

**10th Brazilian / German Workshop on
Applied Surface Science
23.09 - 28.09 2018**

Kurparkhotel Bad Dürkheim, Germany

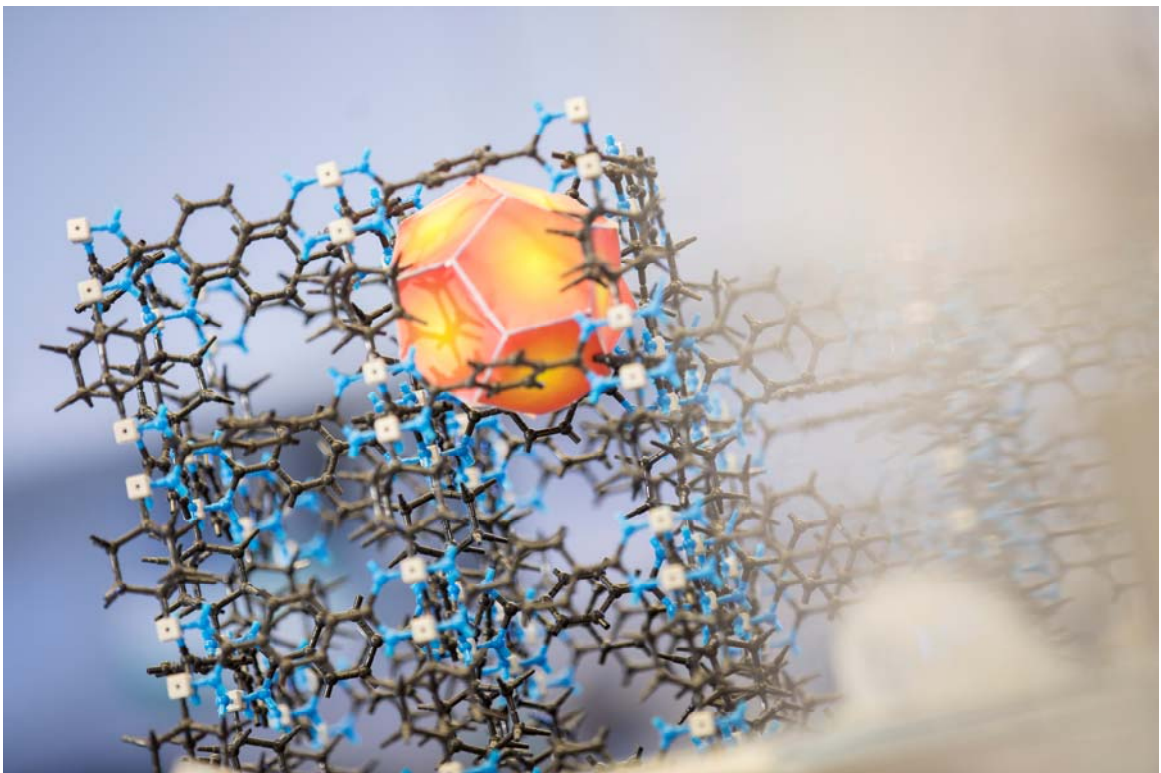


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PROGRAM

Monday, 24th September 2018

8:20 AM – 8:30 AM

César Bof Bufon, Christof Wöll

Opening Remarks

8:30 AM – 9:20 AM

Waldemar A. A. Macedo

Centro de Desenvolvimento da Tecnologia Nuclear - CDTN, Belo Horizonte, Brazil

Growth, Structure and Magnetic Anisotropy in Co-Fe Ultrathin Films and Co-Fe/Pt Multilayers

9:20 AM – 10:10 AM

Katharina Al-Shamery

Institute for Chemistry, Carl von Ossietzky University Oldenburg, Germany

How to Use Nanoscience for Renewable Energy Conversion

10:10 AM – 10:40 AM

Coffee Break

10:40 AM – 12:00 AM

Contributed Oral Presentations

10:40 AM – 11:05 AM

Christian Papp

Lehrstuhl für Physikalische Chemie 2, Egerlandstr. 3, 91058 Erlangen, Germany

Chemical Modification of 2 D Materials

11:05 AM – 11:30 AM

Jörg Libuda

Department of Chemistry and Pharmacy and Erlangen Catalysis Resource Center, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

Model Systems in Catalysis and Energy Science: From Surface Science to Electrochemistry and Photoelectrochemistry

11:30 AM – 11:55 AM

Jürgen Behm

Institute of Surface Chemistry and Catalysis, Ulm University, Ulm, Germany

Electrode - Electrolyte Interactions in Batteries: From a Surface Scientist's Perspective

12:00 PM – 14:00 PM

Lunch

14:00 PM – 14:50 PM

Edmar Avellar Soares

Departamento de Física, ICEX, UFMG, Belo Horizonte, Brazil

The Magnetic Properties of Co Monolayers Intercalated on Graphene/No-Magnetic Metal Interfaces

14:50 PM – 15:40 PM

Pavel Levkin

Institute of Toxicology and Genetics (ITG), Karlsruhe Institute of Technology, Karlsruhe, Germany

Superoleophobic Slippery Lubricant-Infused Surface: Combining two Extremes

15:40 PM – 16:10 PM

Coffee Break

16:10 PM – 17:00 PM

Martin Weinelt

Fachbereich Physik, Freie Universität Berlin, Berlin, Germany

Electron Dynamics in Spin-Orbit Materials

17:00 PM – 17:50 PM

Beatriz Roldán Cuenya

Department of Interface Science, Fritz-Haber-Institute of the Max Planck Society, Berlin, Germany

Size, Shape, Support and Chemical State Effects in the Conversion of CO₂ to Valuable Chemicals and Fuels

17:50 PM – 18:15 PM

Contributed Oral Presentation

Engelbert Redel

Karlsruhe Institute of Technology (KIT), Institute of Functional Interfaces (IFG), Karlsruhe, Germany

SURMOFs and CCNCs as Novel Tuneable Materials for Electronic Devices and Application

Tuesday, 25th September 2018

8:30 AM – 9:20 AM

Hans-Joachim Freund

Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Instrumentation Development and Novel Concepts in Model Catalysis

9:20 AM – 10:10 AM

Wolf-Dieter Schneider

Institut de Physique, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne
Switzerland / Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

From Adatoms to Superlattices: Sensing the Spin of Individual Ce-Atoms

10:10 AM – 10:40 AM

Coffee Break

10:40 AM – 12:00 AM

Contributed Oral Presentations

10:40 AM – 11:05 AM

Irene T. S. Garcia

Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil

*Tungsten Oxide Films Obtained by Anodization in Environmentally Friendly
Conditions: Structural and Optical Properties*

11:05 AM – 11:30 AM

Armin Götzhäuser

Faculty of Physics, Bielefeld University, Bielefeld, Germany

*Functional Nanomaterials from Surfaces: 2D Membranes for Water
Purification*

11:30 AM – 11:55 AM

Lars Heinke

Institute of Functional Interfaces, Karlsruhe Institute of Technology, Karlsruhe, Germany

Switching the Proton Conduction in Nanoporous, Crystalline Materials by Light

12:00 PM – 14:00 PM

Lunch

14:00 PM – 14:50 PM

Aldo J. G. Zarbin

Department of Chemistry, Federal University of Paraná (UFPR), Curitiba, Brazil

Thin Films of Advanced and Multifunctional Materials

14:50 PM – 15:40 PM

Andre Galembeck

Centro de Tecnologias Estratégicas do Nordeste (CETENE), Recife, Brazil

*Luminescent Nanocomposites with High Colloidal Stability and Self-
Healable Metallo-Gels*

15:40 PM – 16:10 PM

Coffee Break

16:10 PM – 17:00 PM

Abner de Siervo

Instituto de Física „Gleb Wataghin“, Universidade Estadual de Campinas, Campinas, Brazil

On-surface Synthesis of Complex Molecular Nanostructures Through Ullmann-Coupling Reactions

17:00 PM – 18:30 PM

Poster Session 1

Rodrigo C. de Campos Ferreira

Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas – UNICAMP, Campinas, Brazil

On-surface Reaction and Diffusion of (tetra-4-chlorophenyl) porphyrin on Cu(111)

Lucas M. Arruda

Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

CAPES Foundation, Ministry of Education of Brazil, 70040-020 Brasília-DF, Brazil

Surface- and Ligand-Dependent Quenching of the Spin Magnetic Moment of Co Porphyrins

Astrid Alí Pereya

Brazilian Center for Research in Physics (CBPF), Brazil

Epitaxial Growth and Characterization of Mn₃O₄ Thin Films on Cu (111)

Jan Kuliga

Universität Erlangen, Erlangen, Germany

Metalation and Coordination Reactions of 2h-meso-trans-di(p-cyanophenyl)porphyrin on Ag(111) with Co-Adsorbed Cobalt Atoms

Leonardo O. M. de SOUSA

Universidade Federal de Minas Gerais, Instituto de Ciências Exatas, Departamento de Física.

Laboratório de Física de Superfícies Sala 4155b, Pampulha - 31270901 - Belo Horizonte, MG - Brazil

Electronic and Structural Properties of Co Monolayers Intercalated at the Graphene/Ni(111) Interface by Photoelectron Diffraction (PED)

Engelbert Redel

Institute of Functional Interfaces, Karlsruhe Institute of Technology, Karlsruhe, Germany

SURMOF Based "Designer Solids" for Microelectronic Devices and Thermoelectric Materials Characterization

Wednesday, 26th September 2018

8:30 AM – 9:20 AM

Wendell Simões e Silva

Brazilian Synchrotron Light Laboratory, Campinas, Brazil

Probing Eletronic Structure with ARPES Using Soft X-ray at Sirius

9:20 AM – 10:10 AM

Hans-Peter Steinrück

Physikalische Chemie, Universität Erlangen-Nürnberg, Germany

Ion Liquid Surface Science

10:10 AM – 10:40 AM

Coffee Break

10:40 AM – 12:00 AM

Contributed Oral Presentations

10:40 AM – 11:05 AM

Ulrich K. Heiz

Department of Chemistry, Technische Universität München, Garching, Germany

Why Co-Catalyst-Loaded Rutile Facilitates Photocatalytic Hydrogen Evolution

11:05 AM – 11:30 AM

Wolfgang Kuch

Institut für Experimentalphysik, Freie Universität Berlin, Berlin, Germany

Reversible PhotoSwitching of Spiropyran Molecules Adsorbed on Metal Surfaces

11:30 AM – 11:55 AM

Artur Böttcher

Institute of Physical Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany

Electron-impact Induced Fragmentation for Soft-Landing of Molecular Ions as a Procedure to Grow Unique Carbon Nanomaterials

12:00 PM – 14:00 PM

Lunch

14:00 PM – 23:00 PM

Conference Outing: Winery in Deidesheim

Thursday, 27th September 2018

8:30 AM – 9:20 AM

Jonder Morais

Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil

Tayloring and Probing the Atomic Arrangement of bi-metallic Nanoparticles

9:20 AM – 10:10 AM

Martin Stutzmann

Walter Schottky Institute and Physics Department, Technische Universität München, Garching, Germany

Optoelectronic Processes at the Gallium Nitride Surface

10:10 AM – 10:40 AM

Coffee Break

10:40 AM – 12:00 AM

Contributed Oral Presentations

10:40 AM – 11:05 AM

Martin Sterrer

Institute of Physics, University of Graz, Graz, Austria

Metalation of Organic Molecules: Tetraphenylporphyrin on MgO(001)/Ag(001) thin films

11:05 AM – 11:30 AM

Petra Tegeder

Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany

Time-Resolved Nonlinear Optics and Photoelectron Spectroscopy at Functional Interfaces: Singlet Fission Dynamics

11:30 AM – 11:55 AM

Paulo B. Miranda

Sao Carlos Physics Institute, University of Sao Paulo, Sao Carlos, Brazil

Structure and Dynamics of Water Adsorbed on the Gypsum (010) Surface

12:00 PM – 14:00 PM

Lunch

14:00 PM – 14:50 PM

Edson Roberto Leite

Laboratório Nacional de Nanotecnologia (LNNano), Campinas, Brazil

The Role of the Ion Segregation in the Photoelectrochemical Performance of Hematite for Solar Water Splitting

14:50 PM – 15:40 PM

Joyce Rodrigues de Araújo

Materials Metrology Division, INMETRO, Duque de Caxias, PENt/COPPE, Universidade Federal do Rio de Janeiro, Brazil

Biocatalysis using Graphene Oxide as a Matrix for Enzyme Immobilization

15:40 PM – 16:10 PM

Coffee Break

16:10 PM – 17:00 PM

Alexandre Reily Rocha

Instituto de Física Teórica (IFT) – Universidade Estadual Paulista (UNESP), São Paulo

Simulating the Electronic Structure of Water Molecules on Metallic Surfaces under an Applied Bias

17:00 PM – 18:30 PM

Poster Session 2

Engelbert Redel

Institute of Functional Interfaces, Karlsruhe Institute of Technology, Karlsruhe, Germany
SURMOF/CCNC Based "Designer Solids" for Photonic, Optical and Energy Applications

Qi An

Institute of Functional Interfaces, Karlsruhe Institute of Technology, Karlsruhe, Germany
Synthesis of Stimuli-responsive and Self-healing Porous Polymers via Dynamic Nitroxide Exchange Reaction

Kai Müller

Karlsruhe Institute of Technology (KIT), Institute of Functional Interfaces (IFG), Karlsruhe, Germany
Surface Defects in HKUST-1 MOFs investigated by Spectroscopy and mass transfer experiments

Letícia M. M. Ferro

Brazilian Nanotechnology National Laboratory, CNPEM, Campinas-SP, Brazil
Planar and Rolled-up Nanomembrane-based Electrochemical Cells

Sascha Koch

Universität Bielefeld, Bielefeld, Germany
Observation of Cross-linking: Transition from SAM to CNM

Tatjana Parra Vello

Brazilian Nanotechnology National Laboratory (LNNano), CNPEM, Brazil
Department of Physical Chemistry, Institute of Chemistry (IQ), UNICAMP, Brazil
Characterization of Surface Metal-Organic Frameworks (SURMOFs) Films for Applications in Electrical Devices

Yuemin Wang

Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
Surface Chemistry of Model and Nanostructured Metal/oxide Systems

Friday, 28th September 2018

8:30 AM – 9:20 AM

Gregor Witte

Faculty of Physics, Philipps-University Marburg, Germany
Template Controlled Growth of Van der Waals Bound Organic Semiconductor Films and Hetero-structures for Investigations of their Optoelectronic Properties

9:20 AM – 10:10 AM

Michael Zharnikov

Applied Physical Chemistry, Heidelberg University, Heidelberg, Germany

Functional Monomolecular Films on Solid Supports

10:10 AM – 10:40 AM

Coffee Break

10:40 AM – 12:00 AM

Contributed Oral Presentations

10:40 AM – 11:05 AM

Andreas Terfort

Institut für Anorganische und Analytische Chemie, Johann Wolfgang Goethe Universität Frankfurt, Germany

Optimization of Charge-Carrier Injection in Organic Electronics by DIPOLAR Self-assembled Monolayers

11:05 AM – 11:30 AM

Nadiia Mameka

Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Geesthacht, Germany

Surface Modification and Bulk Mechanics: Tailoring the Strength of Nanoporous Gold by Self-Assembled Monolayers of Alkanethiols

11:30 AM – 11:55 AM

Hubertus Marbach

Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Germany

Surface-Anchored Metal-Organic Frameworks as Versatile Resists for E-Beam Lithography: Fabrication of sub-10 nm Structures

12:00 PM – 14:00 PM

Closing remarks / Lunch

14:00 PM

Departure

Invited Presentations

HOW TO USE NANOSCIENCE FOR RENEWABLE ENERGY CONVERSION

K. Al-Shamery

*Carl von Ossietzky University Oldenburg, Institute for Chemistry, 26111 Oldenburg, Germany
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Nanoparticles are a key component of many heterogeneous photocatalysts to convert solar into chemically stored energy. However, in order to tailor the catalyst to the specific need of the chemical reaction it is essential to understand a multitude of different aspects. Besides the size and structure of the nanoparticle the interaction between the particle and the support may play an important role. In case of photocatalysis the dynamics of excited charge carriers and the availability at the reaction site has to be understood. Furthermore the reactants also exhibit a specific dynamics. In the talk a colloidal approach will be presented allowing in contrast to classical impregnation-calcination techniques to control the size, shape, particle loading and the study of the nanoparticle support interaction [1]. The ligands stabilizing the colloids may further act to influence the selectivity of the chemical reaction. The work will focus on amine capped platinum and gold nanoparticles deposited at various oxidic supports. For a photocatalytic application nanosized superparticles consisting of nanoparticle building blocks combine the advantages of light absorption in a broad part of the visible range with the high reactivity of single, small sized nanoparticles. Furthermore the electron dynamics at a metal-semiconductor interface will be presented together with size dependent photocatalysis at metal nanoparticles [2].

Keywords: photocatalysis, nanoparticle, superparticle, colloids, gold, platinum.

References

- [1] Siemer, Michael; Mohrhusen, Lars; Grebien, Maximilian; Al-Shamery, Katharina, *Zeitschrift für Physikalische Chemie*, 2019, DOI: <https://doi.org/10.1515/zpch-2018-0004>.
- [2] Al-Shamery, Katharina; Al-Shemmary, Alaa; Buchwald, Robert; Hoogestraat, Dirk; Kampling, Margarethe; Nickut, Patricia; Wille, Ansgar, *European Physical Journal B (Condensed Matter and Complex Systems)*, 2010, 75, 107-114.

BIOCATALYSIS USING GRAPHENE OXIDE AS A MATRIX FOR ENZYME IMMOBILIZATION

J. R. Araujo^{1*}, J. M. Luzardo^{1,2}, C. A. Achete¹, R. A. Simão²

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Graphene oxide (GO), having a large specific surface area and abundant functional groups, provides an ideal substrate for enzyme immobilization [1]. Combining atomic force microscopy (AFM) imaging results of the immobilized enzyme molecules, water contact angle measurements (WCA) and their catalytic activity, we illustrated that the conformation of the immobilized enzyme is mainly determined by interactions of enzyme molecules with the functional groups of GO. In this work, the β -galactosidase (lactase) enzyme has been used for immobilization in membranes of graphene oxide synthesized by two different methods: electrochemically synthesized graphene oxide (EG), and graphene oxide (GO) synthesized via chemical oxidation of graphite followed by its exfoliation in an ultra-sound bath, process known as Hummers methodology [2]. The β -galactosidase enzyme was immobilized in different concentrations (0.5 to 10 mg mL⁻¹) by physical adsorption where the membranes were immersed in a phosphate buffer solution (PBS) containing the enzyme and heated at 30 ° C for 1 h. EG membrane, without enzyme on the surface, showed 22.9° WCA while GO membrane, showed WCA of 55.6 ° indicating that EG has higher hydrophobicity than GO membrane. After enzyme immobilization, WCA showed significant changes, mainly in GO membranes, reaching WCA of 77 ° due to the creation of nanorugosities taking these membranes more hydrophobic. Through AFM images it was possible to see that EG membrane has higher ability to immobilize β -galactosidase enzyme. This fact is related to the hydrophobicity of the EG surface, allowing the enzyme to open their active sites to adsorb in the support, which is called interfacial activation of the enzyme.

Keywords: biocatalysis, atomic force microscopy, enzymes, graphene oxide.

References

[1] Zhang, Jiali; Zhang, Feng; Yang, Haijun; Huang, Xuelei; Liu, Hui; Zhang, Jingyan; Guo, Shouwu, *Langmuir*, 2010, 26, 6083.

[2] Hummers, William; Offeman, Richard, *J. Am. Chem. Soc.*, 1958, 80, 1339.

On-surface synthesis of complex molecular nanostructures through Ullmann-coupling reactions

A. de Siervo

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On-surface synthesis based on the so called *bottom-up approach* has become a common method to produce complex nanostructures, for instance 2D materials and molecular frameworks, under ultra-high vacuum conditions [1]. Typically, molecular precursors are dosed onto a well-defined substrate where the competition between molecule-substrate and molecule-molecule interactions is the most important mechanism to allow molecular diffusion toward stabilized self-assembly structures. Several mechanisms of stabilization are chemically activated by the substrate depending on the molecule functional groups, for example, through hydrogenation and dehydrogenation, metal coordination, polymerization, among others [2]. Ullmann coupling reactions have shown to be one of the most effective ways to architecture covalent-bonded nanostructures. In general, an Ullmann coupling reaction starts with the cleavage of the halogen bond in the molecular precursors as a first step toward the formation of C-C covalent bond [3]. In this work we will discuss the roles of surface adsorption and kinetics in determining the final molecular self-assembly of 5,10,15,20-(tetra-4-chlorophenyl) porphyrin on Cu(111) and Ag(111) assisted by Ullmann reaction. The study combining scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and density-functional theory (DFT) calculations have allowed to image, and unambiguously characterize the initial, intermediate and final species upon reaction. By comparing the calculated energy barrier for an assisted Ullman-coupling reaction and a direct dechlorination of the molecule we are able to determine the most favorable thermodynamic pathway for this reaction.

Acknowledgments

This work was financially supported by FAPESP through projects 2017/08846-7, 2017/09529-5 and 2007/54829-5, as well as by CAPES and CNPq from Brazil.

Keywords: Ullman-coupling, porphyrin, scanning tunneling microscopy, DFT.

References

- [1] Gottfried, J. Michael, *Surface Science Reports*, 2015, 70, 259–379.
- [2] Lafferentz, Leif; et al., *Nature chemistry*, 2012, 4, 215-220.
- [3] Bieri, M.; et al., *Chem. Commun.* 2011, 47, 10239–10241.

THE MAGNETIC PROPERTIES OF CO MONOLAYERS INTERCALATED ON GRAPHENE NO-MAGNETIC METAL INTERFACES

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The possibility of utilizing the rich spin-dependent properties of graphene has attracted much attention in the pursuit of spintronics advances. The promise of high-speed and low-energy-consumption devices motivates the search for layered structures that stabilize chiral spin textures such as topologically protected skyrmions. Here we demonstrate that chiral spin textures are induced at graphene/ferromagnetic metal interfaces. Graphene is a weak spin-orbit coupling material and is generally not expected to induce a sufficient Dzyaloshinskii–Moriya interaction to affect magnetic chirality. We demonstrate that indeed graphene does induce a type of Dzyaloshinskii–Moriya interaction due to the Rashba effect. First-principles calculations and experiments using spin-polarized electron microscopy show that this graphene-induced Dzyaloshinskii–Moriya interaction can have a similar magnitude to that at interfaces with heavy metals. This work paves a path towards two-dimensional-material- based spin-orbitronics.

Keywords: graphene/metal interface, spintronics.

References

[1] Yang, Hongxin; Chen, Gong; Cotta, Alexandre A. C.; N'Diaye, Alpha T.; Nikolaev, Sergey A.; Soares, Edmar A.; Macedo, Waldemar A. A.; Liu, Kai; Schmid, Andreas K.; Fert, Albert; Chshiev, Mairbek, *Nature Materials*, 2018, 17, 605–609.

INSTRUMENTATION DEVELOPMENT AND NOVEL CONCEPTS IN MODEL CATALYSIS

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Action spectroscopy with rare gas messenger atoms is commonly used for the characterization of aggregates in the gas phase. With this method vibrational spectra of the clusters are measured via detection of rare gas desorption following a vibrational excitation. We have constructed an apparatus for the application of action spectroscopy with rare gas messenger atoms to surfaces of solids. Experiments performed for neon covered $V_2O_3(0001)$ show that this method is applicable to surfaces. It is highly surface sensitive in that exclusively vibrations with a large vibrational amplitude at the surface are detected. Unlike IRAS, normalization to a reference spectrum is not required for action spectroscopy data and unlike HREELS, it does not suffer from moderate resolution nor from multiple excitations.¹ Reactions in confined space are relevant in catalysis using micro- and meso-porous materials. We have designed a study to investigate a simple reaction such as water formation from oxygen and hydrogen at a transition metal surface both in open and confined space to be in a position to evaluate the factors influencing the kinetics of those reactions. The space between a Ru(0001) surface and a silica bi-layer film is used to mimic the confined space. The silica bi-layer is completely valence saturated and perfectly inert against the participating species. It is only bound via van-der-Waals forces to the underlying metal surface, and may be produced as a crystalline as well as a vitreous film. This enables us to compare the apparent activation energies of water formation on an open Ru(0001) with the one for the equivalent reaction in confined space. We use a reaction front observed and characterized using a LEEM/PEEM microscope at the BESSY synchrotron.²

Keywords: surface science, instrumentation, oxides, surface reactions.

References:

- [1] Wu, Zongfang; Plucienik, Agata; Feiten, Felix E.; et al., *Phys. Rev. Lett.*, 2017, 119 (13), 136101.
- [2] Prieto, Mauricio J.; Klemm, Hagen W.; Xiong, Feng; et al., *Angew. Chem. Int. Ed.*, 2017, 57, 8749.

LUMINESCENT NANOCOMPOSITES WITH HIGH COLLOIDAL STABILITY AND SELF-HEALABLE METALLO-GELS

A. Galembeck, M. Pelagio-Flores, C. Martinez-Ibanez, S. B. C. Silva, E. Skovroinski

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Some of the most important challenges to develop new electronic materials stand on the transition from “heavy and brittle” to “light, thin, flexible” platforms [1]. In this sense, some processing properties such as being printable and compatible with the fabrication of self-healable devices became important. In this communication, we describe two different materials compatible with this processing features: (i) a moldable and self-healable metallo-gels with mixed ionic-electronic conductivity and; (ii) luminescent nanocomposites formed by nitrogen-doped carbon nanotubes (CN_x) decorated with poly(styrene-co-2-hydroxy-ethyl-methacrylate) [P(S-HEMA)] with high colloidal stability.

The self-healable metallo-gels are formed by the coordination of polyphosphate polyanions with Al³⁺ and Fe³⁺ cations to give a supramolecular network with ionic conductivity reaching 10⁻² S cm⁻¹ [2]. Polyaniline can be formed within the metallo-gel and impairs electronic conductivity to the resulting hybrid material. The samples can be molded by manual handling and can be healed after being broken.

In the CN_x/[P(S-HEMA)] nanocomposites, the polymer nanoparticles were loaded with an europium coordination compound [Eu(btfa)₃(H₂O)₂]. The nanocomposites were designed to maximize the emission properties of the europium ions by combining the antenna effect and a co-polymer matrix which can, in principle, improve the quantum yield. The co-polymer, in its turn, has processing properties lacking in the Eu³⁺ coordination compound and their particle size was tailored to match the diameter of the CN_x nanotubes in such a way that a homogeneous deposition of these particles on the surface of the nanotubes could be achieved. The carbon nanotubes add better mechanical properties and electrical conductivity to resulting material. The nanocomposites present exceptional colloidal stability in water.

Keywords: self-healing; metallo-gel; colloidal stability, carbon nanotubes, latex.

References

[1] Chen, D.; Wang, D.; Yang, Y.; Huang, Q.; Zhu, S.; Zheng, Z., “Self-Healing Materials for Next-Generation Energy Harvesting and Storage Devices”, *Advanced Energy Materials*, 2017, 7, 1700890.

[2] Mendes, L.G.; Galembeck, A.; Engelsberg, M.; Diniz, F.B., *Colloids Surfaces A*, 2006, 281, 99.

THE ROLE OF THE ION SEGREGATION IN THE PHOTOELECTROCHEMICAL PERFORMANCE OF HEMATITE FOR SOLAR WATER SPLITTING

Edson R. Leite

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Energy from the sun can provide sufficient power for all of our energy needs and a potentially efficient route to storing this energy is to convert sunlight into chemical energy in the form of chemical bonds, which is a form of an artificial photosynthesis process. Considering the abundance of H₂O on the planet, water splitting is a natural pathway for artificial photosynthesis. Based on Fujishima and Honda's pioneer work (the authors showed that it is possible to induce the water-splitting by light, using TiO₂ semiconductor as photoanode), worldwide research has focused on the conversion of sunlight into hydrogen as a clean and renewable energy source. In the photoelectrochemical cell, one or both of the electrodes can be a photoactive semiconductor, in which a space-charge (depletion) layer is formed at the semiconductor/liquid junction (SCLJ). Under light irradiation, a pair of electron-hole is generated and the carriers are separated by the space-charge field and the minority carriers (holes for an n-type photoanode) travel to the SCLJ to perform one half of the water-splitting reaction. The main focus of this presentation is to describe and discuss the influence of the nanostructure control in the photoelectrochemistry performance of hematite (α -Fe₂O₃). In special, how to avoid the electron-hole recombination and the influence of the grain boundary in this process. We intend to address a critical discussion about the impact of the dopant segregation at grain boundary in the semiconductors oxides photoanode performance for water oxidation.

SUPEROLEOPHOBIC SLIPPERY LUBRICANT-INFUSED SURFACE: COMBINING TWO EXTREMES

Z. Dong, M. F. Schumann, M. J. Hokkanen, B. Chang, A. Welle, Q. Zhou, R. H. A. Ras, M. Wegener, P. A. Levkin

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The ability to create superoleophobic surfaces repellent towards low surface tension liquids is important for various applications, and has been recently demonstrated using re-entrant or doubly re-entrant microtopographies. Both types of microstructures, however, possess high liquid-solid contact surface area, leading to high adhesion forces. Here, the development of a novel slippery superoleophobic surface with low adhesion is demonstrated via combining the doubly re-entrant microtopography with slippery liquid-infused porous surfaces (SLIPS). This is realized by using 3D direct laser writing to fabricate doubly re-entrant micropillars with dedicated nanostructures on top of each pillar. The top nanostructures stabilize the impregnated slippery lubricant, while the re-entrant geometry of the micropillars prevents lubricant from spreading. The slippery layer reduces the adhesion of a liquid to the pillars, as proved using scanning droplet adhesion microscopy, while the doubly re-entrant micropillars make the surface superoleophobic. This novel interface combining two extremes, superoleophobicity and slippery liquid-infused surface, is of importance for designing superoleophobic and superhydrophobic surfaces with advanced liquid repellent, anti-icing or anti-fouling properties.

Keywords: superhydrophobicity, superoleophobicity, DLW, SDAM, SLIPS, lubricant-infused surfaces.

References

- [1] Ueda, E.; Levkin, P. A., *Adv. Mater.*, 2013, 25, 1234.
- [2] Dong, Z.; Schumann, M.F.; Hokkanen, M.J.; Chang, B.; Welle, A.; Zhou, Q.; Ras, R.H.A.; Wegener, M.; Levkin, P.A., 2018, under revision.

GROWTH, STRUCTURE AND MAGNETIC ANISOTROPY IN Co-Fe ULTRATHIN FILMS AND Co-Fe/Pt MULTILAYERS

W. A. A. Macedo

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The magnetism of nanostructured materials in the form of ultrathin films and multilayers is an important current topic in materials science and technology, and materials with perpendicular magnetic anisotropy (PMA) are of high interest due to their applications in spintronic devices. In this talk, it will be presented and discussed experimental results on the growth, structure and magnetic anisotropy of layered Fe-Co-based nanostructures prepared by molecular beam epitaxy (MBE), and also by magnetron sputtering. We have investigated the influence of chemical order in the magnetic anisotropy of alternated Fe/Co monolayers epitaxially grown on Cu₃Au(001) by MBE. The stoichiometry, structure, morphology and magnetic properties of the films were characterized in-situ using XPS, LEED, RHEED, STM and MOKE measurements, respectively. Our results indicate that the chemical order and also the surface layer play an important role in establishing the film magnetic anisotropy. The effective magnetic anisotropy can be tuned from in-plane to out-of-plane depending on which material (Fe or Co) the alternated film is terminated, contrary to codeposited FeCo films, that present only in-plane magnetic anisotropy [1]. We have also investigated the influence of the preparation (growth rate of the Pt buffer layer) on the perpendicular magnetic anisotropy in Pt/[Co₆₀Fe₄₀/Pt]₅ multilayers grown by magnetron sputtering. Highly crystallized, atomically flat (111) fcc-textured [CoFe/Pt] multilayers were obtained. Our investigation show that the formation of an ordered phase of Pt₅₀Co₃₀Fe₂₀ with a fcc (111) texture, which is affected by the growth rate of the Pt buffer, regulates the anisotropy field in the multilayer system, evidencing a magnetocrystalline origin of the observed perpendicular anisotropy [2].

Keywords: perpendicular magnetic anisotropy, Co/Fe/Cu₃Au(100), Co₆₀Fe₄₀/Pt.

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TAYLORING AND PROBING THE ATOMIC ARRANGEMENT OF BI-METALLIC NANOPARTICLES

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Regardless of all efforts devoted to the synthesis of bimetallic nanoparticles (NPs) with controlled shape and structure, the underlying relationship between their atomic arrangement and reactivity are still under debate. In this work, bimetallic PtPd NPs with approximately 5 nm mean diameter were synthesized to achieve distinct atomic distributions: nanoalloys or core@shell. The samples were probed by Medium Energy Ion Scattering (MEIS) and space-resolved elemental analysis via energy dispersive X-ray (EDX) spectroscopy in STEM (Scanning Transmission Electron Microscope) mode. The complementary association of STEM-EDX profiling with MEIS, which simultaneously surveys millions of NPs, becomes a powerful tool for a statistically representative structural analysis. As result, the measurements provided key details such as core size, shell thickness and composition, and even distinguished core@shell from core@alloy structures. PtPd nanoalloys and Pd-core structures were successfully obtained while the attempt to produce Pt-core NPs actually resulted in a mixture of nanoalloy and core@alloy structures (core = Pt or Pd). In order to correlate structure and reactivity, catalysts were prepared using these PtPd NPs, and their performance was evaluated under “operand” conditions. Different EXAFS measurements were performed under reducing and oxidizing atmospheres. Particularly, in one of the experiments the catalysts were tested toward the direct decomposition of NO reduction [1]. The Pd K and Pt L₃ edges EXAFS signal were collected and simultaneously, the effluent gases from the reactor were analyzed by a mass spectrometer. The results shed some light on the structural evolution during the NO abatement, at the atomic level, and demonstrated its influence on the NPs’ reactivity.

Keywords: Pt, Pd, nanoparticles, in situ, MEIS , XPS, XAS.

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SIMULATING THE ELECTRONIC STRUCTURE OF WATER MOLECULES ON METALLIC SURFACES UNDER AN APPLIED BIAS

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Understanding the local structure of water at the interfaces of metallic electrodes is a key issue in aqueous-based electrochemistry. Nevertheless a realistic simulation of such a setup is challenging, particularly when the electrodes are maintained at different potentials. To correctly compute the effect of an external bias potential applied to truly semi-infinite surfaces, we combine Density Functional Theory and Non-Equilibrium Green's Function (methods. This framework allows for the out-of-equilibrium calculation of forces and dynamics, and directly correlates to the chemical potential of the electrodes, which is introduced experimentally. In this work, we apply this methodology to study the electronic properties and atomic forces of a water molecule at the interface of a gold surface. We find that the water molecule tends to align its dipole moment with the electric field, and it is either repelled or attracted to the metal depending on the sign and magnitude of the applied bias, in an asymmetric fashion.

Keywords: electrochemistry, density functional theory, non-equilibrium Green's functions.

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SIZE, SHAPE, SUPPORT, AND CHEMICAL STATE EFFECTS IN THE CONVERSION OF CO₂ TO VALUABLE CHEMICALS AND FUELS

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Tailoring the chemical reactivity of nanomaterials at the atomic level is one of the most important challenges in catalysis research. In order to achieve this elusive goal, we must first obtain a fundamental understanding of the structural and chemical properties of these complex systems. In addition, the dynamic nature of the nanostructured films and nanoparticle (NP) catalysts and their response to the environment must be taken into consideration. To address the complexity of real-world catalysts, a synergistic approach taking advantage of a variety of cutting-edge experimental methods (EC-AFM, SEM, TPD, AP-XPS, XAFS, GC) has been undertaken.

This talk will provide new insights into the thermal hydrogenation and electrocatalytic reduction of CO₂. Important aspects that will be discussed are: (i) the design of size- and shape-controlled catalytically active NPs (Cu, Cu-Zn, Cu-Ag) and plasma-activated nanostructured metal films (Ag, Cu), and (ii) the investigation of structure/chemical state-reactivity correlations in situ and under operando reaction conditions in realistic reaction conditions, i.e., at high pressure or under potential control [1-4]. The results are expected to open up new routes for the reutilization of CO₂ through its direct conversion into valuable chemicals and fuels such as carbon monoxide, methane, ethylene, methanol, ethanol, and propanol.

Keywords: nanostructured films, nanoparticle catalysts, electrocatalysis, carbon dioxide hydrogenation, carbon dioxide electroreduction.

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FROM ADATOMS TO SUPERLATTICES: SENSING THE SPIN OF INDIVIDUAL CE-ATOMS

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Recently, correlation-driven transport asymmetries, reminiscent of spin-polarized transport in a magnetic field, have been observed in the tunneling spectra between two magnetic impurities, one at the tip of a scanning tunneling microscope, the other one on the sample surface [1]. Here we apply this technique in zero magnetic field and at a temperature of 0.5 K, to reveal the spin of an individual Ce adatom on the surface of a CuN ultrathin film. The presence of the Ce 4f spin manifests itself in the differential conductance spectra recorded in a tunneling junction between a PtIr tip, functionalized with a Ce-cluster at its apex, and a single Ce adatom on the sample surface. By identifying this cluster as a Ce-trimer at the tip apex via its Kondo and spin excitation spectrum, a fundamental understanding of the manifestations of the 4f spin in Ce adatoms is obtained. The three Ce adatoms forming the trimer are shown to couple ferromagnetically to a total spin of 3/2 with a degenerate Kondo ground state of spin 1/2 [2]. The degeneracy of the ground state of the Ce-trimer at the tip is gradually lifted by decreasing the tunneling resistance (decreasing the tip surface distance) and thereby increasing the interaction with the 4f spin of a single Ce adatom at the sample surface. The induced splitting of the Ce trimer Kondo resonance of about 2 meV corresponds to an effective magnetic field of 5 Tesla [3]. Thus, employing the vertical atom manipulation capabilities of the STM, the functionalized tip is used as a spin detector for single magnetic Ce adatoms in the absence of an external magnetic field. This achievement validates an alternative route to the study of magnetic nanostructures [4], circumventing the application of spin-polarized STM tips. When individual Ce adatoms assemble to create a superlattice on Ag(111) with an interatomic lattice spacing of 3.2 nm [5], a Kondo lattice is formed. The differential conductance spectra obtained on single Ce-adatoms within the superlattice reveal a considerably broadened Kondo resonance of about 70 meV as compared to the one of 1 meV found for isolated Ce-trimers, indicating the presence of antiferromagnetic indirect exchange interactions (RKKY) in the superlattice[6]. In the light of these results, the present study opens new insights into the interplay between Kondo physics, localized spin-flip excitations, and the magnetic exchange interaction.

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ION LIQUID SURFACE SCIENCE

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Ionic liquids (ILs) are salts with melting points below 100 °C. Typically, they are characterized by an extremely low vapour pressure. Since their physical and chemical properties can be tailored over a wide range, they represent a fascinating class of liquid materials with interesting applications in catalysis. Two important concepts in this context are Supported Ionic Liquid Phase (SILP) and Solid Catalyst with Ionic Liquid Layer (SCILL). In both, a high surface area solid substrate is covered with a thin IL film. In SILP, the film contains a homogeneously dissolved transition metal complex; in SCILL, the film modifies catalytically active surface sites at the support. The interfaces of the IL with the gas phase and with catalytic nanoparticles and/or support materials are thus of critical importance. These interfaces can be investigated in great detail under well-defined ultrahigh vacuum conditions using surface science methods such as in situ deposition of ultrathin IL films on solid supports. From angle-resolved X-ray photoelectron spectroscopy, not only information on the surface and bulk composition of non-functionalized and functionalized IL films or the reactivity of catalytically active metal complexes in ILs can be deduced, but also their interfaces can be studied on the molecular level. The obtained information includes the adsorption geometry and growth mode of IL on various support materials. A number of examples will be discussed.

OPTOELECTRONIC PROCESSES AT THE GALLIUM NITRIDE SURFACE

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Gallium nitride (GaN) and its related lower band gap InGaN alloys have met increasing interest in the photocatalysis community due to the advantageous optical and electronic properties of this material system (band edge positions, direct band gap, bipolar doping, chemical stability). Especially InGaN nanowire arrays with a large surface-to-volume ratio have attracted a lot of attention lately. In this presentation we will discuss recent results concerning optoelectronic processes occurring at the surface of GaN epitaxial layers (c-plane) and at the sidewalls (m-plane) of GaN nanowires exposed to different environmental conditions (vacuum, ambient air, liquid electrolytes) and under above-band gap illumination. Photoconductivity, photoluminescence, surface photovoltage and cyclic voltammetry measurements were employed to investigate charge transfer processes between the bulk of GaN and the GaN surface and between the GaN surface and the external environment [1,2]. Implications of our results for applications of GaN in photocatalysis will be analyzed.

Keywords: GaN, surface states, nanowires, photocatalysis, charge transfer processes.

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ELECTRON DYNAMICS IN SPIN-ORBIT MATERIALS

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Topological insulators (TIs) and Rashba materials host surface states with spin structure. This makes them promising materials for the generation of spin-polarized currents. The TI Bi₂Se₃ is intrinsically n-doped and exhibits an occupied and an unoccupied topological surface states at the Γ point with a Dirac cone dispersion. It has been disputed, whether photocurrents, induced in Bi₂Se₃ with circularly polarized light stem from these Dirac cones. We studied the momentum distribution of electrons excited with circularly polarized light and find dichroic photoemission, both at resonant and off-resonant excitation. While a two-dimensional (E,k_y)-cut perpendicular to the plane of incidence would support the commonly assumed coupling of the photon angular momentum to the electron spin, it is inconsistent with the observed azimuthal (k_x, k_y) – patterns. Instead it reflects the surface point group. The only anti-symmetric patterns appear in the energy range, in which surface and bulk states hybridize. In general, a threefold-symmetric dichroic signal does not support unidirectional photocurrents. Nevertheless, the residual asymmetry of up to 3.5% in our photoemission spectra is compatible with previously observed helicity-dependent photocurrents.

BiTeI is a layered semiconductor without inversion symmetry. Strong spin-orbit coupling leads to a giant Rashba-splitting of the BiTeI surface and bulk bands. We studied the population dynamics of excited carriers in pure and Mn-doped BiTeI. Applying a 6.2-eV probe pulse, we monitor the Rashba-split surface state and conduction band on the Te-terminated surface. Its surface state has a nearly isotropic free-electron-like dispersion with a positive effective mass. Excitation with a 1.5-eV pump pulse generates hot electrons with picosecond decay times. The lifetimes of electrons do not depend on the sample temperature (50 vs 300 K). In contrast, we find a very different behavior for hole lifetimes. They are overall smaller than corresponding electron lifetimes, and show a strong temperature dependence. We attribute this difference to the opening of an plasmon emission channel.

Keywords: Topological insulator, Rashba, Surface State, Femtosecond Electron Dynamics.

*This work results from two collaborations between groups at FU Berlin¹, FAU Erlangen², LMU München³, St. Petersburg State University⁴, Novosibirsk State University⁵ and Tomsk State University⁶.

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PROBING ELETRONIC STRUCTURE WITH ARPES USING SOFT X-RAY AT SIRIUS

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Angle-resolved photoemission Spectroscopy (ARPES) has been shown to be very powerful tool to study a variety of materials because of its capability of directly measuring the spectral function. It gives information on direction, speed and scattering process of the electrons, in that way, mapping the reciprocal space of the material. ARPES experiments are performed on a wide variety of systems. Among the most famous systems we can point out complex oxides, Weyl semimetals and topological insulators. In the last few years, studies using this technique have shed light on the concepts and helped the understanding of these new types of materials [1,2]. In this presentation, I am going to talk about the ARPES technique and the experimental set up of ARPES endstation attached to IPE beamline. IPE will be one of the first beamlines to be constructed at Sirius, the 4th generation synchrotron light source still under construction in Brazil. That machine will provide to Brazilian community the state of art for such experiments allowing users to probe bulk states as well as states near the surface, with the same high quality, using soft X-rays. I will also show some ARPES data acquired at the PGM beamline in LNLS facilities and discuss the results and the perspectives for them in this brand new Beamline at SIRIUS. In particular, I will discuss the results of the ZnO(0001) metallization after HCL etching which has been performed at the PGM beamline in LNLS with the photon energy of 103.5 eV. Photons with this energy have a high surface sensitivity which makes them useful to probe the electronic structure on the interface of the substrate and small ordered structures grown/adsorbed on their surfaces.

Keywords: ARPES, SIRIUS, Zinc Oxide, Topological Insulators, Weyl Semimetals.

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TEMPLATE CONTROLLED GROWTH OF VAN DER WAALS BOUND ORGANIC SEMICONDUCTOR FILMS AND HETERO-STRUCTURES FOR INVESTIGATIONS OF THEIR OPTOELECTRONIC PROPERTIES

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Despite the recent success of optoelectronic organic devices such as photovoltaic cells, the fundamental understanding of the involved photo-physical processes is still incomplete. This is mainly due to the complex microstructure of blends utilized in customary devices that hampers precise microscopic interface studies. Polycyclic aromatic molecules such as oligoacenes are versatile building blocks which form crystalline films and can also be modified chemically, e.g. by fluorination which turns the p-type pentacene (PEN) into the n-type perfluoropentacene (PFP). By tuning the growth kinetics and employing template effects, crystalline molecular films of predetermined molecular orientation and even specific polymorphs can be prepared that enable detailed optical studies [1]. For the case of PFP heteroepitaxial crystalline films can be grown onto alkali halide substrates which render polarization and directional resolved optical measurements on individual crystalline molecular domains possible. Based on time- and polarization-resolved pump-probe experiments this allows identifying correlations between molecular packing motifs and singlet-exciton fission processes [2]. Furthermore, structural and optical properties of molecular acceptor/donor hetero-systems are discussed at the examples of PEN/PFP. Using the concept of templated film growth affords the realization of hetero-stacks with well-defined molecular interfaces either in standing or lying molecular orientation [3], which allow to explore the energetics and dynamics of charge transfer excitons at the interfaces [4].

Keywords: Organic Semiconductors, Excitons.

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THIN FILMS OF ADVANCED AND MULTIFUNCTIONAL MATERIALS

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We are reporting during the last years that liquid-liquid (L/L) interfaces are suitable confined medium to stabilize thin films of unprocessable materials, easily transferable to several ordinary substrates enabling their studies in thin films-based devices. In this work will be presented the strategies and synthetic approach to prepare thin, transparent, homogeneous and conducting films of different carbon nanostructures (carbon nanotubes and graphene), as well as their nanocomposites with metal nanoparticles, conducting polymers and inorganic materials like Prussian blue and analogues. Also, a novel chemical (bottom up) synthetic route to graphene and graphene/polymer nanocomposite, based on L/L interfaces, will be presented. Application of these films as i) transparent and flexible electrodes; ii) electrodes for batteries; iii) electrochromic materials ; iv) sensors; v) active layers in photovoltaic devices; vi) SERS substrates; vii) supercapacitor and viii) catalysts, with improved and unusual performances, will be presented and discussed in light of the structure and morphology of the nanostructured films.

Keywords: liquid/liquid interfaces; carbon nanostructures; nanocomposites; energy applications.

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FUNCTIONAL MONOMOLECULAR FILMS ON SOLID SUPPORTS

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Self-assembled monolayers (SAMs) are 2D polycrystalline films of semi-rigid molecules that are chemically anchored to a suitable substrate. Blocking the substrate off the ambient, a SAM gives the surface a new physical and chemical identity, which can be precisely adjusted by the selection of the SAM constituents. These can be flexibly designed by a suitable combination of the individual building blocks, which are a docking group that makes the anchoring to the substrate, a tail group that is exposed to ambience, and a spacer that separates the docking and tail groups. The flexibility of the SAM design and the possibility to prepare these films on almost any substrate result in a variety of applications, such as e.g. tailoring surface properties, sensor fabrication, molecular and organic electronics (injection barrier and growth mode), and conventional and chemical lithography. In most cases, these applications rely on a specific architecture of SAM constituents and SAM as a whole as well as on precise knowledge of the SAM properties. In the overview talk, I will describe the basic properties and architecture of SAMs, address the current state of understanding of the molecular self-assembly, and give representative examples for design of application-relevant SAMs on noble metal, semiconductor, and insulator substrates. The emphasis will be put on tailoring molecular structure to achieve specific structural organization of the fabricated films as well as to create a definite chemical identity of the functionalized substrate. These are prerequisites for well-defined chemical and physical properties of the modified surface. Examples of application-related molecular design will be given, viz., in the areas of molecular and organic electronics [1,2], nanofabrication, sensor fabrication [3], and biofunctionalization [4].

Keywords: Self-assembled monolayers, molecular electronics, nanofabrication, sensors.

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Contributed Oral Presentations

ELECTRODE - ELECTROLYTE INTERACTIONS IN BATTERIES: FROM A SURFACE SCIENTIST'S PERSPECTIVE

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The close connection between Surface Science and Heterogeneous Catalysis, both on the experimental and on the theory side, is well established, and bridging the materials and pressure gap initially separating these disciplines has become a highly active field [1]. Such relations have recently developed also between the fields of Surface Science/Heterogeneous Catalysis and Electrochemistry/Electrocatalysis [2]. A similar relation and hence a similar approach seems to be promising also for the understanding of electrode – electrolyte interactions in batteries, which driven by the recent rise of Electrochemical Energy Technologies in concepts for future sustainable energy supplies have attracted considerable interest recently [3,4]. In the present contribution I want to illustrate the potential of Surface Science studies for the microscopic, molecular scale understanding of electrode – electrolyte interactions and processes, but also point out key differences, using simple processes such as the adsorption / desorption of organic electrolyte molecules or their decomposition as the first step to the build-up of the solid-electrolyte interphase as examples [5]. Another example refers to diffusion of charge carriers in electrode materials [5,6]. The potential of combined experimental and theoretical studies is demonstrated.

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ELECTRON-IMPACT INDUCED FRAGMENTATION FOR SOFT-LANDING OF MOLECULAR IONS AS A PROCEDURE TO GROW UNIQUE CARBON NANOMATERIALS

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Electron-impact induced ionization, heating and fragmentation of large molecules, in vacuum can provide ionized molecular fragments which after passing through a mass filter system are collected on an inert surface to form stable supported nanomaterials. The softly-land molecular radicals become stabilized by the migration-mediated formation of covalent inter-molecular bonds thus generating oligomers. The material properties (e.g., the film morphology) can be tuned by choosing the mass, ionic state, the impact energy and the temperature of the ionic molecular fragments. The capabilities of this approach [1], will be demonstrated for the example of non-IPR fullerene solids ([C₆₈], [C₅₈], [C₅₀]...). Electron impact efficiently converts the IPR fullerenes into reactive non-IPR cages as building blocks. The properties of the resulting materials (HOMO-LUMO gap, the sublimation enthalpy, ionization potential and the material hardness) scale with the size of the non-IPR cages.

The procedure has also recently been applied to partly dehydrogenate Coronene molecules and to collect the resulting radicals, C₂₄H_{12-n}, n<4, on an inert HOPG surface. The sublimation of the *activated* Coronene films evidences monomers and dimers as the main volatile film components which in turn show that polymers can be formed in the solid films. We have additionally exploited this approach to convert planar fluorinated PAHs into curved cups or even closed cages.[2] (via HF elimination in custom-designed planar PAHs). The resulting carbon cups are planned to be used as nuclei for CVD-based growth of chirality selected carbon nanotubes. In future, we propose to apply this approach as a synthetic pathway towards bulk-scale fabrication of low-mass non-IPR cages not yet accessible with other strategist.

Keywords: electron-impact induced fragmentation, novel carbon materials.

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TUNGSTEN OXIDE FILMS OBTAINED BY ANODIZATION IN ENVIRONMENTALLY FRIENDLY CONDITIONS: STRUCTURAL AND OPTICAL PROPERTIES

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The anodization process of tungsten foils allows oxide layers to be obtained with special optical and chromic properties [1]. The process is usually driven with strong acids and/or considerable concentrations of neutral electrolytes. This work reports the obtention of tungsten oxide films by anodization of tungsten foils in environmentally friendly conditions: with small amount of neutral electrolyte in aqueous media [2]. A 2⁴-factorial design permitted to understand the influence of variables, such as electrolyte concentration, glycerol as modifying agent, applied voltage and thermal annealing (300 °C, 60 min) on the structural and optical properties of the films. The films were characterized by atomic force microscopy, Raman spectroscopy, ellipsometry and photoluminescence spectroscopy. The applied voltage during anodization affects directly the roughness, thickness and the refractive index of the films. Two competitive reactions take place on the anode's surface: oxidation of tungsten and chlorine evolution. The continuous growth and dissolution of the oxide layer contribute to the production of porous oxide films with small refractive index and extinction coefficient. Among the variables, thermal annealing contributes to the development of crystalline phase, increasing particle size and, also, promoting the texturization of the oxide layers. The films were photoluminescent and emitted light between 300 to 630 nm, when excited at 266 nm. The development of crystallinity is strongly correlated with the observed decreasing in PL emission bands; this behavior can be attributed to the annihilation of the luminescent centers during the annealing process.

Acknowledgements

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Keywords: oxide films; anodization; optical properties; photoluminescence.

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FUNCTIONAL NANOMATERIALS FROM SURFACES: 2D MEMBRANES FOR WATER PURIFICATION

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Clean water is a global challenge, and membrane filtration is a key technology to achieve it. There are growing research efforts to explore the use of 2D carbon materials as nanoconduits for molecular transport and separation [1]. Surface science plays a prominent role in these activities as molecular surfaces layers can serve as precursors in the fabrication of nanomembranes. Here, we report on the fabrication and application of carbon nanomembranes (CNMs) with sub-nanometer channels that prove to be excellent water filters, combining a high selectivity with an exceptionally high water permeance. The CNMs are fabricated via the electron induced cross-linking of self-assembled monolayers (SAMs) [2]. CNMs made from terphenylthiol SAMs result in a ~1.2 nm thick membrane perforated by sub-nanometer channels with diameters below ~0.7 nm and areal densities of $\sim 10^{18} \text{ m}^{-2}$. When tested as filter membranes, it was found that the CNMs efficiently block the passage of most gases and liquids. However, water passes through with an exceptionally high permeance of $\sim 1.0 \times 10^{-4} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ [3]. This suggests that water fast and cooperatively translocates through a channel with a rate of $\sim 66 \text{ molecules} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. As the fabrication of CNMs is scalable, this finding can open new paths towards the use of 2D materials in water purification.

Keywords: Self-Assembled Monolayer, Carbon Nanomembranes, Filtration.

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SWITCHING THE PROTON CONDUCTION IN NANOPOROUS, CRYSTALLINE MATERIALS BY LIGHT

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Proton conducting nanoporous materials attract substantial attention with respect to applications in fuel cells, supercapacitors, chemical sensors and information processing devices inspired by biological systems. Here, a crystalline, nanoporous material which offers dynamic remote-control over the proton conduction is presented.^[1] This is realized by using well-defined surface-mounted metal-organic frameworks (SURMOFs) with azobenzene pendant groups that can undergo light-induced reversible isomerization between the stable *trans* and *cis* states.^[2] The *trans-cis* photoisomerization results in the modulation of the interaction between SURMOF host framework and guest molecules, 1,4-butanediol and 1,2,3-triazole; enabling the switching between the states with significantly increased (*trans*) and reduced (*cis*) conductivity. Quantum chemical calculations show that the *trans-to-cis* isomerization results in the formation of stronger hydrogen bridges of the guest molecules with the azo groups, causing stronger bonding of the guest molecules and, as a result, a smaller proton conductivity.^[1]

Keywords: Proton conduction, photoswitching, azobenzene, metal-organic frameworks, thin films.

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WHY CO-CATALYST-LOADED RUTILE FACILITATES PHOTOCATALYTIC HYDROGEN EVOLUTION

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Hydrogen generated from renewable feedstocks is envisioned to act as a potential fuel for clean transportation. In the last decade research focusing on increasing the efficiency of hydrogen production has tremendously been intensified by following both conventional and novel approaches. Photocatalytic water splitting facilitated by co-catalyst loaded semiconductor particles is one promising way for clean hydrogen production. Recently, such systems have been reported to exceed efficiencies of over 1% in a scalable solar-to-hydrogen production. Surprisingly, detailed mechanistic insights are still scarce despite of the intense research efforts undertaken in the past. Such knowledge, however, may be vital for the development of devices, which economically outperform electrolyzers driven by a solar cell. So far, there is general agreement that two different effects contribute to the hydrogen evolution rate, the charge carrier dynamics and the chemical reactions. For the latter, both partial reactions are usually treated somewhat independently from each other, following the concepts of photoelectrocatalysis. For most of the systems it is believed that the oxidation reaction is the rate-determining step, while the evolution of hydrogen occurs on a much faster time scale. The latter is usually viewed as a two-electron reduction of H^+ . If such a separate picture of both half-reactions is valid, the choice of particular semiconductor materials is subject to certain restrictions, for example the position of the band edges with respect to the electrochemical potential of the two half-reactions. In this regard, there is still a lively discussion whether rutile is capable of enabling the evolution of molecular hydrogen or if its conduction band edge is too low in energy. Evidenced by the study of the photocatalysis of methanol as model reaction, we show that H_2 evolution is indeed possible on a rutile single crystal decorated with small platinum clusters as co-catalysts. Experiments under well-defined conditions reveal the exact reaction mechanism, which does not occur along the (generally expected) reduction of H^+ by photoelectrons. Instead, the Pt co-catalysts only act as a thermal recombination site for hydrogen atoms. The mechanism also explains why only very little amounts of co-catalyst already facilitate efficient H_2 formation. We believe that this mechanism has to be considered in other photocatalytic systems, too, in particular for those that enable hydrogen surface diffusion.

Keywords: photo catalysis, alcohol reforming, hydrogen evolution, platinum clusters, titania.

REVERSIBLE PHOTOSWITCHING OF SPIROPYRAN MOLECULES ADSORBED ON METAL SURFACES

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Photochromic isomerization of molecules allows to remotely control systems on the molecular level by illumination only. Of particular interest for applications is the group of spiropyran, which can be switched from a closed form to an open form by UV light and reversibly back by visible light. Their drastic change of chemical reactivity, electric dipole moment, and geometry upon ring opening or closing attracts great attention. For utilization in nanoscale systems such as for molecular electronics, however, immobilization on a surface is mandatory, which strongly affects the switching ability. In nitro-spiropyran adsorbed on Au(111), for example, the back reaction to the closed form was found to be quenched [1]. Here we report reversible switching of adsorbed molecules from the closed to the open form by ultraviolet light and back to the closed form by temperature increase after replacing the nitro group with an electron-donating naphtho group to destabilize the open form and by using semimetallic Bi(111) as substrate to minimize van-der-Waals interaction [2]. Exchanging further the spiropyran by spirooxazine leads to a modified energy landscape of the excited states, which allows, presumably by avoiding a triplet state after excitation, a true bidirectional photochromism even on the Au(111) surface. This is demonstrated by comparison of near-edge x-ray absorption spectra to density-functional theory simulations and by in-situ differential reflection spectroscopy. Illumination with UV and red light triggers the photoconversion of the molecules from the closed to the open form and back, respectively, thus offering full optical and reversible control of the isomerization in direct contact with a single crystal surface [3]. Our results demonstrate that when molecules capable of switching in solutions are appropriately redesigned, even photochromic switching in direct contact with a metal surface can be achieved.

Keywords: Molecular switches, Surfaces, Spiropyran, Photochromism, NEXAFS.

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MODEL SYSTEMS IN CATALYSIS AND ENERGY SCIENCE: FROM SURFACE SCIENCE TO ELECTROCHEMISTRY AND PHOTOELECTROCHEMISTRY

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Designing complex interfaces is the key to the development of new functional materials in energy technology and energy-related catalysis. In our work, we explore model systems, which provide detailed insight into the chemistry and physics at such functional interfaces. Complex, yet atomically-defined model systems are studied both under ‘ideal’ surface science conditions and under ‘real’ conditions, i.e. in contact with gases, liquids, in electrochemical, and in photoelectrochemical environments. The approach is illustrated showing examples from our recent research.[1-4] First, we investigate model systems for complex oxide-based electrocatalysts. We describe how such model electrodes are prepared and characterized by surface science methods in ultrahigh vacuum and, subsequently, are studied in liquid electrolytes preserving their atomic structure. We investigate the role of particle size effects and identify the origin of metal–support interactions. In the second example, we scrutinize organic-oxide hybrid interfaces. Here, functional organic layers are anchored to atomically-defined oxide surfaces using specific linker groups, e.g. carboxylates or phosphonates. We investigate the anchoring mechanism and show that binding motifs, molecular orientation, and stability are controlled by the structure of the surface. Combining surface science and electrochemical studies, we identify the role of the charged interface in the anchoring reaction. Finally, we investigate molecular systems for solar energy storage. Scrutinizing norbornadiene-based photoswitches, we show that such molecules can be anchored to surfaces and photochemically converted under surface science conditions. Further, we demonstrate photochemical conversion and electrochemically triggered back-conversion with high reversibility.

Keywords: Model catalysis, heterogeneous catalysis, electrocatalysis, hybrid interfaces, energy storage and conversion.

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SURFACE MODIFICATION AND BULK MECHANICS: TAILORING THE STRENGTH OF NANOPOROUS GOLD BY SELF-ASSEMBLED MONOLAYERS OF ALKANETHIOLS

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A spontaneous chemisorption of functionalized organic molecules has emerged as a flexible and efficient way to control and modify the surface properties of flat substrates, nanoparticles, and nanoporous structures [1, 2]. While most of the studies focus on the mechanical properties of the resulting self-assembled organic monolayers (SAMs), very few attentions have been paid to the influence of SAMs on the behavior of the underlying substrates. Here, we exploit SAMs of alkanethiols to modify a surface of nanoporous gold (NPG) and probe the impact of the organic layers on the mechanical response of the bulk nanoporous samples. Made by dealloying, NPG provides a three-dimensional, freestanding and mechanically stable framework with extremely large surface area and open porosity [3, 4]. By testing the mm-sized specimens upon the SAMs formation in different thiol solutions, we reveal a substantial, up to 50%, the strength enhancement due to alkanethiol adsorption. In the contribution, we will discuss origins of the modified plastic behavior and outline future perspectives of SAMs for functionalization of free surfaces of nanostructured materials that can be profitably used to control their mechanical performance.

Keywords: Self-assembled monolayers, Alkanethiols, Dealloying, Nanoporous, Surface tension, Surface stress.

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SURFACE-ANCHORED METAL-ORGANIC FRAMEWORKS AS VERSATILE RESISTS FOR E-BEAM LITHOGRAPHY: FABRICATION OF SUB-10 NM STRUCTURES

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We explored Surface-Anchored Metal-Organic Frameworks (SURMOFs)^[1] as versatile resists/substrates for two specific Focused Electron Beam Induced Processing (FEBIP) techniques. The combination of such powerful lithographic protocols with the huge versatility of MOF materials allows for the fabrication of nanostructures with unique properties. The FEBIP methods applied here rely on the local decomposition of the volatile precursors Fe(CO)₅ and Co(CO)₃NO, either by the direct impact of the focused electron beam (Electron Beam Induced Deposition, EBID) or through the interaction of the precursor molecules with preirradiated/activated surface areas (Electron Beam Induced Surface Activation, EBISA).^[2] We demonstrate the huge potential of the approach for two different types of SURMOFs (HKUST-1 and Zn-DPDCPP). Application of our “surface science” approach, i.e. working in an ultra-high vacuum environment, allows to obtain well-defined deposits with any of the precursor/SURMOF combinations. Local Auger Electron Spectroscopy (AES) reveals that deposits from Fe(CO)₅ exclusively consist of iron, whereas deposits from Co(CO)₃NO contain cobalt, nitrogen and oxygen. EBISA experiments were successfully conducted with Fe(CO)₅ on both SURMOFs, whereas EBISA with Co(CO)₃NO on both SURMOFs does not result in deposit formation, making the process chemically selective. Most importantly we demonstrate the fabrication of “nested-L test structures” with Fe(CO)₅ on HKUST-1 with unusually narrow line width (average FWHM value 9.6 nm, smallest width 7.5 nm). This resolution can be considered extraordinary high, since the diameter of the electron beam was larger than 6 nm. We attribute this finding to reduced electron proximity effects, i.e. reduced electron scattering and quenching of secondary electrons within the SURMOF material.

Keywords: nanofabrication, gas-assisted electron beam lithography, SURMOFs.

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STRUCTURE AND DYNAMICS OF WATER ADSORBED ON THE GYPSUM (010) SURFACE

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Gypsum, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, is an abundant, low-cost mineral that is widely used in the construction industry (“plaster of Paris”) and is also of high medical and environmental relevance, but little is known about its surface structure and its interaction with water. We will present a combined experimental/theoretical study that provided a molecular-level understanding of the gypsum/water interface. We have investigated the structure and dynamics of adsorbed water from vapor at room temperature on the (010) Gypsum single crystal surface, by combining Sum Frequency Generation (SFG) vibrational spectroscopy and *ab initio* molecular dynamics (AIMD) simulations. The SFG spectra of Gypsum in low relative humidity (RH \sim 0.1%) showed anisotropic arrangement of (structural) surface water molecules and the presence of dangling OH groups. The AIMD simulations allowed a detailed assignment of the SFG spectra and showed that the cleaved (010) surface rearranges to have only 25% of the OH groups pointing away from the surface. At higher RHs, the first adsorbed water layer binds to these OH groups and forms an anisotropic arrangement, but with the amount of free OH groups significantly suppressed and with a slower surface diffusion with respect to bulk water. Upon adsorption of a second water layer, although the topmost layer of molecules is more disordered and dynamic than the previous one, its structure is still influenced by the Gypsum surface underneath, because it has a much reduced amount of free OH groups with respect to the free surface of water. The theoretical results corroborated the experimental ones and provided further insights into the surface structure that could not be obtained only from the experiments, such as an accurate atomic characterization of the surface structure.

Keywords: Gypsum, water, adsorption, sum-frequency vibrational spectroscopy, molecular dynamics simulations.

CHEMICAL MODIFICATION OF 2 D MATERIALS

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Understanding the chemical reactivity of 2D materials such as graphene and hexagonal-boron nitride (h-BN) is of fundamental importance for obtaining flexible and tunable materials for devices and electronic applications, as well as for fundamental science to obtain concepts for the chemistry on such materials. The interaction of graphene and h-BN with oxygen and atomic hydrogen will be discussed in details and the results for the two substrates will be compared. While in the case of atomic hydrogen, graphene forms graphane, i.e. fully hydrogenated graphene, for h-BN hydrogen can bond and intercalate, depending on the exposure. [1, 2] Interestingly, graphene does not react with molecular oxygen, even when supplied with a high kinetic energy of 0.7 eV, while h-BN readily forms bonds to oxygen, intercalates or even reacts, depending on the substrate temperature. Further insights to the bonding and reaction mechanisms of hydrogen and oxygen are obtained from DFT calculations.

Keywords: 2 D materials, Hydrogenation, Oxygen.

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SURMOFs AND CCNCs AS NOVEL TUNEABLE MATERIALS FOR ELECTRONIC DEVICES AND APPLICATIONS

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Here we present a particularly interesting class of surface-anchored (metal-organic frameworks and coordination network compounds) materials SURMOFs and (conductive coordination network compounds) CCNCs for the fabrication e.g. of 1D (Photonic Band Gap) PBG materials [1,2] as optical sensors, low-k dielectric thin films [3], optoelectronic/electrochromic switchable coatings/devices [4] microelectronic devices, e.g. RRAM devices. An outlook will be given on the characterization of conductive and porous CCNCs thin film materials as well as for further electronic characterization of SURMOFs and CCNCs.

Keywords: SURMOFs, CCNCs, Devices, Applications.

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METALATION OF ORGANIC MOLECULES: TETRAPHENYLPORPHYRIN ON MgO(001)/Ag(001) THIN FILMS

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The metalation of free-base tetraphenyl porphyrin (2H-TPP) on various metal surfaces has been extensively studied in the literature due to their potential in a variety of future technologies. On most metal surfaces, porphyrins and metallporphyrins adsorb in a flat adsorption geometry and form a square superstructure by self-assembly at/ or above room temperature. Much less investigated is the adsorption and metalation of porphyrins on oxide surfaces. However, metalation of 2H-TPP has been reported, e.g., on MgO [1,2] and TiO₂ [3]. Here, we present a comprehensive investigation of the adsorption and metalation of 2H-TPP on Ag(001) and MgO(001)/Ag(001) using LEED, TPD, STM, XPS and UPS. While the molecule adsorbs unmodified on the bare Ag(001) substrate, metalation of 2H-TPP on the MgO(001)/Ag(001) substrate is confirmed. We demonstrate that metalation of the 2H-TPP on Ag(100) can also be achieved by dosing with atomic Mg. Furthermore, we analyse the film-growth and electronic structure for both the unmetalated and metalated molecules. Of particular interest is, for both metalated monolayers, a hitherto unreported molecular state nearly 1eV below the Fermi level. This new state will be discussed in terms of charge transfer from the substrate into the molecule.

Keywords: Porphyrins, Metalation, Charge Transfer, Thin Oxide Films,

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TIME-RESOLVED NONLINEAR OPTICS AND PHOTOELECTRON SPECTROSCOPY AT FUNCTIONAL INTERFACES: SINGLET FISSION DYNAMICS

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Understanding the dynamics of electronically excited molecular states after optical excitation in organic semiconductors is necessary for improvement and optimization of potential molecule-based devices such as organic photovoltaic cells or organic light emitting diodes. Using femtosecond time-resolved second harmonic generation (SHG) [1,2] and two-photon photoemission (2PPE) spectroscopy [3] we investigated the dynamics of electronically excited states after optical excitation in several organic molecules. This includes the singlet fission dynamics. For instance, in triiso-propylsilylethynyl-pentacene (TIPS-Pn) adsorbed on Au(111) we proposed a coherent excitation of the singlet and multiexciton (ME) state, both decaying with the same time constant of 160 ± 60 fs. The triplet state stabilizes on a time scale of 1.6 ± 0.9 ps and decays to the ground state. The latter occurs within 620 ± 190 ps [4].

Keywords: fs time-resolved spectroscopy, organic semiconductors, exciton dynamics.

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OPTIMIZATION OF CHARGE-CARRIER INJECTION IN ORGANIC ELECTRONICS BY DIPOLAR SELF-ASSEMBLED MONOLAYERS

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Organic electronics is an area of science about to become mature, as it is already being integrated in many commercial devices. While a significant part of the effort is focused on optimizing the organic semiconductors in a rational and innovative manner, the problem of charge-carrier injection from the metallic electrodes into the semiconductors is tangled in an empirical way with often no working hypothesis. In this project, we developed a concept of structurally very similar molecules, that carry an internal dipole moment and are able to form self-assembled monolayers (SAMs) on coinage metal surfaces. For the induction of the internal dipole moments, pyrimidine rings were employed, which can be introduced either with the nitrogen atoms pointing toward the metal surface or away from it. The resulting monolayers permitted to vary the work function of the surfaces over a range of ± 0.5 eV, permitting a level alignment to adjacent organic semiconductors. In addition, the molecules were designed to facilitate the ordered, upright growth of the semiconductor, promoting the formation of large crystallites. These measures together result in a significantly improved performance of the final devices, as could be demonstrated in organic field-effect transistors (OFETs) and set-ups consisting of several of those.

Keywords: Dipolar SAMs, level alignment, semiconductor growth, organic field-effect transistors.

References: Will be presented at meeting

Poster Presentations

EPITAXIAL GROWTH AND CHARACTERIZATION OF Mn_3O_4 THIN FILMS ON Cu (111)

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Artificial photosynthetic system has been a long-standing challenge due to its difficult development and study¹. Among others, manganese is an essential element for photosynthesis, since light harvesting and electron transfer in natural systems involves Mn-Ca-O complexes². It is well known that the electronic property of manganese oxide depends on its form: single crystal, nanoparticles and thin films. Here, we are studying manganese oxide thin films grown on metallic surface, to avoid charging effects due to an insulating nature of these films, and to understand how the substrate affects the Mn oxides crystallographic and electronic structures. To this end, we prepared several Mn oxide films and characterized them their electronic properties by X-ray and Ultraviolet photoelectron spectroscopies (XPS/UPS) and their crystallographic structure and morphology by Low energy electron diffraction (LEED) and Atomic force microscopy (AFM), respectively. In particular, we focused on the growth and characterization of Mn_3O_4 films on Cu (111) deposited by e-beam epitaxy in UHV. We have observed distinct and well-defined structural phases as a function of film thickness measured by LEED. XPS and UPS measurements gave information about their electronic properties and the influence of the substrate in determining them. AFM images show a Mn_3O_4 films relatively flat with presence of dispersed pyramidal shaped structure.

Keywords: manganese oxide thin films, electronic structure, XPS, UPS.

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SYNTHESIS OF STIMULI-RESPONSIVE AND SELF-HEALING POROUS POLYMERS VIA DYNAMIC NITROXIDE EXCHANGE REACTION

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Dynamic covalent polymers are complex supramolecular assemblies from discrete molecular building blocks, that can reversibly assemble and disassemble. The dynamic process of the reaction allows the exchange of the molecular components at equilibrium to achieve thermodynamic minima of the system.^[1]

Thermal radical nitroxide exchange reaction (NER) has been successfully applied for the synthesis and tailoring of polymers. In these processes, thermal C-O bond homolysis of alkoxyamines leads to transient carbon-centered radicals and persistent nitroxide radicals. If homolysis of an alkoxyamine is performed in presence of additional nitroxide radicals, the thermodynamic product can be obtained.^[2-4]

Herein, we report the first synthesis of a dynamic porous polymer via NER. Taking advantage of the reversible covalent chemistry, the synthesis of a dynamic polymer with self-healing and stimuli-responsive properties was achieved. Besides, the radical mechanism of the NER also allowed to follow the kinetics of the polymer formation and the self-healing process using electron paramagnetic resonance (EPR).

Keywords: porous polymers, stimuli-responsive, nitroxide exchange reaction.

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SURFACE- AND LIGAND-DEPENDENT QUENCHING OF THE SPIN MAGNETIC MOMENT OF Co PORPHYRINS

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The bonding flexibility of metalloporphyrin molecules makes them versatile candidates for spintronic applications [1]. The magnetic properties of these molecules, which result from the metallic ions at their center, can be readily influenced by changes to the molecules' ligands. We investigate the electronic and magnetic properties of cobalt octaethylporphyrin (CoOEP), deposited on two similar single crystal substrates, Cu(100) and Cu(111), with x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD). A significant magnetic moment is observed from the cobalt ions of the molecules deposited on Cu(100), but it is completely quenched on Cu(111). Further investigations are performed by subjecting the molecules to an annealing process on both substrates that causes an intramolecular reaction on the CoOEP, resulting in a cobalt tetrabenzoporphyrin (CoTBP) [2]. The new molecules on both substrates have a quenched magnetic moment and are seen to have similar electronic properties as the CoOEP molecules deposited on Cu(111). We propose that the CoOEP molecules on Cu(100) display an unusual mixed-valence configuration [3] caused by the hybridization of the cobalt ion with the copper substrate, which leads to an intermediary spin magnetic moment, $S = 0.7$. Such a configuration allows for the quench of the cobalt ions' magnetic spin moment in CoOEP/Cu(111), where the adsorption geometry is expected to be different, and in CoTBP.

Keywords: Magnetic molecules, on-surface reaction, XAS, XMCD.

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ELECTRONIC AND STRUCTURAL PROPERTIES OF CO MONOLAYERS INTERCALATED AT THE GRAPHENE/Ni(111) INTERFACE BY PHOTOELECTRON DIFFRACTION (PED)

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In the present work, we studied the atomic structure of the Graphene/Ni(111) interface intercalated with monolayers (ML) of Cobalt by Photoelectron Diffraction (PED), LEED and XPS. The metal intercalation was performed evaporating monolayers of Cobalt in a Graphene/Ni(111) substrate previously prepared, with intermediate annealing and sputtering cycles, in an Ultra-High Vacuum (UHV) system equipped with cleaning, heating and evaporation facilities, at a base pressure of 1×10^{-10} bar. The experimental results show a possible structural surface transition between 3ML and 4ML of deposited Cobalt. Simulations performed with the Multiple Scattering Calculation of Diffraction[1] (MSCD) indicate the formation of a Ni-Co alloy for small amounts of evaporated Co (0.5ML, 1ML and 2ML), with the structure of bulk Nickel, agreeing with previous results of the Graphene/Ni(111) system[2].

Acknowledgements:

We acknowledge financial supporting from LNLS, FAPEMIG, CNPq and INCT of Carbon Nanomaterials

Keywords: surface, alloy, photoelectron diffraction, graphene.

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PLANAR AND ROLLED-UP NANOMEMBRANE-BASED ELECTROCHEMICAL CELLS

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Electrochemical cells (ECs) are devices usually composed of electrodes immersed in electrolyte solution. As primary functions, ECs generate electrical energy from chemical reactions or facilitate chemical reactions by means of electricity [1]. Such features have allowed ECs to be applied in the development of both chemical and biological sensors. Technologically, the miniaturization of ECs has become interesting, and microelectrodes have been used in the EC manufacturing allowing diverse applications at the micro/nanoscale [2]. Working on such a trend, nanomembranes (NMs) can be used to bring microelectrodes effectively within the nanoscale by using the standard methods of microfabrication. The NMs are freestanding structures that have nanoscale thickness even with macroscopic lateral dimensions. Composed of metal or oxide thin films, the NMs display mechanical features that allow the manipulation of their strain energy to build three-dimensional (3D) structures [3]. In the present work, NM-based electrochemical cells (NanoMECs) have been developed and analyzed. Planar and 3D nanoMEC architectures are fabricated using photolithography and thin-film depositions on glass substrates. The characterization of each architecture is performed individually by assessing the ferri- and ferrocyanide ($\text{Fe}(\text{CN})_6^{3-/4-}$) redox couple via cyclic voltammetry. In comparison to the planar architecture, it is expected that the 3D one enriches the set of future applications involving ECs by intensifying the device response and/or improving the ECs' recognition area for possible applications such as sensors and biosensors.

Keywords: electrochemical cell, microfabrication, nanomembrane, voltammetry.

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OBSERVATION OF CROSS-LINKING: TRANSITION FROM SAM TO CNM

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When electrons hit a metallic substrate, secondary electrons are emitted. These can interact with surface-bound molecules, and in the case of an aromatic self-organized monolayer (SAM), this can lead to the formation of carbon nanomembranes (CNM). CNMs are insulating, and mechanically stable, quasi two-dimensional carbon layers having a thickness of approx. 1 nm. They can be produced by electron bombardment of systems of e.g. aromatic molecular layers grown on numerous solid substrates [1]. It has been shown that dissociative electron attachment (DEA) plays a key role in the radicalization and cross-linking of such SAMs [2]. Furthermore, we found that CNMs have intrinsic pores leading to exceptional permeation and filtration properties [3]. However, to control CNMs and develop them specifically for tuning their intrinsic properties, it is necessary to understand the processes at the molecular and atomic level at all stages of cross-linking as well as the transition from a SAM to a CNM. Here we present a thorough STM study of the electron radiation impact on a terphenylthiol SAM on Au(111) at different doses and primary energies. First, we investigated the effects of electron bombardment of SAMs with different doses and a primary electron energy of 50eV. With STM we have observed the occurrence of defects, new molecular phases and polymerization nuclei. In a second experiment, we used the focused beam of a scanning electron microscope mounted above the STM as an electron source of 1keV. This allowed a localized STM observation of the formation of irradiation induced changes with molecular resolution without leaving or losing the STM scan position. For the first time, we were able to directly observe the continuous transition from SAMs to CNMs at the molecular level.

Keywords: carbon nanomembranes, cross-linking, STM.

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METALATION AND COORDINATION REACTIONS OF 2H-MESO-TRANS-DI(P-CYANOPHENYL)PORPHYRIN ON AG(111) WITH COADSORBED COBALT ATOMS

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The controlled fabrication of functional molecular nanoarchitectures on surfaces is in the focus of our research activities. Thereby, we follow a bottom-up approach in which we rely on the adsorption behavior, i.e., self-assembly and *in situ* reactions of porphyrin derivatives as prototype functional molecules.¹⁻³ In this context, we investigated the metalation⁴ and coordination⁵ reactions of Co with 5,15-bis(para-cyanophenyl)-10,20-bisphenylporphyrin (2HtransDCNPP) on a Ag(111) surface by scanning tunneling microscopy. At room temperature, 2HtransDCNPPs self-assemble into a well-ordered supramolecular structure stabilized by van der Waals interactions and intermolecular hydrogen bonding. The supramolecular structure consists of two types of intermittently occurring rows. Within row *I*, all molecules are orientated along the same direction while this azimuthal orientation is rotated by 90° in the neighboring row *II*. This adsorption behavior is interpreted as due to electrostatic repulsion of neighboring cyano groups in row *I* and *II*. The metalation of 2HtransDCNPP can be realized by pre- or postdeposition of Co atoms onto the Ag(111) surface.⁶ In case of Co postdeposition a subsequent heating step to 500 K is necessary. Interestingly, with “excess” Co material one observes the formation of peculiar motifs appearing as 3 to 7 protrusion motifs in STM, with the dominating motif being a 5-protrusion appearance. The corresponding motifs could be identified as 2 to 6 CotransDCNPPs coordinated by central Co atoms through the N atoms in the peripheral cyano groups.⁶ The identification of the involved species was realized among other considerations through bias-dependent STM.

Keywords: STM, porphyrin, supramolecular structures.

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SURFACE DEFECTS IN HKUST-1 MOFs INVESTIGATED BY SPECTROSCOPY AND MASS TRANSFER EXPERIMENTS

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The performance of many metal-organic frameworks (MOFs) is hindered by their limited stability, which arise from several defects. Exposure to water or humid air leads to the destruction of the surface of MOFs of type HKUST-1. These defects can tremendously decrease the uptake and release rates of guest molecules.^[1] Well-defined thin MOF films of HKUST-1 are used for spectroscopic investigations, i.e. Infrared, UV-vis and X-ray photoelectron spectroscopy, as well as for uptake experiments using a quartz crystal microbalance. It is found that the surface defects, which are caused by exposure to humidity, can be healed in the synthesis solvent at elevated temperatures. A model for the defect structure is proposed through theoretical calculations.^[2]

Keywords: defects, metal-organic frameworks, thin films.

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SURMOF BASED "DESIGNER SOLIDS" FOR MICROELECTRONIC DEVICES AND THERMOELECTRIC MATERIALS CHARACTERIZATION

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SURMOF based "Designer Solids" and Organic thin film materials will be presented as non-volatile RRAM Devices. Additionally fully thermoelectric characterization have been performed with on ZT Test Cips (from Linseins Messgeräte GmbH). Thermoelectric Properties and Seebeck measurements of pristine and loaded HKUST-1 SURMOF thin films will be presented.

Keywords: SURMOFs, Organic thin film, RRAM, Devices, electrical and thermoelectric characterizations.

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SURMOF/CCNC BASED "DESIGNER SOLIDS" FOR PHOTONIC, OPTICAL AND ENERGY APPLICATIONS

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SURMOFs and CCNCs applications will be presented; in the Applications field of low-k and dielectric materials, optoelectronic properties, novel photonic band gap materials as well as for single component SURMOF PV applications.

Keywords: SURMOFs, CCNCs, Application, Devices, Optics, Photonics, PV.

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ON-SURFACE REACTION AND DIFFUSION OF (TETRA-4-CHLOROPHENYL) PORPHYRIN ON CU(111)

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The study of the on-surface chemistry of porphyrin-based molecules using metallic single-crystal became quite attractive, mainly because these molecules presents diversity of coordination chemistry with metals. The idea is to control the interactions between molecules and substrate in order to group them in complex two-dimensional networks that present interesting physical-chemical properties [1, 2].

Here, we present a study of the molecular self-assembly of the porphyrin-based molecule 5,10,15,20-(tetra-4-chlorophenyl) porphyrin (2H-TCIPP) on Cu(111) under ultra-high vacuum conditions. X-ray photoelectron spectroscopic (XPS) and scanning tunneling microscopy (STM) measurements as a function of temperature were performed to study the dynamics of the formation of molecular arrangements. Quantitative information on the diffusion and rotation barriers were obtained by the well-known Arrhenius approach [3]. Density Functional Theory (DFT) calculations were also useful in identifying the molecular adsorption configuration on the surface. The DFT simulation together with STM data indicated that the configuration of the adsorbed molecule on Cu(111) agrees very well with the so-called “inverted structure” [4]. Finally, the thermodynamic study shows that metal coordination (C-Cu-C) after molecule dechlorination is the most stable structures in the intermediate process of the Ullmann reaction.

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Keywords: 5,10,15,20-(tetra-4-chlorophenyl)porphyrin, Ulmann coupling, Arrhenius approach, STM, XPS, DFT:

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CHARACTERIZATION OF SURFACE METAL-ORGANIC FRAMEWORKS (SURMOFS) FILMS FOR APPLICATIONS IN ELECTRICAL DEVICES

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Surface Metal-Organic Frameworks (SURMOFs) is a new class of nanostructured materials based on the tridimensional networks of metallic clusters and organic ligands. These structures have important characteristics such as crystalline orientation, high porosity and superficial area [1]. The SURMOFs can directly be grown on a support surface functionalized with self-assembled monolayers (SAMs) [1]. The possibility of incorporating this supported film onto devices and sensor platforms leads to the studies of film's morphology, crystallinity and interface quality. Previous studies have investigated the nucleation and film growth of the first layers [2,3] and defined the preferential crystallographic orientation of SURMOF selecting the SAMs end-group [3]. However, to the best of our knowledge, no study focusing on the SAMs chain length dependence of the growth properties has been performed. In this sense, we evaluated the influence of SAMs chain length on the preferred crystalline orientation of SURMOF HKUST-1. The results show a preferential growth in [100] direction when the SAM chain length increases. The study was carried out considering a conductor and an insulator surface (Au and Al₂O₃, respectively), in order to evaluate their influence on the nucleation and growth of HKUST-1. These results are crucial when SURMOFs are applied to electrical devices, associating the characteristics of the films with their electrical properties, considering both solid/solid and solid/liquid interface.

Acknowledgments:

The authors acknowledge the Brazilian funding agency FAPESP (projects 2014/25979-2 and 2016/25346-5).

Keywords: Surface Metal-Organic Frameworks, Self-Assembled Monolayers, Electrical Devices

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SURFACE CHEMISTRY OF MODEL AND NANOSTRUCTURED METAL/OXIDE SYSTEMS

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Nanostructured metal oxides and oxide-supported metals have attracted enormous attention because of their widespread applications, especially in heterogeneous catalysis and photocatalysis. The atomic arrangement on oxide surfaces and at metal-oxide interfaces determine their physical and chemical properties, and the ability to control and optimize structural parameters is of crucial importance. However, an atomic-scale understanding of the structure and electronic properties of many catalytic nanomaterials is still a challenging task, which makes the fabrication and engineering of these systems largely empirical. We present here our recent work on ceria (CeO_2), ZnO as well as TiO_2 -supported AuPd bimetallic nanoparticles (NPs) [1-4]. These systems were studied with the help of probe molecules (such as CO, O_2 and N_2O) and a sophisticated ultrahigh vacuum-infrared apparatus which allows both polarization-resolved IRRAS (IR reflection-absorption spectroscopy) on model crystals and temperature-dependent IR measurements on powders. On the basis of a thorough understanding of various ceria surfaces, we were able to gain atomic-level insights into the surface chemistry of ceria nanoparticles. Our results provided detailed information on the location of O vacancies and the relevant dioxygen activation on different surfaces. It was found that the rod-shaped ceria NPs undergo complex reconstruction and surface faceting exposing a high density of defects. The photoreactivity of ceria can be enhanced considerably by the generation of surface oxygen vacancies. In the case of ZnO, we demonstrate that the metal support plays a vital role in the structure and activity of ultrathin ZnO films. Finally, we will discuss the chemical nature of the high reactivity of TiO_2 -supported AuPd NPs for the CO oxidation reaction.

Keywords: Surface chemistry; Infrared spectroscopy; CeO_2 ; ZnO; TiO_2 -supported AuPd alloy.

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	SUNDAY, 23rd	MONDAY, 24th	TUESDAY, 25th	WEDNESDAY, 26th	THURSDAY, 27th	FRIDAY, 28th
		Openening Remarks Bof Bufon and Wöll				
8:30 - 9:20		Macedo	Freund	Silva	Morais	Witte
9:20 - 10:10		Al Shamery	Schneider	Steinrück	Stutzmann	Zharnikov
10:10 - 10:40		Coffee break	Coffee break	Coffee break	Coffee break	Coffee break
10:40 - 12:00		Papp Libuda Behm	Garcia Gölzhäuser Heinke	Heiz Kuch Böttcher	Sterrer Tegeder Miranda	Terfort Mameka Marbach
12:00 - 14:00		Lunch	Lunch	Lunch	Lunch	Closing remarks Lunch
14:00 - 14:50		Soares	Zarbin		Leite	
14:50 - 15:40	Levkin	Galembeck	Araújo			
15:40 - 16:10	Coffee break	Coffee break	Coffee break			
16:10 - 17:00	Weinelt	Siervo	Rocha			
17:00 - 17:50	Roldán	Poster Session 1	Poster Session 2			
17:50 - 18:15	Redel					
19:00	Dinner	Dinner	Dinner	Dinner		