Nanostructuring for Efficient Energy Conversion

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Electricity—Humans like it!

**Earth at Night 2001** : Human-made lights highlight particularly developed or populated areas of the Earth’s surface, including the seabords of the eastern United States.

US electricity demand (0.418 TW in 2002)

NASA/courtesy of nasaimages.org. Credit: NASA/Goddard Space Flight Center Scientific Visualization Studio
Electricity

- A favorite form of energy is electricity

- Where does electricity come from?
  - Even though electricity is a very useful form of energy, there are very few direct sources of electrical energy on earth. (One example is a lightning storm.)
  - Electricity is really a secondary energy source, which we get by converting another type of energy into it.

- The original source of energy can be
  - Nuclear
  - Wind
  - Sun
  - Hydrodynamic
  - Chemical energy
But

- Most of the electricity we use comes from chemical energy, namely burning fossil fuels

Global Energy Consumption (EJ)

Exajoule = $10^{18}$ Joules

85% of world-wide energy consumption is from fossil fuels

Carbon Dioxide Emissions

Burning fossil fuels generates carbon dioxide, CO₂.

Why is CO₂ a problem?

- Most of this carbon dioxide is being poured directly into the atmosphere, where it adds to the existing CO₂ levels.
- The CO₂ concentrations in the earth’s atmosphere have already risen by over 25% in the past century.

- CO₂ is a greenhouse gas. Increasing its concentration in the earth’s atmosphere leads to a warming of the earth. “Global warming”
- Changes to the ocean acidity
Global Potential of Solar Energy

Exergy sources scaled to average consumption in 2004 (15 TW)

Global solar resource: 120,000 TW

Slide from Paolo Bosshard, GCEP

( Hermann, Energy, 2006)
Transportation

• We still need portable, stored energy
  o We need portability for many applications
  o We also need energy on demand

• Some choices
  o Chemical fuels
  o Batteries / Electrochemical cells
  o Electrical energy storage
Together these two sectors make up 2/3 of US energy demand.
No Single Solution

- Energy problem is so large that multiple solutions will be needed.
- No single technology can meet the world’s growing energy needs while reducing emission of greenhouse gases.
- A collection of energy technologies must work in concert to produce, store, and consume the 28 TW of energy that humans will demand by 2050.
Same Underlying Phenomena

- The diverse energy devices needed, such as photovoltaics, fuel cells, and batteries, all exploit **similar physical and chemical phenomena**.

- By identifying and exploiting common threads, we can lay the groundwork for new generations of many families of devices.

- Each process
  - Creates a positive and negative charge carrier (electron and hole)
  - Moves the charge
  - Recombines charge
A Photovoltaic Device Splits, Transports, and Recombines Charge

- Photovoltaic devices convert light into electrical energy

- Typically consist of semiconductor materials
  - Light is absorbed
  - Charge carriers (electrons and holes) are created
  - Charge carriers are separated
  - Current flows in a circuit
Fuel cells do the same

*Fuel cells are devices that convert chemical energy into electrical energy*

- Generate charged species (ions, electrons)
- Move the charged species (ions, electrons)
- Recombine

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2 \text{e}^- \]

\[ 2\text{H}^+ + \frac{1}{2} \text{O}_2 + 2 \text{e}^- \rightarrow \text{H}_2\text{O} \]
Photoelectrocatalysts do the same

*Photoelectrocatalysts convert light energy into chemical energy*

- Generate charged species (electrons, holes, ions)
- Move the charged species
- Recombine

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

\[
H_2O + 2h^+ \rightarrow \frac{1}{2} O_2 + 2H^+
\]
How can we improve this process?

Answer: **Make things smaller**

- Charges don’t have as far to move

- Separation and recombination of charge may improve
  - If chemical reaction, can get more active surfaces for better reaction rates (kinetics)

- More light may be absorbed
  - If induced by light, may get better absorption by tuning bandgap through quantum confinement
CNEEC seeks to understand and solve cross-cutting fundamental problems at the nanoscale to improve materials properties such as light absorption, charge transport, and catalytic activity. These efforts are aimed at efficient energy conversion and storage in advanced devices such as photovoltaics, fuel cells, and batteries.

**RESEARCH PLAN AND DIRECTIONS**

We will use nanostructuring to tune thermodynamics, enhance kinetics, manage photonics, and accelerate charge transport in materials, each of which will be used to improve performance and efficiency in energy conversion devices.
Thematic Research Groups of the Center

• Manipulate sub-nanometer particles – namely electrons, photons, ions, atoms, and molecules – by tuning material properties through nanostructuring.

Three thematic research efforts:

1. Tuning Thermodynamics/Kinetics by Nanostructuring (TRG1)
2. Photon Management (TRG2)
3. Optimizing Charge Transport at Reduced Sizes and Dimensions (TRG3)
The CNEEC Team at Stanford

Co-Directors

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Stacey Bent (ChE)
Fritz Prinz (ME)

Executive Director

Turgut Gür (MSE)

Tom Jaramillo (ChE)
Yi Cui (MSE)
Xiaolin Zheng (ME)
Bruce Clemens (MSE)

DOE-EFRC Center on Nanostructuring for Efficient Energy Conversion
Two Examples

- Earth abundant materials for photovoltaics
  - Nanoscale device geometry for better collection of charge carriers

- Nanostructured photoelectrocatalysts
  - Independently tunable properties for light absorption and surface reaction
Two Examples

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Photovoltaics at Large Scale

- Constant growth and technology improvement for the past 20 years.
  - Prices of modules decrease on average 7.5% yearly.
  - Production has increased on average 18% per year; even faster recently.
  - Still – not good enough – current PV is just a few percent of all new generation capacity
    - Low level of deployment of solar energy
    - 2007: 2.6GW 2008: 5.95GW 2030: >11.2GW
  - It will take many decades before PV modules can substantially contribute to electricity generation. 30 TW of power needed by 2050

- For PV to contribute a significant part of the energy portfolio, cost per kWh needs to be reduced
  - Currently ~20¢/kWh
  - Target ~5¢/kWh

- Intermittency issue will also need to be addressed
Solar Cells

- A solar cell converts light into electrical energy
- A good solar cell should:
  - Absorb sunlight well
  - Convert the energy from the sunlight into electrical energy with good efficiency
    - Efficiency = percentage of solar power converted to electrical power
  - Not cost too much
The Need for Photon Management in PV (and PEC)

PV and PEC materials exhibit a large mismatch between electronic and optical lengths scales

- Thick cells are desirable from a photonics standpoint to enable efficient light absorption
- Thin cells are desirable from an electronics standpoint to enable efficient charge extraction

Both approaches have their advantages and disadvantages:

- **Thin Cell**
  - Excellent absorption
  - Poor charge extraction
  - Expensive

- **Thick Cell**
  - Poor absorption
  - Excellent charge extraction
  - Inexpensive

**Solution?!**

We need:

- Excellent absorption
- Excellent charge extraction
- Inexpensive

**Stanford University**

**Mark Brongersma**
Minority Carrier Diffusion Length Can Limit Charge Collection in PV

\[ L_x = \sqrt{\tau_x D_x} \]

- \( \tau_x \) = lifetime
- \( D_x \) = diffusion coefficient (depends on \( \mu \) - mobility)

- Characterizes how far the photogenerated carrier can travel before it is lost via recombination.

Why not just make the layers thinner than \( L_d \)?

Not enough absorption.
Interdigitated Architecture

- Maximization of photon absorption and minimization of required diffusion length
- Layers thinner than minority carrier diffusion length
- Full collection of photogenerated carriers is possible
- Interpenetrated architecture insures full absorption of incident photons with $E \geq E_g$. 
Interdigitated Architecture

Array of Si nanowires
Self-Organized Nanostructured Photovoltaics

Self-organizing nanostructured solar cells

Desired length scale (100’s nm) and morphology (platelets, cylinders) achieved by:

- Growth-controlled phase segregation
- Templated phase segregation
Modeling Nanostructured PV Geometry

- Nanostructuring leads to an increase in dark current
- This can more than offset the gain by increased photo-carrier collection

\[
\frac{I_{\text{light}}}{AJ_0} = \frac{\int_{AM1.5G}^{BG} \left(1 - e^{-a_{\lambda x}}\right) \left(\frac{\pi R^2 I_\lambda}{hc/\lambda}\right) q d\lambda}{\left(\pi R^2 + 2\pi R x\right) q \left(\frac{D_n n_i^2}{L_n N_a} + \frac{D_p n_i^2}{L_p N_d}\right)}
\]

- Modeling is carried out to determine optimal nanostructured geometry and materials properties

A solar cell that produces energy is also a diode in forward bias

Planar Extended junction
Test system:

- **Cu₂ZnSnS₄ (CZTS)**
  - P type semiconductor
  - 9.6% efficiency: Cu₂ZnSn(S,Se)₄ (Mitzi et al)
  - 6.7% efficiency (Katagiri et al)
  - 1.45 eV Eg
- CZTS has kesterite structure
- Compare with CuInGaSe₂ – 19.5% efficient – thin film architecture
- Earth abundant materials
Earth Abundance

Relative abundance of the chemical elements in Earth’s upper continental crust

Abundance, atoms of element per 10^6 atoms of Si

Rock-forming elements

Major industrial metals in Bold

Precious metals in Italic

Rare earth elements

Rarest “metals” Os Ir

U.S. Geological Survey Fact Sheet 087-02
PV Absorber Deposition Methods

Our approach

- **Chemical Bath Deposition (Bent)**
  - In conjunction with:
    - Metal Ion Exchange
    - Sulfidization
  - Solution-based deposition technique used for rapid, economical growth of thin films on a variety of substrates.
  - Applicable to a wide range of materials (CdS, ZnS, SnS)

- **Sputter Deposition (Clemens)**
  - Reactive sputter deposition
  - High quality films
Chemical Bath Basics

- Deposition of thin films on a solid substrate from a reaction occurring in solution (aq)

Simple view

\[ aM^{n+}(aq) + bX^{m-}(aq) \rightleftharpoons M_aX_b(s) \]

\[ M_aX_b(s) \rightleftharpoons aM^{n+}(aq) + bX^{m-}(aq) \quad K_{sp} = [M^{n+}]^a[X^{m-}]^b \]

CZTS

\[ Sn^{2+}(aq) + S^{2-}(aq) \rightleftharpoons SnS(s) \quad K_{sp} = 10^{-26} \]

\[ Zn^{2+}(aq) + S^{2-}(aq) \rightleftharpoons ZnS(s) \quad K_{sp} = 3 \times 10^{-25} \]

\[ Cu^{2+}(aq) + S^{2-}(aq) \rightleftharpoons CuS(s) \quad K_{sp} = 5 \times 10^{-36} \]
CBD Mechanisms

- Need a “time release” method for controlling $[M^{2+}]$ and $[S^{2-}]$ in solution to prevent homogeneous nucleation (precipitation)

- Use ligands to complex with metals

- Use $S^{2-}$ as a product from a slow decomposition reaction
CZTS Fabrication Method

- **Large area scalable**
  - high throughput
- **No expensive equipment**
  - open air
  - no high vacuum
  - aqueous
- **Controllable**
  - CBD is well-established for CdS in CIGS and CdTe devices
CBD Process for CZTS

ZnS (via CBD)
SnS
Cu₂S
Molybdenum
SiO₂ substrate

Sulfidization for 120 minutes at 500°C

Cu₂ZnSnS₄
Molybdenum
SiO₂ substrate

ZnS
SnS
Cu₂S
Mo
Glass

Cu₂ZnSnS₄ pre-sulfidization

Cu₂ZnSnS₄ post-sulfidization

Artit Wangperawong
CZTS Efficiency Trends

Best Research-Cell Efficiencies

From www.nrel.gov/ncpv/thin_film/docs/kaz_best_research_cells.ppt
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Photoelectrocatalysts

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]

\[ \text{H}_2\text{O} + 2\text{h}^+ \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ \]

\[ 2\text{H}_2\text{O} \xrightarrow{\text{hv}} 2\text{H}_2 + \text{O}_2 \quad \Delta E = 1.23 \text{ eV} \]

**Key Material Properties**

a) Bandgap  

b) Band alignment  

c) Catalytic surface  

d) Stability
Solar Spectrum

AM1.5 Solar Spectrum

Intensity vs. Wavelength (nm)
Absorption of Light

- There is an optimal bandgap for a PEC device using solar radiation
  - Only photons with energy above the bandgap of the semiconductor will excite e-h+ pairs
  - The energy of photons above the bandgap is not utilized, because holes and electrons quickly relax to band edges, giving off heat

- If $E_g$ is too low, lots of light absorbed, but insufficient energy to drive redox reactions and absorption of high energy photons leads to energy loss

- If $E_g$ is too large, absorb just a fraction of the solar spectrum

- For AM1.5, $E_g \approx 2$ eV is ideal for single-layered PEC devices

\[
\begin{array}{cccc}
\lambda(\text{nm}) & 475 & 510 & 650 \\
E_{ph}(\text{eV}) & 2.61 & 2.43 & 1.91 \\
\end{array}
\]
Challenge in PEC

Not many semiconductors with bandgap ~ 2.0 eV are also catalytically active and stable in solution

Possible solution: Nanoengineered materials
Possible Nanoscaled PEC Geometry

Nanostructured semiconductor for light absorption

Nanoscale coating for stability and catalysis
**Nanostructured Semiconductors for PEC**

**Example: MoS$_2$**

- MoS$_2$ can be quantum confined from its bulk bandgap of $\sim$1.2 eV to a more suitable bandgap for water splitting ($\sim$1.8 – 2.2 eV)

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**Size (L)**

**Bandgap ($E_g$)**

**Improved water splitting ability**

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*Figure courtesy Zhebo Chen*

Manganese Oxides as Catalyst

<table>
<thead>
<tr>
<th>Metal</th>
<th>Abundance (mg/kg)</th>
<th>Price ($/kg)</th>
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<tbody>
<tr>
<td>Platinum</td>
<td>5.0*10^{-3}</td>
<td>43000</td>
</tr>
<tr>
<td>Iridium</td>
<td>1.0*10^{-3}</td>
<td>13000</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>1.0*10^{-3}</td>
<td>2800</td>
</tr>
<tr>
<td>Manganese</td>
<td>9.5*10^{2}</td>
<td>3</td>
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</tbody>
</table>


Atomic Layer Deposition (ALD)

1) Pulse reactant into the reactor
2) Purge to remove excess reactant
3) Pulse counter-reactant
4) Purge to remove products/excess counter-reactant
5) Repeat 1-4 as many times as desired

Stanford University
ALD is a powerful film deposition method

- Advantages to ALD:
  - Excellent conformality
  - Excellent uniformity
  - Elimination of detrimental gas phase reactions

- Major disadvantage:
  - Slow deposition rate (100-300 nm/hr typical)

Al₂O₃ deposition in DRAM
Infineon Technologies
(www.future-fab.com)
Atomic Layer Deposition of MnO$_x$

Manganese Precursor

200 cycles on Si substrate at 250°C

Growth Rate (Å/cycle) vs. Pulse Time (s)

Number of Cycles vs. Thickness (nm)

Mn(EtCp)$_2$/N$_2$ purge/H$_2$O/N$_2$ purge (2s/5s/6s/10s)

150°C
200°C
250°C

Sang Wook Park
Experimental Process

\[ \text{Mn(EtCp)}_2 + \text{H}_2\text{O} \rightarrow \text{MnO} \]

480ºC Annealing

Rotation @1600rpm

Electrolyte (0.1M KOH)

Counter Electrode (Pt)

Reference Electrode (Hg/HgO)

Working Electrode (Glassy Carbon)

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Morphology on Glassy Carbon

1000 cycles of MnOₓ on GC substrate under 250°C

Bare glassy carbon

ALD before annealing

ALD after annealing

Increased Surface Area

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Sang Wook Park
Linear Sweep Voltammetry

**Experimental Condition**
- Rotation rate = 1600rpm
- Sweep rate = 20mV/s
- Temperature = 23°C
- Electrolyte = 0.1M KOH, O₂ sat.
- Reference electrode = Hg/HgO
- Counter electrode = Platinum wire

**Nobel Metal Benchmark Catalyst**
Pt, RuOₓ on GC - electrodeposition
(Courtesy of Dr. Choi)

**Good Catalytic Activity**

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

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \]
Conclusions and Outlook

• There is no single solution to the energy challenge. We need to work on a broad portfolio of approaches.

• CNEEC carries out a cross-cutting program of basic research in understanding how to use **nanostructuring** to achieve step-out improvements in energy conversion efficiencies.

• Build nanoscale structures to achieve the following objectives
  - Tune thermodynamics and kinetics
  - Manage photonics
  - Accelerate charge transport

• The long-ranging goal is to achieve improved conversion efficiencies in photovoltaics, batteries, photoelectrochemical fuel synthesis, fuel cells, supercapacitors, and hydrogen storage
Acknowledgments

- CZTS
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  - Kristine Pangan-Okimoto

- MnO$_x$
  - Sang Wook Park
  - Yelena Gorlin
  - Dr. Shin-Jung Choi
  - Prof. Tom Jaramillo

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