



## Program and Book of Abstract of the 1<sup>st</sup> workshop



18 December 2023, 15:00 and 19 December 2023 9:00

Presentations from all the PhD students involved  
in the 4 different Curricula

Homogeneous **Catalysis**: Mechanisms and Applications

Heterogeneous **Catalysis**: Synthesis, Characterization and Applications

Bio**Catalysis**

Novel Technologies for **Catalysis**

Program Coordinator: Prof. Luigi Vaccaro

*University of Perugia, Italy*

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<http://www.dccb.unipg.it/catalisi>



*1st Workshop of the Italian PhD Program in Catalysis  
Perugia, 18<sup>th</sup> December 2023*

*Palazzo dei Priori, Sala dei Notari*

14:40 -15:00 Registration

15:00 Welcome greetings – **Magnifico Rettore Prof. Maurizio Oliviero, Delegata alla didattica Prof.ssa Carla Emiliani,**  
Presentation of the Teaching Board – *Luigi Vaccaro*

*Homogeneous Catalysis  
Chair: Luigi Vaccaro (UNIPG/DCBB)*

15:35 – 15:45 OP1 **Astone Armando** (UNISA)  
*Title: Organocatalytic asymmetric synthesis of epoxides bearing quaternary stereocenters*

15:45 – 15:55 OP2 **Barilli Matteo** (UNIPV)  
*Title: Upcycling of NdFeB SmCo magnets. From e-waste to high-value products. Green&Digital Transition*

15:55 – 16:05 OP3 **Iapadre Debora** (UNIVAQ)  
*Title: Sustainable methodologies via organo-, photo and supramolecular catalysis*

16:05 – 16:15 OP4 **Mancini Jacopo** (UNI Tor Vergata)  
*Title: Catalytic C(sp<sup>3</sup>)-H bond hydroxylations promoted by dioxiranes*

16:15 – 16:25 OP5 **Mannoni Giulia** (UNIUD)  
*Title: Development of highly efficient ruthenium catalysts for sustainable hydrogenation reactions*

16:25 – 16:35 OP6 **Rubello Giovanni** (UNIPD)  
*Title: Gold-based cooperative catalytic systems for the valorization of phenols derived from biomasses*

16:35 – 16:45 OP7 **Tropiano Sofia** (UNICAL)  
*Title: Study of new catalytic processes for the conversion of CO and CO<sub>2</sub> into high value added products*

16:45 – 16:55 OP8 **Zurzolo Simone** (UNISI)  
*Title: Industrial and agricultural solid waste for sustainable catalytic processes*

16:55 – 17:30 *Coffee Break*

*Heterogeneous Catalysis*  
Chair: Barbara Bonelli (POLITO)

- 17:30 – 17:40 OP9 **Catalini Francesco** (UNICAM)  
*Title: The role of catalysis for the development of hybrid filter matrices for sustainable organic transformations*
- 17:40 – 17:50 OP10 **Ferraro Giorgia** (UNIVE)  
*Title: Study and characterization of catalytic systems and their recovery/regeneration*
- 17:50 – 18:00 OP11 **Itri Giulia Maria** (UNIRC)  
*Title: PHOTOWASTE – Synthesis of a new heterogenous photocatalyst for the photoreforming of aqueous solutions of biomass residues*
- 18:00 – 18:10 OP12 **La Greca Eleonora** (UNICT)  
*Title: Catalytic, photocatalytic and photothermo-catalytic reforming reactions for the H<sub>2</sub> production and the subsequent CO<sub>2</sub> valorization*
- 18:10 – 18:20 OP13 **Plavi Federica** (UNIPV)  
*Title: Development and Radiobiology of New Boron Entities*
- 18:20 – 18:30 OP14 **Sang Tian** (UNIPG/DCBB)  
*Title: Synthesis of heterocycles via sustainable heterogeneous C(sp<sup>3</sup>)-H functionalization processes*
- 18:30 – 18:40 OP15 **Trovarelli Letizia** (UNITO/UNIPG/DCBB)  
*Title: Synthesis, characterization, and testing of Metal Organic Frameworks (MOFs) for CO<sub>2</sub> separation and conversion in Mixed Matrix Membranes (MMMs).*

Free time: students are invited to organize a joint activity to know each other, open personal and scientific collaborations

**Dinner “Il Cantinone” at 20:00**

**19<sup>th</sup> December 2023**  
**Palazzo dei Priori, Sala dei Notari**

*Heterogeneous Catalysis*  
Chair: Marco Bandini (UNIBO)

- 9:00 – 9:10 OP16 **Palit Shilpa** (POLIMI)  
*Title: Legislation and policy guidelines for greener sustainable processes*
- 9:10 – 9:20 OP17 **Sciarretta Sara** (UNIVAQ)  
*Title: Development of adsorbents for gases of technological interest from recovered raw materials*

*Biocatalysis*

- 9:20 – 9:30 OP18 **Bigliardi Martina** (UNIMI)  
*Title: Biocatalytic synthesis of bioactive compounds exploiting the acyltransferase from *Mycobacterium smegmatis**
- 9:30 – 9:40 OP19 **Morrone Nelly** (UNIFI)  
*Title: Holistic development of chemical and biological catalysis approaches for the conversion of waste renewable resources into high value-added molecules*
- 9:40 – 9:50 OP20 **Niola Edelberto Oscar** (UNINA)  
*Title: Artificial metalloenzymes for biomass transformation*
- 9:50 – 10:00 OP21 **Voicu Paul George** (UNITO)  
*Title: Engineering of new redox enzymes for the sustainable production of molecules with high added value*

*Novel Technologies for Catalysis*  
Chair: Claudia Antonetti (UNIFI)

- 10:00 – 10:10 OP22 **Edoardo Bazzica** (UNIPG/DCBB)  
*Title: Green and circular strategies for biowaste valorization*
- 10:10 – 10:20 OP23 **Bruschetta Chiara** (UNITO)  
*Title: Technologies for the Intensification of Eco-sustainable Catalytic processes*
- 10:20 – 10:30 OP24 **Bucchieri Michele** (POLITO)  
*Title: Synthesis and characterization of photocatalysts enhanced by upconversion systems and/or plasmonic nanomaterials to exploit sunlight in reactions of environmental interest.*





December 18<sup>th</sup>-19<sup>th</sup>, 2023

Palazzo dei Priori – *Sala dei Notari*

Perugia

1<sup>st</sup> workshop



**PhD Coordinator:** Prof. Luigi Vaccaro  
*University of Perugia, Italy*

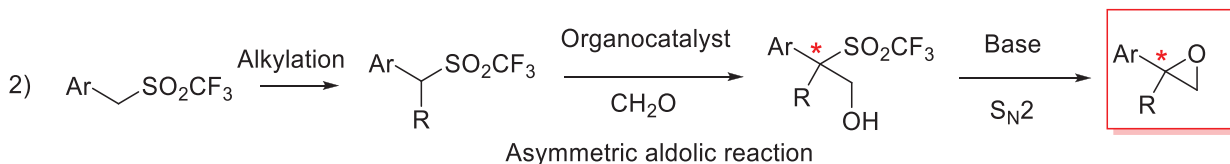
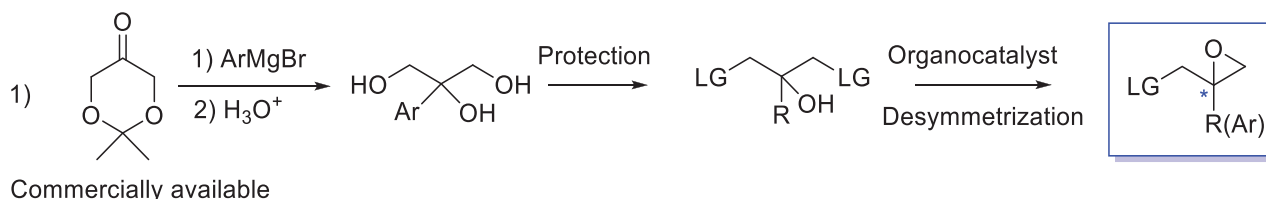
**Abstract of the Oral Presentations**

**Armando Astone**

Local Institution: Università degli studi di Salerno

## Organocatalytic asymmetric synthesis of epoxides bearing quaternary stereocenters

Supervisors: Alessandra Lattanzi, Sara Meninno



### Thesis abstract:

Chiral epoxides are widely used as versatile synthetic intermediates, thanks to the regioselective opening of the oxirane ring, which allows to obtain functionalized molecules, with a well-defined stereochemistry of the centers.<sup>1</sup> Metal or organocatalyzed asymmetric epoxidation of olefins with oxidants represents the most convenient method for obtaining epoxides. Among these methods, Sharpless, Jacobsen and Shi's epoxidation should be mentioned. The synthesis of enantioenriched epoxides can be achieved by non-oxidative methods, like sulfur ylides route, or via the Darzens reaction.<sup>2</sup>

Although there are several methods for obtaining epoxides, there is a lack of general methodologies that allow the preparation of chiral 1,1-disubstituted terminal epoxides. Terminal epoxides are the most synthetically useful, since ring opening occurs in a highly regioselective manner, and consequently they can be exploited as intermediates for the synthesis of derivatives.<sup>3</sup>

This PhD project aims to develop new and more sustainable enantioselective approaches for the synthesis of novel classes of chiral enantioenriched terminal epoxides. In particular, our attention will be focused on catalytic processes mediated by organocatalysts derived from the *Chiral Pool*, including Cincona alkaloids, or other optically pure commercial compounds such as diamines or amino alcohols.

A desymmetrization process of triols will be investigated to directly access enantioenriched terminal protected epoxy-alcohols.

Moreover, an organocatalytic approach to non-functionalized chiral terminal epoxides will be studied. In this case, we envision to exploit the EWG properties of the triflone group as i) a proper activator for the generation of nucleophilic carbon in the asymmetric aldol reaction step and then ii) its ability to act as leaving group in the second step.

The synthetic utility of the enantioenriched terminal epoxides will be demonstrated by their transformation into biologically and/or pharmacologically active molecules.

<sup>1</sup> Wang, C.; Luo, L.; Yamamoto, H. *Acc. Chem. Res.* **2016**, *49*, 193.

<sup>2</sup> a) Gao, Y.; Klunder, J. M.; Hanson, R. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765. b) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801. c) Zhu, Y.; Wang, Q.; Cornwall, R. G.; Shi, Y. *Chem. Rev.* **2014**, *114*, 8199.

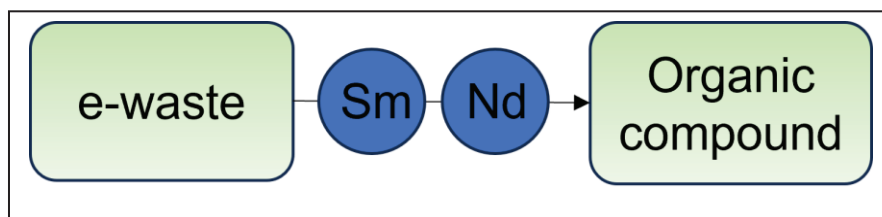
<sup>3</sup> Cho, I.; Prier, C. K.; Jia, Z.-J.; Zhang, R. K.; Görbe, T.; Arnold, F. H. *Angew. Chem. Int. Ed.* **2019**, *58*, 3138.

**Matteo Barilli**

*University of Pavia*

**Upcycling of NdFeB SmCo magnets. From e-waste to high-value products.  
Green&Digital Transition**

**Supervisors:** Prof. Giuseppe Zanoni



**Thesis abstract:**

The pressing need to address sustainable development in order to face of the climate crisis, resource scarcity, and planetary boundaries has highlighted the importance of seeking alternative paths. To this end, utilizing secondary sources for raw materials has become a critical activity. NdFeB and SmCo magnets, are widely used in electronics, so their accumulation is starting to be a huge problem all around the world.

Magnet valorisation could solve the problem of waste accumulation and the loss of value associated with it, while also addressing environmental concerns related to primary mining and metal processing. Currently, there is no market for EoL (End of Life) magnets due to the lack of sustainable processes that integrate zero-waste and circular economy approaches. Upcycling is the best option to develop a sustainable process, able to valorise the entire magnet in other applications with quality standards, respecting planetary boundaries and decreasing the use of primary raw materials. The upcycling of magnets is scarcely documented, leaving potential for innovation in this area.

Sm and Nd can be used in a lot of organic process such as: catalysts with lewis acid properties in different condition where lot of lewis acid are inhibited (such as water condition), or as a single electron transfer reagent. For these reasons the aim of this PhD project will focus on development of new methods for upcycling and uses of crucial raw materials in organic chemistry to establish and improve the impact of this chemistry in the circular economy.





**Debora Iapadre**

*Local Institution: Università degli Studi dell'Aquila*

## **Sustainable methodologies via organo-, photo and supramolecular catalysis**

**Supervisors:** Armando Carlone  
Fabio Pesciaoli



### **Thesis abstract:**

The main research topic of my PhD will be about the conceptualization and the development of methodologies in homogeneous catalysis for the synthesis of enantioenriched compounds. In order to carry out chemical reactions in a stereoselective way I will explore organocatalysis, photocatalysis and supramolecular systems. To date organocatalysis represents one of the three pillars of asymmetric catalysis; its impactful contribution to the scientific community and industry is testified by the 2021 Nobel Prize for Chemistry, awarded to B. List and D. MacMillan for the development of asymmetric organocatalysis. Light-driven transformations (photochemistry/photocatalysis) are powerful activation modes for the construction of organic building blocks for synthesis. Furthermore, supramolecular systems for molecular recognition may be an interesting option to explore in catalysis. This will take me at the interface with Ragazzon's group that works on molecular machines, where I will spend part of my PhD.

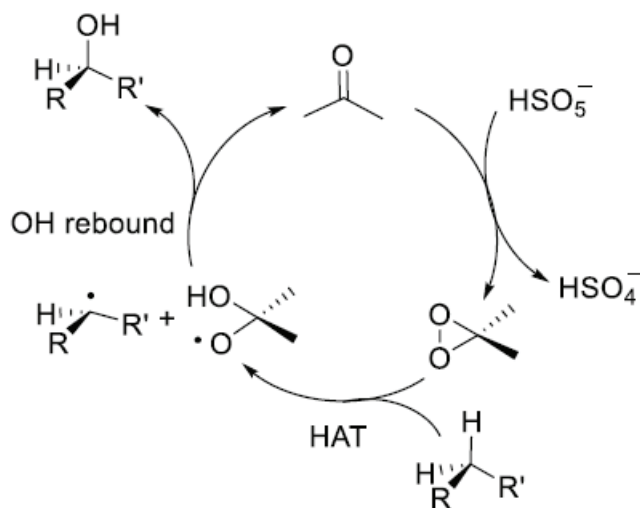
I will spend most of my PhD at University of L'Aquila, under the supervision of Professor Armando Carlone. The interest of the group is widespread through organic chemistry, with a particular focus on organocatalysis, photocatalysis, synergistic catalysis and applied chemistry in industry. During the next three years I will spend my period abroad in the group of Professor Guilio Ragazzon in Strasbourg, focusing my research on self-assembled supramolecular systems and molecular machines in order to drive chemical reaction and explore new strategies in this field. Moreover I will have the possibility to expand my knowledge and skills spending six months in Fater S.p.A., exploring the world of detergents and surfactants for a more sustainable production and use.

**Jacopo Mancini**

*Local Institution : Università degli studi di Roma « Tor Vergata »*

## Catalytic C(sp<sup>3</sup>)-H bond hydroxylations promoted by dioxiranes

**Supervisors:** Prof. Massimo Bietti, Prof.ssa Michela Salamone



### Thesis abstract:

C(sp<sup>3</sup>)-H bonds functionalization represents one of the most investigated approaches to develop new synthetic methodology. Because of their ubiquity in organic molecules, the possibility to directly functionalize such bonds offers the opportunity to simplify synthetic paths, avoiding the introduction and subsequent functional group manipulation, thus representing a powerful method for late-stage functionalization of molecules of pharmaceutical interest, natural products and biomolecules. Control over site-selectivity and stereoselectivity represent crucial aspects associated to these processes.

In this regard, various methodologies have been developed, among which those that exploit hydrogen atom transfer (HAT) reactions have attracted considerable interest because they offer the opportunity to replace H with a large variety of functional groups under mild conditions. These procedures typically employ heteroatom based radicals or radical-like reagents like metal-oxo complexes and dioxiranes. This latter class of reagents can be conveniently generated from ketone precursors and, in addition to being able to epoxidize C=C double bonds, has found particular interest in C(sp<sup>3</sup>)-H bond oxygenations. In such transformations, dioxiranes show high selectivity for tertiary C-H bond hydroxylation that proceed with stereoretention. Initially employed as stoichiometric reagents, catalytic procedures for C(sp<sup>3</sup>)-H bond oxygenations that allow in situ generation of the dioxirane have been recently developed.

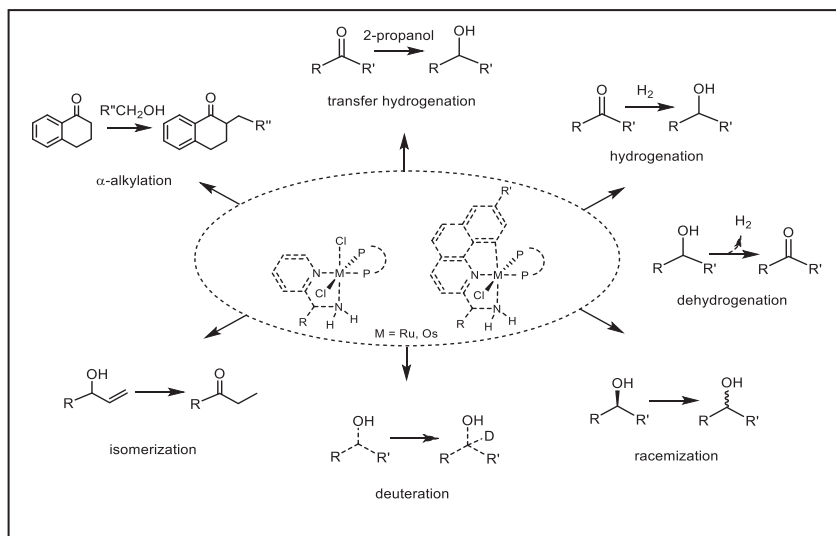
With these concepts in mind, the first aim of my PhD work will be to improve the catalytic efficiency of C(sp<sup>3</sup>)-H bond oxygenations promoted by dioxiranes. This will be pursued through a detailed screening of precursor ketones, solvents, additives and experimental conditions. With the optimal conditions in hand the reactions will be employed to implement site-selectivity and stereoselectivity in C(sp<sup>3</sup>)-H bond oxygenations of different substrate classes, investigating in detail the role of substrate and dioxirane structure as well as of medium effects on the reaction outcome.

**Giulia Mannoni**

Local Institution : University of Udine

**Development of highly efficient ruthenium catalysts for sustainable hydrogenation reactions**

Supervisors: Walter Baratta and Daniele Zuccaccia



**Thesis abstract:**

The production of high value compounds under sustainable conditions requires the development of efficient catalytic processes capable of carrying out reactions that limit the production of by-products, with low energy demand and with the ultimate goal of replacing traditional, non-catalyzed processes. Among the green solvents that can be used, water is a non-toxic solvent, inexpensive and abundant, reducing the environmental impact associated with its use and disposal.

Ruthenium is a transition metal that continues to be of great interest due to its relatively low cost, high performance in numerous catalytic transformations, such as carbonyl hydrogenation and alkenes metathesis reactions. Hydrogenation and hydrogen transfer reactions of aldehydes and ketones are key catalytic processes in the industry for the preparation of alcohols using H<sub>2</sub> or 2-propanol and formic acid, which is soluble in H<sub>2</sub>O, as non-toxic reagents with low environmental impact.

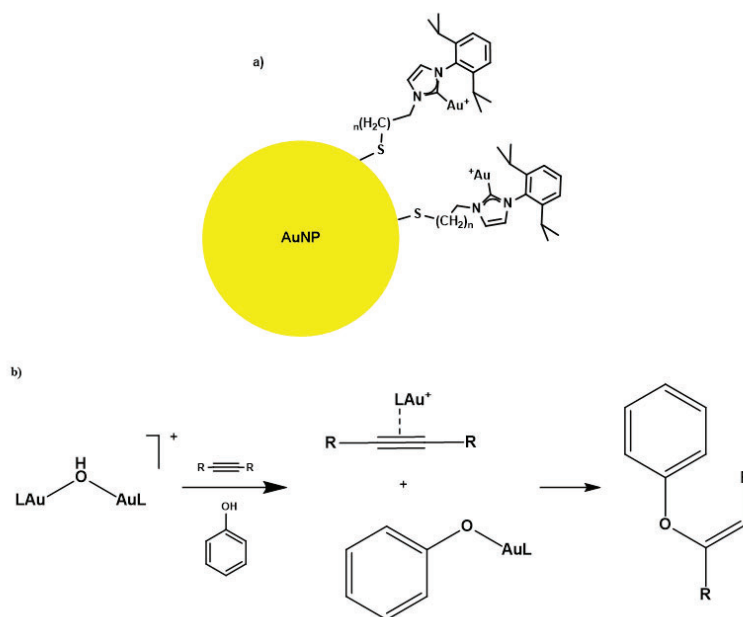
The design of ruthenium catalysts for reactions characterized by a high atom economy is a central topic for the synthesis of high-value intermediates. Based on these considerations, the project aims to develop new ligands able to increase the solubility of ruthenium complexes in water. To achieve this, phosphonic ligand and water-soluble heterocyclic compounds such as ampy and modified benzoquinolines containing carboxylic or sulfonic functions on the heterocycle or aromatic rings will be used and synthesized. The obtained ligands and ruthenium complexes will be characterized by multinuclear NMR spectroscopy. These catalysts will be tested in the model reduction reactions of short-chain carbonyl compounds with low-pressure H<sub>2</sub>, alcohols and formic acid in water. In addition, the reduction of carbonyl substrates resulting from the degradation of biomass (furfural, HMF, cinammaldehyde) will be also explored. For the most promising systems, mechanistic studies will also be conducted using NMR to identify the key relevant ruthenium complexes present in the catalytic cycle with the ultimate aim of redesigning the catalysts to increase the efficiency.

**Giovanni Rubello**

Local Institution: Università degli Studi di Padova

**Gold-based cooperative catalytic systems for the valorization of phenols derived from biomasses**

**Supervisors:** Cristina Tubaro  
Laura Orian



a) Gold complexes grafted to nanoparticle's surface. b) Dual gold-activation in hydrophenoxylation reaction.

**Thesis abstract:**

The lignin is an amorphous polymer constituted by phenolic monomeric units, as paracoumaryl, coniferyl and synapil alcohol. Nowadays, this material is a waste of the agricultural and paper industry and it's mainly used for the energy production through combustion.<sup>[1]</sup> In order to valorise this type of biomass, the phenols derivatives can be chemically transformed to obtain fine chemical products, more useful for economic, chemical and environmental purposes. The capability of NHC-gold(I) complexes to activate alkynes towards several transformations, such as hydrophenoxylation reaction, is well known.<sup>[2]</sup> This reaction is an example of cooperativity phenomenon that occurs when two catalysts are involved in a single catalytic cycle, participating in a double activation of the substrates. To favor the reaction, the proximity and pre-organization of the gold centers can be controlled by grafting the NHC-gold(I) complexes to the surface of monolayer-protected gold nanoparticles. The NHC ligand will be functionalized with an alkyl chain with a terminal thiol group to allow the interaction with the nanoparticle. Moreover, the selectivity of the reaction (selectivity for the reagents or the products, as well as regio- and stereoselectivity) could be enhanced and controlled thanks to the confinement effect due to the chemical properties of the monolayer.

[1] T. Wang, H. Li, X. Diao, X. Lu, D. Ma, N. Ji, *Ind. Crops Prod.*, **2023**, *199*, 116715.

[2] C.H. Leung, M. Baron, A. Biffis, *Catalysts*, **2020**, *10*, 1210.

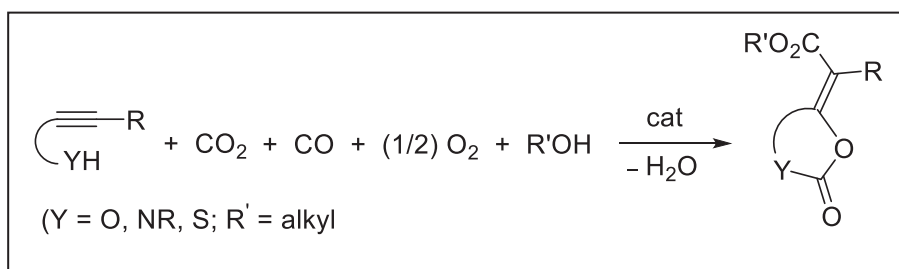
**Sofia Tropiano**

*Local Institution: Università della Calabria, dipartimento di CTC*

**Title of the PhD research**

**Study of new catalytic processes for the conversion of CO and CO<sub>2</sub> into high value added products**

**Supervisors:** Prof. Bartolo Gabriele, Girolamo Giordano, Tiziana Marino, Raffaella Mancuso



**Thesis abstract**

This research project is aimed at developing new catalytic methods for the conversion of CO and/or CO<sub>2</sub> into high value added compounds. The importance of catalytic activation of carbon dioxide and/or carbon monoxide as a C-1 feedstocks is of primary importance both in academia and in industry, due to their large availability and the possibility to convert simple building blocks in important compounds.

In particular, during the PhD will be studied and developed innovative catalytic approaches for incorporating CO<sub>2</sub>/CO into unsaturated molecules, such as functionalized alkynes, in order to produce important cyclic carbonyl derivative, such as carbamates, cyclic ureas and other heterocyclic compounds of industrial and pharmaceutical interest. To promote this type of carboxylation and cyclization reactions, the use of metal catalysts in possible combination with organocatalysts will be implemented in order to sequentially activate the substrates taking part in the catalytic transformation.

The project is divided into several lines of research, concerning the use of different types of substrates aimed at the synthesis of various compounds with pharmacological or technological activity, as shown in above equation. The use of non-conventional solvents, such as ionic liquids and deep eutectic solvents, as well as of heterogeneous catalysts will also be exploited for realizing the goals of the PhD project.

The final objective is to propose new sustainable catalytic strategies to transform waste gases into organic compounds of industrial and pharmaceutical value, thus contributing to the reduction of environmental impact and the development of new scientific applications.



**Simone Zurzolo**

*Local Institution: University of Siena*

## **Industrial and agricultural solid waste for sustainable catalytic processes**

**Supervisors:** Elena Petricci

### **Solid waste materials in sustainable catalytic processes**

While liquid waste management has been widely and successfully explored,<sup>1</sup> Solid Waste Materials (SWMs) from agriculture and industrial processes find limited applications being treated as special waste. In this scenario, the possible valorization of SWMs for the development of green<sup>2</sup> and circular<sup>3</sup> processes can represent a great opportunity for their management. The idea is to properly treat SWMs from different industrial sectors to produce additives and new catalysts, after the extraction of all their active principles by using different technologies such as microwaves, biomass derived solvents and others methods.<sup>4</sup> A plethora of reactions will be investigated, using different SWMs based metal catalysts (*i.e.* Pd, Rh, Ru, Ir) to be applied on transformations such as, but not limited to, hydroformylation (HF),<sup>5</sup> carbonylation (CA),<sup>6</sup> hydrogen borrowing reactions (HB),<sup>7</sup> cross-couplings (CC),<sup>8</sup> and hydroaminomethylation (HAM).<sup>9</sup> The biological activity of the SWM derived extracts will be performed to find interesting matrices for cosmetic and/or nutraceutical applications, while for each process the heterogeneous or homogeneous catalyst will be fully characterized and its recovery and reused carefully evaluated. The Life Cycle Assessment (LCA)<sup>6</sup> calculation of the different processes will be performed and compared to the classical protocols and the transformation applied in industry. Sardinian White Wool (SWW) has been chosen as the model SWM for our purposes. With the use of this biomass, it has been possible to develop a protocol for the Regioselective HF of terminal alkenes in collaboration with Prof. Porcheddu in the University of Cagliari. This solvent-free method exploits commercially available ligands and catalysts and mild reaction conditions taking advantages from microwave irradiation. The reaction is of general applicability on different terminal alkenes and it is possible to recover both the catalyst and ligand without using organic solvents. The efficiency and sustainability of the process is supported by LCA analyses that compare the classic HF methods with the one here reported. This is just a proof of concept of the possible application of SWMs in the development of low impact catalytic processes in a zero waste approach able to valorize all the chemical information contained in the waste matrix.

#### References:

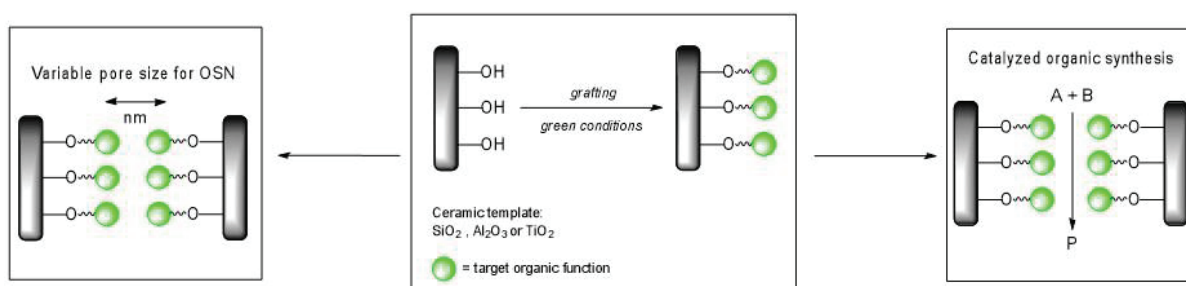
- <sup>1</sup> Seggiani, M. *et al.* *Desal. Water Treat.* **2014**, *52*, 1647.
- <sup>2</sup> Anastas, P.T.; Warner, J.C. *Chem. Rev.* **2007**, *107*, 2167.
- <sup>3</sup> Elser, M. *Accenture Report.* **2017**. <https://www.accenture.com>
- <sup>4</sup> Chemat, F.; Vian, M. A.; Fabiano-Tixier, A. S.; Nutrizio, M.; Jambrak, A. R.; Munekata, P. E. S.; Lorenzo, J. M.; Barba, F. J.; Binello, A.; Cravotto, G. *Green Chem.*, **2020**, *22*, 2325.
- <sup>5</sup> Migliorini, F.; Dei, F.; Calamante, M.; Maramai, S.; Petricci, E. *ChemCatChem.* **2021**, *13*, 2794.
- <sup>6</sup> Aya, I.; Gevorgyan, A.; Skrydstrup, T.; Bayer, A. *Org. Process Res Dev.* **2020**, *11*, 2665.
- <sup>7</sup> Reed-Berendt, B. G.; Latham, D. E.; Dambatta, M. B.; Morrill, L. C. *ACS Cent. Sci.* **2021**, *7*, 4, 570.
- <sup>8</sup> Campeau L.C.; Hazari, N. *Organometallics*, **2019**, *14*, 38, 3.
- <sup>9</sup> Migliorini, F.; Monciatti, E.; Romagnoli, G.; Parisi, M.L.; Taubert, J.; Vogt, M.; *et al.* *ACS Catal.* **2023**, *13*, 2702.

**Francesco Catalini**

University of Camerino

**The role of catalysis for the development of hybrid filter matrices for sustainable organic transformations**

**Supervisors:** Prof. Serena Gabrielli,  
Prof. Enrico Marcantoni



**Thesis abstract:**

The development of organic-functionalized inorganic membranes can significantly impact both the academic and industrial worlds, not only for the ability of nano-porous membranes to improve the Organic Solvent Nanofiltration, but especially for the catalytic activity of specific organic functionalization we can selectively graft on the inorganic surface of the membranes. Together with the application of environmental-friendly experimental conditions, such as: performing the recovery and reuse of the catalyst, working from less to no-solvent conditions and under no-toxic conditions for human health, the development of hybrid filtrating nanomembranes represents a perfect merge between the need for a green chemistry approach to synthetic chemistry and the leading interest for efficient organic transformations.

First, we must define three primary inorganic matrix candidates for this purpose, such as  $\text{SiO}_2$ ,  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{TiO}_2$  matrices, which could be used as nanoparticles or porous membranes. The choice of ceramic instead of polymeric matrices is due for the OSN application, because of the swelling-affinity of polymers under the presence of certain organic solvents.

Then, several organic groups could be chosen for functionalization, concerning the application's aim, such as filtration, catalysis, or others. The target organic function is applied to the ceramic membrane through grafting techniques, exploiting the presence of hydroxyl groups on the surface for silanization of organic molecules, for example, APTMS, MPTMS, and others, such as amino acids derivatives. The nature of the organic functions is also related to the formation of the desired pores size, which can be managed by changing the dimension of the grafted organic molecule.

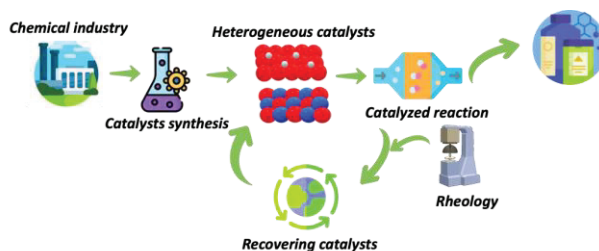
Finally, the obtained hybrid membrane, selectively customized, is submitted for characterization and investigation of the target activity, i.e., solvent retention in the case of OSN application and catalytic efficiency in the case of organic synthesis application.

**Giorgia Ferraro**

Local Institution: Ca' Foscari University of Venice

## Study and characterization of catalytic systems and their recovery/regeneration

Supervisors: Michela Signoretto  
Nicola Ballarini



### Thesis abstract:

The chemical industry is a significant emitter of greenhouse gas, that have to be reduced. This challenge can be solved with the advancements of catalysis<sup>1</sup>. The present research will be done in collaboration with Clariant, a Swiss multinational chemical company, that is continuously investing in catalyst solutions, helping to decarbonize the chemical industry, for a great number of applications, including sustainable chemical and fuel production. The aim of the research is the study and characterization of catalytic systems used in several process in a worldwide scale, in order to reintegrate them in the productive cycle, as a part of a sustainable and circular perspective<sup>2</sup>. This is possible if heterogeneous catalysts are employed, thanks to their easy separation from the products, therefore their consequent recyclability. In particular, supported metal catalysts (Ni/Al<sub>2</sub>O<sub>3</sub>, Pd/C) and mixed oxides (Fe/Mo, Cu/Mn oxides) will be studied. The first are composed by a support that permits to reduce the amounts of the expensive active metal component, which is dispersed as small particles, it increases the available metal surface area which is related to the catalytic activity, and it provides mechanical resistance<sup>3</sup>. The second, thanks to the synergistic effect of the ion metal pair and their variable oxidation states ( $M_1^{n+}$ ,  $M_2^{(n+1)+}$ ), present high performances in catalyzing the reaction. However, due to this complexity on their structure, they need several steps to be separated and purified enough to make possible to integrate them in a virtuous production cycle without degrading chemical and physical performances<sup>4</sup>. Rheology, i.e. the study of the deformation and the flow of matter, will be employed to stress out both the recovered catalyst and the one obtained from the recycling production process in order to evaluate their partial or total recovery and reinstatement for the same or different applications. Abrasion resistance tests, density measures, chemisorption, temperature programme reduction/oxidation/desorption (TPR, TPO, TPD), nitrogen physisorption, X-Ray Diffraction (XRD), Scanning/Tuning Electron Microscopy (SEM, TEM) will be carried out on the catalysts and the spent ones. From this study, the catalytic process parameters will be optimized to minimize the energy, water and time required for the process.

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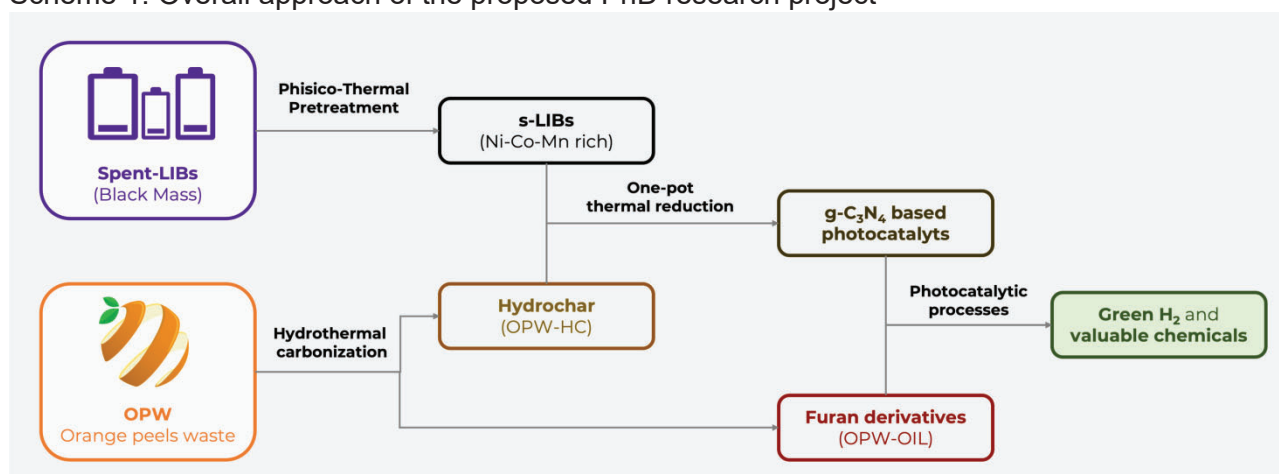
**Giulia Maria Itri**

*Local Institution: Università degli studi Mediterranea di Reggio Calabria*

**PHOTOWASTE – Synthesis of a new heterogenous photocatalyst for the photoreforming of aqueous solutions of biomass residues**

**Supervisors:** Francesco Mauriello

Scheme 1. Overall approach of the proposed PhD research project



**Thesis abstract**

This PhD project focuses on the design and development of low-cost and robust heterogeneous carbon nitride based photo-catalysts coupled with s-LIBs and OPW-HC and in their application in the production of value-added chemicals by a sustainable photocatalytic processes in the context of circular economy (Scheme 1).

The specific objectives of the projects can be summarized as follows:

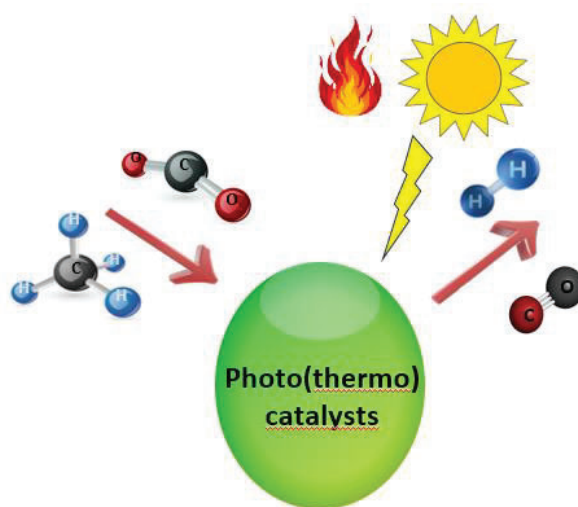
- design and prepare new heterogeneous photo-catalysts based on g-C<sub>3</sub>N<sub>4</sub> (from melamine or urea) and containing Co-Ni-Mn from the s-LIBS (i.e. the mixture of anode and cathode materials obtained from the mechanical shredding of s-LIB known as “black mass”) and the hydro-char deriving from the hydrothermal carbonization of orange peel waste (OPW-HC);
- perform a detailed structural and physico-chemical characterization of the prepared catalytic systems to identify the crucial properties of the photo-catalyst;
- study the photo-reforming process for the sustainable production of green H<sub>2</sub> with the simultaneous upgrading of the furans derived from OPW into precious chemical substances, appropriately modifying the characteristics of the catalyst, the reaction conditions and the photocatalytic set-up.

**Eleonora La Greca**

*Local Institution: University of Catania, National Research Council (CNR),*

## **Catalytic, photocatalytic and photothermo-catalytic reforming reactions for the H<sub>2</sub> production and the subsequent CO<sub>2</sub> valorization**

**Supervisors:** Prof. Salvatore Scirè  
Prof. Roberto Fiorenza  
Dr. Leonarda Francesca Liotta



### **Thesis abstract**

Since the industrial revolution, the increasing use of conventional fossil fuels led to severe environmental consequences, including global warming and resource depletion. For those reasons, in the last years the international community, is promoting ambitious policies and pursuing ecofriendly goals. Among them, it is worth noting that, the European Green Deal aims to make Europe a carbon-neutral economy by 2050. The current energy production model, characterized by increasing greenhouse gas (GHG) emissions and fossil fuel depletion, necessitates an urgent transition to low-carbon energy market, with sustainable energy carriers as hydrogen (H<sub>2</sub>). The traditional methods for H<sub>2</sub> production, also contribute to CO<sub>2</sub> emissions and are depending on non-renewable feedstocks. Green approaches, such as water electrolysis, photocatalysis, and photoelectro-catalysis, offer some alternatives, but they often have important drawbacks such as the high cost and energy consumption.

To address these challenges, this project will explore catalytic, photocatalytic and photothermal-catalytic reforming reactions, with the aim to improve the H<sub>2</sub> production, valorizing at the same time, a greenhouse gas, as the CO<sub>2</sub>. In particular, the dry reforming, the chemical looping reforming and photoreforming reactions will be studied. The nature of the catalysts is crucial in determining their thermal stability, oxygen storage capacity, redox and basic properties that affect the catalytic and photo-catalytic behavior. For this purpose, Ni catalysts supported on CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, La-doped ceria-based Perovskites and modified carbon nanotubes appear as good candidates and will be initially investigated.

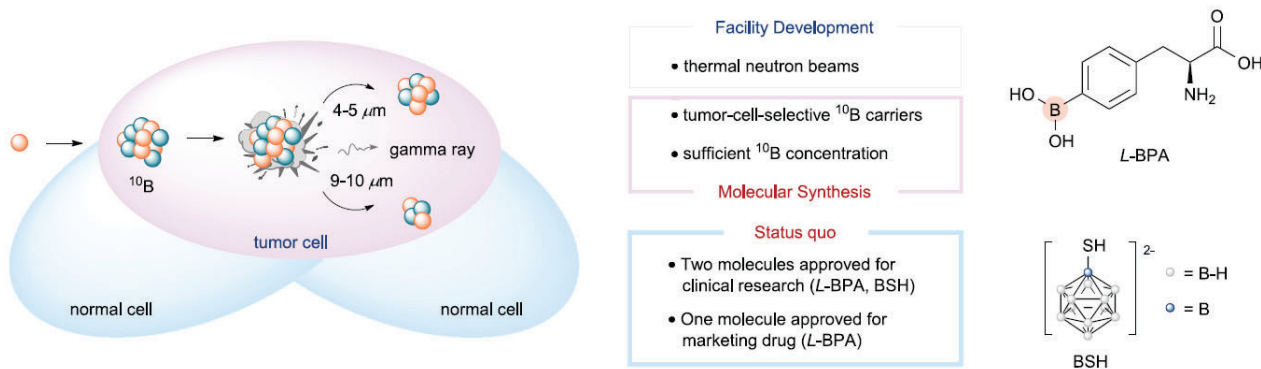
The project foresees a circular scenario in which the reforming reactions will produce syngas and pure H<sub>2</sub>, with zero CO<sub>2</sub> emissions. The synthesized catalysts will be investigated by advanced characterization techniques, thanks to international collaborations, to deeply understand the structure-activity relationships with the aim to propose at the end a versatile and sustainable energy production system in line with global environmental objectives.

**Federica Plavi**

Local Institution: Università degli Studi di Pavia – Lab B2

## Development and Radiobiology of New Boron Entities

Supervisors: Giuseppe Zanoni



### Thesis abstract:

Boron Neutron Capture Therapy (BNCT) is an emerging treatment modality aimed at improving the therapeutic ratio for traditionally difficult to treat tumors. BNCT is based on the nuclear reaction known as boron neutron capture. Natural boron has two stable isotopes, namely  $^{10}\text{B}$  and  $^{11}\text{B}$ . A relevant nuclear property of the  $^{10}\text{B}$  isotope is the high cross section for neutron capture, which has permitted the therapeutic use of boron compounds for BNCT.

$^{10}\text{B}$  atoms are nonradioactive isotopes and they can adsorb low energy neutrons (thermal neutrons). This leads to the production of an  $\alpha$  ( $^4\text{He}$ ) particle and a recoiled lithium nucleus ( $^7\text{Li}$ ). These particles deposit high energy along their short path ( $< 10 \mu\text{m}$ ), approximately the size of a single cell. Therefore, the BNC reaction occurs within one cell.  $^{10}\text{B}$  atoms selectively accumulate inside the malignant cells which are surrounded by normal cells, the thermal neutron irradiation can selectively destroy the malignant cells by the two heavy particles,  $^4\text{He}$  and  $^7\text{Li}$ . The efficacy of BNCT is highly dependent on the selective delivery of boronated compounds to the tumor, while avoiding significant uptake in normal tissues. The ideal properties of a BNCT agent includes high tumor uptake, low normal tissues uptake, rapid clearance from tissue after treatment, and low toxicity.

The development of  $^{10}\text{B}$ -drugs has become an urgent task for BNCT technology. Only two boron containing molecules, L-Boronophenylalanine (L-BPA) and Sodium Borocaptate (BSH), have been approved by FDA for clinical investigation, and only L-BPA has been approved as the world-first marketing BNCT drug.

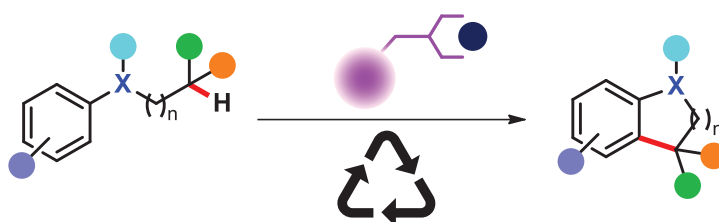
For this reason, the goal of the project is the development of new  $^{10}\text{B}$ -entities, based not exclusively, on L-BPA.

**Sang Tian**

Local Institution: Università di Perugia

## Synthesis of heterocycles via sustainable heterogeneous C(sp<sup>3</sup>)-H functionalization processes

Supervisors: Prof. Luigi Vaccaro  
Prof. Stefano Santoro



### Thesis abstract:

Transition metal catalyzed C–H bonds functionalization field has undergone an ever-increasing development in recent years, emerging as a powerful synthetic organic tool. Despite the challenges related to the intrinsic inertness of C–H bonds and the need for selectivity, this class of transformation represent a sustainable synthetic alternative to create new C–C bonds.<sup>1</sup>

To address the above-mentioned issues the catalyst design plays a crucial role. Moreover, to move towards a sustainable synthesis, in addition to the atom- and step- economy intrinsic to the direct C–H functionalization, other strategies should be considered. In the context of waste minimization, resource security and recycle, the design of efficient heterogeneous catalysts is a key tool.

Since the early 2000s the green SOC group investigated the employment of polymer-supported heterogeneous catalysts for different organic transformations gaining great experience in this field.

The first example reported an Amberlyst IRA900-fluoride resin used to catalyze the  $\beta$ -azidation of  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>2</sup> Later the efficiency of this type of ammonium fluoride catalyst was demonstrated for diverse transformations developing other ammonium fluoride-based catalysts.<sup>3</sup>

Thanks to the experience of the Green SOC group and the careful design of the cross-linker, named SPACER,<sup>4</sup> a novel class of heterogeneous catalysts POLITAG has been recently developed. The pincer type ligands of POLITAG can efficiently immobilize anionic Pd<sup>2+</sup> complexes or Pd<sup>0</sup> nanoparticles affording catalysts efficient in cross-coupling reactions and C–H activation processes.<sup>5,6</sup>

This long time experience led to the synthesis of supported NHC catalyst used in several C–H activation processes for the synthesis of heterocycles and in diverse enantioselective C–H activation protocols.<sup>7,8</sup>

These catalysts will be finely tuned to catalyze different direct C–H functionalization processes aiming at a sustainable synthesis of heterocycles with a waste minimization approach.

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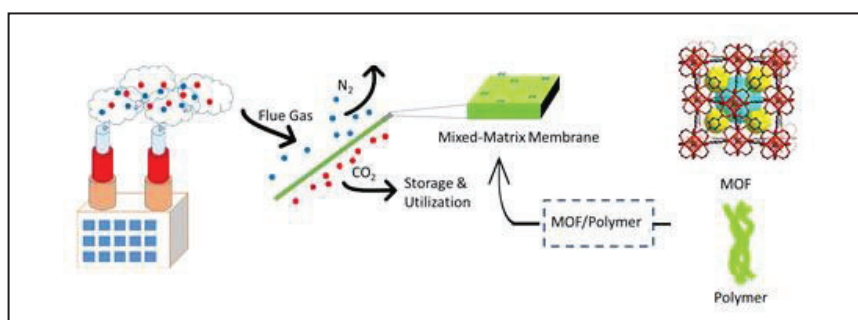
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**Letizia Trovarelli**

*Local Institution : University of Perugia*

**Synthesis, characterization, and testing of Metal Organic Frameworks (MOFs) for CO<sub>2</sub> separation and conversion in Mixed Matrix Membranes (MMMs).**

**Supervisors:** Prof. Ferdinando Costantino, Prof. Valentina Crocellà.



**Thesis abstract:**

Nowadays one of the impellent challenges around the world is certainly global warming. Carbon dioxide, the by-product of fossil fuels, is the dominant greenhouse gas and an increase in its concentration in the atmosphere is no longer tolerable. In this scenario, Carbon Capture and Sequestration (CCS) and Carbon Capture Utilization (CCU) technologies that effectively capture CO<sub>2</sub> from exhausted gases released from combustion process will play a major role, also in the prospective to convert captured CO<sub>2</sub> in new valuable products.

In the light of this, Metal Organic Frameworks (MOFs) represents an important class of materials to reach this purpose. MOFs are composed by a metal ion or a cluster of ions that act as Lewis acid site (LASs) that have been shown to interact with CO<sub>2</sub>.

An important parameter to consider when selecting a material in the CO<sub>2</sub> capture field are the quantity adsorbed and the selectivity with respect to other molecules present in gas mixture, such as N<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O.

Thanks to these promising properties, MOF-based materials can be used as a fillers to produce Mixed Matrix Membranes (MMMs), composite consisting by a crystalline porous filler dispersed in a polymer matrix. This new class of materials have been selected as a promising next-generation membranes, as they outperform commercially available membranes in CO<sub>2</sub> capture technologies.

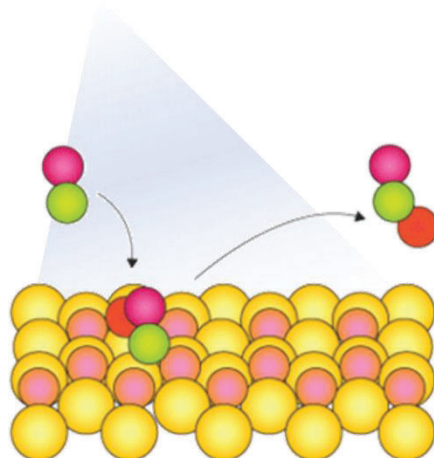
As CO<sub>2</sub> is a stable molecule, it requires the use of a catalyst to convert into chemicals. However, the catalytic reduction of CO<sub>2</sub> requires harsh conditions such as high pressures and temperature. Therefore, a possible CO<sub>2</sub> conversion pathway would be the photocatalytic mechanism, where the organic linker is the light absorbing material that transfers the electron to the metal (ligand to metal charge transfer) and then the metal reduces the CO<sub>2</sub> to CO through the RWGS reaction and subsequently to hydrocarbons.

**Shilpa Palit**

*Università degli Studi di Perugia & Politecnico di Milano*

**Legislation and Policy Guidelines for Greener Catalytic Processes**

**Supervisor:** Prof. Gianvito Vilé



**Thesis abstract:**

The application of advanced photocatalytic technologies has emerged as a promising avenue for the transition towards scalable engineering methods, offering the potential to significantly reduce, if not entirely eliminate, the environmental impacts of traditional processes. However, the implementation of photocatalytic technologies raises numerous questions, particularly regarding safety, sustainability, and adherence to regulatory frameworks. The regulatory landscape is currently undergoing updates, with the EU Commission actively engaged in revising regulations on photocatalysis.

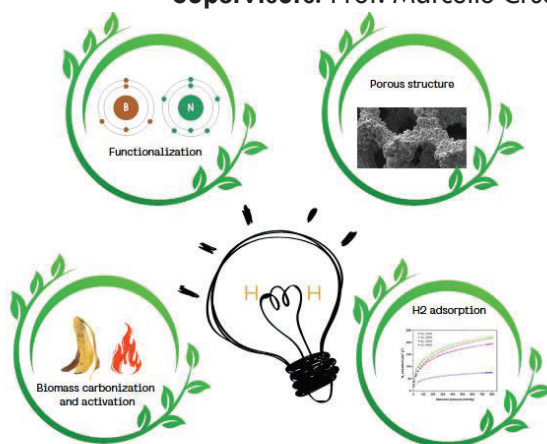
The primary objective of this PhD thesis is to gain an in-depth understanding of the regulations, and standards concerning photocatalytic processes, such as C-X photoredox catalysis and photocatalytic wastewater remediation. The research will thus involve investigating and examining the use of new single-atom-based catalytic technologies, considering both economic and sustainability perspectives. Furthermore, this work will encompass an internship at the Joint Research Centre in Ispra, a part of the European Commission. This internship aims to provide a practical dimension to the study, facilitating a comprehensive exploration of the subject matter.

**Sara Sciarretta**

*Local Institution: Università degli Studi dell'Aquila*

## **Development of adsorbents for gases of technological interest from recovered raw materials**

**Supervisors:** Prof. Marcello Crucianelli and Dott. Andrea Lazzarini



### **Thesis abstract:**

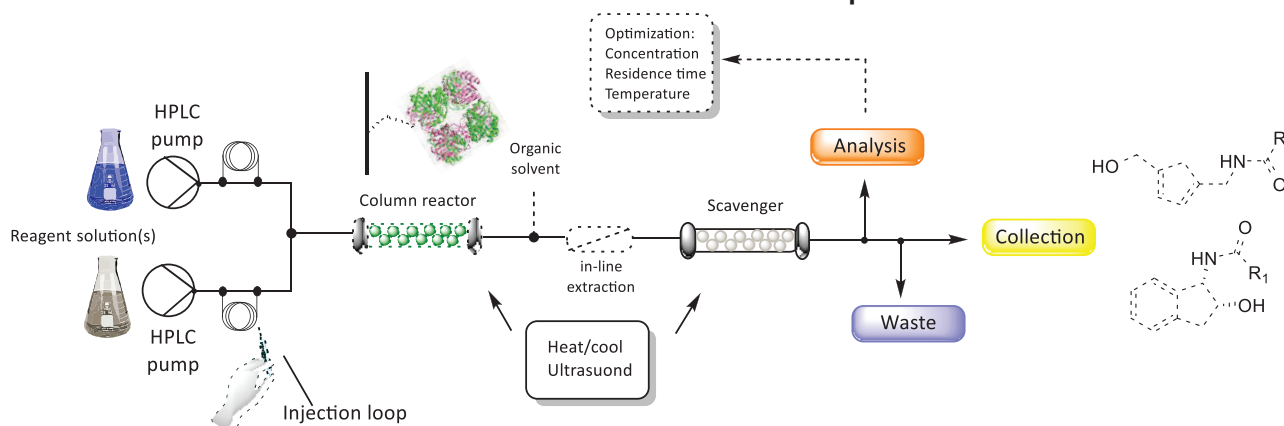
The current global economy is desperately hungry for energy and even in the case of increased energy production from non-renewable raw materials (primarily fossil and nuclear), the environmental costs will be enormous. Therefore, it is important to develop efficient technologies and materials to convert electrical energy into chemical energy, usable as needed. One of the most promising molecules for this purpose is hydrogen. This molecule has enormous potential both as a traditional energy carrier (usable with already established technologies) and as a molecule of high industrial value. One of the major limitations to its widespread use lies in the current technologies for its storage and transport. Due to its low energy density, it needs to be concentrated. However, this storage method can be extremely dangerous. Therefore, the development of materials for the rapid release of hydrogen (physisorption) is of great practical interest. In this scenario, activated carbons play a leading role being characterized by a high surface area and obtainable from recovered raw materials. The project aims to examine a selection of recovered raw materials, undertake a comprehensive characterization of them and, subsequently, conduct a study on different activation methods to identify the optimal and mildest procedure, for each biomass. To make interactions with the gas more specific and stronger, they will also be carefully functionalized and doped. The first doping method considered is boronation. Indeed, boron has a very similar atomic radius to carbon and this characteristics allows easier introduction of the element into the carbonaceous matrix. Additionally, the electron deficiency of boron is exploited to enhance the interaction with hydrogen. In order to store also other gases of technological interest, like CO<sub>2</sub> and CH<sub>4</sub>, doping with other elements and metals will also be properly examined.

**Martina Bigliardi**

Università degli Studi di Milano

**Biocatalytic synthesis of bioactive compounds exploiting the acyltransferase from *Mycobacterium smegmatis***

Supervisor: Dr. Martina Letizia Contente



**Thesis abstract:**

The acyltransferase from *Mycobacterium smegmatis* (MsAcT) is able to perform transesterification reaction of different species of primary alcohols and amines, with a variety of acyl donors, in aqueous environment at room temperature and with high acyltransferase/hydrolase ratio, differing from lipases and esterases. Moreover, the engineered S11C MsAcT mutant, in which the serine residue of the catalytic triad has been substituted with a cysteine, shows a wider substrate scope offering the possibility of synthesizing valuable thioesters and tertiary amides in a greener way.

In this project, MsAcT WT and S11C will be tested for acyl transfer reactions against building blocks of bioactive compounds, such as amino alcohols, secondary alcohols and amines with particular attention on chemo-, regio- and stereo-selective syntheses.

Subsequently, alternative acyl donor species (i.e., anhydrides, lactones, lactams, carbonates) will be investigated as low-cost and more sustainable alternatives to vinyl esters, in order to expand the range of donors available for the functionalization of alcohol and amine groups.

Since enzyme immobilization is an innovative tool improving catalyst stability, its recovery and reuse, thus impacting on the efficiency, productivity and greenness of synthetic processes, MsAcT and S11C variant will be immobilized and assayed for operational stability and reusability. Different immobilization strategies forming covalent bonds between the matrix and the enzymes (i.e., agarose carriers) will be used to obtain robust catalysts for flow processing.

Exploiting the results of MsAcT immobilization, continuous enzymatic syntheses for the preparation of valuable compounds will be carried out as they merge together the advantages of flow reactors with the selectivity and mild reaction conditions of biocatalysts. To further enhance system automation, in-line work-up and purification steps can be added when necessary downstream the process, thus ensuring reduction of manual handling while increasing the safety of the operator.

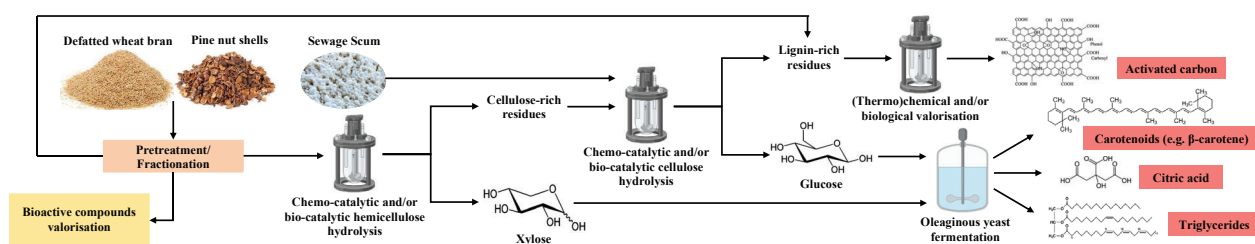


**Nelly Morrone**

*University of Pisa, Department of Chemistry and Industrial Chemistry, GreenCat Research Group*

**Holistic development of chemical and biological catalysis approaches for the conversion of waste renewable resources into high value-added molecules**

**Supervisors:** Prof. Anna Maria Raspolli Galletti, Prof. Claudia Antonetti, Dr. Nicola Di Fidio



### Thesis abstract:

The intensive exploitation of fossil raw materials to produce fuels and building blocks of current industrial production has determined several critical issues. Biomass represents a promising alternative to fossil sources and biorefineries assume a central role, leading to the conversion of biomass into chemicals, intermediates, materials and fuels. Third-generation biomasses and wastes, mainly composed of cellulose, hemicellulose, lignin and bioactive compounds, can be converted into valuable bio-products and bio-fuels. The exploitation of each fraction of the feedstock is fundamental to increase the sustainability. Since cellulose, hemicellulose, lignin and exctratives require specific reaction conditions for their conversion into bio-products and bio-fuels, the cascade multi-step approach could ensure the highest valorisation of each biomass component.

The main purpose of this research project is to design, investigate and optimise the conversion of different wastes, such as defatted wheat bran, pine nut shells and sewage scum to triglycerides, citric acid and carotenoids through an innovative approach based on the synergistic combination of chemical and biological catalysis.

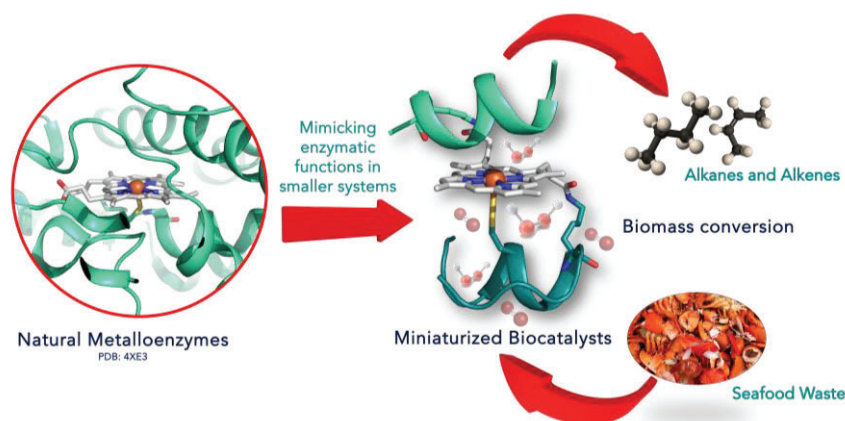
Firstly, the chemical characterisation of each biomass will be carried out. Tailored pretreatment and/or fractionation approaches will be investigated to extract bioactive compounds for subsequent exploitation. Chemical and enzymatic catalysis will be optimised to valorise both polisaccarides and lignin. Homogeneous acids and cellulolytic mixtures will be evaluated for the hydrolysis reaction. The main reaction parameters will be optimised by a chemometric approach. The obtained hydrolysates will be used as a substrate for the fermentation of oleaginous microorganisms to produce target molecules and the process parameters will be optimised. Lignin-rich residues collected after the pretreatment or the hydrolysis will be valorised through the synthesis of aromatics, activated carbons, resins or functionalised materials by implementing (thermo)chemical or biological approaches. The project involves the implementation of LCA studies to evaluate the environmental and economic sustainability of the optimised processes.

**Edelberto Oscar Niola**

Local Institution: University of Naples Federico II, Department of Chemical Sciences

**Artificial metalloenzymes for biomass transformation**

**Supervisors:** Flavia Natri  
Angelina Lombardi



**Thesis abstract:**

The urgent need of eliminating environmental pollutants has propelled the scientific community toward the continuous exploration of sustainable and innovative technologies. An abundant and unutilized material is seafood waste, which contains chitin, lipids and fatty acids (FAs). In this context, the final goal of this PhD project is the development of artificial metalloenzymes for biomass transformation. To this end, artificial biocatalysts, featuring metalloporphyrins as active site, will be designed, in order to promote selective oxidation reactions with high efficiency and using environmentally friendly oxidants, like molecular oxygen and hydrogen peroxide.<sup>[1]</sup> Miniaturization and *de novo* design strategies will be used for selecting the optimal peptide sequences encompassing the essential requirements for tuning metalloporphyrin activity.<sup>[2]</sup> Taking inspiration from the mimochrome family of artificial metalloenzymes,<sup>[3]</sup> small-sized heme-protein models with peroxidase and peroxygenase catalytic activity will be designed as models of cytochrome P450 (CYPs)<sup>[4]</sup> and fungal unspecific peroxygenases (UPOs).<sup>[5]</sup> CYPs are able to enzymatically convert FAs to alkanes and alkenes, while UPOs are emerging as promising biocatalysts in synthetic chemistry, for the wide portfolio of oxyfunctionalization reactions they catalyze. Starting from these target natural enzymes, through a stepwise process involving design, synthesis, and characterization, the most promising artificial biocatalysts, in terms of robustness, efficiency, and selectivity, will be selected and exploited in the conversion of recalcitrant substrates derived from marine waste biomass into low-carbon biofuels.

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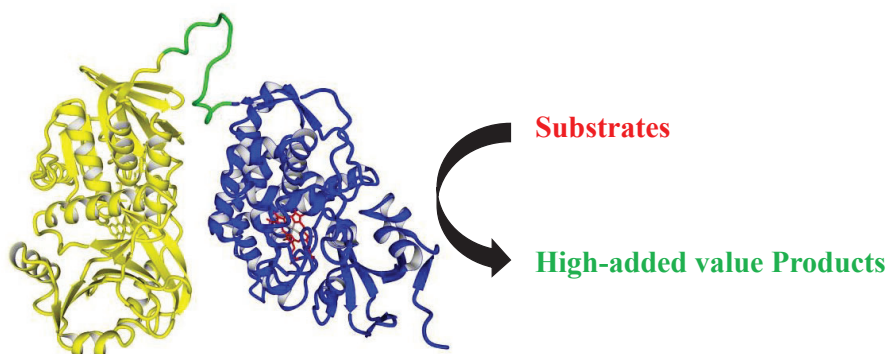
**George Paul Voicu**

*Università degli Studi di Torino*

**Engineering of new redox enzymes for the sustainable  
production of molecules with high added value**

**Supervisors:** Gianluca Catucci, Gianfranco Gilardi

**Thesis abstract:**



Redox reactions represent some of the most important chemical events in biochemistry. The vast majority of reductions and oxidations involving organic molecules rely on redox enzymes. Redox enzymes act as highly specialized and performant biocatalysts.

Among all, cytochromes P450 (CYPs) attract for their unique catalytic features. CYPs are a super-family of monooxygenase enzymes able to oxidize a miscellaneous variety of substrates. C-C and C-H bond selective oxidation can be easily achieved using these enzymes, bypassing the difficulties of organic synthesis. Bacterial systems possess a unique biotechnological potential since they are soluble and usually more stable. P450 BM3 (CYP102A1) is regarded not only as a model of such biocatalysts but also as an example of successful protein engineering. Protein engineering allows the modification of the chosen CYP system. The process will lead to a better catalytic activity as well as the incorporation of new features. Another method to improve or to generate new catalysts considers the fusion of different protein domains. It allows the creation of chimeras, new proteins that can present specific desired properties. As all CYPs, BM3 uses molecular oxygen to trigger its redox activity. The electrons needed for oxygen activation are retrieved from NADPH through a reductase domain. The use of such expensive cofactors negatively impacts on the usage of CYPs in biotechnological processes. The use of  $H_2O_2$  in alternative to NAD cofactors would revolutionize the application of CYPs in industrial processes. A possible solution is already provided: it consists in the creation of a chimeric system between the P450's heme domain and monomeric sarcosine oxidase (MSOX). The oxidase produces  $H_2O_2$  locally in a concentration that does not affect the stability of the enzyme.

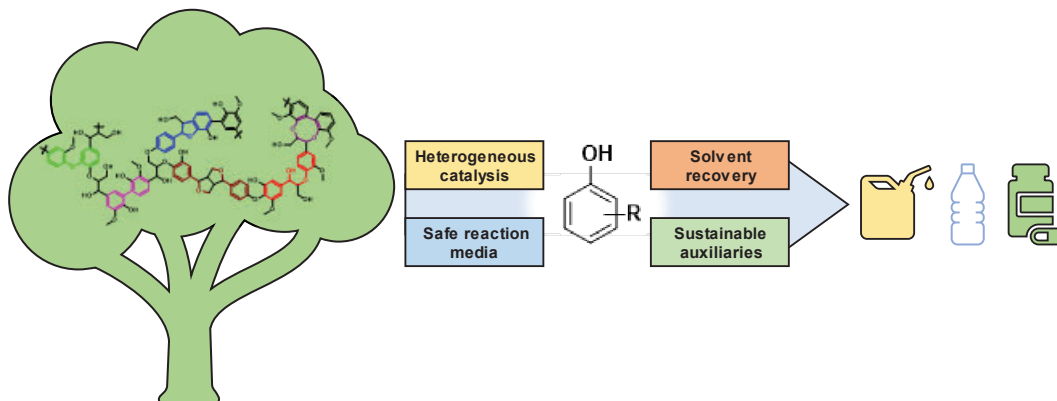
The end goal is the large-scale utilization of this cytochrome. Protein engineering supports the industrial transfer of P450s by enhancing specific features, namely thermostability, activity, and self-sufficiency.

**Edoardo Bazzica**

Local Institution: Università degli Studi di Perugia

## Green and circular strategies for biowaste valorization

Supervisor: Prof. Luigi Vaccaro



### Thesis abstract:

The present PhD project focuses on the valorization of products derived from biomass through the formation of value-added chemical compounds, following the principles of Green Chemistry. The increasing demand for petroleum, the decrease in petroleum resources, and environmental concerns bring to the need to the development of sustainable processes for the production of fuels and chemicals.<sup>1</sup> Plant biomass, with its ability to sequester CO<sub>2</sub> during plant growth, emerges as the best sustainable source of organic carbon and biofuel.

Lignocellulosic biomass, derived from agricultural and forestry residues, represents an abundant source of biomass.<sup>2</sup> Its transformation allows the production of biobased chemical products through processes such as hydrolysis, gasification, and pyrolysis.<sup>3</sup> Lignin, a key component of lignocellulosic biomass, can be utilized for the production of functionalized aromatic chemical compounds.<sup>4</sup>

The project focuses on the valorization of phenols derived from lignocellulosic biomass. The objective is to develop sustainable synthetic protocols in accordance with the principles of Green Chemistry. The use of heterogeneous catalytic systems, sustainable solvents, and flow reactors is anticipated to maximize energy efficiency. The ultimate goal is to improve the scalability of renewable feedstock upgrading processes, generating high-value chemical compounds, biofuels, and pharmaceutical products.

The project is structured around three specific objectives: the design of new heterogeneous catalytic systems, the identification of sustainable solvents, and the development of flow reactors to enhance energy efficiency. The overall aim is to contribute to the development of sustainable processes for the production of high-value chemical compounds, addressing environmental challenges and promoting innovation in the chemical industry.

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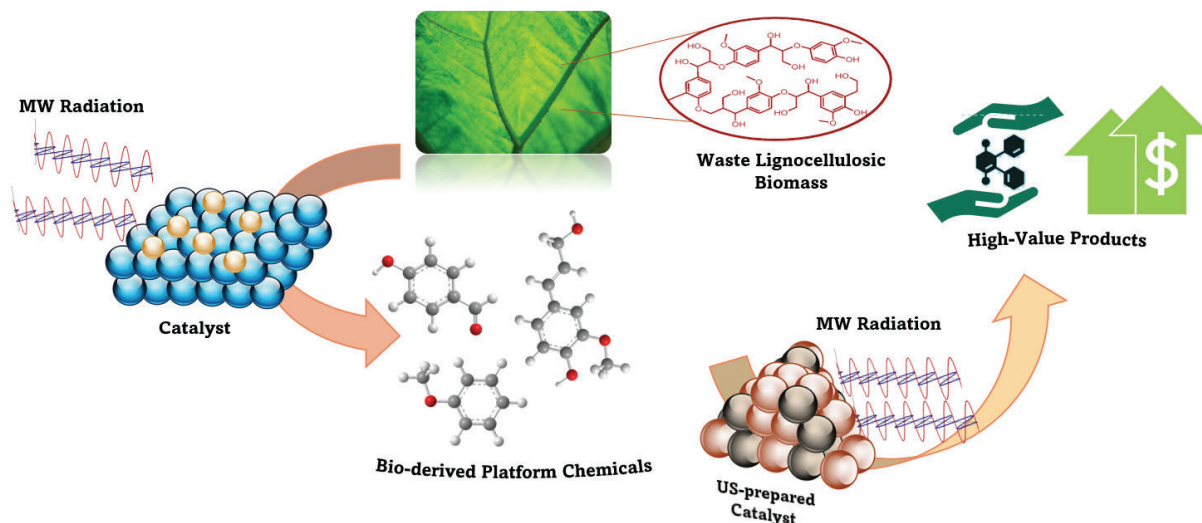
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**Chiara Bruschetta**

Local Institution: Università degli Studi di Torino

## Technologies for the Intensification of Eco-sustainable Catalytic processes

Supervisors: Maela Manzoli, Giancarlo Cravotto



### Thesis abstract:

Lignocellulosic biomass is the most abundant and available renewable source, and the main components are cellulose, hemicellulose, and lignin. These biopolymers are a source of platform chemicals that can be converted into high value-added products, especially when considering waste biomasses. However, the development of energy-efficient and eco-sustainable conversion processes is limited by the complexity of lignocellulosic biomass chemistry, which hampers the exploitation of current catalytic processes to effective valorisation. Therefore, the combination of innovative technological approaches and robust heterogeneous catalysts developed *ad hoc* represents an efficient strategy to overcome these limits.

In this doctorate project new sustainable catalytic processes using enabling technologies such as ultrasound (US) and microwaves (MW) combined with heterogeneous catalysis will be developed for waste biomass conversion into added value products, according to a biorefinery approach. US create severe physicochemical environments via acoustic cavitation, to obtain highly dispersed and robust catalysts and to improve the accessibility of recalcitrant biomass. On the other hand, MW-assisted processing of biomass can help improving heat transfer. Indeed, the effect of MW irradiation at a molecular level, in the case of lignocellulosic biomass, leads to a physical disruption of the internal composition of cells, which increases the rate of mass transfer. Furthermore, the use of heterogeneous catalysts under MW irradiation may selectively generate “hot spots” that can dramatically accelerate reaction rates.

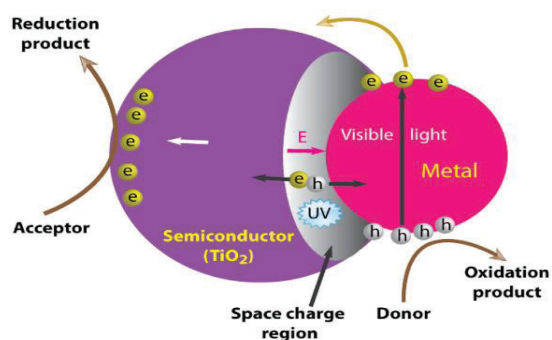
The aim of this project is to investigate different types of catalytic systems by screening different compositions to design catalysts that can selectively activate specific bonds of waste biomass to obtain platform chemicals. These can then be used in further steps both for conversion to high value-added products and for the synthesis of biopolymers using other *ad hoc* synthesized catalysts.

**Michele Bucchieri**

*Local Institution: Politecnico di Torino*

**SYNTHESIS AND CHARACTERIZATION OF PHOTOCATALYSTS ENHANCED BY UPCONVERSION SYSTEMS AND/OR PLASMONIC NANOMATERIALS TO EXPLOIT SUNLIGHT IN REACTIONS OF ENVIRONMENTAL INTEREST.**

**Supervisors:** Barbara Bonelli  
Francesca S. Freyria



**Thesis abstract (max. 300 words):**

TiO<sub>2</sub> is one of the most studied materials in the field of photocatalysis, because is non-toxic, environmentally friendly, providing a high photocatalytic activity (in the UV) and good chemical stability, etc. Among the different polymorphs of TiO<sub>2</sub>, the most exploited ones in this field are: anatase, rutile and brookite.

Even if TiO<sub>2</sub> is characterised by a high extinction cross section in the UV, it has a low photon harvesting efficiency in the IR and in the visible range (since its band-gap is around 3 eV); in order to improve its photocatalytic activity under sunlight, TiO<sub>2</sub> can be coupled with plasmonic metal nanoparticles (PMNPs) and/or upconversion systems (UCSs).

PMNPs are light-harvesting nanomaterials able to collect visible light near their surface, generating very efficiently photoexcited charge carriers; in particular this occurs when the wavelength of the incident light is longer than the size of the PMNP, causing a resonant collective oscillation of its free electrons; the elevated electric fields, generated near the surface, are able to trigger different reactions providing high reaction yield and good product selectivity.

UCSs have the ability to convert two or more low-energy photons (generally in the IR range) into one high-energy photon (generally in the UV-visible range). UCSs generally consist of a pair formed by a sensitizer species that has the task to absorb a lower-energy incident radiation and an annihilator/emitter system which, once collected the excitation energy from the sensitizer will emit via fluorescence a higher-energy radiation.

The task of my PhD project consists of synthesizing and characterizing a new generation of TiO<sub>2</sub>-based photocatalysts enhanced by PMNPs and/or UCSs. Such new systems will be validated in reactions of environmental interest, since they should be able to harvest and exploit sunlight more efficiently with respect to bare TiO<sub>2</sub>, resulting into higher reaction yield and product selectivity.

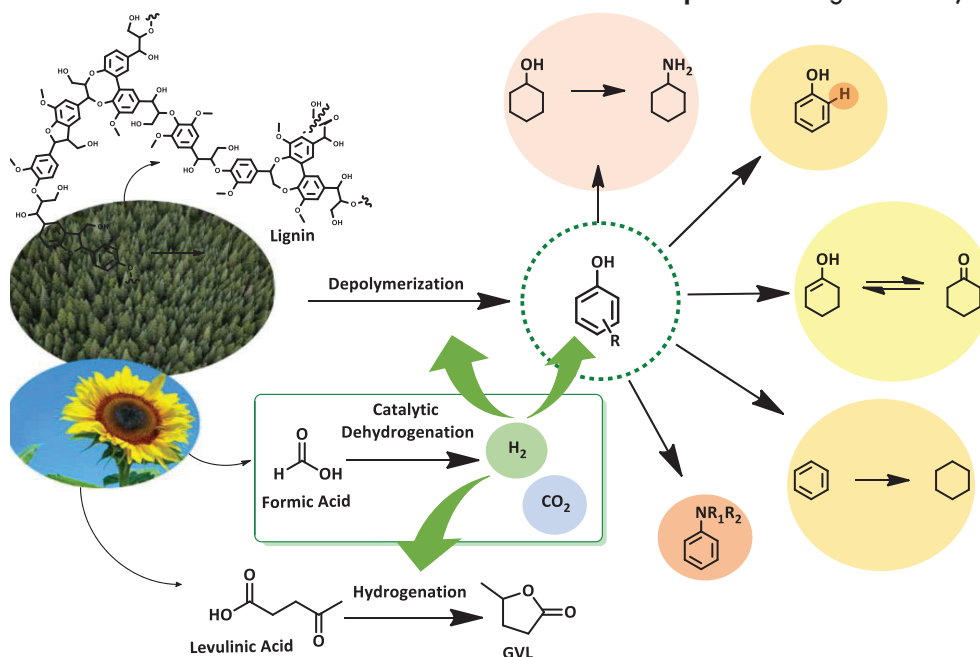
**Marta Ciani**

Università degli studi di Perugia

Dipartimento di Chimica, Biologia e Biotecnologie

## Circular catalytic processes of the valorization of waste and the production of hydrogen from LOHCs

Supervisor: Luigi Vaccaro, Francesco Ferlin



### Thesis abstract:

The urgent need to substantially decrease  $CO_2$  emissions is steering the transformation of our existing carbon-based energy system toward a more sustainable paradigm focused on renewable sources. Hydrogen, acknowledged as a clean energy carrier, encounters challenges in terms of transport and storage. Liquid Organic Hydrogen Carriers (LOHCs), equipped with hydrogen storage capacity, provide a solution by enabling on-site hydrogen generation for direct utilization in producing valuable chemicals. Specific LOHCs, derived from biomass such as formic acid, isopropanol, or methanol, facilitate a circular process for biomass valorization. Hydrogen stored as formic acid can partake in diverse transformations of biomass-derived platform molecules, including levulinic acid and lignin. Lignin, a significant byproduct in the cellulose and paper industry, undergoes controlled reductive depolymerization using LOHC-generated hydrogen, yielding variously substituted phenols as renewable starting materials. The development of recyclable heterogeneous catalytic systems, utilizing Pd and Ni, allows the utilization of hydrogen produced from formic acid and its salts in the hydrogenation processes of phenol. This leads to the primary formation of cyclohexanone, a pivotal synthetic intermediate that itself functions as an LOHC.

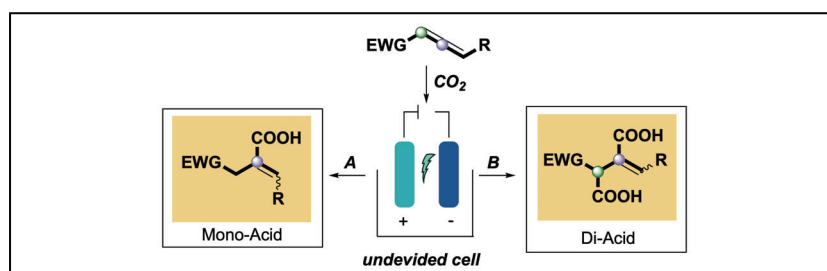
Formic acid, phenols, and heterogeneous catalysts play integral roles in reductive amination, hydrogen borrowing, and dearomatization/rearomatization processes, yielding a diverse array of high-value chemicals. Opting for heterogeneous catalysis represents a greener choice, facilitating the recovery and recycling of the catalyst. The selection of the support material becomes crucial in effectively producing hydrogen from various LOHCs derived from both biomass and non-biomass sources, particularly formic acid. Two types of supports are under consideration: POLITAG, cross-linked polystyrenes with the significant advantage of being easily modified, and activated carbon obtained from biomass. Furthermore, employing flow reactors and microwave reactors enhances the scalability of these processes, improves intrinsic safety, and provides better control over reactivity and reaction parameters.

Mauro Garbini

Alma Mater Studiorum – Università di Bologna

*Development of new homo- and heterogeneous catalytic protocols for the valorization of CO<sub>2</sub>*

Supervisors: Marco Bandini



**Thesis abstract:**

In the first part of my PhD research, I will focus on the development of novel homogeneous catalysis systems for the valorization of CO<sub>2</sub>, by harnessing the advantages of electrocatalysis. The use of electrocatalysis as an enabling technique offers distinct advantages, including enhanced control over reaction conditions, the ability to access unique and challenging chemical transformations, and the potential for the development of environmentally sustainable processes. Here, specific organic scaffolds will be employed for the CO<sub>2</sub> fixation, by merging metallic catalyst and electroChem. The preparative electrochemical reactions relied on the use of the “Electrasyn 2.0” apparatus in which different parameters can be easily set and tuned to rapidly optimize an efficient preparative redox process: reaction voltage, current, Faraday per mole of the substrate, electrodes and electrolytes.

Electron-deficient compounds hold great significance in the context of fixation of CO<sub>2</sub>, making them a fascinating focus of investigation. In this context, 1,3-disubstituted allenes are a class of chemically tunable starting materials in which we fix CO<sub>2</sub> under site-selective manner.

The goal of this project is to investigate the electrocatalytic reduction of electron-deficient sites of allenes, aiming to capture CO<sub>2</sub> (atmospheric pressure) during the reaction, for the preparation of substituted itaconic acids. Preliminary results indicated a peculiar electrochemical parameters/ reaction outcome correlation. In particular, by altering the current (mA), total charge (F/mol) and reaction temperature, one (Cond. A) or two molecules (Cond. B) of CO<sub>2</sub> could be captured in the allenyl scaffold in a regio- and stereoselective manner.

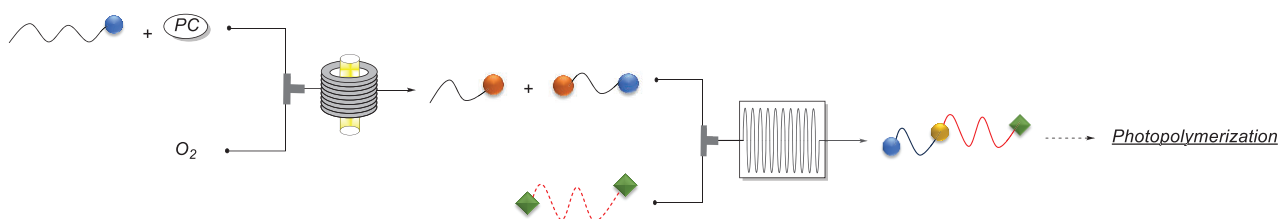


**Sara Stocchetti**

*Local Institution: Università degli Studi di Cagliari*

**From biomass to catalysis. An integrated platform for the development of new catalysts and their application in the synthesis of biobased monomers and polymers.**

**Supervisors:** Francesco Secci, Alberto Luridiana



*Figure: Flow process for the realization of new organic building blocks.*

**Thesis abstract:**

In the context of this project, novel catalytic processes are introduced to convert biomass fractions into valuable chemicals, playing a pivotal role in sustaining the chemical industries.<sup>1</sup> A series of initiatives will be undertaken to establish an integrated platform that harnesses biomolecules sourced from industrial and agricultural waste. This platform will be dedicated to the synthesis and post-functionalization of organic building blocks and photoactive molecules tailored for light-driven applications. The overarching objective is to propel environmentally conscious practices and promote the development of greener materials within the bioeconomy, ultimately reducing dependence on fossil hydrocarbon sources.<sup>2</sup> Furthermore, the project will focus on the development of new continuous flow synthetic (multistep) processes and enabling technologies for the production of organic fine chemicals.<sup>3, 4</sup> Special attention will be given to the synthesis of low-viscosity polyesters with a high carbon content derived from vegetable sources, specifically for the production of biolubricant bases.

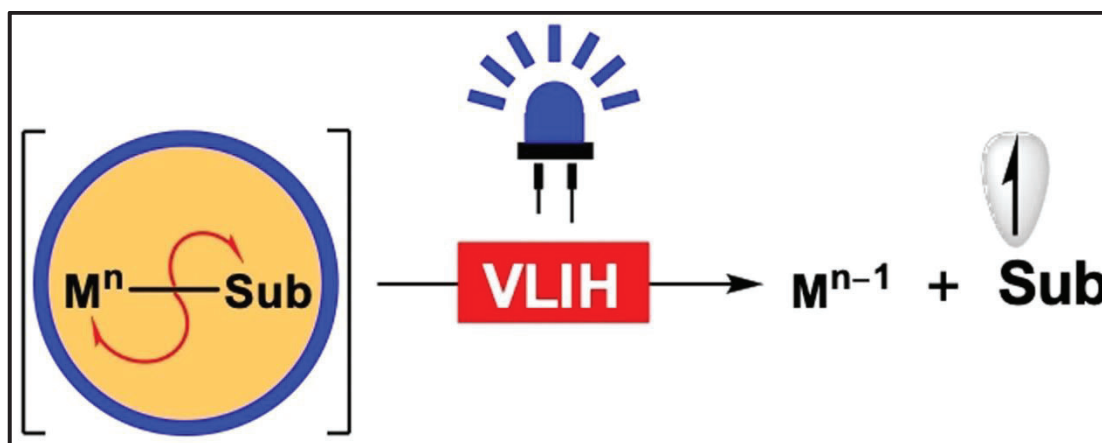
1. ACS Catal. 2018, 8, 2129–2165.
2. ACS Sustainable Chem. Eng. 2021, 9, 5486–5505.
3. Chem. Sci., 2023, 14, 4230.
4. ACS Macro Lett. 2020, 9, 123–133.

**Madan Mohan Urma**

*Università degli Studi di Sassari*

**Development of new photocatalysts based on earth-abundant metals  
and their applications in sustainable organic methodologies**

**Supervisors:** Prof. Lidia Vera Giovanna De Luca



The use of earth-abundant metal complexes in photoredox catalysis offers a complementary mode of activation for organic substrates through visible-light-induced homolysis (VLIH) of metal-substrate bonds

**Thesis abstract:**

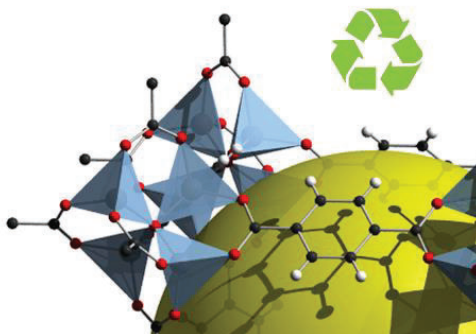
Over the last decade, the prevalence of the visible light photoredox catalysis have exploded exponentially. With majority of photocatalytic process included heavy metal such as Ru(II) or Ir(III) complexes and organic dyes which have been studied extensively over the decade. This type catalyst generally based on outer-sphere single-electron transfer (SET) or energy transfer (EnT) processes for organic transformation for the substrate. Unfortunately, with such metals being rare in earth, it is expensive and not viable for commercial large scale photochemical process. Alternate to rare earth metal based photocatalyst, earth-abundant metal-based photocatalysts are being employed in visible light photoredox catalysis for their low cost and low environmental impact, through overcoming their intrinsic limitations of having ultrashort excited-state lifetimes compared to Ru(II) or Ir(III) based photocatalysts. This type of catalysts are based on Visible-light-induced homolysis (VLIH), which is defined as the process that starts with the generation of suitable ligated metal-substrate complexes ( $M^n$ -Sub) that can both absorb light and cleave homolytically to yield metal complexes ( $M^{n-1}$ ) and substrates (Sub) for further transformations. Visible-light-induced homolysis (VLIH) along with Ligand-to-Metal Charge Transfer (LMCT) Photochemistry will change the upcoming landscape of the field of photochemistry.

**Maristella Simone**

Department of Pharmacy-Drug Sciences, University of Bari Aldo Moro (Italy)

## **Innovative Synthesis of MOFs in DESs and Their Application in Metal-Catalysis**

**Supervisors:** Vito Capriati, Filippo Maria Perna, Paola Vitale



### **Thesis abstract:**

Over the past decades, metal-organic frameworks (MOFs) have emerged as an extensive class of crystalline materials with ultrahigh porosity and enormous internal surface areas. Despite their obvious usefulness, most cross-coupling reactions facilitated by MOFs continue to heavily rely on air-sensitive, precious metal catalysts, typically involving Pd. These processes often mandate the use of degassed toxic and flammable volatile organic compounds as solvents. In addition, the prevailing synthetic methods employed for their preparation typically require harsh reaction conditions and prolonged heating of precursors under autogenous pressure.

Deep Eutectic Solvents (DESs) represent an emerging class of green and bio-renewable solvents. They are mixtures of hydrogen bond donors and hydrogen bond acceptors, usually Lewis or Brønsted acids and bases, exhibiting a melting point much lower than either of the individual components. The application of DESs in the synthesis of MOFs is still in its infancy. DESs properties make them excellent candidates for the preparation of MOFs, whose morphology and porosity are known to be strongly influenced by the nature of the solvent besides that of the organic linkers.

Through meticulous adjustments to the composition and structures of MOFs, synthesized in DESs, employing either alkaline-earth (Ae) or first-row d-block transition metals, this research endeavors to harness the unique capabilities of these tailored MOFs in demanding cross-coupling reactions. Examples include Suzuki-Miyaura, Mizoroki-Heck, Sonogashira, Ullmann, and Goldberg reactions, typically run with Pd complexes. Going considerably beyond the current state of the art, this research will also delve into uncharted territory by exploring novel MOF-Ae and MOF-d-catalyzed cross-coupling reactions employing organolithiums, organozinc, and even organosodium reagents in DESs. The ultimate goal is to target crucial intermediates essential for the synthesis of Active Pharmaceutical Ingredients (APIs).