O 39: Poster Session: Heterogeneous Catalysis and Surface Dynamics

Time: Tuesday 18:00–20:00 Location: P2/EG

O 39.1 Tue 18:00 P2/EG

SURMOF ZIF-67 Thin Films for Catalytic Water Oxidation Reaction — •Jimin Song, Alexei Nefedov, Stefan Heissler, Christof Wöll, and Yuemin Wang — Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344, Eggenstein-Leopoldshafen, Germany

Metal-organic frameworks emerged as promising electrocatalysts to tackle urgent energy and environmental problems. Surface-coordinated MOF thin films (SURMOFs) were grown via a liquid phase epitaxial layer-by-layer method, endowed with precisely controlled thickness, preferred growth orientation and highly-ordered surface. For the first time, high-quality crystalline ZIF-67 SURMOF thin films were fabricated and employed in water oxidation reaction (OER). The transformation from ZIF-67 to CoOOH was observed after the water oxidation reaction by applying IRRAS, Raman and XPS measurements. Meantime, the thickness of the thin film decreased from 100 nm to 20 nm. The overpotential was reduced from 468 to 375 mA/cm2 by doping with boron and nickel.

O 39.2 Tue 18:00 P2/EG

SFG microscopy of ferroelectric domains in Barium Titanate — •Dorothee Mader[1], Daniel Lourens[2], Maarten Kwaaitaal[2], Richarda Niemann[1], Sören Wasserroth[1], Sandy Gewinner[1], Marco De Pas[1], Wieland Schöllkopf[1], Martin Wolf[1], Andrei Kirilyuk[2], Sebastian Maehrlein[1], and Alexander Paarmann[1] — [1]Fritz Haber Institute of the Max Planck Society, Berlin, Germany — [2]Radboud Universiteit, Nijmegen, The Netherlands

Phonons exhibit a mostly unexplored leverage on ferroic order and its dynamics. Exploring the possibility of phonon-driven changes to the ferroelectric order provides an attractive route for potential applications of ferroelectric devices. Here, infrared-visible (IR-VIS) sumfrequency generation (SFG) microscopy with IR-sub-wavelength resolution [1] is employed combining resonant phonon excitation and ferroelectric domain imaging of barium titanate [BTO]. BTO is a noncentrosymmetric perovskite oxide with a strong ferroelectric polarization in its tetragonal phase at room temperature.Typically, BTO samples exhibit a multi-domain structure. Using the FHI Infrared (IR) free electron laser (FEL) in the range of 400-800 cm^{-1} different phonon modes of BTO are accessible. After characterization of the samples using linear optical techniques like polarization microscopy and infrared spectroscopy, the nonlinear optical properties of the ferroelectric domains are investigated using SFG-microscopy. By mapping phonon resonances in domains and domain walls, this approach may enable in-depth understanding of the underlying physics of domain formation. [1] R. Niemann et al., Appl. Phys. Lett. 120, 131102 (2022).

O 39.3 Tue 18:00 P2/EG

Investigating Heterogeneous Catalysts by Design of Experiments — •Christian Kunkel, Frederic Felsen, Sina Stocker, Christoph Scheurer, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin, Germany

Bringing new and improved heterogeneous catalysts to market can be economically and ecologically rewarding. Yet, catalyst development is tedious, as a plethora of experimental factors in synthesis, formation and operation potentially influence achievable educt conversion and/or product selectivity. In the planning phase of an investigation, such influences can often only inadequately be assessed based on literature knowledge, individual experience and chemical intuition, resulting in a too narrow scope of experimentation. Data-driven approaches are less biased, potentially offering a way out. Still, the amount of recordable experimental data remains to be a limiting factor even with modern (automated) multi-reactor setups, where only a few dozen data points are acquired in reasonable time. In this contribution we therefore illustrate the practical application of highly-efficient optimally designed experiments. Leveraging simultaneous factor-changes, these jointly extract a maximum of information from each experimental run. Using examples from our ongoing investigation of thin-film and powder catalysts, we illustrate how this approach leads to significant insights on catalytic behavior over a larger number of factors. With additional information coming from multiple characterization techniques, we also demonstrate how catalyst development can strongly benefit from jointly coordinated data-driven experimental efforts.

O 39.4 Tue 18:00 P2/EG

Operando sXRD study of copper-zinc-alumina (CZA) model systems under methanol synthesis conditions — •Erik Beck[1,2], Vedran Vonk[1,2], Heshmat Noei[1,2], and Andreas Stierle[1,2] — [1]Centre for X-ray and Nano Science, Hamburg, Germany — [2]German Electron Synchrotron DESY, Hamburg, Germany

Methanol synthesis from gas mixtures of H2, CO and CO2 is an important industrial process in which copper-zinc-alumina (CZA) has been identified as a high performing catalyst. Typically, the products and reactants are gases used at pressures of >30 bar and a temperature of 250-300 degree C. Because of the dynamic nature of the catalyst under such industrial conditions, the underlying mechanisms and reaction paths are still under debate, since the traditional surface science techniques cannot be used at such high pressures. In order to bridge this pressure gap and gather structural information of the system in real operando conditions, we designed a special experimental setup for synchrotron-based high pressure SXRD. By using dedicated Cu and Zn UHV MBE growth chambers, we were able to prepare epitaxial model systems of the CZA catalysts composed of epitaxial Cu nanoparticles on Al2O3 single crystal surfaces. We performed operando high energy x-ray diffraction experiments on such model catalysts at up to 30 bar and 300degC at the High Energy Materials Science Beamline at DESY and we were able to follow the structural changes of the Cu nanoparticles during oxidation and reduction in different gas compositions.

O 39.5 Tue 18:00 P2/EG

Surface phase transitions in doped manganite thin films — •Leonard Schüler, Tim Titze, Stefan Mathias, Daniel Steil, and Vasily Moshnyaga — I. Physikalisches Institut, Georg-August-Universität Göttingen

The symmetry breaking at the surface of strongly correlated $La_{1-x}Sr_xMnO_3$ (LSMO) thin films leads to a modification of orbital occupation compared to the bulk resulting in the formation of intrinsic magnetic and electric surface phases. To obtain a phase diagram of possible surface states, LSMO films with Sr doping over the complete range $x = 0 - 1$ were prepared by metalorganic aerosol deposition and have been investigated by both surface-enhanced Raman spectroscopy (SERS) and pump-probe optical (SE-PPR) reflectivity. Temperature-dependent SERS reveals magnetic phase transitions by anomalous frequency shifts of the MnO_6 octahedra's stretching mode resulting from spin-phonon coupling, as well as changes in Mn orbital occupation inferred by enhanced Raman activity of vibrational Jahn-Teller modes at the surface. Furthermore, ultrafast dynamics studied by SE-PPR reveals a surface phase transition, which is not present in the bulk LSMO.

O 39.6 Tue 18:00 P2/EG

Laser pump X-ray probe investigations of the dynamics at the liquid-vapour interface of alkali halogenide salt solutions — •Lukas Petersdorf[1], Svenja Hövelmann[1,2], Rajendra Giri[1], Nicolas Hayen[1], Karin Hansen[1], Philipp Jordt[1], Andrea Sartori[1], Matthias Greve[1], Florian Bertram[2], Olaf Magnussen[1], and Bridget Murphy[1,3] — [1]University of Kiel (IEAP), Kiel — [2]DESY, Hamburg — [3]RHL, Kiel

Detailed knowledge of the surface of alkali halogenide solutions is fundamental for understanding atmospheric effects and developing technological applications such as solar thermal cells. Surface dynamics of such systems ranging from fs to s, can be studied in detail by pump-probe techniques. Our Laser pump-X-ray probe studies are based on photoionization processes at the interface induced by a 258 nm laser pulse and pumping electron solvation dynamics and ion rearrangements. With auspicious quantum yield and surface structure, the pump-probe studies were performed on salt solutions (NaI, RbBr, ErCl3). We apply the surface sensitive techniques time resolved XRR and GIXRF to investigate the responding structural changes. A sensor monitored sample environment allows us to distinguish between laser induced and solution dependent dynamics. Upon laser excitation, changes in the specular reflectivity occur on the ms to s scale. Electron density and surface roughness change near the interface indicate a rearrangement of the ion concentration. Within the framework of the DAPHNE4NFDI project, the analysis will be supported by artificial neural networks in order to allow in-operando experimental decisions.