International Union for
Vacuum Science,
Technique, and
Applications

Zaragoza Scientific
Center for Advanced
Modeling

IUVSTA-ZCAM METAL-OXIDE ULTRATHIN FILMS AND NANOSTRUCTURES: EXPERIMENT MEETS THEORY

July 3rd – 7th, 2024

Zaragoza Scientific Center for Advanced Modeling, Zaragoza, Spain

ORGANIZING COMMITTEE

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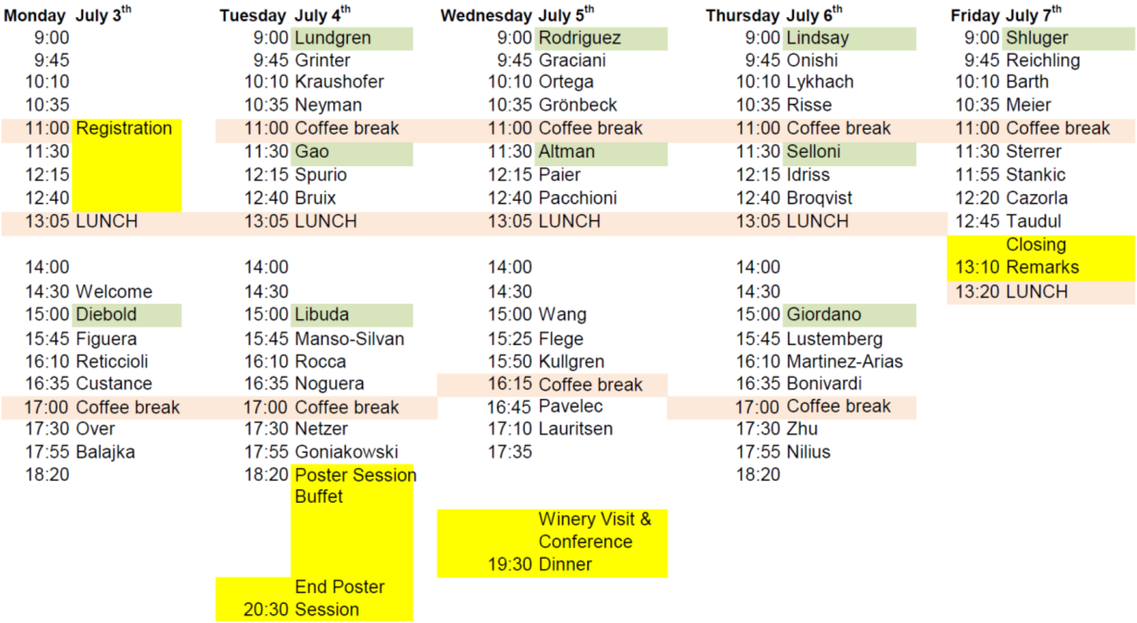
IUVSTA-ZCAM METAL-OXIDE ULTRATHIN FILMS AND NANOSTRUCTURES: EXPERIMENT MEETS THEORY

July 3th – 7th, 2023
ZCAM, Zaragoza, Spain



Monday July 3th		Tuesday July 4th		Wednesday July 5th		Thursday July 6th		Friday July 7th	
9:00		9:00	Lundgren	9:00	Rodriguez	9:00	Lindsay	9:00	Shluger
9:45		9:45	Grinter	9:45	Graciani	9:45	Onishi	9:45	Reichling
10:10		10:10	Kraushofer	10:10	Ortega	10:10	Lykhach	10:10	Barth
10:35		10:35	Neyman	10:35	Grönbeck	10:35	Risse	10:35	Meier
11:00	Registration	11:00	Coffee break	11:00	Coffee break	11:00	Coffee break	11:00	Coffee break
11:30		11:30	Gao	11:30	Altman	11:30	Selloni	11:30	Sterrer
12:15		12:15	Spurio	12:15	Paier	12:15	Idriss	11:55	Stankic
12:40		12:40	Bruix	12:40	Pacchioni	12:40	Broqvist	12:20	Cazorla
13:05	LUNCH	13:05	LUNCH	13:05	LUNCH	13:05	LUNCH	12:45	Taudul
								13:10	Closing Remarks
14:00		14:00		14:00		14:00		13:20	LUNCH
14:30	Welcome	14:30		14:30		14:30			
15:00	Diebold	15:00	Libuda	15:00	Wang	15:00	Giordano		
15:45	Figuera	15:45	Manso-Silvan	15:25	Flege	15:45	Lustemberg		
16:10	Reticcioli	16:10	Rocca	15:50	Kullgren	16:10	Martinez-Arias		
16:35	Custance	16:35	Noguera	16:15	Coffee break	16:35	Bonivardi		
17:00	Coffee break	17:00	Coffee break	16:45	Pavelec	17:00	Coffee break		
17:30	Over	17:30	Netzer	17:10	Lauritsen	17:30	Zhu		
17:55	Balajka	17:55	Goniakowski	17:35		17:55	Nilius		
18:20		18:20	Poster Session Buffet			18:20			
				19:30	Winery Visit & Conference Dinner				
		20:30	End Poster Session						

Day 1 – July 3th, 2023

Welcome:

- 14:30 to 14:40 – **Adrián Velázquez, ZCAM-Director**
- 14:40 to 15:00 – **Welcome by the Organizers**

Session I
Chair: Michael Reichling

- 15:00 to 15:40 – **Ulrike Diebold**
  Surface science of functional oxides: Perovskites

- 15:45 to 16:10 – **Juan de la Figuera**
  The Verwey transition of magnetite: From surfaces to nanostructures

- 16:10 to 16:35 – **Michele Reticcioli**
  Electronic states and polarons on polar surfaces

- 16:35 to 17:00 – **Oscar Custance**
  Characterization of molecular H_2O, CO_2 and CO on the $CeO_2(111)$ surface with high-resolution atomic force microscopy

17:00 to 17:30: Coffee Break

Session II
Chair: Niklas Nilius

- 17:30 to 17:55 – **Herbert Over**
  Crucial step in the HCl oxidation reaction over single-crystalline $CeO_{2\ x}$(111): A combined experiment-theory approach

- 17:55 to 18:20 – **Jan Balajka**
  The structure of the reconstructed Al_2O_3(0001) surface

Day 2 – July 4th, 2023

Session III
Chair: Paola Luches

- 9:00 to 9:45 – **Edvin Lundgren**
  Surface dynamics under reaction conditions

- 9:45 to 10:10 – **David C. Grinter**
  Soft X-ray spectroscopy of spinels for photocatalysis: Theory & experiment

- 10:10 to 10:35 – **Florian Kraushofer**
  Particle encapsulation on reducible oxides under near-ambient pressures

- 10:35 to 11:00 – **Konstantin Neyman**
  Oxidation of platinum at sub-nano scale: Insights from catalytic experiments and DFT modelling

11:00 to 11:30: Coffee Break

Session IV
Chair: Gianfranco Pacchioni

- 11:30 to 12:15 – **Yi Gao**
  Towards the operando simulation of metal nanocatalysts

- 12:15 to 12:40 – **Eleonora Spurio**
  Influence of oxide shells on plasmonic properties of Cu nanoparticles

- 12:40 to 13:05 – **Albert Bruix**
  Addressing the complexity of working oxide catalysts in computational modelling studies

13:05 to 15:00: Lunch

Session V
Chair: Jeppe V. Lauritsen

- 15:00 to 15:45 – **Jörg Libuda**
  Atomic layer deposition of transition-metal dichalcogenides on functionalized oxide interfaces: In-situ spectroscopic studies of the initial nucleation processes

- 15:45 to 16:10 – **Miguel Manso-Silvan**
  Chemical heterogeneous nucleation of reducible metal oxides and physical transformation into metallic or dichalcogenide thin films

- 16:10 to 16:35 – **Mario Rocca**
  Interface oxygen induced internal structures of ultrathin MgO islands grown on Ag(100)

- 16:35 to 17:00 – **Claudine Noguera**
  Two-Dimensional mixed oxide honeycomb monolayers probed at the atomic level: $(V,Fe)_2O_3$/Pt(111) and $VFeO_6$/Ru(0001)

17:00 to 17:30: Coffee Break

Session VI
Chair: Jolla Kullgren

- 17:30 to 17:55 – **Falko P. Netzer**
  2D molybdenum oxide nanostructures: The interplay of strain and the chemical potential of oxygen

- 17:55 to 18:20 – **Jacek Goniakowski**
  Understanding the structural diversity of freestanding and NiAl-supported Al_2O_3 ultrathin films through DFTB-aided global optimization

18:20 to 20:30: Poster Session – Buffet

Day 3 – July 5th, 2023

Session VII
Chair: Arturo Martínez-Arias

- 9:00 to 9:45 – **José A. Rodriguez**
  Metal-oxide interfaces for energy production and a cleaner future

- 9:45 to 10:10 – **Jesús Graciani**
  Nanostructured oxides for conversion of CO_2 to methanol and ethanol

- 10:10 to 10:35 – **Enrique Ortega**
  Using molecular beams to simulate surface reactions that require high-pressures

- 10:35 to 11:00 – **Henrik Grönbeck**
  Interface reactions dominate low-temperature CO oxidation activity over Pt/CeO_2

11:00 to 11:30: Coffee Break

Session VIII:
Chair: Kersti Hermansson

- 11:30 to 12:15 – **Eric I. Altman**
  2D silicates from ultimate membranes to robust ferromagnets

- 12:15 to 12:40 – **Joachim Paier**
  Combining experiment with theory in studying structure and dynamics of silica bilayers on Ru(0001)

- 12:40 to 13:05 – **Gianfranco Pacchioni**
  Two-dimensional oxides as new catalytic materials

13:05 to 15:00: Lunch

Session IX
Chair: Pablo G. Lustemberg

- 15:00 to 15:25 – **Yuemin Wang**
  Structure evolution of pristine and Pt-deposited ceria nanoparticles in reactive gases

- 15:25 to 15:50 – **Jan Ingo Flege**
  In situ identification of the active sites during oxidation of Ce_2O_3 on Ru(0001) by CO_2

- 15:50 to 16:15 – **Jolla Kullgren**
  Superoxide ions on the edge – the key to understanding hydrogen reduction of nanoceria?

16:15 to 16:45: Coffee Break

Session X
Chair: Falko P. Netzer

- 16:45 to 17:10 – **Jiri Pavelec**
  Optimized infrared reflection absorption spectroscopy for metal oxides: Overcoming challenges of low reflectivity and sub-monolayer coverage

- 17:10 to 17:35 – **Jeppe V. Lauritsen**
  Mixed Co-Fe oxides on Au(111) in electrochemical water splitting

19:30: Winery Visit & Conference Dinner

Viñedos Rhey
Paraje del soto s/n, Cuarte de Huerva, 50410 (Zaragoza)
Bus transportation will be provided.

Day 4 – July 6th, 2023

Session XI:
Chair: Geoff Thornton

- 9:00 to 9:45 – **Robert Lindsay**
  Oxide interfaces: Playing away from UHV

- 9:45 to 10:10– **Hiroshi Onishi**
  Transient amperometry of O_2 evolution reaction on metal-oxide photocatalysts under water

- 10:10 to 10:35 – **Yaroslava Lykhach**
  An atomistic picture of electronic metal support interaction and the role of water

- 10:35 to 11:00 – **Thomas Risse**
  Water on Fe_3O_4(111)/Pt(111) revisited

11:00 to 11:30: Coffee Break

Session XII
Chair: Joachim Paier

- 11:30 to 12:15 – **Annabella Selloni**
  Structure and chemistry of aqueous oxide interfaces from molecular simulations

- 12:15 to 12:40 – **Hicham Idriss**
  Surface reactions of uranium oxides thin films and single crystals

- 12:40 to 13:05 – **Peter Broqvist**
  Toward an efficient f-in-core/f-in-valence switchable description for DFTB calculations of Ce 4f states in ceria

13:05 to 15:00: Lunch

Session XIII
Chair: Hicham Idriss

- 15:00 to 15:45 – **Livia Giordano**
  Electronic structure-based descriptors for oxide properties and functions

- 15:45 to 16:10 – **Pablo G. Lustemberg**
  Vibrational frequencies of CO bound to CeO_2(111), (110), and (100): A consistent theoretical description using density functional theory

- 16:10 to 16:35 – **Arturo Martínez-Arias**
  Copper-ceria CO-PROX catalysts: exploration by low temperature CO adsorption infrared

- 16:35 to 17:00 – **Adrián L. Bonivardi**
  $CuGaO_2$ delafossite as a high-surface area model catalyst for Cu^+-activated reactions

17:00 to 17:30: Coffee Break

Session XIV:
Chair: Oscar Custance

- 17:30 to 17:55 – **Junfa Zhu**
  Ceria-supported Cu-based bimetallic model catalysts: Structures and properties

- 17:55 to 18:20 – **Niklas Nilius**
  Optical properties of cuprous oxide measured in the STM: Excitons, plasmons and color centers

Day 5 – July 7th, 2023

Session XV:
Chair: Rubén Pérez

- 9:00 to 9:45 – **Alexander Shluger**
  Mechanisms of charging and structural modification of amorphous oxide films in devices

- 9:45 to 10:10– **Michael Reichling**
  Quantification of nanoscale charges with a force microscope

- 10:10 to 10:35 – **Clemens Barth**
  Charging single metal nanoparticles on a thin Al_2O_3 film by the AFM tip

- 10:35 to 11:00 – **Matthias Meier**
  Reactivity of FeO_x-based single-atom catalysts: Role of the support, metastable configurations, and electronic structures

11:00 to 11:30: Coffee Break

Session XVI:

Chair: Javier Fernández-Sanz

- 11:30 to 11:55 – **Martin Sterrer**
  Assembly and reactions of porphyrins on iron oxide thin film surfaces

- 11:55 to 12:20 – **Slavica Stankic**
  2D Indium: Self-organization over MgO cubes

- 12:20 to 12:45 – **Claudio Cazorla**
  First-principles modeling and high-throughput screening of piezo-photocatalytic materials for green hydrogen production

- 12:45 to 13:10 – **Beata Taudul**
  Raman activity in anatase TiO_2 (nano)materials : an *ab initio* investigations of surface and size effects

13:10: Closing Remarks

13:20 to 15:00: Lunch

TALKS

Surface Science of Functional Oxides: Perovskites

Ulrike Diebold
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ulrike.diebold@tuwien.ac.at

Perovskite oxides with the chemical formula ABO_3 belong to some of the most tunable inorganic materials. They are applied in emerging fields such as novel electronics and energy conversion, where their surfaces and interfaces play a significant role in their functionality. Compared to binary oxides, the surface science of perovskites is far less developed, representing an attractive opportunity for future research.

In the talk, I will focus on two materials: $SrTiO_3$(001) and $La_{0.8}Sr_{0.2}MnO_3$(001), commonly called STO and LSMO, respectively. While STO exhibits a whole range of reconstructions depending on the Sr:Ti stoichiometry [1], we found a way to prepare (metastable) 1×1 terminated surfaces by cleaving STO single crystals in UHV [2]. The cleavage procedure was developed based on the experience with $KTaO_3$ [3], a polar cubic perovskite. It was based on the hypothesis that the surface's BO_2 and AO terminated regions are imprints of (induced) ferroelectric polarization domains. Indeed, cleaved STO surfaces always exhibit a defect density of 14±2% Sr vacancies/adatoms on the SrO/TiO_2 terminations, which form to compensate for the induced polarity. The size of these termination domains varies with doping level, and highly conductive STO samples span several hundreds of μm. The two terminations have drastically different electronic structures and work functions, leading to a sizeable photovoltage development upon uv irradiation. However, cleaved STO surfaces are metastable, and heating ultimately leads to previously-observed reconstructions [4].

The LSMO(001) samples were grown by PLD on STO(001) substrates. Only a careful tuning of the surface stoichiometry leads to high-quality thin films [5]; off-stoichiometries result in a rich phase diagram, as has been observed for the LSMO (110) orientation [6]. Interestingly, the MnO_x-terminated terraces form a robust surface structure that exhibits the characteristics of a quasicrystalline order.

Work supported by the Austrian Science Fund FWF (SFB-F81 'Taming Complexity in materials modeling' (TACO)) and by the European Research Council (Grant agreement No. [883395], Advanced Research Grant 'WatFun')

[1] S.Gerhold, Z. Wang, M. Schmid, and U. Diebold, Surf. Sci. Lett., 621 (2014) L1-L4
[2] I. Sokolović, M. Schmid, U. Diebold, and M. Setvin, Phys. Rev. Mater., 3 (2019) 034407
[3] M. Setvín, M. Reticcoli, F. Poeltzleitner, J. Hulva, M. Schmid, L. A. Boatner, C. Franchini and U. Diebold, Science, 359 (2018) 572-575
[4] I. Sokolović, G. Franceschi, J. Xu, Z. Wang, J. Pavelec, M. Riva, M. Schmid, U. Diebold, and M. Setvín, Physical Review B, 103 (2021) L241406
[5] M. Riva, G. Franceschi, Q. Lu, M. Schmid, B. Yildiz, U. Diebold, Phys. Rev. Mater., 3, 043802 (2019)
[6] G. Franceschi, M. Schmid, R. Heller, M. Stöger-Pollach, U. Diebold, and M. Riva., Phys. Rev. Mater., 5 (2021) L092401

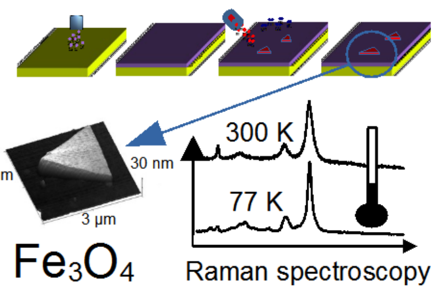
The Verwey transition of magnetite: from surfaces to nanostructures

Juan de la Figuera[1]
[1]Instituto de Química Física Blas Cabrera (IQF)
juan.delafiguera@csic.es

Magnetite, the oldest know magnetic material, is a mixed-valence iron oxide with a cubic, inverse spinel crystalline structure at room temperature. Magnetite undergoes a phase transition, the Verwey transition, upon cooling at a temperature of 120 K for bulk crystals. Below the phase transition, the resistivity increases by two orders of magnitude, the magnetic anisotropy increases, and the crystallographic structure changes to monoclinic. The origin of these changes has been debated for a century, and this has pushed forward developments in solid-state physics such as the study of the Mott transition.

We have studied the effect of the Verwey transition on the surfaces of magnetite bulk crystals, mostly with the (100) orientation [1-3]. The magnetic easy axis change, and microtwins appear which give rise to a distinctive microstructure. However, the role of dimensionality in the transition is still under scrutiny. In order to gain insight into the role of size effects in the transition, we have started to study how the Verwey transition occurs in micron-wide magnetite crystals grown by high-temperature, oxygen-assisted molecular beam epitaxy on Ru(0001) [4]. These crystals are highly perfect and have a range of thicknesses from sub-nanometer to hundreds of nanometers. We explore their structure and properties through the Verwey transition by photoemission microscopy as well as by Raman spectroscopy. Our results indicate that for crystals thicker than 20 nm, the charge order and the structure of the crystals below the Verwey transition resemble those of bulk samples. However, for thinner crystals, although a transition to a new phase takes place, its charge order and structure differ from those characteristic of the bulk material, highlighting the role of size effects in the Verwey transition.

This work is supported by the Grants PID2021-124585NB-C31 and TED2021-130957B-C54 funded by MCIN/AEI/10.13039/501100011033 and by “ERDF A way of making Europe” and by the "European Union NextGenerationEU/PRTR"



[1] J. de la Figuera et al., Phys. Rev. B 88, 161410® (2013).
[2] J. de la Figuera and C. Tusche, App. Surf. Sci. 391, 66 (2016).
[3] L. Martín-García, et al., Sci. Rep. 8, 5991 (2018).
[4] A. del Campo, et al., J. Phys. Chem. C 126, 13755 (2022).

Electronic States and Polarons on Polar Surfaces

Michele Reticcioli[1], Z. Wang[2], D. Wrana[3], M. Setvin[3], Cesare Franchini[1,4]
[1]University of Vienna (Austria), Center for Computational Materials Science
[2]Vienna University of Technology (Austria)
[3]Charles University of Prague (Czech Republic)
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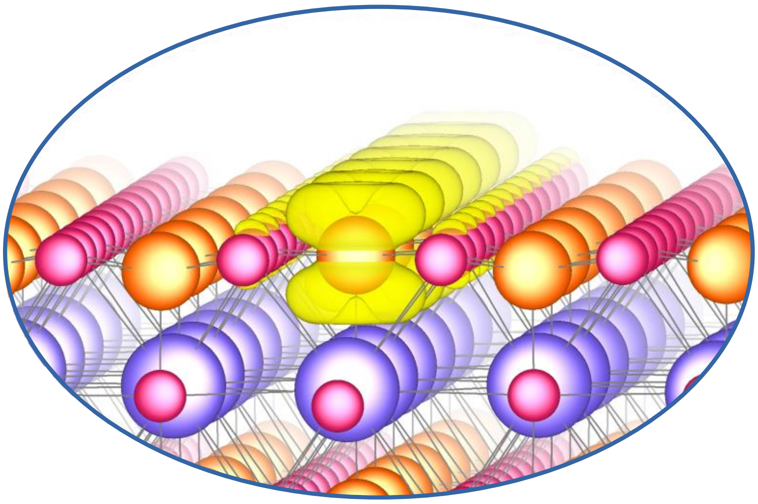
Polar surfaces of oxides exhibit an internal electric field and intrinsic excess charge that might be exploited for a wide range of applications, such as catalysis or electron-hole separation for solar light harvesting. However, there is very limited fundamental understanding of the processes induced by the surface polarity.

In our study we attempt to shed some light on the nature of the electric field and the interplay with surface charge. Our density functional theory calculations and scanning-probe microscopy measurements on $KTaO_3$(001) show spontaneous localization of the excess charge in the form of electron and hole polarons [1]. In the absence of external perturbations, the internal electrostatic potential keeps the electron-hole polaron pairs spatially separated.

The coupling of the excess charge with the surface dipole moments shows strong effects on the functionality of the material. In particular, by dosing CO molecules, we observed an enhanced binding energy for adsorbates coupling with bipolaronic states on the $KTaO_3$ surface [2].



[1] M. Reticcioli, Z. Wang, M. Schmid, D. Wrana, L. A. Boatner, U. Diebold, M. Setvin, C. Franchini, "*Competing electronic states emerging on polar surfaces*" Nature Communications 13(1), 4311 (2022).

[2] Z. Wang, M. Reticcioli, Z. Jakub, I. Sokolović, M. Meier, L. A. Boatner, M. Schmid, G. Parkinson, U. Diebold, C. Franchini, M. Setvin, "*Surface chemistry on a polarizable surface: Coupling of CO with $KTaO_3$(001)*", Science Advances 8(33), 2–8 (2022).

Characterization of molecular H_2O, CO_2 and CO on the CeO_2(111) surface with high-resolution atomic force microscopy

Oscar Custance[1], Kyungmin Kim[2], Daiki Katsube[3], Masayuki Abe[2], Shigeki Kawai[1]
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[2]Osaka University, 1-3 Machikaneyamacho, 560-0831 Toyonaka, Osaka, Japan
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Water, carbon monoxide and carbon dioxide are involved in numerous reactions for which cerium dioxide serves as catalyst or reducible support [1]. While there is wealth of information about the adsorption on these molecular species on the CeO_2(111) surface from theoretical studies [2-5], knowledge from an experimental point of view is still scarce.

In this contribution, we present a study of the adsorption and behaviour of H_2O, CO and CO_2 molecules on CeO_2(111) thin-films grown on a Cu(111) substrate using high-resolution atomic force microscopy operated at 4.8K. Constant height force imaging of the water molecules has allowed us to experimentally corroborate the theoretical results for the adsorption of individual water on CeO_2(111) [2, 3]. Unprecedented resolution has also enabled us to observe the adsorption of a water molecule on the surface extends beyond the cerium atom it binds to, affecting the surrounding area. We also present experimental information about the condensation of CO and CO_2 molecules on the surface. As predicted by theoretical studies, the adsorption energy of these molecules is quite small in comparison with the case of H_2O. This characteristic manifests in a high mobility of the CO and CO_2 molecules on the surface that renders challenging the experiments. At variance with the simulation of individual molecules on CeO_2(111) surface [2], the competition between the molecule-substrate and the molecule-molecule interactions depicts a non-trivial identification of the adsorption geometry of the molecules at the condensate.

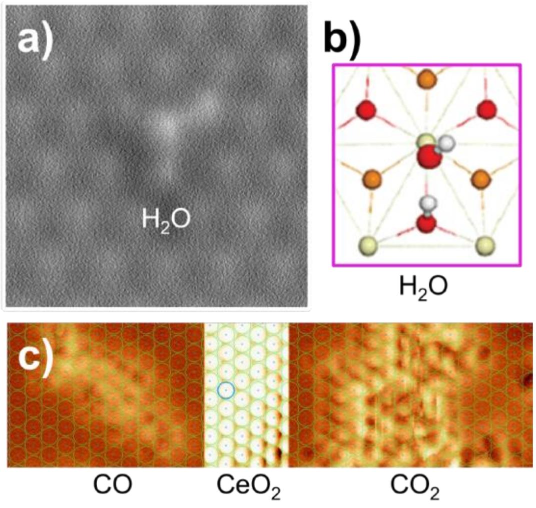

Figure: **a)** High-resolution AFM image of a single water molecule measured on the CeO_2(111) surface at 4.8K. **b)** Comparison with the theoretical prediction for the adsorption geometry of a water molecule; image adopted from ref. [3]. **c)** High-resolution AFM image measured at 4.8K of a CeO_2(111) surface region containing CO and CO_2 molecular condensates, and triangulation with respect to the atomic structure of the ceria surface.

[1] D. R. Mullins, Sur. Sci. Rep. 70, 42 (2015).
[2] M.B. Watkins, A.S. Foster and A. L. Shluger, J. Phys. Chem. C, 111, 15337 (2007).
[3] D. Fernandez-Torre et al. J. Phys. Chem. C 116, 13584 (2012).
[4] P. Lustemberg, et al. Phys. Rev. Lett. 125, 256101 (2020).
[5] N. Baumann, et al. J. Chem. Phys. 154, 094702 (2021).

Crucial Step in the HCl Oxidation Reaction over Single-Crystalline $CeO_{2\ x}$(111): A combined Experiment-Theory Approach

Volkmar Koller[1], Pablo Lustemberg[2], Sabrina M. Gericke[3], Alfred Larsson[4], Alexander Luciano-Spriewald[1], Christian Sack[1], Alexei Preobrajenski[5], Edvin Lundgren[4], Veronica Ganduglia-Pirovano[2], **Herbert Over**[1]

1) Physical Chemistry Department, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany; 2) Instituto de Catálisis y Petroleoquímica (ICP-CSIC), C/Marie Curie 2, 28049 Madrid, Spain; 3) Combustion Physics, Lund University, Box 118, 22100 Lund, Sweden; 4) Synchrotron Radiation Research, Lund University, Box 118, 22100 Lund, Sweden; 5) MAX IV Laboratory, Lund University, Box 118, 22100 Lund, Sweden

The catalytic oxidation of HCl by molecular oxygen (Deacon process) over ceria allows to recover molecular chlorine from omnipresent HCl waste in various large-scale industrial processes: [1-3] $4\ HCl + O_2 \rightarrow 2\ Cl_2 + 2\ H_2O$; $\Delta_rH = -114$ kJ/mol.

Based on powder CeO_2 experiments, density functional theory (DFT) calculations Amrute et al. [4] proposed a reaction pathway for the HCl oxidation over single crystalline CeO_2(111) surface. The most critical reaction step in the Deacon process over CeO_2(111) is predicted to be the displacement of tightly bound chlorine in a surface oxygen vacancy position of ceria (Cl_{vac}) towards a less strongly bound cerium on-top (Cl_{top}) position. Unfortunately, this step is highly endothermic by more than 2 eV. Based on a dedicated model system, namely the re-oxidation of a fully chlorinated single crystalline Cl_{vac}-CeO_{2-x}(111)- $(\sqrt{3} \times \sqrt{3})$R30° surface structure, [5] we provide spectroscopic insights (synchrotron based techniques of high resolution core level spectroscopy (HRCLS) and X-ray adsorption near edge structure (XANES)) into this fundamental reaction step. Along with first principles theory based on density functional theory calculations this displacement reaction $Cl_{vac} \rightarrow Cl_{top}$ is predicted to be induced by an adsorbed peroxo surface species (O_2^{2-}), making the displacement step exothermic with an activation barrier of as low as 1.04 eV. *The peroxo species is shown to be pivotal for the re-oxidation of* Cl_{vac}-CeO_{2-x}*(111), and it is considered critical instrumental to understand the action of ceria in oxidation catalysis.*

[1] K. Seki, Development of RuO_2/Rutile-TiO_2 Catalyst for Industrial HCl Oxidation Process. *Catal. Surv. Asia* **2010**, *14*, 168.
[2] J. Pérez-Ramírez; C. Mondelli; T. Schmidt; O.F.K. Schlüter; A. Wolf; L. Mleczko; T. Dreier Sustainable Chlorine Recycling via Catalyzed HCl Oxidation: From Fundamentals to Implementation. *Energy Environ Sci.* **2011**, *4*, 4786-4799.
[3] H. Over, R. Schomäcker, What Makes a Good Catalyst for the Deacon Process? *ACS Catal.* **2013**, *3*, 1034-1046.
[4] P. Amrute; C. Mondelli; M. Moser; G. Novell-Leruth; N. López; D. Rosenthal; R. Farra; M.E. Schuster; D. Teschner; T. Schmidt; J. Pérez-Ramírez Performance, Structure, and Mechanism of CeO_2 in HCl Oxidation to Cl_2. *J. Catal.* **2012**, *286*, 287-297.
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The structure of the reconstructed $Al_2O_3(0001)$ surface

Johanna Hütner[1], Andrea Conti[1], David Kugler[1,2], Florian Mittendorfer[1], Ulrike Diebold[1],
Michael Schmid[1], **Jan Balajka**[1]

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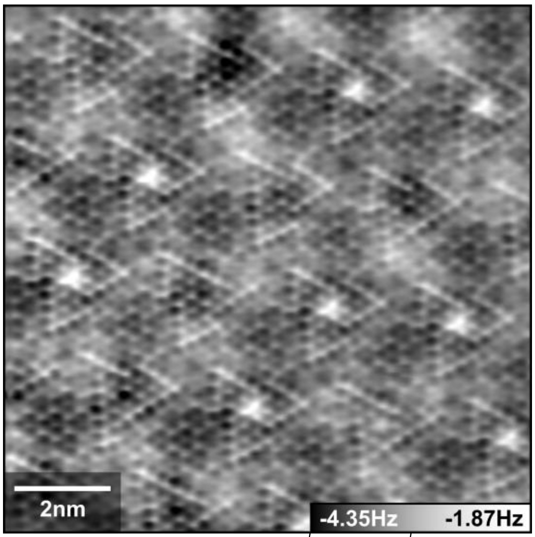
[2] CEITEC, Brno, Czech Republic

corresponding author: jan.balajka@tuwien.ac.at

Corundum α-Al_2O_3 is an important ceramic widely used in electronics, optical applications, or as catalyst support. Despite its importance, the atomic structure of the most stable (0001) termination has not been conclusively determined. Detailed studies of Al_2O_3 surfaces have been stymied by its insulating nature, preventing the use of many surface science methods.
Structural models based on surface X-ray diffraction (SXRD) [1] and atomic force microscopy (AFM) [2] concluded the $(\sqrt{31} \times \sqrt{31})R\pm9°$-reconstructed $Al_2O_3(0001)$ surface formed upon high-temperature annealing is terminated by one or two layers of metallic Al strained to lattice-match the oxide substrate.
We imaged the reconstructed $Al_2O_3(0001)$ surface with noncontact AFM (nc-AFM) using specifically functionalized tips for chemically-sensitive contrast. In particular, CuO_x terminated tips [3] enabled us to directly identify oxygen and aluminum atoms in the topmost layer.
With the aid of *ab-initio* calculations, we propose a structural model of the $(\sqrt{31} \times \sqrt{31})R\pm9°$-reconstructed $Al_2O_3(0001)$ surface consistent with atomically resolved nc-AFM images and area-averaging spectroscopic data. Unlike prior models, the surface does not contain a metallic Al layer but consists of oxygen and aluminum atoms arranged in similar structural units as reported in thin AlO_x films [4,5].



NC-AFM image of $(\sqrt{31} \times \sqrt{31})R\pm9°$-reconstructed $Al_2O_3(0001)$ acquired with a CuO_x-terminated tip (qPlus, 4 K)

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Surface dynamics under reaction conditions

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Catalysis is an important process and is widely applied on an industrial scale for many applications in either gas or in liquid phase. Industrial catalysts are complex materials, and consequently the gas/liquid-surface interaction between simplified single crystal surfaces and molecules in controlled environments has been studied for decades. We have in recent years explored the possibilities to perform experiments at conditions closer to those of a technical catalyst, at elevated pressures and in an electrolyte. In this contribution, recent results using in situ/operando techniques [1-5] will be presented. Armed with structural knowledge from ultra-high vacuum experiments, the dynamics of the gas or electrolyte induced structures and phases can be observed in real time. The strength and weaknesses of the experimental techniques will be discussed.

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Soft X-ray Spectroscopy of Spinels for Photocatalysis: Theory & Experiment

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As active components in photocatalytic water splitting, spinel oxides (general formula AB_2O_4) have attracted much attention with regards to their electronic structure. In addition to variation in oxidation states for reducible spinels, the effect of coordination geometry is also of key importance to the electronic structure. One parameter of merit is the inversion degree, which indicates the relative populations of tetrahedral and octahedral sites within the lattice.

In our group, we have employed soft X-ray spectroscopy (XPS and NEXAFS) to understand the behaviour of various spinels under conditions that approach those encountered in catalysis with an aim to understand better the surface behaviour. We complement these experimental results with DFT modelling of the spectra and the materials. Particle size, composition, and thermal treatments are all observed to play important effects in the behaviour of the spinels.

In this talk I will present our recent results as well as providing an explanation of the in-situ and operando soft X-ray capabilities at the B07 beamline at Diamond Light Source. [1]

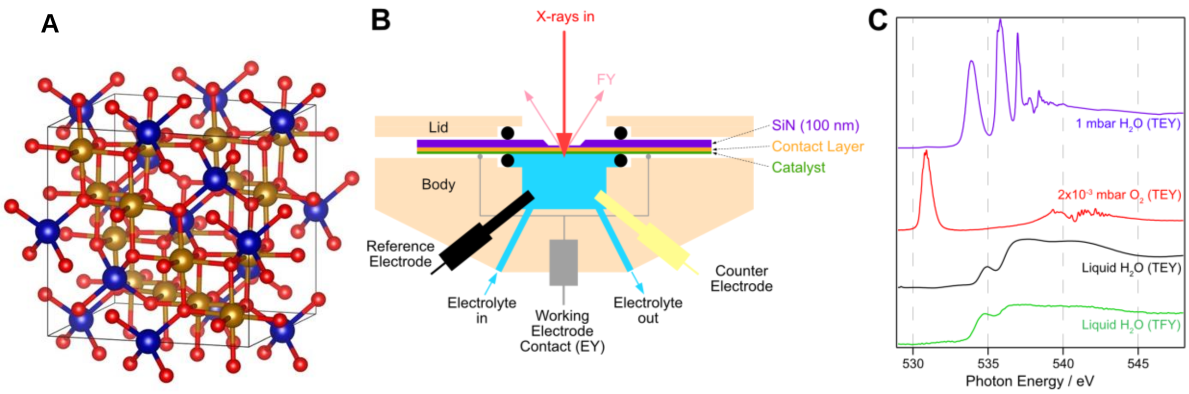

Figure 1. A. Structure of a normal (non-inverse) spinel (gold: Oh, blue: Td, red: oxygen); **B.** Schematic of the B07-B electrochemical cell; **C.** O K edge XAS of various oxygen-containing species.

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Particle encapsulation on reducible oxides under near-ambient pressures

Florian Kraushofer, Matthias Krinninger, Philip Petzoldt, Moritz Eder, Sebastian Kaiser, Johanna E. Reich, Tim Kratky, Sebastian Günther, Martin Tschurl, Ueli Heiz, Barbara A.J. Lechner
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Catalysts on reducible oxide supports often change their activity significantly at elevated temperatures due to the strong metal-support interaction (SMSI), which induces the formation of an encapsulation layer around the noble metal particles. However, the impact of oxidizing and reducing treatments at elevated pressures on this encapsulation layer remains controversial, partly due to the ‘pressure gap’ between surface science studies and applied catalysis.

In the present work, we employ near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and scanning tunneling microscopy (NAP-STM) to study the effect of reducing and oxidizing atmospheres on the SMSI-state of well-defined oxide-supported Pt catalysts at pressures from UHV up to 1 mbar. On a $TiO_2(110)$ support, we can either selectively oxidize the support or both the support and the Pt particles by tuning the O_2 pressure [1]. We find that the growth of the encapsulating oxide overlayer is inhibited when Pt is in an oxidic state. Our experiments show that the Pt particles remain embedded in the support once encapsulation has occurred. On $Fe_3O_4(001)$, the encapsulation stabilizes small Pt clusters against sintering [2]. Moreover, the cluster size and the cluster footprint on the support affect its diffusivity and can therefore be used to tune the sintering mechanism. Very small clusters of up to 10 atoms even still diffuse intact after encapsulation.

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[2] S. Kaiser et al., *ACS Catalysis* 13, 6203-6213 (2023).

Oxidation of platinum at sub-nano scale: Insights from catalytic experiments and DFT modelling

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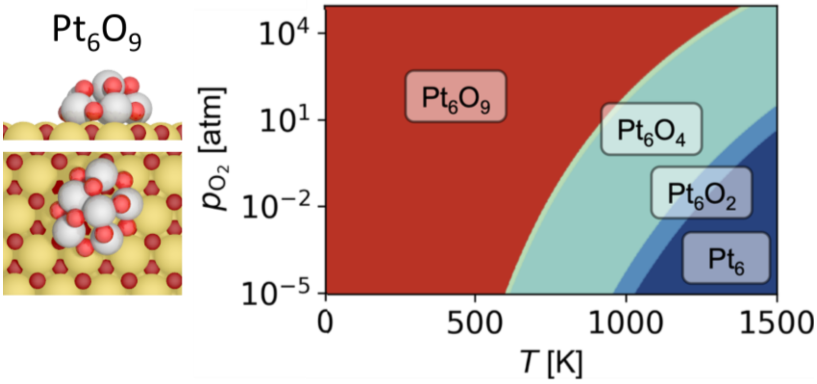
Platinum is among the metals most resistant to oxidation at ambient conditions. Nevertheless, platinum in the sub-nanoscale state may not be as stable to oxidation and formation of oxide clusters. Indeed, experiments indicate formation of small ceria-supported PtO_x clusters in Pt/CeO2 catalytic materials even at low oxygen pressure [1]. Such clusters were proposed to expose active sites that enable efficient CO oxidation starting at temperatures below 0ºC.

We explored oxidation of small free-standing and CeO_2(111)-supported platinum clusters using a DFT-based global structure optimization algorithm in combination with *ab initio* thermodynamics [2]. These studies revealed thermodynamically stable, strongly oxidized supported Pt clusters at O_2 pressures below 0.01 atm and temperatures up to several hundred ºC. Such high stability indicates that the clusters with Pt-O-Pt bonds on CeO_2(111) support are more abundant than metallic Pt clusters and Pt cations embedded in ceria. The calculated PtO_x clusters exhibit O-Pt-O and Pt-O-Pt motifs typical for coordination compounds formed by Pt cations. Interestingly, modelling of CO adsorption on the PtO_x clusters and subsequent CO_2 desorption strongly suggests that such surface structures can enable CO oxidation at extraordinarily low temperatures, in line with the experimental observations [3].

In this presentation we will discuss data of the above mentioned DFT modelling studies of the PtO_x/CeO_2 systems, in relation with the experimental data on their structure and oxidative catalytic activity. A general conclusion is that studies of small Pt clusters should consider their oxidized states, even at quite low oxygen pressures, as ignoring the PtO_x states may hinder obtaining a complete understanding.



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Towards the Operando Simulation of Metal Nanocatalysts

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China
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The morphologies, surface compositions, and surface structures determine the activities of nanocatalysts. Conventional experiments tune the nanocatalysts by controlling their initial structures, morphologies and compositions before the reactions. In the past two decades, extensive in-situ experiments have demonstrated that the structures, morphologies and composition may change significantly during the reactions comparing to those before/after the reactions, which indicates the conventional methods may not be efficient to tune the properties as expected. Owing to the difficulty and high-cost of in-situ experiments, how to understand and even predict these changes during the reactions becomes extremely important for the nanocatalysts. However, previous theories were mostly focused on the model systems in vacuum, the models to handle the complex systems under operando conditions are still lacking.

Herein, we developed a multi-scale model by combining the first-principles calculations, adsorption isotherm, kinetic Monte Carlo simulation, and Wulff construction method. This model can describe and predict the static morphologies, structures, and surface compositions of metal catalysts and their dynamic changes under the varied reaction conditions (size, composition, temperature, pressure, gas/liquid, mixed gas, substrate, and etc) and further correlate with the catalytic activities quantitatively [1,2]. Moreover, the reliability of our model is confirmed by comparing the theoretical results with the independent experimental results [3,4]. Our model lays the foundation for the future development of theory to precisely predict and tune the catalytic reactions in operando conditions [5,6].

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Influence of oxide shells on plasmonic properties of Cu nanoparticles

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Nanostructures of copper metal and its corresponding oxides are very promising materials in the field of catalysis, photovoltaics, electronics, and optics, both for their optimal properties, for example in terms of optical response and conductivity, and as lower-cost materials [1]. Copper tends to easily oxidize in ambient conditions, forming stable oxides like CuO and Cu_2O. The last one, in particular is a semiconductor with a direct bandgap of ≈ 2.2 eV with promising characteristics for photovoltaic or photocatalytic applications [2]. The oxidation of Cu thin films and nanoparticles (NPs) has been demonstrated to strongly depend on the temperature and pressure conditions [3], and the exposure to oxygen influences the position and the shape of the plasmonic band of the NPs [2].
We show here the study of the effects of pressure and temperature conditions on the plasmonic and morphological properties of Cu NPs, either self-assembled via MBE on the substrate or deposited via reactive magnetron sputtering and inert gas aggregation. Figure 1 shows the optical response of four different samples: as-grown NPs present a relatively broad plasmonic band, compatible with a partial oxidation of the NPs, while the response of the NPs grown in an oxygen partial pressure suggests a stronger oxidation. Contrarily, the plasmonic peak of Cu NPs grown in UHV and co-deposited with MgO or post-processed in an oxygen partial pressure of 10^{-6} Torr at 450°C is narrow and intense, compatible with the response of metallic NPs. The morphology of these two samples (figure 2) shows the formation of protective shells of MgO or Cu_2O respectively, suggesting a possible way to cap the NPs and to preserve the plasmonic properties of metallic Cu.

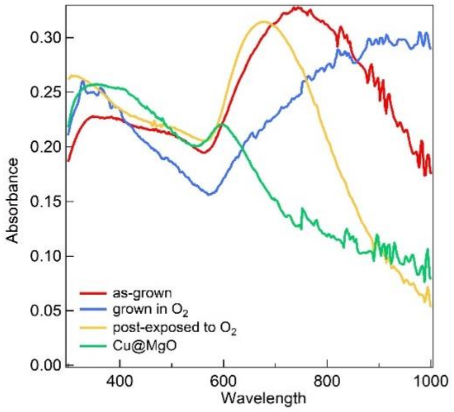

Figure 1 optical absorbance of Cu NPs in the different conditions

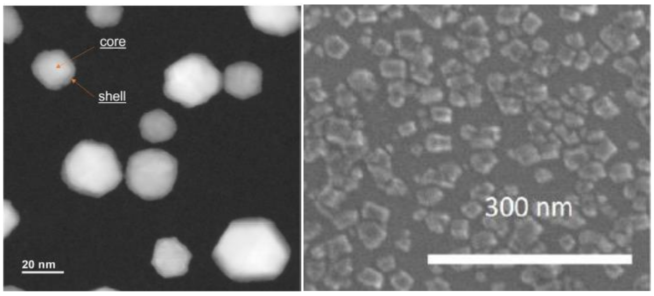

Figure 2 morphology of Cu NPs with (a) a Cu_2O and (b) a MgO protective shell

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Addressing the complexity of working oxide catalysts in computational modelling studies

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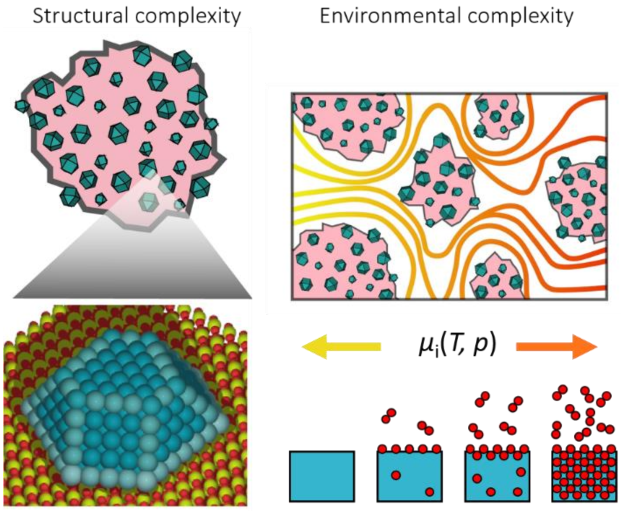
The improvement of spectroscopic techniques has enabled the *in situ* characterization of catalysts under operating conditions, often revealing a highly dynamic behaviour of the active phase. For example, metals and metal-oxides usually employed as catalysts frequently undergo significant chemical and structural transformations during operation. In contrast, the conceptual framework and structural models used to rationalize the catalytic properties of such materials has traditionally relied on a rather static picture of the catalyst substrate. In addition to this so-called environmental complexity, the structural complexity of such these nanostructured materials further hinders the characterization of their response to reaction conditions [1].

Establishing reliable structural models of working catalysts is particularly relevant in computational modelling studies relying on quantum mechanical calculations. To overcome the challenges arising to the aforementioned complexities, novel computational approaches have been developed to determine the structure and composition of targeted materials and conditions, combining quantum mechanics, structure prediction (i.e. global optimization) algorithms, ab initio thermodynamics, and, more recently, also machine-learning methods [2].

During my talk, I will introduce some of these approaches and showcase their capacity by presenting different case studies involving the characterization of the structure and oxidation states of technologically relevant catalytic materials [3, 4]. Current efforts from our group towards the development of grand canonical global optimization methods will also be discussed [5].



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[5] https://github.com/jquinl/GrandCanonicalGA

Atomic Layer Deposition of Transition-Metal Dichalcogenides on Functionalized Oxide Interfaces: In-Situ Spectroscopic Studies of the Initial Nucleation Processes

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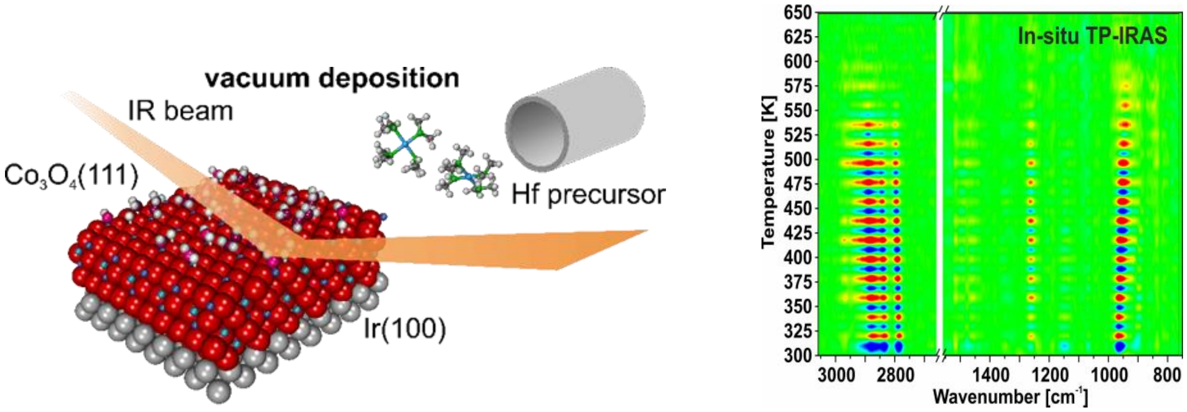
Low-dimensional semiconductors, in particular transition-metal dichalcogenides (TMDCs), have attracted a lot of interest due to their unusual electrical and optical properties. Besides MoS_2, a promising alternative TMDC is HfS_2, which shows higher charge mobility and a proper band gap. In order to build electronic devices based on TMDCs, the controlled deposition is a key prerequisite. Here, innovative deposition methods such as atomic layer deposition (ALD) open new possibilities. In order to achieve continuous, defect-poor, and pinhole-free ultrathin films, however, the nucleation step of the ALD process is critical.

In this presentation, we summarize surface science model studies, exploring the molecular mechanisms and microkinetics of ALD of HfS_2 on well-defined substrates. In specific, we investigated the initial nucleation processes on an atomically defined $Co_3O_4(111)$ surface. The nucleation and growth steps were monitored in-situ by time-resolved infrared reflection absorption spectroscopy (IRAS). HfS_2 was grown by sequential dosing of tetrakis-(dimethylamido)-hafnium (TDMAH) and D_2S onto the surface which exposes well-defined OD groups and partially dissociated OD/D_2O aggregates. We show that the initial half-cycle of the ALD process comprises of several regimes. The reaction with mobile OD/D_2O species controls the stoichiometry of the nuclei formed, which change drastically during a single deposition half-cycle. Our findings demonstrate that the initial nucleation step of the ALD procedure is a very complex process in which it is essential to control not only the classical growth parameters such as temperature and flux, but also the nature and the mobility of the OD/D_2O aggregates on the surface.

In a second part of the study, we explore the nucleation behavior on the same $Co_3O_4(111)$ surface after coating by functionalized and non-functionalized self assembled monolayers (SAMs). The coating allows us to control the nature and density of the nucleation centers with great precision. The adsorption and reaction of TDMAH with the functionalized films is again monitored in-situ by time-resolved IR spectroscopy.



In-situ IRAS study of the deposition of Hf_2S on $Co_3O_4(111)$ by ALD.

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Chemical heterogeneous nucleation of reduceable metal oxides and physical transformation into metallic or dichalcogenide thin films

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The sol-gel process offers a variety of adaptable protocols for the nucleation of metal oxides [1]. We have recently been attracted by this method for the clustering of metal oxides on silicon. We want to bring into discussion the results of nucleation and reduction of Mo and W, that helped an ulterior physical transformation into dichalcogenides (Se, Te) by closed space vapor transport process. We have additionally reached nanostructured metallic Sn films by microwave plasma annealing of the deposited SnO_2 films. We show results of the morphological, structural and functional characterization of these thin films. We show original microstructures, like out of plane standing or porous transition metal dichalcogenides very attractive for catalytic processes or nanocluster metal films in optimization as transparent conductive films.

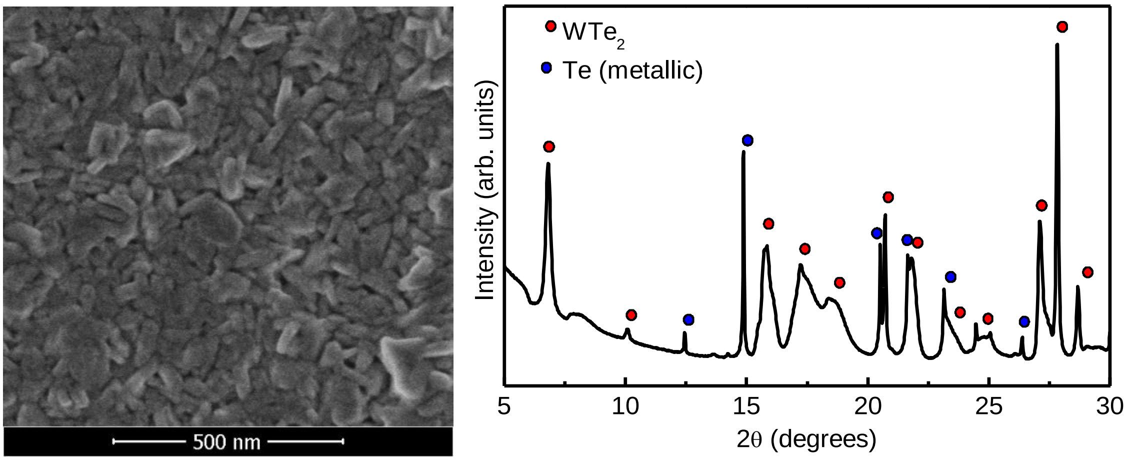

Figure 1. SEM image of WTe_2 films prepared by isothermal closed space tellurization of reduced WO_3 films (left). XRD diagrams of the same (right) showing the formation of WTe_2 (OCD: 96-231-0356) with excess metallic Te (OCD: 96-202-0223).

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Interface Oxygen Induced Internal Structures of Ultrathin MgO Islands Grown on Ag(100)

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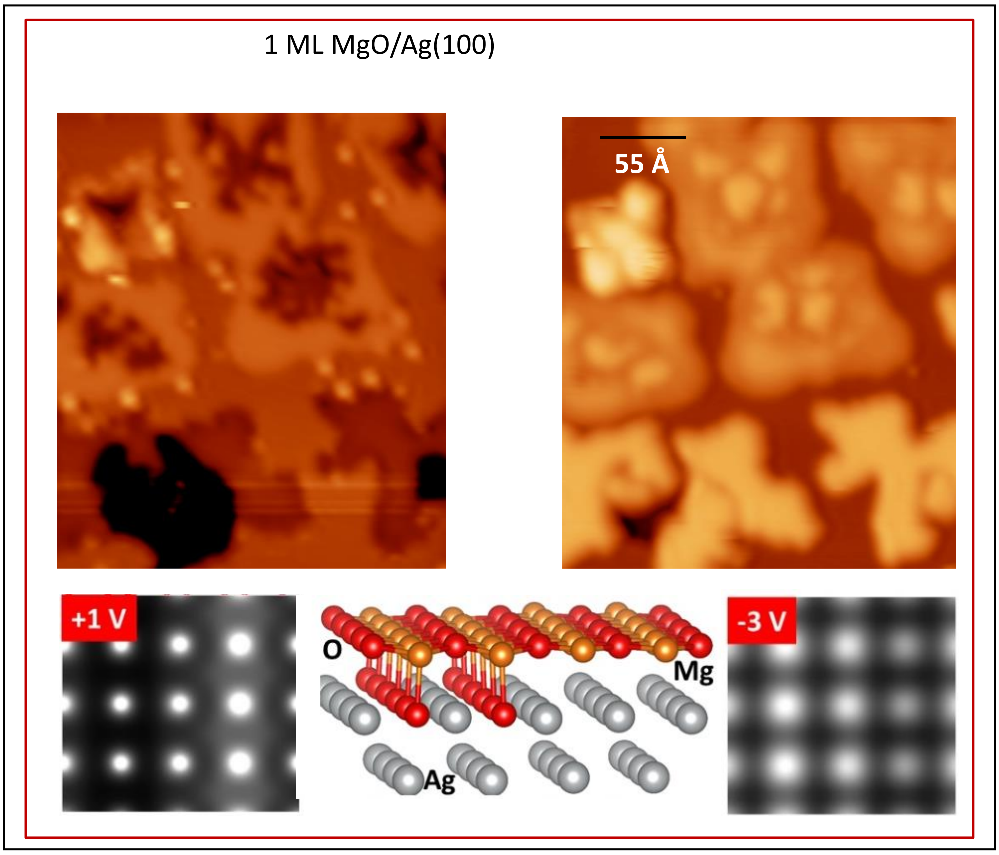
When imaged by scanning tunnelling microscopy (STM) at constant current under non topographic conditions, nanosized MgO islands grown on Ag(100) may show a fractal dark internal structure and/or appear embedded in the surface. On the contrary, when imaged under topographic conditions, the same islands appear as nearly flat plateaus. Islands showing different contrast and a different contrast dependence on sample bias have been often reported in the literature, but a thorough explanation is still missing. Here we demonstrate, on the basis of experimental data and computational results, that such structure is due to the accumulation of oxygen at the MgO islands−substrate interface. Interestingly, interfacial oxygen concentrates at the center of the islands.



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Two-Dimensional mixed oxide honeycomb monolayers probed at the atomic level: $(V,Fe)_2O_3$/Pt(111) and $VFeO_6$/Ru(0001)

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The growing demand of methods for engineering the properties of nanomaterials such as metal-supported ultra-thin oxide films fosters an efficient use of cation doping or mixing. Recently, with the help of DFT modelling, we have shown that the low dimensionality of the oxide film and its interaction with a substrate may induce cation mixing characteristics and charge states, which differ from those present in the corresponding bulk oxides [1,2].

With the use of scanning tunnelling microscopy (STM) experiments and density functional theory (DFT) calculations, we have investigated the properties of mixed V-Fe oxide honeycomb monolayers supported on two different metal substrates. On Pt(111), the mixed film displays a $V_{2-x}Fe_xO_3$ stoichiometry and preserves a rumpled epitaxial honeycomb structure in a wide range of Fe contents (0 – 40%) [3]. The Fe cations can be traced by their specific STM signature, and the changes in their distributions at increasing Fe content are well reproduced in Monte Carlo simulations.

In contrast, under the same experimental conditions, a self-organization scheme is at work on Ru(0001), which selects only V/Fe film compositions close to 50% and leads to honeycomb layers of unique $VFeO_6$ stoichiometry with excess oxygen anions located at the metal/oxide interface [4]. It results from a singular, geometry-driven mixing scenario in 2D which, because of the high interfacial oxygen content, is reminiscent of that known for bulk ternary oxides.

In both cases, the characteristics of cationic mixing are principally driven by a strong effective attraction between neighbouring Fe and V cations. On Pt(111) it results from an important electron transfer from the V cations towards the substrate. On Ru(0001), it is additionally enhanced by a significant site effect.

Comparison between Pt(111) and Ru(0001) thus exemplifies how the choice of the metal substrate may induce largely different mixing behaviors. Such versatility opens a way toward a thorough fundamental understanding of the principles that underlie oxide alloying in 2D and its possible use in various applications.

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2D Molybdenum Oxide Nanostructures: The Interplay of Strain and the Chemical Potential of Oxygen

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MoO_3 is a reducible oxide with tunable electronic properties, which makes it suitable for a wide range of nanotechnological systems, amongst them ´smart windows´, batteries, photoelectrodes, thin film capacitors, sensors, or chemical catalyst systems [1,2]. Of particular interest is the technological use of the so-called Mo oxide nanosheets, i. e. free-standing several atomic layers thin platelet systems that can be fabricated by simple, wet chemical preparation procedures. Although typically not completely uniform, they have potential for optoelectronic, sensor or biotechnological applications. The particular structural and electronic properties of oxide nanosheets, however, still need careful scientific scrutiny. This work aims to contribute to this characterization.

Here we have investigated the structure of two-dimensional (2D) $MoO_{3(-x)}$ model systems under various stress levels and different chemical potentials of oxygen. Stress has been introduced in the oxide layers by epitaxial growth of MoO_3 from 1-3 monolayers via MBE on a Pd(100) single crystal substrate. The chemical potential of oxygen has been established during growth by the oxygen pressure and the substrate temperature. The oxide deposits have been characterized in a surface science approach by LEED, STM, XPS, and work function measurements.

The first oxide monolayer wets the Pd surface in a commensurate c(2x2) structure and forms a well-ordered anti-phase nanoscale domain lattice; the latter is an effective way to release the primary interfacial strain [3]. A DFT derived structure model consists of a MoO_2+O bilayer, which is based on a cubic MoO_3 structure. The deposition of a second oxide layer results in a restructuring of the oxide phase, a change of symmetry and the formation of rectangular islands with a coincidence lattice and misfit dislocations to release strain. A double layer sheet of the α-MoO_3 structure constitutes a stable DFT structure model. Changing the deposition conditions and the chemical potential of oxygen leads to the growth of MoO_3 nanostructures in the form of arrays of square clusters and nanowires. A reduction of the chemical potential of oxygen during oxide deposition and a nominal coverage of 2-3 monolayers creates defective MoO_{3-x} films with ordered arrays of point defects.

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Understanding the structural diversity of freestanding and NiAl-supported Al_2O_3 ultrathin films through DFTB-aided global optimization

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(Sub)nanometer-thin alumina films are frequently encountered due to the self-limited oxidation of Al and its alloys (e.g., NiAl or FeAl), and seem to display an even larger structural variety than bulk alumina itself. Understanding the intrinsic stability of freestanding films constitutes an important first step in itself, especially when the interaction with the substrate is weak. Using a combined tight-binding/DFT global optimization approach, we identify particularly stable θ(100)-type films along with a host of novel stable thin film structures [1]. Several among them correspond to cuts from relatively high energy bulk structures, e.g. dehydrated boehmite, pseudo-CaIrO3, defective rocksalt and LuMnO3, which are not commonly associated with alumina. DFT calculations allow to rationalize this stability reversal with respect to α-Al2O3 and to identify the underlying mechanisms: breaking of a low density of relatively weak Al-O bonds, filling of Al surface vacancies, and polarity-induced relaxation of the whole film.

In case of supported alumina films on the NiAl(100) substrate, their observed structure has been tentatively assigned to a distorted θ-alumina polymorph, but the film stoichiometry, the nature of its surface and interface terminations, as well as the mechanisms that stabilize the θ phase remain unknown. Using the same global optimization approach, we explicitly demonstrate that ultra-thin θ(100)-type films correspond indeed to the structural ground state of alumina supported on the (2×1)-NiAl(100) substrate [2]. Moreover, our results prove that non-stoichiometry may be easily accommodated by the supported θ(100) film structure via an excess or deficiency of oxygen atoms at the very interface with the metal substrate. Finally the comparison between the experimental and theoretical electronic characteristics (STM and XPS) of supported θ(100)-type films provides clues on the detailed structure of the experimentally observed films.

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Metal-Oxide Interfaces for Energy Production and a Cleaner Future

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Carbon dioxide (CO_2) and methane (CH_4) are among the most dangerous greenhouse gases and there is a general desire to transform these pollutants into high value chemicals. They are at the center of many operations in C1 chemistry. The transformation of CO_2 and CH_4 into alcohols or other hydrocarbon compounds is challenging because of the difficulties associated with the chemical activation of these highly stable molecules by heterogeneous catalysts. Pure metals and bimetallic systems used for this task usually have trouble when binding CO_2 or CH_4 and, thus, low catalytic activity. The creation of metal-oxide interfaces opens new routes for the selective transformation of CO_2 and CH_4 [1-5]. Here, we will discuss a series of in-situ studies investigating different mechanisms or approaches for C-O and C-H bond activation on conventional metal/oxide [1-3] or inverse oxide/metal configurations [4-5].

Metal support interactions have been found in X/CeO_2(111) surfaces (X= Ni, Co, Fe, Pt, Pd) that facilitate the reforming of methane with CO_2 or water to produce syngas [1-3,6] or directly methanol [7]. On the X/CeO_2(111) surfaces, the methane molecule can be activated at room temperature, opening the possibility for the conversion of CH_x fragments into high value chemicals [1-3,6,7].

Under the reducing conditions of CO_2 hydrogenation, a metal/oxide catalyst can undergo structural transformations that lead to inverse oxide/metal configurations [8,9]. Indeed, ZnO/Cu(111), CeO_x/Cu(111), and ZrO_2/Cu(111) exhibit an activity for the $CO_2 \rightarrow CH_3OH$ conversion that is 2-3 orders of magnitude higher than that of a benchmark Cu(111) catalyst [8,10,11]. These inverse oxide/metal systems also have sites that can transform CH_4 directly into CH_3OH at moderate temperatures [4,5,12]. Fundamental studies involving these catalysts will be discussed.

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Nanostructured oxides for conversion of CO_2 to methanol and ethanol

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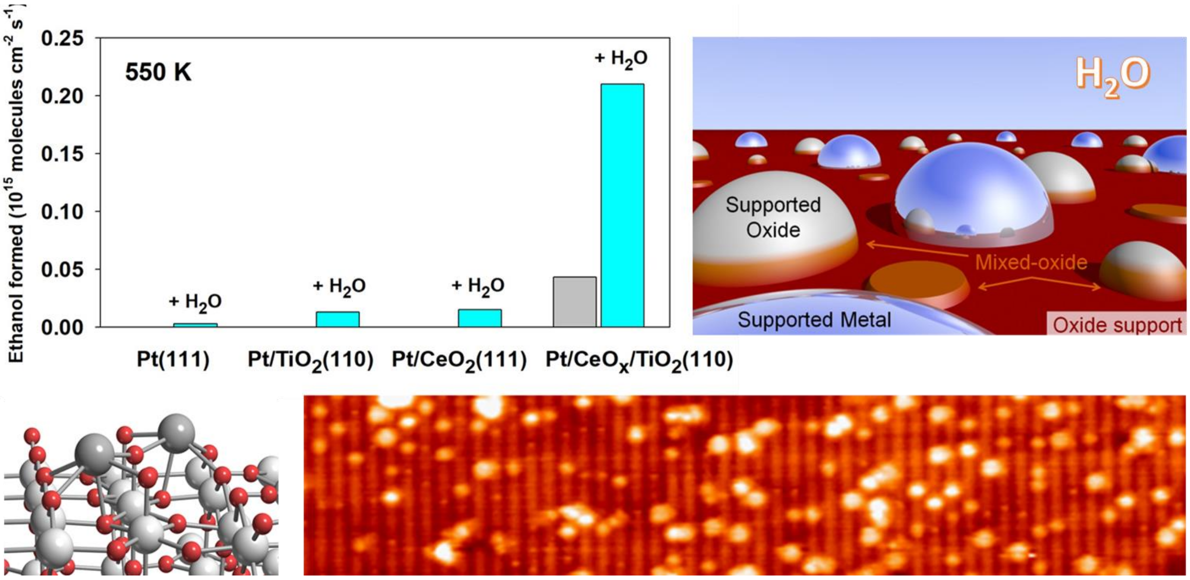
The surface chemistry of alcohol synthesis from CO_2 hydrogenation has been investigated [1, 2,3] using kinetic testing, ambient pressure x-ray photoelectron spectroscopy (AP-XPS) and DFT calculations over a multicomponent system where Pt and ceria nanoparticles coexisted on a titania template, $Pt/CeO_x/TiO_2(110)$ [4]. Due to its high ability to bind and activate CO_2, not seen for typical Cu-ZnO catalysts, the Pt-CeOx-TiO_2 interface is excellent for the hydrogenation of CO_2 to methanol with some ethanol also being produced (21% selectivity). The results of AP-XPS and DFT calculations indicate that the active state involves a mixture of Ti^{4+}/Ti^{3+}, Ce^{3+} and Pt^0/Pt^+. A fast pathway for the formation of CH_3O species is only plausible when Ce^{3+} and Pt are present. The addition of water to the reaction feed facilitates the first hydrogenation of CO_2 and substantially enhances the surface coverage of C-containing species (CH_3O, HCOO, CO_3, CH_x), facilitating the formation of C-C bonds and the production of ethanol (38% selectivity). [4]



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Using molecular beams to simulate surface reactions that require high-pressures

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A molecular beam is a collimated stream of gas formed by a supersonic expansion from a high source-pressure, of up to 150 bar[1]. This process leads to a stream of molecules of well-defined translational kinetic energy (E_{kin}), with a very narrow energy distribution. Using a reactive molecular beam with the appropriate E_{kin} one can speed surface reactions of high activation energy (E_{act}), which otherwise require elevated pressures if a random, Maxwell-Boltzman gas is used. Combining O_2 molecular beams and X-ray photoemission spectroscopy (XPS) in Ultra-High Vacuum (UHV) we revisited the oxidation of the Cu(111) surface. By tuning the energy of the O_2 beam we achieved the same sequence of surface oxides obtained in Ambient Pressure Photoemission (AP-XPS) experiments[2], in which the Cu(111) surface was exposed to a random O_2 gas of increasing pressure (P_0), up to 1 mbar. The comparison of molecular beam and random gas spectra at different E_{kin} and P_0 values, respectively, follows the expected trend derived from the different number of molecules that overcome the activation barrier for the Cu oxidation in each case. Based on this, we elaborate a general E_{act}-P_0 equivalence curve, through which we postulate that molecular beams tuned at $E_{kin} = E_{act}$ are an ideal tool to investigate gas/surface reactions that involve high activation energies, making it possible to simulate, in standard UHV-XPS experiments, high, industrial-range (> 10 bar) pressures, very far from the AP-XPS working range[3].

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Interface reactions dominate low-temperature CO oxidation activity over Pt/CeO_2

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First-principles-based kinetic Monte Carlo simulations and kinetic experiments are used to explore CO oxidation over Pt/CeO_2 [1]. The simulations compare CO oxidation over a ceria-supported ∼1 nm particle with simulations of a free-standing particle and Pt(111). The onset of the CO oxidation over ceria supported Pt is shifted to lower temperatures compared to the unsupported systems thanks to a Mars–van Krevelen mechanism at the Pt/CeO_2 interface perimeter, which is not sensitive to CO poisoning. Both the Mars–van Krevelen mechanism and the conventional Langmuir–Hinshelwood mechanism over the Pt nanoparticle are contributing to the conversion after the reaction onset. The reaction orders in CO and O_2 are compared experimentally for Pt/CeO_2 and Pt/Al_2O_3. The reaction orders over Pt/CeO_2 are close to zero for both CO and O_2, whereas the corresponding reaction orders are −0.75 and 0.68 over Pt/Al_2O_3.

In addition to reaction kinetics, the possibility to observe vacancies in CeO_2 with X-ray photoelectron spectroscopy will be discussed [2].

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2D Silicates from Ultimate Membranes to Robust Ferromagnets

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Silica and silicates represent a relatively under-explored class of two-dimensional (2D) materials that nonetheless display interesting and potentially useful properties. When deposited onto late transition metal surfaces, silica spontaneously forms a 2D van der Waals structure constructed of mirror image planes of rings of corner sharing SiO_4 tetrahedra with crystalline and amorphous polymorphs possible. The rings are large enough that small molecules may pass through without any need to create defects making it an intriguing system to create *ultimate* permeance membranes. We have isolated the layers from the growth substrate and tested the permeance of the amorphous phase for noble gases and a range of organic molecules. Despite expectations based on size, He does not permeate the SiO_2 layer but water and larger organic molecules with substantial vapor pressures can. Theoretical and experimental analyses indicate that permeation does not occur ballistically but rather through an adsorption, diffusion, transmission mechanism; since He does not adsorb, it does not permeate.[1] On the other hand, comparison of a series of straight chain and branched alcohols show that size- and shape-selective permeation is possible.[2] Transition metal (TM) silicates with a layer of corner-sharing SiO_4 tetrahedra atop an octahedrally-coordinated TM oxide layer can also be readily prepared by depositing the TM plus Si on a late TM surface and heating in oxygen; first row TM cations spanning Ti to Ni are possible. The layers break inversion symmetry making them piezoelectric and the inclusion of magnetic cations creates opportunities for magnetic phases that respond to strain and electrostatic fields. We have studied the magnetic order in single layers of these materials theoretically and experimentally. Scanning tunneling and low energy electron microscopies reveal well-ordered layers that completely cover the surface and remain intact after extended storage in ambient conditions. X-ray magnetic circular dichroism (XMCD) measurements reveal that single layer Cr silicate on Pt(111) is ferromagnetically ordered up to at least 80 K.[3] Experiment and theory indicate that Cr is nominally 3+ but electron deficient compared to typical Cr^{3+} compounds. Theoretical analysis reveals that this electron deficiency enhances ferromagnetic ordering while tying it to inefficient screening by the Pt substrate. This finding highlights the potential to control the magnetic order by doping and/or electrostatic gating. Meanwhile, XMCD measurements revealed ferromagnetic ordering in single layer Fe silicate up to room temperature. In this case, spectroscopic characterization reveals mixed valence Fe and suggests that the presence of Fe^{2+} is essential to the observed room temperature ferromagnetism. Room temperature ferromagnetism is seen for Fe silicates on Pd and Au(111) substrates, indicating that the substrate is not critical to this observation. To stabilize the Fe^{2+} state, we have also investigated mixed $Cr_2FeSi_2O_x$ layers. As a first step towards releasing the layers from the growth substrate, we have studied reactions of the layers with water and hydrogen using ambient pressure x-ray photoelectron and reflection absorption infrared spectroscopies.

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Combining experiment with theory in studying structure and dynamics of silica bilayers on Ru(0001)

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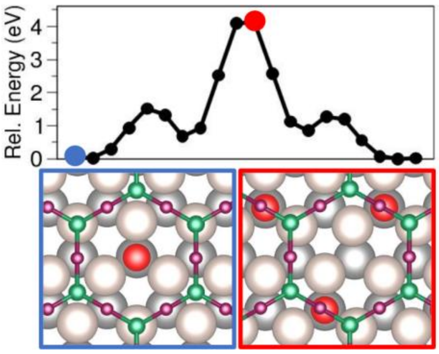
Model systems are valuable in breaking down complexity of more involved materials into manageable components [1]. Previously, well-defined silica bilayer films have been used to study the properties of the inner walls of the pores of zeolites, as a limiting case with zero curvature, hence infinite pore volume [2]. Importantly, this bilayer is only bound by dispersion interactions to the substrate, thus acting like a membrane, which opens ways to study reactions in confined space [3]. Recently, the formation of water within the silica bilayer and the oxygen covered Ru(0001) substrate has been studied by surface science techniques [4]. These observed reactions were best explained by considering lateral and vertical bilayer motion relative to the substrate due to changes in the interfacial oxygen concentration during the reaction [4,5]. Due to lacking experimental evidence for the dependence of the position of the silica bilayer on the oxygen coverage of Ru(0001), a detailed LEED I/V study on that very system has been made [6]. It has been complemented by a detailed set of DFT calculations combined with MD simulations. We will show that energy barriers induced upon moving the silica bilayer film parallel to the Ru surface will strongly depend on the oxygen coverage, i.e., the interfacial oxygen content. Dynamics simulations provide insights into the low frequency phonon motions parallel to the surface (centre of mass motion) again as a function of oxygen coverage. Our results justify the split position approach employed in the present LEED I/V study. This means that sufficiently small Pendry-R factors are only achieved upon superposition of multiple silica bilayer structures varying in registry to the oxygen covered substrate.



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Two-dimensional oxides as new catalytic materials

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About twenty years have passed since it became apparent that two-dimensional oxides grown on a metal represent a new class of materials with unprecedented physical and chemical properties [1]. In fact, the geometric and electronic structures of these ultrathin films differ from those of the bulk counterparts [2]. The formation of a metal oxide interface generates novel phenomena with some aspects in common with semiconductor physics [3]. These effects can be exploited to better understand industrial catalysts or even to design new heterogeneous catalysts. In fact, thin oxide films can play a role in catalysis thanks to their structural flexibility, nanoporosity, or ability to selectively favor charge transfer. Among the systems that we investigated recently, we will discuss the nature of ZnO ultrathin films [4,5] and their relationship with Cu/ZnO/Al_2O_3 industrial catalysts for methanol synthesis [6].

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Structure evolution of pristine and Pt-deposited ceria nanoparticles in reactive gases

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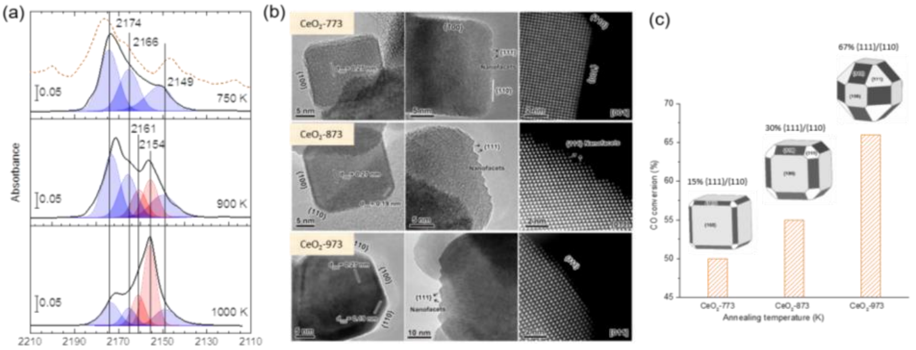
Ceria-based catalysts are highly active for numerous chemical reactions relevant for energy and environment technologies. A fundamental understanding of the surface structure and active sites of metal/ceria systems is among the most important and challenging topics in catalysis. Despite extensive investigations, many crucial issues have remained unresolved. This is primarily due to the great complexity of nanostructured metal/ceria materials and the lack of accurate reference data acquired for well-defined model systems based on a thorough surface science study.

Here, we present our recent spectroscopic investigations on pristine and Pt-deposited ceria systems in the form of both well-defined single crystals and nanoparticles by combining IR spectroscopy (polarization-resolved IRRAS and IR transmission) and X-ray photoelectron spectroscopy (XPS). The systematic spectroscopic results, in conjunction with microscopic spectroscopy (STEM) and density functional theory (DFT) calculations, allowed us to gain in-depth insight into structural, electronic and reactive properties of pristine and Pt-decorated ceria systems under different conditions [1-3].

For the cubic ceria nanoparticles, a two-step mechanism was proposed for the polarity compensation of the polar (110) surface, where an initial O-terminated (2x2) reconstruction is followed by a severe refaceting at elevated temperatures to yield {111}-dominated configurations. This substantial surface restructuring is accompanied by the formation of under-coordinated defect sites and O vacancies, which account for the enhanced catalytic activity for CO oxidation reaction [1]. For Pt/CeO_2, we focused on the structural and electronic changes of ceria-supported Pt species (nanoparticles, small clusters, single atoms) in reactive gases at different temperatures. It was found that the charge state and size of Pt species can be tuned in a controlled manner depending on the oxidation/reduction conditions. Furthermore, our results revealed significant modification of the ceria surface resulting from strong interactions with Pt. These results provided solid basis for mechanistic understanding of CO oxidation over Pt/ceria catalysts [2,3].



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In situ identification of the active sites during oxidation of Ce_2O_3 on Ru(0001) by CO_2

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Cerium oxide is of great technological interest due to its relevance in various catalytic applications. An inverse model catalyst such as cerium oxide on Ru(0001) can be used to understand the fundamentals behind catalytic processes. For the production of methanol from CO_2 and H_2, oxygen vacancies, as found on reduced ceria, are necessary to activate the CO_2 molecules [1]. Ceria reduction may be achieved by, e.g., exposure to H_2 at elevated temperatures [2] or by thermal treatment [3]. We have studied the interaction of CO_2 with thermally reduced cerium oxide islands on Ru(0001) in situ with low-energy electron microscopy (LEEM) and spatially resolved x-ray absorption spectroscopy (XAS-PEEM) at the ELETTRA nanospectroscopy beamline. The structure and composition of the islands were analyzed by XAS-PEEM and dynamic (real-time) intensity-voltage (I(V))-LEEM measurements. In particular, the oxidation state was derived from specific islands by fitting the data by a linear combination of reference spectra of Ce_2O_3 and CeO_2, respectively. Partial reoxidation by exposure to CO_2 was achieved at 550 °C, which agrees well with previous studies that oxidized cerium oxide on other metal substrates [4,5]. From this analysis we derive a correlation of the oxidation state and the size of the island, revealing that larger islands are reduced less throughout this process, which is possibly related to the higher thickness of these islands (Fig. 1). Furthermore, the different probing depths of I(V)-LEEM and XAS-PEEM allow comparing the oxidation state of the topmost layers and the bulk. Also, fitting the I(V)-LEEM data by a linear combination of reference spectra was used to derive a pixel resolved map of the cerium cation oxidation state providing further insights and enabling statistical analysis of the distribution of reactive sites of the cerium oxide on the few nanometer scale.

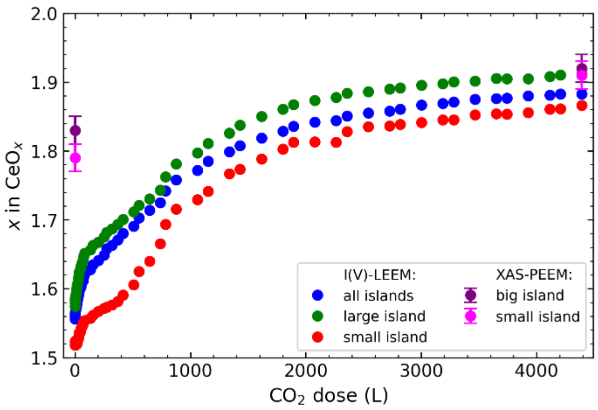

Figure 1: Reoxidation of cerium oxide islands by exposure to CO_2 at 550 °C obtained from *in situ* XAS-PEEM and I(V)-LEEM analyses.

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Superoxide ions on the edge – the key to understanding hydrogen reduction of nanoceria?

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Using an extensive data-set of density functional theory derived reaction energies and reaction barriers and subsequent microkinetic modelling, we propose a new mechanism that explains experimentally observed temperature programmed reduction (TPR) spectra for small (3-6 nm) CeO_2 nanoparticles exposed to hydrogen presented in Refs. 1 and 2. In our mechanism, which is schematically illustrated in the Figure below, dissociation of hydrogen takes place at the extended {111} facets, while the actual conversion to water takes place at the ridges where protons are transferred to superoxide species strongly adsorbed at these ridges. The hydrogen migration barrier and the availability of Ce^{3+} ions dictate the shape of the TPR spectra. In conclusion, our simulations provide quantitative support for the interpretation that superoxide ions are responsible for the dramatically increased reactivity of small CeO_2 nanoparticles. In addition, we also make comparison to temperature programmed desorption experiments.

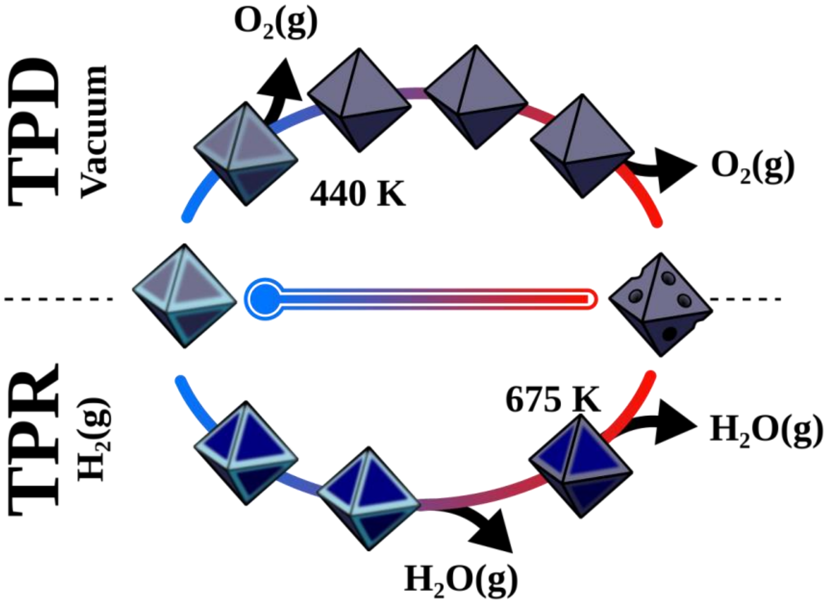

Figure 1. A schematic illustration showing the evolution of a small CeO_2 nanoparticle in a TPR or TPD experiment as the temperature as predicted from our DFT-based microkinetic modelling. Turquoise and dark blue color indicates superoxide ions and hydroxide groups (protons), respectively.

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Optimized Infrared Reflection Absorption Spectroscopy for Metal Oxides: Overcoming Challenges of Low Reflectivity and Sub-Monolayer Coverage

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Infrared reflection absorption spectroscopy (IRAS) is a wide-spread technique in heterogenous catalysis, and it is an ideal tool for the comparison of real and model catalysts [1]. Most surface science groups perform IRAS studies either directly on metal single crystals, or on (ultra-)thin metal oxide films grown on such samples [2]. Achieving high-quality data from metal-oxide single crystal surfaces is difficult because their low reflectivity necessitates averaging many individual measurements with long acquisition times [3]. The goal of this work was to develop an IRAS setup for studying the adsorption of molecules on model "single-atom" catalysts. Here, the low reflectivity of oxide support is exacerbated by the sub-monolayer coverage of adsorbates on single adatoms. In the contribution, I will present the novel IRAS system we have developed to overcome these two challenges.

The main improvements over commonly-used setups are a high numerical aperture, an optimized optical path, control of the incidence angle range, and high mechanical stability. The high numerical aperture of the optical system leads to an increase in the amount of light reflected from a small single crystal sample. This is achieved by placing both the illumination and collector mirrors inside the UHV chamber close to the sample. To minimize the loss of signal, optimization of the optical path was performed using a ray tracing program. The other limit is the small area on the sample that is covered with adsorbates: in our setup, a molecular beam delivers adsorbates with a spot diameter of 3.5 mm [4]. Infrared light is reflected only from this area.

The reflectivity and absorbance of non-metallic samples varies strongly with incidence angle, and can even change a sign, leading to cancellation. The optimum angle ranges are different for every material. As our setup has a large range of incident angles, we can use this to our advantage: Using two adjustable aperture plates, we can vary the minimum and maximum incidence angle from 49° to 85° to maximize the signal for each single crystal sample. Angle control also allows us to optimize the signal for both p-polarized and s-polarized light independently.

We successfully executed and compared D_2O and CO absorbance measurements on a rutile $TiO_2(110)$ surface, and our results agree with the established literature [3]. By properly selecting the incidence angle range, we achieved a signal-to-noise ratio of ~16 for 1 ML CO adsorbed on TiO_2 with only 150 seconds of measurement time.

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Mixed Co-Fe oxides on Au(111) in electrochemical water splitting

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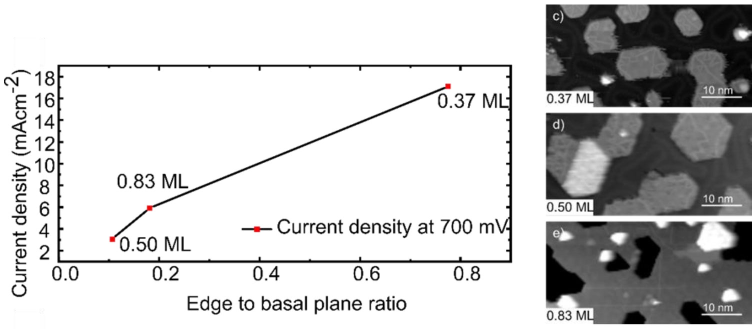
Mixed transition metal oxides are used extensively in heterogeneous catalysis and electrocatalysis. The surface morphology, metal mixing and role of interchangeable oxidation states, however, in many cases generate a structure sensitivity, which needs to be better understood. For example, in elecrocatalytic water splitting, nanostructured catalysts with a mixed composition of e.g. Co-Fe and Ni-Fe are active earth-abundant alternatives for the oxygen evolution reaction (OER), but the long-term stability and understanding of the enhanced activity of mixed oxides compared with unary oxides is still limited. A key problem is the missing fundamental insight on how the morphology and interface structure of mixed oxides ultimately regulate electrocatalytic properties.

To develop a better understanding of CoFe oxide catalysts in OER reaction, we use scanning tunneling microscopy (STM) and photoemission spectroscopy to characterize the structure and chemical composition of mixed Fe/Co oxide nanoislands on a Au(111) surface [1]. Atom-resolved STM images directly show where single Fe dopants preferentially locate within the Co oxide. Starting from a series of well-defined Co oxide nanoislands with a variable Fe content, we can therefore compare how the oxide surface structure and chemical composition develops after the sample has been used as the working electrode in a homebuilt electrochemical cell during OER [2]. Combining insight from STM and XPS we can follow the formation of the active Co(Fe) oxyhydroxide (CoOOH) phase from the initial oxide. Based on this information we have proposed a model where the main effect of Fe doping in Co oxide is that of a structural stabilizer that acts to stabilize smaller particles with more active sites residing on the edges of CoOOH layers [3,4].



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Oxide Interfaces: Playing away from UHV

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Preparing and/or probing metal oxide interfaces away from ultra-high vacuum (UHV) can be hugely challenging but is of immense importance for elucidating properties of technological relevance. In this presentation, I will outline some of the endeavours of my group and collaborators to contribute to this area. Firstly, work conducted on wet-chemically prepared single crystal metal oxide surfaces will be described, focusing on structure determinations of rutile-TiO_2(110) and rutile-TiO_2(011) with surface X-ray diffraction (SXRD). It will be demonstrated that non-UHV surface preparation can lead to significantly different surface terminations. The potential importance of these results will be discussed, including enhancing our understanding of the superhydrophilicity and photocatalytic activity of titania interfaces.

In the second part of the presentation, I will describe measurements to understand the occurrence of atmopheric corroson prior to surface condensation of bulk liquid water, i.e., at a relative humidity (RH) below 100%. The focus will be on the interaction between water vapour ($0\% \lesssim$ RH $\lesssim 100\%$) and an oxidised surface of polycrystalline zinc; the latter is an important material for atmospheric corrosion control. We shed new light onto the phenomenon of atmospheric corrosion through the application of two *in situ* surface spectroscopies, namely near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and vibrational sum frequency spectroscopy (VSFS). Combining evidence emerging from both spectroscopies, we conclude that water does not simply grow atop a sharply terminated zinc substrate, as often proposed, but accumulates through capillary condensation in the ubiquitous layer of adventitious carbon covering the surface.

Transient Amperometry of O_2 Evolution Reaction on Metal-Oxide Photocatalysts under Water

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Oxygen evolution at water–solid interfaces is a key reaction for sustainable energy production. Although some intermediate states have been detected in transient absorption spectroscopy, the O_2 evolution kinetics after the multi-step, four-electron oxidation of water remain unknown. In this study, we applied micrometer-sized electrode to operando O_2 detection over an efficient metal-oxide photocatalysts for the overall water-splitting reaction.

A platinum electrode of 10 µm in radius is moved close to a photocatalyst film in an electrolyte solution. The reaction product of interest, O_2 in this study, is released on the film, diffused across the electrode–film gap, and converted to a current on the electrode (Figure 1).

By monitoring electrode current in the order of nanoampere, O_2 evolution rate was determined with a time resolution of 0.1 s over two perovskite-structured photocatalysts; $SrTiO_3$ doped with Al cations and $NaTaO_3$ doped with Sr cations.

The evolution rate did not respond instantaneously to excitation light irradiation on the $SrTiO_3$ photocatalyst. When light was turned on, the photocatalyst film was inactive for evolution and light activated in seconds; first photons impinging the film were utilized for activating the photocatalyst and then second or latter photons drove steady evolution [1]. The evolution rate over the $NaTaO_3$ photocatalyst is being evaluated and will be compared with the rate on the $SrTiO_3$ photocatalyst.

Transient O_2 adsorption and desorption were recognized in addition to steady, photocatalytic O_2 evolution on the $SrTiO_3$ photocatalyst [2]. We hypothesized that electrons excited to the conduction band were transferred to O_2 in water thorough Ti cations neighboring an oxygen anion vacancy on Al-doped $SrTiO_3$. The negatively charged O_2 was then bound to the Ti cations. By contrast, it was neutralized and released when shaded through electron back-transfer to the conduction band. The hypothesized mechanism for O_2 adsorption and desorption is comparable with the photoinduced O_2 desorption known to occur on anion vacancies of $TiO_2(110)$ [3].

Microelectrode amperometry demonstrated here will be useful for understanding many other reaction kinetics at liquid–solid interfaces.

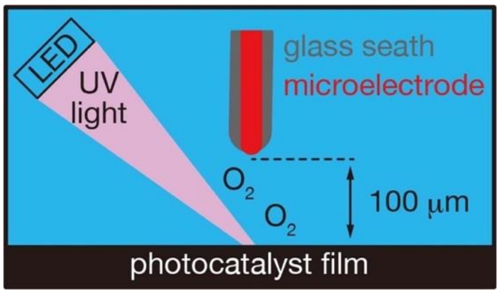

Figure 1. Time-lapse O_2 detection in water.

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An atomistic picture of electronic metal support interaction and the role of water

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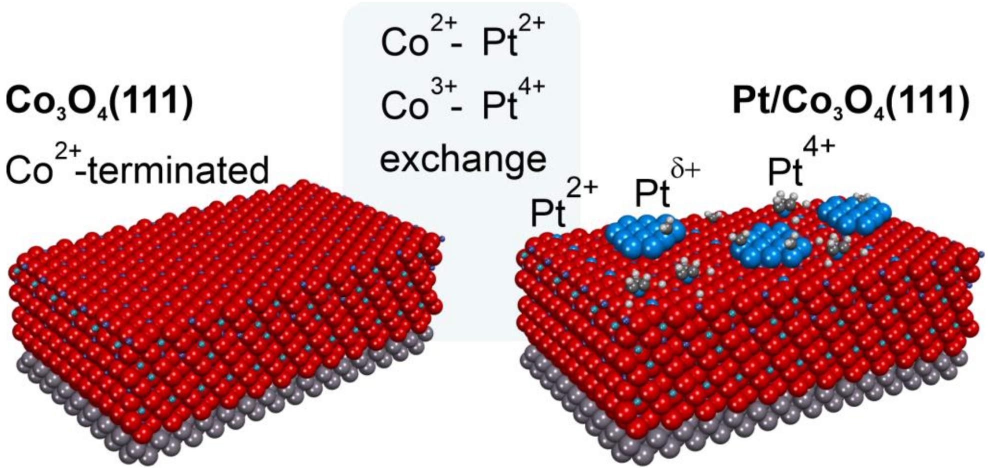
Electronic metal support interaction (EMSI) can be potentially employed to anchor noble metals on the surfaces of reducible oxides in the form of cations [1,2]. The latter serve as active catalytic sites in single-atom catalysts (SAC) [3]. The atomic dispersion of noble metals on the energetically the most favorable, oxygen-terminated oxide surfaces is controlled by defects. However, the nanostructuring of the reducible oxides may not provide sufficient number of defects to achieve high density of atomically dispersed noble metals for SAC. We present a comprehensive picture of the EMSI between platinum and a $Co_3O_4(111)$ support terminated by Co^{2+} cations which can be employed for the fabrication of SACs with a high density of single-atom sites on the defect-free supports. The corresponding mechanism involves temperature controlled substitution of surface Co^{2+} and sub-surface Co^{3+} cations by Pt^{2+} and Pt^{4+} species, respectively. The cationic exchange with Co^{2+} cations is coupled with the partial reduction of $Co_3O_4(111)$, while the exchange with Co^{3+} cations is driven by the charge disproportionation within the Pt deposit. In the presence of co-adsorbed water, the Pt^{4+} species are stabilized at the surface in the form of triaqua complexes. We use scanning tunneling microscopy and synchrotron radiation photoelectron spectroscopy in combination with density functional theory to monitor the charge transfer and determine the nature and coordination environment of the Pt species on $Co_3O_4(111)$.



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Water on Fe_3O_4(111)/Pt(111) revisited

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The interaction of water with iron oxide surfaces can be considered a prototypical example of the complex interplay between the chemical interaction of water with redox active metal oxides which strongly dependent on the details of the surface structure as well as the intermolecular interactions between adsorbed water molecules. The system discussed in this contribution was first investigated by the group of the late Werner Weiss.[1] However, several groups have subsequently extended our understanding of this system considerably using both experimental as well as theoretical techniques (e.g. [2]). Recent studies using TPD and LEED showed the formation of ordered structures of the water molecules in the temperature range between 200 and 250 K and DFT calculations provided structural models encompassing the formation of water aggregates (dimers, trimers) to explain these observations.[3] While direct evidence for water aggregation was shown on Fe_3O_4(001) using both STM and AFM corresponding measurements on the (111) oriented surfaces have not yet reported.[5] Further insight into the nature of the adsorbed species was gained from IR spectroscopy -in part by combination with DFT calculations- assigning the observed bands to different species such as free O_sH and O_wH (oxygen from lattice and water), water dimers or water-OH species.[4, 3, 6, 7]

In this contribution we will present a recent study combining IRAS and STM. The latter showed the formation of ordered water structures on the Fe_3O_4(111) surface which can be understood by the formation of water aggregates as previously reported on the (001) surface. Furthermore, we will present results from IRAS experiments comparing the rather complex spectral evolution as a function of coverage and temperature and will focus the discussion aspects not yet satisfyingly explained. Whereas recent DFT calculations predict the presence of “free” O_sH-groups with oxygen atoms belonging to the iron oxide lattice up to rather large coverage (8 molecules per 2x2 unit cell) the IRAS data show that the IR signal associated with these OH groups disappear prior to the saturation of the monolayer signal. To this end, it is also worth mentioning that the signals observed in IR spectra for water adsorbed at 300 K are distinctly different to those taken after adsorption at 250 K. In particular, the latter exhibits a signal assigned to a hydroxyl group form with lattice oxygen while the signals at 300 K lack indications for the presence of such species even though comparable adsorption energies are deduced for low coverage [6, 7]. The coverage and temperature dependent IRAS spectra will be discussed in light of these discrepancies.

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Structure and Chemistry of Aqueous Oxide Interfaces from Molecular Simulations

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Photo-electrocatalysis involving complex oxide-water interfaces is a highly promising technology for the sustainable production of fuels. However, probing these complex interfaces and gaining atomistic insights is still very challenging for current experimental methods, and is often only possible through computational simulations. Ab initio simulations provide the best accuracy, but are generally limited to small system sizes and time-scales due to their high computational cost. Machine learned potentials that reproduce the accuracy of ab initio methods while allowing the exploration of larger systems and timescales have recently emerged as a promising alternative. In this talk I will illustrate these issues by discussing some of our recent work on the application of ab-initio based molecular simulations to understand the structure and dynamics of interfacial water on photoelectrochemically relevant oxide surfaces. Specific topics will include proton transfer at the aqueous TiO_2 and IrO_2 interfaces, the water dissociation fraction and the hydroxyl lifetimes at the interface.

Surface Reactions of Uranium Oxides Thin Films and Single Crystals.

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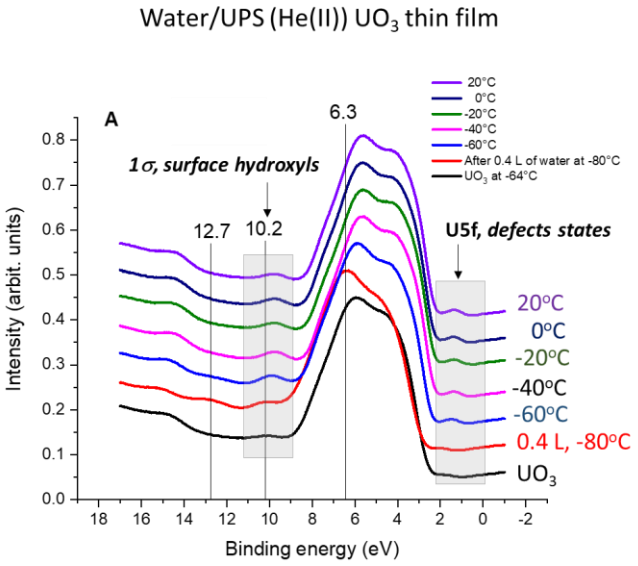
The surface reactions of model oxides with oxygen containing compounds provides many needed fundamental information related to redox and acid-base interactions. We present the surface reactions of water with uranium oxides (UO_2, U_2O_5 and UO_3) thin films and those of ethanol with both UO_2 thin film and (100) single crystals. One of the intriguing phenomena is the observation that, for a few oxides, water seems to reduce (not oxidize) the substrate. Ultraviolet Photoelectron Spectroscopy (UPS) has been used to study the reactions for this purpose. It was found that on UO_2, water adsorbs largely in a molecular state while on U_2O_5, it partially dissociates, forming surface -OH groups and a fraction of uranium cations were reduced from U(V) to U(IV). On UO_3 a similar reduction process is seen (reduction of a fraction of U(VI) to U(V) cations), albeit less pronounced (figure 1A). The chemisorbed H_2O and -OH states via their molecular orbitals $1b_2$, $3a_1$ and $1b_1$ (for H_2O) and 1σ and 1π (for -OH) were further analyzed. The $3a_1$-$1b_1$ (ΔE) binding energy difference was taken as a measure for the bond strength. It was larger on UO_2 and U_2O_5 (2.9-3.0 eV) than on UO_3 (2.2 eV). TPD of Ethanol over UO_2 showed desorption due to both molecular and dissociated adsorption. The dissociated form resulted in dehydrogenation of a fraction of ethoxides to acetaldehyde. As shown in figure 1B, the dehydrogenation is not related to prior presence of surface oxygen defects but is intrinsic to UO_2 redox property. Modelling of TPD results is currently in progress to extract relevant kinetic parameters and compare them to other 3d-transition metal oxides.



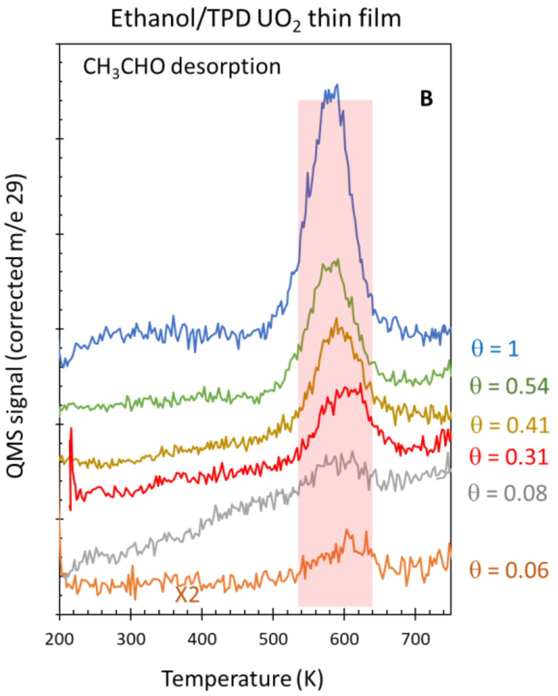


Figure 1. A, UPS of water on UO_3 thin film heated at the indicated temperatures. B, Acetaldehyde (CH_3CHO) desorption during ethanol-TPD as a function of surface coverage.

Toward an efficient f-in-core/f-in-valence switchable description for DFTB calculations of Ce 4f states in ceria

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The Density Functional Theory (DFT) is one of the pillars of modern computational materials science. The success of the DFT method rests on its favorable scaling behavior and its (often) respectable accuracy. However, the method is still too computationally demanding to address the complexity of many materials under realistic conditions. Therefore, the method often serves as a reference method in modern multi-scale simulation protocols. One example of a computationally challenging group of materials is the reducible oxides with their strongly correlated electronic d and f states. Accurate treatment of these systems generally requires many-body theory (higher-order quantum mechanical methods) treatment or, within DFT, hybrid (non-local exchange) functionals, together with efficient minimization algorithms to ensure proper convergence to the correct electronic ground state. These challenges stimulate research activities to develop new methods, or schemes and protocols, for electronic structure calculations with improved computational efficiency. Our approach has been to utilize the computational efficiency of the Self-Consistent Charge Density Functional Tight-binding (SCC-DFTB) as implemented in the DFTB+ code [1] in conjunction with recent developments in repulsive potential fitting using either two-body [2-3] or many-body machine learning potentials [4].

In more detail, we have developed a computational protocol for efficient studies of partially reduced redox-active oxides based on the SCC-DFTB method [5]. The protocol is demonstrated for ceria which has become a prototypical reducible oxide material with its signature Ce *4f* states being populated in the reduced state. The underlying idea of the developed protocol has been to achieve a consistent (and harmonized) set of Slater–Koster (SK) tables with connected repulsive potentials that enable switching on and off the *in-valence* description of the Ce *4f* states without serious loss of accuracy in structure and energetics. The implicit treatment of the Ce *4f* states, with the use of f-in-core SK-tables, is found to lead to a significant decrease in computational time. More importantly, it allows for explicit control of the oxidation states of individual Ce atoms. This makes it possible to “freeze” the electronic configuration, thereby allowing the exploration of the energetics for various meta-stable configurations. We anticipate that the outlined strategy can help to shed light on the interplay between the size, shape, and redox activity for nanoceria and other related materials.

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Electronic structure-based descriptors for oxide properties and functions

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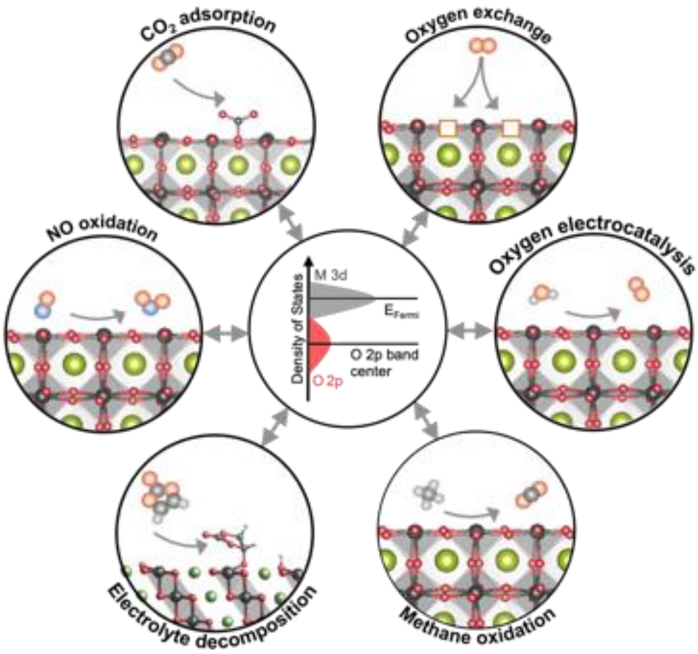
The use of easily accessible descriptors has proven to be a powerful method to advance and accelerate discovery and design of new materials. The position of the oxygen electronic 2*p* band center has been proposed to capture the basic physical properties of oxides including oxygen vacancy formation energy, diffusion barrier of oxygen ions, and work function [1]. In this talk we discuss how the energy of the oxygen 2*p* states can be used as a descriptor for oxide bulk and surface chemical properties. We show how the oxide redox properties vary linearly with the position of the oxygen 2*p* band center with respect to the Fermi level. Moreover, we highlight how the adsorption strength of relevant reaction intermediates at the surface of oxides can be strongly correlated with the energy of the oxygen 2*p* states, which affects the catalytic activity of reactions such as oxygen electrocatalysis [2], oxidative dehydrogenation of organic molecules [3,4], and NO oxidation [5]. Such descriptors for the oxide catalytic activity can be used to understand trends and changes in reaction mechanisms among different catalysts and to predict new catalysts with improved activity. We discuss how this descriptor can be expanded across different materials and structural families, including possible generalizations to compounds outside oxides.



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Vibrational Frequencies of CO Bound to CeO_2(111), (110), and (100): A Consistent Theoretical Description using Density Functional Theory

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This presentation reviews the facet-dependent adsorption of CO on all three low-index oxidized and reduced CeO_2 surfaces. The focus lies on the effect of the CO coverage on the IR vibrational modes and on the performance of state-of-the-art quantum-mechanical methods in their description. A comparison with a high-resolution IR spectroscopy study performed on single crystal samples is used to assign different CO vibrational bands observed on all three low-index ceria surfaces (see Figure). The hybrid DFT approach with the HSE06 functional and saturation coverage yields good agreement in contrast with commonly applied DFT(PBE)+U method that does not provide reliable CO vibrational frequencies. The failure of conventional density-functional theory (DFT) is explained in terms of its inability to accurately describe the facet- and configuration-specific donation and backdonation effects. The study demonstrates that CO is highly affected by the structure of cerium oxide surfaces and the presence of oxygen vacancies. The theoretical-experimental approach can help to better understand ceria nanoparticles and determine the nature of their exposed facets.

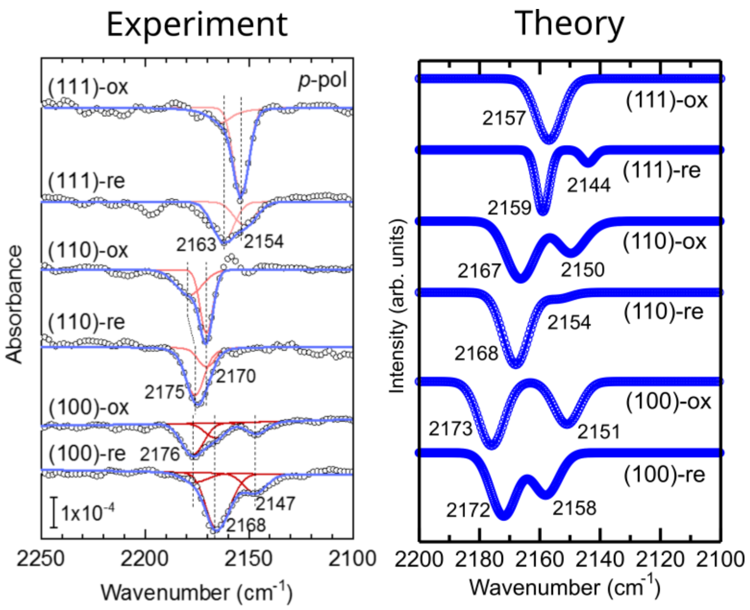

Figure: p-polarized IRRAS spectra at 75 K (left) and DFT-HSE06 calculation (right) of 1 ML CO adsorption on the oxidized and reduced (111), (110) and (100) ceria surfaces

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Copper-ceria CO-PROX catalysts: exploration by low temperature CO adsorption infrared

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Catalysts combining copper and cerium oxides are an economically interesting alternative for various processes involved during production-purification of H_2 generated from hydrocarbons or biomass [1,2]. In particular, they show promising characteristics for the preferential oxidation of CO (CO-PROX) required for achieving CO concentrations below about 100 ppm in the hydrocarbon reforming H_2-rich stream in order to minimize the poisoning of low temperature fuel cell electrodes. Active sites for such process have been proposed to be located at the interface between the two component oxides [2]. However, details about them are basically unknown. In the present work, we examine catalysts of copper supported on two different nanostructured ceria supports (cubes, spheres). The results of basic characterization by XRD, Raman, TPR, EPR, HREM and XPS [3,4] are complemented by STEM-HAADF combined with high yield XEDS, which allows achieving important details about the structural properties of the systems. In turn, the results of catalytic tests are complemented by DRIFTS under CO-PROX conditions and CO is employed as probe molecule at low temperature after selected situations for the catalysts. In turn, theoretical exploration by DFT is employed to rationalize the results obtained. Important similarities are observed in the type of carbonyls formed on the bare supports which reveal that an important faceting and reconstruction of the (100) faces of the nanocubes takes place and finally carbonyls on (111) and (110) faces predominate in any case [5]. Despite such similarities, different types of copper species are apparently formed as a function of the shape of the support and which determine important catalytic differences between the systems.

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$CuGaO_2$ Delafossite as a High-Surface Area Model Catalyst for Cu^+-Activated Reactions

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Copper is one of the goldilocks metals in catalysis. Deciphering the local atomic environment and oxidation state of active centers in supported copper catalysts, as well as the design of materials to control their stability under reaction conditions remains a great challenge today.
In general, it has been highlighted that copper species in the intermediate oxidation state 1+ (Cu^{1+}) play a key and beneficial role in a wide variety of important heterogeneous catalytic reactions, such as the synthesis of methanol [1,2], water gas shift reaction [3,4], reforming reactions [5], electrochemical reduction of CO_2 [6], dehydrogenation and hydrogenation reactions [7,8], epoxidation of propylene [9] and CO oxidation [10], among others.
In this work, well-defined copper and gallium delafossite ($CuGaO_2$, Cu^{1+} and Ga^{3+}) was synthesized to maximize the number of stable Cu^{1+} sites on a high surface area model-catalyst. An exhaustive multimodal characterization was carried out by combining high resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), ambient pressure X-ray photoelectron spectroscopy (AP-XPS), *operando* IR spectroscopy, and density functional theory (DFT) calculations in order to determine the morphology and nature of active surface sites on $CuGaO_2$. We show here how $CuGaO_2$ in the form of porous nanoplates, mainly exposing (110) facets with Cu^{1+} and Ga^{3+} cations in well-defined surface positions, can be used as a model to explore the activity and stability of Cu^{1+}-activated reactions.
Our results also show that the delafossite structure is preserved after calcination or reduction pretreatments (in pure O_2 or H_2, respectively), and has the potential to develop new technical catalysts. Extensive reduction of the mixed-oxide leads to a stable catalyst with higher activity for CO oxidation, as a result of the formation of geminal dicarbonyl species on $Cu^{\delta+}$, with $0 < \delta < 1$, under reaction conditions.

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Ceria-supported Cu-based bimetallic model catalysts: Structures and properties

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Copper-containing cerium oxide materials have obtain intensive attention in catalysis, especially in electro-catalysis, due to their superior catalytic performance in many important industrial and environmental catalytic applications, such as water-gas shift (WGS) reaction,[1] and CO oxidation, [2] etc. The superior activity of Cu/CeO_2 has been ascribed to a synergistic effect which is related to the strong interaction between Cu and ceria.[3] By summarizing the literature, it is evident that such synergism normally involves several interrelated factors: the presence of defects like oxygen vacancies; the facilitation of the interplay between the Ce^{3+}/Ce^{4+} and Cu^{2+}/Cu^{+} redox couples; the enhanced reducibility of mixed CuO/ceria composites as compared with those of the individual counterparts. Despite those factors accounting for the improved catalytic activity of CeO_2 supported Cu-based catalysts, the underlying mechanism of the effect and the accurate amount of electrons transferred from per Cu atom to CeO_2 at the Cu/CeO_2 interface are still unclear. This is due to the complexity of the copper-ceria interaction as well as the limited availability of the in-situ sophisticated techniques, which greatly prohibit the molecular level understanding of synergistic mechanism of Cu/CeO_2 system.

In this presentation, we report our recent studies on Cu and Cu-based bimtallic systems on the well-ordered CeO_2(111) thin films by synchrotron radiation photoemission spectroscopy (SRPES) together with scanning tunneling microcopy (STM), low electron energy diffraction (LEED) and infrared reflection absorption spectroscopy (IRAS). The growth, electronic structure and thermal stability of Cu, Cu-Co and Cu-Ni on CeO_2(111) were systematically investigated. Through these model catalyst studies, we aim to gain a fundamental insight into the nature and the extent of copper-ceria interactions as well as the structures of Cu-based bimetallic catalysts, which could help shed some light on the origin of the catalytic performance of CeO_2 supported Cu-based catalysts. By preparing studies like this provide a basic understanding that is crucial for the rational design of novel, more efficient, and greener catalysts.

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Optical Properties of Cuprous Oxide measured in the STM: Excitons, Plasmons and Color Centers

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Cuprous oxide, one of the few p-type binary oxides, is known for its rich optical response. A set of para and ortho-excitons including multiple Rydberg states hereby competes with a pronounced defect luminescence mediated by copper and oxygen vacancies. Whereas the full arsenal of non-local optical methods has been utilized to interrogate the emission response of Cu_2O, spatially resolving optical techniques were not employed so far. This presentation discusses how STM luminescence spectroscopy can be applied to probe the optical properties of bulk and thin-film Cu_2O at the nanoscale.

Both sample systems display identical XPS signatures, diffraction patterns and surface configurations.[1] The latter is governed by the nano-pyramidal reconstruction of $Cu_2O(111)$, composed of Cu_4O units that occupy every third Cu-O six-ring of the bulk-cut surface.[2] Moreover, robust p-type conductivity and a 2.1 eV band gap are revealed for both systems. In classical photoluminescence, free and defect-bound excitons are detected for the bulk crystal, while only defect-mediated luminescence from single and double charged O vacancies are found for the Cu_2O films.[3] This difference reflects the reduced crystallographic quality, i.e. the higher number of non-radiative decay channels, for the thin films.

STM luminescence of the bulk crystal is controlled by Cu-vacancy emission with a small remnant of the free-exciton peak.[4] Photon maps of the surface are entirely homogenous due to the long radiative lifetime of the Cu_2O optical modes that destroys any correlation between the points of excitation and decay in the experiment. Conversely, the oxide films exhibit a broad emission band ranging from 700 to 950 nm that is compatible with cavity plasmons stimulated by inelastic electron tunneling. Although the spectra contain no direct signature of Cu_2O defects, the mechanism of STM luminescence is largely controlled by O vacancies in the oxide surface.[5] Resonant tunneling into V_O defect states in the band gap opens efficient channels for plasmon excitations, and gives rise to a sharply peaked emission maximum at 2.2 V sample bias. Corresponding photon maps display highly localized emission centers that can be assigned to single or few O vacancies in the surface. Our approach thus renders individual oxide color centers accessible to the experiment, even if their topographic signature cannot be resolved in respective STM images.

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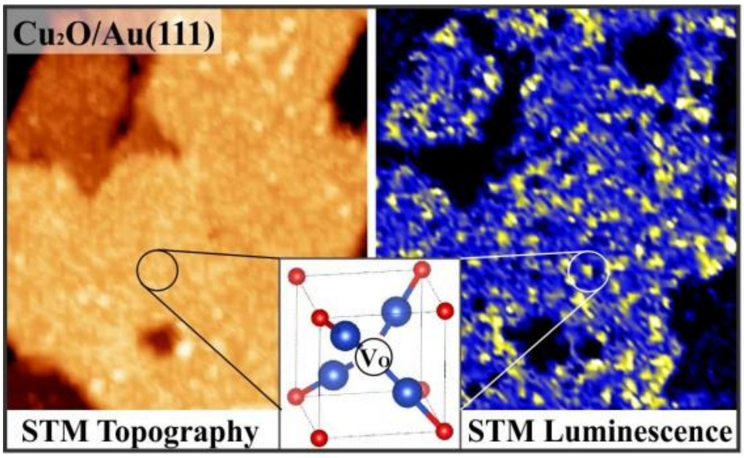

Fig. 1: STM topography and corresponding luminescence map of a $Cu_2O/Au(111)$ thin film, showing the emission response of single oxygen vacancies.

Mechanisms of charging and structural modification of amorphous oxide films in devices

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Thin films of amorphous (a) oxides are ubiquitous as photocatalysts, protective coatings, photo-anodes, and in memory applications, where they are exposed to excess electrons and holes. We investigate the role of electron and hole trapping and hydrogen incorporation inside amorphous films of SiO_2, HfO_2, Al_2O_3, Ga_2O_3, TiO_2, and ZnO and at interfaces with Si and metals in creation of new defects, oxide structural degradation and conduction. The initial models of amorphous structures are produced using classical force-fields and the LAMMPS package. The volume and geometry of all structures are fully optimized using density functional theory (DFT) as implemented in the CP2K code with the range-separated hybrid PBE0-TC-LRC functional, as described in detail in [1]. The results demonstrate that hole injection into all amorphous oxides leads to hole localization at low-coordinated O sites in the amorphous network [2]. Injected extra electrons localize in amorphous SiO_2 and HfO_2 at structural precursors in deep states about 3.0 eV below the mobility edge [2]. However, electrons do not localize in a-ZnO and electron trapping in a-Al_2O_3 and a-Ga_2O_3 is shallow and metastable. Trapping of up to two electrons at intrinsic sites results in weakening of Si-O and Hf-O bonds and emerging of efficient bond breaking pathways for producing neutral O vacancies and interstitial O_i^{2-} ions with low activation barriers [2]. These barriers, as well as barriers for migration of the O_i^{2-} ion (< 0.5 eV) are significantly reduced by bias application. Creation of O vacancies facilitates trap-assisted tunnelling through oxide films and is responsible for oxide charging and leakage current. Hydrogen incorporation from metal electrodes leads to creation of additional defects in the oxide. Atomistic simulations of defect creation in amorphous oxide films are combined with kinetic simulations of trap assisted tunnelling of electrons and ionic diffusion through oxide [3,4]. They provide the mechanisms and time evolution of oxide charging and degradation. These mechanisms are used to simulate the kinetics of dielectric breakdown in devices and explain the performance of resistive random-access memory devices.

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Quantification of nanoscale charges with a force microscope

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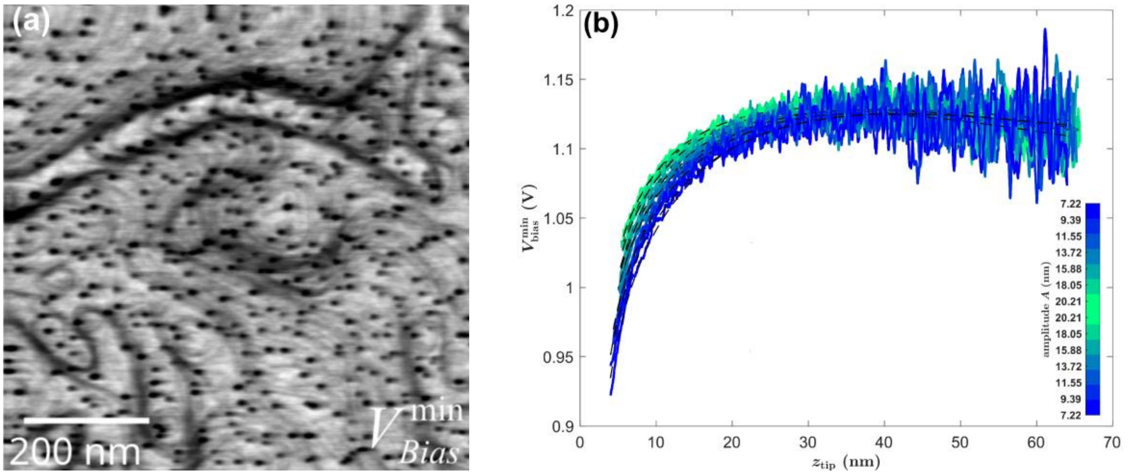
The quantitative measurement of charges at the nanoscale yields important insight into fundamental physico-chemical processes, and may be specifically important for the elucidation of surface reactions on oxides. It is straightforward to detect charges by probing with the tip of a dynamic atomic force microscope, however, quantitative measurements are still a challenge as a large number of parameters and effects contribute to the measured force signal. We introduce the fundamental framework for charge force microscopy (CFM) as a tool for the precise quantification of charges and discuss charges located in, on or above the surface of a dielectric substrate supported by a metal electrode. We present a comprehensive analysis of CFM signal generation and unravel the dependency of the CFM signal on the probe oscillation amplitude, on system parameters such as the substrate dielectric constant or the tip geometry, and on the vertical and lateral position of charges. Most importantly, we demonstrate how to untangle the influence from nearby charges when quantifying the magnitude of a central charge of interest in presence of many surrounding charges. We find that charge quantification from regular imaging bears many ambiguities, while mapping the CFM signal perpendicular to the sample surface yields sound results. We introduce an experimental procedure for CFM measurements utilising the force curve alignment (FCA) method [1] to derive precise force curves in the presence of charges and introduce a methodology to quantify the charge of the object under investigation based on a spectral analysis of the side band CFM signal by Lock-In detection. We first experimentally determine the tip-electrode capacitance as a function of tip-surface distance by analysing the second harmonic of the CFM signal and then determine the charge by a fit of the CFM model to the tip-surface distance curve of the first harmonic of the CFM signal $V_{\text{Bias}}{}^{\text{min}}$. We demonstrate the practicability and precision of the method by results from experiments measuring the charge of a nanoscale gold cluster on a CeO$_2$(111) surface. Figure (a) shows a CFM survey measurement showing the distribution of many clusters on the surface by their CFM contrast. Figure (b) is a plot of the CFM signal $V_{\text{Bias}}{}^{\text{min}}$ as a function of the tip-surface distance (z_{tip}) for one set of measurements. Each set includes the variation of the oscillation amplitude A in a systematic ascending and descending order and the processing of the measured force-distance curves with the FCA method. Dashed curves are model fits well representing experimental data. The reliability of such analysis is demonstrated by discussing the influence of surrounding charges on the result as evident in the measurement, the reproducibility of results and by a statistical error analysis.



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Charging Single Metal Nanoparticles on a Thin Al_2O_3 Film by the AFM Tip

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Charges on oxide supported metal nanoparticles (NP) are of general interest due to their impact on the electronic/electrostatic properties of the NP and their interaction with defects of the underlying oxide support and with other nearby NPs. Whereas the first aspect is of general importance in catalysis, the second one is of particular interest in nanoelectronics because a detailed analysis of the charge interaction with the oxide and with other nearby nano-objects can explain phenomena that are related to leakage currents and device characteristics and performance.

It is shown that by using room temperature noncontact AFM (nc-AFM) and Kelvin probe force microscopy (KPFM) in ultra-high vacuum (UHV), a ~ 5 nm small, alumina supported AuNP can be directly charged by the AFM tip (see Figure 1). Due to Coulomb blockades, the NP charging appears in the form of large and discrete peaks in detuning (Δf) versus bias voltage curves. Finite element method (FEM) calculation reveal that the large peaks can only be observed when the insulated NPs in the vicinity of the main NP adjust accordingly their electrostatic potentials as soon as the main NP gets charged. In view of the relatively high number of transferred electrons into the NP, we anticipate that during the charging, the electrons are immediately transferred from the NP to the interface formed with the ALD grown alumina or into alumina subsurface regions directly underneath.

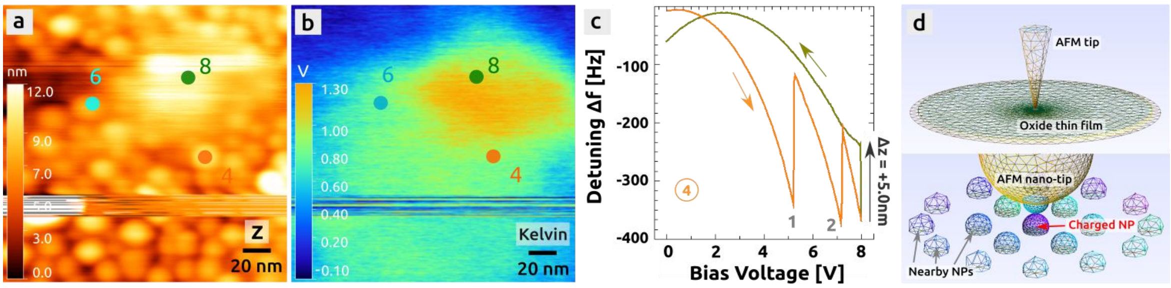

Figure 1: Charge manipulation experiments conducted at single AuNPs supported on a ALD grown, 40 nm thick Al_2O_3 film on Si(001). (a,b) Topography (a) and CPD image (b) after the charging of NPs 4, 6 and 8. Detuning (Δf) vs voltage curve obtained during the charging of NP 4. Three-dimensional tip-NP model for the FEM setup. From Ref. [1].

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Reactivity of FeO_x-based single-atom catalysts: Role of the support, metastable configurations, and electronic structures

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Single-atom catalysts are often supported by cheap oxides, such as iron oxides. As a model system [1,2], magnetite (Fe_3O_4), specifically its (001) [3] facet has been used because it offers stable sites for the adsorption of single atoms of catalytic active metals up to high temperatures [4,5]. The support affects single-atom stability and properties. Fe vacancies in the subsurface of the reconstructed Fe_3O_4(001) unit cell can allow single metal atoms to incorporate into the surface layer. As a result, metal atoms can often be accommodated in a more favorable configuration than if they were simply adsorbing on the surface. Changes in their atomic environments strongly affect their electronic structures [6], with drastic consequences for catalysis. Changes in the support can affect not only ground states but also reaction mechanisms and activation barriers. I will show how single Pt atoms become mobile upon CO adsorption, forming dimers, which oxidize CO via a Mars van Krevelen reaction using a surface oxygen atom [7]. The support is temporarily altered, reducing overall activation barriers and permitting CO oxidation otherwise inaccessible at the observed experimental temperatures. While the surface has a dynamic behavior, the initially observed Pt dimers also don't remain static. As a result of the metastability [8] of Pt dimers at higher temperatures, the overall reaction path is drastically altered.

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Assembly and reactions of porphyrins on iron oxide thin film surfaces

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Tailoring the properties of molecules of the tetrapyrrole family by metalation and functionalization is potentially useful for targeting specific applications, e.g., in the fields of catalysis, sensing, optoelectronics, and magnetism. To this end, on-surface preparation strategies, mostly carried out on metal surfaces, for variously functionalized porphyrins and phthalocyanines have been developed, that provided detailed insight into their hierarchical organization and allowed their structural, electronic, and chemical properties to be studied in detail [1-3]. Atomic-scale investigations into the interfacial properties of, e.g., oxide/porphyrin hybrid systems with scanning tunneling microscopy have recently emerged (e.g., porphyrins on $TiO_2(110)$ [4] or Co(100) [5]). Iron oxides are particularly interesting because of their magnetic properties. Fe_3O_4, which has a high Curie temperature and is a half-metal at room temperature, has potential to be used in spintronic devices. Moreover, it has been shown that also ultrathin FeO(111) films display ferromagnetic behavior [6].

In this contribution, we will present recent scanning tunneling microscopy results of the adsorption of porphyrins (2H-tetraphenylporphyrin, 2H-diphenylporphyrin, 2H-porphine) on ultrathin FeO(111) films on Pt(111) and Au(111), and on thick $Fe_3O_4(111)$ films. On monolayer FeO(111), due to the Moiré structure that forms with Pt(111) (and Au(111)) and the corresponding periodic work function variation, the molecules occupy specific sites depending on coverage (Fig. 1a). While in the full monolayer regime, an ordered, dense monolayer forms on top of the Moiré, the different electronic properties due to the electronic alignment of the molecules with the substrate are still visible (see Fig. 1b). On the thicker $Fe_3O_4(111)$ films, we have observed specific ordering of the molecules (Fig. 1c) and the formation of cyclodehydrogenation products after heating to elevated temperature (Fig. 1d). Finally, we will also discuss the self-metalation of the porphyrins on the iron oxide surfaces.

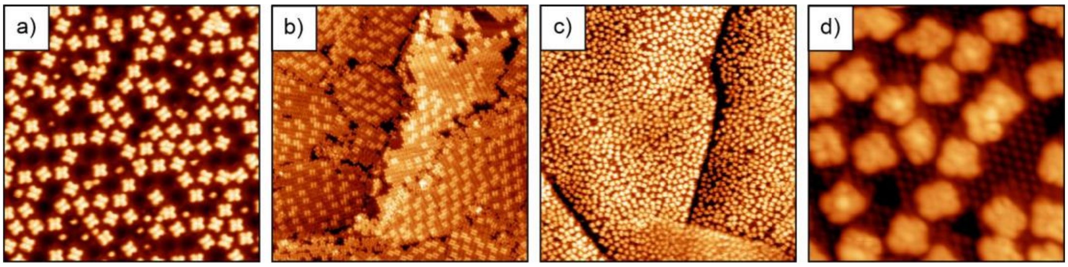

Fig. 1: STM images of 2H-TPP on (a,b) FeO(111)/Pt(111) and (c,d) $Fe_3O_4(111)$/Pt(111).

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2D Indium: Self-organization over MgO cubes

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When deposited on wide-gap oxide surfaces the metal-support interaction is rather weak which results in poor wetting and the growth of metals in a three-dimensional (3D) fashion. The interplay between surface and interface energies governs the equilibrium shapes which for sufficiently large clusters are given by Wulff-Kaishew theorem and represented by truncated polyhedron [1,2].

We have previously shown that silver on MgO smokes adopts systematically the shape of a truncated octahedron [3]. Stepped MgO surfaces or contact lines between stacked crystallites were shown to completely dominate the nucleation behavior of silver providing conditions for its growth close to the equilibrium. (100)Ag//(100)MgO epitaxy was evidenced and the Ag(110) facet identified for the first time in case of supported silver particles.

In the present study we report on the site-specific growth of metallic indium on MgO smoke. We combined TEM experiments and atomistic simulations to analyze the indium adsorption/ adhesion on MgO surfaces of different orientations. In contrast to Ag, indium shows a strong tendency to selectively wet MgO surfaces in form of uniformly organized 2D layers. On small MgO cubes In was observed only in corners whereas the edges of larger cubes provide enough space to additionally accommodate uniformly and almost equidistantly distributed indium layers (Figure (a)). These observations are in line with theory that predicts strong adhesion energy for In on (110) and (111) MgO surfaces. On the contrary, no indium was observed on (100) MgO surface for which also the calculated adhesion energy was weak. According to STEM and corresponding EDX mapping (Figures (b), (c) and (d)), the layers of higher z-contrast are indium rich while the oxidized form is ruled out. Generally shown to precede the adhesion of In to an oxide support, the formation of In_2O_3 cannot be, however, unambiguously excluded – at least in the interface layer. The corresponding studies are still in progress.

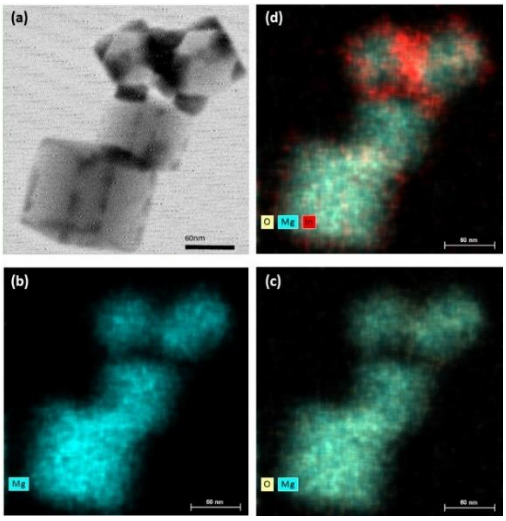

Figure: (a) STEM image and corresponding EDX mapping for Mg (b), MgO (c) and MgOIn (d), showing that the layers of higher z-contrast are indium rich. The image in (a) also shows the indium distribution over MgO cubes as a function of their size.

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First-Principles Modeling and High-Throughput Screening of Piezo-Photocatalytic Materials for Green Hydrogen Production

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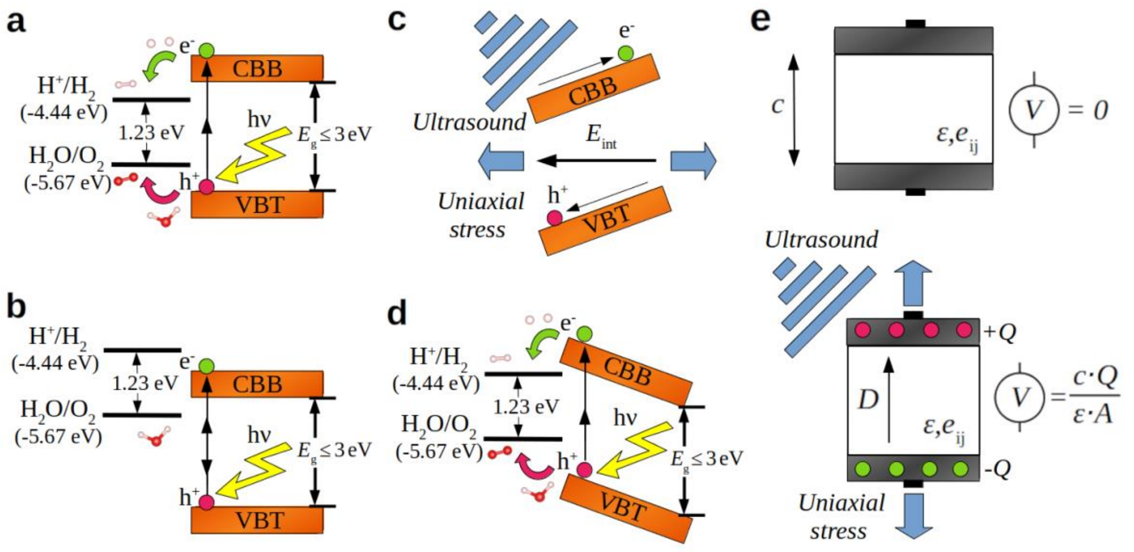
Photocatalytic materials are pivotal for the implementation of disruptive clean energy applications like the generation of hydrogen from water-splitting under sunlight. However, efficient and cost-effective materials able to catalyse the chemical reactions of interest when exposed to visible light are scarce due to the stringent electronic conditions that they must satisfy. Chemical and nanostructuring experimental approaches are capable of improving the catalytic performance of known photoactive compounds, however, the variability of the as-synthesised nanomaterials and the sophistication of the employed synthesis methods make systematic design of photocatalysts difficult. Here, we present the results of recent computational first-principles studies on semiconductor materials that have the potential to improve the rational engineering of piezo-photocatalysts for green hydrogen production. First, we theoretically show how the application of uniaxial stress (or, equivalently, ultrasound) in the archetypal bulk piezoelectric $BaTiO_3$ can modify its optoelectronic and catalytic properties in a significant and predictable manner [1]; analogous computational results are also show for transition metal dichalcogenide monolayers [2]. And second, we present a high-throughput screening of piezo-photocatalytic materials performed over ~1,000 polar compounds that relies on a simple electrostatic model and first-principles calculations [3]. Interestingly, a number of previously overlooked binary and tertiary piezo-photocatalysts emerge as very promising from our computational screening owing to their superb optoelectronic and band-alignment tunability under applied strain.



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Raman activity in anatase TiO_2 (nano)materials : an *ab initio* investigations of surface and size effects

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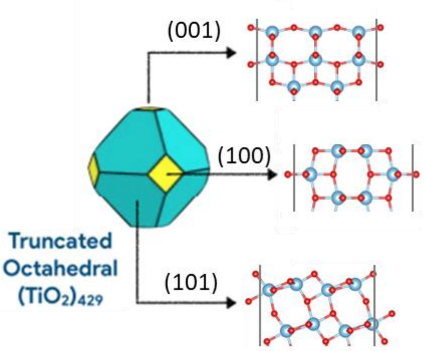
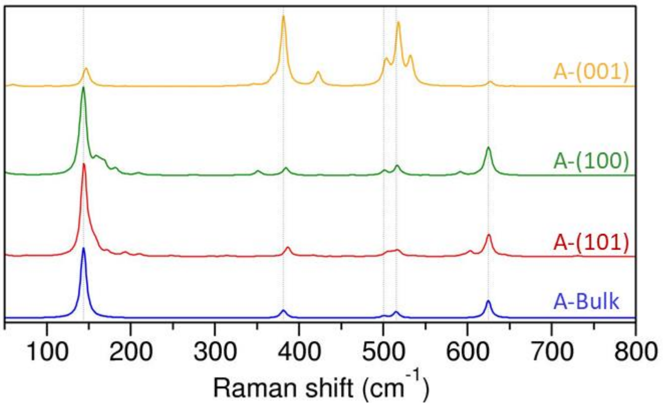
Nanosized titanium dioxide (TiO_2) materials are widely used in various technological devices as well as everyday products, including drugs and food additives. However, their properties and applications depend on their size and surface [1], as they can be extremely reactive in contact with the environment. It was found that crystalline TiO_2 nanoparticles prefer the anatase structure for diameters up to about 10-14 nm and above this size they crystallize in a rutile structure. Therefore, it is crucial to characterize the surface structure and understand its implications on the properties of nanomaterials. In this regard, Raman spectroscopy has proven to be a powerful and non-destructive tool for materials characterization and has been widely used in the field of nanomaterials [2-3]. Yet, many of structure-property relations of TiO_2 nanomaterials are based mostly on the experimental peak assignment and still not fully understood.

In our work we address this gap by performing *ab initio* investigations of the Raman response for a set of TiO_2 anatase-based models, selected to identify the main features present in the Raman spectra. The TiO_2 nanoparticles are modeled as a set of anatase-based surfaces with (101), (100) and (001) terminations. The state-of-the-art density functional theory, as implemented in the CRYSTAL17 code, is used to calculate vibrational modes and Raman spectra for the selected surfaces. We provide an assignment of the most intense peaks in the calculated spectra and identify the vibrating atoms. This allowed us to distinguish between surface and bulk vibrations and to assess the sensitivity of Raman spectra to the surface termination. To address the size-dependency of the Raman response, we analyzed the relationship between peak position/intensity and the slab thickness. Our results show that *ab initio* calculations are powerful tools to assign Raman signals origin, with potential use to predict how different structural features may affect the observed spectra.

Acknowledgements: funding for project from the EU H2020 R&I programme CHARISMA 952921 and Nanoinformatix 814426





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POSTERS

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16. **Verónica M. Sánchez**
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Femtosecond laser-induced transformations on thin-films of 2D Transition-Metal Dichalcogenides

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In this work we study the transforming effect, both compositional and morphological, of ultrashort laser pulses on thin films of 2D materials. The objective, besides studying the laser-matter interaction in 2D materials, is to demonstrate the versatility of laser irradiation as a post-synthesis process to improve or locally change the thin-film properties. Specifically, we study the transformation of a WTe_2 thin films fabricated by a mixed synthesis process of chemical nucleation and vapor phase transformation, forming randomly oriented 2D out-of-plane flakes over a silicon substrate [1]. Both pre- and post-irradiated thin films have been characterized by various techniques.

Irradiating at 1030-nm wavelength a decomposition of WTe_2 is observed. It is evidenced by a greater presence of crystalline Te and the appearance of a higher concentration of WO_3 in the resulting films. Morphologically the formation of periodic structures interestingly occurs. This structuring confers an anisotropy in the optical and electrical properties that can be beneficial for the applications. However, a drawback is a fusion-resolidification process that tend to eliminate the originally 2D out-of-plane flakes for the tested conditions. On the other side, by irradiating at 258-nm wavelength, a very different transformation is produced. From the morphological point of view, the film undergoes nano-pores formation because of a possible selective ablation process. Micro-Raman spectroscopy confirms the permanence of WTe_2, the partial removal or amorphization processes of Te and the disappearance of WO_3.
Finally, resistivity tuning (values and induced anisotropies) has been produced by ultraprecise selective thinning using direct femtosecond laser writing. This post-synthesis process demonstrates that resistivity can be tuned by changing the laser parameters (pulse energy, line width, line separation, etc.) keeping the material characteristics (as shown by EDX compositional maps).

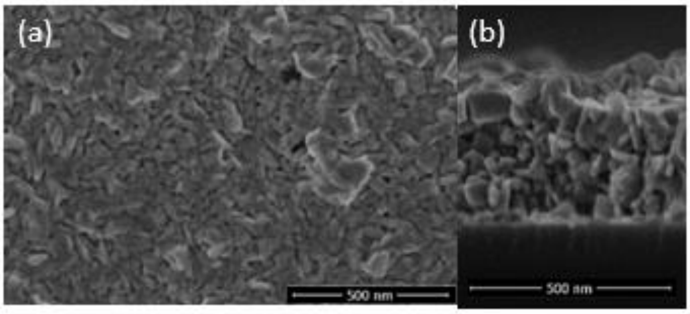

Figure 1. SEM micrograph from the surface of WTe2 (a) and a cross-section (b).

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Enhanced Methanol Production over a Cu/MgO Catalyst: the key role of Cu^+ species and water-enabled conversion

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CO_2 is a harmful but critical greenhouse gas and, as such, improved catalysts for its conversion into other useful carbon forms are ever-increasingly pursued.[1] The CO_2 hydrogenation reaction is interesting because, in addition to the removal of CO_2, it can produce methanol, which is useful both as a fuel and as a chemical building block to synthesize many products.[2] Cu-doped and Cu-supported catalysts on non-redox metal oxides (SiO_2, MgO, Al_2O_3) show some but insufficient activity for this reaction, which can be improved adding promoters.[3] Layered double hydroxides of a hydrotalcite-like structure (HT), $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{z+}\cdot[A_{z/n}{}^{n-}\cdot mH_2O]^{z-}$, are precursors of oxides that favor well dispersed metal species, and some have already shown interesting catalytic activity for this reaction as well.[4] In this work, a Cu/MgO model is used to represent a non-promoted copper-based and HT-derived mixed oxide catalyst for the CO_2 hydrogenation to methanol, and its catalytic activity is studied at the DFT level and compared to experimental results. Firstly, a computational model is built and tested to provide the key features needed to be representative of the system experimentally employed in a previous work.[5] Then, the study of the reaction mechanism is explored i) assuming that hydrogen dissociation and spillover occurs primarily at existing Cu NPs and ii) following the stabilization of an experimentally-observed and key monodentate formate species (that occurs primarily at Cu^+ single-atom sites). The results indicate that the latter is stable because the surface is hydroxylated, which is typical for this type of catalysts. Furthermore, these water/hydroxyl species are the ones that participate in the easy formation and reaction of such formates, as well as make the pathway from formate to methanol highly selective.

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Significant reducibility of ultrathin atomic layer deposited ceria towards H_2 exposure at room temperature

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In the last decades, atomic layer deposition (ALD) has gained prominence in the materials and surface science communities owing to its high potential for integration as a scalable process in microelectronics. ALD's largest strengths are its well-controlled layer-by-layer deposition and growth conformity on 3D structures [1]. Yet, the ALD technique is also well known to lead to amorphous and defective, non-stoichiometric thin films, resulting in modified materials properties that may even preferentially be used in certain applications. Interestingly, initial in situ X-ray photoemission spectroscopy (XPS) measurements of ceria ALD-deposits on Al_2O_3/Si, sapphire, and SiO_2 substrates confirm a Ce^{3+}/Ce^{4+} mixture dependent on the substrate interaction, deposit thickness, and morphology. Using near-ambient pressure XPS, we have significantly reduced ultrathin (< 10 nm) ceria films deposited by ALD by exposing them to different H_2/O_2 partial pressures at significantly lower temperatures (300 – 525 K) than thicker films grown by physical vapor deposition techniques [2]. Notably, the total amount of reduction to Ce^{3+} is found to depend on the deposit thickness and initial ceria/substrate interaction. Furthermore, the intrinsic defects related to the ALD method seem to play a critical role in the reversible reduction at room temperature.

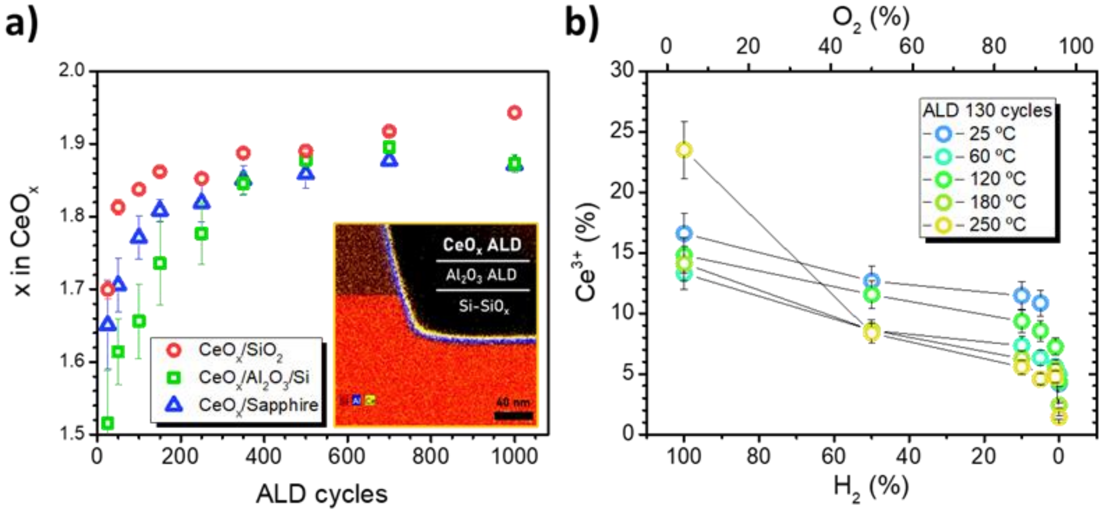

Figure a) Ce^{3+}/Ce^{4+} ratio as a function of the total number of ALD cycles and substrate; insert, transmission electron microscopy (TEM) cross-section image of the ALD-ceria ultrathin deposit. Figure b) percentage of Ce^{3+} states as a function of H_2/O_2 mixture for different sample temperatures

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An experimental and theoretical study of spinel oxides for photocatalysis

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Spinel oxides have been identified as potential photocatalysts for reactions such as water splitting. Their general formula, AB_2O_4, can also be written as $(A_{1-x}B_x)[B_{2-x}A_x]O_4$ where () represents the tetrahedral sites, [] represents the octahedral sites, and x is the degree of inversion ($0 \leq x \leq 1$). The degree of inversion can be used as a tuning parameter to control the electronic and therefore photocatalytic properties of spinels. A combination of density functional theory (DFT) calculations and experimental techniques have been used to study various transition metal spinel oxides. Powder samples of $ZnFe_{1-\gamma}Ga_{\gamma}O_4$ (γ = 0, 0.5, 1) showed catalytic activity for the oxygen evolution reaction (OER). DFT simulations demonstrated suitable band gaps and alignments for OER. Further calculations showed that thermal treatment of these spinels could be used to influence their inversion degree, and potentially to engineer and improve their behaviour in photocatalysis.

Redox Behavior of the Inverse Ceria/Cu(111) Catalyst Characterized by LEED, STM, nc-AFM and KPFM

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The inverse catalyst *cerium oxide (ceria) on copper* has attracted much interest in recent time because of its promising catalytic activity in the water-gas-shift reaction and in the methanol production through CO_2 hydrogenation. For such reactions it is important to know the redox behavior of the catalyst, in particular in view of the reduction by H_2.

We comment on the redox behavior of ceria nanoparticles (NP) and the underlying Cu(111) support after several redox cycles of high-temperature O_2 and H_2 anneals. In particular the surface morphology, atomic structure and composition are characterized after each redox step by low energy electron diffraction (LEED), scanning tunnelling microscopy (STM), non-contact atomic force microscopy (nc-AFM) and Kelvin probe force microscopy (KPFM) [1].

We show that whenever the ceria-copper system is reduced, the ceria NPs and the Cu(111) support can be fully re-oxidized during an anneal at 550 °C in O_2, with the copper oxide partially exhibiting a new oxide structure as verified by LEED and STM (Figure 1a and b). In turn, the copper support can always be entirely reduced during a kilo Langmuir strong H_2 anneal at 550 °C. However, after such a reduction step, the ceria NPs stay close to their almost fully oxidized state of CeO_2.

Apart from the surface morphology, atomic structure and composition and involved redox mechanisms, we also discuss phenomena of local work function (WF) changes (Figure 1c) that appear after a redox step has been done. Furthermore, we also briefly discuss a possible alloying between cerium and copper during a reduction step and compare it with the ceria-platinum catalyst.

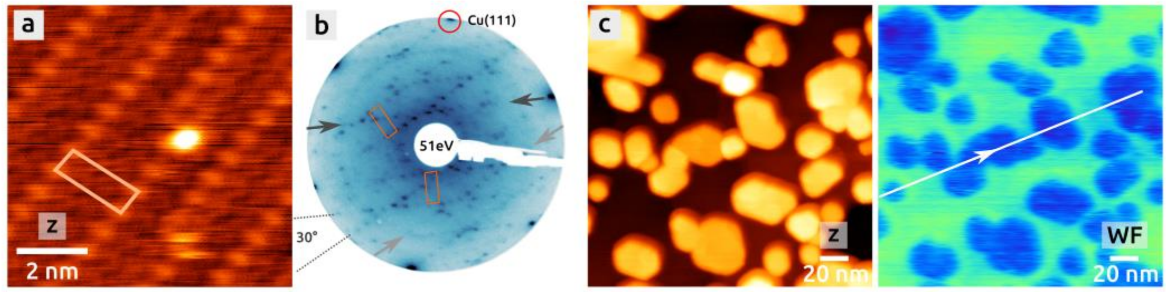

Figure 1: The ceria/Cu(111) surface after a 1.3 kL long O_2 oxidation at 550°C (a,b) and after a 54 kL long H_2 reduction at 550°C (c). (a) The new surface oxide imaged by STM with the size and shape of the unit cell (light orange parallelogram), (b) The corresponding LEED with same unit cell (orange), (c) Topography (Z) and WF image obtained in a KPFM measurement, showing strong WF variations after a reduction step. From Ref. [1].

Tuning the energy of monochromatic molecular beams to overcome high activation barriers in gas-surface studies

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Catalysts are expected to be instrumental to accelerate the energy transition from a fossil-fuel-based society to one that is based on renewable carbon resources. One of the main challenges is to find ways to activate/dissociate the two major greenhouse gases (CO_2 and CH_4) in order to convert them into harmless products. Several promising routes have been found recently. For instance, combined near ambient pressure XPS and DFT studies have shown that low-coverage Ni-CeO_2(111) is a highly efficient catalyst for methane activation [1]. Moreover, direct conversion of methane to methanol was observed adding water as reactant [2]. The complexity of these reactions and the high barriers involved in CH_4 and CO_2 dissociation at surfaces demand the development of alternative experimental tools.

The combination of X-ray photoemission spectroscopy (XPS) with molecular beams (MB) is well suited for such studies. A MB is a collimated stream of gas formed by a supersonic expansion from a high source pressure (up to 150 bar). This process leads to a downstream beam of well-defined translational energy, with a very narrow energy distribution (10-30%). Nowadays it is possible to produce monochromatic, supersonic beams of a variety of reactive molecules, such as CH_4, CO_2, H_2O, and H_2, with fine-tuning of their various degrees of freedom (average velocity, rotational and vibrational energies) [3]. Energies beyond 1 eV are readily obtained, using CO_2 beams experiments performed at energies up to 2 eV have been recently reported [4]. We will summarize results obtained in our group using H_2 and CH_4 MB, where the high quality of the MB allows observing diffraction features from solid surfaces [5,6], and more recent results obtained with O_2 beams with incident energies up to ca. 1 eV to study in detail the oxidation of Cu(111).

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Sol-Gel synthesis of Se-doped Ta_2O_5 porous films for photocatalytic applications

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Due to its higher conduction band, Ta_2O_5 constitutes an attractive alternative to TiO_2 during photocatalytic and photoelectrochemical processing [1]. This can favor the formation of additional radical species that contribute to improving the efficiency towards the degradation of organic pollutants [2], improve the kinetics of reduction reactions during the water splitting process [1], etc. In the present study, Se-doped Ta_2O_5 porous thin films have been synthesized by the Sol-Gel method and characterized. The obtained thin films have been subjected to either a thermal annealing or a plasma annealing process. It has been observed that by changing the concentration of precursors and the annealing process, the morphology and pore size, as well as the crystallinity and band gap can be modified. The porous nature of the surface will favor the efficiency of the photocatalyst due to a higher specific surface area.

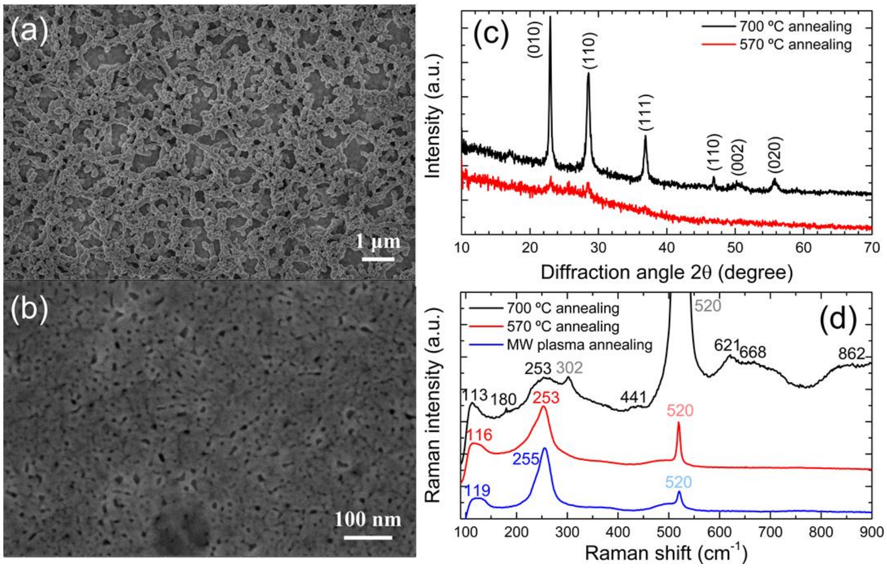

Figure 1. SEM images of porous Se-doped Ta_2O_5 films prepared by using (a) 0.1 M $TaCl_5$ and 0.2 M $SeCl_4$ precursors, and (b) 0.025 M $TaCl_5$ and 0.1 M $SeCl_4$ precursors. (c) X-ray diffraction pattern and (d) Raman spectra of Se-doped Ta_2O_5 after different annealing processes for films prepared by using 0.1 M $TaCl_5$ and 0.2 M $SeCl_4$ precursors.

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Transition from 3D to 2D buckled metal clusters on α-Al_2O_3(0001)

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The crystallography of interfaces plays a crucial role in the formation of supported nanoparticles, affecting their growth, energetics, adhesion on supports, morphology, and related properties. Metal/α-Al_2O_3(0001) systems are of considerable interest due to their countless applications in catalysis, microelectronics, and functional coatings. However, the determination of the interface structure remains an ongoing challenge, prompting a wealth of atomistic simulations. In this context, the geometry of Ag nanoparticles will be experimentally determined using extended x-ray absorption fine structure (EXAFS) to explore local environments and confronted to atomistic simulations.

The EXAFS spectra were analysed using ATHENA/ARTEMIS codes and Fourier Transforms, and calculations regarding the α-Al_2O_3(0001) sites were performed within the framework of a DFT approach. The average Ag-Ag (d_{Ag-Ag}) and Ag-O (d_{Ag-O}) interatomic distances and coordination numbers have been determined as a function of the cluster size. As the cluster size decreases, there is a simultaneous reduction in both d_{Ag-Ag} and coordination number providing unambiguous fingerprints for the dimensionality of the Ag clusters. Size-dependent interface structures are also evidenced. At low coverage, silver atoms sit on surface Al sites to form buckled 1 ML-thick islands associated with Ag-Ag distances (2.75 Å) which fit the alumina lattice. Upon increasing Ag coverage, as 3D clusters appear, interface Ag atoms tend to leave Al sites to sit atop oxygen atoms while the d_{Ag-Ag} distance increases. These structural transformations from 2D Ag islands to macroscopic 3D clusters are accompanied by changes in adhesion energy of Ag/α-Al_2O_3(0001).

Infrared Absorption of Metal-Oxide Photocatalysts Excited under Water: Operando Spectroscopy with an ATR Prism

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Chemical conversion of materials is completed in milliseconds or seconds by assembling atoms over metal-oxide photocatalysts. Bandgap-excited electrons and holes reactive on this time scale are important for efficient atom assembly to yield the desired products. In this study, attenuated total reflection (ATR) of infrared (IR) light was applied to characterize the electronic absorption of long-life charge carriers excited in $NaTaO_3$ and TiO_2 photocatalysts under liquid, particularly water. This was a difficult task since water absorbs IR light for probing, while excitation light is absorbed by photocatalyst particles. An ATR assembly with a diamond prism is key for guiding the excitation light to the volume probed by IR light. Photocatalyst nanoparticles were placed on the prism, covered with liquid, and irradiated by steady UV light of LED through the prism (Figure 1).

Electrons excited in rutile particles formed small polarons characterized by a symmetric absorption band spread over 10000–700 cm^{-1} with a maximum at 6000 cm^{-1}. Electrons in anatase particles created large polarons and produced an asymmetric absorption band that gradually strengthened at wavenumbers below 5000 cm^{-1} and sharply weakened at 1000 cm^{-1}. UV-light power dependence of the absorption bands was observed in N_2-exposed decane liquid to deduce electron–hole recombination kinetics. With light power density P greater than 200 W m^{-2} (rutile) and 2000 W m^{-2} (anatase), the polaron absorptions were enhanced with absorbance being proportional to $P^{1/2}$. The observed 1/2-order power law suggested recombination of multiple electrons and holes randomly moving in each particle. Upon excitation with smaller P, the power-law order increased to unity. The unity-order power law was interpreted with recombination of an electron and a hole that were excited by the same photon. Further, an average lifetime of 1 ms was estimated with electron polarons in TIO-6 when weakly excited at $P = 20$ W m^{-2} to simulate solar-light irradiation [1].

$NaTaO_3$ particles doped with Sr or La cations presented an asymmetric absorption band with a maximum at 1400 cm^{-1}, which was enhanced by the addition of hole scavengers and disappeared in the presence of electron scavengers. This absorption was compared with the absorption in anatase, and it was suggested that excited electrons were accommodated as large polarons in $NaTaO_3$ efficient for artificial photosynthesis [2].

The ATR-based method demonstrated here is applicable to a broad range of photocatalysts functional under liquid.

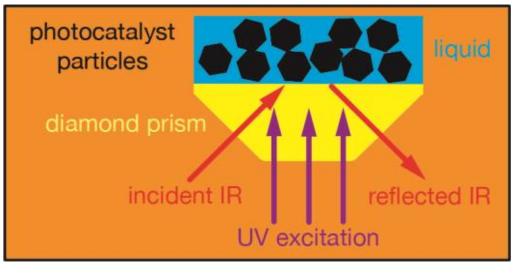

Figure 1. An ATR assembly for operando IR spectroscopy.

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Revealing defects on anatase TiO_2 (101) - a competitive study with non-contact atomic force microscopy and scanning tunneling microscopy

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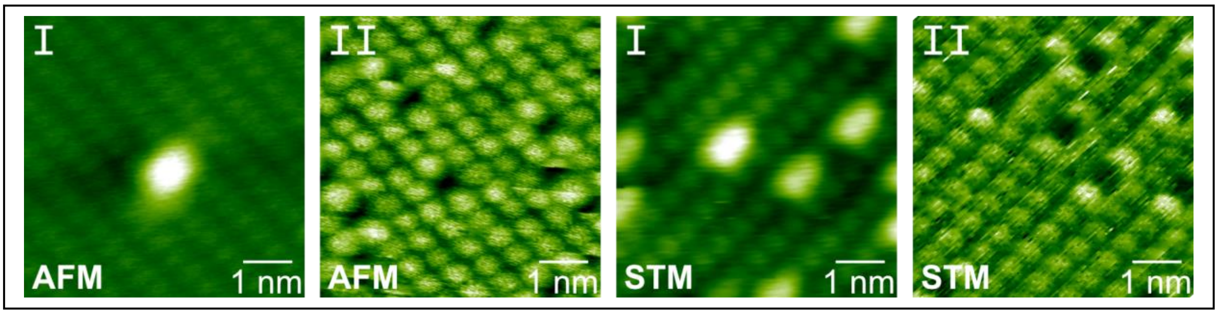
In this study, we have conducted a comparison of the atomic structure of the (101) surface of anatase using non-contact atomic force microscopy (NC-AFM) and scanning tunneling microscopy (STM). Anatase crystals, whether natural or synthetic, often exhibit surface and subsurface defects, but identifying them using scanning probe microscopy (SPM) can be challenging. During NC-AFM and STM measurements, we frequently observed changes in contrast resulting from different tip terminations that develop after scanning over surface defects or step edges of islands. As a result, we have introduced two imaging modes for NC-AFM and STM topography images that can be distinguished by the position of the surface defects. In contrast (I), the irregularities are imaged as protrusions and appear as bright spots between the atomic rows. In contrast (II), the irregularities are imaged as being directly on top of the atomic rows. Using these imaging modes, we were able to identify and distinguish between various types of surface and subsurface defects on the anatase (101) surface. Our results show that NC-AFM and STM can provide complementary information about the atomic structure of materials, and that the combination of these two techniques can greatly enhance our understanding of surface and subsurface defects. Furthermore, the imaging modes introduced in this study can be useful for characterizing other materials with surface defects and could lead to the development of new techniques for identifying and analyzing such defects.



Atomic-Level Understanding of Metal Promotion in In_2O_3-catalyzed CO_2 Hydrogenation

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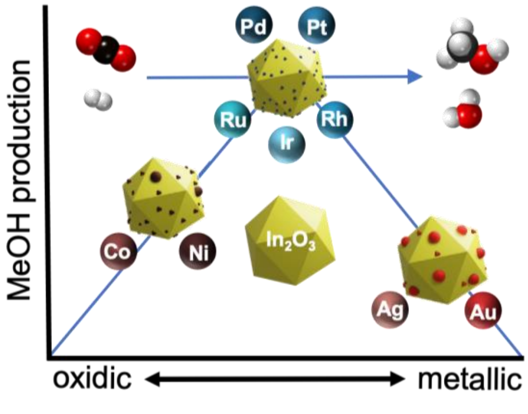
Methanol is a versatile energy carrier and a key chemical platform. Therefore, its production via thermocatalytic hydrogenation of CO_2 with green hydrogen is envisaged to play a crucial role in tackling climate change. In this scenario, In_2O_3 was identified as a highly selective catalyst and several metal dopants were explored to enhance its performance. However, the rationalization of the promotional effects and the design of an optimal system are hindered by the lack of systematic catalyst preparation. Herein, we used flame spray pyrolysis (FSP) as a standardized synthetic method to introduce nine different metal promoters into indium oxide. Detailed experimental characterization and density functional theory simulations show that the speciation of metal dopants leads to different catalyst architectures dictating the degree of promotion [1]. Pd, Pt, Rh, Ru, and Ir are atomically-dispersed on the In_2O_3 surface surpassing the methanol activity and selectivity of the undoped metal oxide. These dopants hinder the undesired CO formation and foster hydrogen activation. Co and Ni form large oxidic and alloy-containing clusters, respectively, leading to a non-significant improvement in catalytic performance. Finally, Ag and Au sinter into metallic nanoparticles and they do not show any promotional effect. This study elucidates that the metal dopant speciation at the atomic-level of detail is paramount to rationalise In_2O_3 promotion and the FSP potential to synthesize intricate catalytic systems that can be employed in energy transformations.



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Dynamic redox-coupling of ceria-based Single-Atom Catalysts

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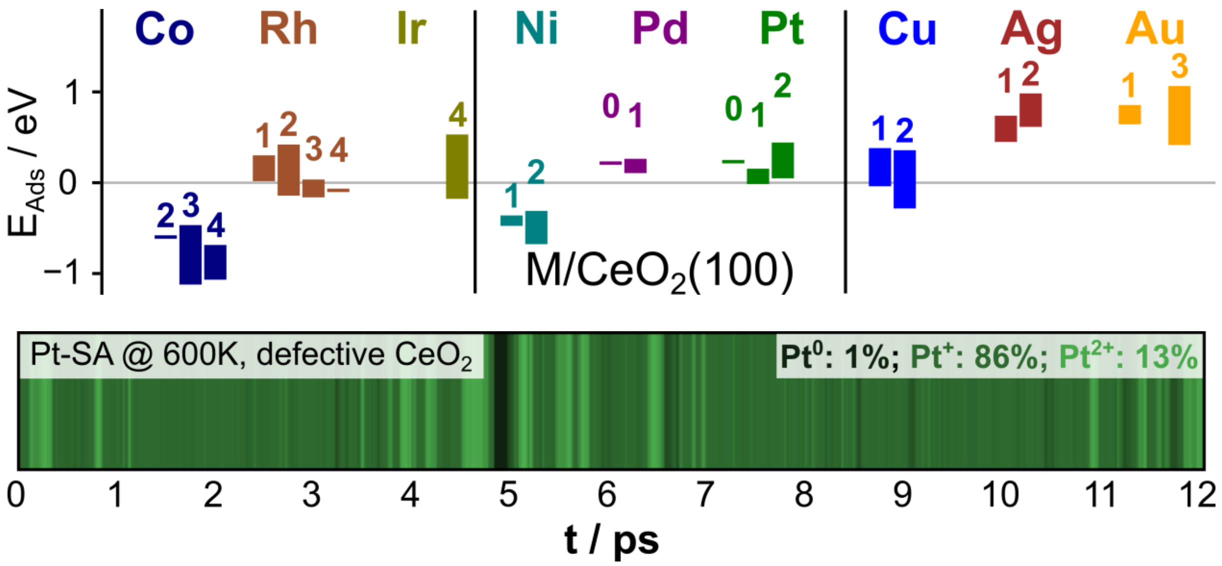
Single-Atom Catalysts (SACs) have emerged as a new frontier in catalysis providing the best noble metal utilization. Atomic dispersion renders the systems highly fluctuous, however, experimental techniques often provide spatial and temporal averages, making full characterization challenging. Reducible oxide supports like ceria further allow for a strong redox coupling with the metal and can facilitate electron-transfer between both [1]. In our work, we discovered the high prevalence of metal oxidation state (mOS) dynamics for a variety of ceria-based SACs [2], making the common assignment of a fixed oxidation state a too simplistic approximation. We employed data-driven techniques to rationalize charge transfer processes at the metal/oxide interface using fundamental physical descriptors. Lastly, we explored the influence of intrinsic support vacancies and local polaron structure on the dynamic behaviour, showing that surface reduction is a viable route for the stabilization of unusual metal charge states [3].



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Oxygen chemistry of halogen-doped CeO_2(111)

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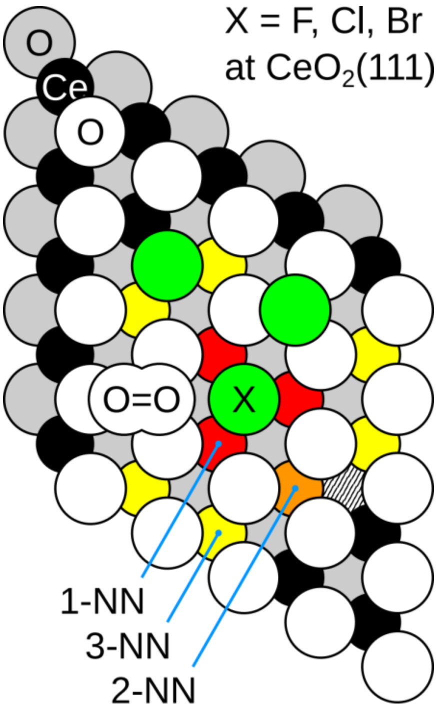
One of the ways in which the catalytic activity or selectivity of a metal oxide can be modified is via doping, which can be either intentional or unintentional [1]. Historically, research on the effects of dopants in CeO_2 has focused primarily on metal cations, but in recent years, the potential relevance of halogen dopants has been increasingly recognised [2,3].



Halogen-doped CeO_2(111), and the additional species considered in this study: Ce^{3+} ions at different locations; a sub-surface oxygen vacancy; an adsorbed O_2 molecule; and an adsorbed halogen atom.

With this in mind, we carried out density functional theory (DFT) calculations of F, Cl and Br species at CeO_2(111), focusing on their influence on elementary reactions related to the surface oxygen chemistry [4]. Specifically, we considered the effects of substitutional halogen dopants on **1.** O vacancy formation, **2.** Molecular O_2 adsorption and **3.** 'Surface re-oxidation' i.e. the displacement of a halide ion on to the surface by ½O_2.

While the effects of halogen dopants on O vacancy formation are marginal, they are more marked for O_2 adsorption, due to electron transfer from the Ce^{3+} ion associated with the halogen dopants, which results in an adsorbed superoxide (O_2^-) molecule. Most significantly, we find that the energy change involved in the 're-oxidation' of the surface depends strongly not only on the identity of the halogen, but also on whether or not a second halogen impurity, with its associated Ce^{3+} ion, is present; if it is, then the process is greatly facilitated, permitting low-energy surface oxygen exchange without requiring the formation and healing of oxygen vacancies.

Overall, our results demonstrate the existence of a rich variety of ways in which the oxygen chemistry of CeO_2(111) may be modified by the presence of halogen dopants.

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Origin of the Hydrophobic Behaviour of Hydrophilic CeO_2

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The hydrophobic nature of rare-earth oxides is intriguing. One example is the CeO_2(100) surface which, despite its strongly hydrophilic nature, has experimentally been demonstrated to exhibit hydrophobic behaviour when immersed in water [1, 2].

In order to understand this puzzling and counter-intuitive effect we performed a detailed analysis of the structure and dynamics of a water film "on top of" a ceria(100) surface. This was done by way of an ab-initio molecular dynamics (AIMD) simulation of a 3D slab model of a water film confined between two ceria surfaces. The simulation demonstrates that the first water layer, in immediate contact with the hydroxylated CeO_2 surface, is responsible for the effect and behaves as a hydrophobic interface with respect to the liquid water fiilm "above it" [3].

We find that hydrophobicity is manifested in several ways, namely by **...**

... A considerable **diffusion enhancement** of the confined liquid water as compared with bulk water at the same thermodynamic condition.

... **Weak adhesion** energy of the water film on the hydroxylated ceria surface.

... The small number of **H-bonds formed between** the hydrophobic water layer and the rest of the water film.

... The fact that the (100) surface appears to sustain a **water droplet** (additional simulations, see Fig. 1)

These findings introduce a new concept in water/rare-earth oxide interfaces: hydrophobicity mediated by specific water patterns on a hydrophilic surface.

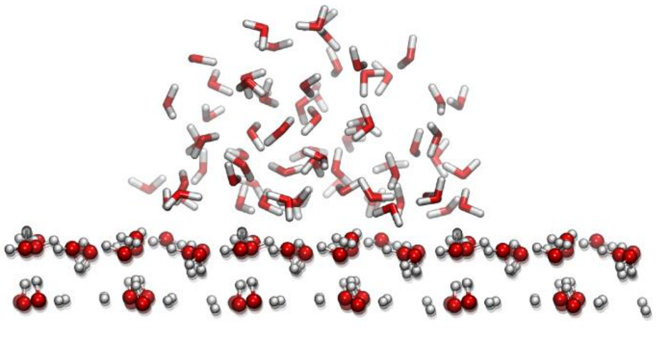

Fig. 1. AIMD simulation of a water droplet (at 310 K) on a fixed model surface of a structured water layer formed on the hydroxylated CeO2 (100) surface.

The droplet persists with a contact angle of circa 90°after 40 ps.

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Automated Real-Space Lattice Extraction and Atom Counting for Atomic Force Microscopy Images

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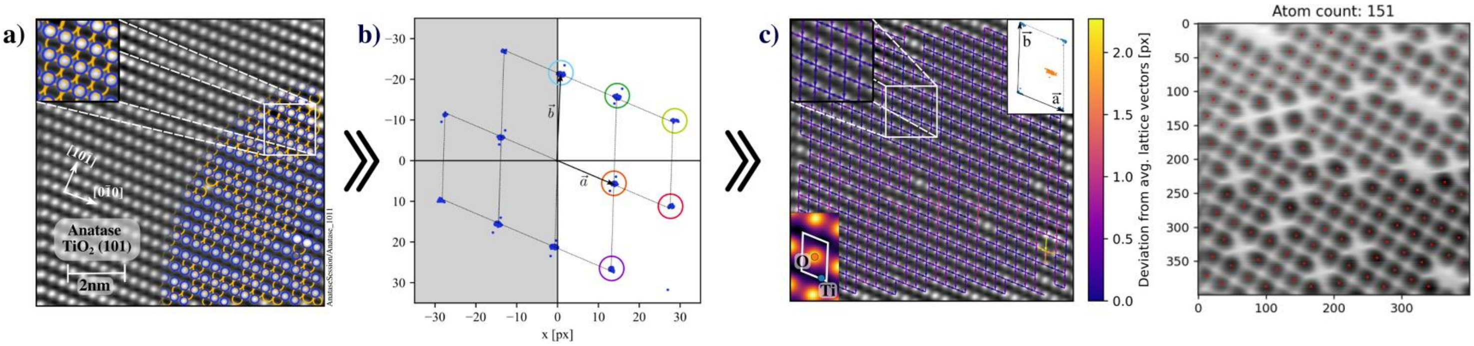
The analysis of atomically resolved images is a time-consuming process which requires solid experience and substantial human intervention. In addition, the acquired images contain a large amount of information such as crystal structure, presence and distribution of defects, and formation of domains, which need to be resolved in order to understand a material's surface structure.

We introduce the free and open source tool AiSurf [1], developed to inspect atomically resolved images via Scale-Invariant Feature Transform and Clustering Algorithms, inspired by the work of Laanait et al. [2].

AiSurf extracts primitive lattice vectors, unit cell symmetry and structural distortions from the image, with no pre-assumption on the lattice and minimal user intervention. The method is applied to a variety of AFM images for different surfaces with different levels of complexity. The code is tested against atom misclassification and artifacts, thereby faciltating the interpretation of scanning probe microscopy images. In addition, recent results on automated atom counting will be shown; this feature can be useful to estimate the feature (e.g. atoms) coverage in images. Recent developments on automated image denoising might also be shown.



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Theoretical study of Fe_3O_4 (111) and (001) surfaces and their reactivity towards H_2O_2

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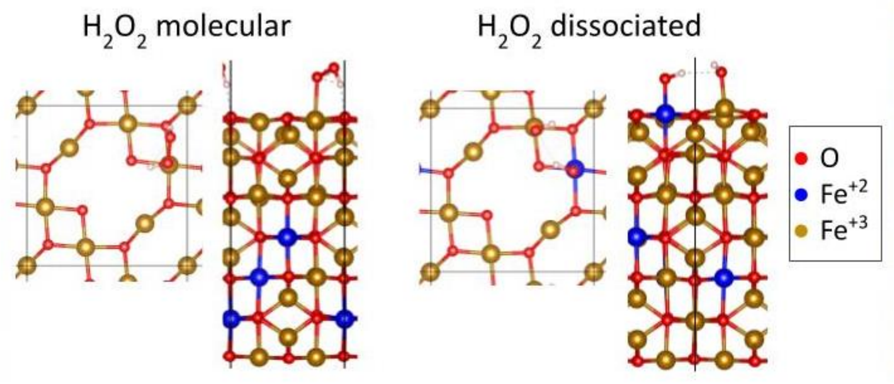
Fe_3O_4-based nanozymes are nanomaterials that have the inherent ability to mimic the catalytic activity of peroxidase-like enzymes [1]. These materials are being increasingly used for generating or scavenging reactive oxygen species through catalytic reactions for industrial or therapeutic applications. Fe_3O_4 is a mixed-valence compound that consists of both Fe^{2+} and Fe^{3+} ions which promotes the transfer of electrons between the two ions, resulting in a unique catalytic behaviour [2]. The most stable Fe_3O_4 terminations are the (111) and (001) surfaces facets [3]. In this work, density functional theory (DFT) was used to study the relative stability of the Fe_3O_4 (111) and (001) surfaces, the latter one considering the observed $(\sqrt{2}\times\sqrt{2})R45°$ surface reconstruction. H_2O and H_2O_2 adsorption on undoped and Cu-doped Fe_3O_4 (001) surfaces was rationalised in terms of the adsorption energy and the oxidation state and charge of the Cu and Fe species. Also, we determine the solvent effect on the H_2O_2 adsorption by including an implicit solvent model.



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Anisotropic iron-doping patterns and water dissociation on mixed Co-Fe oxide bi-layer nanoislands on Au(111)

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Mixed transition metal oxides (TMOs) have found wide applications in industry, e.g. as supports, electrodes, catalysts and sensors, due to their superior electronic, magnetic and/or catalytic properties.[1-3] Unlike the case in unary TMOs of which the structure/phase mainly defines the properties, it remains challenging to link the atomic-scale structures and compositions to the interesting physiochemical properties of mixed TMOs. A few key questions regarding how the heterogonous atoms and host oxides mix in various phases for nanoparticles and their coordinating interactions with external environments, e.g. atomic arrangement at the interface of TMOs and structure motifs for specific functions, are still under debate.

With a view on the properties of a class of mixed TMOs of relevance for electrocatalysis, we focus on the structure and distribution of Fe species within the Co-Fe oxides, as well as the interaction between water and the mixed oxide surface. Herein, we have synthesized a range of Co-Fe oxide bilayer nanoislands with well-defined Fe contents on Au(111) substrate. Using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) on such atomically defined Co-Fe oxides/Au(111) system, we investigate the link between Fe content in the Co-Fe oxides and the resulting atomic structure, particularly the preferential doping sites of the Fe species. Ultimately and by means of water exposure at vacuum condition, the hydroxylation behavior as a function of Fe content is studied in detail.

Our findings show that Fe dopant distribution within CoO nanoislands is highly anisotropic and affect-ed by both the moiré structure of the basal plane and the under-coordinated edge types. We further observe the moiré structure exhibits a strong template effect on the distribution of the OH groups. With the interpretation of the trend of hydroxylation as a function of Fe the content, we reveal the detailed atomistic mechanisms leading to the formation of OH in connection with the Fe species.

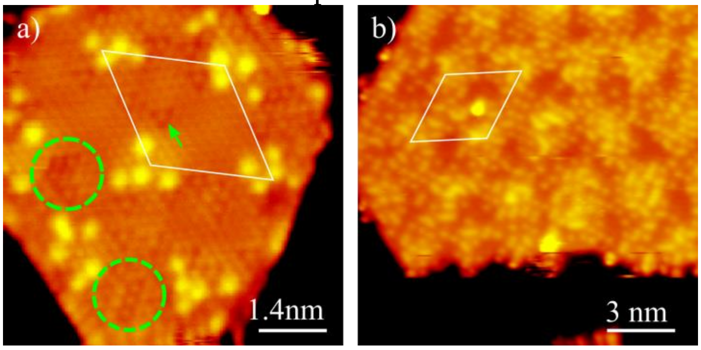

Figure 1. STM images showing distributions (a) Fe species and a small amount of OH, (b) intense OH within Co-Fe oxides. The green arrow and dashed circles indicate the single site and clusters of Fe, respectively. The white rhomb indicates the moiré unit cell.

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