



SEDUTA DEL COLLEGIO DEI DOCENTI DEL 36° CICLO

17 Ottobre 2023

Il Collegio dei Docenti del 36° ciclo del Dottorato di Ricerca in Scienze Fisiche e Chimiche dell'Università di Palermo, regolarmente convocato in modalità telematica dal Coordinatore Prof. Marco Cannas, si riunisce sulla piattaforma Microsoft Teams alle ore 16,30 del giorno 17.10.2023 con il seguente ordine del giorno:

1) Adempimenti dottorandi per l'esame finale di conseguimento del titolo di dottore di ricerca (1° sessione)

2) Varie ed eventuali

Presiede il Coordinatore Prof. Marco Cannas, svolge le funzioni di segretario il Prof. Giuseppe Lazzara

Sono presenti

M. Cannas, A. Pettignano, G. Lazzara, F. Messina, F. Ciccarello, F. Ferrante, G.M. Palma, A. Napoli, G. Micela, R. Iaria, T. Di Salvo, D. Valenti, S. Agnello, M. Miceli

Sono assenti giustificati

C. Fazio, F. Reale, S. Milioto, G. Cusumano, S. Miccichè, R. Passante, G. Buscarino, G. Marsella, B. Militello.

Sono presenti inoltre i cotutor A. Sciortino, G. Cavallaro, C. Pinto

Il Presidente, prof. M. Cannas, verificato il numero legale, dichiara aperta la seduta e passa a discutere il primo punto all'ordine del giorno:

1) Adempimenti dottorandi per l'esame finale di conseguimento del titolo di dottore di ricerca

Il presidente illustra la circolare ricevuta dall'Ufficio Dottorati sugli adempimenti necessari per il conseguimento del titolo di dottore di ricerca per gli allievi del 36° ciclo. L'esame finale si potrà svolgere in tre distinte sessioni, così distribuite nell'A.A. 2023/24.

I sessione: 15 novembre – 19 dicembre 2023

II sessione: 20 febbraio – 3 marzo 2024

III sessione: 26 giugno – 6 luglio 2024

Il collegio, dopo ampia discussione stabilisce le date di scadenza per ogni adempimento e per ogni sessione di esame finale, come riportato nel seguente schema:

Scadenza per sessione	Attività previste prima dello svolgimento della prova d'esame	Responsabile
I sessione: 27 ottobre 2023 II sessione: 15 dicembre 2023 III sessione: 19 aprile 2023	Convocazione collegio dei Docenti in merito a: <ul style="list-style-type: none">• Formulazione della relazione del dottorando sulle attività svolte nel corso di dottorato e sulle eventuali pubblicazioni;• Formulazione del parere per il titolo di Doctor Europaeus;• Formazione Commissioni giudicatrici per il conseguimento del titolo di dottore di ricerca;• Nomina Valutatori esterni.	Coordinatore



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I sessione: 30 ottobre 2023 II sessione: 18 dicembre 2023 III sessione: 22 aprile 2023	Il Coordinatore invia la scheda con la proposta di nomina di commissione alla UO Dottorati di Ricerca.	Coordinatore
	Pubblicazione Commissioni giudicatrici. Notifica del Decreto Rettorale tramite posta elettronica al Coordinatore del corso che informerà i componenti della Commissione.	U.O. Dottorati di Ricerca
I sessione: 5 novembre 2023 II sessione: 4 gennaio 2024 III sessione: 12 maggio 2024	Il Dottorando invia la TESI di dottorato al Coordinatore del corso.	Dottorando
I sessione: 6 novembre 2023 II sessione: 5 gennaio 2024 III sessione: 13 maggio 2024	Il Coordinatore invia la TESI ai Valutatori	Coordinatore
I sessione: 4 dicembre 2023 II sessione: 2 febbraio 2024 III sessione: 10 giugno 2024	Valutatori inviano i giudizi sulla TESI al Coordinatore	Valutatori
I sessione: 5 dicembre 2023 II sessione: 3 febbraio 2024 III sessione: 11 giugno 2024	Il Coordinatore informa il Dottorando, il Collegio dei Docenti, il Tutor e l'Ufficio Dottorati, sull'esito della valutazione e invia i giudizi dei valutatori alla UO Dottorati e al dottorando interessato.	Coordinatore
I sessione: 10 dicembre 2023 II sessione: 9 febbraio 2024 III sessione: 18 giugno 2024	Il Dottorando compila online la domanda di ammissione all'esame finale, paga la tassa dovuta e contestualmente carica i documenti previsti: <ul style="list-style-type: none">• copia documento in corso di validità firmato;• dichiarazione coordinatore in caso di Doctor Europaeus;• giudizio valutatore 1;• giudizio valutatore 2;• frontespizio tesi;• presentazione collegio dei docenti;• decreto ammissione o proroga all'esame. Nel caso di documenti non ancora posseduti dal dottorando, la procedura rimane aperta per il caricamento dei suddetti, che deve essere effettuato prima dello svolgimento dell'esame finale.	Dottorando
I sessione: 10 dicembre 2023 II sessione: 9 febbraio 2024 III sessione: 18 giugno 2024	Il Dottorando invia la TESI definitiva in formato elettronico al Coordinatore e la carica su IRIS. Il Coordinatore rilascia al dottorando il documento di "Avvenuto deposito".	Dottorando e Coordinatore
I sessione: 11 dicembre 2023 II sessione: 12 febbraio 2024 III sessione: 19 giugno 2024	Il Coordinatore invia le TESI al Presidente della Commissione d'esame.	Coordinatore
I sessione: 11 dicembre 2023 II sessione: 12 febbraio 2024 III sessione: 19 giugno 2024	Dottorando invia email all'indirizzo mail-protocollo@unipa.it con oggetto [Documenti esami finali dottorando <cognome nome>, <Dottorato>, <ciclo>], allegando: 1 frontespizio della tesi firmato; 2 documento di "Avvenuto deposito" rilasciato dal Coordinatore; 3 dichiarazione deposito legale tesi di dottorato; 4 eventuale richiesta di embargo della tesi.	Dottorando
	ESAMI per il conseguimento del titolo di dottore di ricerca. Sosteranno l'esame per il conseguimento del titolo di Dottore di ricerca solo i dottorandi che sono in regola con il pagamento delle tasse.	Commissione d'Esame e Dottorando



In accordo al cronoprogramma, il presente collegio dei docenti dovrà occuparsi dei seguenti punti:

- formulazione della relazione del dottorando sulle attività svolte
- formulazione del parere per il titolo di Doctor Europaeus
- proposta di formazione delle commissioni giudicatrici
- nomina dei valutatori esterni

per gli allievi che terminano il loro dottorato il 31/10/2023 e intendono sostenere l'esame finale nella prima sessione (15 novembre - 19 dicembre 2023).

Martina Maria Calvino (Tutor: Prof. Giuseppe Lazzara; Cotutor: Dr. Giuseppe Cavallaro)

Il collegio prende visione della relazione del dottorando (allegato 1 al verbale).

Il collegio propone che la commissione giudicatrice per l'esame finale sia composta da:

Membri effettivi

- 1) Francesco Ferrante, Università degli Studi di Palermo
- 2) Pavel Siler, Brno University, Faculty of Chemistry, Institute of Materials Science (Czech Republic).
- 3) Celia Duce, Università di Pisa, Dipartimento di Chimica e Chimica Industriale

Membro supplente

Alberto Pettignano, DiFC, Università degli Studi di Palermo

Il collegio nomina i valutatori esterni:

- 1) Yuriy Stetsyshyn Institute of Chemistry and Chemical Technology, Lviv Polytechnic National University, (Ucraina)
- 2) Rawil Fakhrullin Institute of Fundamental Medicine and Biology, Kazan Federal University, (Russia).

Per l'allieva Marta Maria Calvino, il collegio attesta che sono soddisfatti i criteri per conseguire il titolo di Doctor Europaeus, ed esprime un parere positivo



Marco Reale ((Tutor: Prof. Fabrizio Messina; Cotutor: Dr. Alice Sciortino)

Il collegio prende visione della relazione del dottorando (allegato 2 al verbale).

Il collegio propone che la commissione giudicatrice sia composta da:

Membri effettivi

- 1) Simonpietro Agnello, Università degli Studi di Palermo
- 2) Marinella Striccoli, CNR - Istituto per i processi chimico-fisici (IPCF), Bari
- 3) Francesca Arcudi, Università degli Studi di Padova

Membro supplente

Carlo Maria Carbonaro, Università degli Studi di Cagliari

Il collegio nomina i valutatori esterni:

- 1) Jean-Sébastien Lauret, Université Paris-Saclay (Francia)
- 2) Elena V. Ushakova, ITMO University, St Petersburg, (Russia).

2) Varie ed eventuali

Non ci sono varie ed eventuali.

Il verbale è approvato seduta stante. La seduta si chiude alle ore 17:00.

Il Presidente

Prof. Marco Cannas

Il Segretario

Prof. Giuseppe Lazzara



Allegato 1

PHD IN PHYSICAL AND CHEMICAL SCIENCES, XXXVI COURSE

PhD Candidate: Martina Maria Calvino

Transcript of Records

Tutor: Prof. Giuseppe Lazzara

Cotutor: Dr. Giuseppe Cavallaro

COURSES/SCHOOL/EXAM SCORES:

- **School:**
- [ILL Soft Matter Summer School](#), 4-6 July 2023, Grenoble, France.
- [Network for Equilibria and Chemical Thermodynamics, Advanced Research](#), 27 August 2022, NECTAR TS on Calorimetry COST Action CA18202, Ljubljana, Slovenia.
Exam Score: A
- [Summer School and Workshop in Calorimetry and Thermal Analysis 2022 - Calorimetry and thermal methods in material science](#), 19-24 June 2022, CNRS, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Université Lyon, Lyon, France.
Exam Score: A
- [Thermodynamics and Energetics in Soft Matter Systems](#), 27 May – 22 July 2021, ILL Grenoble, France.
- [School of Physical Chemistry - Supramolecular Interactions in Biological Systems](#), 15-24 June 2021.
- **Courses:**
- [Potenzialità e utilizzo della microscopia elettronica a scansione \(SEM\): Microscopio Fei-Thermofisher versa3D](#), 10 May 2023, Aten Center, University of Palermo.
- [Organic/Inorganic nanocomposites: properties and applications](#), 05-09 July 2021, Dr. G. Cavallaro, University of Palermo.
Exam Score: A
- [Thermodynamic techniques for the characterization of nanostructured materials](#), 21-25 June 2021, Dr. G. Cavallaro, University of Palermo.
Exam Score: A
- [DSC – MDSC – TMA – TGA – DMA – Rheology](#). 12 April – 7 May 2021, TA Instruments.
- [Training Atomic Force Microscopy \(AFM\)](#), 13 January 2021, ATeN Center, University of Palermo.



CONFERENCES/WORKSHOP ATTENDED:

Oral Communications presented by Calvino M.M.:

- *XLIX National Congress of Physical Chemistry (CDCF2023)*, 4-7 September 2023, Torino, Italy. Calvino, M. M., Topgaard D., Cavallaro, G., Lazzara, G., Milioto S., Distinctive properties of Patch Halloysite Nanotubes: NMR study of water confinement and rheological behavior.
- *EMI2023 International Conference*, 27-30 August 2023, Palermo, Italy. Calvino, M. M., Lisuzzo, L., Cavallaro, G., Lazzara, G., Milioto S., Pickering Emulsions Stabilized by Halloysite Nanotubes: a versatile starting material for geopolymers and coating layers preparation.
- *Mediterranean Conference on Calorimetry and Thermal Analysis (MEDICTA 2023)*, 19-21 July 2023, Porto, Portugal. Calvino, M. M., Cavallaro, G., Lisuzzo, L., Lazzara, G., Milioto S., HNT based geopolymers incorporating wax microparticles as sustainable building materials with coating applications.
- *Frontiers in Water Biophysics*, 19-24 May 2023, Erice, Italy. Calvino, M. M., Topgaard D., Cavallaro, G., Lazzara, G., Water diffusion in nanoclays: an NMR study.
- *XVII International Clay Conference ICC 2022*, 25-29 July 2022, Istanbul, Turkey. Calvino, M. M., Cavallaro, G., Lazzara, G., Lisuzzo, L., Milioto S., Halloysite based geopolymers filled with beeswax and halloysite stabilized microparticles with enhanced thermo-mechanical performances.
- *XLVIII National Congress of Physical Chemistry - Physical Chemistry and the Challenges of the Ecological Transition*, 4-7 July 2022, Genova, Italy. Calvino, M. M., Cavallaro, G., Lazzara, G., Lisuzzo, L., Milioto S., New clay-based geopolymers filled with halloysite stabilized microparticles and beeswax.
- *I Italian National Congress on Geopolymers - New frontiers in innovative and green materials for cultural heritage conservation and building industry*, 24-25 February 2022, Catania, Italy. Calvino M. M., Cavallaro G., Lisuzzo L., Milioto S., Lazzara G. New hybrid halloysite based geopolymers with beeswax and microwax particles.
- *SCI 2021 - XXVII National Congress of the Italian Chemical Society*, 14-23 September 2021. Calvino M. M., Lisuzzo L., Cavallaro G., Lazzara G., Milioto S. Shelf-life prediction of paracetamol formulations by non-isothermal thermogravimetry.
- *School of Physical Chemistry 2021 – Supramolecular Interactions in Biological Systems*, 15-24 June 2021. Calvino M. M., Lisuzzo L., Cavallaro G., Lazzara G., Milioto S. Shelf-life prediction of paracetamol formulations through non-isothermal thermogravimetry.



- **Posters presented by Calvino M.M.:**
- [ILL Soft Matter Summer School, 4-6 July 2023, Grenoble, France](#). Calvino M. M., Topgaard D., Cavallaro G., Lazzara G., Milioto S. Investigation of the Properties and Applications of Clay Nanoparticles: From NMR Analysis of Water in Nanoclays to Halloysite-based Geopolymers for Building Materials.
- [BeGeo Scientists – I Congresso Nazionale dei Giovani Geoscientziati, 7-10 October 2021, Napoli, Italy](#). [Calvino M. M.](#), Lisuzzo L., Mazzoleni P., Stroschio A., Lazzara G., Cavallaro G., Barone G., Milioto S. Thermogravimetric characterization of local Sicilian clays and advanced geopolymeric materials.
- [XLII National Conference on Calorimetry, Thermal Analysis and Applied thermodynamics, 27-28 January 2021, Udine, Italy](#), [Calvino, M. M.](#), Lazzara, G., Cavallaro, G., Milioto, S. Thermogravimetric analysis of local Sicilian clays.
- **Workshop:**
- [Heritage Science today: From Archaeological Sites to Museums, 05-06 May 2021, University of the Basque Country UPV/EHU](#).

TECHNICAL REPORTS:

6 Technical Reports (one every six months) for the characterization of sicilian soils/geopolymers/clay-based materials provided by the PI (Edil Ponti S.r.l. company) within the *Sicilia Eco Tecnologie Innovative* (S.E.T.I.) project - Cod.Progetto 2017-NAZ-0204, PO FESR Sicilia 2014/2020– Azione 1.1.5. The PhD scholarship was financially supported by the SETI project.

PAPERS PUBLISHED:

Related to the project:

1. Calvino M. M., Lisuzzo L., Cavallaro G., Lazzara G., Pipitone C., Giannici F., *Beeswax/halloysite microparticles embedded within a geopolymeric layer for the protective coating of steel*. Materials Letters 330 (2023) 133257. (<https://doi.org/10.1016/j.matlet.2022.133257>)
2. Calvino M. M., Lisuzzo L., Cavallaro G., Lazzara G., Milioto S., *Halloysite based geopolymers filled with wax microparticles as sustainable building materials with enhanced thermo-mechanical performances*. Journal of Environmental Chemical Engineering 10 (2022), 108594. (<https://doi.org/10.1016/j.jece.2022.108594>)
3. Calvino M. M., Cavallaro G., Lisuzzo L., Milioto S., Lazzara G., *Separation of halloysite/kaolinite mixtures in water controlled by sucrose addition: the influence of the attractive forces on the sedimentation behavior*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 641 (2022) 128530. (<https://doi.org/10.1016/j.colsurfa.2022.128530>)



4. Calvino M. M., Pasbakhsh P., Cavallaro G., Lazzara G., Milioto S., *Hydrogel Based on Patch Halloysite Nanotubes: a Rheological Investigation*. Submitted to Journal of Colloid and Interface Science.
5. Calvino M. M., Topgaard D., Cavallaro G., Lazzara G., Milioto S., Investigation on the diffusion and relaxation of water in nanoclays exploiting NMR techniques. In Preparation.

Other ISI papers:

6. Calvino M. M., Cavallaro G., Lazzara G., Milioto S., *Talc concentration effect on shelf life of acetaminophen tablets*. Journal of Thermal Analysis and Calorimetry (2023) (<https://doi.org/10.1007/s10973-023-12389-6>)
7. Barbata L.G., Scavuzzo D., Ettlinger R., Calvino M.M., Lazzara G., Gelardi F.M., Agnello S., Cannas M., Russell E. Morris, Buscarino G., *Origin of the solid-state luminescence of MIL-53(Al) and its connection to the local crystalline structure*. Microporous and Mesoporous Materials 361 (2023) 112747 (<https://doi.org/10.1016/j.micromeso.2023.112747>)
8. Ciaramitaro V., Piacenza E., Lo Meo P., Librici C., Calvino M.M., Conte P., Lazzara G., Chillura Martino D. F., *From micro to macro: Physical-chemical characterization of wheat starch-based films modified with PEG200, sodium citrate, or citric acid*. International Journal of Biological Macromolecules 253 (2023) 127225. (<https://doi.org/10.1016/j.ijbiomac.2023.127225>)
9. Calvino M. M., Lazzara G., Cavallaro G., Milioto S., *Inclusion complexes of triblock L35 copolymer and hydroxyl propyl cyclodextrins: a physico-chemical study*. New Journal of Chemistry 46,13 (2022) 6114-6120. (<https://doi.org/10.1039/D2NJ00486K>)
10. Calvino M. M., Lisuzzo L., Cavallaro G., Lazzara G., Milioto S., *Lifetime predictions of non-ionic and ionic biopolymers: kinetic studies by non-isothermal thermogravimetric analysis*. Emergent Materials (2021). (<https://doi.org/10.1007/s42247-021-00259-6>)
11. Calvino M. M., Lisuzzo L., Cavallaro G., Lazzara G., Milioto S., *Non-isothermal thermogravimetry as an accelerated tool for the shelf-life prediction of paracetamol formulations*. Thermochimica Acta 700 (2021) 178940. (<https://doi.org/10.1016/j.tca.2021.178940>)

GRANTS

- **Attendance Grant** for the *Mediterranean Conference on Calorimetry and Thermal Analysis (MEDICTA 2023)*, given by "Associazione Italiana di Calorimetria e Analisi Termica (A.I.C.A.T.)", 19-21 July 2023, Porto, Portugal.
- **Travel Grant** for the *NECTAR TS on Calorimetry, COST Action CA18202 - Network for Equilibria and Chemical Thermodynamics Advanced Research*, given by COST Association, August 27th, 2022, Ljubljana (Slovenija).



- **Attendance Grant** for the *I Italian National Congress on Geopolymers - New frontiers in innovative and green materials for cultural heritage conservation and building industry*, given by “Italian Ceramic Society (I.Cer.S.)” 24-25 February 2022, Catania, Italy.
- **Attendance Grant** for the *SCI 2021- XXVII National Congress of the Italian Chemical Society*, given by “Italian Chemical Society – Division of Physical Chemistry”, 14-23 September 2021.
- **Attendance Grant** for the *XLII National Conference on Calorimetry, Thermal Analysis and Applied Thermodynamics*, given by “Associazione Italiana di Calorimetria e Analisi Termica (A.I.C.A.T.)”, 27-28 January 2021.

RESEARCH WORK ABROAD

Research visit from 06/10/2022 to 30/04/2023 at the Division of Physical Chemistry at Lund University (Sweden) under the supervision of Prof. Daniel Topgaard. The research project investigated the role of water and its confinement in different natural nanoclays. Moreover, NMR techniques allowed to study the self-diffusion and relaxation of water in these systems. The results acquired have been used to write a manuscript, currently in preparation.

MEMBER OF THE ORGANIZING COMMITTEE

13th European Symposium on Thermal Analysis and Calorimetry, 19-22 September 2022, University of Palermo, Italy.

THESIS TITLE:

Halloysite Nanotubes as Versatile Aluminosilicate Precursors for Composite Geopolymers: design, preparation and physico-chemical characterization

ABSTRACT:

The aim of this PhD thesis was the preparation and characterization of new halloysite based geopolymers with a preliminary focus on specific features of the nanoclays used as aluminosilicate precursors.

In the initial part of this project, the main objective was to purify samples of natural halloysite nanoclay since they are often contaminated by a certain level of platy kaolinite nanoparticles, which varies depending on the geological deposit from which they were sourced. In this regard, an easy strategy for the separation of halloysite/kaolinite mixtures in sucrose aqueous solution was proposed, by exploiting the ability of sugar to control the attractive forces of the clay nanotubes as well as the colloidal stability of kaolinite nanoplates in aqueous solvent. The optimization of the separation protocol was achieved in 10 wt% of sucrose solution, at which different sedimentation behaviours of the two nanoclays were observed.

Considering the distinct properties evidenced thanks to the different morphology of these nanoclays, NMR techniques were used to explore the self-diffusion and transverse relaxation time of water in



platy kaolinite and two types of halloysite nanotubes. Various hydration levels were tested, revealing the existence of different water populations. Results indicated that the unique structure of Patch halloysite, with longer and thinner nanotubes, influences both the water diffusion and relaxation features compared to the other nanoclays. Furthermore, it was demonstrated that Patch halloysite,

due to its unique fibrous structure, exhibits distinct rheological properties compared to halloysite sourced from other natural sources, enabling the formation of hydrogel even at low concentrations. Accordingly, a detailed rheological study on patch samples at different concentrations was presented. Following the first part of this research, regarding the characterization of the nanoclays that can be used as precursors in geopolymeric synthesis, a novel protocol for the preparation of halloysite based geopolymers filled with beeswax microparticles was proposed. According to the morphological and structural investigations, microwax spherical particles have been homogeneously dispersed within the geopolymeric network conferring excellent properties to the hybrid geopolymers. For comparison, halloysite based geopolymers filled with variable amounts of beeswax showed that their properties depend on their composition, reflecting the random dispersion of the beeswax. Relevant improvements of the flexibility and heat storage capacity can be achieved only by adding a large amount of beeswax, meaning one order larger than filling with microwax particles. Due to the presence of phase change materials confined in the geopolymeric network, the increased heat storage capacity, combined with the enhanced flexural performances, make this hybrid material suitable in many fields. Additionally, it was demonstrated that the resulting material can be exploited for coating applications as a protective layer on steel substrates. Remarkably, the presence of microwax particles significantly altered the wettability of the steel, enhancing the hydrophobic properties of its surface. These findings have implications for the development of new green clay-based materials and their applications in different fields.

The PhD Board Dean

Prof. Marco Cannas



Allegato 2

PHD IN PHYSICAL AND CHEMICAL SCIENCES, XXXVI COURSE

PhD Candidate: Marco Reale

Transcript of Records

Tutor: Prof. Fabrizio Messina

Cotutor: Dr. Alice Sciortino

Courses/school/exam scores:

- Course: Thermodynamic Techniques for the Characterization of Nanostructured Materials (with final exam); Exam Score: A
- Course: Organic/Inorganic Nanocomposites: Properties and Applications (with final exam) Exam Score: A
- School: School on the Fundamentals of Semiconductive Quantum Dots (with final exam); Exam Score: A
- Course: Time-resolved Photoluminescence
- Course: Femtosecond Spectroscopy
- Course: Atomic Force Microscopy
- Course: Raman Spectroscopy
- Training: “X-rays Photoelectron Spectroscopy”
- Training: “Confocal imaging from basic to advanced”
- Training: “Potenzialità della Microscopia Elettronica ed utilizzo del microscopio a scansione FEI-ThermoFisher Versa 3D”

Conferences/workshop attended:

- Nanoge Online School on Fundamentals of Semiconductive Quantum Dots, 11-13 May (Online)
- eMRS Fall 2021, 20-23 September 2021 (Online)
- 7th Nano Today Conference, 15-18 November 2021 (Online)
- eMRS Spring 2022, 30 May- 3 June 2022 (Online)
- Carbon 2022, 3-8 July 2022 (London)
- eMRS Spring 2023, 29 May- 2 June 2023 (Strasbourg)
- SiO2023, The 14th International Conference on SiO₂, Dielectrics and Related Devices 12-14 June 2023 (Palermo)



Talks:

- **M. Reale**, A. Sciortino, G. Buscarino, A. Emanuele, N. Mauro, M. Cannas, F. Messina, "Self-assembled Carbon dot-Plasmonic nanohybrids with remarkable charge separation and photocatalytic properties", eMRS 2021 Fall
- **M. Reale**, S. Chandra, G. Buscarino, A. Emanuele, M. Cannas, A. Sciortino, F. Messina, "Photoinduced charge separation in self-assembled Carbon dot- Plasmonic functional nanohybrids", eMRS 2022 Spring
- **M. Reale**, A. Sciortino, M. Cannas, E. Maçoas, A. G. Campaña, F. Messina, "Structural-Photophysical Relationships in Atomically-Precise Distorted Nanographenes", Carbon 2022 (London)
- **M. Reale**, S. Chandra, G. Buscarino, A. Emanuele, M. Cannas, O. Ikkala, A. Sciortino, F. Messina, "Modulation of Optical Properties in Self-Assembled Carbon dot-Plasmonic functional Nanohybrids", eMRS Spring 2023 – Strasbourg
- **M. Reale**, A. Sciortino, M. Cannas, E. Maçoas, C. M. Cruz, A. G. Campaña, F. Messina, "Tailoring the photophysics of atomically-precise distorted nanographenes by structural engineering", eMRS Spring 2023 – Strasbourg

Posters:

- **M. Reale**, A. Sciortino, G. Buscarino, A. Emanuele, N. Mauro, M. Cannas, F. Messina, "Charge Separation and Photocatalysis in Carbon dot-Plasmonic nanohybrids", 7th Nano Today Conference, 15-18 Nov 2021

Papers published:

- M. Reale, S. Chandra, G. Buscarino, A. Emanuele, M. Cannas, O. Ikkala, A. Sciortino, F. Messina, "Photoinduced charge separation in functional carbon– silver nanohybrids", Physical Chemistry Chemical Physics, 2022, 24, 12974-12983 (10.1039/D2CP00668E)
- M. Reale, A. Sciortino, M. Cannas, E. Maçoas, A. H. G. David, C. M. Cruz, A. G. Campaña, F. Messina, "Atomically Precise Distorted Nanographenes: The Effect of Different Edge Functionalization on the Photophysical Properties down to the Femtosecond Scale", Materials, 2023, 16, 835 (10.3390/ma16020835)
- M. Reale, A. Sciortino, C.M. Cruz, M. Cannas, E. Maçoas, A.G. Campaña, F. Messina, "The photophysics of distorted nanographenes: Ultra-slow relaxation dynamics, memory effects, and delayed fluorescence", Carbon, 2023, 206, 45-52 (10.1016/j.carbon.2023.02.001)
- J. P. Mora-Fuentes, M. D. Codesal, M. Reale, C. M. Cruz, V. G. Jiménez, A. Sciortino, M. Cannas, F. Messina, V. Blanco, A. G. Campaña, "Heptagon-containing nanographene embedded into [10]cycloparaphenylene", Angewandte Chemie International Edition, 2023, 62, 21, e202301356 (10.1002/anie.202301356)
- A. Pramanik, A. Sciortino, M. Reale, P. Pasbakhsh, G. Cavallaro, M. Cannas, G. Lazzara, F. Messina, "Naturally Occurring Halloysite Nanotubes as Light Scatters for Stable Random Lasing Applications", ACS Applied Nano Materials, 2023, 6, 17, 15896-15905 (10.1021/acsanm.3c02840)



- F. C. Herrera, V. Sireus, P. Rassu, L. Stagi, M. Reale, A. Sciortino, F. Messina, G. J. A. A. Soller-Illia, L. Malfatti, P. Innocenzi, "Chemical Design of Efficient Photoelectrodes by Heterogeneous Nucleation of Carbon Dots in Mesoporous Ordered Titania Films", *Chemistry of Materials*, 2023

Thesis title: Nanocarbons as building blocks for optical hybrid structures

Abstract: Carbon nanomaterials play a central role in the field of nanoscience. In particular, luminescent zero-dimensional nanocarbons (0DNCs) such as Carbon Dots (CDs) and nanographenes (NGs) are garnering significant attention for their efficient light harvesting properties and tunable optical properties. CDs are a relatively recent class of nearly-spherical nanoparticles, typically smaller than 10 nm, consisting of a carbonaceous core a surface shell that can be decorated by a variety of chemical functional groups. On the other hand, NGs are nanosized graphenic fragments with precisely defined structures, synthesized through precise organic chemistry methods that provide tight control over their atomic structure. These 0DNCs can be considered as the carbon-based counterparts of semiconductor quantum dots, which have been just recognized with the Nobel Prize in Chemistry 2023, possessing the advantage of absence of toxic chemical elements with respect to their inorganic analogues. 0DNCs display exceptional optical properties, such as bright optical transition in the visible range and photoinduced charge or energy transfer behaviours. In addition, 0DNCs exhibit an exceptional structural flexibility, which arises from the unique chemistry of carbon, allowing for the design and functionalization of their structures as desired. Because of all these qualities, 0DNCs represent ideal building blocks for creating innovative hybrid structures. By combining them with other opportunely chosen materials, the properties of the different components can be synergistically exploited, enhancing or modulating existing properties or introducing entirely new functionalities absent in the original components. This capability has led to the creation of a diverse range of multifunctional nanohybrids, which are currently a subject of very large scientific interest due to their countless potential applications.

Within this context, the aim of the thesis is to perform a fundamental photophysical study of specific 0DNC-based hybrid materials, based on the use of either NGs or CDs as fundamental building blocks. Firstly, a comprehensive photophysical characterization of a palette of various atomically-precise NGs is performed to investigate the impact of structural variations or slightly different edge functionalization on their optical properties. After the study of their standalone properties, specific NGs are selected to build all-carbon hybrids by coupling them with fullerenes or polystyrene microparticles. In the first case, the supramolecular interactions between a properly functionalized nanographene and fullerenes are exploited to promote photoinduced charge-transfers. In the second case, polystyrene microparticles serve as microresonators to modulate the emission features of the NGs they are doped with to obtain fluorescent microtags with unique spectroscopic characteristics. Moving to the second category of hybrid nanomaterials, various carbon/plasmonic nanohybrid structures are designed through the coupling of a specific type of CDs with silver and gold nanoparticles. Depending on their mutual separation, metallic nanoparticles can act as a charge reservoir to produce charge pair separation or help to modulate the optical properties of CDs *via* plasmonic plasmonic interactions. The results demonstrate the versatility of nanocarbons to form multifunctional hybrid materials, paving the way for diverse applications in the ever-evolving landscape of nanotechnology.

The PhD Board Dean

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