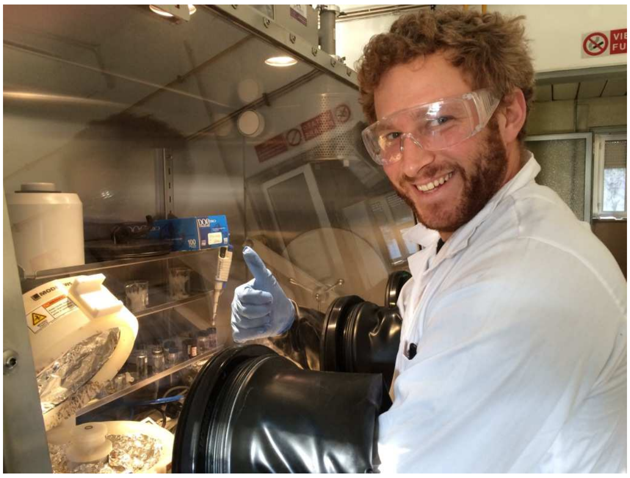
UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI CHIMICA

SmartMatLab Workshop



http://users2.unimi.it/smartmatlab/wordpress/

fse per il tuo futuro

fondazione cariplo

UNIONE EUROPEA
Fondo europeo di sviluppo regionale

Regione Lombardia

istm
istituto di scienze e tecnologie molecolari

POR COMPETITIVITÀ 2007-2013
CON L'EUROPA PER CRESCERE INSIEME

COMITATO SCIENTIFICO

Dipartimento di Chimica Università degli Studi di Milano

Elena SELLI

Maddalena PIZZOTTI

Patrizia MUSSINI

Gianfranco TANTARDINI

Giuseppe D'ALFONSO

Monica PANIGATI

Gian Luca CHIARELLO

Maria Vittoria DOZZI

CNR – ISTM

Rinaldo PSARO

Alberto BOSSI

Alessio ORBELLI BIROLI

SmartMatLab Workshop Program

Aula 403 del settore didattico Celoria

15 Novembre 2017

9.00 – 9.30	Apertura dei lavori **Chiara Tonelli**, Prorettore per la Ricerca **Laura Prati**, Direttore Dipartimento di Chimica **Elena Selli**, PI Progetto SmartMatLab
9.30 – 10.00	IL1 – **Stefano Caramori**, Università di Ferrara *Photoelectrodes for Solar Energy Conversion and Water Remediation*
10.00 – 10.30	IL2 – **Francesco Galeotti**, CNR ISMAC *Self-assembled Nano- and Microstructures for Optoelectronics*
10.30 – 11.00	IL3 – **Paolo Vacca**, SAES GETTERS *Functional Chemicals for Active Packaging*
11.00 – 11.30	Coffe Break
11.30 – 12.00	IL4 – **Michele Muccini**, CNR ISMN *Organic Light Emitting Transistors Technology*
12.00 – 12.15	OC1 – **Alberto Bossi**, CNR ISTM *Chemistry & OLEDs: the Journey of Blue and NearIR Emitters from the Hood to the Device*
12.15 – 12.30	OC2 – **Francesca Tessore**, Dipartimento di Chimica *Porphyrin Sensitized Solar Cells: the Challenge of Photostability*
12.30 – 12.45	OC3 – **Gian Luca Chiarello**, Dipartimento di Chimica *Exploiting Photonic and Electronic Properties of Semiconductor Thin Films to Enhance their Photocatalytic Performance*
12.45 – 13.00	OC4 – **Mirko Magni**, Dipartimento di Chimica *Going beyond the Surface: a Glance inside Smart Conducting Molecular Surfaces through a Multitechnique Approach*
13.00 – 14.00	Lunch Break
14.00 – 14.30	IL5 – **Claudio Fontanesi**, Università di Modena *Spin Dependent Electrochemistry: Water Splitting on Anodes Made of Chiral Materials*
14.30 – 14.45	OC5 – **Maciej Zalas**, Adam Mickiewicz University in Poznan, Poland *Materials and Dyes for Dye-sensitized Solar Cells*

14.45 – 15.00	OC6 – **Silvia Cauteruccio**, Dipartimento di Chimica *Heteroaromatic Systems as Organic Semiconductors and Luminescent Au(I) Complexes for Biological Application*
15.00 – 15.15	OC7 – **Andrea Previtali**, Dipartimento di Chimica *Cyclic Triimidazole Derivatives: Intriguing Cases of Multiple Emissions and RT Ultralong Phosphorescence*
15.15 – 15.30	OC8 – **Valeria Comite**, Dipartimento di Chimica *The Assessment of the Carbonaceous Component in Black Crusts Damaging the Stone Surfaces of Historical Monuments (from Trevi Fountain Roma to Square San Marco Venice)*
15.30 – 15.45	OC9 – **Elisa Albanese**, Università di Milano Bicocca *Heterojunction for Solar Energy Conversion: Electronic Band Alignment Modelling*
15.45 – 16.00	OC10 – **Craig Evans**, Politecnico di Milano *Physical Chemistry Techniques for Antimatter Research*
16.00 – 16.30	IL6 – **Francesco Sannicolò**, Università di Milano e Laboratori Alchemia *Applying the "Inherent Chirality" Concept to the Design of Functional Molecular Materials with Impressive Enantiorecognition Properties*
16.30	Chiusura del workshop

Sarà possibile visitare il laboratorio SmartMatLab durante le pause del convegno.

Invited Lectures (IL)

Photoelectrodes for Solar Energy Conversion and Water Remediation

Stefano Caramori,[a] Carlo Alberto Bignozzi,[a] Vito Cristino,[a] Serena Berardi,[a] Michele Orlandi,[b]
Gelsomina Longobucco,[a] Luisa Pasti[a]

[a] *Dipartimento di Scienze Chimiche e Farmaceutiche dell'Università di Ferrara, Via Luigi Borsari 46, 44121, Ferrara*
[b] *Dipartimento di Fisica dell'Università di Trento, Via Sommarive 14, 38123, Povo (Tn)*

cte@unife.it

WO_3 [1], hematite (α-Fe_2O_3) [2] and WO_3-$BiVO_4$ are wide band gap semiconductors that can be obtained under nanocrystalline form and serve as the photo-anodic compartment (i.e. the oxygen evolving compartment) of a photoelectrochemical cell for solar fuel production. In this contribution some results about the charge transfer dynamics at the semiconductor/electrolyte interface gained by combining Transient Absorption Spectroscopy and Electrochemical Impedance Spectroscopy are reported. Viable approaches to improve the photoelectrochemical response of these materials are also discussed. Finally, we focus on the environmental applications of these materials, by considering the degradation of some Contaminants of Emerging Concern which are present in potable water and are impervious to conventional decontamination techniques [3].

References

[1] a) V. Cristino et al. *Langmuir*, **2011**, *27,* 7276-7284; b) V. Cristino et. al. *J. Mater. Chem. A,* **2016**, *4*, 2995-3006.
[2] a) N. Dalle Carbonare et. al. *PCCP*, **2015,** *17* 29661-29670; b) M. Orlandi et. al. *ACS Applied Mater. & Interf.*, **2016**, *8*, 20003-20011.
[3] G. Longobucco et al. *Applied Catalysis B: Environmental*, **2017**, *204,* 273-282.

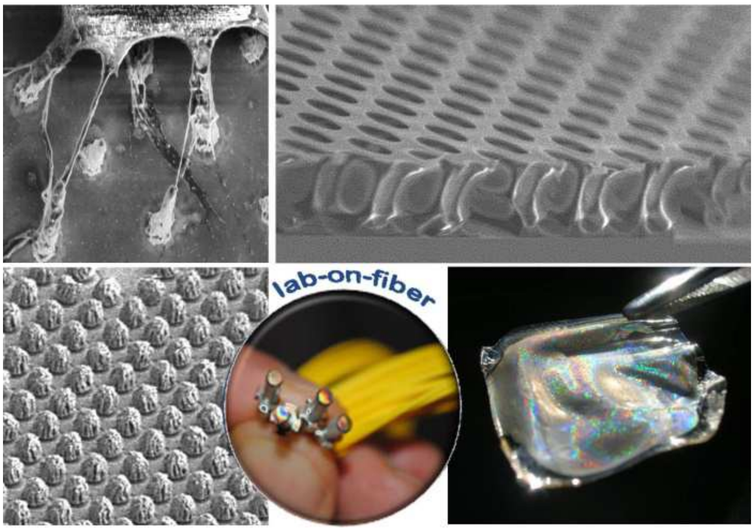
Self-assembled Nano- and Microstructures for Optoelectronics

Francesco Galeotti

ISMAC-CNR, Via A. Corti 12, 20133 Milano
galeotti@ismac.cnr.it

Nanostructured surfaces can offer different advantages compared to flat ones in terms of interaction with the external medium, interaction with target molecules and biomolecules and interaction with light. Just as nature teaches us, nanostructures are able to provide some specific properties like self-cleaning, super-hydrophobicity, antireflection or iridescence, that are dictated mostly by morphological organization than by the chemical composition of the material. Because manipulating the matter at the nano- and microscale is rather complex, nanofabrication of well-defined structures normally requires advanced technological instrumentation and expensive processes. Self-assembly, in this contest, is a valuable alternative toll for realizing nano- and microstructures with high resolution, high throughput and at relatively low-costs.

This contribution will focus on the exploitation of some different self-assembly processes for the preparation of structured surfaces based on polymeric materials [1-3]. The techniques here employed, based on breath figures templating, colloidal assembly and phase separation, allow the development of functional surfaces with properties appealing for different field of optoelectronics, from light emitting devices to solar cells and biosensors.



References

[1] M. Pisco, F. Galeotti, G. Quero, G. Grisci, A. Micco, L.V. Mercaldo, P.D. Veneri, A. Cutolo, A. Cusano, *Light: Science and Applications*, **2017**, *6*(5), e16229.

[2] V. Vohra, F. Galeotti, U. Giovanella, T. Anzai, E. Kozma, C. Botta, *Applied Physics Letters*, **2016**, *109*(10), 103702.

[3] F. Galeotti, W. Mróz, M. Catellani, B. Kutrzeba-Kotowska, E. Kozma, *Journal of Materials Chemistry C*, **2016**, *4*(23), 5407.

IL3

Functional Chemicals for Advanced Packaging Solutions

Paolo Vacca, Alessandra Colombo, Miriam Riva, Gaetano Campanella, Sergio Santoro

SAES Getters S.p.A., Corporate LABs, viale Italia 77, Lainate (MI)
paolo_vacca@saes-group.com

New approaches for efficient packaging solutions are continuously under scrutiny to ensure longer shelf life coupled to safety store conditions. In this regard, the development of new materials is a fundamental step in introducing innovative functions in conventional configurations and knowledge intensive approaches need relevant efforts in R&D activities. For the last seventy years, SAES core technologies have enabled the preparation of innovative materials to meet the customer needs in several industrial application up to the more recent definition of an innovative technology platform based on Functional Chemicals. Starting from the SAES getter technology, new approaches have been designed to prepare nanoparticles and microcapsules by adopting both bottom-up and top-down procedures able to guarantee high flexibility in properties tuning. These materials represent a tremendously versatile and promising platform to prepare new systems with tunable reactivity and to enable their efficient integration in proprietary organic formulations.

Functional Chemicals based on nanozeolites, submicro metal-oxides and polymer capsules area adopted to produce innovative coating for advanced packaging solutions where new functional properties in terms of solid-gas interaction for both VOC adsorption/releasing and gas permselectivity are introduced. The integration of these functionalities in organic formulations has enabled the development of a new family of dispensable products (Fig.1). A right combination of metal oxides and siloxane matrices are adopted to produce dryer pastes to guarantee dry conditions in organic electronics and implantable devices ensuring suitable shelf life in combination with active sealants [1]. For demanding applications (e.g. OLED devices in top emission configuration and flexible OPV modules) where getter functionalities have to be coupled to high transparency and fast process constraints (inkjet printing), a composite system based on inorganic salt dispersed in a polymeric acrylic matrix has been developed [2,3]. Finally, the continuous exploitation of SAES ZeoTec based on solgel hydrothermal synthesis is allowing the development of engineered zeolites with designed characteristics able to ensure selective getter functionalities for active packaging applications [4].

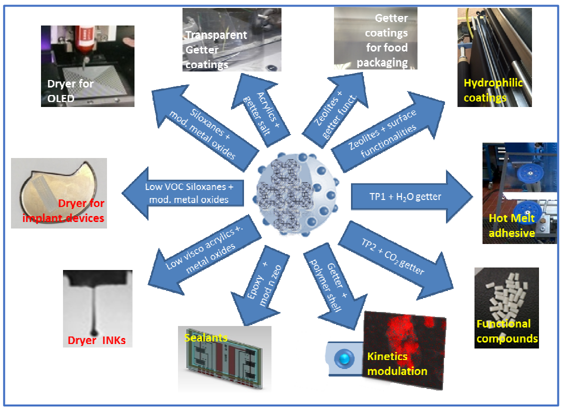


Fig. 1. Overview of new products based on SAES Functional Chemicals.

References

[1] P. Vacca, in *Organic and Printed Electronics, Fundamentals and Application* (Edited by G. Nisato, D. Lupo and S. Ganz), Pan Stanford Editor, **2016.**

[2] P. Vacca, *Dispensable polymeric precursor composition for transparent composite sorber materials*. PCT 2012, WO045557A1.

[3] V. Crocellà, E. Groppo, A. Dani, A. Castellero, S. Bordiga, S. Zilio, A. De Simone, P. Vacca, *Applied Spectroscopy*, **2017**, *71*, 2278-2285.

[4] M. Riva, A. Colombo, P.Vacca, *Active Packaging*, WO2016125050A1.

Organic Light Emitting Transistors Technology

Michele Muccini

CNR-ISMN, via P. Gobetti 101, 40129 Bologna, Italy
michele.muccini@cnr.it

Organic light-emitting transistors (OLETs) combine the current modulating function of a transistor with light emission, and offer new simplified solutions for nanoscale light sources and highly integrated organic optoelectronics. By benchmarking the planar transistor structure of OLETs with the vertical diode architecture of OLEDs, it is clear that OLETs have the potential to achieve similar optoelectronic and photonic performances with much simpler architectures and lower production costs.

Given the recent results in the fabrication of bright, efficient and reliable devices, it is expected in the near future that the full compatibility of OLETs with well-established electronic and photonic planar technologies will allow the development of viable technological solutions in various application field, including display technology and sensing. However, the practical implementation of the OLET technology requires the development of carefully engineered device structures capable of reducing driving voltages and enhance the photonic performances.

We will analyze the electronic, optoelectronic and photonic properties of semiconducting materials, which make them suitable for single-layer or multi-layer OLETs. In addition, we report on the realization of highly integrated multifunctional optoelectronic organic device by introducing a high-capacitance photonic crystal as a gate dielectric into a transparent single-layer ambipolar organic light-emitting transistor (OLET). These results have the potential to enable the realization of highly integrated optoelectronic smart systems based on organic light-emitting transistors.

References

[1] M. Muccini, *Nature Materials,* **2006**, *5*, 605.
[2] R. Capelli, S. Toffanin, G. Generali1, H. Usta, A. Facchetti, M. Muccini, *Nature Materials,* **2010**, *9*, 496.
[3] W. Koopman, et al., *Nano Lett.*, **2014**, *14,* 1695.
[4] M. Muccini, S. Toffanin, *Organic Light Emitting Transistors: towards the next generation display technology, Ed. John Wiley & Sons, New York,* **2016**.
[5] M. Natali, S.D. Quiroga, L. Passoni, L. Criante, E. Benvenuti, G. Bolognini, L. Favaretto, M. Melucci, M. Muccini, F. Scotognella, F. Di Fonzo, S. Toffanin, *Adv. Funct. Mater.*, **2017**, 1605164.

Spin Dependent Electrochemistry: Water Splitting on Anodes Made of Chiral Materials

Claudio Fontanesi

Department of Engineering, "Enzo Ferrari", Via Vivarelli 10, 41125, Modena
claudio.fontanesi@unimore.it

The spin-dependent electrochemistry (SDE) method [1] can be exploited to improve the efficiency of hydrogen production obtained via electrochemical/photo-electrochemical dissociation of water, i.e. water splitting. Indeed, the water splitting process is hampered by its poor overall efficiency, which is still a major concern. The main problem is the overall low current density, eventually making the H_2 evolution an expensive and sloppy process. This drawback is quantitatively expressed by the need to apply a larger potential with respect to the thermodynamic value: over-potential (η). The larger contribution to η is due to the multi-electron-transfer/multi-step oxygen evolution reaction (OER), causing $\eta \geq 0.6$ V. Remarkably, in the overall OER reaction, two water molecules are oxidized to yield a single O_2 molecule in its triplet ground state. Thus, spin correlation is supposed to play a role in the O_2 production: the radicals which react to finally form O_2, must have their electronic spin co-aligned in the laboratory frame. The singlet O_2 ($^1O_2$) is about 100 kJ mol^{-1} higher in energy than triplet oxygen ($^3O_2$). Altogether, the efficiency of the hydrogen production depends strongly on the anode design to enhance production of the triplet oxygen. Many reports have indicated that during water splitting, oxygen is produced as a final product from the disproportionation of hydrogen peroxide. This has been explained as part of a complex multi-step process in which hydrogen peroxide is formed first [2]. This is consistent with the fact that the formation of hydrogen peroxide is kinetically favorable compared to oxygen, but it has a high thermodynamic value, approximately 0.60 V higher than that of oxygen. Hydrogen peroxide formation results a competing process with respect to OER, and has a negative effect on the overall hydrogen production efficiency. Details concerning the exploitation of SDE (exploiting anodes prepared with chiral materials) in the water splitting process can be found in the literature [3,4]. A patent is pending on the chiral water splitting method [5].

References

[1] D. Mishra, T.Z. Markus, R. Naaman, M. Kettner, B. Gohler, H. Zacharias, N. Friedman, M. Sheves, C. Fontanesi, Spin-dependent electron transmission through bacteriorhodopsin embedded in purple membrane, *Proc. Natl. Acad. Sci.*, **2013**, *110*, 14872.

[2] M. Favaro, C. Valero-Vidal, J. Eichhorn, F. M. Toma, P. N. Ross, J. Yano, Z. Liu, E. J. Crumlin, Elucidating the alkaline oxygen evolution reaction mechanism on platinum, *J. Mater. Chem. A.*, **2017**, *5*, 11634.

[3] W. Mtangi, V. Kiran, C. Fontanesi, R. Naaman, Role of the Electron Spin Polarization in Water Splitting, *J. Phys. Chem. Lett.*, **2015**, *6*, 4916.

[4] W. Mtangi, F. Tassinari, K. Vankayala, A. Vargas Jentzsch, B. Adelizzi, A.R.A. Palmans, C. Fontanesi, E.W. Meijer, R. Naaman, Control of Electrons' Spin Eliminates Hydrogen Peroxide Formation During Water Splitting, *J. Am. Chem. Soc.*, **2017**, *139*, 2794.

[5] R. Naaman, C. Fontanesi, W. Mtangi, Water Splitting Method and System, WO/2016/056011, **2016**.

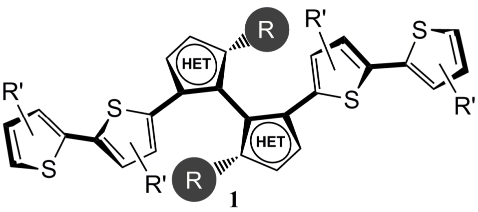
Applying the "Inherent Chirality" Concept to the Design of Functional Molecular Materials with Impressive Enantiorecognition Properties

Francesco Sannicolò,[a,b] Tiziana Benincori,[c] Simona Rizzo,[d] Patrizia R. Mussini,[a] Arnaboldi Serena,[a] Roberto Cirilli,[e] Monica Panigati,[a] Rocco Martinazzo,[a] Marco Pierini,[f] Andrea Marchesi,[b] Giovanna Longhi[g]

[a] *Università degli Studi di Milano, Dipartimento di Chimica, via Venezian 21, 20133, Milano (Italy)*
[b] *Laboratori Alchemia S. R. L., via San Faustino 68, 20134, Milano (Italy)*
[c] *Università degli Studi dell'Insubria, Dipartimento di Scienza e Alta Tecnologia, via Valleggio 11, 22100, Como (Italy)*
[d] *C.N.R., Istituto di Scienze e Tecnologie Molecolari, via Venezian 21, 20133, Milano (Italy)*
[e] *Istituto Superiore di Sanità, Dipartimento del Farmaco, Viale Regina Elena 299, 00161, Roma (Italy)*
[f] *Università di Roma 1, Dipartimento di Chimica e Tecnologia del Farmaco, Piazza Aldo Moro, 5, 00185 Roma (Italy)*
[g] *Università degli Studi di Brescia, Dipartimento di Medicina Molecolare e Traslazionale, Viale Europa 11, 25123, Brescia (Italy)*

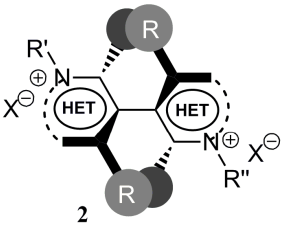
francesco.sannicolo@unimi.it

The classical design of chiral functional molecular materials involves attaching chiral pendants to molecules containing the functional groups able to bestow a specific property on the material. According to this strategy, chirality is conveyed to the functional groups "from outside" and, consequently, their enantiodiscrimination properties are modest. The "inherent chirality" concept requires that the stereogenic element responsible for molecular chirality and the functional group responsible for the specific properties of the material coincide. The consequence is that chirality and specific properties are indissolubly connected. This strategy is very successfully applied to design non-conventional chiral electrocondutive poly-conjugated heterocyclic oligomers [1,2] (and corresponding polymers [3]) and of chiral Ionic Liquids (CILs) [4] having general structure **1** and **2** respectively. In these systems chirality is produced by a torsion in the electoconductive backbone in the former case and, in the latter, by a distortion from coplanarity of two interconnected imidazolium or pyridinium rings, which are typical functional scaffolds of ILs. Coating electrodes with films resulting from the oxidation of enantiopure oligomers **1** [5], or addition of traces of **2** to achiral IL media [4] gave impressive unprecedented differences (up to 400 mV) between the oxidation peak potential of the enantiomers of several probes, differing in structure, functional groups and stereogenic element.



1

HET = 5 membered heteroaromatic ring



2

HET = 5 or 6 membered heteroaromatic ring

References

[1] F. Sannicolò, S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P.R. Mussini, M. Panigati, M. Pierini, S. Rizzo, *Angew. Chem. Int. Ed.*, **2014**, *53*, 2623.

[2] F. Sannicolò, P.R. Mussini, T. Benincori, S. Arnaboldi, G. Appoloni, M. Panigati, E. Quartapelle Procopio, R. Martinazzo, R. Cirilli, W. Kutner, K. Noworyta, A. Pietrzyk-Le, Z. Iskierko, K. Bartold, *Chem. Eur. J.*, **2016**, *22*, 10681.

[3] F. Sannicolò, P.R. Mussini, T. Benincori, R. Cirilli, S. Abbate, S. Arnaboldi, S. Casolo, E. Castiglioni, G. Longhi, R. Martinazzo, M. Panigati, M. Pappini, E. Quartapelle Procopio, S. Rizzo, *Chem. Eur. J.*, **2014**, *20*, 15257.

[4] S. Rizzo, S. Arnaboldi, V. Mihali, R. Cirilli, A. Forni, A. Gennaro, A.A. Isse, M. Pierini, P.R. Mussini, F. Sannicolò, *Angew. Chem. Int. Ed.*, **2017**, *29*, 2111.

[5] S. Arnaboldi, T. Benincori, R. Cirilli, W. Kutner, M. Magni, P.R. Mussini, K. Noworyta, F. Sannicolò, *Chem. Sci.*, **2015**, *6*, 1706.

Oral Communications (OC)

Chemistry & OLEDs: the Journey of Blue and NearIR Emitters from the Hood to the Device

Alberto Bossi,[a] Marta Penconi,[a] Marco Cazzaniga,[a,b] Sagar Kesarkar,[a] Davide Ceresoli,[a] Fausto Cargnoni,[a] Clara Baldoli,[a] Patrizia Mussini[b]

[a] *Istituto di Scienze e Tecnologie Molecolari del CNR, Via Fantoli 16/15 e Via Golgi 19, Milano*
[b] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano*

alberto.bossi@istm.cnr.it

Among optoelectronic devices, organic light emitting diodes (OLEDs) are considered the new reference technology suited for display and lighting applications thanks to their intrinsic low driving potentials (2-5 V) and broad color tunability. Although this technology has already been introduced in the market [1], two big challenges still remain to be solved: i) the instability and degradation of blue-emissive organic materials and ii) the lack of efficient emitters to extend the OLED *applications* into the nearIR region ($\lambda_{NIR} > 700$ nm) for automotive, surveillance and phototherapy.

In the former case, the study of the degradation pathway leading to OLED failure is essential to meet the device lifetime and efficiency requirements [2]. Our approach combines photophysical and thermal studies, device fabrication and chemical analysis with a thorough theoretical investigation. We were able to define the boundary conditions for the suppression of degradation in a model blue OLED based on the archetypal FIrpic complex (Fig. 1a) [3]. In the NIR field, we undertook a rational structure-property engineering of Ir(III) emitters with *iso*quinoline-benzothiophene ligand (Fig. 1b) identifying $Ir(iqbt)_2dpm$ as leading system with high NIR quantum efficiency of 16% and short radiative lifetime. Phosphorescent OLEDs were fabricated by solution processes and vacuum thermal evaporation showing state-of-the-art efficiencies exceeding 3% (Fig. 1b) [4].

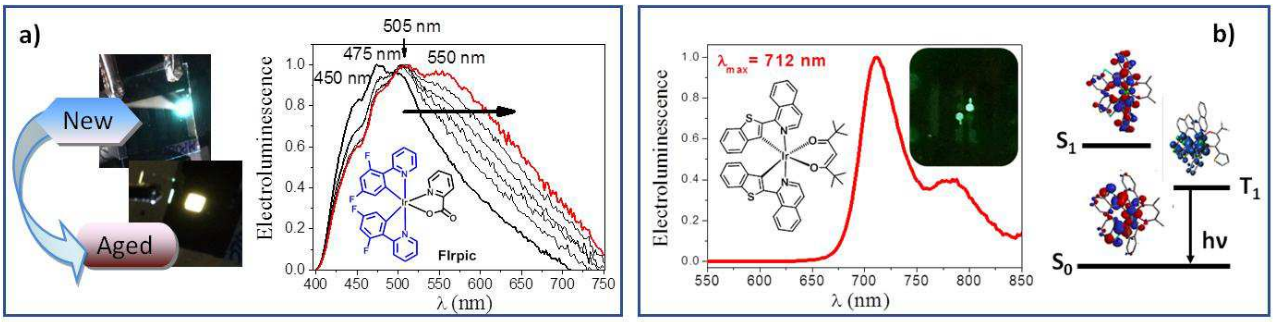


Fig. 1. (a) "Aging" effects on working *blue*-OLED: perceivable color alteration, electroluminescence spectral evolution, and chemical structures of FIrpic). (b) NIR emissive $Ir(iqbt)_2dpm$ complex and its OLED application under IR night vision camera.

References:

[1] D.J. Gaspar, E. Polikarpov, in *OLED Fundamentals: Materials, Devices, and Processing of Organic Light-Emitting Diodes*, CRC Press, **2015**.

[2] S. Scholz, D. Kondakov, B. Lüssem, K. Leo, *Chem. Rev.* **2015,** *115*, 8449−8503; I.R. de Moraes, S. Scholz, B. Lüssem, K. Leo, *Org. Electron.* **2011,** *12*, 341−347.

[3] M. Penconi, M. Cazzaniga, F. Cargnoni, A. Bossi, D. Ceresoli, *in preparation.*

[4] S. Kesarkar, W. Mroz, M. Penconi, M. Pasini, S. Destri, M. Cazzaniga, D. Ceresoli, P.R. Mussini, C. Baldoli, U. Giovanella, A. Bossi, *Angew. Chem. Int. Ed.* **2016**, *128*, 2764-2768; M. Penconi M. Cazzaniga, S. Kesarkar, P.R. Mussini, D. Ceresoli, A. Bossi, *Photochem. Photobiol. Sci.*, **2017,** 16, 1220.

Porphyrin-Sensitized Solar Cells: the Challenge of Photostability

Francesca Tessore,[a] Gabriele Di Carlo,[a] Alessio Orbelli Biroli,[b] Maddalena Pizzotti[a]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, UdR INSTM, via C. Golgi 19-20133 Milano*
[b] *Istituto di Scienze e Tecnologie Molecolari del CNR (CNR-ISTM), via C. Golgi 19-20133 Milano*
francesca.tessore@unimi.it

Dye-sensitized solar cells (DSSC) are a highly promising alternative to conventional photovoltaic silicon-based devices [1]. A key-role is played by the dye and porphyrin sensitizers have drawn great interest because of their excellent light-harvesting properties mimicking photosynthesis [2,3]. In 2014 a device based on a D-π-A Zn^{II} porphyrin with a $[Co(bpy)_3]^{2+/3+}$ redox couple attained an unprecedented photon-to-current conversion efficiency (PCE) of 13.0% [4], higher than that reported for the best Ru(II)-based dyes traditionally employed in DSSC. However, a still quite unexplored topic is the stability towards photodegradation of Porphyrin Sensitized Solar Cells [2], an issue of outstanding importance for their potential application in Building Integrated Photovoltaics (BIPV), for which the greenish color displayed by porphyrin complexes could be very appealing [5,6].

Therefore two β-substituted Zn^{II}-tetraarylporphyrins, bearing hexyloxy chains ($–OC_6H_{13}$) in the *ortho*-position of each aryl ring (so to prevent detrimental $\pi–\pi$ aggregation) and a carboxylic or a cyanoacetic acceptor group (to be anchored to TiO_2 surface) have been synthesized [7]. Thanks to the facilities of the SmartMatLab Centre hosted, prototype solar cells of both dyes have been assembled on FTO glasses (1.25x2.0 cm, with an active area of 0.196 cm^2) coated with a 6 μm thick transparent TiO_2 layer (20 nm nanoparticles), in air or under nitrogen atmosphere, uptaking the dye by two different solvent mixtures (EtOH:THF = 9:1 or EtOH:toluene = 1:1), and using a I^-/I_3^- redox couple. Some cells have been coated also with a UV filter adhesive film purchased by Solaronix. The photostability of the devices has been evaluated through UV-Vis spectroscopy after radiation of the solar cells with a Solar Simulator (under 1 sun illumination through an AM 1.5G filter), monitoring the changes in absorption maximum and intensity of the Q bands of the dye after regular time intervals (0’, 90’,180’, 240’, 300’, 360’, 540’, 720’, 900’, 1080’, 1260’, 1440’, 1620’ and 1800’). Moreover, the starting PCE of the cells have been compared to that after 1800’ irradiation.

References

[1] B. O’Regan, M. Grätzel, *Nature*, **1991**, *353*, 737.
[2] E.G. –W Diau, L.–L. Li, *Chem. Soc. Rev.*, **2013**, *42*, 291.
[3] M. Urbani, M. Grätzel, M.K. Nazeeruddin, T. Torres, *Chem. Rev.*, **2014**, *114*, 12330.
[4] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B.F.E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M.K. Nazeeruddin, M. Grätzel, *Nat. Chem.*, **2014**, *6*, 242.
[5] S. Yoon, S. Tak, J. Kim, Y. Jun, J. Kang, *Build. Environ.*, **2011**, *46*, 1899.
[6] A. Covezzi, A. Orbelli Biroli, F. Tessore, A. Forni, D. Marinotto, P. Biagini, G. Di Carlo, M. Pizzotti, *Chem. Commun.*, **2016**, *52*, 12642.
[7] A. Orbelli Biroli, F. Tessore, V. Vece, G. Di Carlo, P.R. Mussini, V. Trifiletti, L. De Marco, R. Giannuzzi, M. Manca, M. Pizzotti, *J. Mater. Chem. A*, **2015**, *3*, 2954.

Exploiting Photonic and Electronic Properties of Semiconductor Thin Films to Enhance their Photocatalytic Performance

Gian Luca Chiarello, Elena Selli

Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy
gianluca.chiarello@unimi.it

Photoelectrochemical cells (PECs) are the most promising devices for solar energy harvesting and storage, leading to water cleavage with separate H_2 and O_2 production. Fabrication of suitable, stable and active photoelectrodes is the crucial task for the future development and application of such devices. Two methods for the fabrication of photoelectrodes thin films will be presented: *i*) Self-assembled, vertically oriented TiO_2 nanotubes (NTs) thin films, directly grown on a Ti foil by electrochemical anodization; and *ii*) radio frequency magnetron sputtering (RF-MS). In particular, this presentation will focus on the possibility of enhancing the quantum efficiency of the semiconductor thin films by exploiting both electronic and photonic properties.

In the case of the electronic properties, the separation of the electron-hole pairs can be effectively achieved at the heterojunction between two overlapping layers possessing the proper electronic band gap configuration. Recently we demonstrated that the total pressure during WO_3 deposition by RF diode sputtering affects the position of the conduction band (CB) energy very likely due to the different extent of crystal structure distortion induced by oxygen vacancies [1]. The equivalent n-n heterojunction at the interface of a double-layer coating deposited at two different pressures creates a built-in electric field that facilitates the photopromoted electron transfer toward the lower laying CB material. This led to a decrease of the interfacial charge transfer resistance (R_{ct}) as measured by impedance spectroscopy and to a *ca.* 30% increase in the PEC performance compared to the monolayer and to a 93% faradaic efficiency. In the presence of methanol, an outstanding 4-fold photocurrent density increase up to 6.3 mA cm^{-2} was attained over the bilayer.

Concerning the photonic properties, the ordered 2D structure of the nanotube (NT) array confers them the photonic crystal properties due to the periodic modulation of the refractive index. This provokes the formation of a photonic band gap (PBG), *i.e.* a range of forbidden wavelengths in certain directions that cannot propagate through the structure due to Bragg diffraction and scattering. Furthermore, the group velocity of the light slowing down at the frequency edges of the PBG generates the so called “slow photon effect”. Hence, the PBG can be exploited to confine, control, and manipulate photons with the ultimate goal to intensify light absorption. We found that the photocatalytic performance of a series of TiO_2 NT array significantly increased with increasing the applied potential during the synthesis (*i.e.* with increasing the NT inner diameter) [2]. IPCE measurements revealed that such unexpected behavior is due to a red shift of the activity threshold ascribed to the parallel shift of the PBG position as confirmed by theoretical calculations. This demonstrates the important role played by ordered hierarchical structures in improving the photocatalytic performance by confining and manipulating light.

References

[1] G.L. Chiarello, et al., *J. Mater. Chem. A*, **2017**, *5*, 12977.

[2] G.L. Chiarello, A. Zuliani, D. Ceresoli, R. Martinazzo, E. Selli, *ACS Catal.*, **2016**, *6*, 1345.

Going beyond the Surface: a Glance inside Smart Conducting Molecular Surfaces through a Multitechnique Approach

Mirko Magni,[a] Serena Arnaboldi,[a] Claudia Malacrida,[a] Alessio Orbelli Biroli,[b,c] Tiziana Benincori,[d]
Francesco Sannicolò,[a] Patrizia Mussini[a,c]

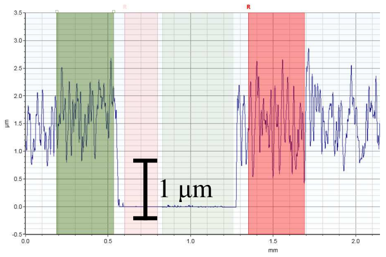
[a] *Dipartimento di Chimica dell'Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy*
[b] *Istituto di Scienze e Tecnologie Molecolari del CNR (CNR-ISTM), Via Golgi 19, 20133 Milano, Italy*
[c] *SmartMatLab Centre, Via Golgi 19, 20133 Milano, Italy*
[d] *Dipartimento di Scienza ed Alta Tecnologia dell'Università dell'Insubria, Via Valleggio 11, 22100 Como, Italy*

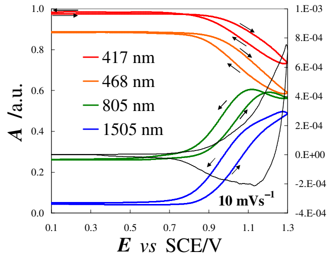
mirko.magni@unimi.it

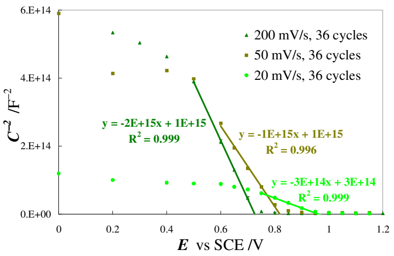
Conducting organic polymers, COPs, are smart materials that merge some of the most interesting properties of common polymers (*e.g.* flexibility, processability, etc.) with high electrical conductivity of metals. Research in this field is currently attracting increasing attention, since these innovative materials are very promising for a great variety of applications, from energetics to electronics and sensoristics, even from an industrial point of view.

Chirality makes COPs even smarter materials, opening the way to enantioselective electroanalysis/electrosynthesis. In particular the "inherent chirality" concept proposed by our groups some years ago actually represented a breakthrough, significantly improving all other literature approaches so far proposed, making possible deposition of conducting homochiral oligomeric films acting as effective, efficient and robust enantioselectors toward a great variety of chiral analytes, in different media [1-3].

The further natural step is the comprehension of the actual working mechanism of these intelligent surfaces. To reach such intriguing target a deep and multivariate characterization is mandatory, to reveal as much properties as possible that could be finally combined to depict a complete portrait of these conducting inherently chiral films. In this short presentation we will glance at these smart chiral conducting molecular surfaces, following an ideal tour from outside (*i.e.* surface appearance) to their inner parts (*i.e.* optical and electronic features).







The support of Fondazione Cariplo/Regione Lombardia (Project 2016-0923) and SmartMatLab are gratefully acknowledged.

References

[1] F. Sannicolò, P.R. Mussini, T. Benincori, R. Martinazzo, S. Arnaboldi, G. Appoloni, M. Panigati, E. Quartapelle Procopio, V. Marino, R. Cirilli, S. Casolo, W. Kutner, K. Noworyta, A. Pietrzyk-Le, Z. Iskierko, K. Bartold, *Chem. Eur. J.*, **2016**, *22*, 10839. (and references therein)

[2] S. Arnaboldi, T. Benincori, R. Cirilli, W. Kutner, M. Magni, P.R. Mussini, K. Noworyta, F. Sannicolò, *Chem. Sci.*, **2015**, *6*, 1706.

[3] F. Sannicolò, S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P.R. Mussini, M. Panigati, M. Pierini, S. Rizzo, *Angew. Chem. Int. Edit.*, **2014**, *53*, 2623.

Materials and Dyes for Dye-sensitized Solar Cells

Maciej Zalas,[a, b, c] Agata Wawrzyńczak,[a] Paulina Półrolniczak,[d] Jan Sobuś,[e, f] Grzegorz Schroeder,[a] Stefan Jurga,[e] Elena Selli,[b, c] Błażej Gierczyk,[a] Alberto Bossi,[c, g] Patrizia Romana Mussini,[b] Maciej Klein,[h, i] Radosław Pankiewicz,[a] Małgorzata Makowska-Janusik,[j] Łukasz Popenda,[e] and Waldemar Stampor [f]

[a] *Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89 B, 61-614 Poznań, Poland*
[b] *Department of Chemistry, University of Milan, Via Golgi 19, 20133 Milano, Italy*
[c] *SmartMatLab Centre, Via Golgi 19, 20133 Milano, Italy*
[d] *Institute of Non-Ferrous Metals Division in Poznań Central Laboratory of Batteries and Cells, Forteczna 12, 61-362 Poznań, Poland*
[e] *NanoBioMedical Centre, Adam Mickiewicz University in Poznań, Umultowska 85, 61-614 Poznań, Poland*
[f] *Quantum Electronics Laboratory, Faculty of Physics, Adam Mickiewicz University in Poznań, Umultowska 85, 61-614 Poznan, Poland*
[g] *Istituto di Scienze e Tecnologie Molecolari – CNR, via Fantoli 16/15, 20138 Milano, Italy*
[h] *Department of Physics of Electronic Phenomena, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland*
[i] *Distributed Energy Department, The Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences, Fiszera 14, 80-231 Gdansk, Poland*
[j] *Institute of Physics, Faculty of Mathematics and Natural Science, Jan Dlugosz University, Al. Armii Krajowej 13/15, 42-200 Częstochowa, Poland*

maciej.zalas@amu.edu.pl

Dye-sensitized solar cells (DSSCs) seem to be promising devices efficiently converting sunlight to electricity, because of their relatively high efficiency, simple fabrication methods and low cost of production. Typical DSSC is composed of dye-sensitized nanocrystalline semiconducting oxide, liquid or solid electrolyte and a counter electrode. All the components above have an important role in determination of the photovoltaic device performance, but there are different opinions about which part of the DSSC device, the semiconductor or the dye, plays the main role in the photoelectric process taking place in the cell upon its illumination. The use of a mesoporous titania electrode, characterized by a high internal surface area, was a milestone for the DSSCs development. It brought about 1000 times increase in the dye load, in the form of a monolayer on the surface of a porous electrode, in comparison with the result of non-porous semiconductor materials applied earlier. On the other hand, the dye is often called "the heart of the system" which indicates its key role in determination of the device photovoltaic performance. Dye molecule is responsible for the photon absorption process, which is a beginning of the whole photovoltaic process. Both, semiconductor materials and dyes are developed in SmartMatLab laboratories and the selected results will be presented.

OC6

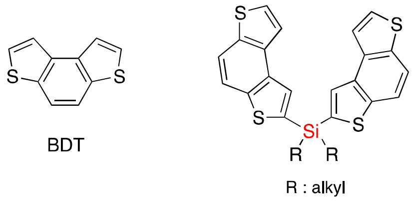
Heteroaromatic Systems as Organic Semiconductors and Luminescent Au(I) Complexes for Biological Application

Silvia Cauteruccio,[a] Alberto Bossi,[b] Emanuela Licandro[a]

[a] *Dipartimento di Chimica. Università degli Studi di Milano. Via Golgi 19, 20133 Milano*
[b] *Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM-CNR), Via Fantoli 16/15, 20138, Milano*

silvia.cauteruccio@unimi.it

Silicon-containing polymers, having a regular alternating arrangement of silanylenes and π-electron systems in a polymer backbone, are of great interest as photoresists, semiconducting materials, and precursors of silicon carbide [1]. On the other hand, much attention has been paid to thiophene-based heteroaromatic compounds due to their important photoelectric properties, and their use as charge transport materials in broad range of applications including OFETs, OLEDs and Solar Cells. Thiophene units bridged by silylene σ-linkages, including both small molecules and polymers, have been therefore studied extensively, because of their stability, in many optoelectronic applications [2]. In this context only simple thiophene rings have been studied, hence living plenty of space for further structural engineering including the use of polyconjugated thiophene-based systems. For several years our group has been working on synthesis and functionalization of benzo[1,2-*b*:4,3-*b*']dithiophene (BDT, Figure 1) derivatives [3], which are an interesting class of π-conjugated systems in functional organic materials [4], and are key intermediates for the synthesis of inherently chiral thiahelicenes [5].



1

Fig. 1. BDT and general structure of silicon-based BDTs.

In this communication we will report our new field of investigation where we have focused on the development of π-conjugated BDT units bridged by silylene σ-linkages of general formula **1**, as key intermediate to prepare active molecular or polymeric photoelectronic systems. We will discuss the synthesis of structures **1** along with the study of the optical, chemical and electrochemical properties.

References

[1] C. Moreau, F. Serein-Spirau, C. Biran, M. Bordeau, P. Gerval, *Organometallics*, **1998**, *17*, 2797, and references therein.
[2] J. Ohshita, A. Kunai, *Acta Polym.,* **1998**, *49*, 379.
[3] S. Cauteruccio, D. Dova, C. Graiff, C. Carrara, J. Doulcet, J.R. Stephenson, E. Licandro, *New J. Chem.,* **2014**, *38*, 2241.
[4] C. Kim, T.J. Marks, A. Facchetti, M. Schiavo, A. Bossi, S. Maiorana, E. Licandro, F. Todescato, S. Toffanin, M. Muccini, C. Graiff, A. Tiripicchio, *Organic Electronics,* **2009**, *10*, 1511.
[5] E. Licandro, C. Rigamonti, M.T. Ticozzelli, M. Monteforte, C. Baldoli, C. Giannini, S. Maiorana, *Synthesis,* **2006**, 3670.

Cyclic Triimidazole Derivatives: Intriguing Cases of Multiple Emissions and RT Ultralong Phosphorescence

Andrea Previtali,[a] Elena Lucenti,[b] Alessandra Forni,[b] Chiara Botta,[c] Lucia Carlucci,[a] Clelia Giannini,[a] Daniele Marinotto,[a] Stefania Righetto,[a] Elena Cariati[a]

[a] Department of Chemistry, Università degli Studi di Milano and INSTM RU
via Golgi 19, 20133 Milano, Italy.
[b] ISTM-CNR, Istituto di Scienze e Tecnologie Molecolari, INSTM RU
via Golgi 19, 20133 Milano, Italy.
[c] ISMAC-CNR, Istituto per lo Studio delle Macromolecole, INSTM RU
Via Corti 12, 20133 Milano, Italy.

andrea.previtali@unimi.it

Solid luminogens' performances are determined by both their inherent electronic properties and packing status. Intermolecular interactions have been exploited to produce persistent room-temperature phosphorescence (RTP) from organic molecules. However, the design of organic materials with bright RTP and the rationalization of the role of interchromophoric electronic coupling remain a challenging task. Cyclic triimidazole, **1**, has been demonstrated as a promising scaffold due to its crystalline induced room temperature ultralong phosphorescence (RTUP) associated with H aggregation [1]. In addition, its derivatives represent a significant example of multifaceted emission. In particular, dual fluorescence, RTUP, phosphorescences from molecular and supramolecular units are observed. H aggregation in **1**, **2** and **4**, is responsible for the red RTUP, Br atoms in **3** and **4** favour yellow molecular phosphorescence, while halogen bonded Br···Br tetrameric units are involved in the blue-green phosphorescence of **4** [2].

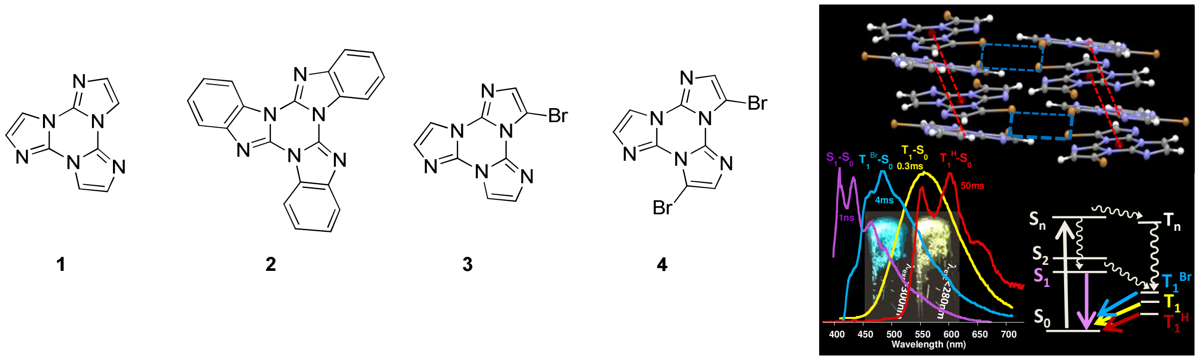


Fig. 1. Left: chemical structures of compounds **1**, **2**, **3** and **4**. Right: X-ray structure, emission bands and Jablonski diagram for compound **4**.

References

[1] E. Lucenti, A. Forni, C. Botta, L. Carlucci, C. Giannini, D. Marinotto, A. Previtali, S. Righetto, E. Cariati, *J. Phys. Chem. Lett.*, **2017**, *8*, 1894.

[2] E. Lucenti, A. Forni, C. Botta, L. Carlucci, C. Giannini, D. Marinotto, A. Pavanello, A. Previtali, S. Righetto, E. Cariati, *Angew. Chem.*, in press.

The Assessment of the Carbonaceous Component in Black Crusts Damaging the Stone Surfaces of Historical Monuments
(from Trevi Fountain Roma to Square San Marco Venice)

V. Comite,[a] P. Fermo,[a] L. Barbagallo,[a] M.F. La Russa,[b] S.A Ruffolo[b]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy;*
[b] *Università della Calabria, Dipartimento di Biologia, Ecologia e Scienze della Terra (DiBEST), Via Pietro Bucci 87036, Arcavacata di Rende, CS, Italy*

valeria.comite@gmail.com

The issue of conservation of the monumental heritage is mainly related to atmospheric pollution that causes the degradation of stone surfaces. Black crusts can be formed as a result of different chemical and physical reactions between the stone surface and environmental factors (such as gaseous pollutants and aerosol particulate matter, PM). These black layers present on the stone monuments reflect the composition of the aerosol particulate matter to which the surfaces are exposed. In particular elemental carbon (EC, also known as black carbon, typically emitted by combustion processes) is the PM component responsible for the characteristic black color of the crusts where it is embedded together with calcium sulphate due to the conversion of calcium carbonate, the main constituent of the stone. Organic carbon (OC) represents the other carbonaceous component of PM and it is present in the black crusts, too. It is of both primary or secondary origin and is linked to numerous sources (traffic, heating plants, biomass burning, etc.).

A deep knowledge of the crust composition in terms of OC and EC optical properties is mandatory in order to get information on the sources responsible for the surface darkening.

OC/EC in PM samples are generally quantified by a reference method (TOT, Thermal Optical Transmittance) not suitable for the analysis of these components in the crusts. A new approach for OC/EC quantification based on a thermal protocol and including CHN and TGA analyses, has been set-up. The method validation has been performed analyzing suitable reference standard samples prepared by mixing different chemical species in order to simulate the composition of the black crusts present on the monument surfaces. Real samples of black crusts coming from historical monuments placed in Rome, Milan and Venice have been analyzed.

OC9

Heterojunctions for Solar Energy Conversion: Electronic Band Alignment Modelling

Elisa Albanese, Gianfranco Pacchioni

Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, via R. Cozzi 55 – 20125 Milano, Italia

elisa.albanese@unimib.it

The photocatalytic production of solar fuels allows, through the electronic excitation of a semiconductor, to convert and store the energy of photons into chemical energy. Many drawbacks characterize the most promising semiconductor oxides and hinder their use as photocatalytic materials. Here, we report an experimental and theoretical work pointing to investigate novel photocatalysts based on oxide/oxide heterojunctions with improved photocatalytic activity. In particular, we focused on two promising oxide heterojunctions, $WO_3/BiVO_4$ and ZnO/CeO_2. The first one showed interesting results in the crucial electron-hole separation and carrier migration [1]. For ZnO/CeO_2 same experimental works reported improved photocatalytic activity with respect to bare ZnO (and also to TiO_2) [2]. However, the mechanism through which PC processes occur on such composite is still under debate. The simulation of heterojunction (see Fig. 1) and of the electronic band alignment can give an important contribution to the fundamental understanding of the physical mechanisms, which are at the basis of the increased and extended photoactivity.

The calculations were performed with hybrid DFT functional (B3LYP and HSE06) as implemented in CRYSTAL14 code because of its capability to accurately predict the electronic structure of complex materials. We adopted a particular approach to tune the fraction of exact exchange (α) of the hybrid DFT functional through the reciprocal of the dielectric constants of the considered material. To reproduce the band offset of the two systems the accurate lineup average electrostatic potential at the interface method of Van de Walle and Martin [3] as recently applied by Conesa [4] has been used. Large supercells have been built and fully relaxed.

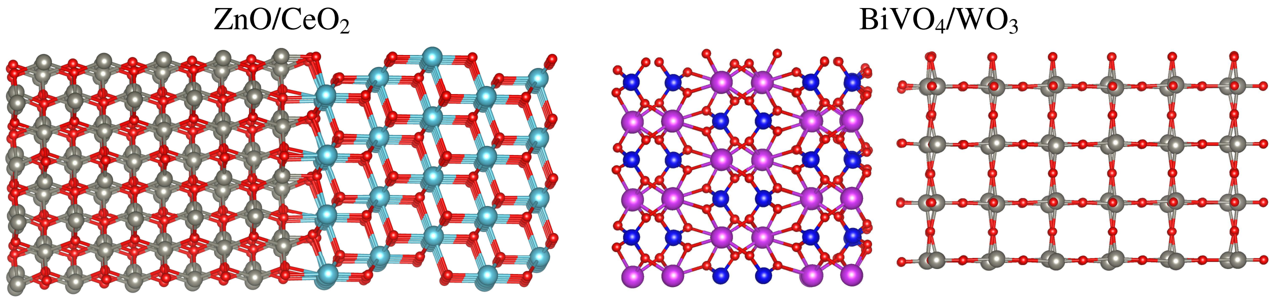


Fig. 1. 2D ZnO/CeO_2 and $BiVO_4/WO_3$ heterojunction models.

References

[1] S. J. Hong, S. Lee, J. S. Jang, J. S. Lee, *Energy Environ. Sci.,* **2011**, *4*, 1781.

[2] M.C. Paganini, D. Dalmasso, C. Gionco, V. Polliotto, L. Mantilleri, P. Calza, *ChemistrySelect*, **2016**, *1*, 3377-3383.

[3] C.G. Van De Walle, R.M. Martin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, **1986**, *34*, 5621–5634.

[4] J.C. Conesa, *J. Phys. Chem. C,* **2012**, *116*, 18884–18890.

Physical Chemistry Techniques for Antimatter Research

C. Evans,[a,b] R. Martínez Vázquez,[c] S. Aghion,[a,b] D. Marinotto,[d] M. Longhi,[d] G. Barucca,[e] P. Mengucci,[e] D. Chrastina,[e] M. Giammarchi,[b] R. Ferragut[a,b]

[a] *LNESS, Department of Physics, Politecnico di Milano, via Anzani 42, 22100, Como, Italy*
[b] *National Institute for Nuclear Physics, Milan Unit, via Celoria 16, 20133 Milan, Italy*
[c] *Istituto di Fotonica e Nanotecnologie - CNR, Politecnico di Milano, Piazza Leonardo da Vinci, 32 - 20133 Milano, Italy*
[d] *Dipartimento di Chimica, Università degli Studi di Milano, Via Gogli 19, 20133 Milano, Italy*
[e] *Dipartimento SIMAU, Università Politecnica delle Marche, 60131 Ancona, Italy*

craig.evans@polimi.it

The AEgIS collaboration, a CERN based experiment wants to create antihydrogen (the antimatter equivalent of hydrogen) through charge exchange [1]. This requires a large source of cold positronium (Ps) atoms, the bound state of a positron and an electron. The widely used method for Ps production is in the reflection geometry. Positrons enter a silica-based mesoporous material, form Ps inside the pores and thermalize as they exit into vacuum. It is predicted (through simulation) that changing this geometry from reflection to transmission would increase the quantity of cold Ps being emitted into vacuum [2].

To accomplish this, in collaboration with the SmartMatLab, a sol-gel mixture of TEOS ($Si(OC_2H_5)_4$), water (pH=1.25 with HCl) and ethanol to a molar ratio of (1:5:3.8) based on [3], A cationic surfactant (CTAB: $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$) was added to 0.1 CTAB/Si molar ratio and then diluted with ethanol (ratio 1:1). The resulting diluted sol-gel was then spin-coated onto a Si (111) substrate. A cylindrical oven was used to remove the surfactants via calcination, leaving a mesoporous silica thin film (740-760 nm thicknesses).

A polystyrene/toluene-based layer was administered onto the substrate prior to the sol-gel, this layer would then be removed via dissolution to release the sol-gel and allow transferal [4]. A laser-irradiated, chemically etched, holed substrate with transmission ~69% [5] was used as the secondary substrate to allow self-standing to be possible.

A continuous positron beam (energy range 0.1 – 20 keV) was implemented to characterize these films to find the Ps production properties within the pores. It was found that at low implantation energies (~1 keV), the estimation for the ortho-Ps (o-Ps) formation yield was ~65%. The pore diameter determined to be 3-4 nm (obtained via a positron lifetime measurement).

XRD and HRTEM was used to determine the nanostructure, it was found that the silica had a disordered structure with differing morphology at the air/bulk and bulk/substrate interfaces.

Ink-jet printing techniques as an alternative grid-like structure will also be presented.

References

[1] M. Doser et al. (AEgIS col.), *Class. Quantum Grav.*, **2012**, *29*, 184009.
[2] S. Aghion, *PhD Thesis. Politecnico di Milano, Italy*, **2015**.
[3] S. Besson, T. Gacoin, C. Jacquiod, C. Ricolleau, D. Babonneau, J. Boilot, *J. Mater. Chem.*, **2000**, *10*, 1331.
[4] R. Bandyopadhyaya, E. Nativ-Roth, R. Yerushalmi-Rozen, O. Regev, *Chem. Mater.*, **2003**, *15*, 3619.
[5] K.C. Vishnubhatla, N. Bellini, R. Ramponi, G. Cerullo, R. Osellame, *Optics Express*, **2009**, *17*, 8686.