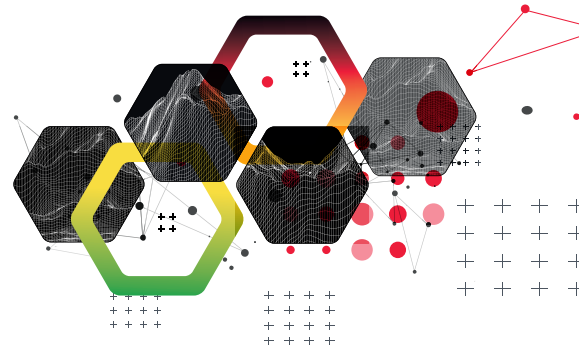


11th Brazilian German Workshop on Applied Surface Science

19.04.2022 – 24.04.2022
MANAUS/AM – BRAZIL



PROGRAM AND ABSTRACTS BOOK

ORGANIZATION



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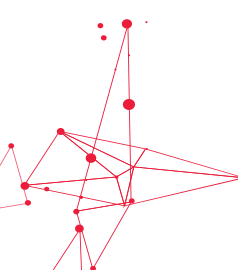


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General Information

This workshop will be the eleventh meeting of scientists in surface science and nanoscience from Brazil and Germany stimulated by the successful previous editions of the Brazilian-German Workshops on Applied Surface Science.

The main topics addressed at this workshop deal with fundamental problems (theory and experiment) in surface science and nanoscience, and corresponding applications. Particular emphasis is given to nanostructured materials, thin films, polymers, devices, and catalysis, all of which seem to be an active area in both countries and represent promising future perspectives.

We sincerely hope many colleagues and students from Brazil and Germany will participate in this workshop and take advantage of the optimal conditions for discussions and personal contacts.

Organizing Committee

Prof. Dr. Carlos César Bof Bufon, MackGraphe - Instituto Presbiteriano Mackenzie, São Paulo, SP, Brazil.

Prof. Dr. André Avelino Pasa, Universidade Federal de Santa Catarina, Florianópolis, SC, Brazil.

Prof. Dr. Waldemar Augusto de Almeida Macedo, Centro de Desenvolvimento da Tecnologia Nuclear - CDTN, Belo Horizonte, MG, Brazil.

Prof. Dr. Hans-Peter Steinrück, Universität Erlangen-Nürnberg, Erlangen, Germany.

Prof. Dr. Christof Wöll, Karlsruhe Institute of Technology, Karlsruhe, Germany.

Prof. Dr. Katharina Al-Shamery, Institute of Chemistry, School of Mathematics and Natural Sciences, Carl von Ossietzky University, Oldenburg, Germany.

Prof. Dr. Hans-Joachim Freund, Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany.

Local Organizing Committee

Prof. Dr. Sergio Humberto Rodrigues, MackGraphe - Instituto Presbiteriano Mackenzie, São Paulo, SP, Brazil.

Prof. Dr. Lizandro Manzato, Instituto Federal do Amazonas, Manaus, AM, Brazil.

Ms. Débora Mitie Morita, MackGraphe - Instituto Presbiteriano Mackenzie, São Paulo, SP, Brazil..

Previous editions of the Workshop

Brazilian-German Workshop I, Mangaratiba, RJ, Brazil, 3 - 7 April, 1995.

German-Brazilian Workshop II, Berlin, Germany, 21 – 25 September, 1998.

Brazilian-German Workshop III, Itapema, SC, Brazil, 5 – 9 March, 2001.

German-Brazilian Workshop IV, Tegernsee, Germany, 21 – 26 September, 2003.

Brazilian-German Workshop V, Mangaratiba, RJ, Brazil, 3 – 9 April, 2006.

German-Brazilian Workshop VI, Titisee, Germany, 14 – 19 September, 2008.

Brazilian-German Workshop VII, Buzios, RJ, Brazil, 3 – 8 April, 2011.

German-Brazilian Workshop VIII, Bamberg, Germany, 15 – 20 September, 2013.

Brazilian-German Workshop IX, Maresias, SP, Brazil, 11 – 14 April, 2016.

German-Brazilian Workshop X, Bad Dürkheim, Germany, 23 – 28 September, 2018

Program overview – 11th BGW 2022 Manaus, Brazil

	TUESDAY, 19th	WEDNESDAY, 20th	THURSDAY 21st	FRIDAY, 22nd	SATURDAY, 23rd	SUNDAY, 24th	
7:30 - 8:20		REGISTRATION					
8:20 - 8:30		Opening Remarks					
8:30 - 9:00		Lecture 1 - HANS-JOACHIM FREUND	Lecture 9 - FELIPE CRASTO DE LIMA	Lecture 15 - HANS-PETER STEINRÜCK	Lecture 18 - ANTONIO GOMES		
9:00 - 9:30		Lecture 2 - CAUJÉ DE OLIVEIRA	Lecture 10 - THOMAS HEINE	Lecture 16 - ABNER SIERVO	Lecture 19 - SABINE MAIER		
9:30 - 10:00		Coffee break	Coffee break	Coffee break	Coffee break	Check-out	
10:00 - 10:30		Lecture 3 - JÖRG LIBUDA	Lecture 11 - ANTONIO AZEVEDO	Lecture 17 - MARTIN STERRER	Lecture 20 - SWETLANA SCHAUERMANN		
10:30 - 11:30		Oral 1 - LEONARD G. GURA	Oral 7 - MILTON A. TUMELERO	Oral 10 - SIMON JAEKEL	Oral 13 - LUIZ ALBANO		
		Oral 2 - INGRID D. BARCELOS	Oral 8 - ANDREAS TERFORT	Oral 11 - FLORIAN SCHWARZ	Oral 14 - CECILIA SILVA		
		Oral 3 - MAX NIEDERREITER	Oral 9 - ALEXANDRE COTTA	Oral 12 - EVA FREIBERGER	Oral 15 - HICHAM IDRIS		
11:40 - 14:00		Lunch	Lunch	Lunch	Lunch	Lunch	
14:00 - 14:30		Lecture 4 - ALDO ZARBIN	Lecture 12 - PETRA TEGEDER		Lecture 21 - AXEL GROß		
14:30 - 15:00		Lecture 5 - CHRISTOF WÖLL	Lecture 13 - CARLOS GRAEFF		Lecture 22 - UBIRAJARA PEREIRA		
15:00 - 15:30		Coffee break	Lecture 14 - NARCIZO DE SOUZA-NETO		Coffee break		
15:30 - 15:40			Poster presentations (3 min each)				
15:40 - 16:10	Arrival	Oral 4 - SERGIO H. DOMINGUES	Poster section	Optional Tour in Manaus	Oral 16 - ERIC SAUTER		
16:10 - 16:40		Oral 5 - NOAH COELESTIN AL SHAMERY			Oral 17 - NATALIE WALESKA		
16:40 - 17:10		Oral 6 - LEANDRO MERCES			Oral 18 - NILS BRINKMANN		
17:10 - 17:40		Lecture 6 - LUIZ GUSTAVO CANÇADO			Oral 19 - TATIANA PARRA VELLO		
17:40 - 18:10		Lecture 7 - KATHARINA AL-SHAMERY			Closing Remarks		
19:00	Dinner	Lecture 8 - DANIEL UGARTE	Dinner	Thematic Dinner	Dinner	Departure	

Program

Wednesday, 20th April 2022

8:20 AM – 8:30 AM

Opening Remarks

8:30 AM – 9:00 AM

Hans-Joachim Freund

Fritz Haber Institut der Max Planck Gesellschaft, Berlin, Germany

Model systems for heterogeneous catalysts at the atomic scale

9:00 AM – 9:30 AM

Cauê Ribeiro

Embrapa Instrumentation, São Carlos, SP, Brazil

Towards the application of semiconducting materials as photo(electro)catalysts for energy conversion

09:30 AM – 10:00 AM

Coffee Break

10:00 AM – 10:30 AM

Joerg Libuda

Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, German

Model interfaces in catalysis and materials science: from surface science to the electrified solid/liquid interface

10:30 AM – 11:30 AM

Contributed Oral Presentations

10:30 AM – 10:50 AM

Leonard Gura

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Chemical capturing surface dynamics with spiral high-speed STM

10:50 AM – 11:10 AM

Ingrid D. Barcelos

Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, SP, Brazil

Probing polaritons in low-dimensional materials with synchrotron infrared nanospectroscopy

11:10 AM – 11:30 AM

Max Niederreiter

Institute of Physics, University of Graz, Graz, Austria

Charge transfer in copper-phthalocyanine on metallic and oxide surfaces

11:30 PM – 14:00 PM

Lunch

14:00 PM – 14:30 PM

Aldo J.G. Zarbin

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

Preparing and processing multicomponent materials at liquid/ liquid interfaces: thin films for enlarging technological applications

14:30 PM – 15:00 PM

Christof Wöll

Institut für Funktionelle Grenzflächen, Karlsruher Institut für Technologie, Germany.

Reticular networks supported on solid substrates: Chances and Challenges

15:00 PM – 15:40 PM

Coffee Break

15:40 PM – 16:40 PM

Contributed Oral Presentation

15:40 PM – 16:00 PM

Sergio Humberto Domingues

MackGraphe – Mackenzie Institute for Research in Graphene and Nanotechnologies, Mackenzie Presbyterian University, São Paulo, Brazil

Development of nanocomposites for energy storage systems

16:00 PM – 16:20 PM

Noah Coelestin Al-Shamery

School of Materials Science and Engineering, Nanyang Technological University, Singapore

Investigation of melanin-based energy storage systems via chemical derivatization

16:20 PM – 16:40 PM

Leandro Mercês

Brazilian Center for Research in Energy and Materials (CNPEM), Campinas SP, Brazil. University of Campinas (UNICAMP), Campinas SP, Brazil.

Organic/inorganic hybrid nanodevices: from charge-transfer reactions to sensor applications

16:40 PM – 17:10 PM

Luiz Gustavo Caçado

Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil

Metrological framework for quality control of mass-produced graphene

17:10 PM – 17:40 PM

Katharina Al-Shamery

Carl von Ossietzky University Oldenburg, Institute for Chemistry, Oldenburg, Germany

How to use nanoscience for renewable energy conversion

17:40 PM – 18:10 PM

Daniel Ugarte

DFA-IFGW-UNICAMP, R. Sergio B. de Holanda 777, 13083-859 Campinas SP, Brazil
Quantitative structural characterization of nanomaterials by precession e-diffraction

Thursday, 21st April 2022

8:30 AM – 09:00 AM

Felipe Crasto de Lima

Illum - Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, São Paulo, Brazil.

The robustness of topological insulators

9:00 AM – 09:30 AM

Thomas Heine

School of Science, Faculty of Chemistry and Food Chemistry, TU Dresden, Germany

The potential of 2d polymers for light harvesting applications

09:30 AM – 10:00 AM

Coffee Break

10:00 AM – 10:30 AM

Antonio Azevedo

Departamento de Física, UFPE, Recife, PE, Brasil

Investigation of spin and orbital hall effects in heterostructures

10:30 AM – 11:30 AM

Contributed Oral Presentations

10:30 AM – 10:50 AM

Milton A. Tumelero

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

Rationalizing spin-orbit proximity effect in soc/fm multilayers: the role of interface

10:50 AM – 11:10 AM

Andreas Terfort

University of Frankfurt, Department of Chemistry, Institute of Inorganic and Analytical Chemistry, Frankfurt, Germany

From self-assembled monolayers to highly functional substrates for cryo-transmission electron microscopy (cryo-tem)

11:10 AM – 11:30 AM

Alexandre A. C. Cotta

Departamento de Física, Universidade Federal de Lavras (UFLA), Lavras, MG, Brazil;
Centro de Desenvolvimento da Tecnologia Nuclear, CDTN, Belo Horizonte, MG, Brazil

Study of magnetic anisotropy and induced spin polarization in fe/co/cu₃au(001): an experimental and first-principles investigation

11:30 PM – 14:00 PM

Lunch

14:00 PM – 14:30 PM

Petra Tegener

Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany

Electronic properties of interfaces with n-heteropolycyclic molecules

14:30 PM – 15:00 PM

Carlos F. O. Graeff

São Paulo State University (UNESP), School of Sciences, Department of Physics, Bauru, Brazil

From nature to organic (bio)electronics: melanin-inspired materials

15:00 PM – 15:30 PM

Narciso M. Souza-Neto

Brazilian Synchrotron Light Laboratory (LNLS), Campinas, SP, Brazil

Condensed matter at Sirius, the new Brazilian synchrotron

15:40 PM – 18:10 PM

Poster presentations/ Poster Section

Alisson Ceccatto dos Santos

“Gleb Wataghin” Institute of Physics, State University of Campinas. Campinas -SP, Brazil

On-Surface Synthesis of Two-Dimensional Porous Network on Metal Surfaces

Ana Claudia Fingolo

Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Centre for Research in Energy and Materials (CNPEM), Campinas/SP, Brazil

Postgraduate Program in Material Science and Technology (POSMAT), UNESP, Bauru/SP, Brazil

Zif-8 derived ZnO functional devices

Isabela da Costa Tonon

“Gleb Wataghin” Institute of Physics, State University of Campinas. Campinas -SP, Brazil

Epitaxial growth of HfS₂ on Ag (111): semiconductor response and oxidation of the monolayer

Jade Barreto

Brazilian Center for Research in Physics, 22290-180, Rio de Janeiro, RJ, Brazil

Core-level binding energy shifts in MnO(001) thin films grown on Au(111)

João Vitor Paulin

Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Centre for Research in Energy and Materials (CNPEM), Campinas/SP, Brazil

A step forward eumelanin-based micro and portable devices

Leonard Gura

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Chemical capturing surface dynamics with spiral high-speed STM

Lilian Rodrigues de Oliveira

Federal University of Amazonas, Manaus, Amazonas, Brazil

Synthesis and characterization of poly(p-anisidine): experimental and theoretical approach to molecular structure, electrical and spectroscopic properties.

Noah Coelestin Al-Shamery

School of Materials Science and Engineering, Nanyang Technological University, Singapore
Investigation of melanin-based energy storage systems via chemical derivatization

Rubem Raphael dos Santos Caetano

Brazilian Center for Research in Physics, 22290-180, Rio de Janeiro, RJ, Brazil
Study the structure of MN_3O_4 (110) by STM

Salomão dos Santos Costa

Laboratory of Technological Materials Processing (LPMAT), Department of Materials Engineering, Federal University of Amazonas, Manaus, Amazonas, Brazil
Temperature influence on the electrical properties of $Na_2Ti_3O_7/Na_2Ti_6O_{13}/POMA$ composite.

Wagner Wlysses Rodrigues de Araujo

Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Centre for Research in Energy and Materials (CNPEM), Campinas/SP, Brazil
Development of self-coiling nanomembranes for 3D ultracompact capacitively coupled contactless conductivity detection

Yan Matheus Colares Pinto

Laboratory of Technological Materials Processing (LPMAT), Department of Physics, Federal University of Amazonas, Manaus, Amazonas, 69067-005, Brazil
Effect of LiOH concentration in flexible composites for application in solid state electrolyte.

Friday, 22nd April 2022

8:30 AM – 9:00 AM

Hans-Peter Steinrück

Universität Erlangen, Erlangen, Germany.
The surface science of ionic liquids

9:00 AM – 9:30 AM

Abner de Siervo

University of Campinas (UNICAMP), Campinas, São Paulo, Brazil.
On-surface synthesis of new functional 2D materials: a molecular "Lego"

09:30 AM – 10:00 AM

Coffee Break

10:00 AM – 10:30 AM

Martin Sterrer

Institut für Physik, Universität Graz, Österreich, Austria.
Metalation of Organic Molecules: Tetraphenylporphyrin on $MgO(001)/Ag(001)$ thin films.

10:30 AM – 11:30 AM
Contributed Oral Presentations

10:30 AM – 10:50 AM

Simon Werner Soo-Chun Jaekel

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

Self-Assembly and Thin Film Growth Dynamics of an Ionic Liquid on Au(111) Investigated in Real Space

10:50 AM – 11:10 AM

Florian Schwarz

Institute of Physics, University of Graz, Universitätsplatz Graz, Austria

Self-metalation of 2HTetraphenyl Porphyrin and 2H-Porphine on an Oxide Surface.

11:10 AM – 11:30 AM

Eva Marie Freiburger

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

An HR-XPS Study On Bromine on h-BN/RH(111).

11:30 PM – 14:00 PM

Lunch

14:00 PM – 18:00 PM

Optional Tour: Meeting of the Waters - Manaus

19:00 PM – 21:00 PM

Thematic Dinner

Saturday, 23rd April 2022

8:30 AM – 9:00 AM

Antonio Gomes Souza Filho

Federal University of Ceará (UFC), Fortaleza, Ceará, Brazil.

2D materials under high pressures: probing strain transfer and adhesion

9:00 AM – 9:30 AM

Sabine Maier

Universität Erlangen-Nürnberg, Erlangen, Germany.

On-surface synthesis: A bottom-up strategy to low-dimensional carbon-structures.

09:30 AM – 10:00 AM

Coffee Break

10:00 AM – 10:30 AM

Swetlana Schauermann

Institut für Physikalische Chemie, Universität Kiel, Kiel, Germany.

Understanding Ligand-Directed Heterogeneous Catalysis: When the Dynamically Changing Nature of the Ligand Layer Controls the Hydrogenation Selectivity.

10:30 AM – 11:30 AM

Contributed Oral Presentations

10:30 AM – 10:50 AM

Luiz Gustavo Simão Albano

Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, São Paulo, Brazil.

Surface-Supported Metal-Organic Framework Vertical Heterojunctions for Hybrid Electronic Devices.

10:50 AM – 11:10 AM

Cecilia de Carvalho Castro e Silva

MackGraphe – Mackenzie Institute for Research in Graphene and Nanotechnologies, Mackenzie Presbyterian University, São Paulo, Brazil

Exploring Field-Effect Transistors Based on Graphene for the Ultrasensitive Detection of Biomarkers

11:10 AM – 11:30 AM

Hicham Idriss

Institute of functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Karlsruhe, German

Electron Transfer Reaction by Time Resolved (TRS) and Core Level Spectroscopy (XPS) and STM on Au/TiO₂(110) Single Crystal Systems.

11:30 PM – 14:00 PM

Lunch

14:00 PM – 14:30 PM

Axel Groß

Institut für Theoretische Chemie, Universität Ulm, Deutschland, Germany.

Structure of catalyst surfaces under operating conditions from first principles.

14:30 PM – 15:00 PM

Ubirajara Pereira Rodrigues-Filho

University of São Paulo (USP), São Paulo, São Paulo, Brazil.

Organic-Inorganic hybrid photocatalytic membranes for in-flow water purification.

15:00 PM – 15:40 PM

Coffee Break

15:40 PM – 16:40 PM

Contributed Oral Presentation

15:40 PM – 17:00 PM

Eric Sauter

Karlsruhe Institute of Technology, Institute of Functional Interfaces, Germany
Surface Ligand Infrared Spectroscopy: In-Situ Characterization of Noble Metal Clusters and Metal Oxides at Work.

16:00 PM – 16:20 PM

Natalie Jessica Waleska

Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany
Reactivity and Passivation of Fe Nanoclusters on h-BN/Rh(111).

16:20 PM – 16:40 PM

Nils Sebastian Brinkmann

Institute of Chemistry, Oldenburg, Germany.
Activation of Amines and Alkenes at Pt(111) Surface For C-N Bond Formation.

16:40 PM – 17:00 PM

Tatiana Parra Vello

Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, São Paulo, Brazil
Improving Electrical Conductivity Mediated by Pyrrole Loading in Monolithically Integrated Surmofs Templates

17:00 PM – 18:00 PM

Closing remarks

Sunday, 24th April 2022

08:00 PM – 12:00 PM

Check-out/Lunch - Departure

Invited Talks

LECTURE 01

MODEL SYSTEMS FOR HETEROGENEOUS CATALYSTS AT THE ATOMIC SCALE

Hans-Joachim Freund¹

1 Fritz Haber Institut der Max Planck Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

We have created model systems for heterogeneous catalysts on the basis of thin oxide films. This permits us to apply the toolbox of surface science for characterization and reaction studies. In the presentation I will discuss two case studies to demonstrate how those systems may be studied at the atomic scale. The first one discusses a novel characterization technique, namely surface action spectroscopy, using concepts developed in gas phase studies to record vibrational spectra of extremely dilute specimen based on messenger desorption. We demonstrate the extreme surface sensitivity of this technique by applying it to surface states of oxide surfaces, i.e. vanadia as well as iron oxides. The second case study deals with a reaction in confined space using a model system based on a thin silica film, which is only bound to a metal substrate by dispersive forces, leaving a space between the oxide film and the metal substrate. Here we study water formation from intercalated oxygen, adsorbed on the metal surface and hydrogen provided from the gas phase in operando, and deduce the details of the kinetics of the reaction in confined space in direct comparison to the equivalent open space reaction. To this end we use a spectro-microscope, operated at BESSYII and developed in the group, which allows to observe tempo-spatial distribution of reactants and deduce apparent activation energies. Those experimental observations are interpreted on the basis of DFT calculations and kinetic models.

TOWARDS THE APPLICATION OF SEMICONDUCTING MATERIALS AS PHOTO(ELECTRO)CATALYSTS FOR ENERGY CONVERSION

Caue Ribeiro¹

1 Embrapa Instrumentation, São Carlos, SP (Brazil)

caue.ribeiro@embrapa.br

The emergence of climate problems related to greenhouse gas emissions lead to the conclusion that, only through the natural cycles of these gases, especially CO₂, catastrophic scenarios in the coming decades are unavoidable. Essentially, the latest IPCC report emphasized the importance of seeking mitigation of CH₄ emissions, due to its high global warming capacity (> 15 CO₂eq), and seeking technological initiatives for the decarbonization of the global economy. In this sense, recycling CO₂ and CH₄ emissions using renewable energies, such as solar, depends on the development of electrochemical routes that can process them with high efficiency, good selectivity and long-term use. For that, the discovery and design of photo(electro)catalysts play a fundamental role. These materials should be based in earth-abundant materials (cost-effective), stable under high potentials (inert) and with adequate conductivity. Currently, several semiconductors as TiO₂, BiVO₂, ZnO, CuO, Cu₂O, among others, are under investigation as photoanodes or photocathodes. Finally, the concept of the photo(electro)chemical cell is challenging, demanding knowledge in supports for catalysts (immobilization), membranes for ion separation, and fluid-dynamics. In this presentation, a review of the concepts of photoelectrocatalysis applied to CO₂ reforming (reduction) and CH₄ reforming (controlled oxidation) is proposed, comprising a comparison of photoelectrocatalytic systems against other alternatives (e.g., high temperature reactions), along with the specific challenges (catalyst discovery, system design, scaling) emphasizing some case studies from our research group.

MODEL INTERFACES IN CATALYSIS AND MATERIALS SCIENCE: FROM SURFACE SCIENCE TO THE ELECTRIFIED SOLID/LIQUID INTERFACE

Joerg Libuda¹

*1 Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany
joerg.libuda@fau.de*

Understanding the chemistry at solid/liquid interfaces is essential for many applications in electrocatalysis, energy-related catalysis, and materials science. In our work, we explore fundamental mechanistic and kinetic phenomena at solid/liquid interfaces using atomically defined model systems prepared under surface science conditions.

In a first step, we explore the geometric and electronic structure of the model systems in ultrahigh vacuum by surface science methods such as X-ray photoelectron spectroscopy, scanning tunneling microscopy, infrared reflection absorption spectroscopy, and temperature programmed desorption. In the second step, we transfer the samples from ultrahigh vacuum into the liquid environment. We show that for various types of model systems such transfer is possible while preserving the atomic surface structure of the model interface. In the liquid environment, we study growth processes, catalytic processes, or (photo)electrocatalytic processes in situ, e.g. by cyclic voltammetry, scanning flow cell experiments, electrochemical IR spectroscopy, electrochemical scanning tunneling microscopy, differential electrochemical mass spectrometry, and electrochemical X-ray photoelectron spectroscopy.

In this presentation, we review recent work along this research strategy, covering examples from electrocatalysis, photoelectrochemistry, and materials science. In the first example we show that we can transfer ordered cobalt oxide thin films into liquid electrolytes to follow their structural dynamics under potential control.[1] In the second example, we scrutinize the interaction of noble metal nanoparticles with oxide interfaces in liquid electrolytes.[1,2] In the third example we investigate the growth of functional molecular films on ordered oxide surfaces in liquid environments.[3] Finally, we discuss recent experiment using ionic liquid films used as catalytic modifiers for selective electrocatalytic transformations.[4]

Keywords: Oxide interfaces, solid/liquid interfaces, electrochemical interfaces, metal support interaction, organic thin films, ionic liquids

References

- [1] C. Stumm, et int., O. Brummel, J. Libuda, Adv. Funct. Mater. 2021, 31, 2009923.
- [2] F. Faisal, et. int., O. Brummel, J. Libuda, Nat. Mater., 2018, 17, 592.
- [3] M. Bertram, et int., O. Brummel, J. Libuda, J. Chem. Phys. 2020, 152, 044708.
- [4] T. Yang, et int., O. Brummel, J. Libuda, submitted.

LECTURE 04

PREPARING AND PROCESSING MULTICOMPONENT MATERIALS AT LIQUID/ LIQUID INTERFACES: THIN FILMS FOR ENLARGING TECHNOLOGICAL APPLICATIONS

Aldo J.G. Zarbin¹

*1 Department of Chemistry, Federal University of Paraná (UFPR), CP 19032, CEP 81531-980,
Curitiba, PR, Brazil
aldozarbin@ufpr.br*

This talk will demonstrate the huge potentiality coming from the interface between immiscible liquids to synthesize, stabilize and process complex materials as transparent and conductive thin films to be applied in different technological systems and devices [1]. Examples of multicomponent materials combining carbon nanostructures (nanotubes, graphene), 2D materials, Prussian blue analogues, metal nanoparticles and conducting polymers will be presented, highlighting unique preparative routes, characterization techniques, study of properties and the structure/properties relationship, thin film deposition over several solid substrates and application in transparent aqueous metal-ion batteries; flexible supercapacitors; electrochromic devices; solar cells; as transparent electrodes and as catalysts.

Keywords: Nanocomposites; metal-ion battery; transparent and conductive films; carbon nanostructures

References

[1] Zarbin, A.J.G., *Mater. Horizons*, 2021, 8, 1409-1432.

METROLOGICAL FRAMEWORK FOR QUALITY CONTROL OF MASS-PRODUCED GRAPHENE

Luiz Gustavo Cançado¹

*1 Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil
cancado@fisica.ufmg.br*

Liquid-phase exfoliation (LPE) is considered, among all forms of producing 2D materials, as the most scalable one. However, production scalability, with quality, can only be reached if critical parameters such as temperature, processing time, and energy are optimized. Postprocessing is also important: the proper choice of electrostatic or steric stabilizers can make the suspensions stable. Mass separation through centrifugation is usually employed to improve homogeneity. All these procedures should be monitored, aiming at the requirements that make the material suitable for the target application. However, because LPE usually generates 2D nanosheets with broad distributions of thickness and lateral size, it is hard to find the right parameters that summarize the yielded material. For this purpose, robust statistical analysis is required. In this talk, I will present statistical methods that summarize and provides deep understanding of morphological attributes of mass-produced nanoflakes from 2D materials. The protocol is based on atomic force microscopy (AFM) [1,2], Raman spectroscopy [3,4] and tip-enhanced Raman spectroscopy (TERS). The information gathered is rarely accessible even in conventional methods considered as statistical ones, such as thermal or spectroscopic analysis. The key factor is that the statistical essence our protocols is not related to the measurement itself but to the large number of nano-objects individually scrutinized, having their morphological parameters extracted one by one. The amount and type of information that can be extracted from this routine indicate that this is the most adequate way to analyze batch produced nanomaterials, in which the size and shape of each individual nano-object matters to the physicochemical properties of the whole.

Keywords: graphene, characterization, mass-production

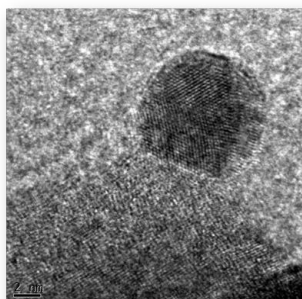
References

- [1] T. F. D. Fernandes et al, 2D Mater., 7 (2020) 025045.
- [2] Hélio Chacham et al., ACS Appl. Nano Mater., 3 (2020) 12095.
- [3] Luiz Gustavo Cançado et al. 2D Mater., 4 (2017) 025039.
- [4] Diego L. Silva et al., Carbon, 161 (2020) 181.

HOW TO USE NANOSCIENCE FOR RENEWABLE ENERGY CONVERSION

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The transformation of solar energy directly into chemical energy may become a key for a future sustainable society. Heterogeneous catalysis plays a major role in chemical industry to lower activation barriers in chemical production. Therefore, new (photo)catalysts are needed for the development of sustainable production processes in a circular economy. The catalysts are normally complex hybrid systems, often consisting of metal nanoparticles on oxidic supports. Catalytic reactions may involve a large number of elementary steps. However, in order to tailor the catalyst to the need of a specific chemical reaction it is essential to understand a multitude of different aspects. Single defects and dopants at the oxidic support may be responsible for the population of various reaction paths. In case of the use of metal nanoparticle cocatalysts, the size, composition and structure of the nanoparticle, as well as the interaction between the particle and the support may be essential. Molecules adsorbed at the nanoparticles may act as reactants, poisons or spectators. Ultra High Vacuum (UHV) techniques are useful to study single molecule surface interactions to get an insight into the most important elementary steps. In the talk the relevance of different Ti^{3+}/Ti^{4+} ratios in a $TiO_2(110)$ single crystal will be demonstrated as an example to influence partial oxidation, deoxygenation or C-C-coupling reactions of alcohols and aldehydes [1]. In order to study the interaction of metal nanoparticle cocatalysts a colloidal approach will be presented allowing to control the size, shape, particle loading and the study of the nanoparticle support interaction in contrast to classical impregnation-calcination techniques. The ligands, such as amines, stabilizing the colloids may further influence the selectivity of the chemical reaction [2],[3].

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QUANTITATIVE STRUCTURAL CHARACTERIZATION OF NANOMATERIALS BY PRECESSION E-DIFFRACTION

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Nanomaterials require detailed and reliable characterization at various scales from atomic-, to micro- and, macroscopic level. TEM microscopy is widely applied to characterize nanosystems due to the intrinsic high spatial resolution. Nevertheless, the strong electron-matter interaction may generate multiple scattering events, and severe sample modification. This renders difficult the interpretation of diffracted beam intensities or image contrast in TEM measurements. Precession electron diffraction (PED) has risen as a very interesting approach to reduce the contribution of many event scattering (technically called dynamic diffraction) to the diffracted signal. In fact, PED yields intensities can be described as “quase-kinematical” [1], allowing a very detailed structural characterization based on diffraction based methods and kinematical modeling, traditional assumptions in X-ray/neutron scattering. We will analyze different examples that show the high relevance of the PED approach for t fine characterization of nanomaterials. We will discuss the high potential of PED-based Pair Distribution Function (PDF) to characterize an ensemble of nanoparticles in a TEM [2,3]. Also, when precession diffraction is acquired with a scanning nanobeam, we may combine real and reciprocal space information to derive fine details of the strain field of defects such as dislocations with high spatial resolution in individual nanoobjects [4].

Keywords: precession electron diffraction, pair distribution function, nanodiffraction, TEM

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THE ROBUSTNESS OF TOPOLOGICAL INSULATORS

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Topological insulators (TIs) are quantum states of matter with an insulating energy gap in the bulk and metallic boundary states that are robust against non-time-reversal breaking perturbations. Topological phases of matter in both two- (2D) and three-dimensional (3D) systems gained significant interest due to their exotic properties and potential applications [1]. Further exploring the robustness of such topological phases could lead to the development of non-strict grown protocols aiming for large-scale synthesis. Here we clarify, the robustness of some 2D and 3D topological insulators against chemical disorder [2], vacancies [3], and amorphization [4].

Keywords: Topological Insulator, Density Functional Theory

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LECTURE 10

THE POTENTIAL OF 2D POLYMERS FOR LIGHT HARVESTING APPLICATIONS

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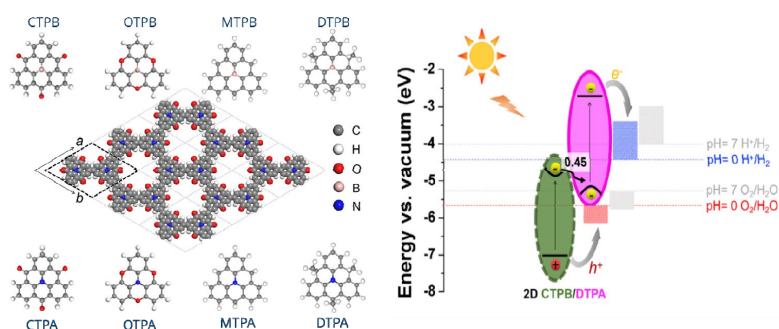
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Decentralized production of green hydrogen by solar-fueled water splitting is key for a successful transfer to a zero emission energy supply. Our goal is the development of materials that are efficient photocatalysts without additional need for infrastructure, have long-term stability, and transform a considerable part of the solar spectrum to chemical and electric energy.

To achieve this goal we take advantage of various options that are offered by conjugated 2D polymers, in particular

- full conjugation to allow for band dispersion and high charge carrier mobility
- lattice symmetry that determines electronic band structure
- functionalization to in-plane control conjugation and photocatalytic performance
- functionalization with heteroatoms to shift bands with respect to vacuum

As example system we use honeycomb-kagome structures based on hetero-triangulenes [1,2]. If designed properly, they can be arranged in tandem cells where hydrogen and oxygen evolution is spatially separated, and no additional catalyst, voltage or sacrificial agent is required-(Figure) [3].



Keywords: 2D polymers, on-surface synthesis, topological polymers, density-functional theory

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INVESTIGATION OF SPIN AND ORBITAL HALL EFFECTS IN HETEROSTRUCTURES

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Unlike normal electronics, where only the electron charge is used, spintronics exploits the spin angular momentum of electrons to store, encode, access, process and transmit information. Thus, pure spin current, which is the flow of spin without charge transport, is a ubiquitous concept in spintronics. Few year ago, the concept of orbital angular current, which is the flow of electrons with a finite orbital moment, emerged as a theoretical proposal, and the first experimental data were reported in 2020¹. In this talk we will discuss two challenging investigations. In the first study, we investigated YIG/Bi heterostructures, where YIG = Y₃Fe₅O₁₂, using the spin pumping technique, and concluded that Bi shows negligible spin-charge conversion. By adding a top layer of Pt, we found that the spin current flowing through the Bi is converted into charge current at the Pt layer. In addition, the pumped spins exhibit an unusual relaxation mechanism driven by the strong diamagnetic response of Bi. We propose that the Bi acts as a binary classifier device that categorizes pumped spins into relaxed spins and those that will flow upwards and eventually reach the top layer of Pt. In the second study, we will show intriguing experimental results of the generation of orbital currents and their interaction with pure spin current in the trilayer structure of CuOx/Pt/YIG. It will be shown how both currents can be generated by means of the spin pumping and spin Seebeck effects. Keeping the thicknesses of the CuOx and YIG layers fixed and varying the thickness of the Pt layer, it is possible to investigate the conversion of angular current in spin current by measuring a transverse electric voltage due to the inverse spin Hall effect.

Keywords: Spintronics, Orbitronics, Spin Hall effect, Orbital Hall effect

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ELECTRONIC PROPERTIES OF INTERFACES WITH N-HETEROPOLYCYCLIC MOLECULES

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For improvement and optimization of the performance of organic molecule-based devices, such as photovoltaic cells and thin-film transistors comprehensive insight into the physical and chemical properties of the organic molecules at surfaces is necessary.

N-heteropolycyclic aromatic compounds are promising candidates for n-channel semiconductors. The introduction of nitrogen atoms into the π -backbone of the polycyclic aromatic hydrocarbons stabilizes the frontier orbitals and increases the electron affinity, while the size of the HOMO-LUMO (optical) gap is nearly unaffected. By using two-photon photoemission spectroscopy (2PPE) and high resolution electron energy loss spectroscopy (HREELS) we determined quantitatively transport, singlet and triplet states as well as electronic spectra of several N-heteropolycyclic molecules adsorbed on Au(111) [1-4]. Using angle-resolved 2PPE we identified strongly dispersing occupied and unoccupied electronic states, which result from hybridization between localized molecular states and delocalized metal bands at the metal/organic interface [2, 3].

We acknowledge funding by the German Research Foundation through the SFB 1249 (N-Heteropolycycles as Functional Materials) and the Cluster of Excellence (3D Matter Made to Order).

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FROM NATURE TO ORGANIC (BIO)ELECTRONICS: MELANIN-INSPIRED MATERIALS

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Melanin is a generic term evoked for a broad class of indole/quinone-based natural pigment, mainly known due to its primary role in photoprotection. Besides, throughout the last couple of decades, synthetic melanin and melanin-like materials garner a lot of attention as a soft biocompatible functional material for bioelectronic and optoelectronic material due to their water-dependent conductivity and excellent biocompatibility [1]. In the earlier days, the limited solubility and the low electronic conductivity of this class of compounds have hindered their progression in organic electronics and bioelectronics helms. Currently, such issues have been overcome by different strategies. In our research group, we combine organic and physical chemistry of condensed matter to develop different melanin derivatives and study their physicochemical properties. We have found years ago, that by synthesizing melanin in DMSO thin films could be produced [2]. In this synthesis melanin are functionalized with sulfonated groups which makes this derivative soluble in DMSO. We have also synthesized melanin under oxygen pressure in water. Under this condition melanin is functionalized with CO₂ and the synthesis time is accelerated. This CO₂ rich melanin is closer to natural melanin and is less insoluble in water. The results obtained suggest that these new melanin derivatives are quite attractive alternatives for the manufacture of (bio) electronic devices. We have produced a pH sensor using an extended gate field effect transistor (EGFET) based on melanin thin films as active layer. The results revealed that EGFETs with melanin deposited on ITO and on gold substrates showed sensitivities ranging from 31.3 mV/pH to 48.9 mV/pH, depending on the melanin precursor solution and the substrate used for deposition. In another work [3] we demonstrate a highly sensitive pH sensor ($62 \text{ mV pH}^{-1} \pm 7$) over a pH range from 5 to 8, with high stability and superior performance when compared with a number of existing devices and making it suitable for physiological applications. Hence, the chemical tailoring procedures and physical-chemical properties of melanin-inspired material will be presented emphasizing their technological problems and applications.

Acknowledgements

We gratefully acknowledge the financial support of São Paulo Research Foundation (FAPESP; grants 2013/07296-2, 2015/23000-1, 2017/24839-0, 2018/02411-1), National Council for Scientific and Technological Development (CNPq, grant: 304541/2018-4) and CAPES (grant: Procad: 88881.068492/2014-01).

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CONDENSED MATTER AT SIRIUS, THE NEW BRAZILIAN SYNCHROTRON

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Sirius, the new Brazilian synchrotron light source under commissioning at Campinas-SP, one of the brightest and first fourth-generation machines in the world, is opening up a plethora of opportunities to study areas such as condensed matter physics with conditions yet nonexistent, including surfaces and nanostructures.

Today we have several challenges to provide a complete understanding of physical mechanisms in condensed matter phenomena, as superconductivity for example. That in part can be tackled by employing experimental x-ray techniques, such as XRD, XMCD, RIXS and ARPES, available at Sirius to access, for example, how electronic states are affected depending on multiple factors (temperature, interface, crystallinity, applied fields and pressure, etc). This information could in principle be used to test, validate or propose new physics theories in ways not yet imagined.

In this talk I will give an overview of several possibilities for condensed matter and materials research with synchrotron techniques at diverse conditions and sensitivities. In addition to an overview of the general possibilities at Sirius, I will show a few examples of studies in thin surfaces/interfaces and nanometer sized structures together with x-ray techniques.

THE SURFACE SCIENCE OF IONIC LIQUIDS

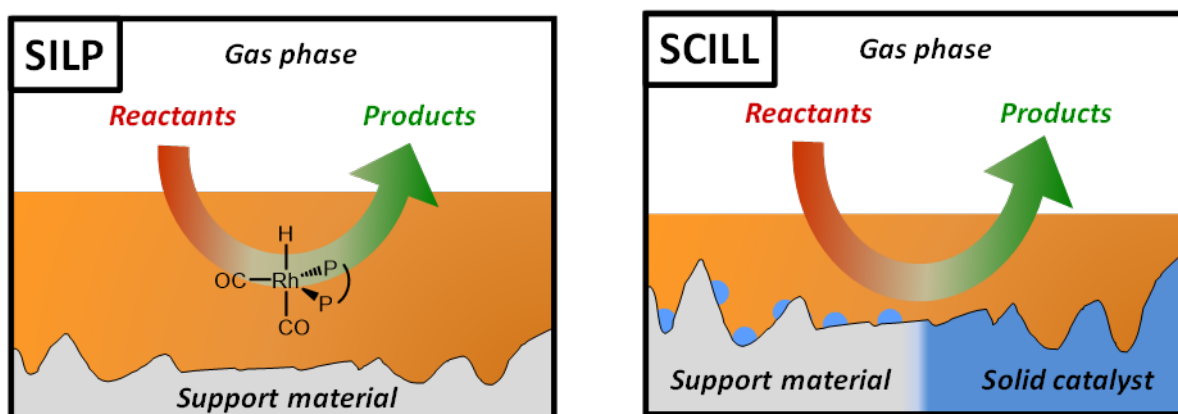
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Ionic liquids (ILs) are salts with melting points below 100 °C. Typically, they are characterized by an extremely low vapour pressure. Since their physical and chemical properties can be tailored over a wide range, they represent a fascinating class 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 like angle-resolved XPS, STM and AFM, along with in situ deposition of ultrathin IL films on solid supports. 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.



Keywords: Ionic Liquids, SIPL, SCILL, adsorption, photoelectron spectroscopy, STM, AFM

ON-SURFACE SYNTHESIS OF NEW FUNCTIONAL 2D MATERIALS: A MOLECULAR “LEGO”

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In the last decades, several 2D materials (e.g., graphene, hexagonal boron nitride, artificial metal-organic frameworks - MOFs) have been intensively studied, revealing interesting physical phenomena and unique electronic, optical, and mechanical properties. These materials are promising for innovative technological applications, such as new catalysts, sensors, electronic and photonic devices, magnetic networks, etc. A fascinating technique for preparing these materials is the so-called on-surface synthesis [1] which is a bottom-up technique that uses specifically “designed” precursors as molecular building blocks (such as pieces of a LEGO[®]) to create, on-demand, new materials with the desired atomic and electronic structure. In this seminar, I will show recent examples in which we applied different growth and functionalization strategies to produce new semiconductors and 2D MOFs[2-4], whose electronic and atomic structures have been characterized by X-ray photoemission spectroscopy (XPS) and scanning tunneling microscopy/ spectroscopy (STM/STS) techniques.

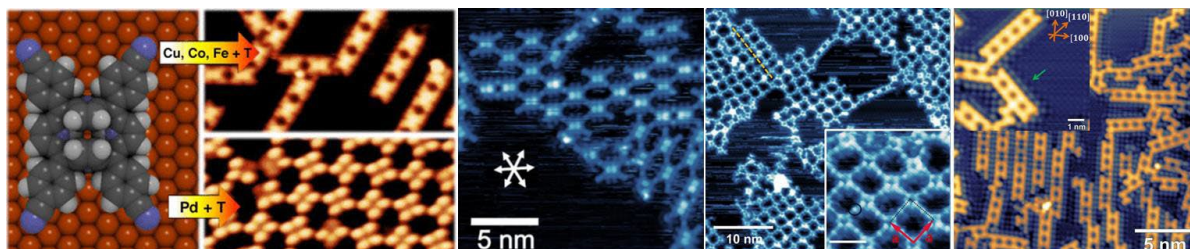


Figure 1- Few examples of organometallic networks formed by on-surface synthesis, which will be addressed in this seminar.

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MODEL IRON OXIDE THIN FILM SURFACES AT THE SOLID-LIQUID INTERFACE

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Surface science model investigations of solid-liquid interfaces have recently gained interest due to the important role of solid-liquid interfaces in general, and, in view of present and future environmental and technological challenges, electrochemical interfaces in particular. In this talk, we will present results of our recent investigations using iron oxide thin films as substrates for model studies of processes occurring at oxide-liquid interfaces. The model systems applied here are the well-known Pt(111)-supported FeO(111) ultrathin film and the 10 nm thick Fe₃O₄(111) film. These films have been characterized in ultrahigh-vacuum and were subsequently exposed to aqueous electrolytes, where various processes have been investigated. We will focus on the stability of the films in solutions of different pH, both with and without applied potential, and the influence of organic molecules (e.g., catechol, phthalic acid) on the dissolution of the films. As an example for model studies of catalyst preparation, we discuss the pH-dependent deposition of Pd precursor and subsequent formation of Pd nanoparticles on Fe₃O₄(111). Finally, we will present results for Pd-Fe₃O₄(111) model catalysts, which have been tested in the electrochemical oxidation of ethanol in alkaline electrolytes. Here, the main focus is laid on the particle size dependent stability of the model catalysts and the restructuring of Pd surfaces in electrochemical environment.

Keywords: Iron oxide films, model catalyst, electrochemistry

2D MATERIALS UNDER HIGH PRESSURES: PROBING STRAIN TRANSFER AND ADHESION

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Raman spectroscopy is a versatile tool nondestructive tool widely used to characterize two-dimensional (2D) systems such as graphene and MoS₂, among others. Since electrons and phonons are specially coupled to each other due to the reduced dimensionality, this technique provides detailed information about the structure and electronic properties of these layered systems thus allowing one to probe in the phonon spectra many features such as the numbers of layers and their interactions with the environment. Most of these 2D materials are sitting on substrate and the understanding on how the substrate affects the physical properties of these atomic thickness layers is a key point for fully characterize and understand the materials as well as to exploit them in different applications. In this regard, strain is an important variable to consider because the adhesion of the 2D material, which is basically surface, depends on the nature of the substrate. One key question is how the strain is transferred from the substrate to the 2D material. The use of hydrostatic pressure has been an effective method modulate the interactions between the 2D materials with substrates and environment and Raman spectroscopy has been important for investigating these strained 2D nanomaterials because the Raman cross section for these systems is very large, even for a single layer. In this talk, we discuss results obtained using high-pressure Raman studies of graphene [1,2] and MoS₂ [3] sitting on different substrates. Depending on the pressure transmitting medium, number of layers, and compressibility of the substrate, the analysis of the Raman modes tells us how the stress is transferred from the substrate to the 2D material, thus allowing us to propose a model for studying the adhesion, and even the delamination, of the 2D systems by using high-pressure Raman technique.

Keywords: 2D materials, Graphene, MoS₂

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ON-SURFACE SYNTHESIS: A BOTTOM-UP STRATEGY TO LOW-DIMENSIONAL CARBON-STRUCTURES

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On-surface synthesis via covalent coupling of adsorbed molecules on metal surfaces has attracted significant attention in recent years due to its potential to fabricate low-dimensional carbon materials with atomic precision. To understand and control the surface-chemistry-driven synthesis, many efforts have been made to design smart precursors, explore novel reaction schemes, and utilize templating effects from the substrate.

My presentation focuses on high-resolution scanning probe microscopy experiments combined with density functional theory to demonstrate recent highlights on the assembly of surface-supported low-dimensional carbon structures. First, the assembly and electronic structure of planar π -extended cycloparaphenylene macrocycles, which represent the first nanographene with an all-armchair edge topology, will be discussed [1]. Exclusive paraconjugation at the macrocycle's periphery yields delocalized electronic states, and calculations predict global aromaticity in the doubly charged system. In the second part, I will outline the host-guest chemistry and the electronic properties of covalent and metal-organic 2D networks that are assembled via debromination reactions on metal surfaces [2-4].

Keywords: On-surface synthesis, Covalent organic frameworks, Metal-organic frameworks, Scanning Probe Microscopy

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LIGAND-DIRECTED HETEROGENEOUS CATALYSIS: WHEN THE DYNAMICALLY CHANGING NATURE OF THE LIGAND LAYER CONTROLS SELECTIVITY

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Selectivity of multi-pathway surface reactions depends on subtle differences in the activation barriers of competing reactive processes, which is difficult to control. One of the most promising strategies to overcome this problem is to introduce a specific selective interaction between the reactant and the catalytically active site, directing the chemical transformations towards the desired route. This interaction can be imposed via functionalization of a solid catalyst with ligands, promoting the desired pathway via steric constrain and/or electronic effects. The microscopic-level understanding of the underlying surface processes is an important prerequisite for rational design of a new class of ligand-functionalized catalytic materials.

In this contribution, we present a mechanistic study on formation and dynamic changes of a ligand-based heterogeneous Pd catalyst for chemoselective hydrogenation of β,α -unsaturated aldehyde acrolein.¹ Deposition of allyl cyanide as a precursor of a ligand layer renders Pd highly active and nearly 100 % selective toward propenol formation by promoting acrolein adsorption in a desired configuration via the C=O end. Employing a combination of real space microscopic (STM) and in operando spectroscopic (IRAS) surface sensitive techniques, we show that an ordered active ligand layer is formed under operational conditions, consisting of stable butylimin species. In a competing process, unstable amine species evolve on the surface, which desorb in the course of the reaction. Obtained atomistic-level insights into the formation and dynamic evolution of the active ligand layer under operational conditions provide important input required for controlling chemoselectivity by purposeful surface functionalization.

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STRUCTURE OF CATALYST SURFACES UNDER OPERATING CONDITIONS FROM FIRST PRINCIPLES

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There is the well-known structure and pressure gap between surface science on the one hand and heterogeneous and electro-catalysis on the other hand: under operating conditions the structures of catalyst surfaces can be very different from those under ultra-high vacuum conditions. Also any reliable atomistic modelling of structures and processes at catalysts surfaces should take the influence of the environment appropriately into account, otherwise the relevance of this modelling with respect to catalysis might be limited. However, there are elegant concepts to address this issue by combining atomistic quantum chemical studies with grand-canonical schemes [1] which are coined *ab initio* Thermodynamics in heterogeneous catalysis and Computational Hydrogen Electrode in electro-catalysis. In this contribution I will briefly review and contrast these approaches, discuss the challenges associated with them, and illustrate them using examples from heterogeneous and electro-catalysis related to the structure of titania supported tungsten-doped vanadia catalysts for the selective catalytic reduction [2], electrode surfaces in the presence sulfate-containing electrolytes [3] and bifunctional catalysts for the oxygen evolution and reduction reaction [4].

Keywords: catalyst surfaces, operating conditions, quantum chemistry, grand-canonical approach

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LECTURE 22

ORGANIC-INORGANIC HYBRID PHOTOCATALYTIC MEMBRANES FOR IN-FLOW WATER PURIFICATION

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Due to the ever-increasing release of anthropogenic pollutants in the environment, many efforts have been directed towards development of improved technologies and materials capable of efficient removal of organic and inorganic contaminants. Given their unique electronic, surface and structural properties, inorganic nanomaterials show improved contaminant removal performances by adsorption and/or (photo)catalytic reactions. However, the use of nanomaterials-based water decontamination technologies generally suffers from severe drawbacks inherent to the nanometric nature of the adsorbents/catalysts which limit their applicability. In this context, our recent research focus on the development of hybrid organic-inorganic materials, that combine unique photocatalytic behavior of inorganic nanostructures (MoS₂, TiO₂ and BiVO₄) with mechanically stable porous polymer supports (Polyhydroxyurethanes, cellulose acetate or Bacterial Nanocellulose) to achieve functional photocatalytic membranes for in-flow photo-assisted water and wastewater treatment. The prepared hybrid membranes show excellent photocatalytic performance towards removal of model pollutants such as organic dyes and hexavalent chromium when employed in a specifically designed membrane photoreactor operated. under in-flow conditions, representing significant advances on the photocatalytic water treatment field.

Keywords: photocatalytic membrane, bacterial cellulose

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Oral Presentations

CAPTURING SURFACE DYNAMICS WITH SPIRAL HIGH-SPEED STM

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Dynamic processes on surfaces are fundamental in catalysis. To understand these processes, real time and real space observations at the atomic scale are crucial. We show a pathway to capture atom dynamics on the millisecond timescale with scanning tunneling microscopy.

100 years ago, first experimental evidence for mobile surface species was provided based on macroscopic observations [1]. Since then a variety of methods have been developed to study atomic processes on well-defined surfaces. Scanning tunneling microscopy (STM) is a prominent example. While it exhibits remarkable lateral resolutions, time resolution is the limiting factor in conventional STM and dynamic processes are often not accessible due to the low frame rate. In our newly developed high-speed STM, we use custom high-speed electronics and an innovative spiral scan pattern to increase the frame rate up to 120 Hz.

With the high-speed STM, we investigate the well studied system of chemisorbed oxygen on Ru(0001) [2,3]. At room temperature, we detect atomic jump rates within an O(2x2) and an O(2x1) adlayer in the order of 0.1 to 1 Hz. Theoretical density functional theory calculations affirm the high mobility in the oxygen adlayers. In the O(2x2) layer, the occupied intermediate state along the diffusion path was resolved in real space and in real time. In the O(2x1) phase, structural reorientations were resolved that extend from the millisecond time scale to minutes.

To analyze the data acquired with constantly high frame rates over several minutes, we developed software tools. These tools enable to analyze structural changes in future measurements on 2D oxide network films.

Keywords: STM, High-Speed, Surface Diffusion

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PROBING POLARITONS IN LOW-DIMENSIONAL MATERIALS WITH SYNCHROTRON INFRARED NANOSPECTROSCOPY

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Polaritons, which are quasiparticles composed of a photon coupled to an electric or magnetic dipole, are a major focus in nanophotonic research of low-dimensional materials. Polaritons can be active in a broad range of the electromagnetic spectrum (meVs to eVs) and exhibit momenta much higher than the corresponding free-space radiation. Hence, the use of high momentum broadband sources or probes is imperative to excite those quasiparticles and measure the frequency-momentum dispersion relations, which provide insights into polariton dynamics. Synchrotron infrared nanospectroscopy^[1] (SINS) is a technique that combines the nanoscale spatial resolution of scattering-type scanning near-field optical microscopy with synchrotron infrared radiation, making it highly suitable to probe and characterize a variety of polaritons. Here, the advances enabled by SINS on the study of key different types of polaritons from the THZ to mid-infrared will be described. In this talk, I will explore low-dimensional materials^[2,3], including graphene, boron nitride (hBN), talc, tin oxide, and others, as the polaritonic materials and their remarkable optical properties. I will present recent studies in the field of polaritons in contact with different interfaces dielectric/air(metal) and heterostructures using SINS. Furthermore, I will show that these experimental observations provide an attractive platform for understanding light-matter interaction and, therefore, it could be harnessed in compact nanophotonic devices and applications involving subdiffractional light traffic.

Keywords: Synchrotron infrared, phonon polaritons, nanomaterials, nano-photonics, Quantum Materials

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ORAL 03

CHARGE TRANSFER IN COPPER-PHTHALOCYANINE ON METALLIC AND OXIDE SURFACES

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Charge transfer into molecular layers on substrates is a well-known phenomenon. On metallic substrates in particular, one would expect the adsorbates to only exist in one charge state, since the metal ought to even out all charge differences across the surface. However, through a combination of results obtained with scanning tunneling microscopy, scanning tunneling spectroscopy and photoemission spectroscopy in investigating copper-phthalocyanine (CuPc) on both Ag(100) and Ag(111), we can show that here a charged and an uncharged state of CuPc coexist. We attribute this behavior to the combination of the CuPc electron affinity and the substrate work function leading to the CuPc lowest unoccupied molecular orbital to sit right at the Fermi edge, and thus small perturbations of the energy levels favor either the charged or uncharged state.

In order to test this hypothesis we also investigated heterostructures of CuPc and pentacene (5A) on both Ag(100) and on ultrathin magnesium oxide layers. Here we can show that CuPc exhibits more charge transfer than 5A, and is thus more strongly bound to the surfaces resulting in the complete displacement of 5A by CuPc in both cases.

These results further the understanding of charge transfer on metals and oxides and suggest a means of controlling and predicting molecular heterostructures.

Keywords: charge transfer, STM, STS, UPS

DEVELOPMENT OF NANOCOMPOSITES FOR ENERGY STORAGE SYSTEMS

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The demand for energy consumption is increasing, but the solution is not only focused on increasing generation, but also on improving the way of transmitting and storing the generated energy. With that in mind, supercapacitors can be considered the great answer to this question, due its properties, being charged faster and discharging this energy more slowly. Therefore, this work presents the development of nanocomposites involving the combination of conductive polymers (CPs), neat transition metal oxides (TMO) or mixed (MTMO), graphene derivatives (GO and rGO) and transition metal dichalcogenides (TMDs) to produce materials or devices with capacitive properties. In recent works we synthesized, in less than 20 minutes, WO₃/rGO nanocomposites, which showed capacitance close to 300 F.g⁻¹ after 3000 cycles. In another work, WO₃-RuO₂/PAni was prepared with impressive capacitance values when compared to neat PAni. Such performance allows us to prepare a symmetrical device that presented capacitance values of 240 mF.cm². We also present some results related to the one-step hydrothermal synthesis of mixed capacitive systems based on WO₃-WS₂/rGO, as well as the synthesis of more complex systems involving the combination of oxides, dichalcogenides, conductive polymers and graphene derivatives to produce the PAni/rGO/WS₂-MoS₂ nanocomposite and the evaluation of the influences of each material on the total capacitance of the system. The author acknowledges MackGraphe, Mackenzie Presbyterian University (UPM), MackPesquisa, FAPESP, CNPq (306808/2020-0), Capes, and INCT of Carbon Nanomaterials.

Keywords: Electrochemical capacitor; Nanocomposites, Energy storage

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INVESTIGATION OF MELANIN-BASED ENERGY STORAGE SYSTEMS VIA CHEMICAL DERIVATIZATION

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Over the last decade, the interest in using melanin specifically as a material class for applications in technological and biomedical settings has increased drastically [1]. The most recent efforts in chemical modification of eumelanin polymers for battery device applications have mostly focused on increasing their solubility for film processibility [2]. Thus, a vast number of potential derivatives have yet to be studied more deeply that could potentially help in understanding the redox chemistry of eumelanin. Here, synthetic eumelanin (melanin-*Syn*) was chemically modified to include *tert*-butyloxycarbonyl protecting groups added to the indole N-1 nitrogen atoms of the monomers, giving the derivative melanin-*Boc*. The goal was to investigate the importance of metal ion chelation by the secondary amine groups through a functionalized eumelanin coated on conductive carbon paper cathode with a zinc anode in a two-electrode coin cell-system, using ZnSO₄ in deionized H₂O as electrolyte. This was achieved by comparing electrochemical properties of melanin-*Syn* and melanin-*Boc* in electrolytes of different concentration. Cyclic voltammetry-, galvanic charge-discharge-, and battery cycling measurements were carried out. Furthermore, the substances were characterized and compared using NMR-, FTIR-, SEM-, and UV-Vis experiments. The indole nitrogen atoms were found to play an important role in charge transfer processes of melanin-based energy storage systems. The implications of the differences between melanin-*Syn* and melanin-*Boc* for choosing new melanin derivatives will be discussed.

Keywords: melanin, eumelanin, derivative, battery, device, electrochemistry, chelation.

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ORGANIC/INORGANIC HYBRID NANODEVICES: FROM CHARGE-TRANSFER REACTIONS TO SENSOR APPLICATIONS

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Intermolecular charge transfer reactions are key processes in physical chemistry. The charge transfer rates depend on a few system parameters, such as the temperature (T), the electric field (E), the distance between adsorbates, and, especially, the molecular reorganization energy (λ). This microscopic quantity is the energetic cost to rearrange each molecule and its surrounding environment when a charge is transferred.^[1] Despite the evident impact of electron transfer reactions on hopping transport, well-controlled charge transport measurements using monolithically integrated nanodevices have not been succeeded in measuring λ . Here, we show that self-rolling nanomembrane (rNM) devices,^[1] with strain-engineered mechanical properties and on-a-chip monolithic integration,^[2] can overcome this challenge. We employ the rNM technology to manufacture 6 nm thick copper-phthalocyanine (CuPc) nanocapacitors, from which the CuPc charge-transport is thoroughly characterized as a function of T and E . Thereby the CuPc reorganization energy is experimentally determined as $\lambda = (0.93 \pm 0.04)$ eV, whereas density functional theory calculations supported our findings with an atomistic picture of the CuPc charge-transfer reaction.^[1] Our approach presents a consistent route towards electron-transfer experiments and provides insight into the role of λ when it comes to both monolithically integrated nanodevices and chemical sensor applications.^[2]

Keywords: reorganization energy, device, molecular electronics, electrochemistry, transistor.

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RATIONALIZING SPIN-ORBIT PROXIMITY EFFECT IN SOC/FM MULTILAYERS: THE ROLE OF INTERFACE

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The Spin-Orbit Proximity Effect is the raise of Spin-Orbit Coupling at a layer near to the interface with a strong spin-orbit material. It has been seen in several system such as graphene [1] and ferromagnetic layers [2]. The control of the Spin-Orbit Coupling can be a pathway to discover novel and exotic phases in superconductor and semimetallic systems [3]. Here, we study the magnetoelectrical transport, i.e., magnetoresistance and anomalous Hall effect, in Cobalt/Bismuth multilayers looking for traces of spin-orbit proximity effect and evaluate the origin of such effect. Our results point for an increase of Anisotropic Magnetoresistance and Anomalous Hall Resistivity at very low thicknesses of Cobalt. The analysis of the Anomalous Hall Resistivity indicate that the Bismuth layers change the scattering mechanism of Hall effect to the extrinsic skew-scattering type, indicating that the spin-orbit proximity effect could be related to the elastic scattering of cobalt free carriers by bismuth sites at the interface.

Keywords: Spin-Orbit Proximity Effect, Ferromagnetism, Bismuth Multilayers

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FROM SELF-ASSEMBLED MONOLAYERS TO HIGHLY FUNCTIONAL SUBSTRATES FOR CRYO-TRANSMISSION ELECTRON MICROSCOPY (CRYO-TEM)

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Major problems for the cryo-transmission electron microscopy (cryoTEM) of proteins are the stabilization of the nm-thick water film and the preservation of the particles within the field of observation without denaturation. Here we report three approaches to produce TEM grids suitable for the task.

1) Covering the supporting carbon films with a hydrophilic film to suppresses adhesion of proteins. This could be extended by introduction of carbon nanotubes, covered by the same kind of molecular film to aid charge dissipation during observation.

2) The cross linking of a polyglycerol-SAM resulted in ultrathin hydrogel membranes, which help the distribution of the unaltered proteins. Self-perforation of the membranes during the deposition process opened windows for an unaltered observation by the electron beam.

3) The modification of the hydrogel membrane with selective binding sites, by formation on-top of carbon nano-membranes, which in turn are obtained by cross-linking of aromatic monolayers by electron-beam irradiation. The bi-layer system is then modified covalent attachment of a selective binding site, which allows for the selective extraction of the analyte from e.g. protein mixtures.¹

Keywords: self-assembled monolayers; cross-linking; hydrogels; transmission-electron microscopy

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STUDY OF MAGNETIC ANISOTROPY AND INDUCED SPIN POLARIZATION IN Fe/Co/Cu₃Au(001): AN EXPERIMENTAL AND FIRST-PRINCIPLES INVESTIGATION

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Understanding the complex correlations structure-magnetism and the origins of the magnetic anisotropy in ultrathin magnetic heterostructures is an active research area in physics, given its great potential for new technologies in data storage and processing, and devices. In this work we investigated the induced magnetization of interfacial Cu atoms in ferromagnetic Fe/Co ultrathin films grown on an fcc Cu₃Au(001) substrate. To explore the interfacial nature of the induced magnetic moments and its origin, we probed two structures of five alternate Fe and Co monoatomic layers with either Fe or Co in direct contact with the non-magnetic Cu₃Au(001) surface. X-ray magnetic circular dichroism measurements at the L_{2,3} edges of Fe, Co and Cu allowed to extract the spin and orbital magnetic moments of Fe and Co in both structures, and to measure extremely low magnetic moments induced in Cu atoms. The samples were grown and probed in-situ at the PGM beamline. The same systems were also investigated by first principles calculations, in order to obtain the spin and orbital moments of the different atoms for both Fe-Co/Cu₃Au(001) stacks, disentangling the origin of magnetic proximity effects at these ferromagnetic/non-magnetic interfaces. The experimental and theoretical results reveal an induced magnetism only in atoms at the interface layer of the ordered Cu₃Au(001) substrate, i.e., the observed Cu XMCD signal is due to only 0.5 ML magnetic Cu atoms. Such results clearly demonstrate the importance of the structural, electronic, and magnetic interface reconstructions on the appearance of magnetic induced moments, which at the end determine the detailed behavior of the magnetic anisotropy.

SELF-ASSEMBLY AND THIN FILM GROWTH DYNAMICS OF AN IONIC LIQUID ON Au(111) INVESTIGATED IN REAL SPACE

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Ionic liquids (IL) are organic salts with low melting points, often at or even below room temperature. They have shown promise as solvents and electrolytes, but have also become part of novel catalytical concepts involving solid metal catalysts. Amongst these is the Solid Catalyst with Ionic Liquid Layer (SCILL) design, where thin films of ionic liquid cover solid metals, thereby modifying surface properties and active sites of the supporting material.

In this context, our group studied the self-assembly and growth dynamics of thin films of 1,3-dimethylimidazolium-bis[(trifluoromethyl)sulfonyl]imide ([C1C1Im][Tf2N]) on the model surface of Au(111) using scanning probe microscopy[1,2,3]. Our experiments show that the film undergoes distinct phases between the growth of the wetting layer and subsequent multilayers. Further, 2D film growth is shown to be in competition with the growth of a metastable 3D droplet phase, with the dominant growth mode determined by a combination of temperature and nucleus formation.

Keywords: Ionic liquids, Solid-Liquid Interface, STM, AFM

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SELF-METALATION OF 2H-TETRAPHENYL PORPHYRIN AND 2H-PORPHINE ON AN OXIDE SURFACE

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Porphyrins and metalloporphyrins are versatile molecules, which offer a large variability of their properties due to the possibility to attach different ligands or metal atoms to the porphyrin macrocycle. The surface-confined self-metalation reaction describes the replacement of two amine protons in the macrocycle of the porphyrin molecule by a metal atom of the substrate. This reaction was first observed on metal surfaces, but more recent investigations show that it also occurs on oxides such as magnesium oxide (MgO). Previous work has shown that the self-metalation of 2H-tetraphenyl porphyrin (2H-TTP) on MgO is strongly dependent on the morphology of the material and occurs only on surface irregularities but not on a perfect planar surface.

By a combination of results obtained with scanning tunneling microscopy, photoemission spectroscopy, and DFT computations, we show that the self-metalation reaction on MgO can also be induced on planar MgO surfaces. The key to this is the use of only few atomic layers thin MgO films, which are grown on a metallic substrate. Because of the reduction of the work function of the silver substrate by the MgO film, electron transfer occurs into adsorbed 2H-TTP molecules, which then leads to the self-metalation reaction. By chemical tuning of the work function we could furthermore show that states where the molecules are charged and metalated or uncharged and non-metalated can deliberately be generated. These results suggest a method to control the electric and chemical properties of porphyrins on surfaces, which opens the way for selective surface functionalization.

To understand the role of charging, we compare the self-metalation of 2H-TTP and 2H-porphine on ultrathin MgO films. Our results suggest, that charging helps to bring the macrocycle closer to the MgO surface, which facilitates the transfer of an Mg ion from the oxide lattice into the molecule.

Keywords: Charge Transfer, Photoemission Tomography, Porphyrins, Self-Metalation, Thin Film

AN HR-XPS STUDY ON BROMINE ON *h*-BN/RH(111)

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Since the first preparation of graphene, numerous two-dimensional materials (2DM) have been theoretically predicted, synthesized, and characterized. These efforts are motivated by their unique properties rendering them promising for diverse applications.

Hexagonal boron nitride (*h*-BN), a graphene analogue, consists of alternating boron and nitrogen atoms arranged in a honeycomb fashion. On Rh(111), *h*-BN exhibits a Moiré pattern, the so-called nanomesh. To tailor the properties of 2DM towards possible applications, their chemical modification is of high interest. Despite of its chemical inertness, covalent functionalization of *h*-BN has been successful [1]. In the special case of the *h*-BN/Rh(111) nanomesh, the Moiré structure can act as a template, enabling spatially defined modification of the 2DM [2]. Using this template, we now aim for controlled functionalization of *h*-BN/Rh(111) with halogens.

Here, we present a state-of-the-art surface science study on the adsorption and thermally induced reaction of elemental bromine on the *h*-BN/Rh(111) nanomesh. The adsorption of different amounts of bromine was followed *in situ* using synchrotron radiation-based high-resolution X-ray photoelectron spectroscopy (HR-XPS), confirming the template effect of the nanomesh for low coverages. Applying temperature-programmed XPS (TPXPS), we examined the thermal stability of Br₂/*h*-BN/Rh(111). Based on our data, we propose covalent functionalization of the pores and a thermally induced on-surface reaction of bromine. Additionally, ultraviolet photoelectron spectroscopy (UPS) was used to investigate the valence band structure. By shedding light on the controlled chemical modification of the *h*-BN/Rh(111) nanomesh on the molecular level, our work paves the way for purposeful tailoring of the properties of 2DM.

Keywords: two-dimensional materials, hexagonal boron nitride, functionalization, bromine, high-resolution X-ray photoelectron spectroscopy

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SURFACE-SUPPORTED METAL-ORGANIC FRAMEWORK VERTICAL HETEROJUNCTIONS FOR HYBRID ELECTRONIC DEVICES

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The advent of Surface-Supported Metal-Organic Frameworks (SURMOFs) thin-film synthesis has opened new perspectives to integrate Metal-Organic Frameworks (MOFs) structures into electronic devices. Derivative from the layer-by-layer growth on functionalized surfaces, SURMOFs possess the main intrinsic properties of MOFs coupled with the processibility in creating homogeneous thin-films with adjustable thicknesses. However, the characteristic high porosity of SURMOFs is the principal source for the formation of glassy interfaces and atomic disorder during top electrode deposition using conventional evaporation methods. Therefore, the main challenges in such a context are concerned to appropriate methodologies of integration. In this direction, nanomembrane-origami technology can be a valuable alternative, since this approach has the capability of providing self-adjustable top contacts on ultra-thin films without damage. In this work, we demonstrate the fabrication of HKUST-1 SURMOF vertical heterojunctions using rolled-up nanomembranes as the top electrode. The electrical characterization under controlled conditions of humidity and applied electric field revealed unprecedented physical effects, namely, ambipolar resistive switching and negative differential resistance – both with low-power consumption. These effects are interpreted employing density functional theory (DFT) calculations and ab initio molecular dynamics simulations. Furthermore, a low-voltage ternary inverter is also demonstrated. These findings point out how SURMOFs can be envisioned to create novel and hybrid electronic devices, by employing adequate methods of integration and precisely controlling external parameters.

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ORAL 14

EXPLORING FIELD-EFFECT TRANSISTORS BASED ON GRAPHENE FOR THE ULTRASENSITIVE DETECTION OF BIOMARKERS

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Biosensors based on graphene field-effect transistors (GFETs) are highly attractive technology, as they allow real-time label-free electrical detection, scalability, inexpensive mass production, miniaturization, the use of a low volume of sample, and the possibility of on-chip integration of both sensor and measurement systems. Besides that, graphene possesses unique properties such as: i) high charge carrier mobilities and electrical conductivity, ii) flexibility, iii) biocompatibility, iv) facile chemical functionalization, and v) large specific surface area, allowing the immobilization of high density of bioreceptors, leading to increased sensitivity [1]. This presentation will provide an overview of the fundamentals and applications of GFETs, highlighting the use of these in the ultrasensitive detection of breast cancer biomarkers (HER-2 protein) and the Spike (S) proteins of the SARS-CoV-2 virus. Furthermore, we will show how the decoration of graphene by gold nanoparticles and aptamers improved the limited detection of these devices to fM levels. Our results have shown that the GFETs exhibited a high electrical sensitivity in the detection of HER-2 proteins and the S protein, allowing us to explore this technology to detect the breast cancer biomarkers and SARS-CoV-2 virus in real samples, such as blood and saliva, respectively.

Keywords: Graphene, FETs, Bioelectronics, Cancer, COVID-19

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ELECTRON TRANSFER REACTION BY TIME RESOLVED (TRS) AND CORE LEVEL SPECTROSCOPY (XPS) AND STM ON AU/TiO₂(110) SINGLE CRYSTAL SYSTEMS.

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Abstract:

Electron transfer reactions in the photocatalytic hydrogen production rely on the presence of metals of cluster or nanoparticle nature dispersed on top of a semiconductor. The complexity of multi- component photo-catalysts hinders accurate measurements dictating the use of simplified methods. In order to explore part of this complex kinetics, H₂ production rates of an electron donor, such as ethanol, over Au clusters with different sizes and coverage deposited on single crystal rutile TiO₂(110) were studied by scanning tunneling microscopy, online mass spectrometry and complemented by femto second pump probe spectroscopy. It was also found that there is a non- linear increase of the H₂ production rate with increasing gold coverage. The key determining factor appears to be the Au inter-particle distance. Increasing this distance resulted in an increase in the normalized reaction rate. These results are explained in terms of competition between particles for excited electrons to reduce H⁺ (of surface OH groups) to H₂.

A new atomic scale anisotropy in the photoreaction of surface carboxylates on rutile TiO₂(110) induced by gold clusters will also be presented. STM and DFT+U were used to study this phenomenon by monitoring the photoreaction of the prototype hole-scavenger molecule over s-TiO₂, Au₉/s-TiO₂, and Au₉/r-TiO₂. STM results show that adsorption displaces a large fraction of Au clusters from the terraces towards their edges. DFT calculations explains that Au₉ clusters on stoichiometric TiO₂ are distorted upon adsorption. More importantly, the photoreaction rate appears to be directional. A roughly three-fold higher depletion rate is observed in the [001] direction. This is linked to the anisotropic conduction of excited electrons along [001], with subsequent trapping by Au clusters leaving a higher concentration of holes and thus an increased decomposition rate. To our knowledge this is the first-time atomic scale directionality is reported upon photo-excitation of an adsorbate on a semiconductor.

SURFACE LIGAND INFRARED SPECTROSCOPY: IN-SITU CHARACTERIZATION OF NOBLE METAL CLUSTERS AND METAL OXIDES AT WORK

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To achieve a full understanding of chemical processes taking place at the exposed surfaces of metal clusters or at metals deposited on oxide nanoparticles in-situ and operando investigations will be required. For studies of catalytic processes under real conditions, IR spectroscopy offers a number of advantages over other methods. In the present study, surface ligand infrared spectroscopy was used to perform an in-situ investigation of the surface characteristics of cerium oxide single crystals as well as catalytic active Pd-clusters on cerium oxide nanoparticles at low temperature (60 - 200 K) in ultra-high vacuum conditions (10^{-10} mbar). Carbon monoxide as well as water was used as probe molecule for surface characterization as well as the identification of active sites. In addition to single crystals, highly dispersed Pd was investigated on cerium oxide nanoparticles. The adsorption and desorption of carbon monoxide in ultra-high vacuum conditions can be used as a tracking method for available adsorption sites as well as the change in surface structure. The metal particles and clusters were investigated in their oxidized as well as their reduced state, which was achieved by heating the samples in ultra-high vacuum conditions. It could be shown that the identification of the oxidation state, structural changes as well as the effects of cluster formation and sintering can be investigated with infrared spectroscopy as a non-destructive method. This series of experiments show the power of infrared spectroscopy as a tool for in-situ investigations and the characterization of noble metal clusters and metal oxides at work.

Keywords: CO-SLIR, surface characterization, oxide materials, metal cluster, nano particles

REACTIVITY AND PASSIVATION OF FE NANOCCLUSERS ON H-BN/RH(111)

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Iron is a nontoxic and affordable element, which shows high catalytic activity. Iron containing catalysts are used in important industrial reactions, such as the Fischer-Tropsch synthesis and the Haber-Bosch process. Especially, iron nanoclusters are of interest because of their potential utilization in electrochemical devices or high-density data storage applications due to their magnetic properties.

To obtain monodisperse, ordered Fe nanocluster arrays, h-BN was used as a template on the Rh(111) surface. Due to the lattice mismatch, differences in the strength of interaction between the h-BN sheet and the Rh(111) surface occur, leading to corrugation of the nanosheet and the formation of pores and wires.^[1]

We studied Fe nanocluster arrays formed in the pores of h-BN/Rh(111) using in situ high-resolution X-ray photoelectron spectroscopy. CO was used as a probe molecule to investigate the morphology, such as the available adsorption sites and the reactivity of the nanoclusters. On the as prepared Fe clusters, CO was adsorbed at on-top and hollow/edge sites and dissociated at 300 K. For the C and O pre-covered Fe nanoclusters we found a passivation of the catalytic activity as a result of adsorption site blocking, allowing for the determination of the most active sites of the Fe clusters.^[2]

Keywords: heterogeneous catalysis, iron, model catalysis, nanocluster array, XPS

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ACTIVATION OF AMINES AND ALKENES AT Pt(111) SURFACE FOR C-N BOND FORMATION

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Previous own studies on amine-stabilized Pt nanoparticles for spectator-directed catalysis had shown the formation of an additional imine-like surface species besides the amine. However, the origin and identification of this species is still under discussion.^[1]

We want to elucidate, if one of the amine-surface interaction species can serve as an essential intermediate for C-N formation reactions. The anti-Markovnikov addition of amines to alkenes is of particular interest, as it was listed as one of the top ten challenges in catalysis.^[2] While the hydroamination were often carried out homogeneous-catalyzed, the development of heterogenous catalysts is still lagging behind.^[3]

Studies were performed with *N*-Methylaniline and Ethylene at a Pt(111) single crystal as both substrates reacted efficiently in the homogeneous catalysed hydroaminoalkylation with titanium complexes.^[4] Before starting the coadsorption experiments, the adsorption and decomposition of *N*-Methylaniline and Ethylene on Pt(111) surfaces were investigated. For *N*-Methylaniline XPS spectra do not show any additional surface species besides the amine. Therefore, it is an ideal system to test which reactions occur without imine-like species before addressing the more complex chemistry with heterogeneously catalyzed hydroamination/hydroaminoalkylation reactions in the presence of partial imine-formation. Results show that *N*-Methylaniline desorbs molecularly, while Ethylene forms an Ethylidyne species. Carbon residues are formed by the decomposition and influence the surface chemistry, as apparent from temperature dependent desorption spectra.

Keywords: X-ray photoelectron spectroscopy (XPS), Temperature-programmed desorption (TPD), Fourier-transform infrared spectroscopy (FTIR), Pt(111), C-N formation

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IMPROVING ELECTRICAL CONDUCTIVITY MEDIATED BY PYRROLE LOADING IN MONOLITHICALLY INTEGRATED SURMOFS TEMPLATES

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Surface Metal-Organic Frameworks (SURMOFs) is a new class of materials based on the networks of metallic clusters and organic ligands. These structures have essential characteristics such as crystalline orientation, high porosity, and superficial area [1]. This approach originates homogeneous, highly oriented films with thicknesses that achieve the nanometric scale. All these characteristics make SURMOFs attractive candidates for electronic devices [2,3]. Nevertheless, one of the main challenges for using SURMOFs in electronics remains insulator-like characteristics ($<10^{-10}$ S/cm), mainly operating in inert environment. In this sense, the intrinsic high porosity of SURMOFs can offer a unique set of opportunities to improve their electrical conductivity, like inserting conductive materials inside their pores. Here we report an improvement of electrical conductivity in monolithically integrated HKUST-1 SURMOF heterojunctions using pyrrole (Py) loading via vapor. The metallic clusters from SURMOF film act as a template to convert the Py monomers into conductive conjugated polypyrrole (PPy) chains. The polymerization parameters were optimized and monitored by electrical and chemical characterizations. At room temperature, the highest electrical conductivity obtained was about $5 \cdot 10^{-6}$ S/m after 24 h of loading [4]. Additionally, the nanomembrane-based contact allowed profitable electrical characterization under low temperatures. Besides, we demonstrated that PPy@HKUST-1 device could work as a load resistor integrated into a simple basic light-emitting diode circuit. In this way, the integration of high-quality SURMOF thin films and polymerization *in situ* is a versatile approach, enabling their applications to key technological fields.

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Keywords: Metal-organic frameworks, Electronics, Polypyrrole

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Posters

ON-SURFACE SYNTHESIS OF TWO-DIMENSIONAL POROUS NETWORK ON METAL SURFACES

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Recently, on-surface coupling, supramolecular self-assembly, and coordination networks investigations have been widely explored. Graphene nanoribbons, one- and two-dimensional polymers are remarkable examples [1]. The Ullmann coupling reaction has a noteworthy efficiency to build covalent nanostructures from molecular building blocks [2]. Furthermore, the growth of bidimensional porous networks based on nitrogenous molecular precursor it has been promising. Molecular precursors, such as porphyrins, have been explored for these studies since their high degree of functionalization. Moreover, porphyrins are a promising class of functional molecules, due to their chemical stability and electronic properties. For example, brominated precursors present great potential to build nanostructures by Ullmann reaction [2]. Therefore, it is crucial to understand the molecular adsorption behavior, the intermediate complexes, and final products formed to obtain a deeper insight into these on-surface reactions.

In this work, the adsorption behavior of 5,10,15,20-(tetra-4-bromophenyl) porphyrin (H₂Br₄TPP) on Cu(111) surface and the building of ordered porous networks are explored. To shed light on the molecular adsorption behavior and nanostructure characterization we present a combined x-ray photoelectron spectroscopy scanning tunneling microscopy, and density functional theory calculations study. The porphyrins adopt the inverted structure conformation, characterized by the strong interaction between iminic nitrogens and the Cu surface [3]. Moreover, we investigated the dehalogenation reaction, determining the Br adatoms position over Cu(111). The molecules shows no ordering after the deposition at RT. However, adsorbing these precursors with Cu(111) kept at 400K yields a different behavior. The molecules arrange ordered nanostructures with trigonal symmetry. Furthermore, the precursors on the nanoarchitectures adopt the inverted structure conformation [4].

Keywords: On-surface synthesis, Ullmann reaction, Porphyrins, Coordinated networks, Porous network, STM.

Acknowledgments

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ZIF-8 DERIVED ZnO FUNCTIONAL DEVICES**Ana Claudia Fingolo^{1,2}, Tatiana Parra Vello¹, Carlos César Bof Bufon²***1Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Centre for Research in Energy and Materials (CNPem), Campinas/SP, Brazil**2Postgraduate Program in Material Science and Technology (POSMAT), UNESP, Bauru/SP, Brazil**anaclaudiafingolo@outlook.com*

Metal Organic Frameworks (MOF) are a class of materials that attracted great attention in recent decades due to its characteristic's high porosity, crystallinity, and versatility with wide possibilities of functionalization. These compounds are formed by a metallic center, composed of an ion or cluster, coordinated to organic ligands. A prominent example of this class is ZIF-8, which is formed by zinc ions and 2-methylimidazole as ligand. This material has high chemical and physical stability in addition to the most common characteristics of MOFs. When heated above ~450 °C, Zn ions oxidation leads to ZnO formation, with high porosity due to precursor structure, while organic ligand degradation leads to a conductive carbon matrix formation. Conductive carbon presence can improve the electrical properties of the resulting material, which can be an advantage in several applications of this semiconductor. In this work, ZIF-8 thin films were thermally treated for the formation of ZIF-8 derived ZnO using two devices with different architectures, manufactured by photolithography techniques. The films' crystalline structure was analyzed by XRD, and the deposition of ZIF-8 was confirmed. After thermal treatment a large structure shrinkage was observed in topography images obtained by AFM. The functional groups present in the films suffered changes observed through Raman spectroscopy. After treatment two peaks belonging to ZnO were seen. Electrical behavior of the films was compared before and after thermal treatment using a semiconductor analyzer and a probe station. *I vs V* curves (0 to 2V) showed an increase of five orders of magnitude in maximum current before and after treatment.

Keywords: On-surface synthesis, Ullmann reaction, Porphyrins, Coordinated networks, Porous network, STM.

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This work was financially supported by FAPESP, CNPq, and CAPES.

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EPITAXIAL GROWTH OF HfS₂ ON Ag (111): SEMICONDUCTOR RESPONSE AND OXIDATION OF THE MONOLAYER

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The 2D transition metal dichalcogenides (TMDs) have attracted attention for their application in optoelectronics and transistors devices [1] due to property variability when changing the transition metal, the chalcogen element, the number of layers, or the growth conditions [2]. The hafnium disulfide has a calculated indirect bandgap of 1.2 eV, a large mobility of carriers at room temperature (RT), high optical absorption coefficient, and high photoluminescent response from the monolayer [3]. However, this material presents limited literature owing to the synthesis and implementation difficulty for devices development. In this work, we use the gas source molecular beam epitaxy (GSMBE) technique to grow HfS₂ on Ag(111) substrate. Furthermore, the high-purity sources, lower-growth temperatures, and slow growth rate are essential for thickness control. Two samples were grown differing the substrate temperature and the hafnium evaporation time from each other. The first sample was grown with Ag(111) at RT and 5 min of Hf. The second was grown with the substrate at 430 °C and with 15 min of Hf deposition. HfS₂ was successfully grown according to the characterizations results, and the air exposure oxidized the monolayers. Therefore, the formed HfO₂ appears in the X-ray photoelectron spectroscopy (XPS) measurements. The growth with Ag(111) at 430 °C generated HfS₂ islands with a surface area 1064% greater than in RT. Moreover, the scanning tunneling microscopy/spectroscopy (STM/STS) analysis shows preserved small flakes of HfS₂ after the oxidation, with a semiconductor behavior and gap of the order of ~1 eV, in good agreement with the monolayer for the 1T structural phase. This is also supported by the periodicity analysis by LEED (low energy electron diffraction) patterns. In summary, the growth technique is appropriate for this system since the UHV environment is suitable for the growth of HfS₂ without O₂ exposure, which causes oxidation of the monolayer. Furthermore, the current methodology provides HfS₂ monolayers with a single crystallographic phase, a semiconductor bandgap, and a large substrate coverage area. Hence, we can obtain parameters to synthesize high-quality TMDs in laboratory conditions and study them both globally (XPS and LEED) and locally (STM and STS) for potential optoelectronic applications.

Keywords: epitaxial growth, TMDs, hafnium disulfide, HfS₂, XPS, LEED, STM, STS, GSMBE.

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CORE-LEVEL BINDING ENERGY SHIFTS IN MNO(001) THIN FILMS GROWN ON AU(111)

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Understanding the physical origin of core-level photoemission line shapes can offer valuable information on the chemical and physical properties of surfaces. For instance, in a larger number of transition metals oxides, changes in the line shape allow the precise description of their oxidation states and cation site symmetry. And the fact that the binding energies of surface and bulk atoms of metals are shifted has been known for some time, described as Surface Core Level Shifts (SCLS) [1]. Remarkably, there has been much less study of SCLS for oxides despite their possible importance for the chemical and physical properties of surfaces [2-4]. In order to provide further evidence of the relevance of its physical nature, we have introduced a new aspect of interior-, terrace- and edge- atoms corelevel binding energies shifts to describe monolayers of MnO(001) films onto Au(111) substrate. By this means we were able to distinguish the line shape contributions related to different types of atomic sites. We show that their relative intensities and shifted features, is able to provide information about the relative amount of uncoordinated atoms on the surface and, hence, to allow understanding of its possible catalytic properties. Our findings reveal the importance of a detailed surface science characterization to provide the correct interpretation of distinct photoemission line shapes when considering thin film samples as well as nanostructures in general.

Keywords: manganese oxide; thin films; xps; surface core-level binding energies shifts.

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A STEP FORWARD EUMELANIN-BASED MICRO AND PORTABLE DEVICES

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Eumelanin, the primary pigment in humans, is becoming a model biomaterial for bioelectronics and eco-design technologies due to its biocompatibility, biodegradability, easy processing for creating device-quality thin films, and hydration-dependence conductivity [1,2]. Using spin-coating and drop-cast techniques, various devices platforms such as batteries, supercapacitors, ion-to-electron transducers, memories, sensors, and UV-shielding were developed [1,2]. However, these two processes are not entirely compatible with the current tendency towards smaller and portable devices. Here, we explored the standard photolithography microfabrication process to fabricate structures for (bio)electronics applications based on soluble sulfonated eumelanin. We have found that the microfabrication process does not affect the thin-film surface topography, chemical composition, and charge transport behavior of such material. Furthermore, the patterned films had their applicability validated based on the development of a pH-humidity-contact multisensory platform. This sensor showed excellent efficiency over physiological pH, and response and recovery times from human breath and touch were achieved. Our work provides a step toward miniaturized wearable technologies for human healthcare and physiological monitoring based on eumelanin materials.

Keywords: Patterning; photolithography; melanin; eumelanin derivative; sensing

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CAPTURING SURFACE DYNAMICS WITH SPIRAL HIGH-SPEED STM

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Dynamic processes on surfaces are fundamental in catalysis. To understand these processes, real time and real space observations at the atomic scale are crucial. We show a pathway to capture atom dynamics on the millisecond timescale with scanning tunneling microscopy.

100 years ago, first experimental evidence for mobile surface species was provided based on macroscopic observations [1]. Since then a variety of methods have been developed to study atomic processes on well-defined surfaces. Scanning tunneling microscopy (STM) is a prominent example. While it exhibits remarkable lateral resolutions, time resolution is the limiting factor in conventional STM and dynamic processes are often not accessible due to the low frame rate. In our newly developed high-speed STM, we use custom high-speed electronics and an innovative spiral scan pattern to increase the frame rate up to 120 Hz.

With the high-speed STM, we investigate the well studied system of chemisorbed oxygen on Ru(0001) [2,3]. At room temperature, we detect atomic jump rates within an O(2x2) and an O(2x1) adlayer in the order of 0.1 to 1 Hz. Theoretical density functional theory calculations affirm the high mobility in the oxygen adlayers. In the O(2x2) layer, the occupied intermediate state along the diffusion path was resolved in real space and in real time. In the O(2x1) phase, structural reorientations were resolved that extend from the millisecond time scale to minutes.

To analyze the data acquired with constantly high frame rates over several minutes, we developed software tools. These tools enable to analyze structural changes in future measurements on 2D oxide network films.

Keywords: STM, High-Speed, Surface Diffusion

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POSTER 07

SYNTHESIS AND CHARACTERIZATION OF POLY(P-ANISIDINE): EXPERIMENTAL AND THEORETICAL APPROACH TO MOLECULAR STRUCTURE, THEORETICAL AND SPECTROSCOPIC PROPERTIES

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P-anisidine is a derivative of aniline substituted by the methoxy group (-OCH₃) in the para position. Few studies have been carried out aiming at the evaluation of its electrical and spectroscopic properties, as well as its structural aspects. Thus, in order to enable its technological applications, the purpose of this research is to address these properties through the correlation of experimental data provided from techniques such as XRD, NMR and FTIR with theoretical data from computer simulation. Poly (p-anisidine) (PPA) was chemically synthesized using hydrochloric acid, for to optimize of synthesis was applied statistical experimental design DCCR to evaluate the data of each variable involved in the experimental, thus 17 synthesis were to prepared. X-Ray Diffraction (XRD) data were obtained to observe possible structural changes in the PPA. DFT analysis on the molecular structure and vibrational spectra was evaluated, for that experimental for FTIR data to be correlated with theoretical data obtained through computer simulation, for the study the molecular structure of PPA, NMR results were used to propose the molecular system, where two structures were analyzed. For the analysis of the electrical conductivity of the PPA, impedance spectroscopy data were obtained.

Keywords: Poly(p-anisidina), DFT, NMR.

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INVESTIGATION OF MELANIN-BASED ENERGY STORAGE SYSTEMS VIA CHEMICAL DERIVATIZATION

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Over the last decade, the interest in using melanin specifically as a material class for applications in technological and biomedical settings has increased drastically [1]. The most recent efforts in chemical modification of eumelanin polymers for battery device applications have mostly focused on increasing their solubility for film processibility [2]. Thus, a vast number of potential derivatives have yet to be studied more deeply that could potentially help in understanding the redox chemistry of eumelanin. Here, synthetic eumelanin (melanin-*Syn*) was chemically modified to include *tert*-butyloxycarbonyl protecting groups added to the indole N-1 nitrogen atoms of the monomers, giving the derivative melanin-*Boc*. The goal was to investigate the importance of metal ion chelation by the secondary amine groups through a functionalized eumelanin coated on conductive carbon paper cathode with a zinc anode in a two-electrode coin cell-system, using ZnSO₄ in deionized H₂O as electrolyte. This was achieved by comparing electrochemical properties of melanin-*Syn* and melanin-*Boc* in electrolytes of different concentration. Cyclic voltammetry-, galvanic charge-discharge-, and battery cycling measurements were carried out. Furthermore, the substances were characterized and compared using NMR-, FTIR-, SEM-, and UV-Vis experiments. The indole nitrogen atoms were found to play an important role in charge transfer processes of melanin-based energy storage systems. The implications of the differences between melanin-*Syn* and melanin-*Boc* for choosing new melanin derivatives will be discussed.

Keywords: melanin, eumelanin, derivative, battery, device, electrochemistry, chelation.

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STUDY THE STRUCTURE OF $Mn_3O_4(110)$ BY STM

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The structure of $Mn_3O_4(110)$ thin film is investigated by STM. Additional surface science techniques were employed to observe the thin film surface of the Mn_3O_4 film on Cu (111). The ratios of Mn^{3+} and Mn^{2+} cations on manganese oxide surfaces are expected to contribute to the catalytic activity of Mn_3O_4 . However, there is no complete understanding on the surface structure of the thermodynamically stable film of Mn_3O_4 (hausmanite). In this work we observed the surface of $Mn_3O_4(110)$ undergoes lattice distortions that can affect its chemical and physical properties. These properties are known to be relevant to surface reactivity. In particular, the STM images suggest a termination layer of the $Mn_3O_4(110)$ film with a fully oxidized Mn^{2+} layer on the upper surface and Mn^{3+} cations at the Cu (111) interface [1]

Keywords: Scanning Tunneling Microscopy. manganese oxide surfaces

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TEMPERATURE INFLUENCE ON THE ELECTRICAL PROPERTIES OF Na₂Ti₃O₇/Na₂Ti₆O₁₃/POMA COMPOSITE.

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Ceramic-polymeric composites match the excellent physicochemical properties of ceramics with the flexibility and additional properties of polymers[1]. Recently, a new ceramic-polymer composite based on sodium titanate and POMA was reported. Such composite was structurally and electrically characterized and the influence of the POMA content on its properties was presented[2]. In this work a study is carried out on the temperature influence on the electrical properties of the ceramic-polymer composite with sodium titanate and POMA (Na₂Ti₆O₁₃/Na₂Ti₃O₇/POMA). The composites were prepared with different concentrations of polymer (0%, 1%, 10%, 15%, 35% and 50%) in the ceramic matrix. The complex impedance spectroscopy technique was used to execute the electrical characterization of the samples in the temperature range of 25 °C to 100 °C. Depending on the POMA concentration, it was observed a decrease in the samples resistance with an increase in the POMA content. The increase in the samples resistance with increasing temperature can be observed in the Cole-Cole diagrams and it is a typical behavior of materials with PTCR effect[3]. This anomalous effect is clearly seen for all the composites, except for the sample with the highest POMA content (50%). The variation in resistivity values was about two orders of magnitude for all composites that presented PTCR effect. As a function of temperature, the lowest value of resistivity at room temperature (9.20 x 10⁴ Ωcm) corresponded to the sample with 50% POMA. While the highest resistivity value after the resistivity jump (2.20 x 10⁹ Ωcm) corresponded to the sample with 0% POMA.

Keywords: Composites, Electrical properties, PTCR.

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DEVELOPMENT OF SELF-COILING NANOMEMBRANES FOR 3D ULTRACOMPACT CAPACITIVELY COUPLED CONTACTLESS CONDUCTIVITY DETECTION.

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Abstract: There is a plethora of molecular events occurring in a fraction of a second in our body fluids right now. Being able to detect alterations of corporal fluids in an individual is key for precocious treatment of several illnesses. Therefore, devices (microdevices) aimed at improving the lives of individuals in society are in high demand. A class of these devices that is increasingly expanding its applicability are Point of Care (Point of Care) test or Point of Care Testing (POCT) devices and Lab-On-Chip (LOC) type devices.¹ These type of microdevices allow for a quick diagnosis, with safety, efficacy and reliability, and low production costs. Furthermore, it allows a better strategy regarding decision making for the treatment and prognosis of several diseases. Herein we present a concept of a microdevice aimed at capacitively coupled contactless conductivity detection (C4D) technique ^{2,3} to probe fluids in electrochemical environments. The C4D microdevices are based on self-coiling nanomembranes that were produced by microfabrication techniques according to processes previously developed by the research group.⁴ Layers of selected materials are sequentially patterned onto a surface of a glass substrate. Each layer has lateral dimension (width, length) about dozens of micrometers and thickness in nanometer scale. From top to bottom the main 4 layers can be described: (i) a dielectric layer that covers and insulates the electrodes, (ii) the electrodes that are responsible to excitation and detection signals, (iii) the strained layer, that once it is released from the sacrificial layer relax forms a tube-like structure, the so-called r-NMC4D. As proof-of-concept the performance for r-NMC4D was validated with diferente electrolytes. The r-NMC4D exhibits sensitivity compatible with what is found in literature.

Keywords: Capacitively coupled contactless conductivity detection (C4D); rolled-up nanomembranes; self-coiling; electrochemical.

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EFFECT OF LIOH CONCENTRATION IN FLEXIBLE COMPOSITES FOR APPLICATION IN SOLID STATE ELECTROLYTE

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Since the advent of solid state batteries (SSB) many materials have been used as electrolytes to get better ionic conduction through its crystalline structure. Some types of polymers are interesting to be used in battery components because they combine high mobility of charge carriers and flexibility [1,2]. For this purpose, in recent years, composites with lithium salt have been use achieving a significance increase in the conductive properties of this type of materials [3].

In this work, thermoplastic composites have been synthesized, PVA (Polyvinyl Alcohol) blended with LiOH (Lithium Hidroxide Monohydrate) in the following proportions, 0, 1, 3, 5, 7, 9 e 10% in weight. It was prepared via Solvent Casting Method. The process was carried out in the Ultrasonic Bath. The complex impedance study indicated that there is a decrease in the resistance values of the composites up to 7% of LiOH (104 Ω) with the increase of the lithium content. The composites with 9% and 10% LiOH presented higher resistance values (106 Ω), which points to a solubility limit. Therefore, we concluded that the material obtained becomes promising for applications in technological devices.

Keywords: Composite, LiOH, solid state electrolytes.

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