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Model systems for photoelectrochemical water splitting: A surface science approach

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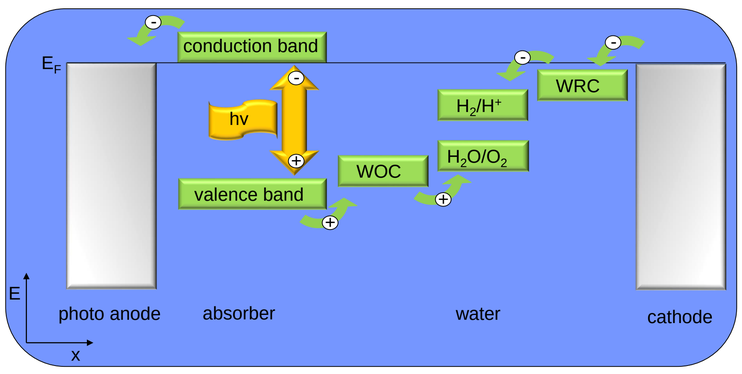
1. Motivation

- water splitting as approach for energy storage of solar light: $2H_2O + hv \rightarrow 2H_2 + O_2$
- H_2 as fuel of the future
- model systems for water splitting photoelectrodes
- mechanistic insight about novel catalyst molecules, photosensitizers and interfaces

Working principle of a photoelectrochemical cell:

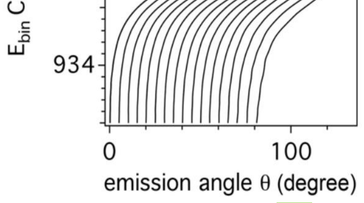
- solar photon is absorbed and creates an electron-hole pair
- possible absorbers: semiconductors or photosensitizers
- charge transfer to water reduction catalyst (WRC) and water oxidation catalyst (WOC)
- dissociation reaction of water:
  $4H^+ + 4e^- \rightleftarrows 2H_2$
  $2H_2O + 4h^+ \rightleftarrows 4H^+ + O_2$



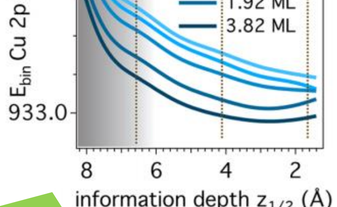
2. Atomically Resolved Band Bending Effects

- heterojunctions of semiconductors and molecules of importance
- angle-resolved x-ray photoelectron spectroscopy (XPS) provides spatial resolution of band bending
- atomically resolved band bending allows extraction of charge density

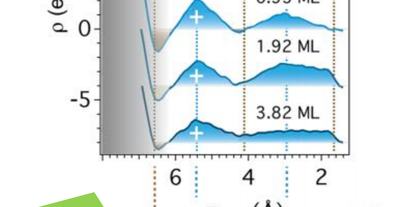
XPS of the Cu $2p_{3/2}$ core level as a function of emission angle for Cu_2O(111)



peak maximum of Cu $2p_{3/2}$ core level as a function of information depth

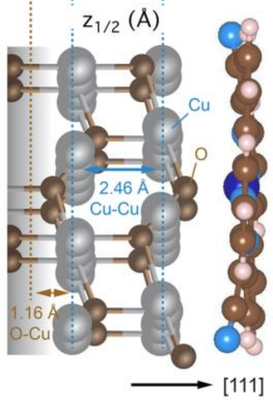


extracted charge density profiles ρ(z) perpendicular to the (111) surface (top) and structural model (bottom)

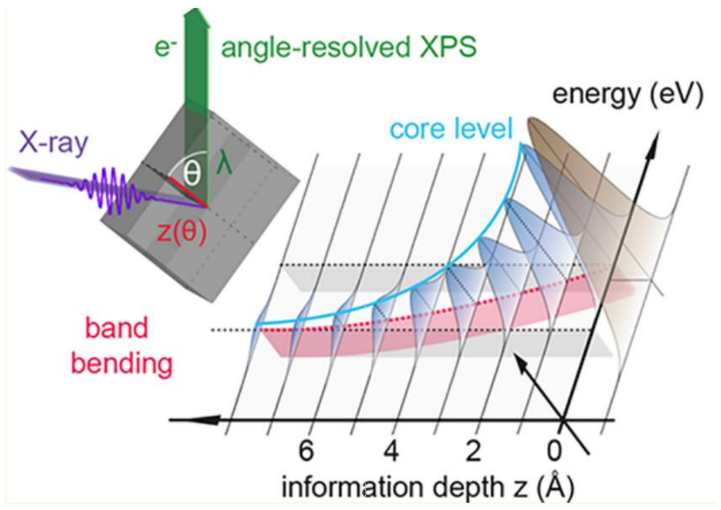


$$z_{1/2}(\Theta) = \ln(2)\lambda_{in}(E_{Kin})\cos(\Theta)$$

$$\rho(z) = -\varepsilon_0\varepsilon_r \frac{\mathrm{d}^2 E_{bin}}{\mathrm{d}\, z^2}$$



working principle of angle resolved XPS: spatial resolution allows probing of band bending

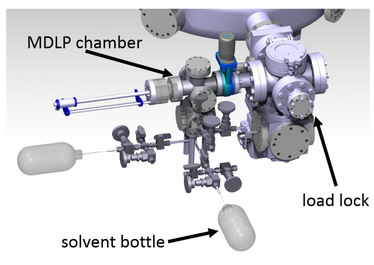


Leuenberger et al., *Nano Lett.*, 17 (2017) 6620

used water reduction catalyst: Co-Pyrphyrin (CoPyr)

3. Wet-chemical Functionalization of Ultrathin Films

CAD model of new setup



- ultrathin alumina films prepared under UHV-conditions
- surface oxide not stable in air [3]
- new chamber developed for wet-chemical deposition of molecules
- high vacuum cleanliness maintained
- $Re(NCS)(CO)_3$(dicabipy) as photosensitizer:
  - molecule density: $n_{Re} = 1.0$ /nm²
  - molecules passivate surface

model of ultrathin alumina films

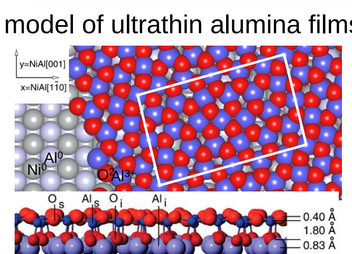
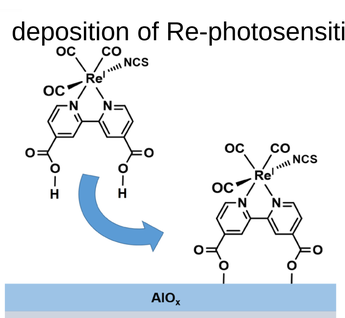
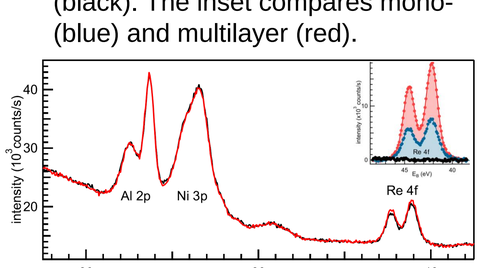


figure: Kresse et al., *Nano Lett.* **308** (2005) 1440

deposition of Re-photosensitizer

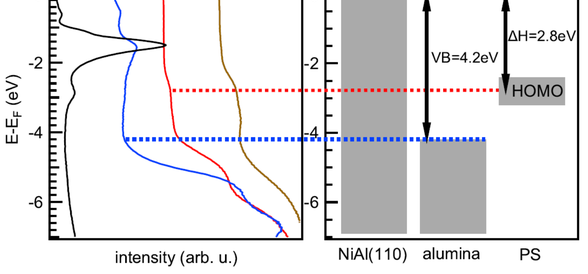


XPS after molecule deposition (red), and after 5 minutes of air exposure (black). The inset compares mono- (blue) and multilayer (red).



4. Energy Alignment and Modulation of Charge Carrier Dynamics

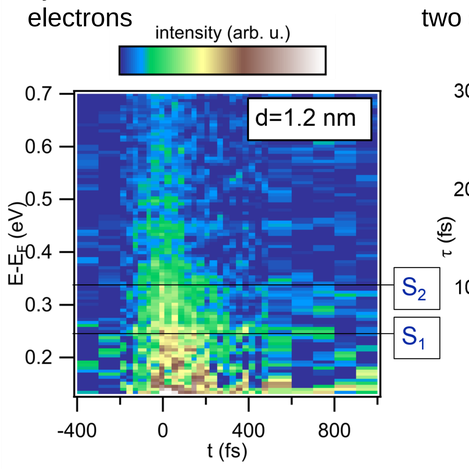
UPS of NiAl substrate (black), alumina film (blue), and Re-photosensitizer (monolayer red, multilayer yellow)



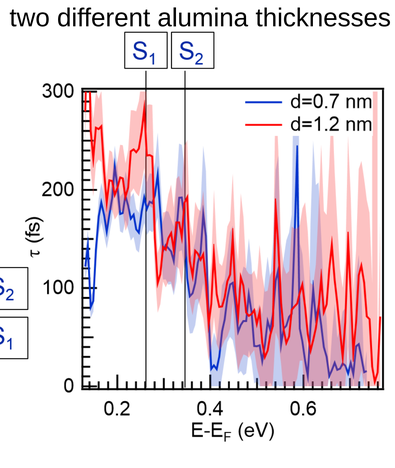
energy alignment in photoelectrode model system

- ultraviolet photoelectron spectroscopy (UPS) from substrates and molecular overlayers
- information about valence band structure, occupied molecular orbitals, ionization potentials and energy alignment
- time-resolved two photon photoemission for electron dynamics (pump-probe experiment)
- lifetime of excited electrons in photosensitizer changes for different alumina thicknesses
- electron injection from molecule to substrate for thinner films
- tunneling relevant process in such devices

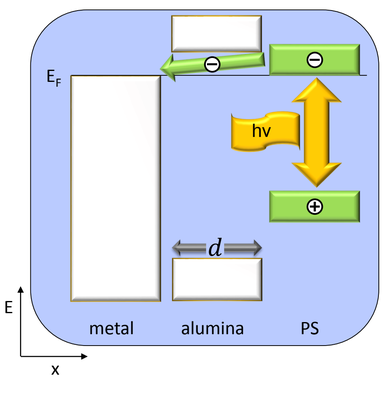
dynamics of the excited electrons



lifetimes of excited electrons for two different alumina thicknesses

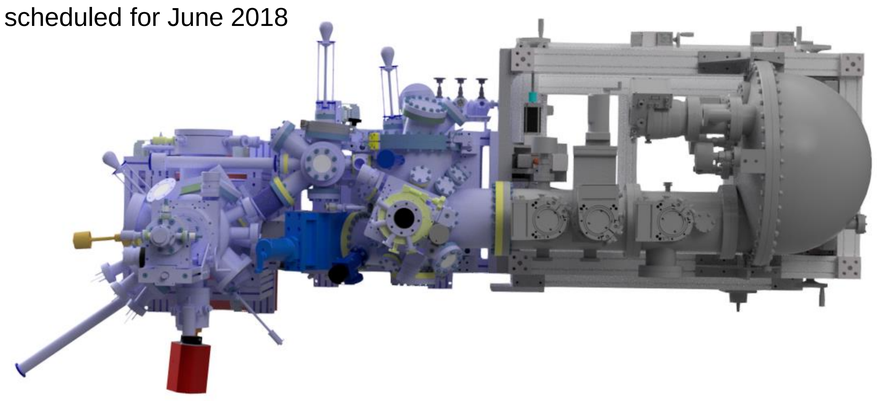


excited electrons in the photo-sensitizer are injected into the metal substrate



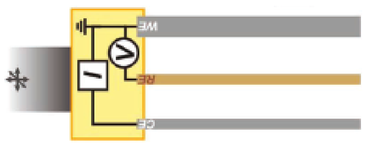
5. Instrument Development: Solid-Liquid Ambient Pressure XPS

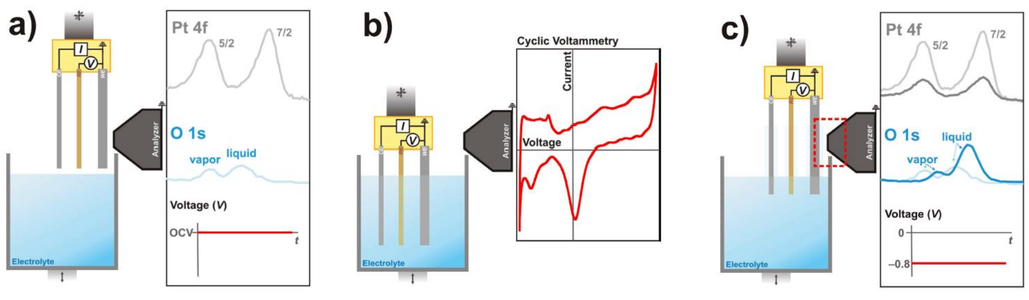
- new endstation attached to existing Scienta HiPP2 analyzer at Paul Scherrer Institute
- in-situ UHV sample preparation capabilities
- solid-liquid interface created by the dip-and-pull method [4]
- commissioning scheduled for June 2018



In situ electrochemical cell
Water vapor pressure
~ 25 mbar

hν = 4 keV





Prior to immersion:
O 1s shows signals from water vapor and from a condensed water film.

During immersion:
Measure cyclic voltammograms, Sample can be cleaned.

After immersion:
Liquid water film pulled out of the liquid, Potential control of liquid water and vapor.

Axnanda et al., *Sci. Rep.*, 5 (2015) 9788

Outlook

- ongoing effort towards studying molecular catalysts and photosensitizers under catalytically relevant conditions
- understanding electron dynamics in model photoelectrodes
- implementing time-resolved corelevel spectroscopy to probe metal-to-ligand charge transfers

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