Basic Research Needs for Solar Energy

- **The Sun is a singular solution to our future energy needs**
  - capacity dwarfs fossil, nuclear, wind . . .
  - sunlight delivers more energy in one hour than the earth uses in one year
  - free of greenhouse gases and pollutants
  - secure from geo-political constraints

- **Enormous gap between our tiny use of solar energy and its immense potential**
  - Incremental advances in today’s technology will not bridge the gap
  - Conceptual breakthroughs are needed that come only from high risk-high payoff basic research

- **Interdisciplinary research is required**
  - physics, chemistry, biology, materials, nanoscience

- **Basic and applied science should couple seamlessly**
World Energy Demand

EIA Intl Energy Outlook 2004
http://www.eia.doe.gov/oiaf/ieo/index.html
Renewable Energy

**Solar**
1.2 x 10^5 TW at Earth surface
600 TW practical

**Wind**
2-4 TW extractable

**Tide/Ocean Currents**
2 TW gross

**Biomass**
5-7 TW gross
all cultivatable land not used for food

**Hydroelectric**
4.6 TW gross
1.6 TW technically feasible
0.9 TW economically feasible
0.6 TW installed capacity

**Geothermal**
12 TW gross over land
small fraction recoverable

Energy gap:
~ 14 TW by 2050
~ 33 TW by 2100
Cost of Solar Electric Power

- Competitive electric power: $0.40/W_p = $0.02/kWh
- Competitive primary power: $0.20/W_p = $0.01/kWh

Assuming no cost for storage

Module cost only double for balance of system

I: bulk Si
II: thin film dye-sensitized organic
III: next generation

Report of the Basic Energy Sciences Workshop on Solar Energy Utilization
Solar Energy Utilization

Solar Electric

- 0.001 TW PV
- $0.20/kWh w/o storage
- 1.5 TW electricity
- $0.03-$0.06/kWh (fossil)

Solar Fuel

- 1.4 TW solar fuel (biomass)
- 11 TW fossil fuel (present use)

Solar Thermal

- 0.002 TW
- 2 TW space and water heating

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Solar Energy Challenges

Solar electric
Solar fuels
Solar thermal
Cross-cutting research
Solar Electric

- Despite 30-40% growth rate in installation, photovoltaics generate less than 0.1% of our electricity less than 0.01% of total energy
- Decrease cost/watt by a factor 10 - 25 to be competitive with fossil electricity (without storage)
- Find effective method for storage of photovoltaic-generated electricity
Solar Energy Conversion

Capture

100 nm-100 μm

 Conversion

Storage

A Monolithic Photoelectrochemical Cell

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Optimum Absorption Threshold

AM 1.5 Solar Spectrum

Irradiance, mW/(cm²-nm)

Wavelength, nm

Too Large Band Gap

Too Small Band Gap
Semiconductor Doping

- cb
- \( E_f \)
- vb

a) undoped, or intrinsic, semiconductor
b) n-type
c) p-type
Band Bending at SC/Metal Junctions

- $E_{cb}$
- $E_{f,sc}$
- $E_{f,m}$
- $E_{vb}$

Semiconductor → Metal

Energy (eV)
The Depletion Region

Charge Density

Electric Field Strength

Electric Potential

\[ E_{\text{max}} = \left( \frac{q N_d}{\varepsilon_s} \right) W \]

\[ |V_{\text{max}}| = \left( \frac{q N_d}{2 \varepsilon_s} \right) W^2 \]
Thermionic Emission

Thus, always

\[-\frac{dn}{dt} = k_{et}n_s - k_{et}^{-1}\]

Rewrite it as:

\[-\frac{dn}{dt} = k_{et}(n_s - n_{so})\]

Now relate flux to current density:

\[J = -q(-\frac{dn}{dt}) = -q k_{et}(n_s - n_{so}) = -q k_e n_{so} (n_s/n_{so} - 1)\]

By substituting for \(n_s/n_{so}\), we obtain:

\[J = -q k_{et} n_{so} \left[ \exp \left( \frac{-qV}{kT} \right) - 1 \right] = -J_o \left[ \exp \left( \frac{-qV}{kT} \right) - 1 \right]\]
The Dark Current

The current given by the equation:

\[ J = -J_0 \left[ \exp \left( \frac{-qV}{kT} \right) - 1 \right] \]
I-V Curves

Photovoltaic I-V Curve

- $V_{oc}$: Open circuit voltage, the voltage when no current flows. $J_{ph} = -J_0$
- $I_{sc}$: Short circuit current, current where $V = 0$
- $P_{max}$: Maximum power point, greatest value of $I \times V$
Carrier Recombination

In an ideal system, electrons and holes will only recombine at the back face of the semiconductor after they have performed work. In a real system, alternative pathways for recombination will shorten the effective carrier lifetime of the sample and lower the efficiency of photovoltaic devices. The dominant recombination pathways are:

- Radiative Recombination
- Thermionic Emission
- Tunneling
- Surface Recombination
- Bulk Recombination
- Depletion Region Recombination
“Solar Paint”

"Fooling "inexpensive particles into behaving as single crystals"

polymer donor
MDMO-PPV

fullerene acceptor
PCBM

inexpensive processing, conformal layers

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Interpenetrating Nanostructured Networks
Revolutionary Photovoltaics: 50% Efficient Solar Cells

present technology: 32% limit for
- single junction
- one exciton per photon
- relaxation to band edge

- multiple junctions
- multiple gaps
- multiple excitons per photon

hot carriers

rich variety of new physical phenomena
understand and implement
Concentrator vs. Flat Plate Arrays

Why not stack several semiconductors to get better energy conversion? A large band gap semiconductor can get higher voltage out of the more energetic photons, then smaller band gap semiconductors underneath can extract additional energy from the remaining photons.

<table>
<thead>
<tr>
<th>UV</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ (3.2 eV)</td>
<td>Metal</td>
</tr>
<tr>
<td>CdS (2.4 eV)</td>
<td>Green</td>
</tr>
<tr>
<td>GaAs (1.44 eV)</td>
<td>Red</td>
</tr>
<tr>
<td>Ge (0.7 eV)</td>
<td>IR</td>
</tr>
</tbody>
</table>

Flat Plate Array

Concentrator Array
Ultra-high Efficiency Solar Cells

- Multiple junctions
- Hot carriers
- Rich variety of new physical phenomena
- Understand and implement

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Dye Sensitization

- Can Use Metal Oxides
- Only Monolayer of Dye
- <<1% Efficiency
Semiconductor Photoelectrochemistry

nanocrystalline solar cell

Dye-sensitized nanocrystalline TiO₂

hv

S

S*

S⁺

Red

Ox

B. O’Regan, M. Grätzel  Nature 1991, 353, 737
Nanocrystalline Titanium Dioxide

• Particle Size ~ 15nm

• Surface Area
  is larger than single crystal
  ~1000 times

• No Quantum Size Effects
  (large electron effective mass)

• Different Electrochemistry
  from single crystal semiconductors

TEM of nanostructured TiO$_2$
Dye Sensitized Solar Cells

- 8-10% Efficient
- >15% Efficiency Possible
- Stability
Dye-Coated TiO₂ Electrodes

OsL'₂(NCS)₂  RuL'₂(NCS)₂  OsL'₂(CN)₂  RuL'₂(CN)₂

OsL₂L'  RuL₂L'  OsL'₃  RuL'₃

TiO₂ coated on conducting glass (INAP), deposited TiCl₄ overnight, heated 450 °C for 30 min, cooled to 120 °C, immersed in ethanolic dye solution for 15-24 h
Energetics of Sensitized TiO$_2$ Solar Cell

To red-shift the absorption spectra, require:
More positive excited state potential, or more negative ground state potential

V vs SCE

\[ E^0' > 0.25 \text{eV} \]

MLCT
Triplet State
\(-E^{0'*} > 0.8 \text{eV}\)

\(-\Delta G^{0'} > 0.25 \text{eV for } I^- \text{ oxidation}\)
Solar Energy Challenges

Solar electric
Solar fuels
Solar thermal
Cross-cutting research
Solar Thermal + Electrolyzer System
Solar Thermal

- heat is the first link in our existing energy networks
- solar heat replaces combustion heat from fossil fuels
- solar steam turbines currently produce the lowest cost solar electricity
- challenges:
  - new uses for solar heat
  - store solar heat for later distribution
Solar Thermochemical Fuel Production

High-temperature hydrogen generation
500 °C - 3000 °C

Scientific Challenges
- high temperature reaction kinetics of metal oxide decomposition
- fossil fuel chemistry
- robust chemical reactor designs and materials

A. Streinfeld, Solar Energy, 78, 603 (2005)

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**Thermoelectric Conversion**

Scientific Challenges
- increase electrical conductivity
- decrease thermal conductivity
- nanoscale architectures
- interfaces block heat transport
- confinement tunes density of states
- doping adjusts Fermi level

thermal gradient $\Leftrightarrow$ electricity

figure of merit: $ZT \sim \left( \frac{\sigma}{\kappa} \right) T$

$ZT \sim 3$: efficiency $\sim$ heat engines
no moving parts

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Solar Energy Challenges

- Solar electric
- Solar fuels
- Solar thermal
- Cross-cutting research
Leveraging Photosynthesis for Efficient Energy Production

- photosynthesis converts ~ 100 TW of sunlight to sugars: nature’s fuel
- low efficiency (< 1%) requires too much land area

Modify the biochemistry of plants and bacteria
- improve efficiency by a factor of 5-10
- produce a convenient fuel: methanol, ethanol, H₂, CH₄

Scientific Challenges
- understand and modify genetically controlled biochemistry that limits growth
- elucidate plant cell wall structure and its efficient conversion to ethanol or other fuels
- capture high efficiency early steps of photosynthesis to produce fuels like ethanol and H₂
- modify bacteria to more efficiently produce fuels
- improved catalysts for biofuels production

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**Smart Matrices for Solar Fuel Production**

- Biology: protein structures dynamically control energy and charge flow
- Smart matrices: adapt biological paradigm to artificial systems

**Scientific Challenges**

- engineer tailored active environments with bio-inspired components
- novel experiments to characterize the coupling among matrix, charge, and energy
- multi-scale theory of charge and energy transfer by molecular assemblies
- design electronic and structural pathways for efficient formation of solar fuels
Bacterial Photosynthetic Reaction Center

*rhodobacter sphaeroides*

1 step distance: 25 Å
Calculated time: ~100 ms

4 steps
ET distance: 55 Å
Total time: < 1 ns

 photons in
1 oxidant & reductant out

BChl: bacteriochlorophyll
BPheo: bacteriopheophytin
Q: quinone

Nature uses two photosystems to span the redox space from $\text{O}_2/\text{H}_2\text{O}$ to $\text{NAD}^+/$NADH.
Defect Tolerance and Self-repair

• Understand defect formation in photovoltaic materials and self-repair mechanisms in photosynthesis

• Achieve defect tolerance and active self-repair in solar energy conversion devices, enabling 20–30 year operation

the water splitting protein in Photosystem II is replaced every hour!
\[ 4H^+ + 4e^- \rightarrow 2H_2 \]

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \]
Efficient Solar Water Splitting

- Demonstrated efficiencies 10-18% in laboratory

Scientific Challenges
- Cheap materials that are robust in water
- Catalysts for the redox reactions at each electrode
- Nanoscale architecture for electron excitation $\Rightarrow$ transfer $\Rightarrow$ reaction

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Fuel from Sunlight

QuickTime™ and a YUV420 codec decompressor are needed to see this picture.
Light is Converted to Electrical + Chemical Energy

Photoelectrochemical Cell

SrTiO$_3$
KTaO$_3$
TiO$_2$
SnO$_2$
Fe$_2$O$_3$
Optimum Absorption Threshold

Irradiance, mW/(cm²-nm)

Wavelength, nm

AM 1.5 Solar Spectrum

Too Large Band Gap

Too Small Band Gap
Solar H$_2$ production on Ru/CulnS$_2$-AgInS$_2$-ZnS solid solution photocatalyst

Solar simulator (AM-1.5)

Rate of H$_2$ evolution
8L/h•m$^2$

Photocatalyst
Reactant: K$_2$SO$_3$ + Na$_2$S

I. Tsuji, H. Kato, and A. Kudo,
Solar H₂ production on Ru/CulnS₂–AgInS₂–ZnS solid solution photocatalyst

Solar simulator (AM-1.5)

Rate of H₂ evolution
8L/h•m²

Absorbance / arb. units

Wavelength / nm

500 600 700 800

BG : 1.77e V

Photocatalyst
Reactant: K₂SO₃ + Na₂S

I. Tsuji, H. Kato, and A. Kudo,
Lessons from Photosynthesis
Mission of JCAP

**Melvin Calvin, 1982:** It is time to build an actual artificial photosynthetic system, to learn what works and what doesn’t work, and thereby set the stage for making it work better.

**10-year JCAP Goal, 2010:** To demonstrate a manufacturably scalable solar fuel generator, using earth-abundant elements, that, with no wires, robustly produces fuel from the sun, 10 times more efficiently than (current) crops.

*Photosynthesis* | *Artificial Photosynthesis*
System Concept

2H₂O → 2H₂ + O₂

Solar PV & membrane

O₂ catalyst anode

H₂O

2H

H₂ catalyst cathode

4H⁺
Constructing the Pieces of a Solar (H₂) Fuel Generator
Structure – Radial Advantage

Impure material but high performance

\[ L_D \bigodot \text{purity} \bigodot \text{materials cost} \]
Enables Application of New Materials

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Relaxes Catalyst Activity Requirements

$$\text{H}^+ \rightarrow \text{H}_2$$

$$\Delta G_{\text{H}^+} \text{ (eV)}$$

$$i_0 \text{ (A/cm}^2\text{)}$$

$$\eta \text{ Experimental (V)}$$

$$\Delta E_{\text{O}^* \text{ DFT (eV)}}$$

- alkaline
- acidic
- CoO_x (neu)
- CoO_x (neu)

$$\text{H}_2\text{O} \rightarrow \text{O}_2$$

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Flexible PDMS-Si Wire Composites

**Fundamental Design Principles and Progress**

- Require >1.23 V of photovoltage
- Require membrane to neutralize pH gradient and separate products
- Require catalytic sites to transform individual $e^- - h^+$ pairs into multi-electron transfer reactions

![Diagram of water splitting and hydrogen production](image)

![Graph of current and potential](image)

7% to $H_2$

(w only 60% absorption)
Solar-Powered Catalysts for Fuel Formation

chloramdomonas moewusii

photosystem II

hydrogenase

$2H^+ + 2e^- \Leftrightarrow H_2$

oxidation

reduction

$2H_2O \xrightarrow{4e^-} CO_2 \xrightarrow{4H^+} HCOOH$,

$CH_3OH$, $H_2$, $CH_4$
Molecular-Nanoscale Interface

**Gaps:** How to combine components into working system; functionality of components individually vs collectively.

**Approach:** Control functionality of integrated components

Exploit 3-D to achieve desired activity and/or functionality

**Starting Points:**
- MnO$_x$: CoO$_x$
- Ni-Mo

Synthesis and catalytic activity of Ru double gyroid vs planar Ru for O$_2$ evolution
Heterogeneous Catalyst Discovery

Gaps: Complement with Ultra-high Throughput Experimentation

Schematic of the process of preparing the substrate and making electrical contact to 130 individual materials on a single piece of FTO-coated glass.

Starting Points:
- $\text{H}_2/\text{CO}_2$: $\text{MS}_x$
- $\text{O}_2$: $\text{MO}_x$
- $\text{MO}_x\text{N}_y$

Outputs: Tie together theory, surface science, electro-chemistry, X-ray spectroscopy, high-throughput experimentation

Activity Metrics/Goals:
- $\sim x 10^2$ for $\text{H}_2$
- $\sim x 10^4$ for $\text{O}_2$
- $> x 10^5$ for $\text{CO}_2$

False color images of the photocurrent of a slide that contained spots of binary mixed-metal oxides (top). Three-dimensional plot (bottom). Top-down view.

Measured OER overpotential vs calculated adsorption energy
Envisioning JCAPs Products

km-scale

mm-scale

cm-scale

m-scale

System/design/process level

Flow channel building blocks

Device/physics level
Basic Research Needs for Solar Energy Utilization

Report of the Basic Energy Sciences Workshop on Solar Energy Utilization

Nathan S. Lewis
Caltech

with
George Crabtree, ANL
Arthur Nozik, NREL
Mike Wasielewski, NU
Paul Alivisatos, UC-Berkeley

April 18-21, 2005
CONCLUSIONS

- Without **massive** quantities (10-20 TW by 2050) of clean energy, CO$_2$ 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 CO$_2$) into O$_2$ and a reduced fuel.
BES Workshop on Basic Research Needs for Solar Energy Utilization

April 21-24, 2005

Workshop Chair: Nathan Lewis, Caltech
Co-chair: George Crabtree, Argonne

Panel Chairs
Arthur Nozik, NREL: Solar Electric
Mike Wasielewski, NU: Solar Fuel
Paul Alivisatos, UC-Berkeley: Solar Thermal

Topics
Photovoltaics
Photoelectrochemistry
Bio-inspired Photochemistry
Natural Photosynthetic Systems
Photocatalytic Reactions
Bio Fuels
Heat Conversion & Utilization
Elementary Processes
Materials Synthesis
New Tools

Plenary Speakers
Pat Dehmer, DOE/BES
Nathan Lewis, Caltech
Jeff Mazer, DOE/EERE
Marty Hoffert, NYU
Tom Feist, GE

Charge
To identify basic research needs and opportunities in solar electric, fuels, thermal and related areas, with a focus on new, emerging and scientifically challenging areas that have the potential for significant impact in science and technologies.

200 participants
universities, national labs, industry
US, Europe, Asia
EERE, SC, BES

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