



# Seminarankündigung

Dienstag, 10. Dezember 2013

15:00 Uhr

WSI, Seminarraum S 101

## “Direct observation of the photo-electrochemical water splitting process with in-situ synchrotron valence band spectroscopy”

Solar hydrogen generation by water splitting in photo-electrochemical cells (PEC) belongs to the holy grail of sustainable energy supply. The search for high-performing, affordable, and corrosion-resistant photo-electrode materials is an on-going quest. Hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is in many respects a promising solution, particularly because it is an abundant and low-cost material with a band gap that makes it operational even for visible-light applications. But in spite of decades of extensive research, hematite still suffers from substantial deficiencies of conductivity. There is a controversy of whether this is based on the premature recombination of electron-hole pairs in the bulk or on the recombination of charge carriers at the surface. Lack of information of the electronic structure of typical PEC electrode materials for bulk and surface may be one reason why progress in the field is lacking.

Our recent combination of electrochemical and x-ray spectroscopy methods has provided new insight in the interaction of DC bias, electrolyte and photo-excitation with hematite. Electrochemical oxidation of sol-gel derived hematite photo-anodes creates a new, stable and hitherto unknown surface state in the upper Hubbard band, as evidenced by O1s near edge x-ray absorption fine structure (NEXAFS) spectra. Anodization of creates at least two new pre-edge structures in the O1s NEXAFS spectra, which can be assigned to  $e_g$  spin up symmetry transitions in the O2p charge transfer band and in the Fe3d-type upper Hubbard band. Upon further analyses, we find a parallel evolution of the relative spectral weight of these transitions with the photocurrent vs. DC bias, strongly supporting that two types of electron holes are contributing to the historically suggested two types of photocurrent in hematite. The fact that our experiment was carried out entirely *in-situ* with exposure of the electrode to visible light (or dark) and electrolyte (or dry) during x-ray spectroscopy strongly supports previous speculations that the electronic structure of the surface, and not only the short hole diffusion length in the bulk, may impede the performance of hematite photo-anodes. Our *in-situ* ambient-pressure and Fe-resonant XPS valence band studies on hematite during oxidation suggest that the charge transfer satellites frequently visible in Fe 2p NEXAFS spectra are indeed active in the valence band right near the Fermi energy.

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