Sunlight-driven water splitting in hematite-based photoelectrochemical cells

Beniamino Iandolo†, Björn Wickman†,‡, Brian Seger‡, Ib Chorkendorff†, Igor Zorić†, and Anders Hellman†

† Department of Applied Physics, Chalmers University of Technology, Göteborg, Sweden

‡ Center for Individual Nanoparticle Functionality, Department of Physics, Technical University of Denmark (DTU), Lyngby, Denmark
Division for Chemical Physics, Applied Physics Department

Group photo on a nice Swedish late-summer day
Outline

1. Plasmon-enhanced water splitting on hematite-based model photoanodes

2. Faradaic efficiency of water splitting on hematite surface

3. Beyond plasmon-enhanced water splitting on hematite
1. Plasmon-enhanced water splitting on hematite-based model photoanodes
Background

- Photoelectrochemical (PEC) cell: a monolithic device in which energy is converted into chemical energy (H$_2$ and O$_2$) at macroscopically different locations.

Solar water splitting:
- Solar cells + electrolyzers
- Photocatalytic cells
- Photoelectrochemical cells
Photoelectrochemical (PEC) cells

\[ 2H_2O + 4hv \rightarrow O_2 + 4H^+ + 4e^- \]

\[ 4H^+ + 4e^- \rightarrow 2H_2 \]

Solar-to-Hydrogen energy conversion efficiency
- light collection
- charge separation
- charge transport
- charge transfer
- reaction selectivity

Requirements on light absorber(s):
- efficiency
- durability
- fabrication costs
Hematite as photoanode for solar water splitting

Hematite (crystalline Fe$_2$O$_3$):

- absorbs visible light ($E_g$ around 2 eV)
- inexpensive
- stable in aqueous environment for pH>3
- non-optimal alignment of conduction band edge and hydrogen evolution potential
- indirect bandgap → low $\eta_{\text{absorption}}$
- low conductivity, short hole diffusion length (4-5 nm) → low $\eta_{\text{transport}}$

Physically thin, optically thick photoanodes:

- nanostructure absorber
- enhance light absorption

Metallic nanostructures supporting localized plasmonic resonances

Beniamino Iandolo, Chalmers University of Technology 2013-04-11
Localized surface plasmon resonance (LSPR)

Electric field enhancement around nanodisk at resonance

\( E_{\text{LSPR}} \) depends on:
- metal
- shape
- size
- refractive index of the nanoenvironment

Zorić et al., ACS Nano 2011, DOI: 10.1021/nn102166t

Beniamino Iandolo, Chalmers University of Technology 2013-04-11
How can LSPR help?

**Light scattering**

- a)

**Near-field enhancement**

- b)

**Hot electron injection**

- c)

**Heat**

- d)

Beniamino Iandolo, Chalmers University of Technology 2013-04-11
Fabrication of hematite-based photoanodes

Model photoanodes, focus on process understanding

a) Physical Vapor Deposition of Fe thin films on indium tin oxide covered substrates

b) Dry thermal conversion of Fe into Fe$_2$O$_3$

c) Functionalization of Fe$_2$O$_3$ with Au nanodisks

Beniamino Iandolo, Chalmers University of Technology 2013-04-11
Fabrication of hematite-based photoanodes

Functionalization based on hole-mask colloidal lithography

Short ordered arrays of nanostructures with control on shape, size, surface coverage and chemistry


Beniamino Iandolo, Chalmers University of Technology 2013-04-11
XRD and SEM characterization

Fe$_2$O$_3$ is the only observable iron oxide phase

Beniamino Iandolo

2012-12-10
Optical characterization

Determination of bandgap energy in hematite films

- Spectrophotometer with integrating sphere to measure extinction $E$ and scattering $S$
- Optical theorem $E = A + S \rightarrow$ absorption $A = \alpha t$, $t =$ thickness, $\alpha =$ absorption coefficient
- Tauc’s formula: $(\alpha h\nu)^{0.5} = A(h\nu - E_G)$, where:
  - $h\nu$: photon energy
  - $E_G$: bandgap energy
  - $A$: constant
  - $0.5$: exponent denoting indirect transition

- Plot $(\alpha h\nu)^{0.5}$ versus $h\nu$ and fit the linear part

Beniamino Iandolo, Chalmers University of Technology 2013-04-11
Optical characterization

Increased light harvesting upon functionalization

Beniamino Iandolo, Chalmers University of Technology 2013-04-11
Photocurrent-potential (J-V) characteristics

- Pt wire counter-electrode,
- 1M KOH electrolyte (pH=13.6)
- Ag/AgCl reference electrode
- solar simulated illumination

Conversion from Ag/AgCl to Reversible Hydrogen Electrode (RHE)

\[ E_{RHE} = E_{Ag/AgCl} + E^0_{Ag/AgCl} + 0.059 \times pH \]
Internal Photon-to-current Conversion Efficiency (IPCE)

\[ IPCE = \frac{hc}{e\lambda} \frac{j_{ph}(\lambda)}{P(\lambda)} \]

- Same 3-electrodes setup as before, constant potential of 1.5 V versus RHE

- Increase in IPCE close to bandgap in Fe\(_2\)O\(_3\)
  - Highest for 25 nm thick hematite
  - Correlation between \(\lambda_{LPSR}\) and spectral position of relative \(\Delta\)IPCE maximum
How did LSPR help?

**Light scattering**

- a) 

**Near-field enhancement**

- b) 

**Hot electron injection**

- c) 

**Heat**

- d) 

Beniamino Iandolo, Chalmers University of Technology
Spectrally resolved measurements and calculations

Geometry used for calculations

![Geometry Diagram]

Calculated extinction difference

Wavelength [nm]

Measured extinction difference

Wavelength [nm]

FDTD calculations by Tomasz J. Antosiewicz, Division for Condensed Matter Theory, Chalmers

Beniamino Iandolo, Chalmers University of Technology 2013-04-11
Evidence that the observed plasmonic improvement can be assigned to enhanced charge generation in Fe$_2$O$_3$.

Iandolo et al., PCCP (2013), 15, 4947--4954

Beniamino Iandolo, Chalmers University of Technology
Mechanism of plasmonic IPCE increase

Beniamino Iandolo, Chalmers University of Technology

V.P. Zhdanov et. al., Physica E 46 (2012): 113–118
2. Faradaic efficiency of water splitting on hematite surface
Faradaic efficiency (FE) evaluation

- Measure the total charge $Q_{\text{tot}}$ from photocurrent integration
- Quantify evolved amounts of $O_2$ and obtain the corresponding $Q_{O_2}$
- Determine FE as $Q_{O_2}/Q_{\text{tot}}$

- 0.1 M KOH
- Calomel - RE
- Pt wire - CE
- Ar purged
- Solar simulated
- 1.56 V vs. RHE
Faradaic efficiency (FE) evaluation

- Peak area $\rightarrow$ $O_2$-concentration (calibrated from known source)
- Subtraction of $O_2$ leaking in from the surrounding
- Volume (entire gas volume in system) determined electrochemically using HER

- **Total amount of $O_2$ evolved, charge $Q_{O2}$**

Beniamino Iandolo, Chalmers University of Technology 2013-04-11
Faradaic efficiency (FE) evaluation

- FE = 1 (within experimental error) for both samples
- for broadband illumination also at plasmonic wavelengths

All the detected charge goes into O\(_2\) evolution

landolo et al., in manuscript

Beniamino Iandolo, Chalmers University of Technology 2013-04-11
Stability test on functionalized hematite

After 16 h reaction, Faradaic efficiency measured to be 98.9%

Iandolo et al., in manuscript
3. Beyond plasmon-enhanced water splitting on hematite
Beyond LSPR-induced improvement

Which mechanism(s) behind IPCE increase at short wavelength?

- Adhesion layer likely to be involved
- The interface properties are crucial:
  - semiconductor-metal
  - semiconductor-semiconductor
  - semiconductor-electrolyte
  - triple junctions

How to study surface properties?

Electrochemical Impedance Spectroscopy (EIS)

Beniamino Iandolo, Chalmers University of Technology 2013-04-11
Electrochemical impedance spectroscopy (EIS)

- A potential $V = V_{DC} + v_{AC}(f)$ is applied between working and reference electrodes.
- The frequency of $v_{AC}$ is swept keeping the same $V_{DC}$ value.
- For each $f$, the total complex impedance $Z(f) = Z'(f) + Z''(f)$ is recorded.
- Then, $V_{DC}$ is changed and the sweep is repeated in the same frequency range.

How to interpret the Nyquist plots data?

An equivalent circuit modeling is required.
EIS on hematite photoanodes

Surface states for holes at the hematite-electrolyte interface

Increased band bending at semiconductor-semiconductor interface

Systematic investigation on our model photoanodes:
- chemistry (metals, oxides)
- surface coverage
- thickness

Beniamino Iandolo, Chalmers University of Technology

Klahr et al., E&E Science, 2012, 5, 7626

Barroso et al., E&E JACS, 2011, 133, 14868–14871


Downloaded by UNSW Library on 01 March 2013

Published on 24 April 2012 on http://pubs.rsc.org | doi:10.1039/C2EE21414H
Conclusions

- Model photoanodes were designed and fabricated

- Functionalization with Ti/Au nanodisks:
  - improves the photocurrent
  - improves IPCE close to the bandgap thanks to increased charge generation in Fe$_2$O$_3$

- FE of O$_2$ evolution is 1 for plasmon-functionalized hematite

- EIS investigation under process at SPREE (UNSW)
Acknowledgments

Michael Zäch
Anders Hellman
Mattias Eng
Brian Seger
Ib Chorkendorff

Igor Zorić

CHALMERS

Björn Wickman