Investigating Model Electrodes for Photocatalytic Water Splitting with Surface Science Techniques

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Principle of Photocatalytic Water Splitting

Motivation: Sustainable energy generation from solar light

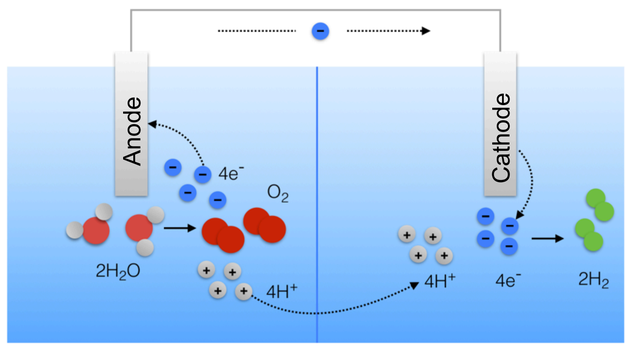


Figure 1: Working principle of a heterogeneous photoelectrochemical cell. On the anode water molecules are split into O_2, protons and electrons. On the cathode protons are reduced to H_2.

- ✓ Storage of solar energy in form of chemical bonds
- ✓ Oxygen as only side product
- ✓ Non-pollutive, cheap, and abundant materials

Cobalt-Pyrphyrin on Cuprous Oxide

Model system for a cathode (1)

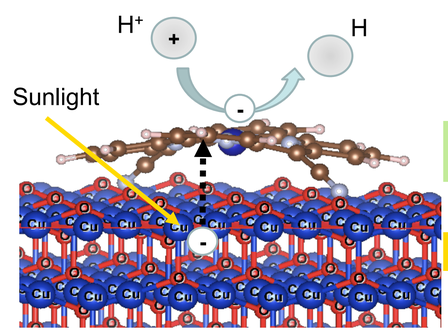


Figure 2: Working principle of the cathode: (1) Photoabsorption in Cu_2O generates free charge carriers; (2) Charge separation and electron injection into the Cobalt-Pyrphyrin molecule; (3) Reduction of the proton to hydrogen gas.

Storage of free electrons

Electron transfer to H^+

Water reduction catalyst

Photoabsorber

Cobalt-Pyrphyrin (CoPyr)

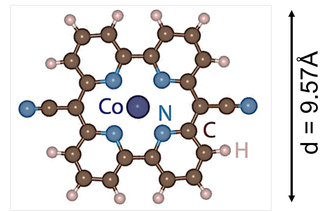


Figure 3: Model of the metalorganic molecule Cobalt-Pyrphyrin. Synthesized on UZH. [3]

Cuprous Oxide $Cu_2O(111)$

Absorption of sunlight

Charge separation

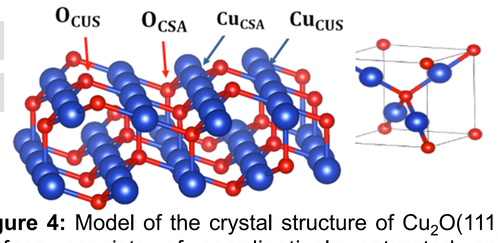


Figure 4: Model of the crystal structure of $Cu_2O(111)$; surface consists of coordinatively saturated and unsaturated copper (blue) and oxygen (red) atoms. [1]

Molybdenum Disulfite on Antimony Selenide

Model system for a cathode (2)

Storage of free electrons

Electron transfer to H^+

Water reduction catalyst → **Molybdenum Disulfite (MoS_2)**

Photoabsorber → **Antimony Selenide (Sb_2Se_3)**

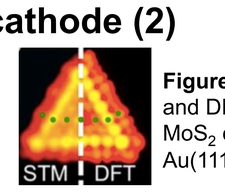


Figure 8: STM image and DFT model of a MoS_2 cluster on Au(111) [5]

Absorption of sunlight

- Direct band gap of 1.0 -1.2 eV
- High optical absorption coeff. [6]

Charge separation

- 1D parallel-stacked ribbons occupied by saturated atoms → low recombination losses [7]

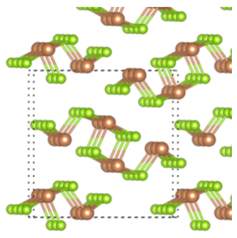
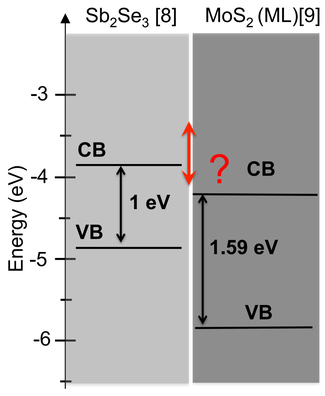


Figure 9: Sb_2Se_3 rystalline structure and unit cell



MoS_2 on Sb_2Se_3: is band alignment suitable for HER?

1st step: Sb_2Se_3 characterization.

XPD

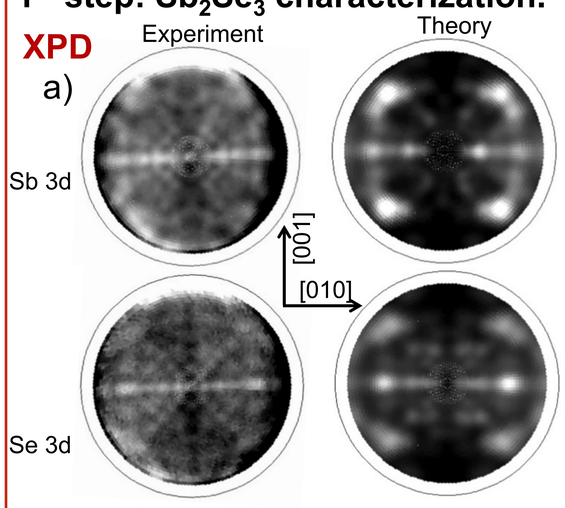


Figure 10: a) Experimental and simulated XPD pattern for Sb and Se 3dcore levels. From the two sets of data, we can conclude the **surface orientation** is **(100)**. b) LEED pattern obtained with E_{e^-}**= 35 eV**. From the diffraction pattern and the crystal structure, the unit cell is located.

STM

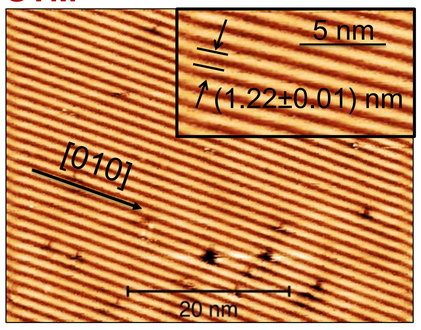
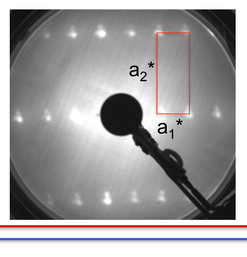


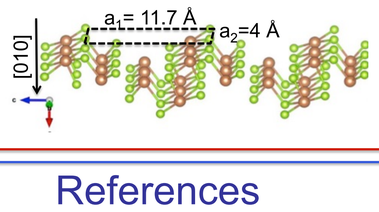
Figure 11: Image conditions: 35 nm x 50 nm, V_{sample} = 1.4 V, I_{tunnel} = 190 pA

LEED

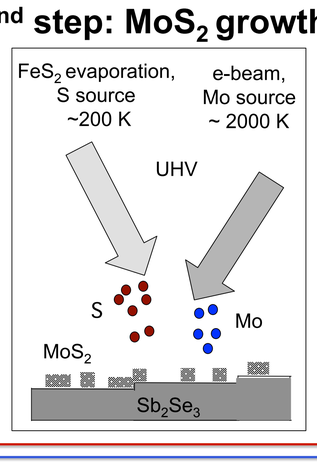
b)



a_1= 11.8 Å
a_2 = 3.9 Å



2nd step: MoS_2 growth



Photoemission Experiments: Energy level alignment

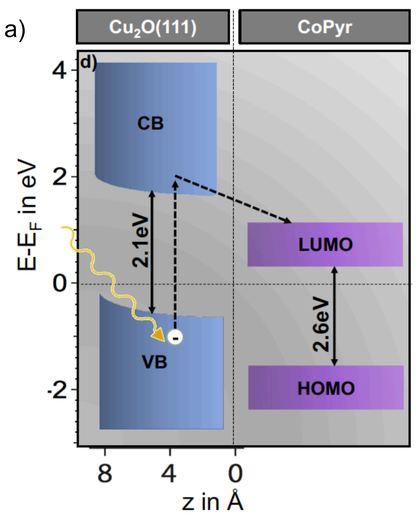
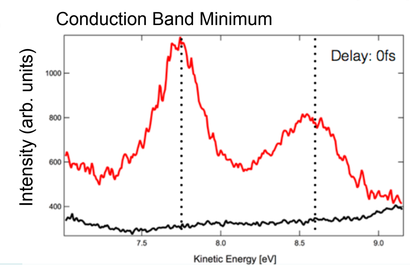


Figure 5: a) Energy level alignment of CoPyr on $Cu_2O(111)$. b) 2PPE spectrum of $Cu_2O(111)$ pumped with 3eV and probed with 6eV ultrashort laser pulse. c) Valence band spectrum of $Cu_2O(111)$ and CoPyr on $Cu_2O(111)$ [2].

Two-Photon Photoemission (2PPE): Unoccupied electronic structure of $Cu_2O(111)$

b)

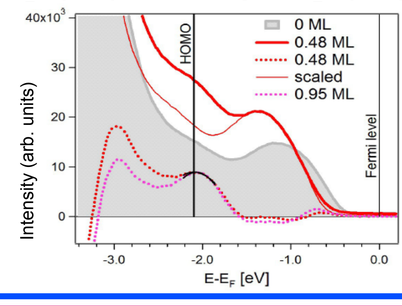


LUMO of CoPyr
$E\text{-}E_F$ = ?
DFT calc.: $E\text{-}E_F$ = 0.5eV

Conduction band minimum of $Cu_2O(111)$
$E\text{-}E_F$ = 1.6eV

UV-Photoemission: Occupied electronic structure of $Cu_2O(111)$ and CoPyr/$Cu_2O(111)$

c)



HOMO of CoPyr
$E\text{-}E_F$ = -2.1eV

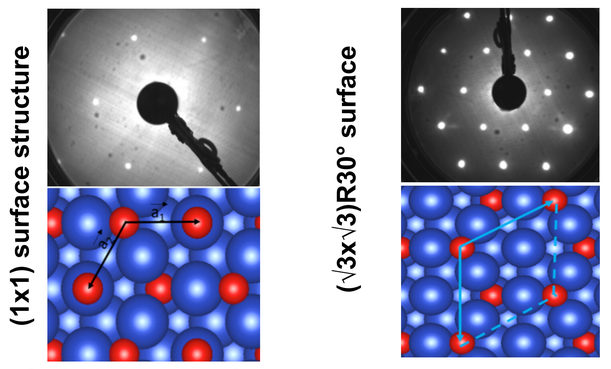
Valence band minimum of $Cu_2O(111)$
$E\text{-}E_F$ = -0.5eV

LEED+STM: Surface structure and adsorption geometry

$Cu_2O(111)$

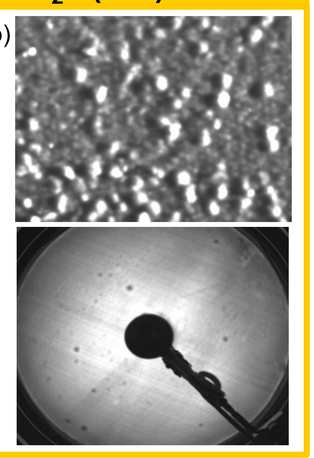
LEED: 2 different surface reconstructions obervable

a)



CoPyr / $Cu_2O(111)$

b)



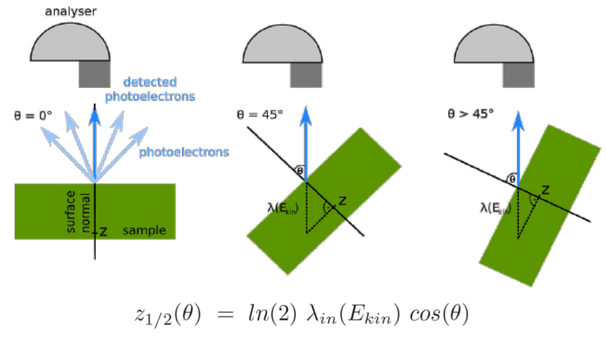
STM: no short range ordering

LEED: no long range ordering

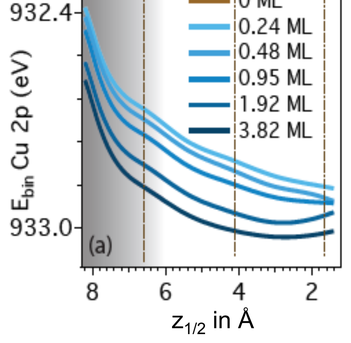
Figure 6: a) LEED images of different surface reconstructions of $Cu_2O(111)$ and model of the related surfaces. b) STM image of a low coverage of CoPyr on $Cu_2O(111)$ and LEED image show that there is no ordering of the molecule. [1]

ARXPS: Band bending of $Cu_2O(111)$

Principle: Probing depth depends on the angle of the sample in respect to the detector



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

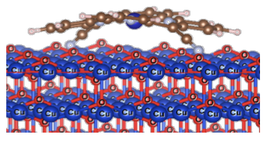


Downward band bending conserved by adsorbing CoPyr

Figure 7: Principle of angle-resolved XPS and band bending of $Cu_2O(111)$ yellow and CoPyr on $Cu_2O(111)$ blue: Downward band bending conserved by adsorbing CoPyr but shape changes. [2][4]

Outlook

Model System



CoPyr

$Cu_2O(111)$

Additional protection layer for stability → Additional layer for electronic junction

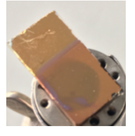
Real Device

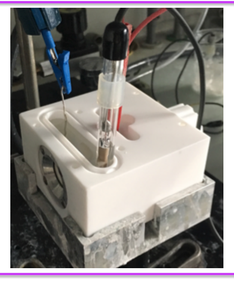
CoPyr

TiO_2

GaO

$Cu_2O(111)$





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Acknowledgments

We gratefully acknowledge financial support by University Research Priority Program Light to Chemical Energy Conversion (LightChEC) and the Swiss National Science Foundation (SNF).