

HL 15: Energy materials (other than photovoltaics)

Time: Tuesday 9:30–11:15

Location: H33

HL 15.1 Tue 9:30 H33

Ab-initio study of the electronic structure of Na₂KSb and NaK₂Sb for photocathode applications — ●RAYMOND AMADOR and CATERINA COCCHI — Institut für Physik und IRIS Adlershof, Humboldt-Universität zu Berlin, Deutschland

In the search for novel materials for electron sources with enhanced quantum efficiency and minimised intrinsic emittance, multi-alkali antimonides are particularly promising in light of their relatively low band gap and electron affinity giving rise to emission in the near-infrared and visible region [1]. To fully exploit their potential, it is essential to reliably understand the electronic structure of these materials. First-principles methods such as density-functional theory (DFT) and many-body perturbation theory are suited for this purpose, as recently demonstrated in the case of CsK₂Sb [2]. Here, we employ DFT to investigate the electronic structure of two Na-based alkali antimonides, namely Na₂KSb and NaK₂Sb. From the analysis of the band structure and the density of states, computed with exciting [3], we clarify the character of the electronic states in the gap region and rationalise their behaviour in comparison with previously investigated Cs-based compounds [2]. Our results represent the first step towards an in-depth characterisation of the photoemission processes in Na-based alkali antimonides.

[1] Musumeci et. al., Nucl. Instrum. Methods Physics 907, 209 (2018) [2] Cocchi, et. al. J. Phys.: Condens. Matter <https://doi.org/10.1088/1361-648X/aaedee> (2018) [3] Gulans et. al., J. Phys.: Condens. Matter 26, 363202 (2014)

HL 15.2 Tue 9:45 H33

The roles of polarons and defects in charge carrier transport in BiVO₄ photoanodes for solar water splitting — ●VIKTORIA KUNZELMANN, IRINA ILICHEVA, ALEX HENNING, and IAN SHARP — Walter Schottky Institute and Physics Department, Technical University of Munich, Garching, Germany

Hydrogen generation by solar water splitting provides a promising route towards the sustainable storage of solar energy. Bismuth vanadate (BiVO₄) has a favorable band gap (2.5 eV) for solar light absorption and it has been demonstrated as a photoanode in photoelectrochemical cells (PEC) with one of the highest solar-to-hydrogen conversion efficiencies using metal oxide electrodes. While it is known that polarons and defects in BiVO₄ limit electron and hole mobilities, and thereby the PEC efficiency, their energetics and influence on macroscopic cell parameters have not yet been determined. This work aims to identify the energy levels of polarons and defects and to understand their effects on the surface photovoltage. Temperature-dependent photocurrent spectroscopy and photothermal deflection spectroscopy are used to investigate interband absorption, self-trapping and localization of carriers as well as their escape mechanisms in polycrystalline BiVO₄ thin films. These measurements yield key ensemble-averaged physical insights that are complemented with the nanoscale spatial characterization of surface photovoltage and charge transport by Kelvin probe force microscopy and conductive AFM, respectively.

HL 15.3 Tue 10:00 H33

Increasing the Spectroelectrochemical Performance of WO₃ Films Prepared by Spin-Coating with Additives — ●THI HAI QUYEN NGUYEN and DERCK SCHLETTWEIN — Justus-Liebig-Universität Gießen, Institut für Angewandte Physik

Tungsten oxide (WO₃) can be widely used as an electrochromic material in smart windows. In the presence of an electrolyte containing small cations such as Li⁺ ions the application of a negative voltage leads to reversible coloration of WO₃ thin films. The electrochromic properties of WO₃ including the charge transfer strongly depend on the internal structure of the films. In this work, thin films of WO₃ were prepared by spin-coating followed by heat-treatment using a precursor solution based on peroxotungstic acid with optional addition of poly(ethyleneglykol) of different molecular weight and similar components. The influence of the additives on the morphology and film structure was examined by SEM and XRD. The electrochromic properties of the films were studied by cyclic voltammetry and chronoamperometry with spectroscopic monitoring in a three-electrode-setup with LiClO₄ in propylencarbonate as electrolyte. The films prepared with additives clearly showed an improvement in the rate and in the extent

of optical switching between the coloring and bleached state with a clearer color impression. The diffusion coefficient of the Li⁺ ions in WO₃ could be increased confirming a facilitated diffusion of the ions through the film network. Hence, the presence of additives created an improved film structure of WO₃ which can be promising for smart windows with high efficiency.

HL 15.4 Tue 10:15 H33

Pre-activating CO₂ for Photocatalytic Reduction at the Semiconductor Surface — HONGTING WU, VERONIKA KÖNIG, PETER BUDWEISER, ●JACEK STOLARCZYK, and JOCHEN FELDMANN — Chair for Photonics and Optoelectronics, Department of Physics, Ludwig-Maximilians-Universität, Munich, Germany

Photocatalytic properties of semiconductor nanostructures are drawing much attention in recent researches because it provides possibilities to harvest solar energy and change it directly into chemical energy. Among all the possible photocatalytic reactions, CO₂ reduction remains to be much more challenging than others due to its stable C-O double bonds and its linear molecular structure. This makes it especially energetically costly to bring a single electron onto the molecule, which is the first step for most CO₂ photo-reduction reaction-chains. Recently Copper (I) compounds have been proved to be promising in forming simple, yet efficient photocatalytic nanostructures for CO₂ reductions. We use Cu₂O nanoparticles with the aim to improve the overall efficiency of CO₂ reduction by exploring ways to pre-activate CO₂ molecules and hence lowering the potential barrier for the initial one electron transfer in the CO₂ reduction reaction-chain.

HL 15.5 Tue 10:30 H33

Photochemical stability of BiVO₄ photoanodes for solar water splitting — ●IRINA ILICHEVA, VIKTORIA KUNZELMANN, and IAN SHARP — Walter Schottky Institute and Physics Department, Technical University of Munich, Garching, Germany

Artificial photosynthesis, the conversion of solar energy into chemical fuels, could be a promising alternative to fossil fuels. One way of realizing this is by photoelectrochemical water splitting. Here, the main challenge is to identify a semiconductor that is simultaneously stable, scalable and efficient. One of the materials showing a suitable electronic structure is the transition metal oxide bismuth vanadate (BiVO₄), which has a band gap of 2.5 eV in the visible range. Metal oxide semiconductors are often studied for their superior chemical stability. However, they can suffer from photochemical instability. Recent studies have shown the dissolution of BiVO₄ thin films under water splitting conditions, even though thermodynamic considerations predict the formation of a self-passivating, stable bismuth oxide surface layer. In this work, we analyze the photochemical stability of polycrystalline BiVO₄ photoanodes by photoelectrochemical methods to gain better insights into the corrosion mechanisms under operating conditions. We intentionally alter the BiVO₄ surface state by different surface pre-treatments in order to favor the formation of a stable bismuth oxide phase and to identify possible chemical and electronic passivation schemes. Changes in the morphology are monitored by scanning electron and atomic force microscopy.

HL 15.6 Tue 10:45 H33

Impact of surface adsorbates on charge carrier transport in metal oxide semiconductors for solar water splitting — ●JOHANNA EICHHORN¹, CHRISTOPH KASTL², ADAM SCHWARTZBERG², IAN SHARP³, and FRANCESCA TOMA¹ — ¹Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, United States — ²Lawrence Berkeley National Laboratory, The Molecular Foundry, Berkeley, United States — ³Technische Universität München, Walter Schottky Institute and Physics Department, Garching, Germany

Photoelectrochemical (PEC) water splitting is a promising route for efficient conversion of solar energy to chemical fuels. In this context, bismuth vanadate (BiVO₄) is one of the most investigated photoanode materials. Here, we employ in-situ photoconductive atomic force microscopy to elucidate the interplay of surface interactions and interfacial charge transport in polycrystalline BiVO₄ films. We demonstrate that the low intrinsic bulk conductivity limits interfacial charge transport. The transport mechanism is attributed to space charge limited current (SCLC) with shallow trap states.[1] By analyzing the SCLC

in selective gas environments, we are able to quantify the impact of surface adsorbates on bulk transport. Surface adsorbed oxygen acts as a shallow trap state and accounts for 40% of the effective trap density in BiVO₄ films.[2] Understanding such limitations of charge transport and transfer in photoelectrodes at the nanoscale and under in-situ conditions will enable the design of next generation PEC materials.

[1] Eichhorn et al., Nat. Commun. 9, 2597 (2018).

[2] Eichhorn et al., ACS Appl. Mater. Interfaces 10, 35129 (2018).

HL 15.7 Tue 11:00 H33

Sn nanoparticles@nitrogen-doped carbon nanofiber composites as high-performance anodes for sodium-ion batteries —
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Recently, sodium-ion batteries (SIBs) have attracted increasing attention as an important supplement and/or alternative to lithium ion

batteries due to the abundance of sodium resources and its much lower cost. A critical issue in current research is the development of earth-abundant and high-performance electrode materials for the extensive applications of SIBs. Sn-based nanocomposites have been identified as one of the promising anodes for SIBs. In this study, the composites of Sn nanoparticles anchored on nitrogen-doped carbon nanofiber (Sn@NCNFs) have been synthesized by an electrostatic spinning technique and used as anodes for SIBs. Morphological and structural characterizations indicate that the Sn nanoparticles anchored uniformly on the surface of NCNFs. The corresponding specific capacity can reach over 600 mA h/g at 0.1 C after 200 cycles. Additionally, these Sn@NCNFs also show excellent high-rate cycling performance and maintain a capacity of up to 390 mA h/g even at an extremely high rate of 1 C for over 1000 cycles. The results demonstrate that this Sn@NCNFs composite is a promising anode material with good reversible capacity and cycling performance for SIBs.