



HYBRID INTERFACES
COST ACTION MP1202



COST Action MP 1202

Rational design of hybrid organic-inorganic interfaces:
the next step towards advanced functional materials

HINT workshop

Interface in Hybrids for Sustainable Energy Applications

**18 - 19 July 2016
Prague, Czech Republic**

Local organizers

Libor Matějka: *Department of Nanostructured Polymers and Composites*

Jiří Brus: *Department of NMR Spectroscopy*



**Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic**

Workshop webpage <http://www.imc.cas.cz/sympo/cost2016>



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WORKSHOP PROGRAMME

Monday, 18 th July (Venue: Lecture Room A)	
9:00 – 9:30	Registration
9:30 – 9:45	Welcome + Opening
9:45 – 10:15	Metal nanoparticles in organic optoelectronics Jiří Pflieger (Institute of Macromolecular Chemistry AS CR, Czech Republic)
10:15 – 10:40	Coffee break
Session 1.1. Chaired by: E. Garskaite	
10:40 – 11:05	New π -conjugated organic molecules and semi-conducting metal oxide nanostructured electrodes for organic-inorganic hybrid solar cells Thierry Toupance (University of Bordeaux, France)
11:05 – 11:30	Modification of TiO ₂ surfaces by polyoxometalates for improvement of stability and efficiency of perovskite solar cells Mahmut Kuş (Selcuk University, Turkey)
11:30 – 11:55	Singlet fission signature in metallo-supramolecular polymer David Rais (Institute of Macromolecular Chemistry AS CR, Czech Republic)
11:55 – 12:20	Electron paramagnetic resonance potential application for the investigations of the properties of energy materials Alberto Fattori (Urbino University, Italy)
12:20 – 14:10	Lunch break
Session 1.2. Chaired by: T. Toupance	
14:10 – 14:35	Giant electrode dependence of tunneling electroresistance and data retention time in organic ferroelectric P(VDF-TrFE) based hybrid, energy-efficient memory devices Sayani Majumdar (Aalto University, Finland)
14:35 – 15:00	New viologen-based composite materials for energy storage application Nianxing Wang (University of Turku, Finland)
15:00 – 15:25	Time-resolved transient optical absorption study of bis(terpyridyl)oligothiophenes and their metallo-supramolecular polymers with Zn(II) ion couplers Miroslav Menšík (Institute of Macromolecular Chemistry AS CR, Czech Republic)
15:25 – 15:50	Large area quantum dot luminescent solar concentrators with high optical efficiencies Lorcan J. Brennan (Trinity College Dublin, Ireland)
15:50 – 16:20	Coffee break



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Session 1.3. Chaired by: M. Kuş	
16:20 – 16:45	Heterostructure NiO/TiO ₂ nanomaterials: heterojunction earth-abundant metal oxide photocatalysts for hydrogen production and organic pollutant remediation Thierry Toupance (University of Bordeaux, France)
16:45 – 17:10	Fate of photogenerated defects in morphology controlled TiO ₂ nanocrystals: the role of crystal surfaces in upgrading the H ₂ yield Matteo Redaelli (University of Milano, Italy)
17:10 – 17:35	Oxide based materials for energy – processing by wet-chemistry approach and surface characterization Edita Garskaite (Vilnius University, Lithuania)
17:35 – 18:00	Pulsed laser-deposited thin films of room-temperature-switchable spin-crossover compounds Ashta C. Ghosh (Université Catholique de Louvain, Belgium)
18:00 – 19:00	Informal dinner

Tuesday, 19th July (Venue: Lecture Room A)

Session 2.1. Chaired by: L. Matějka	
9:00 – 9:25	Evaluation of the performance of organic-inorganic hybrid coatings obtained by sol-gel method to prevent the corrosion of ancient metallic artifacts Carlos J. R. Silva (Universidade do Minho, Portugal)
9:25 – 9:50	Electrochemical characterization of ureasilicate matrices doped with carbon allotropes Rita B. Figueira (Laboratório Nacional de Engenharia Civil, Lisbon, Portugal)
9:50 – 10:15	Interface induced growth and transformation of polymer-conjugated proto-crystalline phases in aluminosilicate hybrids: A multiple-quantum ²³ Na- ²³ Na MAS NMR correlation spectroscopy study Jiří Brus (Institute of Macromolecular Chemistry AS CR, Czech Republic)
10:15 – 10:40	Near-infrared to visible light spectral converters based on organic-inorganic hybrid nanocomposites Beatriz Julián-López (Universitat Jaume I, Castellón, Spain)
10:40 – 11:00	Coffee break
Session 2.2. Chaired by: C. J. R. Silva	
11:00 – 11:25	Ionosilicas as functional materials in the sustainable development: organocatalysis and adsorption/separation of anionic pollutants Peter Hesemann (Institut Charles Gerhardt de Montpellier, France)



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11:25 – 11:50	High performance shape memory epoxy-silica nanocomposites Libor Matějka (Institute of Macromolecular Chemistry AS CR, Czech Republic)
11:50 – 12:15	Effect of graphite nanoplatelets on properties of conductive microfibrillar composite Ivan Kelnar (Institute of Macromolecular Chemistry AS CR, Czech Republic)
12:15 – 12:40	Solid state NMR study of the effect of TEOS addition to ureasilicate matrices for corrosion protection (STSM work) Rita B. Figueira (Laboratório Nacional de Engenharia Civil, Lisbon, Portugal)
12:40	Farewell Lunch



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PRESENTATIONS

P1	Metal nanoparticles in organic optoelectronics Jiří Pflieger (Institute of Macromolecular Chemistry AS CR, Czech Republic)
P2	New π -conjugated organic molecules and semi-conducting metal oxide nanostructured electrodes for organic-inorganic hybrid solar cells Thierry Toupance (University of Bordeaux, France)
P3	Modification of TiO ₂ surfaces by polyoxometalates for improvement of stability and efficiency of perovskite solar cells Mahmut Kuş (Selcuk University, Turkey)
P4	Singlet fission signature in metallo-supramolecular polymer David Rais (Institute of Macromolecular Chemistry AS CR, Czech Republic)
P5	Electron paramagnetic resonance potential application for the investigations of the properties of energy materials Alberto Fattori (Urbino University, Italy)
P6	Giant electrode dependence of tunneling electroresistance and data retention time in organic ferroelectric P(VDF-TrFE) based hybrid, energy-efficient memory devices Sayani Majumdar (Aalto University, Finland)
P7	New viologen-based composite materials for energy storage application Nianxing Wang (University of Turku, Finland)
P8	Time-resolved transient optical absorption study of bis(terpyridyl)oligothiophenes and their metallo-supramolecular polymers with Zn(II) ion couplers Miroslav Menšík (Institute of Macromolecular Chemistry AS CR, Czech Republic)
P9	Large area quantum dot luminescent solar concentrators with high optical efficiencies Lorcan J. Brennan (Trinity College Dublin, Ireland)
P10	Heterostructure NiO/TiO ₂ nanomaterials: heterojunction earth-abundant metal oxide photocatalysts for hydrogen production and organic pollutant remediation Thierry Toupance (University of Bordeaux, France)
P11	Fate of photogenerated defects in morphology controlled TiO ₂ nanocrystals: the role of crystal surfaces in upgrading the H ₂ yield Matteo Redaelli (University of Milano, Italy)
P12	Oxide based materials for energy – processing by wet-chemistry approach and surface characterization Edita Garskaite (Vilnius University, Lithuania)



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P13	Pulsed laser-deposited thin films of room-temperature-switchable spin-crossover compounds Ashta C. Ghosh (Université Catholique de Louvain, Belgium)
P14	Evaluation of the performance of organic-inorganic hybrid coatings obtained by sol-gel method to prevent the corrosion of ancient metallic artifacts Carlos J. R. Silva (Universidade do Minho, Portugal)
P15	Electrochemical characterization of ureasilicate matrices doped with carbon allotropes Rita B. Figueira (Laboratório Nacional de Engenharia Civil, Lisbon, Portugal)
P16	Interface induced growth and transformation of polymer-conjugated proto-crystalline phases in aluminosilicate hybrids: a multiple-quantum ^{23}Na - ^{23}Na MAS NMR correlation spectroscopy study Jiří Brus (Institute of Macromolecular Chemistry AS CR, Czech Republic)
P17	Near-infrared to visible light spectral converters based on organic-inorganic hybrid nanocomposites Beatriz Julián-López (Universitat Jaume I, Castellón, Spain)
P18	Ionosilicas as functional materials in the sustainable development: organocatalysis and adsorption/separation of anionic pollutants Peter Hesemann (Institut Charles Gerhardt de Montpellier, France)
P19	High performance shape memory epoxy-silica nanocomposites Libor Matějka (Institute of Macromolecular Chemistry AS CR, Czech Republic)
P20	Effect of graphite nanoplatelets on properties of conductive microfibrillar composite Ivan Kelnar (Institute of Macromolecular Chemistry AS CR, Czech Republic)
P21	Solid state NMR study of the effect of TEOS addition to ureasilicate matrices for corrosion protection (STSM work) Rita B. Figueira (Laboratório Nacional de Engenharia Civil, Lisbon, Portugal)



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ABSTRACTS



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P1

Metal nanoparticles in organic optoelectronics

Jiří Pfleger

Downscaling metal fillers to nanometer scale in semiconducting polymer composites brings new phenomena, which can be exploited in advanced optoelectronic applications. Besides the increased electrical conductivity due to the presence of metallic filler such nanocomposites were suggested to work as photochemical catalysts, optical sensors, SERS probes or nonvolatile rewritable memories. Phenomena based on resonance excitations of surface plasmons – collective oscillations of free electrons excited in noble metal (such as Ag and Au) nanoparticles (NPs) by incident light can be used e.g. for localized fluorescence quenching or for better harvesting of absorbed light in photovoltaic energy conversion applications by the enhancement of charge transfer at the donor-acceptor interface located near the NP surface.

Various procedures of plasmonic composites preparation will be shown on the example of poly(3-alkylthiophene), P3AT: (i) simple mixing a polymer solution with an organosol of Au or Ag NPs, (ii) in-situ reduction of metal salts in the polymer solution using a phase transfer agent, (iii) preparation of P3AT derivatives with cationic groups, which are soluble in water miscible solvents, and hence can be mixed with NPs hydrosols, and (iv) laser ablation of Au or Ag target in a proper solvent and subsequent mixing of the sol with a polymer solution. The electrical and optical properties of these composites will be discussed. Also a more defined system consisting of a metal NPs layer prepared by physical vapor deposition onto surface of very thin spin-cast films of poly(3-hexylthiophene) was prepared for a more detailed study of underlying phenomena that accompany the plasmonic effects involved in the optoelectronic behavior of the composites.

Transient optical absorption studies showed, besides the laser pulse induced heating of electrons in conduction band of a metal nanoparticle resulting in spectral broadening of the plasmonic resonance peak, also several excited states relaxation processes in P3AT. Exciton absorption decayed faster, showing increased probability of excitons dissociation due to their interaction with NPs. As seen from the long-lived photobleaching signal the dissociation of excitons resulted in long living species. These observations could be explained by an enhanced photogeneration of long-living polarons with optical absorption in longer wavelength. In similar structures with admixed fullerene forming bulk heterojunction solar cell and Au NPs the power conversion efficiency under white light illumination was improved by about 25%.



P2

New π -conjugated organic molecules and semi-conducting metal oxide nanostructured electrodes for organic-inorganic hybrid solar cells

Céline Olivier¹, Yohann Nicolas¹, Lionel Hirsch², Thierry Toupance^{1*}

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The ever ongoing efforts to harvest efficiently renewable energy resources to address energy demand increase and global warming issues have led to various new solar cells concepts over the past two decades. In this context, dye-sensitized solar cells (DSCs) based on the sensitization of a porous semiconducting metal oxide layer, as anatase titania, with an organic or a metallo-organic dye appeared to be a suitable alternative to conventional photovoltaic devices due to their rather high efficiency, i.e. up to 14% for liquid-based systems, low cost, easy manufacturing and aesthetics. However, this technology still suffers from some limitations related to the photocatalytic properties of titanium dioxide, of the limited light harvesting ability of conventional dyes and the presence of a corrosive liquid electrolyte.

In this context, various approaches will be described to draw new prospects in this field, in particular new photoanode materials combined with suitable post-treatment to tune the interface with organic dyes and, also, original π -conjugated organic molecules for efficient solar light harvesting. Thus, high energy conversion yield and life times for hybrid solar cells base on sensitized tin dioxide electrodes (SnO_2) will be described.¹ New π -conjugated organic chromophores, compatible with non corrosive electrolytes or hole transporters, leading to enhanced solar light harvesting and improved stability of the corresponding devices will be then presented.² Finally, new perspectives in the field of organic-inorganic hybrid solar cells will be given.

Reference:

- 1 L. Cojocaru, et al. J. Mater. Chem. A 1 (2013) 13789.
- 2 a) S. De Sousa, et al. ChemSusChem. 6 (2013), 993. b) Y. Nicolas, et al. Chem. Eur. J. 20 (2014) 3678. c) J. Massin, et al. Dyes Pigments 118 (2015), 76.



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P3

Modification of TiO₂ surfaces by polyoxometalates for improvement of stability and efficiency of perovskite solar cells

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²*Chemical Engineering Department, Selçuk University, Konya, Turkey*

³*Cal Vocational School, Pamukkale University, Denizli, Turkey*

⁴*Chemistry Engineering Department, Selçuk University, Konya, Turkey*

New generation perovskite solar cells exhibited great improvement in the last decades [1-3]. High efficiency and low cost makes this technology interesting for researches. However there is still some problems must be solved for perovskite solar cells such as stability and reproducibility.

In this work, Polyoxometalates were used for modification of TiO₂ surfaces to improve the efficiency and reproducibility of solar cells. TiO₂ layer were obtained by spray pyrolysis. Spin coating method was used for POM, Perovskite and HTM (P3HT) coating. POM modification improves the efficiency in comparison with nonmodified reference solar cells. Different techniques such as SKPM, AFM etc were used to investigate the reasons for those observations.

References:

1. M. Green, et all. Nat Photon 2014, 8 (7), 506-514.
2. J. M. Ball, et all. Energy & Environmental Science 2013, 6 (6), 1739.

Acknowledgements : We want to thank to TUBITAK (PN: 113Z254) for financial support.

P4

Singlet fission signature in metallo-supramolecular polymer

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In the Singlet Fission (SF) photophysical process in organic solids, a photoexcited molecule in an organic solid (a low-spin “singlet” exciton) shares its energy with a neighboring unexcited molecule to produce a correlated pair of excited molecules (two high-spin “triplet” excitons). It was recently proposed as an approach to 3rd generation photovoltaics (PV), potentially raising the top limit for efficiency of single-junction PV solar cells from 30.4 % up to 44.4 % by reducing the thermalization losses.¹ The majority of experimental work up to now has been focused on characterization of SF phenomenon of the crystalline aromatic hydrocarbons of the acene type, mainly tetracene and pentacene and their derivatives,² in which the reported triplet excitons yields reach theoretical maximum of 200 %. However, from the photovoltaic point of view, only a small number of devices where SF plays an important role was reported up to the present date.³ The limited choice among the presently available SF materials is a recurrent hurdle in devices development, and points out the importance of the search for new materials. In this report, we present photophysical investigation of series of structurally-related materials based on bis-terpyridine-oligothiophene metallo-supramolecular polymers (MSP).⁴ In our contribution, we will report about the SF process in material depicted in Fig. 1 in solution as well as in solid with transient absorption experiments. To our best knowledge, the SF was not reported before in MSPs, thus our study brings the material class as plausible candidates for the 3rd gen. PV research.

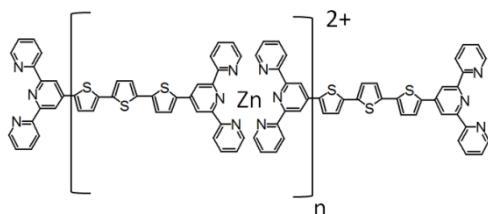


Fig. 1. Chemical structure of the studied compound

References:

1. Hanna, M. C, et. al. Appl. Phys. 100 (2006) 074510.
2. M. B. Smith, et. al. J. Chem. Rev. Macromolecules 110 (2007) 6891.
3. J. Lee, et. al. Accounts of Chemical Research 46 (2013) 1300.
4. D. Rais, et. al. J. Phys. Chem. A 119 (2015) 6203.

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P5

Electron paramagnetic resonance potential application for the investigations of the properties of energy materials

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Electron paramagnetic resonance (EPR) spectroscopy is an experimental technique widely employed in fundamental science in particular in material chemistry. The EPR technique is based on the detection of paramagnetic species ie that have an unpaired electron. Samples could also be investigated even if they don't have unpaired electrons adding paramagnetic species according to two experimental techniques called spin probe and spin label. The spin probes are nitroxide radicals which are selected to work as probes of environmental properties, that is, to insert in specific active site of the studied system to monitor, like a camera, the chemical, structural, and dynamical modifications. Spin-labels are stable radicals that can be chemically bonded to other molecules making them detectable by EPR. In this way, the spin label will follow the fate of the labeled molecule. In alternative, we may add a non-paramagnetic species called spin trap which is able to stabilize short-life radicals (shorter than the EPR detection time) by creating long-life radical adducts. In our lab we performed a computer aided analysis of the EPR spectra in order to investigate different systems using all the techniques above mentioned. This contribution presents an overview of various studies performed in our laboratory mainly on hybrid interfaces characterizing and investigating, adsorption properties of dyes in dye sensitized solar cells (DSSC) [1], and paramagnetic properties of materials constituting one of the recent most studied solar technology based on perovskite planar and mesoscopic, solar cells.

References:

1. A. Fattori, M. Cangiotti, L. Fiorani, S. Lucchi, M. F. Ottaviani Langmuir 30 (2014) 13570.

Acknowledgements: HINT COST Action MP1202 is acknowledged.



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P6

Giant electrode dependence of tunneling electroresistance and data retention time in organic ferroelectric P(VDF-TrFE) based hybrid, energy-efficient memory devices

Sayani Majumdar

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We report an electrode-dependent robust and electrically-controllable tunneling electroresistance (TER) of magnitude up to $10^5\%$ at room temperature in FTJs with 3 nanometer-thick, spin-coated films of ferroelectric co-polymer P(VDF-TrFE) (70:30) on conducting-oxide electrodes. A conductive-tip atomic force, piezo-force microscopy and transport measurements on P(VDF-TrFE) thin films covering Indium-Tin-Oxide (ITO), $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO), Nb-doped SrTiO_3 (Nb-STO) and Au electrodes clearly demonstrate that TER effect appears due to modulation of barrier height caused by electrically-induced polarization reversal in P(VDF-TrFE) molecules. Time-dependent measurements by Kelvin probe microscope reveal that surface potentials in P(VDF-TrFE) are most stable on Nb-doped STO, followed by LSMO, ITO and Au. Relaxation of surface potential in more conducting electrodes indicate presence of leakage currents that creates an electric field inside the ferroelectric acting in opposite direction to the polarizing field causing poor retention of polarization. This finding points out that strong depolarizing field can also arise due to leakage current in metallic electrodes with efficient charge screening properties. Therefore, leakage currents should be minimized in organic ferroelectric tunnel junctions for future non-volatile, energy-efficient memory elements.

P7

New viologen-based composite materials for energy storage application

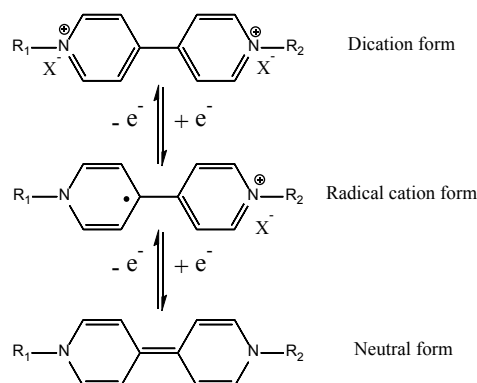
Nianxing Wang^{1,2}, Zsófia Lukcas³, Bhushan Gadgil^{1,2}, Pia Damlin¹, Csaba Janáky³,
 Carita Kvarnström^{1*}

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Viologens, usually named 1,1'-disubstituted-4,4'-bipyridinium salts, have been in focus for increasing attention due to their unique properties.^[1] The special colour change and the stable redox property are the two main features which made the viologens work as a frequently used functional material. The viologen can undergo two redox processes with three redox forms: dication form, radical cation form and neutral form, which are shown in Scheme 1. In previous work, a new viologen-based composite film was synthesized electrochemically from cyanopyridine based precursors and graphene oxide in ionic liquid.^[2] The composite material has been characterized by several electrochemical, physicochemical and imaging techniques, which have revealed several interesting properties of the composite materials that have huge potential to be applied in the energy storage applications.



Scheme 1. Three redox forms of viologen

[1] P. M. S. Monk, *The viologens: physicochemical properties, synthesis, and applications of the salts of 4, 4'-bipyridine*, John Wiley & sons Ltd, West Sussex, England, 1998, p.

[2] a) N. Wang, P. Damlin, B. M. Esteban, T. Ääritalo, J. Kankare and C. Kvarnström, *Electrochimica Acta* 2013, 90, 171-178; b) N. Wang, A. Kähkönen, P. Damlin, T. Ääritalo, J. Kankare and C. Kvarnström, *Electrochimica Acta* 2015, 154, 361-369.

P8

**Time-resolved transient optical absorption study of
bis(terpyridyl)oligothiophenes and their metallo-supramolecular polymers
with Zn(II) ion couplers**

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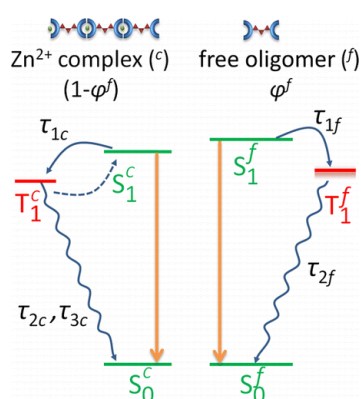


Fig.1. Studied compounds.

α,ω -Bis(terpyridyl)oligothiophenes spontaneously assemble with Zn(II) ions giving conjugated constitutional dynamic polymers (dynamers) of the metallo-supramolecular class, which potentially might be utilized in optoelectronics (Fig.1). Their photophysical properties, which are of great importance in this field of application, are strongly influenced by the dynamic morphology. It was assessed in this study by using ultrafast pump-probe optical absorption spectroscopy. We identified and characterized relaxation processes running in photoexcited molecules of these oligomers and dynamers and show impacts of disturbed coplanarity of adjacent rings (twisting the thiophene–thiophene and thiophene–terpyridyl bonds by attached hexyl side groups) and Zn(II) ion couplers on these processes. Major effects are seen in the time constants of rotational relaxation, intersystem crossing, and de-excitation lifetimes. The photoexcited states formed on different repeating units within the same dimer chain do not interact with each other even at very high excitation density. The method is presented that allows determining the equilibrium fraction of unbound oligothiophene species in a dimer solution, from which otherwise hardly accessible values of the average degree of polymerization of constitutionally dynamic chains in solution can be estimated [1].

References:

1. D Rais et al., J. Phys. Chem. A 119 (2015) 6203.

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P9

Large area quantum dot luminescent solar concentrators with high optical efficiencies

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With the ever increasing demand for society to move away from fossil fuel based energy sources, our approach to sustainable energy generation must become tailored to the requirements of the modern, urban population. The next generation of energy-harvesting devices should not be solely confined to energy harvesting solar or wind farms, but should be seamlessly integrated into modern architecture, in the development of zero or low energy consumption buildings of the future.

Luminescent solar concentrators (LSCs) have the potential to significantly contribute to solar energy harvesting strategies in the built environment.^[1] For the practical realization of LSC technology, the ability to create large area devices, which contain considerable volumes of high quality luminescent species, is paramount. In this study we report on the development of several large area (90 cm² top face) and high efficiency planar organic-inorganic composite LSCs, based on a lauryl methacrylate, ethylene glycol dimethacrylate co-polymer (LMA-co-EGDM) doped with CdSe@ZnS/ZnS core-shell quantum dots (Fig.1). The champion LSC has

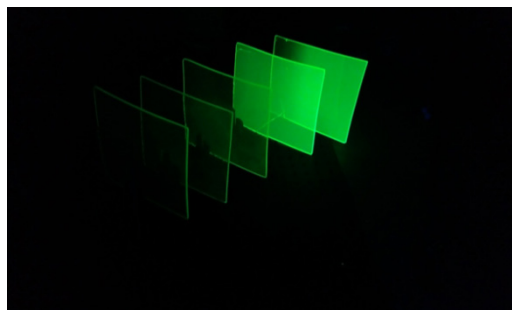


Fig. 1 Photographic image of 5 large area (10 × 9 × 0.3 cm) CdSe@ZnS/ZnS quantum dot doped LMA-co-EGDM LSCs of increasing QD concentration under UV illumination.

demonstrated an operating efficiency of 6.60 %, under full spectrum illumination (250-1050 nm), and has been employed to generate a 14 fold increase in the short circuit current (J_{sc}) of an optically-matched solar cell, when compared to an un-doped polymer slab. This result represents one of the highest optical efficiency values ever reported for a QD-doped LSC.^[2-4] The devices have displayed promising optical stability under accelerated testing conditions and display reasonably low optical reabsorption losses. These results highlight the significant promise of hybrid QD-polymer composites for the practical realization of highly efficient LSCs.

References:

- [1] M. G. Debije, P. P. C. Verbunt, *Advanced Energy Materials* 2 (2012) 12.
- [2] F. Meinardi, A. Colombo, K. A. Velizhanin, R. Simonutti, M. Lorenzon, L. Beverina, R. Viswanatha, V. I. Klimov, S. Brovelli, *Nat Photon* 8 (2014) 39.
- [3] F. Meinardi, H. McDaniel, F. Carulli, A. Colombo, K. A. Velizhanin, N. S. Makarov, R. Simonutti, V. I. Klimov, S. Brovelli, *Nat Nano* 10 (2015) 878.
- [4] Y. Zhou, D. Benetti, Z. Fan, H. Zhao, D. Ma, A. O. Govorov, A. Vomiero, F. Rosei, *Advanced Energy Materials* 2016, DOI:10.1002/aenm.201501913.



P10

Heterostructure NiO/TiO₂ nanomaterials: heterojunction earth-abundant metal oxide photocatalysts for hydrogen production and organic pollutant remediation

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In the broad context of environmental issues related to the continuous energy demand increase arising from the global population growth, semiconductor heterogeneous photocatalysis appeared to be a versatile concept for green technology, and was directed to a wide range of purposes as hydrogen production, and depollution. Nonetheless, the recombination of charge carriers constitutes one of the main limitations to achieve high photocatalytic efficiencies. Development of heterostructure photocatalysts by coupling two semiconductors with suitable band edge position, such as p-type and n-type semiconductors, can reduce recombination phenomena by vectorial transfer of charge carriers. On the other hand, the scarcity of some elements requires the development of photocatalysts with earth-abundant elements and a careful control of the polymorphs obtained is needed to rationalize the photocatalytic properties.

In this context, earth-abundant NiO/anatase TiO₂ heteronanostructures were prepared by a straightforward one pot sol-gel synthetic route followed by a suitable thermal post-treatment. The resulting 0.1-4wt% NiO-decorated anatase TiO₂ nanoparticles were characterized by X-ray diffraction, electron microscopy, Raman and UV-visible spectroscopy and N₂ sorption analysis, and showed both high crystallinity and mesoporosity. The careful determination of the energy band alignment diagram by a suitable combination of XPS/UPS and absorption spectroscopy data revealed significant band bending at the interface of p-n NiO/anatase TiO₂ heterojunction nanoparticles. Furthermore, these heterojunction photocatalysts exhibited improved photocatalytic activity in organic dye degradation and H₂ production by methanol photoreforming compared to pure anatase TiO₂ and commercial P25 and could be recycled several times without any noticeable change in photocatalytic activity. Thus, an average H₂ production rate of 2693 μmol h⁻¹g⁻¹ was obtained for heterojunction 1 wt% NiO/anatase photocatalyst, which is one of the most efficient NiO/anatase TiO₂ system ever reported. Enhanced dissociation efficiency of photogenerated electron-hole pairs resulting from internal electric field developed at the interface of the NiO/anatase TiO₂ p-n heterojunctions was found to be at the origin of this unprecedented photocatalytic activity.

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P11

Fate of photogenerated defects in morphology controlled TiO₂ nanocrystals: the role of crystal surfaces in upgrading the H₂ yield

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The promising performance in H₂ photoproduction of anatase TiO₂ nanocrystals exposing specific surfaces have been explored in depth both theoretically and experimentally [1]. However, a clear assessment of the role of their crystal faces in the photocatalytic process is still under debate. In this direction, tracking by electron spin resonance (ESR) spectroscopy the photogenerated defects in shape controlled TiO₂ nanocrystals, have been demonstrated a powerful tool for gathering useful information.

This background prompted us to investigate the H₂ production by methanol photosteam reforming of anatase nanocrystals with nearly rectangular-(RC), rhombic-(R) and nanobar-(NB) shapes, having exposed {001}, {101} and {010} surfaces, and related this reactivity both to the type of crystal faces and to amount and stability of the charge trapping centers [2]. The ESR spectra revealed that the amount of Ti³⁺ (electrons traps) parallels the H₂ evolution rate and becomes maximum for the RC nanocrystals which display the highest area of {001} surfaces and the lowest of {101} ones, but also involve a significant area of {010} faces. This points out that the H₂ production cannot be related only to the envisaged reducing {101} facets, but that the {010} ones play a key role. More in depth, we suggest that the contiguous {001}, {101} and {010} facets may form a highly effective “surface heterojunctions” within a single RC particle, which allows the selective migration of the photogenerated electrons not just toward the {101} surfaces but also to the {010} ones, and of holes toward the {001}. This transfer increases the lifetime of the charge carriers, thus enhancing the photoefficiency of RCs compared to that of NB and R samples. These outcomes and the adopted strategy suggest the importance of tuning the paramagnetic defects by crystal facet engineering, in order to critically understand and further optimize the functional properties of metal oxide nanocrystals [3].

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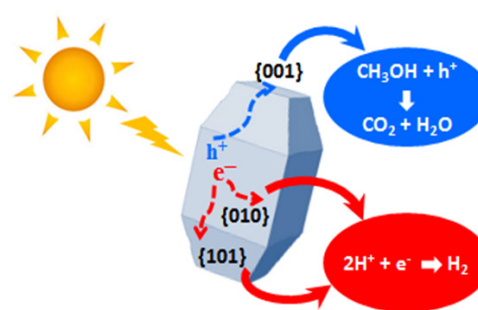


Figure 1. Hydrogen evolution in shape controlled anatase nanoparticles with {001}, {101} and {010} surfaces.



P12

Oxide based materials for energy – processing by wet-chemistry approach and surface characterization

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Owing to their unique properties, oxide based materials in the form of powders and films are used in numerous technological applications, such as flat panel displays, energy efficient windows, photovoltaic devices, light emitting diodes, electrodes for lithium ion battery and photocathodes for photoelectrochemical water reduction [1-4].

In order to achieve desirable properties of the material, precise control of phase homogeneity, particle size and morphology is necessary. So the synthesis method is important for controlling the properties, cost and possible applications of the materials.

Thin films can be deposited by a wide range of techniques, but wet chemical methods to fabricate thin films have potentially many advantages compared to physical methods. They are relatively simple and less expensive techniques, and the composition and homogeneity down to the molecular level can readily be controlled. Aqueous based sol-gel methods have the additional advantage that the environmental and health risks are considerably lower compared to methods based on organic solvents.

Here we report on the development of an environmentally friendly aqueous sol-gel process applied to prepare nano-crystalline oxide based particles, nanostructures as well as high quality thin films by dip/spin-coating and hard templating. Some aspects of chemistry of the proposed synthesis route are discussed and the relationship between solution chemistry and the morphological and structural features of produced oxide nanostructures as well as coatings are addressed.

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P13

Pulsed laser-deposited thin films of room-temperature-switchable spin-crossover compounds

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Spin crossover (SCO) compounds are a class of functional materials able to switch their spin state upon various external perturbations such as temperature, light and pressure. Hence, this class of hybrid inorganic-organic materials were proposed as potential candidates for several technological applications such as in thermal displays, memory devices and sensors and more recently in hybrid electronics and optoelectronics. However due to the fragility of the SCO phenomenon which critically depends on the molecular environment (e.g. packing, crystallinity, solvent molecules, anions, etc.) and the poor processability, their development for the proposed applications have been restricted.[1] In this context, a great effort has been made towards the growth of highly controlled thin solid films and the fabrication of nanostructures in order to evolve specifically dedicated procedures for technological applications.

Till now, the most popular methods to obtain thin films of SCO complexes include Langmuir–Blodgett (LB) deposition,[2] dip coating,[3] spin coating,[4] constructive methods, vacuum sublimation, dispersing complexes into a polymer matrix, and intercalating complexes in layered materials host matrixes. In this context, we use the Pulsed Laser Deposition (PLD) technique for the first time, to the best of our knowledge, to grow (deposit) thin film of [Fe(pz)Pt(CN)₄] SCO nanoparticles on different substrates. The PLD method offers the possibility to produce versatile multicomponent materials without any byproduct contaminations and represents cost-effective solution in the search of one-chamber systems assuming the deposition conditions are exactly controled in order not to destroy the deposited molecular structures. The first structure observations of the prepared films using scanning electron microscopy (SEM) and Raman microscopy reveals discontinuous crystalline structure with very low surface roughness, whereas in order to obtain the reasonably spin transition, the uniformity is necessary. Further work on the selection of the PLD growth parameters is in progress in order to produce controlled, uniformal, crystalline and contamination free SCO thin films for the future nano-electronic devices.

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P14

Evaluation of the performance of organic-inorganic hybrid coatings obtained by sol-gel method to prevent the corrosion of ancient metallic artifacts

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Coating and/or use of corrosion inhibitors can be a simple, effective and widely procedure for the protection of metallic cultural heritage [1-2]. The development of coatings based on organic-inorganic hybrid gel materials obtained by sol-gel method results in stable and inert layers showing high barrier protection and good adhesion to metallic substrate [3].

In this work, the effectiveness of several organic-inorganic hybrid gel coatings based on functionalized silicates to prevent/mitigate the corrosion of zinc, lead, iron, copper and brass when exposed to different environments were tested. Samples of the metals were coated with the different hybrid gel materials by dip-coating method and its effectiveness as corrosion barriers were evaluated by potentiodynamic methods. For comparison purposes, uncoated metal samples were also studied. The protective barrier of these materials was studied in aqueous solutions both in the absence and presence of chloride ions, to reproduce marine conditions.

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P15

Electrochemical characterization of ureasilicate matrices doped with carbon allotropes

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In the past several years, developments in materials' technology such as hybrid sol-gel films have led to the production of a new generation of multifunctional materials. The combination of organic with inorganic and carbon based materials allow to obtain innovative materials with a broad spectrum of useful properties for diverse applications. Among several others, carbon-based materials such as carbon nanotubes (CNTs), carbon nanofibers (CN) and carbon black (CB). The CNTs' diameters can range from <1 nm for single-wall carbon nanotubes (SWCNTs) up to tens of nanometer for multi-walled carbon nanotubes (MWCNTs). Moreover, SWCNTs can be either metallic or semi-conducting and MWCNTs are mostly metallic. CNTs also exhibit strong chemical and mechanical stability with very high thermal conductivity. On the other hand, ureasilicates matrices are considered as promising materials and have been studied in different applications such as optical¹ and coatings for corrosion mitigation². In this work ureasilicate matrices doped with CNTs, CN, graphite, carbon black and activated carbon were produced. A comparative study of the electrochemical properties of ureasilicate matrices doped with different carbon-based materials was carried out in order to obtain materials with suitable properties for optoelectronic device applications. The samples were characterized by electrochemical impedance spectroscopy (EIS).

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P16

**Interface induced growth and transformation of polymer-conjugated proto-crystalline phases in aluminosilicate hybrids:
A multiple-quantum ^{23}Na - ^{23}Na MAS NMR correlation spectroscopy study**

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Nanostructured materials typically offer enhanced physicochemical properties because of their large interfacial area. In this contribution, we present a comprehensive structural characterization of aluminosilicate hybrids with polymer-conjugated nano-sized zeolites specifically grown at the organic-inorganic interface. The inorganic amorphous Al-O-Si framework is formed by alkali activated low-temperature transformation of metakaoline, whereas simultaneous copolymerization of organic co-monomers creates a secondary epoxide network covalently bound to the aluminosilicate matrix. This secondary epoxide phase not only enhances the mechanical integrity of the resulting hybrids but also introduces additional binding sites accessible for compensating negative charge on the aluminosilicate framework. This way, the polymer network initiates growth and subsequent transformation of protocrystalline short-range ordered zeolite domains that are located at the organic-inorganic interface. By applying an experimental approach based on 2D ^{23}Na - ^{23}Na double-quantum (DQ) MAS NMR spectroscopy we discovered multiple sodium binding sites in these protocrystalline domains, in which immobilized Na^+ ions form pairs or small clusters. It is further demonstrated that these sites, the local geometry of which allows for the pairing of sodium ions, are preferentially occupied by Pb^{2+} ions during the ion exchange. The proposed synthesis protocol thus allows for the preparation of a novel type of geopolymer hybrids with polymer-conjugated zeolite phases suitable for capturing and storage of metal cations. The demonstrated ^{23}Na - ^{23}Na DQ MAS NMR combined with DFT calculations represents a suitable approach for understanding the role of Na^+ ions in aluminosilicate solids and related inorganic-organic hybrids, particularly their specific arrangement and clustering at interfacial areas [1].

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P17

Near-infrared to visible light spectral converters based on organic-inorganic hybrid nanocomposites

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Up-converting nanoparticles (UC NPs) able to efficiently transform NIR radiation into visible light have opened new possibilities in photonics, photovoltaics, sensors and biomedical applications [1-3]. Nevertheless, the development of transparent and easy-to shape materials showing multiple light conversion effects remains a challenge for the deployment of new technologies, especially for light emitting diodes, displays and solar concentrators.

This presentation shows a general synthetic strategy to prepare transparent organic-inorganic hybrids with multimodal spectral converting properties. Some examples of complex nanocomposites with potential application in the field of energy will be addressed. In particular, we'll pay attention on the synthesis of lanthanide-doped nanoparticles (such as ZrO_2 and NaYF_4) dispersed into organically-modified silane matrices (di-ureasils and polydimethylsiloxane) that can be easily processed as monoliths and films (Figure 1). The most intriguing features of the nanocomposites from a structural and optical point of view will be discussed, demonstrating that the inclusion of nanocrystals within the hybrid matrices has no adverse effects on the luminescent properties of both constituents. Therefore, these multifunctional systems are attractive for many technological applications in energy.

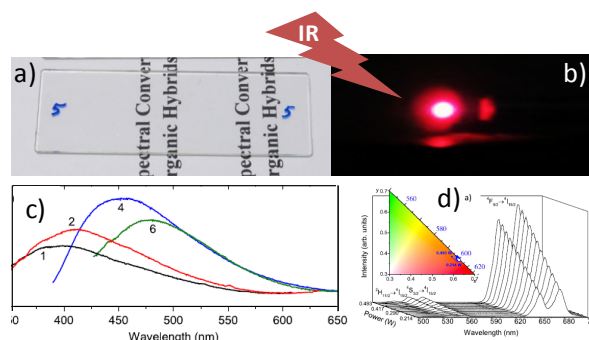


Figure 1. (a,c,d) UC ZrO_2 -diureasil nanocomposite: picture of a film(a), emission spectra upon excitation in the UV-VIS range (c) and at 980 nm (d). (b) Red emission of the pure UCNPs pumped at 980 nm.

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P18

**Ionosilicas as functional materials in the sustainable development:
Organocatalysis and adsorption/separation of anionic pollutants**

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Ionosilicas are defined as silica based materials containing covalently tethered ionic groups.¹ These materials, situated at the interface of silica hybrid materials and ionic liquids, have large potential in catalysis, molecular recognition and separation. This talk will focus on applications of ionosilicas as versatile materials for energy applications for the sustainable development: ionosilicas are versatile heterogeneous organocatalysts and efficient adsorbents for anionic pollutants.

We recently studied ionosilicas as heterogeneous organocatalysts in Henry-, Knoevenagel and Biginelli-reactions^{2,3} as well as for cycloadditions of carbon dioxide to epoxides.⁴ Generally, very high catalytic activities together with good re-usability of the ionosilica based heterogeneous organocatalysts were observed. However, our studies indicate that the catalytic activities of mesoporous ionosilicas depend on various parameters such as the nature of the grafted cationic species, the nature of the counter ion, the hydrophobicity of the surface and the condensation degree of the silica support. Furthermore, synergetic effects may further modify the catalytic properties of the materials. For this reason, ionosilicas cannot simply be considered as simple silica supported Ionic Liquids, but a variety of parameters related to support and supported ionic species must be taken in consideration.

On the other side, ion exchange involving ionosilica materials appear as an interesting way for the sequestration of charged species. In this field, we recently showed that ionosilicas can efficiently adsorb various anionic pollutants such as organic dyes and drugs, but also more specific anions such as iodine and pertechnetate.⁵ These two latter anions are of particular interest in the nuclear waste management. As there is still a need for efficient anion adsorbing materials, ionosilicas open new opportunities in the areas of wastewater management and the nuclear fuel cycle.

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P19

High performance shape memory epoxy-silica nanocomposites

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The shape memory polymers (SMP) represent the class of smart materials able to store the energy and release it upon an external stimulus. The high performance shape memory (SM) epoxy-silica nanocomposites have been synthesized. The structure of the corresponding SMP was designed on the basis of the determined relationships between structure, mechanical properties and SM performance. The recovery stress, as a crucial SM property of high performance systems, is governed by the material toughness while the efficiency of the SM performance is controlled by morphological homogeneity and viscoelastic behaviour of the polymer as well as by experimental conditions of the SM procedure. The nanocomposites were prepared by in situ generation of nanosilica in the epoxy matrix. The non-aqueous sol-gel procedure was applied and the ionic liquid (IL) was used at synthesis as a multifunctional agent controlling morphology and mechanical properties. The thermomechanical properties were tuned and T_g of SMPs were adjusted by optimization of crosslinking density of the epoxy matrix and flexibility of polymer chains, by introducing physical crosslinks and silica nanofiller to increase rubbery modulus and by application of the IL at synthesis in order to narrow glass transition. Tensile properties, toughness, were determined to be enhanced by silica nanofiller and by application of the IL. Moreover, the bimodal epoxy networks showed a very high toughness and enabled a high extensibility of the SMP. The effect of polymer viscoelasticity and relaxation, as a property deteriorating the efficiency of SM performance, is reduced by increasing a system elasticity and homogeneity; by enhancing crosslinking density and by application of the IL. Based on the knowledge of the corresponding relationships and structural effects, the SM nanocomposite was synthesized showing the high recovery stress $\sigma_r = 3.9$ MPa or high deformability $\epsilon_b = 103$ %. The shape fixity and recovery of the polymer shape under nonconstrained conditions were nearly 100 %. They were proved to be controlled mainly by the material thermomechanical properties such as moduli at deformation and setting temperatures, and broadness of the glass transition. The study contributed to the better understanding of the SM behaviour of polymers.

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HINT workshop:

*Interface in Hybrids for Sustainable Energy Applications
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P20

Effect of graphite nanoplatelets on properties of conductive microfibrillar composite

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Modification of polymer materials including introduction of polymer non-typical properties like electrical conductivity using physical methods is of constant interest. In situ formation of reinforcing short polymeric fibers by melt or cold drawing of polymer blends to get microfibrillar composites (MFC) provides perfect dispersion and bonding. The limited parameters of these polymer-polymer composites can be improved by application of nanofillers. Due to high complexity of NF effects in multicomponent drawn systems, both synergistic and antagonistic effects may occur. In this study we have successfully applied graphite nanoplatelets (xGnP) to upgrade MFC based on PCL/PLA combination. The role of xGnP is quite complex; its addition only allow drawing by eliminating unstable extrusion in combination with reinforcement and electrical conductivity. Structure-properties relationships of composite material for broad range of applications are discussed.



P21

Solid state NMR study of the effect of TEOS addition to ureasilicate matrices for corrosion protection (STSM work)

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Ureasilicate (U(X)) coatings are able to behave as a physical barrier improving corrosion protection in highly alkaline environments ($\text{pH} > 12.5$)¹⁻³ and chloride ion diffusion to the substrate⁴, thus decreasing the corrosion reaction rate on the metal surface of hot dip galvanized steel (HDGS). To further improve the corrosion protection properties of these coatings, different contents of tetraethoxysilane (TEOS) were added into the reaction mixture during the preparation of the U(X) matrices in which the content of 3-isocyanate propyltriethoxysilane (ICPTES) was also changed. TEOS and ICPTES addition have the effect of increasing the inorganic component of the matrix. In this study the increasing of the inorganic components on corrosion resistance is reported for the ureasilicates synthesized with higher molecular weights of Jeffamine (approximately 600, 900 and 2000 g mol⁻¹). The increase of the inorganic components on the structure of the OIH sol-gel films was investigated by solid state Nuclear Magnetic Resonance (NMR) and atomic force microscopy (AFM). The mechanical properties were characterized by Vickers nano-indentation tests. The variation of Jeffamine:ICPTES ratio and the addition of TEOS seems not to affect the organic structure of the hybrid materials. The NMR results indicate that the TEOS addition causes a reduction of the condensation of the hybrids. The addition of TEOS improves the mechanical properties of the OIH coatings synthesized.

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