi-Nottiani, D.; Bruni, G.; Cucca, L.; Janner, D.; Milanese, D.; Visai, L. Congresso Nazionale Biomateriali 2021, Lecce, 11-14/07/2021. "Promising bioglasses for medical applications". Poster.
130. Ripani, G.; Messina, G.M.L.; Mazzuca, C.; Dettin, M.; Zamuner, A.; di Napoli, B.; Marletta, G.;

Palleschi, A. 35th Conference of the European Colloid and interface Science, Athens, Greece, 05-10/09/2021. “From Nanoaggregates to Mesoscale Ribbons: The multistep self-organization of amphiphilic peptides. Experimental and Molecular Dynamics study”. Poster.

131. Romano, M.; Zoppi, N.; Ritelli, M.; Chiarelli, N.; Bergese, P.; Radeghieri, A.; Colombi, M. ISEV Meeting 2021, virtual meeting, 18-21/05/2021. “Extracellular Vesicles in Hypermobile Ehlers-Danlos syndrome: deconstructing the fibroblast secretome to define bioactive molecules and disease mechanisms”. Poster.
132. Rossi, F.; Parisi, M.L.; Sinicropi, A.; Basosi, R.; Longo, S.; Cellura, M. XV Convegno della Rete Italiana di LCA, Reggio Calabria (RC), 22-24/09/2021. “State-of-the-art analysis of environmental assessment studies on Concentrated Solar Power systems”. Oral presentation (short).
133. Ruffino, R.; Li Destri, G.; Marletta, G. 35th Conference of the European Colloid and Interface Society (ECIS), Athens (Greece), 05-10/09/2021. “Fine control of nanoparticle monolayer structure at the air/water”. Poster.
134. Ruffino, R.; Li Destri, G.; Tuccitto, N.; Marletta, G. XXVII Congresso della Società Chimica Italiana (Congresso online), 14-23/09/2021. “’Distorted’ self-assembly of polymer thin films at nano-curved surfaces”. Oral presentation.
135. Sacco, P.; Lopez, F.; Marsich, E.; Donati, I. XXVII Congresso della Società Chimica Italiana, 14-23/09/2021. “Biopolymer-based platforms for cell mechanosensing and regenerative medicine”. Oral presentation.
136. Salis, A.; Cappai, L.; Mura, M.; Carucci, C.; Monduzzi, M.; Parsons, D.F. XXXV Conference of the European Colloid & Interface Society, ECIS 2021, 05-10/09/2021. “Specific buffer effects on the interactions between biomacromolecules at the same nominal pH”. Oral presentation.
137. Savi, P.; Di Summa, D.; Natali S.I.; Dassano G.; Ruscica, G.; Pelosato, R. 2021 International Conference on Electromagnetics in Advanced Applications, ICEAA 2021, 2021, pp. 403-404. “Drywall coated with biochar as electromagnetic interference shielding material”. Oral presentation.
138. Schirone, D.; Tartaro, G.; Gentile, L.; Palazzo, G. 35th Conference of the European Colloid and Interface Society, Athens, 05-10/09/2021. “Building up an HLD framework for cationic surfactants”. Poster.
139. Schirone, D.; Tartaro, G.; Gentile, L.; Palazzo, G. Interfaces International Conference 2021, Pula (CA), 21-25/09/2021. “Extending HLD model to Cationic Surfactants”. Poster.
140. Severini, L.; D’Andrea, A.; Domenici, Dabagov, S.B.; Guglielmotti, V.; Hampai, D.; Micheli, L.; Placidi, E.; Titubante, M.; Mazzuca, C.; Paradossi, G.; Palleschi, A. XXVII Congresso della Società Chimica Italiana- modalità virtuale, 14-23/09/2021. “Ultrasound-stimulated PVA microbubbles as removal tool for adhesive tapes from cellulose-based materials” Oral presentation.
141. Severini, L.; D’Andrea, A.; Domenici, F.; Dabagov, S.B.; Guglielmotti, V.; Hampai, D.; Micheli, L.; Placidi, E.; Titubante, M.; Mazzuca, C.; Paradossi, G.; Palleschi, A. 35th Conference of the European Colloid and interface Science, Athens, Greece, 5-10/09/2021. “PVA microbubbles stimulated by Ultrasounds as a “green” tool for removal of modern adhesive tapes from cellulose-based materials”. Oral presentation.
142. Severini, L.; Di Napoli, B.; Franco, S.; Tumiati, M.; Buratti, E.; Titubante, M.; Nigro, V.; Gnan, N.; Micheli, L.; Ruzicka, B.; Mazzuca, C.; Angelini, R.; Missori, M.; Zaccarelli, E. 35th Conference of the European Colloid and interface Science, Athens, Greece, 05-10/09/2021. “Micro-sized cleaning gels as innovative tool for the preservation of paper materials” Poster.
143. Severini, L.; Di Napoli, B.; Franco, S.; Tumiati, M.; Buratti, E.; Titubante, M.; Nigro, V.; Gnan, N.; Micheli, L.; Ruzicka, B.; Mazzuca, C.; Angelini, R.; Missori, M.; Zaccarelli, E. XXVII Congresso della Società Chimica Italiana, modalità virtuale, 14-23/09/2021. “Gellan gum-based microgels as a promising tool for paper preservation”. Poster.
144. Stella.,L. 7th European Joint Theoretical/Experimental Meeting on Membranes (EJTEMM 2020), Graz, Austria, 07-09/04/2021. “A journey in the complex world of host defense peptides: from in silico to cellular studies” (virtual meeting). Invited lecture.
145. Tadini-Buoninsegni, F; Sfragano, P.S.; Palchetti, I. XXVII Congresso Nazionale della Società Chimica Italiana, online conference, 14-23/09/2021. “Modulation of Ca2+-ATPase transport activity by pharmacologically relevant compounds”. Oral presentation.
146. Talarico, L.; Consumi, M.; Leone, G.; Tamasi, G.; Bonechi, C.; Rossi, C.; Magnani, A. Interfaces. International Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity. Pula (CA), 21-25/09/2021. “Solid Lipid Nanoparticles produced via Coacervation Method as promising carriers for controlled release of Quercetin”. Poster.
147. Tamasi, G.; Bonechi, C.; Consumi, M.; Bisozzi, F.; Cangeloni, L.; Rossi, C. Interfaces. International

Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity, Pula (CA), 21-25/09/2021. “Occurrence of solanesol in potato (Solanum tuberosum L.) leaves at different vegetative stages of the plant”. Poster.

148. Tamasi, G.; Bonechi, C.; Leone, G.; Andreassi, M.; Consumi, M.; Sangiorgio, P.; Verardi, A.; Rossi, C.; Magnani, A. Interfaces. International Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity. Pula (CA), 21-25/09/2021. “Varietal and geographical origin characterization of peaches and nectarines by combining analytical techniques and statistical approach”. Poster.
149. Tamasi, G.; Consumi, M.; Leone, G.; Bonechi, C.; Rossi, C.; Magnani, A. Interfaces. International Conference. From new materials to life Science-Structure, Interactions, Dynamics and Activity, Pula (CA), 21-25/09/2021. “Combined experimental and multivariate model approaches for glycoalkaloid quantification in tomatoes” Poster.
150. Tartaro, G.; Gentile, L.; Palazzo, G. 35th Conference of the European Colloid and Interface Society, Athens, 05-10/09/2021. “Scale lengths in AOT sponge phases in the presence of squalene”. Oral presentation.
151. Tartaro, G.; Gentile, L.; Palazzo, G. Interfaces International Conference 2021, Pula (CA), 21-25/09/2021. “Microstructure and phase behaviour in AOT/brine/Squalane sponge phases”. Oral presentation.
152. Tocco, D.; Salis, A.; Yoshi, M.; Hartmann, M. XXXV Conference of the European Colloid & Interface Society, ECIS 2021, 05-10/09/2021. “Immobilization of Aspergillus sp. Laccase on Gd-BTC and TbBTC MOFs and MFI Zeolite”. Oral presentation.
153. Torsi, L. 7th International Fall School on Organic Electronics (IFSOE-2021), online event, Moscow, Russian Federation, 12-16/09/2021. “Sensing at the zeptomolar concentration level with large area bioelectronic interfaces”. Invited Plenary Presentation.
154. Torsi, L. 8th International Symposium on Sensor Science, online event, 17-28/05/2021. “Why a diffusing single-molecule can be detected in few minutes by a large capturing bioelectronic interface”. Invited Lecture.
155. Torsi, L. Exner Medal 2021 (Postponed 2022), Vienna (Austria), 18/05/2022. “Single-molecule detection with a large transistor endows a clinician with the attacker advantage”. Plenary Presentation.
156. Torsi, L. IEEE-NANO2021 - The 21st IEEE International Conference on Nanotechnology, online event, 28-30/07/2021. “Single molecule bio-electronic smart system array for clinical testing”. Invited Plenary Presentation.
157. Torsi, L. MENA International conference on Biosensors 2021, Riyadh (Saudi Arabia), online event, 24-25/02/2022. “Ultimately sensitive potentiometric organic bioelectronic sensors”. Invited Lecture.
158. Torsi, L. The 1st International Electronic Conference on Biosensors, online event, 02-17/11/2020. “Ultimately sensitive potentiometric organic bioelectronic sensors”. Invited Plenary Presentation.
159. Torsi, L. XIX Brazilian Materials Research Society Meeting (XIX B-MRS), online event, 30/08-03/09/2021. “Sensing at the zeptomolar concentration level with large area bioelectronic interfaces”. Invited Plenary Presentation.
160. Tuccitto, N.; Calì, F.; Fichera, L.; Li-Destri, G.; Messina, G.M.L.; Licciardello, A.; Marletta, G. Congresso Nazionale SCI, online, 2021. “Quantum Dots Enable Digital Communication Through Biological Fluids”. Oral presentation.
161. Venanzi, M.; Cavalieri, F.; Cimino, R.; Gatto, E.; Savioli, M. Interfaces, Santa Margherita di Pula (CA), Italy, 21-25/09/2021. “Peptides on surfaces: where the interface matters”. Oral.
162. Vettori, I.; Bassu, G.; Macchiagodena, M.; Paglia, M.; Fratini, E. Interfaces conference Pula (CA), 21-25/09/2021. “Hydrogels improvements through freeze-casting and anti-freezing additives”. Poster.
163. Vettori, I.; Bassu, G.; Macchiagodena, M.; Paglia, M.; Fratini, E. ACS Fall, Atlanta (Georgia, U.S.), 22-26/08/2021. “Hydrogels improvements through freeze-casting and anti-freezing additives”. Oral presentation.
164. Zendrini, A. Showcase of International collaborative projects and networks on Extracellular Vesicles. 2nd EVIta Symposium, Lucca, Italy, 20-22/09/2021. “BOW: Biogenic Organotropic Wetsuits”. Oral presentation.
165. Zendrini, A.; Alacqua, S.; Previcini, V.; Todaro, F.; Martini, G.; Ricotta, D.; Bergese, P.; Radeghieri, A. 2nd EVIta Symposium, Lucca, Italy, 20/09-22/09/2021. “Specific antithrombin glycoforms adsorb onto plasma extracellular vesicles”. Oral presentation.
166. Baglioni, P. 95th JSCM Anniversary Conference, Tokyo (Giappone), 22-28/10/2022. “Colloid and

Surface Chemistry for the Conservation of Cultural Heritage". Keynote lecture.

167. Baglioni, P. Apache project dissemination, Porto Alegre (Brasile), 02-12/04/2022. "New green materials for VOCs removal". Invited lecture.
168. Baglioni, P. Autoorg 2022, Porto Alegre (Brasile), 31/10-07/11/2022. "Structure and Dynamics of Gels for the Preventive Conservation of Art". Plenary lecture.
169. Baglioni, P. Cooperazione bilaterale italo-francese nelle scienze per il patrimonio culturale, Roma, 15/09/2022. "Materiali e tecnologie verdi per la conservazione del patrimonio culturale". Invited lecture.
170. Baglioni, P. McGee Lecture, Richmond (USA), 27-30/04/2022. "New methods and materials for the conservation of cultural heritage from Renaissance frescos to modern & contemporary art". Keynote lecture.
171. Baglioni, P. Nano-systems research and application on cultural heritage, Lisbona (Portogallo), 15-17/05/2022. Invited lecture.
172. Baglioni, P. Nano systems: research and applications on cultural heritage, Parigi (Francia), 17-18/11/2022. "Nano- Science and its contribution to the conservation of Cultural Heritage". Invited lecture.
173. Baglioni, P. Polymer Networks Group 2022, Roma, 12-16/06/2022. Plenary session.
174. Balestri, A.; Montis, C.; Lonetti, B.; Harrisson, S.; Farias-Mancilla, B.; Berti, D. Macrogiovani 2022, Aula Magna, University of Florence, 16-17/06/2022. "New amphiphilic block copolymers as stabilizers for lipid drug delivery nanoparticles". Oral presentation.
175. Bassotti, E.; Telling, M.; Gabrielli, S.; Paradossi, G.; Chiessi, E. "Structure and dynamics of biopolymers in the amorphous state at low hydration"PNG 2022, Rome (Italy), 12-16/06/2022. Poster.
176. Bassu, G.; Laurati, M.; Fratini, E. 36th Conference of the European Colloid and Interface Society 04-09/09/2022. "Confining effects of transparent PEG hydrogels on microgel transport". Poster.
177. Bassu, G.; Laurati, M.; Fratini, E. PiCSU Chemistry PhD Symposium Firenze (FI), 19-21/01/2022. "Poly(ethylene glycol)-based hydrogels as transparent porous network for diffusivity studies (Picsu)". Oral presentation.
178. Bassu, G.; Laurati, M.; Fratini, E. Polimer Networks Group Rome (RM), 12-16/06/2022. "Micro-gel in transparent porous hydrogel: synthesis, morphological characterization, and diffusivity studies". Oral presentation.
179. Bassu, G.; Laurati, M.; Fratini, E. XLVIII Congresso Nazionale di Chimica Fisica Genova (GE), 04-07/07/2022. "Diffusive transport of micro-gel in transparent micro-sized porous hydrogel". Oral presentation.
180. Berti, D. National School of Nanomedicine, CNR, Rome, 08/06/2022. "Nanoparticles meet Organized soft assemblies: Challenges and opportunities for the biomedical field". invited lecture.
181. Berti, D.; Cardellini, J.; Caselli, L.; Montis, C. 51th Conference of the German Colloid Society, Berlin (Germany), 28-30/09/2022. "Membrane Phase Drives the Assembly of Gold Nanoparticles on Biomimetic Lipid Bilayers". Invited Keynote Lecture.
182. Bolzoni, F.; Cabrini, M. Giornata di Studio AIM: Il ruolo dei materiali nell'economia dell'idrogeno,. 27/01/2022. Oral presentation.
183. Cabrini, M.; Carugo, F.; Carozza, A.; Lorenzi, S.; Pastore, T.; Barbieri, G.; Cognini, F.; Moncada, M. Stainless Steels, Duplex & Maraging. Precipitaton Hardenable Stainless Steels, Bardolino (Verona), 15/06/2022. "Effect of macro and microstructural features on the corrosion behavior of additive manufactured alloy 625". Oral presentation.
184. Cabrini, M.; Lorenzi, S.; Coffetti, D.; Coppola, L.; Pastore, T. XIII INSTM Conference, Sestriere (TO), 23-26/01/2022. "Effect of reversible and irreversible traps on hydrogen diffusion in pipeline steels". Oral presentation.
185. Cancelliere, R.; Micheli, L.; Suffredini, E.; Bellucci, S.; Betta, G.; Ferrigno, L.; Maffucci, A.; Miele, G. 21a Conferenza Nazionale Sensori e Microsistemi, AISEM 2022, 10-11/02/2022. "Coronavirus label-free immunosensor: preliminary results". 10-11/02/2022. Poster.
186. Capsoni, D.; Fusaro, C.; Bruni, G.; Milanese, C.; Berbenni, V.; Galinetto, P.; Albini, B.; Boiocchi, M.; Conti, D.M. XLVIII Congresso Nazionale di Chimica Fisica, Genova (GE), 04-07/07/2022. "Optimizing the electrochemical performances of ZnS anodes for SIBs". Poster.
187. Cardellini, J.; Caselli, L.; Lavagna, E.; Salassi, S.; Montis, C.; Rossi, G.; Berti, D. EuChemS Chemistry Congress, Lisbon, 28/08-1/09 2022. "Membrane Phase Drives the Assembly of Gold Nanoparticles on Biomimetic Lipid Bilayers". Oral presentation.
188. Cardellini, J.; Caselli, L.; Montis, C.; Berti, D. Italia Soft Days 2022, Bari, 29-30/09/2022. "Membrane Phase Drives the Assembly of Gold Nanoparticles on Biomimetic Lipid Bilayers". Oral presentation.

189. Carucci, C.; Pablos, J.L.; González, B.; Izquierdo-Barba, I.; Colilla, M.; Piludu, M.; Monduzzi, M.; Salis, A.; Vallet-Regí, M. XLVIII National Congress of Physical Chemistry, Physical Chemistry,and the Challenges of the Ecological Transition, 04-07/07/2022. "Immobilization of enzymes onto mesoporous silica nanoparticles to combat antibiotic resistance". Oral presentation.
190. Carucci, C.; Scalas, N.; Sechi, G.; Tozzi, M.; Piludu, M.; Monduzzi, M.; Salis, A. Biological Surfaces and Interfaces: Forces at biological interfaces, FEBS 2022, 19-24/06/22. "Physico-chemical strategies to improve antibacterial drug delivery systems". Oral presentation.
191. Carugo, F.; Barbieri, G.; Cabrini, M.; Cognini, F.; Lorenzi, S.; Moncada, M.; Pastore T. XIII INSTM Conference, Sestriere (TO), 23-26/01/2022. "Metallurgic defects and corrosion behavior af alloy 625 obtained by means of metal fused filament fabrication". Oral presentation.
192. Caselli, L.; Cardellini, J.; Montis, C.; Ridolfi, A.; Valle, F.; Brucale, M.; Bergese, P.; Berti, D. Japan Colloid Lecture, 08/02/2022. "Nanoparticles meet organized lipid assemblies: challenges and opportunities for the biomedical field". Invited Plenary Lecture.
193. Caselli, L.; Ridolfi, A.; Cardellini, J.; Paolini, L.; Zendrini, A.; Radeghieri, A.; Brucale, M.; Valle, F.; Montis, C.; Berti, D.; Bergese, P. ISEV Meeting 2022, Lyon, France, 25-29/05/2022. "Detecting the collective nanomechanical fingerprint of EV populations by Colloidal NANoplasmonics (CONAN)". Oral presentation.
194. Caselli, L.; Ridolfi, A.; Cardellini, J.; Sharpnack, L.; Paolini, L.; Brucale, M.; Valle, F.; Montis, C.; Bergese, P.; Berti, D. ACS Fall 2022, 21-26/08/2021. "Probing the mechanical properties of synthetic and biogenic nanosized lipid vesicles with a plasmon-based nanoruler". Oral presentation.
195. Chelazzi, D. APACHE 2022 Symposium, Federal University of Rio Grande do Sul, Cultural Center, Porto Alegre, RS, Brazil, 06/04/2022. "New materials and methods for the preventive conservation of art". Invited speaker.
196. Chelazzi, D. International School of Cultural Heritage 2022, Fondazione Scuola dei beni e delle attività culturali (via del Collegio Romano 27-00186 Roma), 20/05/2022. "European best practices: case study". Invited speaker.
197. Chelazzi, D. Workshop "Active & intelligent Packaging materials and display cases as a tool for preventive conservation of Cultural HEritage", Budapest, Main Hall - Hungarian National Museum, 1088 Budapest, Múzeum krt. 14–16, Hungary, 29/06/2022, evento di formazione e training del progetto H2020 APACHE (https://cordis.europa.eu/project/id/814496/it) aperto e diretto a end-users, professionisti e scienziati della conservazione. "Innovative "green" gels as new art cleaning pollutant absorbers in conservation". Organizzazione e partecipazione al workshop con oral presentation.
198. Chelazzi, D. Workshop "APACHE School", evento di formazione e training sui materiali e metodologie prodotti nel progetto H2020 APACHE ("Active & intelligent Packaging materials and display cases as a tool for preventive conservation of Cultural HEritage" https://cordis.europa.eu/project/id/814496/it) aperto e diretto a end-users, professionisti e scienziati della conservazione. Firenze, Auditorium Sant'Apollonia, 24-26/05/2022. Organizzazione del workshop e partecipazione diretta alle attività di "Practical demonstration" (24 maggio 14:00-17:00) e "Round Table" (26 maggio, 11:30-12:15). https://www.apacheproject.eu/apache-school/.
199. Chelazzi, D. Workshop dell'APACHE 2022 Symposium, Federal University of Rio Grande do Sul, Cultural Center, Porto Alegre, RS, Brazil, 07/04/2022. "Innovative "Green" Gels as New Pollutant Absorbers in Preventive Conservation". Invited speaker.
200. Chelazzi, D.; Cianci, C.; Poggi, G.; Modi, F.; Giorgi, R.; Laurati, M. E-MRS 2022 Spring Meeting Technical Sessions, virtual conference, 30/05-03/06/2022. "Composite colloidal dispersions for the consolidation of historical silk". Oral presentation.
201. Chelazzi, D.; Cianci, C.; Poggi, G.; Modi, F.; Giorgi, R.; Laurati, M. PNG 2022 Polymer Networks Group, Università La Sapienza, Roma, Piazzale Aldo Moro 5, 12-16/06/2022. "Green" fibroin/nanocellulose colloidal dispersions for the consolidation of aged silk". Oral presentation.
202. Chelazzi, D.; Cianci, C.; Poggi, G.; Modi, F.; Giorgi, R.; Laurati, M. XLVIII Congresso Nazionale di Chimica Fisica "La Chimica Fisica e le Sfide della Transizione Ecologica", Genova, 04-07/07/2022. "Fibroin and nanocellulose composite films as new adhesives for aged textiles". Oral presentation.
203. Conti, D.M; Bruni, G.; Galinetto, P.; Albini, B.; Boiocchi, M.; Capsoni D. XLVIII Congresso Nazionale di Chimica Fisica, Genova (GE), 04-07/07/2022. "Self-standing electrospinned carbon nanofibers anodes: influence of carbonization temperature on the electrochemical performances". Poster.
204. Conti, D.M; Bruni, G.; Girella, A.; Spada, D.; Galinetto, P.; Albini, B.; Boiocchi, M.; Quinzeni, I.; Capsoni, D. XLVIII Congresso Nazionale di Chimica Fisica, Genova (GE), 04-07/07/2022.

"Optimizing the electrochemical performances of Na3MnZr(PO4)3 and Na3MnTi(PO4)3 cathodes for SIBs: the role of conductive carbon amount in tape-casting and self-standing electrodes". Poster.

205. Coppola, C.; Pecoraro, A.; Muñoz-García, A.B.; Infantino, R.; Dessì, A.; Reginato, G.; Basosi, R.; Pavone, M.; Sinicropi, A. XLVIII Congresso Nazionale della Chimica Fisica, Genova (GE), 04-07/07/2022. "Density Functional Theory study on the electronic properties of a novel TPA and PTZ-based hole transport material and its interfacial features with MAPI perovskite". Oral presentation.
206. Coppola, C.; Pecoraro, A.; Muñoz-García, A.B.; Infantino, R.; Dessì, A.; Reginato, G.; Basosi, R.; Pavone, M.; Sinicropi, A. XL Convegno Nazionale della Divisione di Chimica Organica della SCI - CDCO 2022, Palermo (PA), 11-15/09/2022. "A first-principles study on the electronic properties of a novel TPA and PTZ-based hole transport material and its interfacial features with MAPI perovskite". Oral presentation.
207. Cuomo, F.; Trivisonno, M.C.; Iacovino, S.; Falasca, L.; Messia, M.C.; Marconi, E. 12° convegno AISTEC: Cereali e Scienza: resilienza, sostenibilità e innovazione, Portici (NA), 15-17/06/2022. "Riutilizzo sostenibile delle trebbie di birra per la produzione di pasta ad alto contenuto proteico e di fibre". Oral presentation.
208. d'Ettorre, A; Avelar, M.; Parisi, M. L.; Basosi, R.; Santucci, A.; Sinicropi, A. DBCF Ph.D. Day 2022, Siena (SI), 04/02/2022. "MD and QM/MM investigation of long-range electron transfer pathways in bacterioRhodopsin mutants as photosensitizers for TiO2 semiconductor". Poster.
209. Ferraro, G.; Fratini, E.; Assanelli, G.; Notari, M.; Baglioni, P. XLVIII National Congress of Physical Chemistry, Genova, 04-07/07/2022. "Lacunarity as image descriptor for the evaluation of the dispersion degree of carbonaceous substrates in lubricants". Oral presentation.
210. Ferraro, G.; Susini, V.; Rossi, V.L.; Sanesi, A.; Fratini, E. E-MRS 2022 Spring Meeting. Virtual Conference, 30/05-03/06/2022. "One-pot preparation of amino acids-doped carbon nanostructures as fluorescent pH sensors". Oral presentation.
211. Ferraro, G.; Susini, V.; Rossi, V.L.; Sanesi, A.; Fratini, E. XLVIII National Congress of Physical Chemistry, Genova, 04-07/07/2022. "Use of carbon-based nanodots as fluorescent probes in pH sensors: direct monitoring of bacterial growth". Poster.
212. Fichera, L.; Li-Destri, G.; Tuccitto, N. XLVIII National Conference of the Physical Chemistry Division of the Italian Chemistry Society, Genova, 2022. "Fluorescent Carbon Dots Enable Secure Communication Among Connected Implanted Medical Devices". Oral presentation.
213. Fratini, E. CHESS School, virtual event, February 2022. "Introduction to Neutron Scattering". Oral presentation.
214. Frosi, I.; Milanese, C.; Colombo, R.; Papetti, A. V edizione del simposio "Argomenti di Nutraceutica" Satellite SINut, Pavia, 22/01/2022. "Prodotti di scarto della filiera cerealicola come fonti di nutraceutici ad attività antiglicante". Oral presentation.
215. Illankoon, W.A.M.A.N.; Milanese, C.; Girella, A.; Medina-Llamas, M.; Magnani, G.; Pontiroli, D.; Riccò, M.; Collivignarelli, M.C.; Sorlini, S. 29th European Biomass Conference, virtual event, 9-12/05/2022. "Biochar derived from the rice industry by-products as sustainable energy storage material". Poster.
216. Kipyator, M.J.; Rossi, F.; Parisi, M.L.; Sinicropi, A. DBCF research day 2002, Siena (SI), 28/06/2022. "Harmonization and extension of life cycle assessment studies focused on perovskite/silicon tandem solar cells". Poster.
217. Loffredo, M.R.; Troiano, C.; Bobone, S.; Casciaro, B.; Mangoni, M.L.; Stella, L. Pre-clinical development of antimicrobial peptides. International Workshop and Symposium, Strasbourg, 13/05/2022. "Quantification of the association of antimicrobial peptides with live bacterial cells: what have we learned?". Invited lecture.
218. Lucchesi, G.; Barletti, B.; Errico, S.; Chiti, F.; Grasso, G.; Zasloff, M.; Caminati, G. XLVIII National Congress of Physical Chemistry Physical Chemistry and the Challenges of the Ecological Transition, Genoa (Italy), 04-07/07/2022. "Aggregation behaviour of trodusquemine and its interaction with biomimetic membranes". Poster.
219. Lucchesi, G.; Giordano, D.; Fratini, E.; Caminati, G. XLVIII National Congress of Physical Chemistry Physical Chemistry and the Challenges of the Ecological Transition, Genoa (Italy), 04-07/07/2022. "New lead-free perovskite: synthesis and characterization of Mg-based solar cells". Oral presentation.
220. Lucchesi, G.; Giordano, D.; Muzzi, B.; Caminati, G. First Symposium for Young Chemists: Innovation and Sustainability, Rome (Italy), 20-23/06/2022. "Synthesis and characterization of a new lead-free perovskite solar cell". Keynote oral communication.

221. Lucchesi, G.; Giordano, D.; Muzzi, B.; Caminati, G. International workshop on Plasmonics, Turin (Italy), 07-08/07/2022. “Silver Nanowires Plasmon Enhancement of Photovoltaic Efficiency in Lead-Free Perovskite Solar Cells”. Poster.
222. Mateos, H. 3rd NALS (Nanomaterials Applied to Life Sciences 2022) International Conference, Santander, Spain, 27-29/04/2022. “Is L1CAM a good marker for neuronal exosomes?”. Poster.
223. Mateos, H.; Mallardi, A.; Palazzo, G. 11th Colloids, Lisbon, Portugal, 12-15/06/2022. “Surfactant Interactions with Feline Coronavirus”. Oral presentation.
224. Mazzuca, C.; Severini, L.; D'Andrea, A.; Domenici, F.; Paradossi, G.; Redi, M.; Dabagov, S.; Hampai, D.; Guglielmotti, V.; Micheli, L.; Placidi, E.; Palleschi, A. 25th Polymer Network Group International Workshop, Roma, 12-16/06/2022. “From hydrogels to microbubbles: tailoring PVA networks into green application for cleaning of cultural heritage objects”. Oral presentation.
225. Messia, M.C.; Cuomo, F.; Quiquero, M.; Trivisonno M.C.; Falasca, L.; Miani, M.G.; Marconi, E. 12° convegno AISTEC Cereali e Scienza: resilienza, sostenibilità e innovazione, Portici (NA), 15-17/06/2022. “Integrazione di frazioni di germe di grano duro deoleato in formulazioni per pasta secca ad alto contenuto proteico e di fibre”. Poster.
226. Messina, G.M.L.; Campione, P.; Marletta G. 19th International Conference on Nanosciences & Nanotechnologies, Thessaloniki, Greece, 05-08/07/2022. “Electroactive polymer films for Biolelectronics: P3HT-MWCNT properties”. Poster.
227. Messina, G.M.L.; Marletta, G. Insplorion webinar, 04/03/2022. “Nanoplasmonic Sensing for smart biointerfaces”. Keynote presentation.
228. Milanese, C. Ciclo di incontri “Dalla crisi ambientale allo sviluppo sostenibile”, Collegio Borromeo, Pavia, 18/05/2022. “Produzione e stoccaggio di idrogeno verde”. Invited oral presentation.
229. Milanese, C.; Frosi, I.; Papetti, A.; Girella, A.; Berbenni, V.; Magnani, G.; Pontiroli, D.; Riccò, M. 3rd International Conference on Materials Science and Engineering, virtual event, 18-22/04/2022. “Energy storage in superactivated carbon from agrifood wastes”. Invited Oral presentation.
230. Montis, C.; Caselli, L.; Ridolfi, A.; Berti, D.; Nylander, T. ACS Fall 2022, 21-26/08/2021. “Lamellar and non-lamellar lipid films as synthetic models of biological membranes: the role of symmetry at nano-bio interfaces”. Oral presentation.
231. Musicò, M.; Zenatelli, R.; Romano, M.; Zendrini, A.; Cretich, M.; Urbinati, C.; Rusnati, M.; Pomarico, G.; Bergese. P.; Radeghieri, A. ESC Conference 2022, Szeged, Hungary, 26-30/06/2022. “Protein Corona and EV surface engineering”. Oral presentation.
232. Nieri, T.; Falsini, S.; Mugnai, L.; Papini, A.; Gonnelli, C.; Ristori, S. SYNC2022, Roma, 20-23/06/2022. “Preparation and administration of nanoparticles from plant polymers against grapevine phytopathogenic fungi”. Oral presentation.
233. Palazzo, G. 11th Colloids, Lisbon, Portugal, 12-15/06/2022. “Solution microstructure of the polymeric solubilizer Soluplus®”. Oral presentation.
234. Palchetti, I.; Tadini-Buoninsegni, F. 72nd Annual Meeting of the International Society of Electrochemistry, Jeju Island (Korea), hybrid conference, 29/08-03/09/2021. “A bioelectrochemical approach for monitoring drug interactions with membrane transporters”. Poster.
235. Papetti, A; Frosi, I.; Milanese, C. Global Summit on Food Science and Technology (GSFST) 2022, Dubai & Virtual, 17-19/03/2022. “Recovery of bioactive compounds from corn (Zea mays L.) wastes”. Oral presentation.
236. Porcheddu, A.; Delogu, F.; Colacino, E. 10th International Conference on Mecanochemistry and Mechanical Alloying, Cagliari, 06-10/06/2022. “Mechanochemistry: Modern Technologies and Ancient Rites”. Oral presentation.
237. Radeghieri, A. XVII Congresso Nazionale SIES 2022, Roma, Italy, 31/03-02/04/2022. “Extracellular Vesicles – recent advances and perspectives”. Oral presentation.
238. Ridolfi, A.; Conti, L.; Brucale, M.; Frigerio, R.; Gori, A.; Cardellini, J.; Montis, C.; Berti, D.; Bergese, P.; Cretich, M.; Valle, F. ISEV Meeting 2022, Lyon, France, 25-29/05/2022. “High-throughput nanomechanical differentiation of lipoproteins and extracellular vesicles”. Oral presentation.
239. Ristori, S.; Falsini, S.; Clemente, I.; Nieri, T.; Mugnai, L.; Schiff, S.; Gonnelli, C. Symposium in the honour of Isabelle Grillo, Grenoble, France, 20-22/04/2022. “Engineered soft-matter nanosystems for delivery of bioactive molecules at large scale”. Oral presentation.
240. Rossi, F.; Basosi, R.; Sinicropi, A.; Parisi, M.L. XVI Convegno della Rete Italiana di LCA, Palermo (PA), 22-24/06/2022. “End-of-life scenarios of a Parabolic Concentrated Solar Power system”. Oral presentation.
241. Rossi, F.; Parisi, M.L.; Basosi, R.; Sinicropi, A. SETAC Europe 32 Annual Meeting, Copenhagen (DK), 15-19/05/2022. “Prospective LCA of perovskite solar cells for building integrated applications”.

Poster.

242. Schirone, D.; Olsson, U.; Gentile, L.; Palazzo, G. 36th Conference of the European Colloid and Interface Society, Chania, 04-09/09/2022. “Rheo-titration experiment for detection of optimum formulation conditions”. Poster.
243. Schirone, D.; Olsson, U.; Gentile, L.; Palazzo, G. Second national meeting of the Swedish Chemical Society, Linkoping, 20-22/06/2022. “Rheo-titration experiment for detection of optimum formulation conditions”. Oral presentation.
244. Stella, L. Biovaria 2022, Munich, 11-12/05/2022. “Targeting oncogenic phosphatase SHP2 by inhibiting its protein-protein interactions”. Oral presentation.
245. Stella, L. Regional Biophysics Congress 2022, Pécs, Hungary, 22-26/08/2022. “From liposomes to cells: filling the gap between biophysical and microbiological studies of the activity and selectivity of host-defense peptides”. Invited plenary lecture.
246. Tadini-Buoninsegni, F; Sfragano, P.S.; Palchetti, I. 73rd Annual Meeting of the International Society of Electrochemistry, online.event, 12-16/09/2022. “A biosensing approach based on solid supported membrane to monitor the activity of membrane transporters”. Oral presentation.
247. Tadini-Buoninsegni, F. 16th International Conference on Na,K-ATPase and Related Transport ATPases – P-Type ATPases in Health and Disease, The Banff Center, Banff, Alberta (Canada), 06-11/09/2022. “Recording the transport activity of P-type ATPases on solid supported membranes”. Invited Lecture.
248. Torsi, L. Advances in Surfaces, Interfaces and Interphases, online event, 15-18/05/2022. “Sensing at the zeptomolar concentration level with large area bioelectronic interfaces”. Invited Plenary Presentation.
249. Torsi, L. BioEL 2022 - 7th International Winterschool on Bioelectronics, Kirchberg (Austria), 12-19/03/2022. “Sensing at the zeptomolar concentration level with large area bioelectronic interfaces”. Invited Plenary Presentation.
250. Torsi, L. Exner Medal 2021 (Postponed 2022), Vienna (Austria), 18/05/2022. “Single-molecule detection with a large transistor endows a clinician with the attacker advantage”. Plenary Presentation.
251. Torsi, L. LOPEC 2022, Monaco di Baviera (Germania), 22-24/03/2022. “Sensing at the zeptomolar concentration level with large area bioelectronic interfaces”. Invited Plenary Presentation.
252. Torsi, L. MENA International conference on Biosensors 2021, Riyadh (Saudi Arabia), online event, 24-25/02/2022. “Ultimately sensitive potentiometric organic bioelectronic sensors”. Invited Lecture.
253. Torsi, L. Symposium Exner Medal, Vienna (Austria), 16/05/2022. “From Bench to Bedside – Biotech not lost in translation!”. Plenary Presentation.
254. Torsi, L. Workshop LOPEC 2022|h-ALO, Monaco di Baviera (Germania), 23/03/2022. “The single molecule bio-electronic smart system array for clinical testing”. Pitch Oral Presentation.
255. Venanzi, M.; Savioli, M.; Gatto, E.; Cimino, R.; Bocchinfuso, G.; Cavalieri, F.; Ferrante Carrante, N.; Placidi, E.; Garay-Peres, H.; Lopez-Abad, M.; Lasa Musacchio, A.; Del Carmen Dominguez-Horta, M. 17th Naples Workshop on Bioactive Peptides, Naples, 16-18/06/2022. “Aggregation properties of a therapeutic peptide for rheumatoid arthitis: a spectroscopic and molecular dynamics study.” Poster.
256. Vettori, I.; Macchiagodena, M.; Bassu, G.; Fratini, E.; Pagliai, M.; Baglioni, P. XXXVIII Reuniòn Bienal RSEQ Granada (Spain), 27-30/06/2022. “From HEMA monomers to poly-HEMA systems simulations”. Oral presentation.
257. Vettori, I.; Macchiagodena, M.; Bassu, G.; Fratini, E.; Pagliai, M.; Baglioni, P. Workshop della Divisione di Chimica Teorica e Computazionale – DCTC, Firenze (FI), 08/04/2022. “Water role in hydrogels: from solvent-monomer interactions to water states in poly-HEMA systems”. Poster.
258. Vettori, I.; Macchiagodena, M.; Bassu, G.; Fratini, E.; Pagliai, M.; Baglioni, P. 1° PhD in Chemical Sciences at UniFi - PiCSU Symposium, Firenze (FI), 19-21/01/2022. “Monomeric 2-hydroxyethyl methacrylate (HEMA) and acrylic acid (AA): structural influences on solute-solvent interactions and spectroscopic properties”. Oral presentation.
259. Zendrini, A.; Guerra, G.; Sagini, K.; Vagner, T.; Di Vizio, D.; Bergese, P. ISEV Meeting 2022, Lyon, France, 25-29/05/2022. “At which size does the membrane-to-lumen protein partition switch?”. Oral presentation.
260. Zendrini, A.; Guerra, G.; Sagini, K.; Vagner, T.; Di Vizio, D.; Bergese, P. 2nd Lugano Exoday, Lugano, Switzerland, 13/04/2022. “On the surface-to-bulk partition of proteins in extracellular vesicles”. Oral presentation.

Theses (undergraduate, master and PhD)

U.O. Bari

Master in Chemistry (Laurea magistrale)

- Blasi, F. “Interactions of detergent formulations with phospholipid vesicles as model for surfactants potential virucidal activity” (2021)
- Laera, C. “Early Detection of Xylella fastidiosa with PoC” (2022)

PhD in Chemical and Molecular Sciences

- Mateos, H. “Surfactant-Polymers Interactions at interfaces” (2020)
- Lapenna, A. “Tools for the design of new colorimetric assays: gold nanoparticles and plasma immobilised enzymes” (2021)
- Sarcina, L. “Disposable Bio-electronic HIV Sensor Powered by Bio-Fuel-Cell” (2022)
- Tartaro, G. “Properties in microemulsions: from composition to microstructure” (2022)

Post-Doc

- Imbriano, A. “SiMBiT-Single molecule bio-electronic smart system array for clinical testing”

U.O. Bergamo

Bachelor in Engineering for Technologies of Health (Laurea triennale)

- Bonaccorso, M. “Caratterizzazione meccanica del poliuretano” (2020)
- Degli Agosti, M. “Rivestimenti osteoconduttivi per l’artoplastica totale dell’anca” (2020)
- Maffeis, A. “Impiego dell’Additive Manufacturing per Ti6Al4V in ambito biomedico” (2020)
- Milesi, S. “Ingegneria dei tessuti e ruolo dei biomateriali per la rigenerazione del sistema nervoso centrale (SNC)” (2020)
- Tiraboschi, C. “Dispositivi cardiaci: i casi di infezione a seguito di impianto pacemaker” (2020)
- Zanchi, L. “Innovazioni e applicazioni delle tecnologie additive nella protesi totale di ginocchio” (2020)

Bachelor in Building Engineering (Laurea triennale)

- Mazzoleni, M. “Analisi dei fenomeni di danneggiamento della fontana della Piazza Caduti 6 Luglio 1944 in Dalmine” (2021)

Bachelor in Mechanical Engineering (Laurea triennale)

- Pistacchio, C. “Failure analysis del pedana freno di una moto da enduro” (2020)
- Cattaneo, M.; Ferrari, S. “Studio tramite digital image correlation del comportamento meccanico di giunti saldati per fiction stir welding” (2021)

Master in Mechanical Engineering (Laurea magistrale)
- Borgonovo, A. “Studio della diffusione dell’idrogeno in acciai di grado x65 sottoposti a carico ciclico” (2020)
- Sala, S. “Studio della corrosione ad alte pressioni parziali di CO2” (2020)
- Agazzi, L. “Comportamento a corrosione e caratterizzazione microstrutturale di leghe di nichel 625 prodotte per additive manufacturing” (2021)
- Capelli, D. “Comportamento a corrosione di una lega di alluminio ottenuta mediante tecnologia SLM” (2021)
- Cortinovis, N.; Trussardi, G. “Studio del comportamento a corrosione della lega Ti6Al4V per applicazioni biomedicali: effetto della tecnologia additiva” (2021)
- Galizzi, N. “Corrosione sotto sforzo di leghe di alluminio indurenti per precipitazione saldate tramite friction stir welding” (2021)
- Gritti, L. “Determinazione della fugacità di idrogeno e del coefficiente di diffusione mediante permeazione elettrochimica in diversi acciai X65” (2021)
- Maggi, T.; Cogni, G. “Correlazione tra fugacità di idrogeno gassoso e sovratensione elettrochimica” (2021)
- Marchesi, G. “Effetto della velocità di condensazione sulla corrosione in CO2 umida” (2021)
- Orlando, S.; Perini, G. “Effetto delle nanocariche sull’effetto barriera di rivestimenti a base epossidica” (2021)

Master in Engineering of Building (Laurea magistrale)
- Quartararo, D.; Viganò, G. “Corrosione nei macrodifetti delle strutture in calcestruzzo” (2021)

PhD in Engineering and Applied Science
- Crotti, E. “Sustainable Alkali-Activated Slag Mortars: Study of durability and smart properties” (2021)

U.O. Bologna

Master in Industrial Chemistry (Laurea magistrale)
- Dos Anjos Timas, B. “Applicazione di tecniche untarget molecolari e chimiche per la ricerca di allergeni vegetali in alimenti” (2020)
- Palazzetti, C. “Attività enzimatica ed inibizione della tirosin-fosfatasi A (MptpA) di Mycobacterium tuberculosis in funzione del pH” (2021)

Master in Molecular and Industrial Biotechnology (Laurea Magistrale)
- Girella, A. “Comportamento catalitico della tirosin-fosfatasi di Mycobacterium tuberculosis (MptpA) e di alcune varianti sito-specifiche” (2020)
- Guadalupi, C. “Identificazione simultanea di allergeni vegetali in matrici alimentari mediante real-time pcr e next generation sequencing” (2020)
- Lapenna, A. “Purificazione e caratterizzazione cinetica della DNA Polimerasi del virus responsabile della Peste Suina Africana (2020)
- Pasti, A.P. “Analisi cinetica e strutturale delle transizioni allosteriche pH-dipendenti in lattato deidrogenasi eucariotiche” (2020)

- Cimone, V. “Analisi del comportamento cinetico della tirosin-fosfatsi A di Mycobacterium tuberculosis (MptpA) in funzione del pH” (2021)
- Cinti, N. “Engineering and design of an artificial protein platform for a de novo enzyme selection” (2021)
- Puglisi, A. “Produzione di un potenziale vaccino termostabile contro la COVID-19 e analisi della termostabilita' di enzimi indotta da saccarosio e trealosio” (2021)
- Ruffolo, F. “Espressione in E. coli, purificazione e caratterizzazione cinetica della lattato deidrogenasi A umana” (2021)
- Simongini, M. “Improving enzymes' stability by chemical and protein engineering strategies” (2021)
- Baco, S. “Massively parallel precision editing of natural sequence variation to identify new mechanisms and genetic targets that alleviate cellular ER stress” (2022)
- Bartolini, G. “Strategies to produce prenylated flavonoids in Saccharomyces cerevisiae” (2022)
- Cibin, I. “Cinnamic and p-coumaric acid degradation in Yarrowia lipolytica” (2022)
- Maltoni, G. “Ottimizzazione del processo di produzione e purificazione della proteina chimerica CRM197-RBD, un potenziale componente di vaccini contro SARS-CoV-2” (2022)
- Scutteri, L. “Potenziamento dell’attività antitumorale di CRM197 tramite innesto di attività proteasica nei confronti di HB-EGF” (2022)
- Sordi, S. “Isolamento e caratterizzazione della lattato deidrogenasi umana in forma monomerica” (2022)

U.O. Brescia

Bachelor in Biomedical Laboratory Techniques (Laurea Triennale)

- Ioli, M. “Sviluppo di un metodo per monitorare la captazione di nanomedicinali mediante analisi metabolica cellulare in real-time” (2021)

Bachelor in Biotechnology (Laurea triennale)

- Letti, G. “Extracellular vesicles from Ascaris suum: biophysical and immunomodulatory properties” (2020)

Master in Medical Biotechnology (Laurea magistrale)

- Alacqua, S. “Preliminary study of protein corona of extracellular vesicles” (2020)
- Benedetti, P. “Field flow fractionation methods in extracellular vesicles research” (2020)
- Rinaldi, D. “Interaction of human plasma with nanoparticles from daily life plastic items” (2021)
- Pedrali, D. “Valutazione dell’impatto di vescicole extracellulari isolate in media di coltura su cellule stromali mesenchimali umane” (2022)

Master in Medicine (Laurea magistrale)

- Cherubini, F. “OrigEV: muscular exosomes characterization in patients with intensive care unit-acquired weakness” (2022)

PhD in Precision Medicine

- Romano, M. “Bioevaluation of synthetic and biogenic nano-building blocks for the development of hybrid nanomedicines” (2022)

PhD in Technology for Health

- Paiardi, G. “Glycan-protein interactions in pathological processes: development of new molecular and cellular models for glycobiology-oriented studies” (2021)

Post-Doc

- Paolini, L. “evFOUNDRY – The Extracellular Vesicle Foundry”
- Zendrini, A. “BOW – Biogenic Organotropic Wetsuits”
- Romano, M. “Development of a biotechnological nanoparticle platform for the delivery of antitumor therapies using Patient Derived-organoid library of Breast cancer”

U.O. Cagliari

Bachelor in Biotechnology (Laurea triennale)

- Contu, E. “Studio comparativo di formulazioni liquido cristalline non lamellari per la somministrazione orale” (2021)
- Medda, M. “Effetto del taurocolato di sodio e dello Span 80 sulle proprietà chimico fisiche delle dispersioni acquose di monooleina contenenti antiossidanti e fluorofori” (2021)

Bachelor in Chemistry (Laurea triennale)

- Scalas, N. “Adsorbimento e rilascio del sulfametizolo da nanocarriers di silice come sistema di drug delivery per contrastare la resistenza antibiotica” (2020)

Master in Chemistry (Laurea magistrale)

- Mura, M. “Nanoantibiotic Design of multifunctional MSN nanosystems containing both antibiotic and copper ions to combat bone infection” (2020)
- Musu, G. “Characterization of a mixture of thermosensitive polymers based on Pluronic F127 and Sodium-Carboxymethylcellulose: effect of sodium salts on Sol-Gel transitions” (2020)
- Collu, A.D. “Tailor-made composite oxides as next-generation photocatalysts for solar energy capture” (2021)
- Russo, G. “Effect of added electrolytes on the Sol-Gel transition of thermosensitive polymeric systems” (2021)
- Sechi, G. “Poly-L-lysine functionalised silica nanoparticles as a pH responsive drug delivery system for quercetin release” (2021)

PhD in Chemical Science and Technology

- Fornasier, M. “Biosurfactant based liquid crystalline nanoparticles for nanomedicine applications” (2021)
- Delpiano, G.R. “Synthesis and characterization of nanostructured adsorbents for the removal of inorganic and organic pollutants from water” (2022)

- Tocco, D. “The importance of Laccase immobilisation in Biocatalysis: towards biomass pre-treatment” (2022)

Post Docs
- Pira, A. “The Immobilisation of Enzymes for Biocatalytic Flow Reactors” (03/2021 - 03/2022)

U.O. Campobasso

Bachelor in Food Sciences and Technology (Laurea triennale)
- Aprile, A. “Ruolo di molecole bioattive antiossidanti in prodotti alimentari a base di olio extravergine di oliva” (2021)
- Patriarca, E. “Rivestimenti edibili per preservare la shelf life dei prodotti alimentari” (2022)

Bachelor in Biological Sciences (Laurea triennale)
- Nigro, P. “Nanoparticelle ibride di acido poli(lattico-co-glicolico) e lipidi per la somministrazione prolungata di camptotecina nel carcinoma ovarico” (2022)

Bachelor in Medical Engineering (Laurea triennale)
- De Nigris, A. “Messa a Punto e Caratterizzazione di Nanoparticelle di Afnio come Amplificatori del Segnale Radioterapico” (2021)
- Leoni, A. “Proprietà dei biomateriali da utilizzare nei processi di bioprinting” (2021)

Master in Biology (Laurea magistrale)
- Di Tella, D. “Messa a punto e caratterizzazione chimico-fisica di nanoparticelle ibride per la rigenerazione cellulare” (2021)

Master in Food Sciences and Technology (Laurea magistrale)
- Chirascu, C. “Effetto sinergico antiossidante indotto da vitamina C e vitamina E in emulsioni di olio extravergine di oliva” (2020)
- Piacquadio, M. “Studio delle proprietà antiossidanti di molecole bioattive addizionate ad emulsioni di olio extravergine di oliva” (2020)

Master in Health Professions of Prevention Sciences (Laurea magistrale)
- Spaziani, A. “Da sottoprodotto a materia prima: il recupero delle trebbie di birra nell’industria alimentare” (2022)

PhD in Agriculture, Technology and Biotechnology
- Cofelice, M. “Alginate-Based Nanodispersions to Assemble Coatings and Films for Food Applications” (2020)

U.O. Catania

Bachelor in Chemistry (Laurea triennale)

- Farina, R. “Preparazione di substrati per il sensing molecolare” (2020)
- Ferrara, I. “Auto-organizzazione di colloidi nanometrici alle interfacce liquide” (2020)
- Giannone, A. “Studio di colloidi nanometrici all'interfaccia acqua/aria” (2020)
- Isidoro, F. “Studio di surfattanti rispondenti a stimoli luminosi” (2020)
- Leone, A. “Preparazione e studio di substrati polimerici elettroconduttori per applicazioni bioelettroniche” (2020)
- Caccetta, G. “Orientazione di proteine modello: uno studio di nanoplasmonica” (2021)
- Cafà, F. “Processi di adsorbimento di biomolecole su superfici chelanti” (2021)
- Calascibetta, E. “Effetto della forza ionica sull'auto-organizzazione di nano-colloidi all'interfaccia acqua-aria” (2021)
- Dativo, G. “Monostrati di Langmuir fotosensibili: transizioni e reversibilità” (2021)
- Fabiano, L. “Processi cinetici di adsorbimento di biomolecole su superficie” (2021)
- Giaquinta, R. “Effetto della curvatura su scala nanometrica sull'auto-organizzazione di film di polimeri semicristallini” (2021)
- Laferrera, C. “Studio delle proprietà Meccaniche di superfici biofunzionalizzate” (2021)
- Laudani, F. “Processi di autoorganizzazione in monostrati di Langmuir fotosensibili” (2021)
- Longo, C. “Immobilizzazione spazialmente risolta di Fibronectina su superfici nanostrutturate funzionalizzate” (2021)
- Lucifora, G. “Cinetica di adsorbimento di biomolecole su superfici chelanti” (2021)
- Marino, M. “Studio Di Monostrati di Nanoparticelle all’Interfaccia Acqua-Aria” (2021)
- Pettiglione, A. “Caratterizzazione Interfacciale di Surfattanti Fotosensibili” (2021)
- Randisi, N. “Processi di nanoconfinamento e di orientazione di proteine modello” (2021)
- Savastra, C. “Film ultrasottili di copolimeri a blocchi su substrati con curvatura nanometrica” (2021)
- Thevarajah, A. “Studio di adsorbimento di biomolecole su superfici nanostrutturate” (2021)
- Fiore, K. “Metodologie di funzionalizzazione per l’ottenimento di biosuperfici intelligenti” (2022)
- Giustolisi, F. “Preparazione di Film Sottili Polimerici su Substrati Nanoporosi” (2022)
- Mancini Alaimo, S. “Structure of polyelectrolyte multilayers through Surface Plasmon Resonance” (2022)

Bachelor in Materials Science (Laurea triennale)

- Campione, P. “Studio di compositi polimerici di P3HT-MWCNT elettroattivi per la bioelettronica” (2021)
- Corsaro, P. “Preparazione e caratterizzazione di nanocompositi ibridi di PEDOT-PSS per biointerfacce elettriche” (2021)
- Cucuzza, E. “Metodologie di funzionalizzazione di superfici per il riconoscimento molecolare” (2021)

Master in Chemical Sciences (Laurea magistrale)

- Amata, D. “Studio dei Processi di Isomerizzazione Interfacciale in Monostrati di Langmuir Fotosensibili” (2022)

Master in Materials Chemistry (Laurea magistrale)

- Contino, T. “Caratterizzazione di Struttura e Forza di Nano-Colloidi 2D su Superfici e Interfacce Liquide” (2021)
- Mangano, M. “Effetti combinati di energia libera di superfice e curvatura nanometrica sull’auto-organizzazione di film sottili di poli(3-esiltiofene)” (2021)
- Pappalardo, P. “Proprietà e Stabilità di Monostrati di Langmuir Fotosensibili” (2022)

PhD in Materials Science and Nanotechnology

- Fichera L. “Nanomaterials as information particles for application in wave-denied environments” (2022)
- Ruffino, R. “Self-assembly of soft matter under 2D nanoconfinement” (2022)

U.O. Firenze

Bachelor in Biotechnologies (Laurea triennale)

- Africano, A. “Sintesi di nanocapsule biocompatibili di lignina, loro caratterizzazione e studio del loro uptake in vivo come spray fogliare” (2020)
- Ceccherini, S. “Studio dell'effetto di microplastiche trasportate in atmosfera su Tillandsia usneoides” (2021)
- Gori, G. “Nanovettori lipidici derivanti da Nannochloropsis Oceanica come carrier di antiossidanti naturali” (2021)
- Korotkikh, E. “Interazione di proteine amiloidi con sistemi biomimetici contenenti Trodusquemina” (2021)
- Marini, S. “Caratterizzazione di nanoparticelle di lignina contenenti olio di Neem e capsaicina” (2021)
- Masini, M. “Nanovettori di polimeri vegetali misti come strategia sostenibile per le colture vitivinicole” (2021)
- Ponticelli, L. “Nanocapsule di lignina ingegnerizzate come agenti antiparassitari” (2021)

Bachelor in Chemistry (Laurea triennale)

- De Santis, I. “Fasi lipidiche liotropiche come sistemi biomimetici per lo studio dell’interazione con nanoparticelle inorganiche” (2020)
- Farris, T. “Sintesi e caratterizzazione di organogel a base di olio di ricino” (2020)
- Grazi, P. “Nuovi stabilizzanti per dispersioni di mesofasi lipidiche di natura liquido-cristallina” (2020)
- Mascii, E. “Effetto della lunghezza di catena nella struttura e proprietà meccaniche di criogel a base PVA/PVA” (2020)
- Barielli, L. “Deposizione controllata di nanoparticelle d'oro su microsfere di polistirene” (2021)

- Bilardo, C. “Studio dell’interazione del gingerolo e della demetossicurcumina con un trasportatore di membrana” (2021)
- Cammarota, P. “Sviluppo di un sensore elettrochimico nanostrutturato per applicazioni di interesse ambientale” (2021)
- Modi, F. “Consolidanti innovativi per seta e tessili d’interesse storico-artistico” (2021)
- Adamo, C. “Sistemi ibridi formati da nanoparticelle di Au e aggregati lipidici o copolimerici: effetto delle proprietà interfasali sulla risonanza plasmonica” (2021)
- Cardesi, E. “Sviluppo di un saggio elettrochimico per la determinazione di esosomi” (2022)
- Cervelli, L. “Studio dell’interazione di nanoparticelle a base lipidica con modelli di membrane biologiche” (2022)
- Ciabini, C. “Determinazione di sequenze di RNA di interesse clinico mediante un saggio elettrochimico” (2022)
- Giampietro, V. “Preparazione e caratterizzazione di nanoparticelle inorganiche con coating lipidico” (2022)
- Pellegrini, G. “Studio chimico fisico di sostanze polimeriche esacellulari da scarti industriali nell'ambito di un programma di economia circolare” (2022)
- Petroni, R. “Influenza di parametri chimico-fisici in processi di desorbimento e trasferimento di colorante su fibre tessili” (2022)
- Puri, E. “Sviluppo di un immunosensore elettrochimico nanostrutturato per la determinazione di estrone” (2022)
- Sostegni, A. “Interazione di tensioattivi con fibre tessili: comprensione dei processi di desorbimento e trasferimento di coloranti” (2022)
- Yiqi, G. “Interazione tra aggregati misti lipidici-copolimerici e nanoparticelle di oro: proprietà interfasali e risonanza plasmonica” (2022)

Bachelor in Diagnostics and Materials for Conservation and Restoration (Laurea magistrale)

- Dore, B. “Interazioni tra nanoparticelle di amido Jin Shofu e pigmenti a base metallica” (2021)

Master in Agriculture

- Varuni, M. “Messa a punto di idrogel a base di biopolimeri di tipo ‘Alginate-like’ per applicazioni in campo agronomico” (2020)

Master in Biotechnology for environmental management and sustainable agriculture (Laurea magistrale)

- Barone, A. “Caratterizzazione di microplastiche (MPs) in campioni di sabbia della costa brasiliana mediante analisi micro-FTIR” (2020)

Master in Chemical Sciences (Laurea magistrale)

- Cialli, O. “Formulazioni a base di biopolimeri estratti da matrici naturali: il caso del Funori, caratterizzazione e proprietà applicative” (2020)
- Morganti, A. “Approccio chimico-fisico alle interazioni tra coloranti tessili e tensioattivi” (2020)

- Bassu, G. “Sintesi e caratterizzazione chimico-fisica di gel a base HEMA/AA” (2021)
- Ciraolo, R. “Messa a punto di idrogel per il rilascio controllato di principi attivi” (2021)
- Donati, M. “Nanoparticelle inorganiche coperte da bistrato lipidico biomimetico: preparazione e caratterizzazione strutturale” (2021)
- Pecori, G. “Sviluppo di sensori fluorescenti per l'identificazione di perossidi” (2021)
- Antonello, L. “Messa a punto e valutazione di idrogel funzionalizzati per applicazioni in campo agronomico” (2022)
- Comparini, L. “Self assembly di nanoparticelle d'oro su membrane biomimetiche ibride lipidiche e copolimeriche” (2022)
- Diddi, A. “Studio dell’effetto di complessi di rutenio su Ca2+-ATPasi” (2022)
- Forzatti, M. “Synthesis, Design and Photophysical Characterization of low-dimensional Perovskites towards Optoelectronic Applications” (2022)
- Giordano, D. “Sintesi e caratterizzazione di perovskite a base di magnesio per celle solari flessibili” (2022)
- Mattii, F. “Preparazione e caratterizzazione di nanomateriali ibridi per applicazioni biologiche” (2022)
- Serventi, F. “Effetto di un nuovo neuroprotettore sul processo di fibrillazione della alfa-sinucleina in modelli di membrana” (2022)

Master in Materials Science and Food Technology (Laurea magistrale)

- Pagliai, P. “Stabilità Colloidale in Olio Extravergine di Oliva Velato” (2020)
- Petrucci, A. “Sviluppo e caratterizzazione di emulsioni di Pickering per applicazioni in ambito alimentare” (2020)
- Pacini, V. “Sintesi e caratterizzazione di nanoparticelle di fosfato di calcio per la stabilizzazione di emulsioni di Pickering” (2021)
- Padulo, S. “Studio della stabilità di emulsioni di Pickering per applicazioni alimentari: effetto del fosfato di calcio su sistemi stabilizzati con idrossiapatiti commerciali” (2022)

Master in Pharmaceutical Chemistry and Technology (Laurea magistrale)

- Tozzetti, M. “Ottimizzazione e validazione di un nanosensore della proteina FKBP12” (2022)

Master in Sciences and Materials for the Conservation and Restoration (Laurea magistrale)

- Porpora, F. “Consolidamento di reperti ossei mediante nanoparticelle di idrossiapatite: efficacia e impatto sull'analisi paleogenetica” (2020)
- Capodiferro, S. “Foxing: Caratterizzazione chimico-fisica e messa a punto di un sistema per la rimozione delle macchie” (2021)
- Cianci, C. “Preparazione, caratterizzazione e applicazione di sistemi ibridi di fibroina e nanocristalli di cellulosa per il consolidamento della seta” (2021)
- Marradi, G. “Consolidamento inorganico per il trattamento di ossa archeologiche: le nanoparticelle di idrossiapatite” (2021)
- Meoli, A. “Consolidamento delle ossa archeologiche: la sintesi di nanoparticelle di idrossiapatite tramite microemulsione inversa e l’impatto del consolidamento sulla datazione del 14C” (2021)

- Maiano, A. “Le pellicole cinematografiche a base di triacetato di cellulosa: un protocollo multi-analitico per il monitoraggio della sindrome dell’aceto” (2022)
- Olivadese, F. “Organogel chimici innovativi per la pulitura di superfici pittoriche” (2022)

PhD in Chemical Sciences
- Caselli, L. “Combining inorganic nanoparticles with lamellar and non-lamellar lipid bilayers: from interaction to design of smart hybrid nanodevices” (2020)
- Menicucci, F. “Development and characterization of green nanovectors for agricultural applications (2020)
- Rossi, M. “Gels Based Systems For The Development Of Functional Materials” (2020)
- Guaragnone, T. “Novel formulations of polyvinyl alcohol-based peelable systems for the cleaning of metal artefacts” (2021)
- Balestri, A. “Smart amphiphilic copolymers as building blocks for hybrid lipid-copolymer systems and devices” (2022)
- Casini, A. “Nanostructured systems for the consolidation of matte and porous modern paintings” (2022)
- Clemente, I. “Compartimentalized algal-based nanocarriers as vectors for antioxidants: structural and functional characterization” (2022)
- Lucchesi, G. “Effetto plasmonico in metamateriali nanostrutturati: dalle celle solari a perovskite ai nanosensori per la diagnostica di malattie neurodegenerative” (2022)
- Vettori, I. “Water state in HEMA-based hydrogels: a theoretical and experimental investigation” (2022)

U.O. Pavia

Bachelor in Biotechnologies (Laurea triennale)
- Segato, I. “LDHs (layered double hydroxides) come host per l’aumento della solubilità dei farmaci: il caso del Meloxicam” (2020)
- Vancheri, A. “Halloysite. Misure di spettroscopia IR, diffrazione X, porosimetria, microscopia elettronica a scansione ed analisi termica (TG,DSC) finalizzate all’individuazione delle diverse forme” (2022)

Bachelor in Chemistry (Laurea triennale)
- Bertucci, N. “Covalent Organic Frameworks (COFs): sintesi e classificazione” (2020)
- Bruscagin, M. “Nanoparticelle di Fe_3O_4@MOF per terapia antitumorale combinata” (2020)
- Cacace, A. “Nuove frontiere nella lotta contro il cancro: le tecniche PDT e PTT” (2020)
- Casanova Borca, A. “La superconduttività in Pnictidi e Ossipnictidi a base di Ferro” (2020)
- Cremonesi, G. “Materiali anodici avanzati per le batterie al Sodio” (2020)
- Fusaro, C. “Applicazioni elettrochimiche di nanomateriali a base di metalli di transizione e loro ossidi abbondanti sulla crosta terrestre” (2020)

- Manzi, M.; “Materiali a cambiamento di fase per lo stoccaggio di energia termica” (2020)
- Romano, M.; “Sintesi di idrossidi a doppio strato” (2020)
- Carta, M. “Uso delle nanoparticelle in criochirurgia per la terapia dei tumori” (2021)
- Casarini, M. “Layered Double Hydroxides (LDH) magnetici per applicazioni biomediche” (2021)
- Ricaldone, E. “Nanocarriers a base di fosfato di calcio per il trasporto e il rilascio controllato di farmaci” (2021)
- Ricci, A. “Computer quantistico: qubit semiconduttori e applicazioni nella Quantum Information Science” (2021)
- Rocchetta, W. “Compositi a Matrice Metallica per Automotive” (2021)
- Scotti, F. “Sistemi emergenti per l’accumulo di energia: le batterie al magnesio” (2022)

Master in Chemistry (Laurea magistrale)

- Conti, D.M. “Synthesis and characterization of high voltage cathode for Sodium-ion batteries: $Na_{0.7}Ni_{0.35}Sn_{0.65}O_2$” (2020)
- Davino, S. “Nanodimensionalità ed elettrochimica: il caso di SnO_2, materiale anodico per batterie a ioni sodio” (2020)
- Fantozzi, E. “Nanoparticelle di $MgFe_2O_4$ drogate con Ag: effetto della sintesi sull'attività antibatterica” (2020)
- Rosa, C. “Nanoparticelle di $ZnFe_2O_4$ pure e sostituite come possibili materiali anodici in batterie al litio” (2020)
- Cardaropoli, L. “Sintesi, caratterizzazioni chimico-fisiche e proprietà della ferrite di calcio $CaFe_2O_4$” (2021)
- Fusaro, C. “Ottimizzazione elettrochimica del materiale anodico ZnS per batterie agli ioni Sodio” (2022)
- Grossoni, F. “Sintesi e caratterizzazione elettrochimica del materiale anodico TiO_2 per batterie agli ioni Sodio” (2022)
- Turci, F. “Da scarti agroalimentari a materiali per lo stoccaggio di energia: preparazione e valutazione delle prestazioni” (2022)

Master in Pharmaceutical chemistry and technology (Laurea magistrale)

- Belloni, G. “Progettazione e caratterizzazione chimico-fisica di formulazioni innovative no smoking” (2020)
- Marino, S. “Progettazione e caratterizzazione chimico-fisica di sistemi innovativi termosensibili per il rilascio di molecole bioattive" (2020).
- Montagna, I. “Formulazioni innovative per la veicolazione orale di farmaci peptidici: preparazione e caratterizzazione chimico-fisica" (2020)
- Nardini, M. “Nuovi eccipienti per farmaci contro il dolore severo in Arnold chiari e siringomielia: preparazione e caratterizzazione chimico-fisica del composito tramadolo-nanotubi di halloysite” (2020)
- Paternieri, M. “Preparazione e caratterizzazione termoanalitica di sistemi farmaceutici a rilascio modificato a base di acidi grassi” (2020)
- Djenou Bouoda, S.K. “Cocristalli di Zaltoprofen e 4,4'-bipiridina” (2021)
- Ghione, I. “Il comportamento termico della glipizide” (2021)

- Longo, M. “Preparazione e caratterizzazione di cocristalli di Piretanide e Niacinamide” (2021)
- Rando, B. “Preparazione e caratterizzazione chimico-fisica di sistemi innovativi a base di HNT funzionalizzati contenenti aloperidolo per il trattamento della corea di Huntington” (2021)
- Maestripieri, M. “Preparazione e caratterizzazione chimico-fisica di miscele di acidi grassi e metformina” (2022)
- Ongato Yanape, Q. “Preparazione e caratterizzazione chimico-fisica di sistemi a base di acidi grassi e clorexidina” (2022)
- Taggiasco, I. “Preparazione e caratterizzazione chimico-fisica di miscele di interesse farmaceutico a base di acidi grassi e Metformina compatibili per il rilascio a temperatura corporea” (2022

Master in Advanced Biotechnologies (Laurea magistrale)

- Rinaldi, A. “Metodi di drug delivery a confronto per uno studio applicativo del Tenoxicam” (2021)
- Bianchi, M. “Sintesi e caratterizzazione di Halloysite magnetica per il recupero di inquinanti emergenti” (2022)
- La Rocca, M. “Nuovi sistemi organici-inorganici per il miglioramento della solubilità dei farmaci: il caso della Furosemide” (2022)
- Turesso, C. “Nuovi approcci di disinfezione: materiali con proprietà biocida” (2022)

Master in Pharmacy (Laurea magistrale)

- Ielo, M.S. “Nanotecnologie per la cura del tumore” (2020)
- Mazzucchi, A. “Polimeri termoresponsivi per applicazioni in ambito farmaceutico e biomedico” (2020)
- Paladino, F. “Nanoparticelle a base di proteine per la somministrazione di farmaci” (2020)
- Pignagnoli, G. “EGFR inibitori nella targeted therapy anti-tumorale: effetti collaterali cutanei, dermocosmesi oncologica e ruolo del farmacista” (2020)
- Pirovano, C. “Nanoparticelle per il trattamento dell’epatocarcinoma: proprietà chimiche e farmaceutiche, meccanismo d’azione e nuove prospettive” (2020)
- Righi, S. “La curcumina come coadiuvante: i possibili utilizzi in nutraceutica e le forme farmaceutiche che ne garantiscono elevata biodisponibilità” (2020)
- Schiraldi, D. “Attività antibatterica dei lipidi” (2020)
- Sopa, A.D. “Nanotubi di halloysite per la veicolazione di antibiotici” (2020)
- Tedesco, C. “Attività antibatterica di sistemi termosensibili a base di polimeri e acidi grassi” (2020)
- Montresor, F. “Infiammazione da cibo e malattie autoimmuni: approcci dietetici preventivi e palliativi” (2021)
- Panaro, V. “Nanoparticelle e Covid 19” (2021)
- Puoti, S. “Preparazione e caratterizzazione chimico-fisica di sistemi binari di acidi grassi e clorexidina per la formulazione di sistemi farmaceutici a rilascio modificato ad attività antibatterica” (2021)
- Rezvani Kashani, M.; “Preparazione e caratterizzazione chimico-fisica di sistemi HNT - insulina per un trattamento innovativo dei pazienti diabetici” (2021)

- Urso, A. “Sindrome di Guillain-Barrè: aspetti generali, patogenesi e attuali terapie” (2021)
- Blandino, A.M. “Quantificazione polimorfica del dexketoprofene trometamolo mediante la tecnica di calorimetria differenziale a scansione” (2022)
- Cazzaniga, M. “I materiali mesoporosi silicei come carrier di farmaci poco solubili” (2022)
- Panarisi, V. “Somministrazione nasale di farmaci” (2022)
- Rusconi, M. “Formulazioni nanoparticellari per il trattamento e la profilassi di infezioni virali: stato dell’arte e prospettive future” (2022)

Master in Urban and Environmental Engineering (Laurea magistrale)
- Francazi Zolotorav, S. “Preparazione e caratterizzazione di biochar da pula di riso per lo stoccaggio di idrogeno allo stato solido” (2021)
- Minardi, M. “Preparazione e caratterizzazione di carbonio superattivato da scarti di melone e riso per lo stoccaggio di energia” (2021)

PhD in Chemical and Pharmaceutical Sciences and Industrial Innovation
- Spada, D. “The key role of high-performance anode materials in Li- and Na- ion batteries” (2021)

U.O. Roma “Tor Vergata”

Bachelor in Chemistry (Laurea triennale)
- Bassotti, E. “Studio computazionale della deformazione meccanica della poli(N-isopropilacrilammide) in vuoto ed in soluzione acquosa” (2020)
- Franci, E. “Effetto della fosforilazione e di mutazioni puntiformi su struttura e dinamica della proteina oncogenica H-RAS: simulazioni di dinamica molecolare” (2020)
- Carneri, F. “Interazione tra peptidi bioattivi e membrane: modelli termodinamici e tecniche sperimentali” (2020)
- Perilli, G. “Il peptide antitumorale killer-FLIP: studio dell’aggregazione e dell’attività su liposomi giganti” (2020)
- Montagnolo, A. “Studio in silico della dinamica molecolare del complesso tra integrina αvβ3 e il peptide ciclico cRGD” (2020)
- Ruggiero, F. “Simulazioni di dinamica molecolare dell’inserimento di peptidi bioattivi in membrana” (2020)
- Bisio, S. “Uso di nanocellulosa come materiale barriera per il packaging alimentare” (2021)
- Carnevale, V. “Valutazione dei metodi di sanificazione e dei metodi di monitoraggio di contaminazione batterica in ambienti chiusi” (2021)
- Cecchetti, S. ““Il fumo di sigaretta: descrizione delle principali tecniche diagnostiche e analisi tramite spettroscopia FTIR” (2021)
- Franci, E. “Effetto della fosforilazione e di mutazioni puntiformi su struttura e dinamica della proteina oncogenica H-RAS: simulazioni di dinamica molecolare” (2021)

- Gosti, C. “Studi preliminari del peptide CLP002 in vista di una sua futura applicazione in ambito teranostico” (2021)
- Pagano, G. “Caratterizzazione tramite dinamica molecolare di un inibitore della proteina RNA-polimerasi del virus SARS-CoV2” (2021)
- Nicoletti, R. “Studio in silico di superfici di Au funzionalizzate conmonolayer peptidici per uso teranostico” (2022)
- Tagliaboschi, P. “Selettività del CLP002 inibitore della morte programmatacellulare: studi preliminari di un suo analogo 'scrambled'” (2022)

Bachelor in Applied Chemistry (Laurea triennale)

- Damiani, A. “Analisi spettroscopiche su materiale fotografico: Caratterizzazione di materiale fotografico risalente al secolo scorso e messaa punto di metodi idonei di pulitura” (2020)
- Milana, A. “Diagnostica per i Beni Culturali, dal laboratorio alle misure in situ” (2020)
- Medalla, B.J.C. ““Determinazione del piruvato: approccio biosensoristico” (2021)
- Raparelli, M. “processi di degrado e metodi di conservazione della street-art” (2021)
- Bruno; L. “Studio della Interazione tra un peptide e il dominio C-SH2 della proteina SHP-2 mediante simulazioni di Dinamica Molecolare” (2022)

Bachelor in Materials Science (Laurea triennale)

- Paciotti, G. “Studio delle traiettorie di micro bolle polimeriche su substrati cellulari in condizioni fisiologiche, con riferimento ad applicazioni in imaging molecolare e rilasci di farmaci” (2020)
- Aceto, D. “Studio tramite dinamica molecolare del polimero PNIPMAM in ambiente acquoso” (2021)
- Di Girolamo, A. “Studio di microcapsule formate da peptidi terapeutici mediante emulsificazione assistita da ultrasuoni” (2022)
- Lucidi, E. “Applicazioni di nanostrutture peptidiche in biomedicina” (2022)

Master in Chemistry (Laurea magistrale)

- De Medici, M. “Gel peptidici: Stato dell’arte e studio di caso di un gel formato da un peptide terapeutico” (2020)
- Della Rocca, G. “Studio di un film polimerico sostenibile basato su scarti alimentari con potenziali applicazioni nel settore delle vernici: risultati preliminari” (2020)
- Di Tinno, A. “Verso lo sviluppo di immunosensore label-free: risultati preliminari” (2020)
- Mazzotta, F. “Detection of Aβ42 aggregation intermediates. Using fluorescent dyes to detect transient structures during the aggregation process” (2020)
- Mantegazza, P.” Caratterizzazione del rilascio da sistemi gel come potenziali dispenser di oli essenziali per la sanificazione di ambienti” (2020)
- Ruscito, A. “Proprietà termiche e meccaniche di microgel di PNIPAM reticolato con diversa architettura e conseguenze sulla loro fagocitosi” (2020)
- Angelini, I. “Ultrasound Frequency-Dependent Targeting: a step toward ultrasound molecular imaging” (2021)

- Borgia, S. “Nanogocce polimeriche a transizione di fase per dosimetria multimodale assistita da ecografia” (2021)
- Di Stefano, C. “Sviluppo di inibitori peptidici delle interazioni proteina-proteina della fosfatasi oncogenica SHP2” (2021)
- D’Andrea, A. “Development of a Paper Cleaning Strategy based on Us-Stimulated PVA Microbubbles” (2021)
- Di Ruzza, F. “Acoustic Radiation Force Effect on the Microbubbles Targeting: a step towards Molecular Imaging of Integrins Expression” (2021)
- Ditri, A. “Microdroplet-DNA assembly for tailored coalescing interaction and tumor cells transfection” (2021)
- Riccitelli, F. “Effetti dei peptidi antimicrobici sulla dinamica delle membrane batteriche” (2021)
- Giannetti, M. “Studi di Stabilità del Principio Attivo Furosemide”(2021)
- Schioppa, S. “Studio in vitro della bioadesione di microbolle con guscio polimerico ed analisi della dinamica di approccio a cellule endoteliali” (2021)
- Quarta, A. “Preparation and charcacterization of protein microcapsules through ultrasound-assisted emulsification” (2022)
- Rossi, G. “Preparation and characterization of therapeutic peptide microcapsules” (2022)

PhD in Chemical Sciences

- Palmieri, D. “Development of multi-responsive phase change contrast agents with hybrid shells of potential theranostic relevance” (2020)
- Righi Riva, F. “In vitro studies of the static and dynamic behavior of Ultrasound Contrast Agents designed for the targeting of αvβ3 integrins” (2020)
- Ripani, G. “Theoretical and computational studies on the structure and binding processes of biomolecules in solution and at interface” (2021)
- Titubante, M. “Multi-analytical approaches for the characterisation and consolidation of ancient and modern manuscripts” (2021)
- Cancelliere, R. “Development of biosensors for clinical and food-safety control” (2022)
- Cimino, R. “Structured micro- and nanosystems based on polysaccharides and peptides for encapsulation of nutrients and therapeutic applications” (2022)
- Savioli, M. “Computational and experimental approaches for the characterisation of nanostructured biopolymers with biological activity” (2022)
- Severini, L. “Development, characterization and assessment of innovative materials for ancient and modern paper artifacts conservation” (2022)

Post Doc:

- Di Napoli, B: “Studio e sviluppo di materiali barriera sostenibili nell’ambito del packaging alimentare” (2020)

U.O. Siena

Bachelor in Chemical Sciences (Laurea triennale)

- Bossio, G. “Polimeri di HGA: caratterizzazione combinata mediante metodi computazionali e spettroscopia UV-Vis" (2020)

- Bretti, D. "Analisi delle componenti inorganiche in semi freschi di Coffea arabica per la caratterizzazione geografica e varietale" (2020)
- Brogi, L. "Material Flow Analysis e Life Cycle Assessment per la caratterizzazione degli impatti ambientali del fine vita dei moduli fotovoltaici a perovskite" (2020)
- Chini, E. "Analisi di risonanza magnetica nucleare di metaboliti primari e secondari in estratti di Diospyros kaki immaturo" (2020)
- Cognini, P. "Sviluppo di metodi di caratterizzazione geografica e varietale di Coffea arabica da studi combinati delle componenti inorganiche ottenute da misure di assorbimento atomico e analisi chemiometrica" (2020)
- Falcai, F. "Confronto fra processi di degradazione della plastica compostabile in sistemi marini" (2020)
- Favale, N. "Geometrie dello stato elettronico di singoletto fondamentale ed eccitato di derivati del Tiocromone ottenute mediante metodi DFT e TD-DFT" (2020)
- La Capra, M. "Study on the mechanical degradation of LDPE and Bio-Plastic bags in sea water" (2020)
- Malpede, M. "Studio dei processi di rilassamento NMR relativo alle interazioni capsaicina-albumina e capsaicina-caseinato" (2020)
- Martile, L. "Applicazione dei metodi DFT e TD-DFT al calcolo delle energie di eccitazione ed emissione verticale di due coloranti per biomedicina" (2020)
- Pagliari, V. "Analisi dell'attività antiossidante idrofila e lipofila dei nutraceutici presenti nei prodotti vegetali mediante spettrofotometria UV-visibile" (2020)
- Pecorelli, N. "Determinazione del potere antiossidante di prodotti da forno tradizionali e fortificati" (2020)
- Polvani, A. "Studi di foto e termodegradazione su shopper biodegradabili e non" (2020)
- Raulli, A. "Calcolo delle geometrie e massimi di assorbimento di tre derivati del 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) mediante metodi DFT e TDDFT" (2020)
- Turchi, F. "Studio delle componenti inorganiche di Valerianella locusta, Cichorium intybus var. foliosum endive, Eruca sativa e altre varianti e valutazioni di processi di lavaggio di nitrati e metalli" (2020)
- Asllani, D. "Caratterizzazione di un estratto vegetale di foglie di olivo (Olea europaea) tramite analisi HPLC-DAD-MS" (2021)
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- Fadini, A. "Analisi chemiometrica della pressione antropica sulle acque del Lago Tanganica" (2021)
- Fornarini, P: "Valutazione dell'attività antiossidante di estratti vegetali da misure EPR di quenching del radicale DPPH e confronto con analisi in spettroscopia

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- Mencaraglia, E. “Caratterizzazione strutturale dell’antigene di Meningococco di tipo A tramite risonanza magnetica nucleare” (2021)
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- Alessandro, R. “Derivati tienopirazinici fluorescenti per un possibile uso in concentratori solari luminescenti (LSC): uno studio mediante metodi DFT e TDDFT” (2021)
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- Giubbi, J. “Valutazione degli impatti ambientali dei processi di produzione di materiali a cambiamento di fase mediante metodologia LCA” (2021)
- Jassal, S. “Valutazione del ciclo di vita dei processi di pirolisi lenta e carbonizzazione idroterma applicati a macroalghe infestanti” (2022)
- Kalasuwe, A.E. “Life cycle analysis of micellar catalysed hydroaminomethylation for aniline production” (2022)
- Maccari N. “Analisi qualitativa di campioni di acqua termale in presenza di bioplastica” (2022)
- Nigro, F. “Studio di matrici polimeriche biocompatibili per il rilascio di acido clorogenico” (2022)
- Rotondi, L. “Analisi LCA di un processo di produzione di una cella solare a perovskite” (2022)
- Shtiqeti, E. “Analisi della variazione spaziale e temporale della qualità dell’acqua in un bacino dell’Oxfordshire (UK)” (2022)
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- Albertella, J. “Estrazione e caratterizzazione spettrofotometrica di estratti di matrici vegetali con proprietà antiossidanti" (2022)

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- Bisozzi, F. "Use of DPPH assay carried out with Uv-Vis spectroscopy for the determination of conversion factors between five antioxidant standards through kinetic analysis and EC50 calculation. Experimental applications and validations in four varieties of salad food" (2020)
- d'Ettorre, A. "Computational study of long-range electron transfer pathways in bacteriorhodopsin as photosensitizer for TiO2" (2020)
- Kipyator, M.J. "Lights and shadows of the environmental impact of perovskite-tandem solar cells technology: a Life Cycle Assessment study" (2020)
- Leti, R. "Arsenic absorption on macroplastics in aquatic environments" (2020)
- Papini, M. "Characterization of the degradation processes of biobags in marine waters" (2020)
- Spinelli, G. "Synthesis and application of a new photoactive molecule (dye) as substitution of chenodeoxycholic acid in co-sensitized with Y123 dye in dssc" (2020)
- Stricchi, G.R. "Identifying geochemical traces of Past land-use by chemometrics" (2020)
- Sonnino, N. "*In-silico* assessment of long-range electron transfer pathways in bacteriorhodopsin-sensitized TiO_2 system" (2022)

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- Di Giusto, M. "Valutazione di biomarkers di stress ossidativo in pazienti diabetici sottoposti a trattamento con empaglifozin" (2020)
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- Helal, O. "The anti-inflammatory properties of nutraceuticals, analysis of the mechanisms proposed" (2022)

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- Sgandurra, G. "Caratterizzazione mediante metodi dft e tddft di nuovi coloranti organici contenenti Indigo" (2021)
- Sorrentino, Y. "Valutazione di biomarker di stress ossidativo/nitrosativo in pazienti con sclerodermia sottoposti a trattamento con bosentan" (2021)
- Cetta, A. "Analisi degli effetti della simulazione dei processi di digestivi sulla stabilità delle componenti nutraceutiche presenti negli alimenti" (2022)
- Concetta Pezzullo, M.C. "Applicazione dei metodi DFT e TD-DFT al calcolo dell'energia verticale per nuovi derivati del 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY)" (2022)
- Di Crisci, M. "Polimorfismo nei cocristalli di acido niflumico e caffeina: caratterizzazione e proprietà fisico-chimiche" (2022)

- Tommasi, S. “Caratterizzazione di un estratto idroalcolico di foglie di caffè (Coffea arabica) tramite tecniche spettroscopiche (NMR) e spettrometriche (HPLC-MS)” (2022)
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PhD in Chemical and Pharmaceutical Sciences

- Jankowska, K. “Early stage biofilm formation: influence of environmental chemistry on P. fluorescens and S. epidermidis attachment and growth” (2020)
- Pardini, A. “Chemical characterization of nutraceutical components in vegetable products” (2020)
- Croce, R. “Strategie innovative al servizio del settore vitivinicolo: quando la spettroscopia FT-MIR incontra la chemiometria” (2021)
- Clemente, I. “Compartmentalized algal-based nanocarriers as vectors for antioxidants: structural and functional characterization” (2022)
- Coppola, C. “Design of novel organic compounds for the development of solar energy conversion devices” (2022)
- Zawadka, A. “Amphiphilic self-assembly polymers with improved environmental profile for home and personal care products” (2022)

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- Mohammadpourasl, Sanaz. “Design and characterization by using computational methodologies and life cycle assessment (LCA) of devices for energy production from renewable energy sources” (2020)
- Rossi, F. “Environmental impact assessment of energy storage technologies in photovoltaic systems” (2021)

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RESEARCH PROJECTS

1A – Alizarin-functionalized silane coatings for the development of wearable textile sensors

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[2] CNR-ISMN, Istituto per lo Studio dei Materiali Nanostrutturati, CNR

Aims

Powered by market requests, which is expected to grow from its current value of 40 billion USD to 160 billion USD by 2026, wearable technology has recently gained the interest of researchers and clinicians. Particularly, wearable sensors provide new avenues to continuously monitor the wearers' health, fitness, and surroundings. These devices can have huge applications in human–machine interfaces, electronic skin, and non-intrusive health monitoring systems. To replace rigid traditional sensors, switchable molecular systems, with stimuli-responsive properties in a wide sensing range (e.g., diarylethenes, rotaxanes, azobenzenes and spiropyrans), have been developed as innovative and promising optoelectronic tools to design smart textiles for detecting external stimuli. Thanks to its capability to provide chelation with several ions, alizarin (ARS) has been investigated as a molecular receptor for investigation of some rare earth and proteins, as well as a colorimetric reagent for cations, such as calcium, copper, lead, chromium. The biodegradability, non-toxicity, medicinal value, as well as pronounced colour transitions between 5.8 and 13, make alizarin one of the human and environment harmless interesting dyestuff in the spectrophotometric determination of pH. In this study, the sol–gel method was used as a straightforward approach to preparing optically transparent alizarin coatings for textile fabrics to develop useful pH-meter wearable systems.

Results

Compared to other pH sensing systems based on alizarin encapsulation or absorption in a polymer matrix, in this study the sol–gel technique was used to obtain a silane-based coating, containing alizarin-covalently bonded, coated on cotton fabric to develop a wearable sensor. The step forward in colloid and interfaces science for the covalent functionalization of alizarin dyestuff by the sol–gel technique is described, particularly highlighting the advantages of this sustainable method in the development of organic–inorganic hybrid coatings for stimuli-responsive wearable sensors. Experimental findings suggest that the sulfonate group may be considered as an efficient nucleophilic substituent in the epoxide ring-opening reaction of GPTMS (trimethoxy-[3-(oxiran-2-ylmethoxy)propyl]silane), thus promoting the formation of a covalent bond between alizarin and alkoxysilane precursor. Moreover, alkoxysilane precursor functionalized by ARS dyestuff reacts to pH change by colour transition due to the ionization of phenolic hydroxyl groups as observed for pure ARS, thus confirming that the silane functionalization does not significantly affect the halochromic properties of the alizarin. The absorbance bands of GPTMS-ARS colloidal solution in the pH range between 6 and 8 is composed of three overlapped bands (454 nm, 492 nm and 520 nm) assigned to the higher delocalization of electrons in the functionalized dyestuff than that pure alizarin. The pH-response of treated cotton fabrics (CO_GPTMS-ARS) was investigated after 1 and 5 washing cycles to avoid no-bonded dyestuff interference by soaking samples separately in pH buffer solutions ranging from 2 to 8. Each textile sample was then characterized by UV–Vis diffuse reflectance spectroscopy and obtained K/S curves, together with corresponding images, are reported in Figure 1.

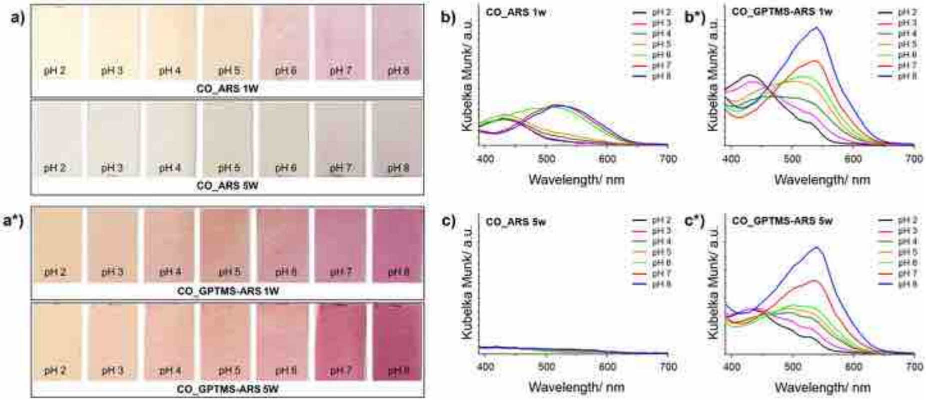

Figure 1. Images of CO_ARS (a) and CO_GPTMS-ARS (a*) after 1 and 5 washing cycles (_1w and _5w, respectively) at different pH and relative Kubelka-Munk spectra (b-c and b*- c*, respectively).

Compared to other methods to produce smart textiles, the synthetic strategy described in this research is much preferable and safer since the observed coating durability represents an added value for the development of novel wearable sensors, as it guarantees that the halochromic molecules as well as the silane-based matrix, do not contaminate the users' skin.

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1A – APACHE (Active & intelligent PAckaging materials and display cases as a tool for preventive conservation of Cultural Heritage)

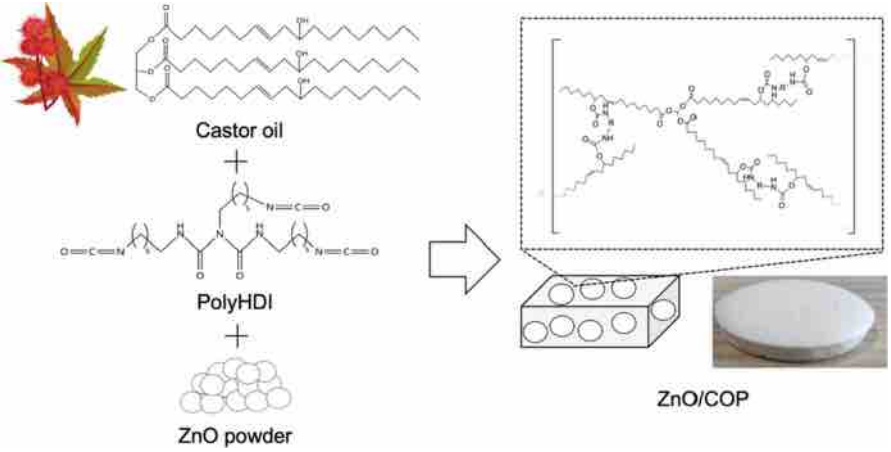
H2020 Grant Agreement number: 814496 — APACHE — H2020-NMBP-ST-IND-2018-2020/H2020-NMBP-ST-IND-2018; 1 January 2019 - 30 June 2022; Total budget: € 7 873 590,90; EU Contribution: € 6 837 732,75; Project Coordinator: CSGI; Number of partners: 26

Aims

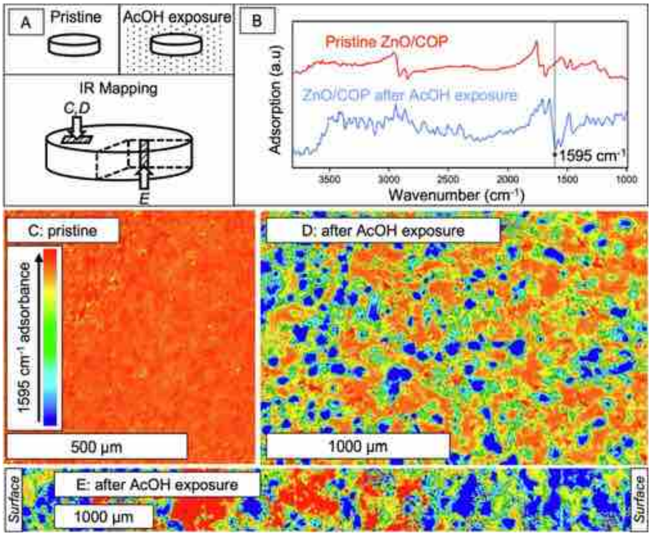
Degradation of movable tangible cultural heritage can be significantly increased by disadvantageous and unstable climate conditions, light and pollution. The purpose of preventive conservation is to avoid and minimize future degradation and loss of cultural heritage. The EU-funded APACHE project has developed new tools to control and prevent degradation: multiscale materials modeling to predict degradation of art-related materials, wireless sensors and low-cost systems to detect unsuitable microclimates, pollution absorbents, and temperature/humidity regulators. CSGI was involved as Project Coordinator and developer of materials for the capture of VOCs like acid, a major pollutant in museum enclosures and storage deposits).

Results

CSGI has developed a class of products based on environmentally friendly composites made of metal oxides (e.g. MgO, ZnO) embedded in a castor-oil polyurethane crosslinked resin (see figure below). Upon exposure, acetic acid interacts with the castor oil polyurethane and diffuses to the surface of metal oxide particles where is stably fixed as metal acetate crystals. Acetate domains form homogeneously on the surface and are distributed evenly within the composite, thanks to weak interactions between the polyurethane matrix and acetic acid that favor the transport of the acid up to reach the metal oxide surfaces, resulting in a synergistic effect. The new composites showed significantly enhanced adsorption capacities of acetic acid surpassing those of the activated carbon benchmark (traditionally used in preventive conservation of artifacts), with the advantage of being easily handled and movable, without the health issues and risks associated to the use of non-confined micro/nano-powders.



Namely, the composites can absorb and retain almost up to their own weigth of acetic acid. FTIR Imaging (see figure below) confirmed the formation of zinc acetate in the composites. The acetate absorption at 1595 cm−1 is imaged as blue and green pixels in the IR false color maps (figure below), showing the distribution of zinc acetate domains on the surface and through the section of the polyurethane network (red-yellow pixels background in panels C-E). The acetate domains are distributed across the entire length of the COPs section (panel7 C). The composites were tested in representative case studies (e.g. storage crates of deposits, frames of paintings, display cases), where they reduced the levels of acetic acid in the enclosures from 1.5-0.6 ppm down to 0.5-0.4 ppm, i.e. close to or corresponding to the threshold limit for AcOH (0.4 ppm) indicated for preventive conservation of artifacts by the Canadian Conservation Institute.



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1A – Carbon-based quantum dots as fluorescent probes in pH sensors: direct monitoring of bacterial growth

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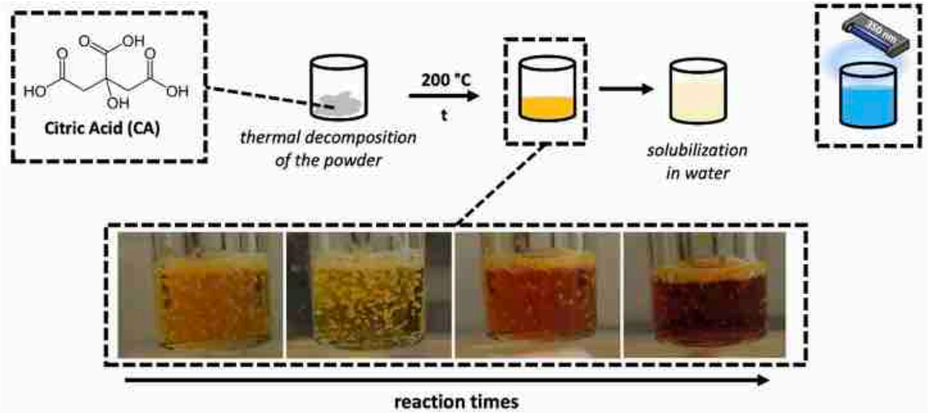
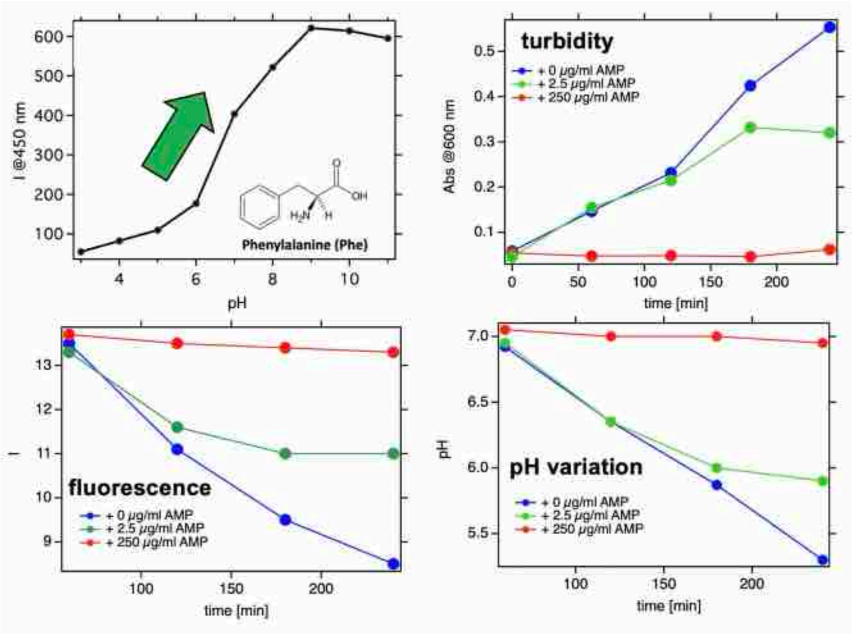
Aims

Quantum dots are well-known fluorophores used in many applications due to their high photostability and brightness. Among them, carbon quantum dots (CQDs) are a relatively new class of carbon nanomaterials which have been extensively studied in the last years to improve their properties towards the final application. Nowadays, most common approaches for CQDs production span from laser ablation, microwave-mediated synthesis, hydro-/solvo-thermal methods and pyrolysis. Here we propose an innovative one-pot synthesis to obtain pH-sensitive CQDs with tunable fluorescence properties. In particular, the procedure is based on the pyrolysis of citric acid (CA) in the presence of different amino acids (i.e., phenylalanine, Phe, or tryptophan, Try). The synthesis has been optimized in terms of decomposition time and dopant concentration to tune the response to pH.



Results

Obtained CQDs result sensitive to very small changes in the pH of the aqueous environment thanks to remarkable variations of their fluorescence. Our results evidence that in the CA/Phe case the fluorescence decreases as the pH decreases with an inflection point at pH 6.6, while the system prepared with Try shows an opposite behaviour with an inflection point shifting at higher pH (i.e. 8.3). This different optical response can be addressed to the different functional groups localised at the surface of the CQDs. These carbon-based nanostructures have been tested, in vitro, for the evaluation of the susceptibility of E. coli ATCC 25922 to ampicillin (AMP) and eventually to estimate the Minimal Inhibitory Concentration (M.I.C.).



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1A – Circular economy for solid state H2 storage

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** Parma University, Mathematical, Physical and Computer Sciences Department*
***Catania University, Physics and Astronomy Department*
****Brescia University, Civil, Environmental, International Cooperation and Mathematical Engineering Department*
***** Institute of Hydrogen Technology, Helmholtz-Zentrum hereon GmbH*

Aims

Ideation and preparation of hydrides and novel carbon-based nanostructures for solid-state H_2 storage from industrial and agricultural wastes; evaluation of their hydrogen sorption properties; determination of the thermodynamic and kinetics parameters of the sorption reactions.

Results

Circular economy and energy storage are very hot topics concerning scientific and technological research and economy. In this framework our activities are developing, regarding in particular solid state hydrogen storage.

Biochar, the carbon side-product in the pyrolysis/gasification of residual waste biomasses, started to receive a widespread attention in the field of energy-storage, thanks to its hierarchical porous structure inherited from biomass precursors, its excellent chemical and electrochemical stability, high conductivity, high surface area and inexpensiveness. In particular, biochar converted to activated carbon (SSA > 1000m^2/g) through a chemical treatment with KOH appears to be a new cost-effective and environmentally-friendly carbon material with great application prospect in the field of energy-storage. We were able to prepare novel hierarchically-porous super-activated carbon materials originating from biochar derived by the pyrolysis of agrifood wastes such as rice bran and husk, and melon and pumpkin peels (Figure 1). The chemical activation process proved to be efficient to remove the majority of impurities other than carbon, stabilizing highly porous hierarchical structures with local graphene-like morphology. The porous compounds obtained by rice bran and husk mixtures demonstrated to behave as excellent electrode materials for high-performance symmetric supercapacitors (SCs), reaching interestingly high specific capacitance and specific energy. On the contrary, the materials obtained by rice bran and the vegetable peels, having specific surface area up to 3000 m^2/g, show a very good hydrogen storage ability, adsorbing up to 4.5 wt % of hydrogen in around 20 seconds at 77K and around 1.5 wt% at room temperature. Work is in progress to optimize the pyrolysis and activation conditions and to improve the performance of the materials by decoration with transition metals and transition metals oxides.

Moreover, to reduce the carbon footprint associated with the production of metals-containing hydrogen storage materials and to reduce their cost, we pursue the possibility of obtaining high-quality hydride-based materials from industrial metals waste. In particular, we developed a method for obtaining high-quality $NaAlH_4$ powders starting from the Al-based automotive recycled alloy DIN-GDAlSi$_{10}$Mg(Cu). The hydrogen storage properties of the material obtained by ball milling NaH and DIN-GDAlSi$_{10}$Mg(Cu) under hydrogen atmosphere were comprehensively explored via a broad range of experimental techniques, e.g. volumetric analysis, ex situ X-ray diffraction (XRD), in situ synchrotron radiation powder X-ray diffraction (SR-PXD), scanning electron microscopy (SEM), and differential thermal analysis (DTA). These investigations show that $NaAlH_4$ was successfully synthesized and that its hydrogen storage performance is comparable with the characteristics showed by high-purity commercial $NaAlH_4$.

The possibility to use waste Mg-Al based alloys as starting material for the production of good quality MgH_2 through the use of industrial mills was also investigated. Hydrogen sorption capacity up to 6 wt% and hydrogenation kinetics efficiency of 26.85% conversion per minute were achieved by 120 min milling a mixture of waste magnesium alloys with 5 wt% graphite. The sample showed full reversibility even after more than 40 hydrogenation/de-hydrogenation cycles without any meaningful drop of hydrogenation/de-hydrogenation rates.

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1A – Degradation of antibiotics in aqueous solution by different metal-doped $LaFeO_3$ photocatalysts

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Department of Engineering and Applied Sciences – University of Bergamo – Italy

Aims

Visible-light oxides are being studied extensively as photocatalysts for removal of pharmaceuticals from the effluents of conventional wastewater treatment plants (WWTPs) [1-6]. Photocatalysts based on pure semiconducting oxides are rarely used, due to the problem of rapid recombination of electron-hole pairs. Doping of the oxide with metal elements is a good strategy to enhance the performance of catalysts. Lanthanum ferrite $LaFeO_3$ (LF) and 10 different metal-doped $LaFeO_3$ nanopowders are evaluated in the photocatalytic degradation of two molecules, ciprofloxacin (CP) and oxytetracycline (OTC), which are frequently detected in surface water bodies as recalcitrant and persistent micropollutants.

Results

Oxides with perovskite structure, such as $LaFeO_3$, allow flexible occupancy of cationic sites by other elements. In fig.1 are shown the chemical element, atomic percentage and the cationic site occupation of each dopant. The effects of La(A)FeO_3 and LaFe(B)O_3 compounds on the photocatalytic degradation of CP and OTC are investigated by irradiating under visible-light and in the presence of H_2O_2. The addition of H_2O_2 increases the photodegradation rate of organic pollutants by removing the surface-trapped electrons, thereby lowering the electron–hole recombination rate and increasing the efficiency of hole utilization for reactions, such as ($OH^- + h^+ \rightarrow \bullet OH$). The influence of doping, specific surface areas (SSA) on the photocatalytic degradation efficiency is assessed. The most extensive photodegradation of OTC, 78%, is detected with Cu 10% and it retains a good response also in the presence of Mg 10% photocatalyst.

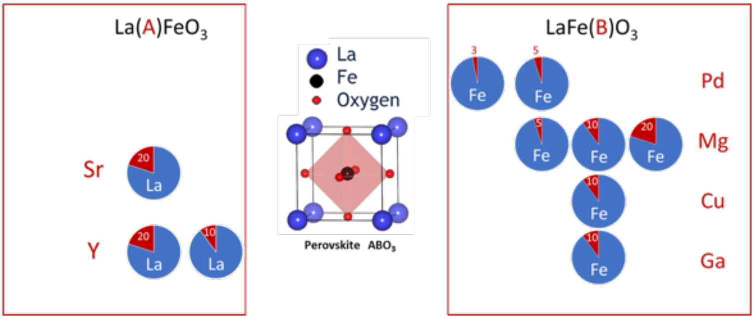

Figure 1: Chemical element, atomic percentage and cationic site occupation of each dopant.

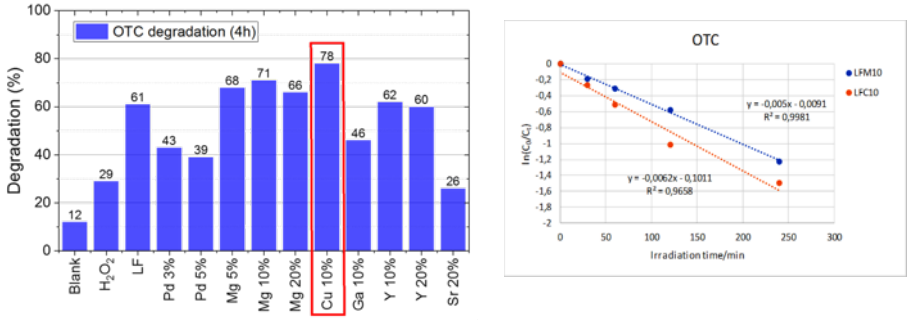

Figure 2: Photocatalytic degradation results after 4h of irradiation. Blank: only solution of pure pollutant (OTC 5x10^{-6} M); H_2O_2: solution of pollutant + H_2O_2 without photocatalyst (left). Pseudo-first order kinetics for the photocatalytic degradation of OTC (5·10^{-6} M) in the presence of 10% Cu (LFC10) and 10% Mg (LFM10) photocatalysts (right).

LFM10, LFY10 and LFY20 photocatalysts show a remarkable photocatalytic activity degrading CP (78%, 71 % and 70% of CP removal, respectively) using the same experimental conditions as for OTC.

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1A –Drug loading on mesoporous silica nanoparticles (MSN) to contrast antibiotic resistance

Part 1: Adsorption and Release of Sulfamethizole from Mesoporous Silica Nanoparticles functionalized with Triethylenetetramine

C. Carucci, N. Scalas, A. Porcheddu, M. Piludu, M. Monduzzi, A. Salis

Aims

According to WHO (World Health organization) antibiotic resistance is one of the most threatening health threats. Antibiotic resistance might be overcome by drug transport by tailored carriers which bring and release the antibiotic exactly at the needed site. This work reports the adsorption and release of a common antibiotic sulfamethizole from bare and triethylenetetramine functionalized mesoporous silica nanoparticles (MSN and MSN-TETA respectively). After the structural carrier characterization, kinetics and thermodynamics of sulfamethizole are studied. This project aims to design a drug delivery system considering the intermolecular interactions between drug and drug carrier.

Results

SAXS patterns of MSN, MSN-Cl and MSN-TETA samples confirmed the original hexagonal MSN structure for bare and functionalized samples (Figure 1A). N_2 adsorption/desorption analysis showed a BET surface area of 942 $m^2\,g^{-1}$ for MSN that decreased after functionalization, with 744 $m^2\,g^{-1}$ and 671 $m^2\,g^{-1}$ for MSN-Cl and MSN-TETA, respectively as expected. These results demonstrated how sample functionalization was compatible with the successful obtainment of the MSN hexagonal structure.

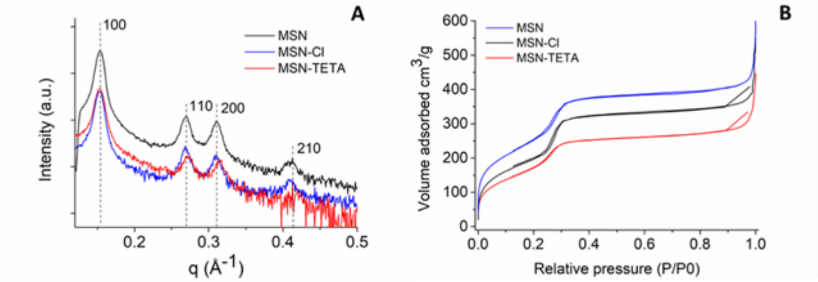

Figure 1. (A) SAXS patterns and (B) Adsorption/desorption N_2 of MSN, MSN-Cl, MSN-TETA samples.

The adsorption kinetics of sulfamethizole on MSN and MSN-TETA was studied. The adsorbed amount (qt, mg/g) of sulfametizole drug as a function of the contact time showed a fast qt increase reaching equilibrium after 5 hours (Figure 2A). Data were analysed with pseudo-first-order and pseudo-second-order kinetic models (Figure 2B-C respectively). Pseudo first order model did not show a good fitting for bare and functionalized MSN. On the contrary, the pseudo-second order model fitted the experimental data (R^2 = 0.99 for both samples).

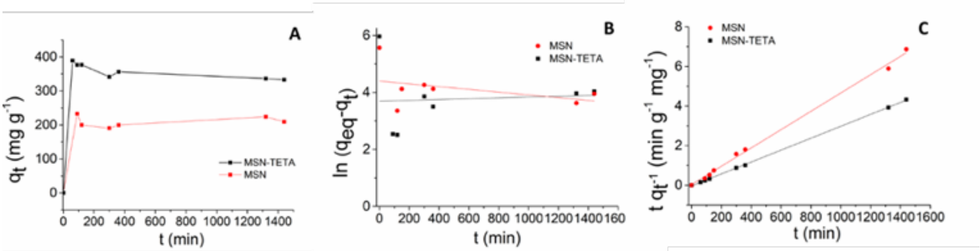

Figure 2. (A) Adsorption kinetics of SMZ on MSN and MSN-TETA fitted with (B) pseudo-first order and (C) pseudo-second order

A new drug delivery system based on sulfamethizole loaded on MSN and MSN-TETA was shown. SAXS and BET structural characterizations confirmed the successful synthesis of MSN having the typical hexagonal structure and the expected decrease of the total surface area due to the presence of the functionalization moieties. The adsorption kinetics on both MSN and MSN-TETA was consistent with a pseudo-second order model. The highest sulfamethizole loading obtained on MSN-TETA rather than bare MSN suggested a favorable interaction between the positive charged TETA and the negative charged drug. The electrostatic interactions between the sulfamethizole and the MSN was shown to be of uttermost importance in the sulfamethizole adsorption and release kinetics.

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1A –Drug loading on mesoporous silica nanoparticles (MSN) to contrast antibiotic resistance

Part 2: A drug delivery system based on poly-L-lysine grafted mesoporous silica nanoparticles for quercetin release

C. Carucci, G. Sechi, M. Piludu, M. Monduzzi, A. Salis

Aims

To optimize the loading and release process of antimicrobial substances from specific carriers, different water/organic solvent mixture can be used. This work focuses on the design and preparation of a drug delivery system based on mesoporous silica nanoparticles (MSN) with different mixtures used during the loading step. The antimicrobial compound quercetin was loaded using two ethanol-water mixtures as solvent, namely EtOH:H_2O mixtures at the ratios 80:20 and 50:50. Quercetin loading and release were studied in bare MSN, functionalized with 3-aminopropyl-triethoxysilane (MSN-NH_2), triethylenetetramine (MSN-TETA) and poly-L-lysine (MSN-NH_2-PLL, MSN-TETA-PLL).

Results

The effect of EtOH:H_2O ratio in the loading step on quercetin release was studied for all MSN samples. When quercetin was loaded using 80:20 EtOH:H_2O ratio, the maximal concentration of released quercetin was 1.8 µg/mL for MSN and MSN-NH_2 increasing up to 2.8 µg/mL for MSN-TETA (Figure 1A). The release kinetic constant, k_1, was very high for bare MSN (80.9 h^{-1}) suggesting a burst release of quercetin. Lower values of k_1, were obtained for MSN-TETA and MSN-NH_2, respectively. With a solvent composition EtOH:H_2O 80:20 quercetin the greatest amount of quercetin was loaded, nevertheless the release performances were very poor suggesting a strong influence of the chosen mixture. The solvent composition EtOH:H_2O 50:50 improved not only the maximal concentration of released quercetin (3.8 µg/mL) but also the kinetics constants with a sustained release showed for the MSN-NH_2 and MSN-TETA samples.

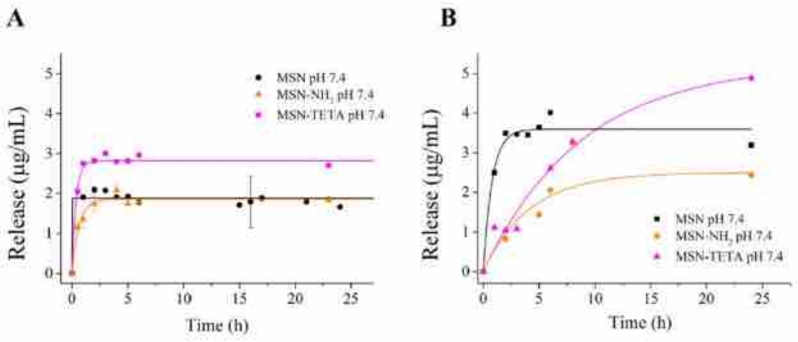

Figure 1. Quercetin release of MSN, MSN-NH_2, MSN-TETA after quercetin loading in a EtOH:H_2O mixture A) 80:20 and B) 50:50.

The PLL grafted samples allowed to reach a released amounts of quercetin in the range 0.2 - 3 µg/mL which matched the concentration range found in plasma after quercetin supplements consumption. Moreover, loading on PLL avoided quercetin oxidation up to 6 h thus improving its stability. The composition of the solvent mixture used to load quercetin onto MSN has been demonstrated crucial to improve the release performance. The results suggest that the solvent composition used in the loading step must be carefully evaluated when dealing with poorly soluble drugs to maximize the drug delivery system performance.

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1A – Fibroin and nanocellulose composite films as new adhesives for aged textiles

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CSGI and University of Florence

Aims

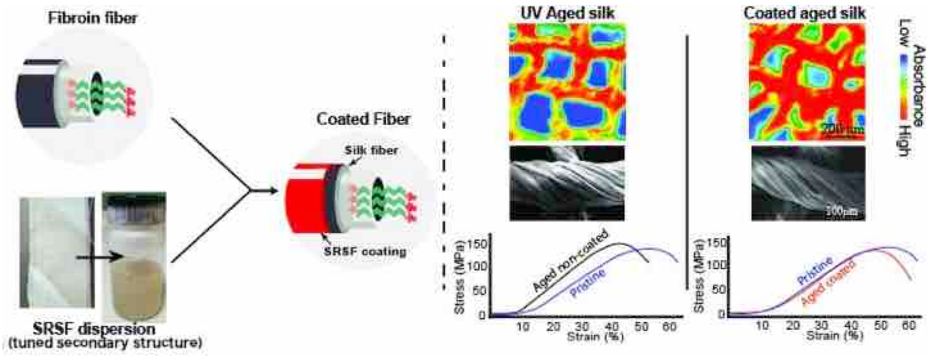
While historical and aged textiles (canvas, silk) constitute a relevant portion of our Cultural Heritage, there is a lack of physico-chemically compatible solutions to provide re-adhesion to the damaged fibers at the micro-scale without introducing potentially harmful adhesives such as those based on synthetic polymers.

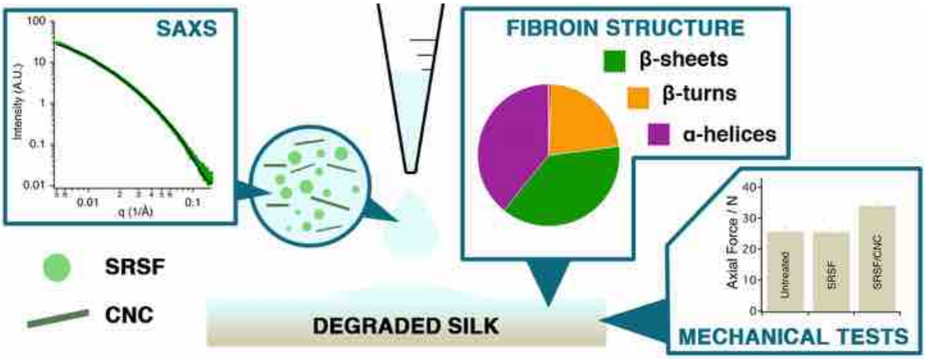
Colloidal systems and advanced functional materials based on biopolymers are optimal candidates to fill this gap. We recently investigated composite dispersions of self-regenerated silk fibroin (SRSF) or SRF and cellulose nanocrystals (CNC), to cast adhesive films able to recover the mechanical properties of aged silk fibers.

Results

SRSF produce films with controlled crystalline/amorphous content depending on the protein concentration in the dispersion; however, there is a limit to the concentration for the sole SRSF dispersions, as crystalline SRSF phases (with scarce chain mobility) cast over aged silk fibers produce brittle films that worsen the fibers' mechanical behavior. Amorphous SRSF films instead improve the flexibility of the aged textiles. Adding CNC to the dispersions speeds up the assembly of SRSF likely thanks to protein organization on the cellulose fibers, and composite films with partially crystalline fibroin (high α-helices content) can be cast even at low fibroin concentration. Noticeably, the composite films produce better improvement than the sole SRSF amorphous films or CNC films obtained from dispersions with the same concentration of consolidant.

The hybrid SRSF-CNC dispersions candidate thus as new promising adhesives for aged silk (and canvas) textiles; in addition, we provided for the first time a semi-quantitative evaluation of the structuring effect of CNC on SRSF assemblies, which can help the development of "green" chemistry solutions in different fields even beyond Cultural Heritage preservation, such as biomaterials and tissue engineering, and the preparation of composites with enhanced properties.





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1A – Inorganic nanomaterials for the consolidation of bone remains

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In collaboration with M. Lari, M.E. Fedi, L. Liccioli, V. Zaro, S. Vai, A. Modi, A. Meoli, S. Barone, G. Marradi, D. Caramelli

Aims

Bones recovered from archaeological excavations are not simply objects of historical and archaeological interest. They can be also considered as a true “Biological Archive” that should be accessible for long-term studies, in fact, ancient human bones are a fundamental resource to understand the uses of past human societies.

Since the twentieth century the products that have been largely used for the consolidation of bone remains are mainly composed by natural and synthetic polymers (vinyl and acrylic polymers, cellulose derivatives, etc.). Unfortunately, the extensive application of these products has many drawbacks mainly due to their low chemical stability that results in simultaneous depolymerization and crosslinking reactions that partially compromise their performances.

Despite the promising results obtained in previous studies where $Ca(OH)_2$ nanoparticles pure or in combination with a solution of diammonium phosphate (DAP) were used as consolidants for degraded bone matrices of historical and archaeological interest, it would be necessary to develop an even more compatible and easily applicable consolidation treatment to be used in situ The most important novelty proposed in the present study is the use of a dispersion of previously prepared hydroxyapatite (HAP) nanoparticles in combination with DAP and $Ca(OH)_2$ nanoparticles. The HAP nanomaterial matches the compatibility criterion and, by synthesizing nanoparticles of proper dimensions, they have the capacity to penetrate the porous support and to fill in almost all fractures and cracks. Moreover, the idea at the basis of the proposed methodology was to try fixing the obtained HAP nanoparticles to the substrate by exploiting the binding properties of a mixture containing DAP and $Ca(OH)_2$ nanoparticles

Another important novelty of this work was the multidisciplinary approach adopted to evaluate not only the performance of the proposed consolidating treatment but also its possible drawbacks for 14C dating and palaeogenetic analyses. Then the efficacy of the consolidation was examined in terms of the impact of the treatment on the physico-chemical and mechanical properties of the treated bones. The results obtained from the consolidated and the untreated fragments indicate that the consolidation process doesn’t have a significant impact on the quality and reliability of both the genetic and on the radiocarbon dating results.

Results

The consolidating effect of the HAP nanoparticles has been evaluated after a pre-treatment with $Ca(OH)_2$ nanoparticles and a following treatment with a DAP aqueous solution. The application of hydroxyapatite nanoparticles affects the overall porosity and the adsorption-desorption isotherms obtained through microtomography that decrease of 35%. Furthermore, after the treatment, the formation of a homogeneous dense phase into the bone matrix is observed as indicated also by the increase of the Vickers microhardness (more than 60%).

Figure 1 shows some SEM micrographs collected before (NT) and after (T) the application of the consolidant. The consolidation treatment leads to the progressive recovery of a much more compact structure and to the formation of a homogeneous texture (Figure T) with an apparent decrease of the dimensions of the open pores. The efficacy of the treatment is also confirmed by microtomography analysis (Figure 1, right) that indicates how the consolidation interests not only the surface of the bone, but also the bulk of the porous matrix.

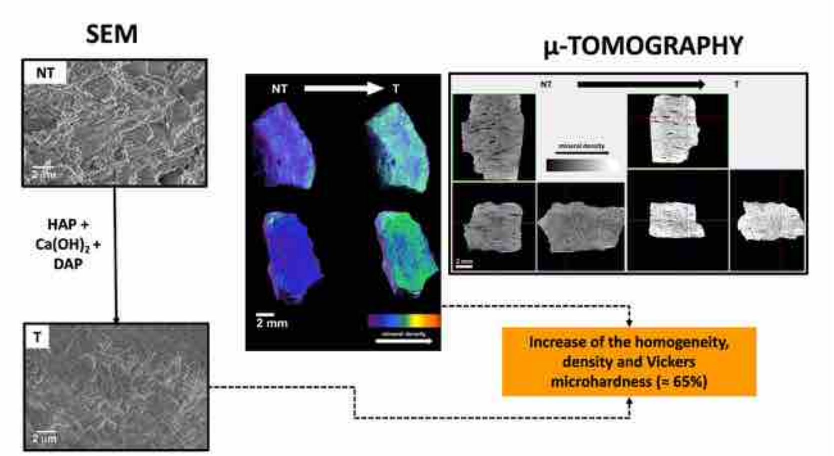

Figure 1. Left: SEM micrographs of Iron Age bone fragments. Images have has been collected from a sample before (NT) and after (T) the consolidation treatment respectively. Right: microtomography analysis of the NT and T samples.

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1A – Intrinsically chiral selectors in electrochemical sensing of biomolecules

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Aims

Intrinsically chiral selectors are those molecules in which the stereogenic scaffold responsible for chirality and the molecular group responsible for their specific properties coincide. This structural feature can be exploited for outstanding enantioselection. The aim of the work is to prepare intrinsically chiral organic molecules, based on azahelicene moieties, able to be used either as chiral additives in ionic liquids or as coating for electrodes, to be used as selectors in cyclic voltammetry experiments for the recognition of chiral biomolecules.

Results

The molecules chosen for the modification of ionic liquids were quaternary salts of aza[6]helicenes, whose enantiomers (the P- and M-helixes constituting the molecular backbone) are configurationally stable at r.t. In particular, 5-aza[6]helicene and 2,12-diaza[6]helicene were synthesized, their enantiomers separated by chiral HPLC and the enantiomers quaternarized by reaction with octyl iodide. In the case of 2,12-diaza[6]helicene it was possible to obtain both monosubstituted N-ethyl-2,12-diaza[6]helicene-2-ium iodide and disubstituted N,N'-diethyl-2,12-diaza[6]helicene-2,12- diium diiodide (Fig.1), which were then reacted with silver bis (trifluoromethane sulfonyl) imidate (bis-triflimidate, NTf_2) for anion exchange. This is necessary because iodide counterion would not be stable in electrochemical experiments, and would also lower the melting point of the resulting salts.

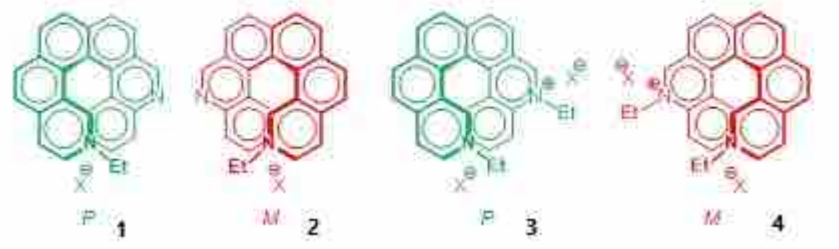

Figure 1. *N*-ethyl-2,12-diaza[6]helicene-2-ium (**1, 2**) and *N,N'*-diethyl-2,12-diaza[6]helicene-2,12-diium (**3,4**) salts

The diazahelicene compounds were investigated as inherently chiral selectors by adding them in low concentration to the achiral IL 1-butyl-3-methylimidazolium bis-triflimidate [$(BMIM)NTf_2$]. From preliminary experiments with 5-aza[6]helicenium salt it was possible to confirm that inherent chirality extraordinarily enhances the enantioselection ability in comparison with chiral ILs designed according to more traditional schemes, involving the separation between chiral and onium moieties. In fact, peak potential separations jump here from a few dozens of mV to more than one hundred. Furthermore, the chiral media obtained from 2,12-diaza[6]helicene was tested a) for enantioselective cyclic voltammetry experiments (CV) with the benchmark electroactive enantiomer probes (R)-(+)- or (S)-(−)- N,N’ -dimethyl- 1-ferrocenylethylamine ((R)-Fc and (S)-Fc; and b) for enantioselective differential pulse voltammetry (DPV) experiments with the enantiomers of an electroactive probe of biological interest, i.e., L- or D-tryptophan, an α-amino acid. Enantiodiscrimination in terms of significant potential differences is observed in all cases, with the same probe enantiomer sequence (i.e., with (R)—undergoing easier oxidation than (S)-), consistently with the inherently chiral selectors having the same configuration. However, the peak potential differences significantly increase with increasing number of alkylated, positively charged nitrogen atoms.

Good linear dynamic ranges for the peak currents enable to add quantification to the configuration assignment based on peak potential.

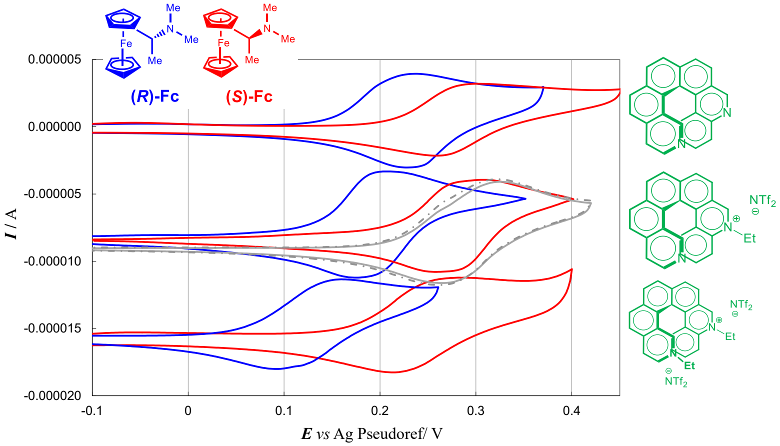

Figure 2: A synopsis of the CV features of (R)-Fc (blue line) and (S)-Fc (red line) solutions on graphite SPE in (BMIM)NTf2 with diazahelicene and its quaternary derivatives as chiral additives (0.02 M).

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1A – Micro-gel in transparent porous hydrogel: synthesis, morphological characterization, and diffusivity studies

Gavino Bassu, Marco Laurati, Emiliano Fratini

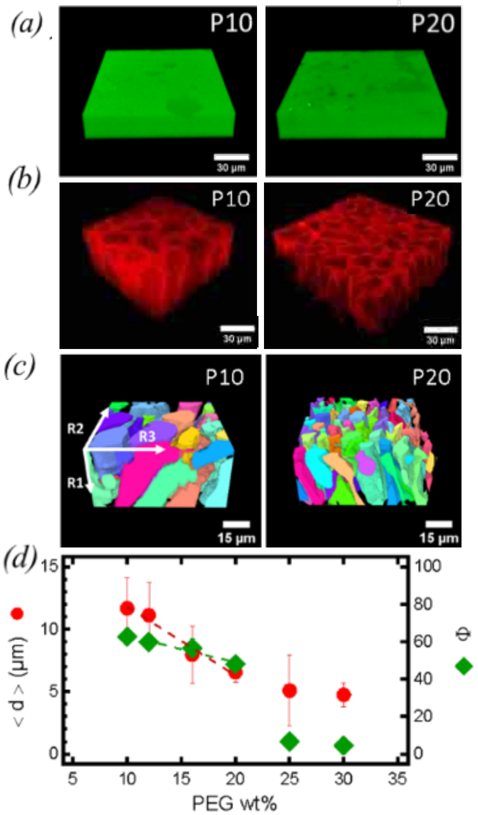
Aims

Even though hydrogels are widely studied for their loading and release properties, large object diffusion through three-dimensional (3D) porous media remains mostly unknown. A better understanding of how micrometric objects move within these porous systems would allow a huge improvement regarding controlled migration processes. Bioremediation, biofertilization, microbial drug delivery and bacterial therapies rely on bacterial migration in disordered 3D porous media. The main problem with the direct visualization of the dynamic motion in micro-porous systems is the complete opacity associated to these networks. As a result, the actual migration models of motile bacteria are limited and based on unconfined 3D or 2D systems. To fill this gap of knowledge transparent 3D porous media are required to study, predict, and control bacterial specific treatments based on these micrometric systems.

Results

We developed a facile synthesis of a 3D transparent porous network of poly(ethylene glycol) (PEG) that allows the study of mobility and the migration properties of microscopic objects loaded into this hydrated structure. Through polymerization of the acrylated-polymeric unit (PEGDA) we synthetized biocompatible hydrogels with high transparency but undetectable porosity on the micro-scale (Fig.1- a). By freeze-drying the hydrogel, we can generate the desired porosity at the micron scale without significantly affecting the optical properties of the polymeric substrate. Laser scanning confocal microscopy revealed the heterogeneity of the micrometric porous network (Fig.1- b). The low opacity of the final hydrogel allowed a deep visualization of the structure, even over 80 µm in depth.

Structural and geometrical characterization of the porous media were carried out by the specific ImageJ's plugin MorphoLibJ (Fig.1- c). Tuning the PEGDA amount in the pre-reaction solution was possible to obtain highly interconnected networks with mean pore diameter ranging from 12 to 6 µm and with asymmetry along one direction. As shown in Fig.1- b, increasing the structural component the average diameter decreases. As a result, the porosity decreases linearly with the PEGDA amount in the range of concentration of 10 to 20 wt%.



Thermo-responsive microspheres of pNIPAM (1.8 µm in diameter) were chosen as a starting point for more complex living systems (i.e. bacteria) to directly probe the stochastic motion through the polymeric network by laser tracking system defining trajectories and mean square displacements. Raw data were processed and analysed by Trackpy, a fast and flexible Particle-Tracking tool, to obtain the mean square displacement) as a function of the Lag time. Consistent with the hydrogel's confinement, the probe exposed sub-diffusive motions with diffusivity directly dependent on the pore size (i.e., polymer composition).

The presented system can be easily modified in terms of the final architecture and interface reactivity allowing to study the effect of the microscopic confining structure on passive or active diffusing systems (i.e. bacteria).

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1A – Molecular Communication through biological liquid

L. Fichera, F. Calì, G. Li-Destri, N. Tuccitto

Aims

Molecular communication allows information to be exchanged in environments where electromagnetic waves are prohibited. It employs the exchange of information particles travelling through fluids. The transmitter releases several chemical messengers inside the communication channel, encoding the message it intends to send in an appropriate way. These messengers will be propagated in the communication channel according to the laws that determine their movement in the environment, until they reach the receiver, which then captures their presence and decodes their content.

Results

Molecular Communication (MoCo), has been applied inside the human body allowing communication between the user (including doctor and patient) and the operating devices or the active devices implanted in biological systems. This innovative communication method consists of using information particles (mainly nanoparticles) as a vector for the message to be transmitted, in a similar way to how communication in nature has been performed for millions of years though the release and detection of hormones.

MoCo is a method of transferring information from one point to another by encoding the message within chemical signals. To date, most of the research concerning MoCo is strongly oriented towards the theorisation and modelling of the transmitter-communication channel-receiver system. The transmitter (TX) releases several chemical messengers inside the communication channel, which encode the intended message in an appropriate way. These messengers will propagate in the communication channel according to the laws that determine their movement in that environment, until they reach the receiver (RX), which then captures their presence and decodes their content. The encoding and transmission of a message occurs as a series of sequential symbols, each in a time slot.

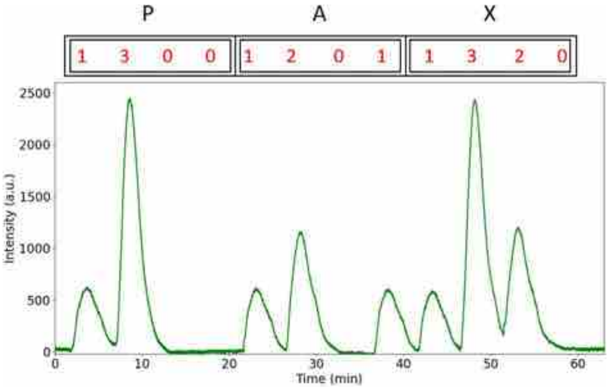

Fig.1 Transmission of the word “PAX” under Quaternary – CSK (Q-CSK) modulation technique

The meaning of the symbol within the time slot depends on the chosen modulation method. Fig. 1 shows an example of a transmitted signal using a multi-threshold multinary Concentration Shift Keying modulation technique. The word “pax” has been converted from text to ASCII quaternary encoding. To do this, we released pulses of nanomessengres over time at three different concentrations (0.5, 1 and 2 mg/mL) for symbols 1, 2 and 3, respectively. Symbol 0 was coded without any release of nanoparticles. The release delay between pulses was 5 minutes and a flow rate of 5 mL/h was used.

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1A – Molecular dynamics on poly-HEMA hydrogels

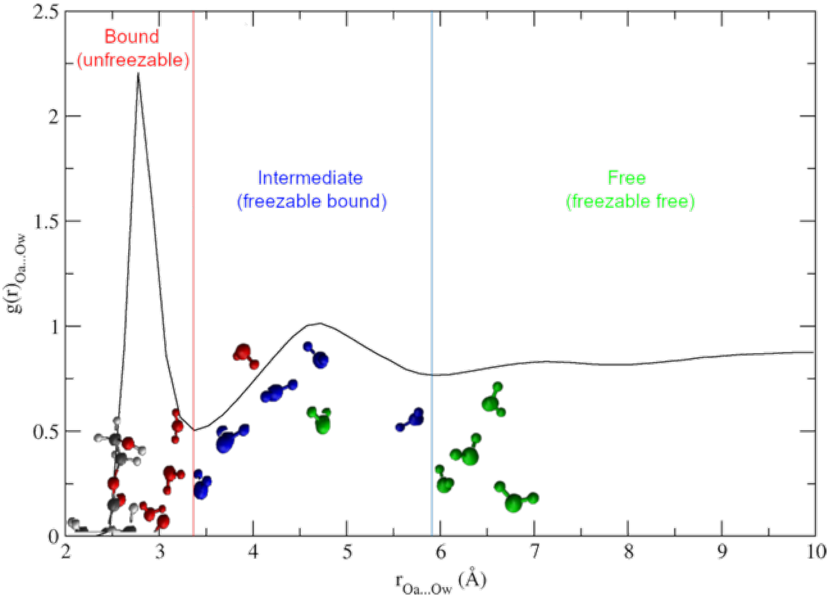
I. Vettori, M. Macchiagodena, G. Bassu, M. Pagliai, E. Fratini, P. Baglioni

Aims

Despite the numerous experimental papers devoted to hydroxyethyl methacrylate (HEMA)-based physical and chemical hydrogels, literature lacks theoretical studies on poly-HEMA systems. Due to their wide application in biomedical fields, transport properties of such hydrogels and the system dynamics might deserve deeper investigations. In this context, the water role was investigated differentiating between three states in low molecular weight physical systems for water content (WC) from 10 to 40% wt using the TIP4P-FB water model within the GROMACS suite. Radial distribution functions were calculated for evaluating the solute-solvent and solvent-solvent interactions. Water diffusion coefficients as well as pairwise and jump distances were computed at various T (273, 298, 360 K, respectively). In addition to low molecular weight hydrogels, high molecular weight systems, resembling both physical and chemical poly-HEMA hydrogels presented elsewhere, were tailored and modelled by modifying GROMACS libraries for the evaluation of inter- and intramolecular interactions and are currently under study.

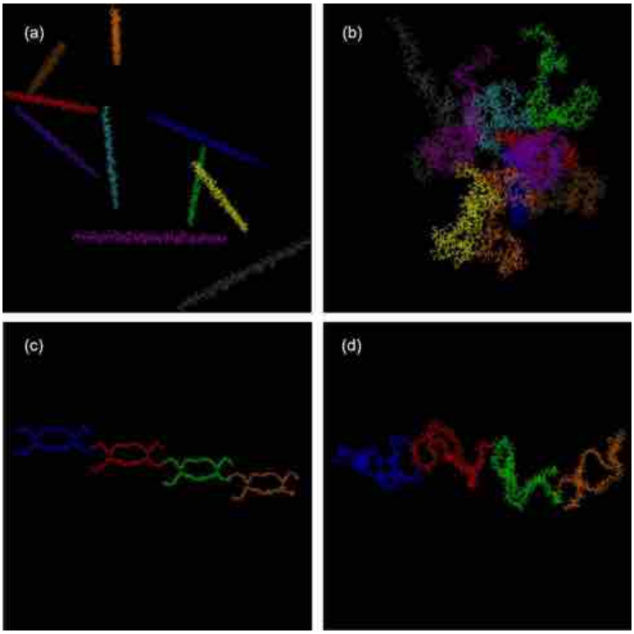
Results

The water classification according to solvation shells is reported in the radial distribution function on the poly-HEMA system at WC 40% wt, differentiating: “bound” water, as the solvent molecules within 3.5 Å from the polymeric chains; (ii) “intermediate” water, as the ones in the 3.5 and 6 Å range and (iii) “free” water, all the rest.



The water states discrimination from a MD point of view sheds light on their different contributions to averaged coefficients that are achieved experimentally, as diffusion coefficients, jump distances (around 0.47 nm), diffusion activation energy (from 10 kJ/mol at WC 10% wt to 18 kJ/mol at WC 40% wt) or hydrogen bond lifetime. Results show that free water fraction is negligible up to WC 20% wt in agreement with experimental findings. From WC 20 to 40% wt, about 2 water molecules coordinate each C-OH group and 1 interacts with the C=O group at 1.8 Å distance. The average diffusion coefficients get larger while increasing WC (from 0.05 ± 0.03 at WC 10% to 0.36 ± 0.11 *10-5cm2/s at WC 40%, at T 298 K); this is in compliance with the increase of the free water fraction, which presents a bulk-like water behaviour, as shown by its individual diffusion coefficient. The polymeric cluster gyration radius follow an enlarging trend while rising WC (from 1.6 at WC 10% wt to 2.5 at WC 40% wt), confirming the water role as a plasticizer within the polymeric network.

Input high molecular weight physical (a) and chemical (c) poly-HEMA structures were minimized in the presence of water eccess up to the desired WC (b and d, respectively) for the next studies.



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1A – Multistep self-organization of amphiphilic peptides

G.M.L. Messina, M. Dettin, A. Palleschi, G. Marletta

Aims

The arrangement of adsorbed molecules and macromolecules at interfaces determines the functional performances of the final interfacial constructs. This is particularly important for biointerfaces, where the effective bioactivity of the biomolecules, is fully determined by the many factors driving folding or unfolding, orientation and proper exposure of epitopes, and density and packing mode of the adsorbed biomolecules.

In the present research work the self-assembly behavior of (i) a single tail alanine-based peptide, and (ii) a double tail alanine– lysine peptide, have been investigated, focusing on the “history” of the early interaction events of aggregation/organization of these two peptide sequences from the bulk solution to their landing at liquid–solid interfaces, which is responsible for the further organization at the mesoscopic scale

Atomic Force Microscopy (AFM), and detailed Molecular Dynamics (MD) simulations have been performed to describe the peptide arrangements occurring on the surface.

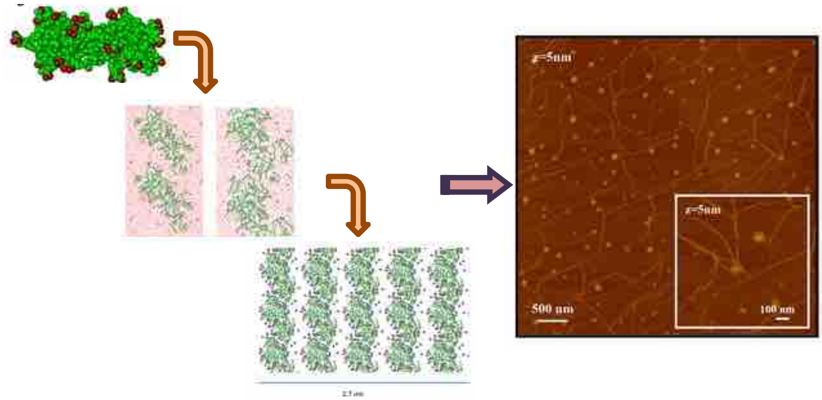
Results

The self-organization of peptides adsorbed on mica surfaces observed in AFM micrographs raises the crucial problem of unraveling the factors driving the observed self-organization behavior, i.e., the very long, narrow and flat nanoribbon networks in the case of double tail and isolated, round-shaped, unstructured nano- aggregates for single tail. In order to tackle this problem, detailed molecular dynamics simulations have been performed.

The self-assembling process involves at first the formation of unstructured aggregates, which in turn forms short and narrow linear assemblies (i.e., nanofilaments), which are the building blocks to finally yield micrometer long nanoribbons. It is important to point out that while the formation of unstructured “primary” round-shaped aggregates occurs for both peptides, only the “double tail” systems are able to evolve up to long range self-organized structures, including networks of nanoribbons.

The formation of the primary aggregates and the further growth of long range assemblies obey to an entangled entropic and enthalpic effects due to the interaction of hydrophobic parts and of strong electrostatic interactions between the charged heads of the peptides, during the formation of larger aggregates.

The overall assembly process implies the matching of thermodynamic state functions, influenced by the presence of the solid–liquid interface, which appears as the stabilization factor of the most ordered long-term equilibrium state, depending on the respective molecular structure.



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1A – Non-Destructive Monitoring of P. fluorescens and S. epidermidis Biofilm under Different Media by Fourier Transform Infrared Spectroscopy and Other Corroborative Techniques

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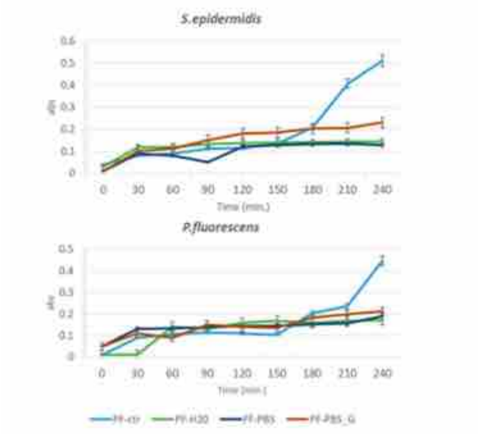
Aims

Most bacteria, when propagated in static liquid culture, grow within the broth phase or quickly sediment to the bottom. External environmental conditions deeply affect the success in surface colonization and the consequent pathogenesis of biofilm related infections. Bacteria are equipped with extracellular polymeric substances (EPS) that permit a prompt formation of surface-related bacterial communities. ATR-FTIR spectroscopy has proven to be a useful analytical tool for monitoring biofilms in situ, being non-destructive, in real-time and under fully hydrated conditions technique. This work focus on the study of the early stages of bacteria attachment to germanium crystal surface, using attenuated total reflectance Fourier transform infrared (ATR-FTIR) technique. A detailed analysis of the whole spectral profile of bacteria under study has been performed to gain more insight at the molecular level into biochemical and physiological changes during the early stages of biofilm development. Pseudomonas fluorescens (PF) and Staphylococcus epidermidis (SE) bacteria were chosen as a model because of their inclination to be surface bound in diverse environmental conditions.

Results

This study highlights the influence of environmental condition on the chemistry of bacteria cell surfaces and biofilm, during the early stage of bacteria attachment to the surface. The amount of bacterial EPS in the different media was monitored by crystal violet assay for the same time interval as spectroscopy experiment. In addition, the presence of bacterial EPS on the ATR crystal was confirmed by O-safranin staining at the end of each experiment. Dominant functional groups of bacterial EPS were, as expected, carboxyl, amide, phosphate, hydroxyl, and carbohydrate related moieties. Both the bacterial species, at planktonic phase, show all the IR bands expected, but with an evident difference in proteins/polysaccharides ratio. SE shows a strong band in Zone III due to polysaccharides vibrational absorption, while, conversely, the PF is characterized by a strong band in Zone I related to protein vibrational absorption, together with a weak polysaccharide absorption. The phospholipids and nucleic acid bands show similar intensities in both bacterial species, as expected, since the initial number of bacteria cells are almost the same and cell division and proliferation occur generally in a longer time with respect to the experiment timing. Concerning the biofilm evolution over the time, both the bacterial species, are detectable on the surface within 45 and 75 min after the inoculation. In water both SE and PF start to produce plenty of proteins in a short time probably because they need to firmly attach to the surface, due to stressful lack of nutrients. The osmotic shock appears to be the driving force forcing the bacteria to attach to the surface. In fact, the presence of PBS (physiological ionic strength but no nutrients) and glucose mitigate this process. An exception was PF where a low amount of proteins was produced when glucose is added. Independently on the environmental conditions (H_2O, PBS, PBS-G) both SE and PF start to increase their polysaccharide content, even if with different kinetics and amounts, probably because of biofilm needs to counteract the lack of nutrients. After 180 min all spectra of SE and PF show an increase of polysaccharide bands intensity with respect to the inoculum with PBS and PBS-G samples. The prevalent structure of the proteins has been highlighted by the second derivative study. PF proteins are mainly in α-helix and β-sheet conformation and their ratio is constant and independent on the media. Only in PBS medium the random coils component is visible. SE protein conformation at inoculum and in H_2O are similar and composed of α-helix, random coils and β-sheet. The random coil conformation seems to decrease in PBS and PBS-G.



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1A – Sfide: A Smart Framework For Virus Detection

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Aims

In the frame of the SFIDE project aiming to construct a smart framework for real-time detection of the presence of viruses in human breathe and in aerosol, such as human Coronaviruses (using low pathogenic strains, selected in the project), we set-up a model label-free immunosensor to verify the selectivity of the selected primary antibody (anti-virus AbI) and the antigen-antibody interaction; in addition the analytical performances of a electrochemical platform is estimated. In this preliminary work, we report about the deep electrochemical characterization of a screen-printed graphite electrode (SPE) interface during the multistep Cov 299E immunosensor build-up, as the prototype of of the proposed system. The immunosensor was assembled on multiwall (MWNT)-modified platforms that are amid the most versatile and customizable enabling surface coatings with a plethora of bio/materials for the construction of a wide variety of electrochemical sensing platforms. The schematic representation of the above-mentioned immunosensor is depicted in Figure 1.

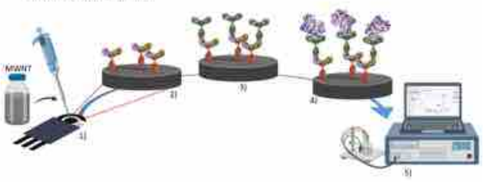

Figure 1. Schematic representation of MWNT-SPE based immunosensor assembly for CoV detection. The graphite SPE are initially drop-casted with 1) MWNT, the nanomodified platforms are exploited for 2) the secondary antibody (anti IgG) and 3) the primary antibody immobilization (anti-CoV). Once the immunological chain is built, the 4) immuno-complex formation is observed.

Results

Layer-by-layer electrochemical characterization of the CoV-immunosensor

Cyclic voltammetry was used to deeply characterize the electrochemical behaviour of the electrode/electrolyte interface at each step of the biosensor fabrication, shown in Figure 2 and Table 1. These results were obtained by using $[Fe(CN)_6]^{3-/4-}$ as an electroactive probe.

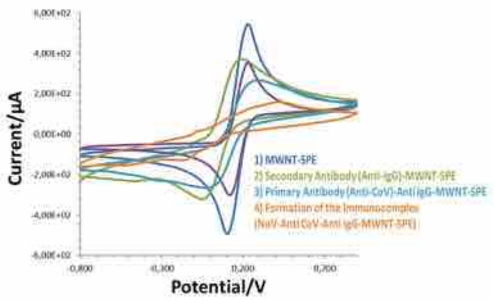

Figure 2. Electrochemical characterization of electrode interfaces during the multistep biosensor build-up. Cyclic voltammograms recorded in 0.005 M $[Fe(CN)_6]^{4-/3-}$ in 0.05 M PBS.

Table 1. Anodic and cathodic peak ratio (Ipa/Ipc), peak-to-peak separation, effective surface area (A) and heterogeneous electron transfer rate constant (k^0) estimated for MWNT-SPE using CV in 0.005 M $[Fe(CN)_6]^{4-/3-}$, in PBS pH 7.4, during CoV-immunosensor fabrication.

Layer	I_{pa}/I_{pc}	ΔE (mV)	A (cm^2)	k^0 (cm/s)
MWNT	1.0 ± 0.2	110 ± 14	0.36 ± 0.05	$(3.5 \pm 0.4)\cdot 10^{-3}$
Anti IgG	1.2 ± 0.2	200 ± 25	0.28 ± 0.02	$(3.3 \pm 0.5)\cdot 10^{-4}$
Anti CoV	1.4 ± 0.4	293 ± 33	0.05 ± 0.01	/
NoV	/	525 ± 39	0.020 ± 0.002	/

Primary antibody optimization and preliminary analytical performance.

Once anti-IgG was immobilized, the ideal anti-CoV concentration were investigated. To this purpose, the electrochemical response (SWV faradic current) of different anti-CoV concentrations (0, 0.5, 1, 2, 5, 10 µg/mL), incubated for 1h on anti-IgG-MWNT-modified SPE (Figure 3a) were tested. By increasing the antibody concentration, a decrease in the recorded faradic current values is observed that can be explained by the following mechanism: the higher the antibody concentration, the higher the molecular crowding on the electrode surface due to the antibody molecular complementarity. The proper antibody concentration to be applied can be obtained considering the 75-80% of the maximum value of the association curve, that for anti-CoV is equal to 5 µg/mL. From the dose-response curve reported in Figure 3b a LOD of 2ng/mL with a good reproducibility of 13% (RSD%) are observed.

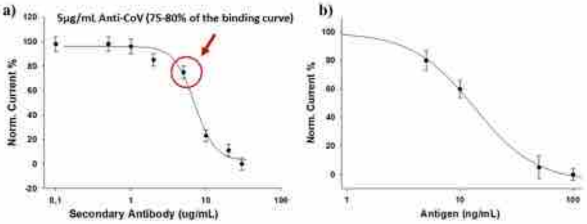

Figure 3: a) Binding curves (dilution of antibody solution) obtained using different concentrations of anti-CoV and b) the dose-response curve, obtained incubating different antigen concentrations. The results were obtained by making use of SWV and 0.05 M $[Fe(CN)_6]^{4-/3-}$ solution, in 0.05 M PBS + 0.01 M KCl, pH 7.4).

Project: Avviso" Fisr Dd 562/2020 - Fondo Integrativo Speciale Per La Ricerca - Codice Progetto Fisr2020ip_02585

1A – Single molecule bio-electronic smart system array for clinical testing

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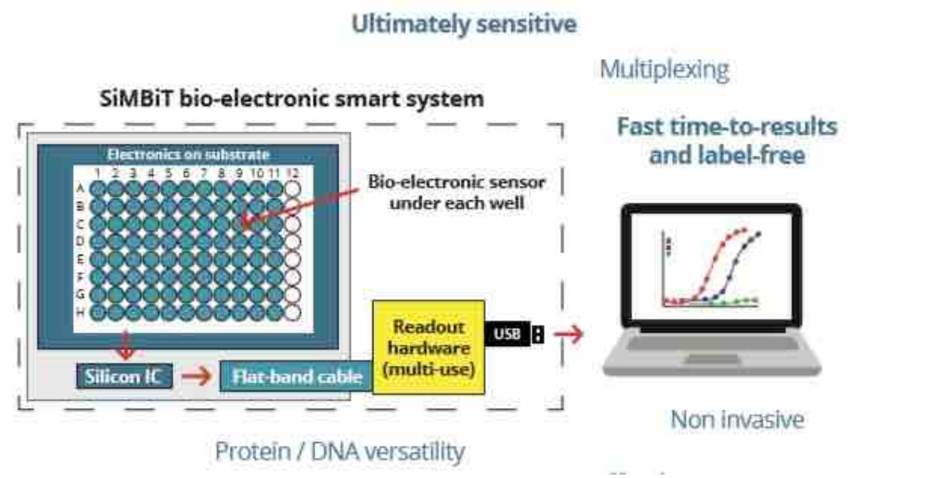
Aims

Digitizing biomarkers analysis by quantifying them at the single-molecule level is the new frontier for advancing the science of precision health. The SiMBiT project will develop a bio-electronic smart system leveraging on an existing lab-based proof-of-concept that can perform single-molecule detection of both proteins and DNA bio-markers. Specifically, the SiMBiT activities will develop the lab-based device into a cost-effective portable multiplexing array prototype that integrates, with a modular approach, novel materials and standard components/interfaces. The SiMBiT platform exhibits enhanced sensing capabilities: specificity towards both genomic and protein markers along with single-molecule detection limits and time-to-results within two hours. This makes the SiMBiT prototype the world best performing bio-electronic sensing system ever. SiMBiT will reach these ambitious goals with a multidisciplinary research effort involving device-physicists, analytical-chemists, bio-chemists, clinicians, electronic- and system-engineers. The platform is also single-use and cost-effective and can work in low-resource settings. The SiMBiT field-effect sensing system will be fabricated by means of future mass-manufacturable, large-area compatible, scalable techniques such as printing and other direct-writing processes. 3D printing of a module is also foreseen. The SiMBiT prototype will demonstrate, for first time, a matrix of up to 96 bio-electronic sensors and a Si IC chip for the processing of all data coming from the matrix, multiplexing single-molecule detection. As the Si IC pins are limited the chip area is reduced and its cost minimized, enabling a single-use assay plate. SiMBiT will apply the multiplexing single molecule technology to the early detection of human pancreatic neoplasms in a well-defined clinical context, performing simultaneous analysis of genomic and protein markers with a minimal sample volume, reduced costs and reduced time-to-results.

Results

The project is dedicated to the fabrication, characterization and optimization of the single sensing device. During the second reporting period of the project, the efforts were focused on the optimization of the biofunctionalization protocol and on the design and validation of the 3D printed sensing gate. The activities of WP2 have been focused on the study and optimization of the bio-functionalization protocol of the gate surface based on a systematic molecular characterization. The outputs on this activity are detailed in D2.3 (M18) and D2.4 (M24). As far as the gate is concerned, the activity carried out aims at the demonstration and validation of a 3D printed gate structure suitable for the development of the final gate cover plate that will fit the standard ELISA plate geometries. The outputs on this activity are given in D4.3 (M24). Moreover, the validation and the assessment of the analytical figures of merit of the final single SiMBiT sensor is reported in D2.5 (M24) and D2.6 (M30), using KRAS and MUC1 markers are detected in phosphate buffer saline solution and in whole blood serum at the single molecule detection limit.



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1A – Synthesis and characterization of magnesium based perovskite for flexible solar cells

G. Lucchesi, D. Giordano, G. Caminati

Aims

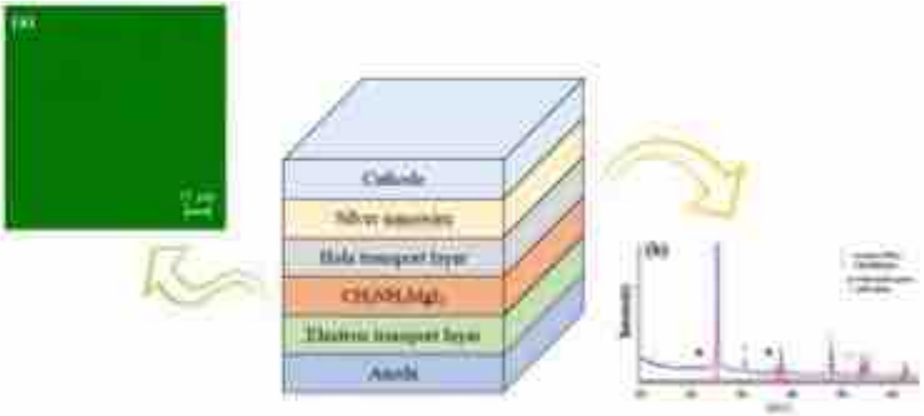
Perovskites are organic-inorganic materials with a ABX3 structure (where A = monovalent organic cation, B = divalent metal, and X = halide) suitable for various fields of application such as solar cells, light emitting diodes and sensors due to their strong light absorption, band gap, excitation lifetime and dielectric properties. The project focuses on the fabrication of non-toxic lead-free perovskite solar cell (PSC) with low environmental impact on flexible substrates.

Results

The chemical composition of the new PSC active layer was chosen according to DFT/LDA calculations substituting the more commonly used lead with magnesium to obtain a CH3NH3MgI3 perovskite structure. The construction of the PSC device was realized in a multistep process: deposition of the electron transport layer, synthesis of the perovskite active layer, deposition of the hole transport layer and of the counter electrode. The synthesis of the photoactive layer was optimized changing the relative volume of the precursor and the annealing temperature.

Spin-coating and doctor -blade was used to deposit a mixture of PEDOT:PSS and graphene oxide on plastic or cotton to obtain conducting flexible anode for the solar cell.

The XRD and SEM/EDX characterization of the Mg-PSC active layer confirmed the presence of the perovskite structure with the expected stoichiometry, the morphology of the active layer obtained both from SEM and Confocal Laser Scanning Microscopy shows the presence of a uniform distribution of the photo-emissive perovskite layer. Different PSC architectures were prepared incorporating a layer of silver nanowires in different positions of the multilayer devices.



The nanowires were deposited either by means of Langmuir-Blodgett or drop-casting technique depending on the layer position. Morphological characterization allowed for the evaluation of the surface density and the packing of the nanowires in the layer; UV-visible spectroscopy revealed distinct peaks due to the presence of the silver surface plasmon resonance.

The photoluminescence and the band gap of the perovskite layer was studied as a function of the preparation procedure. The efficiency and stability of the solar cells were estimated from I-V curves as a function of irradiation and storage time. The addition of silver nanowires was found to increase the conductivity of the electrodes and more importantly the overall efficiency of the PSC

Photoactive layers of magnesium perovskite quantum dots were also preliminary tested to improve the flexibility and the mechanical properties of the active layer. Photoluminescent quantum dots were successfully synthesized using the ligand-assisted reprecipitation method, XRD confirmed the expected perovskite structure of the nanometric.

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1A – Tannins-lignin mixed nanoformulations for improving the potential of neem oil as fungicide agent”

S. Falsini, T. Nieri, S. Schiff, A. Papini, L. Mugnai, C. Gonnelli, S. Ristori

University of Florence, Italy

Aims

Sustainability and circular economy are pushing for the search of natural materials to find new eco-friendly antiparasitic treatments, especially in the case of economically relevant agricultural cultivations such as grapevine. In this project, we propose to deliver neem oil, a potent natural biopesticide, by using *ad hoc* designed nanovectors (nanocapsules) which are fabricated through a scalable procedure from Kraft lignin and grapeseed tannins. The target pathogens are three fungi (Botrytis cinerea, Phaeoacremonium minimum, Phaeomoniella chlamydospora) which are responsible for the noxious grapevine trunk disease. These microorganisms are resistant to a broad spectrum of commercial products and are currently treated with potent, but not harmless, antifungal agents.

Results

Phenolic polymers are scarcely soluble in aqueous media; therefore, to facilitate their solubilization high pH values can be used. In particular, the acid-base titration curve of Kraft lignin showed that full deprotonation is obtained at pH > 13, coinciding with complete solubilization at 1-5% w/w concentration. Thus, we chose to work with lignin solutions at two starting pH vales, i.e. 13.5 and 11.5, in order to evidence the effect of the polymer solubility on the final preparation. Tannins could be dissolved in water at the concentration used for these preparations (≤ 5% w/w), but we maintained the same starting pH as for lignin solutions to allow direct comparison among samples with different composition. The final pH, anyway, was always in the range 6-8. To prepare the neem-loaded nanovectors, lignin and grape seed tannins were dissolved separately or in combination in aqueous KOH. Then 300µL of mixed neem oil and acetone solution 1:1 (v/v) were added to 3mL of polymer solutions and finally high-power sonication was applied to emulsify the oil phase in the water mixture. The structural analysis of the obtained formulations was performed by DLS and showed that lignin and tannins, either alone or in combination at different ratios, yield stable nanovectors, having mean diameter in the suitable range for drug delivery (150-300 nm) and low polydispersity (PdI = 0.1-0.3). However, for the empty nanoparticles, that is the formulations prepared without neem oil, larger size (700-1000 nm) and more polydisperse aggregates (PdI ≥ 0.6) were formed, indicating that in this case the polymer particles didn’t adopt the typical core-shell arrangement of nanocapsules, but rather gave long wormlike micelles. This hypothesis was in agreement with preliminary high resolution investigation carried out by SAXS.

The surface of all the final aggregates was negatively charged and the measured Zeta potential varied approximately from -50 to -80 mV, showing more negative values in samples prepared with high lignin content at starting pH=13.5.

The fungal sensitivity to antimicrobial agents was evaluated *in vitro* through the appearance and extension of a zone around the droplet of administered solution where no fungi growth could be evidenced. The diameter of this inhibition zone (IZD) grew larger with increasing antifungal activity. After 7 days, conidia germinated and the mycelium expanded uniformly on the dishes. The IZD size depended on the sensitivity antimicrobial agents (commercial agents or nanoformulations). P. minimum was the most affected of the three microorganisms tested, both in the treatment with standard pesticides and with neem oil. Figure 1 reports some representative results obtained by *in vitro* tests. Negative controls were water (1A), the commercial pesticide Cumeta Flow (1B) and empty lignin nanoaggregates (1E), showing no or very slight antifungal activity. On the contrary the commercial pesticide Pindarus 25 WDG reduced the P. minimum growth with IZD = 2.68 cm ± 0.2 (1C). Neem oil administered in the form of 78% water emulsion, as recommended by the producer (Natural-mente srl, Florence, Italy), gave a IZD of 3.4 cm ± 0.1 (1D). Pure lignin and mixed (1:1 w/w) lignin-tannins NCs prepared at starting pH=11.5 induced a IZD of 1.8 cm ± 0.1 and 2.7 cm ± 0.2, respectively (images not reported in the figure) at neem oil concentration as low as 0.4%w/w and 1.5% w/v, respectively. However, the most effective formulation was pure lignin NCs prepared at starting pH = 13.5, with IZD = 3.0 cm ± 0.1 and 0.45% w/w neem oil concentration.

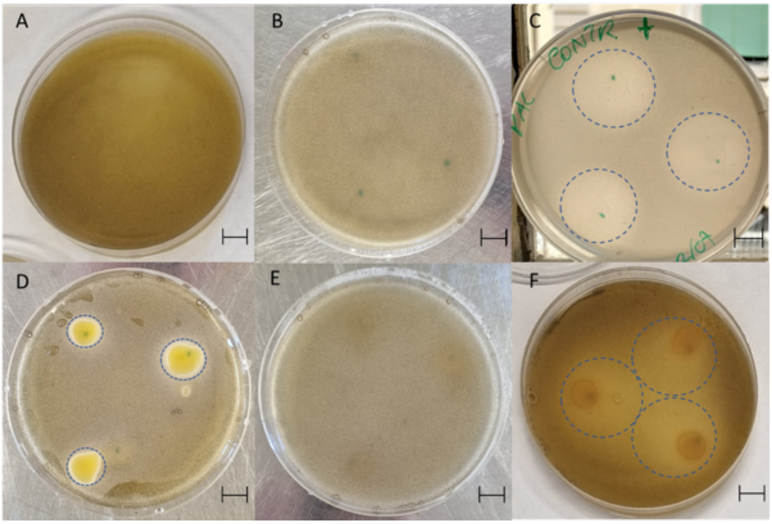


Figure 1. Growth inhibition observed on P. minimum with different antifungal agents (see text for more details). Bar scale = 1cm.

In conclusion, we showed that lignin-based nanocapsules can efficiently deliver neem oil on P. minimum, reducing the antifungal dose by up to ~400 times. This can be correlated with the fact that the interfaces available for the contact between neem oil and the pathogens are greatly enhanced as a consequence of nanodelivery and if a biocidal potentiality exists, it can be magnified accordingly.

1B – Alginate Films Encapsulating Lemongrass Essential Oil as Affected by Spray Calcium Application

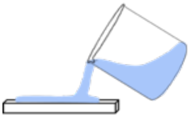
M. Cofelice, F. Cuomo , F. Lopez

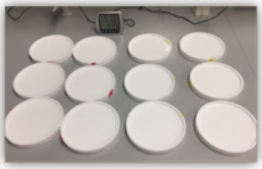
Aims

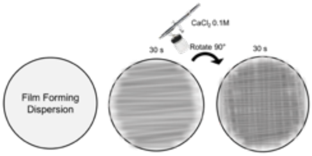
The necessity of producing innovative packaging systems has directed the attention of food industries towards the use of biodegradable polymers for developing new films able to protect foods and to extend their shelf-life, with lower environmental impact. In particular, edible films combining hydrophilic and hydrophobic ingredients could retard moisture loss, gas migration and ensure food integrity, reducing the necessity of using synthetic plastics.

Results

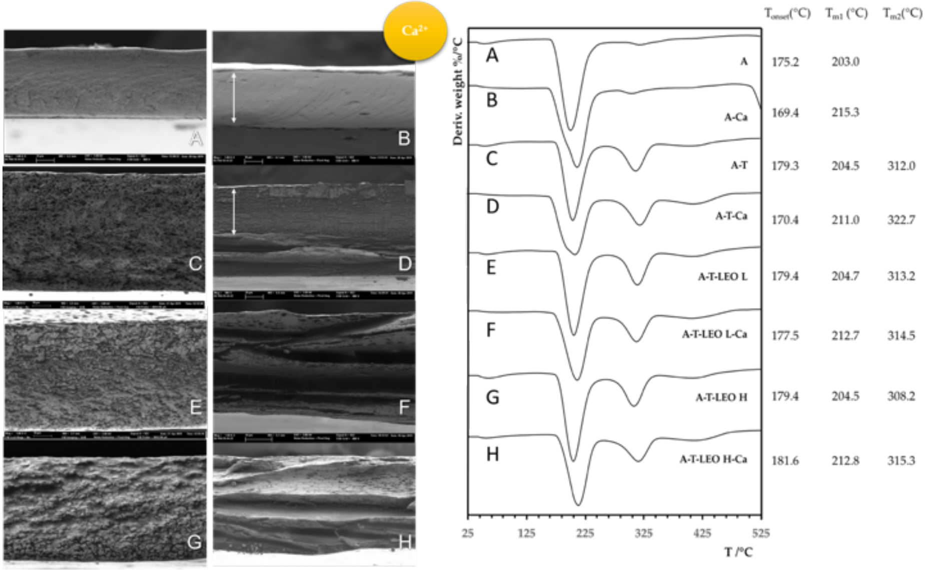
Alginate-based films obtained from emulsions of lemongrass essential oil (at 0.1% and 0.5%) in aqueous alginate solutions (1%), with Tween 80 as surfactant (0.3%), were obtained by casting and characterized as to microstructure and thermal behavior, as well as tensile, barrier and optical properties. Films were also crosslinked through spraying calcium chloride onto the film surface and the influence of oil emulsification and the crosslinking effect on the final film properties were evaluated.







The film microstructure, analyzed through Field Emission Scanning Electron Microscopy (FESEM) revealed discontinuities in films containing essential oil associated with droplet flocculation and coalescence during drying, while calcium diffusion into the matrix was enhanced. The presence of essential oil reduced the film stiffness whereas calcium addition lowered the film’s water solubility, increasing tensile strength and reducing the extensibility coherent with its crosslinking effect.



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1B –Assembly of nanoparticles at liquid interfaces: forces and nanostructures

G. Li Destri, R. Ruffino, N. Tuccitto, G. Marletta

Aims

Understanding nanoscale forces and interactions between nanoparticles (NPs) is essential for both fundamental and technological reasons. Current theories are not able to satisfactorily model and predict the interactions between sub 50 nm NPs. Moreover, the implementation of nanoparticles into new materials and (nano)devices requires to thoroughly understand and control how NPs interact with each other, with the environment and with target molecules/analytes/receptors. In this project, we exploit the irreversible adsorption of nanoparticles at the air/water interface to measure the inter-particle repulsions as a function of the inter-particle distance. In particular, by simultaneously compressing and structurally characterizing the NP monolayers formed at liquid interfaces, it is possible to quantitatively characterize the inter-particle repulsions with sub-nm resolution. The approach, which was applied to a model system consisting of negatively charged NPs assembled at liquid interfaces thanks to the addition of cationic surfactants, demonstrates how short-range repulsions scale with surfactant chain length and flexibility.

Results

The surface tension value and the corresponding structural characterization of surfactant-decorated NP monolayers are reported in Fig. 1 a-b

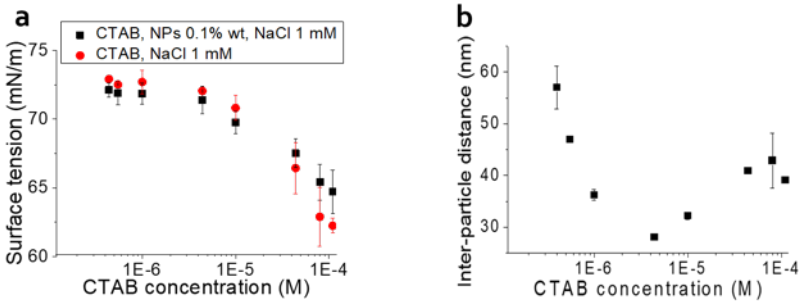

Figure 1: surface tension (a) and inter-particle distance (b) of surfactant-decorated nanoparticle monolayers assembled at the air/water interface as a function of the surfactant concentration.

The inter-particle distance, determined by grazing incidence small angle X-ray scattering (GISAXS), initially decreases with surfactant concentration while, above a threshold concentration characterized by the onset of surface tension reduction, it starts increasing. This suggests that, at low surfactant concentrations, surfactant-decorated nanoparticles predominantly adsorb at the air/water interface while, at higher concentrations, the adsorption of free surfactant molecules prevails. In order to investigate the forces acting between interfacial nanoparticles, any interference arising from free adsorbed molecules must be avoided. Therefore, we performed our combined compression/structural investigation at surfactant concentration lower than 10-5 M. Exemplificative results of this experiment are reported in Fig. 2a, showing how the inter-particle distance gradually decreases with compression while the monolayer surface pressure increases. Compressing nanoparticles beyond its threshold inter-particle distance (Fig. 2a dashed line) leads to nanoparticle desorption and, therefore, to constant inter-particle distance with compression.

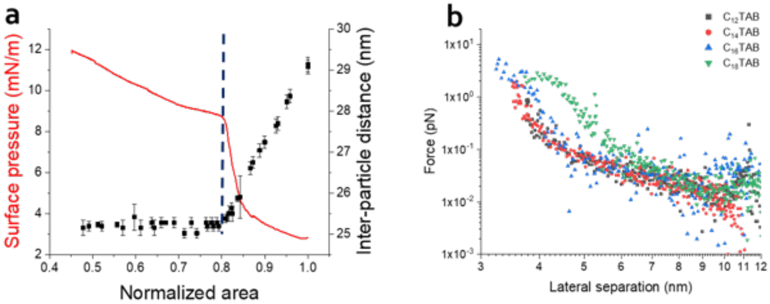

Figure 2: compression isotherm and the corresponding inter-particle distance variation of surfactant-decorated nanoparticle monolayers assembled at the air/water interface (a). Force vs lateral separation curves of of surfactant-decorated nanoparticle monolayers assembled at the air/water interface for surfactants having different tail length.

As nanoparticles desorb only above a given limiting compression rate, it is possible to measure repulsive inter-particle forces at lower compression rates as

$$F = \frac{w}{dx}$$

where w is the compression work determined from the compression isotherm while dx is the corresponding compression-induced inter-particle distance reduction. Exemplificative curves of the inter-particle forces vs inter-particle distance for surfactants having different tail length are reported in Fig. 2b. Two distinct ranges are observed. At long inter-particle distances, inter-particle forces, regardless of the surfactant, scales as L-3 (L= lateral separation), this behavior suggests that long-range forces are predominantly electrostatic. On the contrary, at short inter-particle distances forces increases with increasing the surfactant tail length and concentration. This suggests that short-range forces are predominantly steric. Finally, it is worth to observe how the slope of the short-range forces decreases with increasing the tail length (Figure 2b). Although, at a given lateral separation, steric forces are higher for longer tails, the increase is more rapid for shorter ones. This behavior is attributable to the higher flexibility of longer tails that, when compressed, adopt coiled conformations characterized by an entropic gain proportional to the tail length.

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1B – Behaviour of amphiphatic neuroprotectors at the biomimetic membrane interface

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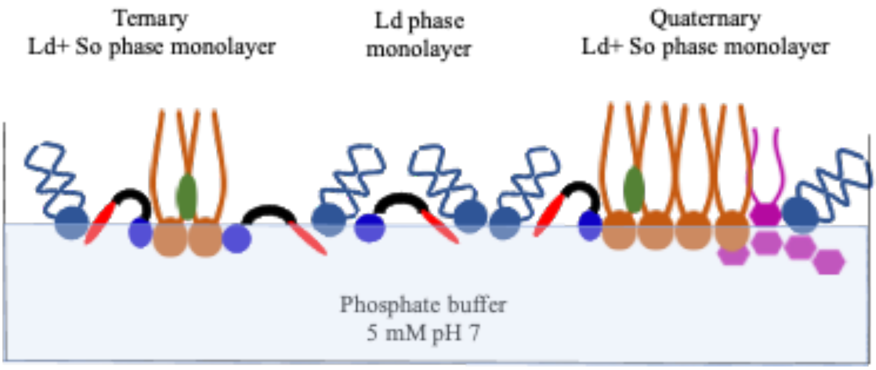
Aims

Many neurodegenerative diseases, including Alzheimer and Parkinson diseases, are associated with the deposition of polypeptide chains into amyloid fibrils. Natural aminosterols are promising drugs against these maladies and one known important mechanism through which they mediate protection is their binding to biological membranes with displacement of amyloidogenic proteins or their oligomers. We studied the behaviour of phospholipid monolayers mimicking the outer layer of the neuronal membrane in the presence of Trodusquemine, an aminosterol that has shown therapeutic benefit in both tau and beta amyloid mouse models of Alzheimer's disease, improving memory and behavior, and reducing hippocampal neuronal loss.

Results

As representative models of the outer layer of the neuronal membrane we selected two different compositions of dioleoylphosphatidylcholine, sphingomyelin, cholesterol and GM1 lipid mixture mimicking either a lipid-raft containing membrane (Ld-So) or a single-phase disordered membrane (Ld). Surface pressure-area isotherms and surface compressional modulus-area combined with Brewster Angle Microscopy (BAM) provided the thermodynamic and morphological information on the lipid monolayer in the presence of increasing amounts of Tro in the monolayer. Preliminary experiments revealed that Trodusquemine forms stable spreading monolayers at the buffer-air interface where it undergoes multiple reversible phase transitions to bi- and tri-layers at the interface. We found that Tro penetrates in the lipid layer for both the selected lipid compositions, but a maximum Trodusquemine uptake in the rafts-containing monolayer was observed for a Lipid/Tro molar ratio equal to 3:2. Statistical analysis of BAM images revealed that Trodusquemine preferentially adsorbs at the border of the lipid rafts inducing a decrease in size of the condensed domains affecting slightly the thickness mismatch.



Removal of GM1 from the lipid Ld-So mixture resulted in an even greater reduction of the size of the lipid rafts suggesting that the presence of GM1 hinders the localization of Trodusquemine at the lipid rafts boundaries.

Taken together these observations suggest that Tro evenly distributes in disordered expanded phases of the membrane model whereas it induces a composition-dependent and long-range reorganization of lipid rafts that should be considered in the context of aberrant protein misfolding at the cell membrane surface.

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1B – BOW – Biogenic Organotropic Wetsuits (Horizon 2020 FET Proactive project, N° 952183)

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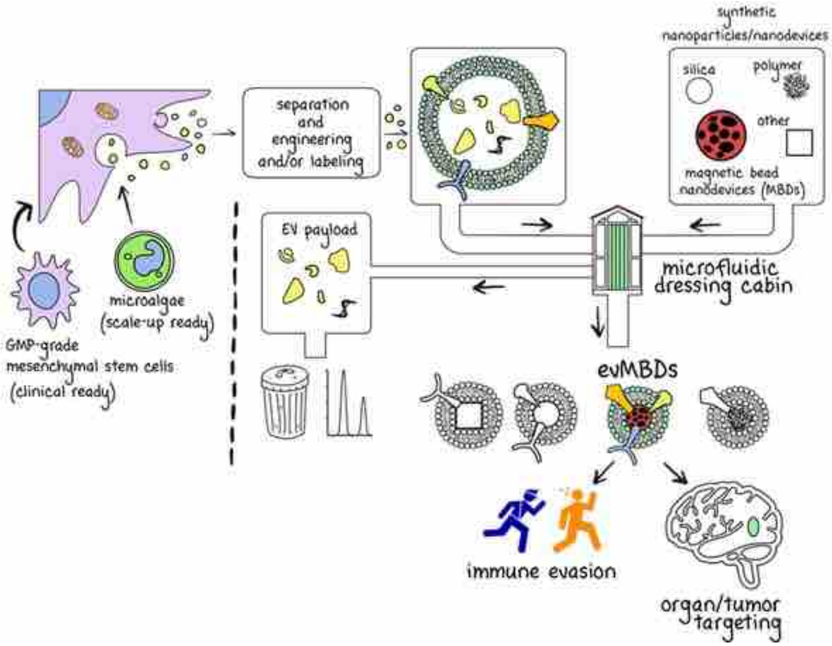
Aims

Extracellular vesicle (EVs) nanoparticles are the universal agents of intercellular and inter-organismal communication. “made by cells for cells” to shuttle lipids, proteins and nucleic acids, EVs mediate physiological processes and help to spread various diseases, including cancer and infections. Their innate navigation performances take origin in the unique structure and composition of their membrane which is to date inaccessible to synthetic mimics. The main goal of the BOW project is to explore and consolidate the technology able to impart biological surface precision, circulation and targeting abilities of EVs to superparamagnetic nanodevices (Magnetic Bead Devices, MBDs) by “dressing” them with a single- or multi-layer “wetsuit” of EV membrane “fabric”.



This will proof and set a general, viable paradigm to recapitulate key biomimetic functions – including camouflage to the immune system and organ site/tumor targeting – to any synthetic nanodevice, while being disruptive as a first example of biogenic nanotechnology. If successful, such a non-incremental technology will promote the progress of implantable nanodevices and nanomaterials towards sustainable production and clinical translation, impacting life quality for people. Major objectives include: (i) production high-grade EVs with biomimetic and organotropic functions, (ii) synthesis and functionalization of MBDs, (iii) engineering a microfluidic device for streamlined fabrication of EV membrane coated MBDs (evMBDs) (iv) evaluation of evMBD biological performances and nanotoxiciy in vitro, ex vivo and in vivo.

Results and References

http://www.bowproject.eu/

1B – Buffer-specific effects and ionic dispersion forces on biophysical interactions

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Aims

The influence of salt on interactions between particles in solution is a core question in engineering and biology. Hofmeister effects showing the influence of specific ions are already well known. Less appreciated is the role of buffer species themselves. Buffer solutions are used to maintain pH, required for optimal protein activity. But in biochemistry the effect of buffer ions has been neglected, with the buffer assumed to be either inert (apart from its effect on pH), or the protocol mandating a specific buffer without consideration of alternatives. But just as Hofmeister effects have been found to be ubiquitous, so too buffer specific effects can be identified on enzyme activity, protein zeta potential, liquid crystal phase transitions. We aim to understand the mechanism and consequences of buffer specificity.

Results

Applying a methodology previously suggested by B. Ninham for understanding Hofmeister effects, we model the interaction of buffer ions with colloid particles using ion dispersion forces. Dispersion coefficients were determined using dynamic polarisabilities evaluated by quantum chemical computation. These dispersion interactions were incorporated into a mean field Poisson-Boltzmann description of the electrolyte. A charge-regulated model was applied to characterise the surface charge of lysozyme protein. This model successfully reproduced buffer specificity observed experimentally in zeta potential measurements at pH 7.1, see Figure 1, including charge reversal observed with citrate buffer.

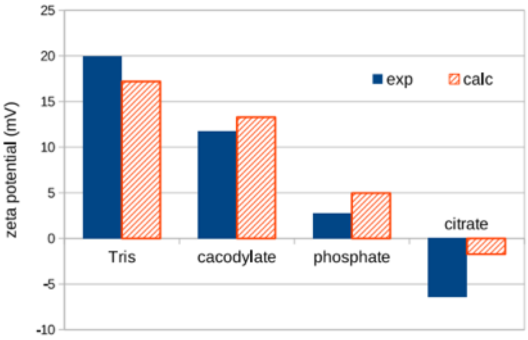

Figure 1. Experimental and theoretical zeta potentials of lysozyme at pH 7.1 in various 50 mM buffer solutions.

Two particular aspects of the model are worth noting. Firstly, the success of the model required explicit treatment of cosmotropic ions as strongly hydrated. That is, the sodium counterion was modelled with 3 hydration water molecules, [Na.3H2O]+, not simply Na+. Secondly, while buffer solutions are conventionally identified via total buffer concentration (e.g. 50 mM of protonated and deprotonated species together), a more consistent comparison of buffer solutions is made via ionic strength. Figure 2, for instance, shows that lysozyme charge reversal can be expected for any anionic buffer with ionic strength greater than 50 mM.

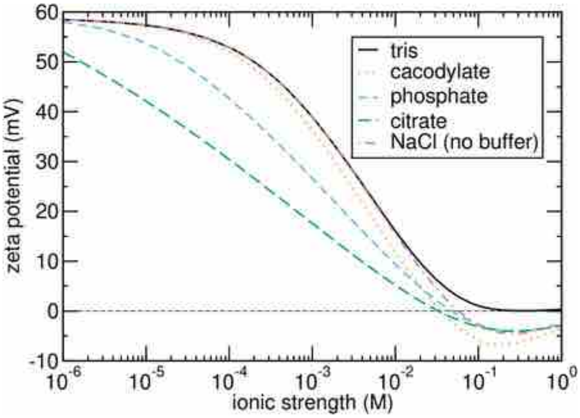

Figure 2. Predicted zeta potential of lysozyme at pH 7.1 as a function fo the ionic strength of buffer solution.

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1B – Calcium ions hyaluronan/gellan gum protective shell for delivery of oleuropein in the knee

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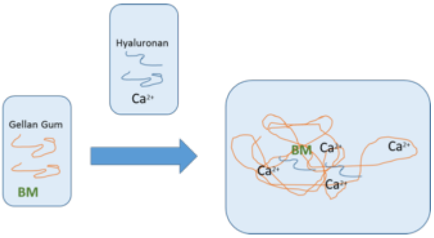
Aims

Oleuropein has several beneficial properties. Strong evidences of its role in preventing osteoarthritis and playing analgesic and sedative effects are gaining. Starting from that, we conjectured that entrapping oleuropein inside a compatible viscosupplement could permit its delivery inside the knee without losing its antioxidant activity and exploiting its analgesic effect against the strong pain associated with injection. Generally, a significant lack of bioavailability in vivo is found using the active principle instead of its original biocomplex, as already observed for other phytotherapeutics. Consistently, the aim of this study is to encapsulate a vegetal bioactive matrix rich in oleuropein in a stable vehicle avoiding strong interactions between the vegetal complex and the polymeric shell to not affect the release or the activity of oleuropein. We prepared calcium ions gellan gum–hyaluronan matrices enriched with a bioactive matrix rich in oleuropein. Different polysaccharide ratios were tested, and the release kinetics and anti-oxidant activity of oleuropein were evaluated. The mechanical performance as well as the cytocompatibility of the system for the foreseen application was also evaluated.

Results

Three different matrices were obtained combining Gellan Gum and Hyaluronan, in different ratios, crosslinked with calcium ions with the aim of creating a protective shell for the delivery of a natural bioactive matrix rich in oleuropein (BM).



The developed formulation did not show any significant interaction with the bioactive substance as highlighted by the burst release in 30 min.

The burst release was necessary to permit oleuropein to quickly exert its anti-inflammatory and analgesic effect after it is injected in the knee. Its activity once released was verified and the used BM seems to have higher antioxidant activity than free oleuropein. Rheological properties were measured to examine mechanical stability of the developed formulations. Parameters were set to verify their performance as viscosupplement. The mechanical response of formulations, in terms of elastic and viscous components, as a function of oscillation frequency was analyzed. All systems showed the ability to reduce their viscosity by applying shear and immediately resume their consistency when the mechanical load is taken off, behaving as self-healing gels. Among the three developed matrices the most promising one is the formulation obtained combining GG and HA in a ratio 2:1. Even if the cytocompatibility of the components is well known and verified, shells cytocompatibility has been analyzed and no cytotoxic effects were found.

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1B – Click-Chemistry Cross-Linking of Hyaluronan Graft Copolymers

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[1]Department of Biotechnology, Chemistry and Pharmacy, University of Siena
[2]Istituto di Scienze e Tecnologie Chimiche "G. Natta"-SCITEC (CNR), Milano

Aims

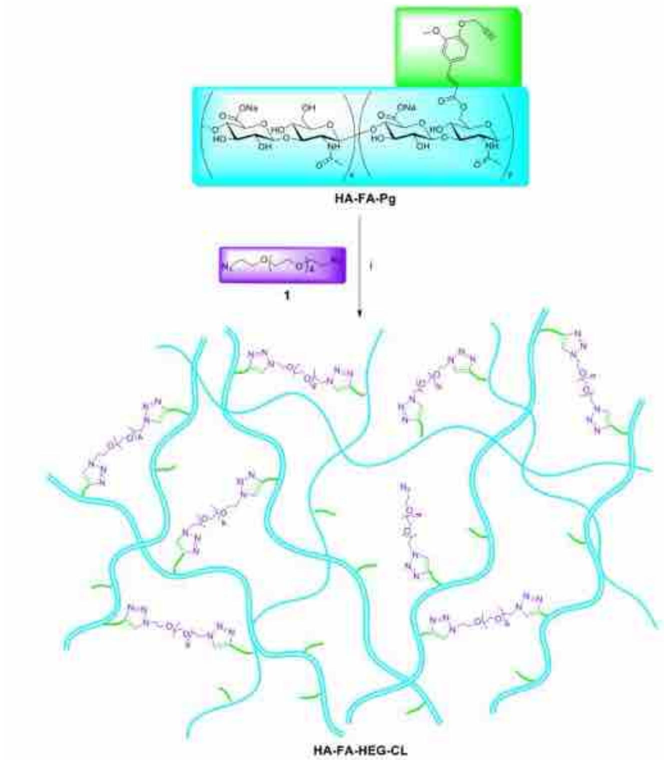
An easy and viable crosslinking procedure by click-chemistry (click-crosslinking) of hyaluronic acid (HA) was developed. In particular, the clickable propargyl groups of hyaluronanebased HA-FA-Pg graft copolymers showing low and medium molecular weight values were exploited in crosslinking by click-chemistry by using a hexa(ethylene glycol) spacer. The resulting HA-FAHEG-CL materials showed an apparent lack of in vitro cytotoxic effects, tuneable water affinity, and rheological properties according to the crosslinking degree that suggests their applicability in different biomedical fields

Results

A click-chemistry crosslinking (click-crosslinking) procedure was developed to obtain cross-linked HA derivatives to be used in the formation of hydrogels.

In particular, the clickable propargyl groups of HA-FA-Pg graft copolymers showing low and medium molecular weight values were employed in crosslinking by click-chemistry through a biocompatible hexa(ethylene glycol) spacer as an example of another possible application of our technology platform based on HA-FA-Pg graft copolymers. A short series of medium weight HA-FA-Pg graft copolymers was synthesized, characterized, and used in a CuAAC dimerization reaction under very mild conditions in the presence of very low amounts of copper(I) catalyst.

The dimerization reaction was also applied to the previously published HA-FA-Pg-3F graft copolymer showing a low molar mass value, and hydrolysis studies confirmed the importance of the dimerization reaction in the formation of cross-linked HA-FA-HEG-CL materials. The interaction of the resulting HA-FA-HEG-CL materials with water led to the formation of hydrogels showing a wide range of gelation features thanks to the possibility of tuning the crosslinking degree.



As a consequence of that, different rheological behaviours have been observed. The tuneable rheological behaviour of HA-FA-HEG-CL materials led to their applicability in different biomedical fields. In particular, HA(270)-FA-HEG-CL-10 seems to be a good candidate for potential application in the treatment of osteoarticular diseases since its shear-thinning ratio perfectly falls in the range of a healthy synovial fluid shear-thinning ratio (70–250).

Moreover, the obtained results allow us to also conjecture their suitability as viscosity enhancers for eye drops. Finally, the data of both qualitative and quantitative cytotoxicity resulting from the experiments (performed according to the UNI EN ISO 10993-5 standards) demonstrates that our click-chemistry cross-linking procedure of HA(270)-FA-Pg graft copolymers is fully biocompatible since the resulting HA(270)-FA-HEG-CL-10, HA(270)-FA-HEG-CL-20, and HA(270)-FA-HEG-CL-40 materials resulted in the avoidance of any in vitro cytotoxic effects.

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1B – Compartmentalized algal-based nanocarriers as vectors for antioxidants: structural and functional characterization

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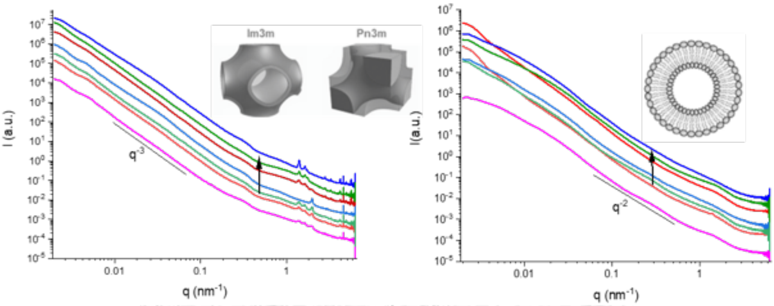
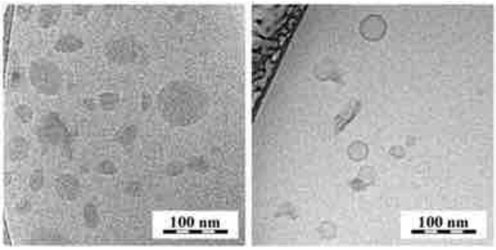
Aims

The delivery of poorly water-soluble natural drugs is a longtime challenge that has led to the development of several solubilizing and encapsulating systems. Particularly, lipid-based vectors are favored thanks to the advantageous properties of lipids as versatile and biocompatible building blocks. Lamellar aggregates possess one or multiple bilayers and show vesicular morphology at larger scale (μm). Nonlamellar mesophases e.g. bicontinuous cubic phases are lyotropic liquid crystalline systems that possess higher inner ordering. In excess water conditions these lyotropic phases are transformed into dispersed liposomes and cubosomes respectively. Lipids can be obtained from a variety of natural sources and biomasses, to develop nanovectors with high carrier-cargo and carrier-target compatibility. In this work, lipid nanovectors were designed and prepared as carriers for a commercially valuable antioxidant i. e. curcumin, whose therapeutic application is typically hindered by poor water solubility, plus two other antioxidants i. e. α-tocopherol and piperine to be used as adjuvants. These three molecules were encapsulated in lipid nanocarriers to improve their biodistribution and bioavailability. Natural-derived lipids were obtained by extraction from two biomasses of the marine microalga Nannochloropsis sp., containing mostly either phospholipids or triglycerides. Two liposomes and cubosomes series of samples with different supramolecular structure were thus obtained and extensively characterized bystructural, morphological, spectroscopic and calorimetric techniques.

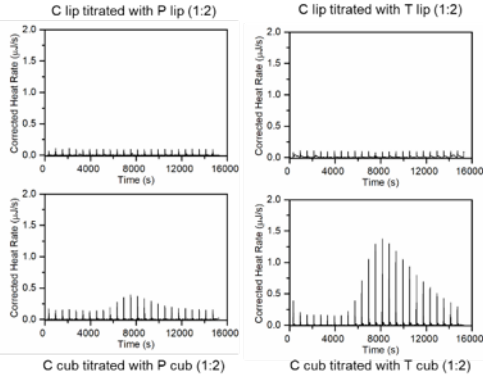
Results

The supramolecular structure and morphology of both aggregate types was investigated by synchrotron SAXS and cryo-TEM, showing cubosome systems with two coexisting cubic symmetries (left, top and bottom figures) obtained from the biomass containing triglycerides and liposomes from the one containing phospholipids (right, top and bottom figures). SAXS diagrams showed enhanced bilayer intercorrelation and ordering when curcumin was loaded in cubosomes at high concentrations. This suggested that carrier-guest interactions were able to influence the bilayer structuring in cubosome systems, but not in liposomes.





Cargo-cargo interactions were explored as well to investigate the possible synergies among co-encapsulated compounds and the effect of the carrier type. ITC measurements were performed by titrating curcumin-loaded liposomes with liposomes containing either tocopherol or piperine (top), and the same was done for cubosomes (bottom).



Results showed that thermal events took place in cubosomes as a response to carrier-carrier and/or cargo-cargo interactions, suggesting easier surface fusion and rearrangements, and stronger effect from curcumin-tocopherol interaction in the confined bilayer space.

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1B –ElectroSpray Ionization Mass Spectrometry Part 1: Specific electrolyte effects on Hemoglobin in denaturing medium

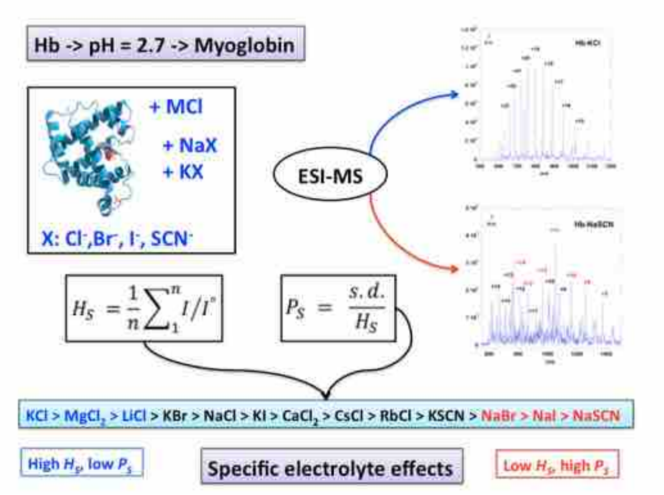
C. Carucci, G. Lusci, T. Pivetta, M. Monduzzi, D.F. Parsons, A. Salis

Aims

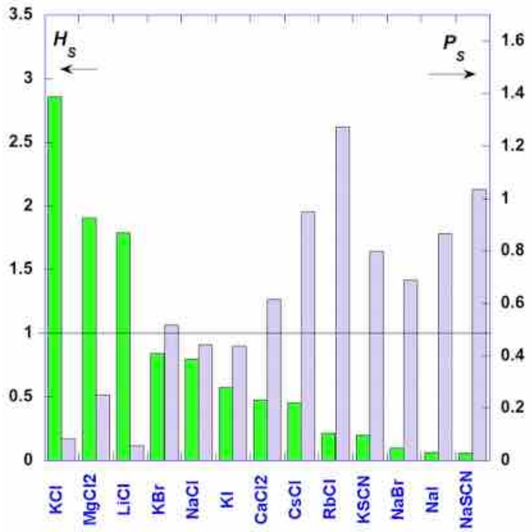
In the last two decades ESI-MS techniques have received great attention for the potential in investigating proteins and their features in terms of stability and interactions. Electrospray ionization is a soft ionization technique that allows to produce intact multiple charged species, without significant fragmentation. In this work the effect of different metal-chlorides, along with sodium and potassium bromides, iodides and thiocyanates, added to Hb in aqueous solutions at pH = 2.7, is investigated. The denaturing condition allowed to minimize the electrostatic attraction between cations and positively charged protein.

Results

Salt concentration was varied to maximize peak intensity and bell-shaped profile in the ESI-MS spectrum. The α-chain of myoglobin is identified as the main pattern of the ESI-MS spectra in all Hb-salt systems. Both peak intensity and quality of the bell-shaped profile of the protein spectrum decrease in the cation order: $K^+ \gg Mg^{2+} > Li^+ \gg Na^+ > Ca^{2+} \approx Cs^+ > Rb^+$ for Hb-Metal Chloride systems, and decrease in the anion order: $Cl^- > Br^- > I^- > SCN^-$ for systems of both Hb-NaX and Hb-KX salts.



To quantify salt addition effects two Hofmeister specific electrolyte parameters H_S, and P_S are proposed. H_S is the mean (Hb-salt)/Hb peak intensity ratio, measured for the nine peaks used for ESI-MS spectra deconvolution, taken at the same *m/z* values of the Hb profile. P_S is the ratio between H_S standard deviation and H_S, and provides a specific perturbation parameter measuring the loss of protein structure. See the equations reported in the figure above. These two Hofmeister parameters give clear evidence of the effects induced either by KCl, $MgCl_2$ and LiCl that enhance protein peak intensity, or by NaBr, NaI, NaSCN and KSCN that induce the protein fragmentation, due to electrolyte-mediated dissociation.



The graph reports the parameters H_S, and P_S for the investigated electrolytes. It can be noticed that anions decrease the quality of ESI-MS spectra in the conventional Hofmeister order $Cl^- > Br^- > I^- > SCN^-$, for both Na and K salts, with Cl^- salts generating higher quality spectra and SCN^- the most degraded.

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1B – ElectroSpray Ionization Mass Spectrometry Part 2: BSA Fragmentation Specifically Induced by Added Electrolytes

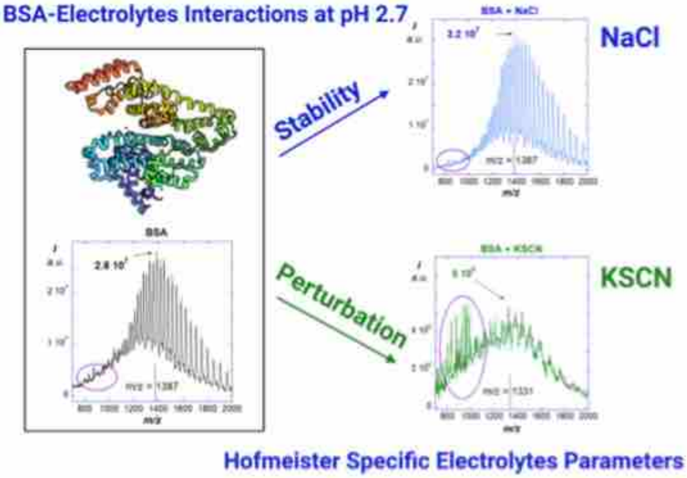
C. Carucci, G. Lusci, T. Pivetta, M. Monduzzi, D.F. Parsons, A. Salis

Aims

Biointerfaces are significantly affected by electrolytes according to the Hofmeister series. This work reports a systematic investigation on the effect of different metal chlorides, sodium and potassium bromides, iodides and thiocyanates, on the ESI/MS spectra of bovine serum albumin (BSA) in aqueous solution at pH = 2.7.

Results

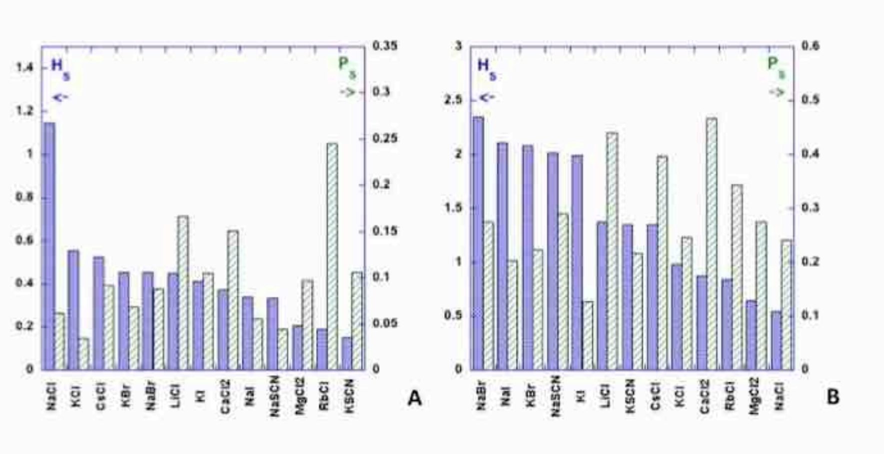
The concentration of each salt was varied to maximize the quality of the ESI/MS spectrum, in terms of peak intensity and bell-shaped profile. The ESI/MS spectra of BSA in the absence and in the presence of salts showed a main protein pattern characterized by the expected mass of 66.5 kDa, except the case of BSA/RbCl (mass 65,3 kDa). In all systems we observed an additional pattern, characterized by at least three peaks with low intensity, whose deconvolution led to suggest the formation of a BSA fragment with a mass of 19.2 kDa. Only NaCl increased the intensity of the peaks of the main BSA pattern, while minimizing that of the fragment. NaCl addition seems to play a crucial role in stabilizing BSA ionized interface against hydrolysis of peptide bonds, through different synergistic mechanisms.



To quantify the observed specific electrolyte effects, two “Hofmeister” parameters (Hs and Ps) are proposed. They are obtained using the ratio of (BSA-Salt)/BSA peak intensities for both the BSA main pattern and for its fragment, according to the following equations:

$$H_S = \frac{1}{n}\sum_{1}^{n} I/I^\circ; \qquad P_S = \frac{s.d.}{H_S}$$

H_S represents the average specific electrolyte effect on the intensity profile of the ESI/MS peaks of BSA protein and of its fragment, both considered as a whole charged ion. The second parameter P_S highlights the significance of H_S being a measure of the structural loss in the charged protein ion ESI/MS profile, caused by specific electrolyte perturbations, as illustrated in the following graphs for BSA main pattern (A) and for BSA fragment (B).



The unique specificity of NaCl in stabilizing the BSA ion and enhancing BSA peak intensities in the ESI/MS spectrum, and also the dramatic effect of replacing Cl^- anion with Br^-, I^-, and SCN^- anion in the Na^+ and K^+ salts systems, should be highlighted.

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1B – Enriched Gellan Gum hydrogel as visco-supplement

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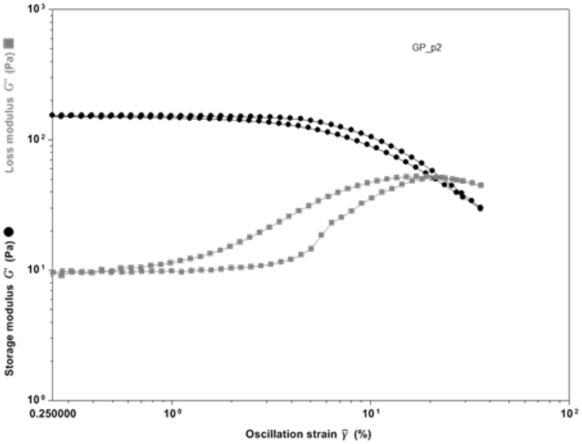
Aims

Osteoarthritis (OA) is a degenerative joint disease caused by a cronic inflammatory state of joints reflected in pain, stiffness and loss of range of motion. The loss of joint functionality mainly derives from the decrease of viscoelastic properties of the synovial fluid, the natural lubricating system present in the cavities of synovial joints. The viscoelastic behavior of synovial fluid depends on hyaluronan (HA), so, when a decrease in its molecular weight or concentration occurs, it leads to pain. The need for development of products with enhanced injectability and yet reasonable viscoelastic behavior for OA treatment is still ongoing. Crosslinking HA significantly improves its viscoelastic properties and residence time but it only slows down HA physiological degradation by hyaluronidases with production of low molecular weight fragments, whose pro-inflammatory action is well known. This has directed research to find adequate hyaluronan substitutes for viscosupplementation. In this context, the hypothesis of this study is that the protection of Gellan Gum (GG) hydrogel with a structural polymer, as poly vinyl alcohol (PVA), could increase the stability of GG towards sterilization and improve its rheological properties, without affecting the injectability. Two different procedures were set up to obtain the mixed hydrogel. This study assessed physicochemical and rheological characterization of the mixed hydrogel and its in vitro performance toward Chondrocytes.

Results

Two different synthesis routes were followed. The first synthesis route, simultaneous crosslinking of PVA and GG by STMP, was unsuccessful, whereas the second procedure, articulated in 2 consecutive crosslinking phases, allowed to synthesize a product, which has proved to be potentially suitable for the foreseen application. The effect of PVA coating on GG-core was analyzed by thermal analysis. GP_p2 showed a higher degree of structuring than the GG_core. However, this did not affect the swelling properties, thanks to the hydrophylicity of both coating and cross-linking agent. The main effect of the coating was observed in terms of viscoelastic characteristics. Both hydrogels have G' and G'' values greater than those of the synovial fluid, and comparable with Synvisc®, which is the most commonly used viscosupplement. Thixotrophy analysis indicated that GG_core and GP_p2 are injectable and therefore usable as viscosupplement.



However, both the resistance to compression and the thixotropic behavior indicate a better performance of GP_p2 hydrogel in comparison with GG_core. Both hydrogels are not cytotoxic and cytocompatible towards chondrocytes.

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1B – Enrichment of olive oil emulsions with antioxidant compounds

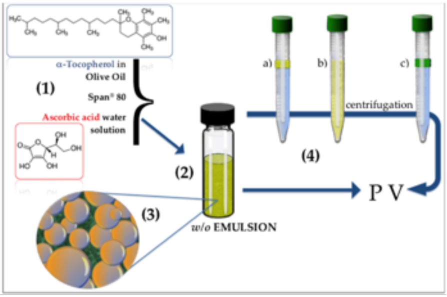
G. Cinelli, F. Cuomo, F. Lopez, F. Venditti, A. Ceglie

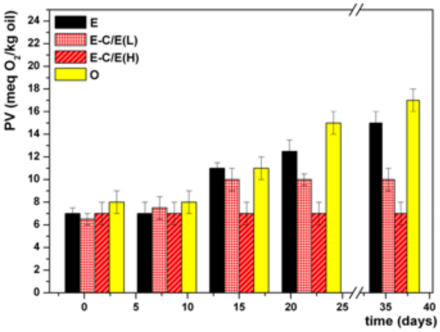
Aims

Water-in oil (w/o) emulsions are heterogeneous systems able to solubilize both hydrophilic and hydrophobic compounds. Thus, hydrophilic vitamin C, lipophilic vitamin E and red wine dry extract (WDE) were loaded in (w/o) emulsions at 1% (w/w) water stabilized by 1% (w/w) Span 80.

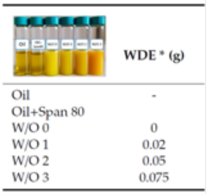
Results

The antioxidant effect of vitamins in emulsions was studied considering the variation of the peroxide values during storage. The oxidation reaction was slowed down in emulsions containing vitamin C, but it was faster by the loading of vitamin E for its high concentration. In emulsions containing vitamin E, indeed, the peroxide values were higher than in emulsions prepared in the absence of vitamins or in oil. The antioxidant activity generated by the co-loading of vitamin C and E was very effective to the point that in presence of high amounts of vitamins the peroxide values did not change in about 40 days of storage, due to the vitamin E regeneration by vitamin C.

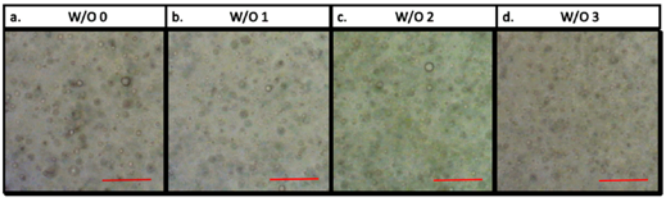


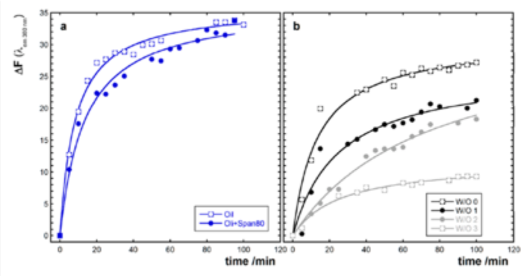


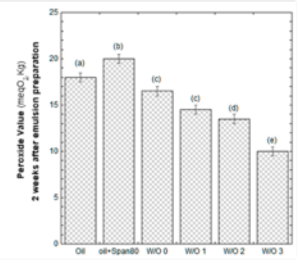
Kinetics of oil oxidation carried out in oil and emulsions in the presence of an increasing amount of WDE, revealed that the presence of WDE slowed down the oxidation rate. The oxidation reaction was monitored in two ways; i.e., with the classical method that consists of the determination of the peroxide value, and with an accelerated test made using the radical initiator (AMVN) and a fluorescent probe revealing the hydroperoxides development (DPPP). Moreover, by comparing the emulsion structures observed by optical microscopy, no differences in term of size of the dispersed aqueous phase were detected with the increase of the wine dry extract concentration.



	WDE * (g)
Oil	-
Oil+Span 80	
W/O 0	0
W/O 1	0.02
W/O 2	0.05
W/O 3	0.075







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1B – Evaluation of the dispersant ability of a lubricant formulation: lacunarity as quantitative descriptor

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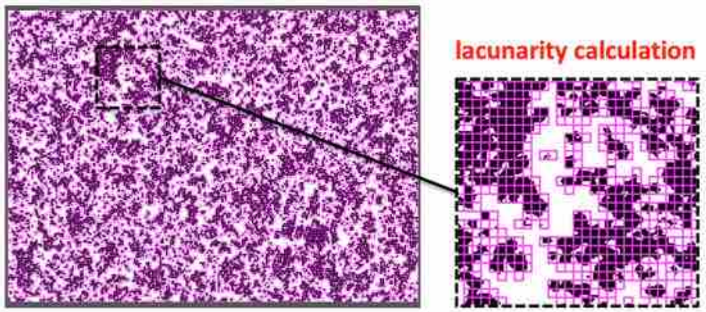
Aims

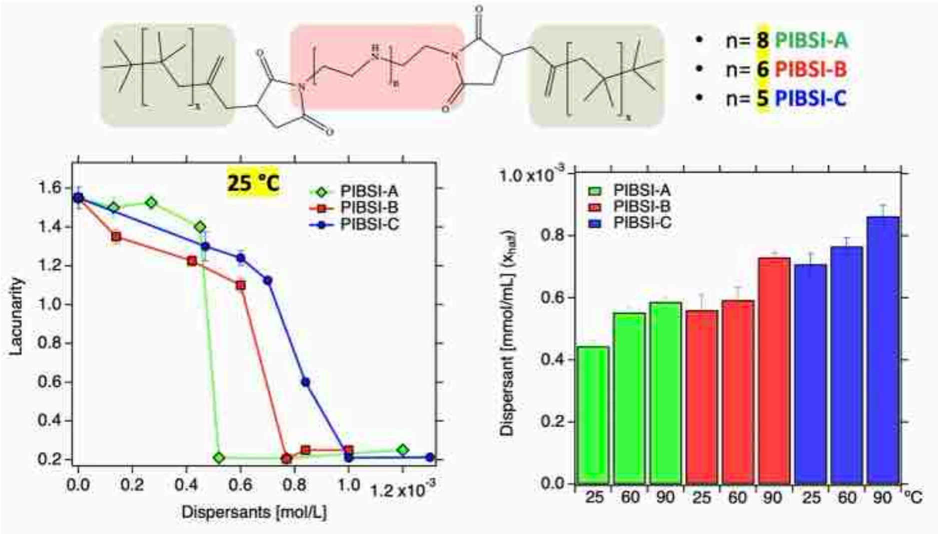
One of the main problems related to the aging of lubricants is the formation and accumulation of carbonaceous deposits inside the matrix. Consequently, the development of additives for the dispersion of these agglomerates is mandatory to increase the performances and life of the lubricant.

Usually, the dispersant performances are evaluated by means of expensive and time-consuming engine tests. Here a new lab-scale method based on optical microscopy for the direct assessment of the dispersing capacity of a lubricant formulation is presented. The degree of dispersion of the investigated samples is calculated directly on optical micrographs using the lacunarity descriptor which is defined as gappiness or heterogeneity associated to an image. We demonstrate that low lacunarity values correspond to well dispersed systems while the presence of aggregates is responsible for an increase of micrograph lacunarity.



Results

The method was validated on reference oils and different commercial carbonaceous substrates showing optimal reproducibility and sensitivity. The obtained results in terms of dispersant ability were coupled with the study of the colloidal behavior of the dispersants in minimal and/or complete formulations establishing a structure-properties relation to explain the different dispersant capacity.



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1B – evFOUNDRY – The Extracellular Vesicle Foundry (Horizon 2020 FET Open project, N° 801367)

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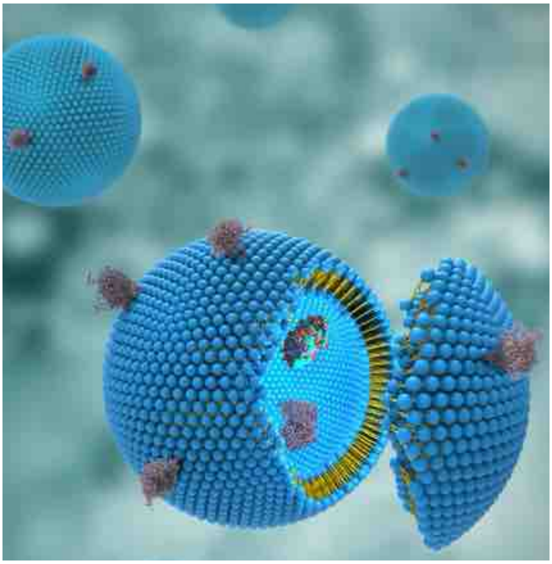
Aims

Extracellular Vesicles (EVs) are natural cell-derived membrane-bound nanoparticles containing proteins and nucleic acids, which are newly recognized as the universal agents of intercellular and interkingdom communication. EVs are reshaping our perspective on life sciences, environment, and public health. They are under intensive investigation as early disease multi-biomarkers, while EV-based personalized therapeutic agents and vaccines have produced enticing results in early-phase clinical trials. +FET-Open project evFOUNDRY targets the unmet knowledge and technology able to streamline the production of therapeutic EVs from sustainable sources, drawing the baseline for future EV bioprocessing, which is necessary for effective EV medical translation and opens to new biogenic nanotechnology.



Results and References

http://www.evfoundry.eu/

1B – Extracellular Polymeric Substances (EPS) extracted from anammox bacteria: structural, mechanical and applicative properties

E. Carretti, D. Berti, T. Lotti, L. Dei

In collaboration with Prof. C. Lubello, Ing. B. Pagliaccia, Ing. R. Campo

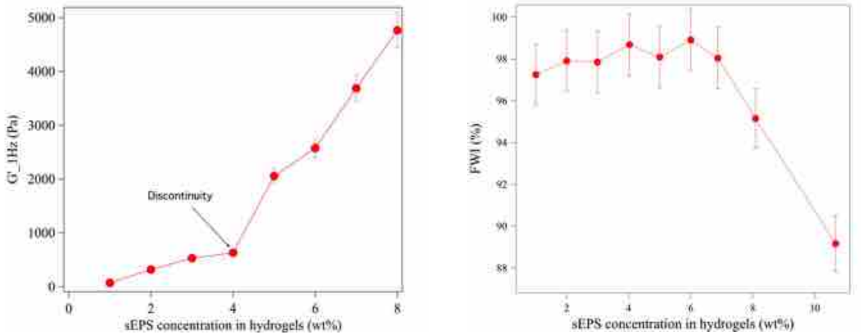
Aims

The recovery of biopolymers from the waste sludge produced in wastewater treatments and their application in other industrial sectors, would substantially increase the environmental and economical sustainability of the process, promoting the development of a circular economy. In this study, extracellular polymeric substances (EPS) extracted from anammox granular waste sludge, were investigated and characterized. Rheological and differential scanning calorimetry measurements on EPS aqueous dispersions indicate that, in the presence of a crosslinker such as Ca^{2+}, the formation of a gel network occurs with a clear dependence of the mechanical and water retention properties on EPS content. Rheological results highlighted a solid-like behaviour (G'>>G") of sEPS-based hydrogels and the power-law fitting of G' vs. sEPS concentration suggest that the expansion of the sEPS network during cross-linking occurs through a percolative mechanism. These findings provide additional information about the mechanisms of sEPS-based hydrogel formation and reveal the peculiar physico-chemical characteristics of sEPS which nowadays are increasingly gaining interest in the context of resource recovery.

As a proof of concept of the applicative potential of EPS, the grease resistance provided to paper by an EPS coating was successfully explored. These results shed light on the structural details of EPS-based hydrogels and pave the way for the possible use of EPS-based materials as a cheap, ecofriendly alternative to commonly adopted paper coatings, in line with a circular economy patter for wastewater treatment. Moreover we also successfully verified the possibility to use EPS as biosorbents for heavy metals present in polluted aqueous solutions. Finally, EPS/Ca^{2+} based gels can be used as tools for the storage and the controlled release of water with possible applications in agronomy.

Results

Figure 1 A shows the G' values at 1Hz vs the sEPS wt%. There is a discontinuity in the slope of the curve that drastically increases for sEPS concentration higher than 4wt%, indicating that above this threshold value, the progressive extension of the 3D network occurs more rapidly as the sEPS concentration increases too.



A B

Figure 1. A: trend of the Storage module (G’) vs. sEPS concentration in hydrogels. B: trend of the Free Water Index vs. sEPS concentration in hydrogels.

Figure 1 B shows the trend of the FWI determined through DSC measurements as a function of the sEPS content into the hydrogels. As seen in the graph, for sEPS concentrations between 2wt% and 6wt%, the FWI remains almost unvaried (97-98%). By further increasing the sEPS content, the amount of not freezable water (that is the fraction of water that, being strongly bound to the polymer network doesn’t freeze even at temperatures below 0^{o}C) increases up to 11wt%.

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1B – Functionalization and characterization of extracellular vesicles for targeted pharmacological therapy towards triple-negative breast cancer (PRIN project, N°. 2017E3A2NR_004)

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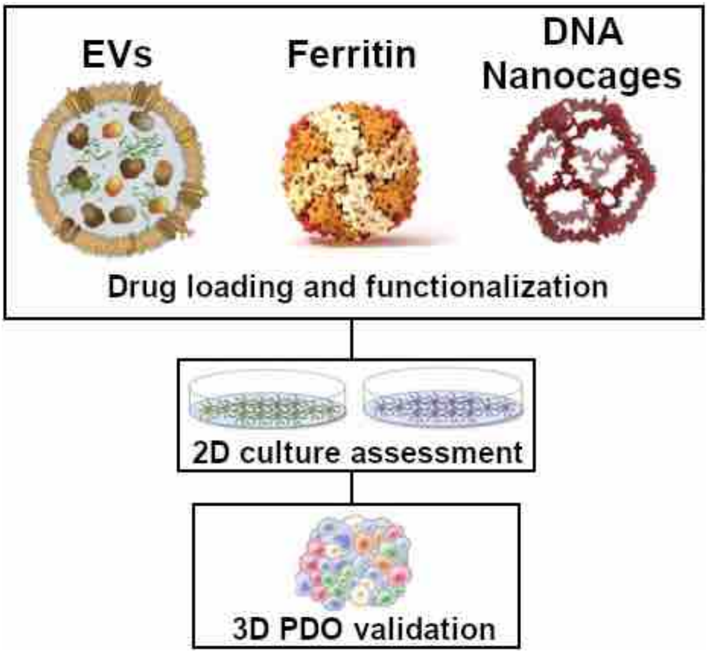
Aims

Bionanoparticles (BNPs) stand at the forefront of emerging technologies for application in materials and life sciences. BNPs represent an advanced tool for the study of molecular interactions, which provides new opportunities for investigating molecular recognition mechanisms and signal transduction processes. An immediate output is envisaged in biomedicine, promising great potential in the development of innovative diagnostic imaging agents and drug delivery systems. The design of engineered BNPs requires careful optimization of physical and biochemical properties, such as size, surface charge and functionalization with appropriate targeting ligands to improve the selectivity toward malignant cells. The project aims to develop an integrated BNP platform for the efficient and safe drug delivery exploiting different classes of BNPs, included Extracellular Vesicles (EVs).



The BNP platforms will be tested, at first, on a panel of 2D cell lines and then, in triple negative breast cancer (TNBC) Patient-Derived Organoids (PDO). TNBC patients have unfavorable prognosis due to chemoresistance sustained involved in the restoration of cellular functions after DNA damage. The use of BNPs could increase antitumor efficacy and decrease chemoresistance exploiting targeted nanodrugs.

Results

EVs were obtained from human-compatible sources with high translational potential and fully characterized with standardized methods developed in our laboratory and recognized in the International Society of Extracellular Vesicles guidelines. EVs were then successfully engineered by functionalizing the EV surface with an anti-EGFR antibody, to maximize the targeting of TNBC cells. Binding assays were performed by means of a Surface Plasmon Resonance biosensor and confirmed the superior capability of the engineered EVs in EGFR binding. Cellular uptake assays targeting TNBC cells were also performed. Engineered EVs were further modified by the encapsulation of a chemotherapeutic agent, thus obtaining BNP-based nanodrug able to precisely deliver the therapeutic payload minimizing off-target effects. Citotoxicity and cell metabolic assays have been performed to detect the modification of cell metabolism and cell viability after treatment with the nanodrug formulation. Other BNP-based formulations (based on ferritin and DNA nanocages) are currently under development and testing.

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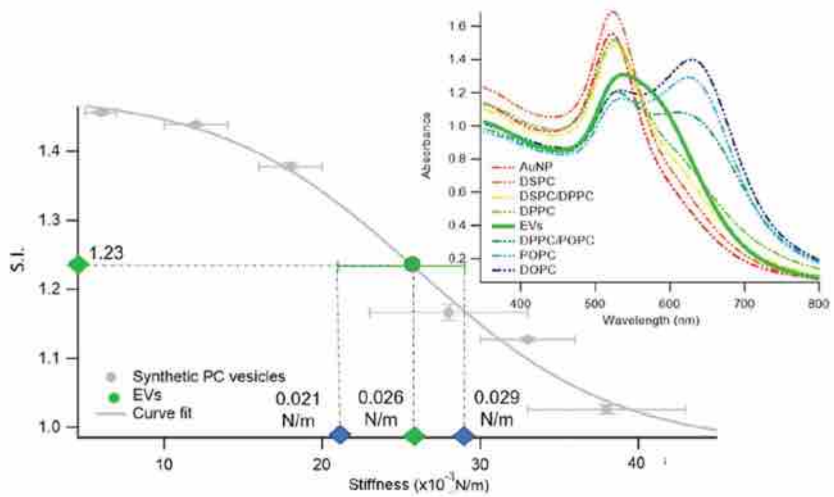
1B – Gold nanoparticles as nanoplasmonic probes for natural and synthetic lipid membranes

L. Caselli, J. Cardellini, A. Ridolfi, F. Valle, M. Brucale, P. Bergese, C. Montis, D. Berti

Aims

Nanosized lipid vesicles are ubiquitous in living systems (*e.g.* cellular compartments or extracellular vesicles, EVs) and in formulations for nanomedicine (*e.g.* liposomes for RNA vaccine formulations). The mechanical properties of such vesicles are crucial in several physicochemical and biological processes, ranging from cellular uptake to stability in aerosols. However, the accurate determination of the mechanical properties of lipid membranes remains challenging and requires sophisticated instruments and data analysis. In this study, we report the first evidence that the surface plasmon resonance (SPR) of AuNPs adsorbed on synthetic vesicles is finely sensitive to the vesicles' mechanical properties and can be used for developing a facile, cost-effective, and high-throughput method to assay the rigidity of dispersions of vesicles of nanometric size and unknown composition at a collective level.



Results

We prepared a library of unilamellar liposomes displaying different rigidities and similar average diameters (100 nm). We exploit AFM-FS to determine the stiffness of liposomes at r.t. which was then used to validate our new optical method.

The vesicles dispersions were incubated with Turkevich-Frens AuNPs. The AuNPs dispersion in the absence of lipid vesicles shows a well-defined SPR peak centred at 522 nm; upon mixing with liposomes, an immediate colour change is visible to the naked eye, which clearly depends on the composition of the target membrane. Specifically, the variation in the SPR profile gradually increases as the stiffness of vesicles decreases, displaying the progressive emergence of a high-wavelength shoulder, eventually resulting in a secondary plasmon peak at about 625 nm. This new spectral feature is the hallmark of the aggregation of AuNPs, whose spatial proximity produces the coupling of the individual AuNPs plasmons. To develop a spectroscopic assay to probe the mechanical properties of lipid vesicles, we extracted from the spectra a quantitative descriptor, the so-called ‘‘stiffness index’’, S.I., accounting for the main variations in the AuNPs SPR profile. The S.I. was used to build-up an empirical ‘AuNPs spectral response’ vs. ‘vesicles’ stiffness’ scale. We found that the relationship between AuNPs plasmon properties and membrane stiffness can be quantitatively described by a sigmoidal relation. Finally, as a proof-of-principle, we successfully tested the assay on a sample of extracellular vesicles. Differently from other methods (e.g., AFM-FS, micropipette etc..) which probe the nanomechanics of single objects, our strategy provides an ensemble-averaged estimation of membrane stiffness, overcoming most of the limitations of the current approaches.

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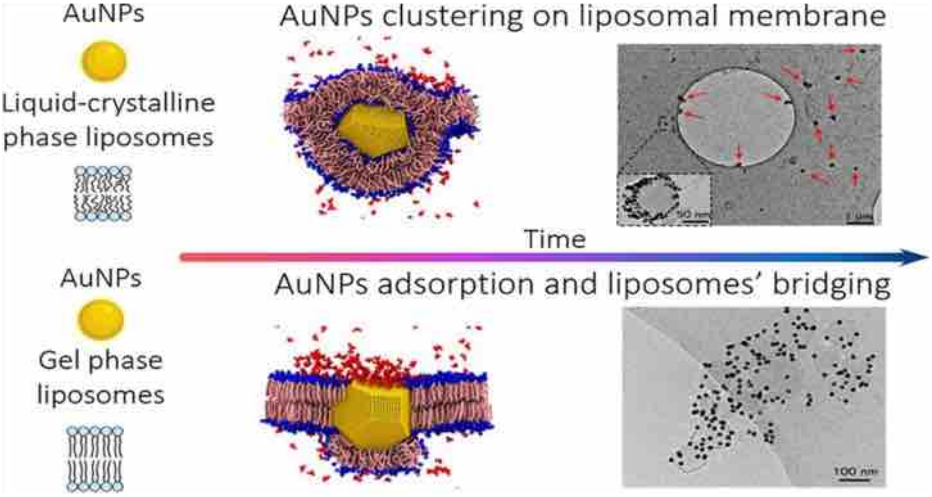
1B – Lipid assemblies-nanoparticles interaction

J. Cardellini, L. Caselli, G. Rossi, C. Montis, D. Berti

Aims

In recent years, many efforts have been devoted to investigating the interaction of nanoparticles (NPs) with lipid biomimetic interfaces, both from a fundamental perspective aimed at understanding relevant phenomena occurring at the nano-bio interface and from an application standpoint for the design of novel lipid−nanoparticle hybrid materials. In this area, recent reports have revealed that citrate-capped gold nanoparticles (AuNPs) spontaneously associate with synthetic phospholipid liposomes and, in some cases, self-assemble on the lipid bilayer. However, the mechanistic and kinetic aspects of this phenomenon are not yet completely understood. In this study, we address the kinetics of interaction of citrate-capped AuNP with lipid vesicles of different rigidities (gel-phase rigid membranes on one side and liquid-crystalline-phase soft membranes on the other).



Results

The formation of AuNPs-lipid vesicle hybrids was monitored over different time and length scales, combining experiments and simulations. First, we propose a new computational model of citrate capped AuNPs, compatible with the coarse-grained Martini force field. The model, which we develop and validate through an extensive comparison with new all-atom molecular dynamics (MD) simulations and UV−vis and Fourier transform infrared spectroscopy data, is aimed at the MD simulation of the interaction between citrate-capped NPs and model phosphatidylcholine lipid membrane and was then used to study the effect of the bilayer rigidity on the very first AuNPs-membrane contact. MD simulations suggest that the outcome of the NP−membrane interaction crucially depends on the membrane lipid phase. Fluid-phase DOPC lipids completely wrap the NP, quickly releasing citrate molecules towards the solution and forming a perfect bilayer around the NP. On the contrary, the NP interaction with the rigid gel bilayer gets stuck at an intermediate stage of NP penetration. The extremely slow diffusion of lipids in the gel phase freezes the NP−membrane complex in a semi embedded configuration. These results highlight that the physical state of the membrane can trigger a series of events at the colloidal length scale, which regulate the final morphology of the AuNPs-lipid vesicles adducts. The structure, morphology, and physicochemical features of the final colloidal objects were studied through UV-Visible spectroscopy, Small Angle X-Ray Scattering, Dynamic Light Scattering, and Cryogenic Electron Microscopy. For lipid vesicles with soft membranes, the hybrids appear as single vesicles decorated by AuNPs, where the AuNPs are in direct contact with each other, while more rigid membranes lead to the hybrid flocculation, with AuNPs acting as bridges between vesicles. Overall, these results contribute to a mechanistic understanding of AuNPs adhesion/self-assembly onto biomimetic membranes, relevant for phenomena occurring at the nano-bio interfaces. The deep comprehension of the main physicochemical parameters which rule the spontaneous association of citrated NPs on zwitterionic membranes paves the way to engineer and finely control lipid-NPs hybrids through simple self-assembly.

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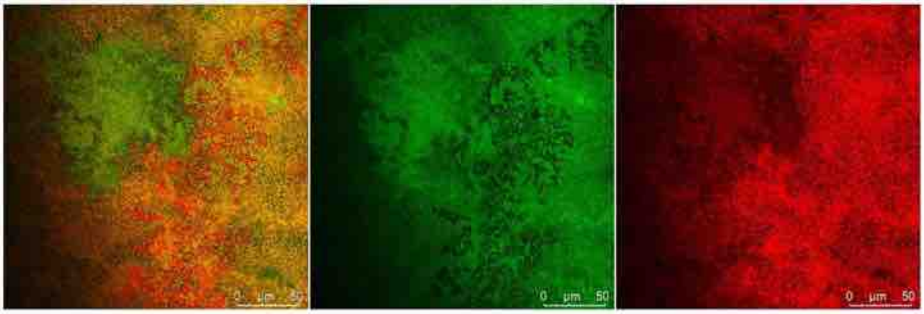
1B – Lipid-Copolymer hybrid systems as complex membranes

A. Balestri, C. Montis, B. Lonetti, D. Berti

Aims

In the last years, hybrid lipid-copolymer assemblies have gained increasing interest for the combination of the best properties of both components, like the bio-relevance of the lipid with the stability and morphological tunability of copolymers building blocks. Lipid assemblies, the major components of cell compartments, can easily adapt to external stimuli and environmental changes, but they possess, on the other hand, mechanical fragility, and a lack of stability. A total synthetic alternative to phospholipids is represented by amphiphilic block copolymers, which can spontaneously self-assemble in aggregates of different shapes in solution. The copolymer addition to the lipid system promotes the stability and mechanical strength of the mixed membrane, as well as allows a wide range of tunability for the thickness of the membrane and, in some cases, determines the formation of complex membranes with lateral phase separation in regions of different fluidities. Composite materials of lipid and polymer provide a potential tool for a wide range of applications, from models mimicking plasma membranes and biosensors to delivery platforms for molecules with pharmacological interest.



Results

A thorough physicochemical understanding and structural control over the assemblies are necessary to translate their potential into applications. For this purpose, a comprehensive physicochemical and structural characterization of hybrid molecular aggregates of the phospholipid 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) and the block copolymer poly(butadiene-b-ethyleneoxide) (PBD-b-PEO) were reported. Hybrid molecular films were investigated as monolayers at the air/water interfaces or as free-standing and solid-supported membranes and characterized with a wide range of experimental techniques. In particular, hybrid supported lipid bilayers (HSLBs) with variable copolymer content were formed through the spontaneous rupture and fusion of hybrid vesicles onto a hydrophilic substrate. Hybrid stable systems with lateral phase separation in lipid- and copolymer-rich regions were highlighted through several techniques, such as differential scanning calorimetry (DSC) and confocal scanning laser microscopy (CSLM).

In conclusion, this investigation improved our fundamental knowledge of hybrid lipid-polymeric assemblies, necessary for their future studies on biological membrane-related phenomena and the construction of 2D complex devices for material science.

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1B – Liquid crystalline nanoparticles applications in nanomedicine

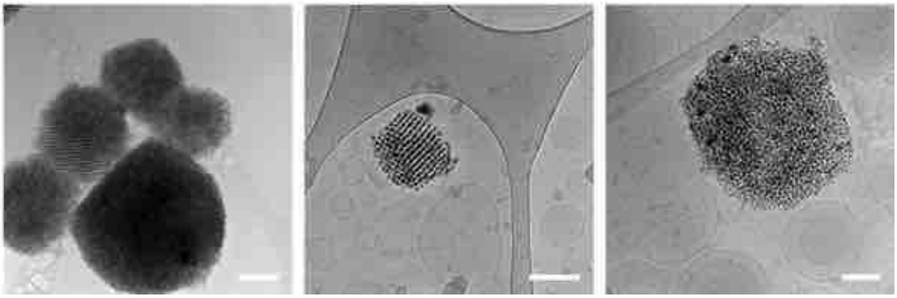
S. Murgia, C. Caltagirone, M. Fornasier, V. Lippolis, M. Mamusa, A. Porcheddu

Aims

Soft nanoparticles characterized by lamellar, bicontinuous cubic, and hexagonal inner structure (namely liposomes, nanoerythrosomes, cubosomes, and hexosomes) were formulated, characterized from a physicochemical point of view, and systematically investigated in vitro to explore their potential as pharmaceutical formulations.

Results

We are currently investigating cubosomes as carriers for photosensitizers to be used in photodynamic therapy (PDT). Particularly, folate decorated cubosomes were loaded with newly synthesized photosensitizers or co-encapsulated with up-converting Er^{3+} and Yb^{3+} codoped $NaYF_4$ nanoparticles and daunorubicin (see figure below). Results proved these formulations as versatile and biocompatible nanosystems for theranostic PDT cancer treatments. Curcumin-loaded cubosomes for topical treatment of cervical cancer were also developed, and their antiangiogenic properties demonstrated. In addition, a polyphosphoester-analog of Pluronic F127 was synthesized and successfully tested as stabilizer for cubosome nanoparticles in water. Advances in this field were reported in several reviews. Antioxidants or Rose Bengal (a drug showing antimelanoma activity) were loaded in hexosomes, vesicle gels, or deformable nanovesicles for topical administration. Results from these investigations proved all these formulations useful in the delivery of drugs to the skin. Finally, surface-modified nanoerythrosomes were effectively formulated and investigated as optical imaging diagnostics useful in diabetes therapy.



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1B – Microfluidics to investigate soft matter materials

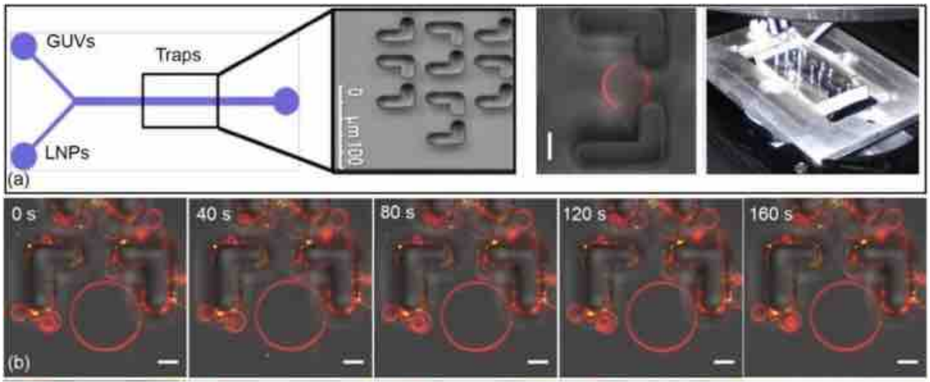
C. Montis, L. Caselli, M. Elias, P. Joseph, D. Berti

Aims

In recent years increasing interest has been devoted to the development of micron-sized soft matter materials for different purposes and applications. For instance, microcapsules are ubiquitous additives in industrial of formulations for encapsulation of poorly soluble or unstable components, while giant lipid vesicles are recognized as valuable biomimetic system, mimicking key characteristics of plasma cells in simplified and controlled conditions. Interestingly, the typical lengthscales of micron-sized soft matter materials perfectly match those of microfluidic devices. Microfluidics can be therefore profitably exploited to synthesize and investigate micron-sized objects. In this contribution, in collaboration with LAAS-CNRS Tolouse (France) we explore the potentialities of microfluidic in characterizing giant lipid assemblies (namely, giant unilamellar vesicles) and their response to exogenous species.

Results

A multifunctional microfluidic device was designed to trap micron-sized objects, specifically, giant unilamellar vesicles, and challenge them with nanosystems designed for biomedical applications. Single-object analysis was performed on the biomimetic membranes to monitor the morphological modifications due to the interaction with the nano-objects. Thanks to this approach, mechanistic insights were gained on the interaction of a nanostructured antimicrobials with Gram-negative bacterial membrane- mimicking systems.



Furthermore, with a similar approach, an on-chip micropipette was developed, to evaluate the mechanical properties of micron sized soft matter objects. The device was applied to the study of giant lipid vesicles and of their mechanical response to exogenous species.

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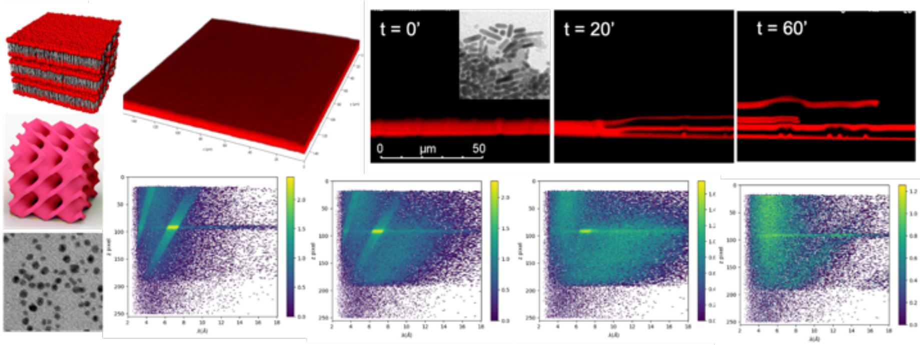
1B – Non-lamellar lipid membranes as biomimetic interfaces for biophysical studies

L. Caselli, A. Ridolfi, G. Mangiapia, T. Nylander, C. Montis, D. Berti

Aims

Lipid polymorphism is ubiquitous in nature, with non-lamellar membranes occurring in different organisms, tissues and biological conditions. In mammalian cells complex non-lamellar lipid arrangements have been found as transient or permanent mesostructures for instance under pathological conditions (e.g., starving, infection, oxidative stress) or during specific phases of cell life (e.g. trafficking phenomena, membrane fusion). However, despite their relevance, the biological role of non-lamellar membranes is far from being completely understood. In this framework, synthetic biomimetic systems can be instrumental to investigate non-lamellar membranes in simplified and controlled conditions, through a physicochemical approach, and gain some hints on their biological role. Over the years, this approach has been successfully applied to the more common planar membranes, with liposomes, giant unilamellar vesicles, supported lipid bilayers employed as proxies for biological membranes. In this study, a similar approach has been employed to prepare, characterize and investigate the behavior of non-lamellar membranes.



Results

Synthetic non-lamellar membranes of cubic arrangement were formed through newly developed protocols, employing either a top-down strategy (i.e., by spin coating a 1-monoolein solution on a solid support) or a bottom-up strategy (i.e., by depositing nanosized particles 1-monoolein on a solid support). The formed membranes were characterized with different techniques, in terms of internal nanostructure (through Small-Angle Scattering, Neutron Reflectometry and Grazing Incidence Small-Angle Scattering), mechanical properties (through Force-Distance Atomic Force Microscopy), morphology (through Laser Scanning Confocal Microscopy). Once characterized, biophysical studies were performed on these platforms to monitor their interaction with nanoparticles of different size, core composition and shape.

A significant difference was found in the interaction of gold and silver nanoparticles capped with the same coating agent, with non-lamellar membranes, highlighting a prominent importance of nanoparticles core nature in driving their interaction with lipid interfaces. Moreover, we found that the topological features of the lipid assembly at the nanoscale control the interaction pathway with nanoparticles. Specifically, confocal microscopy experiments revealed that lamellar membranes exhibit a completely different interaction mechanism with nanoparticles with respect to non-lamellar membranes, and that non-lamellar assemblies with cubic arrangement exhibit a remarkable stability in the interaction with nanoparticles, as compared to lamellar membranes.

Overall, these results will contribute to improve the fundamental knowledge on nano-bio interfaces and, more in general, will provide new insights on the biological function of lipid polymorphism in interfacial membranes as a response strategy.

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1B – Oral delivery of all-trans retinoic acid mediated by liposome carriers

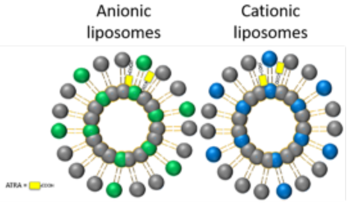
F. Cuomo, A. Ceglie, M.G. Miguel , B. Lindman, F. Lopez

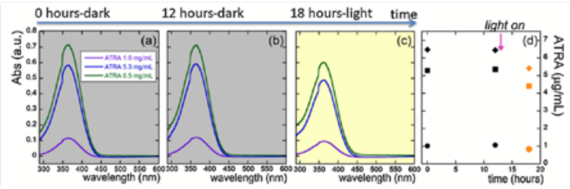
Aims

All-trans retinoic acid (ATRA) is a molecule that finds wide applications in medicine. Driven by the potential applications of liposomes in stabilizing and protecting therapeutic compounds thus enabling effective delivery of encapsulated compounds, recent research efforts have been directed to understanding mechanisms of oral delivery through the gastrointestinal tract. The surface charge of the liposome bilayers can modify the interactions between the aggregates and the gastrointestinal fluids.

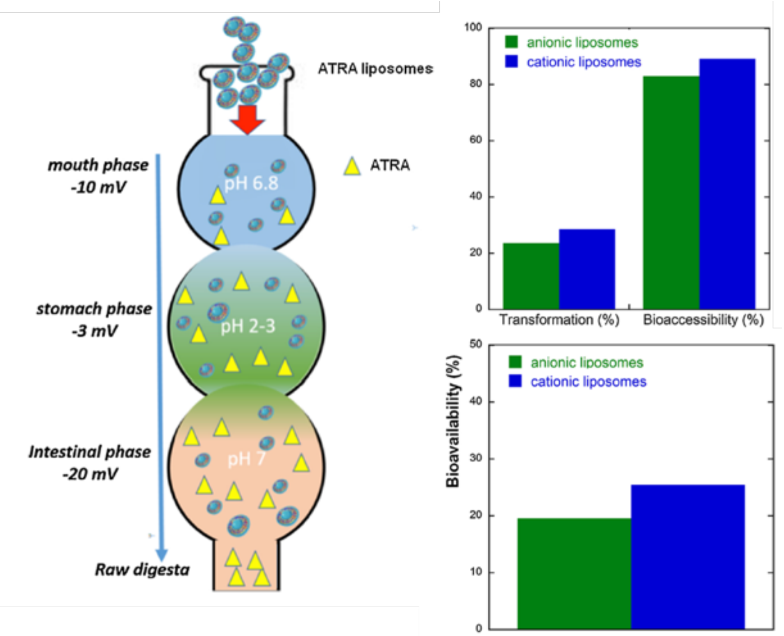
Results

The ability of cationic and anionic liposomes to encapsulate, protect and deliver ATRA in an *in-vitro* digestion process for oral administration has been studied. Stability and encapsulation efficiency of ATRA in negatively and positively charged liposomes enriched with α-tocopherol were investigated by means of UV–vis spectroscopy, dynamic light scattering and ζ-potential. The applicability of the carriers was tested by means of an in-vitro digestion procedure allowing for the measurement of the bioavailability of ATRA. The evidence was provided that the water insoluble molecules, ATRA and α-tocopherol are intercalated in liposome membranes regardless of the surface charge of the vesicle bilayers. Comparisons between cationic and anionic liposomes incorporating retinoic acid show differences in bioavailability.





The digestion model used simulates ingestion from mouth to the small intestinal phase. Here it was proposed that cationic liposomes in the mouth phase interact with mucin that is negatively charged at the pH of the saliva fluid, thus promoting the surface charge inversion and providing a further protection to the loaded molecule during the other digestion phases.



On the whole, this study suggests that liposomes could represent a valuable tool for delivery of ATRA with a different oral administration route. Furthermore, the charge of the liposomes is a very useful handle in controlling the bioavailability; the charge is easily controlled by addition of cationic or anionic surfactants or lipids.

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1B – Phosphorylated xanthan gum-Ag(I) complex as antibacterial viscosity enhancer for eye drops formulation

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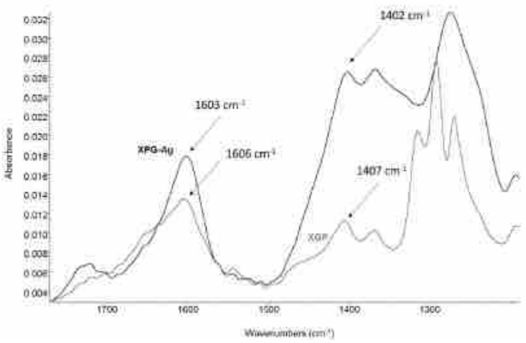
Aims

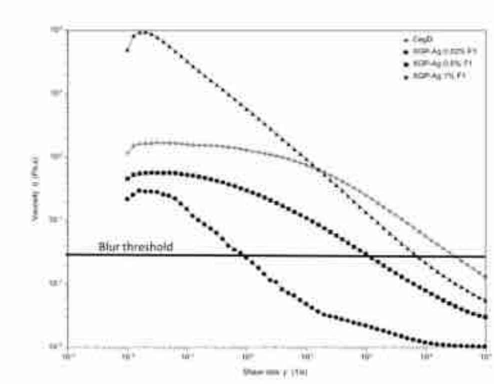
Eye is a very complex organ exhibiting several protective barriers. Efficiency of eye drops is based on increasing their residence time on ocular surface. To this aim any formulation requires adequate viscosity. Beside the viscosity, eye drops require sterility. Quite all eye drops contain benzalkonium chloride (BAC) as antimicrobial agent. Nevertheless, BAC is known to favor the onset of dry eye disease (DED). We aimed to verify the capability of phosphorylated xanthan gum-silver ions complex to guarantee adequate viscosity and antimicrobial properties, two fundamental requirements for effective eye drops.

Results

Phosphorylated xanthan gum-silver ions XGP-Ag(I) complex showed a pH of 7.1 ± 0.3 and an osmolality of 311 ± 2 mOsm/kg, values close to those of human tears. The phosphorylation degree resulted 0.01% w/w. No phosphate ions release was quantified. The Ag content was 0.33% w/w. No silver ions release was quantified. Infrared analysis confirmed both the phosphorylation of XG polymer and the coordination of silver ions by phosphorylated xanthan gum.



Thermal behaviour of XGP-Ag(I) highlighted that the insertion of hydrophilic phosphate groups along the chain increased the water binding capacity of native XG, whereas the coordination of silver ions decreased the water holding capacity. 0.02% w/v, 0.5% w/v and 1.0% w/v solutions of XGP-Ag(I) were prepared to find the formulation showing the best performance for the foreseen application as eye drops. All the prepared formulations were sterilized by filtration (through 0.22 µm filter). All XGP-Ag (I) solutions showed a typical shear-thinning behaviour with viscosity that decreased as a function of shear rate. Eye drops viscosity shoud be comprised in the range 10 mPa·s-30 mPa·s. Among the tested formulations XGP-Ag 0.02% resulted the most promising solution.



All the sterilized formulations guaranteed a visible light transmission higher than 85% and adequate refractive index (i.e. 1.334 ± 0.001). 0.02% XGP-Ag (I) formulation did not show any toxic effect on both NIH3T3 and HMVEC cells proliferation. The capability of 0.02% XGP-Ag(I) formulation to hinder bacterial proliferation was verified on Pseudomans fluorescens and Staphylococcus epidermidis. The obtained results let us to conjecture that XGP-Ag(I) could be used as viscosity enhancer for eye drops.

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1B – Physicochemical Characterization of Hyaluronic Acid and Chitosan Liposome Coatings

C. Bonechi, G. Tamasi, A. Donati, G. Leone, M. Consumi, L. Cangeloni, V. Volpi, A. Magnani, C. Rossi
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Aims

Hyaluronic acid (HA) and chitosan (CH) are biopolymers that are widely used in many biomedical applications and for cosmetic purposes. Their chemical properties are fundamental to them working as drug delivery systems and improving their synergistic effects. In this work, two different protocols were used to obtain zwitterionic liposomes coated with either hyaluronic acid or chitosan. Specifically, the methodologies used to perform vesicle preparation were chosen by taking into account the specific chemical properties of these two polysaccharides. In the case of chitosan, liposomes were first synthesized and then coated, whereas the coating of hyaluronic acid was achieved through lipidic film hydration in an HA aqueous solution. The size and the zeta-potential of the polysaccharide-coated liposomes were determined by dynamic light scattering (DLS).

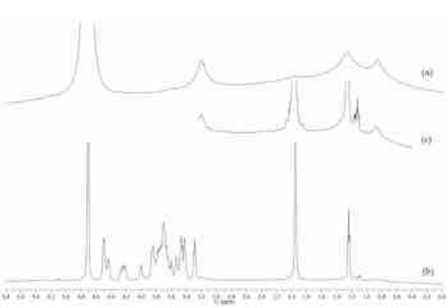
This approach allowed coated liposomes to be obtained with hydrodynamic diameters of 264.4 ± 12.5 and 450.3 ± 16.7 nm for HA- and CH-coated liposomes, respectively. The chemical characterization of the coated liposomal systems was obtained by surface infrared (ATR-FTIR) and nuclear magnetic resonance (NMR) spectroscopies. In particular, the presence of polysaccharides was confirmed by the bands assigned to amides and saccharides being in the 1500–1700 cm-1 and 800–1100 cm-1 regions, respectively. This approach allowed confirmation of the efficiency of the coating processes, evidencing the presence of HA or CH at the liposomal surface. These data were also supported by time-of-flight secondary ion mass spectrometry (ToF-SIMS), which provided specific assessments of surface (3–5 nm deep) composition and structure of the polysaccharide-coated liposomes. The synthesis and the physical chemistry characterization of coated liposomes with HA or CH represent an important step in improving the pharmacological properties of drug delivery systems.

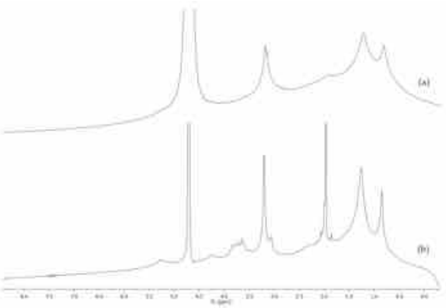
Results

Zwitterionic liposomes coated with two polysaccharides: chitosan and hyaluronic acid, which are widely used for biomedical applications, were synthesized and characterized.

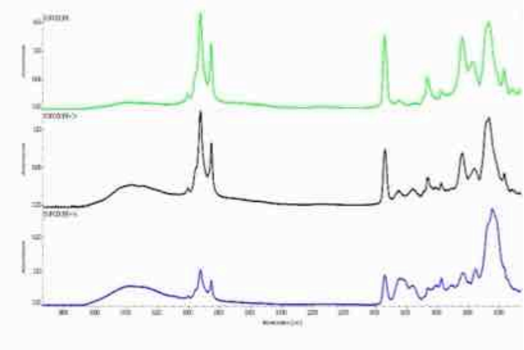
The average size of vesicles being increased after coating with CH and HA, together with the zeta-potential, suggested a proper coating procedure. The zeta-potential of DOPC/DOPE-CH suggested the better physical stability of these preparations, indicating a lower probability of aggregation of liposomes versus time.

The coated liposomes were analyzed by surface infrared (ATR-FTIR) spectroscopy, nuclear magnetic resonance (NMR) and time-of-flight secondary ion mass spectrometry (ToF-SIMS).





The NMR spectrum of HA-coated liposomes showed the presence of large signals typical of vesicles and the presence of proton signals assigned to HA in solution. In the range of 3.3–4.5 ppm, NMR signals of the H1–H5 and H1–H6’ protons of glucuronic acid and acetylglucosamine were evident. The chemical shift and the signal width of the HA proton suggest the presence of HA on the liposome surface, which highlights that the coating process occurred properly and that HA was homogeneously distributed on the liposome surface. The NMR spectra showed the presence of two polymers on the surface of the liposomes. In fact, the proton signals of both liposomes showed broad unresolved peaks, which are typical of aggregates. The comparison of these vesicles suggest that CH coats the vesicles more efficiently.



The analysis of both the infrared and secondary ion mass spectra confirmed the presence of chitosan on the surface of the liposomes. In particular, the ToF-SIMS mass spectra, which investigates the very surface layer of systems (up to a maximum depth of 3–5 nm), provided crucial information on the coating processes.

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1B – Physicochemical properties of hafnium oxide nanoparticles as radio-enhancers

A Minò, L. Ambrosone

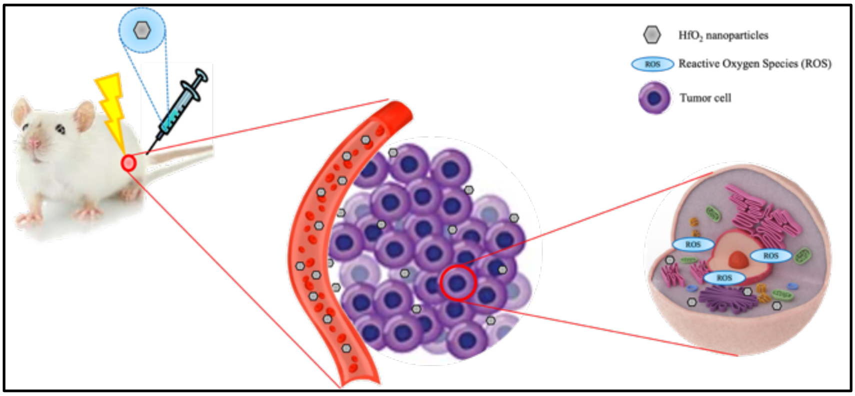
Aims

This research aims to develop a method to produce a new formulation of HfO_2 nanoparticles and to characterize their physicochemical properties as radio-enhancers in cancer therapy.

Results

To improve radiotherapy efficacy, nanotechnologies allow the development of nanomaterials, known as radio-enhancer, which increase the predisposition of tumor tissues to suffer irreparable damage following exposure to radiation. Therefore, radio-enhancers are therapeutic agents that amplify the effects of radiotherapy, allowing to reduce the doses and to limit the damage to the tumor tissues while sparing the healthy ones.

The developed formulation generates HfO2 nanoparticles of 112 nm with a very narrow lognormal distribution. The fluid dynamic properties of their dispersions in water reveal a pseudoplastic behavior with decreasing viscosity as the shear rate increases. The optical properties of the dispersion show a band gap energy of 5.5 eV, corresponding to UVC radiation. This indicates the strengthening capacity against X-rays used for radiotherapy. Therefore, these systems are potential radiotherapy enhancers and can be tested first with Montecarlo simulations and then in vivo on laboratory animals.



1B – Physico-chemical properties of vital dyes in the form of solutions or dispersions for use in medicine

A, Minò, G, Cinelli, F, Lopez, L. Ambrosone

Aims

The research aim is to study the nature of the self-association of dyes in aqueous solutions in order to understand and interpretation the tissue staining in biology and microsurgery.

Results

Although the applications of vital dyes are numerous, some problems such as the questions of how the chemical structure of dye and its tendency to associate in solution are related to the toxic effects observed in-vivo, are still unsolved. Another interesting aspect is the sensitivity of vital dyes to different chemical environments. In this respect Nile Red (NR) has been advantageously applied to probe the local polarity in the study of various heterogeneous systems, including micelles, reverse micelles, dendrimers, liposomes, proteins, and ionic liquids. Furthermore, NR in solution self-associates owing to strong intermolecular van der Waals attractive forces between molecules. It was recently demonstrated that alkan-1ols solvents are significantly more polar than expected based on the measured H-bonding properties of “monomer” alkan-1ols in dilute solution. By varying the length of *n*-alkanols differently hydrophilic environments have been created, where the NR dye is soluble. The NR dimerization equilibrium constant, K, in the first eight n-alkanols was calculated: the hydrophobicity of alkanol significantly reduces the red shift of the NR absorption band. The role of the medium hydrophilicity on the NR spectroscopic response was further investigated. The introduction of water to the binary system NR-alkanol causes a decrease in fluorescence.

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1B – Plasticizers free polyvinyl chloride membrane for metal ions sequestering

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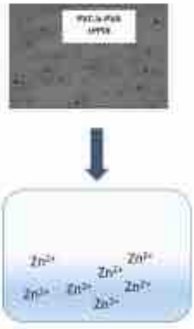
Aims

Rapid and accurate detection of solute species, such as metal ions, is of major importance in several fields, from food analysis to pharmaceutics production. Ion selective membranes (ISMs) remain the most used tool to detect the presence of metal ions in liquid phases. All ISMs are composed of a supporting material, commonly high molecular weight polyvinyl chloride (PVC), a plasticizer, an ion excluder and the ionophore. The plasticizer is the most critical component of ISMs since by it depends the ionophore adsorption in the membrane and hence, sensor performance. Several attempts were used to avoid the use of plasticizer. The objective of this work is the realization of an ion-capturing membrane, suitable for analysis of aqueous solutions, avoiding the plasticizer thanks to microcavities that allow the ionophore to easily penetrate inside the material. This leads to a better sensitivity thanks to the increased active surface. Protophorphyrin IX was used as ionophore. Protoporphyrins are a class of macrocyclic organic compounds that are often applied to ion-selective membranes thanks to their selectivity. Moreover, metalloporphyrins show intensive absorption bands in the visible region making metal detection easily executed.

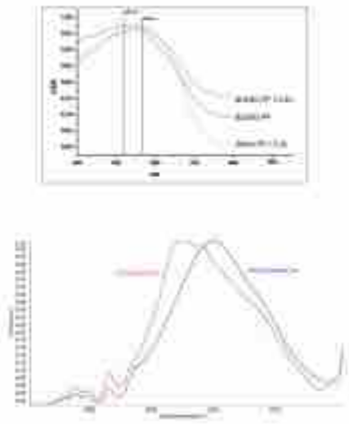
Results

Porous PVC-based membranes enriched with Protoporphyrin IX were prepared as single-use system to capture Zinc ions. Porosity was realized by mixing PVC with PVA as a blend and removing the water soluble component by washing. The procedure permitted to obtain a uniformly distributed porosity (≈2 µm).



FTIR analysis demonstrated both the presence and the removal of the porogenic elements. The presence of ionophore was also verified by FTIR. DSC analysis showed that the effect of porogenic agents and ionophore on glass transition temperature of

PVC do not significantly short the temperature range operation field of the membrane. The effective complexion with zinc ions was verified by UV and IR spectroscopy. Therefore, it is possible to conclude that the PVC-b-PVA membrane is promising for the detection of metal ions of appropriate charge-radius avoiding the use of plasticizers thanks to the micro-cavities that facilitate ion-membrane chemical exchange.



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1B – Poly-vinyl alcohol (PVA) crosslinked by trisodium trimetaphosphate (STMP) and sodium hexametaphosphate (SHMP): Effect of molecular weight, pH and phosphorylating agent on length of spacing arms, crosslinking density and water interaction

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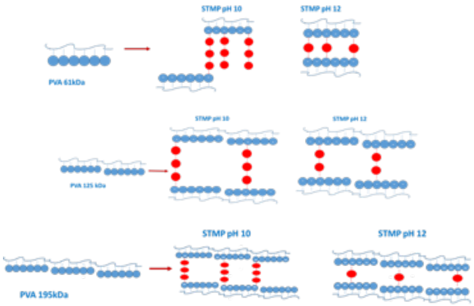
Aims

Recently, a great deal of effort has focused on the design of optimal delivery systems for drugs and bioactive factors, such as nanoparticles, liposomes, dendrimers and aptamers. However, polymeric vehicles still remain the most convenient and versatile way to delivery substances and, among polymers, one of the most utilized is polyvinyl alcohol (PVA). The main concern is about its stability and resistance. Nevertheless, it can be significantly improved by crosslinking it. A major limit in using crosslinking agents is represented by their cytotoxicity. The toxicity of polyphosphates is low and neither mutagenic or carcinogenic effects nor reproductive effects are observed. The mechanism through which polyphosphates can crosslink polysaccharides has been widely studied. On the contrary, there is a lack of investigation on parameters that mostly affect polyphosphate crosslinking capability when PVA is used as polymer. The non-toxic trisodium trimetaphophate (STMP) and sodium hexametaphosphate (SHMP) are used as crosslinker for the preparation of 3D PVA matrices. Specifically, we aim to study the effect of crosslinker and pH on crosslinking density of five different MWs PVA and how the combination of crosslinker, polymer MW and pH affects the interaction of the matrices with water. Understanding the specific interactions that might occur with water, is a useful tool in predicting the properties, as well as indicating what parameters need to be tailored to gain the desired characteristics. Indeed, matrix-water interaction is of foremost importance for the development of an efficient drug delivery polymeric system as well as an absorbent for metal ions or soft tissues substitutes.

Results

Twenty phosphorylated PVA based materials have been obtained using STMP and SHMP as phosphorylating agent working at pH 10 and 12.



MW is the parameter that mostly affects the crosslinking yield, under 61 kDa no crosslinking reaction occurs regardless of phosphorylating agent and pH value. Infrared analysis indicates that pH plays a fundamental role for the crosslinking density affecting both deprotonation of the polymeric chain and the length of the spacing arm. STMP at pH 10 is able to bind polymer chains as triphosphate arm. This guarantees an efficient crosslinking process only in the presence of partially deprotonated chains (high viscosity, PVA 125 kDa and PVA 195 kDa). When STMP is used at pH 12, it is degraded into monophosphate arm, that permits the crosslinking of sufficiently mobile chains able to counteract the repulsion between deprotonated chains. A similar dependence is found also for SHMP. Infrared analysis indicates at pH 10 a shorter crosslinking arm with respect to STMP, pyrophosphate and triphosphate, respectively. At pH 12 a monophosphate arm is found with a similar effect on crosslinking density. For PVA 61 kDa, pH 12 is mandatory for obtaining crosslinked matrices both using STMP and SHMP. Finally, to obtain phosphorylated hydrogels a correct combination of pH, phosphorylating agent and molecular weight need to be selected.

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1B – Recovery, Storage and Recycling of Lacual Sediments

B. Molino, A. Minò, L. Ambrosone

Aims

The research aims at the recovery of submerged silt-clayey sediments and their reuse, in order to reduce the movement, through the combination of plant schemes with a high level of technology.

Results

A mathematical model for determining the sediment volume profile in a reservoir is proposed. The resulting equation is similar to a first-order kinetics with lifetime varying with time. Such model was applied to a large number of dams whose bathymetric reliefs were drawn from the literature. For reservoirs, where the number of bathymetric reliefs is high the model is directly applied and the parameters extracted from a non-linear fitting. Where the number of bathymetric data does not allow a non-linear regression, a straightness test is performed first, then, the parameters computed by the regression line of log Z vs. log t. Finally, for dams where only two bathymetric surveys are available, equations have been provided to estimate the model parameters. These equations have been applied to Altinapa dam (Turkey) and Chimhanda dam (Zimbabwe). Furthermore, a good agreement was verified between the sedimentation profiles obtained by the model and the results estimated by the satellite surveys. The model provides a framework which enables us to correlate data in sensible manner, it tells us what to plot against what, the coordinates we must use to get a smooth line. For engineering work such a framework is extremely useful because it enables to interpolate and extrapolate limited bathimetric reliefs and to manage long-term water of reservoirs. Looking ahead, if one can relate the model parameters to the chemical properties of solids it will become highly predictive for the management of a reservoir and its sed.

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1B – Regulation of substrate dissipation via tunable linear elasticity controls cell activity

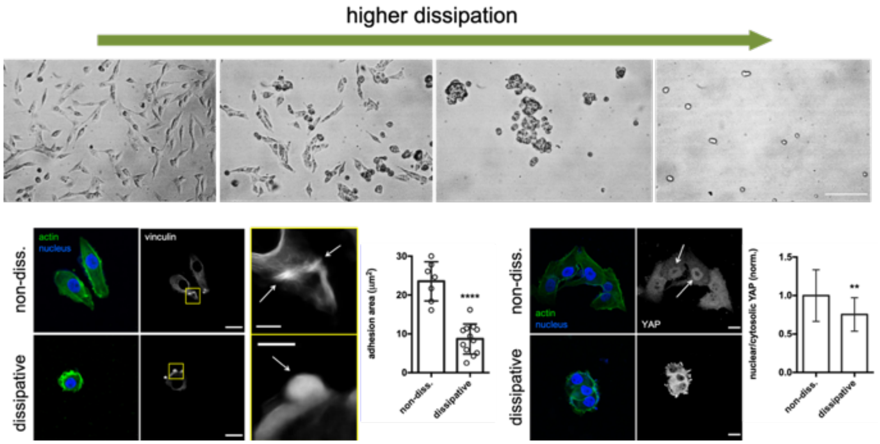
P. Sacco, F. Piazza, C. Pizzolitto, G. Baj, F. Brun, E. Marsich, I. Donati

Aims

Natural tissues and extracellular matrices (ECMs) are not purely elastic materials but exhibit dissipative properties. Despite it has recently emerged as a novel regulator of cellular responses, the contribution of material dissipation to guiding cell-fate decisions is still in its infancy. Here, we report an unprecedented strategy for tuning the dissipation rate of viscoplastic substrates while precisely regulating linear elasticity.

Results

We describe semi-interpenetrating substrates consisting of a rigid hydrogel network intertwined with a branched biopolymer. The release of these weak physical entanglements under loading dissipates the applied stress and leads to the extension of the linear elasticity. Our results reveal a crucial link between this material property and cell response in 2D cultures, impacting on cell migration mode and speed, vinculin-dependent focal adhesion geometry and size, F-actin organization, transmission of forces and YAP nuclear translocation. We show that cells require joint actomyosin contractility and microtubule tension to probe the substrate and decide whether or not to adhere, revealing a clear correlation between force transmission, substrate dissipation rate and amount of anchoring points. Overall, our findings introduce linear elasticity as a novel design parameter for assembling tunable dissipative materials to study cell mechanosensing in 2D and possibly also in 3D cultures.



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1B – Rheological and Nutritional Assessment of Dysphagia—Oriented New Food Preparations

F. Cuomo, F. Lopez, M.C. Messia, E. Marconi

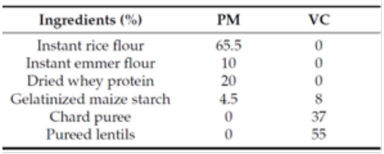
Aims

Dysphagia that involves difficulty swallowing food and liquids is a symptom of different diseases. In some cases, patients who experience this symptom should be fed with modified consistency foods. Dysphagia is often accompanied by malnutrition and dehydration and an interesting approach to dealing with these conditions is to provide patients with nutrient-rich foods. Here, two new food formulations for dysphagia patients are proposed: a cereal-based protein meal (PM) and a vegetable cream (VC).

Results

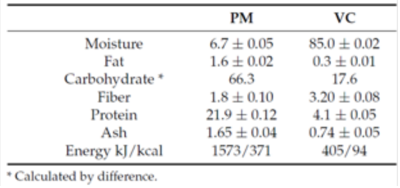
The nutritional aspects evaluated on the new formulations revealed that the protein content in the protein meal was 21.9% and the fiber content in the vegetable cream was 3.2%. These values allowed reaching the claim "high protein" for the protein meal and "source of fiber", for the vegetable cream (EU. Regulation 1924/2006). The nutritional value of proteins in the protein meal assessed by the chemical score was high (CS = 100).

Formulations of PM and VC



Ingredients (%)	PM	VC
Instant rice flour	65.5	0
Instant emmer flour	10	0
Dried whey protein	20	0
Gelatinized maize starch	4.5	8
Chard puree	0	37
Pureed lentils	0	55

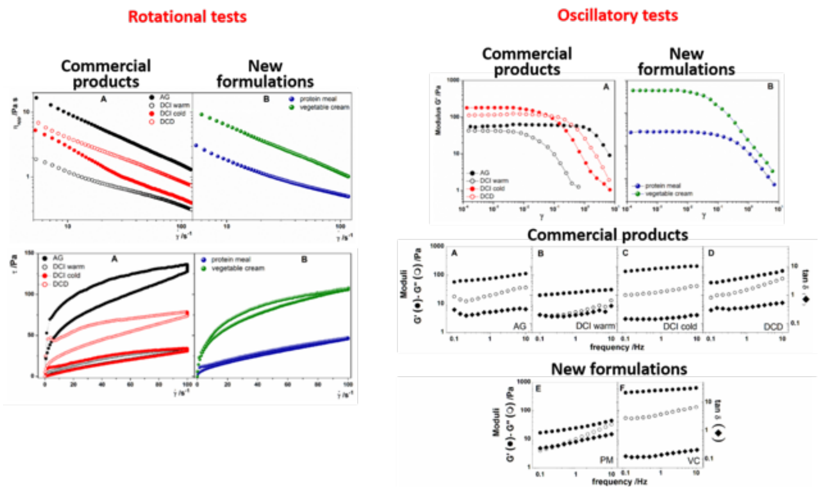
Chemical composition (g/100 g) and energy value of PM and VC



	PM	VC
Moisture	6.7 ± 0.05	85.0 ± 0.02
Fat	1.6 ± 0.02	0.3 ± 0.01
Carbohydrate *	66.3	17.6
Fiber	1.8 ± 0.10	3.20 ± 0.08
Protein	21.9 ± 0.12	4.1 ± 0.05
Ash	1.65 ± 0.04	0.74 ± 0.05
Energy kJ/kcal	1573/371	405/94

* Calculated by difference.

By comparing the rheological characteristics of the new formulations with those of commercial formulations for dysphagia, it emerged that they were comparable for the rheological behavior.



Based on these results, this investigation can be seen as a starting point toward the design of further alternatives for consumers with swallowing disorders. Moreover, considering the ingredients used and the procedure to prepare protein meal and vegetable cream, the proposed formulations could be prepared by non-specialized personnel in conditions of domestic use.

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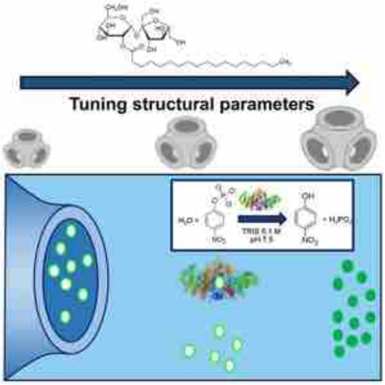
1B – Smart Cubosomes and magnetocubosomes as advanced drug delivery systems

A. Balestri, L. Caselli, C. Montis, B. Lonetti, D Berti

Aims

Despite this intense research on the development of smart and biocompatible drug delivery nanovectors, lipid-based systems, among the first to be developed and brought to the market, remain probably unsurpassed. In this framework, cubosomes offer multiple advantages as drug delivery systems when compared to the most common liposomes, such as an extremely high interfacial area and a remarkable fusogenicity. In this contribution we explore the potentialities of cubosomes as smart drug delivery systems, by endowing simple 1-monoolein cubic structures and cubosomes with different properties, namely: tunable size of the aqueous channel (through the inclusion of an additive); responsivity to static and alternating magnetic field (through the inclusion of hydrophobic magnetic nanoparticles); responsivity to temperature (through the addition of a thermoresponsive stabilizer).



Results

The inclusion of an additive, the sucrose stearate, able to swell the lipid mesophase of phytantriol/H_2O (PHYT/H_2O), was employed to investigate the kinetics of the species p-nitrophenyl phosphate conversion into p-nitrophenol, catalyzed by the enzyme Alkaline Phosphatase, upon alternative confinement of the substrate and the enzyme into the liquid-crystalline system. The combination of a structural study through Small-Angle X-rays Scattering (SAXS), with a colorimetric UV-Vis assay, reports the possibility of fine control on the enzymatic reaction kinetic by tuning the structural parameters of the mesophases depending on the amount of included additive, opening new strategies for confinement and controlled release of therapeutics.

The inclusion of hydrophobic Fe_3O_4 nanoparticles in lipid structure, allows the combination of the lipid biocompatibility with the responsiveness to magnetic stimuli of such nanoparticle, making suitable candidates for a controlled drug delivery and release. The organization of SPIONs within the lipid scaffold can lead to locally enhance

SPIONs concentration and improve magnetic response, overcoming the current limitations of hyperthermic treatments.

The stabilization of non-lamellar lipid nanostructures with a thermoresponsive copolymer, the polymer poly(N,N-dimethylacrylamide)-*block*-poly(N-isopropylacrylamide) (PDMA-*b*-PNIPAM), provides the design of a novel class of drug delivery systems (DDSs). The steric stabilization by a thermo-responsive corona induces additional benefits compared to the standard Pluronic-stabilized formulations like the "sponge effect", for a controlled release of encapsulated molecules, with an increased affinity towards lipid bilayer membranes, for enhanced fusion with the target-cellular site, prompting these new assemblies as promising DDS.

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1B – Sodium hyaluronate-g-2-((N-(6-aminohexyl)-4-methoxyphenyl)sulfonamido)-N-hydroxyacetamide with enhanced affnity towards MMP12 catalytic domain to be used as visco-supplement with increased degradation resistance

G. Leone[1], S. Pepi[1], M. Consumi[1], S. Lamponi[1], C. Rossi[1], A. Magnani[1], M. Fragai[2], M. Martinucci[2], V. Baldoneschi[2], O. Francesconi[2], C. Nativi[2]

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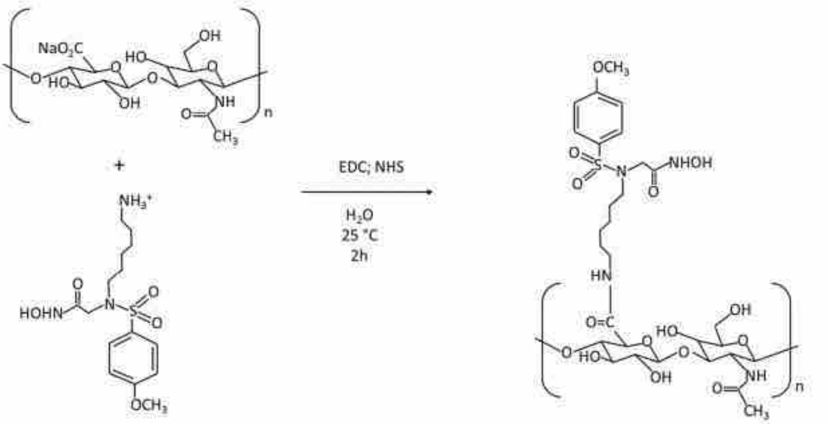
Aims

Hyaluronic acid (HA) is a linear polysaccharide consisting of the repetition of a disaccharide composed of D-glucuronic acid (GLCA) and N-acetyl D-glucosamine (GlcNAc). Viscosupplementation still represents the main field of application for hyaluronic acid. Unfortunately, HA is enzymatically degraded in a short time (hours – days) leading to loss of its lubricating action and formation of low molecular weight fragments (MW < 200 kDa) that represent a pro-inflammatory stimuli. Any inflammatory state is always accompanied by the abnormal activation of specific metalenzymes, matrix metalloproteinases (MMPs), that, if over expressed, lead to the uncontrolled degradation of specific protein substrates. In the last 30 years, MMP inhibitors (MMPI) with high affinity towards these metalloenzymes have been synthesized and tested. However, only a few of these MMPI have come to clinical trials and with little success. Recently, a group of nanomolar inhibitors perfectly soluble in water and therefore with a much better bioavailability compared to those previously has been developed[1]. We aim to prove the suitability of 2-((N-(6-aminohexyl)-4-methoxyphenyl)sulfonamido)-N-hydroxyacetamide (a small molecule with proven inhibition activity towards MMP12) grafted to sodium hyaluronate as viscosupplement. We conjectured that grafting a MMP12 inhibitor (MMPI) along the sodium hyaluronate backbone joined the HA outstanding viscoelastic and lubricating actions, with the inhibition of MMP12 that is directly involved in osteoarthritic disease progression. Moreover, slowing down the HA degradation, the developed compound (HA-MMPI) should reduce the inflammatory effect of the low molecular weight HA fragments that are generated during its physiological degradation.

Results

A combination of IR spectroscopy, elemental analysis, Time of flight secondary ion mass spectrometry and NMR was used to obtain both the confirmation of the grafting procedure and a quantification of MMPI grafted to HA chains. Grafting degree was calculated from CNS elemental analysis using native sodium hyaluronate as reference. A grafting degree of 10 ± 1% was found.



The presence of MMPI does not affect the water binding ability of NaHA. HA-MMPI polymer solution demonstrated viscoelastic behavior similar to that of healthy human synovial fluid h-SF when analyzed in dynamic oscillation conditions showing a viscous response at low frequencies and an elastic response at high frequencies. HA-MMPI cytotoxicity towards HC was assessed as a function of both concentration and incubation time. HC viability is not influenced by any of the different concentrations (from 7 nM to 10 µM) tested. A time dependent proliferation rate can be seen. No dedifferentiation was observed since HC maintain their capability to produce both sGAG and HYP. The maintenance of MMPI affinity towards MMP12 once bound to NaHA was analyzed by fluorimetric assay. No increase of fluorescence was observed at the investigated concentrations of HA-MMPI, indicating that MMPI maintained its nanomolar affinity towards MMP12 also once grafted to hyaluronate chains. In vitro enzymatic degradation kinetics was analyzed to verify if the chemical modification was able to slow down the hyaluronidases action on the samples. From the results of enzymatic test is possible to assess that after 3 h HA-MMPI shows a 10% increased stability to in vitro enzymatic degradation in comparison to native HA, resistance that increased up to about 50% after 24 h.

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1B – Solid Lipid Nanoparticles Produced via a Coacervation Method as Promising Carriers for Controlled Release of Quercetin

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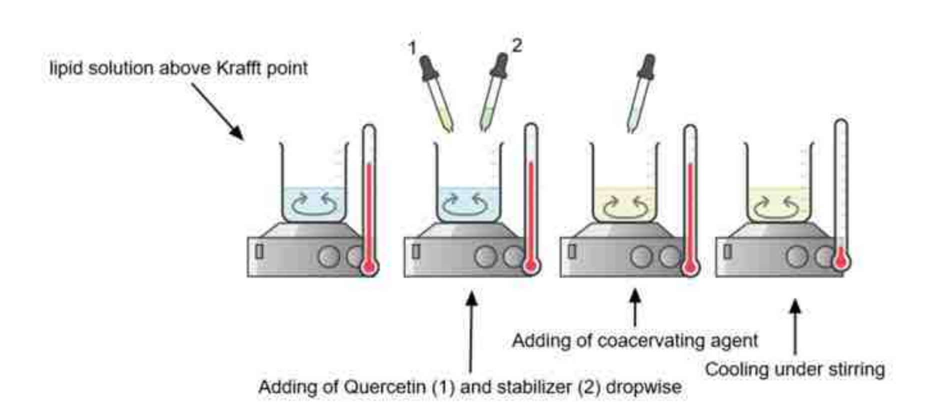
Aims

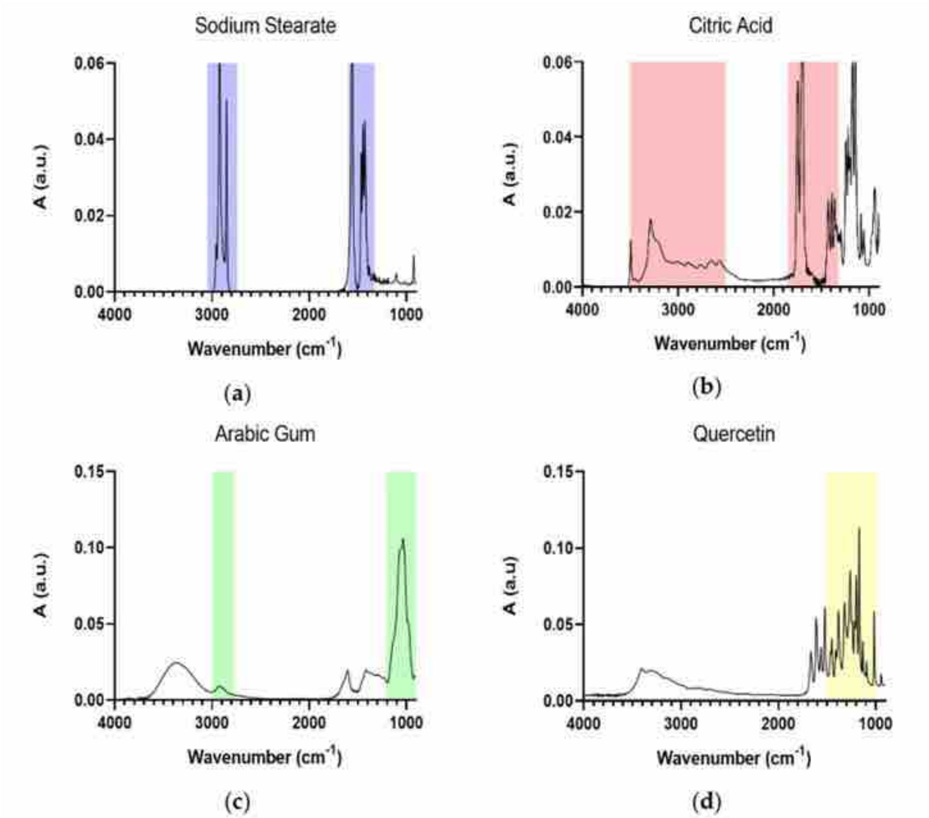
Coacervation is a simple method to obtain solid lipid nanoparticles. It is based on the heating of aqueous solutions with a specific salt of fatty acids above its Krafft point. Although many Solid Lipid Nanoparticles loaded with Quercetin have been already studied, there are not so many examples of loaded SLNs prepared with a coacervation method. Quercetin-loaded SLNs were obtained via the coacervation method. Loaded and unloaded SLNs were qualitatively analyzed using FTIR-ATR, ToF—SIMS, DLS, and Zeta potential. Quercetin encapsulation efficiency, in vitro release, and QuercSLN antioxidant activity against ABTS•+ were evaluated using UV—VIS spectrophotometry methods.

Results

Quercetin-loaded SLNs were obtained via the coacervation method.



This method was demonstrated as a high-loading method for Quercetin and an overall simple process to obtain solid lipid nanoparticles, as confirmed by both DLS and Zeta potential measurements that provided the dimensions and charge of the nanoparticles, and FTIR/ATR and ToF-SIMS that provided the proper SLNs composition.



The filtration process was successful in separating Solid Lipid Nanoparticles by their size, as confirmed by dimensional distributions given by Dynamic Light Scattering data. Moreover, Infrared analysis of the two SLNs portions (the filtered and the recovered from filter) have different composition with the filtered showing a lipid core smaller than the stabilizer shell and the recovered from filter showing a Stearic Acid core greater than the Arabic Gum stabilizing shell. The release profile of QuercSLN followed an exponential plateau pathway within 26 h, evidencing a homogeneous distribution of the drug within the SLNs, and the system showed a controlled antioxidant effect compared to free Quercetin, demonstrating that the encapsulated nutraceutical preserves its antioxidant activity to a large extent (≈81% of that of free Quercetin). Based on these data, Solid Lipid Nanoparticles synthesized via a coacervation method were demonstrated as suitable candidates as systems for the controlled delivery of Quercetin and other lipophilic drugs or nutraceuticals.

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1B – Spontaneous polymerization of benzofulvene derivatives bearing complexed or un-complexed pyridine rings

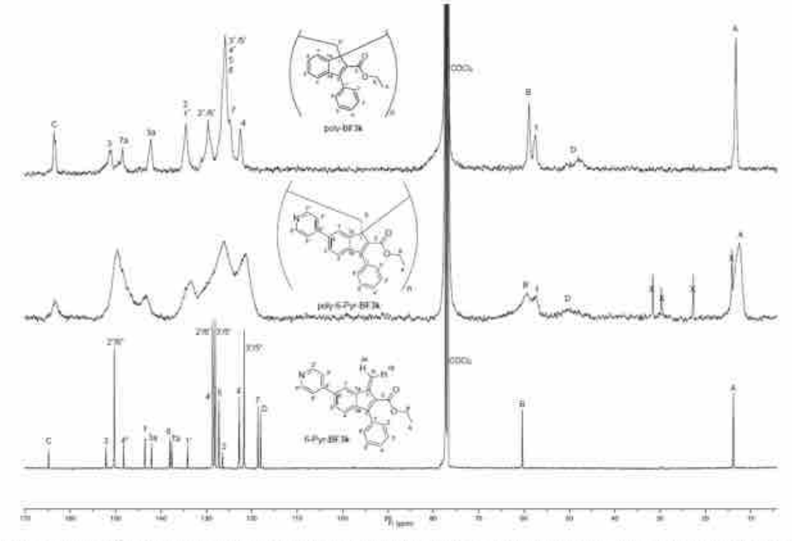
M. Paolino, M. Saletti, A. Reale, V. Razzano, G. Giuliani, A. Donati, C. Bonechi, G. Giorgi, A. Atrei, M. Mauro, A. Scamporrino, F. Samperi, E. Fois, G. Tabacchi, C. Botta, A. Cappelli

Aims

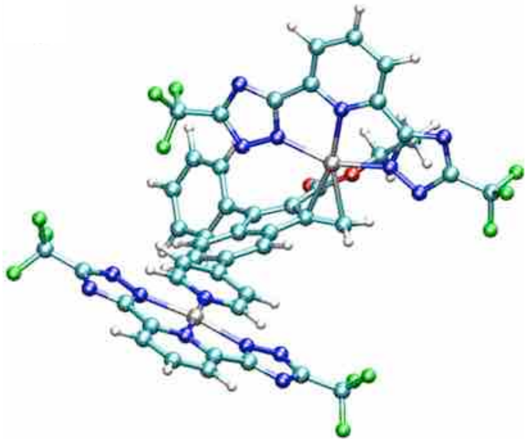
Benzofulvene derivatives bearing complexed and un-complexed pyridine rings are designed and synthesized to assess the effects on the spontaneous solid-state polymerization of the presence in position 6 of the 3-phenylbenzofulvene moiety of bulky substituents capable of establishing metallophilic interactions. Both the benzofulvene monomers are found to polymerize spontaneously upon solvent removal under reduced pressure in the apparent absence of catalysts or initiators. The resulting polybenzofulvene derivatives are characterized by NMR spectroscopy, MALDI-TOF mass spectrometry, and in photophysical studies.

Results

Two benzofulvene derivatives bearing complexed (i.e. 6-PTPC-BF3k) and un-complexed (i.e. 6-Pyr-BF3k) pyridine rings in position 6 of the 3-phenylbenzofulvene scaffold were designed and synthesized to evaluate the effects on the spontaneous solid-state polymerization of the presence of bulky substituents capable of establishing metallophilic interactions. First, the benzofulvene monomer 6-Pyr-BF3k bearing a free pyridine ring was easily prepared and found to polymerize spontaneously by removing the solvent at reduced pressure in the apparent absence of catalysts or initiators. The resulting polybenzofulvene derivative was characterized by NMR spectroscopy, MALDI-TOF mass spectrometry, and in photophysical studies.



The results of MALDI-TOF mass spectrometry characterization supported the polymeric nature of poly-6-Pyr-BF3k, and NMR studies suggested the consistency of the vinyl (i.e. 1,2) thermoreversible polymerization mechanism as already observed in several structurally related polybenzofulvene derivatives. Photophysical characterization studies showed that polybenzofulvene derivative poly-6-Pyr-BF3k displayed a significant fluorescent blue emission centered at 485 nm and characterized by a quantum yield value of 13% and an averaged lifetime of 8.5 ns. On the other hand, benzofulvene monomer 6-PTPC-BF3k showed a more complex polymerization behaviour. In fact, experimental evidence suggested that the spontaneous polymerization of this platinum complex appeared to be in competition with its crystallization probably because of the presence of bulky and rigid platinum complex. In fact, in the formed polymeric material some monomeric unities relieve their bulkiness by transferring the platinum complex moiety to benzofulvene monomer 6-PTPC-BF3k molecules, which are near in the space where the polymerization occurred. Thus, poly-6-PTPC-BF3k appeared to show the features of a copolymer rather than those expected for the corresponding homopolymer, as suggested by MALDI-TOF mass spectrometry and photophysical characterization results.



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1B – Structural characterization of chia mucilage for food processing applications

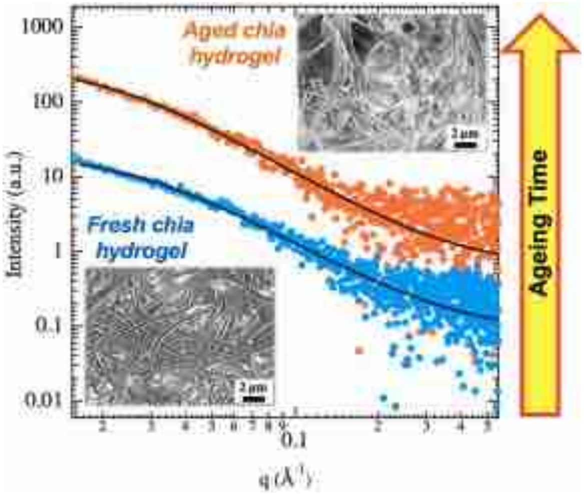
F. Cuomo, E Fratini, S. Iacovino, F. Lopez

Aims

Considering the interest in chia mucilage for various applications, it seems to be of key importance to provide experimental evidence for the change in the microstructure of the biomacromolecule over time and to link the structural changes to the amount of water adsorption observed at the macroscopic level. Therefore, a structural study performed by FTIR spectroscopy, small angle X-ray scattering (SAXS), rheology and microscopy on CM hydrogels was undertaken.

Results

We investigated on the effect of polymer concentration and ageing on the mechanical properties of chia mucilage hydrogels. Rheological characterization highlighted that ageing destabilizes the hydrogel network. Indeed, the hydrogel elastic modules (G’) decreases and the linear viscoelastic range is reduced, as well as the viscosity shows a decrease of the resistance to flow of the viscoelastic fluid. This behavior can be correlated with a structural change observed by microscopy, in particular the formation of less entangled and packed structures. This was further confirmed by SAXS analysis, which helped us to find that the correlation length (i.e., mesh size) of the hydrogel network increases with the ageing of the samples. In view of the wide range of chia mucilage potential applications in food industry, considering the variability of the mucilage composition depending on its origin and on the production procedure, the crucial role of ageing could represent a significant information for food processing involving chia polymer.



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1C – Colloid Interaction Theory and Recovery of Sulfide Minerals

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** University of Cagliari*
° Murdoch University

Aims

DLVO theory has provided a framework for understanding interactions between colloidal particles. Theory however has found less application in industrial mineral processing plants due to inevitable discrepancies between ideal laboratory conditions and the operational reality of working plants. Part of the reason is the oversimplification of chemical models and use of approximate equations that do not well characterise real behaviour. This project aims to close the gap chemists and metallurgists by employing state of the art numerical calculations of lead sulfide (galena) mineral-bubble interactions, including experimentally founded charge-regulated descriptions of the surface charge of minerals.

Results

Galena zeta potentials were measured and used to calibrate a charge regulated model of the surface. A two-site model (acidic site +basic site) was found to reproduce experimental data better than a single amphoteric site. Measured and calculated zeta potentials are show in Figure 1.

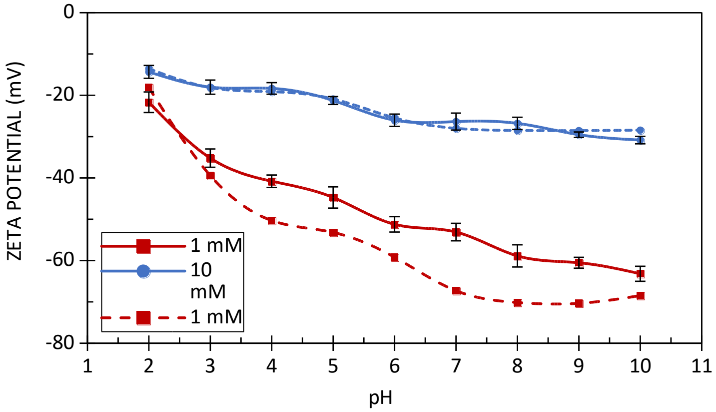

Figure 1. Experimental (solid) and theoretical (dashed) zeta potentials of galena (PbS) in 1 mM and 10 mM NaCl.

Recovery of galena by froth flotation in different salt concentrations and different particle sizes was measured by microflotation using Hallimond tubes. Galena recovery is improved at higher salt concentrations (Figure 2). Theoretical calculations of galena-air bubble interactions interpret this result through an elimination of repulsive interactions driven by ion adsorption layers, with complete particle-bubble attachment (attractive interactions) occurring in 100 mL NaCl conditions.

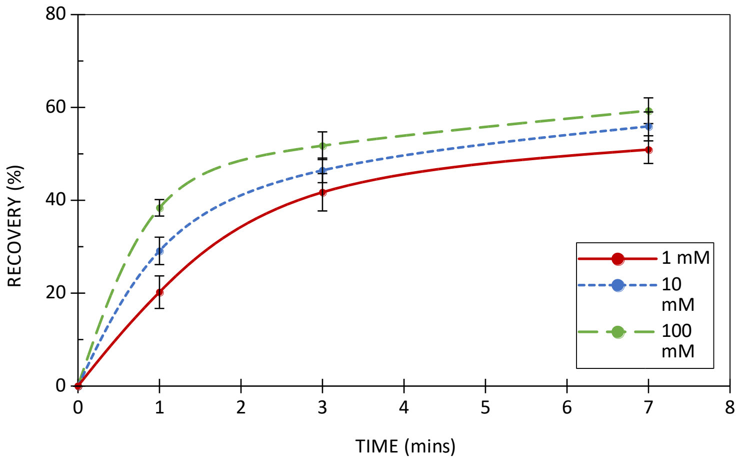

Figure 2. Recovery of galena by microflotation at various NaCl concentrations.

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1C – Exploring the electronic and interfacial properties of triphenylamine- and phenothiazine-based hole transport materials for perovskite solar cells

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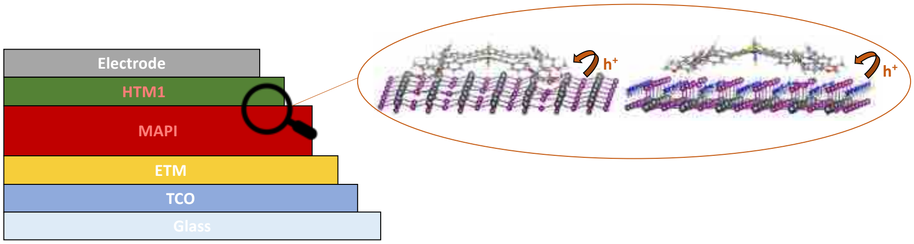
Aims

The aim of the project is the design of a novel class of triphenylamine (TPA)- and phenothiazine (PTZ)-based compounds to be employed as hole transport materials (HTMs) in perovskite solar cells (PSCs). To this end, Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TDDFT) methods have been applied to investigate the well-known electronic and molecular properties that efficient HTMs should possess, as well as the chemical interaction with the parent methylammonium lead iodide (MAPI) perovskite.

Results

Since 2009, PSCs have raised a unique interest in the photovoltaic community leading to a power conversion efficiency of 25.7%. However, a crucial barrier still limiting their commercialization is the lack of long-term stability of the devices, which is mainly associated with the degradation of PSCs components. In this context, the HTMs have a crucial role, as they are responsible for transporting holes and preventing direct contact between the perovskite and the electrode. To overcome the limitations arising from the well-established but unstable Spiro-OMeTAD, great research efforts have been dedicated to the design of novel HTMs. In particular, TPA- and PTZ-based compounds, e.g. PTZ2, have attracted great research interest for their performances comparable to those obtained with Spiro-OMeTAD. In this framework, four novel TPA and PTZ-based molecules (HTM1-4) have been *in silico* designed. The computed properties (i.e., energy levels, electron density and spin density distributions, and absolute chemical hardness) suggest that they have good intermolecular hole transport ability, and they should not compromise the PSCs stability. Furthermore, the calculations of the absorption maxima of neutral and oxidized HTM1-4 indicate that they do not compete with the perovskite absorption in the visible range. Thus, HTM1-4 could be valid alternatives to Spiro-OMeTAD as HTMs. Additionally, key electronic properties related to the hole mobility of one of the designed molecules, HTM1, have been investigated as well. The results revealed that HTM1 has lower reorganization energy than Spiro-OMeTAD and PTZ2, hence its hole mobility could outperform those of the two HTMs, while its oxidation potential is higher in energy than the valence band of MAPI, which would allow its application as HTM in PSCs. The synthesis and the spectroscopic characterization, in perfect agreement with the computed results, further ratified HTM1 as a valid HTM. Then, to assess the mutual polarization effects between the MAPI and HTM1, the HTM1 interaction with either the PbI_2- or MAI-terminated MAPI (001) surface has been analyzed. Bond formations and structural modifications at the interface suggest that HTM1 has good adhesion properties with the MAPI surface. However, our results also point out a lack of driving force for the hole transport. Similar results have been obtained for the other HTMs considered here, suggesting that three factors should be considered in the design process of novel HTMs: i) the intrinsic HTM properties; ii) the chemical interaction with the perovskite; iii) the perovskite composition. In particular, MAPI perovskite has resulted being inadequate when combined with TPA and PTZ-based molecules, hence the exploration of different kinds of perovskite compositions is suggested. As a matter of fact, HTM1 has been further tested without the use of dopants in a methylammonium-free p–i–n PSC, adopting $Cs_{0.17}FA_{0.83}Pb(I_{0.9}Br_{0.1})_3$ as perovskite, demonstrating that it can achieve 17.26% PCE, similarly to that obtained employing the standard PTAA in the same experimental conditions (17.96%). This result confirmed the suitability of HTM1 as HTM, as well as the influence of the perovskite formulation on the hole transport process.



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1C – *In-silico* design of novel organic compounds for the development of perovskite solar cells, dye-sensitized solar cells, and luminescent solar concentrators

C. Coppola, M.L. Parisi, R. Basosi, A. Sinicropi

Aims

The aim of the project is the design of novel organic compounds to be employed in solar energy conversion devices such as perovskite solar cells (PSCs), dye-sensitized solar cells (DSSCs), and luminescent solar concentrators (LSCs). To this end, Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TDDFT) methods have been applied to predict the fundamental physical-chemical properties of the designed compounds, with the aim of assessing their suitability to be employed in such devices.

Results

Nowadays, Silicon (Si)-based solar cells are still the leaders in the photovoltaic market. However, in the last decades, technologies as PSCs, DSSCs, and LSCs are being considered promising alternatives thanks to: i) simple manufacturing processes; ii) the possibility to enhance the light trapping of Si-based solar cells; iii) the advantage to be incorporated into the building-integrated photovoltaics (BIPV). To promote the competitiveness of PSCs, DSSCs, and LSCs in the photovoltaic market, a fundamental point concerns the optimization of some efficiency and instability issues related to such devices' components. In this regard, the *in-silico* design of novel materials is a crucial aspect that can foster the research in this field, offering strategies for the construction of more efficient devices. DFT and TDDFT are the methods of choice for the identification of promising materials in the solar energy field and they are largely applied for predicting the fundamental properties of these compounds.

In particular, the instability of PSCs has mainly been associated with the hole transport materials (HTMs) intrinsic properties and with their inefficient contact with the perovskite. In this regard, a novel family of phenothiazine and triphenylamine-based molecules (HTM1-4), to be potentially employed as HTMs in PSCs, has been designed. The calculation of the structural and electronic properties has revealed that HTM1-4 fulfill all the well-known requirements that make them suitable HTMs candidates. Additionally, the interfacial phenomena between the $CH_3NH_3PbI_3$ perovskite and one of the designed molecules, HTM1, have been investigated as well, providing new insights into the hole transport behavior of phenothiazine and triphenylamine-based HTMs.

The poor efficiency of DSSCs is partially due to the intrinsic properties of the sensitizers and their scarce energy levels matching with the other DSCCs components. To this end, a novel indigo-based D-A-π-A dye (DF90) has been designed and the computation of its electronic and spectroscopical properties has revealed that it can be considered a valid candidate as a sensitizer in DSSCs. Still in the DSSCs framework, DFT and TDDFT methods have been applied to predict the ground state oxidation potentials of 16 D-π-A and D-A-π-A dyes, demonstrating the validity of the applied strategy to accurately predict the dye regeneration driving force, thus helping in the identification of the most promising dyes. Additionally, the effect of the substituents and the effect of enhanced conjugation by inserting a π spacer have been investigated for a novel series of catechol-based molecules, Cat-I-XV, to provide additional knowledge for the design of novel sensitizers in type-II DSSCs.

In the end, to enhance the efficiency of LSCs, a key point to address is the optimization of the fluorophores which are responsible for self-absorption and aggregation-caused quenching (ACQ) phenomena. For such reasons, three novel series of D-A-D fluorophores (BBT2-4, DQ1-5 and TPa-c) have been proposed. The deep investigation of their structural, electronic, and photophysical properties has demonstrated that these molecules have good light-harvesting ability and intense emission properties, associated with large Stokes Shift values. Hence, limited self-absorption phenomena have been predicted, demonstrating that they can be considered as promising fluorophores in LSCs devices.

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1C – MD and QM/MM investigation of Bacteriorhodospin/TiO2 systems

M. Avelar, A. d'Ettorre, C. Coppola, M.L. Parisi, A. Ienco (CNR-ICCOM), R. Basosi, A. Sinicropi

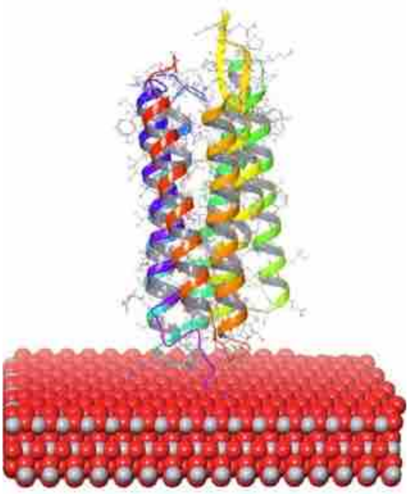
Aims

This work is part of the MIUR Grant-Department of Excellence 2018-2022. The obtained results will be the basis for the improvement of bacteriorhodopsin (bR) performances in bR/TiO2 hybrid systems to be successfully applied in photocatalytic and photoelectrochemical devices.

Results

Bacteriorhodopsin (bR) from Halobacterium salinarum is a light-harvesting integral membrane protein that has been used in both photocatalytic and photoelectrochemical systems to sensitize TiO2. Indeed, several applications are based on the ability of bR to convert solar energy into electricity or chemical fuels, such as H2. Among other environmentally sustainable biomaterials for solar energy conversion, bR holds high promise since it has thermal robustness and keeps functional activity for long-term while absorbing solar radiation to produce photo-induced charge generation.

In this work, we applied molecular dynamics (MD) and hybrid quantum mechanics/ molecular mechanics (QM/MM) methods to model bR on the anatase TiO2 surface. The latter has been modelized with a total of 12276 atoms corresponding of three layers on the c axis and an area of 115x115 Å2. We analyzed different orientations of bR on the TiO2 and applied a hybrid approach7 combining steered molecular dynamics (SMD) and MD simulations in order to get an understanding of the most probable orientations and interactions of the protein on the surface. The following QM/MM simulations showed that the resulting bR/TiO2 models correctly reproduce the blue shift observed when the protein is physiosorbed on the TiO2 compared to the protein in solution. This robust model was then applied to map the long-range ET pathway that allows electrons to be injected into TiO2. This is relevant in order to design novel and more efficient mutants of bR to employ as bio-sensitizers.



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1C – Modelling Capacitance and Stored Energy in Supercapacitors

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Aims

Stored energy devices such as batteries and supercapacitors are a crucial link in the renewable energy economy required minimise the dependence of society on fossil fuels. Improvement of these devices requires a deep understanding of the mechanism controlling the capacity of the devices, whether measured by capacitance or by quantity of stored energy. Mean field (Poisson-Boltzmann) models have found a useful role in understanding interactions between colloidal particles, but utterly fail to adequately describe electrochemical systems once potential differences exceed 0.2 V. Advanced ion-ion correlation theory is capable of providing a suitable description, but adoption is impeded by the complexity of these models. We have reviewed modifications to mean-field theory aiming to identify analytical approximations which provide a simple and useful means of characterising capacitance and stored energy.

Results

The failure of standard Poisson-Boltzmann models to model electrochemical systems arises from the neglect of ion size, with the conventional electrostatic Boltzmann factor unbounded as electrode potential increases. Finite ion size leads to the generation of steric forces, which provide a "push-back" in the Boltzmann factor, keeping ion concentrations bounded to physically meaningful levels.

The Bikerman model provides a simple estimate of steric forces that provides an upper concentration cap on ion concentrations. Once an electrode potential exceeds 200 mV or so (or 10 kT), the counterion forms a steric layer with fixed (capped) concentration. By assuming the model of a composite diffuse layer (CDL) where the steric layer accounts for all charge interactions (i.e when the thickness of the steric layer is much larger than the Debye length of the electrolyte), we derived a simple analytical expressionfor the electric field across the steric layer, which leads to simple analytical expressions for the capacitance and free energy of the electrode.

The capacitance of an electrode in LiPF6, in propylene carbonate solvent. is shown in Figure 1 as a function of electrode potential. A peak in capacitance is found around 200 mV. At higher electrode voltages the capacitance is reduced. The analytical approximation of the CDL steric layer model agrees excellently with numerical calculations using the Bikerman steric forces. The numerically more challenging Carnahan-Starling model steric forces provided a superior description of capacitance, with much a lower capacitance that better matches experimental measurement.

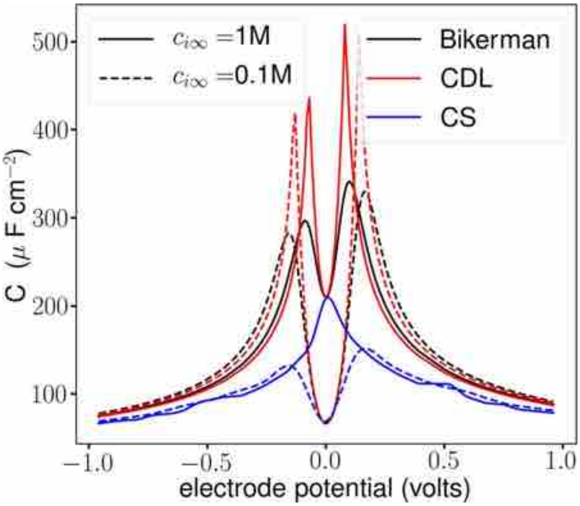

Figure 1. Calculated capacitance of LiPF6 (0.1M and 1M) in propylene carbonate. CDL refers to the analytical approximation using a composite diffuse layer (CDL, i.e. steric layer). CS=Carnahan-Starling model.

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2A – Adsorbent materials and composites for the antibiotics removing in polluted waters

D. Capsoni, M. Sturini, P. Lucini, D.M. Conti

Aims

Antibiotics are considered contaminants of emerging concern (CEC), as they are widely detected in wastewater, surface water, drinking water, and soils in many developed countries, even at trace levels (ng L^{-1}); they easily re-enter the aquatic compartment, as the urban wastewater treatment plants cannot abate them.

Adsorption is considered a consolidated technique for CEC water remediation. It is advantageous (low cost, high efficiency and easy conventional WWTPs integration), and efforts are being done to develop and test new adsorbent materials for antibiotics removing from waters. The ideal adsorbent materials should display high surface area, high stability in aqueous media, and low toxicity. In the present research project, we synthesize and characterize by several techniques (XRPD, SEM-EDS, TEM, TGA, FT-IR spectroscopy) some Zn-based and Fe-based Metal Organic Frameworks (MOFs) as suitable adsorbents to remove Ofloxacin, an antibiotic belonging to fluoroquinolones, from environmental water. The adsorption models and the kinetics are also studied. Secondly, we investigate Fe_3O_4@MOFs composites as magnetic adsorbents, to take advantage of the magnetic component to separate the adsorbent solid phase from the solution.

Results

The adsorption properties of two different zinc-based metal-organic frameworks, the zeolitic imidazolate framework-8 (ZIF-8) and the Zn(II) and benzene-1,3,5-tri-carboxylate ($Zn_3(BTC)_2$) are investigated to remove Ofloxacin (OFL) from polluted water. Both compounds are successfully synthesized and are crystalline, as demonstrated by XRPD, and FT-IR techniques. Both ZIF-8 and $Zn_3(BTC)_2$ display good affinity towards OFL, as it is adsorbed in remarkable amounts (95±10 and 25.3±0.8 mg g^{-1} on ZIF-8 and $Zn_3(BTC)_2$, respectively). The adsorption mechanism differs: a Langmuir model well describes the ZIF-8 profile, while for $Zn_3(BTC)_2$, cooperative adsorption occurs. The kinetic data display a pseudo-second-order and sigmoidal profiles, respectively. Removal efficiencies of 88% for ZIF-8 and 72% for $Zn_3(BTC)_2$ are obtained on tap water samples spiked with OFL 10 $\mu g\ L^{-1}$, thus confirming ZIF-8 and $Zn_3(BTC)_2$ are suitable adsorbent materials for removing fluoroquinolone antibiotics (FQs) from polluted waters. The limited reusability in tap water is explained by the enhanced degradation of the crystalline structure after adsorption in tap water, as demonstrated by XRPD, FT-IR, and SEM analyses. This disadvantage is overshadowed by the satisfactory results obtained in terms of OFL removal efficiency, and by the small adsorbent amount used (10 mg).

MIL-100(Fe) and Fe_3O_4@MIL-100(Fe) are tested as adsorbent materials for the removal of Ofloxacin in environmental conditions, such as tap and river water. The Fe_3O_4@MIL-100(Fe) composite is synthesized by the combined layer-by-layer (5 shell)/hydrothermal route, a new approach which revealed to be interesting and advantageous with respect to the layer-by-layer alone (20 shell), as it gives higher yields of MIL-100(Fe) covering the magnetite cores with the same reagents amount, and it is less solvent and time consuming. The MIL-100(Fe) and Fe_3O_4@MIL-100(Fe) composite are successfully synthesized and both samples are crystalline. The magnetic adduct displays rounded-shaped nanoparticles with diameters in the 200–400 nm range, and a specific surface area as high as 3546 m^2 g^{-1}. The thermogravimetric data are used for the first time to develop a decomposition-reduction model to evaluate the MIL-100(Fe) amount in the Fe_3O_4@MIL-100(Fe) sample.

The Fe_3O_4@MIL-100(Fe) composite indicate an OFL adsorption capacity of 218±7 mg g^{-1}, higher than that obtained with MIL-100(Fe) (123±5 mg g^{-1}). The efficiency of the magnetic composite in the OFL adsorption under environmental conditions is higher than the MIL-100(Fe) alone, too. Moreover, despite the small amount of magnetite (27.3 wt% Fe_3O_4 as determined by TGA data) present in the magnetic composite, it can be easily magnetically recovered after the treatment; this makes Fe_3O_4@MIL-100(Fe) suitable for large-scale applications.

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2A – Amphiphile-based nanofluids for the removal of undesired organic matter from works of art

M. Baglioni,E. Carretti , L. Dei, D. Berti, E. Fratini, D. Chelazzi, T. Guaragnone, R. Mastrangelo, G. Poggi, R. Giorgi, P. Baglioni

Aims

Development of innovative, effective, safe and environmentally-friendly systems for the cleaning of painted surfaces – systems' characterization and cleaning assessment. Improvement of the available formulations with the inclusion of degradable (biodegradable, labile, cleavable) surfactants, which could solve the residues' issue, and/or with more efficient surfactants, having high solubilization power towards small hydrophobic molecules.

Results

The removal of undesired material from the surface of a work of art has always been one of the most important and delicate operations in the conservation of cultural heritage. Surfactant-based aqueous nanostructured fluids (NSFs), such as micellar solutions and microemulsions, represent the most effective, safe and selective cleaning media currently available for cleaning operations in conservation of cultural heritage. Due to their nature, these systems can be used to remove oily grime or hydrophobic substances from hydrophilic surfaces, as in the case of polymer removal from wall paintings and stones.

The nature and properties of surfactants are key to the effectiveness of NSFs, thus the search for highly performing, environmentally-friendly, readily-degradable surfactants is one of the main aims of present studies. The research focus was recently moved from ionic surfactants to nonionic alcohol ethoxylates, which possess interesting (bio)degradability properties and excellent detergent power, and the performances of new classes of surfactants were explored, such as cleavable pH-sensitive autodegradable surfactants. Interesting results were obtained using these innovative surfactants in new NSFs. As a result of these research efforts, nanofluids for the cleaning of cultural heritage have been made available to conservators and restorers as commercial products under the trademark of Nanorestore Cleaning®.

Recently, new surfactants, such as alkyl ester ethoxylates were considered, in view of their excellent solubilization properties, with respect to more common ether ethoxylates. It was shown that alkyl ester ethoxylates are more efficient than their homologue alcohol ether ethoxylates in removing both polymeric coatings and soil from artistic surfaces. This is due to their molecular structure, which includes an ester bond between the hydrocarbon tail and the polyoxyethylene chain, and a hydrophobic capping at the end of the polar head and makes them more efficient in the solubilization of hydrophobic small compounds and in the interaction with hydrophobic polymers. The confinement of NSFs into retentive hydrogels, such as semi-Internpenetrated Polymer Networks (sIPNs) based on poly(hydroxyethyl methacrylate)/poly(vinyl pyrrolydone) or poly(vinyl alcohol)-based twin-chain polymer networks (TC-PNs) obtained as the result of freeze-thaw cycles, results in one of the most advanced solutions for the cleaning of works of art. NSF-loaded TC-PNs were recently and successfully used, within the frame of the EU-funded Nanorestart project, for the cleaning of masterpieces, such as “The Studio” by Pablo Picasso, or, for the first time, for the removal of aged detrimental polymeric coatings from the surface of Nuxalk painted wooden carvings conserved at the American Museum of Natural History.

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2A – Bioplastics and their degradation in composting conditions

E. Carretti, T. Lotti

In collaboration with Ing. F. Ruggero, Prof. C. Lubello, Prof. R. Gori

Aims

The recent regulations, which impose limits on single use plastics and packaging, are encouraging the development of bioplastics market. Some bioplastics are labelled as compostable with the organic waste according to a specific certification (EN 13432), however the conditions of industrial composting plants are generally less favourable than the standard test conditions. Aiming at studying the effective degradation of marketable bioplastic products under composting, the current research stresses novel elements which can strongly influence bioplastics degradation: the simulation of industrial composting conditions and the thickness of bioplastic products, ranging between 50 and 500 µm. The research approaches these critical aspects simulating a composting test of 20 days of thermophilic phase followed by 40 days of maturation phase, on starch-based polymer Mater-Bi® (MB), polybutylene adipate terephthalate (PBAT), polylactic acid (PLA) of different thickness. Conventional low density polyethylene (LDPE) was introduced as negative control. An overall study with Fourier Transform InfraRed (FTIR), ThermoGravimetric Analysis (TGA), Gel Permeation Chromatography (GPC), Scanning Electron Microscope (SEM) and visual inspections was applied. Results highlighted that MB film presented the highest degradation rate, 45 ± 4.7% in terms of weight loss. Both MB and PBAT were subjected to physico-chemical features change, while LDPE presented slight degradation signs. The most critical observations have been done for PLA, which is strongly influenced both by thickness and thermophilic phase duration, shorter than the EN 13432 conditions.

Results

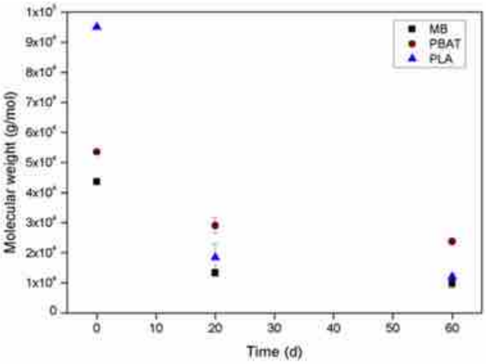

Figure 1. Trend of molecular weight loss (g/mol) for the some bioplastics as a function of time

The implementation of industrial composting conditions to study the plastic degradation highlights that signs of degradation are observable in all the tested materials. First, the decrease of molecular weight, particularly accentuated for PLA and MB.

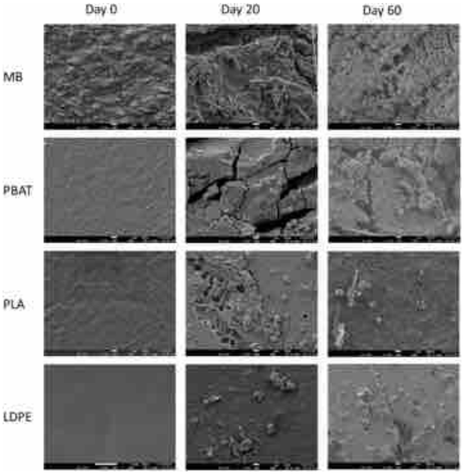

Figure 2. SEM micrographs at different timings of the test carried out on the tested materials

Film MB results in a quite high degradation. Importantly the degradation was higher for the PBAT present in MB than for pure PBAT: in fact, starch grains in MB degraded first, generating cavities which enhanced the degradation of the whole polymer. Despite this, it is noticeable that additional time is required for the complete degradation and therefore assimilability to compost. Furthermore, it emerged the issue of micro and nano fragments detected in the end of the test. Rigid PLA exhibits key features of a progressive degradation (the thickness is a fundamental variable in the degradation process). Finally, a thermophilic phase of 20 days is not sufficient to ensure bioplastics degradation. This result is of great concern, because it highlights that the discrepancy between the standard conditions (e.g. EN 13432) and the industrial composting conditions is an issue to be accounted in the bioplastics management system

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2A – Cementitious formulations to repair damaged concrete-based monuments

M. Tonelli, R. Gelli, R. Giorgi, F. Ridi, P. Baglioni

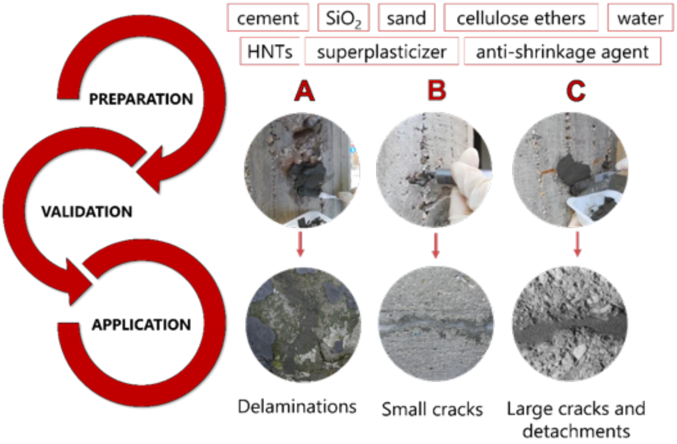
Aims

The aim of the project is to develop innovative formulations containing cement and admixtures to repair XX century concrete-based historical buildings and monuments.

Results

Since historic concrete does not have well developed, universally implemented conservation methodologies for its investigation, repair or long-term maintenance, concrete-based monuments and buildings are at risk. To tackle this issue, we developed different solutions specifically tuned for some of the most common damages that historical buildings may experience, namely delaminations, cracks and detachments. All formulations were prepared using cement and water with different admixtures: silica to improve the adhesion of the repair material to the aged concrete surface, cellulose ethers to tune the rheological properties, superplasticizers to control the setting and water demand, anti-shrinkage agents and halloysite nanotubes (HNTs). HNTs are nanotubular clays perfectly compatible with cement's phases that should reinforce the final material thanks to their 2D shape and whose lumen can be loaded with active molecules to be slowly released in situ.

Initially, different types of admixtures were screened, to enhance the physico-chemical properties of the cement mixture. After optimization, three different formulations were developed: two cement pastes for the repair of delaminated materials and small cracks (< 5 mm) and a mortar containing sand to fill larger cracks (5-10 mm) and repair small detachments (see the figure below).



All formulations were thoroughly characterized to confirm the formation of abundant binder phase, by means of X-Rays Diffraction, Thermogravimetry and Fourier

Transform Infrared Spectroscopy, and its adhesion on the damaged materials through Scanning Electron Microscopy and shear adhesion tests. The porosity of the cements, which is connected to the ingress of harmful substances that accelerate the aging of such materials, was evaluated by means of gas porosimetry and related to the water vapour permeability and absorption. Following established protocols, we also performed shrinkage test, peeling tests and colorimetric analysis, together with chemical and physical degradation tests. HNTs were loaded with different types of molecules, such as corrosion inhibitors and anti-fouling agents, to obtain a specific functional property of the repair material. The release of such molecules was evaluated in simulated rain conditions. The three formulations were successfully used by restorers to repair different monuments throughout Europe, such as the War Memorial of Torricella Peligna (Chieti, Italy, see the figure below).

Together with Portland-based formulations, some quick-repair cracks' sealers based on Magnesium Phosphate Cements (MPCs) containing HNTs as nano-carriers were also developed.

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2A – Definition and validation of harmonised Life Cycle Assessment guidelines for geothermoelectric systems

M.L. Parisi, R. Basosi

Aims

Geothermal energy could play a crucial role in the European energy market and future scenarios focused on sustainable development. Thanks to its constant supply of concentrated energy, it can support the transition towards a low-carbon economy. In the energy sector, the decision-making process should always be supported by a holistic science-based approach to allow a comprehensive environmental assessment of the technological system, such as the life cycle assessment (LCA) methodology. In the geothermal sector, the decision-making is particularly difficult due to the large variability of reported results on environmental performance across studies. This calls for harmonized guidelines on how to conduct LCAs of geothermal systems to enhance transparency and results comparability, by ensuring consistent methodological choices and providing indications for harmonized results reporting. The aim of this project is (i) to identify the main critical aspects of performing an LCA of geothermal systems to provide solutions and technical guidance to harmonize its application., and (ii) perform the validation of the proposed protocol on different geothermal projects.

Results

The extensive activity developed in this project is realized in the framework of the H2020 EU project GEOENVI. Based on the review of the state-of-the-art scientific literature concerning the environmental assessment of geothermal energy exploitation and the large variability of technological variability of power plants, the proposal of harmonised guidelines on how to conduct LCA of geothermal systems is intended to facilitate the achievement of LCAs and ensure comparability among the studies with other renewable energy technologies. The recommendations cover all the life cycle phases of geothermal energy production (i.e., construction, operation, maintenance and end of life) as well as a selection of LCA key elements thus providing a thorough base for concerted LCA guidelines for the geothermal sector.

The guidelines in object would in addition ensure that published LCA results all follow a coherent reporting scheme and therefore guarantee transparency and completeness. The implementation and validation of the modelling approach proposed for LCA studies of geothermal systems was accomplished on a selection of case studies whose life cycle data were provided by the partners consortium of theH2020 EU project GEOENVI. The investigated case studies were selected to be representative of the main available geothermal energy conversion technologies in Europe and they describe real operating or pilot/project power plants located in Italy, France, Iceland, Belgium, Hungary and Turkey.

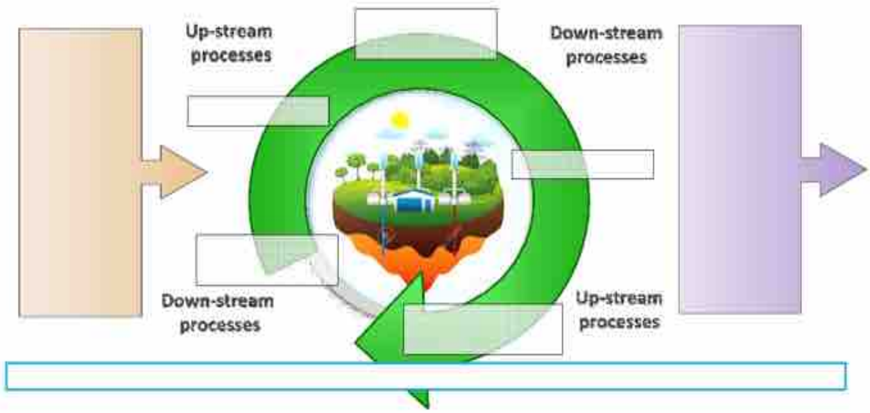

Figure 1: Cradle-to-grave approach for Life Cycle Assessment of geothermal systems and targets of environmental sustainability analysis.

This study shows how the geothermal LCA guidelines developed within the GEOENVI project can be applied to a specific case study. This application highlights some areas where the guidelines can be improved but, more importantly, it shows their importance to ensure the publication of reproducible and comparable LCA studies of geothermal installations. Such results further support the role of geothermal energy for the production of heat and electricity in achieving the European objective concerning greenhouse gases reduction, building on the future electricity mix supply change.

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2A – Eco-friendly alkali activated materials for conservation of cultural heritage and repair of modern reinforced concrete buildings and infrastructures

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Aims:

Building materials are deeply subjected to atmospheric factors and aging, therefore good aesthetical and surface properties are required. In particular, a façade of a building exposed to vehicular traffic has an average duration of 3 years, therefore it requires continuous maintenance to be aesthetically pleasant. Moreover, the subways and tunnels, according to Italian standard, should have a sufficient chromatic value to guarantee adequate brightness. For these reasons, they are subject to very high maintenance costs with also annoying consequences for the periodic construction sites responsible for the redevelopment of internal structures walls. Furthermore, the initial reflectance of porous materials is not always restored through cleaning techniques. Consequently, the addition of nanoparticles of titanium dioxide is an advantageous alternative to maintain the aesthetic properties of building façade, as they are able to provide self-cleaning properties to the materials. The purpose of this study is to evaluate, through natural and accelerated tests, the self-cleaning activity of one-part alkali-activated slag-based mortars manufactured with different titanium dioxide contents.

Results:

Three different one-part alkali-activated slag-based mortars were produced by varying the activator/precursor ratio between 8 and 16. In addition, two cementitious mortars manufactured with Portland cement (grey or white cement) were used as control mix. Different amounts of TiO_2, i.e. 0%, 1%, 3% and 5% with respect to the binder mass to evaluate the impact of titanium dioxide dosage on rheological properties, compressive strength, dynamic elastic modulus, self-cleaning ability (both under natural and accelerated conditions) and resistance to fouling of alkali-activated slag-based materials. Results evidenced that the addition of titanium dioxide nanoparticles have only a marginal effect on the elasto-mechanical properties of mortars at early ages. On the contrary, the 28-day compressive strength of cementitious mixtures linearly increases with the addition of nanoparticles, up to +10% when 5% of TiO_2 nanoparticles with respect to binder mass is used. On the contrary, alkali activated-based mortars do not evidence any improvement in 28-day compressive strength when titanium dioxide nanoparticles were added to the mixtures. The beneficial effect of TiO_2 addition in self-cleaning capability is evident both in cementitious and alkali-activated mortars. In particular, regardless of UV light exposure time, the color variation a% increases almost linearly by increasing the nanoparticles content, with the exception of the grey cement mortar which appears to be little affected by the titanium dioxide dosage.

Comparison of the results obtained for both dyes (rhodamine B (RhB) and methylene blue (MB)) in samples is given in Figure 1, where it can be seen that for no binder there is a good correlation between the values corresponding to RhB and MB at 4 h and 24 h. In fact, all the mortars have more degraded the MB dye than the RhB. The same behavior was found by Zhu et al., who attribute the photodegradation efficiency to the photosensitization of dyes. In particular, superoxide radicals could form from the reaction of electron excited from dyes that have been ejected to the conduction band of photocatalyst and oxygen.

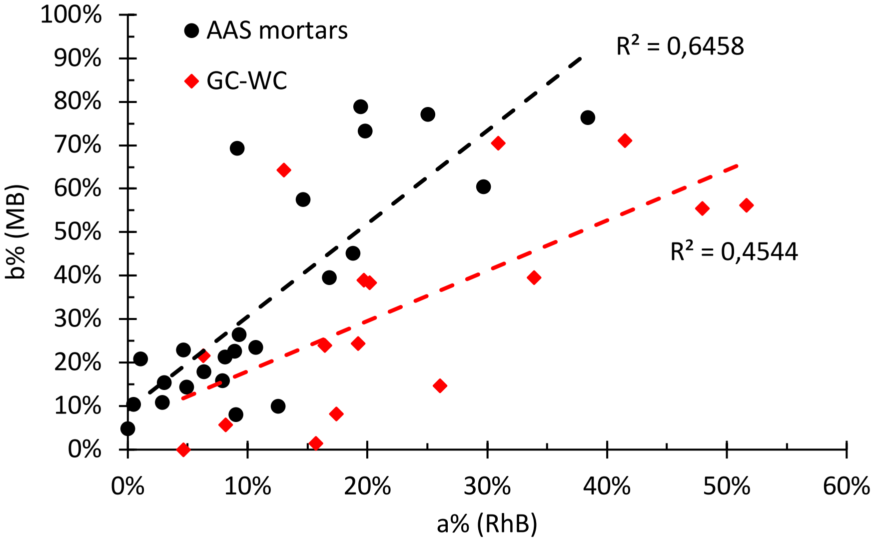

Figure 1 – Comparison of color variation in presence of MB or RhB after 4 and 24 hours under UV light

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2A – Environmental impact assessment of energy storage technologies in photovoltaic systems

F. Rossi, M.L. Parisi, R. Basosi, A. Sinicropi

Aims

This project aims to point out innovative approaches to design residential photovoltaic (PV) systems assisted by storage. For this scope, all the existing methods are currently based on techno-economic criteria whereas environmental life cycle assessment (LCA) is usually applied ex-post to PV installations. This gap is a critical issue because, although PV and storage do not imply a direct release of pollutants, they embed emissions occurring during the construction and end-of-life. Moreover, the problem of natural resources depletion shall not be underestimated because batteries and PV contain several critical raw materials. Therefore, developing new eco-design methods based on an integrated techno-economic and environmental assessment is extremely important to guarantee that their deployment is technically feasible, economically convenient, and environmentally sustainable. More in detail, this project regards residential PV systems, called nano-grids, that are composed of PV and storage; solar home systems (SHSs) are nano-grids that contain batteries as storage technology. In this study, lithium-ion batteries (LIBs) are selected as a reference storage solution.

Results

This project is conducted following five Phases that contain some methodological novelties compared to the existing literature; indeed, the relevance of each Phase is highlighted in a scientific publication:

Phase 1 represents a preliminary analysis where LIBs are compared with alternative energy storage technologies such as pumped hydro storage (PHS), compressed hydrogen storage (CHS) and thermoelectric energy storage (TEES). In this assessment, LIBs result as the most promising technology in terms of environmental impact.

In Phase 2, a novel three-steps methodology for the eco-design of nano-grids is presented (Figure 1a) and it is tested in a case study application located in Italy. More specifically, the three steps composing this eco-design strategy are the following: i) application of design equations for PV, ii) modelling of the performances, and iii) choice of the most sustainable solution based on the LCA results. This approach is a closed loop because the LCA results can suggest evaluating new system configurations. In this study, nickel-cobalt-aluminum and nickel-cobalt-manganese in grid-connected systems result as the most sustainable PV configurations.

Phase 3 represents an extension of the eco-design approach described in Phase 2 to advanced- and post-LIBs and to different countries in Europe. New equations are used to adapt the model proposed in Phase 2 to advanced- and post-LIBs. Among them, solid state LIBs are expected to become the most sustainable solution in the medium term (2025) whereas sodium-ion and vanadium-redox devices turn out as the most promising technologies in the long-term (2030).

In Phase 4 a new three-steps eco-design strategy aiming to a cross-evaluation of the environmental and economic performances of SHSs is defined (Figure 1b). The three steps composing the approach are: i) the LCA and Life Cycle Costing (LCC) of single

SHSs' components and of their energy flows, ii) the implementation of the modelling equations defined in Phase 3 as optimization constraints, iii) the optimal design of SHSs, namely the components optimal sizing and energy management evaluation. Two criteria are adopted for the optimization: the minimization of the SHSs impacts (environmental optimum) and of their costs (economic optimum). Among the proposed eco-design criteria, economic optimal design turns out as the most effective to reduce both the costs and the environmental impacts of the analyzed PV systems

The previous Phases are focused on single nano-grids providing electricity supply to one user. Phase 5 considers the large-scale deployment in Italy of multi-users energy systems called renewable energy communities (RECs). In this Phase, a new feed-in tariffs (FITs) framework is designed to reward RECs' members for the net greenhouse gases emissions that they avoid. Therefore, carbon taxes are used to mathematically correlate the economic incentives and the net environmental benefits of RECs. Accordingly, additional FITs are calculated as function of RECs' electricity throughput to the grid; on the other hand, if economic optimization is used as a design method, RECs' electricity generation depends on FITs. Therefore, this approach is iterative, and it converges to an equilibrium where RECs do not provide additional benefits to the grid in terms of net greenhouse gases avoided emissions. The adoption of the above-mentioned solar compensation mechanism allows for a strong reduction of the national greenhouse gases emissions as well as relevant economic savings for RECs' members.

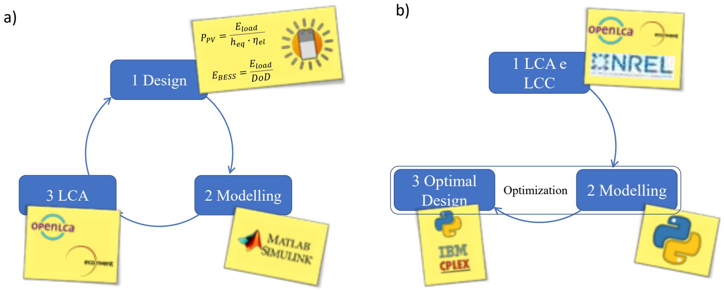

Figure 1 - a) Nano-grids eco-design strategy defined a) in Phase 2 and b) in Phase 4.

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2A – Environmentally friendly ZnO/Castor oil polyurethane composites for the gas-phase adsorption of acetic acid

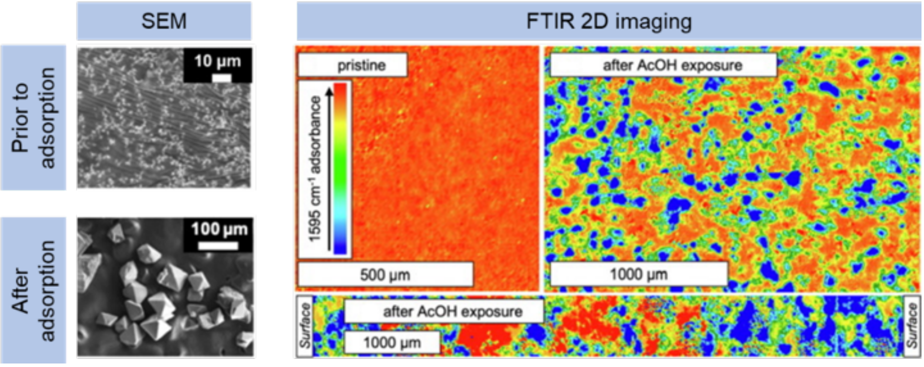
A. Zuliani, D. Bandelli, D. Chelazzi, R. Giorgi, P. Baglioni

Aims

Simple volatile organic acids are common pollutants in museums and art galleries, produced from the degradation of artifacts (*e.g.* paintings) or emitted from wooden frames/boxes and adhesives. As a result, compounds such as acetic acid (AA) can irreversibly damage works of art, making the development of preventive restorative strategies a central aspect in Cultural Heritage science. To this aim, novel adsorbers capable to irreversibly bound pollutants represent the cutting-edge materials to minimize degradative processes in preventive conservation. Herein, a sustainable and scalable synthesis of zinc oxide-castor oil polyurethane hybrids (ZnO/COPs), to be used as AA scavenger, is reported. The final material performances were evaluated in saturated and low concentrations (ppbv-scale) of AA by gravimetry. In addition, structural insights on the materials features prior and after adsorption were accessed by Thermogravimetric analysis (DTG), Infrared spectroscopy (FTIR-ATR), X-Ray diffraction (XRD) and imaging approaches (SEM and FTIR 2D).

Results

Castor oil-polyurethane composites were prepared employing commercially available ZnO particles with varied diameters from 20 nm to 44 μm, and ZnO content from 10 to 60 w%. The resulting materials featured comparable thermal stability, suggesting that the use of ZnO did not alter the three-dimensional structure of the composite. In contrast, adsorption experiments in saturated atmosphere of AA revealed the formation of Zn acetate species (XRD patterns) after 2 weeks of adsorption. In addition, SEM (and SEM-EDX) analysis revealed a variation in the morphology of ZnO particles, resulting in tetragonal pyramid structures with larger size (up to 100 μm) in comparison to the starting particles. Similar results were obtained by FTIR 2D imaging of the composite surface, while the analysis of the composite cross-section also revealed the homogeneous distribution of Zinc acetate, proving the efficient transport of AA in the COP matrix.



Gravimetric analysis during adsorption tests revealed higher AA retention for increasing weight% of ZnO and particle surface area (decreasing particle size); the composites exceeded the adsorption capability of activated charcoal that is commonly employed by conservators for similar applications.
Lower AA concentration (≈ 6000 ppbv) were also tested, with an adsorption capability of 97% after 150 h of exposure. As final test, ZnO/COPs were used for the adsorption of AA in a wooden crate, mimicking the typical storage conditions of piece of arts in both museums and storage facilities, and resulted in the decrease of AA below 250 ppbv already after the first week of usage, far below the 400 ppbv typically suggested for the preventive conservation of Cultural Heritage objects in museums and display cases. Having established a new class of materials able to absorb efficiently AA, our current focus is on the in-depth characterization of the process of diffusion and adsorption through the composite material, as well as the test of additional inorganic adsorbers in order to further extend the range of applicability.

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2A – Fibroin and nanocellulose composite films as new adhesives for aged textiles

D. Chelazzi, G. Poggi, R. Giorgi, A. Cincinelli, M. Laurati, P. Baglioni

Aims

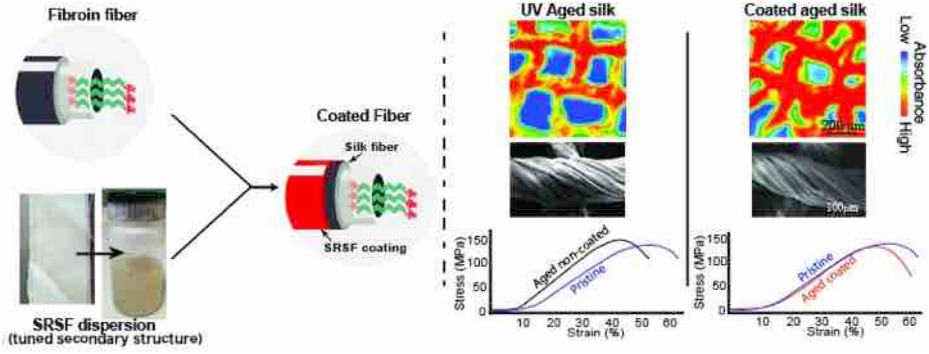
While historical and aged textiles (canvas, silk) constitute a relevant portion of our Cultural Heritage, there is a lack of physico-chemically compatible solutions to provide re-adhesion to the damaged fibers at the micro-scale without introducing potentially harmful adhesives such as those based on synthetic polymers.

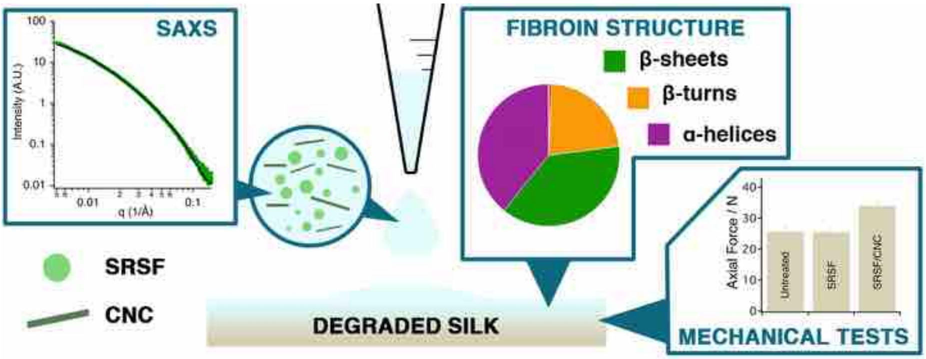
Colloidal systems and advanced functional materials based on biopolymers are optimal candidates to fill this gap. We recently investigated composite dispersions of self-regenerated silk fibroin (SRSF) or SRF and cellulose nanocrystals (CNC), to cast adhesive films able to recover the mechanical properties of aged silk fibers.

Results

SRSF produce films with controlled crystalline/amorphous content depending on the protein concentration in the dispersion; however, there is a limit to the concentration for the sole SRSF dispersions, as crystalline SRSF phases (with scarce chain mobility) cast over aged silk fibers produce brittle films that worsen the fibers' mechanical behavior. Amorphous SRSF films instead improve the flexibility of the aged textiles. Adding CNC to the dispersions speeds up the assembly of SRSF likely thanks to protein organization on the cellulose fibers, and composite films with partially crystalline fibroin (high α-helices content) can be cast even at low fibroin concentration. Noticeably, the composite films produce better improvement than the sole SRSF amorphous films or CNC films obtained from dispersions with the same concentration of consolidant.

The hybrid SRSF-CNC dispersions candidate thus as new promising adhesives for aged silk (and canvas) textiles; in addition, we provided for the first time a semi-quantitative evaluation of the structuring effect of CNC on SRSF assemblies, which can help the development of "green" chemistry solutions in different fields even beyond Cultural Heritage preservation, such as biomaterials and tissue engineering, and the preparation of composites with enhanced properties.





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2A – "Green" Poly(vinyl alcohol)/Starch based cryogels for the cleaning of works of art: application, characterization and investigation of the Amylose/Amylopectin structural role

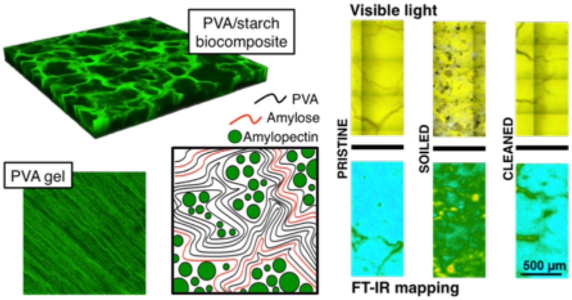
V. Rosciardi, D. Chelazzi, P. Baglioni

Aims

Gels made from synthetic polymers have improved the cleaning of artifacts, but there is the strong need to elaborate new systems through an all-green approach, developing materials with higher eco-compatibility while retaining optimal efficacy. In this perspective, we have developed and studied different biocomposite hydrogels based on poly(vinyl alcohol) (PVA) and rice starch (RS) obtained via freeze-thawing, with water as the only used solvent. Rice starch (RS) is a renewable biopolymer with a high potential for formulating sustainable gels from composites with synthetic polymers, but its interaction with the latter in composite structures is poorly understood.

Results

We characterized the effects of the freeze-thawing process on the gelation of PVA and native starch blends, tuning the starch content from 33 to 66% (w/w), and studying the gels' structure and structure-related properties. The obtained hydrogels showed a highly porous organization due to phase separation events occurring as a consequence of mixing different polymers in solution (i.e. PVA and starch's polymeric components, amylose and amylopectin). Such spongy porous arrangements have been previously reported to be key for dirt removal from painted surfaces and our systems have indeed proved effective when applied on artificially soiled painted mock-ups. Therefore, not only does the partial substitution of PVA with starch diminish the use of the synthetic polymer, with a straightforward advantage in terms of eco-sustainability, but mixing the different components together leads to the formation of a structure that promotes the hydrogels' cleaning effectiveness. The features of the synthesized PVA/starch hydrogels resulted to be broadly tunable in terms of viscoelastic behavior and water release, controllable by simply varying the PVA:starch mixing ratio. Nevertheless, all the considered formulations resulted in the formation of strong gels (i.e., chemical-like gels), despite the predominantly physical nature of the preparation method. As much as a good porosity ensures an efficient cleaning, a good cohesion of the gel grants a safe and residue-free application. Both the aspects have been confirmed through the application of two chosen hydrogels on two different artificially soiled painted surfaces: a poorly bound and water-sensitive tempera, and a highly irregular rough alkyd painting. The excellent outcome of the cleaning operations was assessed by means of micro-FTIR imaging, which also revealed the total absence of any gel residues.



Remarkably, the PVA/starch gels have proven to be as effective as their state-of-the-art commercially available synthetic counterparts, confirming the possibility to formulate greener products for the conservation of Cultural Heritage without compromises in terms of performances and safety. In addition, given their biocompatibility and environmentally friendly character, these systems are easily transferable to transversal fields where "green" and biocompatible confining networks are needed, such as drug delivery, tissue engineering, topical treatments, cosmetics, and many others. However, to be able to finely tune the features of the PVA/starch systems in order to formulate materials that can respond to different applicative needs, a deeper insight into their formation mechanism is necessary. Starch contains two different polymers (amylose and amylopectin), and their behavior in solutions with PVA is still largely unexplored. To investigate the interaction at play between PVA and starch components, as well as their implications on determining the final features of biocomposite PVA/starch networks, we decomposed the real system in its simple components. Investigation on PVA/amylose, PVA/amylopectin, and PVA/amylose/amylopectin systems with variable PVA/polysaccharide ratios allowed a deeper understanding of the possible evolution of a real PVA/starch cryogel. Thanks to CLSM imaging of pre-gel solutions containing fluorescently labeled polymers, we determined the absence of miscibility between PVA and amylose, as well as PVA and amylopectin, in the considered temperature range (25-98°C). Comparing the morphology of PVA/amylopectin solutions and cryogels, the porogen role of amylopectin arises, suggesting that also in PVA/starch networks the observed spongy organization is ascribable to phase separation events specifically regarding amylopectin, rather than amylose. These observations are particularly relevant since they partially clarify the specific contribution of amylose and amylopectin in PVA/starch systems and can therefore help tuning the final properties of these gels.

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2A – Hybrid nanomaterials for the strengthening and deacidification of paper

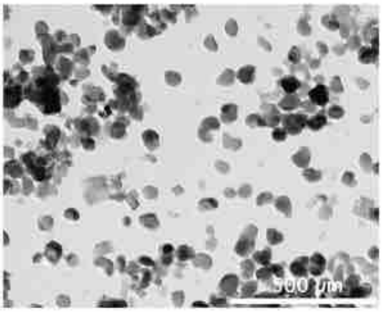
G. Poggi, Q. Xu, C. Resta, M. Baglioni, R. Giorgi, P. Baglioni

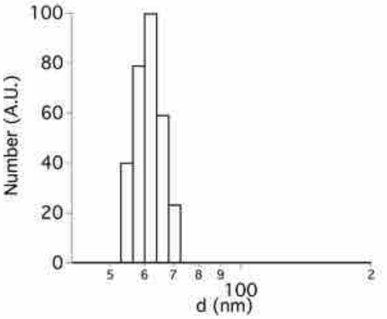
Aims

The acid-catalyzed hydrolysis of glycosidic bonds, that is the most important degradation pathway of paper, results in the decrease of cellulose DP and in the loss of the original mechanical properties. In the case of acidic and strongly mechanically-degraded paper, both a deacidification and a consolidation treatment are required.

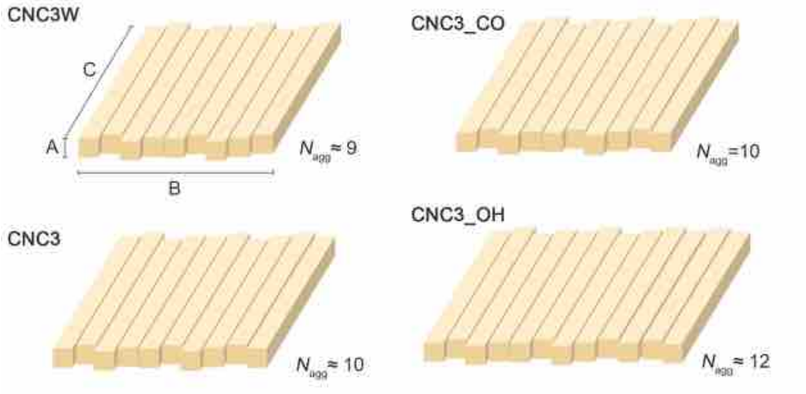
Results

In the framework of the EU project NANORESTART, we have started working on the development of hybrid systems for the concomitant neutralization of acidity and the improvement of the mechanical resistance of paper. The advantages related to the use of a single-step treatment rely in the reduction of cost, treatment time, stress and risk for the artifact. Hybrid systems feature cellulose nanocrystals (CNCs) and alkaline nanoparticles, alternatively calcium hydroxide or calcium carbonate, both obtained via a solvothermal process. The innovative synthetic route of $CaCO_3$ nanoparticles, which is based on the usage of an alkyl carbonate for the conversion of the intermediate reaction products into carbonates, yielded small and highly crystalline nanoparticles already dispersed in an appropriate solvent for applicative purposes.





The mechanical response of CNCs dispersions was studied with rheological measurements. The presence of ethanol in CNCs aqueous dispersion resulted in the overall increase in the viscosity of the system. This behavior is probably due to a decrease in the Debye length, triggered by the lowest permittivity of ethanol with respect to water that allows for stronger interactions between particles. A similar effect, even more pronounced, was obtained after the addition of calcium hydroxide nanoparticles. In fact, the Debye length is also a function of the ionic strength and divalent ions screen the superficial charges of cellulose nanocrystals, favoring their interactions and resulting in the formation of a strong gelled system. A less pronounced effect on the screening of the crystal repulsive forces was displayed after the addition of calcium carbonate, which is significantly less soluble than $Ca(OH)_2$. SAXS measurements confirmed the increase in cellulose interactions after the addition of ethanol and alkaline nanoparticles. In fact, the changes in the aggregation number of CNCs clusters follow the same trend displayed by the mechanical response, i.e., bigger clusters were found in the more gelled system.



After characterization, hybrid systems were applied on aged paper. Mechanical tests, pH and colorimetric measurements were used to evaluate their efficacy. Hybrid systems resulted highly effective in the strengthening and deacidification of acidic and mechanically-degraded cellulosic material, without significant alterations in the visual aspect of samples.

More recently, we have modified the surface of CNC using oleic acid, to favor the dispersion of CNC in pure ethanol. Modified CNC have been mixed with alkaline nanoparticles to have a blended system to be used for the consolidation of highly water-sensitive paper artworks.

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2A – Inorganic nanoparticles and hybrid nano-composites for the consolidation of stone materials

G. Poggi, R. Camerini, D. Chelazzi, R. Giorgi, P. Baglioni

Aims

The development of new technologies based on nano-materials and hybrid formulations enabled to perform compatible and long-lasting consolidation treatments on stone works of art, overcoming the drawbacks related to the use of traditional materials.

Results

Before nanotechnologies looked out in the conservation field, synthetic organic materials were widely applied by conservators for consolidation purposes. Unfortunately, their presence on artistic substrates was shown to be detrimental due to the different physico-chemical properties of polymers with respect to the original artistic materials. Conversely, inorganic nanoparticles exhibit high compatibility with many artistic and architectonic substrates and thus represent a valid alternative to the organic coatings.

In particular, the consolidation and protection of immovable works of art, such as wall paintings, plaster and stone artworks, can be successfully achieved by using alkaline-earth metal hydroxide nanoparticles stably dispersed in short-chain alcohols. The nano-size of the particles, together with the dispersing medium, influences their reactivity and penetration through porous matrices. Furthermore, particles polydispersity greatly affects their performance on stone substrates, as matrices to be consolidated can exhibit wide pores size distributions. It appears thus evident that the processes involved in the preparation of nanoparticles and their dispersion in carrier media play fundamental roles in determining the final effectiveness for specific consolidation issues and the applicability of these conservation tools.

After the disastrous flood of Florence, in 1966, the first compatible consolidation method for wall paintings was developed by Enzo Ferroni and applied by the restorer Dino Dini. The so-called Ferroni–Dini method, designed for the conservation of sulfate polluted wall paintings, consists in applying ammonium carbonate and barium hydroxide aqueous solutions, loaded in poultices, in a two-step procedure. After gypsum removal, the newly formed Ca(OH)2 slowly carbonates in air, binding with the degrading substrate.

An improvement of this method is represented by the direct usage of Ca(OH)2, in the form of colloidal system (alcoholic dispersion), instead of an aqueous solution, which limits the amount of product employable on water-sensitive substrates.

Recently, new formulations of barium and calcium hydroxide nanoparticles have been successfully used for consolidation of degraded wall paintings, even in presence of large amount of salts.

Inorganic nanoparticles can also be combined with organic compounds to obtain tailored and versatile hybrid formulations.

These methodologies are currently used for the consolidation of wall paintings in Italy and other countries, including Mexico, Sweden, Israel, and Denmark.

"Nanorestore®" and "Nanorestore Plus®" are two chemical products based on nanotechnology, produced at the CSGI laboratory, and made available specifically to the conservator community. They are calcium hydroxide nanoparticles dispersed in short-chain alcohols, such as ethanol and 2-propanol.

Siliceous compounds are also largely employed, mainly for treatments of silicate-based stones. Recently, colloidal silica was introduced in traditional formulations for the development of crack-free composite materials for stone consolidation, so to overcome the well-known drawback of the more popular alkoxysilanes.

In this view, hybrid nanotechnologies are providing candidate materials to improve compatibility and versatility of existing products, for specific case studies. For instance, the combination of silica and calcium hydroxide, in the form of nanoparticles, to obtain the in-situ formation of calcium silicate hydrate phases, was studied for surface consolidation treatments of earthen masonry (the so-called adobe bricks). Moreover, the presence of cellulose additives in the formulation allowed to stabilize the system and regulate water release during the formation of the new cementing phase.

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2A – In situ and remote monitoring of pollution in aquatic ecosystems

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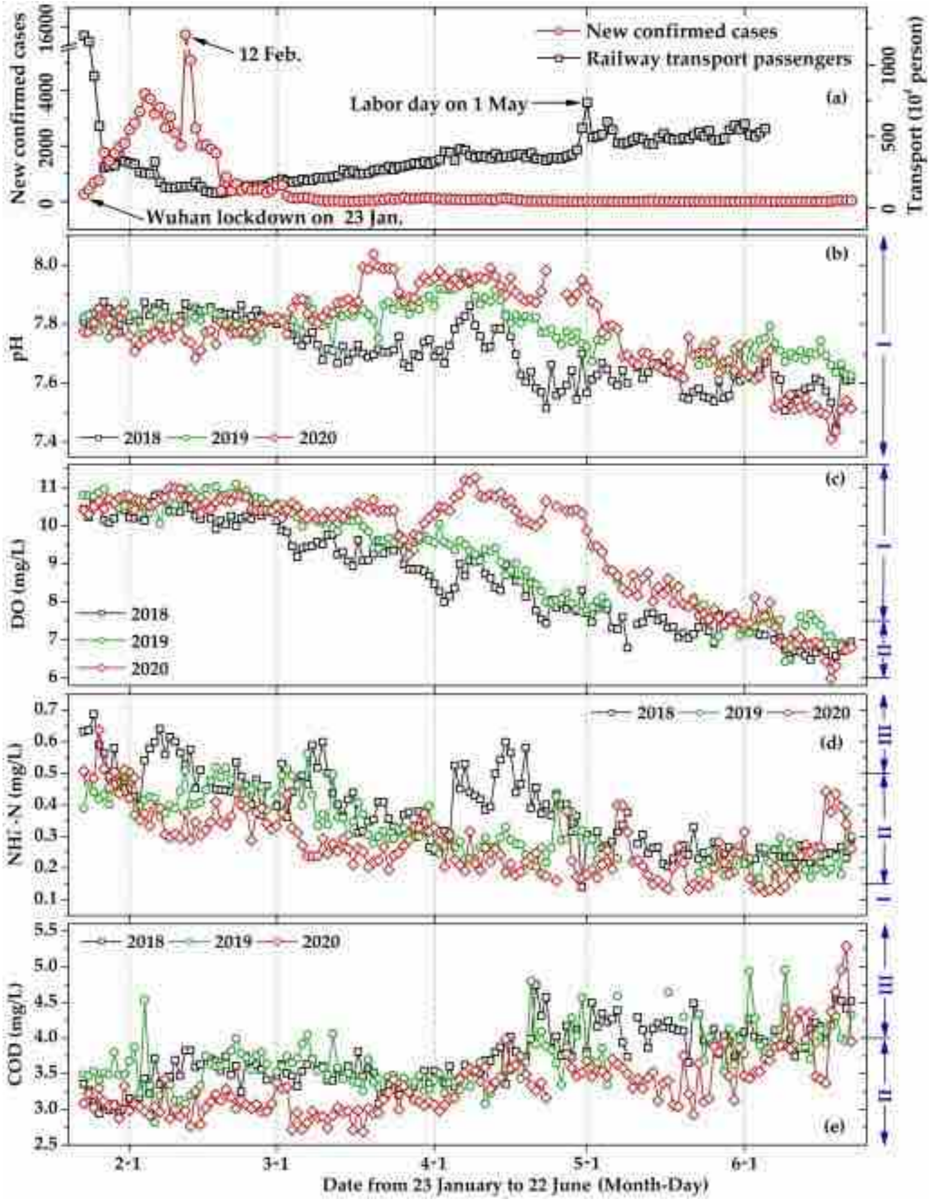
Aims

The impacts of COVID-19 lockdowns on air quality around the world have received wide attention. In comparison, assessments of the implications for water quality are relatively rare. As the first country impacted by COVID-19, China implemented local and national lockdowns that shut down industries and businesses between January and May 2020. Other lockdowns in Europe followed similar patterns. Based on monthly field measurements (N = 1693) and daily automonitoring (N = 65) and using remote sensing multispectral reflectance data, we performed studies analyzed the influence of the COVID-19 lockdown on river water quality in China.

Results

The results showed significant improvements in river water quality during the lockdown period but out-of-step improvements for different indicators. Reductions in ammonia nitrogen (NH4+-N) began relatively soon after the lockdown; chemical oxygen demand (COD) and dissolved oxygen (DO) showed improvements beginning in late January/early February and mid-March, respectively, while increases in pH were more temporally concentrated in the period from mid-March to early May. Compared to April 2019, the Water Quality Index increased at 67.4% of the stations in April 2020, with 75.9% of increases being significant. Changes in water quality parameters also varied spatially for different sites and were mainly determined by the locations and levels of economic development. After the lifting of the lockdown in June, all water quality parameters returned to pre-COVID-19 lockdown conditions. Our results clearly demonstrate the impacts of human activities on water quality and the potential for reversing ecosystem degradation by better management of wastewater discharges to replicate the beneficial impacts of the COVID-19 lockdown.



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2A – Jin Shofu Starch Nanoparticles for the Consolidation of Modern Paintings

A. Casini, D. Chelazzi, R. Giorgi

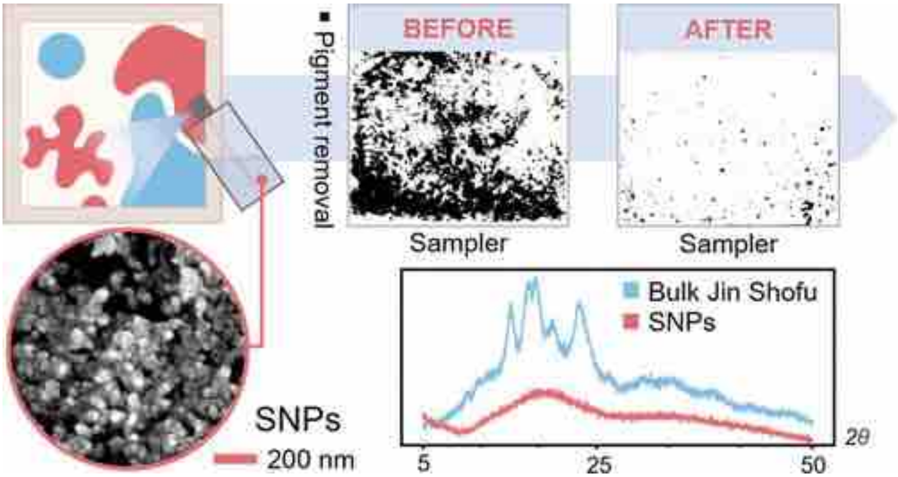
Aims

The preservation of brittle and fragile paint surfaces is undoubtedly one of the most significant issues in contemporary and modern art, both for their technical and optical properties, as well as their aesthetic values. Artists' unfettered experimentation with painting techniques and additive-rich paint formulations have led to artworks with weak powdering surfaces, exacerbated by severe climatic conditions and outdoor pollution. Furthermore, current conservation practice lacks suitable consolidation procedures, and traditional consolidants can result detrimental as optical properties and water permeability of the treated surfaces are dramatically altered.

Alternatively, to enhance penetration into porous paint layers, while avoiding optical modifications, we developed a novel starch-based nanostructured consolidant; the high surface area of the starch nanoparticles (SNPs) is rich with -OH groups, boosting pigment adhesion.

Results

The SNPs were formulated through a bottom-up approach, where gluten-removed Jin Shofu wheat starch was gelatinized and then precipitated in a non-solvent. Wheat starch's low gelatinization temperature is most likely crucial in favoring disassembly in alkali and re-assembly in non-solvent.

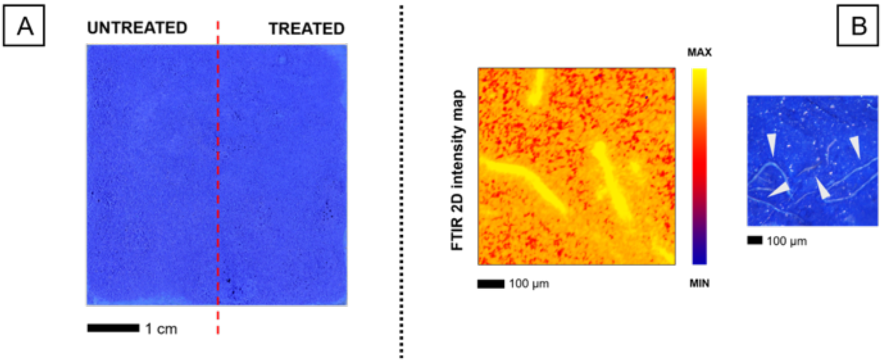


The synthesis conditions can be fine-tuned to produce amorphous SNPs with an adequate polydispersity and dimensions of around 50 nm. Once re-dispersed in an aqueous phase, SNPs form nano-sized gel-like fractal domains by the organization of smaller units in polymer-rich and deficient regions as observed with Cryogenic Electron Microscopy (Cryo-EM). Additionally, by means of infrared spectroscopy (ATR-

FTIR), X-ray diffraction (XRD), and calorimetric measurements (DSC), the amorphous nature of the SNPs was revealed. Short and mobile gluten-removed starch chains, obtained after gelatinization, assemble quickly by non-solvent precipitation, forming disordered, rather than crystalline, nanostructures.

Finally, aqueous and hydroalcoholic SNPs dispersions were satisfactorily tested as consolidant on artificially aged painted mock-ups that mimic degraded modern/contemporary painting surfaces. The efficacy of the consolidation was assessed using an in-house protocol: the SNPs disperse over the paint section and significantly boost pigment cohesiveness while maintaining the painted layer's original optical properties, despite bulk starch dispersions that merely accumulate on the paint surface generating superficial rigid and glossy films.

Overall, SNPs are an excellent example of how biopolymers and renewable sources can be used to create colloidal structures that can improve the resiliency of Cultural Heritage to degradation processes, favoring the transfer of works of art to future generations



(A) Comparison between treated and untreated surface after the application of SNPs (5 g/L) to an artificially aged painted mock-ups that mimic a fragile and powdering painting surface. (B) 2D FTIR Imaging (false color) of starch distribution onto the treated mock-up' surface. Starch nano-hydrogel particles distribute homogeneously and fill cracks in the degraded painted matrix, providing reinforcement acting as micro-junctions and preserving the original paint layers' optical properties.

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2A – Life cycle assessment of recycling strategies for perovskite/silicon tandem solar cells

M.J. Kipyator, F. Rossi, M.L. Parisi, R. Basosi, A. Sinicropi

Aim

The main technological advantage of tandem solar cells is that the combination of multiple devices allows to increase the overall power conversion efficiency (PCE) beyond the single-junction limit. However, like all energy systems, tandem photovoltaic cells are responsible for potential environmental impacts during their life cycle.

The analysis of the eco-profiles of perovskite-silicon tandem (PSK/Si) solar cells have been addressed in various scientific studies. However, in most of these works, the end-of-life phase is excluded due to lack of data; on the other hand, when end-of-life has been included in the assessment, only landfill or incineration has been considered as the end-of-life scenario, thus completely excluding recycling.

In this study, we propose a harmonized comparative scenario-based LCA model focused on recycling as the end-of-life strategy for different PSK/Si tandem configurations. For this scope, the results are focused on Global Warming Potential (GWP) as a reference environmental indicator.

Results

This project addresses the environmental impact assessment of five tandem solar cells configurations, whose fully reproducible life cycle data inventories are available in the literature (Lunardi 1, Lunardi 2, Lunardi 3, Itten, and Celik). In this analysis, the lifetime of a PSK cell is set to 5 years whereas that of the Si cell corresponds to 25 years. Moreover, the aging of PSK cells determines a drop of the efficiency. Based on these considerations, three scenarios are considered:

Scenario 1 (S1): When the PSK cell achieves its end-of-life status, it becomes opaque and this affects the functionality of silicon; therefore, one possible waste management strategy consists of recycling the whole cell after 5 years.

Scenario 2 (S2): Every time the PSK cell achieves the end-of-life status, it is separated from the Si cell and it is replaced with a new device. Therefore, every 5 years, a PSK cell is recycled while the Si cell continues to operate for 25 years.

Scenario 3 (S3): Every time the PSK cell achieves the end-of-life status, the device is not replaced, and the silicon cell continues working with lower efficiency.

According to the histograms in Figure 1, S1 determines the highest impact because of the very short lifespan of the tandem cell. Concerning the other scenarios, the results depend on the percentage contribution of the PVK cell to the overall environmental burden of the tandem device: in case the PSK cell has a small contribution (Itten), replacing the exhausted cell turns out to be the most sustainable solution (S2). On the other hand, in case the PSK cells provide a major contribution to the total, S3 results as the best recycling option to reduce the greenhouse gas emissions of the cell (Lunardi 1, Lunardi 2, Lunardi 3, and Celik).

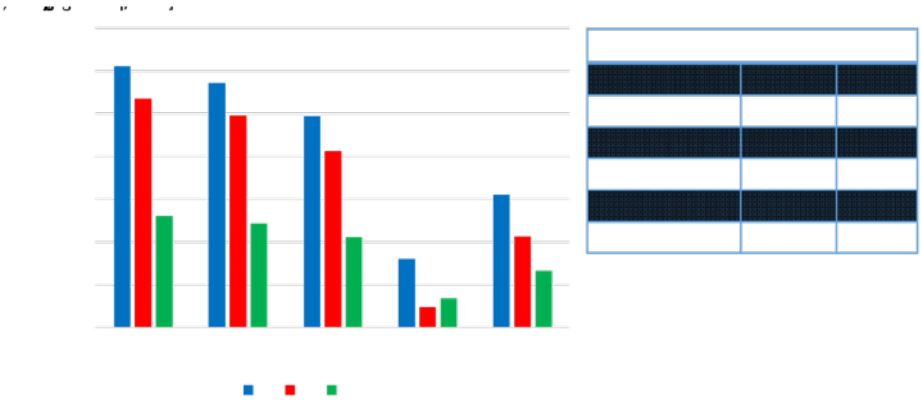

Figure 1: Global Warming Potential (GWP) of the analysed tandem cells as function of the end-of-life scenario and contribution analysis of the PSK and the Silicon cells

Remarkably, the above-mentioned results are calculated considering single values for the lifespan of the tandem cell and for the drop of efficiency due to the opacification of the PSK cell. Therefore, a sensitivity analysis about these parameters is also performed to address their uncertainty.

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2A – Micro-sized cleaning gels as innovative tool for the cleaning of paper materials (Lazioinnova Gruppi di ricerca 2020, funded)

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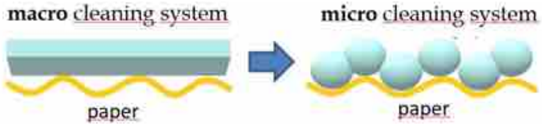
Aims

Since most of the cultural heritage is preserved on paper material, it is essential to develop appropriate conservation strategies. Indeed, the main component of these artifacts is cellulose,that during aging undergoes irreversible degradation processes. Moreover, pollution and water-soluble substances arising from cellulose degradation, accelerate the aging processes, leading to a decrease in paper stability and color changes. A valid alternative to the water bath, that is the a common restoration procedure, is represented by opportune hydrogels that due to their retentive properties, are able to minimize several disadvantages, such as changes in the morphological structure of paper and inks migration. Several hydrogels for cleaning paper artworks have been presented; among them those reported in literature, rigid hydrogels (macrogel) based on the deacylated polysaccharide Gellan gum and calcium acetate (Gg), as effective paper cleaning agent, has been widely characterized. Thus, knowing in depth its behavior, the use of Gellan gum based microgel particles, as innovative paper cleaning agent to improve the efficiency of current cleaning procedures, was proposed (scheme 1).



Scheme 1. comparison between the performances of hydrogels and microgels

Results

It’s known that gelation process under a constant applied shear is able to modify the elastic behavior for various hydrogels, included Gellan gel, as a result of microstructure modification. This procedure allows to obtain stable microgel particles (“weak gels”), whose elasticity depends on Gellan and salt concentrations. Two microgels differing for Gellan (Cw) and salt (Cs) (sodium chloride) concentrations have been prepared: (i) Cw=0.75% and Cs=10mM and (ii) Cw=0.10% and Cs=100mM. The size of microgels particles was demonstrated by DLS measurements to be in the µm range. Physico-chemical characterization, indicates the suitability of the proposed systems for this purpose. From a rheological point of view these microgels cannot support their own weight and can be shaken and poured as normal solutions, ensuring a uniform contact between the gel and the artwork, even in the case of uneven surfaces. Thanks to their reduced size they are able to achieve a better penetration in the porous structure of paper, performing a cleaning action in shorter times respect to hydrogel (scheme1).

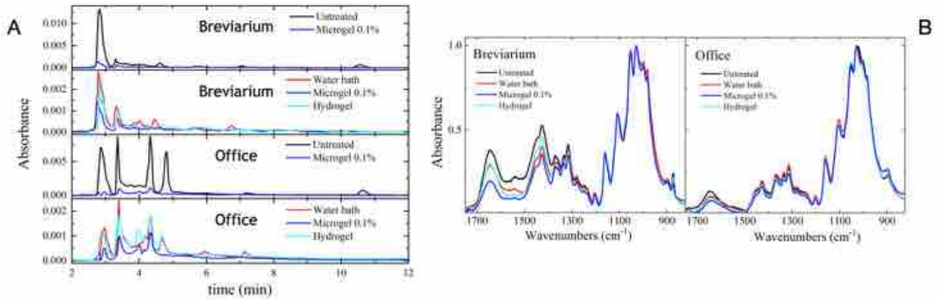


Figure 1. (A) HPLC results for Breviarium and Office samples. (B) FTIR spectra of Breviarium and Office samples. Different colors refer to untreated samples (black), samples cleaned by using water bath (red), Gellan hydrogel (cyan), and 0.10% microgel (blue).

The cleaning efficiency of both proposed Gellan microgels have been assessed on two different kind of paper materials, that are ancient and modern papers. They differ significantly from a chemical standpoint and these differences impact on their stability and mechanical properties. The same paper samples have been treated with Gellan gum hydrogel and water bath, in order to compare our results with established protocols. First of all, SEM and tensile tests have been employed to assess that the proposed treatment methods do not change the morphology and the mechanical properties of paper samples and do not leave residues. pH measurements have been used to demonstrate the removal of acidic molecules responsible for the loss of mechanical properties of the paper due to the hydrolysis of the cellulose chains. Moreover, HPLC measurements, FTIR-ATR (fig.1) and UV-Vis reflectance spectroscopy analysis have confirmed that microgels represent an efficient tool for paper cleaning, resulting in the best treatment with all diagnostic techniques. These results must be emphasized, as the cleaning time is only a few minutes in the case of microgels and about 1 h in the case of water bath or treatment with hydrogels. A comparison between the 0.10% and 0.75% microgel samples, allows to establish that they are rather similar in terms of cleaning efficiency, with an overall slightly superior performance of the 0.10% case. In conclusion these findings establish Gellan gum-based microgels as innovative tool for paper preservation.

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2A – Nanocomposites for the strengthening and deacidification of canvases

G. Poggi, R. Giorgi, P. Baglioni

Aims

Lignocellulosic canvases, used as support in paintings, are progressively degraded by acidity originating from the application of primers, paints, glues or from absorption of acidic gases from the environment. Canvases' degradation causes a decrease in the mechanical properties and may ultimately affect the integrity of the paint layer. Therefore, new materials for the strengthening and deacidification of canvases are needed to grant the preservation of paintings and artworks featuring canvases.

Results

The acidity of canvases made of natural materials is generally of concern as it can lead to loss of mechanical properties and deterioration in less than 100 years. The stability of synthetic canvases is even less known than that of canvases of natural origin. This problem dramatically also concerns jute, which becomes quite acidic in a faster way than linen, and paintings done on this type of canvas become more brittle.

The lining, that is the gluing of a new canvas on the back of the painting, is traditionally used for the consolidation of canvases. However, although inevitable for the most degraded canvases, lining should be avoided due to its invasiveness, because it hides the original canvas and is very resource-intensive.

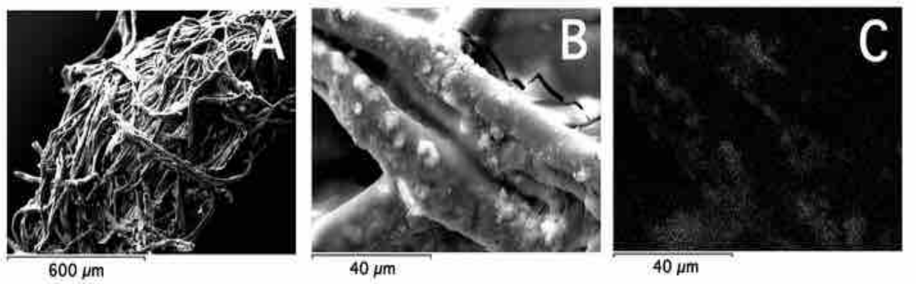
The goal within the EU Project NANORESTART was to develop materials for the mechanical strengthening of canvases of modern/contemporary paintings to be mixed with alkaline nanoparticles to hamper the depolymerization of cellulosic fibers.

One of the most interesting strategies we designed to this aim is based on the use of calcium carbonate nanoparticles dispersed in water/ethanol mixtures. The nanoparticles are intended to neutralize acidity. To stably disperse calcium carbonate nanoparticles in water/ethanol, we use a positively charged polyelectrolyte (PE), i.e. Polyethylenimine (PEI). A cellulose derivative, namely carboxyl methyl cellulose (CMC) is added to the system to induce a strengthening effect of nanocomposite on canvases. When the negatively-charged CMC is added, the presence of PE, prevents the flocculation and probably favors the interactions between nanoparticles and cellulose derivatives. All the systems are composed of small particles, whose size is around 200-300 nm (measured by DLS, analyzed using the cumulant fitting). The pH of systems is alkaline, as required by a deacidification treatment.

Ethanol can be added to the system featuring calcium carbonate nanoparticles and PEI up to a concentration of about 65%. It is worth noting that the addition of ethanol to the systems could ease their penetration inside canvas. On the contrary, CMC based systems are not stable after ethanol addition but could be diluted with water.

During preliminary tests, these systems were tested on two different types of aged cotton canvases: all the tested treatments increase the mechanical resistance of threads, up to 30%. It is also worth noting that all the treatments increased the pH of about 3 units, stabilizing the pH at about 7-8.

The effect of the treatments on cotton fibers was also assessed using Scanning Electron Microscopy. Canvas fibers display several clusters of nanoparticles (B), as clearly shown by EDX map of calcium reported in C.



Based on these experimental test, some of the most promising systems have been tested on iron-tannate dyed cotton, also in combination with nanocellulose and other strengthening agents, such as silica nanoparticles. We show that conservation can only be addressed if the mechanical strengthening is preceded by a deacidification step. We used $CaCO_3$ nanoparticles to neutralize the acidity, while the stabilization was addressed by a combination of nanocellulose, and silica nanoparticles, to truly tackle the complexity of the hierarchical nature of cotton textiles. Silica nanoparticles enabled strengthening at the fiber scale by covering the fiber surface, while the nanocellulose acted at bigger length scales. The evaluation of the applied treatments, before and after an accelerated ageing, demonstrated the potential of using a combined deacidification-strengthening approach in the stabilization of degraded fibrous cellulosic materials.

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2A – Nanofluids and chemical hydrogels for the selective removal of overpaints and graffiti from murals

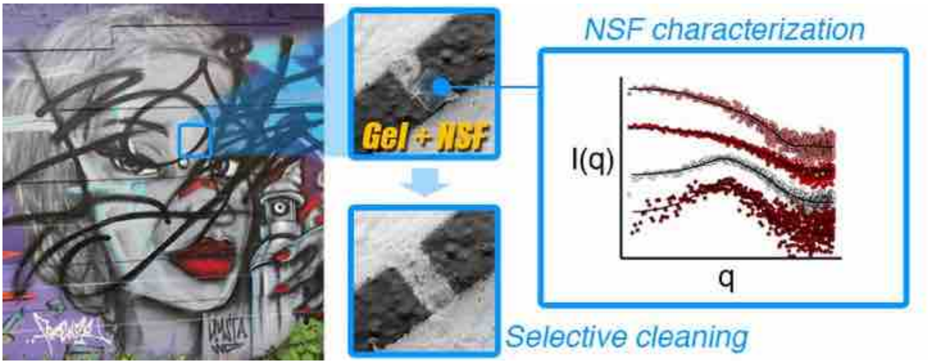
R. Giorgi, M. Baglioni, G. Poggi, P. Baglioni

Aims

Graffiti removal from monuments, such as statues or architecture, is becoming a priority for conservators and restorers. This operation is further complicated when the vandalism is carried out on surfaces that should be preserved, as in the case of writings or tags on historical wall paintings, or even on modern or contemporary pieces of street art. The needed selectivity can then be achieved using nanostructured fluids loaded into highly retentive hydrogels.

Results

The removal of graffiti from paintings that must be preserved is a particularly challenging and relatively new issue in conservation of cultural heritage. This is the case of contemporary street art (by unconventional contemporary artists, such as Banksy or Blu) jeopardized by tags, signs and writings. In these conditions, the cleaning action must be extremely selective, as the binder of the undesired paint is likely to have a very similar chemical nature to the one of the underlying original painting.



Unfortunately, selective and controlled removal of graffiti and overpaints from Street Art is almost unachievable using traditional methodologies. To this aim, in the frame of the Horizon 2020 EU-funded project NANORESTART, the use of nanostructured fluids (NSFs), such as micelles and microemulsions, especially confined into highly retentive chemical hydrogels, was proposed as one of the most promising, selective and controllable cleaning systems for the removal of graffiti and overpaints from street art.

Semi-interpenetrated polymer networks (sIPNs) composed by a tridimensional network of poly(hydroxyehtyl methacrylate)/N,N'-Methylene bisacrylamide (pHEMA/MBA) or polyvinylalcohol (PVA), interpenetrated by a high molecular weight poly(vinyl pyrrolidone) (PVP), or poly(vinyl alcohol)-based twin-chain polymer networks (TC-PNs), obtained as the result of freeze-thaw cycles, can be used as highly retentive hydrogels. These gels were shown to be particularly suited to limit the cleaning action to the surface layers of the treated area. It was recently shown that this methodological approach is effective for the selective removal of a set of modern paints, based on vinyl, acrylic and alkyd binders, laid on similar or the same paints. In particular excellent cleaning results were obtained for the vinyl-on-vinyl and acrylic-on-acrylic samples, while alkyd-on-alkyd specimens were partly resistant to the removal. This represents a substantial improvement over previous formulations used for the same purpose, and a major advancement with respect to the existing methodologies available to conservators. FTIR measurements on the treated areas confirmed that the overlying paint was completely removed without altering the paint layer underneath. Finally, the proposed methodology and cleaning system were assessed in the selective removal of black tags from real pieces of street art, with excellent results.

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2A – Nanostructured fluids for the conservation of cultural heritage – Understanding the mechanism of organic coatings removal

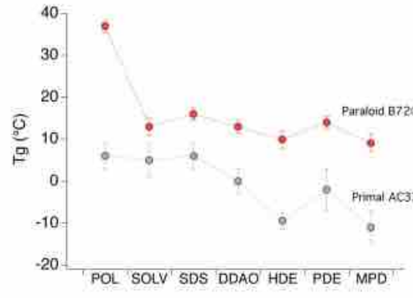
M. Baglioni, D. Berti, C. Montis, T. Guaragnone, M. Raudino, M. Bonini, R. Mastrangelo, D. Chelazzi, R. Giorgi, P. Baglioni

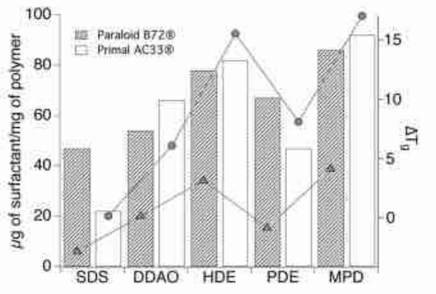
Aims

Understanding the mechanism of interaction between polymer coatings and nanostructured fluids (NSFs) will contribute to improve cleaning formulations in the field of conservation of cultural heritage, and, besides having some scientific relevance from fundamentals standpoint, it may open new perspectives on different applicative fields.

Results

Since the early 1990s, the moment of the very first application of NSFs to art conservation, their effectiveness in removing polymeric coatings from different surfaces was thoroughly demonstrated. Therefore, a major effort has lately been spent in order to investigate the mechanism of polymer removal through which these systems work.





Confocal laser scanning microscopy (CLSM) imaging was combined with differential scanning calorimetry (DSC), fluorescence correlation spectroscopy (FCS), SAXS, SANS, contact angle and surface tension measurements, in order to understand the role of each NSF component in the fluid/polymeric coating interaction. We found that this interaction usually involves dewetting processes, especially in the case of films formed from solvent solutions. Films formed from polymer latexes, on the other hand, are generally swollen even just by water, but they tend not to dewet, due to the presence of a significant amount of amphiphilic additives, which alter their interfacial behavior. It was shown that the nature of solvents in the NSFs plays a major role in the dewetting of polymer coatings, i.e., good solvents for the polymer are needed in order to swell the film and induce the mobility of polymer chains.

On the other hand, surfactant nature is crucial to kinetically favor this process. Surfactants, lowering both the liquid/polymer and liquid/solid interfacial tensions, energetically favor the detachment of the film from the surface, which represents the first step of dewetting processes. Therefore, amphiphile-based systems having very low surface tension may be particularly effective in dewetting polymer films. Then, by means of FCS measurements, it was found that: i) the surfactant present in the NSFs is able to penetrate through the polymer film, that acts as a sort of “sieve” with respect to micelles’ size, and reach the polymer/solid surface interface, where liquid-filled cavities are formed, where micelles are present; ii) during the penetration in the polymer film, part of the micelles is disrupted, with a release of surfactant molecules that promote polymer swelling and softening and further increase polymer chain mobility. Most recently, surfactants were shown to also act synergistically together with organic solvents in lowering the glass transition temperature of polymers below room temperature, which is the prerequisite to increase polymer chains’ mobility, which is needed to kinetically undergo dewetting, even if thermodynamically favored. It was demonstrated that nonionic surfactants are more efficient than zwitterionic/ionic ones in the polymer swelling, and, overall, alkyl ester ethoxylates resulted the most effective among the investigated surfactants. Finally, the results of FTIR imaging on Paraloid B72®-coated mortar tiles provided an explanation for the observed effectiveness of NSFs in real case studies, highlighting the mechanism through which they act and remove aged polymer coatings (cast from solutions).

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2A – New approaches to community monitoring of aquatic pollution

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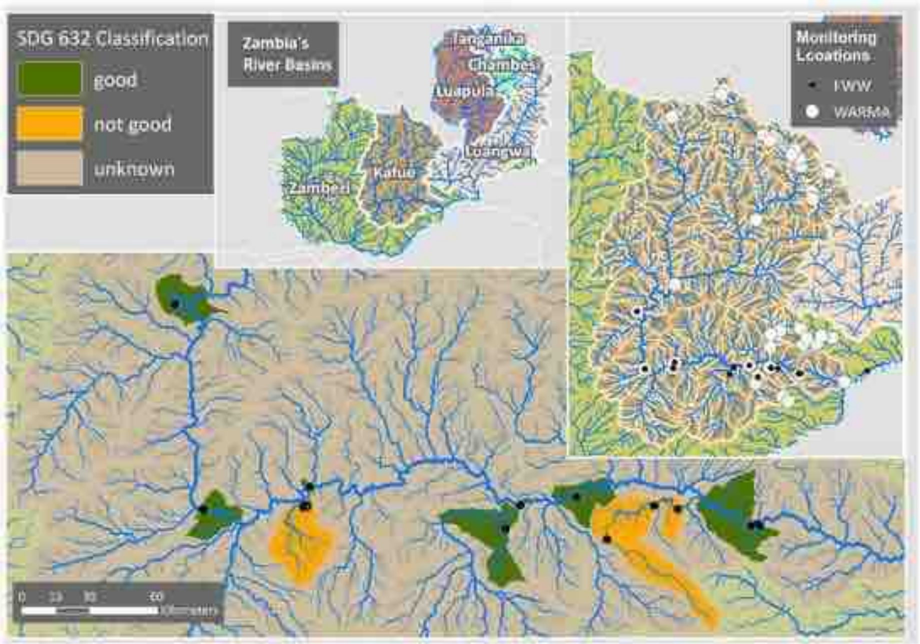
Aims

Citizen science (i.e., the involvement of non-scientists in scientific research) has been increasingly recognized as having a potentially important role to play in delivering the United Nations' (UN) Sustainable Development Goals (SDGs). Central to this role is the ability of citizen science to provide data for SDG indicators, which are the mechanism through which the progress of UN member states measure SDGs. The use of citizen science in this way presents several opportunities for improving the knowledge base that underpins global progress for SDGs, including increasing the frequency of available data, expanding the geographic reach of data, addressing gaps in funding, educating the public about relevant policy issues, and making better use of local knowledge. The challenge remains of developing a low cost but analytically robust approach to monitoring key water quality parameters, and extending this approach to an international context allowing National Statistics Offices (NSO) to use this data for SDG reporting.

Results

We were able to successfully generate indicator scores for European areas using both regulatory and citizen science datasets based on a combination of colorimetric and optical approaches, as well as using both datasets combined. For Zambia, it was possible to generate an indicator score based entirely on citizen science data. To do this, two key adaptations were made to the indicator methodology. Firstly, only two of the five core parameters were used. For complete reporting of indicator 6.3.2, measurements of nitrogen, phosphorus, salinity, acidity, and oxygen are required for surface waters, though in practice many member states do not report all five. Although it is possible to measure all five variables using citizen science methods within the method developed, only nitrates and phosphates are uniformly-used components of existing projects. Although this study demonstrates that it is possible to follow the indicator score calculation mechanisms using existing data, we recommend that future projects incorporate all five core parameters to facilitate complete reporting. Secondly, careful consideration was given to the target values used to accommodate the discrete value classification of nutrient concentrations. Because the indicator methodology is designed to be flexible and to accommodate aggregated datasets collected using a variety of methods, these adaptations represent only very minor alterations to the process and should not prevent the acceptance of citizen science data in national reporting.



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2A – Organogels for the cleaning of artifacts

P. Ferrari, G. Moretti, G. Poggi, D. Bandelli, R. Mastrangelo, D. Chelazzi, R. Giorgi, P. Baglioni

Aims

Gels are particularly useful for the cleaning of works of art as they allow the controlled delivery of cleaning fluids on solvent-sensitive substrates. Owing to the covalent cross-links between polymer chains, chemical gels exhibit mechanical properties that allow their easy handling and their residue-free removal from artistic surfaces after the cleaning intervention. Here we present several strategies for the synthesis of gels to be loaded with organic solvents, which can be also referred as to organogels.

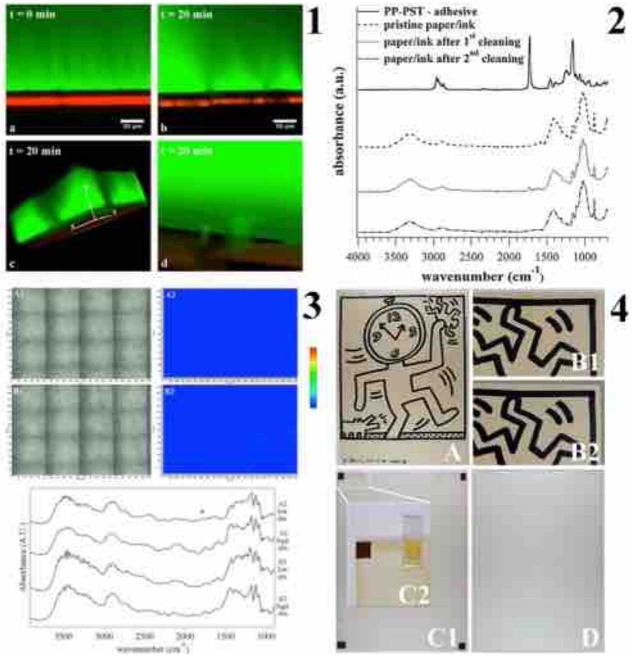
Results

Poly methyl methacrylate (PMMA) organogels obtained by solubilizing MMA together with a dimethacrylate cross-linker in organic solvents, e.g. ethyl acetate (EA), butyl acetate (BA), and metyl ethyl ketone (MEK), were prepared for the removal of aged varnishes from canvas paintings.

To achieve successful organogel applications also to the cleaning of solvent-sensitive paper artworks, more retentive systems were developed. Specifically, a PMMA-MEK organogel was designed for the selective removal of aged wax from inked paper. As compared to previous formulations, the larger amount of cross-linker and the different solvent-monomer ratio actually resulted in decreased solvent content and mesoporosity, as proved by Scanning Electron Microscopy and Small Angle X-ray Scattering analysis; this let a more controlled solvent release.

Afterwards to reduce the eco-toxicological impact of both cleaning fluids and gels processing, the cleaning effectiveness of a class of green solvents (i.e., alkyl carbonates, and particularly diethyl carbonate, DEC), loaded in poly ethyl methacrylate (PEMA) gels was experimented. Because of DEC solubility parameters, efficient interactions between DEC and Pressure Sensitive Tapes (PSTs) components were observed so that PEMA-DEC organogels were tested for the removal of aged PSTs from paper substrates. As proved by Laser Scanning Confocal Microscopy (see figure 1), the embedment of the solvent into the gel network allows a feasible intervention by applying the gel directly on the top surface of PSTs (e.g. a poly propylene PST, PP-PST, is shown in figure 1): in this way the solvent gradually penetrates the PST backing and swells the underlying adhesive, so that the detachment of the PST is allowed minimizing both solvent-artwork contact and mechanical effort. PEMA-DEC effectiveness in removing also adhesive residues after a second gel application performed directly on the paper support was assessed by ATR-FTIR measurements on paper mock-up samples (i.e., PP-PST on paper, see figure 2). Furthermore, the absence of gels residues on mock-ups after the cleaning intervention was verified by 2D FTIR Imaging (figure 3). PEMA-DEC systems were then successfully employed in the restoration intervention of a contemporary drawing by Keith Haring (Untitled, Naples Series, 1983): the use of PEMA-DEC gels let the complete removal of aged poly propylene tapes, avoiding drawbacks usually correlated to methods commonly used by restorers.

Overall, this work validated the use of poly methacrylate organogels as versatile cleaning tools useful for cleaning intervention on different artistic surfaces, furthermore, minimizing the risks of altering the original properties of the artifacts.



More recently, we have developed a solvent-free and cost-effective synthesis of a new class of gels derived from natural resources, based on castor oil and isocyanates mixtures. The development of covalent polyurethane bonds during the curing process induces significant changes in the viscoelastic properties of the systems which result in strong gels with good mechanical properties. Changes in the castor oil and isocyanates ratio and the use of additives allowed us to prepare several formulations whose final properties can be tuned to match those required by specific applications.

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2A – Peelable polyvinyl alcohol highly viscoelastic dispersions loaded with nanostructured fluids: a new class of cleaning tools for works of art

E. Carretti, G. Poggi, E. Fratini, L. Dei, M. Consumi, P. Baglioni

Aims

The development, and the structural and mechanical characterization of an new complex system composed by an oil-in-water microemulsion (μE) embedded in a aqueous 3D Highly Viscous Polymeric Dispersion (HVPD) of poly(vinyl alcohol) (PVA) cross-linked by borax, is here presented together with its possible implications in paintings conservation. The HVPD/μE was characterized by Small Angle X-Rays Scattering (SAXS), Differential Scanning Calorimetric (DSC) and rheology to obtain information about the mutual effect of the μE and of the PVA network on both the nanostructure of the μE, and on the mechanical behavior of the system. Experimental data indicate that the nanostructure of the μE is retained even in the presence of the PVA/borax network whose mechanical properties are enhanced by the presence of the nanofluid.

The high viscosity typical of the system minimizes the capillary penetration of the microemulsion inside the porous matrix constituting the artwork, minimizing the swelling of the binder of the paint layer and the uncontrolled spreading of the liquid phase onto the paint surface. The HVPDs also ensure great control of the cleaning: in fact the high retention reduces the evaporation of the volatile components and, once the system carried out its function, it can be easily and completely removed from the painted surface simply by means of a peeling action without leaving any instrumentally detectable residue onto the treated area.

The effect of HVPD/μE on organic molecules thin films of varnish coatings usually used on easel paintings, was studied for the first time by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). The results showed that an interaction occurred leading to the extraction of the organic molecules within the HVPD/μE.

Results

In previous works it has been observed that the PVA-borate systems, thanks to their elasticity and to their high voscosity, do provide selective, surface-controlled cleaning action as well as facile and benign removal from a painting surface by means of a peeling action. By so doing, residues left on the painted surface from the patina and from the cleaning tool are expected to be minimized. Moreover, the rheological properties can be easily modulated by changing the ratio of PVA to borate or their total concentration. Analogous aqueous PVA/borax-based HVPDs loaded with o/w microemulsions are characterized by a similar behavior.

The HVPD confined o/w microemulsion has been characterized by Small Angle X Rays Scattering (SAXS) and rheology in order to obtain informations about both the structure (i. e. the radius of the nanodroplets and their polydispersity) and the mechanical behavior, with particular attention on the effects induced by the presence of the PVA based 3D network. In particular, the experimental data indicate the persistence of the nanostructure of the o/w microemulsion (this is a fundamental requirement to warrantee the cleaning efficacy of the system) and that the relaxation of the PVA network occurs through a sticky reptation mechanism.

Cleaning test have been carried out on a XIX century Tuscan canvas painting (Figure 1, left). Contact angle, TOF-SIMS (Figure 1, right), Fourier transform infrared (FTIR), and scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) data confirmed that microemulsions were effective in removing polymeric organic coatings from painted surfaces of artistical and historical interest, as demonstrated by the results of several cleaning tests performed onto various painted surfaces of artistical and historical interest. These systems require no after-washing to remove residues, their cleaning action is easily controlled, and they can be removed in one piece by peeling.

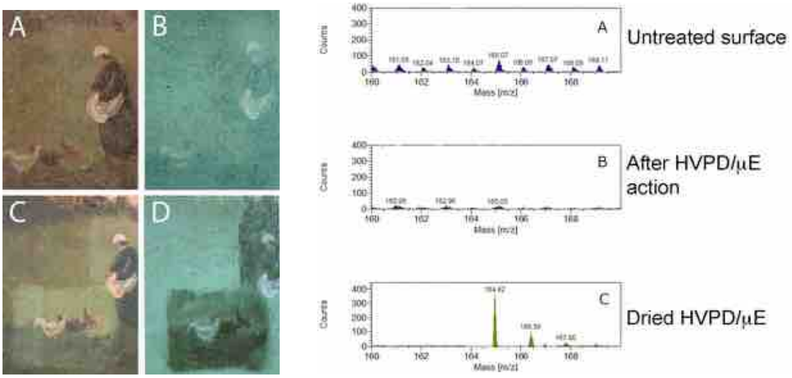

Figure 1. Left: detailed pictures of the XVIII century Tuscan egg-tempera canvas painting before the cleaning test carried out through the HVPD/μE: visible light (A) and UV-induced visible fluorescence (B). The same area of the painting after cleaning procedures: visible light (C) and UV-induced visible fluorescence (D). Right: TOF-SIMS spectra of untreated surface (A), of surface after the interaction time and removal of HVPD/⍰E (B), and of the HVPD/μE system (C) in the 160-170 m/z mass range.

Moreover, recently, we have found that inside the HVPDs, apart organic solvents and o/w microemulsions, it is possible to insert also other molecules like chelates that increase the range of possible applications and support that can be treated with these systems. In particular the preliminary results indicates the potentialities of these systems for the selective removal of sulphates from the surface of carbonatic stones (Figure 2).

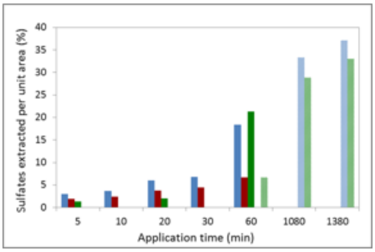

Figure 2. Top: optical micrographs (20x magnification) of the travertine surface before the sulfation treatment (A), the sulfated surface before (B) and after (C) the cleaning test with the HVPD containing 0.5 wt% ammonium carbonate. Bottom: Sulfates extracted per unit area (%) at different contact times based on IC (filled histograms) and ICP (striped histograms) results for the HVPD containing 0.5 wt% ammonium carbonate (light blue), 0.25 wt% EDTA (dark red) and 1 wt% Rochelle salt (green).

2A – Prospective environmental and economic life cycle assessment of a BIPV demonstrator based on perovskite solar modules

F. Rossi, M.L. Parisi, R. Basosi, A. Sinicropi

Aims

The contribution of renewable energy systems is essential to accelerate the energy transition; hence, research on sustainable and high-efficiency energy technologies are considered strategic. Perovskite solar cells (PSCs) have shown a great potential in terms of energetic, economic, and environmental performances. Nevertheless, when scaling up their fabrication from laboratories to industry and to real-world applications, some limitations occur concerning their exploitation. In this study, we present a prospective life cycle assessment (LCA) of a building integrated photovoltaic (BIPV) system focused on the manufacturing and operational phases. The novelty of this work consists of the implementation of a scenario-based approach to evaluate the BIPV system's eco-performances as a function of time compared to the energy mix. An economic assessment is included in the analysis as well.

Results

The PSCs' manufacturing process addressed in this project is based on an existing small-scale line developed by the partners of the H2020 EU project ESPResSO. The scale-up operation consists of identifying those measures that would simplify the fabrication and reduce the consumption of resources, which implies a mitigation of costs and environmental impacts. According to the state-of-the-art literature, the performances of PSCs are affected by a short lifespan, low power conversion efficiency (PCE), and high degradation rate (DR). Representative starting values of these parameters, related to the year 2020, are i) Lifespan = 1 year, ii) PCE = 10% and iii) DR = 4%/yr. As shown in Figure 1, we assume linear variations of these parameters and three scenarios (Pessimistic, Realistic and Optimistic) are proposed for their estimation until 2060.

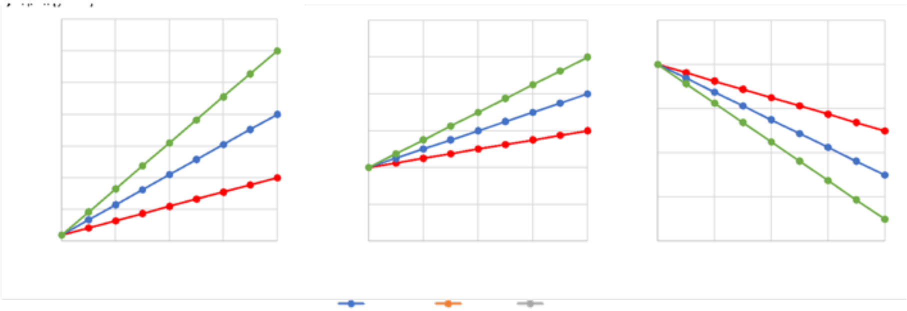

Figure 1 - Future projections of the a) lifespan, b) the PCE, and c) the DR of the PSK modules considering pessimistic (red), realistic (blue) and optimistic (green) scenarios.

To perform a realistic prospective assessment, also the background data provided by the LCA database, in this case Ecoinvent 3.7, should be adapted to future conditions.

In general, background scenarios introduce a high complexity inside a LCA model, but Beltran et al. (2018) created a superstructure that facilitates this operation.

All the charts depicted in Figure 2 highlight that in 2020 the carbon footprint of the BIPV system installed in Cyprus is very close to the burden of the electricity mix and it can be even higher in case of vertical façade installations. In the following years, the environmental impact of PSCs decreases because the energy mix used for the manufacturing processes becomes more sustainable and the operational parameters of PSCs improve along with their technological development. As expected, depending on the scenario, the impact of the BIPV system decreases with a different rate. However, regardless of the selected scenario, the analyzed BIPV system results to be much more sustainable than the national electricity production mix. Accordingly, the largest gap between the BIPV and the grid eco-profiles results to be between 2025 and 2040. Therefore, this is the time range when an extensive deployment of PSK modules in the market could be most effective to reduce the emissions in Cyprus.

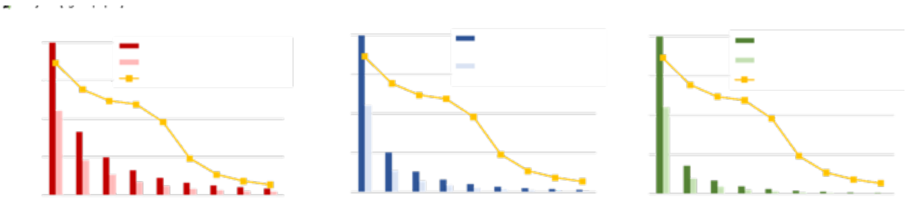

Figure 2: Global Warming Potential of a BIPV system installed in Cyprus considering a) pessimistic, b) realistic and c) optimistic scenarios.

From the economic perspective, the levelized cost of electricity (LCoE) is calculated as a reference indicator to express the economic competitiveness of the BIPV system compared to the current price of electricity in Cyprus (0.2 €/kWh). Particularly, the LCoE of a BIPV system installed in 2020 is approximately assessed in the range 0.5-0.8 €/kWh; therefore, the BIPV demonstrator turns out to be not economically convenient at the status. However, depending on the technological development of the modules, this price will be likely mitigated to 0.1 €/kWh, which is a quite convenient price compared to the grid electricity in Cyprus.

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2A – Prospective Life Cycle Assessment of two-dimensional materials-based perovskite solar panels integrated into a stand-alone solar farm

M.L. Parisi, R. Basosi, A. Sinicropi

Aims

Among the third generation of photovoltaics (PVs), perovskite solar cell (PSC) technology is the most promising one to hit the PV market. Beside the technological development at solar cell level and the upscaling process strengthening, outdoor field tests of large-scale perovskite modules and panels represent a mandatory step to be accomplished in the perspective of industrialization. Recently, the manufacturing of large-area perovskite solar panels engineered with two-dimensional materials was realized and their further integration in a stand-alone solar farm infrastructure allowed to prove the scalability of this technology. The implementation of a prospective Life Cycle Assessment (LCA) approach allowed to calculate the environmental sustainability of the stand-alone solar farm contributing to the eco-design of the product system and demonstrating the very good eco-profile's potential of the generated electricity.

Results

In this project the environmental sustainability assessment, performed through the implementation of a prospective LCA approach, of the first stand-alone solar farm realized in the framework of the European Graphene Flagship and based on perovskite solar panels engineered with two-dimensional materials (Graphene-Perovskite, GRAPE) is addressed. The large area demonstrator (4,5 m2 of total panel area), with a peak power exceeding 250 W, was installed in Crete to work in real outdoor conditions. The continuous monitoring and the direct correlation of the environmental conditions with the outdoor performance of the GRAPE panels provide true metrics for assessing the lifetime of the proposed technology, while offering the possibility of building a life-cycle inventory largely based on high TRL primary data allows to make a robust assessment compared with other LCA studies published in the literature.

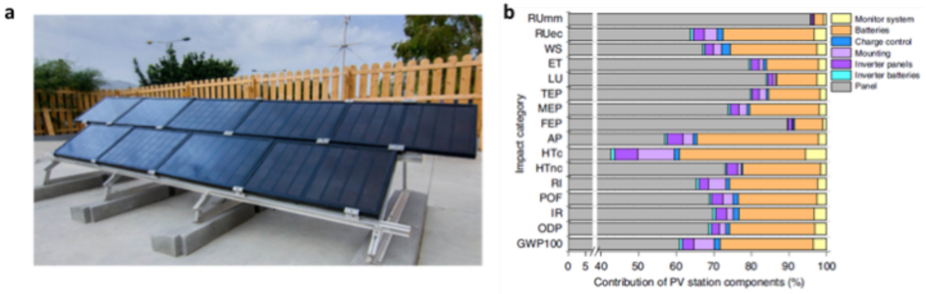

Figure 1: a) Nine GRAPE panels integrated in a stand-alone solar farm-powered infrastructure installed in Crete, Hellenic Mediterranean University campus; b) Characterization of the eco-profile of the GRAPE modules manufacturing process

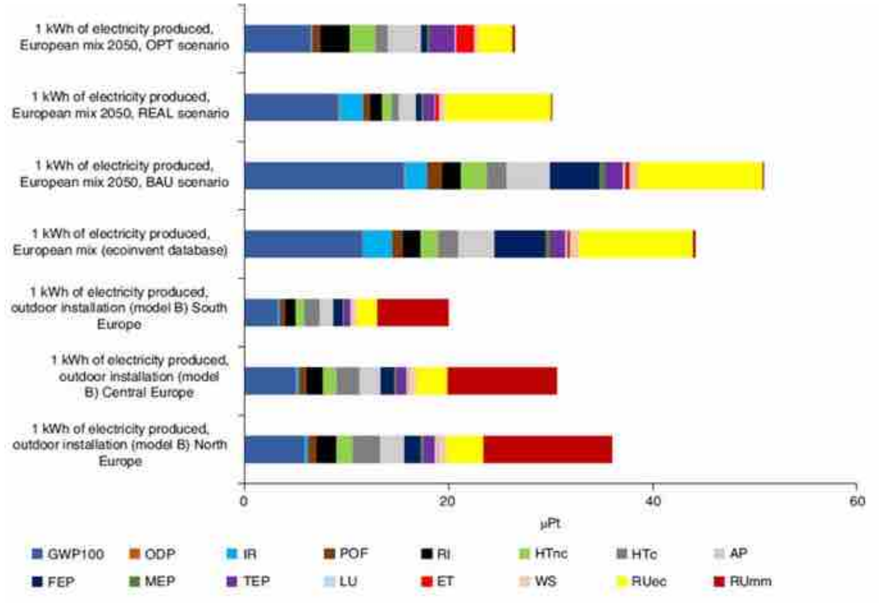

Figure 2 – Eco-profiles of electricity generation. Comparison of the environmental footprint of the optimized GRAPE solar farm (installed in three different European areas), the European electricity mix (taken from the Ecoinvent database) and the 2050 European electricity mix based on Business-as-Usual, Realistic and Optimistic future scenarios.

Based on the detailed characterization of the environment and energy performances of the GRAPE solar modules, the prospective LCA approach allowed to assess the environmental footprint of the electricity generated by the solar farm compared to that provided by the national energy mixes of the EU state members. Results show that producing energy with the GRAPE solar panels would allow to reduce the environmental footprint of 1 kWh electricity of 50% even in a business-as-usual scenario.

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2A – Retentive cleaning systems for the removal of corrosion products from artistic bronzes and iron-based alloys

T. Guaragnone, A. Casini, D. Chelazzi, E. Fratini, P. Baglioni, R. Giorgi

Aims

Development of plasticized PVA-based polymeric systems and pHEMA/PAA gels loading complexing agents for the safe removal of alteration products from Cu-based and Fe-based alloys.

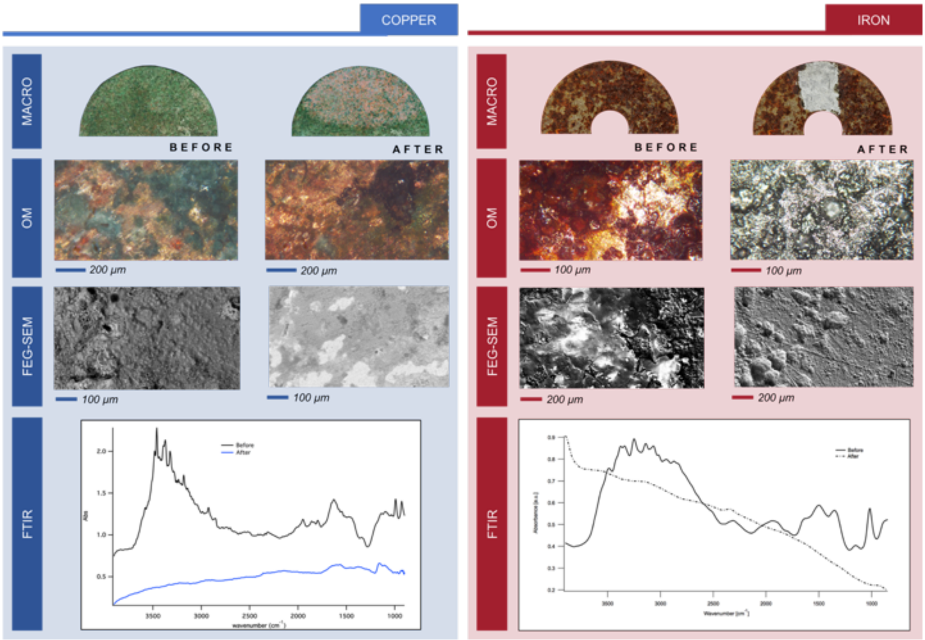
Results

Innovative poly(vinyl)alcohol-based film forming system and poly(2-hydroxyethyl methacrylate) (pHEMA) networks semi-interpenetrated (SIPN) with poly(acrylic acid) (PAA), specifically devised for the controlled and selective cleaning of copper-based and iron-based artifacts were developed.

Traditional cleaning procedures of metallic artifacts are commonly performed by mechanical and/or chemical methods. Both these methods present some limits related to the poor selectivity and invasiveness of the mechanical procedure, and to the scarce control over the reactions involved in the chemical approach.

In the case of copper-based alloys, the cleaning procedure is particularly delicate, it should aim at the complete removal of the defacing and harmful corrosion products of Cu(II) (copper carbonates, sulphates, chlorides, etc.) but preserving the underlying protective cuprite Cu(I) layer. On the contrary, for the iron-based alloys is important the complete removal of all corrosion patinas that are usually powdery and porous layers and unable to protect the metal beneath. Moreover, the presence of high soluble chlorine salts, such as Fe(III)Cl3, can also bring to new rusting processes.

In the case of PVA-based film forming system, the proposed cleaning procedure consists in the application of a PVA-based polymeric solution able to form an elastic film, which can be gently peeled off from the surface upon drying. Plasticizers (different polyols) were added to the solution to obtain a final film with suitable mechanical properties to facilitate the peeling action, while the composition of the volatile fraction (water and ethanol) was adjusted in order tune both, the viscosity of the system and the time required for the film to form. Finally, a complexing agent was loaded in the polymeric dispersion. The main advantage of these cleaning systems consists in the simultaneous chemical and mechanical action, guaranteed by the presence of the complexing agent and the final removal of the film by peeling off.



In case of brittle and mechanically weak metallic surfaces (i.e. archeological artefacts), where the removal or peeling of surface layers might be risky for the artifact integrity, a gel system allows to have e a very controlled action.

Thanks to its mechanical properties, indeed, a pHEMA/PAA gel can be applied repeatedly with no risks to delicate substrates and simply removed in one piece without leaving detectable residues.

Moreover, the capability of PAA to give strong coordination bonds with metal ions *via* carboxylate groups in alkaline conditions, can boost the capture and retention of copper and increase the cleaning performances of the chelating agent confined inside the gel.

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2A – Twin-Chain Polymer Networks for the cleaning of Modern and Contemporary Art

R. Mastrangelo, D. Chelazzi, G. Poggi, E. Fratini, P. Baglioni

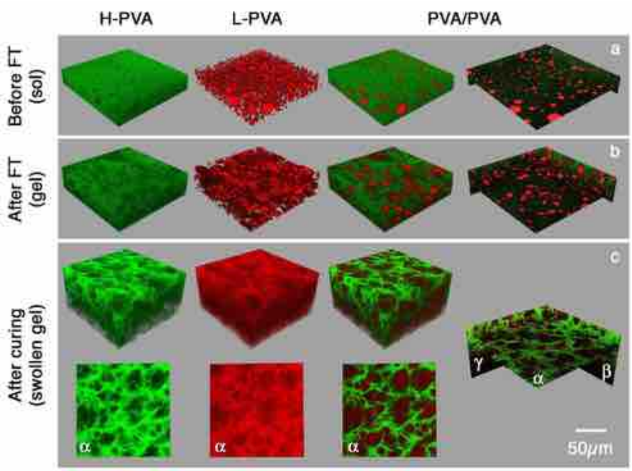
Aims

Artifacts, like easel paintings, are subject to degradation, not only as a result of natural ageing, but also for the exposure to ambient contaminants: grime and soil deposit on surfaces and are often hard to remove. Traditional cleaning techniques in restoration involve the uncontrolled spreading of the cleaning fluid on the surface of the artwork, the use of mechanical methods to remove grime and the possible deposit of residues. The cleaning of Modern and Contemporary paintings is one of the Conservator's most complex tasks: traditional methods are too invasive and risky for their clotted, solvent-sensitive surfaces. The ideal cleaning systems are highly adaptable and retentive gels, with a macroporous structure that allows the diffusion of cleaning fluids throughout the gel matrix and at the gel-substrate interface.

Results

Twin-Chain Polymer Networks (TC-PN) are poly(vinyl) alcohol (PVA)-based cryogels with a sponge-like structure. The micron-sized pores are crucial to ensure high cleaning performances on rough and delicate artistic surfaces. Classically, PVA cryogels are obtained through a freeze-thawing (FT) process. The freezing step induces a water-polymer phase separation: polymer-rich areas are compressed by the growing ice crystals, until PVA crystallites form. PVA crystallites act as junctions, conferring to the hydrogel cohesion and elasticity closer to those of chemical gels. Conversely, ice crystals act as templates in the formation of a ubiquitous porosity. Free water content and water retentiveness are far higher than those characterizing traditional gels used in restoration. In TC-PN, the spontaneous phase separation occurring between a highly hydrolyzed (H-PVA) and a partially hydrolyzed PVA (L-PVA) was exploited to obtain sponge-like hydrogels: L-PVA concentrates in blobs in the pre-gel solutions, acting as a porogen during cryostructuration. H-PVA behaves, instead, as the main structural component. The characterization of the systems morphology at the micron-scale was performed though confocal microscopy and SEM, while the nanoscale features were investigated through SAXS measurements. The porogen causes an increase of the average pores size and a decrease of the correlation length, describing polymer chains crowding in the gel's walls. The number of FT cycles drastically affect the rheological response, as gels crystallinity increases, making the gels stiffer.

The cleaning performances of H-PVA gels and TC-PN were compared on rough and flat surfaces: TC-PN performed better in the removal of artificial soil from glass and mock-ups specifically prepared to mimic Jackson Pollock's dripping technique.



Gels of this type were successfully used in the restoration of Pollock's masterpieces *Two* and *Eyes in the Heat*, on display at the *Peggy Guggenheim Collection*, in Venice.

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2B – Anode materials for enhanced electrochemical performances in SIBs

D. Capsoni, D.M. Conti, C. Fusaro

Aims

Rechargeable batteries play a basic role in the transition to renewable energy systems. Lithium-ion batteries are a mature technology and dominate the market, thanks to their valuable performances in term of energy and power density, cycling stability and rate performances. However, some drawbacks are to be overcome: (i) current performances are not sufficient to satisfy the power demand for energy grids and electric vehicles, due to the limited capacity of commercial electrodes; (ii) availability of Lithium source. Sodium-ion batteries represent a promising choice, as Na is abundant on the Earth crust, but they have two distinctive drawbacks: low cycling stability and poor rate performance at high C-rate. In the present research project, we synthesized and characterized (XRPD, SEM-EDS, TEM, TGA, Raman Spectroscopy) some pure and doped electrode materials and conducing carbon/active material composites, to optimize their electrochemical performances. We investigated TiO_2 and ZnS as anodes for SIBs. The samples showing the best electrochemical performances for each active material, are also used to prepare self-standing electrodes, dispersing the active material into Carbon nanofibers (CNFs) by electrospinning.

Results

TiO_2 is prepared by two synthetic approaches, both simple, feasible, and not expensive: i) thermal decomposition of the Metal Organic Framework (MOF) MIL-125; ii) synthesis by co-precipitation. In both cases the TiO_2 in the anatase crystal structure is obtained. The sample from thermal decomposition of MIL-125 displays large agglomerates (SEM) formed by nanometric rounded particles (diameter: about 10 nm), and slightly better electrochemical performances: for the TiO_2 ball-milled at 100 rpm (slurry composition: 70% active material, 20% super P carbon and 10% CMC binder; electrolyte: $NaClO_4$ in ethylene carbonate and propylenecarbonate (1:1, w/w) with the addition of 5% FEC) an average capacity of 110 mAh/ g at low C-rates and about 80mAh/ g at high C-rate (2C) is obtained. The cell, cycled 200 cycles at 0.2C, displays a small energy loss and a good lifetime.

As concerns the self-standing anodes, a 9% weight percentage of TiO_2 is successfully charged into the CNFs by electrospinning, as confirmed by TGA, and the active material is homogeneously dispersed in the fibers, as demonstrated by SEM, TEM and EDS analysis. The preliminary results obtained by the electrochemical tests suggest the cell displays interesting lifetimes and duration: there was almost no energy loss over 90 cycles at 0.2C.

ZnS anode obtained by two synthesis routes (sol-gel and hydrothermal) is synthesized and characterized and its electrochemical performances are compared. We obtain ZnS/carbon nanoparticles from the sol-gel approach and ZnS/reduced graphene oxide nanoparticles from the hydrothermal one. Both composites are electrochemically tested on slurries prepared by tape-casting. The best electrochemical performances are obtained for the ZnS/reduced graphene oxide (150 mAh/ g at 2C, about 200 mAh/ g after 200 cycles at C/5). Further improvement of the electrochemical performances is obtained by Cu doping (5 and 10% moles); we demonstrate by several characterization techniques the Cu segregates as CuS (covellite phase), thus forming a CuS/ZnS composite.

The ZnS/reduced graphene is implemented into CNFs by electrospinning (10% weight percentage of active material). The self-standing electrode is characterized by several techniques (XRPD, SEM-EDS, TEM microscope, Raman spectroscopy, TGA). The preliminary electrochemical results are encouraging: a high coulombic efficiency (> 99%) was obtained over 200 cycles at C/5. The specific capacity values are comparable to those given by the cells prepared by tape-casting, but an improvement is expected by increasing the active material loaded into the carbon nanofiber.

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2B – Cathodes and anodes materials for lithium and sodium ion batteries

M. Bini, D. Spada, M. Ambrosetti, C. Milanese, A. Girella et al.

Aims

The energy request due to the diffusion on a large scale of electric vehicles and electronic portable devices is rapidly growing. On the other hand, it is also mandatory to reduce the use of fossil fuels for the climate preservation and the progress towards the required green transition. However, the renewable resources (wind or solar) are intermittent, so requiring energy storage systems for the stationary applications. The most diffuse and performing systems are represented by the batteries, particularly lithium ion batteries (LIBs), already marketed by many years, that should however be replaced by more sustainable alternatives, such as sodium ion batteries (SIBs). We synthesized cathodes and anodes materials for LIBs and SIBs with the aim to improve electrochemical performances for SIBs and to unravel the mechanisms at the base of electrochemical performances for LIBs.

Results

Different kind of synthesis routes (wet or solid-state methods, as well as electrospinning) were typically used, with the aim to compare the performances of the synthesized materials and to find the better experimental conditions to obtain peculiar features. The use of doping or substitutions with transition elements could help to improve the structural stability and the electrochemical performances, as well as the nanodimensions, thanks to the shortening of Li+ or Na+ diffusion paths. All the materials were usually characterized from the physico-chemical (X-ray diffraction measurements with Rietveld structural refinements, SEM/EDS, Raman, FT-IR, EPR and Mössbauer spectroscopies) and electrochemical (cyclic voltammetry, galvanostatic measurements and impedance spectroscopy) point of view to study the performances in semi-cells. The determination of the involved reaction mechanisms could be based on Large Facilities measurements (performed at Elettra (Italy), Diamond (UK) or ESRF (France)), such as operando diffraction, EXAFS or Raman spectroscopies. In some cases, DFT calculations allowed to better describe the diffusion paths of sodium into the electrode materials or to study the electronic structure of anodes/cathodes.

This kind of characterization was applied to different materials, allowing to obtain important results (see references). We studied Na0.44MnO2 and Na0.44Mn0.5Fe0.5O2 (with Al, Si and Cu doping), both cathodes for SIBs, demonstrating that the intergrowth of different polymorphs could help obtaining better process reversibility and stability of the electrode materials, particularly during prolonged cycling. Similar findings were obtained on NaNi0.5Mn0.5O2 with Ti, V and Cu doping. We also studied anode materials, for both LIBs and SIBs. In particular, we could verify the reasons of the failure of tin oxides applied in bulk form as anodes in SIBs, while we verified the successful application of self-supported fibrous tin oxide in LIBs. We could also unravel the mechanisms of electrochemical cycling of FeNb11O29, a recent anode for LIBs, by operando techniques as well as by DFT calculation and spectroscopic techniques.

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2B – Material's challenges for hydrogen green economy

M. Cabrini, S. Lorenzi, A. Carrozza, L. Coppola, D. Coffetti, T. Pastore

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Aims

Hydrogen green economy is worldwide proposed to reducing energy consumption and CO_2 emissions, and to store the excess of energy produced by renewable sources. Hydrogen has inherent hazards mainly due to its flammability and explosivity, in addition of damage phenomena of materials, generally called hydrogen environmental embrittlement (HEE). HEE due to corrosion in acidic environments, in the presence of H_2S, in cathodic over-protection or in high temperature and pressure hydrogenation plants, is well known and studied since many decades. Vice versa, there is a lack of knowledge on HEE of carbon steel and other different alloys for compression and transport of gaseous hydrogen at room temperature. The effect of hydrogen inside the material are related to the intrinsic susceptibility of the metals, metallurgical and loading condition, independently from the external hydrogen source.

This research project studies the hydrogen diffusion parameters and environmental embrittlement (HEE) phenomena on different alloys commonly used in transport, conversion and storage of oil, hydrogen and natural gas, biofuel, geothermal steam, and, in general, in any conditions in which there is interaction between metals and hydrogen.

Results

HEE phenomena take place for the simultaneously action of hydrogen and mechanic loading. The presence of hydrogen inside steels reduces their ductility in tensile stress tests at low strain rate (figure 1) (1), increases the low frequency fatigue crack growth (figure 2a) (2) and decreases the total energy to fracture propagation (J-integral vs da) (figure 2b and c) (1).

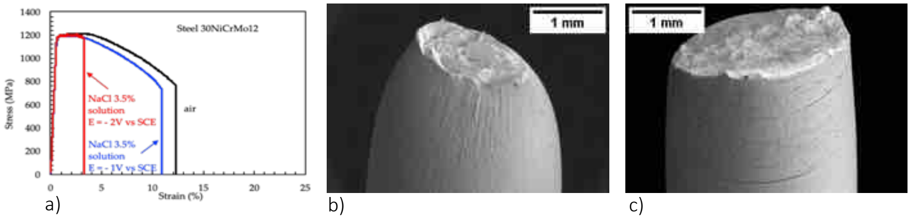
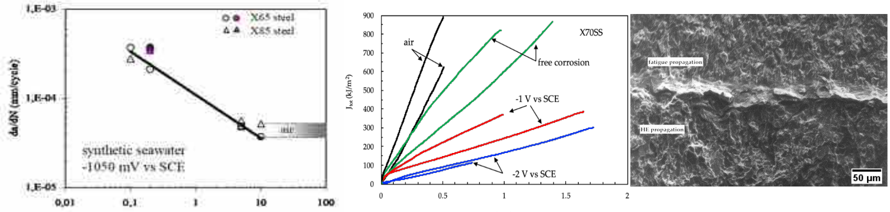


Figure 1: a) stress vs strain curves of the 30NiCrMo12 steel in air and in NaCl 3.5% solution and cathodic protection; SEM images of the specimens of the specimens after the SSR test in NaCl 3.5% (strain rate 10^{-6} s^{-1}) b) at the open circuit potential; (c) polarized at -2 V vs SCE (1)

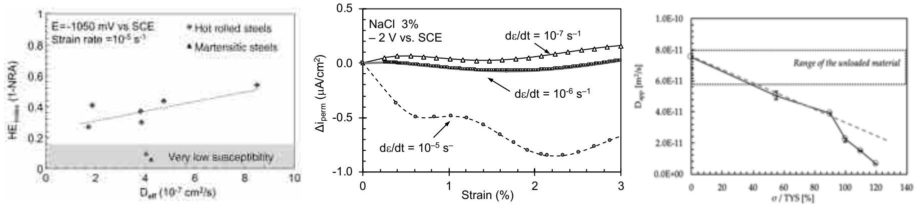
Chemical composition and microstructure influence the critical hydrogen concentration to have HEE. For each materials a relationship could be observed between the hydrogen apparent diffusion coefficient and embrittlement phenomena (figure 3a) (3).



a b c

Figure 2: a) Effect of loading frequency on fatigue crack growth rate in synthetic seawater at 18 MPa·m$^{-½}$ ΔK. Empty symbols denote ΔK constant test; full symbols denote Constant Amplitude test. (2) b) Results of J-integral tests of X70SS steel and c) close-up view of the crack propagation zone of the fracture surface in J-integral test for the X70 steel polarized at -1 V vs SCE in NaCl 3.5% (1)

Hydrogen diffusion inside the metal is strongly influenced by the external stress and strain rate. In slow strain rate tests a decrease in the hydrogen permeation flux (by the Fick’s law in stationary conditions in a DeVanathan Stachurski permeation experiments) can be observed at relatively high strain rates, higher than 10^{-6} s^{-1}, because of the hydrogen traps generates from plastic straining (figure 3b) (3). A similar behavior is observed in cyclic loading tests, in which the apparent hydrogen diffusion coefficient (D_{app}) decreases increasing the average stress (4). Applied cyclic load causes a very small decrease in the hydrogen permeation current at the steady state, mainly hindered by the increase in the passive current (5).



a) b) c)

Figure 3: a) HE indexes from SSR tests at -1.05 mV vs. SCE as function of the average hydrogen diffusion coefficient (2); b) variation of the permeation current with respect to unloaded specimens (Δi_{perm}) as a function of strain and strain rate (API 5L X60 steel under CP at -2 V vs SCE on cathodic side of membrane) (3) c) Apparent diffusivity (D_{app}) as a function of maximum stress and loading condition (4).

These results will be compared with future tests in gaseous hydrogen.

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2B – Microstructure, Properties and Corrosion Resistance of Alloys Produced by Additive Manufacturing

M. Cabrini, S. Lorenzi, L. Coppola, D. Coffetti, A. Carrozza, F. Carugo, T. Pastore

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Aims:

The application of additive manufacturing (AM) technologies to process different materials is industrially relevant, mainly because of cost reduction and the unique microstructure achievable and often, mechanical properties higher than the materials processed by traditional working. Therefore, the qualification of the properties of materials obtained by AM techniques is fundamental, specifically concerning the corrosion behavior. Aim of the research is the analysis of alloys produced using different AM techniques, like material extrusion (MEX), laser powder bed fusion (PBF-LB), electron beam melting (EBM) and directed energy deposition (DED-LB) in terms of process-related defects, microstructure and corrosion behavior. Different alloys were considered: the nickel alloy 625, AlSi10Mg and Ti6Al4V for biomedical purpose.

Results:

PBF-LB and DED-LB processed specimens of alloy 625 provided very high densities. Conversely, the same material processed via MEX was characterized by a significant residual porosity. The highest hardness was provided by the samples manufactured via PBF-LB, DED-LB-processed material had a lower value, due to the coarser dendritic microstructure, instead, the MEX-built specimens were characterized by the lowest hardness, due to the complete disappearance of the dendritic structure. Intergranular corrosion tests showed an excellent behavior of the PBF-LB alloy 625, an acid attack that reveals a dendritic structure on the DED specimens, without penetrating attack, conversely, MEX-built specimens resulted in significant localized attacks in the core region (1.3). The role of different precipitates on the corrosion resistance of the alloy is object of a future research.

The effect of the building platform temperature on the corrosion resistance of the AlSi10Mg alloy obtained by means of PBF-LB was studied in an aerated chloride solution (4-5). Potentiodynamic polarization tests showed two break-down potentials. The first was associated with the initiation of corrosion localized on the edge of the melting pool, while the second with the breakage of the passive film of the matrix. No differences were observed between the breakdown potentials of the specimens as a function of the temperature of the building platform (figure 1), while the time to trigger the selective attack in the potentiostatic tests increases as the plate temperature decreases (figure 2) (6).

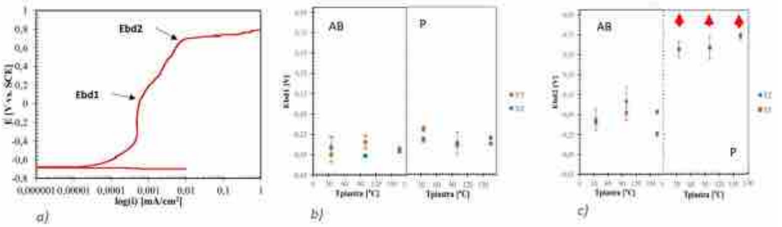
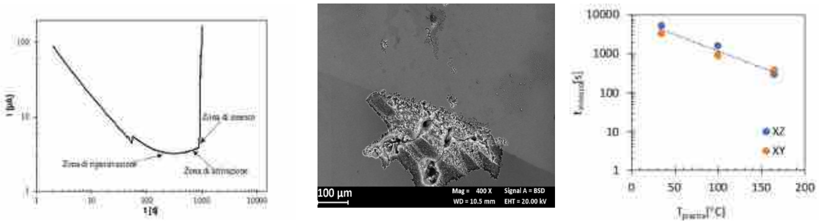


Figure 1: a) example of polarization potentiodynamic curve with the two break-down potentials evidenced b) E_{bd1} and c) E_{bd2} as a function of the building platform temperature



a) b) c)

Figure 2:) example of potenziostatic test, b) specimen after the potentiostatic test; c) time to trigger of the selective attack as a function of the building platform temperature

Ti-6Al-4V alloy PBF-LB produced was microstructurally and electrochemically characterized to investigate the effect of the manufacturing technology on the passive current, index of the ions release, in a simulating body fluid solution. No adverse effect of increase of the passive current density during long-term tests in simulated body fluid was observed with respect to the conventionally-processed material. However, some spikes in current densities, and presumably increases in ion leaching, were detected immediately after the immersion. These spikes were associated with the unmelt powder particles adhered to the surface, formed during LPBF processing. A pickling treatment was shown to partially suppress the initial spikes of current (7-8).

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2C – A biosensing approach based on solid supported membranes to investigate drug interactions with P-type ATPases

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Aims

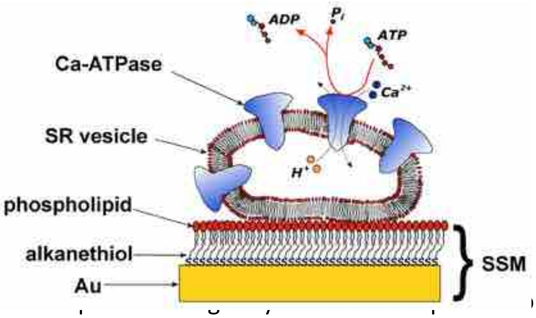
The solid supported membrane, consisting of a hybrid alkanethiol/phospholipid bilayer supported by a gold electrode, is a convenient model system for a biological membrane. The SSM method allows label-free direct electrical measurements of charge movements within a membrane transporter immobilized on the SSM surface, yielding useful information about the transport activity. In the present research project we have used the SSM technique to investigate the interactions of some pharmacologically relevant compounds with sarcoplasmic reticulum Ca2+-ATPase (SERCA), that belongs to a superfamily of membrane transporters known as P-type ATPases. SSM measurements were performed to evaluate at a molecular level the effects of such compounds on ATP-dependent translocation of Ca2+ ions by SERCA. The identification of drugs that can modulate SERCA transport activity may represent an innovative approach to treat various diseases that are associated with Ca2+-ATPase dysfunction.

Results

SERCA, that is localized in the sarcoplasmic reticulum (SR) of muscle cells, hydrolyzes one ATP molecule to transport two Ca2+ ions against their electrochemical potential gradient from the cytoplasm to the SR lumen. Ca2+ uptake in the SR lumen by SERCA plays an essential role in lowering cytoplasmic Ca2+ concentration and inducing muscle cell relaxation. SERCA represents an attractive target for the development of novel drugs with distinct therapeutic potential [1].

SR vesicles containing SERCA were adsorbed on the SSM surface and were subjected to a rapid concentration jump of a suitable substrate, i.e., ATP (Fig. 1). The ATP concentration jump activated the ATPase protein, and an electrical current was detected which was attributed to translocation of Ca2+ ions across the vesicular membrane by SERCA after phosphorylation of the enzyme by ATP [2].

Figure 1: Sche diagram of a SSM w adsorbed SR v containing SERCA drawn to Reproduced from [4



The effects of v n the ion transport activity of SERCA were examined using the SSM method [3]. In the present study, we investigated the mechanism of interaction of a novel small-molecule drug [4] and some selected phytochemicals, i.e. demethoxycurcumin and gingerol, that are known for their antioxidant, anti-inflammatory and anticancer properties. SSM-based electrical measurements indicated that demethoxycurcumin and gingerol affect Ca2+ translocation by SERCA. In particular, gingerol behaves like an activator of the SERCA enzyme, whereas demethoxycurcumin exerts an inhibitory effect on SERCA transport activity. In the case of the small-molecule drug CDN1163, it was shown that CDN1163 reversibly interacts with SERCA and significantly enhances ATP-dependent Ca2+ translocation by SERCA (Fig. 2). These results suggest that CDN1163 interaction with SERCA can promote a protein conformational state that favors the release of Ca2+ ions into the SR lumen, thereby enhancing calcium translocation.

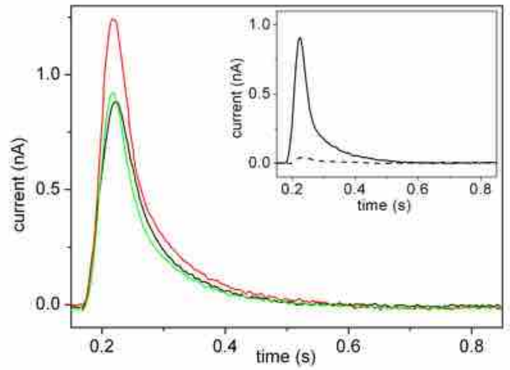


Figure 2: Current signals induced by 100 µM ATP concentration jumps on SR vesicles in the presence of 10 µM free Ca2+ were measured in the absence of CDN1163 (initial control, black line), in the presence of 10 µM CDN1163 (red line), and again in the absence of CDN1163 by replacing the solution containing CDN1163 with one with no CDN1163 added (final control, green line). The inset shows current signals after 100 µM ATP concentration jumps in the absence (black solid line) and in the presence of the potent and highly selective SERCA inhibitor thapsigargin (100 nM, black dashed line). Reproduced from [4].

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2C – Acoustic Markers for Enhanced Remote Sensing of Radiation Doses: Amphora

European Project Horizon 2020
FETOPEN-1-2016-2017
From 01.11.2017 to 30.04.2022
Coordination: Katholieke Universiteit (KU) Leuven

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Aims

Approximately 50% of all cancer patients receive radiation therapy as part of their treatment. The aim is hereby to maximise tumor irradiation and to minimize healthy tissue irradiation. This implies a need for appropriate dosimetry strategies that can effectively measure the actual radiation dose imparted on the tumor. However, state-of-the-art dosimetry cannot quantify the dose distribution in (and around) the tumor, hereby inhibiting the full potential of radiotherapy.

AMPHORA aims to develop a non-invasive in-situ dosimetry system for radiation therapy with the potential of on-line dose assessment by casting ultrasound contrast agents (UCAs) into dose sensing theranostic devices. UCAs will be upgraded to injectable dose-sensitive and targeted devices that gather in tumor tissue and translate imparted radiation dosage into a modulation of their acoustic response upon ultrasound interrogation. Tailored ultrasound imaging and advanced signal processing algorithms will be developed to extract the (change in) acoustic signature of UCAs from backscatter data and to translate this information into a 2D or 3D dose distribution map. The specific objectives of this project are the design, development and pre-clinical validation of the aforementioned UCA based dosimetry system and a customised ultrasound read-out technology.

Results

Within the AMPHORA activities the assessment of the effective radiation dose distribution in (and around) the tumor has been enabled, offering advanced and objective means to compare and evaluate treatment efficacy of different radiotherapy modalities. Such novel technology has the potential to revolutionize quality assurance and treatment follow up in radiotherapy, which also unmistakably will lead to increased patient safety and improved treatment protocols. Moreover, AMPHORA is expected to trigger an avalanche of novel technologies for radiation therapy delivery and to pave the way for other in-vivo UCA based distributed sensing applications. Part of the results is documented by 11 publications, some of them reported in the list below, while other papers are in preparation.

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2C – Allosteric transition of rabbit skeletal muscle lactate dehydrogenase induced by pH-dependent dissociation of the tetrameric enzyme

L.G. Iacovino, M. Rossi, G. Di Stefano, V. Rossi, C. Binda, M. Brigotti, F. Tomaselli, A.P. Pasti, F. Dal Piaz, , S. Cerini, A. Hochkoeppler

Aims

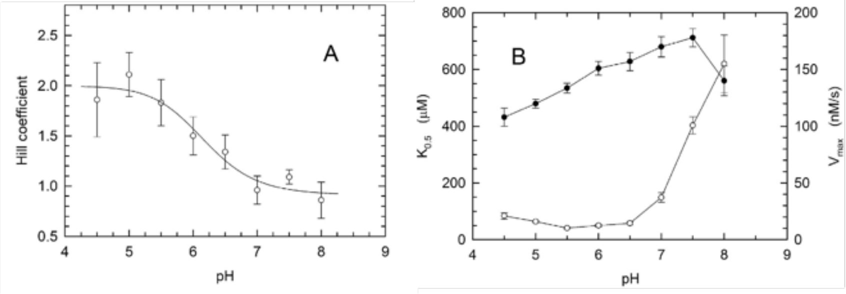
The regulation of muscular lactic acidosis is a very complicated phenomenon. Allosteric transitions are known to occur in prokaryotic lactate dehydrogenases while eukaryotic enzymes are usually considered featuring Michaelis-Menten kinetics. Here we used the rabbit skeletal muscle LDH-A as a model system to investigate the pH-dependence of allosteric transitions. Moreover, the effect of citrate on enzyme stability was also analysed.

Results

Two isoforms of LDH have been identified in vertebrates: the heart (H, LDH-B) and the muscle (M, LDH-A) enzymes. The H form is more abundant in aerobic tissues and is responsible for the oxidation of lactate, while the M form is mainly produced inside white muscle fibers where it is devoted to the reduction of pyruvate.

To investigate the effect of pH on dissociation of the tetrameric LDH-A, we assayed the activity of rabbit skeletal muscle LDH, natural and recombinant, under different conditions. The pyruvate reduction was measured using a spectrophotometric assay and determining the decrease in Absorbance at 340 nm due to the oxidation of β-NADH. To produce the recombinant enzyme *Escherichia coli* BL21(DE3) cells were transformed with pET9a-rLDHA and the expression of rLDH-A was induced with IPTG 1 mM for 15 h at 30 °C. The purification was performed by means of a HiTrap Blue affinity column, a HiTrap Phenyl FF column and a final gel-filtration chromatography.

The kinetics of pyruvate reduction catalysed by the natural enzyme (3 nM) was tested over a pH interval ranging from 4.5 to 8. We observed a sigmoidal dependence of the initial reaction velocities on substrate concentration at pH lower than 7. We indeed found a Hill coefficient ≥1 exclusively at acidic pH values (Figure 1A).



These results indicate the occurrence of allosteric transitions caused by acidic conditions. The pH-dependence of Km and Vmax is shown in Figure 1B: major variations occur in Km values (empty circles) compared to Vmax values (filled circles). In order to verify if post-translational modifications are essential for the enzyme allosteric transitions, analogous assays were performed with the recombinant rabbit LDH-A. The kinetic parameters at pH 5 and 8 are reported in Table:

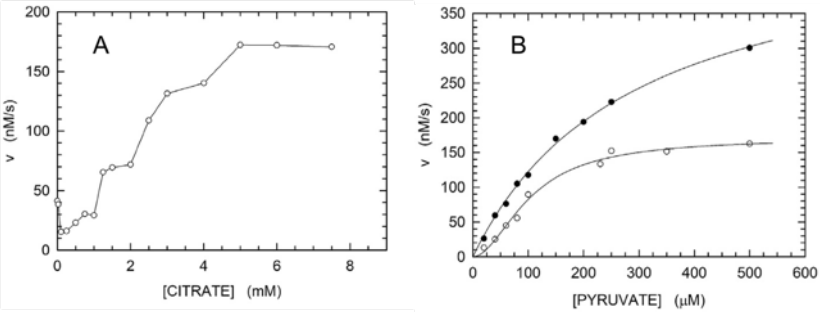
Natural rabbit LDH-A			
	Km (μM)	Vmax (nM/s)	Hill
pH 5	64 ± 3	120 ± 4	2.1 ± 0.2
pH 8	620 ± 102	140 ± 13	

Recombinant rabbit LDH-A			
	Km (μM)	Vmax (nM/s)	Hill
pH 5	164 ± 16	24 ± 2	2.6 ± 0.4
pH 8	1075 ± 163	187 ± 22	

Interestingly, we found that the activity of recombinant enzyme at pH 5 is lower than the natural LDH-A likely due to the lack of some post-translational modifications, as confirmed by mass spectrometry analysis.

The dissociation of the tetrameric lactate dehydrogenase as a function of pH was then studied by DLS measurements (9 μM enzyme). The distribution of tetramer, dimer and monomer was estimated revealing the presence of a tetrameric enzyme only at pH ranging from 6.5 to 7.5, while at lower pH the dimeric/monomeric forms were prevalent. The assembly of the tetrameric enzyme was also promoted by the presence of pyruvate.

Finally, we test if citrate affects the activity of rabbit LDH-A at pH 5. As visible in Figure 2A, low citrate concentrations (0.1-1 mM) induce inhibition of enzyme activity, while higher concentrations (above 2 mM) can activate. A transition to Michaelis-Menten kinetics was visible in the presence of 2.5 mM citrate (Figure 2 B).



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2C – Anethole dithiolethione increases glutathione in kidney by inhibiting γ-glutamyltranspeptidase: biochemical interpretation and pharmacological consequences

D. Giustarini, F. Galvagni, I. Dalle-Donne, A. Milzani, M. Lucattelli, G. De Cunto, D. Bartolini, F. Galli, A. Santucci, R. Rossi

Aims

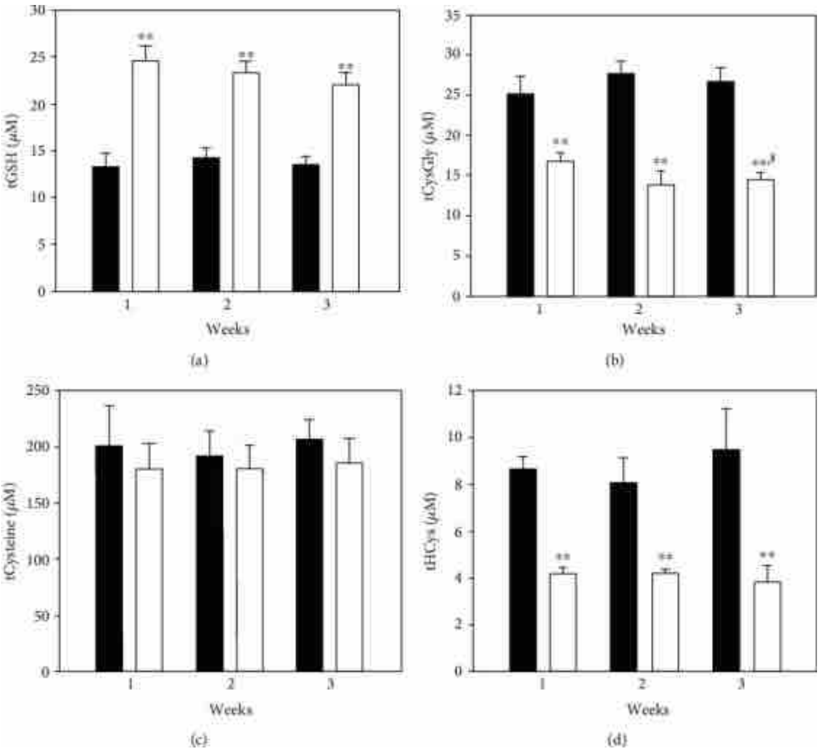
Anethole dithiolethione (ADT) is a marketed drug to treat xerostomia. Its mechanism of action is still unknown, but several preclinical studies indicate that it is able to increase intracellular glutathione (GSH) and protect against oxidative stress. Here, we investigated the molecular mechanisms behind these effects.

Results

Oral treatments of rats with ADT confirmed the increase of GSH concentration in several body tissues, with the kidney showing the most important effect. This effect was paralleled by the decrease of

some systemic and renal biomarkers of oxidative stress. The increase in GSH correlated with a decrease in γ-glutamyltranspeptidase (γ-GT) activity of the different tissues, that, in turn, decreased the production of cysteinylglycine, a thiol that has prooxidant effects as the consequence of its autooxidation. In vitro experiments with tubular renal cells showed that only in the presence of extracellular GSH its concentration inside the cells almost doubled regardless of the presence of ADT. This indicates that intact GSH could be taken by renal proximal tubular cells.

Experiments with isolated perfused rat kidney indicated the presence of a peculiar transport system for GSH, independent from its degradation by γ-GT and suggest that most of the renal GSH depends on its influx from plasma rather than on its synthesis. The activity of ADT as GSH enhancer in both the circulation and the kidney was long-lasting. All these characteristics make ADT a promising drug to protect the kidney, and in particular proximal tubule cells, from xenobiotic-induced damage.



(a) (b) (c) (d)

Total thiols in plasma of rats orally administered 1 mg/kg/day ADT (white columns) or vehicle (dark columns). At 1-week intervals the levels of total thiols, i.e. total glutathione (a), total cysteinylglycine (b), total homocysteine (c), total cysteine (d) were measured. Data are the mean of 3 experiments. $**p < 0.01$ vs. vehicle; $§p < 0.05$ vs. 1-week ADT.

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2C – Biocompatible materials for biomedical applications

M. Bini, M. Ambrosetti, C. Milanese, A. Girella et al.

Aims

A biomaterial is “a substance employed to build objects capable of replacing original living parts of the human body” and, when inserted in the body, it should not produce adverse reactions, i.e. it should be biocompatible. So, biomaterials could be drug delivery systems, materials for prosthesis, surgical equipment or compounds used for the diagnosis. We synthesized mixed oxides, particularly zinc, magnesium or calcium ferrites that can be applied in magneto-fluid hyperthermia (a technique for cancer treatment) or as antibacterial compounds, required due to the increasing antimicrobial resistance to the most diffused antibiotics.

Results

Nanometric $GdFeO_3$ undoped and doped with Ca^{2+} and Mg^{2+} ions were synthesized by microwave assisted, sol–gel, and polyol syntheses and characterized by X-ray diffraction, showing solid solutions formation. Raman spectroscopy confirmed the Ca and Mg substitution on Gd and Fe sites. The magnetic data showed the presence of magnetic domains as consequence of doping with diamagnetic ions, which seem to play a crucial role in the magnetic activity of the compounds. A superparamagnetic behaviour is evidenced; nevertheless, its intrinsic character is not definitely demonstrated. Indeed, the possible presence of traces of magnetic impurities, which are easily obtainable in these samples, such as iron oxides, must be taken into account. $MgFe_2O_4$, a partially inverted spinel phase, could find applications in medicine thanks to the remarkable antibacterial properties attributed to the generation of reactive oxygen species. Undoped and Ag-doped $MgFe_{2-x}Ag_xO_4$ ($x = 0.1$ and 0.3) nanoparticles were prepared using microwave-assisted combustion and sol–gel methods. X-ray powder diffraction, with Rietveld structural refinements combined with micro-Raman spectroscopy, allowed to determine sample purity and the inversion degree of the spinel. The results are discussed in view of the antibacterial activity towards Escherichia coli and Staphylococcus aureus, representative strains of Gram-negative and Gram-positive bacteria. The sol–gel particles were more efficient towards the chosen bacteria, possibly thanks to the nanometric sizes of metallic silver, well distributed in the powders and in the spinel phase, with respect to microwave ones, that, however, acquired antibacterial activity after thermal treatment, probably due to the nucleation of hematite, itself displaying well-known antibacterial properties and which could synergistically act with silver and spinel.

The key property of $ZnFe_2O_4$ spinel is the superparamagnetic behaviour at room temperature, strictly dependent on particle sizes and cation distribution on the spinel sites. We focused on the undoped and Mg (on Zn site) and/or Ga (on Fe site) substituted ferrites synthesized by co-precipitation route. XRPD, SEM and Micro-Raman techniques demonstrated the good quality of the samples and allowed to determine the dopants location into spinel lattice and to estimate an average crystallite size of about 5 nm. A superparamagnetic behavior with maxima magnetization values at room temperature between 4 and 7 emu/g at the highest applied magnetic field of 1T was disclosed, as well as a clear dependence of the blocking temperature on the cationic disorder within the two sublattices, strengthening the magnetic interactions thus moving the transition to an ordered blocked state at higher temperatures. The EPR inspection confirmed the superparamagnetic behavior, excluding extrinsic contribution from iron oxides phases, so demonstrating that the magnetic properties depend on the inversion degree, related to the structural disorder, of the spinel phase.

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2C – Biosensing of FKBP12 and Tacrolimus in Fluid Samples

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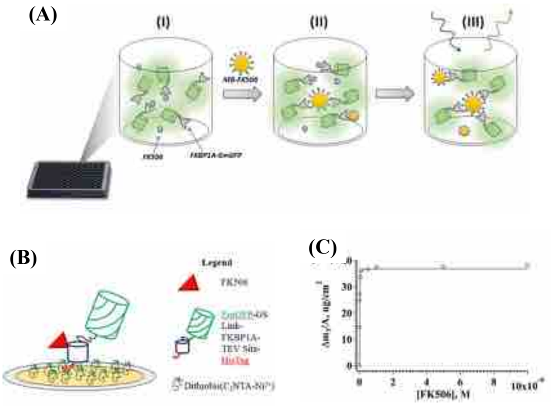
Aims

Tacrolimus (FK506) is an immunosuppressant drug (ISD) used to prevent organ rejection after transplantation. It exhibits a narrow therapeutic window and wide inter- and intra-individual pharmacokinetics fluctuations, requiring therapeutic drug monitoring. The immunosuppressive capacity of FK506 is due to the complex formed with the immunophilin FKBP12. The project describes the construction of two distinct nanosensor platforms for the detection of FK506 and FKBP12 in fluid samples, as a useful alternative to commonly applied antibodies sensing for organ rejection monitoring.

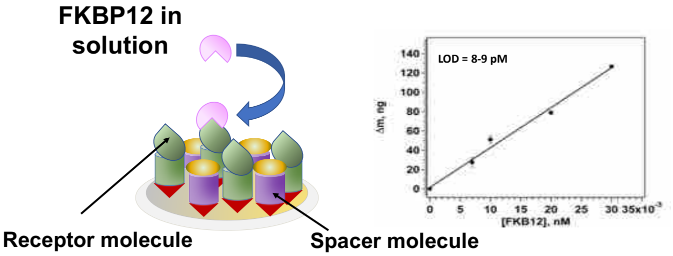
Results

For fluoreceptor-based bioassay development, FK506 is recognized by a recombinant FKBP12 fused to the Emerald Green Fluorescent Protein (EmGFP). The sample is incubated with the recombinant protein and the free FKBP12-EmGFP is captured by magnetic beads (MB) functionalized with FK506 generating the fluorescent signal. FKBP1A-EmGFP exhibits a strong fluorescence at 511 nm upon excitation at 484 nm (max.), an emission quantum yield of 0.70 and a fluorescence lifetime of 3.07 ns. The interaction between the recombinant receptor and the drug has been comparatively evaluated with a quartz crystal microbalance (QCM): the His-tag FKBP12-EmGFP was immobilized on the QCM sensor using a self-assembled layer of Ni-NTA that captures the His-tag moiety of the protein. QMC measurements of spiked samples provided the adsorbed mass of FK506 together with the details of the structure of the recombinant protein layer.



Several parameters have been optimized to improve the sensitivity of the assay, showing a limit of detection of 3 ng mL-1 and a dynamic range of 5 – 70 ng mL-1, fitting the therapeutic requirements. The bioassay has been applied to the analysis of FK506 in whole blood samples, obtaining good recovery rates1.

Direct detection of the protein FKPB12 was accomplished using a nanoarchitecture formed by a tailor-made receptor for FKBP12 diluted in an antifouling matrix, all molecules were designed to allow for chemical immobilization on a QCM and/or SPR sensors2.



QCM measurements as a function of composition of the nanoarchitecture revealed the optimal configuration for FKPB12 sensing in solution.The results showed excellent detection limits and selectivity for FKBP12.

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2C – Chemical characterisation and antihypertensive effects of locular gel and serum of Lycopersicum esculentum l. var. “camone” tomato in spontaneously hypertensive rats

P. Marcolongo, A. Gamberucci, G. Tamasi, A. Pardini, C. Bonechi, C. Rossi, R. Giunti, V. Barone, A. Borghini, P. Fiorenzani, M. Frosini, M. Valoti, F. Pessina

Aims

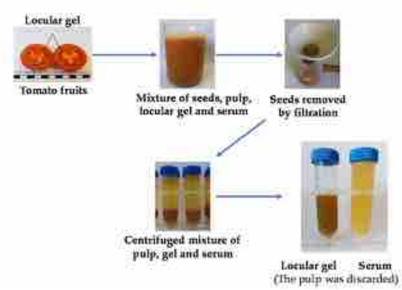
Tomato is widely consumed and rich in healthy components (i.e., carotenoids, vitamins and polyphenols). The aim of this study was to evaluate the chemical composition and antihypertensive effects of locular gel reconstituted in serum of green tomatoes of “Camone” variety. Tomato serum and locular gel were chemically characterised. The antihypertensive effects of the locular gel in serum, pure tomatine, and captopril, administered by oral gavage, were investigated for 4 weeks in male spontaneously hypertensive and normotensive rats. Systolic blood pressure and heart rate were monitored using the tail cuff method. Body and heart weight, serum glucose, triglycerides and inflammatory cytokines, aorta thickness and liver metabolising activity were also assessed. Locular gel and serum showed good tomatine and polyphenols content. Significant reductions in blood pressure and heart rate, as well as in inflammatory blood cytokines and aorta thickness, were observed in spontaneously hypertensive rats treated both with locular gel in serum and captopril. No significant effects were observed in normotensive rats. Green tomatoes locular gel and serum, usually discarded during tomato industrial processing, are rich in bioactive compounds (i.e., chlorogenic acid, caffeic acid and rutin, as well as the glycoalkaloids, α-tomatine and dehydrotomatine) that can lower in vivo blood pressure towards healthier values, as observed in spontaneously hypertensive rats.

Results

Tomato extracts are particularly rich in antioxidants (e.g., carotenoids such as lycopene and vitamin E) which help to reduce blood pressure in patients with mild hypertension never treated with antihypertensive drugs.

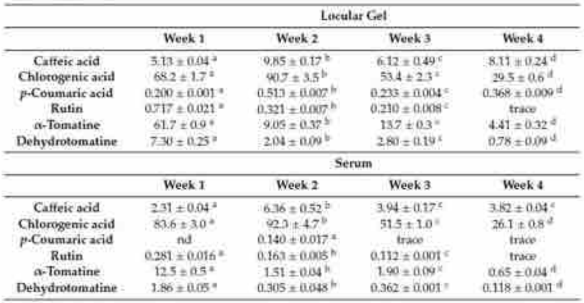
In this study, our attention was mainly focused on the blood pressure lowering effects of tomatoes of the Camone variety. We investigated the gel-serum (Gs), which surrounds the seeds, normally discarded during industrial processing of tomato concentrate, tomato pulp and tomato sauces, and recently chemically characterised.

We used spontaneously hypertensive rats, a well-known animal model of hypertension. These rats are considered suitable for studying the antihypertensive properties of drugs or dietary supplements as the development of hypertension is very similar to that in humans



Our research shows, for the first time, that a quite prolonged treatment with Gs induced a significant decrease in blood pressure, similar to that caused by the antihypertensive drug captopril, with respect to untreated SHRs.

Table 1. Polyphenols and glycoalkaloids content in gel and serum from Camone tomatoes sampled in four different weeks.



	Locular Gel			
	Week 1	**Week 2**	**Week 3**	**Week 4**
Caffeic acid	5.13 ± 0.04 ^{a}	9.85 ± 0.17 ^{b}	6.12 ± 0.49 ^{c}	8.11 ± 0.24 ^{d}
Chlorogenic acid	68.2 ± 1.7 ^{a}	90.7 ± 3.5 ^{b}	53.4 ± 2.3 ^{c}	29.5 ± 0.6 ^{d}
***p*-Coumaric acid**	0.200 ± 0.001 ^{a}	0.513 ± 0.007 ^{b}	0.233 ± 0.004 ^{c}	0.368 ± 0.009 ^{d}
Rutin	0.717 ± 0.021 ^{a}	0.321 ± 0.007 ^{b}	0.210 ± 0.008 ^{c}	trace
α-Tomatine	61.7 ± 0.9 ^{a}	9.05 ± 0.37 ^{b}	13.7 ± 0.3 ^{c}	4.41 ± 0.32 ^{d}
Dehydrotomatine	7.30 ± 0.25 ^{a}	2.04 ± 0.09 ^{b}	2.80 ± 0.19 ^{c}	0.78 ± 0.09 ^{d}
	Serum			
	Week 1	**Week 2**	**Week 3**	**Week 4**
Caffeic acid	2.31 ± 0.04 ^{a}	6.36 ± 0.52 ^{b}	3.94 ± 0.17 ^{c}	3.82 ± 0.04 ^{c}
Chlorogenic acid	83.6 ± 3.0 ^{a}	92.3 ± 4.7 ^{b}	51.5 ± 1.0 ^{c}	26.1 ± 0.8 ^{d}
***p*-Coumaric acid**	nd	0.140 ± 0.017 ^{a}	trace	trace
Rutin	0.281 ± 0.016 ^{a}	0.163 ± 0.005 ^{b}	0.112 ± 0.001 ^{c}	trace
α-Tomatine	12.5 ± 0.5 ^{a}	1.51 ± 0.04 ^{b}	1.90 ± 0.09 ^{c}	0.65 ± 0.04 ^{d}
Dehydrotomatine	1.86 ± 0.05 ^{a}	0.305 ± 0.048 ^{b}	0.362 ± 0.001 ^{c}	0.118 ± 0.001 ^{d}

Data are reported as mean ± SD ($n = 27$) and are expressed as mg/kg fw. Values with different letters in the same row are significantly different (ANOVA with Tukey test, $p < 0.05$). nd, not detected: <limit of detection (LOD); trace: <limit of quantification (LOQ). Caffeic acid, p-Coumaric acid, Rutin and α-Tomatine: LOD/LOQ = 0.10/0.03 mg/L standard. Dehydrotomatine: LOD/LOQ = 0.30/0.10 mg/L standard. Chlorogenic acid: LOD/LOQ = 0.50/0.20 mg/L standard.

The effect of Gs was significant at the end of Week 4, while captopril lowered blood pressure already at Week 2. Tomatine showed a similar trend to Gs, but blood pressure reduction was not significantly different from that of SHRs treated with vehicle.

The long treatment necessary to show the effect of Gs depends on the fact that the used fraction is not a drug. This suggests that tomato Gs supplement can be used as continuous preventive treatment to prevent an increase in blood pressure.

The results suggest that Gs obtained from the Camone tomato variety had beneficial effects on systolic blood pressure and correlated parameters in hypertensive rats. The antihypertensive effects of tomato are a cheap and easy way to restore normal blood pressure and to avoid or delay drug therapy in patients with mild hypertension. The present results provide clear evidence that a diet supplemented with Gs delays the development of hypertension, limiting blood pressure increase, and that the tomato is a rich source of healthy bioactive components.

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2C – Hybrid materials for drug-delivery

M. Bini, G. Bruni, C. Milanese, A. Girella et al.

Aims

A large part of the drugs on the market is poorly soluble in the gastro-intestinal tract, so requiring the administration of high dosages to reach the minimum effective daily dose. The development of systems or methods allowing to improve the drug solubility is a forefront and interesting topic for the pharmaceutical market. The available methods are numerous, including the salt formation, the co-crystal production, the excipients addition or the micronization. In this field, we propose the synthesis of hybrid organic (drug) and inorganic (Layered Double Hydroxides (LDH) or Hydroxyapatite (HAP)) systems to improve the wettability, solubility and drug dissolution rate with respect to the drug alone.

Results

We focused on the synthesis of LDHs based on Mg/Zn and Al ions, in different ratios, to be used for the intercalation of an anti-inflammatory drug (Meloxicam) and a diuretic (Piretanide) one. Both drugs are very poor soluble, so the findings of new way to improve their solubility and dissolution rate is very important for the pharmaceutical market. The hybrids were characterized by X-ray powder diffraction, which is the most important proof to verify the enlargement of the hydroxides layers after the insertion of cumbersome drugs. In addition, SEM/EDS allowed to study the morphology and the distribution of cations in the powders, as well as the possible drug loading, verifying the presence of the elements typical of the drugs. Thermal data, in particular the melting or decomposition temperatures of drugs, are useful to prove the formation of new chemical entities, because of drug intercalation. FT-IR spectroscopy can help to distinguish the drug intercalation into the LDH structure from a simple absorption process. For both Meloxicam and Piretanide we could successfully synthesize the hybrids that showed improved solubility and dissolution rate with respect to the drug alone, as well as to commercial products.

The diuretic Furosemide was instead adsorbed onto HAP surfaces. The hybrids were characterized by the physico-chemical techniques described above, demonstrating the successful synthesis. In this case, we could determine that the hybrids' wettability was improved with respect to the separated entities, so justifying the excellent dissolution rates measured in different media at various pH values.

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Inorganic and Organometallic Polymers and Materials, doi: 10.1007/s10904-022-02302-3 (2022).

2C – Inhibitors of SHP2 protein-protein interactions: a new strategy for a crucial oncogenic target (airc ig2020, lazioinnova gruppi di ricerca 2020, funded)

L. Stella (PI), G. Bocchinfuso, S. Bobone, C. Fulci, C. Storti (and other group members not part of CSGI)

Aims

The Src homology-2 domain-containing phosphatase 2 (SHP2), encoded by PTPN11, is a central node in RAS signaling and cancer and a pivotal target for anticancer therapy. PTPN11 mutations cause ~35% of cases of juvenile myelomonocytic leukemia and occur in other malignancies. In addition, SHP2 is required for survival of RTK-driven cancer cells, contributes to resistance to anti-cancer drugs and modulates immune checkpoints.

SHP2 comprises a catalytic PTP domain, and two SH2 domains (N-SH2 and C-SH2) mediating its interaction with phosphotyrosine-containing binding partners. Under basal conditions, the N-SH2 domain blocks the PTP active site and SHP2 is inactive. Most JMML mutations perturb this autoinhibited structure, enhancing basal phosphatase activity, simultaneously causing an increase in SHP2 affinity for binding partners. Several evidences indicate that the latter effect is the main driver of RAS pathway hyperactivation caused by PTPN11 mutations.

Molecules targeting the catalytic site of the phosphatase are poorly selective; allosteric drugs, stabilizing the autoinhibited conformation, are more promising, but they are ineffective on PTPN11 mutantsdestabilizing the closed state.

In the previous IG2016, we designed and patented peptide-based inhibitors of SHP2 protein-protein interactions, targeting the N-SH2 domain. These non dephosphorylatable phosphopeptidomimetics (NDP) have nM dissociation constants, are resistant to degradation and can be delivered intracellularly by cell penetrating sequences.

NDPs developed in IG2016 represent a promising starting point for a novel therapeutic strategy, but they can be significantly improved and a throughout assessment of their efficacy is required. These molecules are also powerful tools to clarify crucial unanswered questions on SHP2 function and regulation.

The aims of the present project are to:

1-Enhance the affinity, selectivity, and delivery of NDPs, and test their effects in cellular and animal models, bringing them closer to therapeutic applications.

2-Use the NDPs to address questions such as: do SHP2's cognate proteins play a role both as substrates and binders? What is the interdomain arrangement in the active, bound state? How do mutations affect the subcellular localization of the enzyme?

2C – Kinetics of glucosinolate hydrolysis by myrosinase in Brassicaceae tissues: A high-performance liquid chromatography approach

A. Pardini, G. Tamasi, F. De Rocco, C. Bonechi, M. Consumi, G. Leone, A. Magnani, C. Rossi

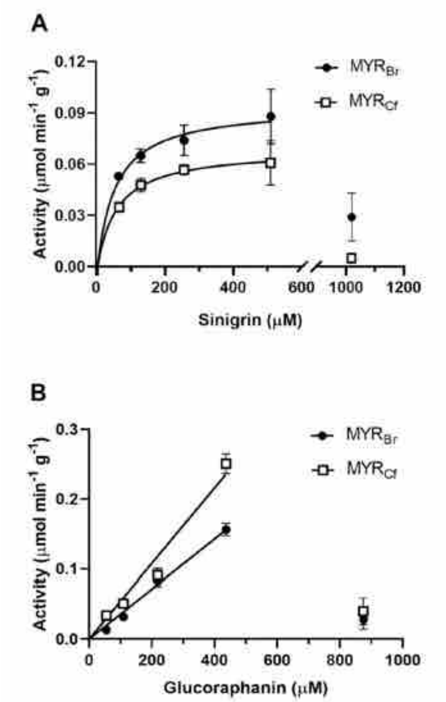
Aims

Glucosinolates are a group of secondary metabolites occurring in all the vegetables belonging to the Brassicaceae family. Upon tissue damage, glucosinolates are hydrolyzed by myrosinase to a series of degradation products, including isothiocyanates, which are important for their health-promoting effects in humans. The glucosinolate myrosinase system has been characterized in several Brassica species, of which white mustard (Sinapis alba) has been studied the most. In this study, a new HPLC-UV assay to evaluate the activities and kinetics of myrosinases in aqueous extracts, which closely represent the physiological conditions of plant tissues, was developed. This method was tested on myrosinases extracted from broccoli and cauliflower inflorescences, employing sinigrin and glucoraphanin as substrates. The results showed a strong inhibition of both enzymes at high substrate concentrations. The main issues related to kinetic analysis on the glucosinolate-myrosinase system were also elucidated.

Results

In this work a new HPLC-UV assay for the determination of MYR activity in aqueous extracts of Brassicaceae tissues is proposed. This method offers the possibility of analyzing samples characterized by high MYR activity, since the reliable operating range of HPLC-UV is much broader with respect to that allowed by traditional spectrophotometric assays. Moreover, through the aid of chromatography it is possible to directly quantify the target GLSs, eliminating possible interferences given by other compounds occurring in the reaction mixtures. The results of preliminary tests performed on MYRSa were compared with those obtained by the UV assay, demonstrating that method is also suitable for kinetic analysis.

The main advantage offered by the HPLC-UV assay is the possibility of analyzing aqueous extracts of Brassicaceae tissues, eliminating the necessity of a preventive purification of the enzyme. This feature can represent a valuable tool to better understand the kinetic behaviors of MYRs in their natural physiological environment. Furthermore, these data can give useful information regarding the capacity of the MYRs naturally occurring in plant material to hydrolyze GLSs.



Michaelis-Menten kinetic plots of MYRBr and MYRCf, employing (A) sinigrin and (B) glucoraphanin as substrates, obtained by the HPLC-UV assays.

The inhibiting effect of high GLS concentration on broccoli MYRs has already been reported (Roman et al., 2018). The analyses performed by the HPLC-UV assay revealed a strong inhibiting effect also on MYRCf at high substrate concentrations.

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2C – Physico-Chemical Properties of Pharmaceutical Systems

G. Bruni, V. Berbenni, C. Milanese, A. Girella, A. Marini

Aims

Co-crystals are an efficient and trendy expedient to tailor the physico-chemical properties of drugs and in particular to enhance the solubility and dissolution rate of poorly water-soluble active principles so that their absorption from the gastro-intestinal tract can be improved and the desired therapeutic benefits can be reached in short times. The proper characterization of solid systems of pharmaceutical interest requires the use of different investigation techniques but surely an important contribution come from DSC measurements. Although differential scanning calorimetry is widely used in pharmaceutical research in the study of solid systems, almost always it is used at a level lower than that which the potential of the investigation technique would make possible. The modest level concerns both the experimental aspects, related to the preparation of samples and the execution of measurements, and the theoretical aspects, related to the processing of the results of the measurements. The present research activity aims to demonstrate, by devoting attention to both aspects, that it is possible to obtain information that could hardly be obtained with other investigation techniques. Systems particularly complex such as that of zaltoprofen/ 4,4’-bipyridine and of probenecid/benzamide constitute excellent tests bed to illustrate the potential of the DSC technique.

Furthermore, a deep study of the thermal behavior of glipizide, a hypoglycemic drug, was carried out with the aim of clarifying whether the recognition of its polymorphic forms can really be done on the basis of the endothermic peak that the literature studies attribute to the melting of the compound.

Results

As for many pharmaceutical solid systems, the thermal behaviors of the binary mixtures zaltoprofen/4,4’ bipyridine (Z/B) and of probenecid/benzamide are without any doubt very complex because of the appearance of several exothermic and endothermic peaks, different from those of the pure components, whose presence, onset temperature, intensity and area strongly depend on the system composition and the heating rate. Here we proved that by a proper experimental design combined with a thorough quantitative analysis of the data it is possible to reach an exhaustive comprehension of the solid phases formed and of the physico-chemical phenomena occurring in the systems.

According to our thermodynamic model, based on a careful qualitative analysis of the DSC traces and on an in-depth quantitative analysis of the melting enthalpies of two eutectic mixtures, Z and B can form two different co-crystals, CC1 with molar composition Z:B = 1:3, and CC2 with composition Z:B = 2:1. Only CC1 is formed for compositions with a Z content less than or equal to that characteristic of CC1, while only CC2 is formed for compositions with a Z content greater than or equal to that characteristic of CC2. For compositions with an intermediate Z content between those of CC1 and CC2 there is a concomitant formation of both the co-crystals CC1 and CC2.

The goodness of our model is proved by an excellent agreement between experimental and expected melting enthalpies and is confirmed by the XRPD, FT-IR and NMR measurements which, in addition, put into evidence that the interaction between the components takes place partially already at room temperature as a consequence of their simple mixing.

As far as the system probenecid/benzamide is concerned, we developed a thermodynamic model that addresses all the single processes which could take place during heating and should appear in the DSC curves if enough time was left to their occurrence and if they didn't hidden reciprocally for kinetics reasons: melting of the metastable eutectic mixture formed by probenecid and benzamide (EU1) with composition $x_{PRO} = 0.2$; crystallization of the cocrystal (CC) with composition $x_{PRO} = 0.5$ and of the excess component with respect to the cocrystal composition; melting of the eutectic mixture formed by the cocrystal and benzamide (EU2) with composition $x_{CC} = 0.4$; melting of the cocrystal. The model here proposed well agrees with the enthalpy values measured for the physical mixtures of different composition.

Furthermore, we obtained new information about the thermal behavior of glipizide, which can be of interest both from a scientific point of view and from a practical point of view, (i.e., for the pharmaceutical industry). First, we shed light on the process responsible for the endothermic peak present in the DSC curves of glipizide, and the reason why different batches of this compound can show the above peak at a different temperature was revealed, correcting the literature data attributing the peak to a melting process whose temperature can be used to differentiate the polymorphic forms of the compound.

Thanks to a proper experimental design, we obtained strong evidence that the DSC peak corresponds to a decomposition process and found a new polymorph of this compound, unknown until now.

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2C – Potential utilization of olive-oil mill by-products for food applications: the 'olive vinegar' case study

A. De Leonardis, A. Iftikhar, V. Macciola

Aims

Both the cultivation of olive trees and the process of industrial production of olive oil generate enormous quantities of solid wastes and dark liquid effluents, most of them with no practical applications and environmental problems. Conversely, these wastes, thanks to their abundance in nutrients, value-added additives and bioactive compounds, could be viewed as “raw materials” for the recovery of high value-added compounds. Nowadays, there is an evident growing interest in obtaining new vinegar variety from alternative substrates, especially from by-products of food industry. Aim of the developed research has been that to realize vinegar from olive-oil mill by-products, specifically from olive-mill wastewater (OMW) and olive leaves (OL).

Results

Olive vinegar obtained from OMW appeared permanently clear, vinous-red colored and without any abnormal smell. Acetic acid level up to 4% is performed by applying both the alcoholic-acetous double fermentation with addition of Saccharomyces cerevisiae starter and the spontaneous acetification without addition of any other starter. OMW vinegar was characterized by huge presence of mineral compounds (ash 2%) and phenol substances (total phenols higher than 4 g/L as GAE), especially hydroxytyrosol. Olive leaf (OL) vinegar was obtained by maceration of dried olive leaves (at a 10:90 w/v leaves/vinegar ratio) in wine vinegar (OL-Wv) and alcoholic 18% vinegar (OL-Alc18). Total phenols of OL-Alc18 was about 5 g/L as GAE, while those of OL-Ww was about 3 g/L evidencing a phenol solving power acetic-acid-concentration-dependent. Oleuropein was found to be the most abundant phenol compounds in the OL vinegar. Both OMW and OL vinegar had shown an excellent antioxidant activity in food.

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2C – Study of cellular alterations induced by exposure to professional ultrasound

ID 43: Project funded by INAIL within the BRiC 2019 initiative
Coordinator: Fabio Domenici

F. Domenici, I. Silvestri, A. Sgura, I. Udroiu, S. Giantulli, D. Palmieri, E. Tortorella, F. Todaro, M. Piermarini, A. Bedini, M. Mattei, R. Cicconi, G. Paradossi, S. Scarpa, S. Morrone

Aims

The project is aimed at expanding and interconnecting the information available to date on the range of structural, ultrastructural and biological effects (including inflammatory, cytotoxic and cytogenetic effects) produced by ultrasound at medium and high frequency under subcavitational conditions on healthy and neoplastic cells (epithelial, connective and endothelial) of human and murine origin and in vivo. The project will be developed through the interplay of three partners operating at the three main Universities of Rome: "Tor Vergata", Dipartimento di Scienze e Tecnologie Chimiche; "Sapienza", Dipartimento di Medicina Molecolare; "Roma3", Dipartimento di Scienze. The in vivo tests will take place at CIMETA, University of Rome "Tor Vergata".

Results

Our results showed that Low Intensity Pulsed Ultrasound exposure at 1 MHz for 1 hour at a spatial average temporal intensity (Ispta) of 65 mW / cm^2 promotes transient activation of proinflammatory interleukin IL-6, both at the level of gene overexpression and protein hypersecretion. This over-expression is triggered by nuclear factor-κB (NF-κB, immunofluorescence test. Furthermore, we observed a slight reduction in cell proliferation dependent on exposure parameters together with alterations in membrane permeability. The results obtained paved the way to further investigations on the molecular mechanisms linked to the triggering of proinflammatory and cytogenetic processes induced by ultrasound, still under development*, in vitro*, *in vivo* and *ex vivo*.

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2C – Substrate activation of the low-molecular weight protein tyrosine phosphatase A (MptpA) from Mycobacterium tuberculosis

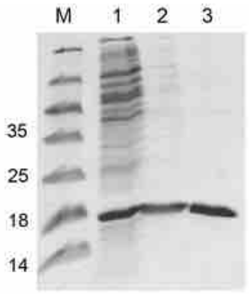
A. Stefan, F. Dal Piaz, , A. Girella, A. Hochkoeppler

Aims

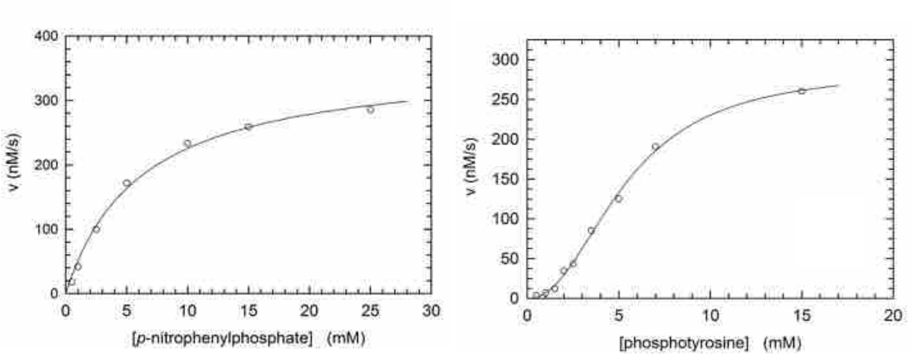
Mycobacterium protein tyrosine phosphatase A (MptpA) is a low-molecular-weight protein tyrosine phosphatase (17.9 kDa) essential for the pathogen to escape the host immune system. In particular, this enzyme is able to inactivate by dephosphorylation the host VPS33B (vacuolar protein sorting 33B) protein. This event inhibits phagosome-lysosome fusion consequently conferring virulence to the pathogen.
MptpA undergoes a significant conformational transition during catalysis from the open to the closed active form. Here we analysed the kinetics of hydrolysis of p-nitrophenyl phosphate and phosphotyrosine as substrates to investigate if MptpA was subjected to substrate activation.

Results

Both prokaryotic and eukaryotic PTPases, HMW and LMW, share the same catalytic C(XXXXX)R motif. The three essential catalytic residues (cysteine, arginine, and aspartate) are located in specific loops called P and D loops, respectively. Once p-Tyr is bound, a large conformational rearrangement of the D-loop, containing the catalytic aspartate, prompts its moving towards the P-loop, converting the enzyme conformation from an open to a closed active form. The understanding of this interconversion between enzyme forms could support the identification of inhibitors targeting the active site. Therefore, the identification of a secondary substrate binding site (allosteric site) could trigger the exploration for highly specific allosteric inhibitors.
We overexpressed MptpA in *Escherichia coli* strain BL21(DE3) and by means of few chromatographic procedures we were able to obtain approximately 15 mg of purified enzyme from 1 L of bacterial culture (Fig 1, lane 3).



The kinetics of *p*-NPP and pTyr hydrolysis was then determined by performing spectrophotometric assays at 405 or 282 nm, respectively. To calculate the kinetic parameters under steady-state conditions the molar extinction coefficient (ε) for p-nitrophenolate was assumed as equal to 18.3 mM^{-1}cm^{-1} and the difference in extinction between tyrosine and phosphotyrosine ($\Delta\varepsilon_{\text{Tyr-pTyr}}$) was determined as equal to 0.96 $mM^{-1}cm^{-1}$. The kinetic of *p*-NPP hydrolysis obeys the Michaelis-Menten equation (Fig. 2, left) whereas in the presence of pTyr the dependence of reaction velocities on substrate concentration showed a sigmoidal dependence, suggesting that the enzyme features allosteric transitions (Fig. 2, right). Accordingly, by fitting the Hill equation to the experimental observations V_{max}, k_{cat}, K_m, and the Hill coefficient were determined as equal to 288 ± 10 nM/s, 0.69 ± 0.02 s^{-1}, 5.36 ± 0.25 mM, and 2.21 ± 0.14, respectively.



The release of *p*-nitrophenolate from *p*-NPP and the fluorescence of the mutant MptpA W152F (containing a single tryptophan at site 48) was then analysed under pre-steady-state conditions using a stopped-flow. Reactions were performed at 20 °C in 50 mM Tris-HCl (pH 8), 2 mM EDTA recording the Absorbance at 405 nm to detect the hydrolysis of *p*-NPP (500 μM) and monitoring the fluorescence of enzyme (2.25 μM) by exciting the sample at 280 nm (emission was detected using a longpass filter). Interestingly, under pre-steady-state conditions, we found that substrate activation is kinetically coupled to the closure of the active site in a competent closed form.

In conclusion, both substrates tested, *p*-NPP and pTyr, were effective in activating MptpA by binding to the allosteric site. This activating site could represent a promising target for the screening of specific MptpA inhibitors.

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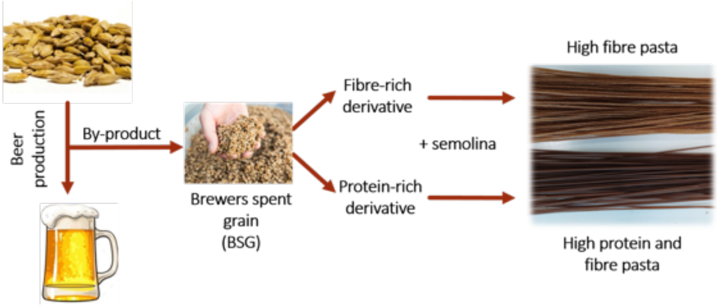
2C – Sustainable Re-Use of Brewer's Spent Grain for the Production of High Protein and Fibre Pasta

F. Cuomo, M.C. Trivisonno, S. Iacovino , M.C. Messia, E. Marconi

Aims

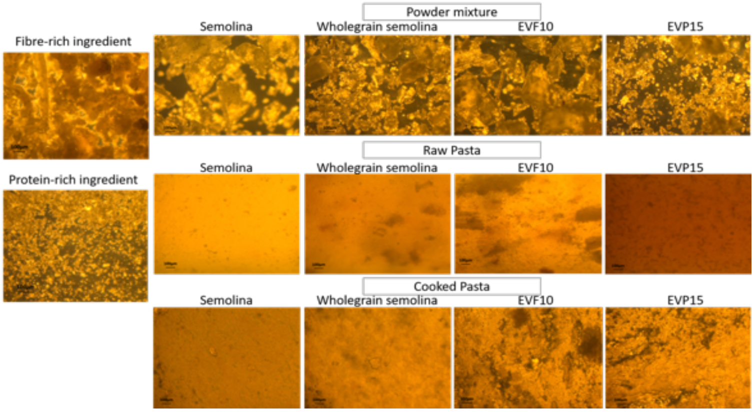
Brewer's spent grains (BSG) are one of the principal by-products of the brewing industry. For protein and fibre content, BSG represents an interesting raw material to be reused for manufacturing many other products. To maximize the nutritional characteristics of this by-product ingredients derived from BSG were included in the design of innovative dry pasta. Two BSG derivative ingredients, one enriched in proteins and the other in fibre were blended with semolina to formulate pasta responding to the claims "High Protein" and "High Fibre" according to EU regulation 1924/2006.



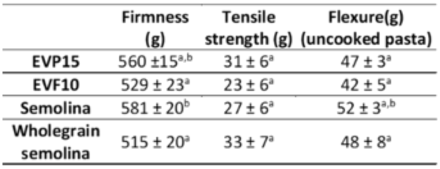
Results

Based on the empirical rheological evaluation, the optimal amount of the two ingredients for producing pasta was determined. In particular, pasta responding to the claims "High Protein" and "High Fibre" was realized using the formulation enriched with 15% of protein-rich ingredient (EVP15) and the claim "High Fibre" and "Source of proteins" using the formulation enriched with 10% of fibre-rich ingredient (EVF10).

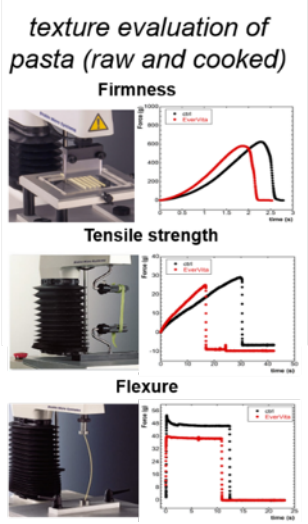
The aspect of pasta made with the two ingredients was quite different. Diffused whitish spots characterized the surface of pasta made with the fibre-rich ingredient. Starting powder formulations, dry spaghetti and cooked pasta were observed at the optical microscope. The fibre-rich ingredient presented long wires of fibre having dimension comparable with the mean particle size (about 320µm) of the ingredient. The same wires were also detectible in powder formulation and in dry and cooked pasta. Smaller structures having similar aspect to the fibres rich ingredient were also visible in dry pasta of wholegrain semolina. The protein-rich ingredient, on the contrary, provided pasta (dried and cooked) with a more homogeneous pattern probably because of the mean particle size of the starting product (50µm), as confirmed by the images of the ingredient at the optical microscope.

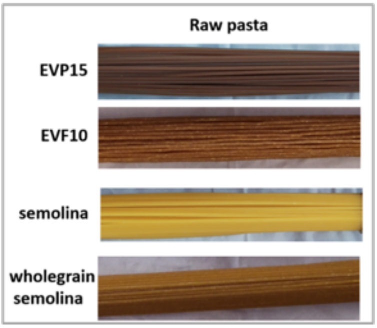


The final products were compared to 100% semolina and 100% wholegrain semolina pasta for composition, color, texture, and cooking quality, revealing excellent quality characteristics, similar to control pasta.



	Firmness (g)	Tensile strength (g)	Flexure(g) (uncooked pasta)
EVP15	560 ±15^{a,b}	31 ± 6^{a}	47 ± 3^{a}
EVF10	529 ± 23^{a}	23 ± 6^{a}	42 ± 5^{a}
Semolina	581 ± 20^{b}	27 ± 6^{a}	52 ± 3^{a,b}
Wholegrain semolina	515 ± 20^{a}	33 ± 7^{a}	48 ± 8^{a}





Pasta evaluation evidenced that the formulated products represented a successful match of technological aptitude, nutritional and sensorial quality, and sustainability.

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2C – Synthesis and biomedical applications of tumor targeting peptidomimetics and conjugates (PRIN2020, funded)

L. Stella (PI of the local unit), S. Bobone, C. Troiano (and other group members not part of CSGI)
National Project coordinated by F. Formaggio, University of Padua

Aims

The present project joins the well established expertise of the participating groups in the design, synthesis, conformational and bioactivity studies of peptides and peptidomimetics. The common goal is to tackle tumors, since peptides are emerging as ideal antitumor drugs, mainly because of their specificity and low off-target effects. The poor pharmacokinetic properties of peptide, including plasma stability, can be overcome by using peptidomimetics, while retaining peptide versatility and feasibility. Three targets were selected to selected to hit a cancer cell by different strategies: (i) over-expressed antigens on the cell surface, (ii) oncogenic protein-protein interactions inside the cell or (iii) the cell membrane itself.

2C – Synthesis and characterization of carriers for improved drugs' solubility and release

D. Capsoni, G. Bruni, D.M. Conti

Aims

Solubility of the drugs is a crucial parameter controlling oral drug absorption in the gastrointestinal tract and its permeability through the gastrointestinal membrane. Poor soluble and permeable drugs often display insufficient and variable bioavailability, leading to negative concerns on safety and effectiveness. Several approaches are developed to enhance the bioavailability of these drugs. Among them, the use of new and suitable substrates/carriers displaying high loading capacity and capable to control rate and released amount of the drugs, seems very promising in terms of simultaneous delivery of various active principles, and advantageous cost-effectiveness ratio. In the present research project, we synthesize and characterize by several techniques (XRPD, SEM-EDS, TEM, TGA, FT-IR spectroscopy) some Metal Organic Frameworks (MOFs) and Layered Double Hydroxides (LDH) as suitable carriers to control the loading and the release of carprofen and zaltoprofen, two poorly soluble active principles belonging to the class of non-steroidal anti-inflammatory drugs (NSAIDs). MOFs display very interesting features suitable to load and control the release of drugs, such as high pore volumes (up to 90% of the crystal cell volume), large surface areas (up to 7000 m^2 / g), multiple topologies and the possibility of tuning the size and shape of the pores themselves by choosing suitably the metal ion and the organic linker. LDHs display an ordered structure able to host/exchange anions into the interlayer space between metal hydroxide blocks. LDH can be successfully intercalated with antibiotics, antihypertensives, anticarcinogens, and anti-inflammatory drugs.

Results

We investigate MIL-100(Fe)/Carprofen, MIL-101(Fe)-NH_2/Carprofen, and MIL-100(Fe)/Zaltoprofen systems.

The MIL-100(Fe)/Carprofen gives the best performances in drug delivery. The MIL-100(Fe) is successfully synthesized and is crystalline. Different temperature conditions were explored to activate the MOF: the MIL-100(Fe) sample activated under dynamic vacuum (10^{-2} bar) at 80 ° C preserves the crystalline structure and displays the highest drug loading value (22.4% wt). The dissolution tests in a pH 4.5 solution (Carprofen is administered orally and pH 4.5 is the acidity of the stomach), demonstrate enhanced dissolution rate (45% of the dose) compared to the carprofen alone (about 8%) in the first hour, related to the release of drug molecules of the surface pores. This evidence suggests the MIL-100(Fe)/Carprofen is a suitable system for the administration of the active principle. At pH 7.5 the Carprofen is highly soluble, and comparable release profiles are observed for the MIL-100(Fe)/Carprofen and the Carprofen alone (release of the 94% wt of the dose in 70 minutes). At this pH a degradation/collapse of the structure is detected by XRPD on the sample recovered after the dissolution test, thus allowing the complete release of drug molecules, even those included in the innermost pores of the MOF.

Secondly, we synthesize a new hybrid organic-inorganic adduct by insertion of the zaltoprofen active principle into the Zn/Al layered double hydroxide. XRPD results demonstrate an increase of the interlayer distance along the *c* axis of the LDH structure, thus confirming zaltoprofen successfully intercalates into the LDH. The active principle inserts as carboxylate anion, as demonstrated by FT-IR spectroscopy, and balances the positive charge of the metal hydroxide block. We investigate the zaltoprofen-LDH interactions by ^{13}C and ^{27}Al solid-state NMR and demonstrate (i) the active principle strongly interacts with the host and the COO- and the OH moieties are involved respectively, (ii) zaltoprofen anions induce local structural changes in the host crystal structure, (iii) similar conformation of the molecules in the zaltoprofen crystal and those inserted into the LDH layers. Dissolution tests at pH 4.5 (gastric environment in fed state) and pH 6.8 (intestinal environment) show improved solubility and dissolution rate of the Zaltoprofen/LDH system (70-80% of the dose released in 2 hours in the two fluids). Moreover, the solubility and dissolution rate seem pH-independent, differently from the active principle alone. The obtained results demonstrate the new LDH/zaltoprofen adduct promote both solubility and dissolution rate of zaltoprofen in different fluids simulating the gastro-intestinal environment, with great advantage for its bioavailability.

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2C – The DNA polymerase from african swine fever virus (ASFV) features high catalytic activity at the expense of recessed DNAs

A. Lapenna, A. Stefan, A. Hochkoeppler

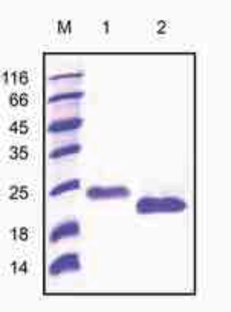
Aims

The ASFV DNA polymerase (Pol X) is the smallest DNA polymerase known (only 174 amino acids) lacking the thumb domain commonly responsible for the binding of the double-stranded portion of the DNA substrate. We present here a study of several DNA substrates containing overhangs or gaps of different length. Our data indicate that ASFV DNA Pol possesses a poor activity in filling DNA gaps, whereas the enzyme features higher activity against DNA substrates containing recessed ends.

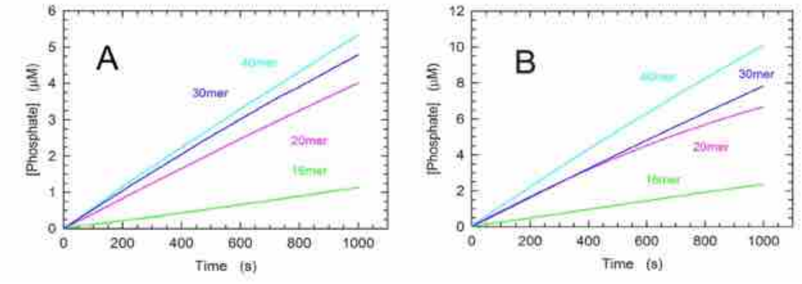
Results

ASFV DNA Pol belongs to the X family of DNA polymerases that includes enzymes essential for DNA repair. All DNA polymerases share a peculiar molecular structure, resembling the shape of an open right hand and containing three main protein domains (denoted thumb, palm, and fingers). In particular, the palm domain is the portion where catalysis occurs, the fingers domain is responsible for the binding of both the template strand and the incoming dNTPs triphosphate, and the thumb domain binds the double-stranded portion of the DNA substrate.

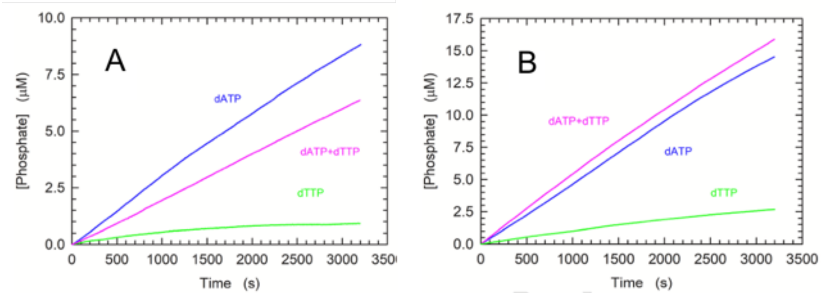
In order to analyse the catalytic activity of ASFV DNA Pol in the presence of recessed or gapped DNA substrates, we produced both the His-tagged and the tag-less enzyme using *Escherichia coli* strain BL21(DE3) as recipient host and pET19b plasmid as expression vector. To purify the His-tagged enzyme we used a HiTrap Chelating affinity column followed by a gel filtration chromatography. For the purification of ASFV Pol X a Cibacron Blue affinity column, a second affinity chromatography with the HiTrap Heparin column and a final gel-filtration were performed. The yield of the tag-less enzyme (lane 2 in gel, Figure 1) was negatively affected by the tendency of the protein to aggregate and was about 2 mg/L, while the yield of the His-tagged enzyme (lane 1 in gel, Figure 1) reached 5 mg/L.



To evaluate DNA polymerase activity, we used the enzyme-coupled assay previously described based on the release of pyrophosphate. Reactions were performed in 100 mM Tris-HCl (pH 8), 10 mM $MgCl_2$, 0.26 mM inosine, 40, 50, and 500 mU/mL of inorganic pyrophosphatase, purine nucleoside phosphorylase, and xanthine oxidase, respectively. Mixtures contained 1 μM dsDNA, 100 μM dNTP (dTTP and/or dATP) and 1.9 μM purified enzyme. We compared the activity of both enzymes at the expense of 4 different recessed DNA substrates, containing polydA overhangs of 1, 5, 15, or 25 bases. Figure 2 shows that faster DNA elongation velocities were detected in the presence of 20mer, 30mer or 40 mer DNAs if compared to the extension of the 16mer DNA substrate. Moreover, we observed a two-fold higher activity of the tagless ASFV Pol X (on right) than the His-tagged protein (on left), irrespective of the substrate used.



We further analysed the catalytic features of ASFV Pol X in the presence of a AT gapped 50-mer DNA substrate containing a polydA and a polydT gap of 15 bases (Figure 3). In the presence of dTTP only, an extremely poor activity was observed (less than 1 nucleotide was incorporated in 1 hour by both enzymes). When the reaction mixture contained dATP only, an initial elongation velocity equal to ca. 3 nM/s (His-tagged protein, left) or 4.5 nM/s (tagless enzyme, right) was detected. Accordingly, ASFV Pol X strongly prefers to incorporate dATP than dTTP.



When we tried a TA gapped 50mer DNA containing a polydT gap followed by a polydA gap, we found that the gap filling at the expense of dATP was three-fold lower than the recessed end extension activity. Our results indicate that ASFV DNA polymerase X features poor activity when filling long gaps and that DNA binding represents the step limiting its catalytic performance.

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2C – Varietal and Geographical Origin Characterization of Peaches and Nectarines by Combining Analytical Techniques and Statistical Approach

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Aims

Prunus persica L. is one of the most important fruit crops in European production, after grapes, apples, oranges and watermelons. Most varieties are rich in secondary metabolites, showing antioxidant properties for human health. The purpose of this study was to develop a chemical analysis methodology, which involves the use of different analytical-instrumental techniques to deepen the knowledge related to the profile of metabolites present in selected cultivars of peaches and nectarines cultivated in the Mediterranean area (Southern Italy). The comparative study was conducted by choosing yellow-fleshed peaches (RomeStar, ZeeLady) and yellow-fleshed nectarines (Nectaross, Venus) from two geographical areas (Piana di Sibari and Piana di Metaponto), and by determining the chemical parameters for the flesh and skin that allow for identification of any distinctive varietal and/or geographical characteristics. A combined analytical and chemometric approach was used, trough rheological, thermogravimetric (TGA), chromatographic (HPLC-ESI-MS), spectroscopic (UVVis, ATR-FTIR, NMR) and spectrometric (ToF-SIMS) analysis. This approach allowed us to identify the characterizing parameters for the analysis of a plant matrix so that the developed methodology could define an easily exportable and extendable model for the characterization of other types of vegetable matrices.

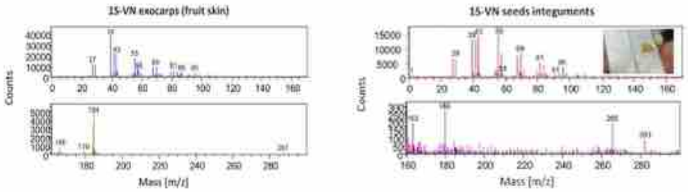
Results

The study developed a method of chemical analysis planned for a full characterization of vegetal products, for human nutrition. In particular, the study was carried out on samples of yellow-fleshed peaches (Prunus persica L. Batsch) and yellow flesh nectarines (Prunus persica L. Batsch, var. Nectarina) of four different cultivars (RomeStar, ZeeLady, peaches; Venus, Nectaross, nectarines) from two geographic areas of Southern Italy, the Sibari Area and the Metaponto Area, located on the Ionian coast of Calabria and Basilicata, respectively. A further sample of commercial nectarine was considered with unknown origin and cultivars. These were chemically characterized by different and complementary analytical techniques, to identify and quantify the chemical composition, with particular efforts to key phytochemical components.

The determinations of the antioxidant capacity (TEAC method, quenching the ABTS°+ radical cation) and total polyphenols (Folin–Ciocalteu method) of mesocarp (flesh pulp) hydroalcoholic extracts revealed as both peaches and nectarines are excellent sources of natural antioxidant polyphenols. HPLC-ESI-MS analysis on mesocarp (flesh pulp) hydroalcoholic extracts, allowed the identification and predominant relative and hydroxycinnamic acids derivatives, with a statistically significant linear relation with findings for antioxidant activity and total polyphenols.

1H-NMR spectra revealed the presence of sugars (sucrose, ⍰- and ⍰-glucose, ⍰-xylose, ⍰-D-fructopyranose) among the main constituents of mesocarp extracts, presenting only minor differences in chemical shift and peaks intensity between samples, in accordance with a chemical composition very similar between peaches and nectarines. The PCA analysis obtained by statistical processing of the 1H-NMR spectra, showed the presence of two outlier samples (ZeeLady-Peach and Nectaross-Nectarine, 2S-NN and 4S-ZP) in accordance with different chemical compositions observed in the high values of chlorogenic acid and neochlorogenic acid from chromatographic measurements.

In agreement with NMR data, IR measurements carried out on lyophilized samples of mesocarps (pulps) and exocarps (skins), confirmed the presence of characteristic bands of –COOH groups of organic acids, –OH groups of sugars, phenols, water, and peptide groups (NH–CO) (amide bands I, II and III) of the proteins. From the comparison between the IR spectra of skin with those of flesh pulp it was established that more intense absorption bands in the region 1800–1500 cm–1 of the exocarp are attributable to cyanidins, while the more intense absorption bands corresponding to sugars between 1200–800 cm–1 are obtained from the mesocarp.



ToF-SIMS analysis confirmed the presence of cyanidin and phosphatidylcholine in the exocarps of peaches and nectarines, and cyanidin, phosphatidylcholine, oleic acid and coniferyl alcohol in the seed integuments. The cluster analysis obtained from the seed integuments constitutes a viable tool for the geographical characterization of peaches and nectarines. The PCA analysis (and cluster analysis), performed on seed integuments ToF-SIMS data, found two varietal grouping for nectarines and peaches and the presence of two outliers.

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2C – Vegetation Indices Data Clustering for Crop Dynamic Monitoring and Classification

S. Marino, A. Alvino

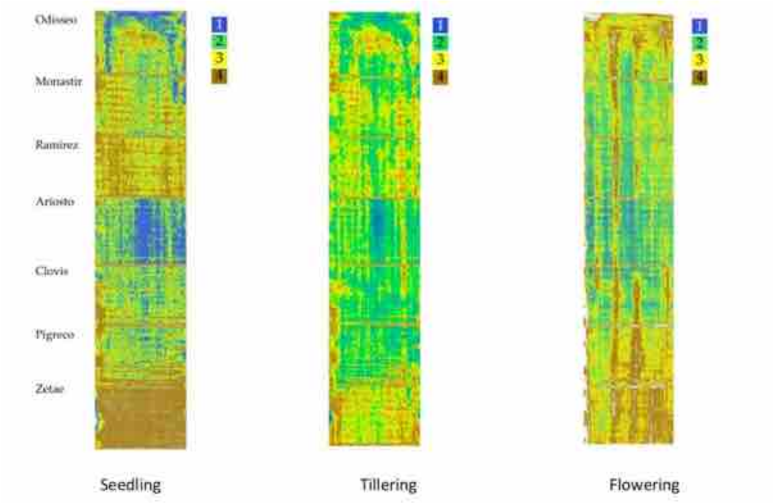
Aims

Monitoring the spatial and temporal variability of yield crop traits using remote sensing techniques is the basis for the correct adoption of precision farming. Vegetation index images are mainly associated with yield and yield-related physiological traits, although quick and sound strategies for the classification of the areas with plants with homogeneous agronomic crop traits are still to be explored.

A classification technique based on spectral information to separate remote sensing data into different groups, using an unsupervised technique such as k-means clustering. The research was performed on seven durum wheat cultivars. Data of three VIs (NDVI, SAVI and OSAVI) collected by a high-resolution UAV were clustered (Ward’s minimum variance approach) at different crop stages (seedling, tillering, and flowering) for delineating clusters area with homogeneous VI values. UAV imagery data were clustered, combining data for three VIs for evaluating a new study approach on remote sensing images in precision agriculture with the aim of improving k-means cluster and completely limit the needs of field data. Agronomic traits (yield and yield components) collected during the crop cycle were used to validate the VI cluster findings and analyze the agronomic crop growth dynamic and classification at every single stage. Furthermore, identified VI clusters at seedling, tillering, and flowering were related to the agronomic yield data collected at harvest. Crop trait dynamics and variability were analyzed. The study aimed to analyze the ability of the cluster method applied to high-resolution UAV VI data to detect yield and yield component dynamics during the crop cycle.

Results

The image segmentation technique combined with multiple VI images collected by a high-resolution UAV at different growing stages allowed the extraction of relevant features associated with yield and yield components. Four clusters were identified and georeferenced; the yield and yield component samples collected were used as ground truth data for validation. In this study, the major findings show that the performance of the remote sensing indices was influenced considerably across the growing stage and cultivars. Furthermore, the most productive areas were always well identified compared to the less productive ones. At the seedling stage, VI clusters led to an identification of areas with greater or less yield potential at harvest, but a lack of a significant relationship with the data collected in this single-stage due to the very small difference between the agronomic yield components. Tillering was the most difficult stage to link VI data to agronomic traits. The widest range of VI values is derived from the crop plasticity and adaptability of wheat. At the flowering stage, VI clusters showed the highest ability to group areas with different agronomic traits and yield. The most productive cultivars were identified by VIs compared to the less productive ones. Some cultivars showed specific spectroradiometric reflectance responses that led to VIs with higher values not related to yield (e.g., Clovis). Some cultivars showed a slight increase in the VI values (and pixel frequency distribution) from seedling to flowering compared to other cultivars (e.g., Odisseo), while others demonstrated the opposite trend (e.g., Ramirez). The cluster method based on multiple VI data can open up a new classification approach in remote sensing data analysis, improving the sensitivity of the grouping procedure while reducing as much as possible the dependence on truth data. The growing stage and cultivar significantly affect the VIs' suitability.



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