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workshop on
nanoenergetics

Nanoenergetics: theoretical and experimental approaches

ICTP, Adriatico Guesthouse
Trieste, Italy
15-16 November 2011



Program

15 November 2011

14:15 - 14:50: Fonda -Fasella Award: E. Miniussi – University of Trieste
"A link between corrugation and thermal stability of epitaxial grapheme"

Chair: S. Lizzit

14:50 - 15:30: A. Morgante - CNR-IOM & University of Trieste
"Charge transfer processes in organic thin films and organic heterostructures of interest for photovoltaic applications"

15:30 – 16:10: T. Pichler - University of Vienna
"Tailoring the electronic properties of low-dimensional carbon solid"

Coffee break

16:40 – 17:20: R. Gebauer - ICTP, Trieste Italy
"A Combined Molecular Dynamics and Computational Spectroscopy Study of a Dye Sensitized Solar Cell"

17:20 – 18:00: C.A. Pignedoli - EMPA - Theory and atomistic simulation group
"Storage of Methane by van der Waals confinement: Sumanene/Ag(111) a preliminary experimental/computational study"

18:00 - 18:40: V. Palermo - ISOF-CNR-Area della Ricerca di Bologna
"Graphene-organic composites as active materials and surface coatings for nanotechnology applications"

Dinner

16 November 2011

Chair: A. Baraldi

9:30 - 10:10: V. Matolin - Charles University, Prague
"Hard X- and Soft X- PES Investigation of Nanostructured PEM Fuel Cell Catalysts"

10:10 – 10:50: H. Amenitsch – Austrian Academy of Sciences
"In situ small angle X-ray scattering to reveal the formation of materials for nanoenergetics"

coffee break

11:20 – 12:00: L. Gregoratti – Sincrotrone Trieste S.c.p.A.
"Chemical imaging with the zone plate based photoemission microscope of Elettra: another step to bridge the Material Gap"

12:00 – 12:40: M. Bonchio - ITM-CNR sezione di Padova/Università di Padova
"Artificial Photosynthesis Challenges: Water Splitting at Nanostructured Interfaces"

Lunch

Chair: S. De Gironcoli

14:30 – 15:10 : G. Pacchioni - University of Milano-Bicocca
"Oxides at the nanoscale as new catalytic materials"

15:10 – 15:50: S. Fabris - CNR-IOM, DEMOCRITOS - SISSA - Theory@Elettra group
"Thermodynamic and kinetic origins of efficient water oxidation by multi-redox catalysts"

15:50 – 16:30: V. Aristov - IFW-Dresden
"Graphene layers on commercial available cubic-SiC(001)/Si wafers: a perspective for mass production of graphene-based electronic"

coffee break

17:00 – 17:40: A. Trovarelli - University of Udine
"Engineering of catalytic materials based on rare earth elements for energy and environmental applications"

17:40 – 18:20: M. Valant - University of Nova Gorica
"Electrocaloric effect in low dimensional oxides"

18:20 Closing remarks

FONDA FASELLA AWARD

A link between corrugation and thermal stability of epitaxial graphene

Miniussi Elisa

Department of Physics, University of Trieste, Italy

In recent years, epitaxial graphene has been the subject of an increasing interest in the fields of nanotechnology due to its outstanding properties.

It is acknowledged that the strength of the graphene-substrate coupling and the ensuing corrugation of the carbon film deeply affect not only the electronic, chemical and geometrical properties of the carbon layer, but also its heat transport properties.

In the present work we introduce a novel approach, based on the combined use of state-of-the-art synchrotron radiation-based techniques and density-functional theory calculations, to investigate the relationship between the corrugation of single-layer epitaxial graphene and its thermal stability. To this purpose, graphene was grown by chemical vapour deposition for the first time on a Re(0001) single crystal. As proved by our results, the strongly interacting nature of this system is reflected in a large corrugation of the graphene film on the substrate, and is responsible for its high temperature thermal instability. In fact, the disruption of the carbon network observed at high temperature turns out to be more likely in the buckled, strongly interacting regions of the moirè cell, although the process requires the presence of diffusing graphene layer vacancies.

Charge transfer processes in organic thin films and organic heterostructures of interest for photovoltaic applications

A. Morgante
CNR-IOM & University of Trieste, Italy

The performances and efficiency of organic material based devices and in particular of photovoltaic cells are strongly affected by charge transfer processes at interfaces (organic-organic and organic-inorganic). To improve the device performances these processes and their correlation with the electronic structure of the interfaces must be understood. Spectroscopic studies based on synchrotron radiation experimental techniques of these hetero-structures will be presented, in particular the application of the Resonant PhotoEmission Spectroscopy (RPES) to various organic molecule based systems. The chemical specificity and the possibility to conduct experiments in the energy domain that provides a time scale for charge dynamics, make the RPES a powerful tool to study organic heterojunctions and in particular to probe the charge transfer processes at organic interfaces. The models used in RPES data analysis to extract the time scale of the excited charge delocalisation and the spatial correlation of core, valence occupied and unoccupied molecular states will be briefly discussed. The application of RPES and other spectroscopic techniques to various interfaces will be reported. The case of ammine terminated organic overlayers will be discuss in connection with recent results of break junction experiments. Measurements carried out on ammine terminated organic molecules have been shown to provide for the first time reliable conductance measurements results. The comparison of RESPES and break junction experiments could elucidate the link between the quantum and the meso-scopic properties of organic-inorganic interfaces.

Tailoring the electronic properties of low-dimensional carbon solids

T. Pichler

Faculty of Physics, University of Vienna

The presentation will give an overview on our current research focus on the electronic properties of carbon based low dimensional quantum solids. These properties are strongly influenced by basic correlation effects. Archetypical examples of these systems are graphene, graphite and single wall carbon nanotubes (SWCNT) which are determined by the local arrangement of their sp^2 hybridised carbon atoms, such that their character is either a zero gap semiconductor, semi-metallic, insulating, semiconducting or metallic. Examples of our recent work on how one can unravel the underlying electronic structure using high energy spectroscopy (electron energy-loss, (resonant) photoemission and x-ray absorption spectroscopy) as a probe will be presented. Special emphasis will be given to the influence of basic correlation effects and local field corrections on the electronic properties of graphite, graphite intercalation compounds and SWCNT. The latter exhibit for metallic tubes a Luttinger liquid behavior.

Furthermore, an overview on how to functionalize them in order to tailor their electronic structure will be given. This includes examples for the three alternative doping routes, namely, substitution, intercalation and endohedral doping (e.g. by filling with fullerenes and metallocenes) as well as examples for the growth of defined inner tubes from the different precursors via a nanochemical reaction. For metallic functionalized nanotubes doping induced changes will be discussed in the framework of a dimensionality crossover which causes a change from a one-dimensional metal to a normal Fermi liquid. The detailed understanding of these fundamental electronic properties of functionalised graphite, SWCNT and graphene is the key to their future success.

A Combined Molecular Dynamics and Computational Spectroscopy Study of a Dye Sensitized Solar Cell

Ralph Gebauer

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Condensed Matter Section - Strada Costiera 11, I-34151 Trieste, Italy.*

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An organic dye sensitized solar cell consisting of a squaraine molecule attached to a TiO₂ surface is modeled using first principles molecular dynamics and time-dependent density functional theory. The system is surrounded by solvent molecules which are treated at the same level of theory as the dye molecule and the surface. The effect of the solvent on the optical properties is investigated by computing many absorption spectra for various configurations along a molecular dynamics trajectory. It is shown that the dynamical effects induced by thermal fluctuations have a strong effect on the optical properties, and that a satisfactory agreement with experiments is only achieved if those thermal effects are accounted for explicitly.

Storage of Methane by van der Waals confinement: Sumanene/Ag(111) a preliminary experimental/computational study

C.A. Pignedoli¹

In collaboration with:

P. Ruffieux¹, R. Jaafar¹, G. Bussi², O. Gröning¹, R. Fasel¹, T. Hirao³, and R. Fasel¹

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³*Department of Applied Chemistry, Osaka University (Japan)*

Sumanene molecules ($C_{21}H_{12}$ fragments of C_{60}) can be adsorbed on metallic substrates forming regular networks of units, with nanometer spacing, capable to host methane molecules.

I will discuss the results obtained from a combined experimental/computational study for the adsorption of sumanene on Ag(111) surfaces and co-adsorption of methane molecules.

Graphene-organic composites as active materials and surface coatings for nanotechnology applications

Vincenzo Palermo

ISOF-Consiglio Nazionale delle Ricerche, Bologna, Italy.

www.isof.cnr.it/nanochemistry/

The term “graphene” refers to a single layer of carbon atoms, arranged in a honeycomb, highly conjugated lattice. The sheets have monatomic thickness and can have a lateral size of hundreds of microns.

While the outstanding physical properties of graphene are well-known, the full potential of graphene chemistry has not yet been fully exploited. Being based on sp^2 carbon atoms, the properties of graphene backbone can be tailored by making use of the many covalent and non-covalent approaches of carbon-based organic chemistry, thereby providing new functionalities to this already exceptional material, as well as enabling its large scale production and solution processing.

Graphene charge mobility is some orders of magnitudes *greater* than the one of silicon; moreover, graphene exhibits a strong chemical affinity with organic molecules, spanning from p-conjugated materials, to fullerenes and DNA.

Here, we give an overview of possible applications of graphene-organic composites, in particular related to recent results obtained in our group on the:

- Covalent functionalization of graphene sheets with optically active oligothiophenes.
- Charge transport in graphene-polythiophene transistors.
- Local current mapping and patterning of reduced graphene oxide.
- Self-assembling of organic molecules on graphene single sheets.

Overall, graphene chemistry can potentially allow seamless integration of graphene technology in organic electronics devices to improve device performance and develop new applications for graphene-based materials. An overview of running and future initiatives of joint research on graphene at European level will be also presented for discussion.

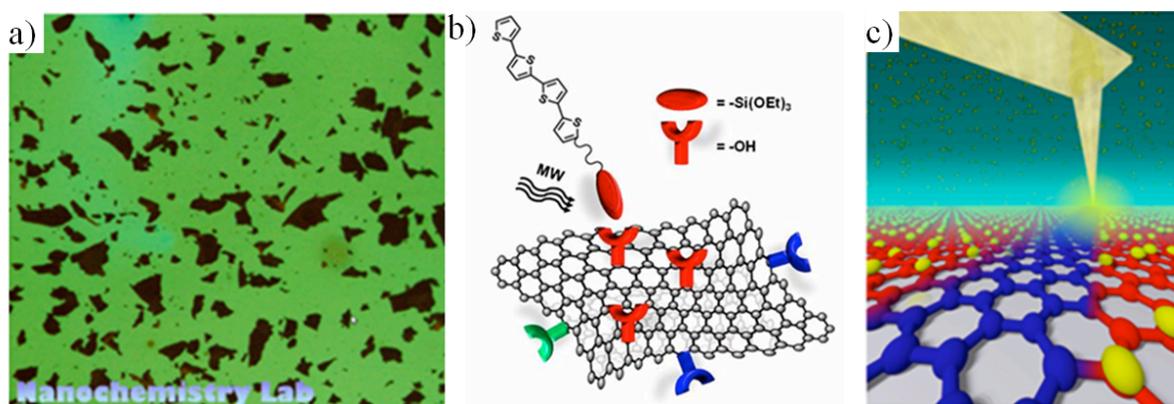


Figure 1: a) fluorescence image of GO single sheets on a T4 self-assembled monolayer, b) Sketch of one-step chemical functionalization of graphene, c) cartoon depicting local GO electrochemical reduction with a scanning probe tip.

1. J.M. Mativetsky, A. Liscio, E. Treossi, E. Orgiu, A. Zanelli, P. Samori, and V. Palermo, *Graphene Transistors via in Situ Voltage-Induced Reduction of Graphene-Oxide under Ambient Conditions*. **Journal of the American Chemical Society**, 2011. **133**(36): p. 14320-14326.
2. A. Liscio, G.P. Veronese, E. Treossi, F. Suriano, F. Rossella, V. Bellani, R. Rizzoli, P. Samori, and V. Palermo, *Charge transport in graphene-polythiophene blends as studied by Kelvin Probe Force Microscopy and transistor characterization*. **Journal of Materials Chemistry**, 2011. **21**(9): p. 2924-2931.
3. M. Melucci, E. Treossi, L. Ortolani, G. Giambastiani, V. Morandi, P. Klar, C. Casiraghi, P. Samori, and V. Palermo, *Facile covalent functionalization of graphene oxide using microwaves: bottom-up development of functional graphitic materials*. **Journal of Materials Chemistry**, 2010. **20**(41): p. 9052-9060.
4. J.M. Mativetsky, E. Treossi, E. Orgiu, M. Melucci, G.P. Veronese, P. Samori, and V. Palermo, *Local Current Mapping and Patterning of Reduced Graphene Oxide*. **Journal of the American Chemical Society**, 2010. **132**(40): p. 14130-14136.
5. E. Treossi, M. Melucci, A. Liscio, M. Gazzano, P. Samori, and V. Palermo, *High-Contrast Visualization of Graphene Oxide on Dye-Sensitized Glass, Quartz, and Silicon by Fluorescence Quenching*. **Journal of the American Chemical Society**, 2009. **131**(43): p. 15576.

Hard X- and Soft X- PES Investigation of Nanostructured PEM Fuel Cell Catalysts

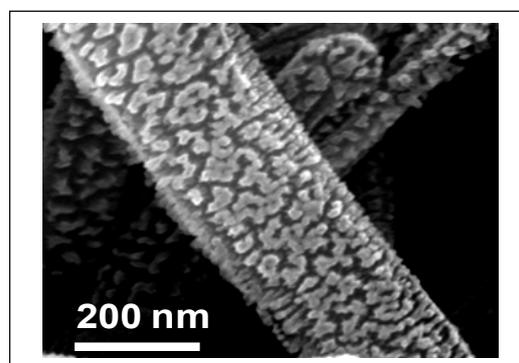
V. Matolin

Charles University in Prague, V Holesovickach 2, 18000 Prague, Czech Republic

Powering of electronic devices by microfabricated power sources, including micro-proton exchange membrane fuel cells (m-PEMFC), are being actually investigated in laboratories world-wide. The possibility of co-fabrication of a power source on the same substrate as the electric circuit offers many advantages, including a reduction in size and weight, increased processing efficiency, and lower cost. The important issue of planar type fuel cells is a preparation of large specific surface area catalysts grown by thin film deposition techniques which are compatible with planar technology.

Recently we showed by fuel cell activity and electron microscopy measurements the possibility of preparation of porous large surface and high activity nanostructured thin film catalysts by depositing the catalysts in form of Pt-Ce-O [1] solid solutions on different carbon substrates by magnetron sputtering. Figure shows example of CNTs coated by the porous Pt-CeO₂ catalyst film.

Chemical composition of the films was investigated by x-ray synchrotron radiation photoelectron spectroscopy in soft and hard X ray region. Resonant PES has been performed by measuring Ce 4f resonant profiles of both Ce⁴⁺ and Ce³⁺ states. The Pt-doped sputtered cerium oxide films contained high concentration of cationic platinum Pt²⁺ and Pt⁴⁺ which were highly active species for hydrogen dissociation to protonic hydrogen H⁺.



***In situ* small angle X-ray scattering to reveal the formation of materials for nanoenergetics.**

Heinz Amenitsch
Austrian Academy of Sciences, Austria

Simultaneous Small and Wide Angle X-ray Scattering (SWAXS) on both, bulk as well on surfaces, is used as standard tool for the structural characterization of materials used in nanoenergetics. Based on some exemplary investigations, this presentation should highlight the use and the information content obtained by using this method. The focus will lay on *in situ* experiments using synchrotron radiation, which reveals simultaneously the supramolecular and atomic structure of the investigated nanomaterials.

The presented topics will cover:

- (i) *in situ* characterization of mesoporous thin films, which find application as low dielectric material in the electronic industry or as photovoltaic materials used in a Grätzel cell [1]
- (ii) *in situ* grazing incidence study of the formation of Copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$, CZTS), which is very promising solar absorber material with a high optical absorption coefficient and an ideal band gap for photovoltaic applications. [2]
- (iii) *in situ*, real-time combined SWAXS investigation during the colloidal synthesis of zinc sulfide nanoparticles, which have potential applications in photonic crystals, photovoltaics and optoelectronic devices [3]

References

- [1] Malfatti, L. *et al.* Mesoporous self-assembled titania films for photovoltaic applications. *Microporous Mesoporous Mater.* **88**, 304-311 (2006).
- [2] Fischereder, A. *et al.* Investigation of $\text{Cu}_2\text{ZnSnS}_4$ formation from metal salts and thioacetamide. *Chem. Mater.* **22**, 3399-3406 (2010).
- [3] J. Novák, T. Rath, A. Pein, A. Fischereder, W. Haas, H. Amenitsch, F. Hofer, G. Trimmel, *in preparation*

Chemical imaging with the zone plate based photoemission microscope of Elettra: another step to bridge the Material Gap

L. Gregoratti, M. Amati and M. Kazemian Abyaneh
Sincrotrone Trieste ScpA

X-ray photoelectron spectroscopy (XPS) has remained the best method for probing the chemical and electronic structure of solid surfaces and interfaces. Using conventional X-ray tubes the yield of the photoelectrons emitted from the atomic electron levels is relatively low, which has imposed severe limitations on the spatial and energy resolution of the laboratory XPS machines. This major obstacle in development of the XPS microscopy has been overcome with the construction of the third generation synchrotron facilities. They provide ultra-bright, spatially coherent and tuneable photon beams, which is of fundamental importance to push the XPS lateral resolution into submicrometer length scales, maintaining a sufficient signal level and an acceptable acquisition time.

The scanning photoemission microscope (SPEM) available at the EscaMicroscopy beamline of the Elettra Synchrotron Light Source allows sample's chemical mapping with a spatial resolution below 100nm and the acquisition of photoemission spectra on regions with the same dimension by using zone plates (ZPs) as focusing elements. With respect to the photoemission spectromicroscopy techniques which require electromagnetic fields to achieve the spatial resolution, e.g. X-PEEM, the ZP-based SPEM is able to probe samples regardless their shape, structure and morphology. This property makes it an ideal tool for studying nanostructures often characterised by huge aspect ratios. Goal of this presentation is to provide an overview of the results and capabilities of the SPEM obtained in the field of nanoenergetics during its 16 years activity. Topics covered will focus on (i) chemical stability of materials used in the fabrication of solid oxide fuel cells (SOFCs) and proton exchange membrane fuel cells (PEMFCs) [1], (ii) characterization of single semiconducting nanostructure [2], (iii) experimental approaches to bridge the material and pressure gaps for catalytic reaction investigations [3].

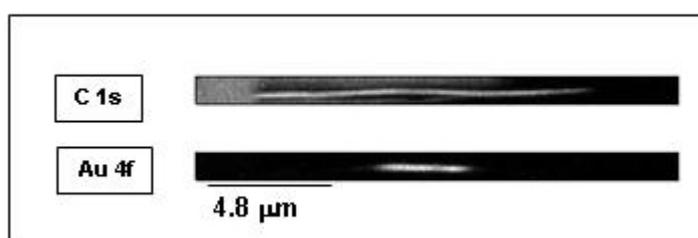


Fig.1: photoemission maps of a multiwall carbon nanotube with a confined Au patch recorded at the C 1s and Au 4f core levels.

- [1] B. Bozzini et al. *ChemSusChem* 4 (8), 2011, 1099–1103.
- [2] F. Jabeen et al. *Nano Research* 3 (10), 2010, 706-713.
- [3] M. Dalmiglio et al. *J. of Phys. Chem. C*, 114 (40), 2010, 16885-16891

Artificial Photosynthesis Challenges: Water Splitting at Nanostructured Interfaces

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Solar-powered water oxidation can be exploited for hydrogen generation by direct photocatalytic water splitting. A recent breakthrough in the field of artificial photosynthesis is the discovery of innovative oxygen evolving catalysts taken from the pool of the nano-sized, water soluble, molecular metal oxides, the so-called polyoxometalates (POMs). These catalysts provide a unique mimicry of the oxygen evolving centre in photosynthetic II enzyme (PSII), sharing a common functional-motif, i.e., a redox-active tetranuclear $\{M_4(m-O)_4\}$ core, and effecting H_2O oxidation to O_2 with unprecedented efficiency. In this scenario, the tetra-ruthenium based POM $[Ru^{IV}_4(m-OH)_2(m-O)_4(H_2O)_4(g-SiW_{10}O_{36})_2]^{10-}$, $Ru_4(SiW_{10})_2$, displays fast kinetics, exceptionally light-driven performance and electrocatalytic activity powered by carbon nanotubes.¹⁻²

Research in the field of artificial photosynthesis for the conversion of water to fuel has recently come to the awakening turning-point that a key issue is the design of efficient catalytic routines that can operate with energy and rates commensurate with the solar flux at ground level. A factual solution to this need implies the mastering of the electron transfer distance, junctions and potential gradients at the molecular level and within a nano-structured environment. Our vision points to a careful choice/design of the nano-structured support, and to a precise positioning of the catalytic domain on such templates, by tailored synthetic protocols. This is a key point to access single-site catalysis approaching the homogeneous behavior.

We report herein a combined synthetic, spectroscopic and mechanistic study on the use of POM catalysts for water oxidation and their combined use with visible light sensitizers and carbon nanostructures CNT. The outcome is a hybrid nanomaterial with unperturbed CNT electrical properties, in close contact with a unique multi-electron catalyst enabling electrocatalytic water splitting with high efficiency at low overpotentials.

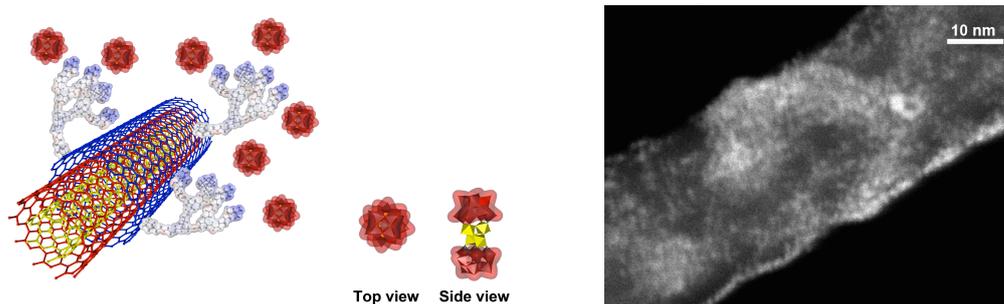


Figure 1. Electrostatic capture of polyanionic $Ru_4(SiW_{10})_2$ (polyhedral structure) by functionalized MWCNT with attached PAMAM dendrons. STEM images of the resulting nano-hybrids, brighter contrast domains are ascribed to the POM catalyst.

References

- [1] a) A. Sartorel, M. Carraro, G. Scorrano, R. De Zorzi, S. Geremia, N. D. McDaniel, S. Bernhard, M. Bonchio. *J. Am. Chem. Soc.* 130, (2008), 5006. b) A. Sartorel, P. Miró, E. Salvadori, S. Romain, M. Carraro, G. Scorrano, M. Di Valentin, A. Lloblet, C. Bo, M. Bonchio. *J. Am. Chem. Soc.* 131, (2009), 16051.

[2] a) F. M. Toma, A. Sartorel, M. Iurlo, M. Carraro, P. Parisse, C. Maccato, S. Rapino, B. Rodriguez Gonzalez, H. Amenitsch, T. Da Ros, L. Casalis, A. Goldoni, M. Marcaccio, G. Scorrano, G. Scoles, F. Paolucci, M. Prato, M. Bonchio. *Nat. Chem.* **2**, 826 (2010). b) M. Prato, M. Bonchio et al. *Chem. Sus. Chem.* (2011) in press.

Oxides at the nanoscale as new catalytic materials

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Oxides at the nanoscale and in particular oxide ultrathin films may exhibit specific surface morphology, physical properties, and chemical reactivity, thus providing new opportunities for the design of innovative materials with special emphasis on nanocatalysis. In this talk we discuss the possibility to functionalize oxide thin films by selective doping and we show how this can be used to tune the shape, electronic structure and reactivity of supported metal nanoparticles.

Thermodynamic and kinetic origins of efficient water oxidation by multi-redox catalysts

Fabris Stefano
CNR-IOM DEMOCRITOS and SISSA

We present a computational study addressing the catalytic cycle of a recently-synthesized inorganic catalyst capable to promote water oxidation with low overpotential and high turnover frequency [Sartorel et al., *J. Am. Chem. Soc.*, 2008, 130, 5006; Geletii et al., *Angew. Chem., Int. Ed.*, 2008, 47, 3896]. This homogeneous catalyst consists of a tetraruthenium-oxo core $[\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4]^{6+}$ capped by two polyoxometalate $[\text{SiW}_{10}\text{O}_{36}]^{8-}$ units and is one of the best catalysts for water oxidation reported to date. The reaction mechanism and thermodynamics underpinning its efficiency are currently under debate. The energetics of the relevant intermediates of the catalytic cycle is studied here with density functional theory calculations. This ab-initio thermodynamics identifies the energetically most demanding step, thus establishing the origin of the catalyst overpotential. The reaction mechanism for water oxidation and O_2 evolution is then addressed with the metadynamics technique. We demonstrate that the catalyst is activated by the formation of a Ru-oxo moiety, which undergoes a nucleophilic attack from a water molecule. The origins of the high efficiency of this metal-oxo catalytic core will be discussed in the context of heterogeneous metal-oxide surfaces and homogeneous metal-organic complexes.

Growth and characterization of graphene layers on cubic-SiC(001)/Si standard wafers

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Graphene synthesis on the surface of alpha-SiC at high pressure of argon [1, 2] is the best method for graphene preparation so far. Nevertheless it does not meet the requirements of industrial mass-production because of the limited size and the costly nature of alpha-SiC wafers sliced from the single crystal ingots. If graphene layers can be fabricated on the surface of thin SiC film grown on a large-diameter standard Si wafer (SiC virtual substrate), its industrial impact would be enormous. Such graphene/cubic-SiC(001)/Si wafer could be easily adapted for graphene-based electronic technologies and thus could be directly patterned by standard Si-electronic lithographic processes. The realizability of graphene synthesis on the surface of cubic-SiC(001) thin film (about 1 μm) deposited on standard Si wafer was already demonstrated in Refs. [3-5]. Here we show our recent data of investigation of graphene grown on SiC(001) virtual substrate. It seems that the results represent a realistic way of bridging the gap between the outstanding graphene properties and their technological applications.

Acknowledgements: This work was supported by the RFBR under grant 11-02-01253. We are grateful to T. Chassagne, M. Zielinski and M. Portail (CRHEA-CNRS, Sophia Antipolice, France) for providing SiC samples.

[1] K.V. Emtsev et al., *Nat. Mater.* **8**, 203 (2009).

[2] M. Sprinkle et al., *Phys. Rev. Lett.* **103**, 226803 (2009).

[3] V.Yu. Aristov et al., *Nano Letters* **10**, 992. (2010).

[4] V.Yu. Aristov et al., Tenth International Conference on the Structure of Surfaces & e-Conference (Hong Kong, China, August 2011), p. 9.

[5] A. Ouerghi et al., *Phys. Rev. B* **83**, 205429 (2011).

Engineering of catalytic materials based on rare earth elements for energy and environmental applications

A. Trovarelli
Udine University, Italy

Rare earth elements have been largely used in the last decade in catalyst formulations for a variety of processes in the area of both chemicals (refining of petrochemical products) and environment (especially dedicated to treatment of exhaust gases from mobile sources). The most significant of the rare earth elements are certainly lanthanum and cerium, their oxides being used as structural and electronic promoters in several applications in the field of environmental catalysis. La_2O_3 is well known as surface area stabilizer of supports based on alumina and zirconia, while the major benefit of cerium oxide is to increase oxygen storage/release properties of three-way catalyst formulations, often in combination with ZrO_2 and other rare earth oxides like PrO_x and TbO_x .

There are also several emerging applications or processes for which rare earth oxides are currently being actively investigated. More specifically cerium oxide is used in several applications for the energy sector as a key component in catalyst materials for reforming, partial oxidation and water gas shift reaction. Other energy-related uses are in the fuel cell technology where CeO_2 and other rare earth materials are fundamental components to reduce the operating temperature of solid oxide fuel cells.

As a contribution to these areas, we have been investigating in the last few years a number of issues concerning the design of mixed transition metal rare earth oxides and vanadates as active materials for fuel cell applications and for use in catalytic reactions involving elimination of soot and NO_x from diesel engine emissions. Some of these issues will be reviewed here, with a special focus on the design and modification of the properties of catalytic materials based on their fundamental structural/morphological characteristics.

Electrocaloric effect in low dimensional oxides

Matjaz Valant

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In the polar crystals the net dipole moment and, consequently, the polarization increases with an application of an external electric field. This causes a decrease in entropy of the system and, in turn, an adiabatic increase in temperature. This phenomenon is called the electrocaloric (EC) effect. The driving force for the research of the electrocaloric materials is the quest for the new alternative cooling technologies that would increase the efficiency of the cooling cycle and eliminate the need for the pollutant refrigerants and compressor unit that consumes high amount of energy.

The development of high EC effect bulk materials continues because the high refrigeration capacity that is required for the cooling medium and large-scale cooling facilities can merely be achieved with any other type of materials than ceramics. However, recent discovery of giant EC effect in thin films has turned the attention to low dimensional structures and application such as micro-cyrocoolers. Because of the experimental difficulties many authors have chosen to theoretically investigate the EC effect in low dimensional oxides. The main parameters of the thin films and their influence on EC effect are theoretically well elaborated. This includes mechanical and electrical boundaries (clamping, misfit strain, electric fields), film thickness, orientation related to EC anisotropy etc. Not only for thin films but also for quantum dots, nanoshells, pn-junctions EC effect have already been studied. The main highlights of the talk will be dedicated to the studies of mechanical boundaries, film thickness and origin of giant EC effect.