Designing New Materials for Solar Energy Conversion

- Global outlook on clean energy, including economics
- Using X-rays to tailor the energy levels in solar cells
- A dream: Follow the fate of charge carriers in real time

F. J. Himpsel, University of Wisconsin Madison
Most of our energy originates from the Sun
Willie Sutton, a notorious bank robber, was asked why he keeps robbing banks. The answer: Because that’s where the money is.

Use the same logic for pursuing solar energy.
Convert solar energy
to the three dominant forms of energy

- Heat: low-tech
- Fuel: atomic, molecular scale (photoelectrocatalysis)
- Electricity: nanometer, picosecond scales (this lecture)
Solar cell production is rising quickly, but from a small base.

Rapid growth in China.

Substantial in Europe.

US is late to catch on.
China took over
1 kW/m² Incident solar power
× ¼ Useful daylight
× 0.20 Efficiency of a solar cell
× 2.6 \times 10^{10} \text{ m}^2 100 \times 100 \text{ (miles)}^2

= 1.3 \text{ TW}

\approx 1 \text{ TW} \quad \text{Electric power generated in the US}

0.7 \text{ TW} \quad \text{could be generated by all the rooftops in the US (NREL study)}
How much would it cost?

0.5 \$/W \text{ Price of solar panels per Watt} \times 1 \text{ TW} \text{ Electric power generated in the US} = 0.5 \ T\$ \text{ (compare the US GDP of } \approx 20 \ T\$) \text{.}

Solar panels make up only a fraction of the cost (and falling).
Cost comparison

- Solar energy is free, fuels are not: $/kW vs. $/kWh

- To get $/kWh, divide by the lifetime of a solar cell. Want long lifetime, short energy payback time.

- Comparisons use levelized cost, which includes the initial investment, lifetime, and fuel cost.

---

**Levelized cost of electricity for Germany**

in EuroCent/kWh, source: Fraunhofer ISE; March 2018

PV = Photovoltaics  = Solar to electricity

- PV roof small
- PV roof large
- PV utility
- Wind onshore
- Wind offshore
- Biogas
- Coal lignite
- Coal hard
- CCGT natural gas
Economics of solar energy

Solar panels make up only a fraction of the total cost.
Major contributions come from the support structure. They scale with the area of the solar cells.

⇒ Reduce the area via higher efficiency
⇒ Design support for solar cells into buildings
⇒ Reduce legal hurdles, create incentives
0.3 $/W now (silicon cells)

1 $/W then
Silicon solar cells dominate, but progress is slow (mainly volume, not Moore’s law).
Lose photons below the band gap.

Lose the kinetic energy of hot electrons.

This part is converted to electrical power.

1100 nm ~ 1.1 eV = band gap of silicon

Lose photons below the band gap.

Lose 1/3

Keep 1/3

Lose 1/3

Efficiency limit of 33% for a single junction

Use multiple junctions in series: tandem cells
Perovskite-on-silicon tandem cell

Perovskite

Halogen cage (Pb inside)

Methylammonium outside

Tandem configurations

Design a solar cell from scratch:
Utilize 4 energy levels, 3 materials

Small energy drop: Large voltage
Large energy drop: Large current

Want both for maximum power
Dye-sensitized solar cells combine 3 materials

Lose half the voltage to fill holes quickly

Measure energy levels with synchrotron techniques

Diamond film as inert, transparent electron donor material

Energy levels from spectroscopy (XAS, XPS, UPS, optical, electrical)

Collaboration with Uppsala (growth, optical), UC Davis (HAXPS), LBL (synchrotron), UC Berkeley (theory)
Energy levels from absorption spectroscopy

ambiguous

UV-VIS

Valence

unique, element-specific

X-Rays

LUMO

Photon Energy

Unoccupied

Core

~

~
**σ** and **π** orbitals in organic molecules

**σ-bond:**
- **σ** orbital
- **σ**-bond

**π-bond:**
- **π**-orbital
- **π**-bond
- **π***-orbital

**π***-orbital

**σ***-orbital

**σ** orbital

**π** orbital

Energy level diagram:
- **σ***-orbital (antibonding, unoccupied)
- **σ** orbital (bonding)
- **π** orbital
- **π***-orbital

2s, 2p bonding and antibonding

Approximate bond energy

**σ**

**π**
Orientation of molecular orbitals via polarized x-rays

Distinguish $\pi^*$ orbitals (perpendicular to the molecule) from $\sigma^*$ orbitals (in-plane)

Calculate energy levels, wave functions

Levels get very dense at higher energies.

Electrons quickly trickle down to the LUMO.

Focus on the LUMO.

Systematics: $N1s \rightarrow \text{LUMO}$ transition in porphyrins

The $N\,1s$ core level shift is due to electron transfer from the metal to the surrounding nitrogens. It tracks the metal electronegativity.

Systematics: Metal $2p \rightarrow 3d$ transitions at the metal atom

The multiplets reveal the oxidation state and the ligand field.

Fe, Mn are stable in both the 2+ and 3+ oxidation states. That facilitates charge separation.

Combine the three components of a solar cell in one molecule with atomic perfection.

Achieved efficiency record for dye-sensitized solar cells (12.3%)

D–π–A (donor–π–acceptor) complexes

Collaboration with U. Autonoma Madrid (synthesis), U. San Sebastian (spectroscopy), LBL (theory)
Design tandem cells with atomic precision?

Connect two dye molecules with an asymmetric molecular wire (= diode). Molecular complexes are atomically perfect.

It would solve the main problem of tandem cells: defects at interfaces.

Fig. 2 $E_{\text{HOMO}}$ (red circles) and $E_{\text{HOMO}} + E_1$ (blue triangles) for all 5000+ porphyrins in our database$^{22,23}$ plotted against the lowest optical transition energy, $E_1$. 

Ørnsø et al., Chemical Science 6, 3018 (2015)
Molecular wires

Lycopene

A single chain of overlapping $\pi$-orbitals forms a molecular wire

Beyond energy levels: lifetimes vs. loss rates

The lifetimes of the charge carriers affect the photocurrent dramatically. When and where are carriers lost? (inside a molecule, across a device)

Add time as variable (fs-ns). Already used in the UV/Vis (nonlinear optics, transient absorption, two-photon photoemission)

Need element-specific X-ray probes. “Heroic” experiments demonstrate proof of principle. Use free-electron lasers to make it mainstream

Probe the carriers along their way out with X-rays.

Pump the center with visible.
“Heroic” demonstration experiments (1 spectrum/day)

Pump the central Fe atom with visible light.

Probe the resulting change in the N1s $\rightarrow \pi^*$ absorption.

Find out when hot electrons arrive at the N cage.

Then look at the surrounding C atoms, then at the electron acceptor, …


See also:
Santomauro,…, Chergui, Structural Dynamics 4, 044002 (2017).
Transmit absorption in the UV/Visible (standard tool)

Bleaching by depopulation of the ground state

Extra transitions starting from excited states

Time constants: $<\text{ps} \rightarrow \mu\text{s}$
Longer for better devices


Where are the carriers lost? At impurities, interfaces?

Use element-specific core levels to identify the location
Messages

• Improve the efficiency of solar cells
  Use tandem cells, but simplify them

• Tailor the energy levels
  Use spectroscopy + computational screening

• A dream experiment:
  Follow electrons/holes across a solar cell
  Pump with visible light, probe with soft X-rays
  Low pulse energy (non-destructive) + high rep-rate (data rate)
Backup Slides
(same sequence as the talk)
Cost of solar installations, breakdown

NREL PV system cost benchmark summary (inflation adjusted), 2010–2017

Chart showing the cost of solar installations for different types of systems, with bars representing various cost components such as module, inverter, and soft costs, for residential PV (5.7 kW), commercial PV (200 kW), and utility-scale PV, fixed tilt (100 MW) and one-axis tracker (100 MW), in USD per Watt DC from 2010 to 2017.
As in the housing market, the location has a strong influence on the true cost of solar (or wind) power:

- **Amount** of sunshine (or wind)

- **Distance** between power plant and user:
  - Long-distance power transmission is costly and lossy

- **Trade-off** between utility scale PV power plants, community solar, individual solar (previous slide)

Examples:
Northern Germany has wind, southern Germany sunshine
Wind power in west Texas, big cities in the east
What to do when the Sun does not shine?

There are many ways to store energy, but no clear winner:
- Batteries, pumping water uphill, storing molten salts, …

For the time being:
- Store conventional fuel, use it in a backup generator:
  - Large scale: Gas-fired power plant (Archimede project in Sicily)
  - Small scale: Fuel cell ("Bloom box" etc.)

My favorite for the long term:
- Convert solar energy to fuel during the day
- Convert fuel to electricity via fuel cells at night (or during winter)
A fuel cell converts fuel directly into electricity without generating heat. That why its efficiency reaches 60% (versus 25% for a diesel generator).

The Apollo program used fuel cells for electric power. When the oxygen tank of Appollo 13 exploded, the crew sent the famous message: “Houston we’ve had a problem.“

Fuel cells are commercially available as backup generators.
Practical solutions

Solar power nicely complements conventional power plants.

• It peaks during the day when the demand is biggest:
  Air conditioning, work place, ...
  Power companies have excess power at night (lower rates!)

• Transients can be made up by fast-ramping power plants:
  Natural gas, stored hydroelectric, ...

• Use a central control system for managing renewable power:
  Predict power fluctuations via accurate weather predictions
  and prepare for any type of glitch (including a solar eclipse).

Silicon solar cells are getting close to their practical efficiency limit (≈25%). Need to capture the full solar spectrum via multi-junctions (tandem cells). Achieved ≈45% in very complex structures. Simplify them.
Core level width from lifetime broadening

The sharpest core levels have \( \approx 10\text{-}1500 \text{ eV binding energy.} \)

\[ \Gamma \text{, PARTIAL AND TOTAL WIDTHS (eV)} \]

**Figure 1.** Theoretical partial and total atomic level widths for K shell. \( \Gamma_A = \text{Auger width, } \Gamma_R = \text{radiative width, } \Gamma = \text{total width.} \)

**Figure 4.** Theoretical partial and total atomic level widths for L\(_3\) subshell. \( \Gamma_A = \text{Auger width, } \Gamma_R = \text{radiative width, } \Gamma = \text{total width.} \)

*Journal of Physical and Chemical Reference Data* 8, 329 (1979)
Decay processes after X-ray absorption

Detect decay products of the core hole (rather than transmitted or absorbed photons)

Absorption

Valence Orbitals

Core Level

Photon in

Emission

Auger electron

Secondary electrons

Electrons out

Photon out

Photoelectron

Electrons out
Probing depths of various particles

- Neutrons: >10^7 nm
- Photons
- Electrons
- Atoms/Ions

Energy (eV):
- 10 eV
- 100 eV
- 1000 eV

Atomic Layers:
- 1000
- 100
- 10
- 1

1s Levels:
- C
- N
- O
Probing depth of electrons

Mean Free Path ($\lambda = 0.1 \text{ nm}$)

Not enough energy to excite plasmons ($\approx 15\text{eV}$)

Fast electrons travel farther

Vary the probing depth by detecting photons vs. electrons