SUNLIGHT-DRIVEN MEMBRANE-SUPPORTED PHOTOELECTROCHEMICAL WATER SPLITTING

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Energy Conversion Strategies

Fuels

- CO₂
- Sugar
- H₂O
- O₂

Photosynthesis

Semiconductor/Liquid Junctions

Electricity

- Fuel
- Light
- Electricity

- SC
- H₂
- O₂

Photovoltaics
Fuel from Sunlight

QuickTime™ and a YUV420 codec decompressor are needed to see this picture.
Photoelectrochemical Cell

Light is Converted to Electrical+Chemical Energy
FTO slide printed with binary combinations of eight metals, pyrolyzed to form mixed metal oxides.

Typical photocurrent map of a slide of metal oxides. The X- and Z-coordinates give each spot’s identity, which is correlated with photo-catalytic activity. Here, combinations of Zn and Co in row #9 show photoanodic current.
Lessons from Photosynthesis
Turner Cell

Membrane-Supported Nanorod PEC H₂ Production
System Concept

Membrane-Supported Nanorod PEC H₂ Production

\[ 2 \text{H}_2 \text{O} \rightarrow \text{Light} \rightarrow 2 \text{H}_2 + \text{O}_2 \]

Diagram:
- **O₂ catalyst anode**
- **Solar PV & membrane**
- **H₂ catalyst cathode**

Water (H₂O) is split into hydrogen (H₂) and oxygen (O₂) under the influence of sunlight, utilizing a catalyst at the anode and cathode.
Why Radial Junction Solar Cells?

- Traditional device design requires long minority carrier diffusion lengths, and therefore expensive materials.
- Radial geometry allows for high quantum efficiency despite short minority carrier diffusion lengths.
Comparison of photovoltaic efficiency for (a) planar and (b) nanowire Si devices as a function of absorber thickness and minority carrier diffusion length

Relatively high efficiencies possible despite low diffusion lengths if depletion region recombination can be minimized


Membrane-Supported Nanorod PEC H₂ Production
Membrane-Supported Nanorod PEC H₂ Production
Enables New Materials

- High efficiencies possible despite low diffusion lengths
  => Inexpensive materials
  - Cheaper traditional materials
    - Silicon as a model system
  - Non-traditional, earth-abundant materials
    - Tandem partners with silicon
Relaxes Catalyst Activity Requirements

Hydrogen Evolution Reaction

Membrane-Supported Nanorod PEC H₂ Production
Why Macroporous Silicon?

- Macroporous silicon can be made from single-crystalline (100) silicon starting material.
- Bulk-limited $V_{OC}$ can be calculated from the Shockley diode equation:

$$V_{OC} = \frac{kT}{q} \ln\left(\frac{J_{ph}}{J_0}\right)$$

$$J_0 = \frac{qD_p n_i^2}{L_p N_D}$$
Making Macropores

5% HF + 10 mM SDS

Bulk Si
Macroporous Silicon

Membrane-Supported Nanorod PEC H₂ Production
I-V Measurements

Membrane-Supported Nanorod PEC H₂ Production
QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.
Testing a Nanorod Array Solar Cell

• Characterize a working nanorod solar cell
  – Ready fabrication of nanorod electrodes to put into a working cell
    • CdSe, CdTe
  – While not an ideal commercial material (toxicity, abundance), CdSe$_x$Te$_{1-x}$
    • is diffusion length limited
    • has ideal bandgap (~1.4 eV)
    • allows for an early test of the theory
The Alumina Template

- Allows for dense, uniform array of rods
- Carefully controlled dimensions
- Easily removable template
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Membrane-Supported Nanorod PEC $H_2$ Production

CdSeTe Nanorods

Porous Alumina
CdSeTe Nanorods
(via electrodeposition)
CdSe layer to prevent shunting
(via sputtering)
Titanium Back Contact
(via sputtering)

Alumina template removed in 1 M NaOH
CdSeTe Nanorods

- Excellent control over the dimensions and composition of these rods is possible
CdSeTe Nanorods

- Very uniform over relatively large area (a few cm²)


**CdSeTe Nanorods**

- Use a liquid junction to make a photoelectrochemical cell
- Measure current-voltage properties in the dark and light and compare nanorod performance to an analogous planar electrode

- Thin sputtered CdSe layer to prevent shunting through back contact – negligible contribution to performance
Why Radial Junction Solar Cells?

- Traditional device design requires long minority carrier diffusion lengths, and therefore expensive materials.

- Radial geometry allows for high quantum efficiency despite short minority carrier diffusion lengths.

Membrane-Supported Nanorod PEC H₂ Production
CdSeTe Nanorods

• Spectral response:

As expected from IV curves, planar usually exhibits better quantum yields – the above curves were chosen because their similar magnitudes allow for ease of shape comparison.

• Shape of the curve is more significant
  • Nanorod samples lose less quantum yield in the red
  • Since longer wavelength light penetrates deeper into the semiconductor, this is an indication that the nanorod geometry is more effectively collecting the carriers
Membrane-Supported Nanorod PEC H₂ Production

**Si Nanorods**

- Nanorod Array Growth Procedure

  - Mounting Wax
  - Porous Alumina
  - Silicon Nanorods
  - Conductive Catalyst Metal (via evaporation)
  - Supportive Nickel Substrate (via electrodeposition)

Alumina template removed in 1 M NaOH
Si Nanorods

- Silicon nanorod array after template is removed
Near-field scanning optical microscopy (NSOM) can measure nanowire photoconductivity as a function of excitation location.

Carrier collection lengths can be studied as a function of nanowire diameter, growth conditions, passivation, etc...

\[ R_{\text{wire}} = 17.9 \text{ M}\Omega \]
\[ R_C = 200 \text{ k}\Omega \]
\[ N_D \sim 5 \times 10^{13} \text{ cm}^{-3} \]
Effective diffusion length

Charge transport by drift and diffusion:

\[ J_n(x) = q\mu_n n(x)E(x) + qD_n \frac{\partial \delta n}{\partial x} \]

Charge continuity for electrons with effective, single-\(\tau\) recombination rate:

\[ \frac{\partial \delta n}{\partial t} = \frac{1}{q} \frac{\partial J_n}{\partial x} - \frac{\partial \delta n}{\partial x} \tau_{n,\text{eff}} + g_n \]

Monitor terminal current as function of injection point:

\[ J_{\text{meas}} = J_n \bigg|_{x=0} + J_p \bigg|_{x=0} \quad \text{when} \quad g_{n,p} \bigg|_{x=x_{\text{inj}}} = I_{ph} \]

Vary \(\tau\) to match measured photocurrent profile:

\[ L_{n,\text{eff}} = \sqrt{D_n \tau_{n,\text{eff}}} = 1.9 \text{ \textmu m} \quad \leftrightarrow \quad \tau_{n,\text{eff}} \approx 1 \text{ ns} \]

\[ L_{p,\text{eff}} = \sqrt{D_p \tau_{p,\text{eff}}} = 2.2 \text{ \textmu m} \quad \square \quad \tau_{p,\text{eff}} \approx 4 \text{ ns} \]

NSOM suggests minority carrier collection length is comparable to wire diameter.
Membrane-Supported Nanorod PEC H₂ Production

Surface Requirements for Semiconductor Heterojunctions

- Low Trap State Density
- Stable in Ambient Conditions
- Facile Interfacial Charge Transfer
An oxide buffer layer is critical for maintaining pattern fidelity during growth.

3 μm array, 500 nm Au, $T_{\text{growth}} = 1000{\degree}\text{C}$, $P_{\text{growth}} = 760$ Torr

**Membrane-Supported Nanorod PEC H$_2$ Production**
Large Area Au-Catalyzed Si Arrays

3 μm array, 500 nm Au, $T_{\text{growth}} = 1000^\circ\text{C}$, $P_{\text{growth}} = 760$ Torr, 30 min growth, 2 mole % SiCl$_4$ in H$_2$
Large Area Au-Catalyzed Si Arrays

3 μm array, 500 nm Au, $T_{\text{growth}} = 1000^\circ\text{C}$, $P_{\text{growth}} = 760$ Torr, 30 min growth, 2 mole % SiCl$_4$ in H$_2$

Nearly 100% vertically aligned, 75 μm length microwire arrays over areas > 1 cm$^2$.
Copper-Catalyzed Si Wire Arrays

3 μm array, 500 nm Cu, $T_{\text{growth}} = 1000^\circ\text{C}$, $P_{\text{growth}} = 760$ Torr, 10 min growth, 2 mole % SiCl$_4$ in H$_2$

Copper produces wire arrays that are structurally equivalent to gold.
Si Wire Array Junctions

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.
Membrane-Supported Nanorod PEC H₂ Production

Surface Requirements for Semiconductor Heterojunctions

- Low Trap State Density
- Stable in Ambient Conditions
- Facile Interfacial Charge Transfer
Surface Passivation

H
Si

PCl₅
benzoyl peroxide
or Cl₂(g)

Cl
Si

CH₃MgCl

CH₃
Si

Measured through STM, $T = 4$ K

Si(111)-CH₃

0.38 nm

1 nm
SEM of Chlorinated Si Nanorod Arrays

- Chlorination with PCl$_5$ is known to cause etching of silicon surfaces

- Functionalized surfaces appear rough, but etching is not destructive
Electrical Performance of Methylated Silicon Nanowires

- Methylated wires (60 nm diameter)
  - Sensitive to gate voltage
  - Maintain higher conductance
- Hydrogen terminated surfaces
  - Deteriorate

Constructing the Pieces of a Solar $H_2$ Fuel Generator
Polymer Embedding of Si Rod Arrays

Silicon rod array on silicon substrate

Cast or grow polymer

Remove from substrate

Silicon rod array in polymer film

PDMS (polydimethylsiloxane)
Large Area Rod Array Removal

Top-down view

- Large area arrays (> 1 cm²) transferred in one piece.

Side view

- Conformal coating from top to bottom of rods

115 μm
Embedded Rod Pattern Fidelity

- Inter-rod angle and spacing is constant before and after PDMS casting and removal.
- Apparent rod diameter differences due to examination of rod tips versus base.

<table>
<thead>
<tr>
<th></th>
<th>Rod diameter (µm)</th>
<th>Shortest inter-rod distance (µm)</th>
<th>Angle (θ, °)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before removal</td>
<td>2.5 ± 2</td>
<td>8.6 ± 2</td>
<td>92 ± 9</td>
</tr>
<tr>
<td>After removal</td>
<td>4.6 ± 4</td>
<td>8.8 ± 3</td>
<td>94 ± 2</td>
</tr>
</tbody>
</table>
Large Area Rod Array Removal

- Large area arrays (> 1 cm²) transferred in one piece.
- Conformal coating from top to bottom of rods.
Regrown Arrays

Membrane-Supported Nanorod PEC H₂ Production
Polymerization from Si Rod Surfaces

Allylated Si base

Methylated Si base

polymer sheath grown around rods
• 1.23 V needed to electrolyze water

• Requires a heterojunction or dual junction

• Single absorber: band gap of 2.0-2.6 eV that straddles the necessary potentials

• Photoanode and photocathode absorbers:
  - Band gaps can better match the solar spectrum (1.1-1.4 eV)
  - Allows for greater flexibility in materials design
  - Efficiency could approach 25%

• Optimal structure would have several light-absorbing layers absorbing different portions of the spectrum with an overall potential greater than 1.23 V
Fe$_2$O$_3$ Nanowires

Membrane-Supported Nanorod PEC H$_2$ Production
**System Concept**

\[
2 \text{H}_2\text{O} \xrightarrow{\text{Light}} 2 \text{H}_2 + \text{O}_2
\]

- **O_2** catalyst anode
- **H_2O**
- **Solar PV & membrane**
- **H_2** catalyst cathode
- **2H_2**
Conclusions

• Without **massive** quantities (10-20 TW by 2050) of clean energy, CO₂ levels will continue to rise

• The only sufficient supply-side cards we have are “clean” coal, nuclear fission (with a closed fuel cycle), and/or cheap solar fuel

• We need to pursue globally scalable systems that can efficiently and cost-effectively capture, convert, and store sunlight in the form of chemical fuels

  – He that can not store, will not have power after four

• Semiconductor/liquid junctions offer the *only* proven method for achieving this goal, but we have a great deal of fundamental science to learn to enable the underpinnings of a cost-effective, deployable technology

  – Nanorods, randomly ordered junctions to generate the needed potential

  – Catalysts to convert the incipient electrons into fuels by rearranging the chemical bonds of water (and CO₂) into O₂ and a reduced fuel
Four Strategies

New Redox Couples

Nonaqueous Solvents

Surface Modification

Inexpensive Semiconductor