Direct observation of two electron holes in hematite with *operando* O1s NEXAFS spectroscopy during photo-electrochemical water splitting

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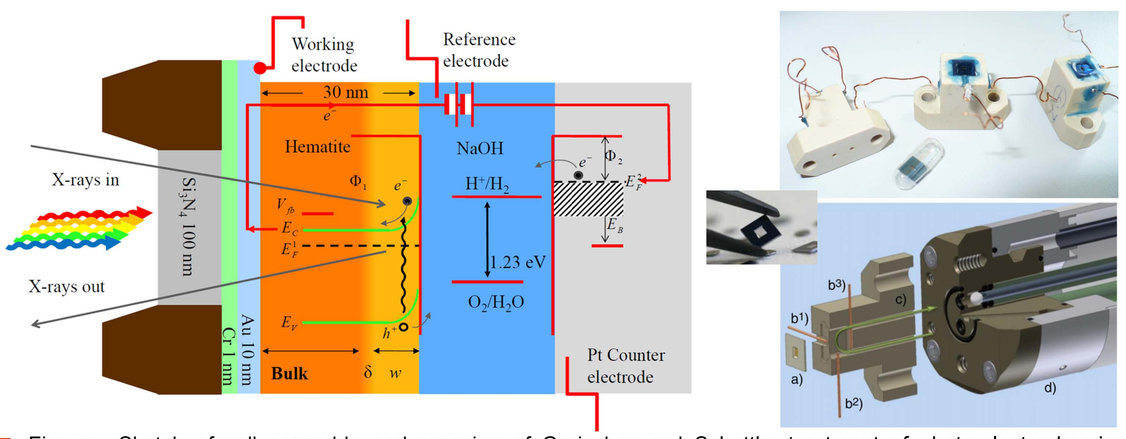
Introduction

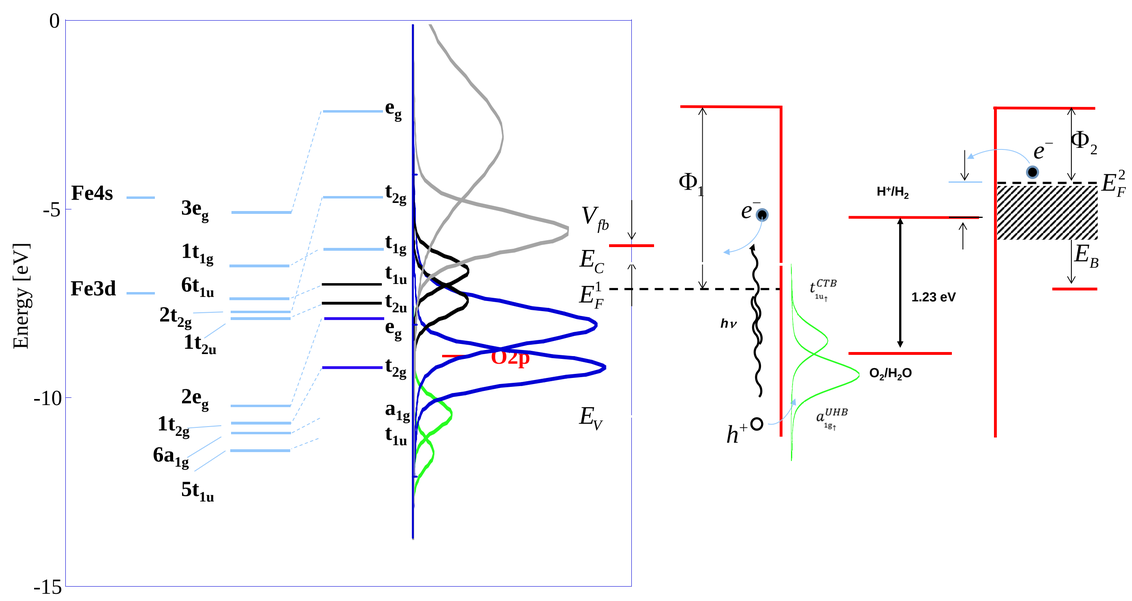
Hematite has been investigated for many decades as a visible light active photoanode for hydrogen generation by solar photo-electrochemical water splitting. In particular, the role of electron holes and charge transfer remains controversial. We have investigated the oxygen evolution of hematite in alkaline aqueous electrolyte under a bias potential during visible light illumination in a photo-electrochemical cell operando with soft X-ray (O 1s) spectroscopy. Only under these conditions, two new spectral signatures evolve in the valence band, which we identify as an O 2p hole transition into the charge transfer band and an Fe 3d type hole into the upper Hubbard band. Quantitative analysis of their spectral weight and comparison with the photocurrent reveals that both types of holes, contrary to earlier speculations and common perception, contribute to the photocurrent.

Spectro-photoelectrochemical cell for soft x-ray studies

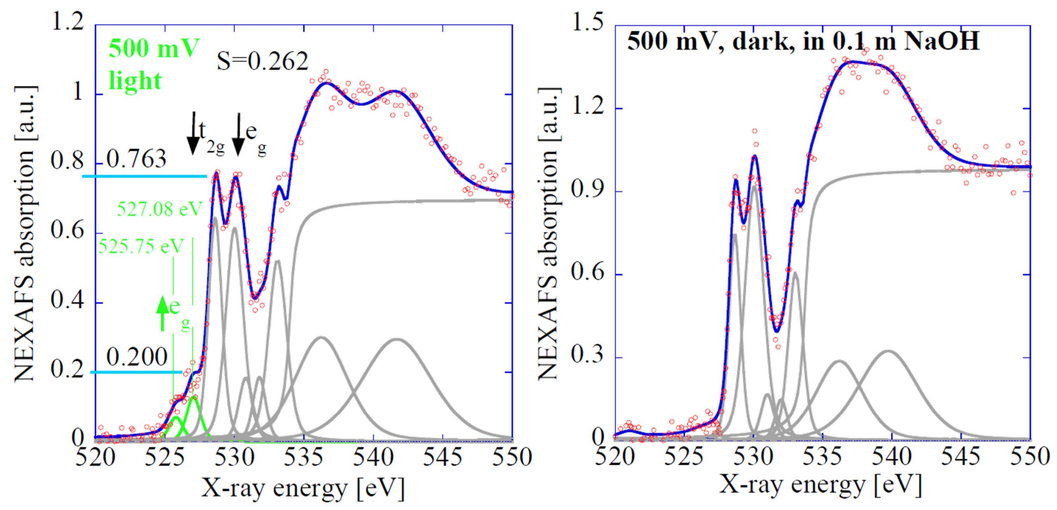


■ Figure: Sketch of cell assembly and mapping of Gerischer and Schottky treatment of photo-electrochemical semiconductor-liquid junction (SCLJ). Right – Liquid NEXAFS cells with Si3N4 frames and 3-electrode terminals.

O1s NEXAFS states match the Fe_2O_3 energy bands



Observation of 2 new peaks upon illumination



$$S^{CTB} = \frac{t^{CTB}_{1u_\uparrow}}{t_{2g_\downarrow} + e_{g_\downarrow}}$$

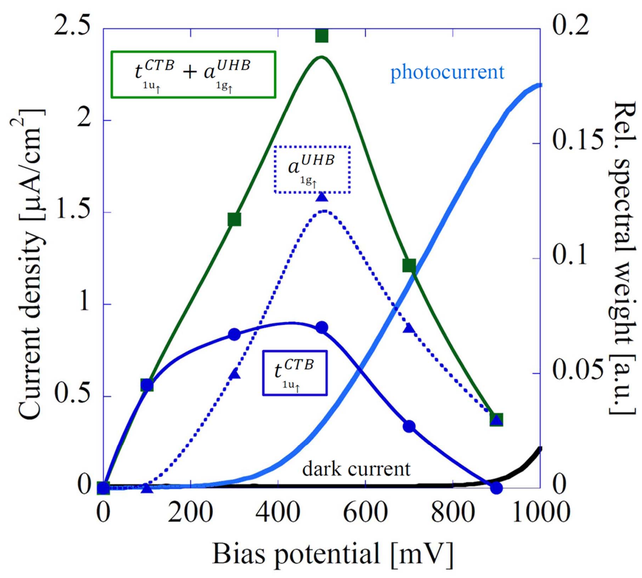
$$S^{UHB} = \frac{a^{UHB}_{1g_\uparrow}}{t_{2g_\downarrow} + e_{g_\downarrow}}$$

■ O 1s NEXAFS spectra recorded at 500 mV bias in light and dark condition shows that light plus potential generates two new transitions in the Fe3d-O2p hybridized states in the valence band.

Comparison with literature on strongly correlated electron systems suggests that the state near the Fermi energy is an O2p type hole into the charge transfer band, and the other one an Fe3d type transition into the upper Hubbard band.

Their relative spectral weight with the t2g-eg dublett can be used for quantitative analyses and correlation with transport properties.

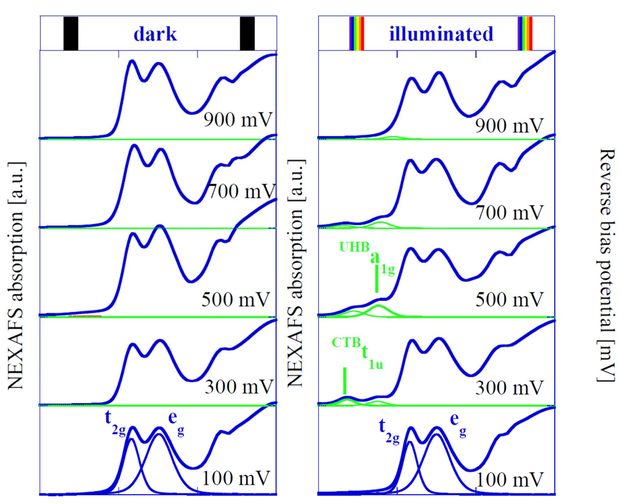
Correlation of photocurrent and hole evolution



$$J_{TOT} = -q\Phi\left[\frac{1-e^{-aw}}{1+aL_p}\right] - \frac{qp_0 D_p}{L_p}$$

The width *w(V)* of the depletion layer extends from the semiconductor-electrolyte junction into the bulk of the semiconductor, and scales with the square root of the potential *V* or the Schottky barrier height *V-V*$_{FB}$ and is pinned by the flat band potential V_{FB}: $w(V) \sim w_0\sqrt{V - V_{FB}}$. The hole state into the CTB shows a square root behavior.

Systematic evolution of hole states during PEC



■ O 1s NEXAFS spectra recorded at bias from 100 to 900 mV under dark (left) and light (right) condition.

This is clear evidence that the two new hole states are formed during illumination with visible light and only when under the proper electrochemical potential.

The «dark» studies rule out that the hole peaks are generated from the soft x-ray beam.

Conclusions

■ This is the first time that an analysis of the electronic structure of a PEC photoanode was carried out online and operando by performing soft x-ray spectroscopy under control of the electrochemical potential. We have directly identified two different electron hole transitions in hematite under PEC operating conditions which arise upon illumination at anodic bias from around 100 to 900 mV vs. an Ag reference electrode and thus validated a long-speculated electronic aspect of hematite. Moreover, in contrast to established perception, the two different holes seem to contribute to photo-electrochemical water oxidation, irrespective their different reactivity. The O 2p hole appears and also disappears at a potential 100 to 200 mV below that of the Fe 3d hole, suggesting that the O 2p hole is more reactive than the Fe 3d hole at the same potential. Surprisingly, the Fe 3d hole, less energetic than the O 2p hole but with a larger spectral weight, is also active for water activation, and there is little difference in their activity.

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