International

3rd Ertl Symposium on
Surface Analysis and Dynamics

09-12 November 2014 in Berlin, Germany

- hosted by the FHI der MPG & Ertl Center, GIST
- http://env1.gist.ac.kr/ertl/new/ERTLCenter

Prof. Dr. Gerhard Ertl
Nobel Laureate 2007
Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin, Germany
"for his studies of chemical processes on solid surfaces"


Ertl center
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November 09-12, 2014
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Supports and Sponsors
BASF
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Gerhard Ertl

Born in 1936 in Bad Cannstadt, Germany. PhD in Physical Chemistry in 1965 from Technische Universität München, Germany. Prof. Emeritus, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany. Ertl has laid the foundation of a scientific discipline through his enormously systematic and thorough studies. He has often returned to the same problem in surface chemistry decade after decade in order to use new experimental methods to obtain answers to questions posed earlier. His ability to describe in detail how an experiment is to be designed and interpreted has helped him to provide the methodological platform for an entirely new area of research.

Ertl Center

Agenda of the Ertl Center

The first period (2008-2010)	The second period (2011-2014)	The third period (2015-beyond)
- Foundation of the center - 1st Ertl symposium	- Center of excellence (COE) in electrochemistry and catalysis research	- Continuous research

Role of the Ertl Center

- Bridge between basic research and industrial applications
- Encouragement of continuous research in Electrochemistry and Catalysis (Surface Science)
- Focused on international collaboration
- Promotion of "practical Learning" movement (DASAN)
- Organization of Ertl symposium

Introduction

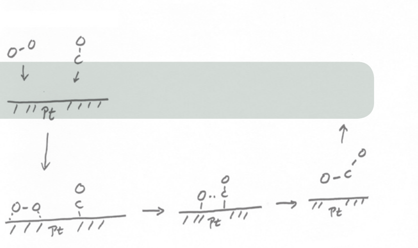
At the beginning of the 21st century our world is facing serious problems with regards to environment, climate, energy conversion, raw materials and food. All these global problems are seeking scientific solutions, especially from physical chemistry and electrochemistry, and in this connection analysis and dynamics are of tremendous importance, in particular for *in-situ* & Operando methods on surface and interface reactions. It is expected that the 3rd Ertl symposium will provide a good opportunity in these attempts, and we wish great success to all the people involved in this enterprise.

Honorary Chair

Gerhard Ertl	Fritz-Haber-Institut der MPG & Ertl Center, GIST

Symposium Chairs

Jaeyoung Lee	Ertl Center & SESE, GIST
Robert Schlögl	Fritz-Haber-Institut der MPG
Martin Wolf	Fritz-Haber-Institut der MPG



Organizing and Scientific Committee

Markus Eiswirth	Fritz-Haber-Institut der MPG & Ertl Center, GIST
Axel Knop-Gericke	Fritz-Haber-Institut der MPG
Hye Jin Lee	Kyungpook National University
Jae Kwang Lee	Ertl Center, GIST
Bongjin Simon Mun	GIST & Advanced Light Source
A. Julia Stähler	Fritz-Haber-Institut der MPG
Hamilton Varela	University of São Paulo & Fritz-Haber-Institut der MPG

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Key Topics

Operando Surface Characterization
Computational Physical Chemistry
Chemical Energy Storage and Conversion
Accelerated Degradation Analysis
Physicochemical (Hydro) Dynamics
Carbon, Hydrogen, Oxygen and Water Reactions

Tutorial Courses : 09 November

Zhi Liu Shanghai Institute of Microsystem and Information Technology & ALS	XPS : From UHV to ambient pressure
Martin Wolf Fritz-Haber-Institut der MPG	Femtochemistry of molecules at metal surfaces

Opening Address

Gerhard Ertl	Fritz-Haber-Institut der MPG & Ertl Center, GIST

Award Lectures (2014 Ertl Prize Winner)

K. Andreas Friedrich	Deutsches Zentrum für Luft-und Raumfahrt
Young Dok Kim	Sungkyunkwan University

Invited Speakers

Francisco Aires	Institute of Researches on Catalysis and Environment in Lyon
Artur Braun	Swiss Federal Laboratories for Materials Science and Technology
Zhifeng Ding	University of Western Ontario
Gerd Ganteför	University of Konstanz
Arnd Garsuch	BASF
Axel Knop-Gericke	Fritz-Haber-Institut der MPG
Axel Groß	Ulm University
Sang Hoon Kim	Korea Institute of Science and Technology
Hiroshi Kondoh	Keio University
Marc T. M. Koper	Leiden University
Katharina Krischer	Technical University of Munich
Hye Jin Lee	Kyungpook National University
Jürgen Leohold	Volkswagen
Jacek Lipkowski	University of Guelph

Zhi Liu	Shanghai Institute of Microsystem and Information Technology & ALS
Olaf Magnussen	University of Kiel
Daniel Mandler	Hebrew University of Jerusalem
Martin Muhler	Ruhr-University Bochum
Bongjin Simon Mun	GIST & Advanced Light Source
Anders Nilsson	Stockholm University & SLAC National Accelerator Laboratory
Masatoshi Osawa	Hokkaido University
Rolf Schuster	Karlsruhe Institute of Technology
Katrin R. Siefermann	Leibniz Institute of Surface Modification
A. Julia Stähler	Fritz-Haber-Institut der MPG
Peter Strasser	Technical University Berlin
Dangsheng Su	Institute of Metal Research & Fritz-Haber-Institut der MPG
Hamilton Varela	University of São Paulo & Fritz-Haber-Institut der MPG
Norbert Wagner	Deutsches Zentrum für Luft-und Raumfahrt
Alastair W. Wark	University of Strathclyde

Abstract Submission by 31 August 2014

150-300 words with illustration and pictures in WORD file
E-mail submission: ertl@gist.ac.kr

Conference Fee & Registration

- Regular participants: €350 Students: €200
  The symposium registration fee includes a copy of the book of abstracts, lunch, coffee break and conference dinner.
- Registration
  http://env1.gist.ac.kr/ertl/new/ERTLCenter

Conference Venue

The 3rd Ertl Symposium on Surface Analysis and Dynamics will be held in the Harnack-House, the conference venue of the Max Planck Society, around 200 meters from U3 Thielplatz. The symposium venue can easily be reached by the well-established public traffic system in Berlin. For details of the location, see:
http://www.harnackhaus-berlin.mpg.de
http://www.fhi-berlin.mpg.de/reach.epl


U3 Thielplatz

Special Issue

The symposium proceedings will be published in a special issue of **Catalysis Today** on Surface Analysis and Dynamics. Articles will be subject to the standard peer review for an Elsevier journal. The Catalysis Today website is active for this special issue and contributions can be uploaded starting **15 November 2014.** The deadline for submission of manuscripts is **28 February 2015.**

Guest Editors : Jaeyoung Lee (Ertl Center, GIST) and Robert Schlögl (FHI der MPG & MPI-CEC)

Program

	09 Nov. Sunday	10 Nov. Monday	11 Nov. Tuesday	12 Nov. Wednesday	Time
08:45-10:20	Arrival	Robert Schlögl	Olaf Manussen	Martin Wolf	95
		G. Ertl / Opening address / 10 Y. D. Kim / AL 01 / 35 M. G. Willinger / OP 01 / 20 R. Schuster / IL 01 / 30	K. A. Friedrich / AL 02 / 35 J. Leohold / IL 08 / 30 S. H. Kim / IL 09 / 30	D. Su / KL 07 / 35 G. Ganteför / IL 16 / 30 P. Strasser / IL 17 / 30	
10:20-10:45		Coffee Break			25
10:45-12:30		Artur Braun	Zhifeng Ding	Hamilton Varela	105
		H. Kondoh / KL 01 / 35 J. D. Ocon / OP 02 / 20 Z. Liu / IL 02 / 30 S. Cherevko / OP 03 / 20	J. Lipkowski / KL 04 / 35 J. Choi / OP 06 / 20 K. R. Siefermann / IL 10 / 30 C. Heine / OP 07 / 20	A. Braun / KL 08 / 35 Y. Tong / OP 10 / 20 B. S. Mun / IL 18 / 30 A. S. Varela / OP 11 / 20	
12:30-13:40		Lunch			70
13:40-15:45	FHI Tour & Registration	Katharina Krischer	Marc T. M. Koper	Rolf Schuster	125
		M. Muhler / KL 02 / 35 A. J. Stähler / IL 03 / 30 A. Garsuch / IL 04 / 30 M. Osawa / IL 05 / 30	K. Krischer / KL 05 / 35 N. Wagner / IL 11 / 30 A. Knop-Gericke / IL 12 / 30 H. J. Lee / IL 13 / 30	Z. Ding / KL 09 / 35 O. Magnussen / IL 19 / 30 Y. Cui / OP 12 / 20 M. T. M. Koper / KL 10 / 35 M. Eiswirth / CR / 10	
15:45-16:10	Jaeyoung Lee	Coffee Break Photograph time (Monday)			25
16:10-18:25	Tutorial 01 / 80 15:45 –17:05 M. Wolf Tutorial 02 / 80 17:05 –18:25 Z. Liu	Dangsheng Su	Peter Strasser	Culture Night	135
		A. Nilsson / KL 03 / 35 H. Varela / IL 06 / 30 I. Herrmann-Geppert / OP 04 / 20 F. Aires / IL 07 / 30 S. V. Levchenko / OP 05 / 20	A. Groß / KL 06 / 35 D. Mandler / IL 14 / 30 O. Diaz-Morales / OP 08 / 20 A. W. Wark / IL 15 / 30 C. Ranjan / OP 09 / 20		
18:30-20:30	**Greetings**	**Poster Session**	**Symposium Dinner**		120
	Welcome Reception	A. J. Stähler A. Knop-Gericke K. A. Friedrich B. S. Mun Y. D. Kim H. J. Lee	Award Ceremony (Ertl Prize & Poster Award)		

09 November (Sunday)

TC (Tutorial Course, 80min), AL (Award Lecture, 35min),
KL (Keynote Lecture, 35min), IL (Invited Lecture, 30min),
OP (Oral Presentation, 20min)

Program		Time
	Tutorical Course : Jaeyoung Lee	
15:45 - 17:05	**TC-01 Martin Wolf** (Fritz-Haber Institute of MPG, Germany) ▶ Femtochemistry of molecules at metal surfaces	80
17:05 - 18:25	**TC-02 Zhi Liu** (Shanghai Institute of Microsystem and Information Technology & ALS, China) ▶ XPS: From UHV to ambient pressure	80
	Greetings : Robert Schlögl	
18:30 - 20:30	Welcome reception	120

Starry Night by Vincent van Gogh in 1889

10 November (Monday)

Program		Time
08:45 - 10:20	Session 1: Robert Schlögl	
	Opening address Gerhard Ertl	08:45
	AL-01 Young Dok Kim (Sungkyunkwan University, Korea) ▶ Initial stage of photo-induced oxidation of poly(3-hexylthiophene-2,5-diyl) layers on bare and TiO_2-covered ZnO	08:55
	OP-01 Marc G. Willinger (Fritz Haber Institute of MPG, Germany) ▶ *In-situ* observation of graphene growth dynamics by environmental scanning electron microscopy	09:30
	IL-01 Rolf Schuster (Karlsruhe Institute of Technology, Germany) ▶ Heat effects upon electrochemical metal deposition	09:50
10:20 - 10:45	Coffee Break	25
10:45 - 12:30	Session 2: Artur Braun	
	KL-01 Hiroshi Kondoh (Keio University, Japan) ▶ *In-situ* analysis of catalytically active surfaces with near ambient pressure XPS	10:45
	OP-02 Joey D. Ocon (Gwangju Institute of Science and Technology, Korea) ▶ Excellent doping-dependent discharge behaviour of p-type germanium in a semiconductor-air cell	11:20
	IL-02 Zhi Liu (Advanced Light Source, USA) ▶ Using "Tender" X-ray ambient pressure X-ray photoelectron spectroscopy as a direct probe of solid-liquid interface	11:40
	OP-03 Serhiy Cherevko (Max-Planck-Institut für Eisenforschung GmbH, Germany) ▶ On-line time- and potential-resolved monitoring of electrochemical noble metal and metal oxide dissolution	12:10
12:30 - 13:40	Lunch	70
13:40 - 15:45	Session 3: Katharina Krischer	
	KL-02 Martin Muhler (Ruhr-University Bochum, Germany) ▶ Short-chain alcohol oxidation over Au/TiO_2 catalysts to probe metal-support interactions	13:40
	IL-03 A. Julia Stähler (Fritz Haber Institute of MPG, Germany) ▶ Ultrafast exciton dynamics at the ZnO(10-10) surface	14:15
	IL-04 Arnd Garsuch (BASF SE, Germany) ▶ Functional films on electrode surfaces - electrolyte additives for lithium ion batteries	14:45
	IL-05 Masatoshi Osawa (Hokkaido University, Japan) ▶ Mechanistic study of formic acid/formate electrooxidation on Pt over a wide pH range	15:15
15:45 - 16:10	Coffee Break	25

10 November (Monday)

Program		Time
	Session 4: Dangsheng Su	
16:10 - 18:25	**KL-03 Anders Nilsson** (Stockholm University, Sweden) ▶ Ultrafast surface chemistry and catalysis	16:10
	IL-06 Hamilton Varela (University of São Paulo, Brazil) ▶ Charge compensation in polymer-metal composites driven by self-organized potential oscillations	16:45
	OP-04 Iris Herrmann-Geppert (Helmut-Schmidt-University, Germany) ▶ Surface analysis of cold gas sprayed TiO_2 photoelectrodes for the water oxidation reaction	17:15
	IL-07 Francisco J. Cadete Santos Aires (Institut de Recherches sur la Catalyse et l'Environnement de Lyon, France) ▶ Study of the behavior of catalytic surfaces in the presence of gases by *in situ* methods	17:35
	OP-05 Sergey V. Levchenko (Fritz Haber Institute of MPG, Germany) ▶ Adsorbate-adsorbate interactions on surfaces at realistic conditions: A first-principles study	18:05
18:30 - 20:30	**Poster Session:** A. Julia Stähler, Axel Knop-Gericke, K. Andreas Friedrich, Bongjin Simon Mun, Young Dok Kim, Hye Jin Lee	120

11 November (Tuesday)

	Program	Time
08:45 - 10:20	Session 5: Olaf Magnussen	
	AL-02 K. Andreas Friedrich (German Aerospace Center, Germany) ▶ Fundamental aspects of polymer electrolyte fuel cell technology and the associated water management	08:45
	IL-08 Jürgen Leohold (Volkswagen AG, Germany) ▶ Batteries for automobiles	09:20
	IL-09 Sang Hoon Kim (Korea Institute of Science and Technology, Korea) ▶ On the effect of substrate reducibility and dopant type on the catalytic activity of metal/metal oxide complex systems	09:50
10:20 - 10:45	**Coffee Break**	25
10:45 - 12:30	Session 6: Zhifeng Ding	
	KL-04 Jacek Lipkowski (University of Guelph, Canada) ▶ IR spectroscopy studies of thin organic films at the solid - liquid interface	10:45
	OP-06 Jinsub Choi (Inha University, Korea) ▶ Preparation of TiO_2 nanotubes with a doping of ruthenium oxide: Potential shock methods *vs.* single anodization	11:20
	IL-10 Katrin R. Siefermann (Leibniz Institute of Surface Modification, Germany) ▶ Ultrafast relaxation dynamics in aqueous environment and charge transfer at a molecule-semiconductor interface	11:40
	OP-07 Christian Heine (Fritz Haber Institute of MPG, Germany) ▶ Ambient pressure soft X-ray absorption spectroscopy of a catalyst surface in action: Closing the pressure gap in the selective n-butane oxidation to maleic anhydride over vanadyl pyrophosphate	12:10
12:30 - 13:40	**Lunch**	70
13:40 - 15:45	Session 7: Marc T. M. Koper	
	KL-05 Katharina Krischer (TU München, Germany) ▶ Peculiar excitation waves during CO electrooxidation on Pt electrodes in an electrochemical flow cell	13:40
	IL-11 Norbert Wagner (German Aerospace Center, Germany) ▶ Production and characterization of carbon-free bi-functional cathodes for the use in lithium-air batteries with an aqueous alkaline electrolyte	14:15
	IL-12 Axel Knop-Gericke (Fritz Haber Institute of MPG, Germany) ▶ The influence of intercalated oxygen on the properties of graphene on polycrystalline Cu under various environmental conditions	14:45
	IL-13 Hye Jin Lee (Kyungpook National University, Korea) ▶ Amplified amepromteric sensing using nanostructured electrodes	15:15
15:45 - 16:10	**Coffee Break**	25

11 November (Tuesday)

	Program	Time
16:10 - 18:25	Session 8: Peter Strasser	
	KL-06 Axel Groß (Ulm University, Germany) ▶ Oxygen interaction dynamics with platinum surfaces: When does O_2 physisorb, chemisorb or dissociatively adsorb?	16:10
	IL-14 Daniel Mandler (The Hebrew University of Jerusalem, Israel) ▶ Nanomaterials and nanocomposites based films	16:45
	OP-08 Oscar Diaz-Morales (Leiden University, The Netherlands) ▶ Oxygen evolution on an iridium-based molecular catalyst: Turnover frequencies, stability and electrolyte effects	17:15
	IL-15 Alastair W. Wark (University of Strathclyde, United Kingdom) ▶ Multimodal optical imaging of individual nanoparticles	17:35
	OP-09 Chinmoy Ranjan (Max Planck Institute for Chemical Energy Conversion, Germany) ▶ *In situ SERS* study of manganese oxides as anode catalysts for oxygen evolution reaction	18:05
18:30 - 20:30	Symposium Dinner & Award Ceremony	120

12 November (Wednesday)

	Program	Time
08:45 - 10:20	Session 9: Martin Wolf	
	KL-07 Dangsheng Su (Institute of Metal Research, China) ▶ Surface-modified nanodiamond for heterogeneous and electro-catalysis	08:45
	IL-16 Gerd Ganteför (University of Konstanz, Germany) ▶ Growth pattern of cluster thin films	09:20
	IL-17 Peter Strasser (Technical University Berlin, Germany) ▶ Electrocatalysts getting in shape: Atomic-scale growth, structure and reactivity of octahedral bimetallic alloy nanoparticles	09:50
10:20 - 10:45	**Coffee Break**	25
10:45 - 12:30	Session 10: Hamilton Varela	
	KL-08 Artur Braun (Empa. Swiss Federal Laboratories for Materials Science and Technology, Switzerland) ▶ Charge transfer across electrochemical and bio-electrochemical interfaces, and its assessment with electroanalytical and x-ray spectroscopy methods	10:45
	OP-10 Yujin Tong (Fritz Haber Institute of MPG, Germany) ▶ Electrochemical oxidation of formic acid on gold electrode: Studied by a surface vibrational spectroscopy	11:20
	IL-18 Bongjin Simon Mun (Gwangju Institute of Science and Technology, Korea) ▶ Surface electronic structures of Pt-TM alloys	11:40
	OP-11 Ana Sofia Varela (Technical University Berlin, Germany) ▶ Non-noble metal based catalyst for efficient and selective reduction of CO_2 and CO	12:10
12:30 - 13:40	**Lunch**	70
13:40 - 15:45	Session 11: Rolf Schuster	
	KL-09 Zhifeng Ding (The University of Western Ontario, Canada) ▶ Interrogating Cu_2ZnSnS_4 nanocrystal films for solar cells	13:40
	IL-19 Olaf Magnussen (Christian-Albrechts University Kiel, Germany) ▶ *In situ* surface x-ray scattering studies of metal deposition and oxidation	14:15
	OP-12 Yi Cui (Fritz Haber Institute of MPG, Germany) ▶ Doping effect in modifying the surface properties of oxide film	14:45
	KL-10 Marc T. M. Koper (Leiden University, The Netherlands) ▶ Chemistry and electrochemistry of water at platinum	15:05
	Closing remarks Markus Eiswirth	15:40
	Culture Night	

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Oral Session

Femtochemistry of molecules at metal surfaces

Martin Wolf

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Chemical reactions occur usually in the electronic ground state, whereby reaction barriers are overcome by thermal activation. Exceptions from this rule are photo-induced or electron stimulated processes, where the activation is mediated by electronic excitation to an excited state which initiates a nuclear motion along the reaction pathway. Examples are photo-chemical processes and chemical reactions induced by electron attachment or charge transfer. A key concept of chemical reaction dynamics relies on the Born-Oppenheimer (BO) approximation whereby electrons are assumed to follow the nuclear motion instantaneously and thus the reaction evolves electronically adiabatically on a BO potential energy surface. Thereby, non-adiabatic coupling effects between the nuclear motion and the electronic degrees of freedom are neglected. However, electronic non-adiabatic processes can occur at metal surfaces where a continuum of electron-hole pair excitations in the metal may lead to a coupling between electronic and nuclear degrees of freedom and a breakdown of the BO approximation. This is relevant for phenomena like interfacial charge transfer, chemicurrents or hot electron induced reactions. The dynamics of such processes occur on ultrafast (typically femto- to picosecond) timescales.

In this talk, I will present several examples for laser-induced electronic non-adiabatic surface femtochemistry at molecule-metal interfaces, namely the associative $H + H \rightarrow H_2$ formation and the oxidation and desorption of CO on Ru(001). These processes are accompanied by pronounced changes of the electronic structure which can be studied directly in the time domain by appropriate spectroscopic techniques. As an outlook I will briefly discuss how the corresponding transient electronic structure changes can be probed using an x-ray free-electron laser employing time-resolved resonant inelastic x-ray scattering (trRIXS). Thereby, the electronic structure of CO molecules on Ru(001) is probed as their chemisorption state changes after excitation with a fs laser pulse and a fraction of these molecules are transiently trapped in a precursor state on ps timescales prior to desorption.

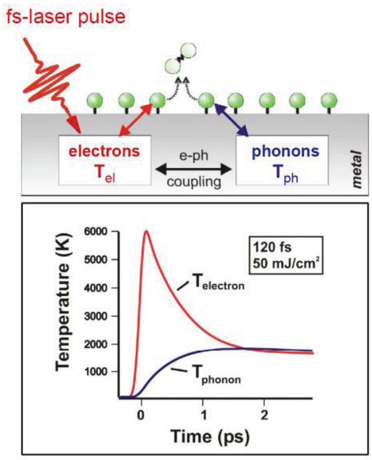

Fig. 1. Femtochemistry at a metal surface: a fs-laser pulse excites electrons in the metal substrate, which equilibrate with lattice phonons on a ps time scale. Surface reactions can be driven either by non-adiabatic coupling to hot electrons (T_{el}) or by activation via lattice phonons ($T_{ph.}$).

XPS: From UHV to ambient pressure

Zhi Liu

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Chemical reactions at gas-solid interfaces play an important role in many processes in the environment and technology. X-ray photoelectron spectroscopy (XPS) is one of the most powerful surface characterization techniques. However, XPS traditionally requires ultra-high vacuum conditions and cannot be used for *in-situ* study at gas-solid interface. The newly developed ambient pressure X-ray photoelectron spectroscopy (APXPS) has become a valuable tool to investigate the elemental composition and chemical specificity of surfaces and adsorbates on the molecular scale at pressures of up to 130 mbar. In this tutorial, I will first introduce the historical development of APXPS over the last forty years, discuss different approaches to minimize scattering of electrons by gas molecules, and give an overview about the experimental systems (mainly gas-solid interfaces). Several examples for the application of APXPS to environmental science, heterogeneous catalysis, and electrochemistry will also be presented. At the end, I will discuss the new development of using APXPS to probe liquid-solid interfaces.

Fig. 1. An APXPS experiment is being conducted on an electrochemical system with a beaker of electrolyte inside of the XPS analysis chamber.


11-14 April, 2010 Oryong Hall
1st Ertl Symposium on Electrochemistry and Catalysis
Prof. Dr. Gerhard Ertl Nobel Laureate 2007
GIST
Gwangju Institute of Science and Technology
1st Ertl Symposium on Electrochemistry and Catalysis
11-14 April 2010 Oryong Hall
PCCP

Initial stage of photo-induced oxidation of poly(3-hexylthiophene-2,5-diyl) layers on bare and TiO_2-covered ZnO

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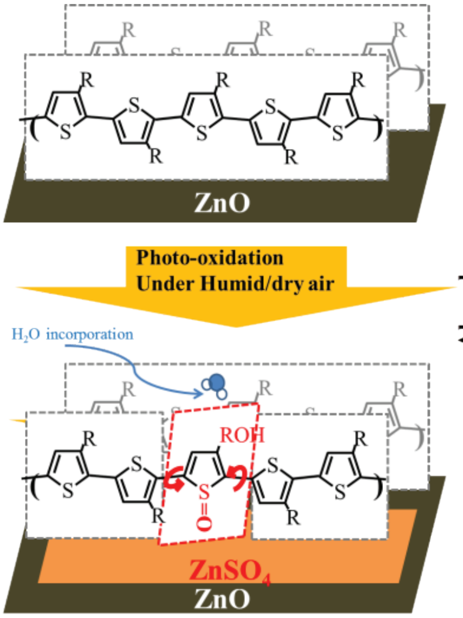
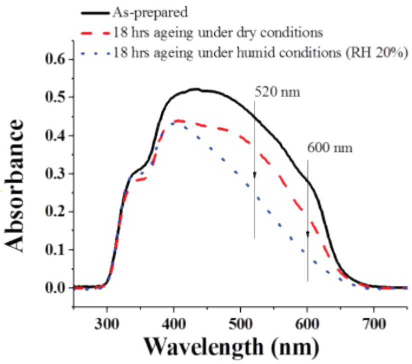
Poly(3-hexylthiophene-2,5-diyl) (P3HT) has been widely used in many electronic devices such as organic photovoltaics, and photo-induced oxidation of P3HT is closely related to the decrease in device efficiency with time. We studied initial stage of oxidation behaviors of P3HT layers on rippled ZnO surfaces under dry or humid atmosphere with visible light irradiation using X-ray photoelectron spectroscopy. In S 2p core-level XPS spectra, only partial oxidation of S into sulfoxide was found with a sustained ring-structure of P3HT on bare ZnO. However, the partial oxidation of P3HT layers resulted in significant changes in optical properties by disturbance of inter- and intra-π-conjugation. When additional TiO_2 layer was inserted between P3HT and ZnO, oxidation of P3HT became more pronounced than on bare ZnO. This result can be attributed to enhanced life-time of electron-hole pairs in P3HT by TiO_2, which blocks defect sites acting as recombination centers of electrons and holes on ZnO surfaces.





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[1] M. -G. Jeong, H. O. Seo, D. H. Kim, K. -D. Kim, E. J. Park, Y. D. Kim, D. C. Lim, *J. Phys. Chem. C*, **118** (2014) 3483.

In-situ observation of graphene growth dynamics by environmental scanning electron microscopy

Z. J. Wang, G. Weinberg, R. Schlögl, M. G. Willinger

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Most promising approaches for industrial scale production of graphene are based on metal catalysed chemical vapour deposition (CVD). Although improvements in graphene quality and yield have been achieved, there remains a lack in the mechanistic understanding of graphene formation. This lack of understanding is due to the fact that most insights on graphene growth have been derived from post growth characterizations, which are in principle incapable of capturing the dynamics of a CVD process. As we have learned from heterogeneous catalysis, a mechanistic insight can (in most cases) only be obtained on the basis of *in-situ* techniques that are capable of capturing the interaction of the catalyst with the environment while the product is formed. Here we report on *in-situ* graphene growth on nickel, copper and platinum catalysts inside a modified environmental scanning electron microscope. Using this method, we are able to visually follow the complete CVD process involving substrate annealing, graphene nucleation and growth and finally, substrate cooling. Due to the high sensitivity of the secondary electron signal to changes at the surface, we are able to visualize the formation and growth of single atom thick graphene sheets.

The *in-situ* experiments presented here reveal the dynamic nature of the process in an unparalleled way and provide important insights on the growth kinetics and the substrate-film interactions at the micron to nanometer scale (Fig. 1). In the case of growth on nickel, temperature and atmosphere induced dissolution and precipitation dynamics can be observed. For the case of copper, it is found that graphene growth above 850°C occurs on a pre-melted, highly mobile surface.

The nucleation and growth behaviour will be discussed and the influence of grain dependent surface dynamics presented. Furthermore, we show that graphene induced copper surface reconstructions occur during cooling.

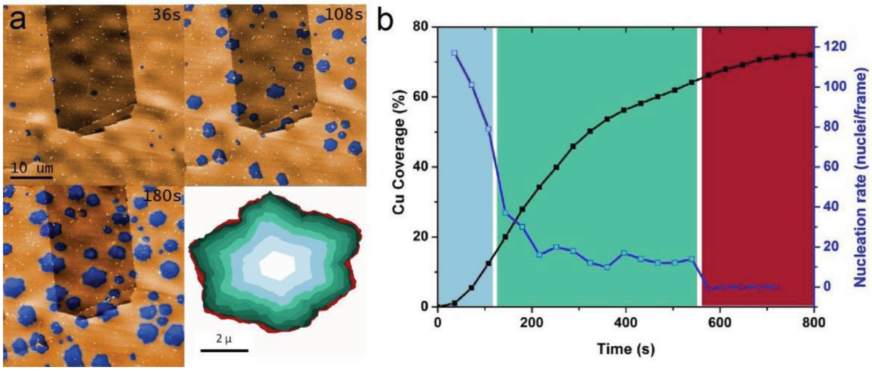

Fig. 1. a) shows colorized snapshots taken during low-pressure CVD growth of graphene on copper at 1000°C. The growth and nucleation behaviour can directly be abstracted from the recorded images as shown in b).

Heat effects upon electrochemical metal deposition

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For electrochemical reactions conducted close to the thermodynamic equilibrium, accompanying heat effects reflect the overall entropy change at the electrode-electrolyte interface, i.e., of the half-cell reaction, including all side processes like double layer charging, coadsorption of anions etc. With a home-built pyroelectric detector, we are able to detect heat effects of electrochemical reactions with conversions down to a few percent of a monolayer. Even heat effects upon double layer charging are accessible.

We will present results on the entropy of complexation of Cu^{2+}, as determined by electrochemical Cu deposition from amine and diamine complexes as well on entropy changes upon the silver underpotential deposition (UPD) on Au(111) films from sulfate and perchlorate solutions. From the differences of the heat effects in both electrolytes, we draw conclusions on the importance of coadsorption processes for the UPD formation.

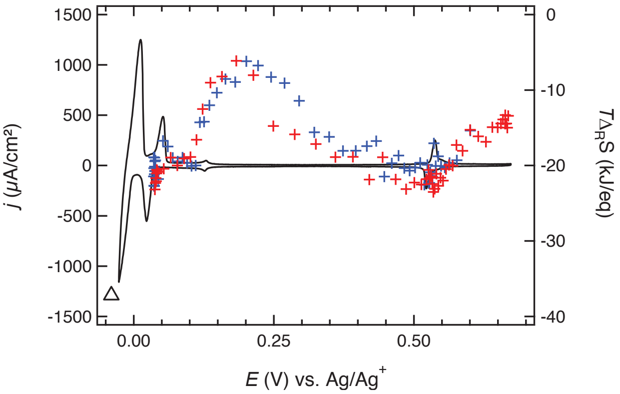

Fig. 1. CV and heat effects upon Ag deposition from a 2.5 mM Ag_2SO_4 / 0.1 M H_2SO_4 solution.

In-situ analysis of catalytically active surfaces with near ambient pressure XPS

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Catalytic surface reactions under working conditions have been studied with various high-pressure compatible surface science techniques. The near ambient pressure (NAP) XPS is one of such techniques and has shed light on the mechanisms of the reactions from the viewpoint of chemical analysis. We built an endstation for NAP-XPS measurements at the Photon Factory [1,2] to study high-pressure-induced surface processes such as formation of high-density adsorption phases, chemical doping and catalytic surface reactions under near realistic conditions. The main chamber of this endstation is equipped with an electron energy analyzer modified for high-pressure experiments and a mass spectrometer (MS) via a differential pumping system as shown in Fig. 1.

We applied this endstation to studies in surface chemistry under NAP conditions. Several high-density adsorption phases have been found, which are formed exclusively under NAP conditions [3,4]. We also studied CO oxidation on Pt-group metal (PGM) surfaces such as Pd, Ir and Ru single-crystal surfaces under NAP conditions in a systematic way [5-8]. Catalytically active surfaces were characterized with operando observations using the NAP-XPS and MS. An example of operando observation for a Pd(100) surface is shown in Fig. 2. At elevated temperatures the Pd surface is activated and dominated by a surface oxide. From comparison of the results for different PGM surfaces, it was found that the catalytically active surface for the CO oxidation can vary depending on type of PGM and surface orientation.

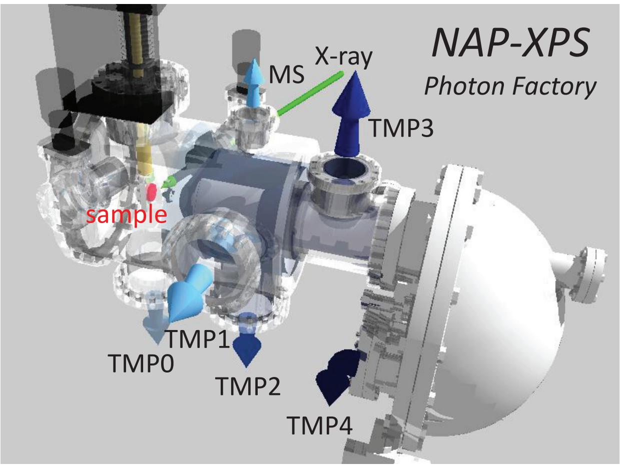

Fig. 1. Illustration of the main chamber of NAP-XPS system at the Photon Factory (KEK-PF).

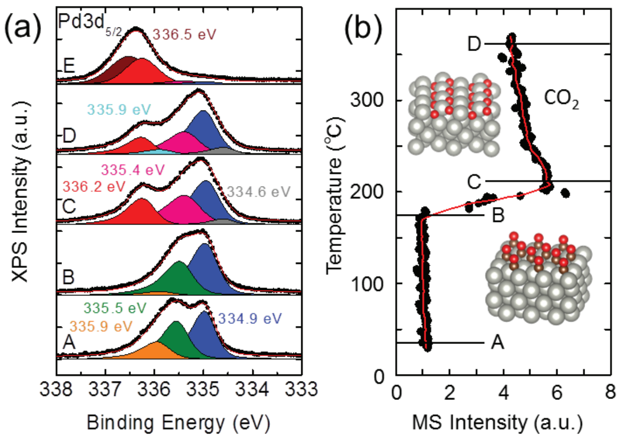

Fig. 2. Operando observation of CO oxidation on a Pd(100) surface using the NAP-XPS (a) and MS (b).

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Excellent doping-dependent discharge behaviour of p-type germanium in a semiconductor-air cell

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Semiconductor-air batteries - a term we first define as metal-air batteries that use semiconductor anodes such as silicon (Si) and germanium (Ge) - have been introduced in recent years as new high-energy battery chemistries [1]. In this paper, we describe the excellent doping-dependent discharge kinetics of p-type Ge anodes in a semiconductor-air cell employing a gelled KOH electrolyte. Owing to its Fermi level, n-type Ge is expected to have lower redox potential and better electronic conductivity, which could potentially lead to a higher operating voltage and better discharge kinetics. Nonetheless, discharge measurements demonstrated that this prediction is only valid at the low current regime and breaks down at the high current density region. P-type Ge behaves extremely better at elevated currents, evident from the higher voltage, more power available, and larger practical energy density from a very long discharge time, possibly arising from high overpotential for surface passivation. A primary semiconductor-air battery, powered by a flat p-type Ge as multi-electron anode, exhibited an unprecedented full discharge capacity of 1,302.5 mAh g_{Ge}^{-1} (88% anode utilization efficiency), the highest among semiconductor-air cells, notably better than new metal-air cells with three-dimensional and nanostructured anodes, and at least two folds higher than commercial Zn-air and Al-air cells [2].

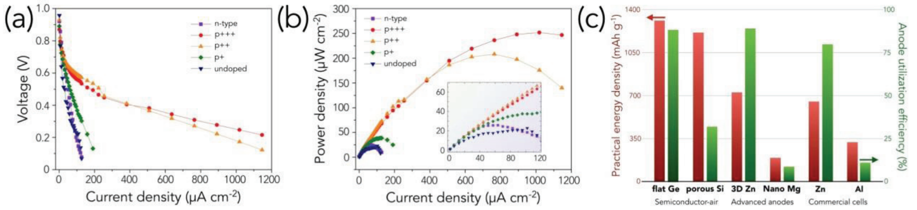

Fig. 1. (a) Current-potential (I-V) curves and (b) power curves for Ge-air cells operated using different anode types. (c) Comparison of the practical energy density and anode utilization efficiency of different metal-air chemistries, emphasizing the advantages of p-type Ge-air cell in terms of high practical energy density and anode utilization.

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Using "Tender" X-ray ambient pressure X-ray photoelectron spectroscopy as a direct probe of solid-liquid interface

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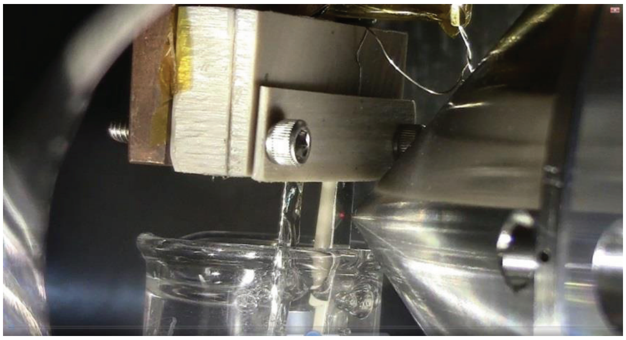
Multiple new ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations are currently under planning or development at US and international synchrotron light sources. Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5 keV- 5 keV). By using X-ray up to 5 keV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. In this talk, I will present results of *in-situ* studies on the electrolyte/electrode interface of a working model electrochemical cell.

We believe the successful development of soft and hard X-ray APXPS endstations will provide energy research community a powerful *in-situ* tool to directly study the electrolyte/electrode interface of many important electrochemical devices.



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On-line time- and potential-resolved monitoring of electrochemical noble metal and metal oxide dissolution

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Noble metals and their oxides constitute a significant part of commercially utilized heterogeneous electrocatalysts. They are extensively used in manufacture of inorganic chemicals (Cl_2/NaOH, H_2, F_2, etc) and synthesis of organic compounds, in fuel cells and sensors, in metals fabrication, refining and finishing, etc. Although noble metals are expensive and sparse, their unique electrocatalytic activity and durability make them the material of choice in many industrial processes [1]. Despite many efforts, it will be challenging to completely replace noble metals by cheaper inorganic or organic counterparts in near future. Therefore, the increase of efficiency, utilization, as well as stability of existing materials and reactions remain essential research directions.

In this presentation I will show our recent results on several noble metals and noble metal oxides electrocatalytic performance studied with a scanning flow cell (SFC) connected to inductively coupled plasma mass spectrometry (ICP-MS) setup shown in Fig. 1. Electrochemical data on activity is thereby recorded in parallel with mass-spectrometric data, which provides time-resolved amounts of dissolved metallic species in electrolyte. In a comparative study on oxidation/reduction and oxygen evolution reaction (OER) on noble metals we have found that degradation of noble metals is of similar nature for all metals [2]. Thus, transition from metallic to oxidized state or vice versa is one of the week points in catalyst stability. Moreover, extensive data on dissolution of Au and Pt allow us to elucidate the degradation mechanism that relates oxidation/reduction and dissolution [3]. Some reactions, e.g. OER, participation of halide anions, etc, may trigger additional destabilization processes. In particular, it is found that during oxygen evolution, the electrode degradation process depends on the mechanism of OER [2,4,5]. The results provide directions on how operation conditions and eventually even material design can be optimized to achieve both, high activity and stability.

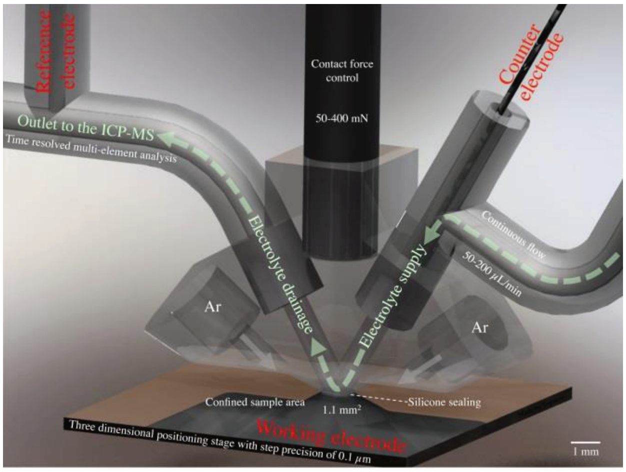

Fig. 1. A sketch showing an electrochemical scanning flow (SFC) cell with outlet connected to inductively coupled plasma mass-spectrometer (ICP-MS).

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Short-chain alcohol oxidation over Au/TiO_2 catalysts to probe metal-support interactions

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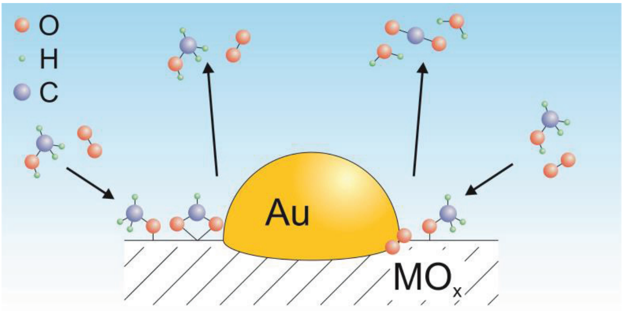
The oxidation of methanol was used as test reaction to investigate the influence of the metal, of the support, and of metal-support interactions in Au/TiO_2 catalysts. Catalytic measurements as well as infrared spectroscopy and temperature-programmed desorption experiments were applied under continuous flow conditions in fixed-bed reactors. A strong effect of the Au loading was found with Au particle sizes in the range from 3 to 7 nm. Methanol combustion yielding H_2O and CO_2 was the main reaction path, but also reactions such as partial oxidation of methanol, steam reforming of methanol, methanol decomposition as well as the selective oxidation of methanol to methyl formate, formaldehyde, or dimethoxymethane were found to occur. Smaller Au particles and a higher amount of small Au particles had a beneficial effect on the activity. Infrared spectroscopy identified methoxy species adsorbed on the metal oxides as intermediates in methanol oxidation. Strongly bound formates acted as reversible catalyst poison. The catalytic activity was found to be correlated with the number of Au atoms at the perimeter of the Au nanoparticles. Correspondingly, oxygen activation is assumed to occur at their perimeter, and the oxide provides methoxy species reacting at the interface.

These investigations were extended to ethanol as reactant. Over pure TiO_2 mainly selective oxidative dehydrogenation to acetaldehyde and water and, to a minor extent, total oxidation to CO_2 and H_2O were found to occur above 500 K. The presence of Au nanoparticles additionally induced the selective oxidation to acetaldehyde and H_2O at temperatures below 400 K. Thus, the Au/TiO_2 catalyst shows bifunctional properties in oxygen activation needed for the selective oxidation of ethanol. Selective low-temperature oxidation is assumed to occur at the perimeter of the Au nanoparticles, which additionally enhance the high-temperature oxidation route on TiO_2 pointing to a Mars-van Krevelen mechanism based on an enhanced reducibility of TiO_2.



Ultrafast exciton dynamics at the ZnO(10-10) surface

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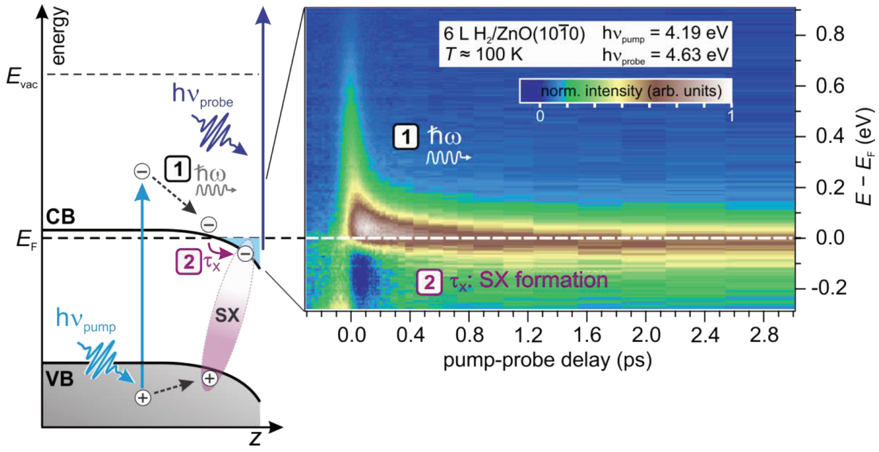
Zinc oxide (ZnO) is a promising electrode material for optoelectronic applications such as excitonic solar cells or organic LEDs. This is due to its transparency to visible light, *n*-type conductivity, the possibility of creating metallic surface layers by exposure to hydrogen, and not least its abundance. Notably, a deep understanding of its highly complex surface properties and the associated surface charge carrier dynamics has not been achieved yet.

We study the ultrafast quasiparticle dynamics in and below the ZnO conduction band using femtosecond time-resolved two-photon photoelectron spectroscopy (2PPE). Above band gap excitation causes hot electron relaxation by electron-phonon scattering down to the bulk conduction band minimum on a 20 to 40 femtosecond timescale. This relaxation process is followed by the ultrafast (200 fs) formation of a surface exciton (SX), which is observed as an increase in 2PPE signal below the Fermi energy E_F. The SX exhibits a remarkable stability, showing lifetimes of several hundreds of picoseconds, most probably due to the lack of unoccupied final states for the electron below E_F. Tuning the excitation density, i.e., the laser light intensity across the Mott limit, the SX formation probability is reduced due to transient screening of the Coulomb interaction in the regime of high electron-hole density. Remarkably, even strong modification of the surface charge density by hydrogen termination does not change the population dynamics of the SX, showing that the exciton is localized in the subsurface region. Thus, its longevity and insensitivity with respect to surface termination make the SX highly relevant for applications involving excitonic interfacial energy transfer such as Förster resonance energy transfer (FRET). Finally, first results on charge and energy transfer across organic/inorganic interfaces will be discussed.



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Functional films on electrode surfaces - electrolyte additives for lithium ion batteries

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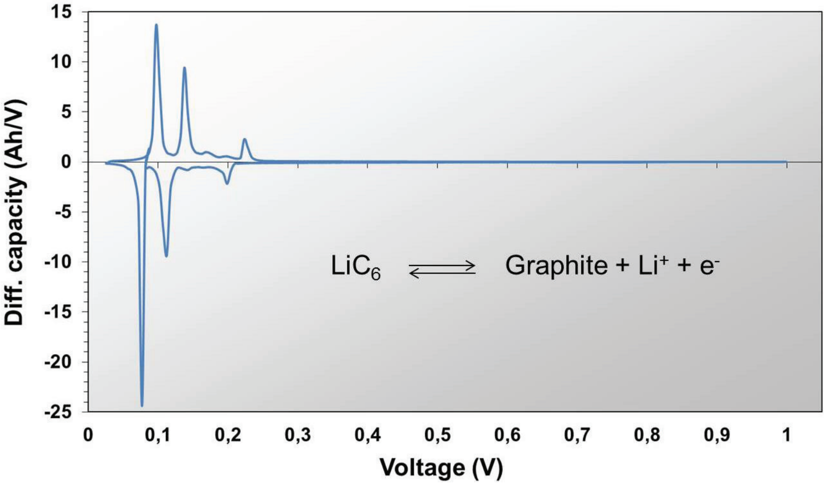
Electrolyte additives used for the modification of the SEI (solid electrolyte interface) normally have high reduction potentials. During the initial charging of a lithium ion cell, an SEI film with the decomposition products from the additive are formed before the potential of the carbonaceous anode is at the onset reduction potential of the bulk electrolyte components. The SEI film grows as the additive and other electrolyte components are decomposed until the resulting surface film reaches a final thickness, which limits electron tunneling. The resulting SEI films are insoluble in the electrolyte, they have a thin film thickness and they exhibit low impedance to lithium ion transport.

Lithium-ion coin cells with additive-contained electrolytes were assembled and tested at various temperatures. The evaluation of the cell cycling performance was further correlated with our surface chemistry studies on the electrodes conducted by SEM, FTIR and XPS, as well as *in-situ* gas analysis by on-line electrochemical mass spectrometry (OEMS). Our results suggest that the SEI layer derived from the electrolyte additive reduction had higher discharge capacity retention and better thermal stability, as a result of the suppression of further electrolyte decomposition at elevated temperature.



Mechanistic study of formic acid/formate electrooxidation on Pt over a wide pH range

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Electro-oxidation of formic acid on Pt in acid is one of the most fundamental model reactions in electrocatalysis. However, its reaction mechanism is still a matter of strong debate. Two different mechanisms, bridge-bonded adsorbed formate mechanism and direct oxidation mechanism, have been proposed by assuming *a priori* that formic acid is the major reactant. Through systematic examination of the reaction over a wide pH range (0-12) by cyclic voltammetry and surface-enhanced infrared spectroscopy (SEIRAS), we will show that the formate ion is the major reactant over the whole pH range examined, even in strong acid. That is, formic acid is oxidized after it has been converted to formate ion though the acid-base equilibrium (Fig. 1). The performance of the reaction is maximal at a pH close to the pK_a of formic acid. The experimental results are reasonably explained by a new mechanism in which formate ion is directly oxidized via a weakly adsorbed formate precursor [1,2]. The reaction serves as a generic example illustrating the importance of pH variation in catalytic proton-coupled electron transfer reactions.

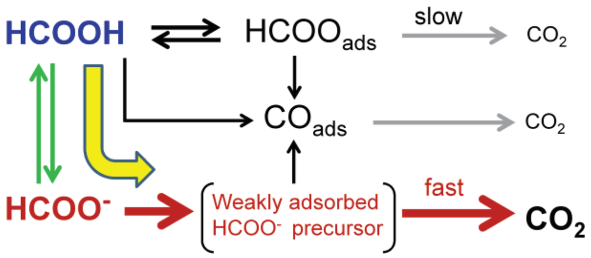

Fig. 1. Reaction mechanism of electrocatalytic HCOOH/ HCOO$^-$ oxidation on Pt.

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Ultrafast surface chemistry and catalysis

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The prospective for the study of chemical reactions on surfaces using X-ray free-electron lasers (Linac Coherent Light Source, or LCLS, at SLAC National Accelerator Laboratory) will be presented. We induced the hot electron and phonon mediated excitation of adsorbates on Ru(0001) with synchronized excitation by a femtosecond optical laser pulse. We have followed the ultrafast evolution of the bond distortions, weakening and breaking, using x-ray absorption spectroscopy (XAS) and x ray emission spectroscopy (XES) resonantly tuned to the oxygen core level with ultrashort x-ray pulses delivered from LCLS, see figure below. Hereby directly follow the time evolution of the molecular orbitals in an atom-specific way on a subpicosecond timescale. Four examples will be shown CO desorption, Oxygen activation, CO oxidation and CO hydrogenation on Ru(0001). We demonstrate that both transient intermediates and the transition state region can be detected in surface chemical reactions.

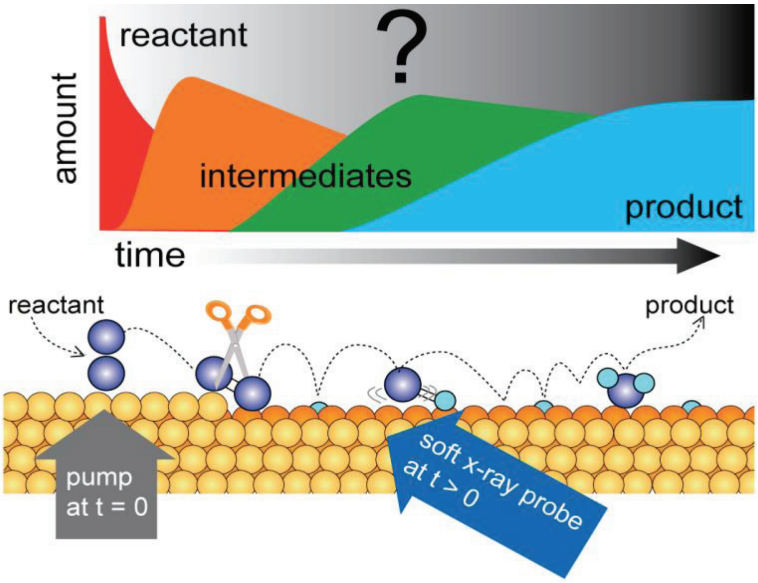

Fig. 1. Elementary steps in a catalytic reaction involving molecular oxygen and hydrogen. The reaction is initiated by optical laser pump and probed with XAS and XES using the LCLS soft x-ray pulse. The concentration of reactants, various intermediates and products can be followed in real time.

Charge compensation in polymer-metal composites driven by self-organized potential oscillations

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Actuators based on conducting polymers have been considered for applications in artificial muscles, mainly due to their considerably large strain and high strength, light-weight, and the possibility of being used in liquid electrolytes, including body fluids, etc [1]. When in association with metallic catalyst layer, i.e. conducting polymer-metal composites (CPMC), an oscillating reaction can be used to drive the actuator in a self-organized manner. Inzelt and Kertész [2] investigated the effect of polyaniline (PANI) pseudocapacitance on the oscillations observed in the electrode potential and in the mass changes, during the electro-oxidation of formic acid. Following this seminal study, we carried out a nanogravimetric study, by means of the Electrochemical Quartz Crystal Nanobalance (EQCN), of a CPMC consisting of a gold surface covered with a PANI film and then deposited Pt, where the oscillatory electro-oxidation of formic acid was studied. Fig. 1 illustrates (a) the current (j) and mass changes (Δm) profiles during the redox processes of an Au/PANI film, and (b) Δm during the potential oscillations for the composite Au/PANI/Pt. The potential and Δm windows visited during the oscillations are comparable to that observed for the redox processes in the PANI film, (a). The self-organized potential oscillations are thus strongly influenced by the electroneutralization process within the PANI film, as reflected by the dominance of this process in the Δm response.

The effect of the ion exchange on the overall properties of the CPMC must thus be considered in connection with the capacitance increase caused by the conducting polymer. We have further explored the role of variables such as the thickness of the PANI film, the oscillatory electro-oxidation reaction and the electrolyte composition on the systems' dynamics.

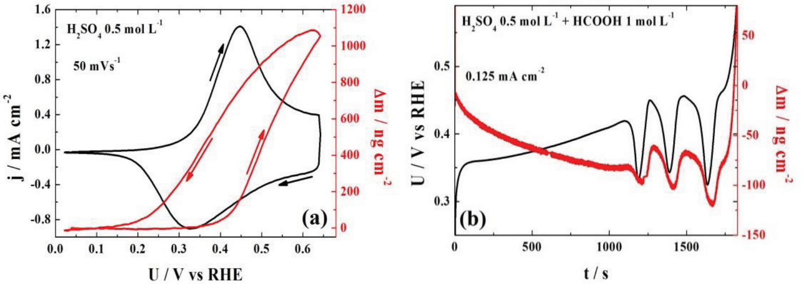

Fig. 1. (a) j and Δm profiles during the redox processes of a PANI film, (b) self-organized galvanostatic oscillations along the electro-oxidation of formic acid on Au/PANI/Pt composite.

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Surface analysis of cold gas sprayed TiO_2 photoelectrodes for the water oxidation reaction

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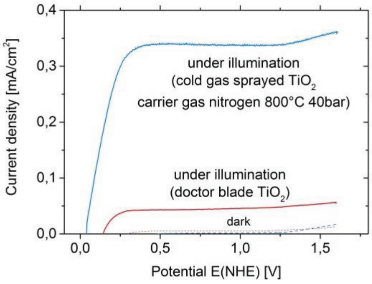
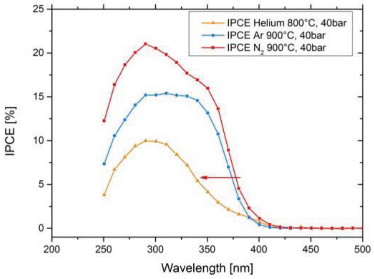
Cold gas spraying (CGS) was successfully probed as innovative manufacturing process for large-area photoelectrodes for the water oxidation [1]. In contrast to wet chemical deposition techniques, the unique technique of CGS enables the coating of substrates with photoactive particles without any further heat treatment steps. The particles are added as a powder to a compressed and heated carrier gas stream and are accelerated in a De Laval nozzle to a velocity up to 1200 m/s. This particle/gas stream is directed towards the substrate on which a thin layer of the photoactive material is formed. In photoelectrochemical measurements combined with surface analysis it was found that nitrogen as carrier gas evokes surfaces states which seems to act as reaction centers for the water oxidation process. In contrast to that reduced photoelectrochemical activity is observed for TiO_2 electrodes obtained from the CGS with argon and helium.

In the following contribution analysis by IPCE, impedance spectroscopy, XPS and surface photovoltage measurement is applied in order to discuss the surface modification of the TiO_2 particles in the CGS process depending on the utilized carrier gas and its effect on the catalytic activity in the photoinduced water reaction.

Furthermore, in the light of these results first attempts to prepare cold gas sprayed $BiVO_4$ and hematite photoelectrodes are presented.





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Study of the behavior of catalytic surfaces in the presence of gases by *in situ* methods

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A catalyst is a very divided material generally composed of active phase nanoparticles supported on a powder support. In such configuration the synthesis methods generally lead to collections of supported nanoparticles in which a large number of parameters vary (size distribution, exposed faces, chemical composition, …). In order to determine the influence of a given parameter on the catalytic behavior of the catalyst we can minimize the influence of other parameters which can be done by using extended catalytic surfaces (single crystal, vicinal, polycrystal) where only a few (ideally one) parameters vary (orientation/surface coordination, chemical composition, …). The study of both types of materials is essential to progress in the understanding of the behavior of the catalysts, verify that the results obtained on extended surfaces can be extrapolated to finite catalysts and ultimately devise the catalytic mechanisms. The sum of this information may then lead to the design of more effective catalysts with specific controlled.

Here we will show examples of studies performed on the morphologic/structural and chemical evolution of extended surfaces under reaction conditions and examples of dynamic real-time modification with high-spatial resolution of supported catalysts.

The study of extended catalytic surfaces requires the use of surface science techniques often developed for UHV operation. Such techniques, can be adapted to operate in (quasi) realistic reaction conditions and are able to yield information on the evolution of catalytic surfaces (structure/morphology, chemical composition/segregation, …) in real-time during the catalytic reaction. In this work we present the study of the evolution of $Pd_{70}Au_{30}$ (110) and $Pt_3Sn(111)$ surfaces during CO oxidation by several surface science techniques developed either at laboratory level (environmental STM and PM-IRRAS) or within synchrotron facilities (Ambient Pressure XPS at ALS-Berkeley, Photon Factory and SOLEIL).

The local study of supported or powder catalysts require high-spatial resolution methods due to the nanometer scale of the materials. Here we present two studies performed *in situ* in an environmental aberration-corrected TEM (the Ly-EtTEM of CLYM, Lyon): one on the evolution of the surface structure/chemical composition of ceria nanoparticles in presence of

CO_2 or O_2; the other, on the dynamic real-time structural/morphologic/chemical modifications of silver nanoparticles supported on amorphous-carbon in presence of O_2 at high temperature.

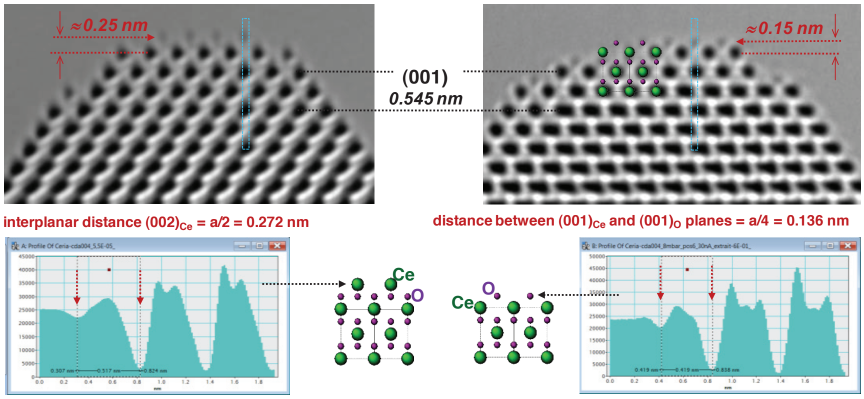

Fig. 1. HRTEM images (top, video frames averaged) and cross-sections of surface contrasts with proposed models (bottom) of $CeO_2[110]$ under vacuum (left) and under 0.8 mbar of CO_2 (right).

Adsorbate-adsorbate interactions on surfaces at realistic conditions: A first-principles study

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Adsorbate-adsorbate interactions can play an important role in adsorption and chemical reactions on metal and metal oxide surfaces, even at low coverage. In the first part of our work, we predict atomic structures of adsorbed complexes that should appear on alkaline earth metal oxide (001) terraces in thermodynamic equilibrium with water and oxygen gases. Density-functional theory combined with the self-consistent many-body dispersion approach [1] is used to calculate total energies. Stable adsorbed water phases are determined using the *ab initio* atomistic thermodynamics. We find a range of H_2O chemical potentials where ordered one-dimensional adsorbed water structures are thermodynamically stable on CaO(001).

This is in agreement with scanning tunneling microscopy studies of CaO films exposed to water [2]. On MgO(001) and SrO(001), thermodynamically stable one-dimensional adsorbed water structures are not found. The formation of the one-dimensional structures on CaO(001) is explained by the balance between adsorbate-adsorbate and adsorbate-surface interactions.

In the second part of our work, we investigate co-adsorption of hydrogen and CH_x (x=1, 2, 3) species on Ru(0001) at realistic temperatures and hydrogen pressures. We find that co-adsorbed hydrogen qualitatively changes the preferred site and the stability of CH_2 species, which is crucial for understanding the mechanism of Fisher-Tropsch synthesis. Our results explains also the recent observation of CH_2 species on methane-dosed Ru(0001) surface [3].

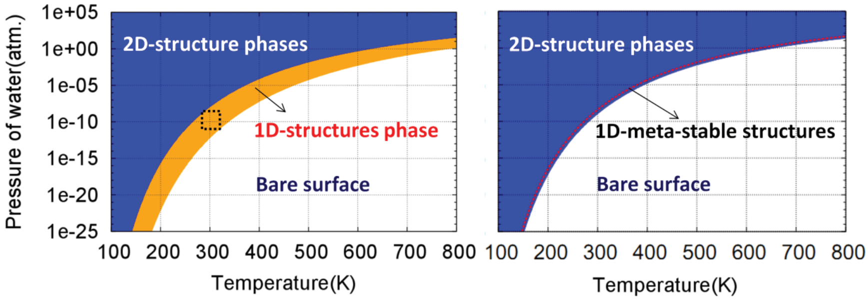

Fig. 1. Surface phase diagram for water adsorbed at CaO(001) (left) and MgO(001) (right).

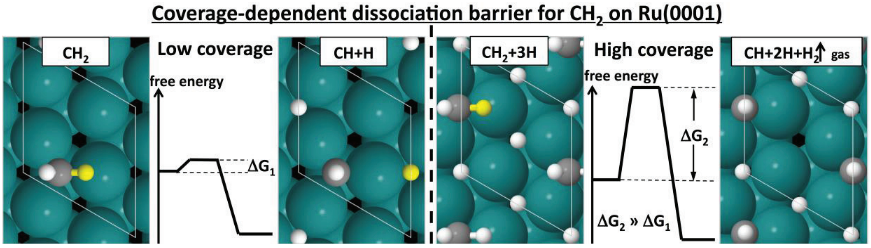

Fig. 2. Dependence of the CH_2 dissociation barrier on the hydrogen coverage on Ru(0001).

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Fundamental aspects of polymer electrolyte fuel cell technology and the associated water management

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Polymer electrolyte fuel cells (PEFC) remain the main fuel cell technology for electric power trains in automobiles. Therefore this technology has benefited from a huge research effort over the past decades. However, still some fundamental properties and interactions of PEFC electrode/electrolyte interface remain elusive due to the experimental difficulty of analysis.

One of the major challenges in the development PEFC is to exploit the whole capacity that inheres a given membrane electrode assembly (MEA) as well as to ascertain superior reliability. In practice, the water management and the corresponding local mass transport effects have to be optimized. Suboptimal operation leads to heterogeneous current distributions, which reduce the efficiency of a MEA and hence that of a PEFC.

In order to investigate factors limiting the performance, the DLR has developed several measurement and visualization techniques to determine the local current density distribution in fuel cells without interfering with the cell operation. This method is applied e.g. to investigate oscillatory performance fluctuations of a single proton exchange membrane fuel cell induced by humidity gradients between anode (wet) to cathode (dry) compartments or degradation of fuel cell performance (see Fig. 1). For the humidity-induced oscillation an insight into the transitions between high and low current operation points is obtained by current density distributions at distinct times indicating a propagating active area with defined boundaries. The observations are in agreement with assuming a liquid water reservoir and changing water fluxes to the cathode due to distinct water content dependent electro-osmotic drag rates and permeation rates (corresponding to liquid-vapour permeation). The results are discussed with regards to water management of fuel cells.

Our research also comprises the characterization of fundamental processes like the conductivity of fuel cell membranes on the nanometer scale by conductive atomic force microscopy. We have investigated the ionic conductivity of different solid electrolyte membranes - mostly perfluorinated sulfonic acid membranes - for fuel cell application by contact mode as well as with different tapping mode atomic force microscopy techniques for several years. This methodological approach yields high resolution images of the conductive surface structure and - by investigating cross-sections - gives insight into the bulk structure and the conducting network. The results demonstrate that the dc current as well as the activation procedure has a prominent influence on the conductivity surface distribution. In addition to conductivity other mechanical properties like i.e. adhesion forces, energy dissipation, and stiffness can be measured simultaneously with the current.

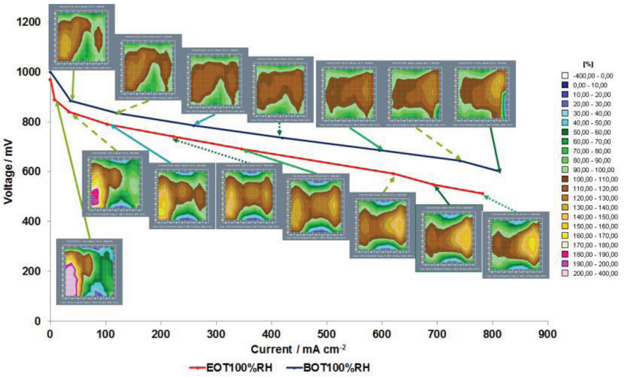

Fig. 1. Comparison between polarization curves measured before of the test (blue) and at the end of the test (red) with the corresponding current density maps.

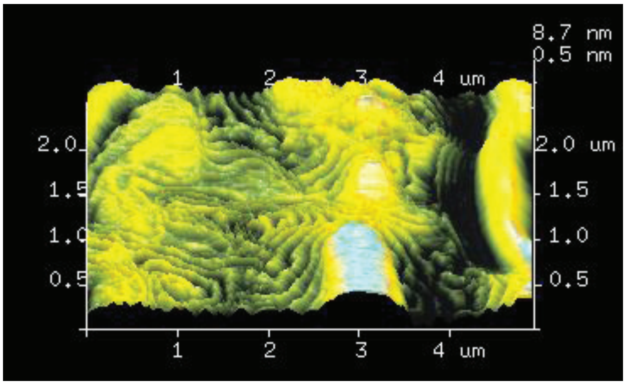

Fig. 2. AFM image of freshly cut cross section of Nafion® 212 after storage at 75% rh showing pronounced steps.

Batteries for automobiles

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On the effect of substrate reducibility and dopant type on the catalytic activity of metal/metal oxide complex systems

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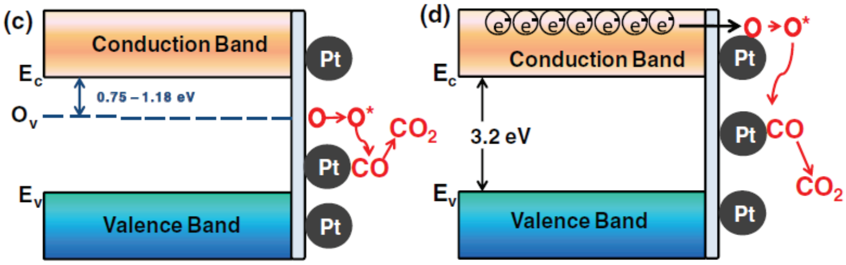
For enhanced catalytic performance, not only intrinsic catalytic activity of catalyst particles is important, but also interaction between catalyst particles and catalyst support materials is critical. In this regards, the strong metal–support interaction (SMSI) effect is an important issue for achieving enhanced catalytic activity for heterogeneous catalysts. Recent studies on Au/TiO_2 suggest that the perimeter area between the Au nanoparticles and TiO_2 is catalytically reactive under CO oxidation [1]. Another study showed that the reaction rate in the oxide–metal model system depends on the oxidation state of the supporting oxide, the free metal surface area, and the number of sites at the interface between the metal and the support [2]. The general concept of the SMSI phenomena means that the catalytic activity changes when metal catalysts are supported on reducible oxides. After reduction at high temperature, migration of the reduced species from the support material to the metal catalytically modifies the metal. In addition to this geometric contribution, the electric field between the metal and support interface changes and generates metallic bonds and compounds in the reduced state. Additionally, metal and semiconductor doping can also lead to changes in the activation energy for catalytic reactions. For the past decade, there have been ongoing discussions on improving catalytic efficiencies using TiO_2 doped with non-metals. In this presentation, we present our studies on the support effect of plasma deposited Pt nanocatalysts on reducible metal oxide supports (CeO_2, Nb_2O_5, and TiO_2) [3] and doping effect on nitrogen (N) and fluorine (F) doped TiO_2 [4].



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IR spectroscopy studies of thin organic films at the solid - liquid interface

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This lecture will review our research involving IR spectroscopy at the solid-liquid interface. After a brief review of basic principles of IR spectroscopy and the laws of reflection of light at interfaces, three methods of Infrared Reflection Absorption Spectroscopy (IRRAS) will be described. The first is subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) or in short potential difference IR spectroscopy. This technique finds application to study reversible adsorption of soluble molecules at electrode surfaces. The methods of optimisation of the SNIFTITS experiment will be discussed. Its application will be illustrated by the case of adsorption of a soluble surfactant such as sodium dodecyl sulphate (SDS) at a gold electrode surface [1]. The second technique to measure IR spectra at interfaces is the photon polarization modulation infrared reflection absorption spectroscopy (PM IRRAS). This technique is used to study films of insoluble molecules a various interfaces. I will discuss application of this technique to study model biological membranes supported at a gold electrode surface [2]. The third technique is the surface enhanced infrared reflection absorption spectroscopy (SEIRAS). It is performed using attenuated total internal reflection (ATR) element covered by nanoparticles of gold. The intensity of the IR signal is then enhanced by a factor of 100. In addition, since the film of metal nanoparticles is conductive it is used to study phenomena at electrified interfaces. I will describe application of this technique to study structure of water in model biological membrane supported at a gold electrode surface [3]. I will emphasize complementarity of SEIRAS and PMIRRAS in application to bio-electrochemical research.

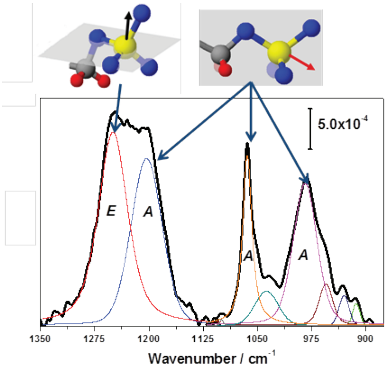

Fig. 1. Sulfate group bands in SDS molecule.

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Preparation of TiO_2 nanotubes with a doping of ruthenium oxide: Potential shock methods *vs*. single anodization

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TiO_2 containing RuO_2 and/or IrO_2 layers has been widely studied for the fabrication of dimensionally stable anodes (DSA), which can be used in severe conditions such as chlor-alkali processes. Recently, we demonstrated that TiO_2 with a doping of RuO_2 and/or IrO_2 can be used as an efficient electrode in water splitting systems. The doping of suitable foreign elements into TiO_2 NTs allows enhancement of catalytic properties in oxygen evolution reaction (OER) and/or hydrogen evolution reaction (HER), which leads to effectively generate oxygen or hydrogen with a low overpotential. Since anodically grown TiO_2 NTs have a geometrical structure with an ultra-high-aspect ratio, homogenously doping of requested catalysts into the NTs is extremely difficult without multi-step processes and facilities. Herein, two novel methods for doping of Ru into high-aspect-ratio TiO_2 NTs are suggested. First, single step anodization is introduced, demonstrating that a choice of suitable electrolytes containing $KRuO_4$ and potential range is very important. As the second method, potential shock method is suggested. In the method, very short high applied potential is imposed on the TiO_2 NTs in $KRuO_4$ electrolyte immediately after the fabrication of anodic TiO_2 NTs.

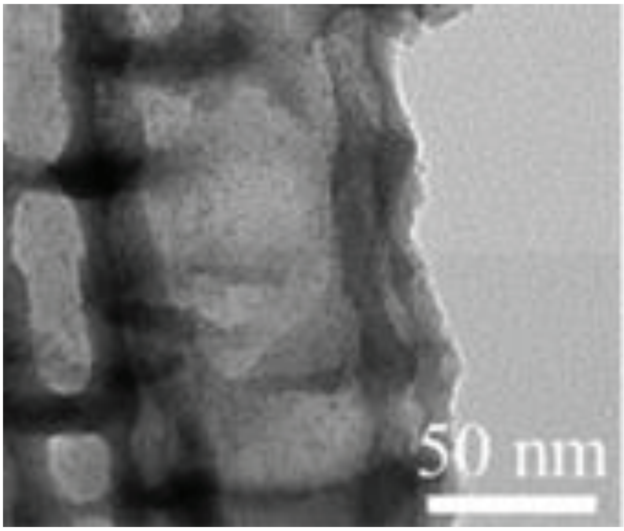

Fig. 1. FE-TEM images of TiO_2 NTs after doping of Ru.

Ultrafast relaxation dynamics in aqueous environment and charge transfer at a molecule-semiconductor interface

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We investigate complex systems with the goal to understand their structure and ultrafast dynamics. In my talk I will present examples from my current research to show how my team and I are developing and using novel experimental techniques - from the field of ultrafast spectroscopy with High-Harmonics and X-ray Free Electron Lasers - to visualize dynamic processes in complex systems:

(1) We perform time-resolved photoelectron spectroscopy experiments on liquid microjets with the goal to monitor relaxation dynamics of electronically excited systems in solution. In these experiments, the liquid sample is excited with a suitable pump-pulse (IR, VIS, UV) and probed by recording photoelectron spectra with a probe pulse in the XUV (38.7 eV) obtained via High-Harmonic Generation. The experiments deliver electron binding energies of excited species as a function of pump-probe delay, allowing unprecedented insights into how electronic structure changes during relaxation dynamics.

(2) I will present time-resolved X-ray photoelectron spectroscopy (TRXPS) as a new tool to achieve an atomic scale perspective of ultrafast charge transfer processes at molecule-semiconductor interfaces. In the proof-of-principle experiment at the Linac Coherent Light Source (LCLS) at SLAC, we have investigated the ultrafast charge separation step in a dye-sensitized solar cell system (N3@ZnO). In this experiment, an ultrashort laser pulse electronically excites the dye (N3) and a time-delayed X-ray pulse is used to record the inner shell photoelectron spectrum of the sample (Fig. 1).

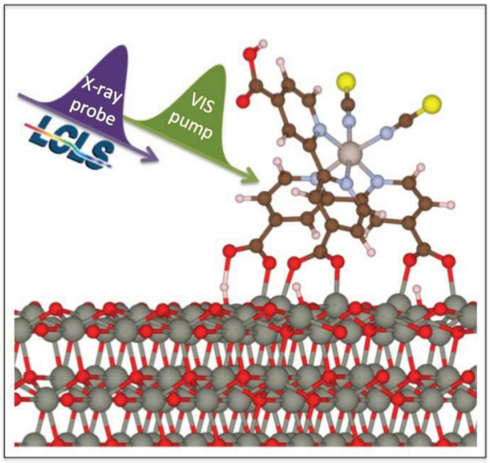

Fig. 1. Experimental scheme to monitor interfacial charge transfer at the atomic scale.

Ambient pressure soft X-ray absorption spectroscopy of a catalyst surface in action: Closing the pressure gap in the selective n-butane oxidation to maleic anhydride over vanadyl pyrophosphate

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The Gibbs free energy, the related chemical potential and surface energy of transition metal oxides are especially triggered by the total oxygen pressure [1]. Since the minimum of the surface energy is related to a certain surface termination, the total oxygen pressure affects the energy and geometric structure of the surface and hence, also catalytic reactions. Hence, *in situ* studies at low pressure can provide misleading information resulting in a wrong view of the surface structure under real catalytic conditions that is responsible for the reaction mechanisms in a fixed-bed reactor. We developed a variable pressure (soft) X-ray absorption spectroscopy system operating in the surface sensitive conversion electron yield mode to study the surface electronic structure under reaction conditions at different total pressures up to 1000 mbar (see Fig. 1) [2]. We probed the vanadium $L_{2,3}$-edges of the polycrystalline catalyst vanadyl pyrophosphate in the industrially important selective n-butane oxidation to maleic anhydride at 10, 100 and 1000 mbar. As a result, we observed indeed a dynamic pressure gap in the studied range. At low pressures (<100 mbar) the surface vanadium oxidation state is solely given by the total pressure of oxygen. The extent of n-butane adsorption and conversion is low and the re-oxidation of the surface can always be achieved up to the state given by the oxygen chemical potential. In contrast, at 1000 mbar the oxidation state is controlled by the catalytic reaction providing a steady state between reduction of the catalyst during n-butane conversion and re-oxidation by oxygen.

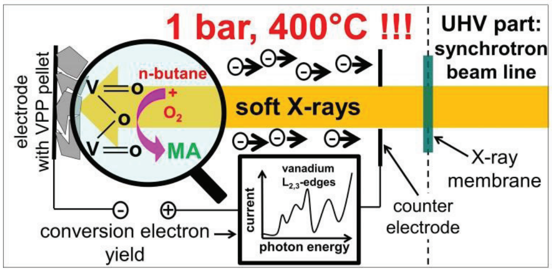

Fig. 1. Sketch of the variable (soft) X-ray absorption setup: The excited electrons are accelerated to the biased counter electrode and multiplied by the gas atmosphere. The resulting current is measured as a function of the photon energy. The ultra-high vacuum (UHV) part is shielded by the X-ray membrane.

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Peculiar excitation waves during CO electrooxidation on Pt electrodes in an electrochemical flow cell

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The electrochemical oxidation of CO on platinum electrodes exhibits a variety of nonlinear phenomena, such as bistability in the current-potential curve and current oscillations under potentiostatic conditions, or the formation of stable spatial domains with different CO coverages, and thus different reactivities, under galvanostatic conditions. In the talk, I will discuss recent results on self-organized reactivity patterns which form during the oxidation of CO in the presence of an electrolyte flow parallel to the electrode. Patterns in the CO coverage are recorded by means of spatially resolved ATR-FTIR spectroscopy. Typical patterns observed are tongue-shaped structures that align parallel to the flow and move in the direction perpendicular to the flow (Fig. 1). These wave fragments possess several peculiar properties: They may split, sending out a second wave in the backward direction; Two colliding waves penetrate each other forming a soliton-type collision state; Open ends do not grow into a spiral wave but propagate with a stable shape. Basic features of the dynamics can be understood on the basis of a model taking into account the reaction kinetics of CO oxidation, diffusion of CO parallel to the electrode and advection of CO, i.e. the transport of CO by the flow. Especially, the role of advection for pattern formation will be elaborated.

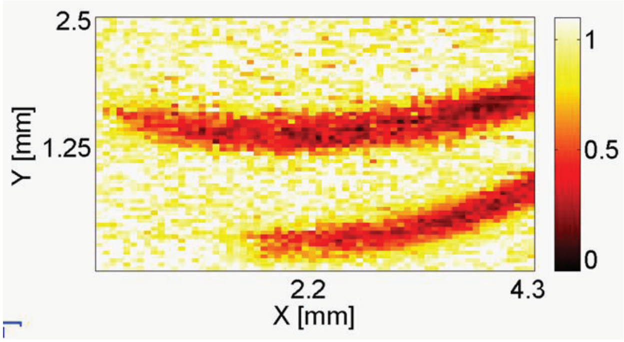

Fig. 1. Snapshot of the CO coverage on a Pt film electrode during bulk CO electrooxidation in the presence of Br ions. Color scale: dark red - no CO adsorbed on the electrode, white: saturation coverage of CO. The electrolyte flows from left to right past the electrode and with time the waves of empty surface move upward or downward.

Production and characterization of carbon-free bi-functional cathodes for the use in lithium-air batteries with an aqueous alkaline electrolyte

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With a theoretical energy density of 11680 Wh/kg and a practical energy density around 1700 Wh/kg Lithium-Air Batteries (LAB) have similar energy densities to gasoline. Furthermore a practical energy density of 1700 Wh/kg would mean a 5-10 fold increase over todays Li-Ion Batteries (LIB) with 100-200 Wh/kg.

Carbon materials are widely used in gas diffusion electrodes due to their high electronic conductivity, relatively low costs and catalytic activity towards oxygen reduction reaction (ORR), the cathodic reaction during discharging an air battery. During charging a lithium-air battery the cathode is operated in oxygen evolution reaction (OER) mode. Carbon materials corrode in OER mode, this leads to degradation and a power loss of the electrode. To improve long-term stability and reduce side reactions as H_2 and CO_2 evolution in OER operation mode carbon-free bi-functional cathodes for aqueous alkaline lithium-air batteries were prepared. Gas diffusion electrodes with silver catalysts show a high activity towards oxygen reduction reaction in alkaline media but a rather poor activity towards oxygen evolution reaction. For the use in future lithium-air batteries with an aqueous alkaline electrolyte the activity of such electrodes must be improved significantly. Combinations of silver with promising oxide catalysts show a significant improvement in OER performance and also long-term stability. Gas diffusion electrodes were electrochemically investigated in a half cell by cyclic voltammetry and electrochemical impedance spectroscopy (EIS) at room temperature and at 50°C, different concentrations of LiOH, different potentials covering all the range of operation of the new developed electrodes. Beside the impedance elements attributed to the structure of the electrode and kinetic parameters of the ORR in the potential range of OER an additional impedance contribution attributed to the formation of an oxide layer can be found.

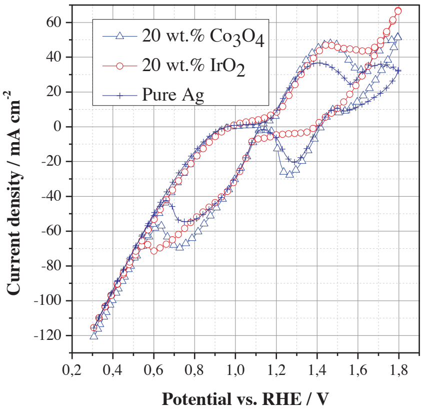

Fig. 1. Cyclic voltammograms of different cathodes measured in 1 N LiOH, 1 mV/s, 25°C in the potential range from 300 mV to 1800 mV *vs.* RHE.

The influence of intercalated oxygen on the properties of graphene on polycrystalline Cu under various environmental conditions

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Intercalation of oxygen at the interface of chemical vapor deposition grown graphene and its polycrystalline copper catalyst can have a strong impact on the electronic, chemical and structural properties of both, the graphene and the Cu. This can affect the oxidation resistance of the metal, the transferability of the graphene as well as its utilization in electronic applications. Here, we show, using near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), X-ray absorption near edge spectroscopy (XANES), energy dispersive X-ray spectroscopy (EDX) and (environmental) scanning electron microscopy (ESEM) that the intercalation is kinetically driven and can be clearly distinguished from carbon etching. The obtained results reveal that a charge transfer between as grown graphene and Cu can be annulled by intercalating oxygen creating quasi-free-standing graphene. This effect is found to be reversible by vacuum annealing proceeding via graphene grain boundaries and defects within the graphene but not without loss of graphene by oxidative etching.

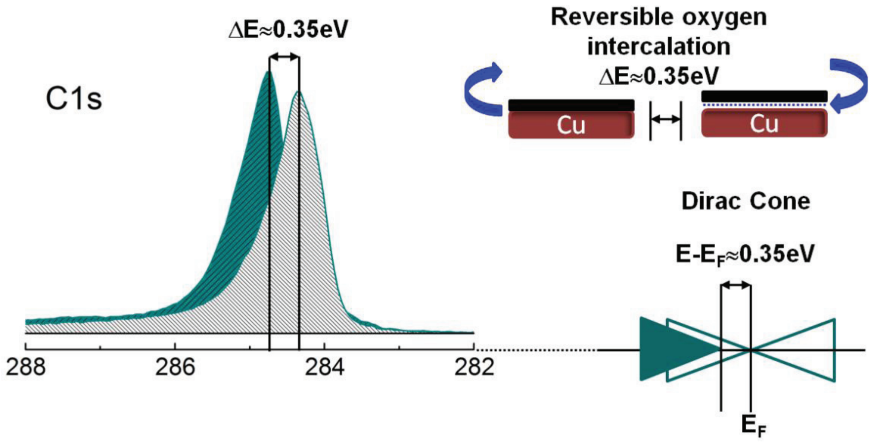

Fig. 1. Schematic overview of the C1s BE shift between coupled and free standing graphene due to the presence of a charge transfer from Cu to graphene also visible in the changed position of the Dirac cone with respect to the Fermi edge.

Amplified amepromteric sensing using nanostructured electrodes

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Gold nanoparticles (NPs) possessing excellent electrochemical and optical properties have been extensively applied to a wide range of environmental and biological research areas. In this presentation, we will demonstrate the use of gold nanoparticles for the fabrication of nanostructured amperometric biosensors in order to improve the sensors performance. Two different methods to incorporate gold NPs onto electrode surfaces will be discussed (see Fig. 1); electroactive enzyme and NP modified biosensors were prepared via i) a covalent linking with 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride/ N-hydroxysulfosuccinimide (EDC/NHSS) and ii) a layer by layer assembly of oppositely charged layers composed of positively charged Au NPs and negatively charged polyelectrolytes and enzymes onto Au NP deposited screen printed carbon electrodes. The sensing performance of both electrode configurations for the detection of biomolecules and toxic agents will be compared and the improvement in the sensitivity of the biosensors originated from Au NPs will be discussed.

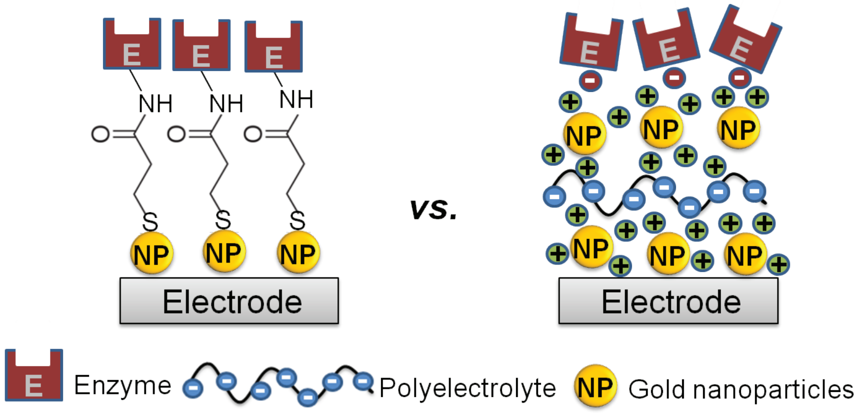

Fig. 1. Schematic showing two differently prepared nanostructured biosensing platforms.

Oxygen interaction dynamics with platinum surfaces: When does O_2 physisorb, chemisorb or dissociatively adsorb?

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The interaction of oxygen with platinum surfaces is not only of fundamental interest, it is also of high technological relevance, for example in the context of the car exhaust catalyst or the oxygen reduction reaction which is one of the central reactions in fuel cells. Upon impinging on Pt(111), O_2 can physisorb, chemisorb or dissociatively adsorb [1]. Interestingly enough, O_2 does not dissociate on Pt(111) at low surface temperatures, even if the initial kinetic energy is much higher than the dissociation barrier. On stepped Pt surfaces, however, O_2 readily dissociates although the barrier between the chemisorption and the dissociative adsorption state is at the steps even larger than on flat Pt(111) [2]. Although some of these issues had been addressed by tight-binding molecular dynamics simulations [3], a complete picture of the complex O_2/Pt interaction dynamics was still missing.

Here we report results concerning the interaction dynamics of O_2 with flat and stepped Pt surfaces that have been obtained by *ab initio* molecular dynamics (AIMD) simulations, as illustrated in Fig. 1. The simulations reproduce the known experimental findings mentioned above, in particular they also reproduce the trapping into physisorbed states at low temperatures and low O_2 incident kinetic energies (see Fig. 1) and the dissociation at the steps. These findings are explained in terms of the energy redistribution along the trajectories together with an analysis of the underlying potential energy surface.

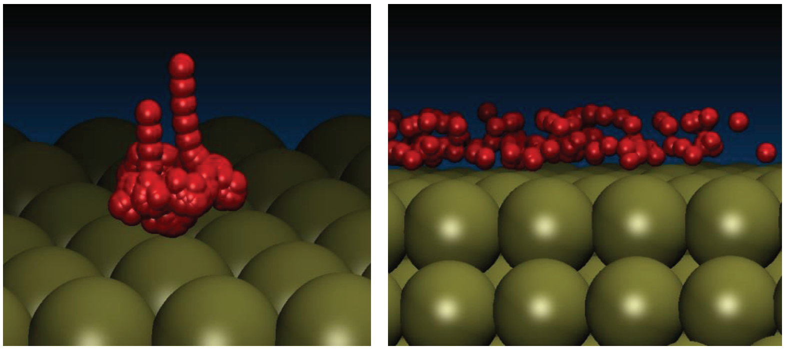

Fig. 1. AIMD simulations of O_2 imping on Pt(111) at low surface temperatures. Left panel: single trajectory with an initial kinetic energy of 100 meV. Right panel: cumulative presentation of the final positions of the O_2 molecules summed up over 200 trajectories. Half of the molecules are trapped into the physisorption state that is further away from the Pt(111) surface.

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Nanomaterials and nanocomposites based films

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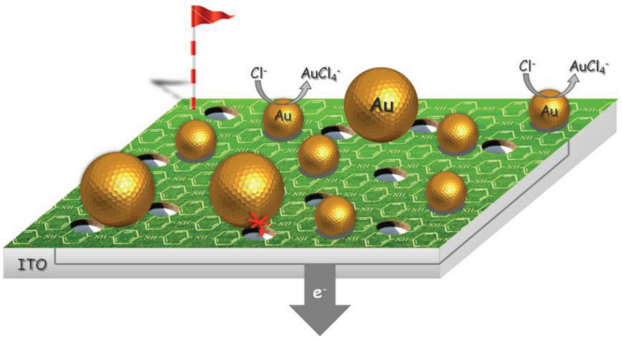
Formation of nanostructured films by electrochemical deposition will be presented. The essence of the method is based on an indirect electrochemical approach in which deposition is driven as a result of changing the environment in the vicinity of the electrode by a potential or current pulse. A few systems will be presented and include films made of: sol-gel materials, organic nanoparticles, carbon nanotubes and electrochromic materials.

The electrochemical deposition of sol-gel films is based on applying either negative or positive potentials to a conducting substrate that alters the pH at the electrode surface, which catalyses the polymerization of sol-gel monomers, leading to the deposition of the appropriate oxide films. Initially, this method has been used by us for the deposition of various sol-gel films. More recently, we have shown that it can also be used for the co-deposition of sol-gel films and a variety of substances ranging from polymers to nanoparticles and nanotubes. Obviously, this enables to form a wide range of coatings that can be used for various applications.

Deposition of organic nanoparticles was enabled similarly upon using long chain carboxylic acids as stabilizers. Homogeneous coating of cardiovascular stents has been accomplished. More recently, we were able to electrochemically drive the deposition of carbon nanotubes and graphene as well as to deposit the electrochromic material tungsten oxide.

The lecture will review the development of this approach and its applicability in different fields such as corrosion prevention and coating biomedical implants.



Oxygen evolution on an iridium-based molecular catalyst: Turnover frequencies, stability and electrolyte effects

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Joost N. H. Reek[2], Marc T. M. Koper[1]

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Organometalic compounds have been extensively studied in the last few years for electrocatalytic water oxidation, which is known to be one of the bottlenecks reducing the efficiency of solar energy conversion into storable fuels. The activity of those catalysts is always measured in solution by using sacrificial oxidant reagents, thus making difficult to properly define the thermodynamic driving force of the reaction. Therefore, an unequivocal comparison between different systems is often complicated due to varying reaction conditions and the associated lack of a clearly defined oxidation potential.

We present a systematic electrochemical and spectroelectrochemical study of the catalytic activity for water oxidation of an iridium-N-dimethylimidazolin-2-ylidene complex adsorbed on a polycrystalline gold electrode. The work aims to understand the effect of the electrolyte properties (anions and acidity) on the activity of the molecular catalyst and check its stability towards decomposition. Our results show that the iridium complex displays a very strong dependence on the electrolyte properties such that large enhancements in catalytic activity may be obtained by adequately choosing pH and anions in the electrolyte (see Fig. 1). The stability of the adsorbed compound was investigated *in situ* by Surface Enhanced Raman Spectroscopy and Online Electrochemical Mass Spectrometry showing that the catalyst is stable under anodic conditions, with no observable evidence for the decomposition to iridium oxide.

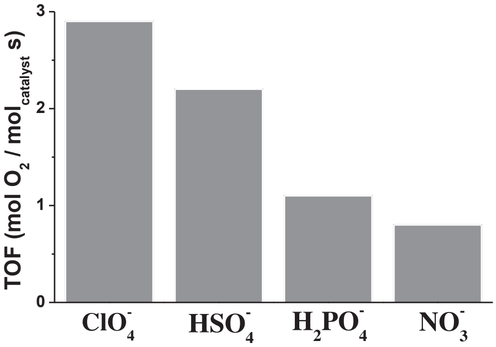

Fig. 1. Turnover frequencies at 1.66 V *vs.* RHE for oxygen evolution reaction at pH 1 in different electrolytes, catalyzed by the iridium complex adsorbed on polycrystalline Au.

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Multimodal optical imaging of individual nanoparticles

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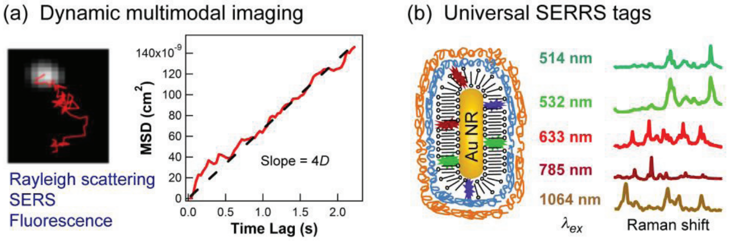
The ability to visualize individual nanoparticles in real-time via more than one optical imaging modality (e.g. Rayleigh scattering, surface enhanced Raman scattering (SERS) and fluorescence) provides a powerful analytical platform which can be potentially applied to a wide range of material development and sensing applications. In particular, the controlled behavior of functionalized metallic nanostructures is a key step in many nanoparticle-enhanced imaging and spectroscopic measurements. This talk will highlight our recent efforts in the development and application of a platform for the *in-situ* tracking of freely suspended (and surface immobilized) nanoparticles. The acquisition of videos via different imaging modalities at frame rates sufficient to determine the diffusion coefficients of individual particles provides a direct route towards characterizing properties such as diffusion coefficient and enhanced spectroscopic signals associated with particle aggregation and molecular adsorption (Fig. 1a).

Also, to fully realize the potential of a dynamic multimodal approach for applications such as real-time biosensing and cellular imaging, there is a need to develop new classes of nanoparticles. The concept of *universal* surface-enhanced resonance Raman tags (UST's) will also be introduced. These are capable of producing bright Raman signals across a much wider range of excitation wavelengths (Fig. 1b) while avoiding the added complexity of particle aggregation. This was confirmed with correlated electron microscopy and confocal Raman measurements (Fig. 1c). In addition to the controlled surface chemistry required for their fabrication, some of the potential applications of these UST's will also be discussed.


(a) Dynamic multimodal imaging
(b) Universal SERRS tags

(c) Correlated SEM and confocal Raman mapping

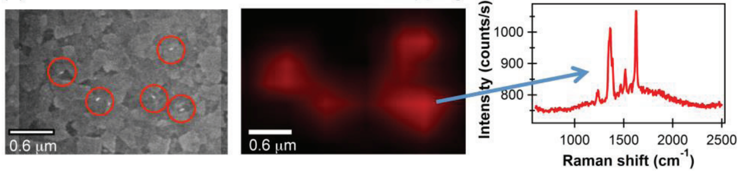


Fig. 1. Schematic highlighting (a) imaging and tracking analysis of single nanoparticle via different imaging modalities, (b) the design of a Au nanorod-dye tag for enhanced Raman over a 514-1064 nm excitation range, and (c) correlated SEM (left) and Raman (middle) analysis of individual tags <50 nm in size.

In situ SERS study of manganese oxides as anode catalysts for oxygen evolution reaction

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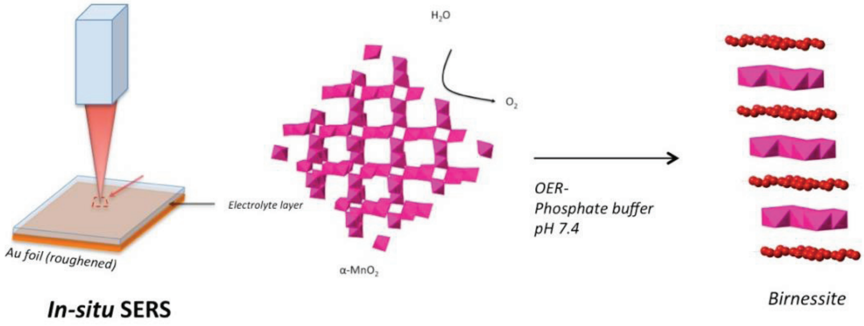
Non noble metal "*earth abundant*" electrocatalysts will significantly reduce the costs and make it possible to use electrochemical water splitting (electrolysis) on a very large scale. Non noble metal catalysts can be an effective replacement even if their electrochemical activities are a fraction of their noble metal counterparts. If these catalysts can be developed to an extent where their operational lifetime would become comparable to their noble metal counterparts, a large part of the problem would be solved. MnO_2 is earth abundant and well known for catalyzing oxygen evolution. A form of MnO_x cluster is known to catalyze water oxidation in photosynthesis. The problem is that the catalyst comes with a significant corrosion problem. Besides that MnO_{2-x} naturally exists in various polymorphs, with various amounts of defects each of which is known to have a different electrocatalytic performance. Poor ballistic electronic conduction (important for good electrode materials) is also a prevalent issue with these oxides.

These catalysts although with immense potential remain a long way from successful implementation within electrolysers. In order to understand the limitations of this catalyst under the operational conditions, it is important to study this material *in situ*. Setup for *in situ* Surface Enhanced Raman Spectroscopy is used for tracking the structural changes of hydrous MnO_x. Electrodeposition of MnO_x on the surface of Au was achieved by passing an anodic current of 50 mC/cm^2 at 1.6 V.

The resulting MnO_2 phase could be termed as the alpha/MnO_2 phase. The structural integrity of the MnO_x was studied by following the Mn-O-Mn stretching various potential ranges in various electrolytes. Onset of phase changes and corrosion could be clearly established. Beside this, other methods such as XRD, SEM, TEM were applied to study these thin films.



Surface-modified nanodiamond for heterogeneous and electro-catalysis

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Carbon nanostructures formed by sp^3-bonding in nanodiamond (ND) have been commercially synthesized by detonation of carbon-based explosives in oxygen-deficient conditions. The diamond nanoparticles are average 3-10 nm in size and can be usually obtained by removing the explosion carbonaceous soot through acid purification treatment. The structure of these particles is believed to be a highly ordered, crystalline sp^3-bonded diamond core, surrounded by few surface layers of more disordered sp^2/sp^3 amorphous carbon, resulting in a variety of oxygen terminations on dangling bonds and defects on surface. The chemical nature of ND surface can be tailored by its surface sp^2/sp^3 hybridization state, defect density and decoration with various types of heteroatom functionalities.

We have used surface-modified ND as catalyst and catalyst support for heterogeneous and electrocatalytic reactions that show unusual performance [1-8]. For oxidative dehydrogenation of n-butane, the ND with sp^2 over-layers exhibited superior performance than other nanocarbon [3]. ND also showed better performance in direct dehydrogenation of ethyl benzene to styrene [2]; Nitrogen and boron doped annealed ND is also electro active for ORR, but the performance is still needed to be optimized. The state-of-the-art of ND catalysis will be presented with an outlook for practical application.

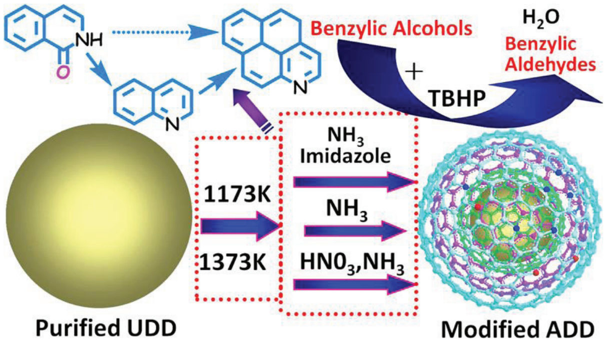

Fig. 1. Illustration of N-functionalized nanodiamond with sp^2 outlayers for heterogenous reactions [8].

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Growth pattern of cluster thin films

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Size-selected ligand-free Mo_n^-, W_n^-, Fe_n^- cluster anions consisting of 10-2000 atoms are soft-landed onto HOPG. The samples are studies with scanning tunnelling microscopy, atomic force microscopy and x-ray photoelectron spectroscopy. At room temperature, clusters of Ag, Au and Pd immediately coalesce forming amorphous 3-dimensional islands. This is not the case for the metal clusters studied here. These clusters stay intact and form a highly porous cluster material [1]. In the STM pictures individual clusters can be distinguished (Fig. 1). The diameter of the spherical objects scales with the size of the deposited clusters. Only small Fen clusters show indications for coalescence. At sub-monolayer coverage a new growth pattern is observed: the clusters arrange in 2-dimensional islands on HOPG. The thickness of the islands corresponds to the diameter of the deposited clusters. It seems the clusters follow a Stranski - Krastanov- growth mode. This indicates that the interaction with the substrate is stronger than the one between neighbouring clusters. Finally, first results on thin film growth of Fe_n^- clusters in the presence of a strong magnetic field will be presented.

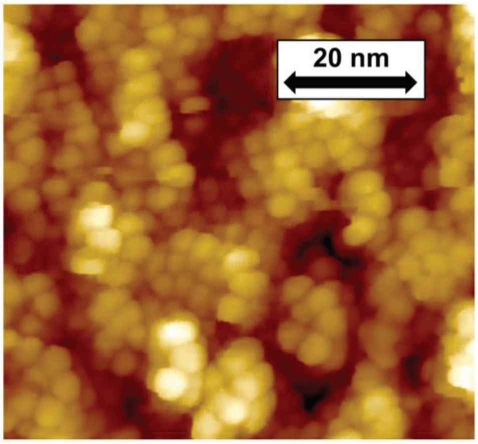

Fig. 1. *Ex-situ* STM picture of the surface of a thin film synthesized by the deposition of $Mo_{275+/-20}$ cluster anions on HOPG at high coverage and with low kinetic energy (< 0,1 eV/atom).

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Electrocatalysts getting in shape: Atomic-scale growth, structure and reactivity of octahedral bimetallic alloy nanoparticles

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Nanostructured core-shell and shape-selected nanoparticles have emerged as attractive families of catalytically highly active materials for the electroreduction of molecular oxygen (ORR) in energy conversion and storage devices. Their structural and compositional transformations upon contact with a corrosive electrolyte and under catalytic reaction conditions are complex, ranging from activation to degradation behavior. The way in which the reactive electrochemical environment affects the shape, structure and composition of electrocatalysts and thereby alter their catalytic activity is of great fundamental and practical importance.

We report on the preparation, structure and catalysis of shape-selected octahedral (Fig. 1) bimetallic Pt alloy nanoparticles for the electroreduction of oxygen in PEM fuel cells [1-5]. Atomic-scale insights are obtained using a unique combination of aberration-corrected microscopy (HR-TEM, STEM), spectroscopic studies (STEM-EELS, XPS), as well as scattering (XRD) and electrochemical techniques. We uncover unexpected self-organized elemental anisotropy, exceptional catalytic activity and unusual degradation behavior of the octahedrally shaped nanoparticle catalysts resulting in concave octahedral. The emergence of elemental anisotropy in bimetallic shaped nanoparticles is discussed.

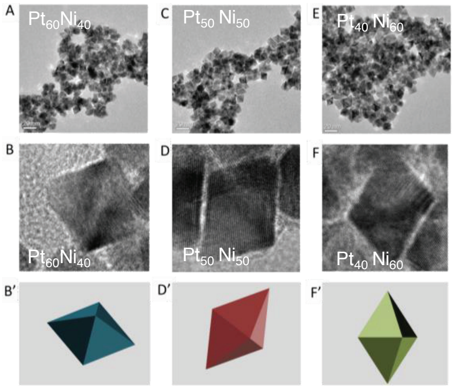

Fig. 1. Octahedral Pt-Ni nanoparticle electrocatalysts of varying overall compositions.

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Charge transfer across electrochemical and bio-electrochemical interfaces, and its assessment with electroanalytical and x-ray spectroscopy methods

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From the perspective of device applications, semiconductor photoelectrochemistry represents one of the most complex fields of physical chemistry. In my talk I will show how with a combination of electroanalytical and x-ray spectroscopic methods one can look into the complex details of physical processes and chemical reactions on surfaces, in double layers and in the depletion layers, which relate their transport properties with electronic structure of the reactor component materials, and how it evolves with synthesis and processing. Hole formation in the absorber causes conductivity in the bulk. Fe2p and Fe3p resonant photoemission spectroscopy shows that a particular electronic signature in the valence band of α-Fe_2O_3 is quenched by exposure to visible light. When α-Fe_2O_3 is connected as photoelectrode, the oxygen x-ray absorption spectra (NEXAFS) show two new states in the pre-edge, which were postulated 30 years ago. They show up when the photoelectrode is illuminated under bias. The variation of the spectral weights *vs*. bias voltage indicates whether holes originate from the depletion layer or from the surface. With the same method, we demonstrate the first spectroscopic proof for hydrogen bond breaking in the water. The spectral shift of the O2p bonding peak in the Fe2p resonant photoemission valence band spectra as obtained from ambient pressure XPS under water oxidation conditions scales in the same way versus the bias potential like the photocurrent, thus showing direct systemic correspondence between photoelectrocatalytic activity and the change in electronic structure. During operation, a water splitting electrode shows remnant changes in its stoichiometry which are visible in the x-ray spectra. It appears that understoichiometric metal oxide ions at the surface could be the electrocatalytic active species which are conjugated with the so-called capacitive defect states. Those become oxidized upon PEC operation and may lose their catalytic power. There exist ways to suppress this process using ultrathin coating layers. Finally I present first studies where algal light harvesting antenna proteins (biofilms) on bio-hybrid electrodes enhance hydrogen production. I emphasize the identification of charge transfer between animate and inanimate matter. I show here some first resonant photoemission studies obtained under physiological photoelectrochemical conditions with an ambient pressure XPS chamber, and compare these with electrochemical impedance spectra.

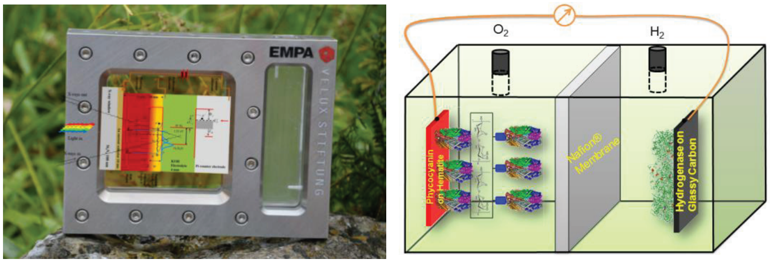

Fig. 1. Solar water splitting reactor with bio-organic photosynthetic components on photoelectrodes.

Electrochemical oxidation of formic acid on gold electrode: Studied by a surface vibrational spectroscopy

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Electrochemical oxidation of formic acid (HCOOH) has attracted much attention from electrochemists in the last several decades, both because it is a promising fuel for a direct formic acid fuel cell [1], and because it is a useful model system for electrocatalytic reactions of higher hydrocarbons [2]. Despite extensive experimental and theoretical work there are still significant debates regarding the oxidation mechanism of formic acid on transition metal electrodes [2-4]. For example, in the past years, novel oxidation mechanisms have been proposed by two groups based on the pH dependent oxidation behaviors [2,4]. One of the reasons for this debate is a lack of experimental techniques that sensitively probe the reaction intermediates at the metal/water interface. In the present study, we employed a surface sensitive vibrational spectroscopy, Sum Frequency Generation (SFG), in combination with a flow thin layer electrochemical cell, to study the electrochemical oxidation of formic acid on gold electrode surface *in situ*. Due to the surface specificity and high sensitivity of the technique, we monitor the potential dependent interfacial populations of relevant reaction intermediates. SFG spectra in both CH and OCO^- symmetric stretching region confirm formate adsorbed in a bidentate geometry is a key reaction intermediate at all potentials, in agreement with recent theoretic predictions [3] and less surface sensitive experimental probes [2]. More importantly, for the first time, we were able to detect and monitor the evolution of surface hydroxyl groups during the oxidation reaction above a threshold potential. This result strongly suggests that at high potentials the oxidation mechanism of formic acid on gold changes as shown in Fig. 1.

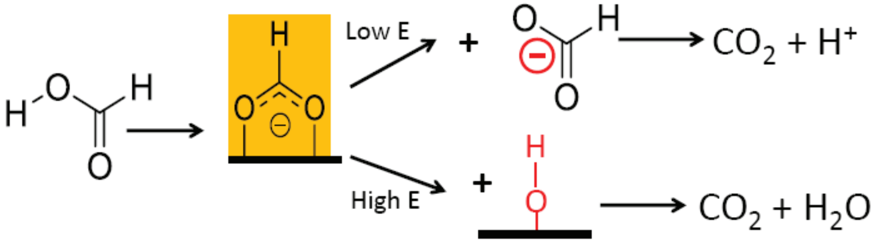

Fig. 1. Scheme for electrooxidation of formic acid on gold electrode.

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Surface electronic structures of Pt-TM alloys

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Recent advances in experimental techniques and theoretical understanding in surface science clearly demonstrate that surface electronic structure make strong influence on its surface chemical properties. Yet, the physical origin on how the electronic structure modifies the chemical properties is not clearly understood.

In this presentation, with the results of angle-resolved photoemission spectroscopy (ARPES) and DFT calculation, the details of surface band structure and atomic orbital character of Pt-transition metal (TM) alloys will be discussed. The analysis of ARPES results indicate that the surface chemical bonding, e.g. surface atomic oxygen, is closely related to the charge polarization between top layer (Pt) and subsurface layer (TM) near Fermi level [1,2]. This charge polarization, which is proportional to surface dipole moment, can provide a clear physical picture on how the chemical properties can be varied on surface.

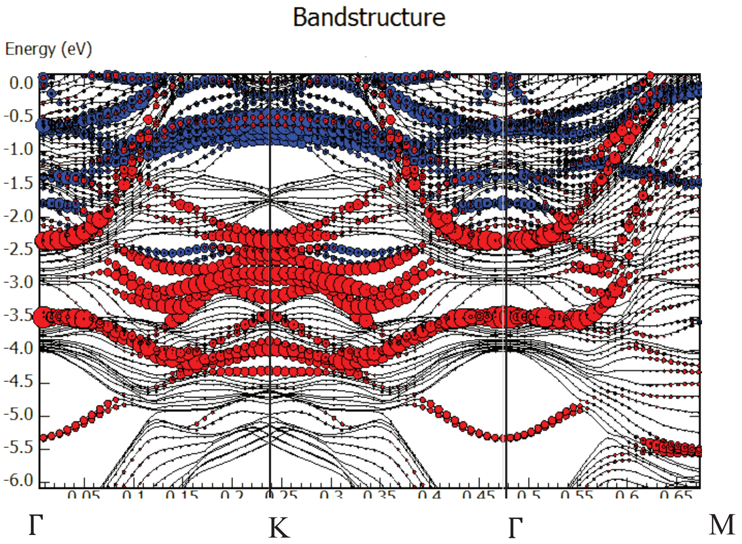

Fig. 1. DFT calculation on $Pt_3Ni(111)$ crystal. Surface Pt in red circle. Sub-surface Ni in blue circle.

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Non-noble metal based catalyst for efficient and selective reduction of CO_2 and CO

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In the past two decades CO_2 electrochemical reduction has attracted attention as an alternative method to produce synthetic fuels using waste CO_2 [1]. Ideally one can directly reduce CO_2 to hydrocarbons. This process, however, has low selectivity and occurs at high overpotential which implies important energy losses [2,3]. Alternatively CO_2 can be reduced to CO, which can be used in the production of synthetic fuels via the Fischer-Tropsch process. Gold has been found to selectively reduce CO_2 to CO at low over potentials [4]. Nevertheless, the viability of this process relays on the development of low cost catalyst with high selectivity towards CO production at low overpotentials.

For this contribution we investigated mono and bimetallic catalysts, synthesized using Fe and/or Mn, polyaniline (PANI) and Ketjenblack (Fig. 1a). These materials have been found to be good catalysts for the Oxygen Reduction Reaction [5] and we now show that they are also promising materials for CO_2 electro-reduction. The catalysts were synthesized by high temperature (900°C) pyrolysis of the starting precursors, followed by acid leaching to remove unreacted metal moieties and a final pyrolysis.

The catalytic activity of these materials was studied by bulk electrolysis in CO_2 saturated 0.1 M $KHCO_3$ (Fig. 1b). We observed a clear dependence of the selectivity of the reaction as a function of potential. The selectivity towards CO is higher at low over potentials. In particular, Mn-Fe/PANI/Ketjen produces CO with more than 80% selectivity, which is comparable to gold. This good catalytic performance indicates that these materials are promising to be used as catalyst in the reduction of CO_2 and CO given their low cost and high selectivity towards CO.

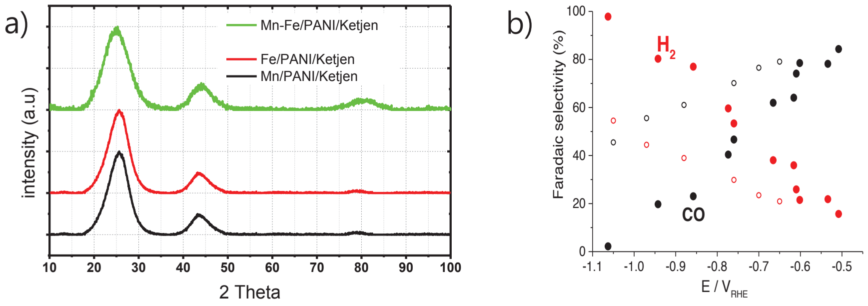

Fig. 1. a) XRD patterns of monometallic Mn/PANI/Ketjen; Fe/PANI/Ketjen; and bimetallic Mn-Fe/PANI/Ketjen catalysts b) Comparison of the faradaic selectivity of gold (open data points) and Fe/PANI/Ketjen (filled data points).

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Interrogating Cu_2ZnSnS_4 nanocrystal films for solar cells

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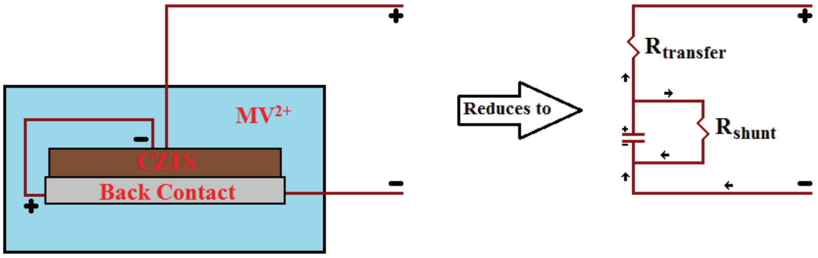
Cu_2ZnSnS_4 (CZTS) nanocrystals (NCs) are made of earth abundant elements with a tunable band gap of 1.45-1.51 eV [1]. This makes CZTS an ideal material for the production of low-cost and efficient solar cells. Photoelectrochemical measurements (PECMs) allow for the quantification of the photovoltaic response based on the current density associated with CZTS films, but cannot account for current losses associated with changes in film quality [2]. Electron flow from the methyl viologen (MV) solution to the back contact competes with transfer to the counter electrode, and can act as a measure of the tightness and thus adhesion quality of the deposited film to the back contact (BC). Cracks and imperfections within the films provide occasions for direct contact between the MV solution and the back contact of the device. Likewise, the adhesion tightness between the deposited thin-film layer and the back contact offers further contact between the two points. This provides increased current losses associated with short circuit pathways within the solution-film system, lowering the perceived output current. Appropriate circuit models in the dark and under irradiation were developed to represent the device based on impedance and intensity modulated photocurrent spectroscopy, respectively. From the model, current losses were compared for dropcast and annealed films of various compositions. High temperature annealing has been shown to enhance photoresponse, but often leads to increased cracking, and more current shunting within the device. The effects of composition on the film quality, and the adhesion between the film and back contact further complicate the relationship by increasing the internal resistance of the device itself, lowering the observed output through PECMs. The CZTS film qualities were quantified based on the determined equivalent circuits for ideal films toward full solar cell devices.



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In situ surface x-ray scattering studies of metal deposition and oxidation

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In situ studies of nanoscale morphological changes during electrode reactions by surface x-ray scattering methods using synchrotron radiation will be presented. These methods provide detailed data on structural changes on the atomic or nanometer scale, as will be demonstrated for the case of Au(001) homoepitaxial electrodeposition and Pt(111) oxidation. Studies of Au(001) deposition in the regime of 3D growth were performed by *in situ* grazing incidence small angle x-ray scattering (GISAXS) [1]. The measurements reveal that the temporal evolution of the lateral island size is governed by well-defined scaling laws with a potential-dependent crossover of the characteristic exponent from 1/3 to 1/4. The latter indicates a pronounced potential dependence of the Ehrlich-Schwoebel barrier governing interlayer transport. Pt oxidation was studied near the onset of oxidation in O_2-free and O_2-containing electrolyte by crystal truncation rod measurements. Furthermore, the nanoscale roughening of the Pt(111) surface during oxidation/reduction cycles was quantitatively studied by *in situ* GISAXS (Fig. 1).

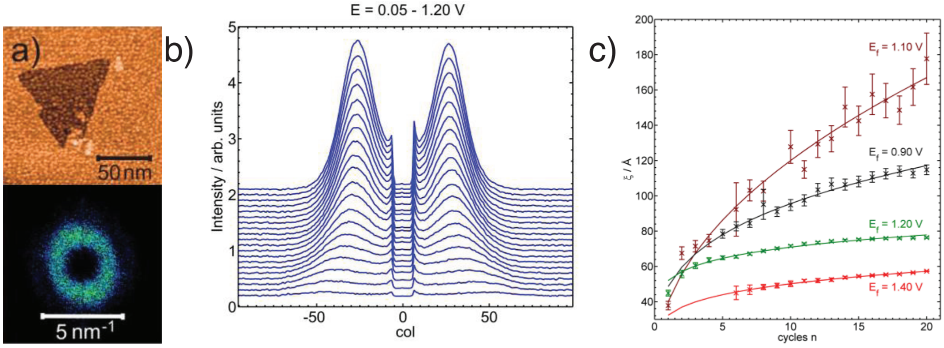

Fig. 1. (a) STM image and corresponding 2D Fourier transform of Pt(111) surface after oxidation/reduction cycles in 0.1 M $HClO_4$. (b) *In situ* GISAXS data for an upper potential limit E_{lim} = 1.20 V *vs*. RHE and (c) resulting characteristic lateral island size as a function of number of cycles for values of E_{lim}.

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Doping effect in modifying the surface properties of oxide film

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Doping is a versatile approach to tailor the physical and chemical properties of oxide thin films. By means of scanning tunnelling microscopy, we demonstrate that small amounts of Mo embedded in a CaO matrix are able to alter the growth behaviour of gold. While 3D deposits form on the pristine oxide, strictly 2D growth prevails on the Mo-doped films. The crossover in particle shape is driven by an electron transfer from localized Mo d-states in the oxide band gap towards the Au islands. Similar charge transfer processes modify also the adsorption characteristic of O_2. In presence of the dopants, the rate for O_2 dissociation via electron injection from the STM tip becomes strongly enhanced. The reason is a partial occupation of the anti-bonding π-orbitals of O_2 due to an electron donation from the Mo-impurities, as suggested from electron spectroscopy data. Doping the oxide support thus opens new routes to modify and improve the properties of a supported metal catalyst.

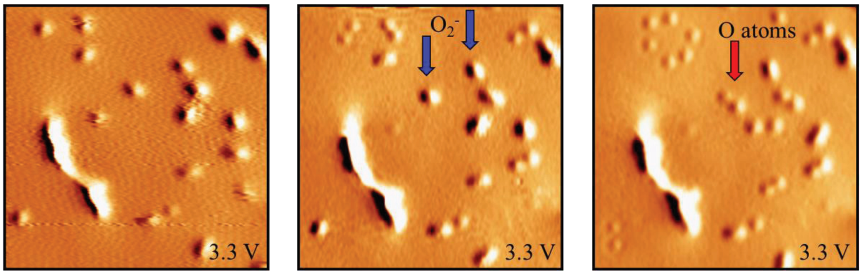

Fig. 1. Dissociation of O_2 on Mo-doped CaO(001) induced by tip scanning.

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Chemistry and electrochemistry of water at platinum

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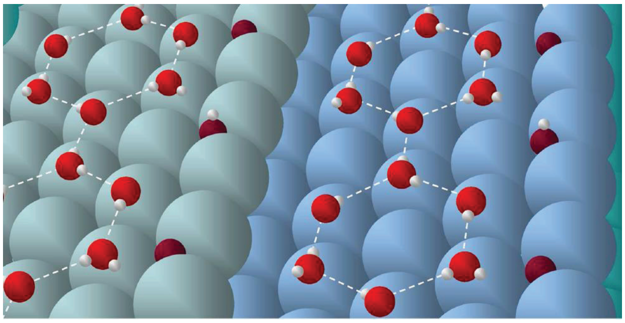
The interaction and dissociation of water at well-defined platinum surfaces, as gleaned from blank voltammetry experiments on stepped platinum electrodes, is compared to modeling experiments in ultra-high-vacuum and to detailed density functional theory calculations on the same platinum surfaces. It is shown that there is a clear distinction between (110) and (100) step sites, both in the adsorption of single species, as well as in the way mono- and multilayers of water interact with clean as well as hydrogen and oxygen-covered stepped platinum surfaces.



Poster Session

FeNi composite on a carbon nanofiber matrix for the electrocatalytic oxygen evolution reaction in alkaline media

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Iridium (Ir) and ruthenium (Ru) oxides are known to be some of the best catalysts for oxygen evolution reaction (OER) in alkaline water electrolysis. The cost of these noble metal oxides, however, remains prohibitive for their commercial use in electrochemical devices. Here, we report the synthesis of FeNi composites embedded within the carbon nanofibers (FeNi-CNFs) as OER electrocatalysts via a facile route of electrospinning and pyrolysis. We demonstrated that FeNi-CNFs show superb OER activity and stability than 20 wt% Ir on Vulcan carbon black. Following detailed physico-chemical and electrochemical characterizations, our results demonstrate that Fe and Ni exhibit synergistic roles in enhancing the OER activity through the uniform formation and widening of pores on the carbon structure, while the CNF matrix might have contributed to the increased durability of the catalyst. This can lead to inexpensive Fe-triad element-based electrocatalysts with high activity and good stability for efficient electrochemical energy conversion and conversion devices.

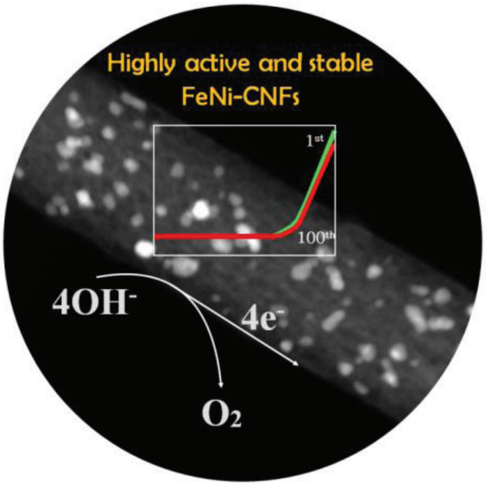

Fig. 1. Schematic illustration of FeNi-CNFs electrocatalysts for oxygen evolution reaction.

Octahedral PtNiCo alloy nanoparticles as active electrocatalysts for oxygen reduction

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Platinum is still the most used catalyst at the cathode of polymer electrolyte fuel cells (PEMFCs) for the oxygen reduction reaction (ORR). Nevertheless, it has been studied that both specific and mass activity can be enhanced by alloying Pt with other non noble metals such as Fe, Co or Ni and by maximizing the exposure of certain facets through the use of shape-controlled nanoparticles [1-4]. In this work, octahedral PtNiCo alloy nanoparticles have been synthesized by the solvothermal method described in [5]. The presence of Co increases the Ni loading in the nanoparticles when both metal precursors are in the same proportion. However, alloyed nanoparticles with very low Co content are formed in this condition. By adding up to 10 times more Co than Ni it is possible to obtain PtNiCo nanoparticles with comparable Ni and Co content, keeping the octahedral morphology in all cases. The electrochemical activity of these catalysts for ORR as well as their stability performance will be studied and compared with commercial Pt/C and PtNi nanoparticles [5].

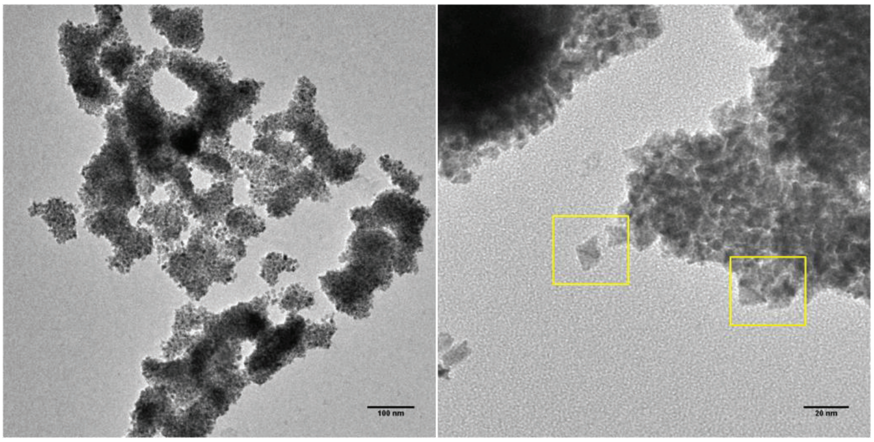

Fig. 1. TEM images of PtNiCo octahedral nanoparticles obtained by solvothermal method.

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Surface catalytic reactivity for energy conversion and storage probed by *in-situ*-electrochemical mass spectroscopy

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Recent trends in electrochemical energy conversion processes have increased the demand for fundamental information about on electrochemical behaviors and the reaction mechanisms. Particular attention to those catalysts involved reactions such as oxygen evolution reaction (OER) and carbon dioxide reduction reaction (CO_2RR), both of which are central to the future sustainable energies either on production of hydrogen or in the conversion of CO_2 into energetically useable molecules, e.g., fuels. Those reactions are essential for solar and electrolytic water-splitting devices and fuel cells.

The differential electrochemical mass spectrum (DEMS) is technique capable to detect volatile production within response time in the millisecond range, by coupling mass spectroscopy in electrochemistry, Fig. 1a. The system consists in application of an online mass spectrometry placed in vacuum chamber supported by two turbo molecular pump in sequence. A hydrophobic membrane promotes the interface of vacuum and electrochemical setup. After being degassing the products of electrochemical reactions can be detected and quantitatively measured in the mass spectrometer. The electrochemical reaction are done with dual thin-layer flow cell composed of two compartments internally connected to each other, one takes the electrochemistry reactions, and the other where the products are exposed and collected into vacuum system. The mass determination products are carried out by a quadrupole mass spectrometer at vacuum pressure around $1x10^{-6}$ mbar.

We present here the principles of DEMS instrument and how this technique have been used to study electrochemical reactions such the electrocatalitic water splitting such as nickel-iron (NiFe) catalysts. Its charging properties well known in battery (NiFe battery) will be presented here as possible explanation for a delay in the oxygen suppressed during the cathodic scan sweep, Fig. 1b.

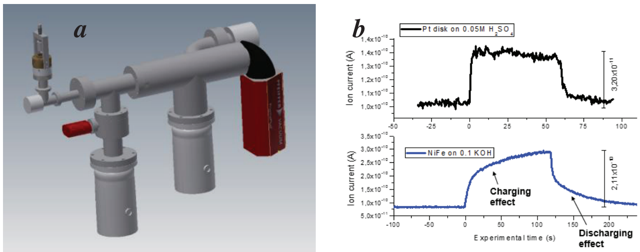

Fig. 1. a) Schematic drawing of the differential electrochemical mass spectrometer. b) DEMS measurements to detect oxygen evolution, studying Pt and NiFe as oxygen evolving catalysts.

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Electrochemical reduction of CO_2 in an organic electrolyte media

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In this presentation we demonstrate the electrochemical reduction of CO_2 in different organic electrolytes dissolved in organic solvents which are immiscible in water for suppressing hydrogen evolution reaction. CO_2 is manifold soluble in organic solvents which paves the possibility of CO_2 reduction with organic electrolytes. Chronoamperometry and linear sweep voltammetry were used to monitor the electrochemical reduction of CO_2 and one of the possible products, HCOOH was anlayzed using UV-vis spectrometry.

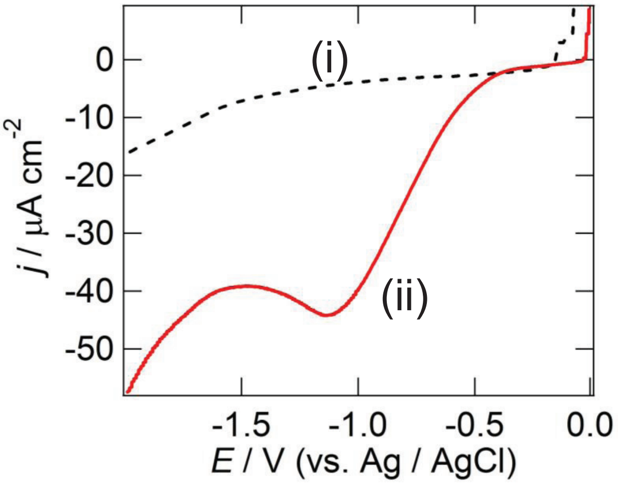

Fig. 1. Linear Sweep Voltammograms for the electrochemical reduction of CO_2 in an organic electrolyte solution using a gold electrode; (i) before CO_2 purging and (ii) after controlled potential electrolysis at -1.5 V *vs*. Ag / AgCl.

On the active catalyst state of cobalt oxide electrocatalysts for oxygen evolution reaction

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Non-noble metal based electrocatalysts for oxygen evolution reaction (OER) which are stable and active in benign environments are essential for the commercialization of electrochemical hydrogen production, especially in developing countries, but the rational design of electrocatalysts needs more fundamental knowledge about the catalyst state under realistic reaction conditions.

In this work, we present new insights into the structure of the oxygen-evolving state of Cobalt oxides in neutral electrolyte extracted from (quasi-)*in situ* x-ray diffraction and absorption spectroscopy experiments [1]. In case of Co_3O_4 thin film model catalysts, we observed reversible changes in oxidation state, cation-cation connection and crystallinity during transition from inactive to the active state. The reversibility of the formation of the active state is further illuminated by the great similarity of the electronic structure as well as surface chemistry of the Co ions before and after oxygen evolution.

In contrast, the pure Co^{2+} oxide shows irreversible changes during transition to the oxygen evolving state towards an X-ray amorphous Co^{3+} oxide consisting of mainly di-μ-oxo bridges similar to the Co-Pi system [2,3]. A comparison of the electrochemical and -catalytic properties of Co_3O_4 and CoO suggest a link between Co redox behaviour, its coordination and the water splitting activity.

Our work guides the way towards the identification of the active catalyst state of Co oxides during oxygen evolution reaction in neutral electrolyte and thus, will help to understand fundamental structure-activity interrelations and will contribute to the development of improved synthesis concepts and electrocatalysts.

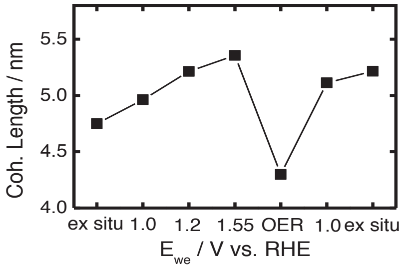

Fig. 1. Structural coherence length of Co_3O_4 as function of catalyst state.

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Exciton formation and decay dynamics in SP6 on ZnO(10-10)

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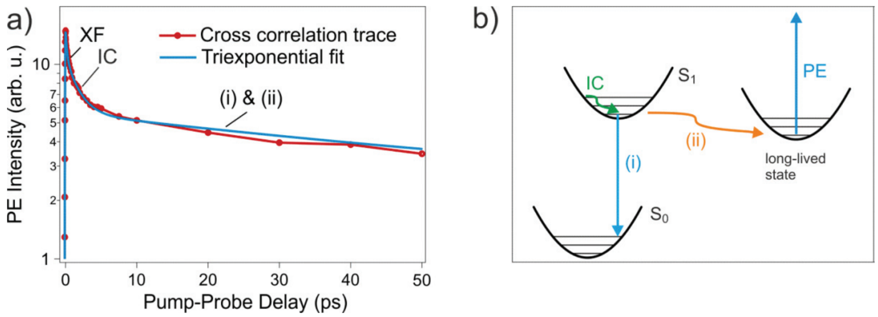
Organic/inorganic hybrid structures exhibit promising properties for the application in various optoelectronic devices, such as organic photovoltaic cells or organic light emitting diodes. A promising transparent electrode material is the wide band gap (3.4 eV) semiconductor zinc oxide (ZnO). On the ZnO surface, the spirofluorene derivative SP6 forms smooth amorphous films from which, after resonant excitation, charge transfer to the ZnO conduction band has been observed [1].

Optical measurements show that resonantly exciting the SP6 molecules from the S_0 to the S_1 leads to internal conversion (IC) by vibrational relaxation on a timescale of 2-6 ps. The exciton population decays on a timescale of 150 ps via competing pathways: (i) electron-hole recombination, (ii) the formation of a long-lived dark state with a lifetime of several μs and (iii) diffusion towards the ZnO interface, where charge separation occurs [2].

We investigate the electronic properties and the excited states dynamics in the SP6 film and at the SP6/ZnO(10-10) interface by means of time-resolved two-photon photoemission (2PPE).

Complementary to the optical experiments time-resolved 2PPE (Fig. 1a) gives access to a fast component with a time constant of a few hundred fs, which may be related to electronic processes which emerge from the exciton formation (XF). These experiments furthermore reveal the binding energy of the dark (triplet) state, inaccessible to optics.

Photon energy-dependent spectra show that the energetic position of the observed signal is independent of the photon energy. Most likely photoemission occurs here via intermolecular energy transfer from the long-lived state instead of emission by the probe photons (Fig. 1b), possible mechanisms will be discussed.



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Electrochemical *in-situ* IR spectroscopy on Pt electrodes: Single crystals, metallic thin-films, Pt nanoparticles, and Pt-doped CeO_2

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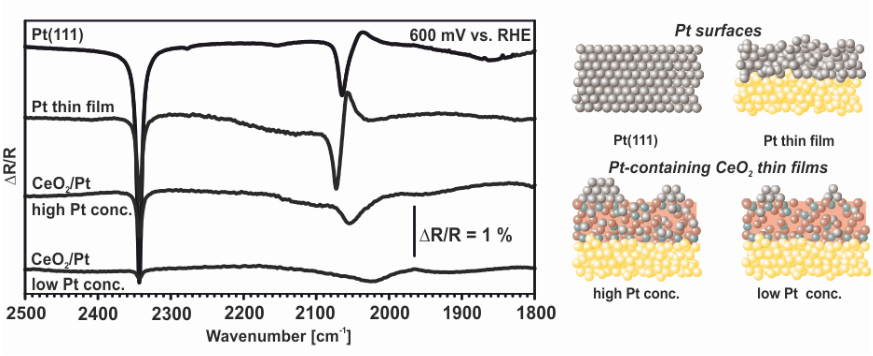
Pt-doped CeO_2 has been identified as a potential novel anode material in proton exchange membrane fuel cells (PEMFC). Providing very high noble metal efficiency, the material may help to decrease the demand for Pt, while simultaneously increasing the tolerance against CO poisoning [1].

To explore the chemical state of the Pt species in the ceria matrix under reaction conditions we apply *in-situ* electrochemical IR spectroscopy. Towards this aim we have set up a new IR spectro-electrochemistry system that includes a state-of-the-art vacuum FTIR spectrometer and an optimized external reflection cell. We demonstrate that the system is functional and provides an excellent signal/noise ratio.

Using this setup, we have investigated methanol oxidation in acidic solution on different Pt catalysts by Linear Potential Scan Infrared Spectroscopy (LPSIRS). Using the CO that is formed during the reaction as a probe for the Pt surface sites, we compare Pt(111) electrodes, Pt thin-film electrodes, and Pt-containing CeO_2 thin-film electrodes with different Pt concentration. All thin-film samples were prepared by magnetron sputtering and characterized by SEM, EDS and cyclic voltammetry. Before measurement we cleaned the surfaces by potential cycling.

On all samples, the IR spectra in the CO stretching frequency region are dominated by the on-top CO band between 2000 and 2100 cm^{-1}. A slight blue shift to 2074 cm^{-1} is observed for the Pt thin film sample in comparison to Pt(111), where the signal appears at 2064 cm^{-1}. Possible explanations involve the co-adsorption of electron withdrawing species and/or an increased CO density. Most importantly, the rougher surface of the thin film induces higher reactivity and leads to earlier CO formation, which is also reflected by the more pronounced s-shape of the CO band (Stark shift). In contrast, the Pt-doped CeO_2 electrodes show a strong red shift and a broadening of the signal, which depend on the Pt concentration. Whereas the corresponding band is observed at 2056 cm^{-1} at high Pt concentration, the band shows a very strong red shift down to 2023 cm^{-1} with decreasing Pt concentration. This observation suggests that, even for low Pt concentration, a fraction of the Pt^{2+} is reduced to Pt^0 and stabilized in form of very small nanoparticles.



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Surface chemistry of glycerol on Pd(111) and Au(111) as a model catalysts

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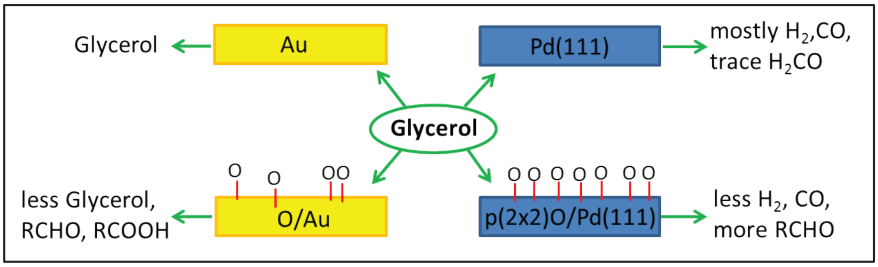
Employing renewable sources from vegetal oil to produce chemicals and energy appears as a promising technological approach to solve human dependence on fuels from fossils. In this way, the new concept of bio-refineries to produce energy and derivatives from biomass comes into the picture. When obtaining biodiesel from biomass conversion, about 10% of the reaction by-product is glycerol. Thus, it is accepted that glycerol will play a very important role in bio-refineries future and it is, therefore, mandatory to search for new processes to upgrade this by-product into more valuable chemicals.

Glycerol is a highly functionalized compound which could be used as a starting material for a great variety of chemical products of industrial interest. It can be upgraded to produce propylene glycol by dehydration followed by hydrogenation. In another aspect, glycerol can be selectively oxidized, in acid or basic conditions, to different products of interest depending if the targeted hydroxyl is in primary or secondary position. Furthermore, glycerol can be reacted with metal catalysts to obtain H_2 and CO (reforming reactions).

Using a combination of surface science techniques, we study the adsorption and further decomposition of glycerol on Pd(111) and Au(111), and are able to distinguish adsorbed intermediates. When the polyalcohol is adsorbed on the metallic Pd surface it primarily decomposes into H_2 and CO, with traces amount of formaldehyde and methane. On the other hand, on the Au(111) surface, it interacts very weakly showing no decomposition. Preliminary results regarding influence on the chemistry observed in the presence of chemisorbed oxygen or surface oxide thin films show that the interaction with both surfaces can be tuned towards different products (Pd) or boost up its reactivity on the coinage metal (Au). These later results are of interest to understand the mechanistic processes of selective catalytic oxidation of glycerol.



Positively charged carbon electrocatalyst for enhanced power performance of L-ascorbic acid fuel cells

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Human implantable devices consume more energy, as its functionality covers not just healing but also monitoring the patient's state of health. Direct ascorbic acid (Vitamin-C) fuel cells offer great potential in supplying power to biocompatible devices owing to a couple of advantages, such as high energy density, a biologically friendly fuel and continuous operation. Recently, it has been reported that high surface carbon with a high oxygen to carbon (O/C) ratio exhibited outstanding electro-catalytic activity toward L-ascorbic acid oxidation, in comparison to platinum group metals [1–4]. The relationship between carbon's surface functional groups and its electro-catalytic activity, however, remains unclear. In this paper, we prepared oxidized carbon samples at different oxidation levels by a simple acid treatment and investigated the correlation between the surface oxygen functional groups in the acid-treated carbon and catalytic activity in the electro-oxidation of L-ascorbic acid. Positively charged carbon, induced by the high electronegativity of surface oxygen, is the dominant factor in enhancing the electro-catalytic activity through easier adsorption of negatively charged reactants.

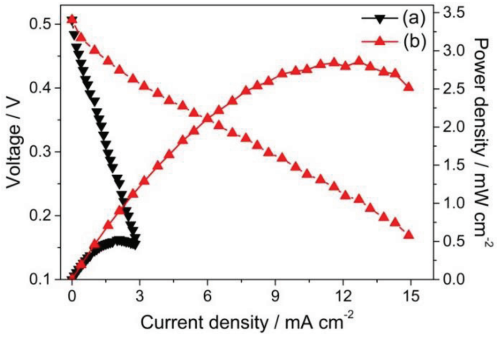

Fig. 1. Polarization curves comparing MEAs prepared with (a) as-received carbon (ARC) and (b) acid-treated carbon for five hours (ATC-5). The cell temperature was 80ºC. The back pressures for both anode and cathode were at ambient pressure. The flow rates of 1 M Vitamin-C and oxygen were 3 and 100 sccm, respectively.

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The activity of the electro-oxidation of liquid fuels under oscillatory regime

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Considerably higher performance has been reported for Polymer Electrolyte Membrane Fuel Cells fed with H_2/CO mixtures when in an oscillatory state [1,2]. In contrast to regular conditions, under oscillatory regime, the anode experiences a periodic self-cleaning state, in which the adsorbed carbon monoxide is periodically oxidized and the activity autonomously restored. We have carried out a systematic comparison of the activity of the electro-oxidation of some liquid fuels (viz. formaldehyde, formic acid, methanol, ethanol, etc.) under regular and oscillatory conditions. Fig. 1 illustrates typical results comparing the activity for the electro-oxidation of formic acid, methanol, and ethanol during a slow voltammetric sweep and under galvanostatic control, where spontaneous potential oscillations prevail in a wide current range. In all cases, the low potentials visited during the oscillations reaches a lower value than that registered along the potentiodynamic sweep, evidencing a high conversion state attained after the oxidation of the adsorbed poison. In particular for formic acid, even the average potential, green dots, lies at less positive values than that under potential control. In addition, results of the rate of changes of the electrode potential during the oscillations are also used to infer on the rate of formation of the poison layer and its oxidation. The analysis helped clarifying the role of poisoning species in each case an provided information that are not accessible via conventional experiments such as chronoamperomeytry and cyclic voltammetry.

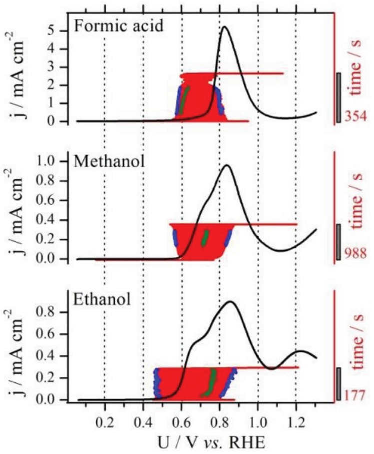

Fig. 1. Cyclic voltammograms (black lines) at 2 mV s^{-1} for the platinum electrode in 0.5 mol L^{-1} of HCOOH (top), CH_3OH (middle) and CH_3CH_2OH (botton) containing 0.5 mol L^{-1} H_2SO_4 aqueous solution. From top to botton, galvanostatics (red lines) obtained at 2.77, 0.77 and 1.1 mA cm^{-2}. Maximum and minimum points are indicated in blue, and the medium points in green. T = 25ºC.

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Investigation of NiFe layered double hydroxide as an electrocatalyst for seawater oxidation

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Generation of hydrogen and oxygen from seawater electrolysis is an attractive process for fuel production since the majority of liquid water available to mankind at the Earth's surface is salty water [1].

Chlorine evolution reaction (CER) is a competing reaction to oxygen evolution reaction (OER) when seawater is used as electrolyte. Despite OER is thermodynamically favoured over CER, the high kinetic lost observed for OER makes CER to be the dominant reaction on many catalytic systems. Therefore, high selectivity and low overpotential for OER reaction are important requirements for an electrocatalyst for seawater oxidation.

Among the noble-metal-free catalysts, NiFe layered double hydroxide (LDH) shows low overpotential for OER reaction in alkaline media [2]. Therefore it has been chosen in our study as potential candidate for seawater oxidation. Its activity and stability have been investigated in slightly basic pH (average pH of seawater being in the range between 7.5 and 8.5) and chloride containing electrolytes (being chloride and sodium ions the main dissolved ions in seawater). NiFe LDH showed good stability in borate buffer electrolyte at pH 9.2 (the pKa) when tested without chloride ions (Fig. 1). However, when NaCl is added (0.5 M concentration) the catalyst deactivates, probably due to corrosion caused by the evolving chlorine. This degradation of the anodic current is not observed in pH 13 (0.1 M KOH) in the presence of the same concentration of NaCl.

More experiments combined with product detection will be performed in order to understand the condition of CER and possibly find modifications of the catalyst that can improve selectivity at near neutral pH.

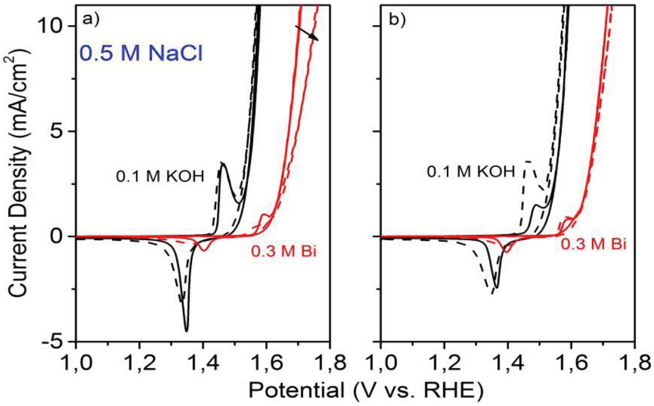

Fig. 1. Stability during cyclic voltammetry. NiFe LDH catalyst supported on carbon Vulcan, measured with a rotating disk electrode (rpm 2800) in pH 13 (0.1 M KOH) and pH 9.2 (0.3 M borate buffer) with (a) and without (b) 0.5 M of NaCl. CV cycle 2 (solid) and cycle 24 (dashed).

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Microwave-assisted solvothermal synthesis of non-precious bifunctional metal catalysts for oxygen reduction and water oxidation

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Mixed nickel iron layered double hydroxides (LDH) are currently the most promising non-novel electrocatalyst for the oxygen evolution reaction (OER) in alkaline media. To enhance the OER activity of non-novel metals towards the oxygen reduction reaction (ORR), will provide a cheap and abundant material for future reversible fuel cell application. This work will present a first attempt for producing a non-novel metal based bifunctional catalyst. Therefore, inspired by Hongjie Dai [1], a much shorter 1.5 h microwave-assisted solvothermal synthesis route to produce 3d transition-metal layered double hydroxides (LDH) was explored. XRD diffractogram confirmed the hydrotalcite like structure for mixed nickel and iron hydroxides. The activity of the catalysts were measured in alkaline aqueous electrolyte using 0.1 M potassium hydroxide, and a 3-electrode setup with a rotating disc electrode (RDE). A high activity of $Ni_{0.20}Fe_{0.80}/C$ for OER was observed with an overpotential of 294 mV at 10 mA cm^{-2}. ORR measurements indicates that nickel based material prefers the 2 e^{-} pathway to produce H_2O_2 in contrast to novel materials like Ir/C and Pt/C.

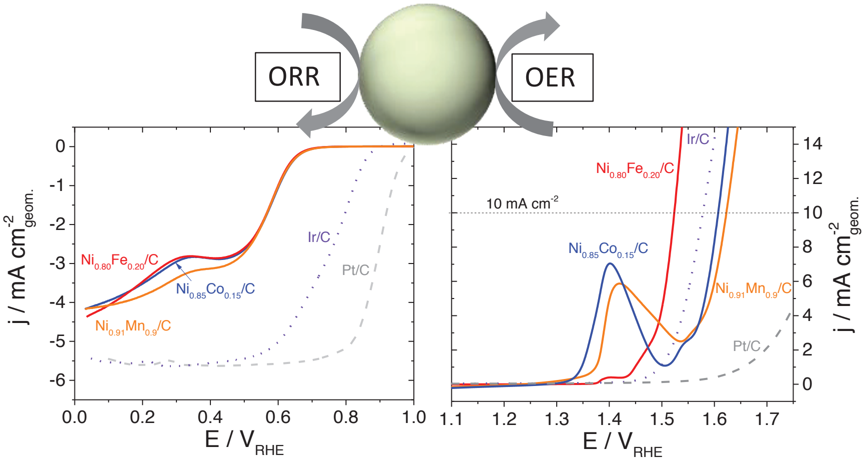

Fig. 1. Linear sweep voltammogram of mixed metal hydroxide of different composition in 0.1 M KOH with rotation speed of 1600 rpm a scan rate of 5 mV/s and a cat. load of 0.2 mg cm^{-2}.

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The surface structure of $V_2O_3(0001)$ A combined STM and IV-LEED study

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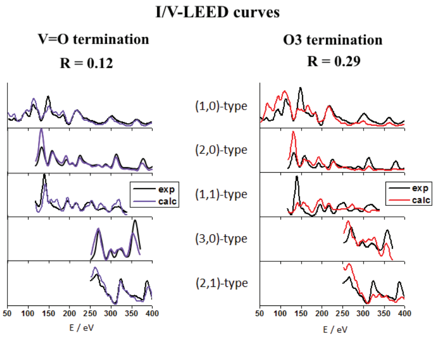
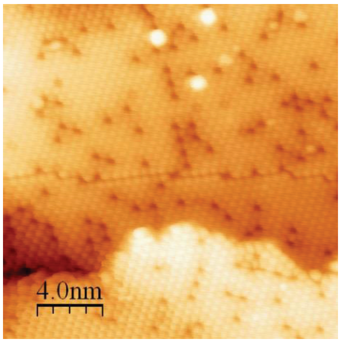
Vanadium oxides are used as industrial catalysts in a variety of oxygen transfer reactions. To unravel the underlying catalytic mechanisms the structures of the relevant surfaces have to be known. While the catalytic activity of the $V_2O_3(0001)$-surface has been demonstrated before [1,2] its surface structure is still under debate. Based on vibrational spectroscopy [3] in combination with STM, XPS and NEXAFS it was widely accepted that the surface is fully covered by V=O groups. Several ion scattering studies published recently [4,5] have questioned this model and suggest an oxygen termination with no or few vanadyl groups instead.

In order to clear up this controversy we have extensively investigated the phase-space of V_2O_3 by varying O_2-pressure and temperature during film deposition as well as in post-annealing steps. Quantitative structure determination with I/V-LEED yielded R-factors of 0.12 for vanadyl-termination and 0.29 for an O_3-termination providing strong evidence that the surface is indeed vanadyl terminated. The comparison of STM images obtained with simulated STM images [6] leads to the same conclusion.

Furthermore a surface phase with a $(\sqrt{3}\times\sqrt{3})R30°$ superstructure could be prepared by oxidation of the original layer. This is in perfect agreement with phase diagrams resulting from DFT calculations [7,8] if and only if the layer was vanadyl terminated before the oxidation.





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Hydrogen evolution as metals and CO interact with surface hydroxyls on MgO(001)

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Hydroxyl groups on metal-oxide interfaces play an important role in catalytic reactions over oxide-supported metal catalysts, through the modification of surface electronic and geometric structure, or by their direct involvement in catalytic reactions. One of the examples is hydrogen evolution, where hydrogen atoms or protons are produced by reactions over the metal-supported oxide surface and recombine to form molecular hydrogen or to proceed reactions. In this contribution, we present results of a surface science study related to hydrogen evolution over hydroxylated MgO(001) to metal (Pd, Au) nanoparticles supported on this surface.

Single crystalline MgO(001) thin films prepared under ultra-high vacuum conditions were hydroxylated by exposure to D_2O at a pressure of 0.05 mbar, yielding a surface hydroxyl - coverage of 0.7 monolayer. The interaction of metals, which were deposited on clean and hydroxylated MgO(001) surfaces by physical vapor deposition, has been investigated with X-ray photoelectron spectroscopy in combination with the Auger parameter analysis as well as infrared spectroscopy. From photoelectron spectroscopic data, conclusions about the changes in chemical nature and morphology of the metal deposits induced by the interaction with surface hydroxyl groups could be drawn. Infrared spectroscopy, on the other hand, allowed to track the interaction of the metals with specific hydroxyl groups upon metal deposition. In subsequent temperature programmed desorption experiments the release of D_2 (from Pd, not from Au) was observed at relatively high temperature (around 400 K), ascribed to the oxidation of metals by surface hydroxyls. For the systems where the hydroxylation was performed for Pd supported MgO surfaces, its thermal annealing was accompanied by D_2 evolution at around 500 K. The metal coverage dependence analysis of by-product suggests the occurrence of the water-gas shift reaction at the periphery of metal particles.

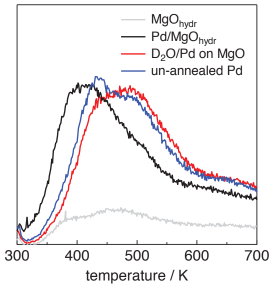

Fig. 1. D_2 TPD spectra taken from hydroxylated MgO (MgO_{hydr}), hydroxylated Pd/MgO and Pd on MgO_{hydr}.

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Platinum dissolution in presence of chlorides

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Platinum is one of the mostly used metals in electrocatalysis. Beside its industrial applications, this is also the material of choice in many fundamental studies. Predominant part of research is devoted to activity of platinum, while stability is often neglected. The use of a scanning flow cell (SFC) connected to inductively coupled plasma mass spectrometry (ICP-MS) enables simultaneous investigation of catalyst activity and stability [1]. In particular, very sensitive time and potential resolved detection of dissolved metal species during various electrochemical experiments can be performed [2,3]. In the current work, platinum dissolution in presence of chlorides will be presented.

Chloride impurities in the electrolyte enhance metal dissolution and catalyst degradation for example in fuel cells. To prevent or minimize catalyst degradation in presence of chlorides, a better understanding of the dissolution reaction mechanism is important. In this work we will show new results on platinum dissolution in presence of traces of chlorides obtained with the SFC-ICP-MS setup. It will be shown that Cl^- ions have an influence on both anodic and cathodic platinum dissolution processes (see Fig. 1). Interesting peculiarities of the platinum dissolution mechanisms in electrolytes with and without chlorides will be discussed.

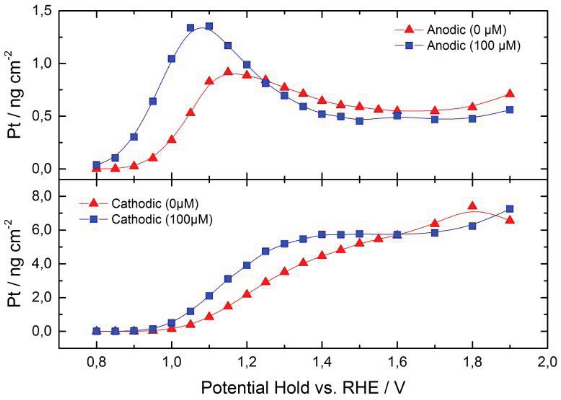

Fig. 1. Amount of dissolved platinum from integrated mass during different potential holds with and without chlorides in 0.1 M H_2SO_4.

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Transition metal containing manganese oxide electrocatalysts for oxygen-evolution reaction

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The storage of electric energy has become one of the main challenges in infrastructure development. Electrocatalytic water splitting is a reasonable way of chemical energy storage in which the anodic oxygen evolution reaction (OER) is the determining factor. Manganese based oxides have attracted particular attention as non-noble metal catalysts for the OER. Due to their abundance, low price and ecological harmlessness, those materials are promising candidates for a commercial application [1].

Here, we report a new microwave based synthesis for manganese mixed oxide nanoparticles. We have introduced Fe, Co or Ni to yield $Mn_{3-x}M_xO_y$ in a range from X=0 to 1. The well characterized (TEM, EDX, XRD) catalysts with a size of 4.5 to 8 nm were tested with respect to electrocatalytic activity and stability for the OER in alkaline media using Rotating Disk Electrode (RDE) measurements [2].

We observed a strong impact of the introduced metal and its fraction in the catalyst. The electrocatalytic activity increased significantly going from Fe to Co and Ni, while the pure manganese and the iron containing catalysts exhibit poor activity and stability. Both aspects increase drastically using cobalt or nickel.

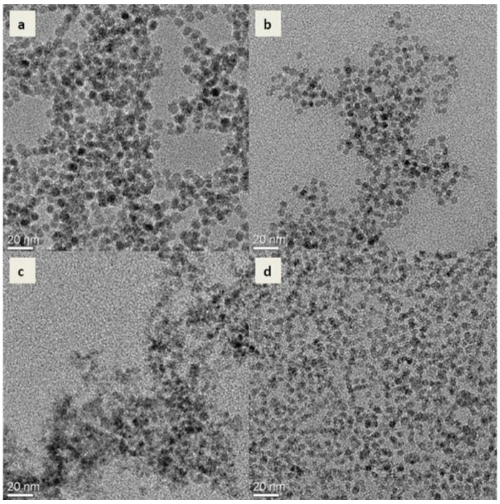

Fig. 1. TEM images of (a) Mn; (b) $Co_{0.46}$, (c) $Fe_{0.57}$, (d) $Ni_{0.54}$.

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Catalytically enhanced effects of mixed NiFe (oxo)hydroxides investigated by X-ray absorption spectroscopy

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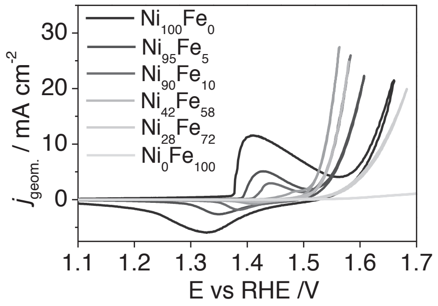
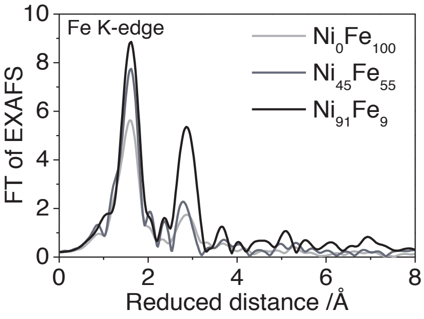
Mixed 3*d* metal oxides of Ni and Fe are highly promising electrocatalysts for water oxidation in alkaline media [1-3], and would be a viable alternative as abundant and cost-efficient material for electrochemical water splitting.

We investigated a mixed NiFe catalyst system prepared by a simple solvothermal route. Doping with different ratios of Ni and Fe showed synergistic positive effects on the oxygen evolution reaction (OER) compared to pure nickel or iron catalysts [1-3], observed as a lowering in the overpotential (η) for OER and an increase in intrinsic activity.

Using synchrotron radiation we recorded X-ray absorption spectra at the K-edges of both Ni and Fe at different mixtures of Ni:Fe given in atomic %. The spectra were consistent with a disordered layered NiFe(oxo)hydroxide structure of, $Ni_xFe_yO_y(OH)_{2x+y}$ [3-5], with increasing degree of disorder at higher Fe ratios. The observed changes in the structure of the different mixtures of Ni and Fe, as well as changes upon operation under OER conditions were addressed in order to investigate the enhanced catalytic effect observed between the two 3*d* metals.





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Commissioning of new near-ambient-pressure XPS at Korean Basic Science Institute and its performance

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Near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) has been considered as one of the best surface science tools for studying *in-situ* chemical and electronic structure of surface. In 2014, Korea Basic Science Institute (KBSI) successfully completes the commissioning of NAP-XPS. The chamber is equipped with SPECS PHOIBOS 150 analyzer and 2-dimensional-delay line detector, which provides improved detection efficiency with a) 2-dimensional angle resolved mode, b) 1-dimensional chemical imaging mode c) time resolved XPS at picosecond scale. The *in-situ* gas-pressure cell is designed to operate at pressure up to 25 mbar with differential pumping system. As a photon source, Al Kα X-ray source can be focused with special monochromator with beam spot size 300 μm. the main chamber is attached to preparation chamber, which houses a low energy electron diffraction (LEED), a high pressure cell (HPC), an ion sputter gun, a multi-cell E-beam evaporators, and a four-axis manipulator with heating and cooling functions. The NAP-XPS at KBSI is now fully operational and expected to play important roles in various field of surface science, e.g. catalysis and energy material science.

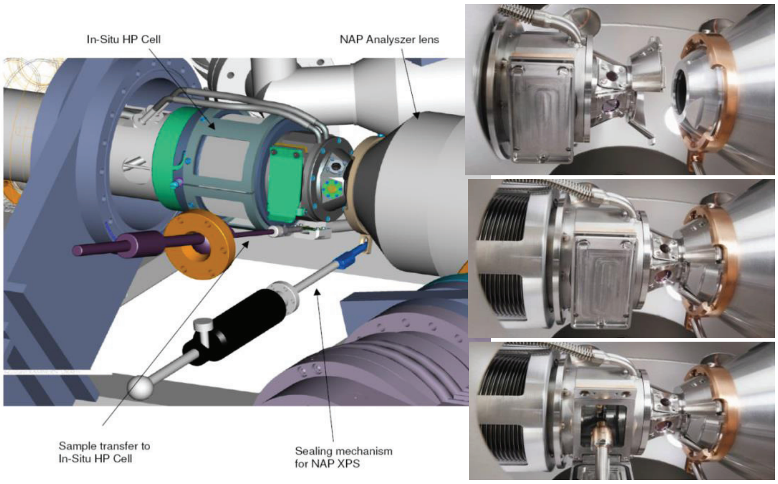

Fig. 1. The schematics of NAP-XPS cell and sample transfer.

Doping and substrate effects on catalytic activity

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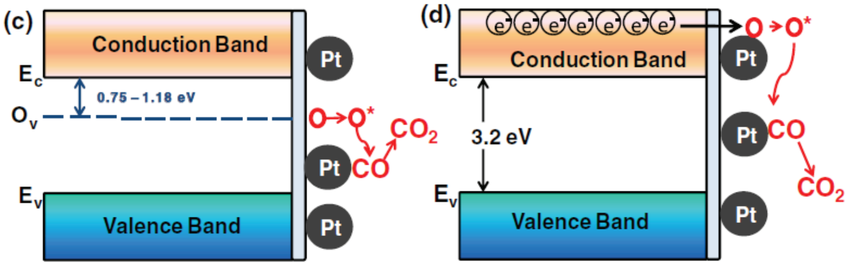
The strong metal-support interaction (SMSI) effect is an important issue for achieving enhanced catalytic activity for heterogeneous catalysts. Recent studies by Fujitani and Nakamura on Au/TiO_2 suggest that the perimeter area between the Au nanoparticles and TiO_2 is catalytically reactive under CO oxidation [1]. Hayek *et al.* showed that the reaction rate in the oxide-metal model system depends on the oxidation state of the supporting oxide, the free metal surface area, and the number of sites at the interface between the metal and the support [2]. The general concept of the SMSI phenomena means that the catalytic activity changes when group VIII metal catalysts are supported on reducible oxides. The group VIII metals include Pt, Pd, Rh, Fe, Ni, and Ir. The reducible metal oxides include cerium dioxide (CeO_2), niobium pentaoxide (Nb_2O_5), and titanium dioxide (TiO_2). After reduction at high temperature, migration of the reduced species from the support material to the metal catalytically modifies the metal. In addition to this geometric contribution, the electric field between the metal and support interface changes and generates metallic bonds and compounds in the reduced state. Additionally, metal and semiconductor doping can also lead to changes in the activation energy for catalytic reactions. For the past decade, there have been ongoing discussions on improving catalytic efficiencies using TiO_2 doped with non-metals. In this presentation, we present our studies on the support effect of plasma deposited Pt nanocatalysts on reducible metal oxide supports (CeO_2, Nb_2O_5, and TiO_2) [3] and doping effect on nitrogen (N) and fluorine (F) doped TiO_2 [4].



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Titania nanotubes prepared by rapid-breakdown-anodization in halogen-free acids

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Titania nanotubes were prepared by anodization in an organic electrolyte without halogen ions (i.e. fluoride, chloride or bromide). Relatively high temperature was required under an applied voltage of 100-200 V for synthesizing tubular structure. High-aspect-ratio TiO_2 nanotubes with an outer diameter of about 60 nm and wall thickness of 10-15 nm were grown as similar as those prepared by so-called rapid-breakdown-anodization (RBA). Various temperatures, voltages, and concentrations were investigated to identify the ranges of occurrence of RBA without halogen ions. Titania nanotubes were randomly found on the surface when the temperature reaches over 323 K at a high voltage. We found that a localized breakdown of TiO_2 happened under a harsh anodic condition without halogen ions, resulting in the formation of nanotubes. Most of all, current density-time transients as a function of anodic conditions showed that there were adequate ranges of current density to prepare nanotubular structures.

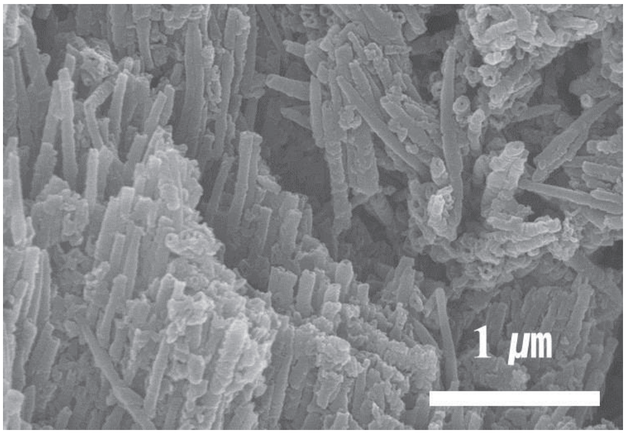

Fig. 1. SEM images of TiO_2 nanotubes prepared by halogen-free rapid-breakdown-anodization.

Characterization of the solid electrolyte interphase in lithium-ion batteries

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Lithium-ion batteries are already widely used in numerous fields of daily life. Their high energy densities as compared to other battery systems make them attractive especially for mobile applications. Nonetheless more research is needed to further increase the safety and cycle-life of lithium-ion batteries.

Carbon anodes are the standard anodes in lithium-ion batteries to date. During the first cycles of a lithium-ion battery a solid film forms on the anode side. This film is known as the solid electrolyte interphase (SEI). It mainly consists of decomposition products of the electrolyte. The SEI is crucial for the cycle-life of the battery as it prevents destruction of the anode by co-intercalation of solvent molecules. Although the SEI has a protective function, it also has negative aspects as it invariably produces irreversible capacity loss. Therefore an ideal SEI is thin but also flexible and homogeneous.

To gain insights into the underlying mechanisms the influence of different electrolytes on the formation of SEI was tested. The layers they generated were examined by spectroscopic and electrochemical methods.

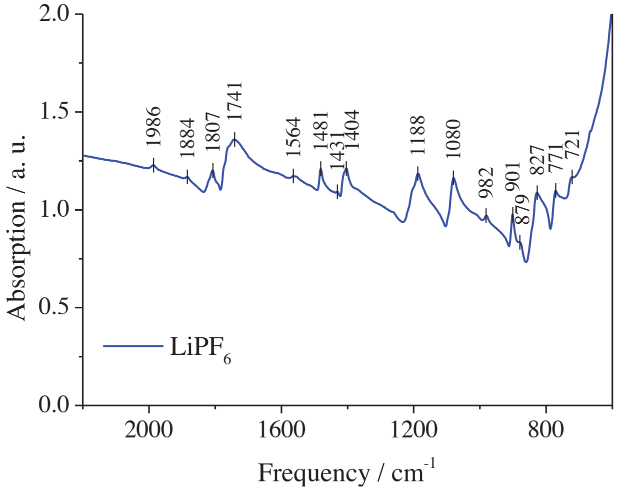

Fig. 1. Fourier transform infrared spectrum on SEI. The used electrolyte was EC:DEC 3:7 wt.%, 1 M LiPF$_6$.

The active sites of Au/TiO_2 and Au/Fe_2O_3 for oxidation reactions

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The discovery that nanoscopic gold particles supported on metal oxides are active for low-temperature CO oxidation has inspire a considerable amount of research directed toward understanding the basis for the activity of Au catalyst [1]. Different factors related to size reduction have been proposed to play a role in Au activation, such as quantum size effects, low coordinated atoms, surface ions and the support interaction [2]. Here we report a surface characterization of the chemical and structural changes of Au/TiO_2 and Au/Fe_2O_3 in CO oxidation reaction.

All measurements were performed in the near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) endstation of the ISISS beamline at HZB/BESSY II (Berlin, Germany). The Au nanoparticles supported on metal oxides were prepared using a deposition-precipitation method [3]. CO was introduced to the chamber at a ratio CO:O_2 = 1:2 keeping the pressure at 0.3 mbar and the temperature at 100°C.

Our observations show the formation of two Au species (Au^0 and $Au^{\delta+}$) on the surface of active Au/TiO_2 (Fig. 1) and Au/Fe_2O_3 samples. TEM images reveal the formation of support layer on top of Au particles. All these results suggest Strong Metal Support Interaction, perhaps the role of the support is to influence the electronic structure of the gold through charge transfer and to stabilize low-coordinated Au atoms possessing unique adsorption properties.

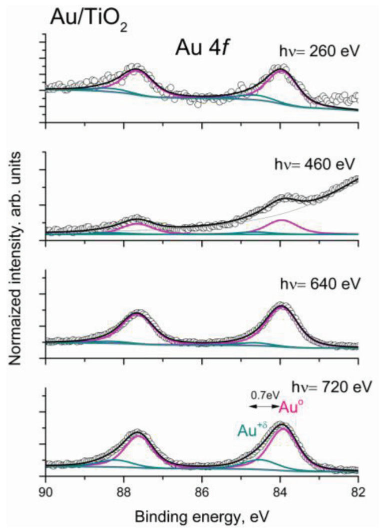

Fig. 1. Au 4f XP spectrum of TiO_2 after CO oxidation.

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Photoelectrochemical properties of hematite nanoparticles synthesized by DC thermal plasma process

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Hematite nanoparticles are widely used for photocatalysis because of its relatively narrow bandgap (2.3 eV) and suitable band position for OER (Oxygen Evolution Reaction), which enables effectively electrolyze water at a low potential with wide wavelength ranges. Therefore, photoelectrochemical water electrolysis using hematite photoelectrode has been conducted for a long time. In this research, two-step route are studied in detail. In the first step, iron nanoparticles are synthesized by DC thermal plasma process, after which are annealed in air atmosphere for the synthesis of hematite nanoparticles. In addition, various types of binders have been tested to improve adhesive properties between substrate and nanoparticles N-type doped hematite with nitrogen is prepared by using NH_3 gas during the DC plasma process in order to shift band position and narrow bandgap. Photoelectrochemical and adhesive properties of the synthesized hematite photoelectrode are measured by LSV (Linear Sweep Voltammetry), TEM (Transmission Electron Microscopy), and UV-Vis spectroscopy.

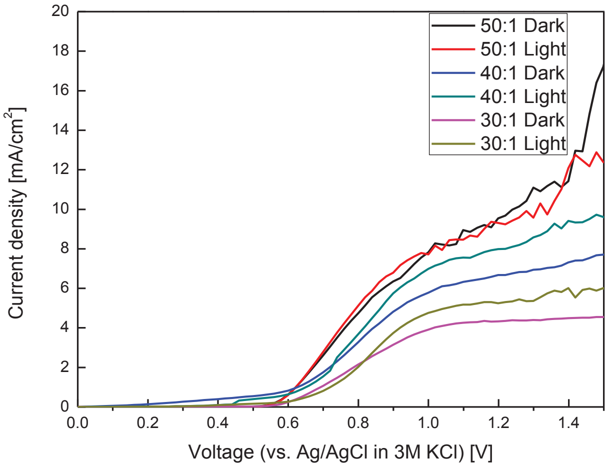

Fig. 1. (Photo) water splitting properties of hematite in terms of different binder compositions.

Investigating the surface stability of Pt skin-layer in $Pt_3Ni(111)$ under oxidation environment with AP-XPS

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Oxygen reduction reaction (ORR) is a key process at cathode side of proton exchange membrane fuel cell (PEMFC), and platinum (Pt) have been utilized as the best catalyst for ORR. Yet, the best Pt catalyst cannot meet the level of ORR performance for the commercialization of PEMFC. In 2007, a model study showed that Pt alloyed with transition metal with the ratio of 3:1 exhibited an enhanced ORR [1]. According to the report, the catalytic activity of $Pt_3Ni(111)$ crystal is 10-fold higher than Pt(111) and the enhancement originates from modified electronic structure of the surface where Pt-skin is formed [2]. However, the unstable surface structure of Pt-skin surface under environment of oxygen and electrolyte prevents its practical use to PEMFC.

In this presentation, using Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS), the stability of surface skin layer is investigated under various temperature and oxygen pressure conditions, e.g. the surface chemical compositions, depth profile, and oxidation states. From the measurements, a segregation of Ni element to the surface is observed, and several species of Ni oxides are identified as a function of oxygen pressure and temperature.

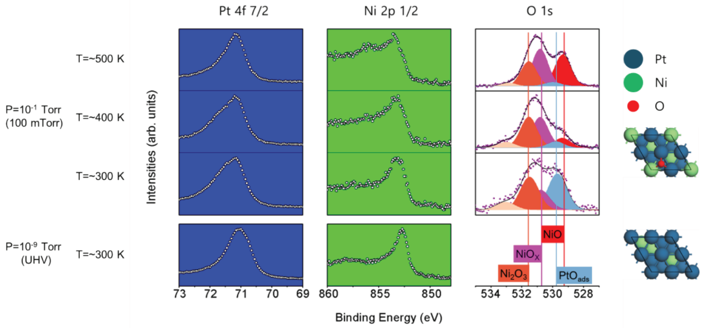

Fig. 1. Core-level XPS spectra of Pt 7/2, Ni 2p 1/2, O 1s regions at UHV, 300 K and 100 mTorr, 300 K, 400 K, 500 K.

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The structural transformations of zinc oxide layers on Pt(111)

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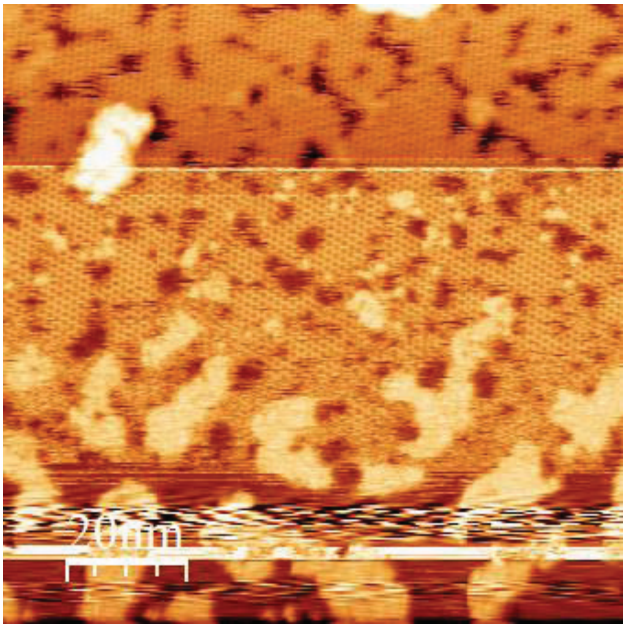
The morphology of ultrathin zinc oxide films grown on Pt(111) was studied as a function of coverage and preparation conditions. The results show that monolayer films exhibit a large variety of structures that may transform into each other depending on ambient conditions. The transformations are accompanied by substantial mass transport across the surface even at room temperature, thus indicating the presence and high diffusivity of migrating ZnO_x species. *In situ* STM experiments show that H_2 plays an important role in the transformation. Comparison with other metal-supported ZnO films shows that the metal substrate plays a critical role in such transformations.



Structural investigation of 45S5 bioglass with calcium-enriched surface

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Bioactive glasses are a group of surface reactive biomaterials, which are able to stimulate more bone regeneration than other bioactive ceramics. The bioactivity strongly depends on the chemical composition and structural arrangement of the surface atoms in the glass. In the present work, the ion-exchange technique was applied aiming to produce a BG45S5 bioglass with a calcium-enriched surface [1]. The BG45S5 composition (46.1 mol% SiO_2, 26.9 mol% CaO, 24.4 mol% Na_2O, and 2.6 mol% P_2O_5) was chosen because it is the gold standard for bioglass biocompatibility and has a well-studied structure and properties. The ion-exchange technique is a fairly simple, reproducible and efficient way to introduce changes in structure and composition to the surface of bioactive glasses, which may lead to an increase of the glass surface reactivity. The use of SEM and XPS spectroscopy allowed estimating the thickness modified and infer over the structural changes on the surface of 45S5 bioactive glass. The entry of calcium in the vitreous network promoted the phase separation of micro-domains rich in silica and phosphate on the surface of the glass. The formation of immiscibility region was attributed a depolymerization of silica network and also, to a possible migration of phosphate species from the bulk. Fig. 1 shows the scheme summarizing the changes in 45S5 from this study; the SEM pictures before and after the ion-exchange process, and XPS spectra of P_{2p} and Si_{2p}.

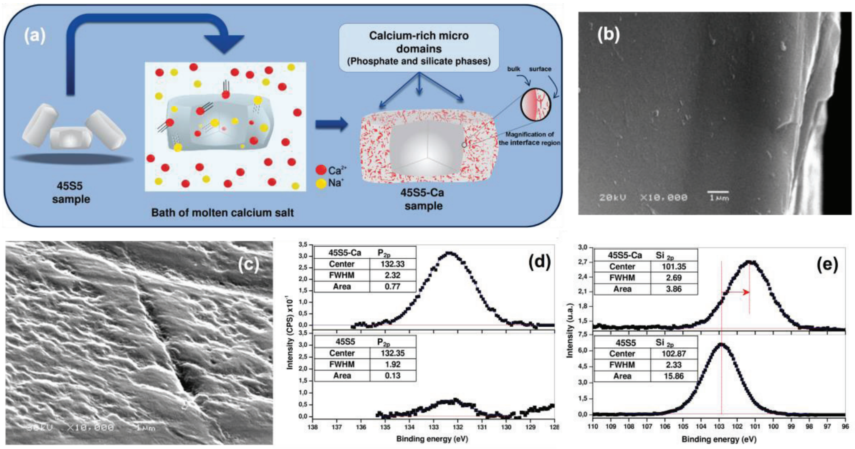

Fig. 1. (a) Scheme summarizing the changes in 45S5 from this study, SEM image from 45S5 (b) before and (c) after ion-exchange process, and XPS spectra of (d) P_{2p} and (e) Si_{2p}.

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Synergy in the electro-oxidation of formic acid assisted by hydrazine

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In the last few years many have been discussed on the mechanism of the electro-oxidation of formic acid, with the plurality of pathways via which the process occurs being the main subject of these works. Despite the uncertainty on the exact mechanism of this process, formic acid is a model molecule for the study of oscillatory behavior in electrochemistry [1]. However, fewer works have been done on the interaction of formic acid with another molecule during the emergency of oscillations. This work proposes to further study the non-linear behavior of the electro-oxidation of formic acid using hydrazine as an additive. This molecule presents an interesting interaction with an oxidized platinum surface [2]. The addition of hydrazine in a system containing formic acid yields an unexpected non-linear result: the emergency of synergy. The response of the system as a whole is different from the individual contribution of its parts. In a galvanostatic measurement, the oscillation time of the system increases more than 20 times with upper potentials that reaches 0.9 V *vs.* RHE. For the hydrazine it is not possible to observe oscillations in this experimental setup and for formic acid, oscillations have maximum potentials near 0.8 V *vs.* RHE. Under potentiostatic conditions, it was possible to observe a stabilization of the oscillatory profile with higher oscillations durations. The voltametric profile shown in Fig. 1 also suggests that a non-additive phenomenon takes place in the system once the currents yielded from the mixture are different from the sum of the individual contributions. We propose that in this case the synergy may be due to the interaction between hydrazine and oxygenated species at the electrode surface, attenuating the spontaneous drift that drives the systems away from their limit cycle, thus causing oscillations to cease [3].

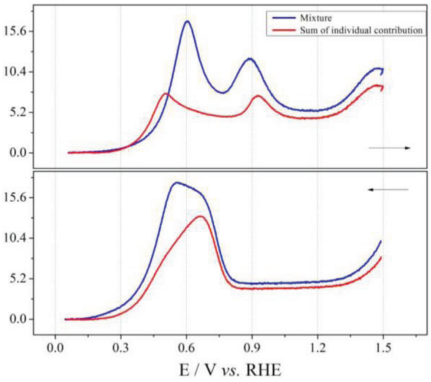

Fig. 1. Cyclic voltammetries at 100 mV s^{-1}. The blue line stands for the result yielded by the mixture [Formic Acid] = 0.5 M + [Hydrazine] = 5 mM. The red line shows the numerical sum of the individual contributions of two separate systems, using the same experimental setup.

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Local imaging and measuring of distortions in the oxygen sub-lattice of complex mixed oxides

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"*It would be very easy to make an analysis of any complicated chemical substance; all one would have to do would be to look at it and see where the atoms are. The only trouble is that the electron microscope is one hundred times too poor*." With this statement in his famous speech "*There is plenty of room at the bottom*" R. Feynman has already highlighted the future importance of transmission electron microscopes (TEMs) in 1959.

Nowadays modern Cs corrected TEMs are powerful enough to obtain point resolution below 50 pm [1,2]. However, direct imaging of light elements next to heavy elements remains complex. In probe corrected scanning transmission electron microscopy (STEM) recent developments tackle this challenge, resulting in the revival of the annular bright field (ABF) detector. In contrary to the contrast detected by the high angle annular dark field (HAADF) method, which is due to Rutherford scattering and proportional to Z^2, the ABF detector is also sensitive to light elements [3,4].

Using the ABF detector, we investigated orthorhombic (Mo, V) oxides crystallized in a structure analog to the M1 structure (ICSD no. 55097) of MoVTeNb oxide. The obtained micrographs were compared with Rietveld refined X-ray diffraction (XRD) data. Fig. 1 shows an ABF image where the oxygen atoms brighten up. Furthermore we directly measured metal-oxygen bond angles and discussed the oxidation states of the metal centers.

Our results prove Feynman´s prediction. Seeing where the atoms are, generates in particular in heterogeneous catalysis a deeper understanding of the functionality of materials on the way towards tailor-made catalysts.

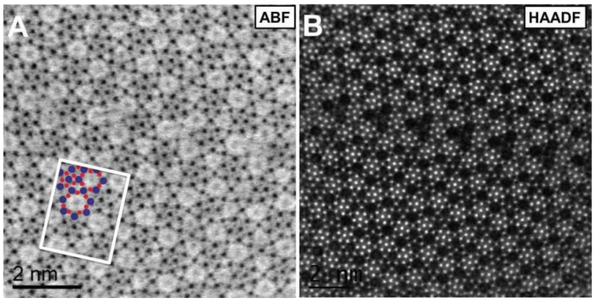

Fig. 1. (A) Atomic resolution ABF-STEM image of (Mo, V)O_x. The white rectangle displays the orthorhombic unit cell, which is in good agreement with the ABF image. Metal sites are partially highlighted with blue circles and oxygen sites are labeled with red circles. (B) Corresponding HAADF image of the same region.

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Redox dynamics of a Ni catalyst - Impact on coking behavior in the dry reforming of methane at high temperatures

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The influence of redox dynamics of a Ni/MgAl oxide catalyst for dry reforming of methane (DRM) at high temperature was studied to correlate structural stability with catalytic activity and coking propensity [1]. Structural aging of the catalyst was simulated by repeated temperature-programmed reduction/oxidation (TPR/TPO) cycles. Despite a very high Ni loading of 55 wt% homogeneously distributed Ni nanoparticles of 11 nm were obtained from a hydrotalcite-like precursor. Redox cycling gradually changed the interaction of the active Ni phase with the oxide support resulting in a crystalline Ni/$MgAl_2O_4$-type catalyst. After cycling the average particle size increased to 21 nm. While still a large fraction of small particles was present, the Ni surface area exhibits a dramatic drop of 72%. Interestingly, the redox dynamics and its strong structural and chemical consequences were found to have only a moderate influence on the activity in DRM at 900°C. However, DRM tests in a fixed-bed reactor indicate a depletion of carbonaceous deposits due to a lower fraction of graphitic carbon. Additionally DRM experiments in a thermobalance revealed coke formation as a continuous process and showed a higher coking rate for the cycled catalyst.

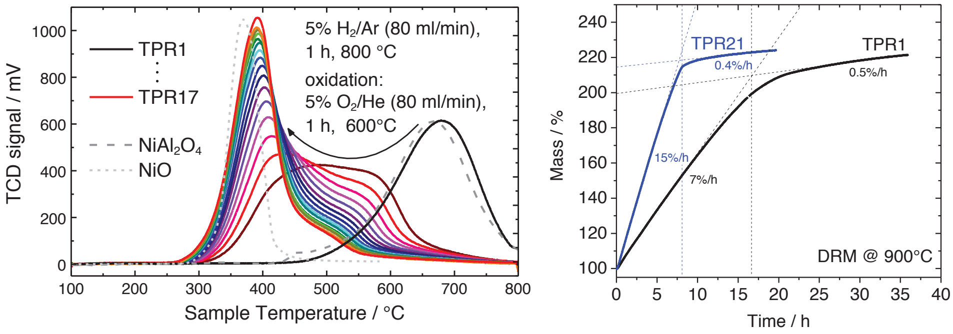

Fig. 1. TPR cycles of Ni/MgAl oxide catalyst and $NiAl_2O_4$ and NiO as references (left); DRM at 900°C in a thermobalance after first reduction and after 18 TPR/TPO cycles (right).

Acknowledgement
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IrO_x core-shell nanoparticle catalysts for efficient electrochemical water splitting

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Water electrolysis, combined with renewable electric power generation technologies, such as solar electric or wind power plants, is expected to emerge as a low-emission method for storing excess electricity or for producing hydrogen fuel as part of a solar refinery [1-5]. Acid Polymer Electrolyte Membrane (PEM) electrolyzers show advantages compared to alkaline electrolyzers in terms of compact system design, operating at high current densities with high voltage efficiency, and providing high gas purity [6]. However, acidic environment in PEM electrolyzers requires noble metal catalysts, e.g. RuO_x, IrO_x for the anodic oxygen evolution reaction (OER) [7,8]. IrO_x appears as a catalyst of choice due to its comparable activity and high stability [3]. However, the scarce nature of Ir requires significant reduction of Ir loading, which is why novel strategies are critically needed to further reduce the amount of Ir in OER catalysts.

Here in, a family of dealloyed metal-oxide hybrid ($M_1M_2@M_1O_x$) core@shell nanoparticle (NP) catalysts is demonstrated to provide substantial advances toward more efficient and less expensive electrocatalytic water splitting. $IrNi@IrO_x$ NPs were synthesized from $IrNi_x$ precursor alloys through selective surface Ni dealloying and controlled surface oxidation of Ir. Detailed depth-resolved insight into chemical structure, composition, morphology, and oxidation state was obtained using spectroscopic, diffraction, and scanning microscopic techniques (XANES, XRD, STEM-EDX, XPS), which confirmed our structural hypotheses (Fig. 1). A 3-fold catalytic activity enhancement for the electrochemical OER over Ir benchmark catalyst was observed for the core-shell catalysts on a noble metal mass basis. Also, the active site-based intrinsic activity was greatly enhanced for the most active $IrNi@IrO_x$ catalyst. This study documents the successful use of synthetic dealloying for the preparation of metal-oxide hybrid core-shell catalysts. The concept is quite general, can be applied to other noble metal nanoparticles, and points out a path forward to nanostructured proton-exchange-electrolyzer electrodes with dramatically reduced noble metal content.

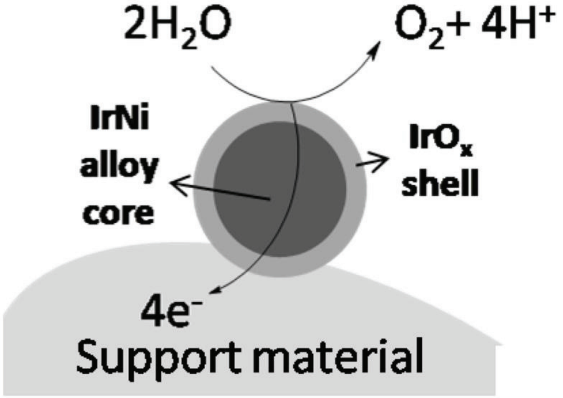

Fig. 1. Oxygen evolution reaction on $IrNi@IrO_x$ core-shell nanoparticle in acidic environment.

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Insights into autonomously-formed oxygen-evacuated Cu_2O electrode for the selective production of C_2H_4 from CO_2

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Carbon dioxide (CO_2) is considered as one of the main contributors to global warming, leading to enormous ecological changes such as desertification and other ecological hazards. Hence, modern technologies are needed to convert CO_2 in the atmosphere to useful compounds, thereby reducing its amount and mitigating its disastrous ecological impact. Of late, electrochemical CO_2 reduction using various catalysts attracts considerable attention as an efficient and viable technological solution [1]. Among all possible products in CO_2 electroreduction, hydrocarbons such as methane (CH_4) and ethylene (C_2H_4) have been catalytically synthesized from CO_2 on Cu electrodes. This is possible because of copper's unique electrocatalytic property in enabling adsorbed carbon monoxide (CO) to further react and produce larger molecules [2]. Cuprous oxide (Cu_2O), in particular, is studied for the production of various organic molecules [3-5]. When looking into previous studies on the use of Cu_2O, however, Cu_2O's role in the CO_2 electrolysis is still not understood. In this study, we attempted to identify how Cu_2O affects the electrochemical process and compared its catalytic performance with Cu electrode. Electrochemical behavior was examined on both of two electrodes and a morphological investigation was also performed before and after CO_2 electroreduction. In contrast with previous studies, our results indicate that Cu_2O bulk structure remains inside the entire Cu_2O layer and it efficiently contributes to the electrochemical process of CO_2 at low overpotential, exhibiting high selective faradaic efficiency of over 20% for C_2H_4 formation even in long-term electrolysis.

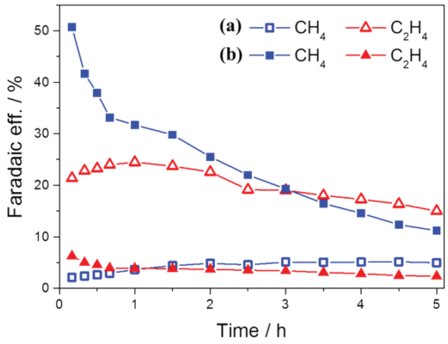

Fig. 1. Faradaic efficiencies toward hydrocarbon production on (a) Cu_2O and (b) Cu evaluated during CO_2 electrolysis at -1.9 V *vs*. Ag/AgCl for 5 h. Cu_2O showed that C_2H_4 was produced more efficiently and stably during the entire CO_2 electrolysis.

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High oxygen-evolution activity and stability of antimony doped-tin oxide (ATO) supported IrO_x nanodendrites in PEM water electrolysers

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Typically only those materials based upon expensive RuO_2 and IrO_2 are regarded as suitable catalysts for OER in PEM water electrolysis [1]. Therefore, the usage of noble metal in PEM water electrolyzer is an important issue for cost reduction. One method to achieve better performances and lower noble metal use is catalyst supports, which may increase the dispersion and surface exposure of catalysts. Herein, we synthesized the antimony doped tin oxide (ATO) bulk powder with high surface area, high crystalline and mesoporous structure. Ir nanodendrites were synthesized using TTAB as surfactant. Ir nanodendrites were deposited on ATO, which was employed as a support material for anode catalysts of PEM water electrolyzers. For comparisons, Vulcan also was used as catalyst support under the same condition. To evaluate the electrochemical stability of catalysts, we applied chronopotentiometry technique for 15 hours and Ir nanodendrites/ATO was highly electrochemical stable compared with other electrocatalysts.

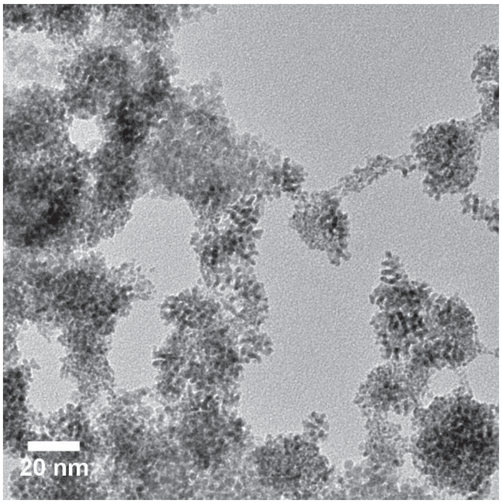

Fig. 1. TEM image of Ir nanodendrties supported on antimony doped tin oxide (ATO).

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Modelling study of activity and stability on Ir(111) and Ir(110) as well as on Ru(0001) single crystals for the oxygen evolution reaction (OER)

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Electrochemical splitting of water has been considered to be a very promising technology for a sustainable hydrogen economy. However, the efficiency of water electrolysis is limited by the oxygen evolution reaction (OER) due to kinetics, which results in a large anodic overpotential [1].

Therefore, the development and optimization of new catalysts for the OER is of great importance in overcoming the challenges in energy conversion [2].

The influence of different crystal faces such as steps, kinks and edges in defined nanosized catalysts is spotlighted as crucial parameter for understanding surface chemistry. Single crystals are suitable model catalysts to study these morphological effects.

Here, we report the preparation and characterization of clean and well-defined single crystalline surfaces of the Iridium(111) and (110) as well as Ruthenium(0001) orientation, which were electrochemically characterized and analyzed towards their oxidation behavior and OER activity. Thus allowing conclusions for preferable crystal faces in nanoparticularly shaped catalysts.

Hereto a new electrochemical cell was designed, using the proposed layout in [3], to perform the thermal restructuring of the surfaces and the following characterization without exposing the single crystals to the laboratory atmosphere.

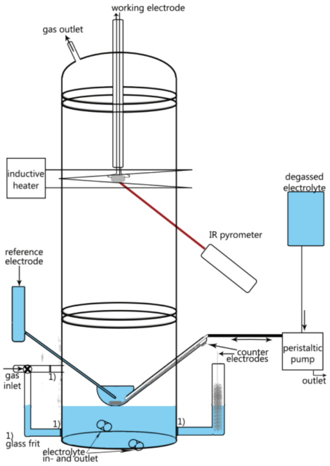

Fig. 1. Sketch - inductive electrochemical cell.

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Reactivity of ultrathin ZnO films supported on Ag(111), Cu(111), and Pt(111)

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Due to the limited thickness that makes them two-dimensional in nature, utrathin films of transition metal oxides may exhibit interesting catalytic properties. As zinc oxide is important component in many catalytic applications, here we studied reactivity of ZnO thin films grown on Ag(111), Cu(111) and Pt(111) with respect to the CO oxidation reaction.

The experiments were performed in an UHV chamber equipped with LEED, AES, QMS and a high-pressure cell for reactivity studies. The ZnO films were prepared by Zn deposition in O_2 ambient followed by annealing in UHV or O_2. The reaction was carried out at 450 K in oxygen-rich conditions (10 mbar CO; 50 mbar O_2; He balance to 1 bar) and monitored by gas chromatography.

For all metal supports, ZnO films grow layer-by-layer in (0001) orientation. For ZnO/Cu(111), the film migrates into the Cu(111) crystal under reaction conditions, and the reactivity is governed by a poorly defined CuO_x oxide film. On Ag(111) and Pt(111), the planar structure of ZnO films is maintained. On Ag(111), the reactivity is gradually suppressed with increasing film coverage. At variance, enhanced reactivity is observed for ZnO layers on Pt(111) with a maximum peaked at sub-monolayer coverage, thus indicating formation of the active sites at the oxide/metal boundary. The support effect is explained by much stronger adsorption of CO on Pt(111) as compared to Ag(111) which reacts with O species provided at the oxide/metal boundary. In addition, the water-gas shift and reverse water-gas shift reactions on ZnO/Ag(111) revealed no promotional effect of ZnO on the reactivity of Ag under the conditions studied.

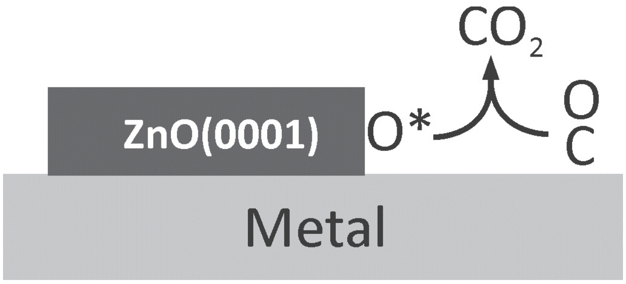

Fig. 1. Schematic of the CO oxidation reaction on ZnO islands supported on metal (Pt, Ag).

An *on line* DEMS investigation of the oscillatory electro-oxidation of formic acid on Sn_{ad}-Pt

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Despite the considerable efforts to understand the mechanisms of the oscillatory electro-oxidation of formic acid (OEFA) on platinum, there still some key questions that remain opened. Especially regarding the role and identity of the species that blocks the surface sites during the oscillatory dynamic [1]. Surface modifiers, such as Sn [2] and Bi [3] are commonly used to enhance the catalytic activity. We present here an experimental investigation of the OEFA on Pt and on Sn modified Pt, as studied by *on line* Differential Electrochemical Mass Spectrometry (DEMS). Fig. 1 illustrates time-series of the electrode potential and of the CO_2 mass signal (m/z=44) for (a) Sn_{ad}-Pt and for (b) Pt. The main differences to be discussed are due to the premature formation of oxygenated species on Sn sites, that freed the surface sites for the direct oxidation path. The potential oscillations on Sn_{ad}-Pt visit lower potential values, in comparison to that on Pt, even with applied current density more than three times higher. We have also estimated the calibration constant for both case and calculated the average number of electrons (NE) per CO_2 molecule during the OEFA. For Sn_{ad}-Pt, NE is close to 2 and for Pt NE is higher than 2 in most applied currents, suggesting a non-CO pathway reaction on pure Pt sites that blocks the surface for further oxidation.

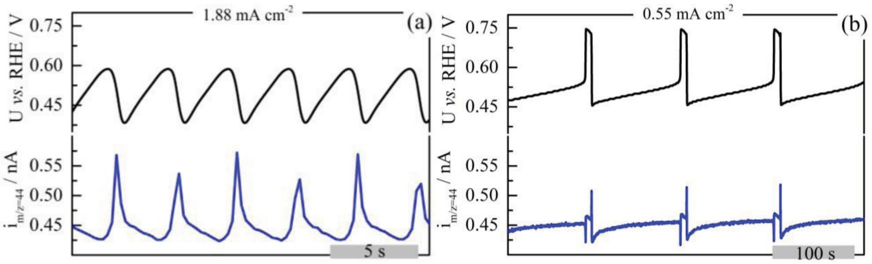

Fig. 1. Temporal series obtained at the electro-oxidation of the formic acid on (a) Sn_{ad}-Pt (θ_{Sn} = 0.78) (b) Pt surfaces. In aqueous solution with $[H_2SO_4]$ = 0.5 mol L^{-1} and [HCOOH] = 0.5 mol L^{-1}.

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Near-Ambient-Pressure-XPS studies of iridium during the oxygen evolution reaction

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Understanding the structural transformation of electrocatalyst surfaces upon the oxygen evolution reaction (OER) is essential for designing novel electrode materials. Using Near-Ambient-Pressure X-ray Photoelectron Spectroscopy (NAP-XPS), the chemical modification of an Iridium electrode surface during the dynamic interaction with water molecules in low temperature gas-phase electrolysis is investigated [1]. The sample consists of a Nafion® proton exchange membrane (PEM) that is sputter-coated on one side with the working electrode material Iridium and on the other side with the counter electrode material Platinum. Mounted on the continuous flow cell shown in Fig. 1, the sample is introduced into the NAP-XPS chamber. The water supplied on the counter electrode side diffuses through the mud crack type electrodes as well as the PEM and supplies the working electrode with the probe molecules. The cell allows for a simultaneous execution of electrochemical and surface sensitive spectroscopic measurements. At working electrode potentials sufficient for the OER to proceed, the resulting gas evolution is evidenced by on-line mass spectrometry while XPS and NEXAFS measurements allow the observation of changes in the electronic structure of Iridium.

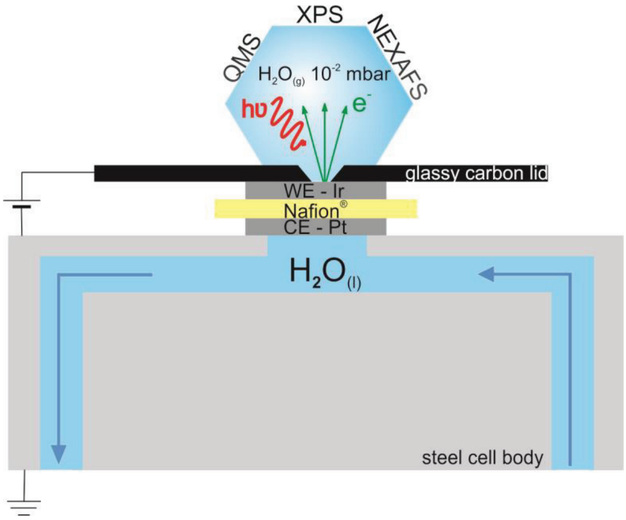

Fig. 1. Continuous liquid flow cell for *in situ* investigation. Water penetrates the porous Pt and Ir films, diffuses through the membrane and generates a water pressure in the range of mbars in the XPS chamber. The working electrode is exposed to the X-rays.

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The effect of random surface defects on the oscillatory electro-oxidation of methanol on Pt(100)

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The oscillatory electro-oxidation of methanol has been subject to many investigations [1,2]. Interesting aspects of the complex mechanism of this system have been provided by studies under oscillatory conditions [1]. In contrast to that for formic acid [3,4], there is no systematic studies of the oscillatory electro-oxidation of methanol on single crystal platinum surfaces. The present work fills this gap and investigate this reaction on Pt(100), Pt(110), and on Pt(111) surfaces. As we found potential oscillations only for Pt(100) surfaces, we have also investigate the role played by random surface defects created on this surface. The amount of surfaces defects was characterized in terms of the voltammetric signature response, and the oscillatory response studied under galvanostatic control. As the main result, observed two distinct oscillation regions depending on the degree of surface disorder, c.f. Fig. 1. Large amplitude oscillations (L) were found in the original Pt(100) electrode, and the appearance of small amplitude oscillations (S) accompanied the creation of surface defects. As recently reported by Mukouyama *et al*. [2], we found that oscillations L we significantly influenced by the presence of partially oxidized species. In contrast, for oscillations S, our results revealed that they depends essentially of surface processes and the need of random surface defects was interpreted as being due to the increase of the coverage of adsorbed carbon monoxide.

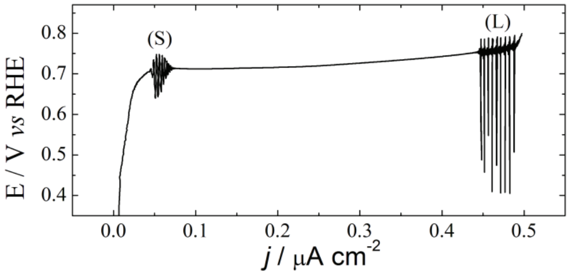

Fig. 1. Galvanodynamic sweeps of the system 0.2 M MeOH + 0.5 M H_2SO_4 on Pt(100) with random defects.

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Structural studies of hydrothermal carbon for the preparation of sustainable binder-free disc electrodes

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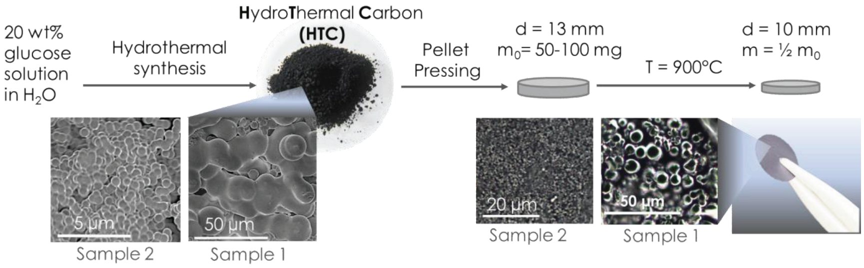
Functional carbon materials, synthesized by hydrothermal carbonization, offer a sustainable material basis from biomass feedstocks [1]. In contrast to highly graphitized supports, such as carbon nanotubes or carbon black, hydrothermal carbon (HTC) provides a higher number of functional groups which are essential for the fixation of catalyst nanoparticles [2]. In addition to particle anchoring, the high number of functional groups leads to beneficial binding properties. Hence, electrodes of desired mechanical stability can be prepared in macroscopic dimensions and devoid of binder additives. Upon thermal annealing the materials exhibit electric conductivity and can be used in electrode applications. The major advantage of this synthesis route is the possibility of post-analysis of used disc electrodes after electrochemical testing. The material quantity allows multiple analytical methods for post-analysis, while structural information are preserved and influences of binder additives are avoided.

Within the present work, we studied structural changes of HTC during the thermal annealing process by TG-MS, *in-situ* Raman spectroscopy and *in-situ* TEM. It could be shown that the spherical particle shape is preserved while the carbon scaffold transformed from a rather molecular state (high intensity of molecular vibrations by FT-IR) into carbonaceous material (characteristic carbon features by Raman spectroscopy). Although electric conductivity could be observed upon thermal annealing to 900°C by 4-point-probe measurements, graphitic structures were detected only locally on the particle surface by TEM. The major volume fraction of the material remained amorphous.



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Electrocatalytic oxygen evolution on iridium oxide thin-film catalysts: Impact of catalyst-substrate interactions and the applied iridium oxide species

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Water electrolysis emerges as key technology for the long-term storage of electrical energy. For this application proton exchange membrane (PEM) electrolyzers have the greatest potential due to low ohmic losses, low kinetic overpotentials and good partial load range [1]. One of the biggest challenges connected with PEM electrolyzers is to provide improved anode catalysts (anode: oxidation of water to oxygen, oxygen evolution reaction OER) which offer high catalytic activity and stability against corrosion [2].

Considering the OER, catalyst substrate interactions are rarely studied. This is remarkable, since the catalyst substrate junction is of great importance for the overall electrocatalytic activity of the system. For common OER catalyst systems, several different catalyst substrate interactions appear plausible, for instance the catalyst can be chemically influenced by the substrate or an interlayer of a new compound can be formed at the junction between catalyst and substrate. This interlayer can have deviating electrocatalytic activity and/or electric conductivity. Understanding and identifying materials at the catalyst substrate junction, their properties and their interactions are therefore of great importance for rational catalyst design.

Here, we present a study of Ir oxide thin-film catalysts on Ti substrates (see Fig. 1), where we first follow the evolution of the chemical nature of the dominant Ir oxide species as function of the annealing temperature. Particular emphasis is placed on the interactions of the Ir oxide film with the Ti substrate and how this interaction alters the Ir oxide properties. In the end, we achieve a correlation between the electrocatalytic OER activity of the Ir oxide films and their chemical state, but also take into account the influence of the substrate.

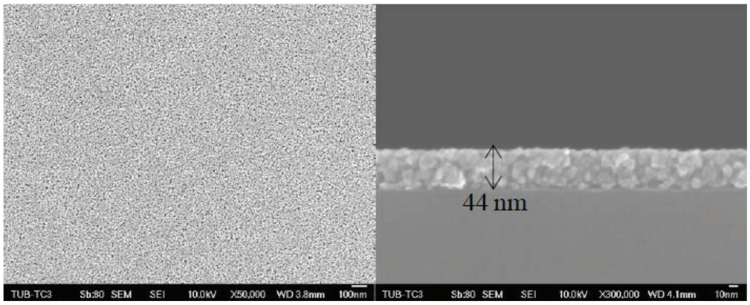

Fig. 1. SEM micrographs of iridium oxide model catalyst, left: top view and right: cross section.

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Tracking of surface metallization and exciton formation at the non-polar ZnO(10-10) and polar ZnO(000-1) surfaces

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Zinc oxide (ZnO) is natively n-type doped, transparent semiconductor (band gap of 3.4 eV), which is abundant and can be easily nanostructured, making it a promising electrode material for organic/inorganic hybrid devices, e.g. organic LEDs or photovoltaic cells. Surface band bending of the conduction band below the Fermi level enables the formation of a metallic charge accumulation layer (CAL) upon adsorption of electron donating molecules or atoms, such as hydrogen. It was shown that the CAL hosts the formation of a remarkably stable subsurface exciton (SX) [1] which is of particular interest in scope of interfacial charge and energy transfer.

We studied the influence of atomic H on two low-index surfaces of ZnO, the mixed-terminated (10-10) and the O-terminated (000-1) surface, using photoemission spectroscopy. On H/ZnO(10-10) the CAL signature passes a maximum intensity at a H dosage of 150 L and subsequent reduction at higher dosages accompanied by a maximum workfunction shift of -0.65 eV. In agreement with theory, this behavior can be accounted to the interplay of O-H and Zn-O bond formation, where O-H is responsible for the CAL formation, while the latter suppresses it [2]. In consistence with the absence of Zn sites, the CAL on the O-terminated ZnO(000-1) exhibits a saturation after ca. 100 L, rather than passing a maximum, and shows a workfunction shift of up to -1.6 eV.

Applying time-resolved two-photon photoemission spectroscopy (tr-2PPE) both ZnO surfaces reveal qualitatively similar physics regarding the fast relaxation processes of hot electrons in the conduction band via electron-phonon scattering and SX formation below the Fermi level. This independence of the surface termination corroborates the subsurface nature of the exciton species on ZnO and the localization of the downward surface band bending at OH-sites.

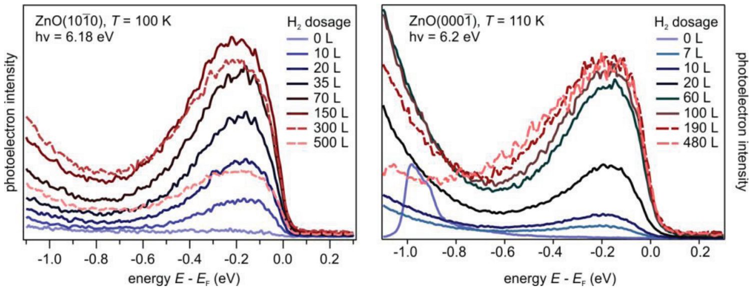

Fig. 1. CAL photoemission signature of ZnO(10-10) [1] and ZnO(000-1) with increasing hydrogen dosage.

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Design and synthesis of carbon-based nanostructures for electrochemical energy conversion

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The transition towards a more sustainable and less polluting society relies on the development of widely accessible, clean and renewable energies. Solid electrodes are key components in all devices where electrochemical reactions take place, such as electrolytic and fuel cells. To make this technology economically competitive and widely available, it is very important to find alternatives to current electrode materials, which contain large amounts of the scarce and expensive metal platinum. In this quest for the next generation of active and durable electrode materials, a central role has been recently attributed to carbon-based nanostructures incorporating heteroatom dopants (N, S, P, B, etc) [1-3], and their analogs additionally bearing non-precious metal species (Fe, Co, Mn, etc) [4-7] (Fig. 1). However, there is limited knowledge on the surface molecular structures responsible for the electrocatalytic activity as well as on the reasons underlying the observed beneficial synergism between different concomitant dopants, and how to rationally design these materials to maximize their occurrence.

Hence, we study and rationalize the design and synthesis of a new generation of doped carbon materials. Main focus is to gain control over not only the nature and content but also the nanometer/molecular scale spatial relative location of dopant atoms and metal oxide clusters. To this end, metal organic frameworks (MOFs) combined with conductive polymers, such as polypyrrole (which introduces N dopant in the final electrode), are explored as sources of electrode carbon materials with controlled nanostructures and original electrocatalytic properties (Fig. 1).

Spectroscopic characterization methods and evaluation of the electrochemical properties are applied to gain further insight into structure-performance relationships, in order to contribute to the rational design of electrode materials with a maximum occurrence of the preferred catalytic atom ensembles.

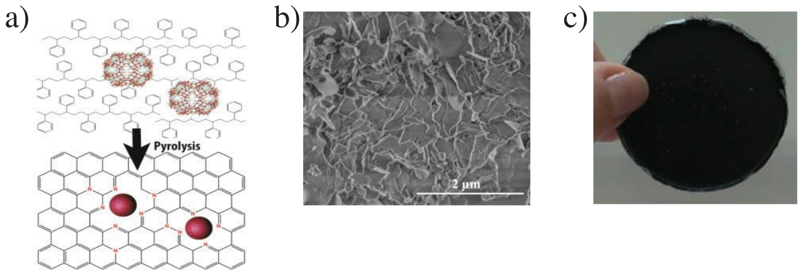

Fig. 1. a) Illustration of the proposed approach to synthesize metal/doped-carbon materials starting from MOF-polymer composites. During pyrolysis treatments, the polymer will provide a source of carbon, the organic linkers of the MOF will introduce doping sites in the vicinity of the metal oxide clusters (purple spheres), which derive from the metallic nodes of the MOF crystal. b) SEM micrograph of nanosheets crystals of a cobalt-based MOF. c) Picture of a film composed of Co-MOF dispersed within a polypyrrole matrix.

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Oscillatory electro-oxidation of ethanol on platinum: The effect of partially oxidized products

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The electro-oxidation of small organic molecules is a key topic in electrocatalysis due to its potential use in energy conversion systems. In particular, the electro-oxidation of ethanol has been topic of several researches in electrocatalysis as it is considered a green, renewable fuel and has low toxicity. We report herein an experimental study of the oscillatory electro-oxidation of ethanol on a polycrystalline platinum electrode. An important peculiarity to be highlighted in this system is the transient character of the potential oscillations in both alkaline and acidic media. Unlikely the cases of methanol, ethylene glycol, and glycerol under comparable conditions [1,2], oscillations in the electro-oxidation of ethanol were usually rather unstable, as exemplified in Fig. 1(a). Rotating electrode experiments, Fig. 1, reveal a strong dependence of the induction period, number of cycles and oscillation's frequency on the mass transport conditions. Altogether, these effects evidence that the removal of partially oxidized products from the electrode vicinity considerably compromises the stability of the oscillator. From the mechanistic perspective, we discuss this finding in terms of the role played by re-adsorption of a C2 species, presumably acetaldehyde, and its eventual dissociation into CO and/or CH_x adsorbates. Furthermore, we have also investigated the role of mass transport on the open circuit interaction of ethanol and oxidized platinum surfaces.

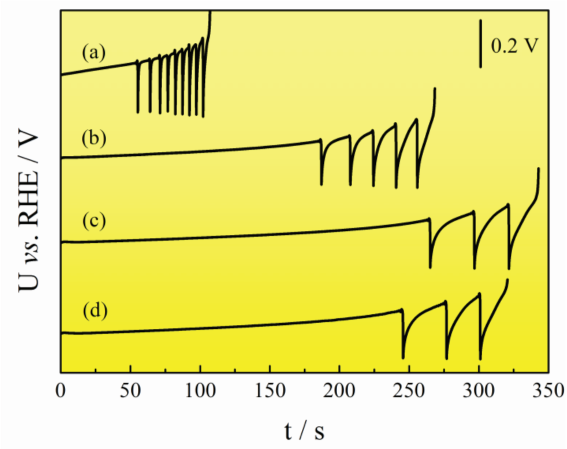

Fig. 1. The effect of mass transport on the oscillatory electro-oxidation of ethanol on Pt: (a) $\omega = 0$, (b) $\omega = 500$, (c) $\omega = 1500$, and (d) $\omega = 2500$ rpm. Electrolyte: [ethanol] = 0.5 mol L^{-1} in [KOH] = 1.0 mol L^{-1}, aqueous solution.

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Investigating the effect of different promoters in doped ZnO supports on Cu/ZnO catalysts for methanol synthesis

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Methanol is of increasing importance as an energy storage and carrier molecule. Although the Cu/ZnO/Al_2O_3 catalyst system has been used for the methanol synthesis for 50 years, it is still not fully understood. Cu is commonly regarded as the active phase, but the role of ZnO and Al_2O_3 is more than that of an inert support [1]. To study the promoter effect in more detail, we have prepared doped model supports ZnO:M (M = Al, Ga, Mg), which have been loaded with copper in a separated step.

The pure supports as well as the impregnated catalyst samples were characterized carefully by XRD, BET, TPR and electron microscopy. By conductivity measurements, UV-visible and EPR spectroscopy, insights into the electronic structure of the support and the role of different promoters were gained. Using a contactless conductivity measurement technique based on the microwave cavity perturbation technique [2], conductivity of the supports in inert, reducing and oxidizing gas environments were measured. Extremely different conductivity behavior was measured for the different supports (Fig. 1a). The impregnated Cu/ZnO:M catalysts were tested in methanol synthesis (Fig. 1b). Interestingly, the intrinsic activity of the catalysts scaled with the measured conductivities of the support suggesting a promotional effect via the modified electronic structure of the doped support.

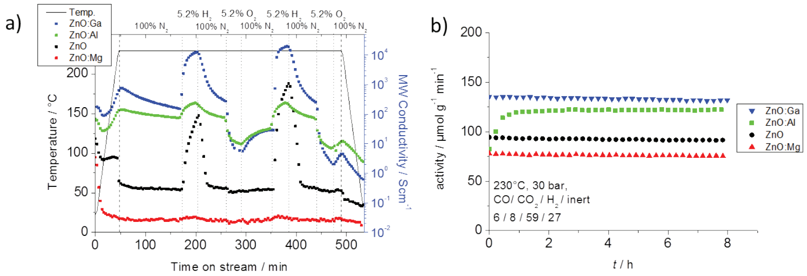

Fig. 1. a) conductivity of ZnO:M supports in different atmospheres; b) activity of Cu/ZnO:M catalysts in methanol synthesis.

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Preparation of 1-dimensional TiO_2 nanotubes with a doping of non-noble catalyst by single anodization

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There are several kinds of noble and non-noble metal(oxide) catalysts, such as Pt, Au, RuO_2, IrO_2, used in water splitting applications. Among them, non-noble catalysts such as WO_3, Ni and Co have great advantages with respect to cost. However, they have relatively low catalytic effects and serious corrosion problems. This triggers to find out new kinds of non-noble metal catalysts in TiO_2.

In this research, preparation of TiO_2 nanotubes with a doping of non-noble metal, such as Mn, on a Ti foil was investigated for enhancing an efficiency of OER (Oxygen Evolution Reaction) in water splitting. Single anodization was carried out in a mixed electrolyte of 1 M phosphoric acid and 1 M sodium hydroxide containing $KMnO_4$. As a result, Mn was doped into concurrently-grown TiO_2 nanotubes, after which was thermally annealed to increase the degree of bonding between the oxide and the manganese catalyst. The optimum condition for suitable amount and compositions of Mn was determined by linear sweep voltammetry to measure OER in KOH. Mn doping was evaluated by the structural analysis using SEM (Scanning Electron Microscope) and TEM (Transmission Electron Microscope) as well as component analysis using EDX (Energy Dispersive X-ray spectroscope).

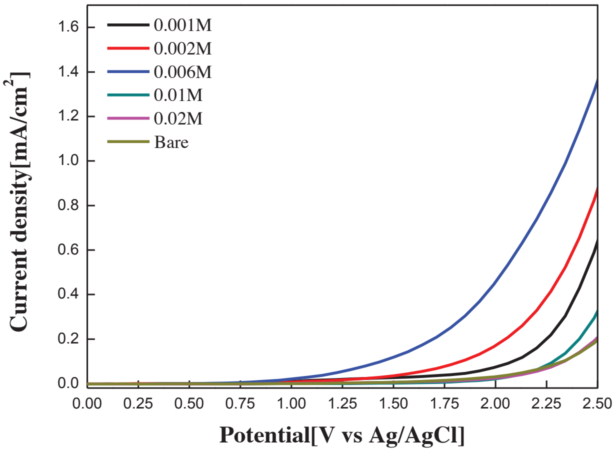

Fig. 1. Water splitting properties of TiO_2 nanotubes in terms of different $KMnO_4$ compositions.

Fuel cell catalysis getting in shape- Atomic-scale structure and catalysis of octahedral alloy nanoparticles

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Nanostructured core-shell and shape-selected nanoparticles have emerged as attractive families of catalytically highly active materials for the electroreduction of molecular oxygen (ORR) in energy conversion and storage devices. Their structural and compositional transformations upon contact with a corrosive electrolyte and under catalytic reaction conditions are complex, ranging from activation to degradation behavior. The way in which the reactive electrochemical environment affects the shape, structure and composition of electrocatalysts and thereby alter their catalytic activity is of great fundamental and practical importance.

We report on the preparation, structure and catalysis of spherical (Fig. 1) and shape-selected (Fig. 2) octahedral bimetallic Pt-Ni alloy nanoparticles for the electroreduction of oxygen in PEM fuel cells [1-7]. Atomic-scale insights are obtained using aberration-corrected microscopy (HR-TEM, STEM), spectroscopic studies (STEM-EELS, XPS), as well as scattering (XRD) techniques.

We uncovered unexpected self-organized core-shell fine structures, discuss the issue of nanoporosity, and highlight the synthesis, exceptional activity and unusual degradation behavior of octahedrally shaped Pt-Ni nanoparticles.

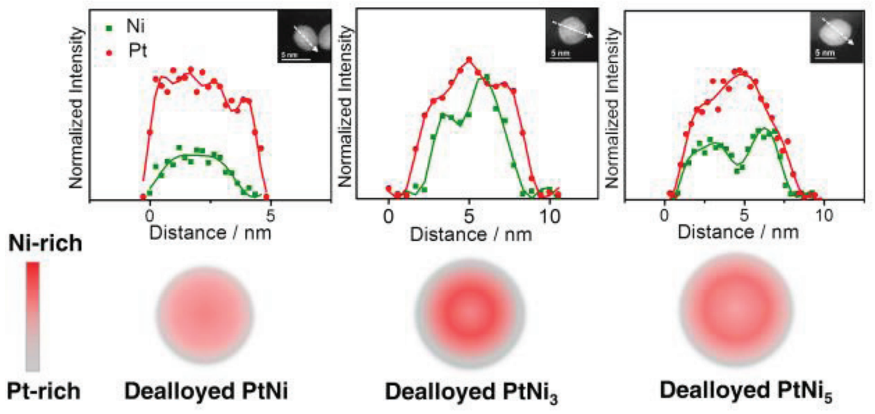

Fig. 1. Aberration-corrected STEM-EELS line scans of dealloyed Pt-Ni core-shell electrocatalysts, showing the formation of unusual near-surface Ni-enriched inner shells.

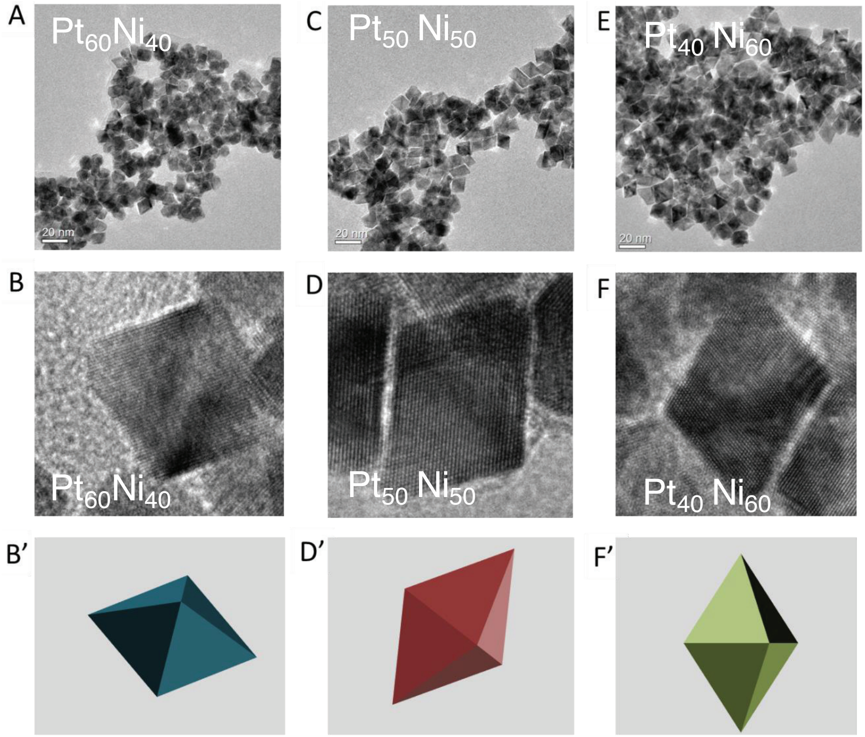

Fig. 2. Octahedral Pt-Ni nanoparticle electrocatalysts of varying overall compositions.

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Electrode materials from thermal annealed carbon with urotropine as N-precursor

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Electrode materials are an integral part in our daily lives in all electrochemical devices, such as mobile phones, electric cars or laptops. Due to the rising importance of global sustainability, efforts have been made to find alternatives to expensive noble and rare earth metal-containing electrode materials. In the last decades, carbon-based electrode materials proved to be a promising option.

The hydrothermal synthesis of carbon materials from biomass is a simple, nontoxic, low-cost, environmentally friendly and highly efficient method [1]. This synthetic technique provides novel carbon-based materials with plenty of possible applications in catalysis or in electrochemistry, as crucial fields for innovative solutions in the energy sector [1,2]. With the introduction of nitrogen, the carbon materials show higher stability towards degradation [3], higher conductivity [2], and high binding capacities for nanoparticles for improved catalytic activity [4].

Within this work, nitrogen-containing carbon materials have been synthesized by hydrothermal carbonization, using glucose as carbon source and urotropine as nitrogen source. The molar ratio of glucose and urotropine has been varied in order to achieve a gradual increase in the N-content. After pressing to pellets and thermal annealing, the obtained N-functionalized carbon materials reveal spherical particles of approximately 2 μm in size with maximal N-content of about 9 wt%.

The obtained materials were tested for their electron transfer properties by electric conductivity measurements and cyclic voltammetry (CV). Electric conductivity shows an increase of the conductivity with increasing the molar ratio of urotropine to glucose. Structural information were gained by Raman spectroscopy, electron microscopy and EELS.

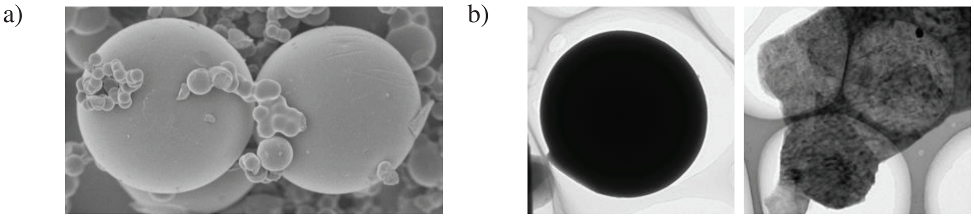

Fig. 1. a) SEM and b)TEM image of a thermal annealed N-functionalized carbon material.

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Towards structure-activity relationships of photocatalysts based on isolated titanate species on SBA-15

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Photocatalysts based on isolated, tetrahedral titanate species are among the most studied systems for the reduction of CO_2 to hydrocarbons since the 1990s [1]. However, correlations that link the photocatalytc properties to structural features of this system are still mostly unknown. Such studies are complicated by the necessity to use reliable means for product quantification and characterization in the ppm-range, together with proper pretreatment procedures of the photocatalyst [2].

In the present contribution, a high-purity gas-phase photoreactor system with GC trace gas analysis has been used to study the catalytic activity of titanate-based photocatalysts for CO_2 reduction (Fig. 1) [3]. Both titanate species grafted onto SBA-15 and incorporated into silica walls are active photocatalysts for the reaction, and methane is the main product. A significant stoichiometric excess of CO_2 is beneficial to improve product yields. This might be attributed to an influence of the reverse reaction [4] or the weak adsorption of CO_2 on the photocatalyst. Either the grafting of ZnO agglomerates or the photodeposition of gold nanoparticles to the isolated titanate on SBA-15 can improve the photocatalytic activity. A titanium-rich shell formed around the photodeposited gold nanoparticles was found to influence the electron transfer in photocatalytic processes [5]. The hole transfer, on the other hand, requires the presence of Ti-O-Si linkages, and Ti-O-Zn linkages appear to be inactive in this respect.

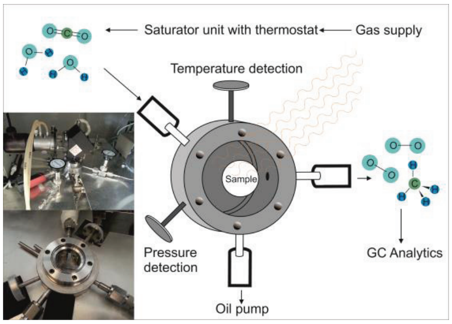

Fig. 1. High-purity gas-phase photoreactor system.

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Exploring the role of nitrogen incorporation in titanium and the effect in their photo and electrochemical properties

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The role of the nitrogen incorporation, its chemical nature, the location in the titanium lattice and its photo-electrochemical performance was investigated by a combination of several spectroscopy and microscopy techniques using samples prepared by CVD of NH_3 at different temperatures and successive treated electrochemically in 1 M of $HClO_4$. We found that nitrogen is incorporated in either the interstitial or substitutional site of the lattice depending on the temperatures modifying strongly their properties explaining the controversial results present in the literature [1-4]. The interstitial nitrogen induces doping (ionic bonds) but suffers from low stability under electrochemical environments in spite to the interstitial (covalent bonds) that is more stable under such conditions. N-doping affects drastically their electrical-optical properties as well as outstanding oxidation and acid corrosion resistance. In addition, the incorporation of N and its ability to absorb visible light has been investigated by a detailed examination of the valence band which revealed the formation of an additional energy level between Ti_{3d} and O_{1s}. This energy level position is shifted by the lack of stability in aggressive electrochemical environments and due to the adsorbed OH species after electrochemical treatment inducing an increase in the band gap which should affects the photocatalytic throughput (see Fig. 1). This effect has not been observed on TiO_2 which suggests that the O_2/H_2O adsorption is enhanced by the incorporation of nitrogen.

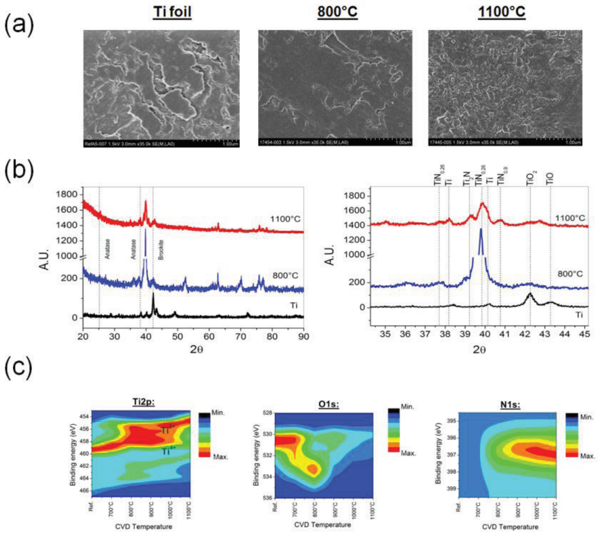

Fig. 1. a) CVD of TiN_x process, temperature vs- time. b) Ti_{2p} XPS spectra *vs*. temperature. c) O_{1s} XPS spectra *vs*. temperature. b) N_{1s} XPS spectra *vs*. temperature.

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Thermal-oxidative degradation of multiwall carbon nanotubes (MWCNTs); Its effect for electrochemical activity and stability

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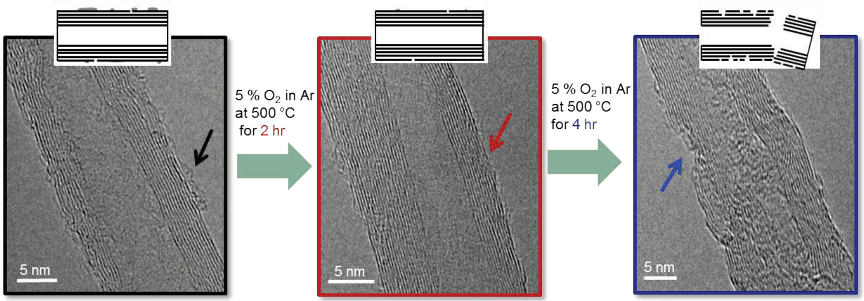
Carbon nanotubes (CNTs) are one of the most economically competitive materials for energy-related technologies and have a variety of physicochemical properties due to their unique structure. Particularly, CNTs are extensively utilized in heterogeneous catalysis and electrocatalysis, either as a catalyst itself or as a catalyst support. However, some applications of CNTs have been limited so far due to the inherent instability of carbon. Carbon is thermally oxidized to gaseous products at high temperature (above circa 400 - 600°C) in oxidative environments. Gas phase oxidation of CNTs damages carbon structures and introduces oxygenated functional groups that represent the sites where the degradation is initiated upon utilization. On the other hand, if it is done in a controlled way, it can positively introduce beneficial oxygenated functional groups for potential applications.

In this study, we report on the thermal oxidative degradation of multiwall carbon nanotubes (MWCNTs). The MWCNTs were thermally oxidized at a temperature at which carbon starts to be oxidized and/or combusted. We monitored the thermal degradation process of MWCNTs over a period of time and its effect on physicochemical properties. Furthermore, to assist in the development of practical applications of CNTs, the thermal and electrochemical behavior of the thermally oxidized CNTs was investigated. With respect to electrochemical characterizations, we focused on the electrochemical oxidation activity and stability/degradation behavior at a high anodic potential. These findings are valuable for the research and application of MWCNTs in energy storage and conversion technology.



Initial MWCNTs **Purification** **Graphite oxidation**

Fig. 1. TEM images and schematic diagrams of the thermal oxidative degradation of MWCNTs.

Assembling capability of silver deposits upon hydrogen electro-oxidation on platinum

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The hydrogen oxidation reaction (HOR) due to the catalytic activity of Pt has been extensively investigated. H_2 adsorbs dissociatively on the Pt surface [1,2]. The overpotential deposition of Ag (OPD) on poly and single crystalline Pt in the presence of H_2 has been investigated by electrochemical techniques and scanning electron microscopy (Fig. 1).

The main goal was to evaluate the assembling capability of Ag deposits, obtained from an aqueous $HClO_4$ and $AgClO_4$ system saturated with N_2 and H_2, and to follow the morphological changes upon HOR. It was found that Ag deposition occurred concomitantly to the HOR and therefore they competed for the Pt sites. Via chronoamperometry and cyclic voltammetry the amount of Ag deposited was determined at certain potential and time, and besides gave some insights about the mechanism of nucleation and crystal growth. A large HOR current remained after depositing more than 50 monolayers of Ag, indicating an open structure. At a deposition potential of -0.120 V (*vs.* Hg^0/Hg_2SO_4) an induction period occurred in the chronoamperometry curve due to the kinetics of nucleation and crystal growth in this region, especially evident for the N_2 saturated system. Under certain conditions, dendritic deposits were formed. It is known that these structures are formed only from a critical OP value and such structures are highly organized, growing in well-defined directions [3]. In conclusion, H_2 electro-oxidation reduces the surface energy, facilitating the adatoms mobility [4], explaining the dendrites and self-assembled structures.
Acknowledgements to CNPq.

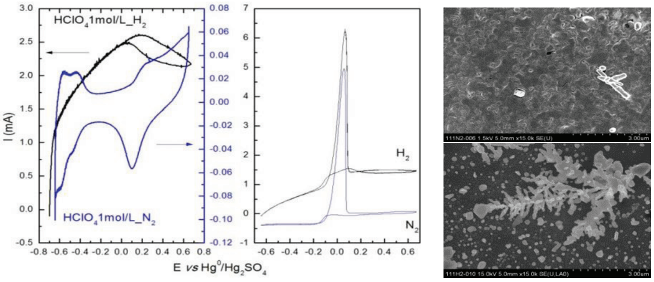

Fig. 1. CVs of a rotating Pt polycrystalline electrode. Scan rate: 50 mV s^{-1} and rotating rate 1500 rpm. SEM images of silver deposited on Pt(111) at = -0.450 V, 60 s. a) N_2 and b) H_2 saturated.

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The effect of temperature on the fast and slow dynamics during the oscillatory electro-oxidation of formic acid on platinum

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We have recently explored the effect of the slow and uncontrollable surface changes in the time-series registered during the electro-oxidation of small organic molecules on platinum [1,2]. The emergence of disparate time-scales results mainly from two sets of surface reactions, one responsible for the core oscillator, and one underlying the slowly evolving surface poisoning that drives the system through the phase space. We studied the effect of temperature on the long-term evolution of these surface processes for the electro-oxidation of formic acid on platinum at five temperatures from 5 to 45ºC. Typical results of the surface evolution are presented in Fig. 1, where the complete time-series is presented together with some snapshots of the different patterns that spontaneously appear despite the constancy of all controllable parameters. As the system evolves, different patterns develop and features such as amplitude, waveform, and oscillation's frequency can be used as a signature of the surface evolution. This evolution was studied at distinct temperatures and characterized in terms of short- and long-term dynamics. As an example of the obtained results, we found that the total oscillating time decreases and increases with temperature in the ranges between 5 to 25ºC, and 25 and 45ºC, respectively. The general dependence is rationalized in terms of the complex interplay between the dynamics of the core oscillator and of the slowly evolving surface poisoning.

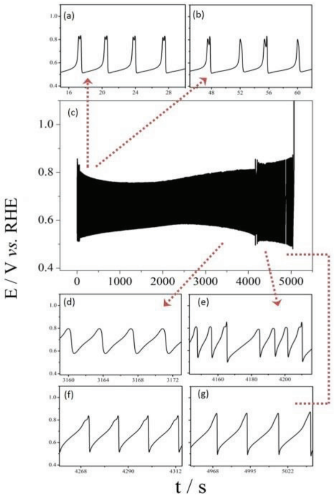

Fig. 1. Galvanostatic experiment obtained at 5ºC. The overall potential time-series is presented in (c). Some zoomed regions in (a), (b), (d), (e), (f), (g) showing the pattern evolution. Electrolyte solution: H_2SO_4 0.5 M + HCOOH 1 M. Pt poly. as working electrode (EA 0.25 cm^2).

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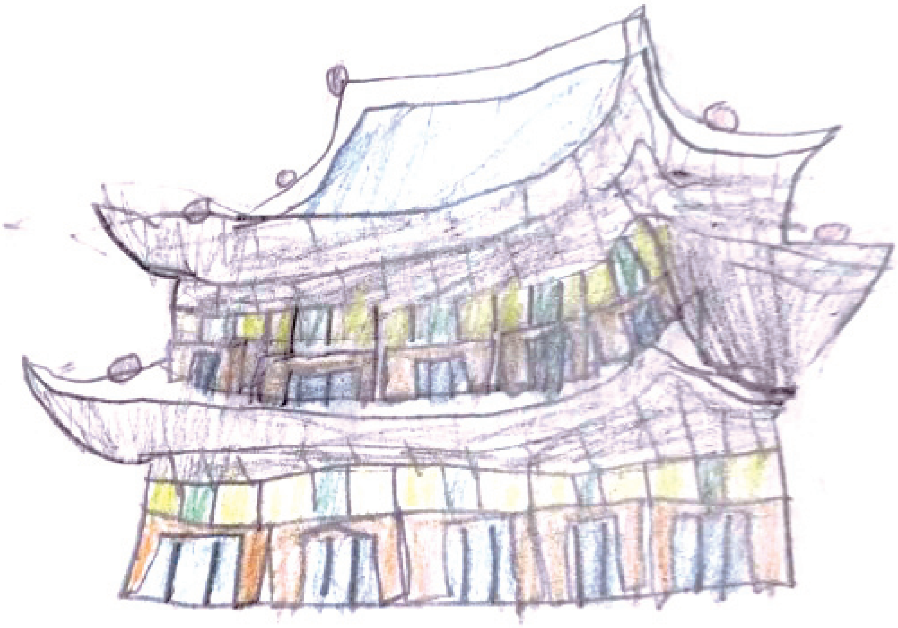

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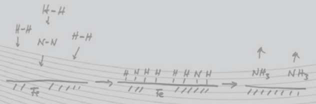

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