Challenges and Solutions for More Sustainable Energy Systems

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Lives and Livelihoods Depend Upon Energy

Energy for food, water, shelter, transportation, industry…
The Global Energy Challenge is Complex

- Environment
- Human needs
- National security
- Economy
We All Agree: The Global Energy System is Under Stress

- 7 billion people and growing
- 2 billion people without modern energy services
- Energy spending now 7% of U.S. economy
- Military fuel supply lines threatens lives
- Nearing 400 ppm CO₂ in the atmosphere
Together these two sectors make up 2/3 of US energy demand.
Electricity—A Favorite Form of Energy

**Earth at Night 2012**: Composite assembled from data acquired by the Suomi NPP satellite in April and October 2012.

*US electricity generation
0.46 TW in 2012*

**Credit**: NASA Earth Observatory/NOAA NGDC
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
Global Energy Consumption

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

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

Projected Energy Demand

Energy Demand (EJ)

50% increase in energy demand by 2030

1 EJ = 10^{18} J

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
- .....
Renewable Global Exergy Flows

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

- Solar and wind are the largest renewable energy resources
  - Solar: 8,600 times current human energy use
  - Wind: 60 times current human energy use
  - But, cost, intermittency and variable global distribution must be addressed
  - Energy storage and a more capable grid will be critical to dealing with intermittency

- Terrestrial and marine biomass resource can contribute
  - Biomass is likely to continue to contribute as an energy resource but with limits due to competition for land use, water, food production …

- Other renewable energy resources may provide local resources but will have limited impact on global energy supply
  - Waves and tides have limited capacity and are widely distributed
  - Ocean thermal energy gradients – small gradients mean low efficiency conversions
Transportation

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

- Some choices
  - Chemical fuels
  - Batteries / Electrochemical cells
  - 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.
One vision for a sustainable energy future

Center on Nanostructuring for Efficient Energy Conversion (CNEEC)

Figure by Zhebo Chen

DOE-EFRC Center on Nanostructuring for Efficient Energy Conversion  http://cneec.stanford.edu
Same Underlying Phenomena

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

- Each process
  - Creates a positive and negative charge carrier (e.g. electron and hole)
  - Moves the charge
  - Recombines charge

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

- 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

![Diagram showing the process of how photovoltaics work](image-url)
Photoelectrocatalysts do the same

*Photoelectrocatalysts convert light energy into chemical energy*

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

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

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

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \]
\[ 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O} \]
How can we improve this process?

Answer: Make things smaller

- Charges don’t have as far to move

- More light may be absorbed
  - If induced by light, may get better absorption by tuning bandgap through quantum confinement

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

Excellent thickness control and conformality

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Thin film solar cell absorption: Example of Cu$_2$ZnSnS$_4$ (CZTS)

- Absorption of sunlight requires a certain thickness of material
- This thickness can be dramatically reduced if typical solar cell materials (semiconductors) are combined with (plasmonic) noble metal nanoparticles

Plasmonic near-field absorbers for ultrathin solar absorbers

- Potential for extreme levels of visible light absorption per unit volume of material
- Efficient (~20%) solar energy conversion theoretically possible with ~10-20 nm thickness of material
- Reduced absorber layer thickness saves scarce materials and reduces costs
- Small volume for absorption reduces the distance charge carriers must travel to the interface
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Quantum Dots

Semiconductor particles a few nanometers in size

Benefits to quantum dots:

- Size quantization effect
  - band gap is tunable by the size of the QD
  - Their absorption spectrum can be tailored by changing their size

- Stability (inorganic)

- Multiple exciton generation (MEG) from a single incident photon

Quantum Dot Sensitized Solar Cells

- Devices employ a layer of quantum dots on TiO$_2$ to absorb solar radiation$^1$
  - Absorption of light in QD forms an exciton (e-h$^+$ pair)
  - Excited electron: through TiO$_2$ to (transparent) anode
  - Excited hole: through either liquid electrolyte or hole-conducting polymer to cathode

Low cost, third generation type solar cell

Can ALD be used to make the sensitizer?

- ALD can grow nanoparticles

⇒ Deposit quantum dots for the sensitizer!

ALD of CdS Films

- Atomic layer deposition (ALD) of CdS by dimethylcadmium and H$_2$S
- CdS films are stoichiometric without contaminants
  - Substrate T : 150 °C
  - Precursors: dimethyl cadmium, H$_2$S
  - 0.4 sec. pulse length, 20 sec. purge length
  - H$_2$S generated in situ from thioacetamide

Atomic layer deposition (ALD) can be used to deposit CdS QDs by operating in the “incubation regime.”

TEM of ALD CdS on planar substrate

- CdS quantum dots of few nm diameter are deposited by ALD

5 ALD cycles

10 ALD cycles

Plan-view TEM images of ALD CdS deposited for (a) 5 and (b)(c) 10 cycles on ALD TiO$_2$ surface on a Cu mesh TEM grid.

Fabrication of QDSSC

1. FTO-coated glass substrate
2. Spray pyrolysis of compact TiO$_2$ layer
3. Doctor-blade on nanoporous TiO$_2$ film
4. ALD of QDs
5. Spin-coat on spiro-OMeTAD hole conductor
6. Evaporate on Ag electrode contact

CdS Quantum Dots by ALD

Increasing ALD cycles
ALD Produces CdS Quantum Dots

- Size quantization effects observed in materials grown by ALD
- QD sizes are ~2-6 nm according to UV-Vis bandgap

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 cycles ALD CdS</td>
<td>3.1</td>
</tr>
<tr>
<td>5 cycles ALD CdS</td>
<td>3.0</td>
</tr>
<tr>
<td>10 cycles ALD CdS</td>
<td>2.7</td>
</tr>
<tr>
<td>15 cycles ALD CdS</td>
<td>2.5</td>
</tr>
<tr>
<td>20 cycles ALD CdS</td>
<td>2.4</td>
</tr>
</tbody>
</table>

TiO$_2$ bandgap: 3.2 eV

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PV Device Measurement

- Working solar cells fabricated with CdS QDs grown by ALD
- Dependence of device performance on QD size is observed

How can we improve this process?

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Photoelectrochemical Splitting of Water

- Can we fabricate improved photoelectrocatalysts for the splitting of water by using nanoscale materials?

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

- Challenge: the material must absorb solar light (semiconductor), catalyze the reaction at its surface, and remain stable.
Possible Nanoscaled PEC Geometry

- Propose to nanostructure semiconducting light absorber to decouple material requirements

- Best catalysts for OER are IrO$_2$ and RuO$_2$

- MnO$_x$ good candidate
  - Cheap and abundant
  - Low overpotential
  - Activity dependent on phase and preparation

Nanostructured semiconductor for light absorption, high surface area

Nanoscale coating for stability and catalysis
Synthesis of $\text{MnO}_x$ Catalyst

ALD procedure:

\begin{align*}
\text{Bis(ethylcyclopentadienyl) manganese} & \quad + \quad \text{Water} \\
& \quad \xrightarrow{170^\circ \text{C}} \quad \text{MnO}
\end{align*}


Growth Rate: $\approx 0.84 \text{ Å/cycle}$

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Synthesis of MnO$_x$ Catalyst

Annealed samples to alter surface area and to access different oxidation states

500 Cycles MnO

10 hours at 480° C in air

Mn$_2$O$_3$

MnO on GC Before Anneal

Mn$_2$O$_3$ on GC After Anneal
Testing MnO\textsubscript{x} as a OER Catalyst
Cyclic Voltammetry (CV)

Used a rotating disk electrode (RDE) configuration:
- Scan rate : 20 mV/s
- 0.1 M KOH electrolyte O\textsubscript{2} saturated
- Rotation Speed : 1600 rpm
- Room temperature
- Hg/HgO reference electrode
- Platinum wire counter-electrode

Minimum applied potential needed
\[ E = -\Delta G / n F \]

Conclusions

- Nanostructured materials can lead to better energy conversion efficiencies
  - Improved transport of charge carriers
  - Better light absorption
  - More active surfaces for catalysis

- Three examples
  - The limit of solar absorption in ultrathin layers was explored using plasmonics
  - Quantum dot solar cells using QDs grown by ALD were demonstrated for the first time
  - Highly active catalyst for the oxygen evolution reaction was created using ALD-deposited MnO$_x$ on glassy carbon
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A Reason for Optimism

• We have recognized that over the coming decades we need to transform our energy system to reduce carbon dioxide emissions.

• Energy resources are plentiful.

• There is no single solution to this challenge. We need to work on a broad portfolio of approaches, with a spectrum of time scales and sources of support.

• We can get started now:
  - Do now: Conservation, energy efficiency, cost effective wind, solar and geothermal energy
  - Coming soon: Low emission base-load electricity generation
    - Next generation lower cost solar photovoltaics
    - Grid integrated energy storage
    - Updated and more capable electricity grid
  - Ongoing: Research to provide plenty of new options