Characterization and Optimization of Photoelectrode Surfaces for Solar-to-chemical Fuel Conversion

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Lawrence Livermore National Laboratory
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Project ID# PD058

Work performed under the auspices of the U.S. Dept. of Energy by LLNL under Contract DE-AC52-07NA27344.

Overview

Timeline

- Start: March 2010
- End: October 2014
- Percent complete: 80%

Project continuation and direction determined annually by DOE

Task 5 Barriers

- AE. Materials Efficiency
- AF. Materials Durability

Budget

Funding received in FY13: $65K

Total funding planned for FY14:
$85K (2% of PI and 50% of PD)

Total DOE Project Value: $490K

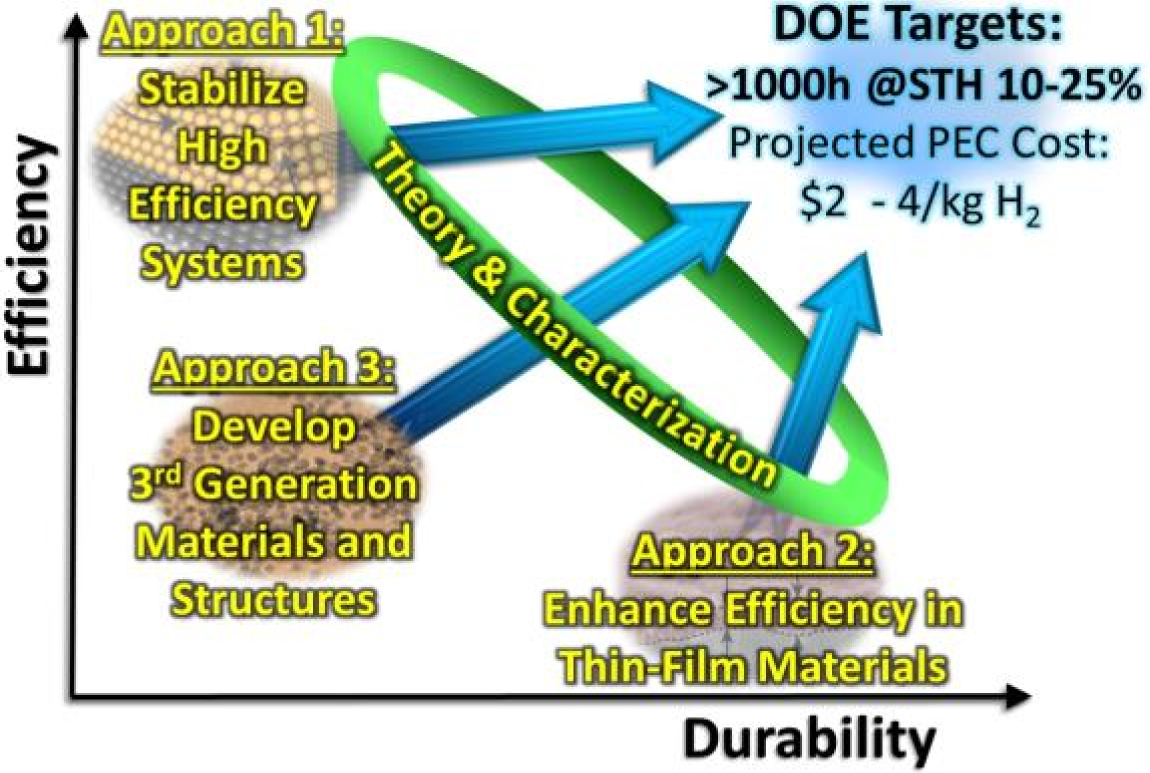
Cost share %: NA

Partners

- DOE EERE PEC Surface Validation WG:
  Deutsch/Wang/Turner (NREL)
  Heske (UNLV)
- Unfunded partners:
  Prendergast (LBNL)
  Otani (AIST Japan)

Project lead: T. Ogitsu, LLNL

PEC H_2 Production Work Group



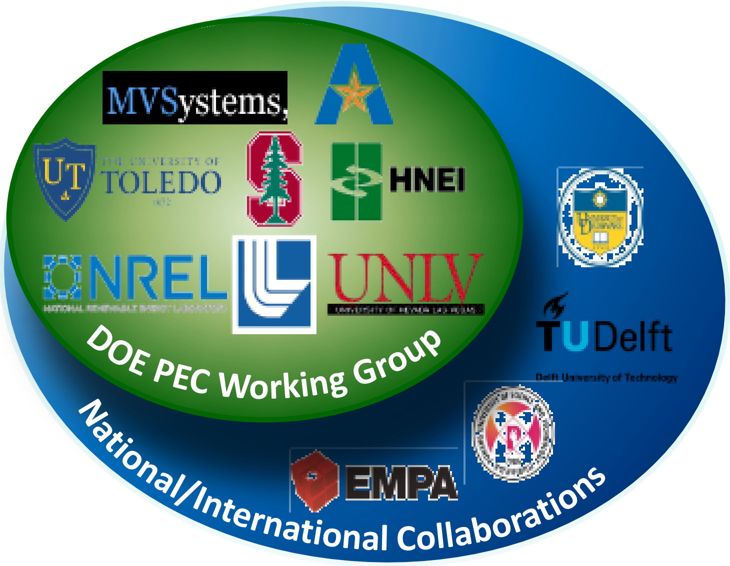
Approach 1: Stabilize High Efficiency Systems

Approach 3: Develop 3rd Generation Materials and Structures

Approach 2: Enhance Efficiency in Thin-Film Materials

Theory & Characterization

DOE Targets:
>1000h @STH 10-25%
Projected PEC Cost:
\$2 - 4/kg H_2



LLNL (theory) together with UNLV (characterization) works on identification of fundamental properties of electrode & interface relevant for H_2 production/corrosion, and share the obtained knowledge with PEC H_2 production WG

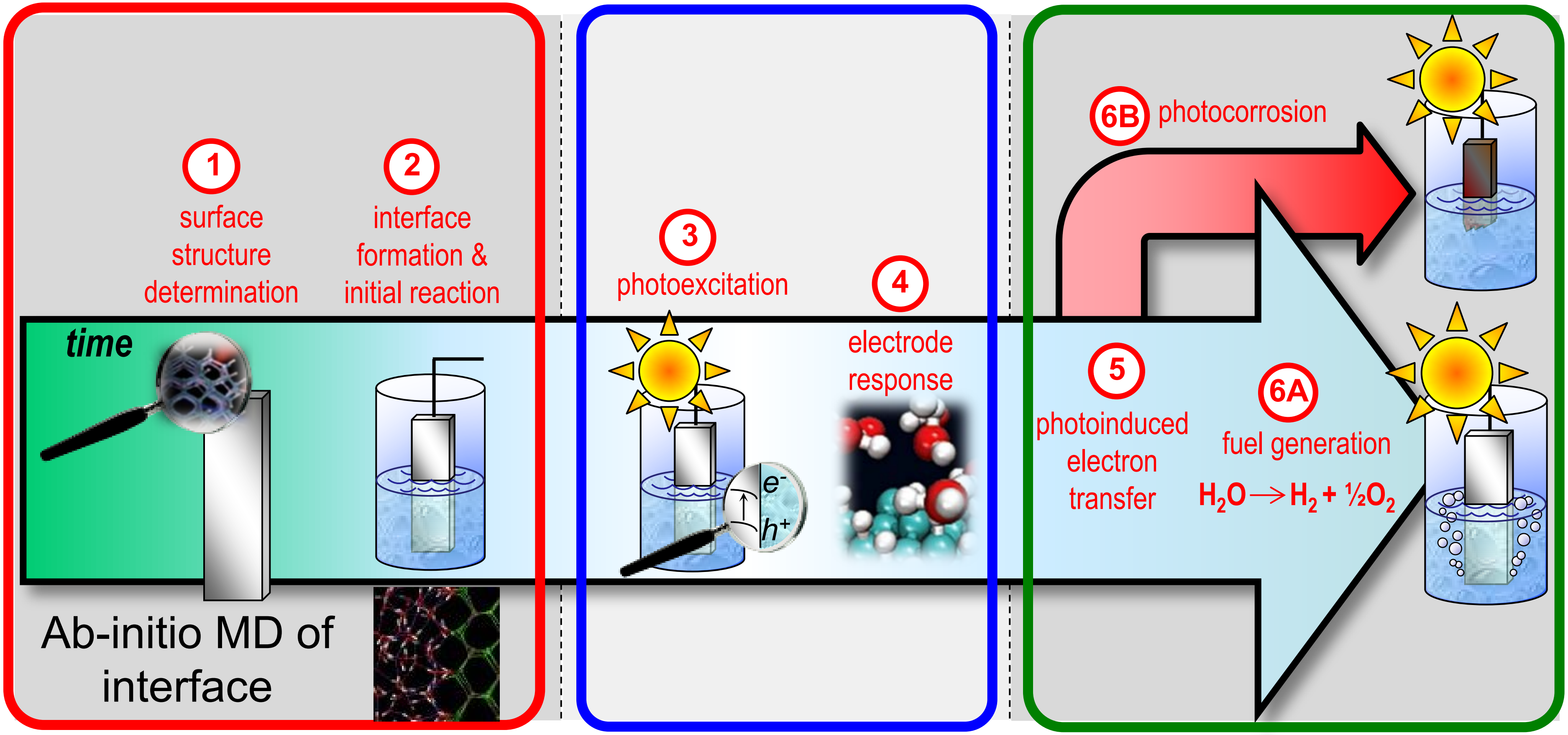
Relevance

- **Objectives**
  - *Develop* ***theoretical tool chest*** *for modeling photoelectrochemical systems*
  - *Compile* ***publications database*** *of research on relevant photoelectrode materials*
  - *Uncover key* ***mechanisms of surface corrosion*** *of semiconductor photoelectrodes*
  - *Understand* ***dynamics of water dissociation and hydrogen evolution*** *at the water-photoelectrode interface*
  - *Evaluate* ***electronic properties*** *of the surface and water-electrode interface*
  - *Elucidate relationship between* ***corrosion and catalysis***
  - *Provide* ***simulated X-ray spectra*** *to UNLV for interpretation of experimental results*
  - ***Share research insights*** *with the PEC WG members*
- **Specific relevance to H_2 program (Task 5)**
  - *Inform experimental efforts to increase* ***Materials Efficiency*** *(Barrier AE)*
  - *Inform experimental efforts to increase* ***Materials Durability*** *(Barrier AF)*

Approach

- Overview: understand relationship between the microscopic property of the electrode-electrolyte interface and the device performance using ab-initio DFT simulations and X-ray spectroscopy
  - Investigate the microscopic mechanisms of the chemistry of corrosion and water dissociation at electrode/electrolyte interfaces using ab-initio molecular dynamics simulation method
  - Identify the electrode properties that affect on electrode stability
    - Comprehensive assessment on the relation between electrode properties and resulting stabilities based both on information available in literature and on information provided by UNLV/NREL
    - Investigate the chemical environment of nitrogen based on measured N K-edge XES of the N treated $GaInP_2$ (NREL/UNLV) and simulated X-ray spectra (LLNL/LBNL)
  - Recruit external collaborators to extend theoretical tool chest
    - M. Huda of UTA on CIGS, E. Zurek of SUNY Buffalo on crystal structure search, A. Correa of LLNL on excited electron dynamics, M. Otani of AIST on simulation of biased interface, B. Yakobson of Rice University on nano-catalyst, T. W. Heo of LLNL on mesoscopic phase field modeling (bridging time & length scale)
  - Expand our survey to the other materials (eg. CIGS)
    - Development of more universal basic knowledge on PEC electrode materials

Stages of the photoelectrochemical reaction



① surface structure determination

② interface formation & initial reaction

Ab-initio MD of interface

③ photoexcitation

④ electrode response

⑤ photoinduced electron transfer

6A fuel generation

$H_2O \longrightarrow H_2 + \frac{1}{2}O_2$

6B photocorrosion

Stage 1: reaction precursors

Stage 2: light absorption

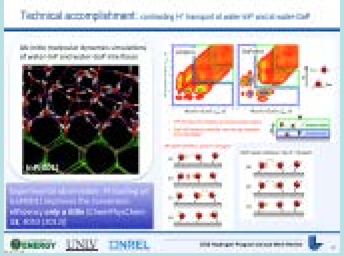
Stage 3: product formation

Milestones and deliverables

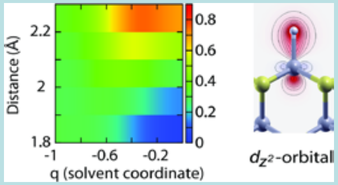
Milestone	Description	% Completed
1	Establish theory/experiment self-consistent material characterization scheme using X-ray spectroscopy with UNLV (the scheme applicable to arbitrary system)	100
2	Characterize surface durability treatments, including chemical environment of N/Pt/Ru in $GaInP_2$, based on theoretical/ experimental spectroscopy (in collaboration with SV Team)	50
3	Disseminate obtained knowledge on the nature of hydrogen bond network at the III-V electrode-electrolyte interfaces	100
4	Study mechanisms of the hydrogen evolution reaction and related corrosion processes	50
5	Dynamical modeling of interfaces under bias	30

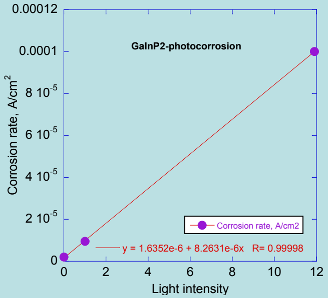
Summary of previous accomplishments in FY13

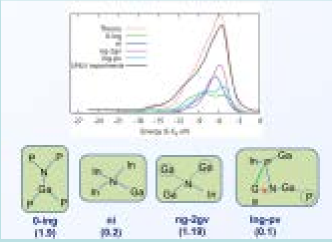
- Study on water-semiconductor interface simulations completed
  - H diffusion at water-InP interface found to be significantly better than that at water-GaP interface
- Study on kinetics of proton discharge process on MoS_2 using ab-initio derived model Hamiltonian completed
- Additional experiments performed by Wang of NREL confirmed the hole trap corrosion mechanism proposed by LLNL in FY11
  - The corrosion current shown to be linear with illumination
- Calculation procedure for N K-edge XES was developed
  - Rational derivation of candidate nitrogen environments for nitrogen bombarded $GaInP_2$ developed
  - Additional set of experiments on reference nitride compounds were initiated by UNLV in order to precisely calibrate the DFT error and fit broadening parameters



Technical accomplishment:







Technical accomplishment 1: Database of PEC research

(in progress)

- Approximately 1750 papers have been collected, indexed, and stored as of April 2014
    - 300 on catalyst, 70 on X-ray spectrum, 150 on water and solvation, 1070 on general PEC/semiconductors, 100 on Chalcogenide/Chalcopyrite, 60 on $GaInP_2$
- Information on relevant papers is shared among team members using online collaboration tools (email and/or photoelectrochemical.sharepointsite.net)
- The team discussions based on literature search and on the UNLV/NREL experimental results led to identification of a few possible causes of electrode performance variability (work in progress)
    - Partial segregation of $GaInP_2$ into GaP/InP
    - CuPt & disordered phases have different band gaps and charge carrier lifetimes
- Further extending review to other materials and methods

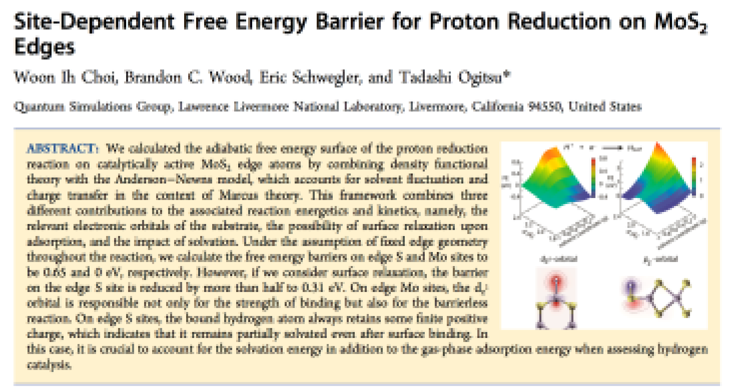
Technical accomplishment 2: Surface Validation (SV) team collaboration (assisting NREL/UNLV)

- 1998: Record STH of 12.4% established by Turner of NREL. *Durability (~24 hours) has been the main issue*
- FY12: One of nitrogen treated samples showed significantly improved durability (up to ~115 hours) by NREL
  - Poor reproducibility was the issue
- FY13: Pt/Ru impurity found by UNLV in the durable sample
  - Systematic study on the effect of Pt/Ru/N initiated (planning through SV team discussion)
- FY14 (as of April): 1st iteration of Pt/Ru/N experiments completed by NREL. Analysis and interpretation underway by SV team
  - *Reproducibility significantly improved yet not satisfactory*
- FY14 (and beyond): Complete analysis/interpretation. Develop research plan to identify and control the non-obvious stability-relevant process parameters (SV team)

LLNL contribution: Offer input/feedback for planning experiments and aid in analysis/interpretation of results; apply general knowledge obtained from compiled literature database.

Accomplishment: 3 publications

1. Catalysis and H_2 evolution



Site-Dependent Free Energy Barrier for Proton Reduction on MoS_2 Edges

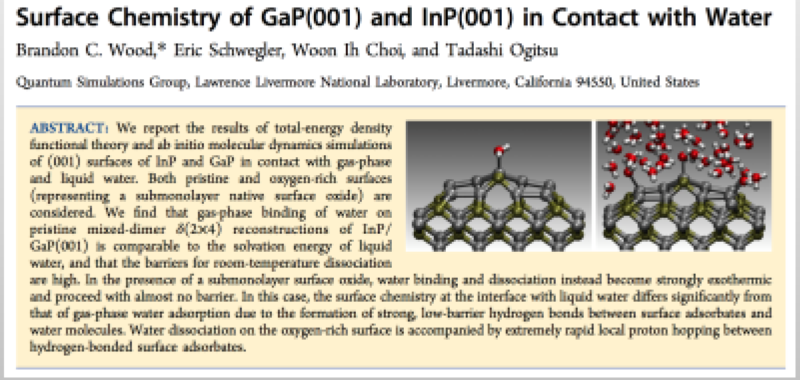
Woon Ih Choi, Brandon C. Wood, Eric Schwegler, and Tadashi Ogitsu*

Quantum Simulations Group, Lawrence Livermore National Laboratory, Livermore, California 94550, United States

ABSTRACT: We calculated the adiabatic free energy surface of the proton reduction reaction on catalytically active MoS_2 edge atoms by combining density functional theory with the Anderson−Newns model, which accounts for solvent fluctuation and charge transfer in the context of Marcus theory. This framework combines three different contributions to the associated reaction energetics and kinetics, namely, the relevant electronic orbitals of the substrate, the possibility of surface relaxation upon adsorption, and the impact of solvation. Under the assumption of fixed edge geometry throughout the reaction, we calculate the free energy barriers on edge S and Mo sites to be 0.65 and 0 eV, respectively. However, if we consider surface relaxation, the barrier on the edge S site is reduced by more than half to 0.31 eV. On edge Mo sites, the d_{z^2} orbital is responsible not only for the strength of binding but also for the barrierless reaction. On edge S sites, the bound hydrogen atom always retains some finite positive charge, which indicates that it remains partially solvated even after surface binding. In this case, it is crucial to account for the solvation energy in addition to the gas-phase adsorption energy when assessing hydrogen catalysis.

Journal of Physical Chemistry C **117**, 21772 (2013)

2. III-V surface chemistry



Surface Chemistry of GaP(001) and InP(001) in Contact with Water

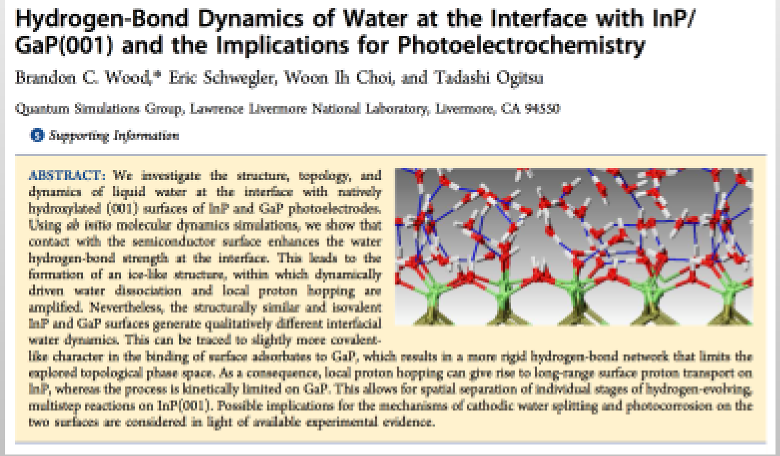
Brandon C. Wood,* Eric Schwegler, Woon Ih Choi, and Tadashi Ogitsu

Quantum Simulations Group, Lawrence Livermore National Laboratory, Livermore, California 94550, United States

ABSTRACT: We report the results of total-energy density functional theory and ab initio molecular dynamics simulations of (001) surfaces of InP and GaP in contact with gas-phase and liquid water. Both pristine and oxygen-rich surfaces (representing a submonolayer native surface oxide) are considered. We find that gas-phase binding of water on pristine mixed-dimer $\delta(2\times4)$ reconstructions of InP/GaP(001) is comparable to the solvation energy of liquid water, and that the barriers for room-temperature dissociation are high. In the presence of a submonolayer surface oxide, water binding and dissociation instead become strongly exothermic and proceed with almost no barrier. In this case, the surface chemistry at the interface with liquid water differs significantly from that of gas-phase water adsorption due to the formation of strong, low-barrier hydrogen bonds between surface adsorbates and water molecules. Water dissociation on the oxygen-rich surface is accompanied by extremely rapid local proton hopping between hydrogen-bonded surface adsorbates.

Journal of Physical Chemistry C **118**, 1062 (2014)

3. Interfacial chemistry



Hydrogen-Bond Dynamics of Water at the Interface with InP/GaP(001) and the Implications for Photoelectrochemistry

Brandon C. Wood,* Eric Schwegler, Woon Ih Choi, and Tadashi Ogitsu

Quantum Simulations Group, Lawrence Livermore National Laboratory, Livermore, CA 94550

Supporting Information

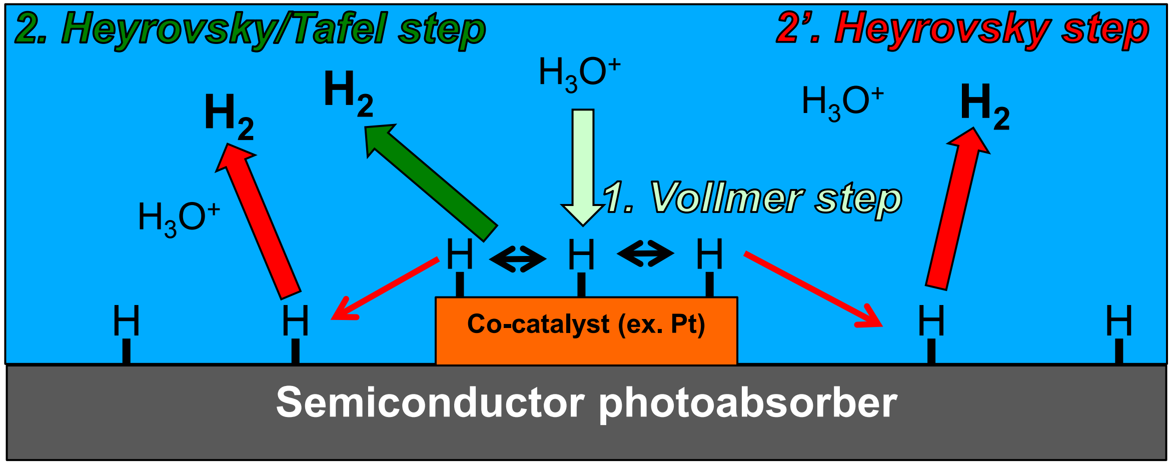
ABSTRACT: We investigate the structure, topology, and dynamics of liquid water at the interface with natively hydroxylated (001) surfaces of InP and GaP photoelectrodes. Using *ab initio* molecular dynamics simulations, we show that contact with the semiconductor surface enhances the water hydrogen-bond strength at the interface. This leads to the formation of an ice-like structure, within which dynamically driven water dissociation and local proton hopping are amplified. Nevertheless, the structurally similar and isovalent InP and GaP surfaces generate qualitatively different interfacial water dynamics. This can be traced to slightly more covalent-like character in the binding of surface adsorbates to GaP, which results in a more rigid hydrogen-bond network that limits the explored topological phase space. As a consequence, local proton hopping can give rise to long-range surface proton transport on InP, whereas the process is kinetically limited on GaP. This allows for spatial separation of individual stages of hydrogen-evolving multistep reactions on InP(001). Possible implications for the mechanisms of cathodic water splitting and photocorrosion on the two surfaces are considered in light of available experimental evidence.

Journal of the American Chemical Society **135**, 15774 (2013)

Accomplishment: Publication + AMR discussions led to a novel HER model

(more detail in technical backup slides)

Our publication + H-spillover reported by Esposito et al. led to a novel PEC HER model

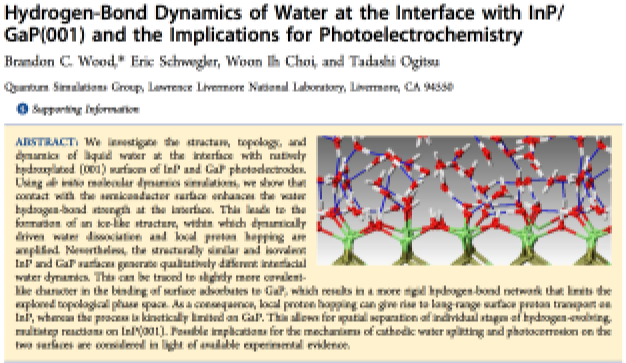


Low H diffusion barrier and low Heyrovsky barrier on semiconductor can activate additional HER channel (red allows)

- Addition of new HER channel involving surface transport (*2'*) could improve overall kinetics
- A numerical model that integrates transport and chemistry is currently being constructed as part of collaborative effort
- The model is designed to estimate optimal geometry/amount of co-catalyst for a given semiconductor/catalyst combination

Theory/experiment collaboration led to the novel HER model

J. Am. Chem. Soc. **135**, 15774 (2013)



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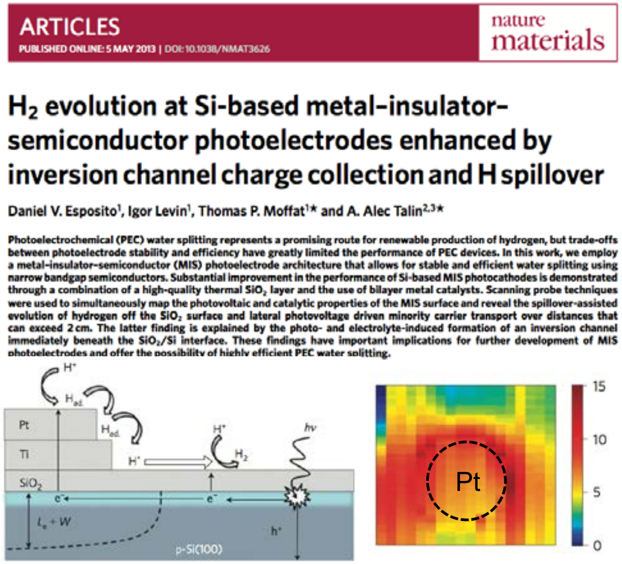
Nature Mat. **12**, 562 (2013)



ARTICLES

PUBLISHED ONLINE: 5 MAY 2013 | DOI: 10.1038/NMAT3626

nature materials

H_2 evolution at Si-based metal–insulator–semiconductor photoelectrodes enhanced by inversion channel charge collection and H spillover

Daniel V. Esposito[1], Igor Levin[1], Thomas P. Moffat[1]* and A. Alec Talin[2,3]*

Photoelectrochemical (PEC) water splitting represents a promising route for renewable production of hydrogen, but trade-offs between photoelectrode stability and efficiency have greatly limited the performance of PEC devices. In this work, we employ a metal–insulator–semiconductor (MIS) photoelectrode architecture that allows for stable and efficient water splitting using narrow bandgap semiconductors. Substantial improvement in the performance of Si-based MIS photocathodes is demonstrated through a combination of a high-quality thermal SiO_2 layer and the use of bilayer metal catalysts. Scanning probe techniques were used to simultaneously map the photovoltaic and catalytic properties of the MIS surface and reveal the spillover-assisted evolution of hydrogen off the SiO_2 surface and lateral photovoltage driven minority carrier transport over distances that can exceed 2 cm. The latter finding is explained by the photo- and electrolyte-induced formation of an inversion channel immediately beneath the SiO_2/Si interface. These findings have important implications for further development of MIS photoelectrodes and offer the possibility of highly efficient PEC water splitting.

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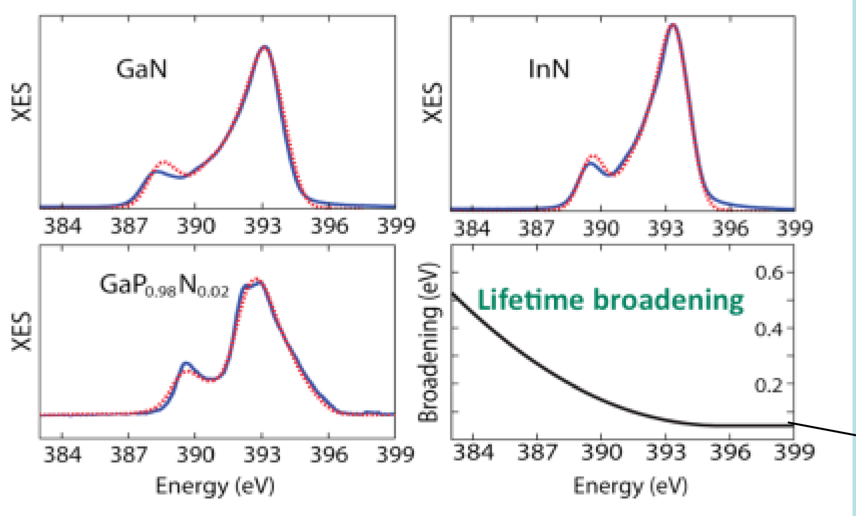
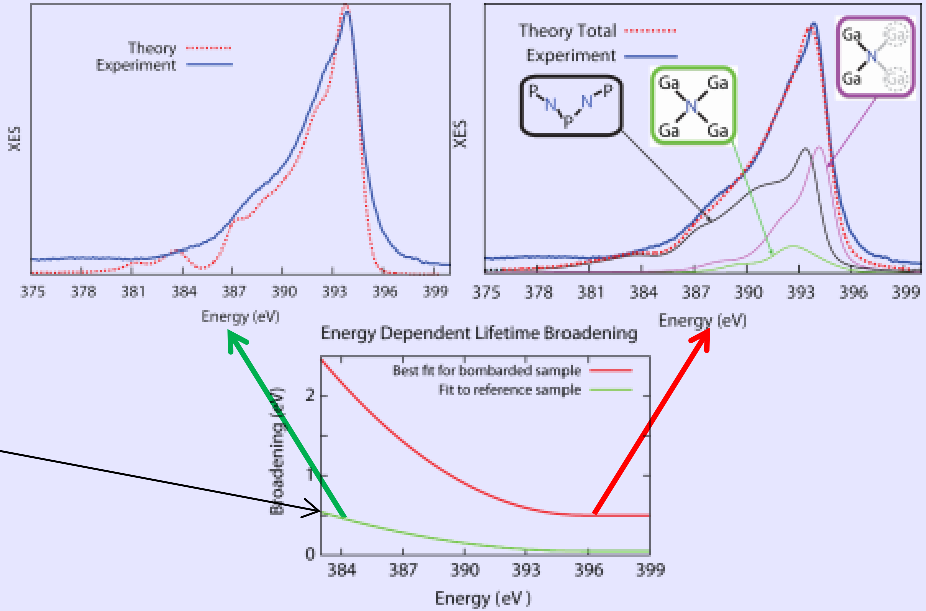
Accomplishments 4: N K-edge XES of GaInP$_2$/N; calibration to UNLV reference experiments completed, draft paper close to ready

Calibration of theoretical XES to exp. completed



- Reference nitride samples provided by NREL/LANL, XES measured by UNLV
- Nitrogen atoms are in well defined tetrahedral coordination with III (Ga/In) atoms
- Broadening parameters and absolute energy scale fitted to the experiments
- Derived species-specific parameters are transferable

Nitrogen environments in GaInP$_2$/N identified

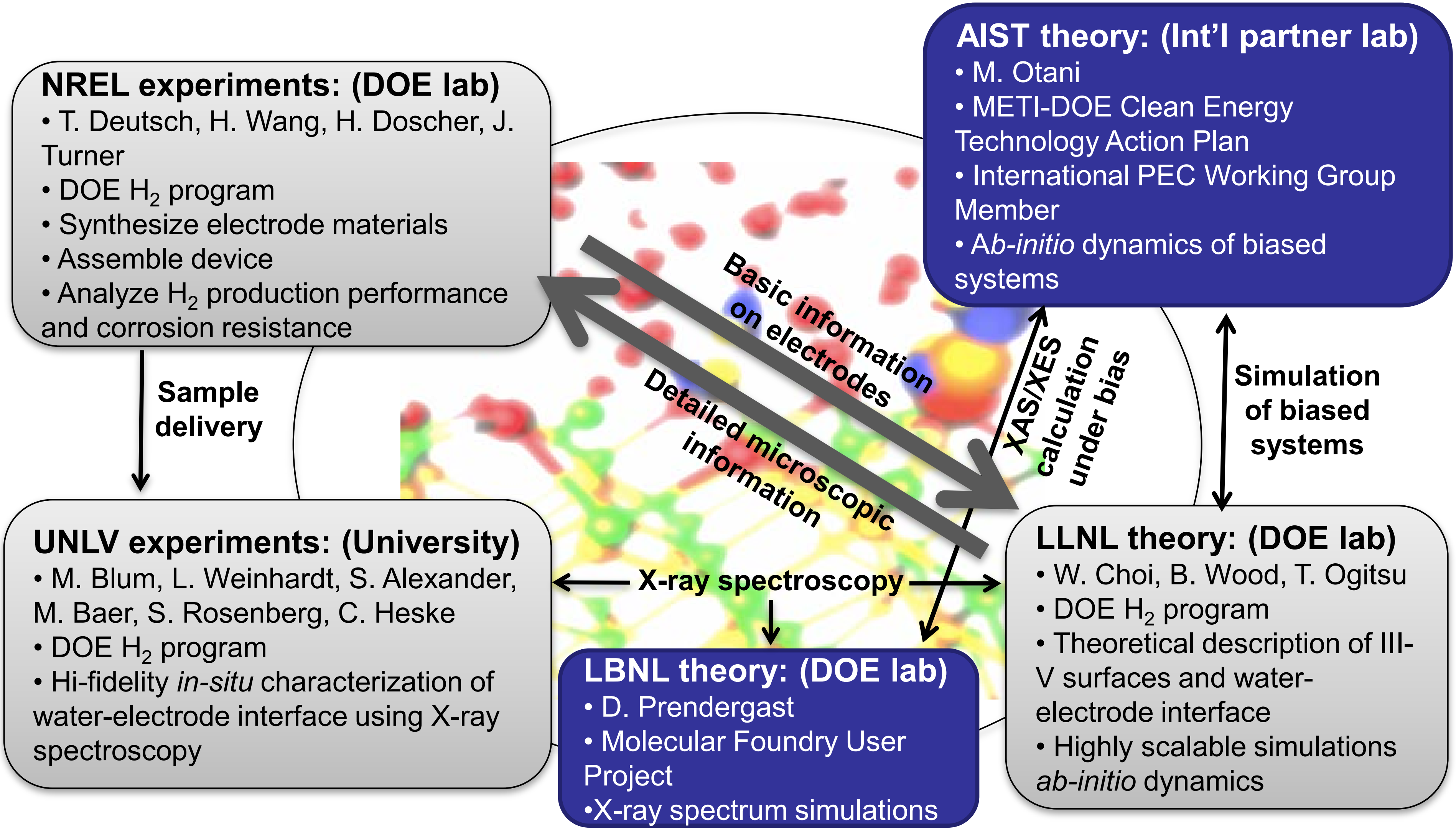


- Minor discrepancy in computed nitrogen environments from uncertainty in lifetime broadening
- Results could change with level of disorder, but no quantitative information yet available
- Use of UNLV experiments for determining broadening being discussed

Key to understanding role of PtRu decoration and N treatment to corrosion mitigation. UNLV/LLNL collaborative capability developed

Collaborations: Theory-experiment feedback cycle

We are moving toward direct comparison between in-operand characterization (NREL/UNLV) and simulation (LLNL/AIST)



NREL experiments: (DOE lab)
- T. Deutsch, H. Wang, H. Doscher, J. Turner
- DOE H_2 program
- Synthesize electrode materials
- Assemble device
- Analyze H_2 production performance and corrosion resistance

AIST theory: (Int'l partner lab)
- M. Otani
- METI-DOE Clean Energy Technology Action Plan
- International PEC Working Group Member
- *Ab-initio* dynamics of biased systems

Sample delivery

Basic information on electrodes

Detailed microscopic information

XAS/XES calculation under bias

Simulation of biased systems

UNLV experiments: (University)
- M. Blum, L. Weinhardt, S. Alexander, M. Baer, S. Rosenberg, C. Heske
- DOE H_2 program
- Hi-fidelity *in-situ* characterization of water-electrode interface using X-ray spectroscopy

X-ray spectroscopy

LLNL theory: (DOE lab)
- W. Choi, B. Wood, T. Ogitsu
- DOE H_2 program
- Theoretical description of III-V surfaces and water-electrode interface
- Highly scalable simulations *ab-initio* dynamics

LBNL theory: (DOE lab)
- D. Prendergast
- Molecular Foundry User Project
- X-ray spectrum simulations

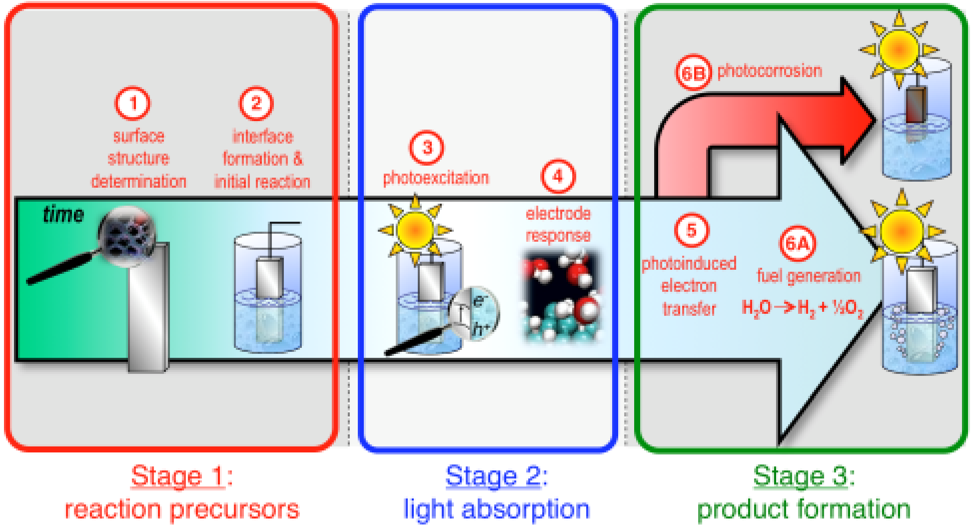
Proposed future work

Milestone	Description	% Completed
1	Characterize surface durability treatments, including chemical environment of N/Pt/Ru in $GaInP_2$, based on theoretical/experimental spectroscopy and publish the results	90
2	Develop a quantitative PEC HER model based on our finding on the H diffusion at the semiconductor-electrolyte interface	20
3	Further develop theoretical/experimental research program for unambiguous identification of the key descriptors that determine electrode durability (with NREL/UNLV)	30
4	Dynamical modeling of interfaces under bias potential spanning microscopic to macroscopic time scales (ultrafast electron dynamics and nonequilbrium electron/ion transport)	30

For successful execution, estimated requirements are two staff scientists plus two Postdocs for theory (LLNL), and one Postdoc and a PhD student for characterization (UNLV)

Example of Response to Reviewers' Comments: "tools not clear"

(further detail in supplemental slides)



- Stage 1: reaction precursors (**current focus**)
  - Tool: Ab-initio Density Functional Theory (DFT) molecular dynamics (MD) simulation
  - Limitations: electrons are always at the ground state (Stage 2: photo excitation cannot be simulated) and time & length scales are limited to 100 ps and 10 nm (Stage 3: product formation cannot be simulated)
- Stage 2: light absorption (in the near future, if necessary)
  - Tool: Time-Domain DFT MD simulation. Implementation completed by collaborators. Test simulations underway. See page 37.
  - Limitation: time scale up to 100 fs. Length scale up to 10 nm.
- Stage 3: product formation (in the future, if support level is increased)
  - Tool: a mesoscale phase-field model for electrochemical devices. Development underway as a collaboration. See page 38.
  - Limitations: need reliable input parameters (from DFT simulations and experiments)

Summary

- Compiled, reviewed, and shared available information on relevant materials and theoretical/experimental methods (approx. 1750)
- Three papers published in FY14, and a few more in preparation.
  - H diffusion at water-semiconductor interface, JACS **135**, 15774 (2013).
  - Water dissociation on GaP/InP(001) surfaces, JPCC **118**, 1062 (2013).
  - Modeling of Vollmer step of HER on MoS_2, JPCC **117**, 21772 (2013).
- Developing a numerical H_2 evolution model that incorporates interface H diffusion (WIP).
- As a part of SV team, continued joint theoretical/experimental study on III-V electrode surfaces (continue through FY14).
- Collaboration with Kristin Persson of LBNL (Materials Project) under discussion.

Technical backup 1-1: why/how lateral proton diffusion on semiconductor could be relevant for improving overall STH efficiency; basic background knowledge of HER

- HER process consists of two steps
- 1st step: Vollmer step
  - $M + H^+ + e^- \rightarrow M\text{-}H$
  - (M is catalyst material)
- 2nd step: Heyrovsky or Tafel step
  - $M\text{-}H + H^+ + e^- \rightarrow M + H_2$ (Heyrovsky)
  - $M\text{-}H + M\text{-}H \rightarrow 2M + H_2$

- Semiconductor surface tend to be V-step limiting
  - high V-step barrier
  - H/T-step barrier not known
- Pt is Heyrovsky or Tafel limiting
  - V-step barrier is low

Technical backup 1-2: why/how lateral proton diffusion could be relevant for improving STH efficiency; if no lateral H^+ diffusion is involved

- For individual Pt and semiconductor PEC HER electrodes, HER current density on Pt and on semiconductor for a given potential V are, $i_{Pt}(V)$ and $i_{semi}(V)$ (mA/cm^2), respectively
- On a semiconductor electrode with its surface area of S, total current density at the potential V will be $I= i_{semi}(V)*S$
- On a Pt electrode with its surface area of S, $I=i_{Pt}(V)*S$
- Suppose the surface of semiconductor electrode, whose total surface area is S_0, is decorated with Pt co-catalyst with surface area of S_1
- Total current of this system is $I_{tot}=i_{semi}(V)*(S0-S1)+i_{Pt}(V)*S_1$
- In the next page, it is shown that $i_{semi}(V)$ near Pt could be enhanced as much as $i_{Pt}(V)$
- If the enhanced current is not due to H provided from Pt via lateral diffusion, where do they come from? (Consider that V-step barrier of semiconductor cannot be as low as that of Pt.)

Technical backup 1-3: why/how lateral proton diffusion could be relevant for improving STH efficiency; evidence shown by Esposito et al (and in our JACS paper)

- On Pt, second step (H/T) is the limiting step.
  - If excess H adsorbed on Pt surface is consumed in some way, the first step (V) could provide more H to the Pt surface
- Let's examine Esposito et al.'s observation (right).
- HER is active at the silicon oxide surface area around Pt co-catalyst (see figure 4-h), and the total current is affected by the property of silicon oxide (see figure 2-b)
- Natural interpretation of these results will be that some of H adsorbed on Pt diffused to silicon oxide surface and evolved as H_2
- If this portion of H_2 evolution can be increased, total STH should be increased (to the point that V-step on Pt cannot supply additional H)

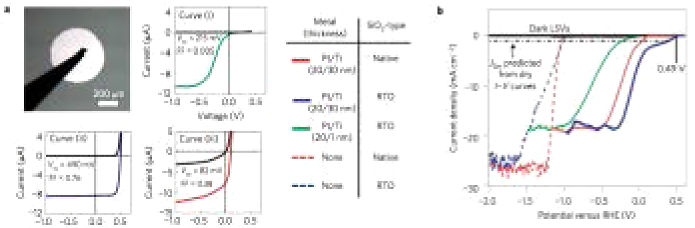


Figure 2 | Current–voltage curves recorded for various samples under simulated AM 1.5 illumination (100 mW cm^{-2}). a,b, Measurements performed in dry conditions (I–V curves) (**a**) and in deaerated 0.5 M H_2SO_4 (LSV curves) (**b**). For dry measurements, I–V curves were recorded for a single collector by contacting its front surface with a W probe as shown in the optical image in **a**. For PEC measurements, the exposed photoelectrode area was 0.43 cm^2. The dash–dot line in **b** represents the expected limiting current (J_{lim}) for the standard photoelectrode (20/30 nm Pt/Ti on 2 nm RTO SiO_2) based on the collector array geometry (138 collectors cm^{-2}) and the dry J_{sc} measured for a single collector in **a**. In **b**, the sudden changes in limiting current at negative potentials in the LSV curves are due to the build-up and detachment of H_2 bubbles from the electrode surface.

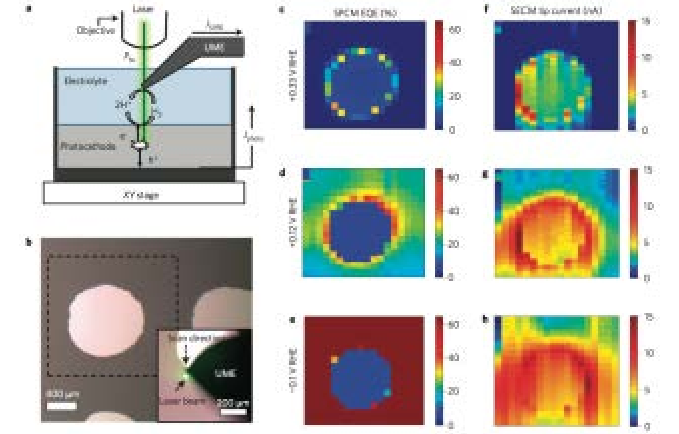


Figure 4 | Simultaneously recorded SPCM/SECM images of standard MIS photocathode. a, Schematic side-view of the SPCM/SECM set-up. **b**, Optical image of standard 20/30 nm Pt/Ti collectors on the MIS photocathode surface immersed in 0.5 M H_2SO_4, with dashed lines marking the region mapped in SPCM/SECM measurements. Inset shows a Pt ultramicroelectrode (UME) with an effective tip radius of ≈12 μm and a 532 nm laser beam (23.5 μW) positioned next to a collector. **c–e**, SPCM EQE images and **f–h**, SECM UME tip current images recorded with the photocathode held at three different applied potentials. In the SPCM images, the EQE is lower when the laser beam is positioned directly over the collector because the metal absorbs/reflects a large fraction of the incident light.

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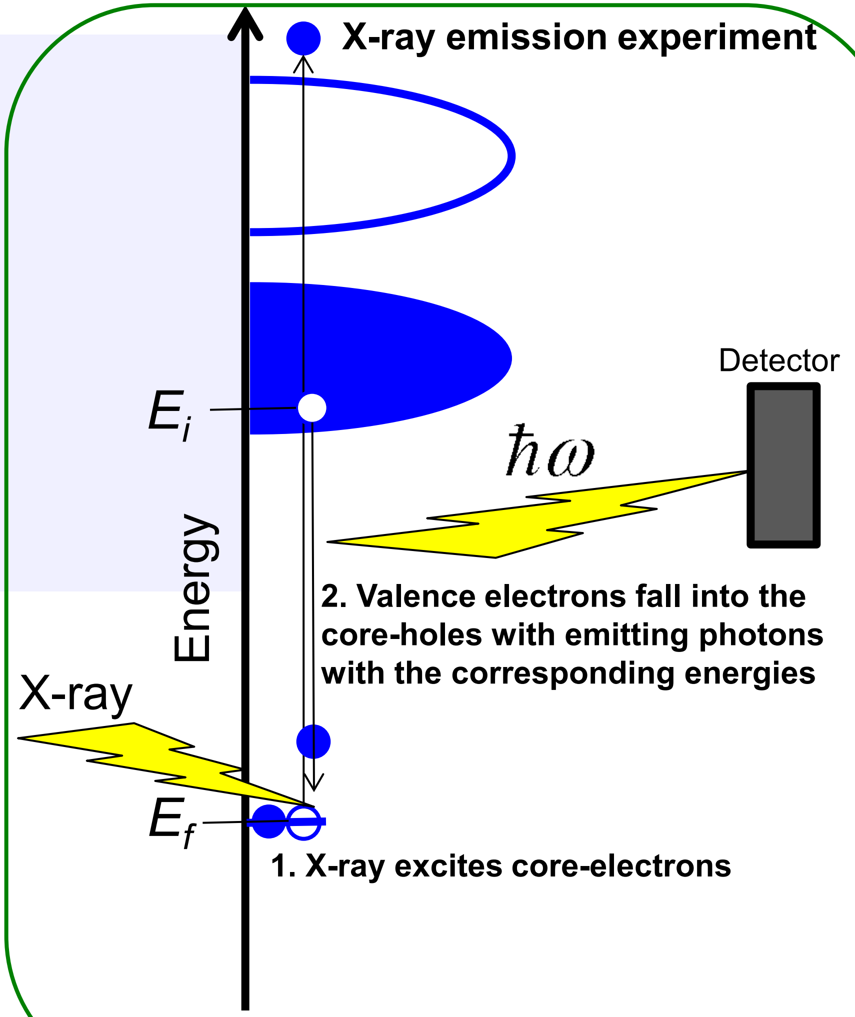
Technical backup 3: X-ray emission spectrum



2. Valence electrons fall into the core-holes with emitting photons with the corresponding energies

1. X-ray excites core-electrons

Performed by UNLV at ALS

X-ray emission spectrum calculations

$$\sigma(E)\propto\hbar\omega\left|\left\langle\psi_i\middle|\vec{\varepsilon}\cdot\vec{r}\middle|\psi_f\right\rangle\right|^2\delta(E_f-E_i-\hbar\omega)$$

Polarization vector of X-ray (take average over x, y, z components in our case)

Initial/final states wavefunctions are calculated with DFT

Issues solved using reference systems (GaN/InN):

- Detector/disorder broadening (Gaussian)
- Lifetime broadening (Lorentzian)
- Accurate calibration of energy scale to correct DFT error completed by comparing to XES of GaN/InN/$GaP_{0.98}/N_{0.02}$, where the samples were provided by Todd Williamson of LANL and XES measured by UNLV team with carefully controlled environment (same beam line, same detector etc).

Issues addresses by rational thinking:

- Candidate N environment atomic orbitals/hybridization/tendency of shift of N 1s core level

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