Solar Fuels From Light & Heat

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Enhance solar utilization

5% Ultraviolet  43% Visible  52% Infrared

Dionne

Photo-electrochemical cell

O₂/H₂O

E₀

Eᵥb

Ectype

hv

H⁺/H₂

Semi-conductor Anode Metal Cathode

Power (W m⁻² nm⁻¹)

1.8 eV

Wavelength (nm)
Combining heat & light: what’s possible?

![Diagram showing the relationship between temperature and solar-to-fuel efficiency.](Diagram)

**Graph 1:**
- **Y-axis:** \( \frac{J_{H_2} \cdot HHV}{P_{\text{sun}}} \)
- **X-axis:** Temperature (T in K)
- **Legend:**
  - Thermal energy
  - Electrical energy

**Graph 2:**
- **Y-axis:** Solar-to-Fuel Efficiency
- **X-axis:** Energy Gap (E_g in eV)
- **Note:** 10% efficiency level marked as unreachable temperature.

Reference:

[chuehlab.stanford.edu](http://chuehlab.stanford.edu)
Can thermal energy make existing materials better?

Low mobility, high stability semiconductor: \( \text{Fe}_2\text{O}_3 \)

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
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<tbody>
<tr>
<td>Ti doped ( \alpha)-Fe(_2)O(_3)</td>
<td>30 nm</td>
</tr>
<tr>
<td>Pt</td>
<td>200 nm</td>
</tr>
<tr>
<td>Al(_2)O(_3)(0001)</td>
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Pulsed-Laser Deposition

TEM

SEM

AFM
Enhancement with temperature & light intensity

0.1 M NaOH pH = 13

Solar simulator
Thermocouple
Nitrogen
Water bath
Stirrer

Enhancement with temperature & light intensity:

Δη ~ 70 mV

E vs RHE [V]

J [mA cm$^{-2}$]

5%Ti-Fe$_2$O$_3$

9 suns
1 sun

0.8 1.0 1.2 1.4 1.6 1.8

0.0 0.1 0.2

1.19 V
1.24 V

72 °C
48 °C
25 °C
7 °C
Enhancement with temperature & light intensity

Baseline: 25 °C 1 sun

72 °C 1 sun

72 °C 9 sun

Relative Potential [V]

\[ V_{eq}, \eta, V_{ph}, V_{on} \]
Thermally-enhanced fill factor

[Graph showing J vs. E for 0.1% Ti-doped Fe$_2$O$_3$ under different temperatures (7 °C, 25 °C, 48 °C, 72 °C) and light conditions (9 suns, dark). The graph indicates an increase in current density (J) with temperature and light exposure.]

$\Delta E$ [V] vs. Temperature

- 0.45 $\rightarrow$ 4.5 mA cm$^{-2}$
- 160 mV
Another low-mobility semiconductor: BiVO₄

Effect of doping

Effect of catalysts

0.5 M K₃PO₄ buffered pH = 7 Electrolyte
Thermally-enhanced saturation current

Significant enhancement in photocurrent without significant decrease with photovoltage

1 mM [IrCl₆]⁴⁻/0.1 mM [IrCl₆]³⁻
Stability

Fe$_2$O$_3$

9 suns, $I = 2$ mA cm$^{-2}$
70°C

BiVO$_4$

1 sun $E = 0.6$V vs. RHE

42°C

25°C

9°C

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Thermally-enhanced PEC

PEC / Solar cells

cooling

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Going > 100°C: an all-oxide approach

< 100 °C

300 - 700 °C

Gas Bubbles

Light Absorber

Liquid Electrolyte

Membrane

Light Absorber

Proton-conducting Oxide

Air

Membrane

eSolar

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A new class of solid state PEC for concentrated sunlight
Compatible with elevated temperature
Single device, isothermal
Photon absorption
Electron/hole pairs excitation
Carrier diffusion
Semiconductor/Mixed Conductor Heterojunction

• Light absorber/MIEC interface:
  – Electrons: thermionic emission
  – Holes: mostly reflected
Semiconductor/Mixed Conductor Heterojunction

2H₂O(g) + 4e⁻ → 2H₂(g) + 2O²⁻

- MIEC/gas interface
  - Electron transfer, HER

Paper submitted
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Semiconductor/Mixed Conductor Heterojunction

- Gas diffusion (stagnation layer)
  - $\text{H}_2\text{O}$: continuously supplied, diffuse to the surface
  - $\text{H}_2$: diffuse away from surface, then removed
Oxygen ions transport to the air side and react with holes
• Broad maximum at ~750 K, 17 %
• Below 700 K: slow thermionic emission
• Above 700 K: insufficient photovoltage
Figure 1
Figure 2
Figure 5

(a) SEM image of macroporous BiVO₄

(b) SEM image of nanoporous BiVO₄

(c) Current density (mA/cm²) vs. E (V) vs. RHE graph for dark current, macroporous BiVO₄, and nanoporous BiVO₄.
Figure 6

(a) Current density (mA/cm$^2$) vs. E (V) at different temperatures.

(b) Current density (mA/cm$^2$) at 0.80 V vs. RHE for different temperatures.

(c) Comparison of current density at 0.80 V vs. RHE for Small BiVO$_4$ NPs and Large BiVO$_4$ NPs at different temperatures.
Figure 8

The figure depicts the relationship between current density and Voltage (V) vs. RHE for different temperatures. It shows a set of curves for 9°C, 25°C, 42°C, 61°C, and 80°C, illustrating how the current density changes with increasing temperature and voltage.