

7<sup>th</sup> Annual Ambient pressure  
X-ray Photoelectron Spectroscopy  
workshop 2020

15<sup>th</sup> – 17<sup>th</sup> December 2020  
Pohang, South Korea

## Greeting

On behalf of Pohang Accelerator Laboratory and Gwangju Institute of Science and Technology, we would like to welcome everyone to the APXPS-2020 workshop. For the first time in the history of the APXPS workshop, the entire program is prepared online due to the COVID-19 pandemic. Nonetheless, with much support and participation from the global communities of APXPS, we have secured total 88 presentations with 173 registrations, which exceed our expectation by far.

As previous workshop, APXPS-2020 is organized as 3-day event, which features plenary/invited presentation, contributed presentation, and poster session. To create more live environment and encourage active participation in the workshop, “Once-a-day Get-together” sessions are arranged and volunteered plenary/invited speakers will deliver real-time online presentation. Also, a special technical session is added for sharing practical information for gas delivery system and related safety regulations in several synchrotron facilities, which can help many potential users in future.

We hope every participant can enjoy the workshop and benefit from the works of our community. The objective of the workshop is to share the latest scientific results related to APXPS technique as well as to provide diverse knowledge in the field of APXPS community, promoting further development of entire APXPS scientific community. Last, but not least, we would like to thank all the sponsors for their gracious contributions.

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## Plenary/Invited speaker

	Giulia Galli	University of Chicago
Plenary talk	Ulrike Diebold	Technische Universität Wien
	Yung-Eun Sung	Seoul National University/Institute for Basic Science
	Jun Yoshinobu	University of Tokyo
	ChunJung Kim	Chungnam National University
	Bilge Yildiz	Massachusetts Institute of Technology
	Jeongjin Kim	Massachusetts Institute of Technology
	Jungwon Park	Seoul National University
	Beibei Wang	Shanghai Tech. University
Invited talk	Marco Favaro	Helmholtz Zentrum Berlin
	Neus Domingo Marimon	Catalan Institute of Nanoscience and Nanotechnology
	Francois Rochet	Sorbonne Université
	Toshihiko Yokoyama	Institute for Molecular Science
	WooChul Jung	Korea Advanced Institute of Science and Technology
	Kug-Seung Lee	Pohang Accelerator Laboratory
	Yi-chun Lu	Chinese University of Hong Kong

Jan Knudsen

Lund University

Luca Artiglia

Paul Scherrer Institute

Iradwikanari Waluyo

Brookhaven National Laboratory

Sanjaya Senanayake

Brookhaven National Laboratory

## Time table

Real-time [RT] Pre-recorded [PR] [P: Plenary I: Invited C: Contributed T: Technical Po: Poster]

### [DAY 1] Tuesday 15 December 2020

- 22:00 – 22:05**     **Opening Remark (Ki-Jeong Kim, PAL)**
- 22:05 – 22:10**     **Welcoming Remark (In Soo Ko, Director of PAL)**
- 22:10 – 22:35     **[I01] Jun Yoshinobu, University of Tokyo**  
*Hydrogen induced chemical processes observed by ambient pressure X-ray photoelectron spectroscopy and other methods*
- 22:35 - 23:00     **[I02] Chunjoong Kim, Chungnam National University**  
*Study about the Energy Storage Mechanism in Dimethylphenazine*
- 23:00 - 23:25     **[I03] Bilge Yildiz, Massachusetts Institute of Technology**  
*In-situ Probing Catalyst Generation and Deactivation with Ambient Pressure X-ray Photoelectron Spectroscopy*
- 23:25 - 23:40**     **Coffee Break**
- 23:40 - 0:15     **[P01] Giulia Galli, Argonne National Laboratory, University of Chicago**  
*Computational spectroscopy from first principles*
- 0:15 - 0:35     **[I04] Jeongjin Kim, Massachusetts Institute of Technology**  
*Bridging the Pressure Gap: Molecular Collision and Adsorption Structure on Single Crystal Model Surfaces between UHV and Ambient Pressure*
- 0:35 - 0:55     **[I05] Jungwon Park, Seoul National University**  
*Liquid phase TEM for studying catalysis and electrochemistry of nanomaterials*
- 0:55 - 1:15     **[I06] Beibei Wang, Shanghai Tech.**  
*Formation and Stability Enhancement of Surface Hydrides for Hydrogenation Reactions with Metal-Oxide Interface*
- 1:15 - 1:35     **[I07] Sanjaya Senanayake, Brookhaven National Laboratory**  
*Sequencing Methanol Synthesis Pathways for the Selective Conversion of C-H bonds using AP-XPS*
- 1:35 - 1:50     **[C01] Baran Eren, Weizmann Institute of Science**  
*Surface chemistry of copper during methanol conversion reactions: An AP-XPS and AP-NEXAFS Study*

Real-time [RT] Pre-recorded [PR] [P: Plenary I: Invited C: Contributed T: Technical Po: Poster]

- 1:50 – 2:05 **[C02] Christopher Goodwin, Stockholm University**  
*Grazing-incidence high-pressure XPS to determine the structure of Pd during catalytic CO oxidization*
- 2:05 - 2:20 **[C03] Fabiano Bernardi, Instituto de Física, Universidade Federal do Rio Grande do Sul (UFRGS)**  
*Probing the electronic nature of the SMSI effect in Pd/TiO<sub>2</sub> nanoparticles*
- 2:20 - 2:35 **[C04] Felix Brausse, Lawrence Berkeley National Laboratory**  
*Exploiting Temporal Correlations in Core-Shell Photoelectron Spectroscopy: Potential Applications for Ambient-pressure Experiments*
- 2:35 - 2:50 **[C05] Freddy E. Oropeza, IMDEA Energy Institute**  
*Interface Energetics of Photoelectrodes Under Relevant Conditions*
- 2:50 - 3:05 **[C06] Heath Kersell, Lawrence Berkeley National Laboratory**  
*A Simultaneous Probe for Chemical and Structural Transformations in Ambient Pressure Environments*
- 3:05 - 3:20 **[C07] Kenneth Goodman, Lawrence Berkeley National Laboratory**  
*Water-gas Shift Reactivity of Size-Selected Ti<sub>x</sub>O<sub>y</sub> nanoclusters supported on Cu(111) utilizing Near Ambient Pressure XPS*
- 3:20 - 3:35 **[C08] Christopher Arble, National Institute of Standards and Technology**  
*Investigation of Radiolytic Damage of Liquid Electrolyte during Focused X-ray Photoelectron Spectroscopy and Microscopy*
- 3:35 - 3:50 **[C09] Haiko Wittkämper, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)**  
*Spectroscopic Insights to Pt-, Pd- and Rh-Ga Alloys as Models for SCALMS Catalysts during Oxidation*
- 3:50 - 4:05 **[C10] Oleg Kostko, Advanced Light Source**  
*Local electronic structure of histidine in aqueous solution*
- 4:05 - 4:10 **[Po01] Ashley Head, Brookhaven National Laboratory**  
*Early Successes & Exciting Developments with the Lab-based APXPS & IRRAS at the Center for Functional Nanomaterials*
- 4:10 - 4:15 **[Po02] Chanyang Song, Gwangju Institute of Science and Technology**  
*Study of oxidation states of SrTiO<sub>3</sub>(001) surface using AP-XPS*

Real-time [RT] Pre-recorded [PR] [P: Plenary I: Invited C: Contributed T: Technical Po: Poster]

- 4:15 - 4:20 **[Po03] Chaya Weeraratna, Lawrence Berkeley National Laboratory**  
*Studying Soft X-ray Spectroscopy of Aerosol Nanoparticles using Velocity Map Imaging*
- 4:20 - 4:25 **[Po04] Chih-Yang Huang, National Taiwan University and Academic Sinica**  
*Probing Adsorbate-Induced Band Bending and Photocatalytic intermediates via Ambient Pressure X-ray photoelectron spectroscopy on CO<sub>2</sub> Reduction Reaction*
- 4:25 - 4:30 **[Po05] David C. Grinter, Diamond Light Source**  
*VerSoX B07-B: A New Beamline for Ambient Pressure X-ray Absorption Spectroscopy and High-Throughput X-ray Photoelectron Spectroscopy*
- 4:30 - 4:35 **[Po06] David Degerman, Stockholm University**  
*Adsorbate coverages and the relation to reaction barriers during CO and CO<sub>2</sub> hydrogenation on Rh single Crystals*
- 4:35 - 4:40 **[Po07] Dongwoo Kim, Gwangju Institute of Science and Technology**  
*The study of bandgap tuning in post-annealed Ga<sub>2</sub>O<sub>3</sub> film with ambient pressure XPS*
- 4:40 - 4:45 **[Po08] Emilia A. Carbonio, BESSY II**  
*Increasing selectivity of direct alkene epoxidation on silver*
- 4:45 - 4:50 **[Po09] Fernando Garcia-Martinez, Centro de Fisica de Materiales**  
*CO oxidation on vicinal Rh surfaces studied with a curved crystal*
- 4:50 - 4:55 **[Po10] Frederic Sulzmann, Fritz-Haber-Institut der Max-Planck-Gesellschaft**  
*Strongly bound oxygen on silver and their role in methanol oxidation*
- 4:55 – 5:00 **[Po11] Giovanni Esteban Gonzales Urrego, Universidad de Antioquia**  
*An Ambient Pressure XPS approach to redox properties change in a Co<sub>3</sub>O<sub>4</sub> thin film modified by Mn cations*
- 5:00 - 5:05 **[Po12] Haamidah Sana, Diamond Light Source**  
*AP-XPS / NEXAFS Study of Thin-Film Al<sub>2</sub>O<sub>3</sub> Catalyst Supports Prepared via Anodization*
- 5:05 - 5:10 **[Po13] Harald Wallander, Malmö University**  
*Oxide formation and reactivity oscillations on Pt<sub>3</sub>Sn(111) during CO oxidation*
- 5:10 - 5:15 **[Po14] Hoan Nguyen, Oregon State University**  
*Ambient Pressure X-Ray Photoelectron Spectroscopy Study of Thermal Decomposition of Acetic Acid on Pd(111)*

Real-time [RT] Pre-recorded [PR] [P: Plenary I: Invited C: Contributed T: Technical Po: Poster]

5:15 - 5:20

**[Po15] Hojoon Lim, Gwangju Institute of Science and Technology**

*Correlation between structural phase transition and surface chemical properties of thin film SrRuO<sub>3</sub>/SrTiO<sub>3</sub> (001)*

## [DAY 2] Wednesday 16 December 2020

**22:00 – 22:10**

**Today's Guide**

22:10 – 22:45

**[P02] Ulrike Diebold, Vienna University of Technology (TU Wien)**

*Well-controlled surface systems for APXPS*

22:45 - 23:10

**[I08] Marco Favaro, Helmholtz Zentrum Berlin**

*Investigation of a model metal/non aqueous electrolyte interface using in situ AP-HAXPES*

23:10 - 23:35

**[I09] Neus Domingo Marimon, Institut Català de Nanociència i Nanotecnologia**

*Water splitting reactions on oxide perovskites by AP-XPS*

**23:35 - 23:50**

**Coffee Break**

23:50 - 0:15

**[I10] Francois Rochet, Sorbonne Université**

*Testing the Cabrera-Mott Oxidation Model for Aluminum in realistic conditions with Near Ambient Pressure Photoemission*

0:15 - 0:35

**[I11] Toshihiko Yokoyama, Institute for Molecular Science**

*Ambient Pressure Hard X-ray Photoelectron Spectroscopy on Polymer Electrolyte Fuel Cells under Working Conditions*

0:35 - 0:55

**[I12] WooChul Jung, Korea Advanced Institute of Science and Technology**

*Direct Electrochemical Oxidation of Methane at Ceria/Gas Interface*

0:55 - 1:15

**[I13] Kug-Seung Lee, Pohang Accelerator Laboratory**

*Introduction of X-ray Absorption Fine Structure and its Application in 8C Beamline at PAL*

1:15 - 1:35

**[I14] Yi-chun Lu, The Chinese University of Hong Kong**

*Probing Metal-Oxygen Reaction Interfaces via In Situ Ambient Pressure X-ray Photoelectron Spectroscopy*

Real-time [RT] Pre-recorded [PR] [P: Plenary I: Invited C: Contributed T: Technical Po: Poster]

- 1:35 - 1:50 **[C11] Matthijs A. van Sprosen, Diamond Light Source**  
*Evolution of Steady-state Material Properties during Catalysis: Oxidative Coupling of Methanol over Nanoporous Ag<sub>0.03</sub>Au<sub>0.97</sub>*
- 1: 50 - 2:05 **[C12] Pinar Aydogan Gokturk, Advanced Light Source, Lawrence Berkeley National Laboratory**  
*Direct observation of chemistry-dependent hydration on polymer thin films: in situ APXPS study*
- 2:05 - 2:20 **[C13] Rafik Addou, School of Chemical, Biological, and Environmental Engineering, Oregon State University Corvallis**  
*Operando Studies of Surface Oxidation Reactions at Gas/Solid Interfaces by Ambient Pressure X-Ray Photoelectron Spectroscopy*
- 2:20 - 2:35 **[C14] Remi Dupuy, Fritz Haber Institute of the Max Planck Society**  
*Cooperative Effect of Carbonaceous Material with Water Enhances the Growth of SiO<sub>x</sub> on Si*
- 2:35 - 2:50 **[C15] Rongtan Li, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, the Chinese Academy of Sciences**  
*Oxygen-adsorption driven high dispersion of Ag nanoclusters revealed by NAP-XPS*
- 2:50 - 3:05 **[C16] J. Trey Diulus, Physics Institute, University of Zürich**  
*Thermal Oxidation of Ru(0001) to RuO<sub>2</sub>(110) Studied with Ambient Pressure X-ray Photoelectron Spectroscopy*
- 3:05 - 3:20 **[C17] Zhengrong Lee, Illinois Institute of Technology**  
*H<sub>2</sub>O Reactivity of TRISO Fuel Layers Probed with Ambient Pressure Photoelectron Spectroscopy*
- 3:20 - 3:35 **[C18] Qiyang Lu, School of Engineering, Westlake University**  
*Understanding Chemical and Electronic Heterogeneity across Solid/Liquid and Solid/Solid Interfaces by Standing-Wave Ambient-Pressure Photoemission Spectroscopy (SWAPPS)*
- 3:35 - 3:50 **[C19] Thorsten Bartels-Rausch, Laboratory of Environmental Chemistry, Paul Scherrer Institut**  
*Precisely mimicking environmental conditions to observe phase changes by near ambient pressure X-ray absorption spectroscopy: supercooled liquid and hydrohalite at interfaces*

Real-time [RT] Pre-recorded [PR] [P: Plenary I: Invited C: Contributed T: Technical Po: Poster]

- 3:50 - 4:05 **[C20] Yifan Ye, Lawrence Berkeley National Lab**  
*Elucidating Ions Adsorption Competition at Electrified Interface by Ambient Pressure X-ray Photoelectron Spectroscopy*
- 4:05 - 4:10 **[Po16] Juan Tapia, Universidad de Antioquia UdeA**  
*Interaction between  $\text{LaMnO}_{3-\delta}$  perovskite (R-3c) surface and small molecules ( $\text{Ar}$ ,  $\text{CO}$ ,  $\text{O}_2$ ,  $\text{H}_2$ ): An XPS-NAP Analysis*
- 4:10 - 4:15 **[Po17] Minsik Seo, Gwangju Institute of Science and Technology**  
*Study of XPS satellite features under elevated pressure condition*
- 4:15 - 4:20 **[Po18] Moonjung Jung, Gwangju Institute of Science and Technology**  
*Investigation of surface chemical states of Pt-based alloys,  $\text{Pt}_3\text{M}$  ( $\text{M}=\text{Ti}$ ,  $\text{V}$ ), during  $\text{CO}$  oxidation by AP-XPS*
- 4:20 - 4:25 **[Po19] Nicolo Comini, University of Zürich**  
*Factors influencing surface carbon contamination in ambient-pressure XPS*
- 4:25 - 4:30 **[Po20] Patrick Loemker, DESY**  
*Observing the Fischer-Tropsch reaction on  $\text{Co}(0001)$  at 150mbar and above using a virtual cell approach and hard X-rays*
- 4:30 - 4:35 **[Po21] Pip Clark, Helmholtz-Zentrum Berlin**  
*A Flow-Focused Droplet Train for Ambient Pressure XPS with tender X-rays*
- 4:35 - 4:40 **[Po22] Rossella Yivliain, Helmholtz-Zentrum Berlin**  
*Ambient pressure X-ray photoelectron spectroscopy studies of electrochemically mediated regeneration of amine solutions for  $\text{CO}_2$  capture technologies*
- 4:40 - 4:45 **[Po23] Ryo Toyoshima, Keio University**  
*In situ oxidation of Pd and Pd-Au alloy surfaces*
- 4:45 - 4:50 **[Po24] Sabrina Gericke, Lund University**  
*Characterization of an  $\text{In}_2\text{O}_3(111)$  model catalyst for methanol synthesis by  $\text{CO}_2$  hydrogenation*
- 4:50 - 4:55 **[Po25] Sheng-Yuan Chen, National Tsing Hua University**  
*Ambient Pressure XPS Study of  $\text{CO}_2$  Photoreduction on  $\text{Cs}_3\text{Bi}_2\text{I}_9$  and  $\text{Rb}_3\text{Bi}_2\text{I}_9$  Perovskite Nanomaterials with Reactivity Enhanced by Ligand Removal*
- 4:55 - 5:00 **[Po26] Tobias Egle, Harvard University**  
*Dynamic metal/metal oxide interface affects PdAg reactivity*

Real-time [RT] Pre-recorded [PR] [P: Plenary I: Invited C: Contributed T: Technical Po: Poster]

- 5:00 - 5:05 **[Po27] Xiangrui Kong, University of Gothenburg**  
*Surface-Catalyzed Oxidation-Reduction on Solvating Aerosol Surfaces*
- 5:05 - 5:10 **[Po28] Xiansheng Li, ETH Zürich and Paul Scherrer Institut**  
*Role of Water on the Structure of Palladium for Complete Oxidation of Methane*
- 5:10 - 5:15 **[Po29] Xueqiang Zhang, Lawrence Berkeley National Laboratory**  
*H<sub>2</sub>O/O<sub>2</sub> interactions with Ir and IrO<sub>2</sub> probed by APXPS*
- 5:15 - 5:20 **[Po30] Yaw-Wen Yang, National Tsing Hua University and NSRRC**  
*APXPS Study of UV Photocatalytic Reduction of CO<sub>2</sub> on ZnO/Cu<sub>2</sub>O Nanoparticle Heterojunction*

## [DAY 3] Thursday 17 December 2020

- 22:00 – 22:05** **Today's Guide**
- 22:05 – 22:10** **Virtual Tour** (Moonjung Jung, Gwangju Institute of Science and Technology)
- 22:10 – 22:45** **[P03] Yung-Eun Sung, Seoul National University**  
*Insights into Electrochemistry from In Situ/Operando Characterization*
- 22:45 - 23:10** **[I15] Jan Knudsen, Lund University**  
*Event-averaged stroboscopic ambient pressure photoelectron spectroscopy as a new tool to follow surface kinetics of catalytic active surfaces*
- 23:10 - 23:35** **[I16] Luca Artiglia, Paul Scherrer Institute**  
*Structure-activity evolution of platinum species supported on ceria exposed to different reaction environments*
- 23:35 - 23:50** **Coffee Break**
- 23:50 - 0:15** **[I17] Iradwikanari Waluyo, Brookhaven National Laboratory**  
*Surface Chemical State of Pt/Cu(111) Single-Atom Alloy in Reaction Conditions Intro.*
- 0:15 – 0:20** **Closing Remark** (Bongjin Simon Mun, Gwangju Institute of Science and Technology)
- 0:20 - 0:35** **[C21] Andrey Shavorskiy, MAX-IV Laboratory, Lund University**  
*Gas Pump X-ray Probe APXPS for Studies in Catalysis with sub-ms Time Resolution*

Real-time [RT] Pre-recorded [PR] [P: Plenary I: Invited C: Contributed T: Technical Po: Poster]

- 0:35 - 0:50 **[C22] Foqia Rehman, Lund University**  
*Time evolution of surface species and oxygen transport during atomic layer deposition of TiO<sub>2</sub> on RuO<sub>2</sub>(110) studied by ambient pressure XPS*
- 0:50 - 1:05 **[C23] Giulio D'Acunto, Lund University**  
*Systematic study of atomic layer deposition of HfO<sub>2</sub> on TiO<sub>2</sub>: space state of temperature and pressure*
- 1:05 - 1:20 **[C24] Juan J. Velasco-Velez, Fritz-Haber-Institute der Max-Planck-Gesellschaft / Max Planck Institute for Chemical Energy Conversion**  
*Correlating APXPS with ESEM, one experimental example: The electrocatalytic CO<sub>2</sub>RR on copper oxide electrodes*
- 1:20 - 1:35 **[C25] Matthew Fraund, Lawrence Berkeley Laboratory**  
*Monitoring photoinduced charge transfer dynamics in nanoparticle-sensitized light-harvesting systems using time-resolved ambient pressure x-ray photoelectron spectroscopy*
- 1:35 - 1:50 **[C26] Mattia Scardamaglia, MAX-IV Laboratory, Lund University**  
*Comparative study of copper oxidation protection with graphene and hexagonal boron nitride*
- 1:50 - 2:05 **[C27] Oleksii Ivashenko, University of Oslo**  
*How surface species drive product distribution during ammonia oxidation, STM and APXPS study*
- 2:05 - 2:20 **[C28] Slavomir Nemsak, Advanced Light Source & University of California Davis**  
*Standing-wave Ambient Pressure Photoelectron Spectroscopy for Extreme UV Lithography Photoresist Analysis*
- 2:20 - 2:35 **[C29] Joachim Schnadt, Lund University**  
*APXPS in the past and in the future: APXPS publication database and a personal view on the future development of the field*
- 2:35 - 2:50 **[C30] Rik V. Mom, Leiden Institute of Chemistry, Leiden University, Fritz Haber Institute of the Max Planck Society**  
*Electrochemical XPS: where do we stand?*
- 2:50 - 3:05 **[C31] Jin Qian, Advanced Light Source**  
*Digital Twin: A Theorist's Playground for APXPS and Surface Science*

Real-time [RT] Pre-recorded [PR] [P: Plenary I: Invited C: Contributed T: Technical Po: Poster]

- 3:05 - 3:20 **[C32] Eoghan Rattigan, Interdisciplinary Nanoscience Centre (iNano)**  
*Cobalt Oxide Nanoisland PROX Catalyst: Mechanisms and Active Phase in Near Ambient Conditions*
- 3:20 - 3:30 **[T1] Doug Taube, ALS, Berkeley**
- 3:30 - 3:40 **[T2] Daniel Brennecke, BESSY, Berlin**
- 3:40 - 3:50 **[T3] Christine Ali, NSLS-II, Brookhaven**
- 3:50 - 4:00 **[T4] Geonhwa Kim, PLS-II, Pohang**
- 4:00 - 4:10 **[T5] Suyun Zhu, MAX-IV, Lund**
- 4:10 - 4:25 **[T6] Andreas Thissen, Specs, Berlin**

## **Computational spectroscopy from first principles**

Giulia Galli

*University of Chicago & Argonne National Laboratory*

We discuss first principles, computational methods and strategies to predict light-activated processes in materials for sustainability (e.g. to understand and design photo-electrochemical cells) and for quantum information science (e.g. color centers in semiconductors). In particular we discuss the study of materials at finite temperature, and emphasize the need for a tight integration between theory, computation and experiment.

## Well-controlled surface systems for APXPS

Ulrike Diebold

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APXPS is arguably one of the most powerful surface analysis techniques, as it offers the possibility to investigate and deeply understand interfacial phenomena relevant in a wide variety of fields. In order to get the most from such experiments, it is essential to have control over the surface of samples at the atomic scale. In the talk I will mainly focus on two systems, where such a control is tricky: the oxide-water interface and the surfaces of multi-component materials, specifically oxide perovskites.

We have recently devised a method that allows dosing liquid water onto a sample without it ever leaving the ultrahigh vacuum (UHV) environment [1]. By condensing water vapor on a liquid nitrogen cooled ‘cold finger’ located in a small side chamber of our UHV chamber, an icicle forms. The low vapor pressure allows opening the gate valve to the main UHV system and inserting the sample. When the icicle melts, the resulting liquid water is so clean that no carbon signal is detected in grazing-exit XPS. This avoids adsorption of organic acids that are common in less clean experiments and can lead to erroneous conclusions [2]. We find that liquid water can change the structure of oxides more profoundly than water vapor, for example it lifts the reconstructions of  $\text{TiO}_2(011)-(2\times 1)$  [3] and  $\text{Fe}_3\text{O}_4(001)-(\sqrt{2}\times\sqrt{2})R45^\circ$  [4]. The acidity of the water drop can be adjusted by adding gases such as  $\text{CO}_2$  [5].

Perovskite oxides (principal chemical formula  $\text{ABO}_3$ ) are promising materials in energy-related applications. At equilibrium they form a series of surface reconstructions that are sensitively dependent on the near-surface stoichiometry, as is shown for the prototypical oxide  $\text{SrTiO}_3$  [6] and for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  [7]. By adjusting the A:B ratio, it is possible to reversibly and reproducibly switch between such surface phases. We find that the standard preparation procedure used for  $\text{BO}_2$ -terminated (001) surfaces [8] yields amorphous overlayers. *In-situ* cleaving provides the most pristine, bulk-terminated (1×1) surfaces [9], we have designed a simple device that allows to do this even for materials that do not cleave easily [10]. These surfaces are metastable, however, and transform when the sample is heated or exposed to water vapor [9].

### References

- [1] Balajka Jan, et al., *Rev. Sci. Instrum.* **89**, 083906 (2018).
- [2] Balajka Jan, et al., *Science*. **361**, 786–789 (2018).
- [3] Balajka, Jan, et al., *J. Phys. Chem. C*. **121**, 26424–26431 (2017).
- [4] Kraushofer Florian, et al., *J. Chem. Phys.* **15**, 154702 (2019).
- [5] Mirabella Francesca, et al., *ChemPhysChem*. **21**, 1788–1796 (2020).
- [6] Wang Zhiming, et al., *Nano Lett.* **16**, 2407–2412 (2016).
- [7] Franceschi, Giada, et al., *J. Mater. Chem. A*. **8**, 22947–22961 (2020).
- [8] Koster Gertjan, et al., *Appl. Phys. Lett.* **73**, 2920 (1998).
- [9] Setvín Martín, et al., *Science*. **359**, 572–575 (2018).
- [10] Sokolović Igor, et al., *Phys. Rev. B*. **3**, 034407 (2019).

## Insights into Electrochemistry from *In Situ/Operando* Characterizations

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Electrochemistry involves dynamic chemical reactions on electrified solid materials interfaced with liquid electrolyte, which has opened a large window of renewable energy harvesting, storage, and conversion applications. In particular, development of functional nanomaterials has provided unprecedented breakthroughs in energy conversion and storage research societies. To understand principle correlations between electrode structure and electrochemical reactions, physicochemical characterizations including X-ray-based spectroscopies on both electrode materials and electrode-electrolyte interfaces have been intensively addressed in the last decades. However, conventional *ex situ* characterization techniques only describe bulk or surface structure of electrodes without considering electrochemical environments or reactions, limiting our understanding of *real* chemical reaction dynamics on electrified solid structures. To overcome this issue, it is of high importance to effectively couple powerful spectroscopy tools with electrochemistry toward *in situ/operando* spectroelectrochemical analysis.

Here, we summarize our continuous efforts to integrate X-ray based characterization techniques into electrochemistry, specifically focusing on understanding correlation between electrode structure and performance in energy conversion and storage systems. Also, importance of constructing *in situ/operando* spectroelectrochemistry will be briefly addressed based on previous researches from our group.

## Hydrogen induced chemical processes observed by ambient pressure X-ray photoelectron spectroscopy and other methods

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Recently hydrogen has been attracting much more attention as a clean energy carrier in our sustainable society as well as conventional chemical resource for hydrogenation. In order to utilize hydrogen in these processes more effectively, it is important to understand and control the dissociation of hydrogen molecules, adsorption, diffusion and absorption of hydrogen atoms at surfaces. It is difficult to elucidate the chemical states of hydrogen directly by using X-ray photoelectron spectroscopy (XPS). On the other hand, the binding energy of core-level is sensitive to the chemical and geometrical environments of hydrogen-reacted atoms. We have constructed and utilized ambient-pressure XPS (AP-XPS) system at the soft X-ray undulator beamline BL07LSU at SPring-8 in Japan [1, 2]. So far, we have studied the adsorption, activation and reaction of CO<sub>2</sub> on model catalysts [1-4], the hydrogen adsorption and absorption processes on Pd alloys [5, 6], etc. using this AP-XPS system.

In this talk, I will present our recent results including the hydrogen adsorption and absorption on Pd(110) by using AP-XPS and scanning tunneling microscopy (STM), the hydrogen adsorption on single atom alloy Pd-Cu model catalysts by using AP-XPS and infrared reflection absorption spectroscopy (IRAS), and the hydrogen adsorption on a Pd deposited MoS<sub>2</sub> surface.

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## Study about the Energy Storage Mechanism in Dimethylphenazine

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Single-molecule organic materials have attracted great attention from the society due to their high theoretical capacity, abundance of the constituents (C, H, N, and O), variety of the structures, and the tunability of their physical and chemical natures. Organic molecules with redox centers revealed the electrochemical activities, which work as electrode materials in the LiB system. Particularly, when phenazine is substituted by two methyl groups, dimethylphenazine showed high operating voltage of ~3.3 V by two-electron redox process at its nitrogen moieties. The understanding about the detailed energy storage mechanism in organic molecules is strongly demanded to engineer them viable as electrode materials. In so far as, bulk analysis tools have been widely used to understand redox mechanism of battery electrode materials. Meanwhile, X-ray photoelectron spectroscopy (XPS) can scrutinize the energy storage mechanism of organic molecules due to their high sensitivity to the chemical state. The change of molecular structure of DMPZ at the various (dis)charge state could be assessed by ex-situ high-resolution XPS. In this talk, study about the energy storage mechanism of organic molecules by spectroscopy will be delivered.

## ***In-situ* Probing Catalyst Generation and Deactivation with Ambient Pressure X-ray Photoelectron Spectroscopy**

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Catalysts design plays a crucial role in both energy storage and fuel synthesis. To enable a precise description of the catalytic reactions, *in situ* characterization of surface chemistry is inevitable. In this talk, I am going to present our recent efforts in using ambient pressure X-ray spectroscopy (APXPS) to understand both the catalyst generation and deactivation under real working conditions.

A recent advance in catalyst design is to exsolve metal nanoparticles at the surface of a supporting oxide. Unlike traditional deposition techniques, the nanoparticle catalysts from exsolution are anchored in the parent oxide, which makes the exsolved nanoparticles more resistant against particle agglomeration. While being a promising pathway, the exsolution efficiency requires further improvement. In the first part of this talk, I will demonstrate the capability to enhance exsolution with biaxial lattice strain on epitaxial  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  thin films. Coupling surface chemical information from APXPS with morphological information from electron and atomic force microscopy, we found that both surface coverage and dispersion of the exsolved  $\text{Fe}^0$  particles can be significantly enhanced with biaxial tensile strain.

Regarding catalysts deactivation, carbon deposition from CO and other carbon-containing fuels (“coking”) is a major cause of the performance degradation of catalysts and electrocatalysts in many energy conversion devices. In the second part of the talk, I will present our investigation into the relationship between gas/solid interface compositional and operational factors that lead to the onset of carbon deposition on thin-film  $\text{CeO}_2$  electrodes at 450 °C in CO/CO<sub>2</sub> atmosphere. During the measurement, electrical bias was applied to drive the redox reaction as well as to change surface oxidation state. With *in-operando* APXPS, we tracked the evolution of surface chemical change during carbon deposition on ceria-based thin-film samples. The surface spectroscopy analysis yielded information about the relationship between carbon deposition, surface defect concentration and surface composition.

## Bridging the Pressure Gap: Molecular Collision and Adsorption Structure on Single Crystal Model Surfaces between UHV and Ambient Pressure

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Industrial catalytic reactions such as CO oxidation and CO<sub>2</sub> reduction are representative energy conversion processes that various strategies have been suggested to enhance catalytic activities by developments of novel catalysts in heterogenous catalysis. However, our knowledge is still not enough to understand fundamental molecular behaviors on the surface when the reactant molecules collide with surface atoms of the catalyst at ambient pressure. In this talk, we will discuss adsorbate-induced geometric and electronic properties of surface alloys between UHV and ambient pressure using atom-resolved microscopy, synchrotron-based X-ray photoemission, and vibrational spectroscopy techniques. The emerged *operando* analysis platforms can support more reliable explorations at the gas-solid interface, which reveals the unexplained surface interactions with intermediates formation under the reaction environment. For example, the dissociated oxygens selectively pull out subsurface transition metal atoms in lattice structures of Pt-Ni [1] and Pt-Co [2] at the elevated pressure of O<sub>2</sub>. The lattice mismatch-driven species evolve interfacial metal-oxide structures in which the spontaneously formed active sites can improve the conversion efficiency of CO gas molecules caused by lowering activation energy barrier on bimetallic catalysts. On the contrary, CO<sub>2</sub> dissociation processes over Pt-Co catalysts show complicated reaction pathways without surface morphology alterations, but a subtle structural difference of monomer/dimer Co formations on the alloy surface would make a selective production of hydrocarbon intermediates depending on a ratio of Pt/Co. The facilitated chemical mechanism will be also compared with an early stage of CO<sub>2</sub> reduction reaction over a Rh model catalyst at ambient pressure [3].

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## Liquid phase TEM for studying catalysis and electrochemistry of nanomaterials

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For the past few decades, nanomaterials of various sizes, shapes, and compositions have been synthesized and utilized in many different applications in heterogeneous catalysts and energy conversion systems. However, due to a lack of analytical tools that can characterize structural changes at the nanoscale level, many of their growth, transformations, and reactions are limitedly understood. The recent development of liquid-phase transmission electron microscopy (TEM) is gaining attention as a new tool to directly observe chemical reactions that occur in solution. Due to its high spatial and temporal resolution, this technique is widely employed to reveal fundamental mechanisms relevant to nanomaterial chemistry. Here, the technical developments for liquid-phase TEM are introduced. In addition, its use in in-situ liquid phase studies of the growth mechanism, 3D structures, surface reactions of heterogeneous catalytic nanoparticles will be discussed. Our in-situ observations with liquid phase TEM elucidate different types of non-classical pathway, including two-step nucleation, amorphous-to-crystalline transition, and coalescence of clusters, are involved in different conditions of catalytic nanoparticle formation. We also observe the diffraction patterns from individual heterogeneous catalytic nanoparticles as they rotate in the liquid cell, and ultimately, we are able to align and invert those images to obtain the 3D atomic structure of individual catalytic particles freely moving in liquid. Obtained 3D density maps unveil internal and surface structural features of those particles that have been either underestimated or unattainable in conventional analysis. Liquid phase TEM is further advanced to have a capability of resolving solution phase reactions of nanomaterials under in-situ electrical biasing conditions. Examples of in-situ biasing liquid TEM studies of electrochemical reactions in Li-air battery system will be also presented.

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## Formation and Stability Enhancement of Surface Hydrides for Hydrogenation Reactions with Metal-Oxide Interface

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The interaction between H<sub>2</sub> and CeO<sub>2</sub> is a center issue to understand the role of CeO<sub>2</sub> for hydrogenation reactions, including CO and CO<sub>2</sub> hydrogenation, etc.<sup>1</sup> Particularly, recent studies have suggested that oxygen vacancies (V<sub>o</sub>) on CeO<sub>2</sub> could facilitate the formation of hydrides (H<sup>-</sup>) at surface and subsurface V<sub>o</sub> sites,<sup>2</sup> despite the homolytic dissociation of H<sub>2</sub> to form two hydroxyl groups is thermodynamically favored on stoichiometric CeO<sub>2</sub>.<sup>3</sup> The catalytic properties of H<sup>-</sup> species have thus attracted increasing attention for hydrogenation reactions.<sup>4,5</sup> Yet, a major challenge remains on how to enhance the formation and stability of surface hydride species over CeO<sub>2</sub>-based catalysts, as such they could be utilized for a wide range of hydrogenation reactions.

Hereby, we propose a strategy to enhance the formation and stability of hydride species with supported Cu sub-nanometer clusters (sub-NCs). We synthesized a series of CeO<sub>2</sub>-supported Cu catalysts and explored their interaction with H<sub>2</sub> via in-situ AP-XPS and H<sub>2</sub>-TPD. Our study showed that the strong electronic interaction between Cu sub-NCs and CeO<sub>2</sub> nanorods (NRs) could enhance the formation and stability of hydride species in both copper and CeO<sub>2</sub>, surpassing the capability of bare CeO<sub>2</sub> or the interface between Cu nanoparticles and CeO<sub>2</sub>. Moreover, the hydride species at interface sites between Cu sub-NCs and CeO<sub>2</sub> exhibited much higher activity for removal of surface hydroxyl and carbon species. Our study has thus provided a guide for the optimum design for heterogeneous catalysts for hydrogenation reactions, including the hydrogenation of CO and CO<sub>2</sub>.

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## Sequencing Methanol Synthesis Pathways for the Selective Conversion of C-H bonds using AP-XPS

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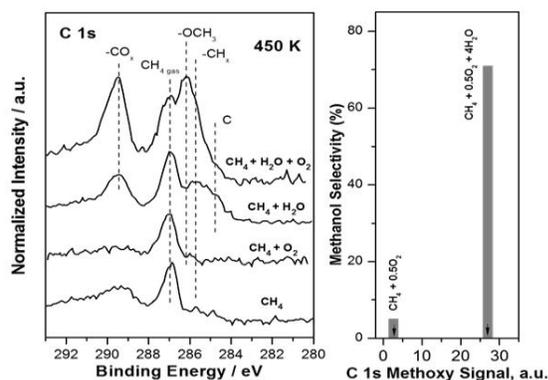


Figure 1. a) C 1s AP-XPS spectra when exposing a  $\text{CeO}_2/\text{-Cu}_2\text{O}/\text{-Cu}(111)$  surface ( $\theta_{\text{CeO}_2} \sim 0.5 \text{ ML}$ ) to different gas reactants at 450 K. b) Methanol selectivity versus the amount of methoxy generated.

Methane remains a valuable yet underutilized resource, with great interest for direct upgrade to valued products. Our recent studies indicate that, in spite of the high stability of methane, systems such as Ni-CeO<sub>2</sub>(111) and CeO<sub>2</sub>-Cu(111) can break C-H bonds even at room temperature, through careful manipulation of interfaces and metal support interactions, using light oxidants (CO<sub>2</sub>, O<sub>2</sub>/H<sub>2</sub>O). The selective oxidation on the surface sites can lead to conversion steps that produce CH<sub>3</sub>OH and CO+H<sub>2</sub>. AP-XPS with the help of DFT has been essential to elucidate C-H activation and oxidation steps with high resolution C 1s and O 1s spectroscopies. Initially, we have employed Dry Reforming (DRM: CH<sub>4</sub>+CO<sub>2</sub> → 2CO+2H<sub>2</sub>) conditions to establish benchmark steps for low temperature oxidative conversion of C-H bonds.

(using CO<sub>2</sub>) on several metal supported CeO<sub>x</sub>, including Pt, Ni, Co, where the active species and reaction mechanism are complex while a strong interaction between small M nanoparticles (M<sup>0</sup>/M<sup>δ+</sup>) and reduced CeO<sub>x</sub> surfaces (Ce<sup>4+</sup>/Ce<sup>3+</sup>) prevail. In parallel, we also established a method for the direct conversion of methane to methanol building on these surface results yielding low methanol selectivity (~30%). Subsequently, and in remarkable contrast we have found that a CeO<sub>2</sub>/Cu<sub>2</sub>O/Cu(111) inverse system is able to activate methane at room temperature and then, with the help of water, performs a highly selective (70%) catalytic cycle, for the production of methanol. The interfacial interaction between CeO<sub>x</sub>-CuO<sub>x</sub> is crucial while the concentration of water has a strong effect on the selectivity towards the production of methanol.

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## Investigation of a model metal/non aqueous electrolyte interface using *in situ*

### AP-HAXPES

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Solar-assisted carbon dioxide reduction reaction (CO<sub>2</sub>RR) offers the possibility to use atmospheric CO<sub>2</sub> and sunlight to produce highly-valuable hydrocarbons such as methane, ethylene, and ethanol. These commodities can be further used as fuels (thereby closing the so-called “carbon cycle”) or for industrial organic chemistry. So far, the majority of the current investigations of CO<sub>2</sub>RR were carried out in water environments. Although this approach is environmental-friendly and constitutes a good strategy for future implementation with solar electrolyzers, three main drawbacks exist: the limited solubility of CO<sub>2</sub> in water (~ 35 mmol/L at room temperature) (i), the competitive hydrogen evolution reaction (HER) occurring when performing CO<sub>2</sub>RR in water that limits the overall Faradaic efficiency (ii), and the difficulty to use molecular homogeneous (photo)catalysts that boost the unless poor selectivity of the reaction (iii). To overcome such limitations, we recently focused our attention on conducting fundamental investigations of different aspects of CO<sub>2</sub>RR performed in non-aqueous environments. In this talk, we will present our recent *in situ* hard X-ray ambient pressure photoelectron spectroscopy (AP-HAXPES) investigations of a model solid/non-aqueous liquid electrolyte interface. The experiments were performed at the SpAnTeX (Spectroscopic Analysis with Tender X-rays) endstation operating at the BESSY II synchrotron facility. The talk will focus on the study of a gold polycrystalline surface in contact with N,N-dimethylformamide (N,N-DMF) solutions, as a function of the applied overpotential and concentrations of the NaI supporting electrolyte. We will conclude this contribution by discussing about future perspectives and technical implementations at the SpAnTeX endstation.

## Water splitting reactions on oxide perovskites by AP-XPS

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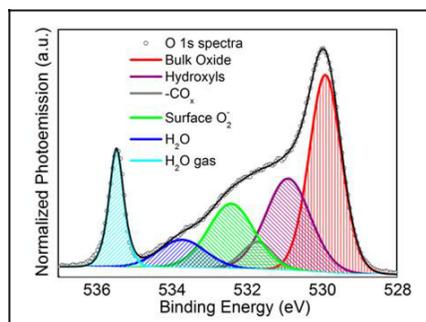
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Water dissociation on oxides is of great interest because its fundamental aspects are still not well understood and it has implications in many processes, from ferroelectric polarization screening phenomena to surface catalysis and oxides surface chemistry. In-situ natural water dissociation and redox processes on metal oxide perovskites which easily expose TiO<sub>2</sub> – terminated surfaces, such as SrTiO<sub>3</sub>, BaTiO<sub>3</sub> or Pb(Zr,Ti)O<sub>3</sub> are studied by ambient pressure XPS, as a function of water vapour pressure. From the analysis of the O1s spectrum, we determine the presence of different type of oxygen based species, from hydroxyl groups, either bound to Ti<sup>4+</sup> and metal sites or lattice oxygen, to different peroxide compounds, and propose a model for the adsorbates layer composition, valid for environmental conditions.[1] From the XPS analysis, we describe the existing surface redox reactions for metal oxide perovskites, happening at different water vapour pressures. Among them, peroxide species resulting from surface oxidative reactions are correlated with the presence of Ti<sup>4+</sup> ions, which are observed to specifically promote surface oxidation and water dissociation as compared to other metals. Finally, surface peroxidation is enhanced by X-ray beam irradiation, leading to a higher coverage of peroxide species after beam overexposure and by ferroelectric polarization, demonstrating the enhancement of the reactivity of surfaces of ferroelectric materials due to the effect of internal electric fields.



**Figure 1:** Decomposition of the O1s XPS spectrum at 700 eV incident X-ray energy of the STO single crystal (001) surface at 1 mbar water pressure into the 5 different contributions from right to left: bulk oxide (the red peak filled with vertical lines), hydroxyl groups (the purple peak with decreasing diagonal lines), carbonate species (the grey peak with horizontal lines), surface oxygen species including peroxides (the green peak with decreasing diagonal lines) and water molecules (the dark blue peak with increasing diagonal lines)

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## Testing the Cabrera-Mott Oxidation Model for Aluminum in realistic conditions with Near Ambient Pressure Photoemission

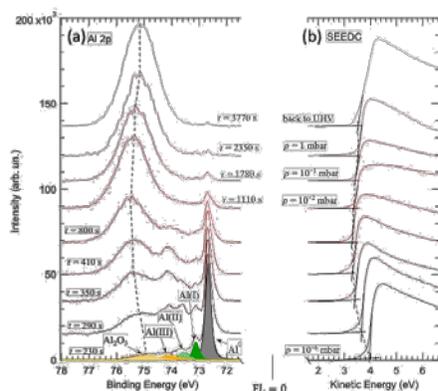
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Using the nascent band theory of solids, N. Cabrera and N.F. Mott designed in the late 1940s a model [1] for the low-temperature oxidation of metals that still stands today as a landmark. The core assumption is that an electric field set up in the growing oxide drives the transport of the ionic species responsible for the oxidation process. Experimentally, the existence of an electrostatic potential has long been sought, directly, in the in-situ measurement of the work function changes, and, indirectly, in the mathematical analysis of the oxidation kinetics. We show that the measurement of the work function is itself insufficient to test the Cabrera-Mott model. Rather, the oxide band structure characteristics (surface dipole energy barrier and band bending) should be followed instead. Addressing the paradigmatic case of the oxidation of the Al(111) single crystal surface in O<sub>2</sub> (1 mbar), we obtain detailed energetic information on the metal/oxide/gas system and we monitor in real-time the oxide growth. By combining the analysis of the oxidation rate with information on the position of the Fermi level in the oxide, we prove that the oxide bands are bent upward, thus validating the central hypothesis made by Cabrera and Mott on the presence of an electric field, but this band bending increases with pressure and oxide thickness. We also investigate whether oxygen anions adsorbed at the oxide/gas interface could be at the origin of the electrostatic potential, taking into consideration the contribution of water inevitably adsorbed on the surface under near ambient pressures.



(a) Al 2p<sub>3/2</sub> spectra after numerical 2p<sub>1/2</sub> stripping ( $h\nu = 149.95$  eV)). We show the spectra acquired in real time under  $10^{-6}$  mbar during the rapid growth regime and then in the successive slow regime. Spectra rescaled in height acquired under  $10^{-2}$ ,  $10^{-1}$  and 1 mbar, and back to UHV are also shown. Changes in the band bending are manifested through changes in the Al<sub>2</sub>O<sub>3</sub> Al 2p<sub>3/2</sub> binding energy. (b) Secondary electron energy distribution curves (SEEDC) rescaled in height corresponding to the Al 2p<sub>3/2</sub> core-levels shown in panel (a).

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## Ambient Pressure Hard X-ray Photoelectron Spectroscopy on Polymer Electrolyte Fuel Cells under Working Conditions

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Ambient pressure X-ray photoelectron spectroscopy is an excellent novel technique that allows us to perform operando observation of chemical reactions such as catalysts under working conditions. Hard X-rays are useful for this purpose since the photoelectron mean free path is elongated due to larger photoelectron kinetic energies. We installed an ambient pressure hard X-ray photoelectron spectroscopy (AP-HAXPES) system in hard X-ray undulator beamline BL36XU in SPring-8 mainly to clarify the degradation and poisoning mechanisms of polymer electrolyte fuel cells (PEFC), financially supported by the New Energy and Industrial Technology Development Organization (NEDO).

The beamline provides brilliant monochromatic hard X-ray microbeams ( $20 \times 20 \mu\text{m}^2$ ) through the focusing mirrors and 4-crystal monochromators. The photon energies available are usually 6, 8, and 10 keV, and the overall resolution of HAXPES is  $\sim 400$  meV in the standard setup. In 2017, we succeeded in the observation of real ambient pressure ( $10^5$  Pa) XPS [1,2]. In 2020, we reported quick HAXPES measurement system for the subsecond time-resolved experiments concerning electrochemical reaction kinetics on the PEFC cathode electrode upon the voltage step trigger [3].

We are interested in the electric potential measurements of PEFC electrolyte. The potential of the electrolyte cannot be measured with a tester probe because electric double layers appears at the interface. AP-XPS provides the electrolyte potential without any difficulties. Using this methodology, we can clarify the location of the chemical species of interest, whether the species is adsorbed on the electrode or dissolved in the electrolyte. Some examples will be presented in this talk.

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## Direct Electrochemical Oxidation of Methane at Ceria/Gas Interface

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One of the key advantages of solid oxide fuel cells is that they can use hydrocarbon fuels in addition to pure hydrogen, and CeO<sub>2-δ</sub> (ceria)-based oxides play an important role in hydrocarbon activation and carbon coking inhibition. However, even for the simplest hydrocarbon molecule, CH<sub>4</sub>, the mechanism of electrochemical oxidation on the ceria surface remains largely unknown. This is due to the complex architecture of typical metal/oxide composite electrodes and the heterogeneity of electrode reactions involving multiple chemical/electrochemical steps.

Here, we present a Sm-doped ceria thin-film model electrochemical cell capable of selectively monitoring CH<sub>4</sub> direct-oxidation on the ceria surface. We also carry out a real-time analysis of the surface adsorbates (e.g., H<sub>ad</sub>, CH<sub>x,ad</sub>, CH<sub>x</sub>O<sub>ad</sub>) and lattice ions during CH<sub>4</sub> electro-oxidation using the synchrotron-based ambient pressure-XPS (AP-XPS). These results, in combination with DFT calculations, enable us to reveal that the ceria surface catalyzes the C-H cleavage and that the overall electrode reaction rate is dominantly determined by the H<sub>2</sub>O formation step. Conclusively, the observations end the longstanding academic debate over the direct use of CH<sub>4</sub> and provide an ideal electrode design for high-performance fuel cells.

## **Introduction of X-ray Absorption Fine Structure and its Application in 8C Beamline at PAL**

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X-ray absorption fine structure (XAFS) refers to the oscillatory structure in the x-ray absorption coefficient just above an x-ray absorption edge. This turns out to be a unique signature of a given material; it also depends on the detailed atomic structure and electronic and vibrational properties of the material. For this reason, XAFS is a very important probe of materials, since knowledge of local atomic structure, i.e., the species of atoms present and their locations, is essential to progress in many scientific fields, whether for biology, chemistry, electronics, geo-physics, metallurgy, or materials science. However, many beamline users measure their samples without understanding basic principles of XAFS and measurement techniques.

In this workshop, a brief introduction of XAFS including basic principles of X-ray absorption, XAFS measurement, and its interpretation. Important examples of XAFS analysis for materials characterization will be presented as well.

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## Probing Metal–Oxygen Reaction Interfaces via In Situ Ambient Pressure X-ray Photoelectron Spectroscopy

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Oxygen reduction and evolution reactions at the electrode/electrolyte interface are at the heart of high-energy-density metal–air batteries. Direct probing of metal–oxygen chemistry at the solid/liquid/gas interface is essential to unravel the reaction mechanism of metal–air batteries. Ambient pressure X-ray photoelectron spectroscopy (APXPS) has been an important tool to advance the fundamental understanding of metal–oxygen battery chemistries.<sup>1-6</sup> For instance, Lu and Crumlin *et al.*<sup>1</sup> and M. Itkis *et al.*<sup>2</sup> applied *in situ* APXPS to examine the chemistry of Li–O<sub>2</sub> battery on a Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> and reduced graphene oxide (RGO) solid cathode, respectively. In addition, Mao *et al.*<sup>3</sup> revealed O<sub>2</sub> redox reactions in Na–O<sub>2</sub> batteries at graphite–O<sub>2</sub> interfaces. Although improved understandings were established via these studies, results obtained in solid-state environments are different from the solid-liquid-gas interfaces<sup>7</sup> in real metal-air batteries. In this presentation, we will discuss our recent efforts in probing metal-oxygen/air reduction/evolution reaction (ORR/OER) via APXPS in ionic liquid-based air batteries. We will discuss the reaction mechanisms and root causes of irreversible cell chemistry in metal-oxygen and metal air batteries revealed by ionic liquid-based air batteries via APXPS, which can be widely applied to study the chemistry of solid/liquid/gas interfaces of metal–air batteries.

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## **Event-averaged stroboscopic ambient pressure photoelectron spectroscopy as a new tool to follow surface kinetics of catalytic active surfaces**

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Ambient pressure x-ray photoelectron spectroscopy (APXPS) is an excellent in-situ characterization technique for catalytic active surfaces as it is able to characterize the surface, adsorbates, and the gas-phase just above the surface simultaneously and while a chemical reaction is running. Unfortunately, the technique is slow with seconds or minutes of acquisition time per spectrum. This limits its use to identifying the equilibrium and majority phases present while the catalyst is active and makes the time domain inaccessible excluding for example studies of kinetic processes.

In this talk I will demonstrate how this limitation can be overcome by the construction of event-averaged data from stroboscopic APXPS data acquired in a cyclic reaction environment. Using a transient gas supply with rapidly changing composition I will show how one can force a surface to oscillate between active and inactive phases in a periodic manner. I will show how the construction of event-averaged data over many transition events gives heretofore unseen vision of reactions on surfaces while the surface changes in response to the sample environment. Ultimately, I will demonstrate that one can record spectra with 60 ms time resolution with an efficient acquisition time of 30 s by averaging over more than 500 events. The scientific case stories in my talk will include examples both acquired in mbar pressures at the HIPPIE beamline, MAX IV, and at 100 mbar at the new POLARIS instrument, DESY.

## Structure-activity evolution of platinum species supported on ceria exposed to different reaction environments

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Atomically dispersed catalysts with isolated noble metal atoms exhibit distinctive performances, which have attracted the interest of several research groups.[1] Special features of such systems include:

- (i) the highest utilization of atoms
- (ii) well-defined active centers, facilitating the design of new catalysts
- (iii) unique catalytic properties of the isolated catalytic sites.[2]

However, contradictory conclusions have been drawn on the intrinsic activity of atomically dispersed species and nanoparticles, generally attributed the transformation of the one into the other[3] and the lack of exhaustive information gathered from in situ/operando characterization methods.[2,4] In this work, we combined in situ and operando spectroscopies with high-level theoretical calculations to investigate the structural evolution of atomically dispersed platinum under different activation and reaction conditions. Platinum active species were probed in situ by ambient pressure x-ray photoelectron spectroscopy and x-ray absorption spectroscopy. The simulated phase diagram of platinum species revealed to be a powerful tool to unambiguously identify the stability domain of Pt<sup>IV</sup>, Pt<sup>II</sup> and Pt<sup>0</sup> as a function of the sample pretreatment and reaction environment (oxygen partial pressure and temperature). Calcination of the samples at high temperature (>600°C) in low oxygen partial pressure/in the presence of steam causes the sintering into nanoparticles. The presence of metallic platinum correlates with the observed increased activity toward the conversion of carbon monoxide at low temperature.

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## Surface Chemical State of Pt/Cu(111) Single-Atom Alloy in Reaction Conditions

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Single-atom alloys (SAA) have recently gained increased interest as highly active heterogeneous catalysts that minimize the use of highly active but expensive metals such as Pt and Pd, by diluting them with a less expensive and more abundant metal such as Cu. While the activity of these catalysts in various reactions has been extensively studied, it is important to fundamentally and systematically characterize the interaction between the SAA surface and common reactant gases, which may alter the surface composition and chemical state of the catalyst, using well controlled model systems in ambient pressure conditions. We used AP-XPS at the IOS (23-ID-2) beamline at the National Synchrotron Light Source II (NSLS-II) to study the surface chemical state of the Pt/Cu(111) SAA model system in the presence of gases relevant in heterogeneous catalysis, both individually and in reaction condition. Our results show that oxidation in  $5 \times 10^{-6}$  Torr O<sub>2</sub> at 400 K results in the formation of a thin Cu<sub>2</sub>O layer on the surface. When the oxide layer is incomplete, the presence of exposed Pt atoms provides active sites for H<sub>2</sub> dissociation, which significantly accelerates the reduction of Cu<sub>2</sub>O by H<sub>2</sub>. When a complete thin oxide layer has been formed, it covers all Pt atoms, thus rendering them inactive for H<sub>2</sub> dissociation. However, we found that the presence of Pt under the oxide layer can still indirectly promote the reduction of Cu<sub>2</sub>O by H<sub>2</sub>. We also explored the surface chemical state of the Pt/Cu(111) SAA system in catalytically relevant reaction conditions such as CO<sub>2</sub> hydrogenation and CO oxidation and found contrasting effects on the stability of the SAA surface.

## Surface chemistry of copper during methanol conversion reactions: An AP-XPS and AP-NEXAFS Study

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Understanding the chemical state of the catalyst over which the methanol-to-hydrogen conversion reactions occur and the interplay with the adsorbed species present is key to the design of improved catalysts and process conditions. We studied polycrystalline Cu foils using x-ray photoelectron spectroscopy and near-edge x-ray absorption fine structure spectroscopy to reveal the Cu oxidation state and identify the adsorbed species during partial oxidation ( $\text{CH}_3\text{OH} + \text{O}_2$ ), steam reforming ( $\text{CH}_3\text{OH} + \text{H}_2\text{O}$ ), and autothermal reforming ( $\text{CH}_3\text{OH} + \text{O}_2 + \text{H}_2\text{O}$ ) of methanol at 200 °C surface temperature and in the mbar pressure range [1]. With AP-NEXAFS, we found that the Cu surface remains metallic throughout partial oxidation and steam reforming reactions, even for oxygen-rich conditions. However, for autothermal reforming the Cu surface shows significant oxidation towards  $\text{Cu}_2\text{O}$ . We rationalise this behaviour on the basis of the shift in equilibrium of the  $\text{CH}_3\text{OH}^* + \text{O}^* \rightleftharpoons \text{CH}_3\text{O}^* + \text{OH}^*$  reaction step caused by the addition of  $\text{H}_2\text{O}$ . This is a crucial finding because  $\text{Cu}_2\text{O}$  formation on the surface can shift the product selectivity from  $\text{CO}_2 + \text{H}_2$  to towards the highly undesired  $\text{CO}_2 + \text{H}_2\text{O}$ . We also detected reaction intermediates such as methoxy, formate, hydroxyl, atomic oxygen, and lattice oxygen with AP-XPS under these reaction conditions. During our studies, when gases are present the surface becomes partly covered by adventitious hydrocarbons, and possibly oxygenated hydrocarbons, which makes the adsorbate coverage hard to assess. This contamination issue remains as a major challenge in the field when working with wet gases.

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## **Grazing-incidence high-pressure XPS to determine the structure of Pd during catalytic CO oxidization**

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POLARIS, the first genuinely high-pressure XPS, is capable of gathering spectra up to and above an atmosphere. The new system opens the possibility to study reactions in regimes previously not possible to explore by typical AP-XPS. Beyond chemical measurements, POLARIS can use x-ray standing waves to probe the catalytic systems' layered structure in situ. The combination of real catalytic environments and measuring the resulting structured surfaces gives rise to unprecedented insight into catalytic surfaces. Herein we present results of the surface structure of palladium during the catalytic oxidation of carbon monoxide. While it is widely accepted that palladium oxide forms and grows epitaxially under certain conditions, the reduction process is much less understood. With POLARS, we studied the resulting palladium structure during oxidation and reduction cycles, showing the active phases of the material, the chemical structure, and the morphologic structure.

## Probing the electronic nature of the SMSI effect in Pd/TiO<sub>2</sub> nanoparticles

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The Strong Metal-Support Interaction (SMSI) effect [1] plays a key role in catalysis influencing directly on the catalytic properties in distinct ways. There are two main factors occurring in the SMSI effect, namely the geometrical and electronic one. The geometrical factor, consisting on the presence of a capping layer from the support covering the nanoparticle's surface, was strongly studied in the past [2]. On the other hand, the electronic nature of the SMSI effect is less studied and, in spite of the past efforts [3], there is still several open questions regarding this issue. In this work, Pd/TiO<sub>2</sub> nanoparticles were characterized with Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD). After, the samples were exposed to a reduction (H<sub>2</sub> atmosphere) and oxidation (O<sub>2</sub> atmosphere) treatments at 300 °C and 500 °C. Ex-situ Ultraviolet Photoelectron Spectroscopy (UPS) measurements were conducted with an He II source ( $h\nu = 40.8$  eV) aiming to probe the electronic properties at the surface of the nanoparticles before and after thermal treatments. Furthermore, Near Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS) measurements with an Al K- $\alpha$  source ( $h\nu = 1486.6$  eV) were performed with H<sub>2</sub> and O<sub>2</sub> pressure of 0.1 mbar, 0.5 mbar and 1 mbar at 300 °C. The system was investigated theoretically with DFT calculations. The results point to the occurrence of the electronic factor of the SMSI effect, which is manifested by a charge transfer between nanoparticles and support. The electronic interaction occurs with the formation of non-bonding O p states at the Pd-TiO<sub>2</sub> interface.

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## **Exploiting Temporal Correlations in Core-Shell Photoelectron Spectroscopy: Potential Applications for Ambient-pressure Experiments**

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We present a novel technique to monitor dynamics in interfacial systems through temporal correlations in x-ray photoelectron spectroscopy (XPS) signals. To date, the vast majority of time-resolved x-ray spectroscopy techniques rely on pump–probe schemes, in which the sample is excited out of equilibrium by a pump pulse, and the subsequent dynamics are monitored by probe pulses arriving at a series of well-defined delays relative to the excitation. By definition, this approach is restricted to processes that can either directly or indirectly be initiated by light. It cannot access spontaneous dynamics or the microscopic fluctuations of ensembles in chemical and/or thermal equilibrium, like the gas—surface equilibrium that forms under ambient-pressure conditions. The correlation-XPS technique presented here is a first step to address and overcome this limitation. The correlation-based technique is implemented by extending an existing optical-laser pump/multiple x-ray probe setup by the capability to record the kinetic energy and absolute (laboratory-)time of arrival of every detected photoelectron. We present results on benchmarking the system performance by monitoring energy-dependent, periodic signal modulations in a prototypical tr-XPS experiment on photoinduced surface-photovoltage dynamics in silicon through both conventional pump–probe data acquisition, and the new, continuous and unsynchronized measurement based on laboratory time. Further, we will discuss the opportunities that this new method opens to ambient-pressure experiments, in particular with respect to investigating gas—liquid and gas—solid interface equilibria.

## Interface Energetics of Photoelectrodes Under Relevant Conditions

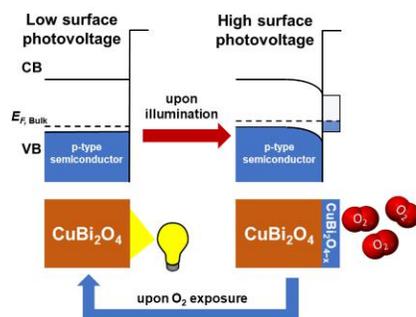
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The surface chemistry of semiconductors has a strong influence on important electronic properties, such as band bending and surface photo-voltage, that determine their performance as photoabsorber in photoelectrochemical cells. We have been studying the stability of surface states and associated electronic properties under relevant reaction conditions of illumination and chemical environments in a series of Cu-based and Fe-based oxide semiconductors using *near-ambient pressure X-ray photoelectron spectroscopy* (NAP-XPS). In this contribution, we will describe a study of the beneficial effect of surface reduction on the photoresponse of  $\text{CuBi}_2\text{O}_4$ <sup>[1]</sup>. A detailed XPS study reveals that visible light irradiation in inert atmosphere leads to the formation of reduced Cu species on the surface of  $\text{CuBi}_2\text{O}_4$ , which triggers a surface photovoltage (SPV) of about 300 mV as measured by the shift of the photoelectron peaks. The stability of reduced surface states and associated SPV under relevant reaction conditions has been further studied by NAP-XPS. Results indicate that reduced surface states remain stable in the presence of Ar and water, but reoxidation of surface Cu occurs in the presence of oxygen, which decreases the measured SPV. In contrast, the SPV of  $\text{Fe}_2\text{O}_3$  is largely favored by the presence of oxidizing environments, reaching up to -250 mV in presence of  $\text{O}_2$ . We relate this observation with the suppression of  $\text{Fe}^{2+}$  formation, which is a chemical species associated with the trapping of electrons from the conduction band (polaron formation) in  $\text{Fe}_2\text{O}_3$  photoanodes<sup>[2]</sup>. Our NAP-XPS studies are correlated with the performance of  $\text{CuBi}_2\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  photoelectrodes, and allow us to identify direct relationships between surface chemistry, surface energetics and the performances of these semiconductor photoabsorbers.



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## **A Simultaneous Probe for Chemical and Structural Transformations in Ambient Pressure Environments**

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Chemical transformations play a crucial role for a wide variety of natural and technological processes in ambient gas environments, from metal migration in geological systems to product formation in heterogeneous catalysis. Ambient pressure X-ray photoelectron spectroscopy (APXPS) provides the composition and chemical state of samples in these environments, as well as the identities of adsorbate species. However, pressure dependent processes (e.g. phase transitions or segregation of subsurface species) can generate structural transformations that also play a critical role in the behavior of materials exposed to ambient gas pressures.

The existence of multiple processes in these systems opens a ‘complexity gap’. A typical approach to address this gap is to separately measure the chemistry and structure of samples in different experiments (e.g. via APXPS and high pressure STM). We will present a new solution to this complexity gap through the development of a simultaneous *in-situ/operando* structural and chemical probe that combines APXPS with ambient pressure grazing incidence X-ray scattering (AP-GIXS). First results with this system will be shown on Ag-behenate and on nanostructured samples, where elevated temperatures and gas pressures into the Torr regime induced structural and chemical transformations observed with this technique. We will then conclude with an outlook discussing future developments for this combination of APXPS and APGIXS.

## Water-gas Shift Reactivity of Size-Selected Ti<sub>x</sub>O<sub>y</sub> nanoclusters supported on Cu(111) utilizing Near Ambient Pressure XPS

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In the nanoscale range, local interface electronic interactions change when a vacancy site is introduced into a supported reducible metal oxide, strongly influencing the potential activity and morphology observed. The presence of these vacancy sites within supported reducible oxides leads to exposure of under-coordinated metal atoms that act as potential active sites for chemical processes to occur, including the water-gas shift reaction (WGSR)<sup>1,2</sup>. In this study, we probe the role of oxygen vacancy sites on the water-gas shift ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ) activity of size-selected Ti<sub>x</sub>O<sub>y</sub> cluster ( $x = 3, 4, 5$  &  $y = 6, 8, 10$ ) supported on Cu(111) using near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). Under WGS reaction conditions (17 mtorr CO + 17 mtorr H<sub>2</sub>O at 300-600K) oxygen vacancy formation was observed on all sizes of the reducible Ti<sub>x</sub>O<sub>y</sub> clusters studied. Dissociation of H<sub>2</sub>O was observed, and CO adsorbed on Cu can be seen, both key to the WGSR. Lastly, the key reaction intermediate formate (HCOO<sup>-</sup>) was observed only in the presence of the Ti<sub>x</sub>O<sub>y</sub> clusters, indicating WGSR activity of these clusters. The observation of formate is consistent with previous work, where Cu coupled with a reducible ox-ide proceeds via an associative mechanism driven pathway, where  $\text{CO(a)} + \text{OH(a)} \rightarrow \text{CO}_2 + \text{H}_2$

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## Investigation of Radiolytic Damage of Liquid Electrolyte during Focused X-ray Photoelectron Spectroscopy and Microscopy

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Traditional UHV soft X-ray photoelectron spectroscopy (XPS) and its recent iteration of APXPS are fundamentally surface sensitive analytical techniques capable of providing elemental and chemical information from an interfacial region. Recently 2D materials have been employed to create a variety of liquid cells where a 2D membrane isolates the UHV of the analysis chamber from the high-pressure sample environment.[1] Herein we report effects of focused X-ray's upon a liquid-solid interface from solvent radiolysis by photo- and secondary electrons. To facilitate this, we employed graphene-capped liquid wells [2] within scanning photoelectron spectro-microscopy (SPEM) endstation to probe liquid-solid electrochemical interfaces under *operando* conditions. The bilayer graphene membrane holds highly electron and X-ray transmittance properties and served as the working electrode of a model electrochemical system of CuSO<sub>4</sub>. Conditions wherein highly focused X-ray irradiation affects the chemical speciation were observed at the liquid–solid interface due to solvent radiolysis by primary radiation, photoelectrons as well as secondary electrons. We recorded radiolytic products by photoemission spectroscopy and characterized their impact on the chemical speciation at the electrified solid-liquid interface. Three different exposure regimes ranging from 0.3 ph s<sup>-1</sup> nm<sup>-2</sup> to 105 ph s<sup>-1</sup> nm<sup>-2</sup> were tested to elucidate the dependence of XPS radiolytic signatures and dose rate. The irradiation dependency was collaborated under similar gray doses with a scanning electron microscope (SEM) which observed the topological deposition of radiolytic byproducts. The observed effects highlight the need for careful consideration of radiolytic processes for artifact-free liquid phase XPS measurements and data interpretation.

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## Spectroscopic Insights to Pt-, Pd- and Rh-Ga Alloys as Models for SCALMS Catalysts during Oxidation

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Palladium, Rhodium and Platinum become very active, selective and stable catalysts for the dehydrogenation of butane and propane when incorporated in a matrix of liquid gallium on oxidic support particles. This catalytic concept was pioneered at FAU and is termed *SCALMS*, for *supported catalytically active liquid metal solutions*. [1] The remarkable properties of these catalysts are attested to the atomic dispersion of the active transition metal in liquid gallium nano-droplets and the dynamics at the liquid metal/gas interface. Our findings link temperature-dependent changes in the reactivity of the catalyst to the dissolution/precipitation of intermetallic transition metal-Gallium phases, leading to transition metal enrichment/depletion of the liquid Ga phase. [3] A special focus of our investigations is the influence of surface oxidation, since Ga is highly prone towards forming a surface oxide layer. [3,4] For real world application, oxidation, due to handling in air or possible traces of oxygen in the feedstock, is almost unavoidable. We present *in situ* oxidation studies for macroscopic Pt-Ga, Pd-Ga and Rh-Ga alloy droplets. In case of rhodium we investigated nanoparticles utilizing synchrotron based XPS and high-resolution temperature dependent transmission electron microscopy. Based on the experiments, ab initio molecular dynamics simulations and density functional theory calculations, we suggest possible coordination of the transition metals as well as their redistribution in the sample surface as a response to the growth of the oxide film.

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## Local electronic structure of histidine in aqueous solution

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Amino acids constitute the elementary building blocks of proteins, are metabolic intermediates, and play important roles in living organisms. To advance our understanding of their roles and functions in biology, it is important to determine the electronic and geometric structure of amino acids particularly in a solvent environment such as water. X-ray spectroscopic techniques are powerful tools for investigations of electronic structure of matter and have been extensively applied to amino acids. However, most of these investigations have been restricted to solid state<sup>1-3</sup> or the gas phase amino acids<sup>4-6</sup> while biochemical systems almost universally occur in aqueous environment. In the gas phase, amino acids exclusively exist in the neutral molecular form,<sup>7,8</sup> and are zwitterionic in the condensed phase.<sup>9</sup> Whereas in biologically relevant aqueous environments, amino acids exist in a wide variety of charge states whose relative populations are determined by the pH of the solution.

In this study C1s and N1s X-ray photoelectron spectra of histidine aqueous aerosols at different pH values were obtained using a velocity map imaging photoelectron spectrometer combined with an aerodynamic lens.<sup>10,11</sup> Application of a building block approach allowed for identification of the protonation state of the individual nitrogen and carbon atoms of aqueous histidine by their respective core-level binding energies. Electron binding energies, extracted from DFT calculations of the histidine at different pH values of solution confirmed assignment of the experimental spectra. This study also demonstrates that velocity map imaging XPS of aqueous aerosols is a powerful technique allowing to probe the electronic structures of biological molecules in their natural aqueous environment.

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## Evolution of Steady-state Material Properties during Catalysis: Oxidative Coupling of Methanol over Nanoporous Ag<sub>0.03</sub>Au<sub>0.97</sub>

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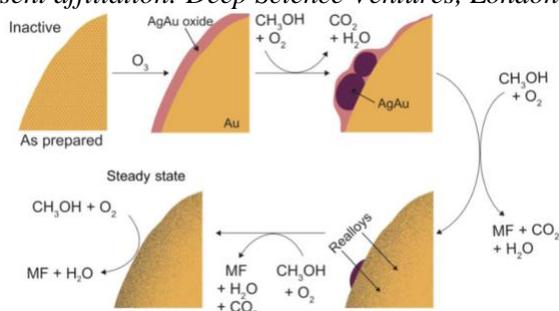
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Activating pretreatments can tune both the surface composition and structure of bimetallic-alloy catalysts. The activation-induced changes in material properties of a nanoporous Ag<sub>0.03</sub>Au<sub>0.97</sub> alloy and subsequent evolution under steady-state conditions for CH<sub>3</sub>OH oxidation are presented [1]. Initial activation in O<sub>3</sub> forms AgO and Au<sub>2</sub>O<sub>3</sub>, driving a strong Ag enrichment in the near-surface region, based on AP-XPS and EXAFS analysis. Exposing this oxidized nanoporous Ag<sub>0.03</sub>Au<sub>0.97</sub> to an O<sub>2</sub>/CH<sub>3</sub>OH mixture reduces both the Ag and Au oxides and results in a highly Ag-enriched surface alloy. Both the oxides and the reduced, highly Ag-enriched alloy fully oxidize methanol to CO<sub>2</sub>. However, at the reaction temperature (423 K), Ag slowly realloys with Au. Although decreasing, Ag remains enriched (29 at.%) in the top few nanometers under steady-state conditions, and the desired product, methyl formate, is selectively produced without significant deactivation. The activation and evolution of the active phase is not uniform: nanometer-scale patches of AgO were observed with environmental TEM, leading locally to Ag-rich alloys after reduction—critical for O<sub>2</sub> dissociation. DFT calculations indicate that the O on the surface assists in stabilizing the Ag. Moreover, the modest reaction temperature (423 K) is crucial for a stable performance. At higher temperatures, bulk diffusion induces sintering and Ag redistribution, leading to a loss of activity. Material properties determining catalytic activity are dynamic and metastable (kinetically trapped). Hence, catalytic activity and selectivity depend on the pretreatment, reaction temperature and gas composition. These observations provide guiding principles concerning the activation of heterogeneous catalysts for selective oxidation.

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## Direct observation of chemistry-dependent hydration on polymer thin films: in situ APXPS study

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Water interactions with polymer surfaces play an important role in nearly all aspects of life including cellular functions, electrochemistry and has important applications in, e.g., water purification, fuel cells, and biosensors. Yet the precise understanding and quantifying in molecular level is still missing or incomplete due to difficulty and/or lack of capability of many surface specific techniques on operating under in situ conditions. To fill this gap, we use ambient pressure Tender X-ray Photoelectron Spectroscopy (APXPS [1-4]). Tender-APXPS combines the chemical specificity, high surface sensitivity and quantitative analysis of the surface composition of traditional XPS and allow studies at pressures up to 20 Torr. In this study, we used 5 different styrenic polymer thin films to understand the effect of functional groups, interaction types and counter ions on water adsorption. Interaction of water vapor with these polymer surfaces were investigated in situ from UHV up to 100% relative humidity (RH) with APXPS. Our results suggest that the interaction of water with polymer surfaces is mediated by polar and charged functional groups. While the hydrophobic polystyrene do not adsorb any water even at 100% RH, -OH and -SO<sub>3</sub> functionalized polymers adsorb and adsorption peak increases with increasing %RH. Additionally, counter ion identity affects the degree of water adsorption on polyelectrolytes. Findings in this study provide direct insight into the critical role of side-chain chemistry in polymer-water interactions while also demonstrating the potential of APXPS with elemental sensitivity to give valuable information about the equilibrium amounts of adsorbed water on polymers to guide the design and control of future materials.

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**Operando Studies of Surface Oxidation Reactions at Gas/Solid Interfaces by Ambient Pressure X-Ray Photoelectron Spectroscopy**

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The Ambient Pressure Surface Characterization Laboratory (APSCL) [1] at Oregon State University is part of the National Science Foundation – National Nanotechnology Coordinated Infra-structure (NNCI) program; [2] the metrology instrumentation includes an integrated SPECS ambient pressure X-ray photoelectron spectroscopy (APXPS) and ambient pressure scanning tunneling microscopy (APSTM) systems. I will highlight several *in-situ/operando* surface reactions at gas/solid interfaces. The initial surface of MoS<sub>2</sub> was exposed to 1 mbar of H<sub>2</sub>O vapor for temperatures ranging from 300 to 573 K, and then again for MoS<sub>2</sub> with increasing surface defect densities. The APXPS from Mo 3*d*, S 2*p*, and O 1*s* core levels indicate that the defective surface is much more reactive to H<sub>2</sub>O, with the formation of Mo-O and Mo-O-S chemical states. In a second study, we have measured the corrosion of an atomically thin film of SiC and ZrN at a H<sub>2</sub>O vapor pressure of 1 mbar, and for temperatures up to 773 K. No oxidation was observed on the SiC surface up to 623 K. For temperatures higher than 623 K, APXPS data show the oxidation of SiC with the formation of SiO<sub>2</sub>. In contrast, the ZrN film reacts at room temperature. As the temperature increases, the ZrN was completely converted to ZrO<sub>2</sub>. In a third example, we studied the thermal oxidation of Si<sub>0.60</sub>Ge<sub>0.40</sub>(001) at 573 K and O<sub>2</sub> pressures of 10<sup>-4</sup>, 10<sup>-2</sup>, and 1 mbar. The oxidation of SiGe follows rapid regime at early stage of oxidation, a transitionary regime, and a quasi-saturated slow regime when the oxide was relatively thick. SiO<sub>2</sub> is thermodynamically more stable than GeO<sub>2</sub> and for a given temperature we determined that there is a critical O<sub>2</sub> partial pressure above which mixed oxide growth occurs and below which there is preferential SiO<sub>2</sub> growth.

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## Cooperative Effect of Carbonaceous Material with Water Enhances the Growth of SiO<sub>x</sub> on Si

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We have investigated the influence of carbonaceous materials on the growth of SiO<sub>x</sub> layers on Si under dry conditions and in the presence of water and/or water vapor. The dip-and-pull experiments were carried out using the SpAnTeX endstation using tender X-rays from the KMC-1 beamline at BESSY II in Berlin.

The Si wafers (n-doped), cleaned using the RCA-method, showed a uniform SiO<sub>x</sub> film thickness of the order of 1 nm at the beginning of the experiments, as determined from Si 2p and Si 1s spectra taken at an incident photon energy of 3 keV. The samples were then exposed to various environments, among them water vapor and gaseous octane and octanoic acid.

In the dip-and-pull experiments the Si wafers were partly immersed into pure water or octanoic acid, as well as mixtures of water and stearic or octanoic acid. The APXPS data clearly show a correlation between the thickness of the SiO<sub>x</sub> layer and the amount of carbon present at the surface. However, this effect is only observed in experiments where the Si wafer was exposed to both water and carbonaceous species. Oxide growth was not observed for experimental conditions where the SiO<sub>x</sub>/Si surface was exposed to only either water or carbonaceous material.

These results thus point to a cooperative effect between water and carbonaceous species that induces SiO<sub>x</sub> growth, which has implications for the preparation, storage and treatment of Si wafers in technological applications.

## Oxygen-adsorption driven high dispersion of Ag nanoclusters revealed by NAP-XPS

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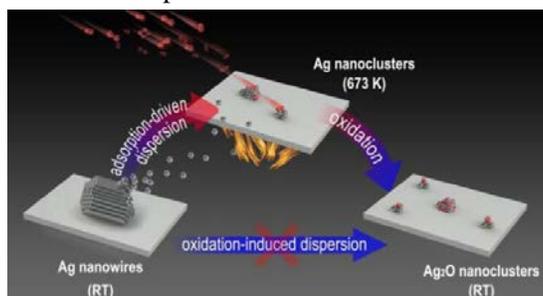
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Dispersion under oxidizing condition is a common phenomenon in oxide supported metal catalysts by an oxidation-induced dispersion mechanism [1]. The strong metal (metal oxide)-support interaction has been reported to be the driving force for the dispersion [1]. However, the confinement environment surrounding the dispersed metal species include not only the support but also the atmosphere. Here, using NAP-XPS, NAP-PEEM, combined with DFT calculation, we unravel a new adsorption-induced dispersion mechanism in a typical oxidative dispersion process. In this report we present XPS results to show the full picture of the dynamic structural evolution in a typical catalyst pretreatment or a reaction process. The strong gas-metal interaction achieved by chemisorption of O<sub>2</sub> on nearly-metallic Ag nanoclusters is the driving force for dispersion at elevated temperature and the oxidation occurs upon cooling process [2].



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## Thermal Oxidation of Ru(0001) to RuO<sub>2</sub>(110) Studied with Ambient Pressure X-ray Photoelectron Spectroscopy

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Ruthenium dioxide (RuO<sub>2</sub>) is a promising oxidation catalyst that has been extensively studied in surface science as a model system.[1] The activity of Ru-based catalysts is correlated to the formation of a RuO<sub>2</sub> film at the surface allowing for enhanced adsorption of reactants,[1] thus understanding Ru(0001) oxidation is imperative for understanding Ru(0001) surface chemistry. Using time-lapsed ambient-pressure X-ray photoelectron spectroscopy (APXPS), we investigate the thermal oxidation of single-crystalline Ru(0001) films toward rutile RuO<sub>2</sub>(110) *in situ*. APXPS spectra were continuously collected while Ru(0001) films were exposed to a fixed O<sub>2</sub> partial pressure of 10<sup>-2</sup> mbar and increasing sample temperatures (room temperature to 400 °C). We initially observe the removal of adventitious carbon and subsequent formation of a chemisorbed oxygen overlayer at 250 °C. Further annealing to 300 °C leads to an increase in oxide uptake and a shift in the Ru-O component of the Ru 3d spectra, indicating the presence of a metastable O-Ru-O trilayer structure.[2] A rapid formation of the RuO<sub>2</sub> rutile phase (approximately 2.6 nm) takes place about four minutes after stabilizing the temperature at 350 °C, characterized by a binding energy shift in both the Ru 3d and O 1s spectra and quantitative analysis of XPS intensities. This observed autocatalytic oxidation process agrees well with previous theoretical models[2] and the data provides the first known spectral identification of one proposed metastable precursor required for full oxidation to rutile RuO<sub>2</sub>. Ultimately, our results provide valuable information for better understanding Ru(0001) surface chemistry and demonstrate the strength of time-lapsed APXPS for investigating surface transformation mechanisms.

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## **H<sub>2</sub>O Reactivity of TRISO Fuel Layers Probed with Ambient Pressure Photoelectron Spectroscopy**

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While the use of TRISO fuels has been long postulated within High Temperature Gas Reactors, an additional use is possible as an accident tolerant fuel in Light Water Reactors (LWRs). Before TRISO fuels can be used in LWRs, the corrosion properties of the different layers of TRISO fuels must be well understood. Photoelectron Spectroscopy (PES) has long been utilized to study the oxidation behavior of materials due to its sensitivity to both element and chemical state. The problem with (PES) has been that it has historically been a technique that required Ultrahigh Vacuum conditions for measurements. This made it difficult to study corrosion in situ. New instruments have expanded the capabilities of PES. It is now possible to measure photoemission spectra at ambient pressure. We have measured the in situ corrosion of a SiC layer grown as a TRISO simulant at a pressure of 1 mbar of H<sub>2</sub>O at temperatures of 500 C using an ambient pressure photoemission system. In addition, we have grown multilayer SiC/ZrN/C systems designed to protect the environment from silver release. We will report on the corrosion chemistry of the SiC, ZrN, and C layers as measured using ambient pressure photoemission.

## Understanding Chemical and Electronic Heterogeneity across Solid/Liquid and Solid/Solid Interfaces by Standing-Wave Ambient-Pressure Photoemission Spectroscopy (SWAPPS)

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Interfaces between two chemically dissimilar materials can strongly influence the functionalities and performance for a wide range of applications. Examples include electrode/electrolyte interfaces in batteries and electrocatalysts (solid/liquid) and oxide heterostructures in quantum materials and oxide electronics (solid/solid). Standing-wave X-ray ambient-pressure photoemission spectroscopy (SWAPPS) can overcome some of the limitations of conventional XPS and AP-XPS technique by combining spectroscopic and scattering techniques, which makes it very suitable for investigating material interfaces.<sup>[1]</sup> In this work, we are going to show how SWAPPS can be used to study material interfaces with high depth resolution by using two case studies: 1) We studied single crystalline LaNiO<sub>3</sub> (LNO) thin films to understand the factors governing the oxygen evolution reaction (OER) electrocatalytic activity. By using standing-wave XPS, we were able to directly probe the differences in surface chemistry of LNO induced by processing temperature, which is linked to electro-catalytic activity and durability. Moreover, by using *in situ* ambient-pressure SWAPPS, we obtained insights into the potential distribution across the electric double layers (EDLs) at LNO/alkaline electrolyte interfaces. 2) Delafossite PdCoO<sub>2</sub> is a “natural” heterostructure consisting of metallic Pd sheets and Mott insulating CoO<sub>2</sub> layers, which shows numerous exotic quantum phenomena.<sup>[2]</sup> We used tender X-ray SW -XPS to reveal individual contribution from each layer in the valence band structure of PdCoO<sub>2</sub>. These two examples highlight the power and versatilities of standing wave XPS, combined with *in situ/operando* ambient pressure XPS, in shedding light into the chemical and electronic heterogeneity across material interfaces.

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## **Precisely mimicking environmental conditions to observe phase changes by near ambient pressure X-ray absorption spectroscopy: supercooled liquid and hydrohalite at interfaces**

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Laboratory experiments are presented on the phase change at the surface of sodium chloride – water mixtures at temperatures between 259 K and 240 K. Environmental relevance comes from the fact that Arctic snow can, due to chemical reactions of its trace constituents such as chloride, have profound and wide-spread impact on the overlaying atmosphere. It is currently unclear when phase changes – that have a profound impact on chemical reactivity - occur at the interface of snow with air. Interest in this topic is additionally driven by the disorder, or pre-melting, observed at the interface [1].

The goal of the experiments reported here was to probe the phase of sodium chloride – water samples at various positions in the phase diagram. Phase changes were observed in-situ by Partial Auger-Meitner electron-yield NEXAFS spectroscopy (NEXAFS) at the Cl K-edge. Detecting electrons results in a high selectivity to the upper few nanometres of the frozen solution – air. We take full advantage of the near ambient pressure set-up [2] that allows us to precisely set and monitor the temperature and water vapour pressure to perform measurements with partial pressures of water between 0.3 mbar and 1.8 mbar and temperatures between 259 K and 240 K.

We find that sodium chloride at the interface of frozen solutions remains as supercooled liquid down to 240 K. Below this temperature, hydrohalite precipitates for which we present the first NEXAFS spectrum. Taken together, this study reveals no differences in the phase changes of sodium chloride at the interface as compared to the bulk.

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## Elucidating Ions Adsorption Competition at Electrified Interface by Ambient Pressure X-ray Photoelectron Spectroscopy

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Discovering the mechanisms governing interfacial electrochemical properties will inform the development of more selective, stable, and efficient interfaces for various important heterogeneous electrochemical reactions. Combining electrochemistry with tender X-ray ambient pressure X-ray photoelectron spectroscopy (APXPS), we can explore the complex molecular interactions of a solid/liquid interface, providing informative knowledge to expedite future material and device innovations.

We investigated the electrified interface between the fluoride ions ( $F^-$ ) in an aqueous solution and copper (Cu) surface using electrochemical methods and *operando* APXPS characterization. We found different electrochemical behaviors and speciation at the interface with different concentrations of  $F^-$  used. We proposed an ions passivation and competition scenario at the solid/liquid interface. High concentration  $F^-$  passivated the Cu surface by repelling water molecules, hindering the formation of  $OH^-$ , at cathodic potentials, and incorporated to the Cu electrode to form  $CuF_2$  at anodic potentials. With low concentration  $F^-$ ,  $OH^-$  formed at the interface under cathodic potentials because of the Cu- $H_2O$  interactions. The  $OH^-$  anions accumulated at the interface and acted like a buffer layer that prevents the  $F^-$  attacking, which we hypothesize forms a sandwich-like F-OH-Cu structure at interface. These observations provided new insights into the Cu- $F^-/OH^-$  interaction in various electrochemical reactions, including Cu corrosion, water splitting and  $CO_2$  reduction reaction with  $F^-$  based electrolyte involved. Our work emphasized again how the electrode/electrolyte interfacial properties determine the electrochemistry behaviors.

## Gas Pump X-ray Probe APXPS for Studies in Catalysis with sub-ms Time Resolution

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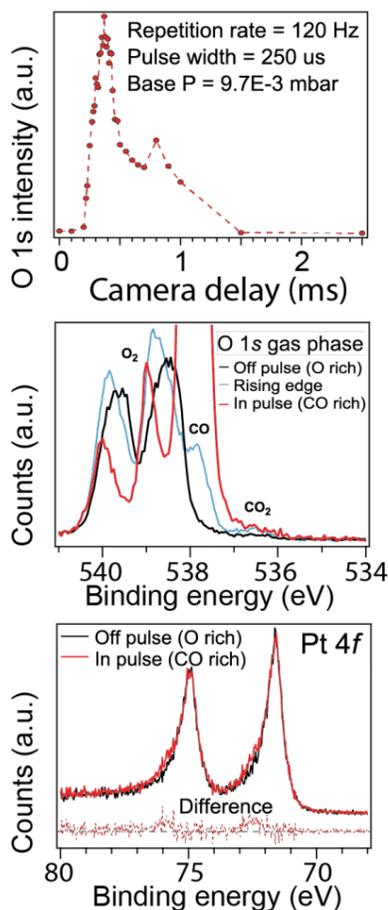
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Studying dynamics and kinetics of chemical reactions on surfaces of e.g. catalysts with time resolution comparable to that of the process itself is an important tool for learning fundamental principles of these reactions. Obtaining such temporal information about intermediate product formation and structural transformations is the key to understanding reaction mechanisms, limiting steps, and overall process efficiency/yield. To do so time-resolved spectroscopical techniques primarily of pump-probe type are valuable experimental tools popular in multiple research communities (e.g. solid-state physics, LDM). With these tools time scales ranging from fs to s with primarily light pump have been investigated using FELs,<sup>1</sup> synchrotrons,<sup>2</sup> and lab-based instrumentation.<sup>3</sup>

Interaction of the short gas pulses with surfaces that are the most relevant for catalysis so far have only been studied in UHV using supersonic molecular beams.<sup>4</sup> Clearly, this is not enough to obtain full understanding of catalytic reaction mechanisms under real conditions. Therefore, new experimental tools allowing such investigations are of high interest at the moment.

In this work we will present technical setup dedicated for injection of short (tens to hundreds of  $\mu$ s) pulses of gas at mbar pressure into a vacuum chamber with frequency varying between 1 Hz to 1000 Hz. We will describe various characteristics of the pure gas pulse such as duration, shape, pressure, dynamics, interaction with background gas present inside vacuum chamber. Finally, we will show results of the time-resolved CO oxidation reaction on the surfaces of Pt and Ag single crystals.



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## Time evolution of surface species and oxygen transport during atomic layer deposition of TiO<sub>2</sub> on RuO<sub>2</sub>(110) studied by ambient pressure XPS

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Atomic layer deposition (ALD) is a thin film deposition technique for depositing uniform and conformal layers on complex three-dimensional topographies. ALD is highly used in different fields of technology, e.g. in microelectronics and solar cell technology. In spite of its intense use in, not least, industrial application, the understanding of the atomic and molecular surface processes underlying ALD is far from complete. An identification and thorough investigation of the role of surface species in the ALD process are therefore very much needed [1].

We performed ambient pressure x-ray photoelectron spectroscopy (APXPS) to study the ALD growth of TiO<sub>2</sub> on the RuO<sub>2</sub>(110) surface in real time, with around 15 second time resolution. We have chosen tetrakis (dimethylamido) titanium (TDMAT) and water as precursors. The result of the measurements is illustrated in Fig. 1, which shows time-resolved ambient pressure x-ray photoelectron spectra taken during the first half-cycle of the ALD process. From the time evolution of the RuO<sub>2</sub> signal we can deduce that the oxide is reduced, and that oxygen is transported to the growing Ti precursor layer, where titanium oxide and the Ru-O-Ti interface are formed. The process is similar to that observed for tetrakis (dimethyl-amido) metal ALD processes on InAs [2] but differs from those on SiO<sub>2</sub> [3]. We have also used the other spectral regions to follow the evolution of the different surface chemical species, methyl methylenimine and dimethylamide bonded to the Ti metal and the surface, respectively [4].

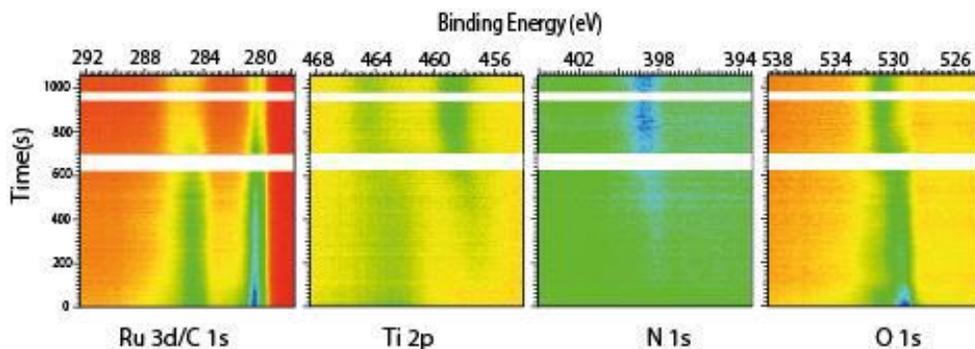


Fig. 1: Time-resolved x-ray photoelectron spectra taken during the first half-cycle of the ALD process.

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## Systematic study of atomic layer deposition of HfO<sub>2</sub> on TiO<sub>2</sub>: space state of temperature and pressure

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Despite the numerous applications of atomic layer deposition (ALD), used mainly in the semiconductor industry to produce thin films with control in thickness and composition, little remains known about the kinetics of the surface chemical reactions, reaction mechanisms and the role of the substrate. In a previous studies of ALD of HfO<sub>2</sub> on InAs, we correlated the self-cleaning process to the formation of HfO<sub>2</sub> during the metal cycle<sup>1</sup>: HfO<sub>2</sub> is formed already during the first half cycle of ALD, as the metal precursor uses the oxygen of the native oxide as an oxidation source. ALD of HfO<sub>2</sub> on oxidized SiO<sub>2</sub> behaves in a different manner: here, the oxide remains stable and, moreover, the reaction mechanism has a bimolecular character<sup>2</sup>.

In the present study, HfO<sub>2</sub> was deposited on anatase TiO<sub>2</sub>(101) by ALD using the tetrakis(dimethylamido)-hafnium (TDMA-Hf) and water precursors in four different conditions, ranging from relatively low pressure (10<sup>-6</sup> mbar) and temperature (300 K) to those that would be used in an actual ALD reactor. During the initial metal half-cycle, HfO<sub>2</sub> is already formed, and here the oxygen atoms are transported from the TiO<sub>2</sub> support to the surface to react with the TDMAHf. The surface chemical reaction of the ligands is highly temperature dependent (N 1s core level in Fig. 1), which implies that temperature is decisive for which surface species are observed and remain on the surface after the reaction. In contrast, the efficiency of the water precursor to react with the ligands is pressure dependent. Our results show clearly that time-resolved APXPS enables us to further the understanding of the surface chemical processes in ALD and to map the influence of the experimental parameters on the surface reactions.

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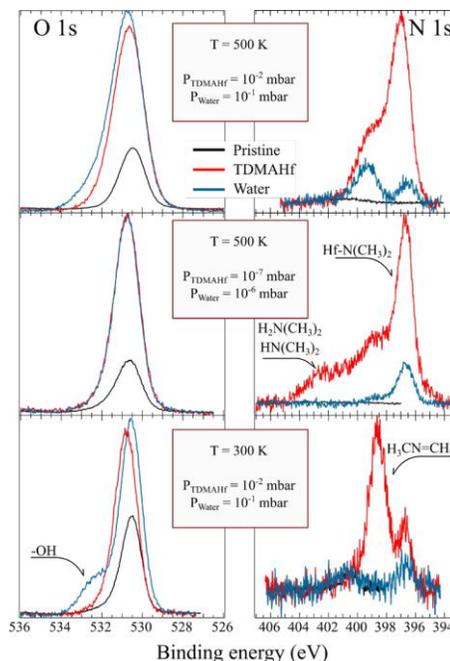


Figure 1 O 1s (left) and N 1s (right) core level spectra ( $h\nu=650$  eV) recorded at different conditions. Black: spectra of the pristine TiO<sub>2</sub> sample, red: after the metal half-cycle, blue: after the water half-cycle.

## Correlating APXPS with ESEM, one experimental example: The electrocatalytic CO<sub>2</sub>RR on copper oxide electrodes

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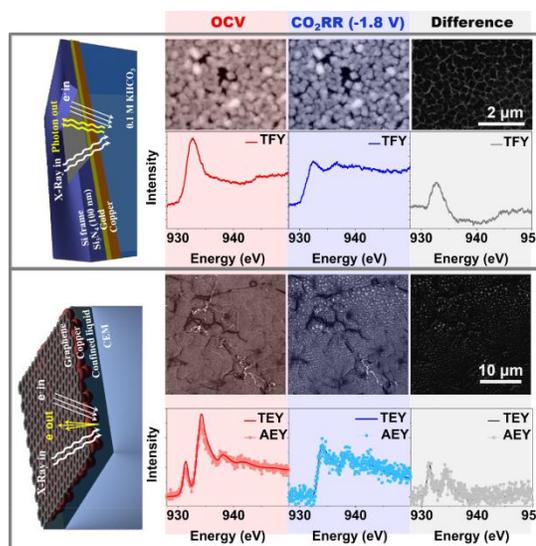
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Combining X-ray spectroscopy with electron microscopy is a valuable method to ascribe the variation in the electronic structure with the changes observed in the material morphology during its operation. Environmental scanning electron microscopy (ESEM) and ambient pressure X-ray photoelectron spectroscopy (APXPS) are operated under the same pressure conditions. It enables to investigate the same specimen with both techniques, including an hypothetical combination of both approaches in the same experimental chamber. We will present how this approach provided an accurate and extended interpretation of the variations that an electrocatalyst undergoes in the course of the reactions [1]. The validation of this approach will be probed with the investigation of



of the CO<sub>2</sub>RR [2,3] on copper oxides based electrodes comparing these results with bulk sensitive techniques based in total fluorescence yield (TFY). Typically, element specific X-ray spectroscopy was used for that purpose being technically challenge to use it in presence of liquids. This technical limitation forced the use of ex situ characterizations and bulk sensitive methods and, thereby, prompted many different interpretations of the active/stable copper oxidation state during the CO<sub>2</sub>RR. In order to provide an unambiguous description of the oxidation state of copper during the electrocatalytic reduction of CO<sub>2</sub> to valuable hydrocarbons, we enabled the detection of surface sensitive photoelectrons using a 2D membrane (graphene) transparent [1]. A schematic comparison of the bulk and surface sensitive approaches used in this work are shown in the figure. It was found that the selectivity to the C-C bond formation takes place on a reconstructed rougher reduced copper surface which controls the dissociation barrier of water and CO<sub>2</sub> [4].

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## Monitoring photoinduced charge transfer dynamics in nanoparticle-sensitized light-harvesting systems using time-resolved ambient pressure x-ray photoelectron spectroscopy

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Photocatalytic production of storable fuels, such as hydrogen through photoelectrochemical (PEC) water splitting, is an attractive and environmentally friendly alternative to fossil fuel usage. Many emerging solar light harvesting schemes use wide-bandgap semiconductors in conjunction with plasmonic metal nanoparticles (NPs) for improved charge separation and increased light absorption at visible wave-lengths. Here, 20 nm gold NPs are deposited on top of nanoporous TiO<sub>2</sub> and studied with picosecond time-resolved ambient pressure x-ray photoelectron spectroscopy (TRAPXPS). The elemental specificity of this technique allows charge transfer to be studied from the perspectives of both electron donor and electron acceptor. Measurements are taken under high vacuum conditions as well as with ~9 Pa of water vapor. Under vacuum, a charge injection efficiency of ~2 electrons per NP (corresponding to ~0.1% photon-to-charge conversion efficiency) is observed. Charge carrier recombination proceeds over two time-scales: 60 ps and ~1 ns.<sup>1</sup> Once water vapor is introduced, charges remain separated significantly longer, and relaxation is described by 3 timescales: ~0.9 ns, ~11 ns, and ~150 ns. Potential physical interpretations for the effect will be discussed.

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## Comparative study of copper oxidation protection with graphene and hexagonal boron nitride

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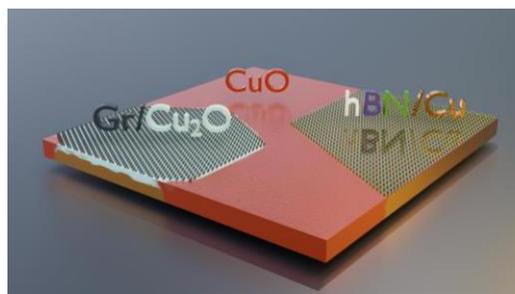
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The use of protective barriers to isolate a metal surface from an aggressive environment is a common way to inhibit its degradation. We used ambient pressure x-ray photoelectron spectromicroscopy (APXPS and nAP-SPEM) to assess in real time the evolution of the copper surface and the contextual protective action of 2D material coatings (graphene and hexagonal boron nitride) towards copper oxidation [1,2]. In an isobaric experiment with 2 mbar of oxygen, the bare copper oxidizes near room temperature, while both 2D materials can retard the onset temperature for the first oxidation of copper by more than 120 °C. However, their protection mechanism is different: boron nitride forms an effective barrier to copper oxidation until it is etched away at high temperatures, leading to a rapid oxidation to cuprous and then cupric oxide. On the other hand, graphene reveals to be a more interesting playground underneath oxygen intercalates and begins a slower undercover oxidation of copper. This different behaviour is ascribed to the metallicity of the graphene that allows a channel for galvanic corrosion of copper, not possible with the insulating hBN [2].

The ability to perform spatially resolved XPS and imaging at high pressure allowed a unique characterization of the oxidation phenomenon by means of photoelectron spectromicroscopy, pushing the limits of this technique from fundamental studies to real materials under working conditions. Oxygen intercalation beneath graphene starts from boundaries and defects, while bilayer flakes can protect at even higher temperatures [1].



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## How surface species drive product distribution during ammonia oxidation, STM and APXPS study

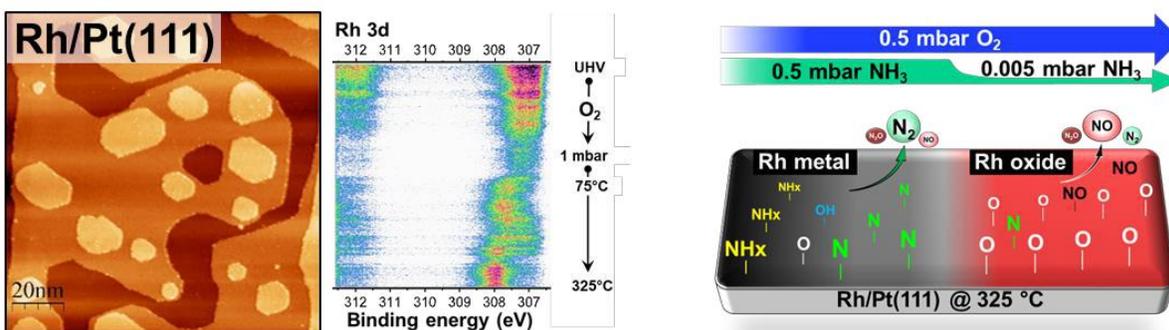
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Ammonia oxidation (Ostwald process, preferred product NO) is an essential step in the chemical for production of artificial nitrogen based fertilizers, and in environmental applications for reducing NO<sub>x</sub> emissions in diesel engines (NH<sub>3</sub> slip reaction, preferred product N<sub>2</sub>). For both processes, PtRh alloys are active catalysts. Although reaction mechanism and kinetics for the oxidation process is established, a direct operando observation of the routes towards N<sub>2</sub> and NO is lacking. In this contribution we fill in this gap and present a combined Scanning Tunneling Spectroscopy (STM) [1] and Ambient-Pressure X-rays Photoelectron Spectroscopy (AP-XPS) study [2] of catalytically active PtRh alloys prepared on Pt(111) and Rh(111) surfaces, measured operando during NH<sub>3</sub> oxidation at 1 mbar.



**Figure 1.** UHV STM (left) and APXPS (middle) demonstrate how surface species (O- and N-) lead to different products during NH<sub>3</sub> oxidation (summarized on the right).

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## Standing-wave Ambient Pressure Photoelectron Spectroscopy for Extreme UV Lithography Photoresist Analysis

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Standing-wave ambient pressure photoelectron spectroscopy (SWAPPS) is by now a well-known technique used for high precision depth analysis of solid/solid and solid/liquid buried interfaces [1]. Recently, the technique was also applied to soft matter samples – polymers used in desalination processes [2] as well as extreme ultraviolet lithography (EUVL) photoresists [3]. In this paper we are reporting results on structural and chemical changes of the commercial chemically amplified photoresist as it's been processed by UV exposure and thermal development. Dramatic changes, both chemical and structural are observed in several constituents of the resist. The chemical depth analysis on ~nm/sub-nm scale, as presented here, is an irreplaceable tool in monitoring the chemical processes in the resist and the results provide valuable input for development of next generation photoresists. The outlook of the paper will then discuss future possible applications of SWAPPS to other soft-matter materials.

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## APXPS in the past and in the future: APXPS publication database and a personal view on the future development of the field

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Within a couple of years from now, ambient pressure x-ray photoelectron spectroscopy (APXPS) is about to enter its sixth decade of existence. By now, on the order of one thousand APXPS publications have appeared (cf. Fig. 1), mainly from around 2005 and onwards [1]. The recent increase in the number of APXPS publications mirrors the installation of an increasing number of APXPS instrument at synchrotron radiation facilities and in laboratory facilities around the world. Clearly, the scientific community is more and more embracing the potential of APXPS in a diversifying spectrum of research areas. Therefore, we have chosen to make an APXPS publication database available to the APXPS community, and by the time of the APXPS workshop this database will have gone online. Our ambition with the database is not only to make available a complete list of APXPS publications, but also to provide you with a tool to easily select APXPS publications according to research field, publication topic (e.g. chemical reaction in the field of catalysis) and type of experiment (lab- or synchrotron-based).

We will present the status and functioning of the database and how you can contribute to it and complete it. This will be combined with an analysis of the development of the APXPS field from the observed publication patterns as well as a personal view of the future possibilities and challenges for the APXPS field. These are exemplified using a few selected case stories from catalysis and thin film deposition.

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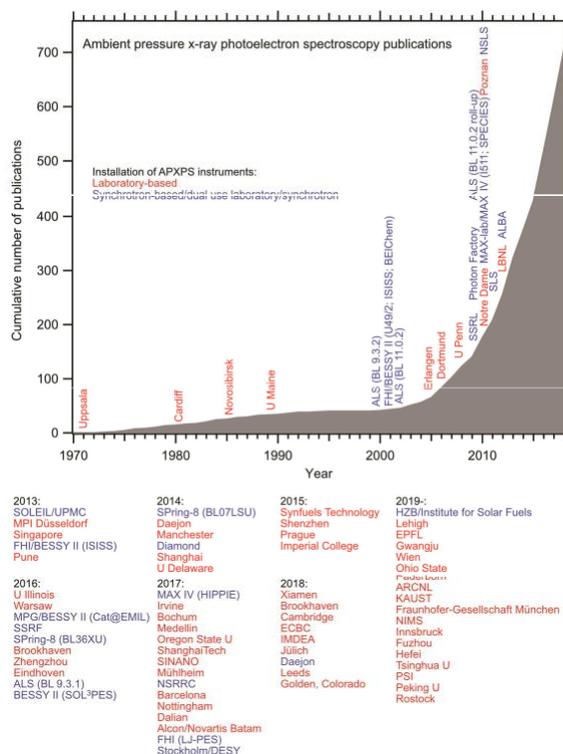


Fig. 1. Updated APXPS timeline [1] with data similar to those shown in [2]. Presented are the cumulative number of APXPS publications and the dates of delivery/installation of new APXPS instruments, with synchrotron light-based instruments shown in blue and laboratory ones in red.

## Electrochemical XPS: where do we stand?

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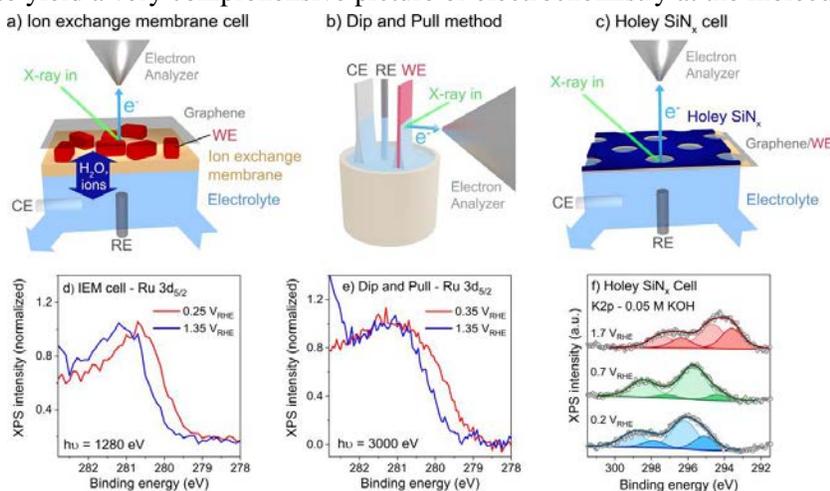
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In search of molecular level understanding of electrochemical reactions, insight into the chemical state of the electrode-electrolyte interface is an essential component. To provide such information, several electrochemical XPS approaches have been developed in recent years. We will compare three of these approaches (see Figure): 1) The ion exchange membrane cell, 2) The Dip and Pull method, and 3) the holey SiN<sub>x</sub> cell. Using the case studies of RuO<sub>x</sub>, IrO<sub>x</sub>, and graphene electrodes, we highlight the capabilities of each approach to probe the chemistry of both the electrode and electrolyte under electrochemical conditions, and discuss opportunities for future improvements.

On the electrode side, we follow the oxidation/reduction of IrO<sub>x</sub> and RuO<sub>x</sub> over a wide potential range. The difference in surface sensitivity of the XPS approaches allows us to see that the redox in these materials only occurs in the near-surface region. On the electrolyte side, we follow the electrostatic potential of SO<sub>4</sub><sup>2-</sup> and K<sup>+</sup> ions near the surface and identify specific interactions with the electrode. Finally, we discuss how the XPS measurements can be combined with XAS and electrochemical measurements to yield a very comprehensive picture of electrochemistry at the molecular level.



## Digital Twin: A Theorist's Playground for APXPS and Surface Science

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The concept of Digital Twin originally came from the industry, which was referring to a “digital copy of the physical asset.” With more than 9000 papers published annually on XPS, the ambitious attempt here is to construct a virtual laboratory infrastructure to solve a variety of technical challenges in data acquisition, control, analysis, and model-driven interpretation. The digital twin is expected to faithfully mimic facilities, including automated workflows with continuous updates from real experiments, which would eventually augment the experimentalists' decision making and execution of optimal experimental strategies to drive physical knowledge acquisition for user facilities. As daunting as it sounds, I will explain the challenges along with the milestones. Specifically, we have come a long way in 1) developing physically accurate quantum chemistry methods that improve the numerical accuracy of XPS binding energy (BE) calculation. 2) realizing that a central piece of chemical reaction network (CRN) is universal in the chemical systems of interest (such as heterogeneous catalysis and reactors): the CRN itself is not directly observable, yet the dynamical behaviours of CRN can be probed through advanced characterization (such as APXPS) and performance experiment (such as the measurement of turn-over-frequency (TOF), tafel slope, overpotential and etc.) 3) sharing a user-friendly, natural chemical language syn-tax Digital Twin v.01 software package, which we welcome collaboration and feedback in any form.

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## Cobalt Oxide Nanoisland PROX Catalyst: Mechanisms and Active Phase in Near Ambient Conditions

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In the pursuit of more sustainable low carbon fuels one of the interesting avenues to explore is the development of better hydrogen fuel cells, specifically proton-exchange membrane fuel cells (PEM-FC). The PEM-FC takes H<sub>2</sub> gas as a fuel, generating current and forming water exhaust. However part of the PEM-FC is poisoned by even trace amounts of CO [1], so an effective way to remove the CO from the feed-gas is needed. This can be achieved through the preferential oxidation (PROX) of CO into CO<sub>2</sub> in the presence of H<sub>2</sub> [2]. CoO<sub>x</sub> has been shown to be an effective PROX catalyst, however the reaction pathway have been previously unknown. Previous work by this group has allowed a CoO<sub>x</sub> on Pt(111) model catalyst, characterized by both STM and XPS, to be grown with a high degree of control, and two distinct morphologies of nanoislands, bilayer and trilayer, characterized by a 2<sup>+</sup> and 3<sup>+</sup> oxidation state respectively [3]. By tracking the oxidation state of the cobalt, using a combination of AP-XPS and NEXAFS, the active phase of the CoO<sub>x</sub> can be determined during PROX reaction, in varying concentrations of H<sub>2</sub> gas. Monitoring the C1s and O1s regions during a temperature series, as in Figure 1, the nature of adsorbates, adsorption sites and the catalytic mechanisms have been determined. We find that in the most selective PROX conditions, CO<sub>2</sub> is produced without H<sub>2</sub>O, the Co is in the 3<sup>+</sup> oxidation state. Moreover, a mechanism by which this occurs has been postulated.

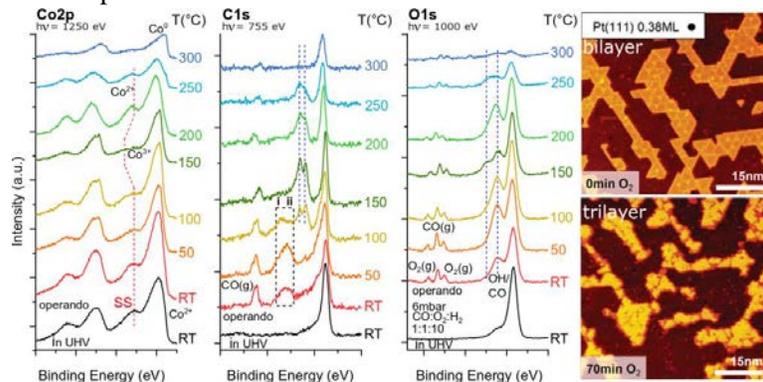


Figure 1: Left AP-XPS of Co2p, C1s & O1s regions, for temperature series from RT to 300°C in PROX reaction conditions (6 mbar CO:O<sub>2</sub>:H<sub>2</sub> in a 1:1:10 ratio) of a 0.5ML CoO<sub>x</sub> nanoisland catalyst on Pt(111). Right: STM of the bilayer and trilayer CoO<sub>x</sub>

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## Early Successes & Exciting Developments with the Lab-based APXPS & IRRAS at the Center for Functional Nanomaterials

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The lab-based APXPS instrument with *in vacuo* IRRAS has been in full user operation for nearly two years at the Center for Functional Nanomaterials (CFN).<sup>1</sup> Early successful studies have used a combination of both techniques, one technique alone, and complementary synchrotron studies. The instrument capabilities will be described using recent science examples. The focused mono-chromatic Al anode provides ample signal to study, for instance, Fisher-Tropsch synthesis,<sup>2</sup> water formation in confinement under silicate films,<sup>3,4</sup> and CO<sub>2</sub> adsorption on metal oxides. Compared with synchrotron radiation, the relatively lower flux of the Al source is ideal to study the electronic structure of insulating metal organic frameworks<sup>1</sup> but remains sufficient for investigations of fractional coverages of size-selected metal oxide clusters deposited on metal single crystalline surfaces.<sup>5</sup> Key to the latter study is a vacuum suitcase used to transport the sample from the deposition chamber to the APXPS or other surface characterization equipment at the CFN.<sup>1</sup> New developments are ongoing, including measuring APXPS data on MEMs chips used in environmental transmission electron microscopy, a cell for gas/solid interface studies at pressures above 10 mbar, a liquid cell for liquid/solid interface investigations, and transient kinetics measurements.

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## Study of oxidation states of SrTiO<sub>3</sub> (001) surface using AP-XPS

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Physical properties of interface at heterogeneous structures have become important as structures of electronic devices have decreased to nanoscale dimension. Any small change in physical or chemical characteristics at interface, such as chemical structure, space charges, or band alignment, can significantly change its transport and electronic properties of devices. As a result, much efforts have been made to the modification and characterization of the interfacial layer with the purpose of obtaining the desired device properties.

For many years, with the intense attention on the complex oxides in the ABO<sub>3</sub> perovskite form, the interface analysis of heterogeneous transition metal oxide materials has become an important topic. In particular, Strontium titanate (SrTiO<sub>3</sub>) has been a well-liked choice as a substrate for the growth of ferroelectric materials due to its superb physical and chemical properties. In a number of cases, the pulsed laser deposition (PLD) is used to deposit overlayer on top of SrTiO<sub>3</sub> and the several fabrication parameters during PLD process has been recognized as important role in changing the interfacial properties, e.g. substrate temperature, surface termination, and oxygen partial pressure. Here, we used ambient pressure XPS (AP-XPS) techniques to study the surface states of SrTiO<sub>3</sub> under similar states to the typical PLD growth condition. Under elevated temperature and oxygen pressure condition, clear chemical shifts to the lower binding energy direction are revealed among all elements. Especially, the spectral change in Sr 3d shows SrO<sub>1+x</sub> layer formation while the shape of the Ti 2p spectra is almost the same during the process of annealing.

## Studying Soft X-ray Spectroscopy of Aerosol Nanoparticles using Velocity Map Imaging

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Aerosols play an important role in the atmosphere, and the physical and chemical properties of aerosols have been studied extensively over the years using X-ray photoelectron spectroscopy. Here we are coupling velocity map imaging (VMI) detection, a powerful technique that has been used mainly for gas phase reactions, with aerosol nanoparticles.<sup>1, 2</sup> The experiment was conducted at the Advanced Light Source synchrotron, Lawrence Berkeley National Laboratory. Our aerosol beam is produced by a constant output atomizer and introduced to a differentially pumped vacuum chamber through an aerodynamics lens system. Then it enters the VMI photoelectron spectrometer, where the nanoparticles interact with the X-ray radiation to produce photoelectrons. These photoelectrons are then collected by a position sensitive microchannel plate detector and recorded as an image in the camera. The main advantage of the VMI spectrometer is, its ability to record both photoelectron spectrum as well as the photoelectron angular momentum information simultaneously.<sup>3</sup> In the present study we are investigating the properties of glycerol-water interactions in the nanoparticles utilizing soft X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS).

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## Probing Adsorbate-Induced Band Bending and Photocatalytic intermediates via Ambient Pressure X-ray photoelectron spectroscopy on CO<sub>2</sub> Reduction Reaction

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Recently, the global warming effect have change the earth climate and the inhabit environment. Therefore, it is urgent to find an effective method to solve this critical issue. Conversion of CO<sub>2</sub> into the solar fuel is a promising strategy to retard the extraordinary climate variation; furthermore, it is also able to solve the energy crisis at the same moment. Among of the photocatalyst materials, Molybdenum disulfide (MoS<sub>2</sub>) of photocatalyst has been extensively studied due to its great potential in CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). In this study, we investigated the crucial intermediate of bent CO<sub>2</sub><sup>δ-</sup> (b-CO<sub>2</sub>) and association with adsorbate-induced band bending of 2D MoS<sub>2</sub> semiconductor [1]. To gain in-depth atomic-level understanding, ambient pressure X-ray photoelectron spectroscopy (APXPS) has been utilized to investigate the electronic and chemical properties of MoS<sub>2</sub> interface under various gaseous condition. The interfacial dipole influenced the band bending and facilitate electron transfer between the H<sub>2</sub>O-adsorbed MoS<sub>2</sub> surface and CO<sub>2</sub> reactant. Moreover, changing the exposure sequences of CO<sub>2</sub> and H<sub>2</sub>O onto MoS<sub>2</sub> produced different b-CO<sub>2</sub> ratio which may further effect intermediates and final hydrocarbon fuels. The results provide fundamental information for developing high-activity catalysts for CO<sub>2</sub>RR.

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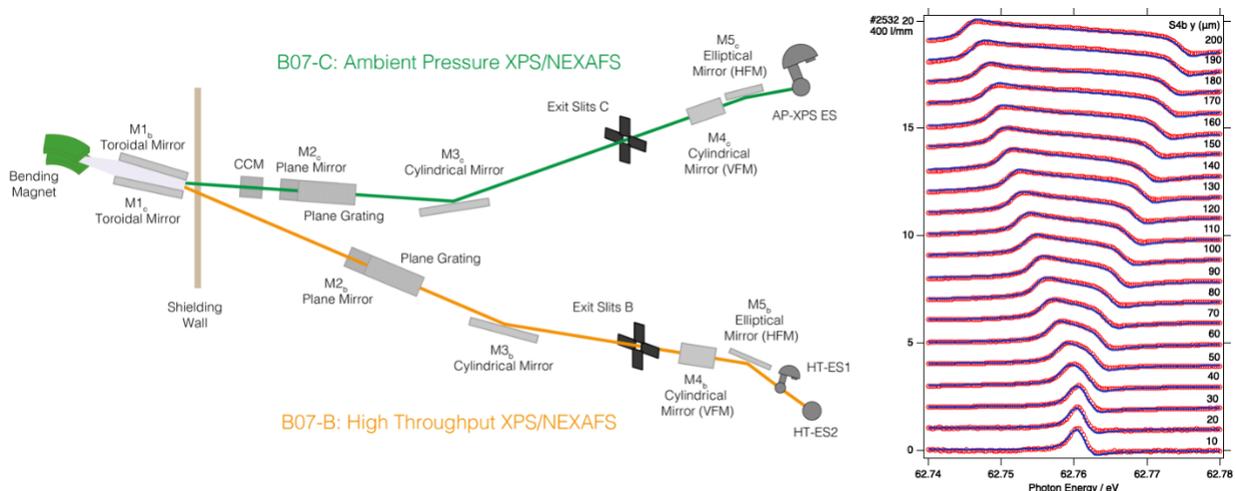
## VerSoX B07-B: A New Beamline for Ambient Pressure X-ray Absorption Spectroscopy Spectroscopy and High-Throughput X-ray Photoelectron Spectroscopy

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We present a new beamline at Diamond Light Source, B07-B, dedicated to soft X-ray spectroscopy under varied experimental conditions. This beamline uses the same bending magnet source as the Ambient Pressure XPS beamline (VerSoX B07-C)[1] but has completely separate optics and control systems allowing simultaneous independent operation of the two beamlines. It is equipped with two experimental endstations: ES-1 for high-throughput XPS measurements under UHV conditions with full sample preparation facilities and automated sample transfers; and ES-2 for ambient X-ray absorption spectroscopy of gas, liquid and solid samples. The beamline covers a wide energy range from 40-2800 eV, and has demonstrated a resolving power >10000 during initial commissioning. We present the experimental capabilities of the beamline and endstations along with a discussion of the X-ray commissioning and optimisation process.



**Figure 1.** The optical layout of the B07 VerSoX beamlines, and He XAS data as a function of B07-B beamline exit slit opening

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## Adsorbate coverages and the relation to reaction barriers during CO and CO<sub>2</sub> hydrogenation on Rh single crystals.

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Energy barriers calculated using density functional theory are staples in the mechanistic understanding of heterogeneous catalytic reactions. Combined with a microkinetic rate model it has been possible to relate the potential energy diagram to the measured turn-over frequency of flow reactor experiments. [1] The recent POLARIS high-pressure x-ray photoelectron spectroscopy endstation allows for another experimental observable to be used: the coverage of adsorbates during the resting state of the reaction [2]. We present a “reverse engineering” approach to the reaction mechanism where a genetic algorithm I utilized to adjust the free energy surface in order to fit the experimental coverages. This approach gives us a tool to hypothesize about reasons for the previously observed mismatches between theory and experiment and ultimately towards a better understanding of the reaction mechanism.

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## The study of bandgap tuning in post-annealed Ga<sub>2</sub>O<sub>3</sub> film with ambient pressure XPS

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Ga<sub>2</sub>O<sub>3</sub> has been a popular choice for optoelectronic devices due to its high chemical/thermal stability, high breakdown voltage, and wide bandgap. Especially, for device application, understanding the band structure at junction in device is of paramount importance. Among many physical parameters, it is widely known that the bandgap of Ga<sub>2</sub>O<sub>3</sub> is affected by oxygen stoichiometry and its crystallinity of the thin film, which can be easily manipulated by post-annealing process. [1]

To identify a role of post-annealing effect on Ga<sub>2</sub>O<sub>3-x</sub> thin film, various techniques, consisted of X-ray diffraction (XRD), ambient pressure X-ray photoelectron spectroscopy (AP-XPS), and UV-vis spectroscopy, were utilized. During post-annealing process, the epitaxial crystallization of thin films is monitored by X-ray diffraction (XRD). Then, ambient pressure X-ray photoelectron spectroscopy (AP-XPS) measurements are carried out under the post-annealing process, *e.g.*, elevated oxygen pressure and temperature condition. With AP-XPS, the enhancement of Ga<sup>3+</sup> peaks are found, *i.e.*, chemical composition of Ga<sub>2</sub>O<sub>3-x</sub> is identified. Furthermore, the bandgap widths from UV-Vis spectroscopy results indicate that the bandgap of Ga<sub>2</sub>O<sub>3-x</sub> thin film is increasing as Ga<sup>3+</sup> component become enhanced. Our works suggest that bandgap of Ga<sub>2</sub>O<sub>3-x</sub> thin film is strongly correlated with the chemical composition of Ga<sub>2</sub>O<sub>3-x</sub> film.

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## Increasing selectivity of direct alkene epoxidation on silver

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Alkene epoxidations are an important class of reactions. These continue to attract considerable academic and industrial interest<sup>1-2</sup>. A longstanding challenge is the development of catalysts for the direct epoxidation of propylene to propylene oxide (PO). From an academic viewpoint, the absence of effective catalysts for this process is intriguing, as the C2 epoxide, ethylene oxide (EO), is easily formed using Ag-catalysts under ethylene and O<sub>2</sub>. This difference in reactivity is attributed to the presence of a labile allylic C-H bond in propylene<sup>3</sup>. Circumventing H abstraction during propylene epoxidation would require a highly selective catalyst. Research of ethylene epoxidation has shown EO selectivity is mediated by the nature of the oxygen species on the catalyst surface. Two broad classes of oxygen have been observed by Ambient Pressure X-Ray Photoelectron Spectroscopy (APXPS), nucleophilic (O<sub>nuc</sub>) and electrophilic (O<sub>elec</sub>) oxygen. O<sub>elec</sub> is a class of covalently bound oxygen<sup>4,5</sup> appearing at high O 1s BE (~530 eV) and is the only species shown to participate in epoxidation (6, 7). O<sub>nuc</sub> is a class of oxygen induced surface reconstructions appearing at low O 1s binding energies (~528 eV). While increasing the concentration of O<sub>elec</sub> may improve PO selectivity, the nature of this species and means of increasing its coverage, has been long debated.<sup>2,7,8,9</sup> Recently, it was demonstrated that the methods used to prepare O<sub>elec</sub> on silver lead to the accumulation of an inactive SO<sub>4</sub>-(7×√3)rect phase surface reconstruction, due to sulfur impurities in ethylene and/or silver.<sup>7</sup> And while active only in combustion, O<sub>nuc</sub> was shown to be required to activate O<sub>elec</sub> (5, 7) by lift the inactive SO<sub>4</sub> induced surface reconstruction to form a metastable adsorbed SO<sub>4</sub> (SO<sub>4,ads</sub>). SO<sub>4,ads</sub> was shown to make EO and to improve EO-production under reaction condition,<sup>7</sup> and was demonstrated to have the spectroscopic properties associated with O<sub>elec</sub>.<sup>7</sup> Thus, the formation of the selective O<sub>elec</sub> requires a high near-surface oxygen concentration.<sup>7</sup> This is difficult to achieve during propylene epoxidation due to its high reducing potential.<sup>10</sup> Therefore, the lack of O<sub>elec</sub> may be a limitation in the direct PO production on silver,<sup>10</sup> though this has still to be proven.

In this work we employed these recent understanding from the catalytic chemistry of ethylene epoxidation and DFT calculations to predictably increase the selectivity of silver towards ethylene and propylene epoxidation. We verify the origins of these changes using APXPS.

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## CO oxidation on vicinal Rh surfaces studied with a curved crystal

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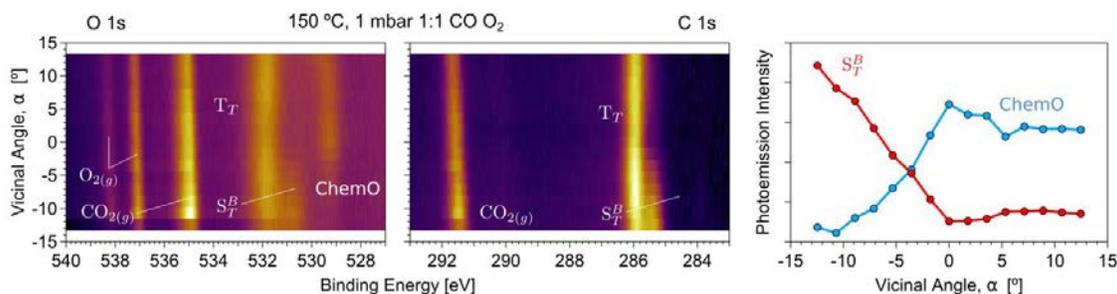
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The study of chemical reactions on single metal surfaces has been aimed at identifying active sites at crystal planes, in order to assess dissimilarities in reactivity between different undercoordinated atoms (*i.e.* terraces or kinks) present on catalysts nanoparticles [1]. By using cylindrical sections of single crystals, the catalytic activity of several surfaces can be compared at the same reaction conditions [2]. Within this approach, we have studied the CO oxidation reaction on a curved Rh crystal featuring different density of A- and B-Steps, with the (111) plane at the center. Using near-ambient pressure X-ray photoemission, we mapped the different reaction stages across the curved surface at different temperatures, in order to probe the different CO and oxygen surface species found individual vicinal planes at the different stages of the catalytic CO oxidation. At low temperature, both steps and terraces are CO-covered, and no CO<sub>2</sub> production is observed. However, after increasing the temperature to 150 °C, we found a very peculiar stage where only atop CO at terraces (TT) and B-Steps (STB) were found, together with a sizeable, macroscopic CO<sub>2</sub> production. Furthermore, chemisorbed oxygen (Chem-O) only appears on terraces at vicinal A-type surfaces, coexisting with STB. We believe that this mixed pre-ignition stage, quite different than those found on analogous Pt and Pd surfaces [2], could be key to understand the peculiarities of this catalytic reaction on Rh vicinal planes. In this sense, Planar Laser-Induced Fluorescent experiments [3] are planned in order to *in-situ* image the step-type-dependent light-off on the same Rh curved sample.



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## Strongly bound oxygen on silver and their role in methanol oxidation

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Understanding the catalytic partial oxidation of methanol to formaldehyde is a long standing problem that is poised to face a resurgence in interest.

Nowadays, formaldehyde is produced industrially by the reaction of methanol over either metal-oxide or silver based catalysts. The two catalysts require different reaction parameters and offer differing selectivity. For example, it is believed that formaldehyde is produced through both a partial oxidation and dehydrogenation pathway over silver based catalysts, while only the former seems to be important for the metal-oxide catalyst. This fact, and the simplicity of the silver based catalyst (modelled catalyst system), motivate our interest in the presented project.

The silver oxygen system has been thoroughly investigated in the last decades. When early studies on X-ray photoelectron spectroscopy (XPS) proved a powerful tool for such investigations [1].

Schlögl's group reported of an oxygen species that is stable at high temperatures and labelled it O<sub>γ</sub>. This oxygen species, with a binding energy of 529.1 to 529.7 eV [2], is described as a subsurface oxygen forming a thin oxide-like-layer on the silver surface. Rocha et al. [2] found two oxygen species formed at 500°C in 0.25 mbar of oxygen, one denoted O<sub>γ</sub> and the other O<sub>α2</sub>. Reichelt et al. [3] later used UHV techniques to show the strongly bound oxygen species could, in some cases, be due to Molybdenum oxide contamination on the silver surface, but the question remains as to the generality of that finding under *in situ* conditions.

We will now report on ways to differentiate between oxygen species attributed to silver and the ones attributed to Molybdenum oxide using synchrotron NAP-XPS in combination with X-ray absorption measurements. Furthermore, we investigated the silver oxygen system under reaction conditions for methanol oxidation.

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## An Ambient Pressure XPS approach to redox properties change in a Co<sub>3</sub>O<sub>4</sub> thin film modified by Mn cations

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The Co-Mn spinel-type materials, just like the spinel compounds (denoted as AB<sub>2</sub>O<sub>4</sub>; A, B=Transition metals), have interesting electronic properties that confer them important capabilities to be used in several applications (i.e. magnetism, energy storage, catalysis, etc.) [1][2]. The main reason is the synergistic effect between Co and Mn when they build the spinel structure, so the different properties of the Co-Mn spinel-type materials can be modulated according to the Co/Mn ratio and their oxidation state [3][4].

In this work, the redox capabilities of a spinel Co-Mn thin film having an approximated composition of CoMn<sub>2</sub>O<sub>4</sub> were tested and compared with a Co<sub>3</sub>O<sub>4</sub>-spinel thin film as a reference sample. The Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) facility located at the University Research Headquarters (SIU-UdeA) University of Antioquia in Medellín-Colombia, was employed to accomplish this research. Both Co<sub>3</sub>O<sub>4</sub> and Co-Mn thin film samples were analyzed under *in-situ* conditions during thermic treatments having H<sub>2</sub> and O<sub>2</sub> atmospheres to perform the reduction and oxidation tests, respectively. Redox capabilities were studied by analyzing changes in oxidation states and composition species of Co, Mn and O. Markable differences were found in the manner of how Co species behave when Mn is present in the spinel-structure. Incorporation of Mn species in the Co-based spinel confers it a relative resistance to be drastically reduced, what could mean better stability in the structure, even at high temperature under both strong reductive and oxidant atmospheres. These results become useful to explain better the performance of Co-Mn spinels in the different applications.

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## AP-XPS / NEXAFS Study of Thin-Film Al<sub>2</sub>O<sub>3</sub> Catalyst Supports Prepared via Anodization

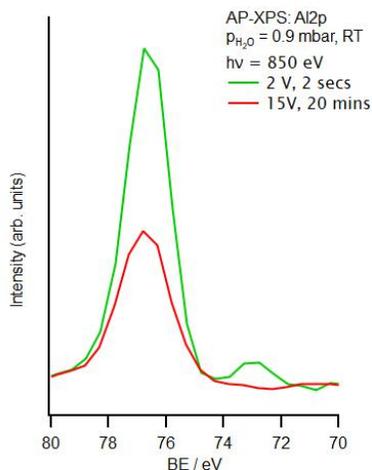
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Natural gas is an abundant energy source that has become useful<sup>1</sup> for several reasons, such as the low amounts of CO<sub>2</sub> and SO<sub>2</sub> generated during combustion.<sup>2</sup> However an issue arises from the presence of unburned methane after natural gas combustion. This is a problem as methane is a far more potent greenhouse gas than CO<sub>2</sub><sup>2</sup>. It is therefore desirable to remove the methane by oxidising it to CO<sub>2</sub> and H<sub>2</sub>O as it leaves the exhaust. The strong C-H bond makes methane the least reactive hydrocarbon.<sup>1</sup> As a result, for methane oxidation to occur a catalyst has to be introduced. Palladium is known to be the most active type of catalyst for methane oxidation;<sup>1,2</sup> however, it becomes unstable when it is exposed to water over a long period of time. Therefore, a Pd-Pt bimetallic catalyst supported on alumina (Al<sub>2</sub>O<sub>3</sub>) is used as the platinum stabilises the palladium and catalytic activity is improved.<sup>2,3</sup>



Photoelectron spectroscopy on alumina-supported catalysts is often hampered by charging of the support. To overcome this issue, thin alumina films of different thickness were synthesised on an aluminium substrate via anodization. In this work, we present a study of the thin film alumina catalyst supports under ambient H<sub>2</sub>O vapour conditions. The reactivity of the support has been studied by soft X-ray spectroscopic techniques at beamline B07, Diamond Light Source. XPS and NEXAFS were used to characterise the behaviour of the material under exposure to water vapour.

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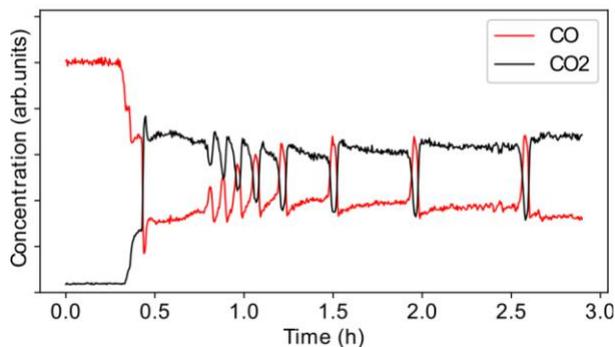
## Oxide formation and reactivity oscillations on Pt<sub>3</sub>Sn(111) during CO oxidation

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Tin oxide formation on a Pt<sub>3</sub>Sn(111) single crystal surface was studied during CO oxidation at *mbar* pressure with APXPS and QMS. As the XPS spectra show, the presence of CO on the surface affects the nature of the oxide that forms. With CO on the surface a more oxidised tin oxide is formed while absence of CO results in a less oxidised form of tin oxide. The oxide can also rapidly change oxidation state if CO is adsorbed or desorbed from the surface. Finally, self-sustained oscillations were observed in the reactivity of the sample, seen in figure 1. The oscillations originally have a high frequency with sharp dips in conversion, with dips becoming less frequent as time passes. This could indicate a relationship between CO presence on the surface, the tin oxide and the number of active sites on the surface.



**Figure 1:** CO and O<sub>2</sub> concentrations above a Pt<sub>3</sub>Sn(111) surface.[1] The temperature was ramped up from room temperature to 300°C (reached at about 0.4h) and maintained there. The total pressure was 1mbar and the flow through the reactor 5.5ml/min.

### References

[1] to be published.

## **Ambient Pressure X-Ray Photoelectron Spectroscopy Study of Thermal De-composition of Acetic Acid on Pd(111)**

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Acetic acid decomposition over Pd(111) is a good model for the decomposition of fatty acids and other oxygenates involved in biofuel production. Our previous density functional theory (DFT) studies on the thermal decomposition of acetic acid on Pd(111) suggested that carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>), are produced by two different reaction pathways: decarbonylation (DCN), and decarboxylation (DCX), respectively. Without water, the DCX, producing CO<sub>2</sub>, is slightly favored over the DCN pathway but in the presence of water, that shifts to mostly CO<sub>2</sub>. To further understand these reaction mechanisms, we have studied this model system using ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and mass spectrometry (MS). AP-XPS allowed us to identify adsorbed reaction intermediates when dosing acetic acid on clean Pd(111), including surface carbon, adsorbed CO, and acetate species. In order to confirm our DFT results, we introduced a 1:1 mixture of water and acetic acid at various pressures and temperatures. When exposing Pd(111) to acetic acid at 300K and range of pressures from 0.001 mbar to 1 mbar, the CO<sub>2</sub>:CO mass peak ratios increased from 1.22 to 2.11. This mass peak ratio also increases from 2.11 to 2.82 in the presence of water at 1 mbar, which suggests that more of CO<sub>2</sub> is being produced in the presence of water. AP-XPS data shows an increase in relative area of CO when co-adsorbed water is present (2.3% to 6.1%, at 1mbar, 300K), suggesting an increase in reactivity. These preliminary studies suggest an enhancement in both of pathways with the addition to water based on the XPS and MS data. Future experiments include lower pressures to separate the contribution of gas phase from the surface reaction as well as varied temperatures.

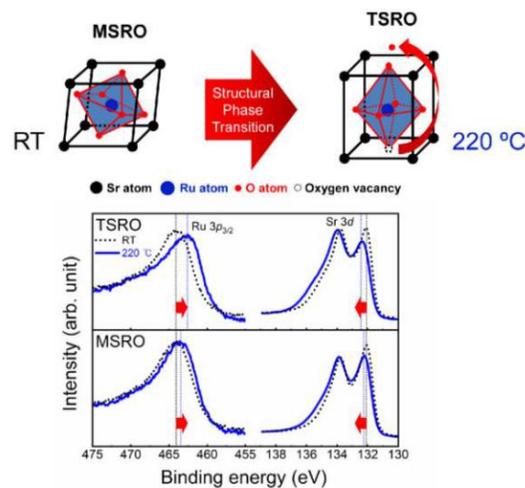
## Correlation between structural phase transition and surface chemical properties of thin film SrRuO<sub>3</sub>/SrTiO<sub>3</sub> (001)

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In field of photovoltaic and electronic devices, SrRuO<sub>3</sub> (SRO) thin film has been attracted much attention due to its fascinating electronic/magnetic properties, *i.e.*, ferromagnetism, superconductivity, etc. It is well known that SRO/STO thin film undergoes the structural phase transition (SPT) from monoclinic phase to tetragonal phase near ~200 °C. The physical origin of the SPT is suspected to be coming from the interfacial constraint between SRO and STO, which is related to the oxygen vacancy. To confirm the correlation between oxygen vacancy and SPT of SRO thin film, in situ x-ray diffraction (XRD) and ambient pressure x-ray photoelectron spectroscopy (AP-XPS) were utilized during SPT. XRD shows that the SPT occurred from monoclinic SRO to tetragonal SRO at ~200 °C regardless of gas environment. With AP-XPS, the surface chemical properties of SRO film changes dramatically during the SPT temperature. The direction of core level shift of Ru and Sr can be understood with the formation of oxygen vacancy along the Sr-O plane. Our results show the evidence of oxygen migration to surface during SPT, indicating the close correlation between oxygen vacancy and SPT in SRO thin films.



## Interaction between LaMnO<sub>3-δ</sub> perovskite (R-3c) surface and small molecules (Ar, CO, O<sub>2</sub>, H<sub>2</sub>): An XPS-NAP Analysis

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The hydrogen-rich stream that is constantly supplied to a fuel cell (FC) commonly comes from reformed hydrocarbons that contain a significant amount of carbon monoxide. This CO must be removed to a level below 10 ppm to avoid deactivation of the platinum electrode. A good alternative for obtaining this low level is the CO selective oxidation (SELOX) [1].

Near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) has become an increasingly popular technique to observe the chemical changes of catalytically active oxide surfaces under more realistic operating conditions (or at least near to) [2].

The main objective was to study the interaction of small molecules with the surface of a LaMnO<sub>3-δ</sub> perovskite. Surface chemical changes such as the O<sub>surf</sub>/O<sub>lattice</sub> and Mn<sup>3+</sup>/Mn<sup>4+</sup> ratio were analyzed as a function of temperature (400, 450, 500, 550, 650 K) and different gas background. A partial reduction was found on the surface when H<sub>2</sub> and CO are used in the reaction and the Mn<sup>3+</sup>/Mn<sup>4+</sup> ratio increases. On the other hand, carbonate species were formed on the surface in the reaction stream and found in the carbon region. In addition, CO<sub>2</sub> was detected, through mass spectrometry, during the reaction at temperatures greater than 500 K. These results allow to suggest that CO is activate at superficial oxygen sites and desorbing itself as CO<sub>2</sub> and in some cases generating very strong interactions forming carbonates.

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## Study of XPS satellite features under elevated pressure condition

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The interaction (inelastic scattering) between surface photoelectrons and gas molecules has been investigated with ambient pressure X-ray photoelectron spectroscopy (AP-XPS) experiment. [1] In AP-XPS spectra, several characteristic satellite features are observed as the pressure increases, which then can be interpreted as the molecular excitation states of gas molecules due to the collisions of photoelectron from surface. [2] Further-more, it is expected that chemisorption of gas molecules can contribute to the structure of these satellite features. [3]

To observe the effect of gas chemisorption on the satellite features from the photoelectron-gas interaction, CO gas molecules are tested on Pt-based alloy surfaces. Each Pt-based surface shows distinct satellite structure, which is related to the different adsorption property of CO on different surface. Our results show that inelastic features under elevated pressure condition can be utilized for studying surface adsorption properties as well as chemisorbed surface electronic structures.

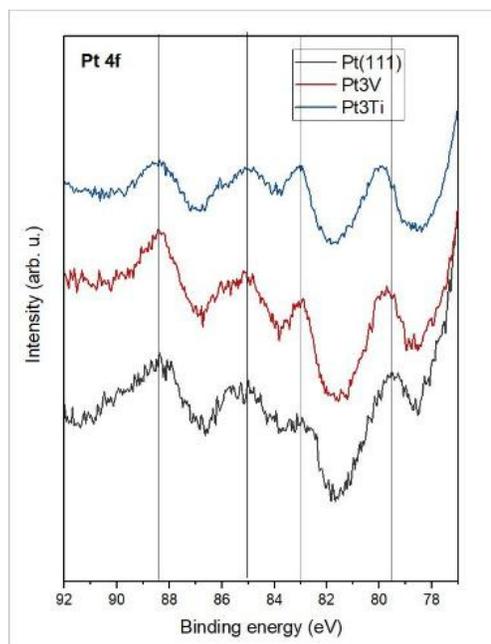


Figure 2. Photoelectron-gas interaction satellite peaks for Pt 4f peak for Pt-based surface

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## **Investigation of surface chemical states of Pt-based alloys, Pt<sub>3</sub>M (M=Ti,V), during CO oxidation by AP-XPS**

Moonjung Jung<sup>1</sup>, Dongwoo Kim<sup>1</sup>, Hojoon Lim<sup>1</sup>, Geonhwa Kim<sup>1</sup>, Youngseok Yu<sup>1</sup>, Minsik Seo<sup>1</sup>,  
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With ambient pressure X-ray photoelectron spectroscopy and mass spectrometer, the modifications of surface state on Pt-transition metal alloy, Pt<sub>3</sub>M (M=Ti,V), are investigated during CO oxidation reaction, *i.e.*, oxygen rich reaction condition, P(CO)/P(O<sub>2</sub>)=0.1. As reaction temperature increases, surface compositions and its chemical states undergoes significant changes. The chemical bonding states between the transition metals and platinum atom shows the sign of charge transfer between them. Also, at the onset of CO oxidation reaction, the oxidation states of 3*d* transition metals increases while the Pt atoms becomes metallic states. Our works provide the basic information on how the 3*d* transition metals in Pt<sub>3</sub>M alloys contributes to the reaction, which can be valuable information for real catalyst design and theoretical modeling for practical reaction condition.

## Factors influencing surface carbon contamination in ambient-pressure XPS

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Surface carbon contamination has an enormous influence on surface science experiments, especially in near-ambient conditions. We performed ambient-pressure X-ray photoelectron spectroscopy experiments towards examining this problem using a large scale (50x10x1 mm<sup>3</sup>) rutile TiO<sub>2</sub>(110) single crystal exposed to water vapor and liquid water. All experiments were performed at the Swiss Light Source, using the recently built Solid-Liquid Interface Chamber (SLIC) endstation connected to the tender X-ray Phoenix I beamline [1]. The experimental results highlight factors and environmental conditions playing roles in the carbon buildup on the surface, such as beam illumination, residual gas pressure and composition, as well as interaction with liquid water. It became evident that beam-induced effects locally increase the amount of carbon. Starting conditions that are independent of the light irradiation determine the initial overall contamination level. The introduction of a few mbar of molecular oxygen allows fast surface cleaning during X-ray illumination. The surface carbon contamination can be completely removed when the partial oxygen pressure is comparable to the partial water vapor pressure, as was tested by exposing the sample to 15 mbar of water vapor and 15 mbar of molecular O<sub>2</sub> simultaneously. Furthermore, our data support the hypothesis that progressive removal of carbon species from the chamber walls takes place following exposure to water vapor. Repeating this exposure multiple times results in reduced contamination. We believe that our findings will be vital for future studies of solid-liquid interfaces with techniques such as the dip-and-pull method [2], where carbon contamination is notorious but rarely mentioned.

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## Observing the Fischer-Tropsch reaction on Co(0001) at 150mbar and above using a virtual cell approach and hard X-rays

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The quest for a sustainable future poses challenges, especially with regard to the storage and distribution of fuels. One possible solution is to store energy in chemical bonds. The underlying process for hydration of carboxides is well-known as Fischer-Tropsch (FT) synthesis and can be performed on various heterogeneous catalysts such as Co. Despite knowing that this catalytic reaction exists, available literature detailing the debated reaction mechanisms is lacking[1, 2]. Indeed, only indirect measurements (e.g. by QMS), observations far away from reaction conditions (XPS < ~10mbar) or after the reaction can be found. As seen by many publications XPS can address the reaction mechanisms in question. However, combining ultra-high vacuum (UHV), as it is required to transfer photoelectrons without scattering and high pressures (above 1 bar), as it is required for the catalytic reaction, has posed significant technical challenges and caused the pressure gap above the ~10mbar range.

The POLARIS setup (Stockholm University) is in operation at P22, PETRA III [3] and aims to overcome this pressure gap by utilizing a virtual cell concept. Here we set out with the goal of observing the FT reaction at pressures as close as possible to the pressures applied in industrial catalysis. Onto the single crystalline cobalt we direct mixtures of CO:H<sub>2</sub>, CO<sub>2</sub>:H<sub>2</sub> and CO:CO<sub>2</sub>:H<sub>2</sub>. We obtain Co2p, C1s and O1s core level isotherms and quantify the adsorbed species under these conditions at 150mbar. We demonstrate the feasibility of measuring surface adsorbates at 1025mbar. Our findings reflect recently published results from operando STM[4] and are compared to findings from post-reaction XPS[5].

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## **A Flow-Focused Droplet Train for Ambient Pressure XPS with tender X-rays**

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Here we present a newly commissioned droplet train that we have designed for measuring the chemical and physical properties of liquids in pressures up to 30 mbar. Our droplet train generates thousands of uniform droplets a second, tunable in diameter between 100 to 500 microns, suitably matching the diameter of our analysis nozzle (300 microns).

We demonstrate how the use of flow-focusing creates a positionally stable droplet train that is less prone to clogging than traditional methods. Flow-focusing uses a gas pressure drop across an orifice to shape a liquid stream flowing through it where the liquid stream does not contact the orifice. We demonstrate flow-focusing with gas pressures below atmospheric pressure, a requirement for implementation into AP-XPS systems. We present results from commissioning experiments on aqueous solutions and colloidal systems. We also show the capability of time-resolved XPS using the droplet train. By changing the height of the droplet generation point above the analysis position nucleation and growth of salt crystallites from aqueous solution can be studied. Depending on the speed of the droplets, we can access delay times between tens of  $\mu$ s and hundreds of ms. The use of tender X-rays renders these measurements more bulk-sensitive than traditional soft X-ray AP-XPS measurements and opens a range of new possibilities for time-resolved XPS measurements of reactions and processes in liquids.

The droplet train module, along with the dip and pull module, is a part of the SpAnTeX end station, which is equipped with a SPECS Phoibos 150 NAP Analyzer capable of measuring up to 10 keV photoelectrons. The SpAnTeX end-station focuses on AP-XPS experiments in the tender X-ray regime (AP-HAXPES). Commissioning experiments were performed at the KMC1 beamline in BESSY II, Berlin.

## **Ambient pressure X-ray photoelectron spectroscopy studies of electrochemically mediated regeneration of amine solutions for CO<sub>2</sub> capture technologies**

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Carbon capture with aqueous amine solutions is a mature technology that has been used for CO<sub>2</sub> removal from point source emissions, such as fossil fuel-fired power plants. Amines are known for their reversible reactions with CO<sub>2</sub>, which make them particularly useful for the separation of CO<sub>2</sub> from many CO<sub>2</sub>-containing gases, including flue gas. However, current aqueous amine-based capture technologies use a high temperature regeneration cycle that can lead to amine decomposition and a high energy penalty. Electrochemically mediated amine regeneration (EMAR) has been proposed [1] as an alternative method to regenerate aqueous amine-based CO<sub>2</sub> capture solutions in order to circumvent these problems. EMAR can help to overcome the high energy consumption and reduce amine decomposition caused by thermal regeneration. During EMAR, the captured CO<sub>2</sub> is released from the amine solution by oxidizing a metallic anode, typically copper. This produces metallic ions that form complexes with amines. Since complex formation is more favorable than CO<sub>2</sub> absorption, the CO<sub>2</sub> is released upon complex formation. Subsequent reduction of the complex at a cathode regenerates the aqueous amines and the solution's ability to capture CO<sub>2</sub>.

We have used the dip-and-pull method in combination with AP-HAXPES [2] to investigate copper-based EMAR systems. We investigated the copper(II)-ethylenediamine (EDA) complex by in-situ AP-HAXPES measurements, to identify and quantify the copper oxidation states and the amounts of EDA bound in complex. To reproduce the EMAR process, a copper electrode was immersed in a Cu(II)-EDA complex solution, and cyclic-voltammetry scans were performed to consecutively oxidize and reduce the Cu(II)-EDA complex on the electrode; AP-HAXPES measurements were conducted at selected potentials at both oxidation and reduction conditions, in order to understand both the state of the copper electrode and the composition of the aqueous solution near the electrode. The experiments were carried out at the SpAnTeX end-station, using tender X-rays from the KMC-1 beamline at BESSY II in Berlin.

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## *In situ* oxidation of Pd and Pd-Au alloy surfaces

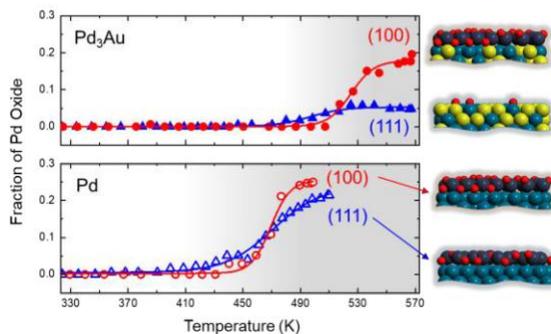
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Pd is well known as a catalytically active material for the CO oxidation. It has been found that O-covered Pd phases accelerate the catalytic CO oxidation by high-pressure surface science techniques. Alloying with secondary elements is regarded as a promising modification for achieving highly functionalized catalysts. In this work, oxidation of monometallic Pd and bimetallic Pd<sub>3</sub>Au alloy surfaces are observed by AP-XPS at 100 mTorr O<sub>2</sub> ambient [1]. Figure 1 shows the evolution of surface oxidation on Pd<sub>3</sub>Au and Pd surfaces. It shows that the alloying with Au hinders the surface oxidation of Pd surfaces. Besides, the oxidation behavior is clearly different between Pd<sub>3</sub>Au(111) and (100) surfaces. The (100) surface has a relatively Pd-rich surface composition, and the surface oxide layer is formed, whereas the (111) surface has an Au-rich surface composition, and the surface oxidation is quite limited. Theoretical simulations reveal that Pd/Au surface composition and atomic arrangement are key factors determining the oxidation behavior.

AP-XPS measurements were carried out at beamline 13B at the Photon-Factory of High Energy Accelerator Research Organization (KEK-PF) in Tsukuba, Japan [2]. The Pd and Pd<sub>3</sub>Au single-crystal surfaces were cleaned by repeated cycles of Ar<sup>+</sup> sputtering, O<sub>2</sub> treatment at 700 K, and annealing up to 1000 K. Au 4f<sub>7/2</sub>, Pd 3d<sub>5/2</sub>, and O 1s XP spectra were recorded with photon energies of 180, 430, and 630 eV, respectively, to detect photoelectrons with almost the same kinetic energies. The surfaces are exposed to the 100 mTorr O<sub>2</sub> ambient.



**Figure 1.** *In situ* oxidation of Pd<sub>3</sub>Au (top) and Pd (bottom) surfaces as a function of temperature. The fraction of Pd oxide is deduced from the intensity of the oxide-induced “four-fold surface Pd” peak in Pd 3d<sub>5/2</sub> XP spectra.

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## Characterization of an In<sub>2</sub>O<sub>3</sub>(111) model catalyst for methanol synthesis by CO<sub>2</sub> hydrogenation

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Methanol synthesis by CO<sub>2</sub> hydrogenation is an attractive method to recycle captured CO<sub>2</sub> from combustion processes of fossil fuels. This utilizes the captured CO<sub>2</sub> and simultaneously creates a sustainable source of methanol. A range of catalysts for methanol synthesis by CO<sub>2</sub> hydrogenation have been studied. In<sub>2</sub>O<sub>3</sub> - catalysts supported on ZrO<sub>2</sub> have shown high activity, 99.8 % selectivity and remarkable stability for CO<sub>2</sub> hydrogenation to methanol under industrial relevant conditions [1].

To investigate the reason behind the high performance of this catalyst for CO<sub>2</sub> hydrogenation, we are investigating a model system of this catalyst consisting of a crystalline In<sub>2</sub>O<sub>3</sub>(111)-film grown on Yttria-stabilized ZrO<sub>2</sub>-substrate [2].

We used X-ray Photoelectron Spectroscopy (XPS) and Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) to study the adsorption of CO<sub>2</sub> and H<sub>2</sub> on the In<sub>2</sub>O<sub>3</sub>(111) surface. We observed the formation of different carbon-based species during the CO<sub>2</sub> adsorption which will be discussed.

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## **Ambient Pressure XPS Study of CO<sub>2</sub> Photoreduction on Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> and Rb<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> Perovskite Nanomaterials with Reactivity Enhanced by Ligand Removal**

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Bismuth halide perovskites exhibit several attractive properties for photovoltaic applications, such as nontoxicity for being lead-free, good light absorption ability, and high chemical stability. One appealing use of bismuth halide perovskite is for photocatalytic application. In the present study, we examine the photo-catalytic reduction of CO<sub>2</sub> on nano-crystalline Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> and Rb<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>. For the nanomaterials fabricated from solution phase, ligand or surfactant molecules need to be present so that the degree of agglomeration of nanoparticles can be controlled. The organic ligands attached to the nano-perovskites can act as a barrier to impede the transportation of photogenerated carriers from perovskite to reactants, decreasing the overall photocatalytic performances. Thus, it is imperative to remove ligands completely while preserving the reactive nature associated with nanoparticles.

Nano-crystalline perovskites were synthesized by top-down method and ligand-free perovskites were prepared by removing oleic acid ligand with ethanol. APXPS investigation of CO<sub>2</sub> UV-photoreduction was performed in mixed CO<sub>2</sub>/H<sub>2</sub>O of mbar pressure. Surface species adsorbed on Bi active sites and the carbon-containing products were closely followed as the photoreaction proceeds. The ligand free perovskite exhibits a larger CO<sub>2</sub> uptake and is more photo-reactive, as compared to ligand-present nano-perovskite. The comparison of photocatalytic efficacy for nano-perovskites prepared by two methods will be presented.

### **Dynamic metal/metal oxide interface affects PdAg reactivity**

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Heterogeneous catalysts are complex materials with multiple interfaces. A critical proposition in exploiting bifunctionality in alloy catalysts is to achieve surface migration across interfaces separating functionally dissimilar regions. Herein, we demonstrate the enhancement of more than 10<sup>4</sup> in the rate of molecular hydrogen reduction of a silver surface oxide in the presence of palladium oxide compared to pure silver oxide resulting from the transfer of atomic hydrogen from palladium oxide islands onto the surrounding surface formed from oxidation of a palladium–silver alloy. The palladium–silver interface also dynamically restructures during reduction, resulting in silver–palladium intermixing. This study clearly demonstrates the migration of reaction intermediates and catalyst material across surface interfacial boundaries in alloys with a significant effect on surface reactivity, having broad implications for the catalytic function of bimetallic materials.

## Surface-Catalyzed Oxidation-Reduction on Solvating Aerosol Surfaces

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Gas-particle interfaces play essential roles in the atmosphere and directly influence many atmospheric processes. For example, many hygroscopic substrates solvate at a deliquescence relative humidity (DRH), but modern observational techniques have revealed that reversible water adsorption and reversible ion solvation already take place at relative humidity (RH) lower than the DRH. These interfacial processes are occurring at microscopic scales sometimes overlooked in the present picture of atmospheric chemistry, where important surface catalysis processes may be missed. In this study, a novel surface-catalytic redox reaction during salt solvation is discovered by using the ambient pressure X-ray photoelectron spectroscopy (APXPS). Classical and first-principle molecular dynamics were performed to support the identification of the solvation preference and spectroscopical signatures of the compounds detected during the deliquescence process.

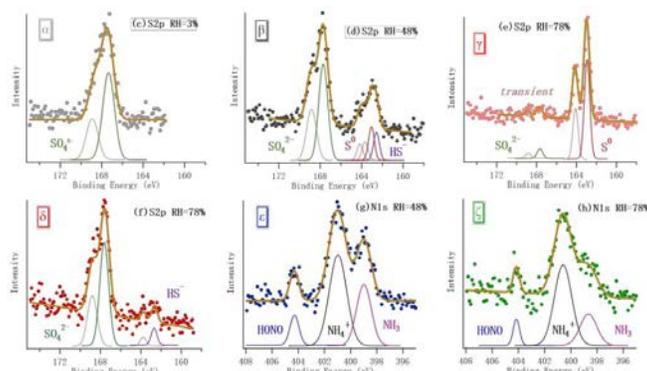


Figure 1 S 2p and N 1s XPS peaks measured at three RHs, and the photon energy were set to 435 eV for sulfur XPS and 665 eV for nitrogen XPS, respectively. The binding energies were aligned to with aliphatic C 1s at 284.8 eV. At RH=3%,  $\text{NH}_4^+$  peak and  $\text{SO}_4^{2-}$  doublet (c) were observed. At RH=48%,  $\text{S}^0$  and  $\text{HS}^-$  doublets (d) and HONO and  $\text{NH}_3$  peaks (g) appeared. At RH=78%, when full deli-quescence was occurring, most sulfate transferred to  $\text{S}^0$  (e) and no nitrogen species could be found (b); when deliquescence finished, the sulfur region was dominated by sulfate again (f) and nitrogen species reappeared (h).

Surface-catalyzed sulfate reducing ammonium oxidation reactions are discovered to spontaneously take place on common inorganic aerosol surfaces. Several key intermediate species including,  $\text{S}^0$ ,  $\text{HS}^-$ , HONO, and  $\text{NH}_3(\text{aq})$  are identified as reaction components associated with the solvation process. Depth profiles of relative species abundance show the surface propensity of key species. The species assignments and depth profile features are supported by classical and first-principle molecular dynamics calculations. A detailed mechanism is proposed to illustrate the complicated processes that lead to unexpected products during salt solvation. This discovery reveals novel chemistry that is uniquely linked to a solvating surface and has great potential to illuminate current puzzles within heterogeneous chemistry.

## Role of Water on the Structure of Palladium for Complete Oxidation of Methane

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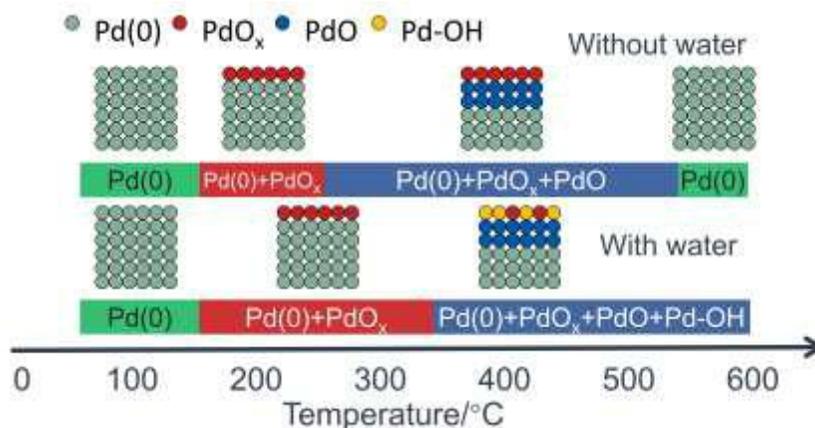
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Palladium-based catalysts are attractive for methane combustion on natural gas vehicles at low temperature. By means of ambient pressure X-ray photoelectron spectroscopy, we investigated the reaction on a palladium foil exposed to different mixtures at increasing temperature. Water affects the long-term catalyst stability and blocks the active sites, ascribed to the hydroxyl inhibition effect. We investigated such an effect both under steady state and transient reaction conditions to understand the mechanism of inhibition. The hydroxyl formation on the surface of palladium blocks the sites for methane activation, postponing the formation of the active palladium oxide phase in the bulk.



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## H<sub>2</sub>O/O<sub>2</sub> interactions with Ir and IrO<sub>2</sub> probed by APXPS

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Hydrogen has become a major player in the transition from fossil fuels to clean and renewable energy. Hydrogen production can be achieved by water splitting, especially via means of electrocatalysis. However, large-scale application of electrocatalytic water splitting is limited by the high overpotentials and degradation of the catalyst during oxygen evolution reaction (OER). Ir-based electrodes are well-known for their balance between activity & stability and are one of the state-of-the-art catalysts for OER [1, 2]. Here, by investigating Ir and IrO<sub>2</sub> polycrystalline films interactions with H<sub>2</sub>O and/or O<sub>2</sub> using ambient pressure X-ray photoelectron spectroscopy (APXPS), we aim to elucidate the initial steps of H<sub>2</sub>O (or O<sub>2</sub>)/Ir-based catalyst interfacial chemistry. These experimental results will be utilized to finetune theoretical parameters and computational models [3, 4] that will be extrapolated to enhance our understanding of OER.

At room temperature, H<sub>2</sub>O adsorbs dominantly in a molecular form, with limited amount of OH-related species, onto Ir; but readily dissociates into H and OH on IrO<sub>2</sub> and progressively enhanced by an increase of H<sub>2</sub>O pressure. Further scission of O-H bond and oxidation of Ir was activated under elevated temperatures. Spectral fittings and quantifications extract information regarding coverage and reaction kinetics of individual surface species, including H<sub>2</sub>O, Ir-O, and OH-related species. As a product of OER, the presence of O<sub>2</sub> also has significant impact on the surface chemistry of Ir-based electrodes. For example, the presence of O<sub>2</sub> leads to immediate oxidation of Ir surface and the formation of Ir-O at room temperature, which can be readily converted into Ir-OH upon the introduction of H<sub>2</sub>O. The formation and interconversion of various surface O-containing species offers a full picture of the chemical structures at the H<sub>2</sub>O (or O<sub>2</sub>)/Ir-based catalyst interface.

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### Acknowledgment

The Ir and IrO<sub>2</sub> samples, thin films grown on Si wafer via physical vapor deposition, were provided by Nemanja Danilovic Group from Lawrence Berkeley National Laboratory.

## **APXPS Study of UV Photocatalytic Reduction of CO<sub>2</sub> on ZnO/Cu<sub>2</sub>O Nanoparticle Heterojunction**

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In this work, we report a UV photocatalytic reduction study of carbon dioxide with water on semiconducting heterojunctions constructed from the nanoparticles of zinc oxide ( $E_g = 3.2$  eV) and crystalline cuprous oxide ( $E_g = 2.0 - 2.2$  eV). Two crystalline types of cuprous oxide were selected based on the anticipated difference in photocatalytic performance: cubic structure terminated with (100) faces, and rhombic dodecahedron (r.d.) terminated with (110) faces. Ambient pressure X-ray photoelectron spectroscopy (APXPS) was used to track the change of reaction species on the photocatalyst surfaces. The ZnO/Cu<sub>2</sub>O (r.d.) is found to be more reactive than ZnO/Cu<sub>2</sub>O (cube) as evidenced by a larger production of carbon species such as carbonate, formate, carbonyl, and methoxy on the surface when the nano-catalysts were exposed to gaseous carbon dioxide and water of mbar pressure and illuminated with UV photons. Further, the heterojunctions composed of Cu<sub>2</sub>O (r.d.) and different ZnO loading ranging from 7% to 40% were found to exhibit altered reaction pathway, yielding more methane instead of methanol as the ZnO loading is increased. The energy band diagrams useful in discerning the catalytic performance of photocatalysts are also constructed by means of APXPS data. The semiconductor interfaces of ZnO/Cu<sub>2</sub>O (r.d.) and ZnO/Cu<sub>2</sub>O (cube) all belong to type II heterojunction but with distinct band offsets between VBM of Cu<sub>2</sub>O and CBM of ZnO, leading to different interfacial recombination rate. The speculated difference in interfacial recombination rate seems to correlate well with the changing UV photocatalytic reactivity between two types of heterojunctions.

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