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Assistant Professor
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Challenges and Opportunities for Personal Electronics Applications

Dee Strand, Chief Scientific Officer, Wildcat Discovery Technologies
Mark Jones, Executive External Strategy and Communications Fellow, Dow Chemical

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Tierra Range, 2015 Chem Champs Runner Up and Student, Centenary College of Louisiana
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Artificial Photosynthesis: Making Fuels Directly from Sunlight

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Artificial Photosynthesis: Direct Production of Fuels from Sunlight

Nathan S. Lewis
Division of Chemistry and Chemical Engineering
California Institute of Technology

NSF CCI, DOE BES, AFOSR, Moore Foundation
Energy Conversion Strategies

Fuels

- Photosynthesis
  - CO₂
  - Sugar
  - H₂O
  - O₂

Electricity

- Semiconductor/Liquid Junctions
  - SC
  - O₂ → H₂
  - H₂O

- Photovoltaics
  - e⁻

Fuel from Sunlight
Lessons from Photosynthesis

Constructing the Pieces of a Solar H₂ Fuel Generator
Oxide Buffer Layer - Pattern Fidelity

An oxide buffer layer is critical for maintaining pattern fidelity during growth.

Large Area Au-Catalyzed Si Arrays

Nearly 100% vertically aligned, 75 μm length microwire arrays over areas > 1 cm².
Polymer Embedding of Si Rod Arrays

Polymer Embedding and Wafer Reuse

Integrated Architectures
Accomplishments and Future Direction

Platinized 6 min, 0.25 M HF 0.5 mM K$_2$PtCl$_4$

EXAMPLE OF EARLY POLYMER-EMBEDDED MICROWIRE ARRAY

- a) Si Wafer
- b) SiO$_2$
- c) Nafion
- d) PEDOT-PSS
- e) 
- f) 

Scale-up
Prototypes
Applied Research
Use Inspired Research
Basic Research
Si Wire/Ionomer Morphology

Dual (Si Wire Array/Nafion)/PEDOT-PSS

Dual (Si Wire Array/Nafion)/PEDOT-PSS

Si wire/QAPSF

Development of a microwire architecture capable of solar-driven water splitting

CORE-SHELL STRUCTURE

CURRENT-VOLTAGE BEHAVIOR AND CONVERSION EFFICIENCY

- Open-circuit potentials are additive:
  - Tandem junction: $E_{oc} = -1.21$ V vs. $E^\circ (O_2/H_2O)$
  - WO$_3$/liquid junction: $E_{oc} = -0.73$ V vs. $E^\circ (O_2/H_2O)$
  - $n$-$p$-$n$-$p^+$-Si junction: $E_{oc} = -0.5$ V vs. $E^\circ (O_2/H_2O)$

- Although unassisted water splitting is observed, STH conversion efficiencies remain low (<0.1%) due to the high band-gap of WO$_3$
Integrated Prototyping Approach in JCAP (cont.)

JCAP’s research prototypes are fully integrated systems

EXAMPLE: MEMBRANE AND MEMBRANE-FREE SOLAR-FUEL GENERATORS

- Identified requirements of the membrane (e.g., crossover rates, ion conductivity, etc.) needed to ensure intrinsically safe operation
- Revealed operational pH of the electrode surfaces even in 1 M buffer
- Revealed intrinsic concentration-polarization based energy losses in this configuration
- Validated the modeling effort with a real experimental system

Near neutral pH testing

The HER-HDS Hypothesis

Acid-Stable, Earth-Abundant HER Electro catalysts

- MoS$_2$ is also an HDS catalyst.
- HER and HDS share key hydric intermediates.
- HDS may be a predictor for HER
- Ni$_2$P was the first target.

Ni$_2$P HER in 1 M H$_2$SO$_4$; 120 mV OVERPOTENTIAL AT 10 mA/cm$^2$
**CoP HER in 1 M H$_2$SO$_4$; 85 mV overpotential at 10 mA/cm$^2$**

![Image of catalyst activity requirements](image)

**Relaxes Catalyst Activity Requirements**

![Graph showing catalyst activity requirements](graph)

![Diagram illustrating catalyst activity](diagram)
Performance Benchmarking of Electrocatalysts in JCAP

JCAP’s benchmarking facility allows for consistent performance evaluation of catalysts

Sensitivity analysis of Solar-Fuel Generators

Simulations indicate that photoelectrode improvements provide the greatest efficiency gains.

Improvements in photon capture and conversion efficiency can offer larger solar-to-hydrogen efficiency gains than reductions in catalyst overpotential.

Current state-of-the-art Earth-abundant catalysts


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Development of Alkaline stable photoanodes (cont.)

Protection of unstable photoanodes with thick TiO₂ overlayers offers another path to stability.

- Efficiency is equivalent to a 9.5% efficient photovoltaic in series with an electrolyzer
- Photocurrent is stable for more than 100 hours

Thick TiO$_2$ overlays are also compatible with III-V semiconductors that have near ideal band gaps

- GaAs: 1.4 eV bandgap
- GaP: 2.3 eV bandgap
- GaAs$_{0.6}$P$_{0.4}$: 1.7 eV bandgap

**Performance of III-V Semiconductors with Thick TiO$_2$ Layers**

**Wire-shape photoanodes stabilized by atomic layer deposited TiO$_2$**

- Stability: >400 hours
- FF remains the same

An Intrinsically Safe, 10% Efficient Solar-to-Hydrogen System with TiO$_2$-Stabilized III-V Tandem and Ni-Mo/NiO$_x$ Electrocatalysts

Blueprint for an Integrated Solar-Fuel Generator
Acknowledgements

Artificial Photosynthesis: Making Fuels Directly from Sunlight

Nathan Lewis
Professor of Chemistry,
California Institute of Technology

Joseph Fortunak
Professor of Chemistry,
Howard University

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