

UNIVERSITY OF GENOVA

*Doctorate Course in Sciences and Technologies
of Chemistry and Materials*

XXIX CYCLE YEARBOOK

The Doctoral School of Chemical and Materials Sciences and Technologies was established in 2005 to activate research doctorates in chemistry or the like. Since 2013 (XXIX Cycle) it has been transformed into one doctorate course with 5 curricula, in which 2 are run in collaboration with the Istituto Italiano di Tecnologia (IIT) (Italian Institute of Technology).

The Doctorate aims to train high quality researchers in all research fields of fundamental chemistry (analytical chemistry, physical chemistry, inorganic chemistry, organic chemistry) and applied chemistry (pharmaceutical chemistry, food and cosmetic chemistry, pharmaceutical technologies, innovative chemical processes, environmental chemistry) as well as materials science, including nanochemistry.

For this purpose, the doctorate programme is structured into five independent curricula:

- Chemical Sciences and Technologies
- Pharmaceutical, Food and Cosmetic Sciences
- Materials Science and Technology
- Nanochemistry
- Drug Discovery and Nanobiotechnologies

The research doctorates gained additional knowledge and skills to those acquired during their previous university studies. In particular, they have been trained to handle and recognize the issues related to specific research sectors, to gain and assimilate the necessary knowledge autonomously and ultimately use it productively to solve them. Furthermore, they have developed their ability to work in groups, to exchange their interdisciplinary skills and give a clear presentation of their research results in both written and verbal form. The research doctorate will therefore be an extremely flexible and versatile figure who will be able to adapt to the new scientific and technological challenges. The balance between gaining and managing skills will enable research doctorates to conduct their important research autonomously with national and multinational companies, research bodies or universities. The doctorate provides an ideal follow-up to university studies, especially for MSc graduates in the following classes LM-13 (Pharmacy and Industrial Pharmacy), LM-17 (Physics), LM-22 (Chemical Engineering), LM-53 (Materials Science and Engineering), LM-54 (Chemical Sciences), LM-71 (Sciences and Technologies of Industrial Chemistry).

Research structure and teaching staff

The Doctoral Course have relied on the collaboration of 4 Departments within the University of Genoa: the Department of Chemistry and Industrial Chemistry, the Pharmacy Department, the Physics Department, the Department of Civil, Environmental and Chemical Engineering, as well as several research units of the Italian Institute of Technology. All these departments are characterized by excellent research standards and numerous collaborations with Italian and foreign industries, universities and research bodies. Besides the structures (laboratories, instrumentation, seminar rooms) provided by these departments, the Doctoral School can rely upon a large number of teaching staff who supervise the PhD students and programme lessons or seminars. All the advisors assigned have counted on substantial research funding and therefore have assured to the Ph. D. students a sufficient budget to carry out the research.

Internationalization

The doctorate course is strongly committed to internationalization and favours the attendance by foreign students. Thus, for the XXIX cycle, 11 out of 24 students were foreigner (46%).

Moreover, all Italian students have been strongly encouraged to spend a secondment period abroad, as stated in the following activity reports.

I hope that this "yearbook" could remain for the new Doctors as a memory of these three years dedicated to the advancement of science, and, we are sure of that, also to the improvement of their own scientific skills and human merits.

To all of them I would like to present my best wishes for a successful and gratifying career!

Adriana Saccone
Director of the Course

MANAGEMENT COUNCILS OF THE COURSE

The course was governed by a Board of Professors, formed by 12 members, and by a Director.

For the XXIV cycle the board of professors was formed by:

- Tiziano Bandiera IIT
- Antonio Barbucci DICCA
- Raffaella Boggia DIFAR
- Olga Bruno DIFAR
- Gabriele Cacciamani DCCI
- Fabio Canepa DCCI
- Maurizio Canepa DIFI
- Gabriele Caviglioli DIFAR
- Massimo Colombo IIT
- Antonio Comite DCCI
- Davide Comoretto DCCI
- Carlo Ferdeghini CNR
- Maurizio Ferretti DCCI
- Paola Fossa DIFAR
- Gianpiero Garau IIT
- Federica Gastaldo DCCI
- Maria Carmela Ianni DCCI
- Roman Krahne IIT
- Silvia Lanteri DIFAR
- Riccardo Leardi DIFAR
- Emanuele Magi DCCI
- Liberato Manna IIT
- Iwan Moreels IIT
- Teresa Pellegrino IIT
- Giovanni Petrillo DCCI
- Mirko Prato IIT
- Marina Putti DIFI
- Gianguido Ramis DICCA
- Annalisa Relini DIFI
- Renata Riva DCCI
- Adriana Saccone DCCI
- Silvia Schenone DIFAR
- Carla Villa DIFAR

RESEARCH ACTIVITY

The total number of credits achieved in 3 years is 180. The research activity is the most important part of the doctorate course. Therefore the School has decided that this activity must correspond to a minimum of 150 credits and a maximum of 160 credits.

The research and course activities of the School are held in the followings Departments: Dep. of Chemistry and Industrial Chemistry (DCCI), Dep. of Pharmaceutical Sciences (DISCIFAR), Dep. of Chemistry and Pharmaceutical and Food Technologies (DICTFA), Department of Chemical and Process Engineering "G.B. Bonino" (DICheP), Department of Physics (DIFI), Italian Institute of Technology (IIT)

At the end of each year, the students presented a written report and an oral presentation on their activity, which were evaluated by the Board of Professor of the doctorate.

COURSEWARE

The remaining 20 to 30 credits are divided into these categories:

- Type A credits: short courses (4-6 hours) given by experts external to the university of Genova. Each course will have a value of 1 credit.
- Type B credits: courses given by the faculty of the School. 1 credit will correspond to 7 hours of lessons. The courses will be either of 2 or 3 credits.
- Type C credits: attendance to seminars held at the Departments involved (or in special cases also elsewhere). 1 credit corresponds to 8 seminars.
- Type D credits: participation to national or international schools for Ph.D. students. Typically a week school will count as 2 credits.
- Type E credits: the student will prepare (also through a bibliographic search) and present a seminar on a particular subject (different from its own research work). A seminar of this kind will correspond to 2 credits.
- Type F credits: only in particular cases, when the student must fill an important gap in disciplines necessary for his/her research work, the student can be invited by the Board of Professors to attend courses activated inside one of the "master" laureas related to the subjects of the school.

Each student has chosen the distribution of these credits according the specific rules independently established by each doctorate course.



Università degli Studi di Genova



**Doctorate in
Sciences and Technologies of
Chemistry and Materials**

CURRICULUM: Nanochemistry

ILARIA ANGELONI

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *December 31th, 2016*

Advisors *Prof. Maurizio Canepa, Dr. Iwan Moreels*

Thesis Title: **Optical properties of colloidal CdSe/CdS nanocrystals.**

Thesis abstract

Thanks to their quantum nature, which allows to tailor their opto-electronic properties using size and shape, colloidal nanocrystals have sparked great interest as a material for photonics. Crucial features are a high photoluminescence quantum efficiency, combined with a controllable photoluminescence spectrum and lifetime. This can be achieved by engineering of band alignment in nanocrystal heterostructures. The first system I have focused on are CdSe/CdS nanorods, which enable us to obtain a configuration where the hole wave function is localized in the core, while the electron wave function can be delocalized into the rod due to a small conduction band offset. I first studied the optical absorption at high energy, in a region where residual quantum confinement is weak and it is thus possible to access the intrinsic optical properties of the material. Then, I applied this knowledge to study the oscillator strength at the band gap, which gives insights into the extent of electron delocalization in the CdS shell. Finally, I used steady-state and time-resolved fluorescence measurements to study CdSe/CdS rod-in-rods, whose band structure is shaped by electric fields induced by interface strain, and dot-in-giant-dots, structures that are nowadays attracting growing interest thanks to the very low thresholds for amplified spontaneous emission and lasing.

ACTIVITY REPORT
Research Activity

The research activity was mainly carried out at Istituto Italiano di Tecnologia (IIT)

Scientific Publications

First author:

- 1) **Angeloni, I. et al.** Disentangling the Role of Shape, Ligands, and Dielectric Constants in the Absorption Properties of Colloidal CdSe/CdS Nanocrystals. *ACS Photonics* **3**, 58–67 (2016).
- 2) **Angeloni, I. et al.** Band-Edge Absorption Properties of Colloidal CdSe/CdS Dot-in-Rods. *submitted*.

Co-author:

- 3) Barthel, M. J., **Angeloni, I.** *et al.* Synthesis of Highly Fluorescent Copper Clusters Using Living Polymer Chains as Combined Reducing Agents and Ligands. *ACS Nano* **9**, 11886–11897 (2015).
- 4) Di Stasio, F., Polovitsyn, A., **Angeloni, I.** *et al.* Broadband amplified spontaneous emission and random lasing from wurtzite CdSe/CdS “giant-shell” nanocrystals. *ACS Photonics* **3**, 2083–2088 (2016).
- 5) Khan, A. H., Brescia, R., Polovitsyn, A., **Angeloni, I.** *et al.* Near-Infrared Emitting Colloidal PbS Nanoplatelets: Lateral Size Control and Optical Spectroscopy. *submitted*.

Communications at Conferences

Poster Communications:

- 1) “*Calculation of the Molar Extinction Coefficient of Colloidal CdSe/CdS Quantum Dot-in-Rods*” presented at the School of Photonics 2014: “Seeing sharp and further with the optical microscope” Cortona, Italy, from 31st March to 4th April 2014.
- 2) “*Calculation of the Molar Extinction Coefficient of Spherical and Anisotropic CdSe/CdS Nanocrystals*” presented at the International Conference of Fundamental Processes in Semiconductor Nanocrystals, Oxford, United Kingdom, from 7th to 10th September 2014.
- 3) “*Calculation of the Molar Extinction Coefficient of Anisotropic CdSe/CdS Nanocrystals*” presented at the E-MRS Spring Meeting, held in Lille, France, from 11th to 15th May 2015.
- 4) “*Optical Absorption to Access the Band Edge Properties of CdSe/CdS Dot-in-Rods*” presented at Plasmonica 2016, held in Genoa, Italy, from 14th to 16th September 2016.

Oral communications:

- 1) Abstract “Optical Properties of Colloidal CdSe/CdS Dot-in-Rods” accepted for oral presentation at Materials2016 in Catania, on 12th December 2016.

Congresses Attended

- 1) School of Photonics 2014: “Seeing sharp and further with the optical microscope”, Cortona, Italy, from 31st March to 4th April 2014.
- 2) “International Conference of Fundamental Processes in Semiconductor Nanocrystals”, Oxford, United Kingdom, from 7th to 10th September 2014.
- 3) E-MRS Spring Meeting 2015, held in Lille, France, from 11th to 15th May 2015. Symposium assistant at Symposium I, Semiconductor nanostructures towards electronic & opto-electronic device applications V, E-MRS Spring Meeting 2015.
- 4) Plasmonica 2016, held in Genoa, Italy, from 14th to 16th September 2016.
- 5) I will attend the conference *Materials2016*, held in Catania, Italy, from 12th to 16th December 2016.

Courseware

Attended:

- 1) "Basic concepts in Nanochemistry", Prof. Manna L. (1 credit)
- 2) "Nanomaterials and Nanocomposites: Processing and characterization", Dr. De Trizio L. and Dr. Arciniegas M. (1 credit)
- 3) "Opto-Electronic Properties of Semiconductor Quantum Dots", Dr. Moreels I. (1 credit)
- 4) "X-rays based Characterization Techniques", Dr. Prato M. (1 credit)
- 5) "Characterization techniques 2", Dr. Genovese A. and Dr. Brescia R. (1 credit)
- 6) "Characterization techniques 3", Dr. Krahne R. and Dr. Casu A. (1 credit)
- 7) "Energy related applications", Dr. Colombo M., Dr. Monaco S. and Dr. Zhang Y. (1 credit)
- 8) "Energy related applications 2", Dr. Manna L. and Dr. Casu A. (1 credit)
- 9) "Laser-matter interactions from fundamentals to applications", Dr. Martì Duocastella (3 credits)
- 10) "Optical Properties of Materials", Prof. Canepa M. and Dr. Bisio F. (3 credits)

Passed:

- 1) "Basic concepts in Nanochemistry", Prof. Manna L. (1 credit)
- 2) "Nanomaterials and Nanocomposites: Processing and characterization", Dr. De Trizio L. and Dr. Arciniegas M. (1 credit)
- 3) "Opto-Electronic Properties of Semiconductor Quantum Dots", Dr. Moreels I. (1 credit)
- 4) "X-rays based Characterization Techniques", Dr. Prato M. (1 credit)
- 5) "Characterization techniques 2", Dr. Genovese A. and Dr. Brescia R. (1 credit)
- 6) "Characterization techniques 3", Dr. Krahne R. and Dr. Casu A. (1 credit)
- 7) "Energy related applications", Dr. Colombo M., Dr. Monaco S. and Dr. Zhang Y. (1 credit)
- 8) "Energy related applications 2", Dr. Manna L. and Dr. Casu A. (1 credit)
- 9) "Laser-matter interactions from fundamentals to applications", Dr. Martì Duocastella (3 credits)
- 10) "Optical Properties of Materials", Prof. Canepa M. and Dr. Bisio F. (3 credits)

During her doctorate, ILARIA ANGELONI has acquired 14 credits of Courseware.

Courses given by invited experts

- 1) "Tecniche di monitoraggio e bonifica di acque e suoli", Dr. Bagatin, 09/10/2014, Chemistry Department (1 credit)
- 2) "Low and Very Low Temperatures: Methods of Producing and Measuring Cryogenic Temperatures", Ivan Čurlík, 17-18/02/2016, Chemistry Department (1 credit)

During her doctorate, ILARIA ANGELONI has acquired 2 credits of advanced courses.

National and International Schools or Workshops

- 1) School of Photonics 2014: "Seeing sharp and further with the optical microscope", Cortona, Italy, from 31st March to 4th April 2014.
- 2) Plasmonica 2016, held in Genoa, Italy, from 14th to 16th September 2016.

During her doctorate, ILARIA ANGELONI has acquired 5 credits of schools and workshops.

Seminars given

- 1) *Disentangling the Role of Shape, Ligands and Dielectric Constants in the Optical Absorption of Colloidal CdSe/CdS Nanocrystals*, IIT, Nanochemistry group meetings, 05/11/2015.
- 2) Optical Properties of Colloidal CdSe/CdS Dot-in-Rods, IIT, 06/12/2015.

During her doctorate, ILARIA ANGELONI has acquired 4 credits of given seminars.

Seminars Attended

- 1) A. Houtepen: *Electrochemical control over charge transfer and trapping in CdSe-CdTe QD Solids*, IIT, 3/03/2014.
- 2) S.Deka: *Nanomaterials as highly active catalyst for multiple significant reactions*, IIT, 25/06/2014.
- 3) D.Dorfs: *Colloidal nanoparticles- shape and composition control* IIT, 26/06/2014.
- 4) N.C.Bigall: *Organization of colloidal nanoparticle building blocks into functional superstructures*, IIT, 26/06/2014.
- 5) N.Gaponik: *Colloidal nanocrystal and their functional architectures*, IIT, 29/09/2014
- 6) S.Sartori: *Neutron scattering for materials research in the field of nitrogen storage for vehicular applications*, IIT, 05/05/2014
- 7) A.Shavel *Copper-based quaternary chalcogenide nanoparticles for the photovoltaic and thermoelectric applications*, IIT, 28/07/2014.
- 8) C.Sinito *Magneto-optical spectroscopy of individual semiconductor nanocrystal* , IIT, 25/09/2014.
- 9) T.Mokari *Synthesis of metal-oxide and metal-oxide based hybrid nanostructures*, IIT, 24/09/2014.
- 10) C.Tortiglione *Unravelling animal biology by functional nanoparticles*, IIT, 19/02/2014.
- 11) L.Torsi *Organic bio-electronic devices for sensing applications*, IIT, 10/11/2014
- 12) I.Kriegel: *Plasmonic heavily doped semiconductor nanocrystals: from fundamentals to their nanoscale application*, IIT, 26/11/2014
- 13) J.I. Climente Plasencia: *Optics of CdSe/CdS nanocrystals: a theoretical overview*, IIT, 05/12/2014
- 14) F. Di Stasio: *Semiconductor Nanocrystals Laser Structures*, IIT, 16/12/2014
- 15) S.Dogan: *Field-Effect Transistors and solar cells made of individual colloidal PbS nanosheets*, IIT, 08/01/2015
- 16) M. Hedayati: *Plasmonic nanomaterials*, IIT, 12/01/2015
- 17) V. Lotito: *Design, fabrication and characterization of plasmonic structures for graphene-based devices and superresolution*, IIT, 19/01/2015
- 18) G. Bertrand: *Designing organometallics for material science: application for solar cells and scintillators*, IIT,19/01/2015
- 19) S.Pergolini: *Chemical Identification at the Nanoscale 100nm IR Spectroscopy, where IR spectroscopy meets AFM*, IIT, 29/01/2015
- 20) G. Konstantatos: *Colloidal Quantum dot Optoelectronics: Photodetectors and Solar Cells*, IIT, 30/01/2015
- 21) D. Braga: *Printed Semiconductors and Novel 2D-Materials in the High Charge Density Regime*, IIT, 30/01/2015
- 22) M. Agostini: *High Energy Lithium-Ion and Lithium-Sulfur Batteries*, IIT, 20/02/2015
- 23) M. Kazes: *Using colloidal quantum dots to boost photovoltaic cell performance*, IIT, 25/02/2015
- 24) A. Freytag: *Versatile Fabrication of Highly Porous Cryogels from Noble Metal Nanoparticles*, IIT, 04/03/2015
- 25) S. Pedetti: *Synthesis and optical properties of II-VI colloidal two-dimensional nanocrystals: homo- and hetero-structures*, IIT, 30/06/2015
- 26) L. Miranda Perez: *Perovskites: an old material for the third generation of PV solar panels*, IIT, 21/04/2016
- 27) G.M.Vanacore: *Spatio-temporal visualization of atomic motions in low-dimensional materials*, IIT, 03/05/2016
- 28) Alexander Weber-Bargioni: *“Visualizing and controlling optoelectronic processes in lead halide perovskites”*, IIT, 14/11/2016

During her doctorate, ILARIA ANGELONI has acquired 2 credits of attended seminars.

Other Activities

Visit at IBM Research – Zurich Laboratory, Rüschlikon, Switzerland, for the period from August 15th to August 26th , 2016. During this period, I learnt about low temperature optical measurements on single quantum dots.



Università degli Studi di Genova
Doctorate School in
Sciences and Technologies of
Chemistry and Materials

Curriculum: Nanochemistry

Preethi Bala Balakrishnan

Start of Doctoral School Program *January 1st 2014*

End of Doctoral school Program *December 31st 2016*

Advisors

Prof. Dr. Teresa Pellegrino (IIT)

Prof. R. Rita (UniGe)

Thesis Title

**Effect of various Iron-Oxide-based Nanocubes-induced Hyperthermia on
In-Vivo NUDE Mice Model for Sub-cutaneous Tumor Treatment**

Thesis abstract

The first two years of my PhD, I optimized and tested the viability and efficiency of various magnetic nanomaterials prepared in my laboratory on various two dimensional and three dimensional cell culture techniques, to act as effective heat mediators in cancer hyperthermia therapy. After studying and evaluating these materials, in my 3rd year PhD I moved onto testing these materials in *In-vivo* model. Overall this chapter will give an insight of in-vivo experiments conducted to show the efficiency of Co-Fe NCs as hyperthermia inducing agents in the presence of an AMF and how it is utilized in treating epidermoid carcinoma in athymic NUDE mice. Initial optimization of the in-vivo study was conducted followed by testing the NPs in a short term study following protocols developed by our collaborators. The information obtained from the short-term study helped us develop an experimental procedure of my own to test the effect of this treatment over a long period of time. With the results obtained from tumor growth analysis, survival study, IR images, TEM, Histo-pathological studies and finally the ICP-elemental analysis, we back up the efficiency of Co-Fe NCs to serve as effective mediates of hyperthermia induced killing of epidermoid carcinoma in animals model.

ACTIVITY REPORT

Research activity

Scientific Publications:

1. Non-Covalent Functionalization of Carbon Nano-Onions with Pyrene BODIPY Dyads for Biological Imaging, RSCAdvances, 2015
2. Star poly(ϵ -caprolactone)-based electrospun fibers as drug scaffold for doxorubicin with prolonged drug release activity (Manuscript completed)

Talks:

1. Annual Presentation January 2014 in University (Project proposal)
2. Educational Seminar with powerpoint presentation to cover the topics of WIN Symposium attended in the month of June, 2014 to the Department students and scholars under supervision of Dr. Teresa Pellegrino
3. Annual Presentation December 2014 in University (1st year work report)
4. Seminar on my 2nd year work to the whole of NACH department under the supervision of Dr. Teresa Pellegrino in IIT, November 12, 2015
5. Annual Presentation December 11th 2015 in university (2nd year work report)
6. Talk at ERC Kick-off meeting conducted by Dr. Teresa Pellegrino, June 6th 2016 (ICARO project), Sestri Levante, Italy
7. Seminar on my 3rd year work to the whole of NACH department under the supervision of Dr. Teresa Pellegrino in IIT, December 6th, 2016

Congress Attended (Credits undecided):

1. **International Conference** "WIN Symposium 2014: Winning combination for precision Cancer Medicine" June 23-24th, Paris, France
2. "Nanomedicine Symposium CEN@Politecnico: Synthesis of Nanomaterials, biological applications and modelling" November 4th 2014, Milano, Italy, **National conference**

3. "Nanomedicine Symposium CEN@Politecnico: Synthesis of Nanomaterials, biological applications and modelling" September 21st 2014, Milano, Italy, **National conference**
4. "**International Conference** on Nanomedicine and Nanobiotechnology" September 28th-30th 2016, Paris, France
5. **Summer School** on Nanomedicine, Utrecht University, June 20th to 24th 2015, Utrecht, The Netherlands

COURSEWARES

*During her three years of doctorate Preethi Bala Balakrishnan has acquired **27.25 + conference and summer school credit (to be decided by university) credits of Courseware.***

Courses Attended and passed:

A-type Courses Given by invite speaker in the university (3 credits):

1. "Metabolomics Profile of Hypoxic Colorectal Cancer Cells", Research Scientist presso il Weatherall Institute of Molecular Medicine, University of Oxford, 8 maggio, Difar sezione Chimica del farmaco e del Prodotto cosmetico, Dott. Alessandro Valli **(1 credit)**
2. "X-ray based experimental techniques and characterization of nano materials" Alberto Morgante, CNR-IOM and Physics Department Trieste University), 31 marzo 2015, h. 14,30–17,30 DCCI Aula 6 **(1 credit)**
3. "Magnetic Hyperthermia: from fundamentals to biomedical applications" Dr. Francisco Terán, CNB-CSIC-Universitario de Cantoblanco, 5 and 6 May 2016 **(1 credit)**

B-type Courses Given by Teachers of NACH, IIT (21 credits):

1. "Basic concepts in Nanochemistry", Prof. Manna L. **(1 credit)**
2. "Nanomaterials and Nanocomposites: Processing and characterization", Dr. De Trizio L. and Dr. Arciniegas M. **(1 credit)**
3. "X-rays based Characterization Techniques", Dr. Prato M. **(1 credit)**
4. "Characterization techniques 2", Dr. Genovese A. and Dr. Brescia R. **(1 credit)**

5. "Characterization techniques 3", Dr. Krahne R. and Dr. Casu A. **(1 credit)**
6. "Opto-electronics", Dr. Iwan Moreels **(1 credit)**
7. "Magnetic Nanoparticles in Biomedicine" Aidin Lak **(1 credit)**
8. "Non-linear excitation microscopy: from theory to tissue imaging", Dr. Paolo Bianchini, IIT **(3 credits)**
9. "Laboratory of Optical Fluorescence Microscopy Methods", Dr. Marta D'Amora, IIT **(3 credits)**
10. "Characterization of Polymeric Materials" Dr. J A. Heredia Guerrero, Dr. L. Ceseracciu, IIT **(4 credits)**
11. "Nanoparticle characterization by Atomic Force Microscopy and Dynamic Light Scattering" R. Rolandi at UniGe **(2 credits)**
12. "Applicazioni della spettroscopia Raman", Prof. Alberto Morgante, CNR-IOM and Physics Department Trieste University, 31 March 2015, DCCI, UniGe **(2 credits)**

National and International Workshops and Schools (credits undecided):

1. Summer School on Nanomedicine, Utrecht University, June 20th to 24th 2015, Utrecht, The Netherlands

Seminars Attended (credits 3.25):

1. C. Tortiglione, "Unravelling animal biology by functional nanoparticles", IIT, 19/02/2014
2. D. Belmonte, "Quantum geochemistry: simulating physico-chemical properties of materials in the deep earth", IIT, 31/03/2014
3. S. Sartori, "Neutron scattering for materials research in the field of hydrogen storage for vehicular applications", IIT, 05/05/2014
4. A. Shavel, "Copper-based quaternary chalcogenide nanoparticles for photovoltaic and thermoelectric applications", IIT, 28/07/2014
5. T. Moksari, "Synthesis of metal and metal oxide based hybrid nanostructures", IIT, 24/09/2014

6. C. Sinito, "Magneto-optical spectroscopy of individual semiconductor nanocrystals", IIT, 25/09/2014
7. N. Gaponik, "Colloidal nanocrystals and their functional architectures", IIT, 29/09/2014
8. L. Torsi, "Organic-Bio electronic devices for sensing applications", IIT, 10/11/2014
9. I.Kriegel, "Plasmonic heavily doped semiconductor nanocrystals: from fundamentals to their nanoscale application" 26/11/2014
10. Plasencia J.I.C., "Optics of CdSe/CdS nanocrystals: a theoretical overview", IIT, 5/12/2014
11. M. Sainato, "Chemi-transistors gas sensors based on multicomponent nanomaterials" 28/05/2015
12. Hedayati Mehdi, "Plasmonic Nanomaterials" 12/01/2015
13. Stefano Passerini, "Materials for sodium Batteries" 16/01/2015
14. Guillaume Bertrand, "Designing organometallics for material science: application for solar cells and scintillators" 19/01/2015
15. Valeria Lotito, "Design, fabrication and characterization of plasmonic structures for graphene-based devices and super resolutions" 19/01/2015
16. Daniele Braga, "Printed semiconductors and novel 2D materials in the high charge density regime" 30/01/2015
17. Gerasimos Konstantatos: Colloidal quantum dots optoelectronics: Photodetectors and solar cells 30/01/2015
18. Motta N., "Graphene towards real world applications: from epitaxy to supercapacitors" IIT 17/02/2015
19. Marco Agostini: High energy Lithium-Ion and Lithium-Sulfur Batteries 20/02/2015
20. Miri Kazes: Using Colloidal quantum dots to boost photovoltaic cell performance 20/02/2015

21. J.C. Arnault: Control of surface chemistry of Nanodiamonds for bio applications 9/11/2015
22. Alexander L. Efros: Semiconductor Nanocrystals: discovery, Milestones and recent theoretical developments 20/11/2015
- 23.
24. BAZZANO ANDREA, "Strumentazione di chimica analitica per l'esplorazione del sistema solare" UniGe, 05/11/2015
25. GARBARINO SILVIA, "The magic of diazomethane: advantages and drawbacks of an elusive reagent" UniGe, 05/11/2015
26. GARDELLA LORENZA, "Self-assembled block copolymers aggregates: application in drug delivery" UniGe, 05/11/2015
27. GHIARA GIORGIA, "Introduzione alle pile a combustibile e ai fenomeni di degrado ad alta temperatura" UniGe, 05/11/2015



Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Chemical Sciences and Technologies

PH.D. CERTIFICATE
of
SAMANTHA CAPUTO



Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisor

Prof. Luca Banfi

Thesis Title

Diastereoselective Ugi reaction of chiral 1,3-aminoalcohols-derived from an organocatalytic Mannich reaction- followed by intramolecular nucleophilic substitutions: convergent multicomponent synthesis of diverse heterocyclic scaffolds

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department of Chemistry and Industrial Chemistry, Samantha Caputo has orally presented her doctorate research work in front of the Commission, formed by

- Prof. Gaetano Granozzi, University of Padova
- Prof. Andrea Pucci, University of Pisa
- Prof. Renata Riva, University of Genova

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

**HAS APPROVED THE THESIS OF SAMANTHA CAPUTO,
CONFERRING ON HER THE TITLE OF**

**RESEARCH DOCTOR IN
CHEMICAL SCIENCES AND TECHNOLOGIES**

Genova, February 24th, 2017

**The Coordinator of the Doctorate Course
(Prof. Adriana Saccone)**



Università degli Studi di Genova
Doctorate School in
Sciences and Technologies of
Chemistry and Materials

Curriculum: Sciences and Technologies of
Chemistry



Samantha Caputo

Start of the Doctorate Program January 1st, 2014

End of the Doctorate Program January 1st, 2017

Advisor Prof. L. Banfi

Thesis Title 1: Diastereoselective Ugi reaction of chiral 1,3-aminoalcohols - derived from an organocatalytic Mannich reaction - followed by intramolecular nucleophilic substitutions: convergent multicomponent synthesis of diverse heterocyclic scaffolds.

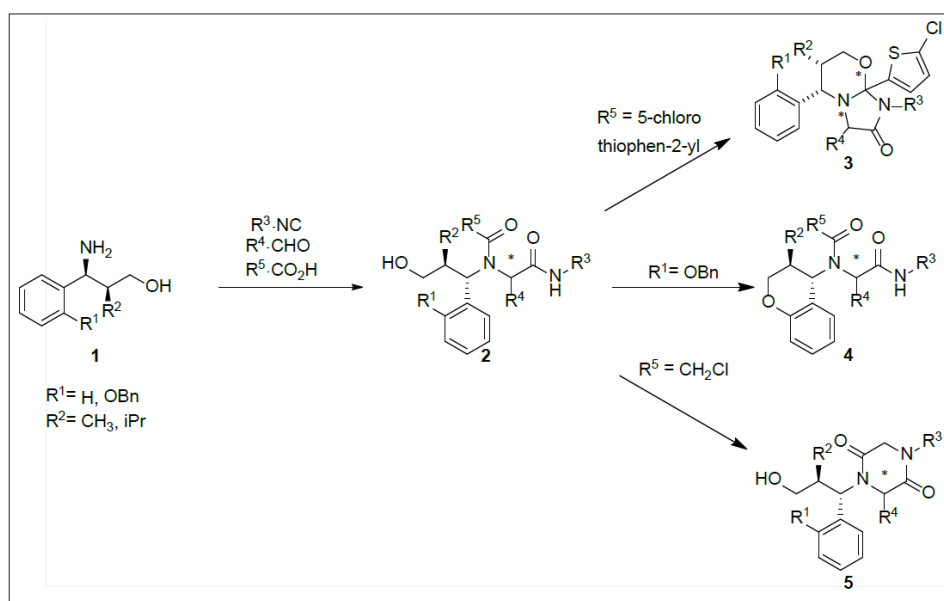
Enantiomerically pure β -aminoalcohols (**1**), produced through an organocatalytic Mannich reaction, were subjected to an Ugi multicomponent reaction under classical or Lewis acid-promoted conditions with diastereoselectivities ranging from moderate to good. This approach represents a step-economical path to enantiomerically pure, polyfunctionalized peptidomimetics endowed with three stereogenic centers, allowing the introduction of five diversity inputs.

After optimization of the Ugi reaction conditions, these adducts (**2**) have been employed as substrates in the synthesis of diverse heterocyclic compounds, through secondary transformations.

For example, without employing any additional functional group, complex bicyclic system (**3**) was obtained.

Other possibilities may be envisaged by adding additional functional groups, beside the alcohol. Thus, chromanes (**4**) could be obtained by employing the alcoholic functional group as electrophilic substrate in a nucleophilic substitution by an additional phenol, under Mitsunobu conditions.

Finally, the use, as nucleophile, of the secondary amide derived from isocyanide, and of an additional alkyl chloride, leads to the 2,5-diketopiperazine scaffold (**5**).



Advisor Prof. R.Lavilla (University of Barcelona)

Thesis Title 2: Multiple Groebke-Blackburn-Bienaymé multicomponent reactions: scope, selectivity and synthetic access to complex heterocyclic scaffolds

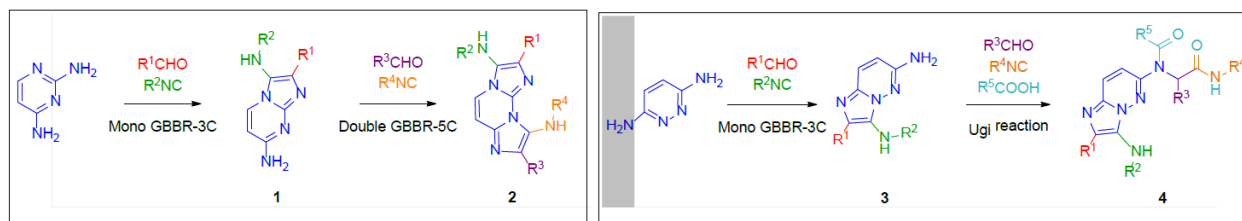
The Groebke–Blackburn–Bienaymé reaction (GBBR) is a multicomponent reaction involving readily available aldehyde, isocyanide and amidine building blocks to form amino substituted N-fused imidazoles. The GBB products can be used for the synthesis of a variety of complex scaffolds via postmodification reactions (e.g. cyclization, metal-catalyzed couplings and even additional MCRs).

GBBR almost exclusively uses aminopyridines as the amidine component. Here we disclose the multiple Groebke–Blackburn–Bienaymé reaction for the one-pot synthesis of therapeutically relevant complex heterocycle, scanning a variety of poly-aminoazine substrates.

For instance, starting from 2,4-diaminopyrimidine, and 3,6-diaminopyridazine and melamine as amidines, we have explored the mono (**1,3**) and double (**2**) GBBR on varying the reaction parameters together with an evaluation of a diverse set of reaction substrates. The GBB adducts were then employed as pluripotent substrates to prepare diverse heterocyclic compounds via postmodification reactions.

For example, the employing of mono GBB adduct from 3,6-diaminopyridazine (**5**) as amine in the Ugi reaction, allowed the introduction of five points of diversity in a two-steps protocol (**4**).

More examples will be discussed together with relevant applications of the adducts.



ACTIVITY REPORT

Research Activity

The research activity was mainly carried out at the Department of Chemistry and Industrial Chemistry (University of Genova). However, Samantha Caputo **has also spent a research period of 9 months abroad**, at the Barcelona Science Park - University of Barcelona (under the direction of Prof. Rodolfo Lavilla Grifols) from 7/1/2016 to 15/9/2016.

Courseware

Courses attended and passed (13 credits)

Courses Given by Teachers of the:

- 1) Biotecnologie Farmaceutice- M. Mazzei (3 CFU); PASSED
- 2) Chimica Bioorganica- L. Banfi (2 CFU); PASSED
- 3) Metodi di preparazione e controllo di forme farmaceutiche innovative- S. Baldassari, G. Caviglioli, B. Parodi, E. Russo (2CFU); PASSED
- 4) Metodologia della ricerca sperimentale- M. Grotti, R. Leardi (3CFU); PASSED
- 5) The Chemical Genetics approach: description and developments"- R. Lavilla (3CFU); PASSED

Courses Given by invited experts (8 credits):

- 1) "Pharmaceutical green chemistry" – Dr. W. Cabri (09/05/2014)
- 2) "Polymers and Composites from Renewable Resources"- Prof. E.A. Gandini (29/09/2015)
- 3) "Polymers and Composites from Renewable Resources"- Prof. E.A. Gandini (30/09/2015)
- 4) "Medicinal chemistry with carbohydrates: the influenza virus and the discovery of sialic acid inhibitors"- Prof.ssa A. Bernardi (13/11/2015)

National and International Schools or Workshops

- 1) Giornate Italo Francesi di Chimica (Torino, 5-6 maggio 2014)
- 2) International Summer School on Organic Synthesis "A. Corbella" (Gargnano, 15-19 giugno 2014)
- 3) International Summer School on Organic Synthesis "A. Corbella" (Gargnano, 14-18 giugno 2015)
- 4) XXXVI Convegno della Divisione di Chimica Organica (Bologna, 13-17 settembre 2015)
- 5) 17th Tetrahedron Symposium (Sitges, 28 giugno – 1 luglio 2016)
- 6) XXXVII Convegno della Divisione di Chimica Organica (Venezia Mestre, 18- 22 settembre 2016)
- 7) Ischia Advanced School of Organic Chemistry (Ischia, 25-29 settembre 2016)

Seminars Attended

- 1) "Flow reactor technology: a flexible tool for reaction optimization and chemical production" – C. Van der Zanden (19/03/2014)
- 2) "Probing multiple low-energy interactions- some new chemistry from old hands – C. Starling (17/10/2014)
- 3) "Le parole delle piante" – V. Butterweck, M. L. Brandi (28/10/2014)
- 4) "Biocatalisi: applicazioni in sintesi farmaceutica" - Dr. M. Massa (28/11/2014)
- 5) "Molecole naturali e xeno-ormesi" - Dr. G. Mele (28/11/2014)
- 6) "Metodi alternativi alla sperimentazione animale" – Dr.ssa B. Pollarolo (28/11/2014)
- 7) "Recenti aspetti d'interesse terapeutico del processo di metastasi tumorale" - Dr.ssa C. Zibana (28/11/2014)
- 8) "Photochemically generated phenyl cations as tunable and versatile intermediates"- S. Protti (13/01/2015)
- 9) "Seeing Molecules: A Survey on Non-Optical Microscopies and their Applications"- M.A. Martin Espinosa (06/11/2015)
- 10) "The hydrogen autotransfer process"- M. Spallarossa (06/11/2015)
- 11) "The magic of diazomethane: advantages and drawbacks of an elusive reagent" – S. Garbarino (06/11/2015)
- 12) "Molecular containers based on aryl extended calix [4] pyrrole" – P. Bellester (22/01/2016)
- 13) " DNA binding and luminescence" – E. Vasquez (18/03/2016)
- 14) "The sweet side of chemistry: Sugars, NMR & Molecular Recognition"- J. Jiménez-Barbero (07/04/2016)
- 15) "Photoredox catalysis" – D. McMillan (07/04/2016)
- 16) "Catalytic C-H activation of aliphatic amine" –M. Gaunt (22/04/2016)

Other Activities

- 1) "Le Giornate di Chimica Organica a Pavia" (Pavia, 15/10/2014)
- 2) Presentazione demo H-Cube Mini (12/05/2015)
- 3) Presentazione de HPLC/MS (21/11/2015)
- 4) Laboratorio didattico di Chimica Organica - Prof.ssa R. Riva (2014, 28 ore; 2015, 32 ore)
- 5) Laboratorio didattico di Chimica Organica- Prof. A. Basso (2016, 48 ore).

Communications at Conferences

Poster Communications

1. Poster CDCO 2015: "DIASTEREOSELECTIVE UGI REACTION FOLLOWED BY INTRAMOLECULAR NUCLEOPHILIC SUBSTITUTIONS: CONVERGENT MULTICOMPONENT SYNTHESIS OF DIVERSE HETEROCYCLIC SCAFFOLDS".
2. Poster CDCO 2016: "DIASTEREOSELECTIVE UGI REACTION FOLLOWED BY INTRAMOLECULAR NUCLEOPHILIC SUBSTITUTIONS: CONVERGENT MULTICOMPONENT SYNTHESIS OF DIVERSE HETEROCYCLIC SCAFFOLDS".
3. Poster IASOC 2016: "GROEBKE-BLACKBURN-BIENAYMÉ MULTICOMPONENT REACTION: A FACILE PROTOCOL FOR THE SYNTHESIS OF N-FUSED IMIDAZOLES HETEROCYCLES".

Publication

1. Diastereoselective Ugi reaction of chiral 1,3-aminoalcohols derived from an organocatalytic Mannich reaction *Beilstein J. Org. Chem.* **2016**, *12*, 139–143.



Università degli Studi di Genova



**Doctorate in
Sciences and Technologies of
Chemistry and Materials**

CURRICULUM: DRUG DISCOVERY

Beatrice Castellani

Start of the Doctorate Program January 1st, 2014

End of the Doctorate Program December 31th, 2016

Advisor: Prof. Daniele Piomelli – Drug Discovery and Development (D3) – IIT.

Thesis Title: Chemical modulation of the bioactive lipid amide signaling

**ACTIVITY REPORT
Research Activity**

The research activity was mainly carried out at Department of Drug Discovery and Development at the Istituto Italiano di Tecnologia (IIT).

Scientific Publications

- 1) Bile Acid Recognition by NAPE-PLD. Margheritis E, Castellani B, Magotti P, Peruzzi S, Romeo E, Natali F, Mostarda S, Gioiello A, Piomelli D, Garau G. *ACS Chemical Biology*, 2016, 11(10), 2908-2914.
- 2) Fluorine nuclear magnetic resonance-based assay in living mammalian cells. Veronesi M, Giacomina F, Romeo E, Castellani B, Ottonello G, Lambruschini C, Garau G, Scarpelli R, Bandiera T, Piomelli D, Dalvit C. *Analytical Biochemistry*, 2016, 495, 52-9.

Communications at Conferences

Poster Communications: The candidate presented the poster with the title “Bile acids modulate fatty-acid ethanolamide signaling” in occasion of the dedicated poster session at the Hercules school program in Grenoble in March 2015.

Oral communications: None

Congresses Attended: None

Courseware

Courses attended and passed (6 credits)

Courses Given by Teachers of the IIT and the University of Genoa:

- 1) What is a drug, Drug discovery process, Target identification and validation (From disease to gene to target), Hit identification (Biomolecular screening): 2 credits.
- 2) Hit identification (Knowledge-based approach, Compound collections and Natural sources): 1 credit.
- 3) Hit to lead and lead optimization [Medicinal chemistry: a) Synthesis of drugs (Prof. Renata Riva); b) Chiral

- drugs; c) Bio-isosterism; d) Improving drug-likeness]): 1 credit.
- 4) Hit to lead and lead optimization (Computational drug design): 1 credit.
 - 5) Hit to lead and lead optimization (Pharmacology, Development process, Patents): 1 credit.
 - 6) The course on "Patents" was given by Dr Lorenzo Rossi and Dr Giuseppe Giardina at the IIT.

Courses Given by invited experts:

- 1) July 6th 2016. SciFinder training. Dr Maria Luisa Quadri.

National and International Schools or Workshops:

- 1) **December 2nd-5th 2014:** 1st Practical Workshop on Advanced Microscopy organized by the IIT Nikon Center.
- 2) **March 2015:** 1-month HERCULES European School held in Grenoble from March 1st to April 1st. The PhD candidate was enrolled in the Session B dedicated to Biomolecular and structure dynamics, which included one week at the French synchrotron radiation facility Soleil, Saint-Aubin (Paris). The program of the school included 8 hours per day of lesson and also practices.
- 3) **October 11th-13th 2016:** "2° MS BioPharma School: Scuola pratica di spettrometria di massa in ambito biofarmaceutico", presso GSK, Siena.
- 4) **October 26th-27th 2016:** "2° MS NatMed School: Scuola pratica di spettrometria di massa nello studio dei sistemi complessi naturali" presso Aboca, Perugia.

Seminars Given: None

Seminars attended over the year 2014:

@IIT:

- 1) On February 2nd, 2014: Dr Cruciani from Molecular Discovery.

@Unige:

- 2) On May 9th, 2014: Dr Cabri from Indena.
- 3) On May 25th, 2014: Dr Pusceddu from Ibimet.

Seminars attended over the year 2015:

@IIT:

- 1) January 27th 2015. "Synergies between chemistry and nanotechnology: applications to neurosciences and energy". Maurizio Prato, professor at Università degli Studi di Trieste.
- 2) April 14th 2015. "Gene Editing: CRISPR/Cas9. The Scientific Basis and Advantages of the GE HealthCare Dharmacon System". Dr Johanna Decastroace, Scientific Support Scientist GE Healthcare – Dharmacon.
- 3) May 29th 2015. "Chemical biology of glycosphingolipid metabolism in man". Dr. Herman Overkleeft. Professor in Bioorganic chemistry at the Leiden Institute of Chemistry at Leiden University.
- 4) July 3rd 2015. "Contribution of chemistry to sphingolipid research". Prof. Gemma Fabriàs. Consejo Superior de Investigaciones Científicas (CSIC), Instituto de Química Avanzada de Cataluña (IQAC-CSIC), Research Unit on Bioactive Molecules (RUBAM), Barcelona, Spain.
- 5) October 15th 2015. "The European Union Nanomedicine Characterization Laboratory (EU-NCL). Dr Luigi Calzolari.

@Unige:

- 6) May 8th 2015. "Metabolomics Profile of Hypoxic Colorectal Cancer Cells". Dott. Alessandro Valli, Institute of Molecular Medicine, University of Oxford.
- 7) May 18th – 19th 2015. "Elementi di Chimica Forense". Dott. Narizzano Riccardo. ARPAL, Genova.
- 8) July 16th 2015. "Modelli per lo studio in vitro del metabolismo umano". Dr. Arti Ahluwalia Professore Associato di Bioingegneria Industriale, Università degli Studi di Pisa.

Seminars attended over the year 2016:

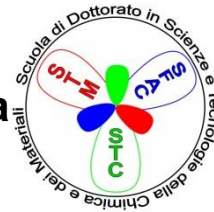
@IIT:

- 1) January 21st 2016. "Carbonic anhydrases as drug targets". Prof. Claudiu Supuran. Università degli Studi di Firenze.
- 2) February 15th 2016. "Ribosomes: a spectacular prebiotic machine". Prof. and Nobel Prize Ada Yonath. Department of Structural Biology, Weizmann Institute, Rehovot, Israele.
- 3) March 2nd 2016. "Toy-like mass spectrometers. An educational tool for the future?". Dr. Enrico Davoli, Istituto di Ricerche Farmacologiche Mario Negri

- 4) September 29th 2016. "A Cannabinoid Link Between Mitochondria and Memory". Prof. Giovanni Marsicano, Université Bordeaux 2.
- 5) September 30th 2016. "Fragment-based drug discovery for identifying single- and multi-target inhibitors of CNS targets". Dr Anders Bach, University of Copenhagen.
- 6) Friday 7th 2016. "Stratification and therapeutic potential of molecular pathways driving cancer aggressiveness". Prof. Giannino Del Sal, University of Trieste.
- 7) November 10th 2016. "Biomolecular interaction analytics using microscale thermophoresis". Dr Francesca Viganò, Application Specialist at NanoTemper Technologies.
- 8) November 25th 2016. "Therapeutic implications of disease-specific broken clocks". Dr Benedetto Grimaldi, Group Leader in cancer research, IIT Genova.

Other Activities

- 1) June – September 2016: tutor in biology for a visiting MSc student from Leiden University.



Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Chemical Sciences and Technologies

PH.D. CERTIFICATE
of
FRANCESCA CIRISANO



Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisors

Dr. Michele Ferrari

Prof. Serena De Negri

Thesis Title

*Preparation and characterization of
superhydrophobic surfaces for anticorrosive
and antifouling applications*

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department of Chemistry and Industrial Chemistry, Francesca Cirisano has orally presented her doctorate research work in front of the Commission, formed by

- Prof. Gaetano Granozzi, University of Padova
- Prof. Andrea Pucci, University of Pisa
- Prof. Renata Riva, University of Genova

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

HAS APPROVED THE THESIS OF FRANCESCA CIRISANO
CONFERRING ON HER THE TITLE OF

RESEARCH DOCTOR IN
CHEMICAL SCIENCES AND TECHNOLOGIES

Genova, February 24th, 2017

The Coordinator of the Doctorate Course
(Prof. Adriana Saccone)



Università degli Studi di Genova
Doctorate School in
Sciences and Technologies of
Chemistry and Materials



Curriculum: Chemical Sciences and Technologies

FRANCESCA_CIRISANO

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *(31 December 2016)*

Advisors

Dr. Michele Ferrari IENI-CNR, Dr. Serena De Negri DCCI

Thesis Title

Preparation and characterization of superhydrophobic surfaces for anticorrosive and antifouling applications.

Thesis abstract

Highly water repellent coatings known as superhydrophobic (SH) are related to surfaces with contact angles above 150° and a very small hysteresis. The small area available for these surfaces when in contact with water address to be exploited in many applications where interactions with aqueous environment are usually strongly to be avoided like for corrosion protection, against biofouling colonization and friction reduction in marine environment. The absence of toxic materials in the final product and in the preparation stage holds to preferable bio-compatible coatings, basing the action on low surface energy exerting physical prevention of bioadhesion of colonizing organisms. With the aim to provide more resistant and long lasting coatings, the SH surfaces under investigation have been studied in presence of pure water and marine waters and in particular the performance, durability and fouling removability is evaluated with immersions in real seawater mesocosms conditioned/not conditioned by the natural photoperiod and the photobiology development focusing on two time scales (days and weeks), emphasizing the role of conditioning film and initial biological slimes formation. Near this study, for evaluate the anticorrosion property of the SHS prepared some tests of free corrosion potential and polarization curves show effectiveness and limitations of the systems under investigation. Moreover, the project will try to incorporate in the SHS capsule-like structures in order to obtain self-healing and anti-fouling materials. In this preliminary stage, capsules have been prepared as a model for the development of self-healing/anti-fouling materials.

ACTIVITY REPORT

Research Activity

The research activity was mainly carried out at the CNR-IENI as part of the flagship project "RITMARE - Italian research for the sea" coordinated by the National Research Council.

During the second year the work was focused

Scientific Publications

Original publications on ISI Journals:

- 1) **Biofouling control by superhydrophobic surfaces in shallow euphotic seawater.** Michele Ferrari, Alessandro Benedetti, Eva Santini, Francesca Ravera, Libero Liggieri, Eduardo Guzman, **Francesca Cirisano**, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, doi:10.1016/j.colsurfa.2014.11.009
- 2) **Toxicity study in blood and tumor cells of laser produced medicines for application in fabrics.** M Carmen

Morán, Tatiana Tozar, Agota Simon, Andra Dinache, Adriana Smarandache, Ionut Relu Andrei, Mihai Boni, Mihail Lucian Pascu, **Francesca Cirisano**, Michele Ferrari, Colloids and surfaces B: Biointerfaces; DOI:10.1016/j.colsurfb.2015.06.041

- 3) **Potentiodynamic study of Al-Mg alloy with superhydrophobic coating in photobiologically active/not active natural seawaters**, Alessandro Benedetti, **Francesca Cirisano**, Marina Delucchi, Marco Faimali, Michele Ferrari, Colloids and surfaces B: Biointerfaces DOI: 10.1016/j.colsurfb.2015.07.045
- 4) **Amphiphobic coatings for antifouling in marine environment**, **Francesca Cirisano**; Alessandro Benedetti; Libero Liggieri; Francesca Ravera; Eva Santini; Michele Ferrari. Colloids and surface A: Physicochemical and Engineering Aspects DOI: 10.1016/j.colsurfa.2016.03.045

Other publications

- 1) **Highly water repellent coatings for application in sea water**. Michele Ferrari, **Francesca Cirisano**, Libero Liggieri, Francesca Ravera, Eva Santini, Alessandro Benedetti, EMASST online library.

Communications at Conferences

Oral communications:

- 1) **Coatings for protection in shallow euphotic seawater** **F. Cirisano**, M. Ferrari, L. Liggieri, F. Ravera, E. Santini, A. Benedetti XXII Congresso AIV Genova 20-22 May 2015
- 2) **Highly water repellent coatings for antifouling in seawater** **F. Cirisano**, M. Ferrari, L. Liggieri, F. Ravera, E. Santini, A. Benedetti IACIS Mainz (Germany) 24-29 May 2015
- 3) **Super hydrophobic coating for sea water biofuelling**. **Francesca Cirisano**, Emilio Olzi, Michele Ferrari, Alessandro Benedetti, 11th Symposium of European vacuum coaters, Anzio 29 September – 1 October, 2014
- 4) **Particles and capsules in superhydrophobic coating for marine application**. **Francesca Cirisano**, Libero Liggieri, Francesca Ravera, Eva Santini, Eduardo Guzmán, Alessandro Benedetti, Michele Ferrari, COST CM1101, Joint Meeting WG 1-3-5-6, Particles at Liquid and Solid Interfaces: Fundamentals and Application, Genoa (Italy) 31 March– 2 April, 2014

Other oral communications:

- 1) **Amphiphobic coatings for protection in seawater environment**, Michele Ferrari, **Francesca Cirisano**, Alessandro Benedetti, Libero Liggieri, Francesca Ravera, Eva Santini, Tenth International Symposium On Contact Angle, Wettability And Adhesion New York-Hoboken (Usa) 13-15 July 2016
- 2) **Superhydrophobic coatings and protection in sea environment**, Michele Ferrari, **Francesca Cirisano**, Libero Liggieri, Francesca Ravera, Eva Santini, Alessandro Benedetti World Congress and Expo on Materials Science & Polymer Engineering (Materials Science-2015) Dubai 26-28 november 2015
- 3) **Superhydrophobic coatings for protection in marine environment**, Michele Ferrari, **Francesca Cirisano**, Libero Liggieri, Francesca Ravera, Eva Santini, Alessandro Benedetti B&D2015 Golm 6-10 July, 2015 in Potsdam-Golm, Germany .
- 4) **Superhydrophobic coatings for protection in sea environment** Michele Ferrari, **Francesca Cirisano**, Libero Liggieri, Francesca Ravera, Eva Santini, Alessandro Benedetti, Fourth International Conference on Natural Polymers, Bio-Polymers, Bio-Materials, their Composites, Nanaocomposites, Blends, IPNs, Polyelectrolytes and Gels: Macro to Nano Scales (ICNP – 2015): April 10, 11 & 12, 2015, Kottayam, Kerala, India
- 5) **Particles and capsules in high water repellent coatings in marine environment**. Michele Ferrari, Libero Liggieri, Francesca Ravera, Eva Santini, Eduardo Guzmán, Alessandro Benedetti, **Francesca Cirisano**, 20th International Symposium on Surfactants in Solution, Coimbra (Portugal), 22-27 June 2014.
- 6) **Superhydrophobic coatings for antifouling and protection in marine environment**. Michele Ferrari, Libero Liggieri, Francesca Ravera, Eva Santini, Eduardo Guzmán, Alessandro Benedetti, **Francesca Cirisano**, *1st edition of European Symposium on Surface Science*, Rome (Italy), 26-28 November 2014.

Poster Communications:

- 1) **Amphiphobic coatings for antifouling in marine environment**, Michele Ferrari, **Francesca Cirisano**, Alessandro Benedetti, Libero Liggieri, Francesca Ravera, Eva Santini, Materials.it 2016. Catania (Italy) 12-16 December 2016
- 2) **Mammalian cell viability on hydrophobic and superhydrophobic fabrics**, Maria del Carmen Moran Badenas, Guillem Ruano I Torres, **Francesca Cirisano** And Michele Ferrari, Nanobiomed, Barcelona 2016 22-24 November 2016
- 3) **Amphiphobic coatings for antifouling in marine environment**, Michele Ferrari, **Francesca Cirisano**, Alessandro Benedetti, Libero Liggieri, Francesca Ravera, Eva Santini, ECIS Rome (Italy) 4-9 September 2016
- 4) **Amphiphobic coatings for protection in marine environment**, Michele Ferrari, **Francesca Cirisano**, Alessandro Benedetti, Libero Liggieri, Francesca Ravera, Eva Santini, Sis 2016 21st International Symposium On Surfactants In Solution (SIS), Jinan, China, During June 5-11, 2016
- 5) **Amphiphobic coatings for protection in seawater environment**, **F. Cirisano**, M. Ferrari, A. Benedetti, L. Liggieri, F. Ravera, E. Santini, Smart and green interfaces conference. Athens (Greece) 4-6 May 2016
- 6) **Biofouling and corrosion protection in sea environment by superhydrophobic coatings** **M. Ferrari**, **F. Cirisano**, L. Liggieri, F. Ravera, E. Santini, A. Benedetti SGI-FunD Symposium 29 – 31 October 2015, Sofia, Bulgaria
- 7) **Corrosion and fouling protection by superhydrophobic coatings**. Michele Ferrari, Alessandro Benedetti, Eva Santini, Francesca Ravera, Libero Liggieri, **Francesca Cirisano**, ECIS 2015 Bordeaux (France) 6-11 September 2015
- 8) **Superhydrophobic coatings for biofouling control in shallow euphotic seawater**. Michele Ferrari, Alessandro Benedetti, Eva Santini, Francesca Ravera, Libero Liggieri, **Francesca Cirisano**, COST Action MP1106 Smart and green interfaces - from single bubbles and drops to industrial, environmental and biomedical applications (SGI) Belgrade (Serbia), 30 March-1 April 2015
- 9) **Rivestimenti superidrofobici in ambiente marino**. Michele Ferrari, **Francesca Cirisano**, Libero Liggieri, Francesca Ravera, Eva Santini, Alessandro Benedetti, TICASS Genoa (Italy) 20 february 2015
- 10) **Superhydrophobic coatings for protection in marine environment**. **Francesca Cirisano**, Michele Ferrari, Libero Liggieri, Francesca Ravera, Eva Santini, Alessandro Benedetti, Winter training school “ Kinetics of wetting/spreading of complex liquids” Loughborough University (United Kingdom) 26-30 January 2015
- 11) **Highly hydrophobic coatings for protection and friction reduction in marine environment**. Michele Ferrari, **Francesca Cirisano**, Libero Liggieri, Francesca Ravera, Eva Santini, Eduardo Guzmán, Alessandro Benedetti, COST Action: MP1106 Meeting Title: MP1106 International Workshop, Saint Charles Campus Of Aix-Marseille University, Marseilles (France) 22-24 April 2014 (Winner poster awards)
- 12) **Particles and capsules for superhydrophobic coatings in marine environment**. **Francesca Cirisano**, Michele Ferrari, Libero Liggieri, Francesca Ravera, Eva Santini, Eduardo Guzmán, Alessandro Benedetti, COST Action MP1106 & CM1101, Joint Training School, Particles at Liquid Interfaces: Fundamentals and Applications, Bonassola (Italy) 2-5 April 2014
- 13) **Surfactant induced synergetic effects on the surface properties of sea water**. Eva Santini, Eduardo Guzmán, Alessandro Benedetti, Francesca Ravera, Michele Ferrari, **Francesca Cirisano**, Libero Liggieri, COST CM1101, Joint Meeting WG 1-3-5-6, Particles at Liquid and Solid Interfaces: Fundamentals and Application, Genoa (Italy) 31 March– 2 April, 2014
- 14) **Highly water repellent coatings for fouling and corrosion prevention in marine environment**. Michele Ferrari, **Francesca Cirisano**, Libero Liggieri, Francesca Ravera, Eva Santini, Eduardo Guzmán, Alessandro Benedetti, COST CM1101, Joint Meeting WG 1-3-5-6, Particles at Liquid and Solid Interfaces: Fundamentals and Application, Genoa (Italy) 31 March– 2 April, 2014

Congresses Attended

- 1) **Joint Meeting of WG1, WG3, WG5 and WG6 of the COST Action CM1101: Particles at liquid interfaces: fundamentals and application**. Genoa (Italy) 31 March- 2 April, 2014
- 2) **11th Symposium of European vacuum coaters**. (invited), Anzio (Italy) 29 September – 1 October, 2014
- 3) **La ricerca che crea innovazione per un future sostenibile TICASS**. Genoa 20 February 2015
- 4) **XXII Congresso AIV** Genoa 20-22 May 2015
- 5) **IACIS Mainz** (Germany) 24-29 May 2015

- 6) **Smart and green interfaces conference.** Athens (Greece) 4-6 May 2016
- 7) **Materials.it 2016.** Catania (Italy) 12-16 December 2016

Other research activity

- Stage at the National institute for lasers, plasma and radiation physics (INFLPR) in Bucarest (Romania) 7th - 17th September 2014 in bilateral inter- governmental project having the title **"Interaction of the laser beams with microdroplets having a controlled content"**.
- Stage at Departamento de Química Física I in Universidad Complutense de Madrid (Spain) 7 th-15th January 2016 in in the framework of the COST-Action CM1101 having the title **"Protective materials for marine environment: antifouling and self-healing surfaces containing capsules"**

Courseware

Courses attended and passed

- Basics of soft matter (2 CFU, Prof. Annalisa Relini, exam passed)
- Methods of preparation and control of innovative pharmaceutical forms (2 CFU Proff. S. Baldassari, G. Caviglioli, B. Parodi, E. Russo, exam passed)
- Polymeric nanocomposites (2 CFU, Prof. Orietta Monticelli, exam passed)
- Surface science (3CFU, Prof. Luca Vattuone exam passed)
- Proprietà ottiche dei Materiali (3 CFU, Prof. M. Canepa exam passed)

Courses Given by invited experts:

- 1) **"Tecnologie di monitoraggio e bonifica di acque e suoli."** Dr. Bagatin: Responsabile dell'Unità di Ricerca delle Tecnologie Ambientali dell'Istituto ENI Donegani (San Donato Milanese), 9/10/14 DCCI
- 2) **"X-ray based experimental techniques and characterization of nano-materials"** Alberto Morgante, CNR-IOM and Physics Department Trieste University 31/3/2015 DCCI
- 3) **"Modern Materials for Energy Saving (Renewable Energy)";** Prof. P. Rogl (Institute of Physical Chemistry, University of Vienna, Austria); 9-10/06/2015, DCCI
- 4) **"Polymers and Composites from Renewable Resources"** Prof. Alessandro Gandini, Politecnico di Grenoble 23,24,29,30/9/2015 CNR Genova

National and International Schools or Workshops

- 1) **"MP1106 & CM1101- Joint Training School on Particles at liquid interfaces: fundamentals and application"** Bonassola, April 2-5, 2014
- 2) **"Winter training school "Kinetics of wetting/spreading of complex liquids"** Loughborough University (United Kingdom) 26-30 January 2015
- 3) **"Eu COST2015 London "Interfacial Science and Fluid Mechanics: Fundamentals, Applications, and Analytical Method"** Queen Mary University of London (United Kingdom) 13-16 April 2015
- 4) **"La rugosità 2D e 3D. Misure non a contatto. Tecniche e normative"** AQM Provaglio d'Iseo (BS) 11 June 2015
- 5) **"IWIW 2016 – International Workshop on Industrial Waste"** DCCI Genova, 17 February 2016

Seminars Attended

- 1) **Rapid Thermal Processing (RTP): a Novel Solvent-Free Enabling Technology for Ultrafast Block-Copolymer Self-Assembly.** Prof. Michele Laus, Università del Piemonte Orientale 11/03/2014 DCCI
- 2) **Study of XIVth century esame corrosion on copper plate.** Prof. Elzbeta Greiner-Wrona, AGH University of science and Technology, Poland, 29/05/14 DCCI
- 3) **Glass as a forever material.** Prof. Elzbeta Greiner-Wrona, AGH University of Science and Technology, Poland 30/05/14 CNR-IENI
- 4) **Recent cosmetic science and formulation technology.** Prof. Yuji Yamashita, del Pharmaceutical and Life science Dept. - Chiba Institute of Science, 3/03/2015 CNR-IENI
- 5) **Recent Developments in the Processing of Ceramics and Glasses.** Prof. Mike Reece (Professor of functional ceramics School of Engineering & Materials Science; Queen Mary University of London (UK)). 17/04/2015, CNR-IENI
- 6) **Pride and Prejudice on Oxygen.** Prof. Joonho Lee (Korea, University, Seoul). 03/06/2015, CNR-IENI

- 7) **Electrochemical Impedance Spectroscopy – a tool for “in situ” investigation of SOFC anodes.** Dott.ssa G. Raikova (Istituto di Elettrochimica e dei Sistemi Energetici (IEES) dell'Accademia Bulgara delle Scienze di Sofia). 22/09/2015, DCCI
- 8) **Surface chemical reaction in graphene/metal interface and materials** Dr. Antonio Politano 21/4/2016 DIFI
- 9) **Design of magnetic nano-architecture** Dott. Davide Peddis (Istituto di Struttura della Materia, CNR – Roma 22/4/2016 DCCI
- 10) **Carbon from historical perspective** Prof. Dr. Javier Narciso Romeo, University of Alicante, Spain 13/5/16 CNR-ICMATE
- 11) **Multi block regression and classification based on PLS regression and extensions** prof. Tormod Naes, Nofina, Oslo - University of Copenhagen, 23/5/16 DIFAR
- 12) **SiC. Synthesis and application** Prof. Dr. Javier Narciso Romeo, University of Alicante, Spain 27/5/16 CNR-ICMATE
- 13) **Diversity oriented synthesis of functional dyes – novel sequences, novel structures, novel properties** Prof. THOMAS J.J. MÜLLER (Heinrich Heine Universität, Düsseldorf) 9/6/16 DCCI
- 14) **Infiltration and their use in the manufacture of composite materials** Prof. Dr. Javier Narciso Romeo, University of Alicante, Spain 10/6/16 CNR-ICMATE
- 15) **Self-assembly of Magnetic Nanomaterials: Design and Physical Properties** Christophe Petit, Sorbonne Universités, UPMC Univ Paris 06, MONARIS, Paris, France 13/6/2016, DIFI
- 16) **Electroceramic materials for energy applications** Dr. Prabhakar Singh Professor *Department of Physics Indian Institute of Technology (Banaras Hindu University)* 21/6/16 DICCA
- 17) **Biointerazione dei reperti in ambiente marino** Dr. Faimale, Dr. Canessa, Dr. Tagliapietra 26/9/16 CNR-ISMAR
- 18) **Fragment-based drug discovery for identifying single- and multi-target inhibitors of CNS targets** Prof. Anders Bach (University of Copenhagen) 30/9/16 IIT



Università degli Studi di Genova
Doctorate School in
Sciences and Technologies of
Chemistry and Materials



Curriculum: Nanochemistry

Graziella Gariano

Start of the Doctorate Program: *January 1st, 2014*

End of the Doctorate Program: *December 31st, 2016*

Advisors:

Luca De Trizio (IIT), Liberato Manna (IIT), Simona Delsante (DCCI)

Thesis Title: Cation Exchange Reactions in Metal Chalcogenide Nanocrystals.

6. Activity report

Research activity

The research activity was carried out at the Istituto italiano di tecnologia (IIT).

Scientific publications

1. Miszta, K. Gariano, G., Brescia, R. *et al.* Selective Cation Exchange in the Core Region of Cu_{2-x}Se/Cu_{2-x}S Core/Shell Nanocrystals. *J. Am. Chem. Soc.* **137**, 12195–8 (2015).

Communications at conferences

Poster communications

1. "Selective Cation Exchange in the Core Region of Cu_{2-x}Se/Cu_{2-x}S Core/Shell Nanocrystals". "ISN2A 2016 – 2nd International Symposium on Nanoparticles/Nanomaterials and Applications", 18th-21st January 2016, Caparica, Portugal.
2. "Selective Cation Exchange in the Core Region of Cu_{2-x}Se/Cu_{2-x}S Core/Shell Nanocrystals". "NaNaX7", 4th-8th April 2016, Marburg, Germany.

Congresses attended

1. "NN14 - 11th International Conference on Nanosciences and Nanotechnologies", 5th-7th July 2014 and "ISFOE14 - 7th International Symposium on Flexible Organic Electronics", 7th-12th July 2014, Thessaloniki, Greece.
2. "SCI&SAYCS 2014 – XIV Sigma-Aldrich Young Chemists Symposium", 27th-29th October 2014, Riccione, Italy.
3. "ISN2A 2016 – 2nd International Symposium on Nanoparticles/Nanomaterials and Applications", 18th-21st January 2016, Caparica, Portugal.
4. "NaNaX7", 4th-8th April 2016, Marburg, Germany.

Courseware

Mandatory credits			+ Other credits
General course (B)	8	Ok	+3
Advanced courses (A)	2	Ok	-
16 seminars	2	Ok	+1
Summer school	1	Ok	+2
Group meetings	4	Ok	-
Total	17		+ 6

During her doctorate, Graziella Gariano has acquired **23 credits** of Courseware.

a) Courses attended and passed (**13 credits**)

- A-type courses: advanced courses on specific topics (**2 credits**):

- 1) “X-ray based experimental techniques and characterization of nano-materials”,
Prof. Morgante A., CNR-IOM and Physics Department Trieste University
(31 marzo 2015, DCCI, Università di Genova) **(1 credit)**.
 - 2) “Elementi di chimica forense”,
Dott. Narizzano R. e Dott.ssa Risso F., ARPAL, Genova
(18-19 maggio 2015, DCCI, Università di Genova) **(1 credit)**.
- B-type courses given by teachers of the IIT **(11 credits)**:
- 1) “Basic concepts in nanochemistry”,
Prof. Manna L. (11, 18 April and 2, 9 May 2014, IIT) **(1 credit)**.
 - 2) “Nanomaterials and nanocomposites: processing and characterization”,
Dr. De Trizio L. and Dr. Arciniegas M. (21-23 May 2014, IIT) **(1 credit)**.
 - 3) “Opto-Electronic Properties of Semiconductor Quantum Dots”,
Dr. Moreels I. (6, 12, 20, 27 June 2014, IIT) **(1 credit)**.
 - 4) “X-rays based Characterization Techniques”,
Dr. Prato M., (4, 14, 18 July 2014 IIT) **(1 credit)**.
 - 5) “Characterization techniques 2”,
Dr. Genovese A. and Dr. Brescia R. (1st, 13th, 14th October 2014, IIT) **(1 credit)**.
 - 6) “Characterization techniques 3”,
Dr. Krahne R. and Dr. Casu A. (12, 17, 19 November 2014, IIT) **(1 credit)**.
 - 7) “Energy related applications 1”,
Dr. Colombo M., Dr. Monaco S., Dr. Zhang Y. (26 November, 4, 9 December 2014, IIT)
(1 credit).
 - 8) “Energy related applications 2”,
Dr. Casu A. and Prof. Manna L. (12, 15, 19, 22 December 2014, IIT) **(1 credit)**.
 - 9) “Photo-physical mechanisms and dynamic investigations in super-resolution microscopy”,
Dr. Vicidomini G. (9, 11, 16, 18 September 2014, IIT) **(3 credits)**.

b) National and International Schools or Workshops (3 credits)

- 1) “8th International Summer Schools on Nanoscience & Nanotechnologies, Organic Electronics & Nanomedicine, ISSON14 ”, 5-12 July 2014 Thessaloniki (Greece) **(3 credits)**.

c) Seminars (7 credits)

- Given **(4 credits)**
- 1) Group meeting talk, IIT, 29/10/2015.
 - 2) Group meeting talk, IIT, 06/12/2016.
- Attended **(3 credits)**

- 1) Tortiglione C., “Unravelling animal biology by functional nanoparticles”, IIT, 19/02/2014.
- 2) Belmonte D., “Quantum geochemistry: simulating physico-chemical properties of materials in the deep Earth”, IIT, 31/03/2014.
- 3) Houtepen A. J., “Electrochemical control over charge transfer and trapping in CdSe-CdTe QD Solids”, IIT, 03/03/2014.
- 4) Sartori S., “Neutron scattering for materials research in the field of nitrogen storage for vehicular applications”, IIT, 05/05/2014.
- 5) Deka S., “Nanomaterials as highly active catalyst for multiple significant reactions”, IIT, 25/06/2014.
- 6) Dorfs D., “Colloidal nanoparticles- shape and composition control”, IIT, 26/06/2014.
- 7) Bigall N. C., “Organization of colloidal nanoparticle building blocks into functional superstructures”, IIT, 26/06/2014.
- 8) Shavel A., “Copper-based quaternary chalcogenide nanoparticles for the photovoltaic and thermoelectric applications”, IIT, 28/07/2014.
- 9) Mokari T., “Synthesis of metal-oxide and metal-oxide based hybrid nanostructures”, IIT, 24/09/2014.
- 10) Sinito C., “Magneto-optical spectroscopy of individual semiconductor nanocrystals”, IIT, 25/09/2014.
- 11) Gaponik N., “Colloidal nanocrystals and their functional architectures”, IIT, 29/09/2014.
- 12) Torsi L., “Organic Bio-Electronic devices for sensing application”, IIT, 10/11/2014.
- 13) Kriegel I., “Plasmonic heavily doped semiconductor nanocrystals: from fundamentals to their nanoscale applications”, IIT, 26/11/2014.
- 14) Di Stasio F., “Semiconductor nanocrystals laser structures”, IIT, 16/12/2014.
- 15) Dogan S., “Field-Effect Transistors and solar cells made of individual colloidal PbS nanosheets”, IIT, 08/01/2015.
- 16) Medhi H., “Plasmonic Nanomaterials”, IIT, 12/01/2015.
- 17) Passerini S., “Materials for sodium batteries”, IIT, 16/01/2015.
- 18) Bertrand G., “Designing organometallics for material science: application for solar cells and scintillators”, IIT, 19/01/2015.
- 19) Lotito V., “Design, fabrication and characterization of plasmonic structures for graphene-based devices and super resolution”, IIT, 19/01/2015.
- 20) Braga D., “Printed Semiconductors and Novel 2D-Materials in the High Charge Density Regime”, IIT, 30/01/15.

- 21) Konstantatos G., “Colloidal quantum dot optoelectronics: photodetectors and solar cells”, IIT, 30/01/2015.
- 22) Agostini M., “High Energy Lithium-Ion and Lithium-Sulfur Batteries”, IIT, 20/02/2015.
- 23) Efros A., “Semiconductor Nanocrystals: Discovery, Milestones and Recent Theoretical Developments”, IIT, 20/11/2015.
- 24) Reiss P., “Insight in the chemistry of metal sulfide nanocrystals and their applications in photovoltaics”, IIT, 25/11/2015.



Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Chemical Sciences and Technologies

PH.D. CERTIFICATE
of
FEDERICA GASTALDO



Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisor

Prof. Mauro Giovannini

Thesis Title

Synthesis, structure and physical properties of ternary intermetallic compounds in R-T-X systems

(R = Ce, Eu, Yb; T = Pd, Pt; X = p-block elements)

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department of Chemistry and Industrial Chemistry, Federica Gastaldo has orally presented her doctorate research work in front of the Commission, formed by

- Prof. Gaetano Granozzi, University of Padova
- Prof. Andrea Pucci, University of Pisa
- Prof. Renata Riva, University of Genova

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

HAS APPROVED THE THESIS OF FEDERICA GASTALDO
CONFERRING ON HER THE TITLE OF

RESEARCH DOCTOR IN
CHEMICAL SCIENCES AND TECHNOLOGIES

Genova, February 24th, 2017

The Coordinator of the Doctorate Course
(Prof. Adriana Saccone)



Università degli Studi di Genova
Dottorato School in
Sciences and Technologies of
Chemistry and Materials



Curriculum: Chemical Sciences

Federica GASTALDO

Start of the Doctorate Program January 1st, 2014

End of the Doctorate Program December 31st 2016

Advisors: Prof. Mauro Giovannini

Thesis Title:

Synthesis, structure and physical properties of ternary intermetallic compounds in R-T-X systems
(R = Ce, Eu, Yb; T = Pd, Pt; X = p-block elements)

Thesis abstract

Rare-earth intermetallic compounds have attracted considerable interest for the past four-decades, because of their use in various technological applications and to interest from the viewpoint of their fundamental properties. These compounds are potentially good candidates to exhibit unusual electronic and magnetic effects, such as superconductivity, intermediate valence, heavy fermion (HF) behavior, Kondo effect and quantum phase transitions [1]. An explorative study on the ternary intermetallics RTX (R = Ce, Eu, Yb; T = Pd, Pt and X = Bi, Sn) is presented. All the samples were prepared by induction melting of the selected elements, and characterized by optical and scanning electron microscopy (SEM) and X-ray powder diffraction (XRPD), in order to detect the existence of new ternary phases and related phase equilibria. Preliminary results on the phase equilibria of these systems will be shown.

[1] T. Muramatsu et al, Phys. Rev. B **83**, 2011, 180404

ACTIVITY REPORT

Research Activity

The research activity was mainly carried out at DCCI (University of Genoa); however, Federica Gastaldo has also spent a brief research period abroad (15 to 27 February 2015, in the group of Prof. Marion Reiffers, Faculty of Humanities and Natural Sciences of University of Prešov, Presov, Slovak Republic

Scientific Publications

- 1) M. Giovannini, I. Čurlík, F. Gastaldo, M. Reiffers, J.G. Sereni
"The role of crystal chemistry in $\text{YbCu}_{5-x}\text{Au}_x$ " *J. Alloys Compd.* 627 (2015) 20-24.
- 2) J.C. Sereni, M. Giovannini, M. Gomez Berisso, F. Gastaldo
"Non-magnetic Anomaly at 1K Arising in Ferromagnetic $\text{Ce}_{2.15}(\text{Pd}_{1-x}\text{Ag}_x)_{1.95}\text{In}_{0.9}$ " *Physics Procedia* 75 (2015) 390-396.
- 3) J.C. Sereni, M. Giovannini, M. Gomez Berisso, F. Gastaldo
"Competition between ferromagnetism and frustrated antiferromagnetism in quasi 2D $\text{Ce}_{2.15}(\text{Pd}_{1-x}\text{Ag}_x)_{1.95}\text{In}_{0.9}$ alloys" *Journal of Physics Condensed Matter* 28 (2016) 475601-475608.
- 4) F. Gastaldo, M. Giovannini, A. M. Strydom, R. F. Djoumessi, I. Čurlík, M. Reiffers, P. Solokha, A. Saccone
"Isothermal section at 600 °C of the Yb-Pd-Sn system ($\text{Pd} \leq 75$ at. %)" *Journal of Alloys and Compounds* 694 (2017) 185-192.

Communications at Conferences

Poster Communications:

- 1) F. Gastaldo, M. Giovannini, A. Saccone
"Explorative study of novel ternary intermetallic compounds in Yb-T-X systems (T = Pd, Pt; X = Bi, Pb, Sn)" 7th JIFC – GICF, Turin, Italy, May 5th – 6th 2014.
- 2) I. Čurlík, F. Gastaldo, M. Giovannini, M. Reiffers
"Crystal structure and physical properties of the novel EuPdSn_2 compound" ICM 2015, Barcelona, Spain, July 5th -10th 2015.
- 3) J.G. Sereni, M. Giovannini, M. Gómez Berisso, F. Gastaldo
"Non-magnetic anomaly at 1 K arising in quasi-2D $\text{Ce}_2(\text{Pd}, \text{Ag})_2\text{In}$ Ferromagnet" ICM 2015, Barcelona, Spain, July 5th-10th 2015.
- 4) R.F. Djoumessi, A.M. Strydom, F. Gastaldo, I. Čurlík, F. Gastaldo, M. Reiffers and M. Giovannini
"Superconductivity in the new cubic correlated compound $\text{Yb}_3\text{Pd}_4\text{Sn}_{13}$ " SCES 2016, Hangzhou, China, May 8th-13th 2016.
- 5) I. Čurlík, F. Gastaldo, M. Giovannini, A. Strydom and M. Reiffers
"Crystal structure and physical properties of the novel Eu compounds" CSMAG'16, Košice, Slovakia, June 13th-17th 2016.

Oral communications:

- 1) F. Gastaldo, M. Giovannini, A. Strydom, I. Čurlík, M. Reiffers
"Structural and physical properties of new compounds in the Yb-Pd-Sn ternary system"
CSMAG'16, Košice, Slovakia, June 13th-17th 2016.

Congresses Attended

- 1) 7th JIFC – GICF, Turin, Italy, May 5th – 6th 2014
- 2) SCTE 2014 – 19th International Conference on Solid Compounds of Transition Elements
June 21st-26th 2014, Genova, Italy
- 3) International Conference: Successful Educational Experiences and Didactic Guidelines in Science Teaching, October 23rd - 24th 2014, Genova, Italy
- 4) ICM 2015– International conference on Magnetism, Barcelona, Spain, July 5th – 10th 2015
- 5) Co.G.I.C.O. 2016 – XII Congresso del Gruppo Interdivisionale di Chimica Organometallica della Società Chimica Italiana, Genova, June 5th – 8th 2016.
- 6) CSMAG'16 – 16th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 13th-17th 2016.

Courseware

Courses attended (type B) (11 CFU):

- 1) Fundamentals of scanning and transmission electron microscopy (passed, 3 credits)
- 2) Mathematic Methods for Chemistry (passed, 2 credits)
- 3) Il metodo di Rietveld in pratica (passed, 2 credits)
- 4) Functional magnetic materials (passed, 2 credits)
- 5) Principi di metallurgia applicata: tradizione e innovazione (passed, 2 credits)
- 6) Synthesis, structure and functional properties of intermetallic compounds (attended, 2 credits)
- 7) Introduction to the RAMAN spectroscopy applied to materials (attended 2 CFU)
- 8) Introduction to functional ceramic materials. Structure, properties, preparation and application (attended 2CFU)

Courses Given by invited experts (type A) (5 credits)

- 1) "Introduction to Thermoelectric Materials" Prof. Peter Rogl (Institute of Physical Chemistry, University of Vienna) June 10th–11th 2014, DCCI.
- 2) "Tecnologie di monitoraggio e bonifica di acque e suoli" Dr. Bagatin: Responsabile dell'Unità di Ricerca delle Tecnologie Ambientali dell'Istituto ENI Donegani (San Donato Milanese) October 9th 2014, DCCI.

- 3) "Yb and Eu Strongly Correlated Electron Systems: from Experiment to Interpretation of Physical Properties" Dr. Ivan Cúrlík (University of Prešov, Slovakia) April 21st -22nd 2015, DCCI.
- 4) "Elementi di chimica forense" – Dr. Narizzano and Dr. Risso (ARPAL, Genova) May 18th – 19th 2015, DCCI.
- 5) "Green analytical chemistry" – Dr. E. Bellido (Department of Analytical Chemistry, Faculty of Sciences, University of Cadiz, Spain) May 26th – 27th 2015, DCCI.

Seminars Attended

- 1) "Fuel cell degradation and its impact on system performance", David Tucker, Senior Scientist, National Energy Technology Laboratory, WV (USA), 29 Aprile 2014, Facoltà di Ingegneria, Genova.
- 2) "Perspectives of future energy research in USA by DoE", David Tucker, Senior Scientist, National Energy Technology Laboratory, WV (USA), 29 Aprile 2014, Facoltà di Ingegneria, Genova.
- 3) "Study of XIVthc. enamel corrosion on copper plates"; Bieta Greiner-Wronowa, AGH University of Science and Technology – Kraków POLAND, 29 Maggio 2014, DCCI.
- 4) "Heterophasic ethylene-propylene copolymer / halloysite nanocomposites using dispersing agents", Dott.ssa Eveline BISCHOFF (Instituto de Química, Universidade Federal do Rio Grande do Sul Porto Alegre -Brasil), 8 Settembre 2014, DCCI.
- 5) "Multiple low energy intermolecular interactions - some new chemistry from old hands", J.M. Charles Stirling, 16 Ottobre 2014, DCCI.
- 6) "Modern Materials for Energy Saving" P. Rogl – June 9th 2015, DCCI.
- 7) "Competition between magnetic phases in the quasi-2D Ce₂(Pd,T)₂In family" J. Sereni, June 19th 2015, DIFI.
- 8) "An automatic method for atom identification in Scanning Tunneling Microscopy images of Fe-chalcogenide superconductors" A.M. Massone, June 19th 2015, DIFI.
- 9) BAZZANO ANDREA, "Strumentazione di chimica analitica per l'esplorazione del sistema solare", November 5th 2015, DCCI.
- 10) GARDELLA LORENZA, "Self-assembled block copolymers aggregates: application in drug delivery", November 5th 2015, DCCI.
- 11) GHIARA GIORGIA, "Introduzione alle pile a combustibile e ai fenomeni di degrado ad alta temperatura", November 5th 2015, DCCI.
- 12) GARBARINO SILVIA, "The magic of diazomethane: advantages and drawbacks of an elusive reagent", November 6th 2015, DCCI.
- 13) MARTINEZ ESPINOSA MARIA ISABEL, "Seeing Molecules: A Survey on Non-Optical Microscopies and their Applications", November 6th 2015, DCCI.
- 14) SPALLAROSSA MARTINA, "The hydrogen auto transfer process", November 6th 2015, DCCI.
- 15) "Conventional and Unconventional Superconductivity: An overview" Prof. Ernst BAUER (Institute of Solid State Physics, Vienna University of Technology) November 9th and 11th 2015, DCCI.
- 16) "Physics in extreme conditions" Prof. M. Reiffers (Faculty of Humanities and Natural Sciences - Prešov University) April 5th and 6th 2016, DCCI.

17) "Low and Very Low Temperatures: Methods of Producing and Measuring Cryogenic Temperatures"
Dr. Ivan Čurlík (Department of Physics, Mathematics and Technics, University of Prešov, Slovakia)
February 17th and 18th 2016, DCCI.

18) "Aspetti e prospettive della moderna industria siderurgica" Ing. Franco Belgrano, Isosistemi srl,
May 5th 2016, DCCI.

Workshops:

1) IWIW 2016 – International workshop on Industrial Waste, February 17th 2016, DCCI.

National and international schools:

1) Scuola Nazionale per Dottorandi in Chimica Inorganica "Nuovi Materiali ed Energie Sostenibili",
Bressanone, Italia, 13-16 luglio 2015.

Other Activities

1) Affidamento di incarico di attività di supporto alla didattica (2014, 2015, 2016) ai sensi del
Regolamento emanato con D.R. n. 569/17.05.2012 e s.m.



Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Materials Science and Technology

PH.D. CERTIFICATE
of
ALICE GIULIANO



Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisor

Prof. Antonio Barbucci

Thesis Title

*Perovskite materials for IT-SOFC
cathodes: improvement of
electrochemical performance and
synthesis of new compounds*

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department Physics, Alice Giuliano has orally presented her doctorate research work in front of the Commission, formed by

- Prof.ssa Elisabetta Finocchio, University of Genova
- Prof. Henrik Rudolph, Netherland Defense Academy
- Prof. Ruggero Vaglio, University of Napoli "Federico II"

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

**HAS APPROVED THE THESIS OF ALICE GIULIANO,
CONFERRING ON HER THE TITLE OF**

**RESEARCH DOCTOR CUM LAUDE IN
MATERIALS SCIENCES AND TECHNOLOGY**

Genova, February 24th, 2017

**The Coordinator of the Doctorate Course
(Prof. Adriana Saccone)**



Università degli Studi di Genova



**Doctorate in
Sciences and Technologies of
Chemistry and Materials**

CURRICULUM Science and Technology of Materials (XXIX ciclo)

ALICE GIULIANO

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *December 31th, 2016*

Advisors: Prof. Antonio Barbucci

Thesis Title: Perovskite materials for IT-SOFC cathodes: improvement of electrochemical performance and synthesis of new compounds

ACTIVITY REPORT
Research Activity

The research activity was mainly carried out at the Department of civil, chemical and environmental engineering (DICCA) – University of Genoa. From October 2015 to April 2016 visiting PhD student at the Bordeaux CNRS laboratory to improve my knowledge on SOFC materials

Scientific Publications

- 1) M. Panizza, A.Barbucci, M.Delucchi, M.P.Carpanese, **A. Giuliano**, M. Cataldo-Hernández, G. Cerisola
"Electro-Fenton degradation of anionic surfactants" Separation and Purification Technology
Reference: Separation and Purification Technology, Volume 118, pp. 394 – 398, 2013
- 2) T.Ou, **A. Giuliano**, M. Panizza, A.Barbucci, G. Cerisola
"Thermochemical recycling of hydrolyzed NaBH₄. Part I: in-situ and ex-situ evaluations"
Reference: International Journal of Hydrogen Energy, Volume 38, Issue 35, pp. 15269 – 15274, 2013
- 3) M. P. Carpanese, **A. Giuliano**, E. Mercadelli, A. Sanson, A. Gondolini, A. Bertei, A. Barbucci
"Experimental approach for the study of SOFC cathodes"
Reference: Bulgarian Chemical Communications, Volume 48, Special Issue B, pp. 23 -29, 2016
- 4) M. P. Carpanese, A. Bertei, D. Clematis, **A. Giuliano**, A. Sanson, E. Mercadelli, C. Nicollella, A. Barbucci
"Understanding the electrochemical behaviour of LSM-based SOFC cathodes. Part I-Experimental and Electrochemical"
Submitted to Solid State Ionics
- 5) **A.Giuliano**, M. P. Carpanese D. Clematis, M. Boaro, A. Pappacena, F. Deganello, L. F. Liotta, A. Barbucci
"Understanding the Redox Behavior in Surface Modified LSCF and BSCF Cathodes for SOFCs"
Submitted to Journal of Power Sources
- 6) **A. Giuliano**, M. P. Carpanese, D. Clematis, M. Panizza, G. Cerisola, A. Barbucci

"Electrochemical and microstructural investigation on LSCF-BSCF composite cathode for SOFCs devices"
Submitted to Electrochimica Acta, Special Issue EIS2016 Congress

- 7) **A. Giuliano**, C. Nicollet, M. P. Carpanese, F. Mauvy, J. C. Grenier
"Influence of the GDC interlayer on the performances of $Pr_{0.8}Sr_{0.2}Fe_{0.7}Ni_{0.3}O_{3-\delta}$ as SOFC cathode"
Submitted to Electrochimica Acta, Special Issue EIS2016 Congress

Communications at Conferences

Poster Communications:

- 1) M. Panizza, A. Barbucci, M. P. Carpanese, M. Delucchi, S. Congiu, **A. Giuliano**, G. Cerisola
"Removal of Coumaric Acid by electrochemically generated Fenton's reagent"
GEI 2013 Giornate dell'Elettrochimica Italiana 22 – 27 Settembre 2013, Pavia
- 2) M. P. Carpanese, S. Congiu, **A. Giuliano**, M. Panizza, Y. A. Ramirez, A. Sanson, E. Mercadelli, P. Pinasco, A. Barbucci
"On Impedance measurements suitability of electrolyte supported SOFC"
11th European SOFC and SOEC Forum, 1 - 4 Luglio 2014, Luzern (Switzerland)
- 3) **A. Giuliano**, S. Congiu, M. P. Carpanese, A. Barbucci
"Study of cathodes for solid oxide fuel cells operating at intermediate temperature"
Advances in medium and high temperature solid oxide fuel cells technology, 14 - 18 Luglio 2014, Udine
- 4) M. P. Carpanese, M. Panizza, M. Delucchi, **A. Giuliano**, S. Congiu, G. Cerisola, M. Boaro, and A. Barbucci
"LSM - impregnated LSCF cathode for Solid Oxide Fuel Cells"
10th European Symposium on Electrochemical Engineering, 28 Settembre - 2 Ottobre 2014, Chia (CG)
- 5) M. P. Carpanese, A. Giuliano, D. Clematis, M. Delucchi, M. Panizza, R. Botter, A. Barbucci
"Effect of cathodic polarization on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ infiltrated electrodes for IT-SOFCs"
Ceramics for Energy CEn 2015, May 14-15 2015, Faenza, Italy
- 6) **A. Giuliano**, M.P. Carpanese, D. Clematis, M. Delucchi, M. Panizza, R. Botter, G. Cerisola, A. Barbucci
"Kinetic mechanisms governing the electrochemical response of Solid Oxide Fuel Cell impregnated electrodes"
Giornate dell'Elettrochimica Italiana GEI, September 2015, Bertinoro, Italy
- 7) **A. Giuliano**, M. P. Carpanese, D. Clematis, M. Panizza, G. Cerisola, A. Barbucci
"Electrochemical and microstructural investigation on LSCF-BSCF composite cathode for Solid Oxide Fuel Cells devices"
10th International Symposium on Electrochemical Impedance Spectroscopy, June 19-24 2016, A Toxa, Spain
- 8) **A. Giuliano**, C. Nicollet, A. Kucharski, F. Mauvy, A. Barbucci, J-C. Grenier
"EIS measurements on $Pr_{1-x}Sr_xFe_{1-y}Ni_yO_{3-\delta}$ perovskite materials as SOFC cathode: methodology and results"
10th International Symposium on Electrochemical Impedance Spectroscopy, June 19-24 2016, A Toxa, Spain
- 9) M. Panizza, A. Barbucci, M. P. Carpanese, D. Clematis, M. Delucchi, **A. Giuliano**, G. Cerisola
"Electrochemical oxidation of synthetic dyes using BDD anode with solid polymer electrolyte"
2nd E3 Mediterranean Symposium: Electrochemistry for Environment and Energy, 14-16 September 2016, Gargnano, Italy

Oral communications:

- 1) M. P. Carpanese, E. Mercadelli, P. Pinasco, A. Sanson, M. Viviani, S. Presto, G. Cerisola, S. Congiu, M. Delucchi, **A. Giuliano**, T. Ou, M. Panizza, A. Barbucci
"Electrochemical performances of monolithic $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ tri-layer as fuelcell and electrolyzer device"

GEI 2013 Giornate dell'Elettrochimica Italiana 22 – 27 Settembre 2013, Pavia

- 2) A. Barbucci, **A. Giuliano**, S. Congiu, A. Sanson, P. Pinasco, M. P. Carpanese
"Study of reliability of SOFC cathode impedances at applied overpotential"
10th International Symposium on Electrochemical Impedance Analysis, 2 - 3 Giugno 2014, Borowetz (Bulgaria)
- 3) **A. Giuliano**
"Characterization and electrochemical measurements of impregnated cathodes for solid oxide fuel cell"
ISE Student Satellite Regional Symposium on Electrochemistry South-East Europe, June 7, 2015, IEES-BAS, Sofia, Bulgaria
- 4) M.P. Carpanese, **A. Giuliano**, D. Clematis, A. Bertei, C. Nicolella, M. Delucchi, M. Panizza, R. Botter, A. Barbucci
"Kinetic mechanism that influence the electrochemical behaviour of different type of cathodic materials for intermediate temperature solid oxide fuel cells"
5th Regional Symposium on Electrochemistry South-East Europe, June 7-11 2015, Pravets, Bulgaria
- 5) M. Delucchi, A. Barbucci, M. Panizza, M. P. Carrpanese, **A. Giuliano**, D. Clematis, G. Cerisola
"(Z)-N-9-octadecenylpropane-1,3-diamine: inhibition effect on metals used in closed-circuit hot-water heating"
Giornate dell'Elettrochimica Italiana GEI, September 2015, Bertinoro, Italy
- 6) **A. Giuliano**, M. P. Carpanese, D. Clematis, M. Panizza, G. Cerisola, A. Barbucci
"Kinetic mechanism, performances and durability of infiltrated cathodes for IT-SOFC application"
10th International Symposium on Electrochemical Impedance Spectroscopy, June 19-24 2016, A Toxa, Spain
- 7) M. P. Carpanese, D. Clematis, **A. Giuliano**, M. Panizza, M. Viviani, S. Presto, A. Barbucci
"Modification of surface chemistry of LSCF and BSCF Electrodes through LSM infiltration"
12th International Symposium on Systems with fast ionic transport ISSFIT-12, July 3-7 2016, Kaunas, Lithuania

Congresses Attended

- 1) 5th Regional Symposium on Electrochemistry South-East Europe, June 7-11 2015, Pravets, Bulgaria
- 2) 10th International Symposium on Electrochemical Impedance Spectroscopy, June 19-24 2016, A Toxa, Spain

Courseware

Attended:

- 1) Introduzione ai materiali ceramici funzionali. Struttura, proprietà, preparazione e applicazioni - Prof. V. Buscaglia - DCCI Aprile 2014 (2 credits)
- 2) Processes for Liquids and Gaseous Biofuels Production - Prof. Attilio Converti - DICCA Novembre 2014 (3 credits) – passed the 13th of March 2015
- 3) Application of Raman spectroscopy - Prof. Marilena Carnasciali – DCCI Aprile 2015 (2 credits)

Passed:

- 1) Introduzione ai materiali ceramici funzionali. Struttura, proprietà, preparazione e applicazioni - Prof. V. Buscaglia - DCCI Aprile 2014 (2 credits)
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- 3) Application of Raman spectroscopy - Prof. Marilena Carnasciali – DCCI Aprile 2015 (2 credits)

During her doctorate, ALICE GIULIANO has acquired 7 credits of Courseware.

Courses Given by invited experts

- 1) X-ray experimental techniques, Prof. A. Morgante, March 31 2015 (3 hours)
- 2) Elementi di chimica forense, Dott. Narizzano, May 18-19 2015 (4 hours)
- 3) Green Analytical Chemistry, Prof. Estrella Espada Bellido, May 26-27 2015 (4 hours)

National and International Schools or Workshops

- 1) Workshop in Fundamentals and application of cerium dioxide in catalysis, University of Udine, July 11 - 14 2014.
- 2) Advances in medium and high temperature solid oxide fuel cells technology - Advanced Professional training, University of Udine, July 14 - 18 2014.
- 3) Ceramics for Energy CEn 2015, International Workshop, May 14-15 2015, Faenza, Italy
- 4) Tecniche Metallografiche, Associazione Italiana di Metallurgia (AIM), Milano, Italy
Corso articolato su 3 moduli per un totale di 41 ore

Seminars Attended

- 1) Atomically dispersed Au-Ox species catalyze the water-gas shift and methanol steam reforming reactions - Prof. Maria Flitzani-Stephanopoulos, Tufts University, Boston (DICCA 24 febbraio 2014)
- 2) FUEL CELL AND FUTURE ENERGY TECHNOLOGIES: prima parte: "Fuel cell degradation and its impact on system performance", seconda parte "Perspectives of future energy research in USA by DoE" - Prof. David Tucker, National Energy Technology Laboratory, WV (Villa Cambiaso - Scuola Politecnica - 29 aprile 2014) (2 hours)
- 3) How to write a scientific paper - Prof. Serge Abrate, Southern Illinois University (Villa Cambiaso - Scuola Politecnica - 8 settembre 2014)
- 4) "ABC" Impedance - (Spettroscopia di impedenza elettrochimica per lo studio dei sistemi elettrochimici) - Prof.ssa Daria Vladikova, Bulgarian Academy of Science (DICCA - 24 settembre 2014)
- 5) Thermal analysis and calorimetry: powerful tools for scientific investigation - Dott. Locardi Federico - UNIGE (DCCI - 30 Ottobre 2014)
- 6) Synchrotron Light for Extended X-ray Absorption Fine Structure (EXAFS). A bright opportunity for (material) science - Dott. Lucchini Mattia - UNIGE (DCCI - 30 Ottobre 2014)
- 7) Corrosione microbiologica: introduzione ai meccanismi e tecniche di studio - Dott. Roberto Spotorno - UNIGE (DCCI - 30 Ottobre 2014)
- 8) Design for today's environment: A material perspective – Prof. Mike Ashby, University of Cambridge (ENSCBP University of Bordeaux-12 Novembre 2015)

Other Activities

- 1) PhD Student Award
"Characterization and electrochemical measurements of impregnated cathodes for solid oxide fuel cell"
ISE Student Satellite Regional Symposium on Electrochemistry South-East Europe, June 7, 2015, IEES-BAS, Sofia, Bulgaria
Sponsored by the International Society of Electrochemistry, the Bulgarian Academy of Sciences, PalmSens and DropSens.
- 2) Internship at ICMBM-CNRS Bordeaux

From October 2015 to April 2016 visiting PhD student at the Bordeaux CNRS laboratory to improve my knowledge on SOFC materials.

3) Incarico di attività di supporto alla didattica

Ai sensi del D. R. n. 569 del 17.5.2012 dell'Università Degli Studi di Genova, come modificato dal D.R. n. 251 del 20.05.2013.

Bando 57/NAV del 11/01/2016 - insegnamento di "Chimica generale ed applicata" cod. 72686



Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Pharmaceutical, Food and Cosmetic Sciences

PH.D. CERTIFICATE
of
CHIARA LACAPRA



Doctorate Course

Pharmaceutical, Food and Cosmetic Sciences

Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisor

Prof.ssa Carla Villa

Thesis Titles

Study and application of innovative green procedures to obtain organic and bio-inorganic compounds of cosmetic and pharmaceutical interests

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department of Pharmacy, Chiara Lacapra has orally presented her doctorate research work in front of the Commission, formed by

- Prof.ssa Olga Bruno, University of Genova
- Prof. Stefano Manfredini, University of Ferrara
- Prof.ssa Nunziatina De Tommasi, University of Salerno

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

HAS APPROVED THE THESIS OF CHIARA LACAPRA

CONFERRING ON HER THE TITLE OF

RESEARCH DOCTOR IN
PHARMACEUTICAL, FOOD AND COSMETIC SCIENCES

Genova, February 24th, 2017

The Coordinator of the Doctorate Course
Prof. Adriana Saccone



Università degli Studi di Genova
Doctorate Course in
Sciences and Technologies of
Chemistry and Materials

Curriculum: SFAC, XXIX cycle

CHIARA LACAPRA

Start of the Doctorate Program: *January 1st, 2014*

End of the Doctorate Program: *December 31st, 2016*

Advisor: *Prof.ssa Villa Carla*

Thesis Title: “Study and application of innovative green procedures to obtain organic and bio inorganic compound of cosmetic and pharmaceutical interests.”

“Studio e applicazione di procedure “verdi” per l’ottenimento di composti organici e bio - inorganici di interesse cosmetico e farmaceutico”.

Thesis abstract: Studio e applicazione di procedure ecosostenibili con lo scopo di preparare “ingredienti” utilizzabili in ambito cosmetico e farmaceutico.

PRIMO ANNO: Il lavoro di ricerca si è sviluppato in due principali ambiti:

In ambito sintetico:

Gli studi sono stati focalizzati su un triterpene pentaciclico, acido 18- β -glicirretico (GTA), parte agliconica del glucoside triterpenoide Glicirizzina (o Acido glicirizzinico) estratto dalla radice della liquirizia e sulla sintesi ecocompatibile di alcuni suoi derivati.

La preparazione convenzionale di questi composti risulta di complessa realizzazione e presenta diversi svantaggi sia in fase sintetica sia nella successiva fase di purificazione, quali l’utilizzo di solventi chimici ad alto impatto ambientale, spesso tossici, lunghi tempi di reazione, complesso work-up con conseguente dispendio energetico e infine l’impiego di reagenti non ecocompatibili, costosi e di difficile approvvigionamento.

Con lo scopo di ottenere diversi esteri dell’acido glicirretico, sono state applicate metodiche *solvent-free* microonde mediate basate sulla semplice miscela dei reagenti, in presenza di sistemi catalitici, che hanno permesso di migliorare le procedure classiche di sintesi e di ottenere i composti con alte rese di reazione.

Le molecole risultate più significative sono state caratterizzate anche da un punto di vista della sicurezza e della funzionalità mediante studi *in vitro* di citotossicità (in linea con il Regolamento Cosmetico europeo 1223/09 che vieta la sperimentazione animale) e di attività antimicrobica, mediante test svolti rispettivamente dai laboratori del DIMES e del DISC di Genova.

In ambito estrattivo, secondo i target della *Green Chemistry* e *Green Extraction* e in prosecuzione di studi in questo ambito, svolti dal mio gruppo di lavoro, la ricerca è stata focalizzata sull'utilizzo di matrici rinnovabili vegetali e fonti energetiche alternative da applicare in campo cosmetico come ingredienti efficienti e sicuri.

I miei studi si sono quindi focalizzati sulla messa a punto di un metodo che permettesse di utilizzare le microonde come unica fonte energetica alternativa e scarti industriali agro-alimentari come matrice vegetale fresca da estrarre, per ottenere ingredienti bioattivi ad alto valore aggiunto e a basso costo da inserire in prodotti cosmetici per esaltarne le proprietà benefiche.

Applicando una metodica nota come *Microwave Hydrodiffusion and Gravity* (MHG), attraverso l'irraggiamento dei prodotti di scarto, è stato possibile il recupero rapido, peculiare e unico delle frazioni acquose di matrici esauste, ancora ricche di ingredienti attivi idrosolubili; questo tipo di estratto non è recuperabile con nessun altro metodo noto. Il processo è rapido (10 minuti circa) e pulito in quanto non prevede l'utilizzo di alcun solvente per il recupero del prodotto di interesse. L' "acqua essenziale" ottenuta è l'acqua di sostentamento e nutrimento della pianta stessa che in fase di processo serve sia da solvente estraente sia da estratto ricco di principi attivi.

L'irraggiamento microonde è stato applicato utilizzando un prototipo di forno microonde multitasking, ideato dal gruppo di ricerca di Genova durante una collaborazione con altre università italiane in materia di riscaldamento dielettrico. Il progetto è proseguito con studi di funzionalità e sicurezza (test *in vitro* eseguiti presso il DIMES di Genova) e gli ingredienti più promettenti sono stati utilizzati per formulare prodotti cosmetici finiti.

I risultati ottenuti e la fattiva collaborazione con un'azienda cosmetica esterna (Luxis Group Srl) hanno permesso di sviluppare un progetto imprenditoriale che è stato presentato al Concorso SMARTcup Liguria 2014 e ha ricevuto il Primo Premio per la sezione *Agro-Food & Cleantech*.

SECONDO ANNO: Il lavoro di ricerca del secondo anno ha toccato diverse tematiche in ambito sintetico, estrattivo e formulativo; gli studi sono stati svolti inizialmente presso la Sezione di Chimica del Farmaco e del Prodotto Cosmetico del Dipartimento di Farmacia dell'Università degli Studi di Genova e sono proseguiti presso la *Penn State University*, sotto la guida del Prof. Sridhar Komarneni, *distinguished professor of clay mineralogy*, nel *Material Research Laboratory*, centro di ricerca universitario specializzato nella progettazione, studio e caratterizzazione di argille naturali e sintetiche, col quale il nostro gruppo di ricerca collabora da diverso tempo.

In ambito sintetico il lavoro si è svolto attraverso la progettazione di argille organofile, *organoclays*, ossia composti ibridi organico-inorganici nei quali le argille, molecole abbondanti in natura, caratterizzate da bassa o nulla tossicità, inerzia chimica e buona biocompatibilità, ospitano nel loro spazio *interlayer* molecole organiche, con lo scopo di veicolarle o proteggerle.

In particolare, presso il dipartimento di farmacia, la ricerca si è focalizzata sulla reazione di scambio cationico microonde-mediata, di due sali ammoniacali quaternari, un filtro solare UVB, derivato della benzilidencanfora e un colorante, lo Steel Blue®, in due argille, la Bentonite sodica e la Laponite, allo scopo di verificare se la Laponite, argilla di sintesi, presentasse delle differenze nel

processo d'intercalazione rispetto alla Bentonite, argilla naturale già oggetto di studi precedenti da parte del gruppo di ricerca.

Presso il *Material Research Laboratory*, invece, la ricerca si è focalizzata sull'intercalazione idrotermale convenzionale e microonde di un tensioattivo anionico, il *Sodium Dodecyl Sulfate*, nell'*interlayer* dell'idrotalcite, argilla anionica *Layered Double Hydroxide*; lo studio è stato preso in esame per l'eventuale successiva realizzazione di altri derivati d'interesse cosmetico e farmaceutico (è attualmente in corso la preparazione di derivati dell'idrotalcite contenenti il *Sodium Dehydroacetate*, noto conservante cosmetico).

Le argille organofile, contenenti il filtro solare, sono state preliminarmente caratterizzate mediante un'analisi spettrofotometrica UV-Vis ed è stato, inoltre, svolto uno studio di funzionalità in vitro, al fine di valutare il rilascio del filtro dai due derivati.

Tutti i derivati sono stati analizzati, presso i laboratori della *Penn State University*, mediante la diffrazione a raggi X (*X-Ray Diffraction- XRD*) allo scopo di valutare l'avvenuto processo d'intercalazione.

In ambito formulativo, al fine di proseguire gli studi relativi a nuovi approcci estrattivi *ecofriendly*, nel "*Green Cosmetic Laboratory*" (DIFAR - Unige), la ricerca si è focalizzata sull'ottimizzazione della procedura *solvent free* microonde-mediata messa a punto sulle vinacce, gli scarti del processo di vinificazione.

Inoltre, al fine di valutare il potenziale utilizzo cosmetico degli estratti, le così denominate "acque essenziali" sono state incluse in nuove formulazioni cosmetiche; il principale obiettivo del lavoro è stato la realizzazione di analisi delle proprietà reologiche e del comportamento dei formulati in seguito a stress termico. Prove di stabilità a lungo termine e altri studi sull'efficacia e la sicurezza sono ancora attualmente in corso.

I buoni risultati ottenuti, presentati mediante progetti imprenditoriali a diversi concorsi locali e nazionali, si sono concretizzati mediante la costituzione di una Spin off cosmetico, ACCADERMICA, In

I risultati di questo lavoro hanno portato alla stesura di un brevetto nazionale la cui domanda è stata recentemente depositata e nel quale sono riconosciuta inventore:

CARLA VILLA CHIARA LACAPRA SILVIA RUM, RAFFAELLA BOGGIA

"Estratto ottenuto da Materiale vegetale, composizione contenente Detto estratto e Dispositivo per la Produzione del Detto estratto".

TERZO ANNO: anche il lavoro di ricerca del terzo anno ha toccato diverse tematiche in ambito sintetico, estrattivo e formulativo.

Ambito sintetico

In prosecuzione degli studi precedenti, il lavoro ha riguardato la progettazione e la preparazione *ecofriendly* microonde mediata di nuovi ibridi bio-inorganici di potenziale impiego in ambito cosmetico.

Nello specifico lo scopo è stato quello di ottenere argille organofile multitasking, mediante l'intercalazione e/o l'adsorbimento, in parallelo, del colorante organico giallo Basic Yellow 87 (1-metil-4-((metilfenilidrazo)metil)piridinio metilsolfato) rispettivamente in Bentonite (BNT, argilla naturale) e Laponite (LAP, argilla sintetica), applicando una metodica idrotermale microonde-mediata, e valutandone vantaggi e limiti in paragone a una metodica tradizionale. E' stato quindi

messo a punto un metodo spettrofotometrico UV-VIS per monitorare l'avvenuta interazione e l'eventuale rilascio del colorante in condizioni fisiologiche dai substrati funzionalizzati.

Ambito estrattivo,

Sono proseguiti gli studi focalizzati sull'estrazione *solvent free* microonde-mediata (metodica MHG) di matrici botaniche e prodotti di scarto dell'industria agro-food, prendendo in considerazione matrici di diversa natura quali: melograno, lavanda, canapa, rosa ed alcune microalghe (*Spirulina* e *Nannocloropsis*).

Inoltre, sul melograno, è stato eseguito uno studio estrattivo microonde-mediato sulla matrice esausta del frutto (ottenuta in seguito alla spremitura del melograno stesso per l'ottenimento del corrispondente succo) utilizzando l'acqua come solvente verde in paragone ad altre metodologie estrattive. Le potenzialità degli estratti sono state valutate in termini di contenuto in polifenoli totali, in ellagitannini e di RSA (*Radical Scavenger Activity*). La ricerca, in collaborazione con la Sezione di Chimica e Tecnologie Farmaceutiche e Alimentari del Dipartimento di Farmacia dell'Università degli Studi di Genova, si è concretizzata con la pubblicazione di un articolo su rivista internazionale, come riportato in seguito.

Ambito formulativo

Sono state ampliate e concluse le prove di stabilità a lungo termine relative a prodotti formulati (contenenti l'estratto delle vinacce messo a punto durante il percorso di dottorato) in seguito alla costituzione dello Spin Off Accadermica. L'approccio formulativo è stato condotto studiando e selezionando appositamente ciascun ingrediente, al fine di garantire sicurezza, efficacia, stabilità ed eco-sostenibilità delle emulsioni.

Di particolare rilievo è risultata la scelta dell'opportuno sistema preservante, non solo in grado di assicurare la corretta conservazione dei prodotti, ma allo stesso tempo presentare un ridotto potenziale irritativo cutaneo.

Questa fase dello studio è iniziata con una ricerca capillare volta ad individuare le miscele di composti, attualmente disponibili in commercio, proposte come alternative (e più sostenibili) rispetto ad alcuni conservanti cosmetici convenzionali. Successivamente è stato sviluppato e portato avanti un test di tollerabilità in uso su volontari, mettendo a punto una formulazione base addizionata delle diverse miscele conservanti, alle percentuali d'uso consigliate dalle aziende fornitrici. Tali formulazioni sono state testate, per il loro potenziale irritativo, mediante uno studio in vivo su 24 soggetti. I risultati dello studio, incrociati con i dati di efficacia conservativa (challenge test eseguiti da un'azienda fornitrice), hanno evidenziato interessanti risposte sui volontari e indicato in modo inequivocabile il sistema preservante più promettente per la linea formulata.

ACTIVITY REPORT

Research Activity

The research activity was mainly carried out at the Department of Pharmacy (UNIGE).

Scientific Publications

- 1) Villa C., Lacapra C., Rialdi V., Corradini A., Picco V., La Mattina L.; "Trucco funzionalizzato ecosostenibile: progettazione e preparazione", *Kosmetica 01*, Feb-2014, pp. 36-39.

- 2) Villa C., Lacapra C., Rosa R., Veronesi P., Leonelli C.; "Ecosustainable development of novel bio-inorganic hybrid materials as UV protection systems for potential cosmetic applications", *Current Pharmaceutical Biotechnology* - volume16, issue12,2015, pp 1070-1077, issn 1389-2010/1873-4316, doi 10.2174/1389201016666150817094847.
- 3) Il lavoro in ambito estrattivo, svolto durante il primo anno di dottorato, ha condotto alla realizzazione di un brevetto nazionale la cui domanda è stata depositata il 31/12/2015, con numero di assegnazione **102015000088909**: Carla Villa, Chiara Lacapra, Silvia Rum, Raffaella Boggia - "Estratto ottenuto da Materiale vegetale, composizione contenente Detto estratto e Dispositivo per la Produzione del Detto estratto".
- 4) Boggia R., Turrini F., Villa C., Lacapra C., Zunin P., Parodi B.- "Green extraction from pomegranate marcs for the production of functional foods and cosmetics", *Pharmaceuticals* 2016, 9, 63; doi:10.3390/ph9040063.
- 5) Nel biennio 2015-2016 autrice di diversi articoli a scopo divulgativo sulla rivista nazionale di settore Kosmetica (edita da Tecniche Nuove, con cadenza mensile).

Communications at Conferences

Poster Communications:

- 1) Villa C., Rum S., Lacapra C.; "Ecofriendly microwave-mediated synthesis of organogelators from renewable sources for cosmetic and pharmaceutical applications"- GIFC (Giornate Italo - Francesi di Chimica), Torino, 5-6 Maggio 2014.
- 2) Villa C., Lacapra C., Rum S., Boggia R., Leonelli C., Rosa R.; "Green microwave extracts from waste matrices for cosmeceutical and nutraceutical applications" - Food Processing Innovation and Green Extraction Technologies: recent advances and applications in human health, Università della Magna Grecia, Catanzaro, 25-26 settembre 2014.
- 3) Villa C., Lacapra C., Rum S., Boggia R., Leonelli C., Rosa R., Bassi A. Danailova J.; "Multidisciplinary sustainable approach for the study of green extracts from waste matrices: solvent-free microwave extraction and in vitro assays as potential cosmeceutical and nutraceutical ingredients" – IFSCC (International Federation of Societies of Cosmetic Chemists), Paris, 27-30 Ottobre 2014.
- 4) Danailova J., Vernazza S., Scanarotti C., Pronzato M.A., Penco S., Lacapra C., Rum S., Villa C., Bassi A.M.; "Multidisciplinary approach to assess the biological potential of bioactive green extracts from exhaust organic matrices, obtained by microwave irradiation"- International Conference Of Alternatives to Animal Experimentation, Portugal, 8-9 Maggio 2015.
- 5) Villa C., Rum S., Lacapra C., Bassi AM., Burlando B., Rialdi V., Boggia R.;" *From grape marc extracts to skin care formulations: a multidisciplinary sustainable approach*"- Cosminnov, Orléans, 24-25 Maggio 2016.
- 6) Turrini F., Lacapra C., Donno D., Villa C., Zunin P., Signorello MG., Beccaro G., Boggia R.; "Green extraction from pomegranate juice by-products and their potential use as natural food/cosmetics preservatives and/or bioactive ingredients"- Green Extraction of Natural Products, Torino, 31 Maggio-1Giugno 2016.

Oral Communications:

- Lacapra C., Villa C., Komarneni S.; "Microwave-mediated preparation of new multifunctional organo Laponites for cosmetic applications" - GIFC- Giornate Italo Francesi di Chimica (Avignone, 25-26 Aprile 2016).

Attended Congresses

- 1) GIFC- Giornate Italo Francesi di Chimica (Torino, 5-6 Maggio 2014).
- 2) 39° Congresso nazionale SICC (Società Italiana di Chimica e scienze Cosmetologiche): Cosmetici e Processi da fonti Alimentari, rinnovabili o sostenibili (Milano, 26 Giugno 2014).
- 3) IFSCC-International Federation of Societies of Cosmetic Chemists- 2014 (Paris, 27-30 Ottobre 2014).
- 4) Making Cosmetics & Formulating Cosmetics 2014 (Milano, 25 Novembre 2014).
- 5) GIFC- Giornate Italo Francesi di Chimica (Avignone 25-26 Aprile 2016).
- 6) Green Extraction of Natural Products (Torino 31 Maggio-1 Giugno 2016)
- 7) Partecipazione alla fiera dell'innovazione SMAU Milano (25-27 Ottobre 2016)
- 8) Making Cosmetics & Formulating Cosmetics 2016 (Milano, 23 Novembre 2016).

Courseware

During his doctorate, Lacapra Chiara has acquired 11 credits of Courseware.

Courses attended and passed (11 credits): “corsi di tipo B”

Courses Given by Teachers of the Doctorate School in Sciences and Technologies of Chemistry and Materials

- 1) Principali piante utilizzate in fitocosmesi e loro costituenti (2 CFU)- Bisio A., DIFAR.
- 2) Metodologia della ricerca sperimentale (3CFU)- Grotti M.,DCCI; Leardi R., DIFAR.
- 3) Metodi di preparazione e controllo di forme farmaceutiche innovative (2CFU)- Baldassari S., Caviglioli G., Parodi B., Russo E., DIFAR.
- 4) Chimica bioorganica (2CFU)- Banfi L., DCCI.
- 5) Caratterizzazione di nano particelle per mezzo della microscopia a forza atomica e dynamic light scattering (2CFU)- Rolandi R., DIFI.

Courses Given by invited experts (“corsi di tipo A”):

1. Graphene on SiC and CU substrates: growth properties and applications (28 Marzo 2014- Coletti C.)
2. Pharmaceutical Green Chemistry (09 Maggio 2014- Cabri W.)
3. Solid state modifications: Principles and applications for drug solubility enhancement (07 Novembre 2014- Gatti P.)
4. “New trends in computer aided drug design (09 Dicembre 2014- Truccinardi T.)”
5. “Elementi di chimica forense (18-19 Maggio 2015- Narizzano Riccardo e Risso Fulvia, ARPAL)”

National and International Schools or Workshops

- 1) Scuola di chemiometria (19-22 Maggio 2014, Genova-DIFAR)
- 2) Scuola di colture cellulari: i metodi alternativi (3-4 Luglio 2014, Genova-DIMES)
- 3) Workshop: Profumo, Scienza e Arte (19 Febbraio 2014- SICC- Milano)
- 4) Workshop: La formazione post lauream e il mondo del lavoro (Federchimica- Milano - 16 Aprile 2014)
- 5) Workshop: Costruirsi un futuro nell'industria chimica (Federchimica- Milano- 30 Maggio 2014)
- 6) Workshop sulla Gestione Responsabile del Prodotto (Federchimica- Milano- 06 Maggio 2015)
- 7) Workshop: Improving American English Pronunciation (EPPIC, English for Professional Purposes Intercultural Center - Penn state University -22 Settembre 2015)

- 8) Workshop: Professional Email Communication (EPPIC, English for Professional Purposes Intercultural Center - Penn state University -13 Ottobre 2015)
- 9) Workshop: Understanding American Culture: Q&A with Invited Panel (EPPIC, English for Professional Purposes Intercultural Center - Penn state University -10 Novembre 2015)
- 10) Workshop: Handling Questions (EPPIC, English for Professional Purposes Intercultural Center - Penn state University -18 Novembre 2015)
- 11) Corso di Formazione: "Integratori Alimentari: quadro normative europeo e nazionale" (Cosmetica Italia- Milano- 11 Febbraio 2016)
- 12) Seminario-Workshop: Qualità:la punta dell'iceberg dell'eccellenza (11 Maggio 2016-SICC-Milano)
- 13) Skin Summer School (University of Pavia- Pavia- 20/22 Giugno 2016)
- 14) Workshop: Dispersioni e nanodisperioni: formulare, stabilizzare, caratterizzare e capire il comportamento reologico (Laboratori Alfatest- 28 Giugno 2016)
- 15) Corso di Formazione: "Laboratori pratici di microbiologia: la valutazione della qualità e della stabilità microbiologica dei prodotti cosmetici" (Eurofins Biolab- Milano- 8 Novembre 2016)
- 16) Giornata di studio "Life Cycle Assessment (LCA) e sviluppo delle figure professionali: esperienze aziendali a confronto" (Milano- 1 Dicembre 2016)

GivenSeminars

- Odori, profumi e feromoni come mediatori chimici olfattivi (18 Novembre 2016).

Attended Seminars

- 1) Allergie e intolleranze alimentari (Restani P. – 13 Febbraio 2014)
- 2) Filiera cosmetica, istituzioni di settore e regolamento cosmetici (Rialdi V. – 04 Marzo 2014)
- 3) Rapid thermal processing. A novel solvent free enabling technology for ultrafast black copolymer self assembly (Laus M. – 11 Marzo 2014)
- 4) Sostenibilità nella filiera cosmetica (Rialdi V. – 18 Marzo 2014)
- 5) Good manufacturing practice (Rialdi V. – 25 Marzo 2014)
- 6) Blue light stress in photoreceptor and related structures (Funk R. - 08 Luglio 2014)
- 7) Biocatalisi: applicazioni in sintesi farmaceutica (Seminario Dottorando XXVII ciclo; Massa M.- 28 Novembre 2014)
- 8) Molecole naturali e Xeno-ormesi (Seminario Dottorando XXVII ciclo; Mele G.- 28 Novembre 2014)
- 9) Metodi alternativi alla sperimentazione animale (Seminario Dottorando XXVII ciclo; Pollarolo B.- 28 Novembre 2014)
- 10) Recenti aspetti d'interesse terapeutico del processo di metastasi tumorale (Seminario Dottorando XXVII ciclo; Zibana C.- 28 Novembre 2014)
- 11) The bond between paper fibers: a fresh look at an old material (Robert Schennach- 17 Febbraio 2015)
- 12) Recent cosmetic science and formulation technology (Yuji Yamashita- 3 Marzo 2015 CNR)
- 13) Il processo autorizzativo dei farmaci in Italia (Domenico Valle- 10 Aprile 2015)
- 14) Calix[n]pyrroles: organic compounds with a potential as drugs and drug delivery tools in Oncology (Franz H. Kohnke-20 Aprile 2015 IST)
- 15) Metabolomics Profile of Hypoxic Colorectal Cancer Cells (Alessandro Valli- 15 Maggio 2015)
- 16) Hsp90 nella terapia antitumorale: dall'analisi conformazionale al disegno di nuovi inibitori allosterici (Gerolamo Vettoretti- 25 Maggio 2015)
- 17) Chemometrics in proteomics studies (Beata Walczak- 22 Gennaio 2016)

- 18) I nutraceutici : i farmaci per le persone sane (Ettore Novellino- 26 Gennaio 2016)
- 19) How to write a successful scientific paper: 1) Writing a Paper and Getting Published; 2) After publication: the continued life of your paper (Elsevier- 17 Luglio 2016)
- 20) Il marketing cosmetico: dalla mission aziendale alla risposta del consumatore (Seminario Dottorando XXIX ciclo; Rum S. - 18 Novembre 2016)
- 21) Giocare sporco: PAINS e composti promiscui (Seminario Dottorando XXIX ciclo; Parricchi A. - 18 Novembre 2016)
- 22) Tubercolosi ed altre patologie polmonari: stato dell'arte e recenti sviluppi terapeutici (Seminario Dottorando XXIX ciclo; Meta E. - 18 Novembre 2016)

Other Activities

- 1) Tutorato didattico di Anatomia umana (primo semestre 2014).
- 2) Visita al Cosmoprof (Bologna -7 Aprile 2014).
- 3) Assistenza agli studenti in laboratorio per il corso di Analisi II (Prof. Spallarossa Andrea) – Corso di Laurea in Farmacia (secondo semestre 2014).
- 4) Giugno 2015 - Costituzione dello Spin-off ACCADERMICA tra l'università di Genova (DIFAR) e l'azienda Luxis S.r.l. con un duplice scopo:
 - Realizzazione di una linea cosmetica per il viso, costituita da sei prodotti (studiata dalla fase di progettazione, alla realizzazione dei “prototipi formulativi” su scala di laboratorio, seguita dall'analisi sensoriale, di sicurezza e stabilità, fino alla fase di scale-up produttivo) da vendersi nelle farmacie sul territorio nazionale contenente il prodotto della ricerca (estratto MW da scarti dell'industria agroalimentare), oggetto di una parte della mia ricerca di dottorato.
 - Organizzazione di corsi di “formazione e accreditamento ECM” tenuti dal team del progetto (Lacpra Chiara e Rum Silvia - PhD SFAC XXIX ciclo; Villa Carla - Docente DIFAR; Guarrera Marcella- Professore a contratto DIMES; Antichi Davide – Cosmetologo e Formulatore; Bacigalupo Emiliano – Esperto in marketing e comunicazione).

Il progetto ACADERMIC, su cui si è basata la costituzione di Accadermica, è risultato vincitore della SMART-Cup Liguria 2014 per la sezione *Agro-Food&Cleantech* ed ha ricevuto un riconoscimento speciale dalla Camera di Commercio di Genova.

Il 4-5 Dicembre è stato presentato a Sassari per concorrere al PNI 2014 (Premio Nazionale per l'Innovazione), dove è stato selezionato tra i 16 progetti finalisti su 58 (tra i 4 finalisti di categoria), ed è stato presentato dal team nel teatro Verdi. Inoltre, il progetto si è classificato al secondo posto nella competizione START-Cup dell'Università degli Studi di Genova, ed ha ricevuto un premio volto alla costituzione della StartUp Cosmetica Innovativa (11 Giugno 2015), della quale faccio parte come socio di capitale.

Successivamente la start up è stata presentata a EXPO 2015, selezionata per concorrere al Premio Luigi Carinelli organizzato da SICC durante il Making Cosmetics 2015, presentata oralmente in occasione del premio “90 secondi per spiccare il volo” organizzato da Panorama, e al “Posidonia Sustainable Green Festival 2016”.

- 5) **Agosto - Dicembre 2015:** svolgimento di un periodo di ricerca negli Stati Uniti come *Visiting Research Scholar*, presso la *Penn State University - Material Reseach Laboratory* (State College- Pennsylvania) sotto la supervisione del Prof. Komarneni Sridhar, *distinguished Professor of clay*

mineralogy. Il lavoro ha avuto come scopo la preparazione di ibridi organici-inorganici, realizzata attraverso processi sintetici idrotermali (convenzionali e microonde mediati), come nuovi potenziali composti d'interesse cosmetico e farmaceutico. I prodotti studiati e sintetizzati sono stati caratterizzati mediante diffrazione a raggi X (XRD), utilizzando lo strumento *PANalytical Empyrean*, dopo il conseguimento della relativa "licenza d'uso" presso la *Penn State University*.

Awards

- Secondo Premio START CUP dell'Università degli Studi di Genova 2013 con il Progetto "ACADERMIC".
- Primo Premio SMARTCup Liguria 2014, settore *Agro-Food & Cleantech* con il Progetto "ACADERMIC"; e diritto di partecipazione come finalisti al Premio Nazionale per l'Innovazione (Sassari 4-5 Dicembre 2014).
- Premio Speciale della Camera di Commercio di Genova per il Progetto "ACADERMIC" assegnato durante il concorso SMARTCup Liguria 2014.
- Start Up ACCADERMICA selezionata dal Vivaio delle Idee per EXPO 2015.
- Premio Start Up Panorama d'Italia al concorso "90 secondi per spiccare il volo".
- Premio Start Up Green al Posidonia Sustainable Friends Festival 2016.
- Lo Spin Off si è aggiudicato un finanziamento di 200.000 euro grazie alla valutazione positiva di un progetto POR FESR, AZIONE 1.1.3 (valorizzazione economica dell'innovazione) .



Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Materials Science and Technology

PH.D. CERTIFICATE
of
ANGELIQUE JEAN LUSUAN



Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisors

Prof. Mario Rocca

Dott.ssa Letizia Savio

Thesis Title

Surface functionalization using amino acids: a characterization from the nanoscopic to the microscopic scale

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department Physics, Angelique Jean Lusuan has orally presented her doctorate research work in front of the Commission, formed by

- Prof.ssa Elisabetta Finocchio, University of Genova
- Prof. Henrik Rudolph, Netherland Defense Academy
- Prof. Ruggero Vaglio, University of Napoli "Federico II"

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

**HAS APPROVED THE THESIS OF ANGELIQUE JEAN LUSUAN,
CONFERRING ON HER THE TITLE OF**

**RESEARCH DOCTOR IN
MATERIALS SCIENCE AND TECHNOLOGY**

Genova, February 24th, 2017

**The Coordinator of the Doctorate Course
(Prof. Adriana Saccone)**



Università degli Studi di Genova



**Doctorate in
Sciences and Technologies of
Chemistry and Materials**

CURRICULUM Science and Tecnology of Materials

Angelique Jean Lusuan

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *December 31th, 2016*

Advisors Prof. Mario Rocca; Dott.ssa Letizia Savio

Thesis Title: *Surface functionalization using amino acids: a characterization from the nanoscopic to the microscopic scale.*

ACTIVITY REPORT
Research Activity

The research activity was mainly carried out at the Department of Physics of the University of Genova.

Scientific Publications

- 1) E.Celasco, G.Carraro, A.Lusuan, M.Smerieri, J.Pal, M.Rocca, L.Savio L.Vattuone; CO chemisorption at vacancies of supported graphene films: a candidate for a sensor? (Phys.Chem.Chem.Phys., 2016, **18**, 18692-18696)
- 2) M.Smerieri, I.Piš, L.Ferrighi, S.Nappini, A.Lusuan, C.Di Valentin, L.Vaghi, A.Papagni, M.Cattelan, S.Agnoli, E.Magnano, F.Bondino, L.Savio; Synthesis of graphene nanoribbons with a defined mixed edge-site sequence by surface assisted polymerization of (1,6) – dibromopyrene on Ag(110) (Nanoscale, 2016, 8, 17843)
- 3) I.Piš, L.Ferrighi, Thanh Hai Nguyen, S.Nappini, L.Vaghi, A.Basagni, E.Magnano, A.Papagni, F.Sedona, C.Di Valentin, S.Agnoli, F.Bondino; Surface-Confined Polymerization of Halogenated Polyacenes: The Case of Dibromotetracene on Ag(110), J. Phys. Chem. C, 2016, 120 (9), pp 4909–4918

Communications at Conferences

Poster Communications:

- 1) Surface-assisted synthesis of graphene nanoribbons on Ag(110) (on-hold for the postponed 5° Workshop Programma PhD organized by Federchimica_Unige)

Oral communications:

- 1) On-surface polymerization of 1,6 – dibromopyrene on Ag(110)

Congresses Attended

Courseware

Passed (7CFU):

- 1) Soft Matter, 2CFU
- 2) Surface Science, 3 CFU
- 3) Catalysts and Industrial adsorbents, 2 CFU

Courses Given by invited experts (2CFU)

- 1) Magnetic hyperthermia: from fundamentals to biomedical applications (DCCI)
- 2) L'impatto delle mie pubblicazioni scientifiche. Come pubblicare con successo sulle riviste scientifiche più importanti a livello internazionale (DCCI)

National and International Schools or Workshops

- 1) On-Surface Synthesis Workshop (June-July 2016), San Sebastian, Spain.

Seminars Attended

- 1) Surface chemical reactions at epitaxial graphene and materials "beyond graphene" (DIFI)
- 2) Raman spectroscopy of carbon nanomaterials: from micro to the nanoscale (DIFI)
- 3) Transport properties of nanostructured graphene (DIFI)
- 4) Towards an atomic scale technology: electronics mechanics with single molecules

Other Activities



Università degli Studi di Genova
Doctorate School in
Sciences and Technologies of
Chemistry and Materials

Curriculum: Nanochemistry

THANH BINH_MAI

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *December 31st, 2016*

Advisors

Dr. Teresa Pellegrino (IIT)

Prof. Orietta Monticelli (UniGe)

Thesis Title

Robust preparation of multi stimuli – responsive polymeric nanomaterials by advanced synthesis protocol for controlled drug delivery systems applications

Thesis abstract

The emergence of hybrid nanomaterials composed of polymer and inorganic nanocrystals (NCs) has fostered the rapidly growing field of materials science since these nanohybrids made of inorganic core and organic shell hold potential for numerous applications ranging from opto-electronic devices to nanomedicine. Indeed, bridging the polymer field and the inorganic nanoscience field can lead to the development of novel nanomaterial classes for advanced applications. Therefore, a versatile and simple grafting from approach based on photo-induced copper mediated radical polymerization for the surface modification of strongly interactive magnetic iron oxides nanocrystals such as nanocubes with thermo-responsive polymers has been realized. The thermo-responsive nanocubes with high absorption rate activated by an alternating magnetic field was demonstrated to be a good candidate for the delivery of chemotherapies for cancer treatment following a heat-triggered release mechanism. In addition, the same synthetic procedure can be applied for the synthesis of pH-responsive polymer functionalized nanocubes representing an interesting class of materials for siRNA delivery. Furthermore, thanks to the extreme versatility, the developed procedure can be extended to the surface functionalization of more complicated heterogeneous nanostructure composed of Au and Fe₃O₄ nanoparticles. As a result, a thermo-responsive dimers can be obtained. Interestingly, the Au domain can be selectively removed to form an accessible surface of iron oxide which is expected to be used for a successive functionalization preserving the heating performance, stability and thermo-responsiveness of the resulting nanomaterials. As a further applications of PI-CMRP, the copolymerization of functional monomers such as activated-ester and polyethylene glycol methacrylate was also studied. The activated ester containing copolymers were used for the nucleophilic reaction with primary amine containing anchoring groups to obtain several multi-dentate ligands for the water transfer of inorganic NCs. An excellent yield of water transfer and long term stability of nanocrystals was observed using such multi-dentate ligands. In addition, the synthesis of the block copolymers of polyethylene glycol and poly(diisopropylaminoethyl methacrylate), a pH-responsive polymer, has been realized and studied for their self-assembly in aqueous solution. The resulting nanostructure including polymeric nano-micelles and vesicles showed a pH transition at 7.0 – 7.1 representing promising candidates for smart drug delivery.

ACTIVITY REPORT

Research Activity

The research activity was mainly carried out at the IIT

Please indicate here if you have spent research periods in foreign countries.

Scientific Publications

Original publications on ISI Journals:

- 1) Synthesis of Thermo-responsive Iron Oxides Nanoparticles with High Specific Absorption Rates as Platform for Cancer Treatment, *Manuscript under preparation*.
- 2) Photo-induced Copper Mediated Copolymerization of Activated Ester Methacrylate and Their Application as Building Block for Preparation of Multi-dentate Ligands, *Manuscript under preparation*.

Communications at Conferences

Poster Communications:

- 1) "Synthesis of cubic iron oxide nanoparticles (IONPs) functionalized with thermoresponsive polymers for applications in hyperthermia and smart drug delivery systems", *Fourth International Conference Frontiers in Polymer Science 2015*, 20 - 22 May 2015, Riva del Garda, Italy.

Congresses Attended

Courseware

During his doctorate, Thanh-Binh Mai has acquired 28 credits of Courseware.

Courses attended and passed (16 credits)

Courses Given by Teachers of the Nanochemistry Department, Italian Institute of Technology:

- 1) Fundamental Crystallographic Concepts, **Prof. Liberato Manna** (1 credit)
- 2) Nanomaterials and Nanocomposites: Processing and Characterization, **Dr. Luca De Trizio and Dr. Milena Arcinigeas** (1 credit)
- 3) Opto-Electronic Properties of Semiconductor Quantum Dots, **Dr. Iwan Moreels** (1 credit)
- 4) X-ray based Characterization Techniques, **Dr. Mirko Prato** (1 credit)
- 5) Fundamentals of Electron Microscopes (TEM and SEM), **Dr. Alessandro Genovese and Dr. Rosaria Brescia** (1 credit)
- 6) Raman spectroscopy and lattice vibrations of nanocrystals, **Dr. Roman Krahné and Dr. Alberto Casu** (1 credit)
- 7) Energy Related Applications 1 (Module VII, cycle XXIX), **Dr. Massimo Colombo, Dr. Simone Monaco and Dr. Yang Zhang** (1 credit)
- 8) Energy Related Applications 2 (Module VIII, cycle XXIX), **Prof. Liberato Manna and Dr. Alberto Casu** (1 credit)
- 9) Characterization of functionalized and water soluble nanoparticles (Module IV-Cycle XXX), **Dr. Teresa Pellegrino, Dr. Markus Barthel and Dr. Vladimir Lesnyak** (1 credit)
- 10) Laboratory of Optical Fluorescence Microscopy Methods (DIBRIS course), **Dr. Marta d'Amora** (3 credits)
- 11) Science and Technology of 2D Materials, **Dr. Francesco Bonaccorso** (1 credit)
- 12) Elementary Electronic Structure of Solids, **Prof. Liberato Manna** (3 credits)

Courses Given by invited experts:

- 1) Advanced course: Bioraffineria di terza generazione: un modello di sviluppo sostenibile integrato nel territorio, **Dr. Luigi Capuzzi** (1 credit)
- 2) Advanced course: Advanced Materials for Renewable Energy (Energy Saving), **Prof. Peter Rogl** (1 credit)

National and International Schools or Workshops

- 1) *Fourth International Conference Frontiers in Polymer Science 2015*, 20 - 22 May 2015, Riva del Garda, Italy.

- 2) *Nanomedicine Symposium CEN @Regione Lombardia: Synthesis of nanomaterials, biological applications and modelling Symposium*, September 21st, 2015, Milano, Italy.
- 3) *ERC ICARO Project Kick off Meeting*, Sestri Levante, Italy, June 11-12th 2016.
- 4) *Summer school: Drug Delivery using Micro and Nanotechnology*, Technical University of Denmark, Copenhagen, Denmark, August 14-28th 2016 (5 ETC credits)
- 5) *Merck Young Chemist Symposium 2016*, Rimini, Italy, October 25-27th 2016.

Seminars Given

- 1) *"Cubic Iron Oxide Nanoparticles Functionalized with Thermo-responsive Polymers for Drug Delivery Applications"*, Nanochemistry Department Group Meeting, IIT, 12-11-2015, 30 min.
- 2) *"Synthesis of Magnetic Nanocomposites and Multifunctional Polymers by Photo-induced Copper Mediated Radical Polymerization"*, Nanochemistry Department Group Meeting, IIT, 06-12-2016, 15 min.

Seminars Attended

- 1) Unravelling Animal Biology by Functional Particles, **Dr. Claudia Tortiglione**, February 19th, 2014
- 2) Electrochemical Control over Charge Transfer and Trapping in CdSe-CdTe QD Solid, **Prof. Arjen J. Houtepen**, March 3rd, 2014
- 3) Neutron scattering for materials research in the fields of hydrogen storage for vehicular applications, **Prof. Sabrina Sartori**, May 5th, 2014
- 4) EKO and EKOS: A New Perspective On Discovery Of Small Molecules To Perturb Protein-protein Interactions, **Dr. Kevin Burgess**, May 30th, 2014
- 5) Nanomaterials as Highly Active Catalysts for Multiple Significant Reactions, **Prof. Sasanka Deka**, June 25th, 2014
- 6) Colloidal nanoparticles – Shape and composition control, **Dr. Dirk Dorfs**, June 26th, 2014
- 7) Organization of Colloidal Nanoparticles Building Blocks into Functional Superstructures, **Dr. Nadia C. Bigall**, June 26th, 2014
- 8) Colloidal nanoparticles and their functional architectures, **Dr. Nikolai Gaponik**, September 29th, 2014
- 9) The Design and Synthesis of Glycotherapeutics and Glycosylated Materials, **Prof. Eoin Scanlan**, October 6th 2014
- 10) Gold nanoparticles as monitoring sensors and delivery system for anti-cancer drugs, **Dr. Elisa Salvati**, October 29th 2014
- 11) Organic Bio-Electronic Devices For Sensing Applications, **Prof. Luisa Torsi**, November 10th 2014
- 12) Plasmonic heavily doped semiconductor nanocrystals: from fundamentals to their nanoscale application, **Dr. Ilka Kriegel**, November 26th 2014
- 13) "Design organometallics for materials science: Applications for solar cells and scintillators" **Dr. Guillaume Bertrand**, January 19th 2015.
- 14) "Design, fabrication and characterization of plasmonic structures for graphene-based devices and superresolution", **Dr. Valeria Lotito**, January 19th 2015.
- 15) "Nano-bio interactions", **Dr. Christoffer Aberg**, July 2015.
- 16) "Semiconductor nanocrystals: Discovery, Milestones and recent Theoretical Developments", **Prof. Alexander S. Efros**, November 20th 2015.
- 17) "Insight in the chemistry of metal sulphide nanocrystals and their application in photovoltaics", **Dr. Peter Reiss**, November 25th 2015.
- 18) "Perovskite: an old material for the third generation of PV solar panels", **Dr. Laura Miranda Perez**, April 21st 2016
- 19) "Colloidal Nanoparticles and Applications", **Prof. Antonios G. Kanaras**, April 28th 2016.
- 20) "Hydration induced spin glass state in a frustrated Na-Mn-O triangular lattice", **Dr. Ioanna Bakaimi**, April 28th 2016.
- 21) "NMR chemosensing with self-organized nanoparticle-based receptors", **Prof. Fabrizio Mancin**, November 3rd 2016.

22) "PhD presentations: XXIX cycle", December 6th, 2016.

Other Activities

- 1) First prize in the pitch challenge, Drug Delivery Micro- and NanoSensors PhD Summer School 2016, Copenhagen, Denmark.
- 2) "Synthesis of Thermo-responsive Iron Oxide Nanoparticles with High Specific Absorption Rates as Platform for Cancer Treatment", Patent in preparation.
- 3) FluoMagneto, BIOUPPER-Start Up Accelerator Competition 2016.



Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Chemical Sciences and Technologies

PH.D. CERTIFICATE
of
MARCO MAURI



Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisor

Prof. Silvia Vicini

Thesis Title

*Synthesis and characterization of
alginate hydrogels for technological
application*

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department of Chemistry and Industrial Chemistry, Marco Mauri has orally presented his doctorate research work in front of the Commission, formed by

- Prof. Gaetano Granozzi, University of Padova
- Prof. Andrea Pucci, University of Pisa
- Prof. Renata Riva, University of Genova

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

HAS APPROVED THE THESIS OF MARCO MAURI
CONFERRING ON HIS THE TITLE OF

RESEARCH DOCTOR IN
CHEMICAL SCIENCES AND TECHNOLOGIES

Genova, February 24th, 2017

The Coordinator of the Doctorate Course
(Prof. Adriana Saccone)



Università degli Studi di Genova



**Doctorate School in
Sciences and Technologies of
Chemistry and Materials**

MARCO MAURI

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *December 31th, 2016*

Advisors *Prof. Silvia Vicini*

Thesis Title

Synthesis and characterization of alginate hydrogels for technological application

ACTIVITY REPORT
Research Activity

The research activity was mainly carried out at the DCCI University of Genoa, with 6 months (from 8th of April to 14th September) spent at the Edinburgh Napier University (Edinburgh, UK) in the research group of professor Rob English, under the supervision of Dr. S. Gagliardi, and Dr. R. L. Williams

Scientific Publications

- 1) **S. Vicini, M. Castellano, M. Mauri, E. Marsano (2015)** *Gelling process for sodium alginate: New technical approach by using calcium rich micro-spheres*. Carbohydrate polymers, 134, 767-774.
- 2) **M. Castellano, R. Cantù, M. Mauri, E. Marsano, S. Vicini (2016)** *Poly(dimethylsiloxane)/TiO₂ Photocatalytic Membranes Obtained by Different Electrospinning Systems*. Journal of Nanoscience and Nanotechnology, 16, 6587-6594.
- 3) **Vicini S., Mauri M., Wichert J., Castellano M.** *Alginate Gelling Process: Use of Bivalent Ions Rich Microspheres* – submitted
- 4) **M. Castellano, S. Vicini, M. Mauri** *Gelation of Sodium Alginate/Hydroxypropyl cellulose blends by using of calcium rich microspheres*. International Journal of Biological Macromolecules, In preparation.
- 5) **R. Vecchiattini, F. Fratini, S. Rescic, C. Riminesi, M. Mauri, S. Vicini** *A methodological approach to the conservation treatments carried out on-site. The abbey of San Fruttuoso di Capodimonte (Genoa, Italy)*. Journal of Cultural Heritage, In preparation.

Communications at Conferences

Poster Communications:

- 1) **M. Mauri, S. Gagliardi, V. Arrighi, R. L. Williams, S. Vicini, M. Castellano, R. English** *“Scaling behavior of hyaluronic acid in aqueous and high ionic strength solutions from rheological measurements”*
IOP conference – Physical aspect of polymer science, Manchester institute of biotechnology, Manchester University, Manchester, 8-10 September 2015
- 2) **M. Mauri, M. Castellano, S. Vicini, S. Gagliardi** *“Alginate and alginate-hyaluronic acid nanofibers membrane made by electrospinning in wet conditions”*
XXII Convegno Nazionale AIM, Genoa, 11-14 September 2016
- 3) **S. Vicini, M. Mauri, M. Castellano** *“Nuovo sistema gelificante a base di alginato e idrossipropilcellulosa per la pulitura di manufatti artistici”*
XXII Convegno Nazionale AIM, Genoa, 11-14 September 2016

Oral communications:

- 4) **M. Mauri** *“New technical approach for a controlled gelling process of sodium alginate”*
XXI Convegno Nazionale AIM, Sezione Macrogiovani, Politecnico di Torino, Turin, 16 September 2014
- 5) **M. Mauri, Silvia Vicini and Maila Castellano** *“Gelling Process of Sodium Alginate with Bivalent Ions Rich Microspheres: Nature of Bivalent Ions”*
8th TOP CONFERENCE – time of polymers and composites, Ischia (NA), 19-23 June 2016

Congresses Attended

- 1) XXI Convegno Nazionale AIM, Sezione Macrogiovani, Politecnico di Torino, Turin, 16 September 2014
- 2) Physical aspect of polymer science - IOP conference – Manchester institute of biotechnology, Manchester University, Manchester, 8-10 September 2015
- 3) 8th TOP CONFERENCE – time of polymers and composites, Ischia (NA), 19-23 June 2016
- 4) XXII Convegno Nazionale AIM, Genoa, 11-14 September 2016

National and International Schools or Workshops

- 1) **Congress-School AIM “Mario Farina” Caratterizzazione di materiali polimerici: tecniche per polimeri in soluzione**, 19-23 May 2014, Gargnano (BS)
- 2) **Recent advances and new perspectives in polymer crystallization**, 29-30 September 2014, DCCI – Genoa
- 3) **Workshop: Il FAI in Liguria, il FAI a San Fruttuoso, l'intervento di conservazione della Torre Nolare dell'Abbazia di San Fruttuoso di Camogli**, 27 October 2014, Dipartimento di Scienze per l'Architettura – Genoa
- 4) **NanoforArt final workshop**, 28 November 2014, Auditorium Santa Margherita, Università Ca' Foscari – Venezia
- 5) **SoftComp topical workshop: Dense suspension flow**, 1-3 June 2015, University of Edinburgh, Edinburgh

Courseware

- 1) Characterization of nanoparticles by atomic force microscopy and dynamic light scattering (2 CFU), 2014 – R. Rolandi
- 2) Basics of scanning and transmission electron microscopy (2 CFU), 2014 – P. Riani
- 3) NMR spectroscopy in characterizing synthetic polymers (2 CFU), 2014 – F. Lucchesini
- 4) Polymeric nanocomposites (2 CFU), 2014 – O. Monticelli
- 5) Basics of soft matter (3 CFU), 2014 – A. Relini
- 6) Analisi multivariata dei dati chimici (3 CFU), 2015 - S. Lanteri, C. Armanino, R. Leardi

During his doctorate, Marco Mauri has acquired 14 credits of Courseware.

Courses Given by Invited Experts

- 1) **Rapid Thermal Processing (RTP): a Novel Solvent-Free Enabling Technology for Ultrafast Block-Copolymer Self-Assembly** – Prof. Michele Laus, Università del Piemonte Orientale. 11 March 2014, DCCI – Genoa
- 2) **Tecnologie di monitoraggio e bonifica di acque e suoli** – Dr. Bagatin, Responsible of research unity of Environment technologies of ENI Donegani Institute, San Donato Milanese. 9 October 2014, DCCI – Genoa
- 3) **The bond between paper fibers: a fresh look to an old material** – Prof. Robert Schennach, Graz University of Technology. 17 February 2015, DCCI – Genoa
- 4) **X-ray based experimental techniques and characterization of nano-materials** – Dott. Alberto Morgante, CNR-IOM and Physics Department Trieste University. 31 March 2015, DCCI – Genoa
- 5) **Polymer and composite from renewable resources** – Prof. Emerito Alessandro Gandini, École internationale du papier, de la communication imprimée et des biomatériaux (INP-Pagora) - Institut Polytechnique de Grenoble (Grenoble INP), FR – Universidade de Sao Paulo, Sao Carlos, BR. 29-30 September 2015, CNR-ISMAL - Genoa
- 6) **Medical chemistry with carbohydrates: the influenza virus and the discovery of sialidase inhibitors** – Prof.ssa Anna Berardi, Università degli Studi di Milano. 13 November 2015, DCCI – Genoa
- 7) **New Methods for food authenticity and safety testing** – Dr.ssa Valeria Merlo, Technical manager & director, Eurofins, Cuneo. 27 November 2015, DCCI - Genoa
- 8) **Nanostructured inks for advanced devices: from research to business** - Alessandro Chiolerio and Sergio Bocchini, Istituto Italiano di Tecnologia, Center for Space Human Robotics, Torino. 22 January 2016, DIFI - Genoa
- 9) **Physics in extreme conditions** – Prof. Marian Reiffers, Faculty of Humanities and Natural science, Presov University, Slovakia. 5-6 March 2016, DCCI - Genoa
- 10) **Advanced materials for renewable energy** – Prof. Peter Rogl, Institute of Physical Chemistry, University of Vienna, Austria. 14 June 2016, DCCI – Genoa

Seminars Attended

- 1) **Heterophasic ethylene-propylene copolymer / halloysite nanocomposites using dispersing agents** – Dott.ssa Eveline Bischoff, Instituto de Química, Universidade Federal do Rio Grande do Sul Porto Alegre, Brazil. 8 September 2014, DCCI – Genoa
- 2) **Conservation of Cultural Heritage in Brazil: the Role of Science and Technology in a Context of Economic Development and Growth** - Prof. Luiz Souza, Federal University of Minas Gerais, Belo Horizonte, Brazil. 5 May 2014, Scuola Umanistica – Genoa
- 3) **Strumentazione di chimica analitica per l'esplorazione del sistema solare** – Bazzano Andrea. 5 November 2015, DCCI- Genoa

- 4) ***Self-assembled block copolymers aggregates: application in drug delivery*** – Gardella Lorenza. 5 November 2015, DCCI- Genoa
- 5) ***Introduzione alle pile a combustibile e ai fenomeni di degrado ad alta temperatura*** – Ghiara Giorgia. 5 November 2015, DCCI- Genoa
- 6) ***The hydrogen autotransfer process*** – Spallarossa Martina. 6 November 2015, DCCI- Genoa
- 7) ***Seeing Molecules: A Survey on Non-Optical Microscopies and their Applications*** - Martinez Espinoza Maria Isabel. 6 November 2015, DCCI- Genoa

Other Activities

- 1) Basic Course of Science and Technology of Polymeric materials (6 CFU)- E. Marsano
- 2) Educational visit at the corporate headquarters of the consortium PROPLAST 30 October 2014
- 3) Work Meetings with Prof. Valeria Arrighi, Heriot-Watt University, Edinburgh, June - August 2015
- 4) Work Meetings with Dr. Alick Leslie, Conservation Science Manager, Historic Scotland, June-July 2015
- 5) Beamtime (21-23 April 2016) at the ISIS Centre, Rutherford Appleton Laboratory in Oxford (UK) (ISIS Application: RB1610271) for Neutron Scattering measurement related to the research project "Structure of Hyaluronic Acid Solutions from dilute to concentrated regime". Principal investigator: S. Gagliardi
- 6) Beamtime (24-28 October 2016) at the ISIS Centre, Rutherford Appleton Laboratory in Oxford (UK) (ISIS Application: RB1700006) for Neutron Scattering measurement related to the research project "Structure of Hyaluronic Acid Solutions in aqueous and salt environment". Principal investigator: S. Gagliardi
- 7) Teaching support: Laboratorio di Chimica Industriale; Modulo II (6 CFU), Laurea magistrale in Chimica Industriale II year, Responsible: Silvia Vicini, hours: 20 – December 2015 - January 2016
- 8) Teaching support: Chimica dei Materiali per il Restauro (6 CFU) Laurea Triennale in Conservazione dei Beni Culturali, Responsible: Silvia Vicini, hours: 9 – April 2016 – May 2016



Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Pharmaceutical, Food and Cosmetic Sciences

PH.D. CERTIFICATE
of
ELDA META



Doctorate Course

Pharmaceutical, Food and Cosmetic Sciences

Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisor

Prof.ssa Olga Bruno

Thesis Titles

New kinases targeted compounds as possible antiangiogenic and antimetastatic agents

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department of Pharmacy, Elda Meta has orally presented her doctorate research work in front of the Commission, formed by

- Prof.ssa Olga Bruno, University of Genova
- Prof. Stefano Manfredini, University of Ferrara
- Prof.ssa Nunziatina De Tommasi, University of Salerno

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

**HAS APPROVED THE THESIS OF ELDA META
CONFERRING ON HER THE TITLE OF**

**RESEARCH DOCTOR IN
PHARMACEUTICAL, FOOD AND COSMETIC SCIENCES**

Genova, February 24th, 2017

**The Coordinator of the Doctorate Course
Prof. Adriana Saccone**



Università degli Studi di Genova
Doctorate School in
Sciences and Technologies of
Chemistry and Materials

Curriculum: Pharmaceutical, cosmetically and alimentary sciences.

ELDA_META

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *December 31, 2016*

Advisor

Prof. Olga Bruno

Thesis Title

New kinases targeted compounds as possible antiangiogenic and antimetastatic agents.

Thesis abstract

Angiogenesis, the formation of new blood vessels from pre-existing ones, is vital for physiological processes during development and in adult during wound healing, tissue growth and repair. Pathological angiogenesis is required for the outcome of several diseases including cancers.

A main role in the angiogenesis process is played by VEGF, which induces key events like endothelial cell sprouting, migration, proliferation and survival. VEGF induces these functions through activation of several serine/threonine kinases in the phosphatidylinositol 3-kinase (PI3K) signaling pathway including protein kinases B (Akt/PKB) and the mitogen-activated protein kinases (MAPK) signaling pathway such as extracellular response kinases 1 and 2 (ERK1/2) and p38MAPK. Moreover activation of ERK1/2 and p38MAPK was found crucial for other processes related to poor prognosis in cancers including tumor cell epithelial to mesenchymal transition (EMT), metastasis and recruitment of bone marrow-derived cells.

Tumor cell proliferation is orchestrated by different factors, and a main role is played by the MAP kinases such as ERK1/2 and p38MAPK, thus finding new inhibitors that could affect the function of these kinases in endothelial cell would help to develop new potential therapeutic agents targeting tumor angiogenesis, tumor microenvironment and tumor cell proliferation.

Neutrophils chemotaxis is a complex process of monocyte cells migration to the site of inflammation; this patho-physiological event is stimulated by chemoattractants such Interleukine-8 (IL8) or formyl-methyl-leucyl-phenylalanine peptide (fMLP). When IL-8 binds to its receptors (CXCR1/2) many downstream serine/threonine kinases are activated including p38MAPKs and ERK1/2 phosphorylation.

The research group where I am actually doing my PhD previously designed and synthesized different compound libraries of pyrazolylureas, imidazopyrazols and imidazopyrazolcarboxamides, able to inhibit the neutrophils chemotaxis by interfering with ERK1/2, Akt and p38MAPK phosphorylation after stimulation with IL8 or fMLP.

In the literature has been evidenced that the intercellular pathways involved in cancer development (angiogenesis, tumor cell proliferation and invasion) are very similar. Given the potent inhibitory actions of our previous library of compounds on MAPK activation and subsequent neutrophil chemotaxis we aimed at designing and synthesizing new series of pyrazolylureas and imidazopyrazolcarboxamides that could interfere with MAPK and PI3K signalling. Our project aims at having compounds able to control tumor cell metastasis by acting on different components of tumour microenvironment as well as on tumor proliferation itself.

During first and second year of my PhD training I designed and synthesized a new library of compounds (pyrazolylureas and imidazopyrazolcarboxamides). I also took part, as a visiting-student in the Prof. Domenicotti's laboratory (Department of Experimental Medicine, University of Genoa) in different biological analyses performed on three selected compounds from the previous series, to evaluate their activity on two neuroblastoma cell lines (ACN and HTLA-230), with the aim of having some preliminary data on this class of compounds on cancer cells movement.

During the third year of the PhD training I pursued my research on the biological evaluation of 27 compounds, selected among the synthesized library, as a visiting doctorate student at the Department of

Pathology and Immunology, University of Geneva (Switzerland) under the supervision of Prof. Beat Imhof. This intership has been possible thanks to the one year "Swiss Government Excellence Scholarship" grant that was assigned to me in 2015. During this year the compounds were screened to evaluate their activity on MAPK and PI3K pathways and also in a wound healing assay as a functional test. From this screening one compound was selected, as the most active one, and further investigated for its activity in tumor cell angiogenesis and proliferation in vitro and in vivo in a tumor mouse model, nonetheless we investigated this compound in order to elucidation its mechanism of action.

ACTIVITY REPORT

Research Activity

The research activity was carried out at the Department of Pharmacy, at the University of Genoa, under the supervision of Prof. Olga Bruno. From September 2015 to August 2016 the research activity was carried out at the Department of Pathology and Immunology, University of Geneva (Switzerland) under the supervision of Prof. Beat Imhof.

Communications at Conferences

Poster Communications

1. 2-Phenyl-2,3-dihydro-1H-imidazo[1,2-b]pyrazole 7-carboxamide and 7-carbohydrazide-benzylidene derivatives: design, synthesis and anti TB activity. Chiara Brullo, Elda Meta, Scott G. Franzblau, Baojie Wan, Rui Ma, Olga Bruno. XXIV National Meeting in Medicinal Chemistry and 10th Young Medicinal Chemists Symposium, Perugia (IT), September 11-14, **2016** P16 .
2. New pyrazole and imidazopyrazole derivatives as potential antimetastatic drugs. Elda Meta European School of Medicinal Chemistry, Urbino (IT) June 26-July 01, **2016** P27.
3. Design and synthesis of 2-Phenyl-2,3-dihydro-1H-imidazo[1,2-b]pyrazole-7 carbohydrazide benzylidene derivatives as potential antitubercular agents. Chiara Brullo, Elda Meta, Scott G. Franzblau, Baojie Wan, Rui Ma, Olga Bruno. 8° Giornate Italo-Francesi di Chimica, P78. Avignon, April 25-26, **2016**
4. New pyrazole and imidazopyrazole derivatives as potential antimetastatic drugs. Elda Meta 5th Workshop of "Programma PhD", "La formazione post lauream e il mondo del lavoro - Nell'Industria Chimica, chi fa Ricerca... fa Carriera?". Genoa (IT) November 24, **2016**.

Oral Communications

1. Development of imidazo-pyrazole derivatives as potential antimetastatic agents in neuroblastoma. E. Meta, M. Massa, C. Brullo, O. Bruno. 7° Giornate Italo-Francesi di Chimica, Torino, May 5-6, **2014** COM23.
2. 3-Cyclopentyloxy-4-methoxyphenyl-isoxazoline derivatives as new PDE4 inhibitors. C. Rotolo, M. Massa, E. Meta, C. Brullo and O. Bruno. 7° Giornate Italo-Francesi di Chimica, Torino, May 5-6, **2014** COM14.
3. New pyrazole and imidazopyrazole derivatives as potential antimetastatic drugs. Elda Meta European School of Medicinal Chemistry, Urbino (IT) June 26-July 01, **2016** (selected among 40 posters to give an oral communication on the presented poster).
4. Design, synthesis and biological evaluation of new antimetastatic compounds. E. Meta, C. Brullo, A. Sidibe, B. Imhof and O. Bruno. XXIV National Meeting in Medicinal Chemistry and 10th Young Medicinal Chemists Symposium, Perugia (IT), September 11-14, **2016**.

Congresses attended:

1. 7° Giornate Italo-Francesi di Chimica, Torino (IT), May 5-6, **2014**.
2. 25ème Journée d'Immunologie, Geneva (CH). June 02, **2016**.
3. XXIV National Meeting in Medicinal Chemistry and 10th Young Medicinal Chemists Symposium, Perugia (IT), September 11-14, **2016**.
4. XXXI edition of "Nuovi Orientamenti nella Sintesi Organica". Milano (IT) Novembre 28, **2016**.

Courseware

During her doctorate, Elda Meta has acquired 16 credits of Courseware.

Courses attended and passed (11 credits)

Courses Given by Teachers of the University of Genoa:

1. Biotecnologie farmaceutiche (3 CFU) – Prof. M. Mazzei
2. Principali piante utilizzate in fitocosmesi e loro costituenti (2 CFU) – Prof. A. Bisio
3. Tecniche strumentali per la determinazione di elementi in traccia di interesse farmaceutico, alimentare, ambientale (2 CFU) – Prof. V. Minganti, Prof. G. Drava.
4. Marker molecolari della qualità e della genuinità degli alimenti (2 CFU), 2015 – Prof. R. Boggia, Prof. P. Zunin
5. Progettazione e sviluppo di inibitori di proteina-chinasi come nuovi agenti antitumorali (2 CFU), 2015 – Prof. S. Schenone.

Courses Given by invited experts:

1. 28/3/2014 Dott. Camilla Coletti: “ Graphene on SiC and Cu substrates: growth, properties and applications”
2. 9 /5/2014 Dott. Walter Cabri: "Pharmaceutical green chemistry"
3. 26-27/5/2014 Dott. Emanuela Pusceddu: "Use of neutrons in the area of food safety"
4. 7/11/2014 Dott. Paolo Gatti : “Solid State Modification: Principles and Applications for Drug Solubility Enhancement”
5. 9/12/2014 Prof. Tiziano Tuccinardi “New trends in computer aided drug design”

National and International Schools or Workshops

1. European School of Medicinal Chemistry, Urbino (IT) June 26-July 01, 2016.

Seminars Given:

1. 18/11/2016 “Advancing scientific discoveries on lung diseases, in particular Tuberculosis infections”.

Seminars Attended

1. 13/02/2014 Dr. Patrizia Restani “Allergie e Intolleranze alimentari”.
2. 19/02/2014 Prof. Gabriele Cruciani “A short story of Molecular Discovery projects”.
3. 04/03/2014 Dr. Rialdi "Filiera cosmetica, istituzioni di settore e regolamento cosmetici”.
4. 18/03/2014 Dr. Rialdi “Sostenibilità nella filiera cosmetica”.
5. 26/03/2014 Dr. Roberto Bagatin: “Tecnologie emergenti di monitoraggio e bonifica per il trattamento di acque e suoli”.
6. 19/03/2014 “Flow reactor technology: A flexible tool for reaction optimisation”.
7. 25/03/2014 Dr. Rialdi: “ Good manufacturing practises”.
8. 17/04/2014 Prof. Giuseppe Poli “Segnali di morte e sopravvivenza cellulare indotti da ossisteroli”.
9. 04/12/2014 Dr. Matteo Massa “Biocatalisi: applicazioni in sintesi farmaceutica” .
10. 04/12/2014 Dr Giacomo Mele “Molecole naturali e Xeno-ormesi”.
11. 04/12/2014 Dr. Benedetta Pollarolo “Metodi alternativi alla sperimentazione animale” .
12. 04/12/2014 Dr. Camilla Zibana “Recenti aspetti d’interesse terapeutico del processo di metastasi tumorale”.
13. 05/03/2015 Prof. Alessandro Morelli "Bioenergetica dei tumori"
14. 08/05/2015 Dr. Alessandro Valli "Metabolomics profile of hypoxic colorectal cancer cells".
15. 25/05/2015 Dr. Gerolamo Vettoretti "Hsp90 nella terapia antitumorale: dall'analisi conformazionale al disegno di nuovi inibitori allosterici".
16. 18/11/2016 Dr. Chiara Lacapra “Odori, profumi e feromoni come mediatori chimici olfattivi”.
17. 18/11/2016 Dr. Anita Parricchi “Giocare sporco: PAINS e composti promiscui”.

18. 18/11/2016 Dr. Silvia Rum “Il marketing cosmetico: dalla missione aziendale alla risposta del Consumatore”.

Other Activities:

Didactics:

1. Academic year 2014-2015: Laboratory assistant of Prof. Bruno Tasso at the course of “Analisi strumentale dei farmaci”, for the fourth year students of the Medicinal Chemistry course at the University of Genoa.
2. Academic year 2014-2015: Teaching tutor of “Physics chemistry” for the second year course of the Medicinal Chemistry course at the University of Genoa.
3. Academic year 2016-2017: Laboratory assistant of Prof. Federica Novelli at the course of “Analisi dei medicinali II”, for the third year students of the Pharmacy course at the University of Genoa.
4. Academic year 2016-2017: Teaching tutor of “Physics chemistry” for the second year course of the Medicinal Chemistry course at the University of Genoa.

Scholarships:

Winner of the “Swiss Government Excellence Scholarship”, for a 12 month experience (September 2015-August 2016) as a visiting student at the University of Geneva (CH), in the Department of Pathology and Immunology, to assess the biological activity of a library of compounds previously synthesized in my first and second year of PhD. Supervisor: Prof. Beat Imhof.

Awards:

Best poster price at the European School of Medicinal Chemistry, Urbino (IT) June 26-July 01, 2016.



Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Chemical Sciences and Technologies

PH.D. CERTIFICATE
of
RICCARDO MINETTI



Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisor

Prof. Adriana Saccone

Thesis Title

*Synthesis, structural characterization
and properties of new polar
intermetallic compounds*

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department of Chemistry and Industrial Chemistry, Riccardo Minetti has orally presented his doctorate research work in front of the Commission, formed by

- Prof. Gaetano Granozzi, University of Padova
- Prof. Andrea Pucci, University of Pisa
- Prof. Renata Riva, University of Genova

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

HAS APPROVED THE THESIS OF RICCARDO MINETTI
CONFERRING ON HIS THE TITLE OF

RESEARCH DOCTOR IN
CHEMICAL SCIENCES AND TECHNOLOGIES

Genova, February 24th, 2017

The Coordinator of the Doctorate Course
(Prof. Adriana Saccone)



Università degli Studi di Genova



**Doctorate in
Sciences and Technologies of
Chemistry and Materials**

CURRICULUM: Chemical Science and Technology

RICCARDO MINETTI

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *December 31th, 2016*

Advisors *Prof. A. Saccone*

Thesis Title: Synthesis, structural characterization and properties of new polar intermetallic compounds

ACTIVITY REPORT
Research Activity

The research activity was mainly carried out at DCCI (University of Genoa); however, Riccardo Minetti has also spent a research period of 6 months (October 5, 2015 to March 25, 2016) abroad, in the group of Prof. Antonio Pereira Gonçalves, at the Departamento de Engenharia e Ciências Nucleares, Instituto Superior Técnico, Bobadela (Lisbon Portugal)

Scientific Publications

- 1) P.Solokha, S.De Negri, R.Minetti, D.Proserpio, A.Saccone; Crystal structures of the new ternary stannides $\text{La}_3\text{Mg}_{4-x}\text{Sn}_{2+x}$ and $\text{LaMg}_{3-x}\text{Sn}_2$, *Journal of Solid State Chemistry*, **233** (2016), 407-414
DOI 10.1016/j.jssc.2015.11.016
- 2) S. De Negri, P. Solokha, R. Minetti, M.Skrobanska, A. Saccone; Isothermal section of the La-Mg-Sn system at 500 °C and crystal structure of the new ternary stannide LaMgSn_2 , in press in *Journal of Solid State Chemistry*.
- 3) P.Solokha, R.Minetti, S.De Negri, A.Saccone. L.C.J. Pereira, A.P.Gonçalves; The new RMgSn_2 series of compounds (R=rare earth metal): synthesis, crystal structure and magnetic measurements, to be sent to *J.Alloys and Compounds*

Communications at Conferences

Poster Communications:

- 1) R. Minetti, P. Solokha, S. De Negri, A. Saccone, "Flux synthesis of intermetallic compounds in the R-Mg-Sn systems (R = rare earth metal)", VII Edizione delle Giornate Italo Francesi della Chimica (GIFC), Torino, 5-6 maggio 2014
- 2) R. Minetti, P. Solokha, S. De Negri, A. Saccone, "Novel intermetallic compounds in the R-Mg-Sn systems (R = rare earth metal)", 19th International Conference on Solid Compounds of Transition Elements (SCTE), Genova, 21-26 giugno 2014

- 3) R. Minetti, P. Solokha, S. De Negri, A. Saccone, "The La-Mg-Sn system: new structures and a new synthesis technique", 14th Edizione del Sigma-Aldrich Young Chemists Symposium (SAYCS) – Riccione, 27-29 ottobre 2014
- 4) R. Minetti, P. Solokha, S. De Negri, A. Saccone, "Exploration of the La-Al-Ge ternary system at 500 °C", XLIV International Conference on Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD) – Loano, 2 giugno 2015

Congresses Attended

- 1) VII Edizione delle Giornate Italo Francesi della Chimica (GIFC), Torino, 5-6 maggio 2014
- 2) 19th International Conference on Solid Compounds of Transition Elements (SCTE), Genova, 21-26 giugno 2014
- 3) XLIV International Conference on Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD) – Loano, 2 giugno 2015

Courseware

Type B courses (12 CFU):

- 1) Synthesis, structure and functional properties of intermetallic compounds, 2014, (2 CFU)- passed
- 2) Basics of scanning and transmission electron microscopy, 2014 (2 CFU)- passed
- 3) Functional magnetic materials, 2014 (2 CFU) - passed
- 4) Mathematical methods for chemistry, 2014 (2 CFU) - attended
- 5) Introduction to functional ceramic materials. Structure, properties, preparation and applications, 2014 – (2 CFU) - attended
- 6) Il metodo di Rietveld in pratica, 2015 (2 CFU)- passed
- 7) Electronic Properties of Solids 2016 (2 CFU) - passed
- 8) Application of RAMAN spectroscopy to materials (2015) (2 CFU) - attended
- 9) Principi di metallurgia applicata: tradizione e innovazione (2016) (2CFU) -passed

Courses Given by invited experts (type A) (5 CFU)

- 1) Tecnologie di monitoraggio e bonifica di acque e suoli – Dr. Bagatin, Responsabile dell'Unità di Ricerca delle Tecnologie Ambientali dell'Istituto ENI Donegani, San Donato Milanese, 9 ottobre 2014, DCCI – Genova
- 2) Elementi di Chimica Forense – Dr. R. Narizzano e Dr. F. Risso, ARPAL Genova, 18-19 maggio 2015 , DCCI
- 3) Modern Materials for Energy Saving (Renewable Energy) – Prof. P. Rogl, Institute of Physical Chemistry, University of Vienna, Austria, 9-10 giugno 2015 DCCI
- 4) X-ray based experimental techniques and characterization of nano-materials – Dr. A. Morgante, CNR-IOM and Physics Department, University of Trieste, 31 marzo 2015, DCCI
- 5) Yb and Eu Strongly Correlated Electron Systems: from Experiment to Interpretation of Physical Properties – Dr. I. Curlik, University of Presov, Slovacchia, 22-23 aprile 2015, DCCI

National and International Schools or Workshops

- 1) International EXPO/SIR Workshop, Università di Bari, Dip. di Scienze della Terra e Geoambientali, Bari, 10-13 giugno 2014
- 2) Scuola nazionale per dottorandi della Divisione di Chimica Inorganica della SCI, "Nuovi Materiali ed Energie Sostenibili" Bressanone, 13-16 luglio 2015

Seminars Given

- 1) R.Minetti, Experimental investigation of New Ternary Intermetallic Systems: an Overview on the Techniques, March 15, 2016, Bobadela, Lisbon, Portugal

Seminars Attended

- 1) **Rapid Thermal Processing (RTP): a Novel Solvent-Free Enabling Technology for Ultrafast Block-Copolymer Self-Assembly** – Prof. Michele Laus, Università del Piemonte Orientale, 11 marzo 2014, DCCI – Genova
- 2) **Fuel cell degradation and its impact on system performance** – David Tucker, Senior Scientist, National Energy Technology Laboratory, WV, 29 aprile 2014, Genova
- 3) **Perspectives of future energy research in USA by DoE** – David Tucker, Senior Scientist, National Energy Technology Laboratory, WV, 29 aprile 2014, Genova
- 4) **Study of XIV-th c. enamel corrosion on copper plate** – Elzbieta Greiner-Wronowa, AGH University of Science and Technology, Kraków Poland, 29 maggio 2014, DCCI – Genova
- 5) **Heterophasic ethylene-propylene copolymer / halloysite nanocomposites using dispersing agents** – Dott.ssa Eveline Bischoff, Instituto de Química, Universidade Federal do Rio Grande do Sul Porto Alegre, Brasil, 8 sett. 2014, DCCI – Genova
- 6) **“ABC” Impedance - (Spettroscopia di impedenza elettrochimica per lo studio dei sistemi elettrochimici)** – Prof.ssa Daria Vladikova dell'Institute of Electrochemistry and Energy Systems – Bulgarian Academy of Sciences, Bulgaria, 24 settembre 2014, DCCI – Genova
- 7) **Thermal analysis and calorimetry: powerful tools for scientific investigation** – Federico Locardi, 30 ottobre 2014, DCCI – Genova
- 8) **Synchrotron Light for Extended X-ray Absorption Fine Structure (EXAFS) – A bright opportunity for (material) science** – Mattia Lucchini, 30 ottobre 2014, DCCI – Genova
- 9) **Corrosione microbiologica: introduzione ai meccanismi e tecniche di studio** – Roberto Spotorno, 30 ottobre 2014, DCCI – Genova
- 10) **The bond between paper fibers: a fresh look at an old material** – Prof. Robert Schennach, 17 febbraio 2015, DCCI – Genova
- 11) **Recent Developments in the Processing of Ceramic and Glasses** – Prof Mike Reece, Professor of functional ceramic, School of Engineering & Materials Science, Queen Mary University of London, 17 aprile 2015, IENI – Genova
- 12) **Electrochemical Impedance Spectroscopy – a tool for “in situ” investigation of SOFC anodes** – Dott.ssa G. Raikova, Istituto di Elettrochimica e dei Sistemi Energetici (IEES) dell'Accademia Bulgara delle Scienze di Sofia, 22 settembre 2015, DIFI – Genova
- 13) **High-valent oxo-rhenium complexes as efficient catalysts for organic reductions** – Joana Rita Maia Bernardo, 13 novembre 2015, IST Lisboa
- 14) **Exploring the magnetic properties of f-electron complexes with potential as single molecule magnets** – Joana Coutinho, 13 novembre 2015, IST Lisboa
- 15) **Design of magnetic nano-architecture** – Davide Peddis, 22 aprile 2016, DCCI – Genova

Other Activities

- 1) Art.33 - Attività di sostegno alla didattica, Corso di Chimica Inorganica 1 con Laboratorio, Laurea triennale CTC, a.a. 2013-2014, 30 ore
- 2) Attività di tutorato – Progetto “Un Tutor Per Ogni Studente”, 70 ore, anno 2014/2015
- 3) Attività di tutorato – Progetto “Un Tutor Per Ogni Studente”, 58 ore (in corso), anno 2016/2017



Università degli Studi di Genova
Doctorate Course in
Sciences and Technologies of Chemistry and Materials

Curriculum: Scienze e Tecnologie Chimiche

Sharif Najafishirtari

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *December 31st, 2016*

Advisors

Dr. Massimo Colombo

Prof. Fabio Canepa

Thesis Title

Nanoparticles for Technological Applications

ACTIVITY REPORT

Research Activity

The research activity was mainly carried out at the IIT Genova, Nanochemistry Dept. for more than 2 years where I developed the synthesis of a number of Nanocrystals (NCs) and applied them in catalytic CO oxidation as a model reaction. In addition to the catalytic measurements, all the characterizations were also performed in IIT. My works resulted in 3 publications as first author and a co-authorship in a collaboration within the group. More work is still ongoing on the last project I started in IIT though it will not be finished and published before the defense.

Also considering a cotutelle agreement, I spent 9 months (from Dec 2015 till September 2016) in the group of Prof. Reiser in Institut für Organische Chemie, Institut für Pharmazie und Chemie, Universität Regensburg. My activities there were mainly focused on the application of the NCs in liquid phase reactions using some of the NCs synthesized in IIT as catalysts. The results of my work in Germany are reported within the annual report of the 3rd year.

Briefly about the results; at first the synthesis protocol of dumbbell-like nanocomposites made of a metallic domain epitaxially connected to a metal oxide one was developed. Two main structures were synthesized, with focus on tuning the size and composition of the metallic domain. The synthesis work focused firstly on Au@Iron oxide heterostructures: NCs were obtained with various sizes of Au domain (nominally 4, 6 and 10 nm) while the size of iron oxide domain was kept ~18 nm. A seeded growth method was employed to form the iron oxide domain on pre-made Au nanoparticles. These NCs were further deposited on alumina supports and their catalytic activities as well as thermal stabilities were evaluated in the oxidation of CO. To benchmark the performances of the synthesized heterostructure, Au catalysts were prepared by their deposition on alumina and iron oxide (having similar sizes as in case of dumbbells) and tested as controlling experiments. The catalyst made of dumbbell NCs of 4 nm Au and iron oxide showed the best performance in CO oxidation suggesting the importance of Au-Iron oxide interface as the active

sites of the reaction, being maximized in this sample. Advanced electron microscopy, XPS and IR spectroscopy studies were carried out in order to characterize the NCs and rationalize the observed trends.

The research went on focusing on the same nanostructure where the composition of the metallic domain was tuned in order to obtain an intermetallic alloy of AuCu while keeping the size of the metallic domain at ~ 6 nm. In this regard, procedures for producing firstly AuCu nanocrystals (NCs) with an atomic ratio of 1:1 and then the corresponding AuCu@FeOx dumbbell nanocomposite were established. The AuCu NCs seeds were the subject of a dedicated study where their transformations upon different pre-treatments (i.e. under oxidizing or reducing atmospheres) and the resulted CO oxidation catalytic activities were studied. The analyses such as EDS-STEM, XRD, SAED and *in-situ* DRIFTS by the probe molecules of CO and NO were applied to characterize the colloidal NCs and to study the transformations and identify the nature of the active sites. The exposure at high temperature (350 °C) to an oxidizing environment caused a phase segregation between Au and Cu, which was found to be detrimental for the CO oxidation reaction. On the other hand, AuCu alloyed NCs were restored when the catalyst was exposed to a reducing environment and the catalytic activity was then significantly enhanced. The CO/O₂ reacting atmosphere also caused changes in the NCs composition and consequently on the reaction rate: for a reduced system the catalytic activity progressively decreased with time on stream, as a consequence of Cu de-alloying and of partial migration on the support surface. On the other hand, when starting from a fully oxidized situation, the reaction environment caused a partial re-alloying of Cu, which in turn resulted in the progressive increase of the catalyst activity. All these transformations were found to be fully reversible.

The AuCu@FeOx dumbbell-like NCs were also successfully synthesized by means of colloidal synthesis having both Au and Cu localized in the metal domain. These dumbbell NCs were further deposited on alumina support and tested in CO oxidation after oxidative pre-treatment which was essential to remove the protecting ligands and activate the catalyst. The complex transformations of these NCs upon activation was thoroughly studied by means of EDS-STEM and XAFS. The oxidation pre-treatment caused the de-alloying between Au and Cu, with Cu atoms likely being incorporated in the iron oxide domain. The resulted structure-activity correlation was further rationalized by comparison of the activity against iron oxide bulk supported AuCu catalyst as well as alumina supported Au@FeOx nanodumbbell having the same size of the metal and metal oxide domains. The AuCu@FeOx sample displayed CO oxidation reaction rates similar to those measured over a Au@FeOx catalyst having a similar Au domain size, highlighting the dominant role of the Au-iron oxide interface for this reaction. The nanosized support of iron oxide in case of dumbbell NCs provided a strong thermal stability of the metallic domains: the sintering of the Au domains was effectively prevented. This in turn yielded a higher activity of the AuCu@FeOx dumbbells when compared against a bulk Fe₃O₄ supported AuCu NCs catalyst, where extensive sintering occurred.

Interestingly, the composition of the oxide domain in case of colloidal AuCu@FeOx NCs was slightly different compared to the Au@FeOx observing a core-shell structure within the oxide domain of a number of NCs with an iron rich core. The number of such NCs were found to be tunable by synthesis conditions. These dumbbell NCs were further deposited on alumina support as before and tested in CO oxidation after oxidative pre-treatment. The NCs having the iron core in the oxide domain were transformed to a hollow iron oxide domain after the activation of the catalysts under oxidative atmosphere while Cu atoms were delocalized from metal domain and dispersed in the iron oxide domain. The catalytic properties of these catalysts were studied along with the characterizations trying to find a correlation between the activity and structural properties of such NCs. The characterizations techniques included TEM, STEM-HAADF-EDS, XAFS, XRD, XPS, CO TPR and etc. The kinetic measurements have been performed on the catalyst suggesting a

trend between the activity and the population of NCs with hollow oxide domain while the activation energy stays the same. EXAFS data have been also simulated to understand the structural properties of the fresh NCs and their evolution upon activation. The work is yet to be finalized before publication.

Finally and during my stay in Regensburg, I explored the catalytic activities of some of the NCs I had synthesized in IIT for liquid phase hydrogenation and oxidation reactions. In this regard, I developed a procedure to prepare magnetically recyclable catalysts using Turbobeads magnetic nanoparticles (NPs) as support (commercially available carbon-coated Co NPs) and pre-made colloidal NCs. I prepared a number of catalysts and applied them in liquid phase oxidation and hydrogenation reactions. The most promising results were the hydrogenation of cinnamylaldehyde to its corresponding unsaturated (or saturated) alcohol using AuCu (or AuCu@FeOx). We have checked the effect of different parameters on the extent of the reaction and found that the reaction takes place at moderately high pressure of 20 bar, the temperature of 50 °C and 24 h. The method for catalyst preparation is straightforward and can be applied for other colloidal NCs of interest as long as they are stable under harsh conditions of sonication. In order to complete this work, it should be extended further in different directions. Briefly, some few more tests are needed in order to fully understand the effects of the reaction parameters on the extent of cinnamylaldehyde hydrogenation as well as the product distribution. The catalysts should be also characterized further before and after reactions. Considering the magnetic nature of the catalyst, some consecutive trials should be performed in order to study the recyclability of the catalyst. The work will be hopefully finalized by the time of the defense.

Scientific Publications

Original publications on ISI Journals:

- 1) **Sharif Najafishirtari**, Rosaria Brescia, Pablo Guardia, Sergio Marras, Liberato Manna, Massimo Colombo; "Nanoscale Transformations of Alumina-Supported AuCu Ordered Phase Nanocrystals and Their Activity in CO Oxidation"; ACS Catalysis 2015, 5, 2154–2163.
- 2) **Sharif Najafishirtari**, Pablo Guardia, Alice Scarpellini, Mirko Prato, Sergio Marras, Liberato Manna, Massimo Colombo; "The effect of Au domain size on the CO oxidation catalytic activity of colloidal Au-FeOx dumbbell-like heterodimers"; Journal of Catalysis 338 (2016) 115–123. **This paper was selected as Editor-in-Chief's Featured Article in June 2016 (certificate is attached).**
- 3) **Sharif Najafishirtari**, Tathiana Midori Kokumai, Sergio Marras, Priscila Destro, Mirko Prato, Alice Scarpellini, Rosaria Brescia, Aidin Lak, Teresa Pellegrino, Daniela Zanchet, Liberato Manna, Massimo Colombo; "Dumbbell-like Au_{0.5}Cu_{0.5}@Fe₃O₄ Nanocrystals: Synthesis, Characterization and Catalytic Activity in CO Oxidation"; ACS applied Materials and Interfaces, **2016**, 8 (42), pp 28624–28632.
- 4) Zahra Hosseinpour, Alice Scarpellini, **Sharif Najafishirtari**, Sergio Marras, Massimo Colombo, Abdolali Alemi, Michaël De Volder, Chandramohan George, and Vladimir Lesnyak; "Morphology Dependent Electrochemical Properties of CuS Hierarchical Super-Structures"; ChemPhysChem 2015, 16, 3418 –3424.

Communications at Conferences

Oral communications:

- 1)

Poster Communications:

- 1) 8th International Conference on Environmental Catalysis, Place: Asheville (US), Date: 24/08/2014-27/08/2014, Contribution: Poster. **“CO oxidation over dumbbell like Au@FeO_y nanoparticles: catalytic activity, thermal stability and effect of gold domain size”** Sharif Najafishirtari, Massimo Colombo, Alice Scarpellini, Mirko Prato, Liberato Manna.
- 2) 24th North American Meeting (NAM) of the Catalysis Society, Place: Pittsburgh Pennsylvania (United States), Date: 14/06/2015-19/06/2015, Contribution: Poster. **“Nanoscale transformations of alumina-supported AuCu ordered phase nanoparticles upon CO oxidation”** Sharif Najafishirtari, Rosaria Brescia, Massimo Colombo, Liberato Manna.
- 3) 7th International Conference Gold2015, Place: Cardiff (UK), Date: 26/07/2015-29/07/2015, Contribution: Poster. **“AuCu ordered tetragonal phase nanocrystals: the effects of nanoscale transformations on CO oxidation catalytic activity”** Sharif Najafishirtari, Rosaria Brescia, Pablo Guardia, Sergio Marras, Liberato Manna, Massimo Colombo.
- 4) 16th International Congress on Catalysis (ICC 16), Place: Beijing (China), Date: 03/07/2016-08/07/2016, Contribution: Poster. **“AuCu@FeO_x dumbbell like heterodimers as catalysts for the CO oxidation: when support size matters”**; Sharif Najafishirtari, Alice Scarpellini, Mirko Prato, Sergio Marras, Priscila Destro, Tathiana Midori, Daniela Zanchet, Liberato Manna, Massimo Colombo.

Congresses Attended

1. 11th International Symposium on the "Scientific Bases for the Preparation of Heterogeneous Catalysts", Place: Louvain-la-Neuve (Belgium), Date: 06/06/2014-10/06/2014.

Courseware

During three years, Sharif Najafishirtari has acquired **29** credits of Courseware.

2 credits for 2 advanced courses in Unige, 9 credits from advanced 9 modules presented in IIT, 2 credits for attending more than 16 seminars, 6 credits for 2 summer schools, 10 credits for more than 6 presentations.

Courses attended and passed (... credits)

Courses Given by Teachers of the

Type A

- 1) Functional Magnetic Materials (Lecturer: Prof. F. Canepa), doctoral course in University of Genova started from 18/03/2014 to 06/05/2014.
- 2) Catalizzatori ed Adsorbenti Industriali (Lecturer: Prof. G. Busca), doctoral course in University of Genova, passed the examination at 26/09/2016.

Type B

- 3) Basic Concepts in Nanochemistry (Lecturer: Prof. L. Manna), Italian Institute of Technology, from 11/04/2014 to 09/04/2014.
- 4) Opto-Electronic Properties of Semiconductor Quantum Dots (Lecturer: Dr. I. Moreels), Italian Institute of Technology, from 06/06/2014 to 27/06/2014.
- 5) X-rays based Characterization Techniques (Lecturer: Dr. M. Prato), Italian Institute of Technology, from 04/07/2014 to 18/07/2014.
- 6) Fundamentals of Electron Microscopy (EM) and Spectroscopy techniques in EM, (Lecturer: Dr. R. Brescia; Dr. A. Genovese), Italian Institute of Technology, from 01/10/2014 to 14/10/2014.
- 7) Electrical properties of nanocrystals and nanocrystal films and Raman spectroscopy and lattice vibrations of nanocrystals, (Lecturer: Dr. R. Krahne), Italian Institute of Technology, from 12/11/2014 to 17/11/2014.
- 8) Fundamentals of magnetism and magnetic properties of nanoparticles, (Lecturer: Dr. A. Casu), Italian Institute of Technology at 19/11/2014.

- 9) Energy related applications, (Lecturer: Dr. M. Colombo; Dr. S. Monaco; Dr. Y. Zhang), Italian Institute of Technology from 12/11/2014 to 17/11/2014.
- 10) Nanomaterials and Nanocomposites: Processing and characterization, (Lecturer: Dr. L. De Trizio; Dr. V. Lesnyak; Dr. M. Arciniegas), Italian Institute of Technology, from 28/01/2015 to 05/02/2015.
- 11) Basics of quantum chemistry; Molecular orbitals in molecules and 1D systems; Concepts of bonding in solids (Lecturer: Prof. L. Manna), Italian Institute of Technology, from 15/12/2014 to 22/12/2014.

Courses Given by invited experts:

- 1)

National and International Schools or Workshops

- 1) *ELITECAT 2015 (Catalysts: preparation, composition and application; Catalyst characterizations and modelisation; Application)*, 6th-10th July 2015, Lyon, France.
- 2) Catsense ATC11 (Physics and Chemistry of Nanoclusters), 7th-11th September 2015, Bruges, Belgium.
- 3) Public Speaking Skills for Scientists, (Lecturer: Jacopo Pasotti), Italian Institute of Technology, from 21/09/2015 to 22/09/2015.

Seminars Given

- 1) Place: University of Genova, Genoa (Italy), Date: 14/02/2014, Contribution: Oral, Title of Contribution: **'Synthesis of Au@FexOy dumbbell nanoparticles with different size of Au and evaluation of their catalytic activity in CO oxidation'**.
- 2) Place: Italian Institute of Technology, Genoa (Italy), Date: 06/11/2015, Contribution: Oral, Title of Contribution: **'Nanosizing of magnetite support for AuCu NCs and its effect on CO oxidation activity'**.
- 3) Place: Institut für Pharmazie und Chemie Universität Regensburg, Regensburg (Germany), Date: 02/02/2016, Contribution: Oral, Title of Contribution: **'Colloidal Synthesis of Nanocrystals as a Tool to Prepare Model Catalysts'**.
- 4) Place: Technische Universität Dresden, Physikalische Chemie, Dresden (Germany), Date: 23/02/2016, Contribution: Oral, Title of Contribution: **'Colloidal Synthesis of Nanocrystals as a Tool to Prepare Model Catalysts'**.
- 5) Place: Institut für Pharmazie und Chemie Universität Regensburg, Regensburg (Germany), Date: 21/06/2016, Contribution: Oral, Title of Contribution: **'Application of colloidal NCs in catalysis of liquid phase reactions'**.
- 6) Place: Italian Institute of Technology, Genoa (Italy), Date: 06/12/2016, Contribution: Oral, Title of Contribution: **'Nanoparticles for technological applications'**.

Also within the framework of the MagneticFun project in which I was enrolled, I gave seminars about the progress of my activity at different stages for our project meetings. This include 5 seminars and presentations in IIT, university of Regensburg, Keele University (Institute for Science and Technology in Medicine) and Trinity College Dublin.

Seminars Attended

- 1) Quantum Geochemistry: Simulating Physico-Chemical Properties of Materials in The Deep Earth; Donato Belmonte; 31/03/2014.
- 2) EKO and EKOS: A New Perspective On Discovery Of Small Molecules To Perturb Protein-protein Interactions; Kevin Burgess; 30/04/2014.
- 3) Nanomaterials as Highly Active Catalyst for Multiple Significant Reactions; Sasanka Deka; 25/05/2014.
- 4) Buckyball Maracas: Size, Shape and Electronic Complementarity between the Carbon Cages and the Clusters for Endohedral Fullerenes; Prof. Luis Echegoyen; 23/05/2014.
- 5) Colloidal nanoparticles – shape and composition control; Dirk Dorfs, 26/05/2014.
- 6) Organization of Colloidal Nanoparticle Building Blocks into Functional Superstructures; Nadja-C. Bigall, 26/05/2014.
- 7) Copper-based Quaternary Chalcogenide Nanoparticles for the Photovoltaic and Thermoelectric Applications; Alexey Shavel, 28/07/2014.
- 8) Novel Strategies for Combining Molecules, Clusters, and Nanocrystals into Functional Inorganic Solids; Maksym V. Kovalenko, 18/09/2014.
- 9) Synthesis of metal-oxide and metal-oxide based hybrid Nanostructures; Taleb Mokari, 24/09/2014.

- 10) Colloidal nanocrystals and their functional architectures; Nikolai Gaponik, 29/09/2014.
- 11) Plasmonic heavily doped semiconductor nanocrystals: from fundamentals to their nanoscale application; Ilka Kriegel, 26/11/2014.
- 12) Optics of CdSe/CdS nanocrystals: a theoretical overview; Juan Ignacio Climente Plasencia, 05/12/2014.
- 13) Field-Effect Transistors and solar cells made of individual colloidal PbS nanosheets; Sedat Dogan, 08/01/2015.
- 14) Plasmonic Materials; Mehdi Hedayati, 12/01/2015.
- 15) High Energy Lithium-ion and Lithium-Sulfur batteries; Marco Agostini, 20/02/2015.
- 16) Using colloidal quantum dots to boost photovoltaic cell performance; Miri Kazes, 25/02/2015.
- 17) Printed semiconductors and novel 2D materials in the high charge density regime; Daniele Braga, 30/02/2015.
- 18) Versatile fabrication of highly porous cryogels from noble metal nanoparticles; Axel Freytag, 04/03/2015.
- 19) The fascinating materials science of epitaxially grown semiconductor materials; Andrew G. Norman; 22/05/2015
- 20) Chemi-transistors gas sensors based on multicomponent nano materials; Michela Sainato, 28/05/2015.
- 21) Semiconductor Nanocrystals: Discovery, Milestones, and Recent Theoretical Developments; Prof. Alexander L. Efros, 20/11/2015.
- 22) Insight in the chemistry of metal sulphide nanocrystals and their application in photovoltaics, Dr. Peter Reiss, 25/11/2015.
- 23) Thermal forces: Moving and manipulating matter with thermal gradients, Prof. Roberto Piazza, 21/10/2016.

OtherActivities

- 1)



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Advisors

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Thesis Title

Nanoparticles for Technological Applications

ACTIVITY REPORT
Research Activity

The research activity was mainly carried out at the IIT Genova, Nanochemistry Dept. for more than 2 years where I developed the synthesis of a number of Nanocrystals (NCs) and applied them in catalytic CO oxidation as a model reaction. In addition to the catalytic measurements, all the characterizations were also performed in IIT. My works resulted in 3 publications as first author and a co-authorship in a collaboration within the group. More work is still ongoing on the last project I started in IIT though it will not be finished and published before the defense.

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- 2) 24th North American Meeting (NAM) of the Catalysis Society, Place: Pittsburgh Pennsylvania (United States), Date: 14/06/2015-19/06/2015, Contribution: Poster. **“Nanoscale transformations of alumina-supported AuCu ordered phase nanoparticles upon CO oxidation”** Sharif Najafishirtari, Rosaria Brescia, Massimo Colombo, Liberato Manna.
- 3) 7th International Conference Gold2015, Place: Cardiff (UK), Date: 26/07/2015-29/07/2015, Contribution: Poster. **“AuCu ordered tetragonal phase nanocrystals: the effects of nanoscale transformations on CO oxidation catalytic activity”** Sharif Najafishirtari, Rosaria Brescia, Pablo Guardia, Sergio Marras, Liberato Manna, Massimo Colombo.
- 4) 16th International Congress on Catalysis (ICC 16), Place: Beijing (China), Date: 03/07/2016-08/07/2016, Contribution: Poster. **“AuCu@FeO_x dumbbell like heterodimers as catalysts for the CO oxidation: when support size matters”**; Sharif Najafishirtari, Alice Scarpellini, Mirko Prato, Sergio Marras, Priscila Destro, Tathiana Midori, Daniela Zanchet, Liberato Manna, Massimo Colombo.

Congresses Attended

1. 11th International Symposium on the "Scientific Bases for the Preparation of Heterogeneous Catalysts", Place: Louvain-la-Neuve (Belgium), Date: 06/06/2014-10/06/2014.

Courseware

During three years, Sharif Najafishirtari has acquired **29** credits of Courseware.

2 credits for 2 advanced courses in Unige, 9 credits from advanced 9 modules presented in IIT, 2 credits for attending more than 16 seminars, 6 credits for 2 summer schools, 10 credits for more than 6 presentations.

Courses attended and passed (... credits)

Courses Given by Teachers of the

Type A

- 1) Functional Magnetic Materials (Lecturer: Prof. F. Canepa), doctoral course in University of Genova started from 18/03/2014 to 06/05/2014.
- 2) Catalizzatori ed Adsorbenti Industriali (Lecturer: Prof. G. Busca), doctoral course in University of Genova, passed the examination at 26/09/2016.

Type B

- 3) Basic Concepts in Nanochemistry (Lecturer: Prof. L. Manna), Italian Institute of Technology, from 11/04/2014 to 09/04/2014.
- 4) Opto-Electronic Properties of Semiconductor Quantum Dots (Lecturer: Dr. I. Moreels), Italian Institute of Technology, from 06/06/2014 to 27/06/2014.
- 5) X-rays based Characterization Techniques (Lecturer: Dr. M. Prato), Italian Institute of Technology, from 04/07/2014 to 18/07/2014.
- 6) Fundamentals of Electron Microscopy (EM) and Spectroscopy techniques in EM, (Lecturer: Dr. R. Brescia; Dr. A. Genovese), Italian Institute of Technology, from 01/10/2014 to 14/10/2014.
- 7) Electrical properties of nanocrystals and nanocrystal films and Raman spectroscopy and lattice vibrations of nanocrystals, (Lecturer: Dr. R. Krahne), Italian Institute of Technology, from 12/11/2014 to 17/11/2014.
- 8) Fundamentals of magnetism and magnetic properties of nanoparticles, (Lecturer: Dr. A. Casu), Italian Institute of Technology at 19/11/2014.

- 9) Energy related applications, (Lecturer: Dr. M. Colombo; Dr. S. Monaco; Dr. Y. Zhang), Italian Institute of Technology from 12/11/2014 to 17/11/2014.
- 10) Nanomaterials and Nanocomposites: Processing and characterization, (Lecturer: Dr. L. De Trizio; Dr. V. Lesnyak; Dr. M. Arciniegas), Italian Institute of Technology, from 28/01/2015 to 05/02/2015.
- 11) Basics of quantum chemistry; Molecular orbitals in molecules and 1D systems; Concepts of bonding in solids (Lecturer: Prof. L. Manna), Italian Institute of Technology, from 15/12/2014 to 22/12/2014.

Courses Given by invited experts:

- 1)

National and International Schools or Workshops

- 1) *ELITECAT 2015 (Catalysts: preparation, composition and application; Catalyst characterizations and modelisation; Application)*, 6th-10th July 2015, Lyon, France.
- 2) Catsense ATC11 (Physics and Chemistry of Nanoclusters), 7th-11th September 2015, Bruges, Belgium.
- 3) Public Speaking Skills for Scientists, (Lecturer: Jacopo Pasotti), Italian Institute of Technology, from 21/09/2015 to 22/09/2015.

Seminars Given

- 1) Place: University of Genova, Genoa (Italy), Date: 14/02/2014, Contribution: Oral, Title of Contribution: **'Synthesis of Au@FexOy dumbbell nanoparticles with different size of Au and evaluation of their catalytic activity in CO oxidation'**.
- 2) Place: Italian Institute of Technology, Genoa (Italy), Date: 06/11/2015, Contribution: Oral, Title of Contribution: **'Nanosizing of magnetite support for AuCu NCs and its effect on CO oxidation activity'**.
- 3) Place: Institut für Pharmazie und Chemie Universität Regensburg, Regensburg (Germany), Date: 02/02/2016, Contribution: Oral, Title of Contribution: **'Colloidal Synthesis of Nanocrystals as a Tool to Prepare Model Catalysts'**.
- 4) Place: Technische Universität Dresden, Physikalische Chemie, Dresden (Germany), Date: 23/02/2016, Contribution: Oral, Title of Contribution: **'Colloidal Synthesis of Nanocrystals as a Tool to Prepare Model Catalysts'**.
- 5) Place: Institut für Pharmazie und Chemie Universität Regensburg, Regensburg (Germany), Date: 21/06/2016, Contribution: Oral, Title of Contribution: **'Application of colloidal NCs in catalysis of liquid phase reactions'**.
- 6) Place: Italian Institute of Technology, Genoa (Italy), Date: 06/12/2016, Contribution: Oral, Title of Contribution: **'Nanoparticles for technological applications'**.

Also within the framework of the MagneticFun project in which I was enrolled, I gave seminars about the progress of my activity at different stages for our project meetings. This include 5 seminars and presentations in IIT, university of Regensburg, Keele University (Institute for Science and Technology in Medicine) and Trinity College Dublin.

Seminars Attended

- 1) Quantum Geochemistry: Simulating Physico-Chemical Properties of Materials in The Deep Earth; Donato Belmonte; 31/03/2014.
- 2) EKO and EKOS: A New Perspective On Discovery Of Small Molecules To Perturb Protein-protein Interactions; Kevin Burgess; 30/04/2014.
- 3) Nanomaterials as Highly Active Catalyst for Multiple Significant Reactions; Sasanka Deka; 25/05/2014.
- 4) Buckyball Maracas: Size, Shape and Electronic Complementarity between the Carbon Cages and the Clusters for Endohedral Fullerenes; Prof. Luis Echegoyen; 23/05/2014.
- 5) Colloidal nanoparticles – shape and composition control; Dirk Dorfs, 26/05/2014.
- 6) Organization of Colloidal Nanoparticle Building Blocks into Functional Superstructures; Nadja-C. Bigall, 26/05/2014.
- 7) Copper-based Quaternary Chalcogenide Nanoparticles for the Photovoltaic and Thermoelectric Applications; Alexey Shavel, 28/07/2014.
- 8) Novel Strategies for Combining Molecules, Clusters, and Nanocrystals into Functional Inorganic Solids; Maksym V. Kovalenko, 18/09/2014.
- 9) Synthesis of metal-oxide and metal-oxide based hybrid Nanostructures; Taleb Mokari, 24/09/2014.

- 10) Colloidal nanocrystals and their functional architectures; Nikolai Gaponik, 29/09/2014.
- 11) Plasmonic heavily doped semiconductor nanocrystals: from fundamentals to their nanoscale application; Ilka Kriegel, 26/11/2014.
- 12) Optics of CdSe/CdS nanocrystals: a theoretical overview; Juan Ignacio Climente Plasencia, 05/12/2014.
- 13) Field-Effect Transistors and solar cells made of individual colloidal PbS nanosheets; Sedat Dogan, 08/01/2015.
- 14) Plasmonic Materials; Mehdi Hedayati, 12/01/2015.
- 15) High Energy Lithium-ion and Lithium-Sulfur batteries; Marco Agostini, 20/02/2015.
- 16) Using colloidal quantum dots to boost photovoltaic cell performance; Miri Kazes, 25/02/2015.
- 17) Printed semiconductors and novel 2D materials in the high charge density regime; Daniele Braga, 30/02/2015.
- 18) Versatile fabrication of highly porous cryogels from noble metal nanoparticles; Axel Freytag, 04/03/2015.
- 19) The fascinating materials science of epitaxially grown semiconductor materials; Andrew G. Norman; 22/05/2015
- 20) Chemi-transistors gas sensors based on multicomponent nano materials; Michela Sainato, 28/05/2015.
- 21) Semiconductor Nanocrystals: Discovery, Milestones, and Recent Theoretical Developments; Prof. Alexander L. Efros, 20/11/2015.
- 22) Insight in the chemistry of metal sulphide nanocrystals and their application in photovoltaics, Dr. Peter Reiss, 25/11/2015.
- 23) Thermal forces: Moving and manipulating matter with thermal gradients, Prof. Roberto Piazza, 21/10/2016.

OtherActivities

- 1)



Università degli Studi di Genova
Doctorate School in
Sciences and Technologies of
Chemistry and Materials

Curriculum: Nanochemistry

Dina Niculaes

Start of the Doctorate Program January 1st, 2014

End of the Doctorate Program December 31st, 2016

Advisors

Dr. Teresa Pellegrino

Prof. Renata Riva

Prof. Miquel A. Pericàs

Thesis Title

Iron oxide nanocubes for magnetically induced hyperthermia

ACTIVITY REPORT

Research Activity & Courseware

During the three-year PhD program, the research activity was mainly carried out at the Italian Institute of Technology, with a ten-month mobility stay at the Institute of Chemical Research of Catalonia (ICIQ), from April 16th 2015 until January 31st 2016, as part of the co-tutelle agreement between the Università degli Studi di Genova and Universitat Rovira I Virgili (Tarragona, Spain).

Scientific publications

Original publications in ISI Journals:

1. Lak, A.; Niculaes, D.; Anyfantis, G. C.; Bertoni, G.; Barthel, M. J.; Marras, S.; Cassani, M.; Nitti, S.; Athanassiou, A.; Giannini, C.; Pellegrino, T.; Facile transformation of FeO/Fe₃O₄ core-shell nanocubes to Fe₃O₄ via magnetic stimulation, *Sci. Rep.*, **2016**, 6, 33295
2. Kakwere, H.; Pernia Leal, M.; Materia, M. E.; Curcio, A.; Guardia, P.; Niculaes, D.; Marotta, R.; Falqui, A.; Pellegrino, T.; Functionalization of strongly interacting magnetic nanocubes with (thermo)responsive coating and their application in hyperthermia and heat-triggered drug delivery, *ACS Applied Materials & Interfaces*, **2015**, 7 (19), 10132

Communications at conferences

Oral communications:

1. 10 minute presentation on '*Controlled multifunctionalization of magnetic nanoparticles for application in biology and catalysis*' at the mid-term review meeting of the Mag(net)icFun network. Place: IIT, Genoa (Italy). Date: 03.06.2014
2. 15 minute presentation on '*Monodisperse iron oxide nanocubes with a core-shell structure*' at the 4th workshop of the Mag(net)icFun network. Place: University of Regensburg, Regensburg (Germany). Date: 27.10.2014
3. 10 minute oral presentation on '*Nano-clusters of iron oxide nanoparticles*' at the 5th workshop of the Mag(net)icFun network. Place: University of Keele, Stoke-on-Trent (United Kingdom). Date: 24.04.2015
4. 20 minute presentation on '*Iron oxide nanocubes coated with thermo-responsive polymers for magnetically induced hyperthermia and drug delivery*' at the 2015 International Chemical Congress of Pacific Basin Societies. Place: Honolulu (United States). Date: 19.12.2015
5. 20 minute presentation on 'Updates on the project: *Nano-clusters of iron oxide nanoparticles*' at the 6th workshop of the Mag(net)icFun network. Place: Trinity College Dublin, Dublin (Ireland). Date: 04.03.2016
6. 30 minute presentation on '*(Core-shell) Iron oxide nanocubes for magnetically induced hyperthermia*' at the final review meeting of the Mag(net)icFun network. Place: University of Regensburg, Regensburg (Germany). Date: 21.11.2016

National and international conferences attended

1. Mag(net)icFun initial training network mid-term review meeting. Place: IIT, Genoa (Italy). Date: 02-03.06.2014
2. Marie Skłodowska-Curie satellite workshop@ESOF 2014. Place: Copenhagen (Denmark), Date: 19-20.06.2014
3. Mag(net)icFun 4th workshop. Place: University of Regensburg, Regensburg (Germany). Date: 27-28.10.2014
4. Nanomedicine Symposium CEN@Politecnico. Synthesis of nanomaterials, biological applications and modelling. Place: Politecnico di Milano, Milan (Italy). Date: 14.11.2014
5. Mag(net)icFun 5th workshop. Place: University of Keele, Stoke-on-Trent (United Kingdom). Date: 23-24.03.2015
6. Workshop 'Supervision training for doctoral candidates: Understanding and Conducting productive and supportive research supervision jointly'. Place: University Rovira I Virgili, Tarragona (Spain). Date: 13.05.2015
7. 65th Interdisciplinary Lindau Nobel Laureate meeting. Place: Lindau (Germany). Date: 28.06-03.07.2015
8. Post-conference to the 65th Interdisciplinary Lindau Nobel Laureate meeting, for young researchers. Place: Konstanz, Tübingen, Stuttgart, Karlsruhe, Heidelberg (Germany). Date: 4-10.07.2015
9. 2015 International Chemical Congress of Pacific Basin Societies. Place: Honolulu, Hawaii (United States). Date: 15-20.12.2015

10. Global Young Scientists Summit@one-north 2016. Place: Singapore (Singapore). Date: 17-22.01.2016
11. Mag(net)icFun 6th workshop. Place: Trinity College Dublin, Dublin (Ireland). Date: 03-04.03.2016
12. ICARO kick-off meeting. Place: Sestri Levante (Italy). Date: 09-10.06.2016
13. Marie Skłodowska-Curie satellite workshop@ESOF 2016. Place: University of Manchester, Manchester (United Kingdom), Date: 28-29.07.2016
14. Mag(net)icFun final review meeting. Place: University of Regensburg, Regensburg (Germany). Date: 21-22.11.2016

Courseware

During my doctorate, I have acquired **23 credits** for courseware.

Courses attended

Courses given by researchers of the Italian Institute of Technology (10 credits):

1. Basics in nanochemistry (2014 - 1 credit)
2. Synthesis of nanocrystals and nanocomposites (2014 - 1 credit)
3. Characterization techniques 1: X-ray based techniques (2014 - 1 credit)
4. Characterization techniques 2: Insights/discussion on electron microscopy (2014 - 1 credit)
5. Characterization techniques 3: Raman spectroscopy and lattice vibrations (2014 - 1 credit)
6. Fundamentals of magnetism and magnetic properties of nanoparticles (2014 - 1 credit)
7. Electronic properties of solids (2016 - **3** credits)
8. Magnetic properties and characterization techniques (2016 - 1 credit)

Courses given by invited experts (1 credit):

1. Magnetic hyperthermia: from fundamentals to biomedical applications (2016 - 1 credit)

National and international summer schools

(6 credits)

1. School on Science Management for Scientists and Engineers (SoSMSE). Place: University of Genoa, (Italy). Date: 11-22.07.2016

Seminars attended

Seminars attended@IIT (2 credits)

1. *Directing Assembly of Integrated Molecular Systems: from Principles to Functional Materials* by Dr. Marco Frasconi, Northwestern University, 07.01.2014.
2. *Self-Assembling Nanomaterials: Quantum Dots and Chemically converted Graphene* by Beatriz. Martín-García, Salamanca University, 03.02.2014
3. *Electrochemical Control over Charge Transfer and Trapping in CdSe-CdTe QD Solids* by Prof. Arjan J. Houtepen, TU Delft, 03.03.2014
4. *Biodegradable polyesters from natural occurring fatty hydroxyacids. The synthesis and characterization of polyaleuritrate* by Josè Jesus Benitez, Materials Science Institute of Seville, 02.04.2014
5. *EKO and EKOS: A New Perspective On Discovery Of Small Molecules To Perturb Protein-protein Interactions* by Prof. Kevin Burgess, Texas A & M University, 30.05.2014

6. *Buckyball maracas: Size, Shape and Electronic Complimentarity between the carbon cages and the clusters for Endohedral fullerenes* by Prof. Luis Echegoyen, University of Texas at El Paso, 23.06.2014
7. *Nanomaterials as Highly Active Catalyst for Multiple Significant Reactions* by Sasanka Deka, University of Delhi, 25.06.2014
8. *Colloidal nanoparticles - shape and composition control* by Dirk Dorfs, Institute of Physical Chemistry and Electrochemistry, Leibnitz Universität Hannover, 26.06.2014
9. *Organization of Colloidal Nanoparticle Building Blocks into Functional Superstructures* by Nadja-C. Bigall, Institute of Physical Chemistry and Electrochemistry, Leibniz University Hanover, 26.06.2014
10. *Copper-based Quaternary Chalcogenide Nanoparticles for the Photovoltaic and Thermoelectric Applications* by Dr. Alexey Shavel, Catalonia Energy Research Institute, 28.07.2014
11. *Synthesis of metal-oxide and metal-oxide based hybrid Nanostructures* by Taleb Mokari, Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, 24.09.2014
12. *Magneto-optical spectroscopy of individual semiconductor nanocrystals* by Chiara Sinito, Laboratoire Photonique, Numérique et Nanosciences, Institut d'Optique Graduate School, CNRS & Université de Bordeaux, 25.09.2014
13. *Cellule Staminali Tumoralì: nuovo bersaglio terapeutico* by Prof. Matilde Todaro, Università degli Studi di Palermo, 26.09.2014
14. *Colloidal nanocrystals and their functional architectures* by Nikolai Gaponik, TU Dresden, 29.09.2014
15. *Gold nanoparticles as monitoring sensors and delivery system for anti-cancer drugs* by Dr. Elisa Salvati, IFOM-IEO Campus, Nanomedicene Lab, 29.10.2014
16. *Organic bio-electronic devices for sensing applications* by Luisa Torsi, University of Bari, 10.11.2014
17. *Field-Effect Transistors and solar cells made of individual colloidal PbS nanosheets* by Dr. Sedat Dogan, University of Hamburg, 08.01.2015
18. *Designing organometallics for material science: application for solar cells and scintillators* by Dr. Guillaume Bertrand, LCAE, CEA Saclay, 19.01.2015
19. *Using colloidal quantum dots to boost photovoltaic cell performance* by Miri Kazes, Department of Physics of Complex Systems, Weizmann Institute of Science, 25.02.2015
20. *Tetravalent DNA Nanostars as Valence-limited Building Blocks* by Dr. Lorenzo Rovigatti, Computational Physics Group@University of Vienna, 02.03.2015

Seminars attended@ICIQ

21. *Synergies between chemistry and nanotechnology: applications to neuroscience and energy* by Prof. Maurizio Prato, University of Trieste, 08.05.2015
22. *Non-nobel metal catalysts for making precious molecules* by Matthias Beller, Leibniz Institute for Catalysis, 19.06.2015
23. *Chemistry of high-valent palladium and nickel* by Melanie Sanford, University of Michigan, 25.06.2015
24. *Strategies to prepare highly luminescent organolead bromide nanoparticle colloids* by Prof. Julia Perez Prieto, University of Valencia, 18.09.2015
25. *From nanoparticles to complex functional materials: a view from the bridge* by Dr. Dorota Koziej, ETH Zürich, 25.09.2015

Seminars attended@IIT

26. *Perovskites: an old material for the third generation of PV solar panels* by Dr. Laura Miranda Perez, Oxford Photovoltaics, 21.04.2016
27. *Hydration induced spin glass state in a frustrated Na-Mn-O triangular lattice* by Dr. Ioanna Bakaimi, Department of Physics, University of Crete, 28.04.2016
28. *Colloidal nanoparticles and applications* by Dr. Antonios G. Kanaras, School of Physics and Astronomy, University of Southampton, 28.04.2016
29. *First-principle predictions of substrate effects on silicone* by Prof. Udo Schwingenschloegl, Physical Science and Engineering Division at KAUST, 09.05.2016
30. *Halocarbons in nanomedicine and nanotechnology: new opportunities and challenges* by Prof. Pierangelo Metrangolo, Politecnico di Milano, 07.10.2016

Seminars given

(4 credits)

1. *Controlled multifunctionalization of magnetic nanoparticles for applications in biology.* Place: IIT, Genoa (Italy), Date: 27.05.2014
2. *Monodispersed iron oxide nanocubes with a core-shell structure for magnetically induced hyperthermia.* Place: IIT, Genoa (Italy), Date: 28.07.2014
3. *1st year of PhD progress report.* Place: University of Genova. Date: 11.12.2014
4. *(Nano)clusters of iron oxide nanoparticles.* Place: ICIQ, Tarragona (Spain), Date: 18.06.2015
5. *Nano-iron oxide-catalyzed oxidation of benzyl alcohol.* Place: ICIQ, Tarragona (Spain), Date: 08.10.2015
6. *Summary of the 2nd year of PhD research activity.* Place: IIT, Genova (Italy), Date: 21.10.2015
7. *Literature seminar: Dosage delivery of sensitive reagents enables glove-box-free synthesis.* Place: ICIQ, Tarragona (Spain), Date: 10.11.2015
8. *PhD meetings: 3rd progress report.* Place: ICIQ, Tarragona (Spain), Date: 04.12.2015
9. *Pellegrino group meeting: 3rd year progress report.* Place: Sestri Levante (Italy). Date: 09.06.2016
10. *3rd year of PhD progress report.* Place: IIT. Date: 06.12.2014

Other

- Italian classes: October–December 2014
- Spanish classes: September–December 2015
- BioUpper startup competition (2016 call)
- Course on High tech entrepreneurship organized in collaboration between IIT and the Department of Economics@UniGe (October–December 2016)



Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Pharmaceutical, Food and Cosmetic Sciences

PH.D. CERTIFICATE
of
ANITA PARRICCHI



Doctorate Course

Pharmaceutical, Food and Cosmetic Sciences

Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisor

Prof.ssa Angela Bisio

Thesis Titles

Isolation of bioactive compounds from medicinal and aromatic plants acclimatized in Liguria

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department of Pharmacy, Anita Parricchi has orally presented her doctorate research work in front of the Commission, formed by

- Prof.ssa Olga Bruno, University of Genova
- Prof. Stefano Manfredini, University of Ferrara
- Prof.ssa Nunziatina De Tommasi, University of Salerno

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

HAS APPROVED THE THESIS OF ANITA PARRICCHI
CONFERRING ON HER THE TITLE OF

RESEARCH DOCTOR IN
PHARMACEUTICAL, FOOD AND COSMETIC SCIENCES

Genova, February 24th, 2017

The Coordinator of the Doctorate Course
Prof. Adriana Saccone



Università degli Studi di Genova
Doctorate School in
Sciences and Technologies of
Chemistry and Materials



Curriculum:

ANITA_PARRICCHI

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *December 31th 2016*

Advisors *Dr. Angela Bisio*

Thesis Title Isolation of bioactive compounds from medicinal and aromatic plants acclimatized in Liguria.

Thesis abstract

Aim of the research is the identification of new bioactive terpenoids from medicinal and aromatic plants (MAPS) acclimatized in the Ligurian region. The research was developed in the following areas:

1. Description of morphological characters of the selected species.

A sample of the species was deposited in herbarium international and checked by an expert of the genre. The morphological characteristics were examined by consulting several reference texts.

2. Extraction of compounds

The biomasses were extracted with appropriate solvents to yield crude extracts, which were subjected to chromatographic methods (classic and HPLC methods) to obtain purified compounds. Identification and structural elucidation of new compounds were carried out by spectroscopic (UV, IR, MS, ¹H-NMR, ¹³C-NMR) and chromatographic (HPLC-DAD) methods.

3. Evaluation of the bioactivity of the isolated compounds

The crude extracts and the isolated secondary metabolites were tested *in vitro* for their biological activity.

4. Quantitative determination of compounds in complex mixtures

The amount of compounds of interest was established through the construction of analytical curves and data statistically analyzed.

ACTIVITY REPORT

Research Activity

The research activity was mainly carried out at the Department of Pharmacy, University of Genoa, Laboratory of Phytochemistry.

Stage period at the University of Prague (Technická 5, 166 28, Prague 6, Czech Republic) from 01/07 to 1/10/15.

Scientific Publications

Original publications on ISI Journals:

1. Bisio A., Schito A.M., Parricchi A., Mele G., Romussi G., Malafronte N., Oliva P., De Tommasi N. 2015. Antibacterial activity of constituents from *Salvia buchananii* Hedge (Lamiaceae). *Phytochemistry Letters*. **14**:170–177.
2. Bisio A., Fraternali D., Schito A.M., Parricchi A., Dal Piaz F., Ricci D., Giacomini M., Ruffoni B., De Tommasi N. 2016. Establishment and analysis of *in vitro* biomass from *Salvia corrugata* Vahl. and evaluation of antimicrobial activity. *Phytochemistry*. **122**:276-285.
3. Bisio A., Parricchi A., Romussi G., De Tommasi N. 2016. Composti bioattivi da specie di *Salvia* di interesse ornamentale: l'esperienza dei Progetti EU-ALCOTRA in Liguria (Italia). In: Summer School of Floriculture 2015 Tradizione e innovazione nel comparto delle colture aromatiche e officinali. RACCOLTA CONTRIBUTI DEI RELATORI E SCHEDE TEMATICHE. In collaborazione con: DISAFA Università degli Studi di Torino CREA FSO Sanremo IRF, Sanremo CeRSAA, Albenga CSF, Regione Liguria. Editore: Società di ortoflorofruitticoltura Italiana (SOI), Firenze. Pp. 205-218.
4. Bisio A, De Mieri M, Milella L, Schito A. M., Parricchi A., Russo D., Alfei S., Lapillo M., Tuccinardi T., Hamburger M., De Tommasi N. Antibacterial and Hypoglycemic Diterpenoids from *Salvia chamaedryoides* : SUBMITTED to *Journal of Natural Product*.

Communications at Conferences

Oral communications:

- 1) Bisio A., Mele G., Parricchi A., Schito A.M., Dal Piaz F., De Tommasi N., 2014. Antimicrobial activity and two new clerodane diterpenoids from the exudate of the aerial parts of *Salvia buchananii* Hedge. Scuola di Fitochimica 2014 della Società Italiana di Fitochimica, Stintino (SS) 2-5 Ottobre.
- 2) Bisio A., Schito A.M., Mele G., Glasl-Tazreiter S., Parricchi A., Romussi G., De Tommasi N., 2014. Secreted material and antimicrobial activity of *Salvia cacaliaefolia* Benth. Società Botanica Italiana 109° Congresso - International Plant Science Conference (IPSC) - Book of Abstracts. Firenze, 2 - 5 September 2014. Firenze, Italia: Società Botanica Italiana. 1: 23.
- 3) Parricchi A., Gbelcova H., D'Acunto W., Bisio A., De Tommasi N., Ruml T. Evaluation of anticancer activity of terpenoids from the aerial parts of *Salvia wagneriana* Polak. Scuola di Fitochimica 2016 della Società Italiana di Fitochimica, Modena 10-12 Giugno.

Poster Communications:

- 1) Bisio A., Mele G., Parricchi A., Pronzato R., De Tommasi N., 2014. A new octaprenylhydroquinone from *Sarcotragus spinosulus*. Trends in Natural Products Research 2014. Book of Abstracts. Czech Republic: Phytochemical Society of Europe (PSE) and Palaky University Olomouc, Centre of the Region Hanà for Biotechnological and Agricultural Research. ISBN 9780956547255. 1: 66.
- 2) Bisio A., Schito A.M., Parricchi A., Mele G., Romussi G., Dal Piaz F., De Tommasi N., 2015. Antibacterial activity of the exudate of *Salvia buchananii* Hedge (Lamiaceae). XIV Congresso della Società Italiana di Fitochimica. "Valorizzazione della Biodiversità Italiana: le proprietà salutistiche delle piante alimentari". 10-12 giugno 2015. Padova. Italia. 1: 48.
- 3) Bisio A., Parricchi A., De Tommasi N., 2015. A new sesterterpene from *Salvia tingitana* Etl. (Lamiaceae). 110° Congresso SBI Onlus. Pavia, 14-18 Settembre 2015.
- 4) Bisio A., De Mieri M., Milella L., Schito A.M., Parricchi A., Alfei S., Vignola L., Hamburger M., De Tommasi N., 2016. Biological activity of constituents of *Salvia chamaedryoides* Cav. 9th Joint Natural Products Conference – GA 2016 - Book of Abstracts. 24th – 27th July 2016. Copenhagen, Denmark.
- 5) Bisio A., Parricchi A., Pedrelli F., De Tommasi N., 2016. Secondary metabolites from *Salvia tingitana* Etl. (Lamiaceae). 111° Congresso della Società Botanica Italiana. Roma, 21-23 Settembre 2016.
- 6) Bisio A., Parricchi A., Pedrelli F., Schito A.M., Glasl-Tazreiter S., De Tommasi N., 2016. Secreted Material and Antimicrobial Activity of *Salvia cacaliifolia* Benth. 2nd Sino-Italian Symposium on Bioactive Natural Products (SISBNP 2016). Napoli, 24-25 Novembre 2016.

Journal Abstract:

- 1) Bisio A., Mele G., Parricchi A., Schito A.M., Dal Piaz F., De Tommasi N., 2014. New clerodane diterpenoids from *Salvia buchananii* Hedge. Book of Abstracts. 62nd International Congress and Annual Meeting of the Society of Medicinal Plant and Natural Product Research. Guimarães, Portugal, 31. August – 4. September 2014. Chair: Prof. Dr. Alberto Dias, Braga – Issue Editors: Prof. Dr. Alberto Dias, Dr. Paulo Silva. *Planta Medica*. Stuttgart, Germania: Thieme Verlag KG. ISSN: 0032-0943, doi: 10.1055/s-0034-1395017. 16(80): P2025.
- 2) Bisio A., Fraternali D., Schito A.M., Giacomini M., Parricchi A., Dal Piaz F., Romussi G., Ricci D., De Tommasi N. 2015. *In vitro* biomass of *Salvia corrugata*: chemical analysis and evaluation of antimicrobial activity. 63rd International Congress and Annual Meeting of the Society for Medicinal Plant and Natural Product Research (GA). August 23 - 27, 2015. Budapest, Hungary. *Planta Medica* 81 - PM_164. DOI: 10.1055/s-0035-1565541

Congresses Attended

1. Phytochemical Society of Europe (PSE): “Trends in Natural Products Research: A Young Scientists Meeting” Olomouc, Czech Republic, 23/06 - 25/06/2014.
2. Society for Medicinal Plant and Natural Product Research - GA: “62nd International Congress and Annual Meeting, 2014” University of Minho, Guimarães, Portugal, 31/08 - 4/09/2014.
3. Società Botanica Italiana: “109° Congresso della Società Botanica Italiana onlus” Firenze, 4/09/2014.
4. Società Italiana di Fitochimica “XIV Congresso della Società Italiana di Fitochimica” 10/06 - 12/06/2015. Padova. Italia. 1: 48.
5. Society for Medicinal Plant and Natural Product Research - GA: “63rd International Congress and Annual Meeting, 2015” Budapest, Hungary, 23/08 - 27/08/2015
6. Society for Medicinal Plant and Natural Product Research- GA: “9th Joint Natural Products Conference 2016” Copenhagen, Denmark, 24/07 - 27/07/2016
7. Società Botanica Italiana: “111° Congresso della Società Botanica Italiana”. Roma, 21/09 – 23/09/2016
8. SISBNP: “2nd Sino-Italian Symposium on Bioactive Natural Products 2016”. Napoli, 24/11 - 25/11/2016

Courseware

During her two years of doctorate, Dr. Parricchi has acquired 12 credits of Courseware.

Courses attended and passed (12 credits)

Courses Given by Teachers of the University of Genoa

- 1) “Principali piante utilizzate in Fitocosmesi e loro costituenti” Dr.ssa A. Bisio (DIFAR) (2 credits)
- 2) “Metodologia della ricerca sperimentale” Prof. M. Grotti (DCCI), R.Leardi (DIFAR) (3 credits)
- 3) “Chimica Bioorganica” Prof. L. Banfi (DCCI) (2 credits)
- 4) “Analisi multivariata dei dati chimici” Prof. R. Leardi, S.Lanteri (DIFAR) (3 credits)
- 5) “Ricerca bibliografica e brevettuale nelle scienze farmaceutiche tramite banche dati” Prof. P.Fossa, C.Brullo (2 credits)

Courses Given by invited experts:

- 1) “Graphene: the magic of carbon”. Dr.ssa Coletti C.
- 2) “Drug Discovery and Development. Industrial Process Design and Pharmaceutical Green Chemistry.” Dr. Cabri W.
- 3) “Tecnologie emergenti di monitoraggio e bonifica per il trattamento di acqua e suoli”. Dr. Bargantin R.
- 4) “Introduction to Thermoelectrics”. Dr. Rogli P.

National and International Schools or Workshops

- 1) Società Italiana di Fitochimica - Scuola di Fitochimica P.Ceccherelli_2014. Le sostanze naturali da abuso: droghe o potenzialità terapeutica? Aspetti storici, botanici, fitochimici, tossicologici e forensi. Stintino (SS) 2-5 Ottobre.
- 2) Società Italiana di Fitochimica - Scuola di Fitochimica P.Ceccherelli_2016. Brassicaceae: Odore pungente e proprietà salutistiche dalla coltivazione alla tavola, dalla chimica agli usi popolari e terapeutici. Modena 10-12 Giugno.

Seminars Given

- 1) Giocare sporco: PAINS e composti promiscui. Università degli studi di Genova. 18 Novembre 2016

Seminars Attended

- 1) Allergie ed intolleranze alimentari. Dr.ssa Restani P.
- 2) Filiera cosmetica, istituzioni di settore e regolamento cosmetici. Dr. Rialdi V.
- 3) Good Manufacturing Practices. Dr. Rialdi V.
- 4) Heterophasic ethylene-propylene copolymer/halloysate nanocomposites using dispersing agents. Dr.ssa Bischoff E.
- 5) Thermal analysis and calorimetry: powerful tools for scientific investigation. Dr. Locardi F.
- 6) Synchrotron Light for Extended X-ray Absorption Fine Structure (EXAFS)-A bright opportunity for (material) Science. Dr. Lucchini M.A.
- 7) Corrosione microbiologica: introduzione ai meccanismi o tecniche di studio. Dr. Spotorno R.
- 8) Le parole delle piante: dall'evoluzione delle molecole segnale ai farmaci. Prof.ssa Butterweck V., Prof. Hamburger M., Prof.ssa Bilia A.R. Palazzo Ducale – Sala del Minor Consiglio – Genova. 28/10/14
- 9) Biocatalisi: applicazioni in sintesi farmaceutica. Dr. Massa M.
- 10) Molecole naturali e Xeno-ormesi. Dr. Mele G.
- 11) Metodi alternativi alla sperimentazione animale. Dr.ssa Pollarolo B.
- 12) Recenti aspetti di interesse terapeutico del processo di metastasi tumorale. Dr.ssa Zibana C.
- 13) Strumentazione di chimica analitica per l'esplorazione del sistema solare. Dr. Bazzano A.
- 14) Self-assembled block copolymers aggregates: application in drug delivery. Dr.ssa Gardella L.
- 15) Introduzione alle pile a combustibile e ai fenomeni di degrado ad alta temperatura. Dr.ssa Ghiara G.
- 16) Il sistema biotina-(strept)avidina nel pretargeting e in applicazioni biotecnologiche. Dr.ssa Croce I.
- 17) Tecnologie avanzate per lo sviluppo di modelli alternativi fisiologicamente rilevanti in vitro. Dr.ssa Danailova J.
- 18) Reazioni palladio-catalizzate: un impatto rivoluzionario in Chimica Farmaceutica. Dr. Desogus A.
- 19) Rivoluzione nella terapia delle malattie parassitarie: Artemisinina come grande successo scientifico. Dr.ssa Francini C. M.
- 20) Odori, profumi e feromoni come mediatori chimici olfattivi. Dr.ssa La Capra C.
- 21) Tubercolosi ed altre patologie polmonari: stato dell'arte e recenti sviluppi terapeutici. Dr.ssa Meta E.
- 22) Il marketing cosmetico: dalla *mission* aziendale alla risposta del consumatore. Dr.ssa Rum S.

Other Activities

- 1) Attività di supporto alla didattica nell'ambito del Corso di Tecnologia, Socioeconomia e Legislazione Farmaceutica I per Farmacia (30 ore), AA 2014-2015, primo semestre.
- 2) Partecipazione all'organizzazione nell'ambito degli eventi del Festival della Scienza 2014, Genova, 24 Ottobre - 2 Novembre, di una conferenza dal titolo "Le Parole delle Piante: dall'evoluzione delle molecole segnale ai farmaci". Relatori: Matthias Hamburger, University of Basel; Anna Rita Bilia, Università degli Studi di Firenze; Veronika Butterweck, University of Applied Sciences and Arts Northwestern Switzerland; Maria Luisa Brandi, Università degli Studi di Firenze. Genova, Palazzo Ducale, Sala del Minor Consiglio, 28 ottobre 2014.
- 3) Attività di supporto alla didattica nell'ambito del Corso di Tecnologia, Socioeconomia e Legislazione Farmaceutica I per Farmacia (30 ore), AA 2016-2017, primo semestre.

Third Year Annual Report-2016

PhD cycle XXIX

Thesis Title: Nanocrystals based LEDs and LASERs

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December, 2016

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Dot-in-rods based red emitting light emitting diode

1. Introduction

Dot-in-rods (DiRs) heterostructures comprising a CdSe core embedded in a CdS rod has been chosen as an emissive material for light emitting diode (LED). CdSe/CdS DiRs anisotropic structures have been widely explored as emitters in lasers [1][2][3], light down-converters and two photon absorbers[4]. But in the application of LEDs it is still lagging behind in performance with respect to the traditional spherical dot-in-dot (DiD) [5][6]. Nevertheless, CdSe/CdS/ZnSe heterojunction nanorods[7] have been recently shown to boost both the efficiency and brightness of LEDs with respect to spherical DiDs, possibly due to favorable band offset and enhanced light out coupling. In other recently reported DiRs [8] LEDs shows 6 % EQE by using polyelectrolytic electron transport layer with mobile Br⁻ counter anions still has the limited luminance around 1200 cd/m².

So far, colloidal nanocrystals-LEDs mentioned above having the aliphatic long chain phosphoric or oleic ligands, since the high temperature synthesis of such nanocrystals required high boiling point ligands like OHPA (463°C) and TOPO (411°C) as a stabilizer. To utilize the optical properties of DiRs semiconductor nanocrystals in optoelectronic application efficiently, it is also required to improve the electrical and charge transport properties of DiRs.

Here, it demonstrated that using the ligand exchange method on DiRs film can be directly affects the performance of LEDs. The ligand exchange procedure, described in previous chapter, is applied on DiRs films to study the LEDs performance. However, ligand exchange procedure has a detrimental effect on the optical

properties of DiRs. Since the core is protected by CdS shell and ligand exchange method can damaged the surface of CdS which results a decrease in photoluminescence quantum yield (PLQY). Therefore, ligand-exchange affects influence the luminance and so the overall efficiency of LEDs. Recently, the unit quantum yield DiRs[9] reported. In this synthesis, multi-steps shell growth is adapted to achieve the thick CdS shell. Here, we modified the typical synthesis [10] of DiRs via seeded growth, which required one step to achieved thick shell of CdS. The advantage of thick CdS shell is that it protect the CdSe core well and has less detrimental effect on the PL quantum yield over the treatment of ligand exchange[1].

2. LEDs based on dot-in-rods with native ligands

2.1 Method and material

The ITO patterned substrates are cleaned in an ultrasonic bath first with acetone and later with isopropanol and dried with Nitrogen. Exposure to oxygen plasma for 10 minutes at 15W followed to remove any remaining organic contamination. Oxygen plasma treatment also helps to decreases the roughness of ITO. The PEDOT:PSS (Ossila) was spin coated on cleaned ITO at 5000 rpm for 60 sec and baked at 140 C for 10 min. The PEDOT:PSS coated ITO/glass substrates transferred into the glove box. The TFB (American dyes), serves as hole transport layer (HTL), dispersed in chlorobenzene at concentration of 8.5 mg/mL and stirred for overnight. The TFB solution spin coated at 4000 rpm for 45 sec and baked at 150 C for 30 min. For the blend HTL, F₄TCNQ (Sigma aldrich) were dissolved in 5 mg/mL TFB m-xylene solution at the ration of 1:01. Poly-TPD and PVK are used as bi-HTL. For Bi-hole HTL, 8 mg/mL Poly-TPD dissolved in chlorobenzene and 1.8 mg/mL of PVK dissolved in m-xylene spin coated at 2000 rmp for 60 sec and annealed at 170 and 110 C for 20 and 30 mins respectively. Then the CdSe/CdS DiRs in toluene were spun at 2000 rpm for 60 sec and baked at 70 C for 30 min. And finally ZnO (zinc oxide) nanoparticles, electron transport layer, dispersed in ethanol at 25 µl/mL and spin coated at 3000 rpm for 60 sec. Then the device was transferred to thermal evaporator in another chamber of the same glove box to deposit 100 nm of aluminum at 3×10^{-6} Torr pressure.

All the devices were encapsulated with glass cover slip inside the glove box. The characterization of the encapsulated devices was performed in ambient air.

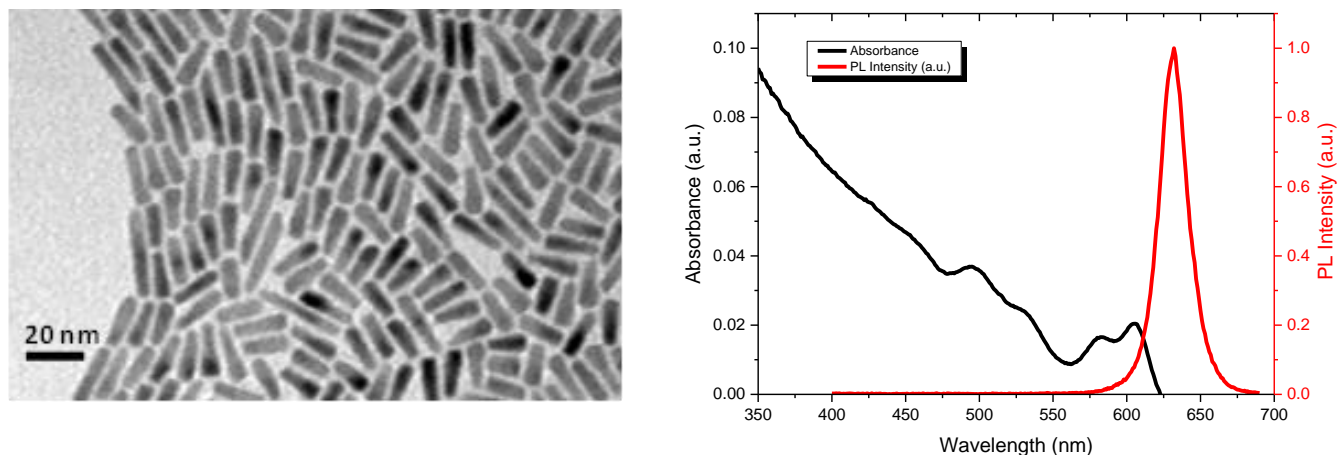


Figure 1 A) TEM image of CdSe/CdS dot-in-rods. The dimensions of DiRs are length 21.0 nm, width 9.0 and core diameter 4.33 nm. B) Absorption and photoluminescence spectrum of the DiRs dispersed in toluene. The peak wavelength of the PL spectrum is 634 nm .

2.2 Hole/electron transport layer for efficient LEDs performance

The performance of LEDs mainly depends on inefficient charge injection in active layer and efficient radiative charge recombination. The choice of hole transport and electron transport layer may directly affect the efficiency of LEDs. In this work, various hole transport materials was examine as hole injecting layer in LEDs. In the Figure 2 hole transport material are shown used in the LEDs. For the efficient charge injection the energy offset between HOMO level of HTL and the valance level maxima (VBM) of emissive material should be comparable. The VBM of nanocrystals used in this work is 5.7 eV from vacuum level measured with ultraviolet photoemission spectroscopy (UPS) measurements.

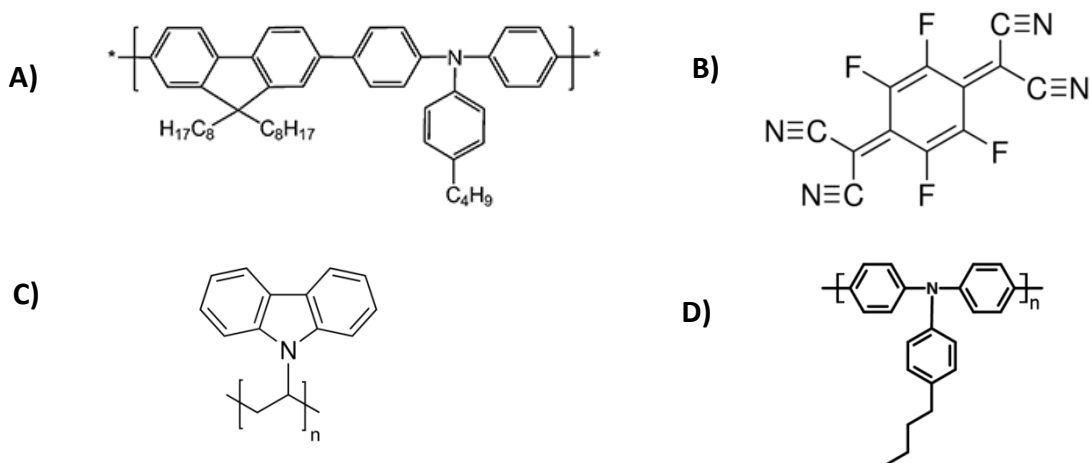


Figure 2 Hole transport material A) Poly(9,9-dioctylfluorene-alt-N-(4-n-butylphenyl)-diphenylamine) (TFB), B) 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), C) Poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine]Poly(4-butylphenyldiphenylamine) (Poly-TPD) and D) Poly(9-vinylcarbazole) (PVK) used to study DiRs light emitting diodes.

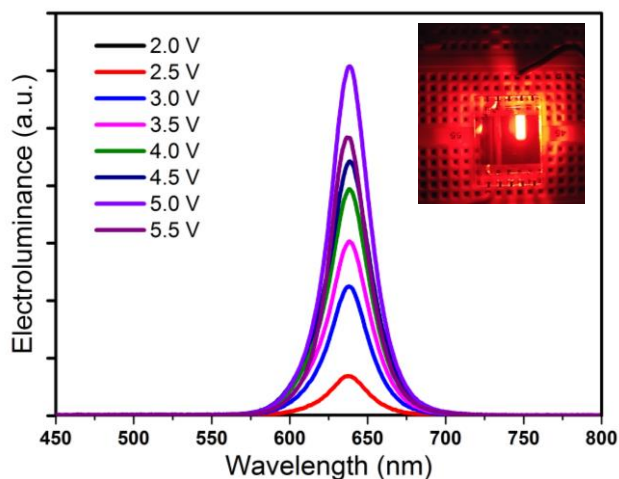


Figure 3 Electroluminescence of the LED at various voltagess. The inset shows the photograph of red LED.

In the Figure 3, the electroluminescence is shown of the device is shown as the function of voltage. The electroluminescence has no shift over the increase of voltage and the spectra became narrower at higher voltage.

The Figure 4 shows current density-voltage-luminance (J-V-L) characteristics of LEDs where the electron injecting layer (ZnO) was optimized for best performance. The device shows low turn on voltage 1.9 V at 0.1 cd/m², however the luminance is less than 100 cd/m². Due to low current density the EQE is measured as 2.4% .the low current density indicates that charge injection was poor in these devices. After examine the TFB layer, we noticed that the TFB layer is dissolved in toluene solvent. Since the DiRs NCs was spin-coated from toluene solvent which leads to dissolve the TFB layer.

In order to prevent the TFB, HTL over toluene exposure, the TFB is blended with F₄TCNQ at 1:0.1 concentration. In Figure 5, the performance of blend-HTL is shown. By blending the TFB layer, hole injection is improved in emissive layer and an increased luminance 130 cd/m² is observed. The current density is also increased from 10 to 80 mA/cm². However the EQE is still low due to not sufficient hole injection in device.

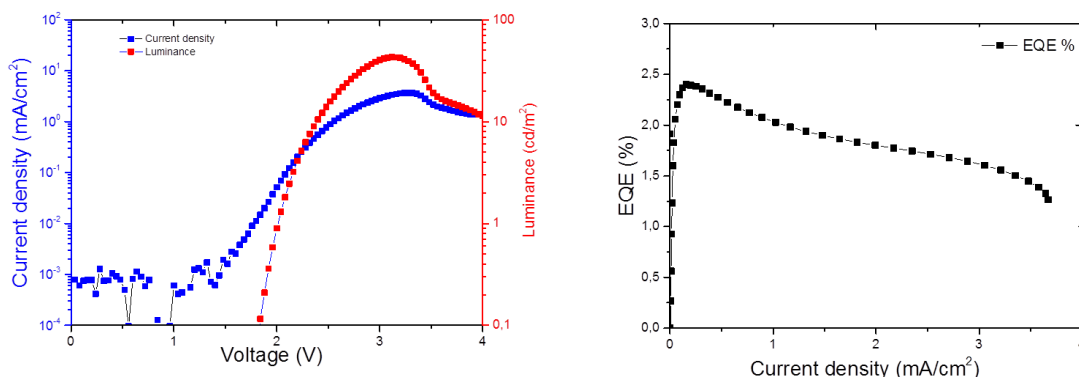


Figure 4: J-V_L characterization of LEDs consist TFB as a hole transport layer. In these devices the active layer is of ODPa capped DiRs and ZnO NPs used as electron transport.

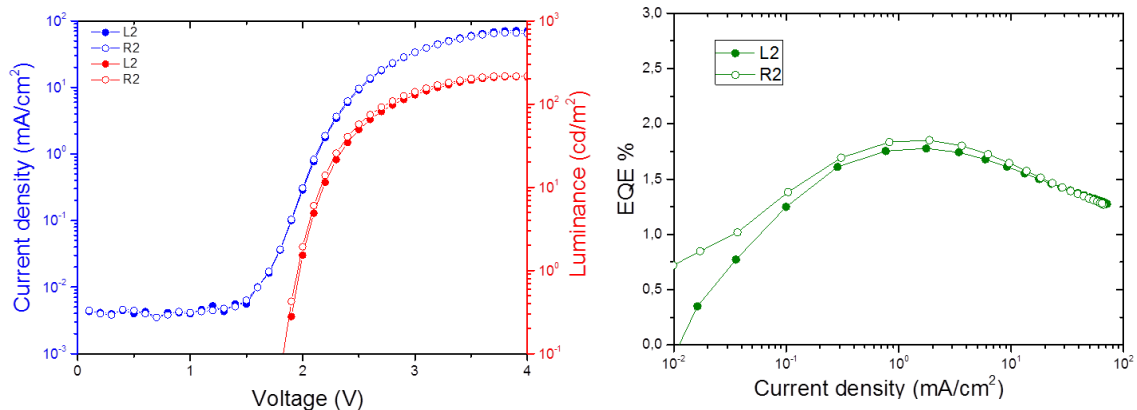


Figure 5 J-V-L characteristics of LEDs consist TFB: F₄TCNQ (1:0.1) blend as a hole transport layer.

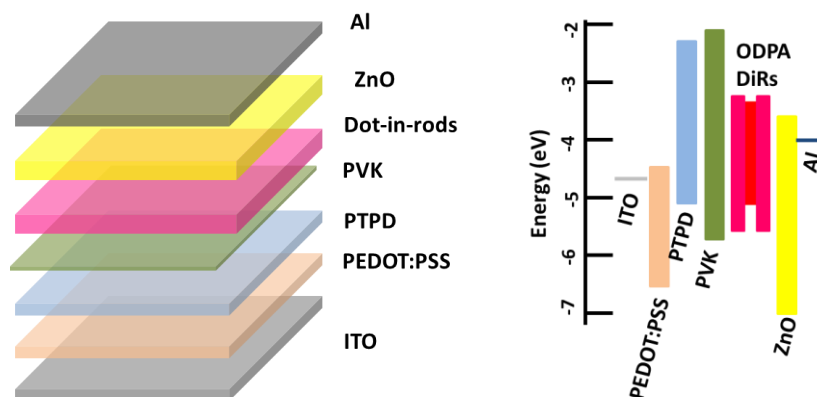


Figure 5 The schematic of LEDs device with Bi-hole transport layers poly-TPD and PVK is shown in a). The LEDs consist ETL as ZnO nanoparticles. b) the energy level diagram of the device.

The previous section states the single hole transport structure disadvantages, where the most important one is the poor charge injection. Therefore other structures have been demonstrated in order to improve LEDs performances. Figure 5 illustrates the bi-hole transport structures. In this structure, PVK is introduced, in order to create small potential offset where holes are easily inject to active layer (Figure 5). The two materials are chosen such that the poly-TPD can block the electron to reach at anode and hole injection becomes efficient, so this design also meets the need to compensate the unbalanced of charge. Since each carrier type is confined

to active material the bi-hole transport layer structure also increases charge recombination. Another advantage of this structure has the low turn on voltage at 1.9 V.

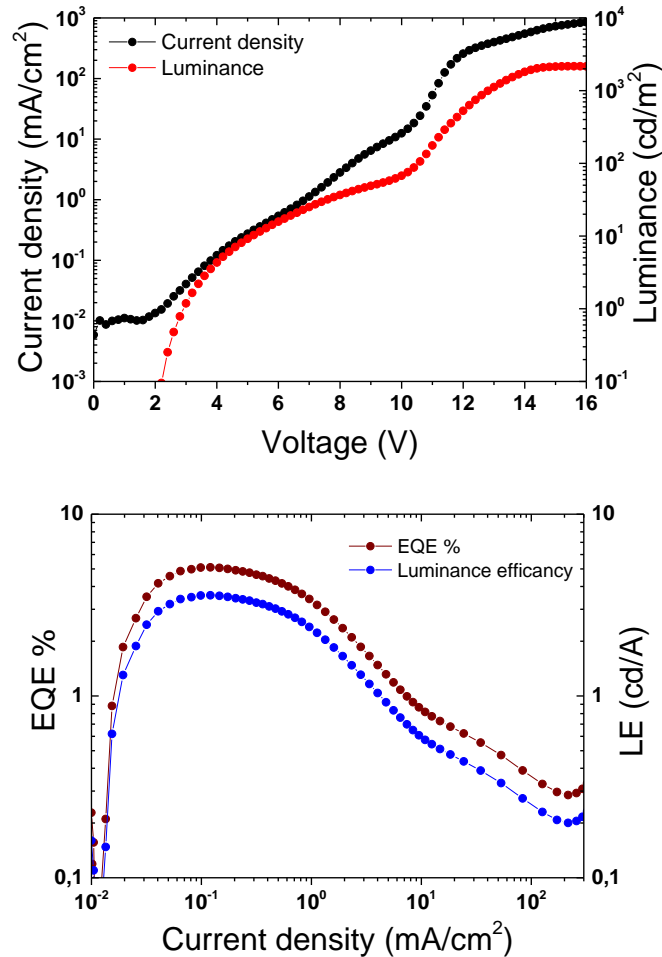


Figure 6 J-V-L characterization of LEDs consist poly-TPD and PVK as hole transport layer. The curves represent devices having different thickness of ZnO, electron transport layer. In these devices the active layer is of NRs with ODPA ligands.

The typical J-V-L and EQE-J curves are shown in Figure 6 for ODPA-DiRs LED. The bilayer- transport struce enhanced the device performance due to improved charge balance in the device. The luminance and EQE of device is measured 2200 cd/m² and 5.1 %. However the device shows the efficiency roll-off i.e. the EQE starts decreasing as the current density increases. This can be explain as when the injected charges from the electrode to the active material are higher than the charges transported in the material, the charge start accumulated into the NCs layer and space charge is created. In this situation the further charge injection

inhibited until equilibrium is reached with a non-uniform electric field and uniform current inside the active materials. In this regime the auger recombination takes place and luminance start decreasing and so the overall performance.

3 Ligand exchanged dot-in-rods based LEDs

3.1 Results and discussion

To study the effect of ligand exchange on LED performance the ODPA ligand is exchanged with MPA, AET and SCN molecules. The ligand exchange on DiRs leads to a shift in the energy levels of DiR nanocrystals. The energy level position of DiR NCs is examined with ultraviolet photoemission spectroscopy (UPS). Figure 7 presents the UPS spectra of MPA, AET and SCN modified NCs along with the native ODPA capped DiRs.

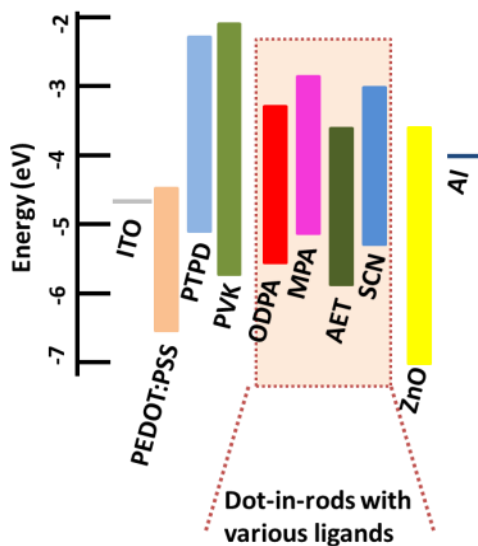


Figure 7 a) energy level diagram of LEDs structure used for ligand exchanged DiRs LEDs. DiR NCs are exchanged with MPA, AET and SCN which shift the energy levels of DiRs .

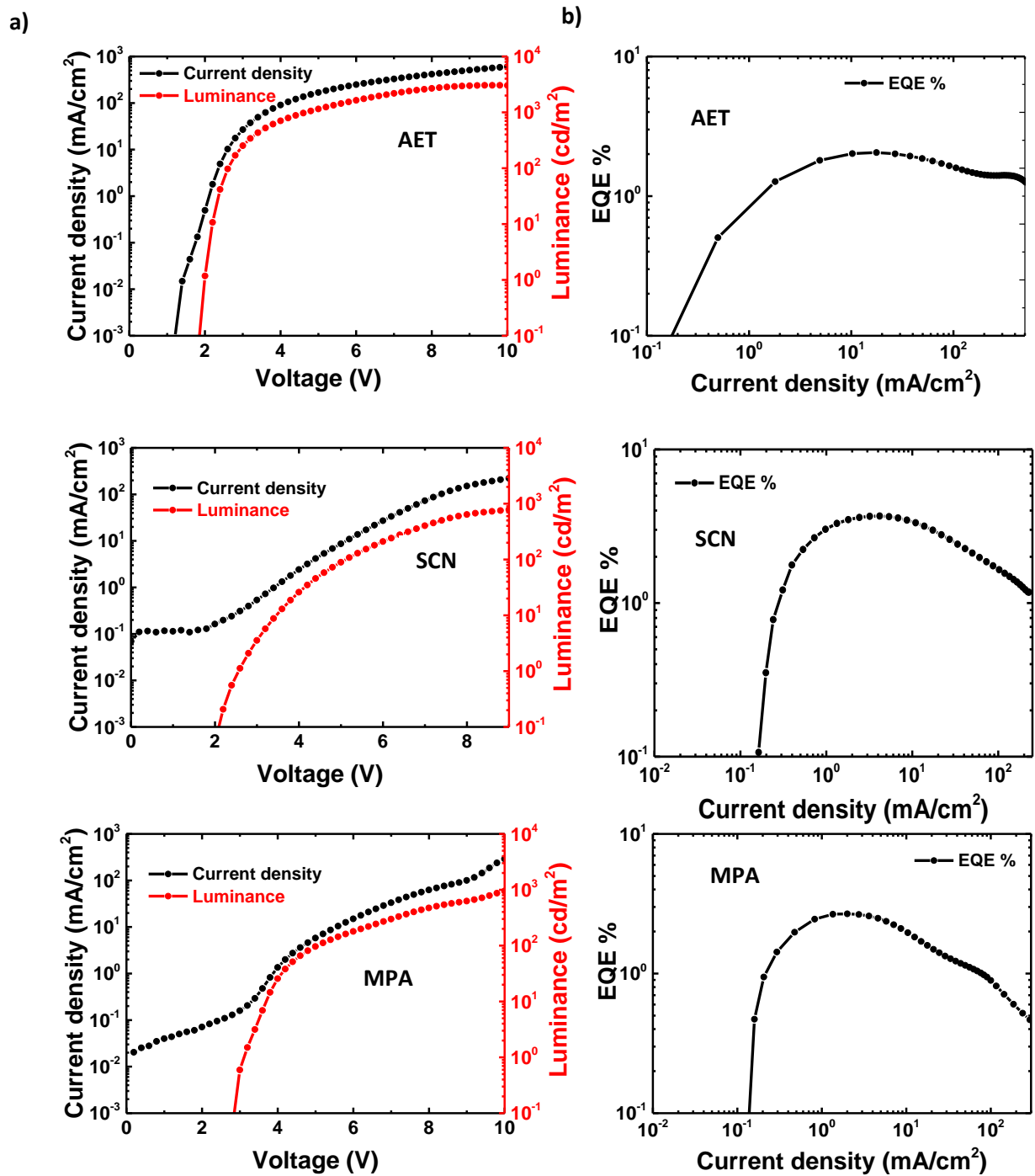


Figure 8 J-V-L and EQE characteristics of AET, SCN and MPA ligand-exchanged LEDs.

Table1: The performance of DiR LEDs with various ligands.

Ligands	PLQY %	Emission wavelength EL (nm)	Turn on voltage	Peak luminance	Peak EQE %
ODPA	48	640	1.9	2200	5.1
MPA	46	640	2.3	900	2.4
AET	38	640	1.9	3052	2.0
SCN	42	640	2.0	790	3.6

The ligand-exchanged AET, MPA and SCN DIRs performance is shown in figure 8. With AET ligand, the efficiency roll-off of completely vanished. It indicates that the charge transport in devices increases sufficiently after ligands. Therefore, an increment in charge density and the luminance is observed. The AET ligand exchanged LEDs shows 3052 cd/m² luminance which is higher than the ODPA capped LEDs, However, the other two ligands show a decreased luminance and EQE of the LEDs. This can be explain from the shift in energy levels of DIRs NCs after ligand exchanged. The shift in energy level can introduced different energy off set between HTL, ETL and DIRs which may reduce the charge injection in the active layer. In table 1, the parameter related to ligand-exchanged LEDs devices are presented.

4 Conclusion

The ODPA capped CdSe/CdS dot-in-rods LED has shown low turn on voltage, high efficiency and narrow EL spectra. We have applied the ligand exchanged on DIRs films by layer-by layer method. Think CdS shell preserve the PL quantum yield from ligand-exchange. Ligand-exchange on dot-in-rods LEDs reduced efficiency roll-off. AET ligand eliminates efficiency roll-off and enhanced the luminance. However, MPA and SCN ligands have shown low EQE which can correlate with LEDs structure. Since the LEDs was optimized for ODPA ligands.

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Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Materials Science and Technology

PH.D. CERTIFICATE
of
FEDERICO REMAGGI



Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisors

Prof. Daniele Marrè

Dott. Luca Pellegrino

Thesis Title

*Development of Innovative ultra low
magnetic fields detectors*

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department Physics, Federico Remaggi has orally presented his doctorate research work in front of the Commission, formed by

- Prof.ssa Elisabetta Finocchio, University of Genova
- Prof. Henrik Rudolph, Netherland Defense Academy
- Prof. Ruggero Vaglio, University of Napoli "Federico II"

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

**HAS APPROVED THE THESIS OF FEDERICO REMAGGI,
CONFERRING ON HIS THE TITLE OF**

**RESEARCH DOCTOR IN
MATERIALS SCIENCE AND TECHNOLOGY**

Genova, February 24th, 2017

**The Coordinator of the Doctorate Course
(Prof. Adriana Saccone)**



Università degli Studi di Genova



**Doctorate in
Sciences and Technologies of
Chemistry and Materials**

Curriculum: Scienza e Tecnologia dei Materiali

FEDERICO REMAGGI

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *December 31th, 2016*

Advisors

Prof. Daniele Marrè

Dr. Luca Pellegrino

Thesis Title: Development of innovative ultra low magnetic fields detectors

ACTIVITY REPORT

Research Activity

The research activity was mainly carried out at Department of Physics and SPIN-CNR Laboratory

Scientific Publications

1)

Communications at Conferences

Poster Communications:

1. F. Remaggi, N. Manca, L. Pellegrino, C. Bernini and D. Marrè, “**(La,Sr)MnO₃-based microelectromechanical systems as low magnetic field detector**”, ISOE 2016, Cargese, France
2. F. Remaggi, L. Pellegrino, N. Manca, V. Ceriale, C. Bernini and D. Marrè, “**Study of (La,Sr)MnO₃ thin film magnetic properties by Micro Electro Mechanical Systems**”, NMC2016, Delft, The Netherlands
3. F. Remaggi, L. Pellegrino, N. Manca, C. Bernini and D. Marrè “**Towards Micromechanical Sensors with (La,Sr)MnO₃ Epitaxial Films**”, EUROSENSOR 2016, Budapest, Hungary

Oral communications:

1. F. Remaggi, L. Pellegrino, N. Manca, V. Ceriale, C. Bernini and D. Marrè, “**(La,Sr)MnO₃-based microelectromechanical systems**”, SUPERFOX 2016, Turin, Italy

Congresses Attended

1. **“Dagli atomi al cervello”** - Politecnico di Milano, January 27th, 2014;
2. **“Superfox 2014”** (Conference on Superconductivity and Functional Oxides), Rome, September 24th - 26th, 2014;
3. **“Novel Materials and Devices for NEMS”**, INRiM Istituto Nazionale di Ricerca Metrologica, Turin, February 25th, 2015;
4. **“Euroensors 2016”**, Budapest, Hungary, September 4th-7th, 2016
5. **“Superfox 2016”**, Turin, September 19th-21st, 2016

Courseware

Attended:

- 1) Materiali Ceramici Funzionali
- 2) Materiali Magnetici Funzionali

Passed:

- 1) Acquisizione Dati e Controllo
- 2) Tecniche Microscopiche e Spettroscopiche

During his doctorate, FEDERICO REMAGGI has acquired 9 credits of Courseware.

Courses Given by invited experts

1. Dr. Camilla Coletti, Center for Nanotechnology Innovation @ NEST, Istituto Italiano di Tecnologia, Pisa: **“Graphene on SiC and Cu substrates: growth, properties and applications”**
2. Dr. Bagatin, Responsabile dell'Unità di Ricerca delle Tecnologie Ambientali dell'Istituto ENI: **“Tecnologie di monitoraggio e bonifica di acque e suoli”**
3. Dr. Ivan Curlik: **“Yb and Eu Strongly Correlated Electron Systems: from Experiment to Interpretation of Physical Properties”**
4. Prof. Ernst Bauer: **“Conventional and unconventional superconductivity: An overview”**
5. Prof. RNDr. Marian Reiffers, DrSc., FlnstP., Faculty of Humanities and Natural Sciences - Presov University (Presov, Slovakia): **“Physics in Extreme Conditions”**

National and International Schools or Workshops

1. **“NMC 2016”** (International Workshop on Nanomechanical Sensing), Delft, The Netherlands, June 22nd-24th, 2016

Seminars Given

- 1) F. Remaggi, **“Development of innovative ultra low magnetic field detector”**, CNR SPIN, Genoa, July

Seminars Attended

1. 11 Marzo 2014 Michele Laus, Università del Piemonte Orientale: **“Novel Solvent- Free Enabling Technology for Ultrafast Block-Copolymer Self-Assembly”**;
2. 27 Marzo 2014 Dr. Lara Benfatto, Università La Sapienza/CNR: **“What is new and interesting in the physics of pnictides? A hint from transport properties”**;
3. 09 Aprile 2014 Alexey Kavokin, Professor at the University of Southampton: **“Thermoelectric and thermomagnetic effects in solids: a unified approach”**;

4. 21 Novembre 2011 Vittorio Pizzella, Istituto di Tecnologie Avanzate Biomediche (ITAB), Università di Chieti: ***“Measures of Cerebral Connectivity by Means of Magnetoencephalography”***;
5. 26 Novembre 2014 Dr. Francesco Giazotto, NEST, Istituto Nanoscienze-CNR e Scuola Normale Superiore di Pisa: ***“Hybrid superconducting coherent caloritronics”***;
6. 13 gen 2015, Dott. Stefano Protti, Università di Pavia: ***“Photochemically generated phenyl cations as tunable and versatile intermediates”***;
7. 16 gen 2015, Paolo Solinas, CNR Spin: ***“A Josephson radiation comb generator”***;
8. 16 gen 2015, Luca Pellegrino, CNR Spin: ***“All-Oxide MEMS: review and perspectives”***;
9. 30 gen 2015, Alberto Martinelli, CNR Spin: ***“Iron based superconductors: phase diagram and phase transitions”***;
10. 30 gen 2015, Vittorio Foglietti, CNR Spin: ***“Transport properties of Barium Zirconate thin films: structural defects at interfaces and their effect on protonic conduction”***;
11. 13 feb 2015, Michele Piana, CNR Spin: ***“Compartmental analysis of positron emission tomography data”***;
12. 13 feb 2015, Federico Caglieris, CNR Spin: ***“Thermoelectric properties of Iron Based Superconductors”***;
13. 17 feb 2015 Prof. Robert Schennach, Institute of Solid State Physics, CD-Laboratory for Surface Chemical and Physical Fundamentals of Paper Strength Graz University of Technology (Austria): ***“The bond between paper fibers: a fresh look at an old material”***;
14. 27 feb 2015, Gianmarco Bovone, CNR Spin: ***“Synthesis of amorphous and nano structured boron for superconductive applications”***;
15. 27 feb 2015, Francesco Bisio, CNR Spin: ***“Graphene and plasmonics”***;
16. 27 mar 2015, Shrikant Kawale, CNR Spin: ***“Overview of Iron Chalcogenide superconducting thin films: Growth, properties and potentiality for Low Temperature-High Field applications”***;
17. 27 mar 2015, Takafumi Hatano, Nagoya University: ***“Electrostatic and electrochemical tuning of transport properties in oxide-based FETs”***;
18. 24 apr 2015, Andrea Gerbi, CNR Spin: ***“Scanning tunneling microscopy investigation of 11 iron-based superconductors and parent compounds: characterization of nanoscale inhomogeneities”***;
19. 24 apr 2015, Giacomo Dolcetto, CNR Spin: ***“Two-dimensional topological insulators: theory, experiments and applications”***;
20. 08 mag 2015, Alessandro Braggio, CNR Spin: ***“High frequency measurements of fractional excitations in FQHE and topological insulators”***;
21. 08 mag 2015, Alessandro Leveratto, CNR Spin: ***“Quantum Transport in ZnO/(Zn,Mg)O heterostructures”***;
22. 05 giu 2015, Riccardo Moroni, CNR Spin: ***“Growth and characterization of magneto-plasmonic nanostructures”***;
23. 03 lug 2015, Renato Buzio, CNR Spin: ***“Electron transport, resistance switching and nanoscale inhomogeneity at the Au/Nb:SrTiO₃ Schottky junction”***;
24. 03 lug 2015, Fabio Canepa, CNR Spin: ***“The intriguing world of magnetic nanoparticles”***;

Other Activities

- 1) Tutor Didattico per il corso di “Fisica Generale” c/o Ingegneria Biomedica, Università di Genova AA 2016/17
- 2) Dipartimento di Fisica (DIFI) “Formazione alla ricerca Scientifica – Stages PLS (Piano Nazionale Lauree Scientifiche)” con stage dal titolo “Studio di Materiali Superconduttori”, 2014, 2015, 2016



Università degli Studi di Genova
Doctorate in
Sciences and Technologies of
Chemistry and Materials
Curriculum: Pharmaceutical, Food and Cosmetic Sciences

PH.D. CERTIFICATE
of
SILVIA RUM



Doctorate Course

Pharmaceutical, Food and Cosmetic Sciences

Start of the Doctorate Program

January 1st, 2014

End of the Doctorate Program

December 31st, 2016

Advisor

Prof.ssa Carla Villa

Thesis Titles

Development of ecofriendly materials in sustainable delivery models for cosmetics and dermocosmetics applications

Defense Date

February 24th, 2017

On February 24th, 2017, at the Department of Pharmacy, Silvia Rum has orally presented her doctorate research work in front of the Commission, formed by

- Prof.ssa Olga Bruno, University of Genova
- Prof. Stefano Manfredini, University of Ferrara
- Prof.ssa Nunziatina De Tommasi, University of Salerno

The written Dissertation had been previously sent to the Commission members. After careful examination of the Dissertation, of the student's oral presentation, of the overall activity of the student during the three years of doctorate studies, the Commission

HAS APPROVED THE THESIS OF SILVIA RUM
CONFERRING ON HER THE TITLE OF

RESEARCH DOCTOR IN
PHARMACEUTICAL, FOOD AND COSMETIC SCIENCES

Genova, February 24th, 2017

The Coordinator of the Doctorate Course
Prof. Adriana Saccone



Università degli Studi di Genova
Doctorate Course in
Sciences and Technologies of
Chemistry and Materials

Curriculum:

SILVIA RUM

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program.....

Advisors

Prof. Villa Carla

Dott. Kirilov Plamen (Université Claude Bernard – Lyon1)

Thesis Title: Development of ecofriendly materials in sustainable delivery models for cosmetics and dermocosmetics applications.

First years

In pursuing our interest in eco-friendly and benign synthetic procedures, following the Green Chemistry principles, the aim of this research was the development of a mild synthetic process to obtain organogelators from natural renewable sources, using solvent-free techniques, under microwave activation as an alternative energetic source.

The coupling of microwave technology with solvent-free conditions in organic synthesis represents a new particularly efficient, powerful and attractive strategy. Significant improvements in yields or reaction conditions can be achieved, together with speed and considerable simplification of work-up and low environmental impact.

Taking into account all these statements, starting from sorbitol, in this work we have studied the solventless synthesis of some derivatives, such as 1,3:2,4-Dibenzylidene sorbitol (DBS) which are able to lead to the formation of gelling networks in the presence of an organic liquid medium, at very low concentrations.

A number of experiments were performed to evaluate the most efficient catalytic conditions. The best procedure was obtained using a simple heterogeneous mixture of reagents and *p*-toluenesulfonic acid (PTSA) as the catalyst, without any solvent or support. Sorbitol and the opportune benzaldehyde were mixed together in stoichiometric amounts with 10% PTSA and irradiated using two kinds of microwave ovens (Prolabo Synthewave mono-mode reactor and an assembled multipurpose multi-mode prototype) at 90-100°C for 5 minutes.

The purified products were tested to evaluate their potential gelling behavior by mixing them with several selected lipophilic vehicles and heated up to the organogelator fusion temperature.

The results showed very high yields (upper to 70 %) in 5 minutes at 100 °C without solvents, very interesting in rapport to the conventional synthesis.

Second year

My research during the second years of PhD was carried out at the Pharmacy department of Genoa University, the initially purpose of my works was the optimization of the DBS and derivatives reactions studied last years.

Taking into account all studies done, we wanted to improve the studies about the best promise products in terms of performance and eco-sustainability. Starting to the basic condensation reaction we have studied two different acid catalysts heterogeneous, normally used as ions exchange resin, for the optimization of reaction conditions. The results were compared with homogeneous ones to evaluate the efficiency in terms of yield, purity, simplicity of greenness procedure.

Starting to the sorbitol and three aromatic aldehydes of natural source (**a**- benzaldehyde, **d**-cuminaldehyde, **g**- cinnaminaldehyde) was developed a synthesis dry-media microwave assisted. This method has led to good yields by a simple reagent mixture in presence of a ions exchange resin in catalytic quantity. In order to highlight the advantages of microwave activation, MW reactions which led to the best results were performed at the same conditions but in a thermo-stated oil bath and results compared. An additional advantage is that the catalyst can be regenerated and can be used several times.

In formulation field, the organogels studied last years were dispersed in a water phase and its behavior was analyzed. In collaboration with University Claude Bernard of Lyon, were developed characterization studies of organogels to evaluate theirs properties, stability, potential applications. In particular the goals of this work will be the cinnamon derivatives for his properties as sunscreen, and potential application in sunscreen formulations. This work led to a research paper on scientific international journal :

Kirilov Plamen, Le Cong Anh Khanh, Denis Alice, Rabehi Halima, Rum Silvia, Carla Villa, et al. "Organogels for cosmetic and dermo-cosmetic applications" H&PC Today - Household and Personal Care Today Vol. 10(3) (part 1) e 10(4) (part 2) 2015

Always in formulation field, as prosecution of the studies related to the extraction solventfree of cosmetic ingredients from waste of the agrofood industry, were formulated different cosmetic and dermo-cosmetics preparations containing "essential waters" derived by the marc grape. Close to studies of rheological behavior and stability, with the acquisition of specific equipment's ,it was possible to set a procedure to evaluate the efficacy of the formulation through measures of skin hydration by the determination of the TEWL (transepidermal water loss) and skin elasticity.

The good results obtained, introduced as business idea in different local and national competitions, it have brought to the constitution of a Spin-off of the University (Accadermica) ,which I'm currently partner of capital and adviser.

This has allowed to submit a patent application, in which as inventor is recognized: Carla Villa, Chiara Lacapra, Silvia Rum, Raffaella Boggia

"Extract obtained by vegetal materials , the composition containing the extract and device for the production of the extract."

Third year

During the third year of my doctoral thesis my work was focused on various activities, firstly I achieve the optimization of the mass reaction of the first year for obtaining new organogelators molecules derived from a sugar derivative of sorbitol. In particular my aim was to obtain a heterogeneous supported catalyst, to evaluate the differences compared to heterogeneous catalysts. I evaluate the total environmental impact of all of reactions carried out during the three years of research, in order to choose the best reaction methodology and its better conditions, taking into account Green Chemistry principles thus taking into account all different conditions and factors that could influence the process.

To continue my work on organogelators molecules, I took care of the formulation of a basic hydrophilic gel that could incorporate the extract of marc obtained from my research group (on which our group has deposed a national patent), thanks to the collaboration with Accadermica Spin Off, which allow the realization of the formulation. This work led to the presentation of the results at an international conference, CosmInnov 2016 through a poster titled: "FROM GRAPE MARC EXTRACTS TO SKIN CARE FORMULATIONS: A Multidisciplinary SUSTAINABLE APPROACH" - Villa Carla, Chiara Lacapra, Silvia Rum, et al.

In the last months of my thesis I spent a period (from September to December 2016) in France, at the Laboratoire Green of the University of Avignon, where I had the possibility to know the other side of Green

Chemistry, in particular the alternative green solvents used for the extraction of natural products that can find a final application in the cosmetics fields.

The goals of this part of my project was the study of alternative green solvents in comparison to conventional solvents for the extraction of vegetable matrices. The study was divided into two parts, the first was developed through a computational study to predict the solubility of the plant matrix of our interest, assessing the composition by several references. During The second part, we performed the extraction of the vegetable matrix selected for our study (seeds of the Neem) with different solvents, and following we characterize the obtained extract in terms of chemical-physical properties (Neem oil). The choice to study Neem oil comes from its very interesting potential application in cosmetics field, and in particular regarding properties as moisturizer and emollient, its natural origin and the possibility to obtain these ingredients within the Green Chemistry principles. All these statement can be considered a real added value.

“Sviluppo di materiali ecocompatibili in sistemi di veicolazione sostenibili per applicazioni cosmetiche e dermocosmetiche”.

Primo anno

L'obiettivo del mio lavoro è stato lo sviluppo di un procedimento di sintesi per sostanze gelificanti utilizzando sorgenti rinnovabili, mediante tecniche solvent-free, attraverso l'attivazione microonde come fonte di energia alternativa, soddisfacendo il nostro interesse nelle sintesi eco-sostenibili, secondo i principi della Green Chemistry.

L'accoppiamento della tecnologia a microonde e di condizioni solvent-free nelle sintesi organiche rappresenta una strategia particolarmente efficace. Sono stati infatti riportati significativi miglioramenti nelle sintesi, in termini di tempo e resa, con procedimenti veloci e semplici con un impatto ambientale molto basso.

In questo lavoro, partendo dal sorbitolo, sono state studiate le sintesi senza l'utilizzo di solventi di alcuni derivati, come 1,3:2,4-sorbitolo dibenzilidene (DBS), i quali sono in grado di formare un networks di gelificazione in presenza di un veicolo lipofilo, a concentrazioni molto basse.

Diversi esperimenti sono stati eseguiti allo scopo di valutare le condizioni catalitiche più efficienti. La migliore procedura è stata ottenuta utilizzando una miscela eterogenea di reagenti e acido paratoluensolfonico (PTSA) come catalizzatore, senza l'utilizzo di solventi o supporti. Il sorbitolo e la benzaldeide opportuna sono stati miscelati in quantità stechiometriche con PTSA al 10% e irradiati mediante l'utilizzo di due diversi tipi di microonde (reattore Prolabo mono-modale e (Prototype multipurpose multimodale) ad una temperatura tra i 90 e i 100°C per 5 minuti. Infine il prodotto ottenuto è stato lavato con opportuno solvente organico ed essiccato in stufa.

I prodotti purificati sono stati testati in maniera da valutare il loro potenziale potere gelificante. Differenti quantitativi dei composti selezionati sono stati miscelati con un opportuno veicolo lipofilo organico e scaldati fino alla temperatura di fusione dell'organogelificante.

Secondo anno

La mia ricerca durante il secondo anno di Dottorato è stata svolta presso il Dipartimento di Farmacia dell'Università di Genova ed è stata in parte rivolta all'ottimizzazione delle reazioni senza solvente per la sintesi di organogelificanti, sviluppate nel corso dello scorso anno.

Tenendo conto dei risultati ottenuti abbiamo voluto ampliare e migliorare lo studio sui prodotti più promettenti in termini di performance e di ecosostenibilità.

Partendo dalla reazione solvent-free già sviluppata, abbiamo preso in considerazione due catalizzatori acidi eterogenei normalmente utilizzati come resine scambiatrici ottimizzando le condizioni di reazione. I risultati sono stati messi in paragone con un catalizzatore omogeneo per valutarne l'efficienza in termini di resa, purezza, semplificazione della procedura e greenness.

Partendo dal sorbitolo e da tre aldeidi aromatiche di origine naturale (a-benzaldeide, d-cuminaldeide, g-cinnamaldeide) è stata messa a punto una sintesi microonde mediata in dry media che ha permesso l'ottenimento con buone rese dei corrispondenti di-benziliden-derivati usando una semplice miscela di reagenti in presenza di quantità catalitiche di resina scambiatrice.

La reazione presenta diversi vantaggi rispetto alla sintesi convenzionale in bagno ad olio, in particolare per l'eliminazione dei solventi e la notevole riduzione dei tempi di reazione. Inoltre la procedura è snellita in termini di purificazione del prodotto e il catalizzatore può essere facilmente recuperato e riciclato.

Il lavoro è quindi proseguito in ambito formulativo, utilizzando principalmente gli organogel presi in considerazione lo scorso anno e studiando nuovi sistemi acquosi che potessero contenerli in forma dispersa.

In collaborazione con l'Università Claude Bernard di Lione, è in via di sviluppo la loro caratterizzazione al fine di valutarne proprietà, stabilità e applicazioni; in particolare oggetto di studio è il derivato dell'aldeide cinnamica, interessante per le sue proprietà filtranti UV, potenzialmente utilizzabile in prodotti per la protezione solare.

Parte di questa ricerca si è concretizzata con la pubblicazione di un lavoro su una rivista scientifica internazionale di settore:

Kirilov Plamen, Le Cong Anh Khanh, Denis Alice, Rabehi Halima, Rum Silvia, Carla Villa, et al. "Organogels for cosmetic and dermo-cosmetic applications" H&PC Today - Household and Personal Care Today Vol. 10(3) (part 1) e 10(4) (part 2) 2015

Sempre in ambito formulativo, come prosecuzione degli studi relativi all'estrazione senza solvente di ingredienti cosmetici da scarti dell'industria agroalimentare, sono state formulate diverse preparazioni cosmetiche e dermocosmetiche contenenti le "acque essenziali" ottenute dalla vinaccia. Accanto a studi di comportamento reologico e stabilità, con l'acquisizione di apparecchiature specifiche è stato possibile

mettere a punto una procedura per valutare l'efficacia dei prodotti formulati attraverso misure di idratazione tramite la determinazione della TEWL (transepidermal water loss) e di elasticità cutanea

I buoni risultati ottenuti, presentati come idea imprenditoriale in differenti competizioni locali e nazionali, hanno portato alla costituzione di uno Spin off dell'Università (Accadermica) di cui sono attualmente socio di capitale e consigliere.

Questo ha inoltre permesso di depositare una domanda di brevetto in cui sono riconosciuta come inventore:

Carla Villa, Chiara Lacapra, Silvia Rum, Raffaella Boggia

“Estratto ottenuto da materiale vegetale, composizione contenente detto estratto e dispositivo per la produzione del detto estratto”.

Terzo anno

Durante il terzo anno della mia tesi di dottorato ho seguito diverse attività, in primo piano l'ulteriore ottimizzazione della reazione messa a punto il primo per l'ottenimento di nuove molecole organogelificanti derivanti da un derivato zuccherino del sorbitolo. In particolare mi sono concentrata sull'ottenimento di un catalizzatore eterogeneo supportato, per valutare le differenze rispetto ai catalizzatori eterogenei classici. È stata poi effettuata una valutazione in generale dell'impatto ambientale delle reazioni condotte durante i tre anni di tesi, per scegliere la reazione e le condizioni di elezioni in termini nell'ambito delle Green Chemistry quindi prendendo in considerazione diversi fattori.

Per proseguire il mio studio sulle molecole organogelificanti, mi sono occupata della formulazione di un gel a base idrofila che potesse incorporare l'estratto della vinaccia ottenuto dal mio gruppo di ricerca (del suddetto estratto è stato anche depositato un brevetto nazionale), il tutto con la collaborazione dello Spin Off Accademica che ha permesso la realizzazione dello studio della formulazione. Lo studio si è concretizzato con la presentazione del lavoro ad un congresso internazionale di settore, CosmInnov 2016 dal titolo: “FROM GRAPE MARC EXTRACTS TO SKIN CARE FORMULATIONS: A MULTIDISCIPLINARY SUSTAINABLE APPROACH” - Carla Villa, Chiara Lacapra, Silvia Rum, et Al.

Negli ultimi mesi della tesi ho svolto un periodo presso l'Université d'Avignon –Francia (Settembre-Dicembre 2016) in cui ho seguito un progetto sulla Green extraction, per poter completare il mio percorso che si è subordinato nell'ambito della Green chemistry e poter quindi conoscere ulteriori applicazioni dell'estrazione verde, già da anni seguita dal mio laboratorio di ricerca. Lo scopo dello studio è stato lo studio di solventi alternativi green ai solventi convenzionali per l'estrazione di matrici vegetali. Lo studio si è articolato in due parti, la prima tramite lo studio computazionale della predizione della matrice vegetale scelta, valutandone la composizione dai vari riferimenti bibliografici e poi facendone una predizione di solubilità. La seconda la parte sperimentale di estrazione a partire dalla matrice vegetale scelta (semi del Neem) con i diversi solventi selezionati, e la successiva caratterizzazione chimico-fisica dell'estratto (olio di Neem). La scelta dello studio dell'olio del Neem deriva dalle sue forti proprietà nel campo della cosmesi viste le sue particolari proprietà come idratante e emolliente, inoltre la sua derivazione naturale e la

possibilità di ottenere l'ingrediente sempre all'interno dei principi della Green Chemistry risulta essere un valore aggiunto.

ACTIVITY REPORT

Research Activity

Scientific Publications

Original publications on ISI Journals:

1. Kirilov P¹, Rum S, Gilbert E, Roussel L, Salmon D, Abdayem R, Serre C, Villa C, Haftek M, Falson F, Pirot F Int J Cosmet Sci. Aqueous dispersions of organogel nanoparticles - potential systems for cosmetic and dermo-cosmetic applications. *Internantional Journal of Cosmetic Science* 36(4):336-46 (2014). doi: 10.1111/ics.12131.
2. KIRILOV PLAMEN, LE CONG ANH KHANH, DENIS ALICE, RABEHI HALIMA, RUM SILVIA, VILLA CARLA, HAFTEK MAREK, PIROT FABRICE "Organogels for cosmetic and dermo-cosmetic applications" *H&PC Today - Household and Personal Care Today Vol. 10(3) (part 1) e 10(4) (part 2) 2015*
3. Brevetto nazionale la cui domanda è stata depositata il 31/12/2015, con numero di assegnazione **102015000088909**: Carla Villa, Chiara Lacapra, Silvia Rum, Raffaella Boggia - "Estratto ottenuto da Materiale vegetale, composizione contenente Detto estratto e Dispositivo per la Produzione del Detto estratto".
4. S. Rum, C. Breil , N. Rakatomanamana, C. Villa, F. Chemat - "Bio-based solvents as an alternative to hexane for extraction of *Neem (Azadiractha indica A. Juss) seeds oil for potential cosmetic applications*". *Waiting for approval to Industrial Crops and Products*
5. Autrice di diversi articoli a scopo divulgativo sulla rivista nazionale di settore **Kosmetica**, con cadenza mensile, nel biennio 2015-2016 (edita da Tecniche Nuove).

Awards

- Primo Premio SMARTCup Liguria 2014, settore Agro-Food & Cleantech con il Progetto "ACADERMIC"; e diritto di partecipazione come finalisti al Premio Nazionale per l'Innovazione (Sassari 4-5 Dicembre 2014).
- Secondo Premio START CUP dell'Università degli Studi di Genova 2013 con il Progetto "ACADERMIC".
- Premio Speciale della Camera di Commercio di Genova per il Progetto "ACADERMIC" assegnato durante il concorso SMARTCup Liguria 2014.
- Start Up ACCADERMICA selezionata dal Vivaio delle Idee per EXPO 2015.

- Premio Start Up Panorama d'Italia al concorso "90 secondi per spiccare il volo".
- Premio Start Up Green al Posidonia Sustainable Friends Festival 2016.
- Lo Spin Off si è aggiudicato un finanziamento di 200.000 euro grazie alla valutazione positiva di un progetto POR FESR, AZIONE 1.1.3 (valorizzazione economica dell'innovazione)

Communications at Conferences

Poster Communications:

- 1) P. Kirilov, S. Rum, E. Gilbert, L. Roussel, D. Salmon, C. Serre, C. Villa, M. Haftek, F. Pirot, F. Falson - "Green" Gelled Nanoparticle Dispersions – Potential Systems for Sunscreen Applications - 9th World Meeting on Pharmaceutics, Biopharmaceutics and Pharmaceutical Technology (PBP 2014), Lisbon Portugal, Mar 31 - Apr 3, 2014.
- 2) Villa C., Rum S., Lacapra C.; "Ecofriendly microwave-mediated synthesis of organogelators from renewable sources for cosmetic and pharmaceutical applications"- GIFC (Giornate italo - francesi di Chimica), Torino, 5-6 Maggio 2014.
- 3) Villa C., Lacapra C., Rum S., Boggia R., Leonelli C., Rosa R.; "Green microwave extracts from waste matrices for cosmeceutical and nutraceutical applications" - Food Processing Innovation and Green Extraction Technologies: recent advances and applications in human health, Università della Magna Grecia, Catanzaro, 25-26 settembre 2014.
- 4) Villa C., Lacapra C., Rum S., Boggia R., Leonelli C., Rosa R., Bassi A. Danailova J.; "Multidisciplinary sustainable approach for the study of green extracts from waste matrices: solvent-free microwave extraction and in vitro assays as potential cosmeceutical and nutraceutical ingredients" – IFSCC (International Federation of Societies of Cosmetic Chemists), Paris, 27-30 Ottobre 2014.
- 5) J. Danailova, S. Vernazza, C. Scanarotti, M.A. Pronzato, C. Lacapra, S. Rum, C. Villa, et all. "Multidisciplinary approach to assess the biological potential of bioactive green extracts from exhaust organic matrices, obtained by microwave irradiation"- International Conference Of Alternatives to Animal Experimentation- Portugal, 8th, 9th May, 2015
- 6) Silvia RUM, Plamen KIRILOV, Carla VILLA:
"Microwave-mediated green synthesis of organogelators from renewable sources for cosmetic and pharmaceutical applications" - 15th International Conference on Microwave and High Frequency Heating - AMPERE 2015, Krakow, Poland, September 14-17, 2015
- 7) Oral communication: "Acadermic: Formulazioni Cosmetiche ecosostenibili da scarti dell'industria Agroalimentare" – Premio Luigi Carinelli 2015- Making Cosmetics- Milano, 24-25 Novembre 2015

- 8) Oral communication : “Solvent-free synthesis of sugar derivatives used as cosmetics ingredients for different dermatological applications” - Villa C., Rum S. - *8èmes Journées Franco-Italiennes de Chimie – Avignon 25-26 aprile 2016*
- 9) Carla Villa, Silvia Rum, Chiara Lacapra, Anna Maria Bassi, Bruno Burlando, Vincenzo Rialdi, Raffaella Boggia
“From grape marc extracts to skin care formulations: a multidisciplinary sustainable approach” – 4th *CosmInnov (Cosmetic Innovation Day) – Orleans 24-25 Maggio 2016*

Congresses Attended

- 1) Making Cosmetics (Milano 25/11/15)
- 2) GIFC (Torino 5-6/5 2014)
- 3) IFSCC (Paris 27-30/10 2014)
- 4) Making Cosmetics (Milano 24-24/11/2015)
- 5) JfiC (Avignone 25-26 Aprile 2016)
- 6) CosmInnov 2016 (Orléans 24-24 Maggio 2016)
- 7) Green extract of natural products (Torino 31 Maggio 2016)
- 8) 3^{ème} Journée Scientifique sur les Substances Naturelles (Avignone 6 Dicembre 2016)

Courseware

During his doctorate, Silvia Rum has acquired credits of Courseware.

Courses attended and passed (“11” credits): corsi di tipo B

Courses Given by Teachers of the Doctorate School in Sciences and Technologies of Chemistry and Materials

- 1) Biotecnologie Farmaceutiche (3 CFU), Docente: Prof. Mauro Mazzei (DIFAR)
- 2) Caratterizzazione di nanoparticelle per mezzo della microscopia a forza atomica e Dynamic Light Scattering (2 CFU), Docente: Prof. Ranieri Rolandi (DIFI)
- 3) Principali piante utilizzate in Fitocosmesi e loro costituenti (2 CFU), Docente: Prof. Angela Bisio (DIFAR)
- 4) Marker molecolari della qualità e della genuinità degli alimenti (2CFU), Docenti: R.Boggia, P. Zunin (DIFAR)
- 5) Ricerca bibliografica e brevettuale nelle scienze farmaceutiche tramite banche dati (2CFU). Docenti: P. Fossa, C. Brullo (DIFAR)

Courses Given by invited experts (corsi di tipo A):

1. Graphene on SiC and CU substrates: growth properties and applications (28 Marzo 2014- Coletti C.)
2. Solid state modifications: Principles and applications for drug solubilità enhancement (07 Novembre 2014- Gatti P.)
3. “New trends in computer aided drug design (9 Dicembre 2014- Truccinardi T.)”
4. “Yb and Eu Strongly Correlated Electron Systems: from Experiment to Interpretation of Physical Properties" (21-22 aprile 2015 - Dr. Ivan Curlik)

National and International Schools or Workshops

- 1) Skin Summer School 2014 – Quality requirement for raw materials and cosmetics products – Pavia (23-25 Giugno 2014)
- 2) Workshop: Profumo. Scienza e Arte (SICC-Milano- 19/02)
- 3) Workshop: Inspection of Cosmetics (25/6) – Pavia
- 4) Ampere 2015- Summer School in High Energy Processing Ultrasound & Microwave Technologies (Cracovia 9-12 Sett. 2015)

Seminars Given

- Il marketing cosmetico: dalla mission aziendale alla risposta del consumatore (18 Novembre 2016)

Seminars Attended

- 1) Filiera cosmetica, istituzioni di settore e regolamento cosmetici (Rialdi Vincenzo- 04/03)
- 2) Rapid thermal processing. A novel solvent free enabling technology for ultrafast black copolymer self assembly (Michele Laus- 11/03)
- 3) Sostenibilità nella filiera cosmetica (Rialdi Vincenzo- 18/03)
- 4) Good manufacturing practice (Rialdi Vincenzo- 25/03)
- 5) Blue light stress in photoreceptor and related structures (Prof Richard Funk-Dresda-08/07)
- 6) Seminario XXVII ciclo (in programma 28/11): Biocatalisi: applicazioni in sintesi farmaceutica
- 7) Seminario XXVII ciclo (in programma 28/11): Molecole naturali e Xenormesi
- 8) The bond between the paper fibers: a fresh look at an old material (Dott. Schennach - 17/2/15).

- 9) Recent cosmetics science and formulation technologie (Yamashtia - 3/3/15 CNR)
- 10) Hsp90 nella terapia antitumorale: dall'analisi conformazionale al disegno di nuovi inibitori allosterici. (Dott. Gerolamo Vettoretti – 25/4/15)
- 11) Natural products approximation for HTS compound libraries design (Giordanetto F. – 22/12/2015)
- 12) I nutraceutici: I farmaci per le persone sane (Novellino E. - 26/1/2016)
- 13) Electroceramic materials for energy applications. (Dr. Prabhakar Singh Professor – 21/6/2016)
- 14) Odori, profumi e feromoni come mediatori chimici olfattivi (Dr.ssa Chiara Lacapra – 18/11/2016)
- 15) Giocare sporco: PAINS e composti promiscui (Dr.ssa Anita Parricchi – 18/11/2016)
- 16) Tubercolosi ed altre patologie polmonari: stato dell'arte e recenti sviluppi terapeutici (Dr.ssa Elda Meta – 18/11/2016)
- 17) Evolution of microscopy on the PACA Avignon site: Context, installation of new devices, operation and accessibility within the framework of platform 3A . (Isabelle BORNARD, UR- Avignon – 21/11/2016)
- 18) Microfluidic and millifluidic droplets: new tool for the formulation of innovative particles, biomimesis and cell encapsulation. (Denis RENARD, UR BIA - Avignon 21/11/2016)
- 19) Spatial and reaction dynamics of microbial biofilms (Romain BRIANDET Micalis- Avignon 21/11/2016)
- 20) Microfluidic mapping of complex reactional landscapes. (Yannick RONDELEZ, ESPCI- Avignon 21/11/2016)

Other Activities

- 1) ACADERMIC: Spin-off tra l'università di Genova (DIFAR) e l'azienda Luxis con un duplice scopo:
 - Realizzazione di una linea cosmetica da vendersi nelle farmacie sul territorio nazionale contenente il prodotto della ricerca (estratti MW da scarti dell'industria agroalimentare).
 - Organizzazione di corsi di “formazione ” tenuti dal team del progetto (Lacapra Chiara e Rum Silvia - PhD SFAC XXIX ciclo; Villa Carla - Docente DIFAR; Antichi Davide - Cosmetologo/ formulatore; Bacigalupo Emiliano- Marketing e comunicazione) MARCELLA GUARRERA.
- Il progetto è risultato **vincitore della Smart-Cup Liguria** 2014 per la sezione Agro-Food-Cleantech ed ha ricevuto un riconoscimento dalla Camera di Commercio di Genova. Il 4-5 Dicembre è stato presentato a Sassari per concorrere al PNI 2014 (Premio Nazionale per l'Innovazione).

- Nel 2015 si è classificato al secondo posto della Start Cup 2013 II call dell'Università degli Studi di Genova
- Successivamente è stato selezionato per una presentazione orale al Vivaio delle idee organizzato da Italia Camp ad EXPO 2015.
- Selezionato al Premio Luigi Carinelli organizzato da SICC durante il Making Cosmetics 2015.
- Il progetto è stato inoltre presentato al “Posidonia Sustainable Green Festival 2016”.

2) Visita al Cosmoprof (Bologna -7 Aprile 2014).

3) **Settembre - Dicembre 2016:** svolgimento di un periodo di ricerca presso l'Université d'Avignon (Francia) presso il Laboratoire Green. Il tema della mia ricerca è stata l'estrazione di matrici vegetali con solventi alternativi verdi. Il lavoro si è articolato tra una parte pratica (sperimentale) e una teorica tramite l'utilizzo di due software innovativi (Hansen Solubility Parameters and COSMO-RS) per la simulazione della solubilità dei componenti della matrice vegetale selezionata.



Università degli Studi di Genova
Doctorate School in
Sciences and Technologies of
Chemistry and Materials



Curriculum: Nanochemistry

Renyong Tu

Start of the Doctorate Program: January 1st, 2014

End of the Doctorate Program: December 31st, 2016

Advisors:

Prof. Maurizio Ferretti, Prof. Liberato Manna, Dr. Luca De Trizio

Thesis Title: Synthesis of Copper Telluride Nanostructures and Cation Exchange Reactions in Cu_{2-x}Te Nanocubes

Thesis abstract: Over the last decade, Cu-based nanocrystals such as copper chalcogenides have received intensive attention due to their localized surface plasmon resonance (LSPR) and numerous copper chalcogenide nanocrystals with well-defined composition, shape, and uniform size have been developed. Among these copper chalcogenides, most of reports are focusing on copper sulfides and copper selenides. Therefore, exploring and developing the procedures to obtain various morphologies of Cu_{2-x}Te nanocrystals will be extremely valuable, not only for their LSPR applications, but also for cation exchange (CE) reactions to achieve nanomaterials with unprecedented structural and novel properties. At the same time, CE reactions at the nanoscale, which replace host cations within the relatively rigid anion host lattice by other cations (i.e. guest cations) while tend to reserve the initial anion sub-lattice, have become one of most powerful post-synthetic strategies for novel metastable crystalline phases, monodisperse III–V nanocrystals, complex heterostructure, homogenous alloys and various doped materials.

Here, we start from the influence of solvents and ligands on controlling the phases and morphologies of copper telluride nanostructures. By using different solvents and surfactant ligands, together with different experimental parameters, we successfully obtained copper telluride nanostructures with different phases and morphologies, including pseudo-cubic nanocubes, nanowires, nanoplates, nanosheets, and tetragonal nanorods and nanosheets. Afterward, Cu_{2-x}Te nanocubes were chosen as a template for synthesis of other nanostructured materials based on CE reactions. We found that the coordination number of the guest cations play a key role in our CE processes. Specifically, Sn^{2+} or Pb^{2+} ions adopt an octahedral coordination (coordination number is 6 or $\text{CN} = 6$), resulting in the formation of a polycrystalline cubic SnTe or PbTe shell around the parent Cu_{2-x}Te NCs at the early stage and then proceeding further to the total replacement of Cu^+ ions and the formation of polycrystalline cubic SnTe or PbTe NCs to end. On the other hand, Cd^{2+} and Hg^{2+} ions adopt a tetrahedral coordination (coordination number is 4 or $\text{CN} = 4$), leading to the

formation of Janus-like particles with sharp epitaxial CdTe/Cu_{2-x}Te and HgTe/Cu_{2-x}T interfaces in partial CE reactions and monocrystalline hexagonal CdTe and HgTe NCs in total CE reactions.

ACTIVITY REPORT

Research Activity

The research activity was carried out at the IIT

Scientific Publications

Original publications on ISI Journals:

- 1) Xie, Y.; Bertoni, G.; Riedinger, A.; Sathya, A.; Prato, M.; Marras, S.; **Tu, R.**; Pellegrino, T.; Manna, L. *Chem. Mater.* **2015**, *27*, 7531-7537.
- 2) Rieginger, A.; Avellini, T.; Curcio, A.; Asti, M.; Xie, Y.; **Tu, R.**; Marras, S.; Lorezoni, A.; Rubagotti, S.; Iori, M.; Capponi, P. C.; Versari, A.; Manna, L.; Seregini, E.; Pellegrino, T. *Journal of the American Chemical Society*, 15145-15151.
- 3) **Tu, R.**; Xie, Y.; Bertoni, G.; Lak, A.; Gaspari, R.; Rapallo, A.; Cavalli, A.; De Trizio, L.; Manna, L. *J. Am. Chem. Soc.* **2016**, *138*, 7082-7090.

Courseware

During his doctorate, Renyong Tu has acquired 13 credits of Courseware.

Courses attended and passed (11 credits)

B type Courses given by Teachers of IIT (11 credits)

- 1) Basics concepts in Nanochemistry, by Liberato Manna (1 credits)
- 2) Nanomaterials and Nanocomposites, by Luca De Trizio & Milena Arciniegas, (1 credits)
- 3) Opto-Electronic Properties of Semiconductor Quantum Dots, by Iwan Moreels, (1 credits)
- 4) X-rays based Characterization Techniques, by Mirko Prato, (1 credits)
- 5) Characterization Techniques 2, by Alessandro Genovese & Rosaria Brescia, (1 credits)
- 6) Characterization Techniques 3, by Dr. Krahne R. and Dr. Casu A. (1 credits)
- 7) Energy related applications, by Dr. Colombo M., Monaco S. and Dr. Zhang Y. (1 credit)
- 8) Energy related applications 2, by Dr. Manna L, and Dr. Casu A. (1 credit)
- 9) Electronic properties of solids, By Liberato Manna (3 credits)

Courses Given by invited experts: (2 credits)

- 1) "Green Analytical Chemistry", Prof. Estrella Espada Bellio, Facultad de Ciencias / Faculty of Science Universidad de Cádiz, Spain (26th -27th May 2015, DCCI, Università di Genova) – 1 credit.
- 2) "Medicinal chemistry with carbohydrates: the influenza virus and the discovery of sialidase inhibitors", Prof. ssa Anna Bernardi, Università di Milano (13th November 2015, DCCI, Università di Genova) – 1 credit.

National and International Schools or Workshops (3 credits)

- 1) Summerschool Utrecht: nanomaterials: science and applications. 15-26 August 2016, Utrecht, Netherland.

Seminars Given (4 credits)

- 1) Study of Cation Exchange Reactions in Cu_{2-x}Te Nanocubes. 4th, December 2015, IIT.
- 2) Synthesis and shape control copper tellurides and mechanism study of cation exchange reactions in Cu_{2-x}Te nanocubes. 6th, December 2016, IIT.

Seminars Attended (2 credits)

- 1) Electrochemical Control over Charge Transfer and Trapping in CdSe-CdTe QD Solids. By Prof. Arjan J. Houtepen, March 3rd, 2014.
- 2) Nanomaterials as Highly Active Catalyst for Multiple Significant Reactions. By Prof. Sasanka Deka, June 25th, 2014
- 3) Optics of CdSe/CdS nanocrystals: a theoretical overview. By Dr. Iwan Moreels, December 5th, 2014.

- 4) Designing organometallics for material science: application for solar cells and scintillators. By Dr. Guillaume Bertrand, January 19th, 2015.
- 5) Design, fabrication and Characterization of plasmonic structures for grapheme-based devices and superresolution. By Dr. Valeria Lotito, January 19th, 2015.
- 6) Semiconductor Nanocrystals: Discovery, Milestones, and Recent Theoretical Developments. By Prof. Alexander L. Efros, November 20th, 2015.
- 7) Insight in the chemistry of metal sulfide nanocrystals and their application in photovoltaics. By Dr. Peter Reiss, November 25th, 2015.
- 8) Materials for therapy: Cerium oxide nanoparticles as novel antioxidant drugs. By Prof. Enrico Traversa, February 2nd, 2016.
- 9) Recent advances with FIB-milled microcavities. By Lucas Flatten, January 19th, 2016.
- 10) Materials for therapy: Cerium oxide nanoparticles as novel antioxidant drugs. By Enrico Traversa, February 4th, 2016.
- 11) Perovskites: an old material for the third generation of PV solar panels: By Dr. Laura Miranda Perez. April 21st 2016.
- 12) Hydration induced spin glass state in a frustrated Na-Mn-O triangular lattice. By Dr. Ioanna Bakaimi. April 28th, 2016.
- 13) Spatio-temporal visualization of atomic motions in low-dimensional materials. By Dr. Giovanni Maria VANACORE. May 3rd, 2016.
- 14) The Power of intermolecular interactions in organic semiconductors: from threaded molecular wires to PCBM single crystals. By Prof. Franco Cacialli. May 5th, 2016.
- 15) First-principles predictions of substrate effects on silicone. By Prof. Udo Schwingenschloegl. May 9th, 2016.
- 16) Nano-photonics phenomena in van der Waals heterostructures. By Prof. Dmitri N. Basov. June 8th, 2016.
- 17) From chemical complexity to functional complexity: tailoring multifunctional low dimensional materials and devices. By Prof. Paolo Samori. November 14th, 2016.
- 18) Visualizing and controlling optoelectronic processes in lead halide perovskites. By Dr. Alexander Weber-Bargioni. November 14th, 2016.
- 19) PhD presentations, by PhD students of Chemistry and Materials-XXIX cycle, December 12th, 2016.



Università degli Studi di Genova



**Doctorate in
Sciences and Technologies of
Chemistry and Materials**

CURRICULUM NANOCHEMISTRY

Carmine Urso

Start of the Doctorate Program *January 1st, 2014*

End of the Doctorate Program *December 31th, 2016*

Advisors *Prof. Manna L., Prof. Saccone A., Dr. De Trizio L.*

Thesis Title: *Nanocrystals for energy conversion and storage applications*

ACTIVITY REPORT
Research Activity

Scientific Publications

- 1) Kriegel I., Urso C., Viola D., De Trizio L., Scotognella F., Cerullo G. and Manna L., *Ultrafast Photodoping and Plasmon Dynamics in Fluorine–Indium Codoped Cadmium Oxide Nanocrystals for All-Optical Signal Manipulation at Optical Communication Wavelengths*, J. Phys. Chem. Lett., (2016), 7, 3873.
- 2) Carmine Urso, Mariam Barawi, Roberto Gaspari, Gianluca Sirigu, Ilka Kriegel, Margherita Zavelani-Rossi, Francesco Scotognella, Michele Manca, Mirko Prato, Luca De Trizio and Liberato Manna, *Colloidal Synthesis of Bipolar Off-Stoichiometric Gallium Iron Oxide Spinel-Type Nanocrystals with Near-IR Plasmon Resonance*, submitted

Communications at Conferences

Poster Communications:

Colloidal synthesis of transparent A₂BO₄ spinel-type plasmonic nanocrystals, NanaX7 4-8 April 2016 Marburg (Germany)

Colloidal Synthesis of Plasmonic Bipolar Ga₂FeO₄ Spinel-type Nanocrystals, accepted for Materials.it 12-16 December 2016 Aci Castello (Italy)

Congresses Attended

- 1) “7th International Symposium on Flexible Organic Electronics, ISFOE14”, 7-10 July 2014 Thessaloniki (Greece)

- 2) "11th International Conference on Nanoscience & Nanotechnologies, NN14", 8-11 July 2014 Thessaloniki (Greece)
- 3) "Nanoscience with Nanocrystals, NanaX7", 4-8 April 2016 Marburg (Germany)
- 4) I will attend "Italian National Conference on Materials Science and Technology, Materials.it", 12-16 December 2016 Aci Castello (Italy)

Courseware

- 1) "Basic concepts in Nanochemistry", Prof. Manna L. (1 credit)
- 2) "Nanomaterials and Nanocomposites: Processing and characterization", Dr. De Trizio L. and Dr. Arciniegas M. (1 credit)
- 3) "Opto-Electronic Properties of Semiconductor Quantum Dots", Dr. Moreels I. (1 credit)
- 4) "X-rays based Characterization Techniques", Dr. Prato M. (1 credit)
- 5) "Characterization techniques 2", Dr. Genovese A. and Dr. Brescia R. (1 credit)
- 6) "Characterization techniques 3", Dr. Krahn R. and Dr. Casu A. (1 credit)
- 7) "Energy related applications", Dr. Colombo M., Dr. Monaco S. and Dr. Zhang Y. (1 credit)
- 8) "Energy related applications 2", Dr. Manna L. and Dr. Casu A. (1 credit)
- 9) "Synaptic basis of brain pathology", Dr. Fassio A. and Dr. Baldelli P. (2 credit)

During his doctorate, Carmine Urso has acquired 10 credits of Courseware.

Courses Given by invited experts

- 1) "Tecniche di monitoraggio e bonifica di acque e suoli", Dr. Bagatin, (1 credit)
- 2) "X-ray based experimental techniques and characterization of nano-materials", Dr Morgante (1 credit)

During his doctorate, Carmine Urso has acquired 2 credits of Courses given by invited experts.

National and International Schools or Workshops

- 1) "8th International Summer Schools on Nanoscience & Nanotechnologies, Organic Electronics & Nanomedicine, ISSON14", 5-12 July 2014 Thessaloniki (Greece)

Seminars Given

- 1) "Ga₂FeO₄ nanocrystals", 27 November 2015 at IIT, 2 credit
- 2) "Nanocrystals for energy conversion and storage applications", 06 December 2016 at IIT, 2 credits

During his doctorate, Carmine Urso has acquired 4 credits of seminars given.

Seminars Attended

1. "Unravelling animal biology by functional nanoparticles", Dr. Tortiglione C., 19 February 2014 at IIT, 0.125 credit
2. "Electrochemical control over charge transfer and trapping in CdSe-CdTe QD Solids", Dr. Houtepen A., 03 March 2014 at IIT, 0.125 credit
3. "Quantum Geochemistry: simulating physico-chemical properties of materials in the deep Earth", Dr. Belmonte D., 31 March 2014 at IIT, 0.125 credit

4. "Neutron scattering for materials research in the field of nitrogen storage for vehicular applications", Dr. Sartori S., 05 May 2014 at IIT, 0.125 credit
5. "Colloidal nanoparticles- shape and composition control", Dr. Dorfs D., 25 June 2014 at IIT, 0.125 credit
6. "Organization of colloidal nanoparticle building blocks into functional superstructures", Dr. Bigall N. C., 25 June 2014 at IIT, 0.125 credit
7. "Synthesis of metal-oxide and metal-oxide based hybrid nanostructures", Dr. Mokari T., 24 September 2014 at IIT, 0.125 credit
8. "Magneto-optical spectroscopy of individual semiconductor nanocrystal", Dr. Sinito C., 25 September 2014 at IIT, 0.125 credit
9. "Colloidal nanocrystal and their functional architectures", Dr. Gaponik N., 29 September 2014 at IIT, 0.125 credit
10. "Organic Bio-Electronic devices for sensing applications", Dr. Torsi L., 10 November 2014 at IIT, 0.125 credit
11. "Plasmonic heavily doped semiconductor nanocrystals: from fundamentals to their nanoscale application", Dr. Kriegel I., 26 November 2014 at IIT, 0.125 credit
12. "Optics of CdSe/CdS nanocrystals: a theoretical overview", Dr. Climente Plasencia J. I., 5 December 2014 at IIT, 0.125 credit
13. "Semiconductor nanocrystals laser structures", Dr. Di Stasio F., 16 December at IIT
14. "Field-Effect Transistors and solar cells made of individual colloidal PbS nanosheets", Dr. Dogan S., 08 January 2015 at IIT, 0.125 credit
15. "Design, fabrication and characterization of plasmonic structures for graphene-based devices and superresolution", Dr. Lotito V., 19 January 2015 at IIT, 0.125 credit
16. "Designing organometallics for material science: application for solar cells and scintillators", Dr. Bertrand G., 19 January 2015 at IIT, 0.125 credit
17. "Chemical Identification at the Nanoscale 100nm IR Spectroscopy, where IR spectroscopy meets AFM", Dr. S. Pergolini, 29 January 2015 at IIT, 0.125 credit
18. "Colloidal Quantum dot Optoelectronics: Photodetectors and Solar Cells", Dr. G. Konstantatos, 30 January 2015 at IIT, 0.125 credit
19. "Materials for sodium batteries", Dr. S. Passerini, 16 February 2015 at IIT, 0.125 credit
20. "High Energy Lithium-Ion and Lithium-Sulfur Batteries", Dr. Marco Agostini, 20 February 2015 at IIT, 0.125 credit
21. "Using colloidal quantum dots to boost photovoltaic cell performance", Dr. Miri Kazes, 25 February 2015 at IIT, 0.125 credit
22. "Semiconductor Nanocrystals: Discovery, Milestones, and Recent Theoretical Developments", Dr. Efros, 20 November 2015 at IIT, 0.125 credit
23. "Insight in the chemistry of metal sulphide nanocrystals and their application in photovoltaics", Dr. Peter Reiss, 25 November 2015 at IIT, 0.125 credit
24. "Spatio-temporal visualization of atomic motions in low-dimensional materials", Dr. Giovanni Maria Vanacore, 3 May 2016 at IIT, 0.125 credit
25. "First principles predictions of substrate effects on silicone", Prof. Udo Schwingenschloegl, 09 May 2016 at IIT, 0.125 credit

During his doctorate, Carmine Urso has acquired 2 credits of seminars attended.



Università degli Studi di Genova
Doctorate School in
Sciences and Technologies of
Chemistry and Materials



Curriculum: Nanochemistry

Chunzheng_Wu

Start of the Doctorate Program January 1st, 2014

End of the Doctorate Program 31/12/2016

Advisors

Dr. Massimo Colombo (IIT), Prof. Liberato Manna (IIT), Prof. Antonio Comite (DCCI)

Thesis Title

Nanocatalysts designed by in-situ galvanic replacement reactions

Thesis abstract

Galvanic replacement reactions become increasingly attractive in design and preparation of nanocatalysts. These reactions are driven by the different reduction potentials of two metal elements. By precisely controlling the degree of the replacement, nanoparticles with various morphology/porosity and controllable compositions could be obtained. The change of morphology and composition mainly have two effects on their catalytic performance. Firstly, the formation of holes and pores result in larger surface area, exposing more active sites to the reacting environment. Secondly, the presence of two components might result in a synergetic effect between them. Usually this kind of effect can influence the activity, selectivity, or stability of the catalysts. Until now, most of the researches were focused on the galvanic replacement between two metals or between one metal and one metal oxide, while the replacement between two metal oxides and their related synergetic effect on catalysis has not been studied. Besides, the present galvanic replacements are performed in colloidal solutions, which have a lot of drawbacks (like poor reproducibility...) and can only be applied to the catalysts prepared via colloidal deposition methods.

In this work, an in-situ galvanic replacement process was developed. Instead of doing the replacement in colloidal solutions, I performed a galvanic replacement selectively on oxide NPs supported on various substrates, and the effects of working conditions were studied systematically. Then, this method was applied to prepare $Mn_xM_yO_4$ based and $Au-Mn_xM_yO_4/SiO_2$ based catalysts ($M = Fe$ or Ce). The application of $Mn_xM_yO_4$ based catalysts in CO oxidation, NO oxidation, and Fisher-Tropsch synthesis and the application of $Au-Mn_xM_yO_4/SiO_2$ in CO oxidation reaction is studied.

ACTIVITY REPORT

Research Activity

The research activity was mainly carried out at the IIT

Please indicate here if you have spent research periods in foreign countries.

Scientific Publications

Original publications on ISI Journals:

- 1) Chunzheng Wu, Rosaria Brescia, Mirko Prato, Sergio Marras, Liberato Manna and Massimo Colombo*. Tuning the CO oxidation catalytic activity of supported metal-metal oxide heterostructures by an aqueous phase post-treatment process, J. Mater. Chem. A, 2016, 4, 18075-18083.

Communications at Conferences

Poster Communications:

- 1) "Preparation of Au-Mn_{3-x}Fe_xO₄/SiO₂ nanocatalysts through an in-situ post-treatment strategy", Designing New Heterogeneous Catalysts: Faraday Discussion (2016.04.04-06).
- 2) "A Fe-doping effect on Au/SiO₂ catalysts for the CO oxidation reaction", The 16th International Congress on Catalysis (2016.07.03-08).

Congresses Attended

1. 2014.07.06-10, Louvain-la-Neuve (Belgium), The 11th International Symposium on the "Scientific Bases for the Preparation of Heterogeneous Catalysts"
2. 2016.04.04-06, London (UK), Designing New Heterogeneous Catalysts: Faraday Discussion.
3. 2016.07.03-08, Beijing (China), The 16th International Congress on Catalysis.

Courseware

During his doctorate, Chunzheng Wu has acquired 20 credits of Courseware.

Courses attended and passed (11 credits)

Courses Given by Teachers of the Nanochemistry Department, IIT:

1. Liberato Manna, "Crystallographic fundamental" (1 credit)
2. Milena Arciniegas and Luca De Trizio, "Nanomaterials and Nanocomposites: Processing and characterization" (1 credit)
3. Iwan Moreels, "Opto-Electronic Properties of Semiconductor Quantum Dots" (1 credit)
4. Mirko Prato, "Characterization techniques 1: X-rays based Characterization Techniques" (1 credit)
5. Alessandro Genovese and Rosaria Brescia, "Characterization techniques 2" (1 credit)
6. Roman Krahne, "Characterization techniques 3" (1 credit)
7. Massimo Colombo, Simone Monaco and Yang Zhang, "Energy related applications" (1 credit)
8. Liberato Manna, "Quantum chemistry" (1 credit)
9. Liberato Manna, "Electronic properties of solids" (3 credits)

Courses Given by invited experts: (2 credits)

- 1) 2015.05.26-27, Prof. Estrella Espada Bellido, "Green Analytical Chemistry" (1 credit)
- 2) 2015.11.09-11, Prof. Ernst BAUER, "Conventional and Unconventional Superconductivity: An overview" (1 credit)

National and International Schools or Workshops (1 credit)

- 1) 2015.07.06-10, Lyon (France), "ECOLE DE CATALYSE ELITECAT 2015"

Seminars Given (4 credits)

- 1) 2014.02.24, "A Research on Metal@Mesoporous-SiO₂ Core-Shell Nanocatalysts" (2 credit)
- 2) 2015.10.29, "Nanocatalysts designed by galvanic replacement" (2 credit)

Seminars Attended (2 credits)

- 1) 2014.03.31, Dr. Donato Belmonte, "Quantum geochemistry: simulating physic-chemical properties of materials in the deep earth"
- 2) 2014.05.05, Prof. Sabrina Sartori, "Neutrons scattering for materials research in the field of hydrogen storage for vehicular applications"
- 3) 2014.06.25, Prof. Sasanka Deka, "Nanomaterials as highly active catalyst for multiple significant reactions"
- 4) 2014.09.24, Prof. Taleb Mokari, "Synthesis of metal-oxide and metal-oxide based hybrid nanostructures"
- 5) 2014.09.25, Dr. Chiara Sinito, "Magneto-optical spectroscopy of individual semiconductor nanocrystals"
- 6) 2015.01.19, Dr. Valeria Lotito, "Design, fabrication and characterization of plasmonic structures for graphene-based devices and superresolution"
- 7) 2015.02.20, Dr. Marco Agostini, "High Energy Lithium-ion and Lithium-Sulfur Batteries"
- 8) 2015.03.04, Axel Freytag, "Versatile Fabrication of Highly Porous Cryogels from Noble Metal Nanoparticles"
- 9) 2015.03.18, Dr. Massimo Colombo, "Structure-activity relationship in CO oxidation over bimetallic AuCu Nanocrystals: the role of nanocrystals size, composition and support interaction"
- 10) 2015.11.09, Dr. Arnauld, "Control of surface chemistry of nano diamonds for bio-applications"

- 11) 2015.11.20, Prof. Alexander L. Efros, "Semiconductor Nanocrystals: Discovery, Milestones, and Recent Theoretical Developments"
- 12) 2015.11.25, Dr. Peter Reiss, "Insight in the chemistry of metal sulphide nanocrystals and their application in photovoltaics"
- 13) 2016.12.11, Veronica Salgueirino, "Synthesis and Chemical Manipulation of Nanoparticles for a Magnetic Improvement"
- 14) 2016.02.04, Prof. Enrico Traversa, "Materials for therapy: Cerium oxide nanoparticles as novel antioxidant drugs"
- 15) 2016.04.21, Dr. Laura Miranda Perez, "Perovskites: an old material for the third generation of PV solar panels"
- 16) 2016.04.28, Antonios G.Kanaras, "Colloidal nanoparticles and applications"
- 17) 2016.05.03, Dr. Giovanni Maria Vanacore, "Spatio-temporal visualization of atomic motions in low-dimensional materials"
- 18) 2016.11.14, Prof. Paolo Samori, "From chemical complexity to functional complexity: tailoring multifunctional low dimensional materials and devices"