Challenges and Solutions for More Sustainable Energy Systems

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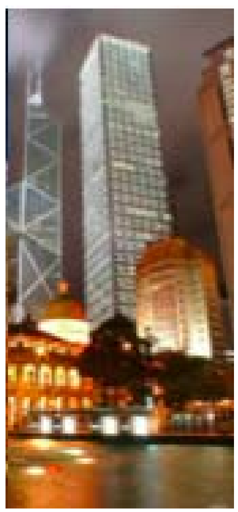
Lives and Livelihoods Depend Upon Energy

Energy for food, water, shelter, transportation, industry…



The Global Energy Challenge is Complex

Environment

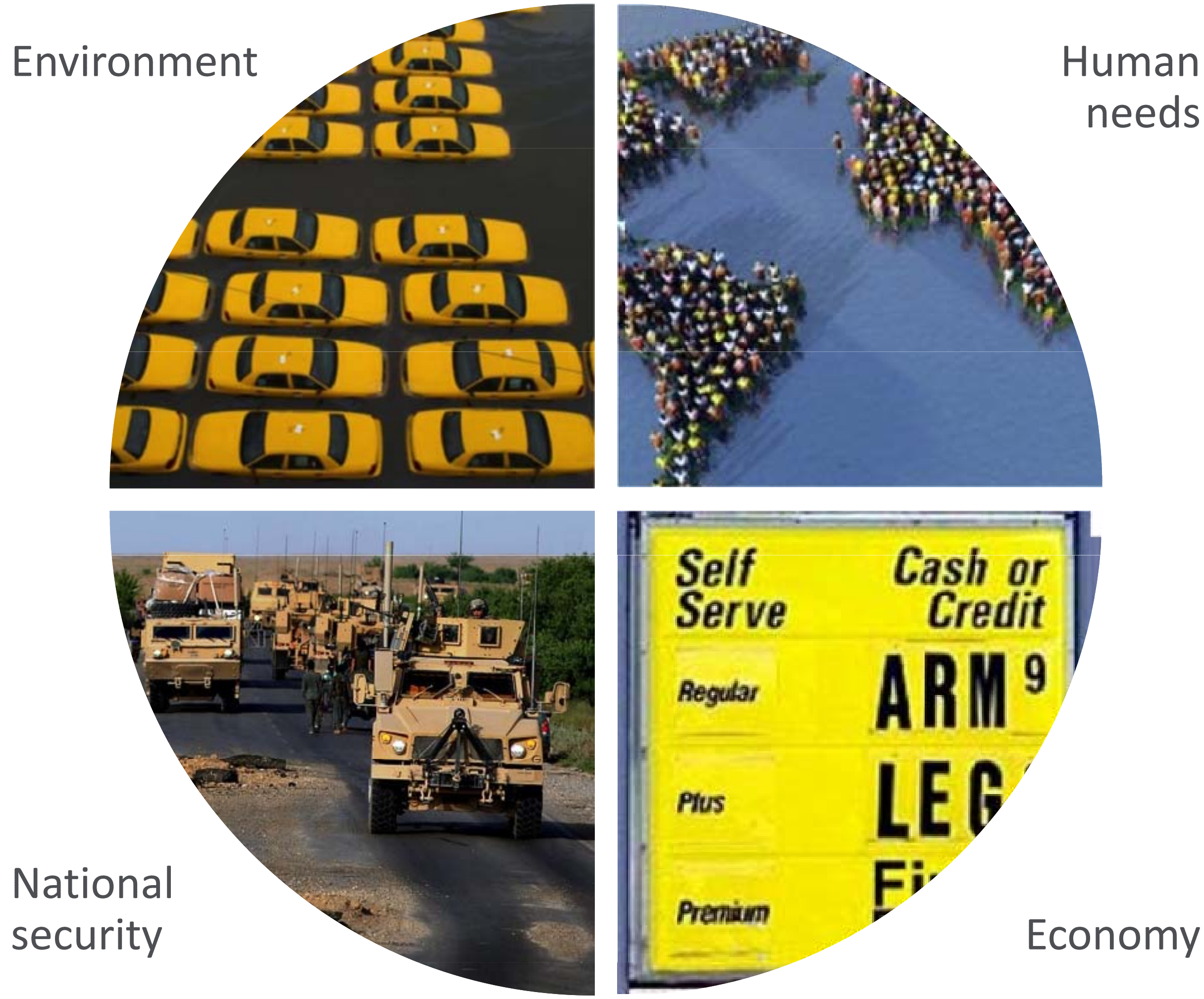
Human needs

National security

Economy

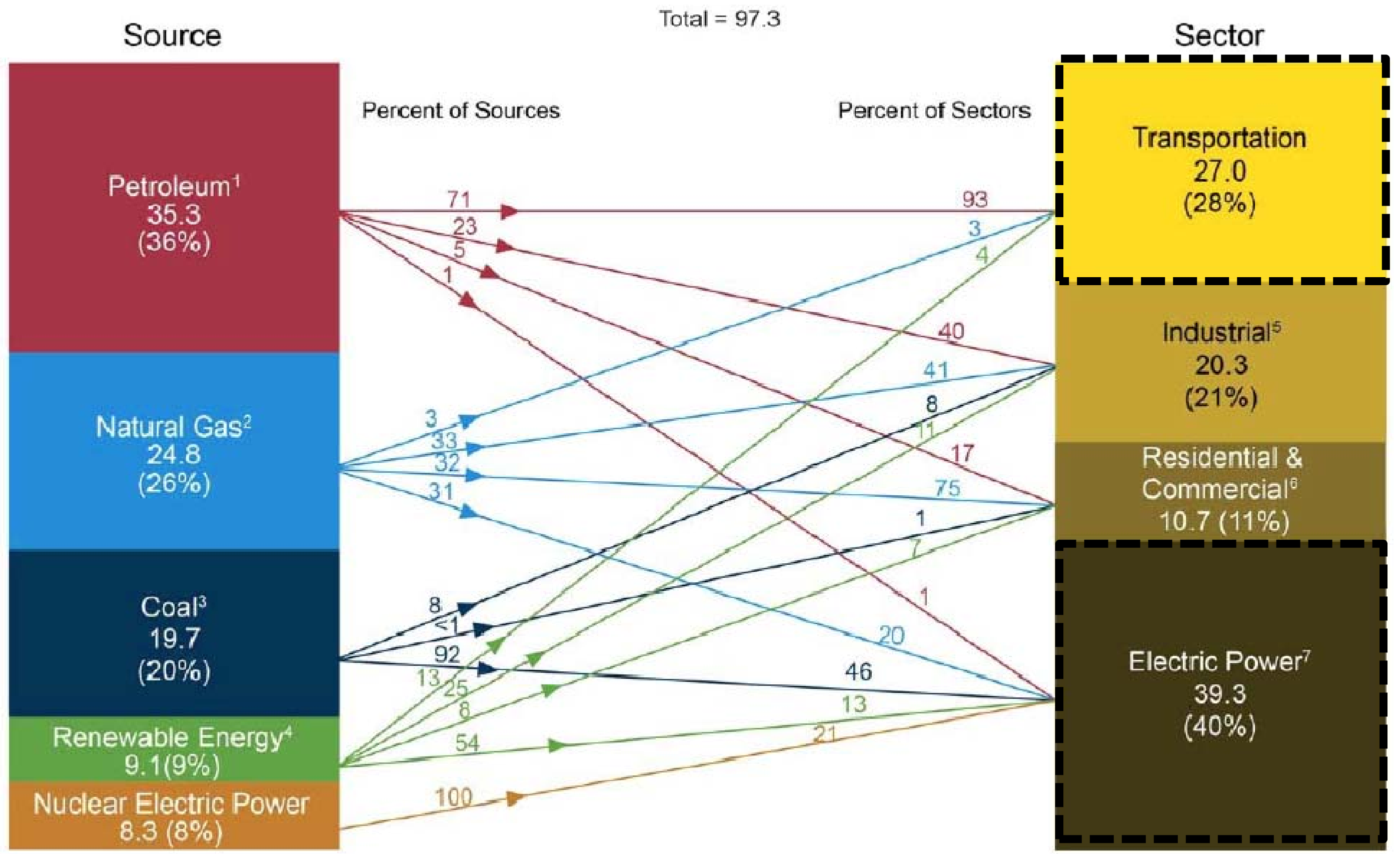
We All Agree: The Global Energy System is Under Stress

- 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 CO_2 in the atmosphere



U.S. Energy Consumption by Sector

Figure 2.0 Primary Energy Consumption by Source and Sector, 2011
(Quadrillion Btu)

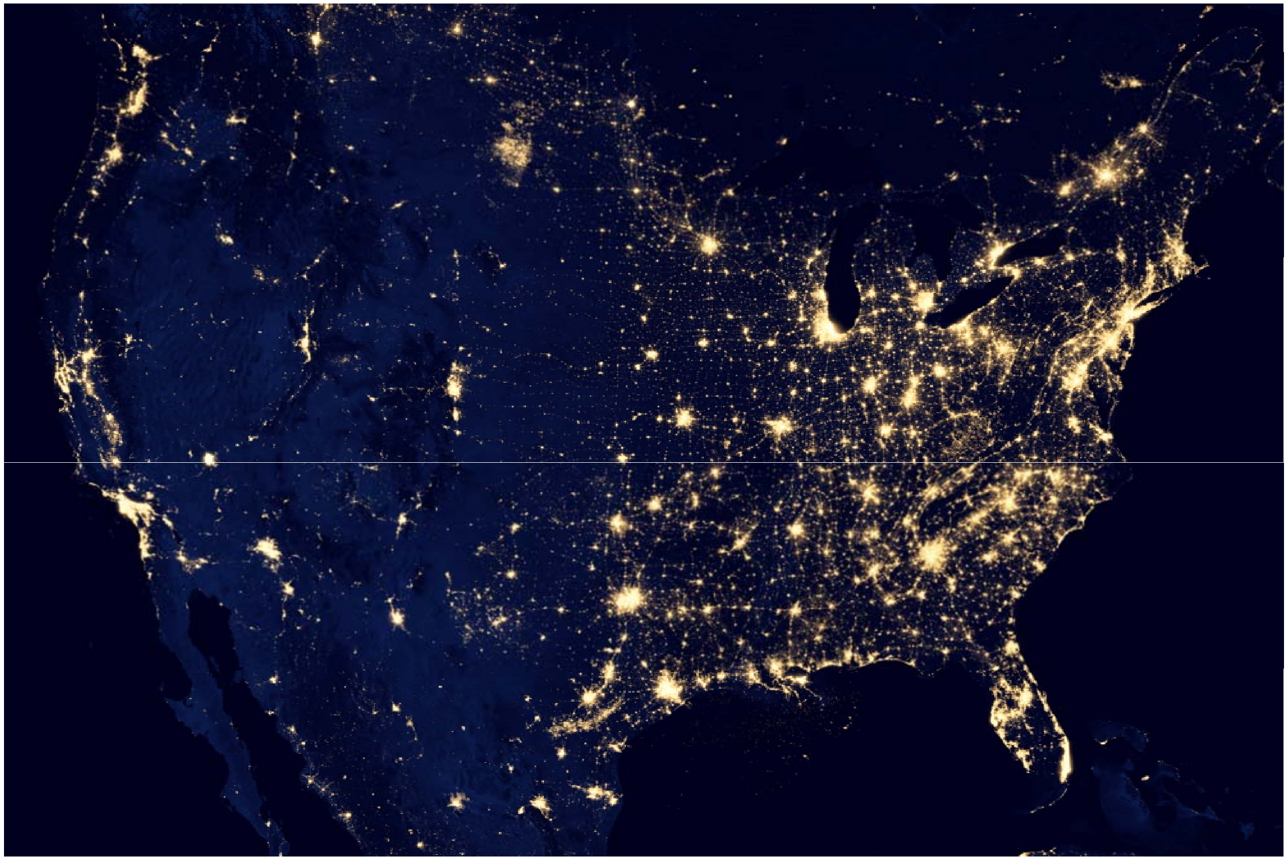


Together these two sectors make up 2/3 of US energy demand

U.S. Energy Information Administration / Annual Energy Review 2011

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

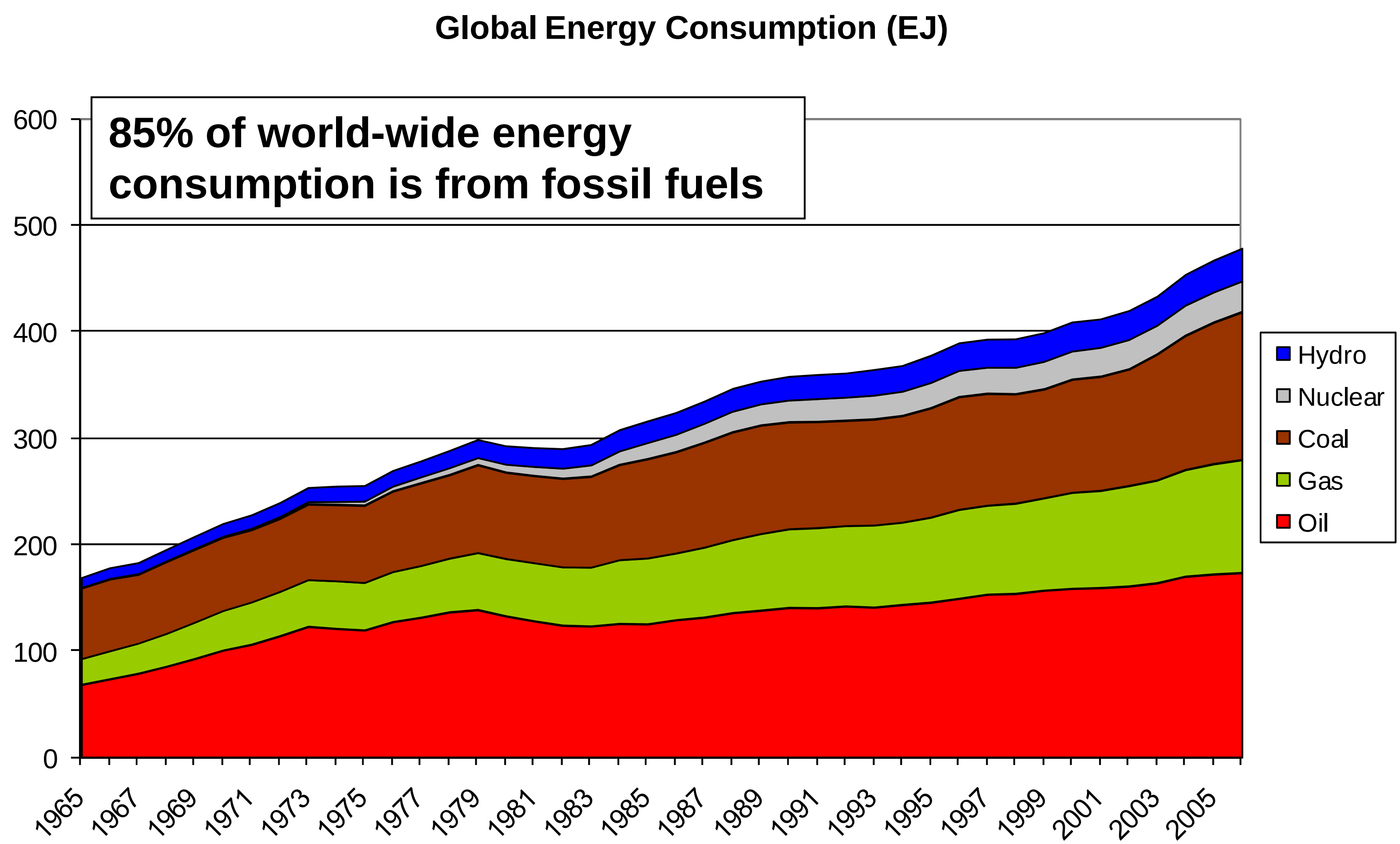
Credit: NASA Earth Observatory/NOAA NGDC

Electricity

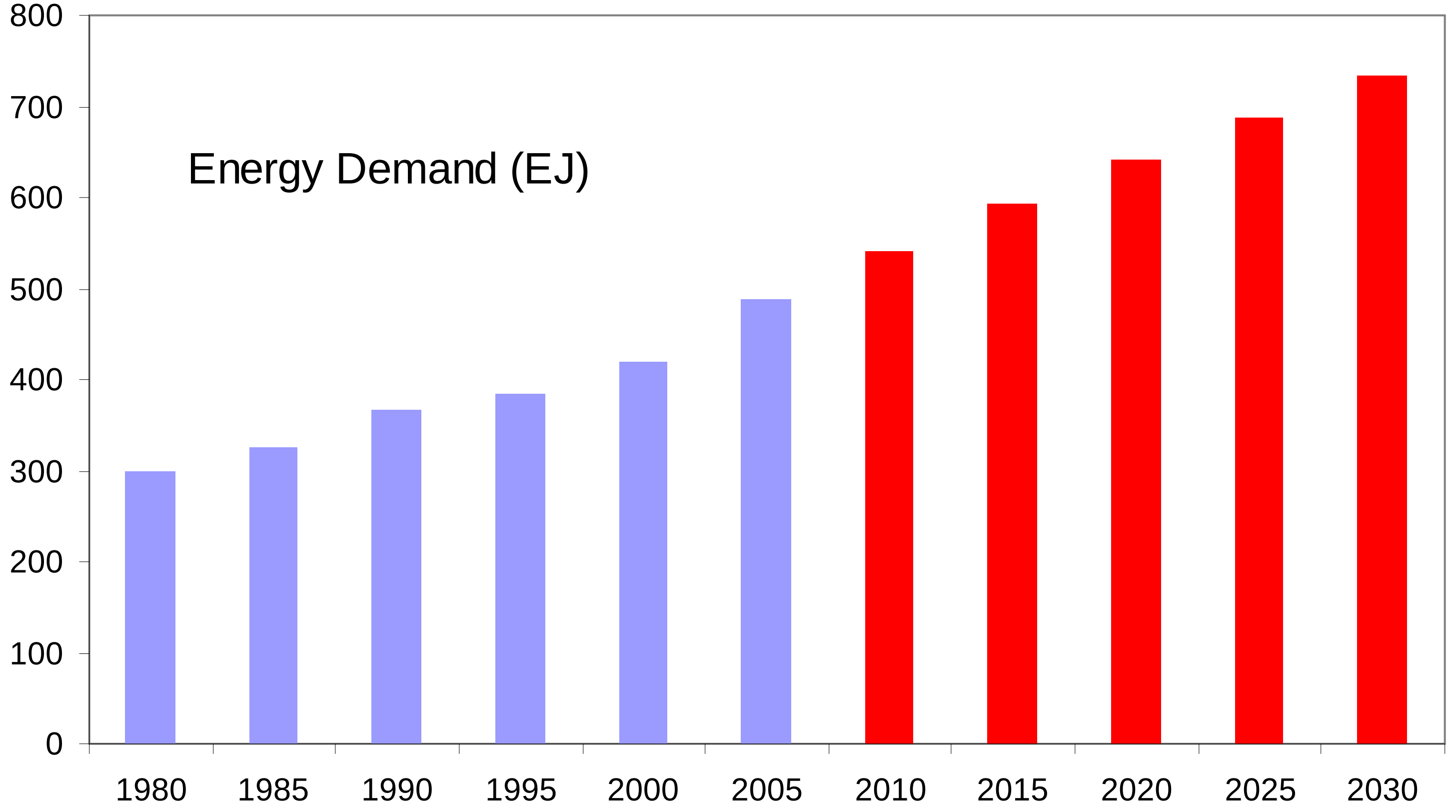
- A favorite form of energy is electricity
- Where does electricity come from?
  - Even though electricity is a very useful form of energy, there are very few direct sources of electrical energy on earth. (One example is a lightning storm.)
  - Electricity is really a secondary energy source, which we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



Projected Energy Demand



50% increase in energy demand by 2030

1 EJ = 10^{18} J

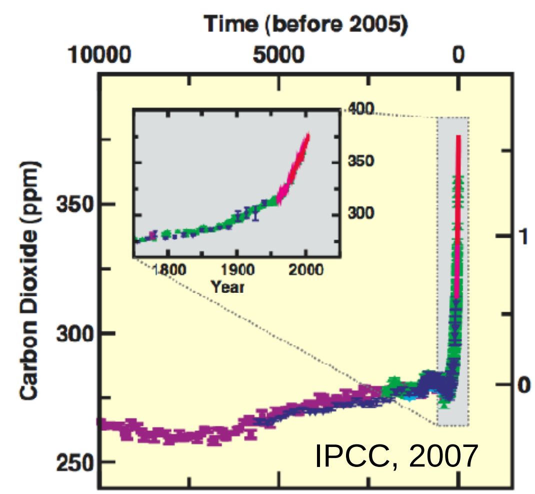
EIA, International Energy Outlook, 2008

Carbon Dioxide Emissions

Burning fossil fuels generates carbon dioxide, CO_2.

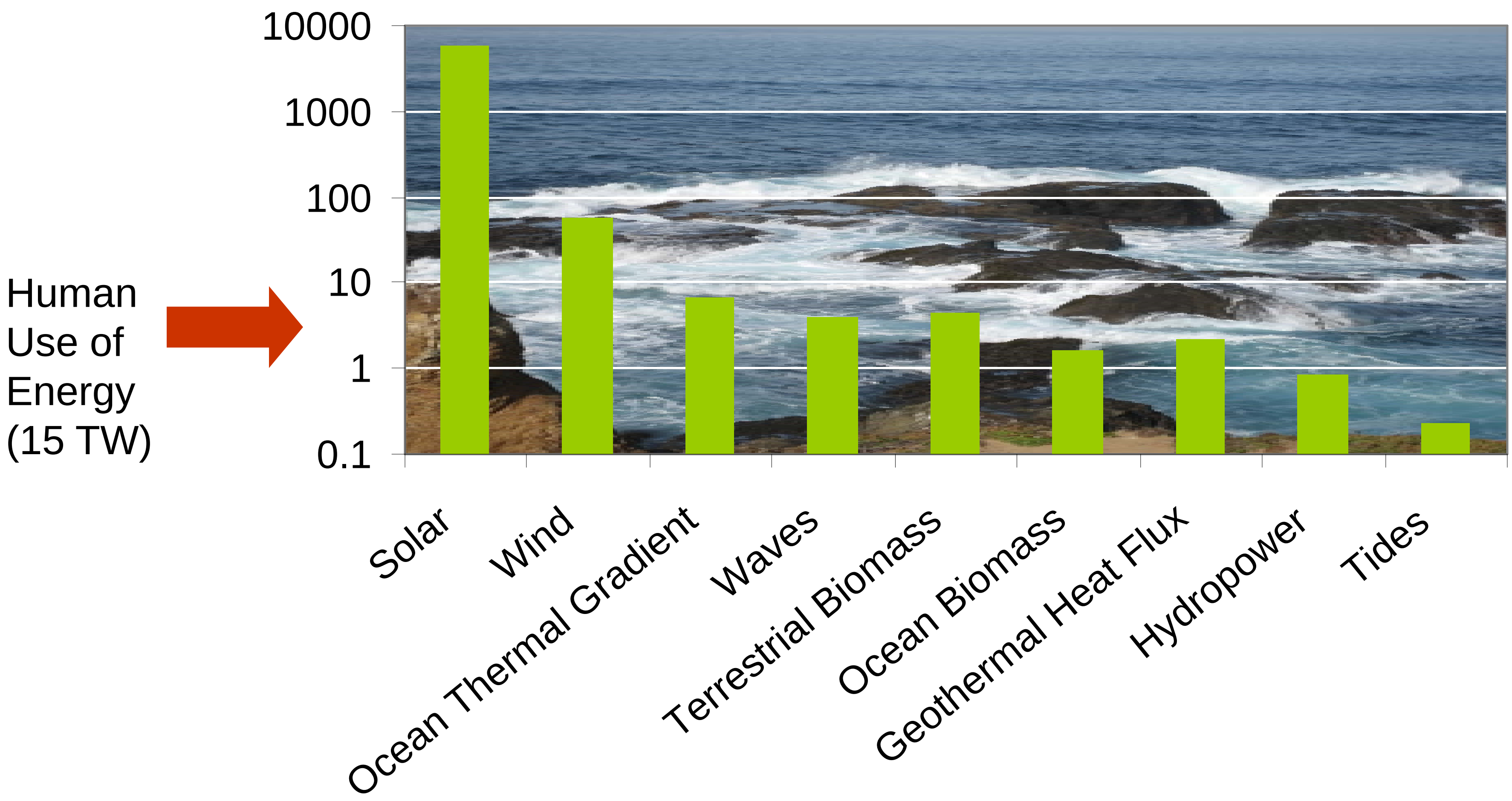
Why is CO_2 a problem?

- Most of this carbon dioxide is being poured directly into the atmosphere, where it adds to the existing CO_2 levels.
- The CO_2 concentrations in the earth's atmosphere have already risen by over 25% in the past century.



- CO_2 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

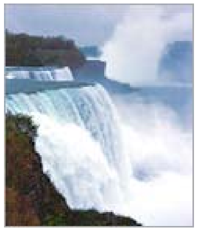


Exergy sources scaled to average consumption in 2004 (15 TW)

From Hermann, 2006: Quantifying Global Exergy Resources, Energy 31 (2006) 1349–1366

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

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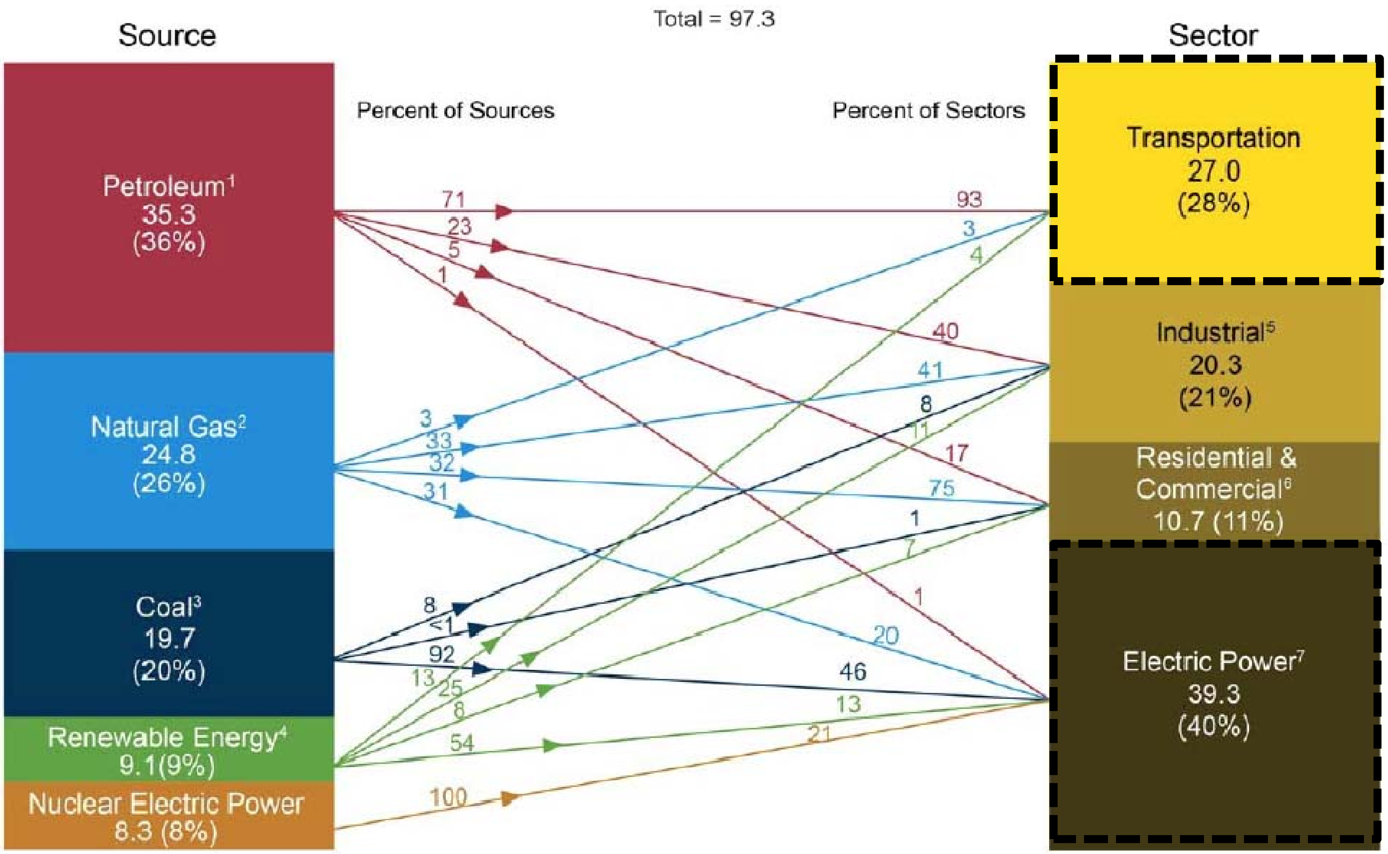

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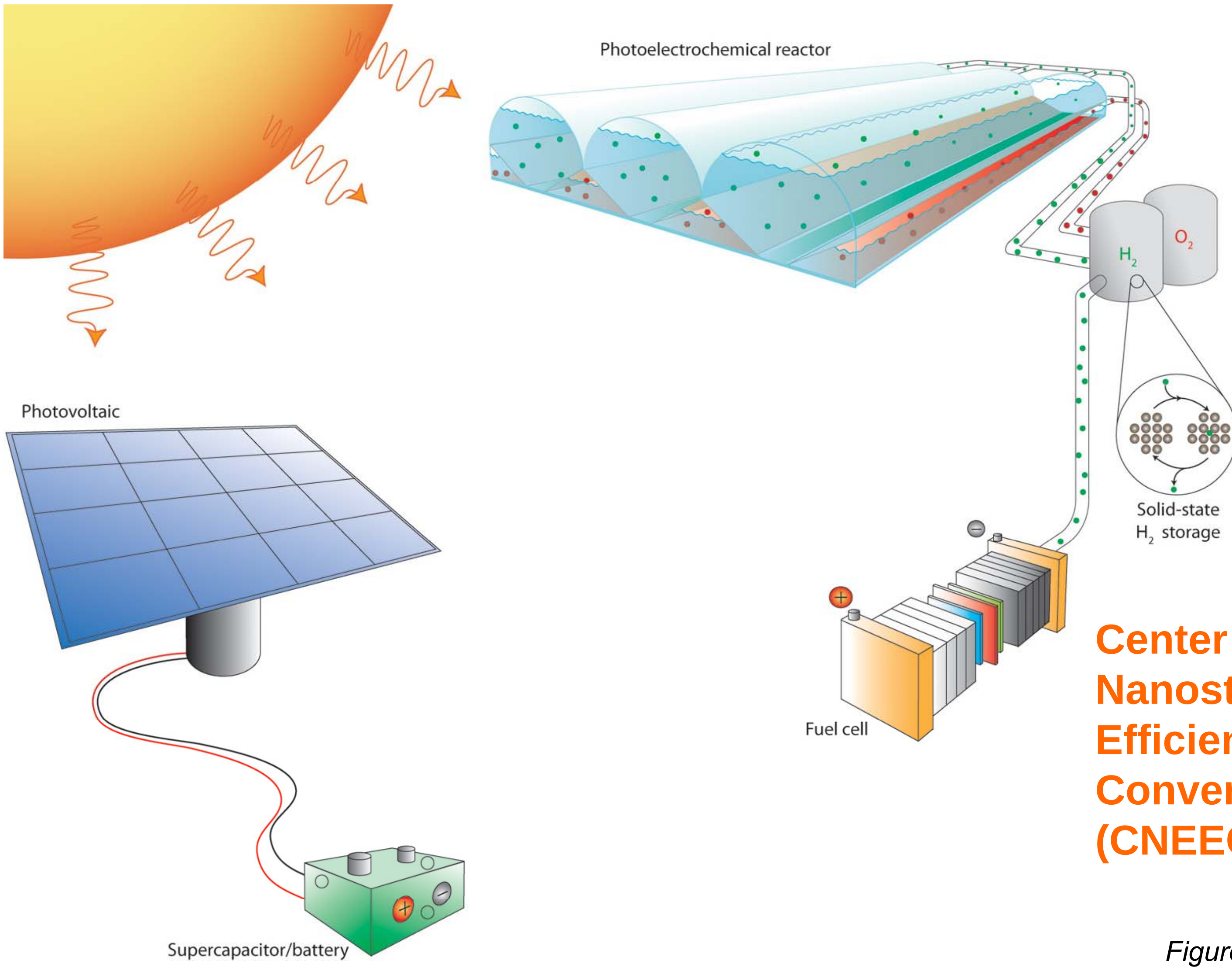
No Single Solution

- 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

Same Underlying Phenomena

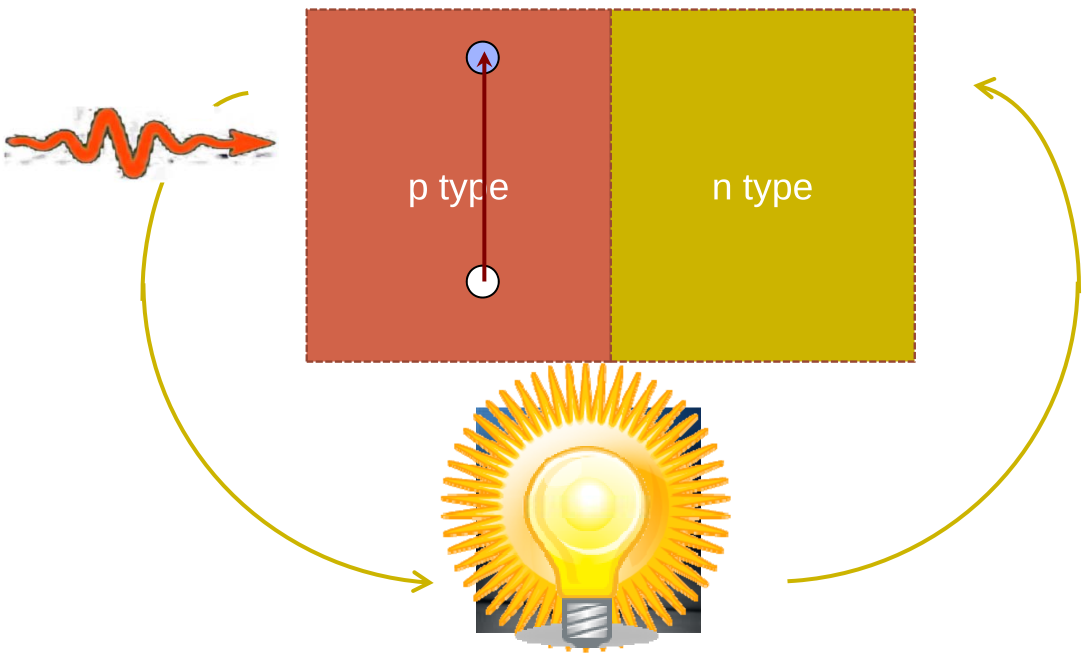
- The diverse energy devices needed, such as photovoltaics, fuel cells, and batteries, all exploit **similar physical and chemical phenomena**.

- 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?

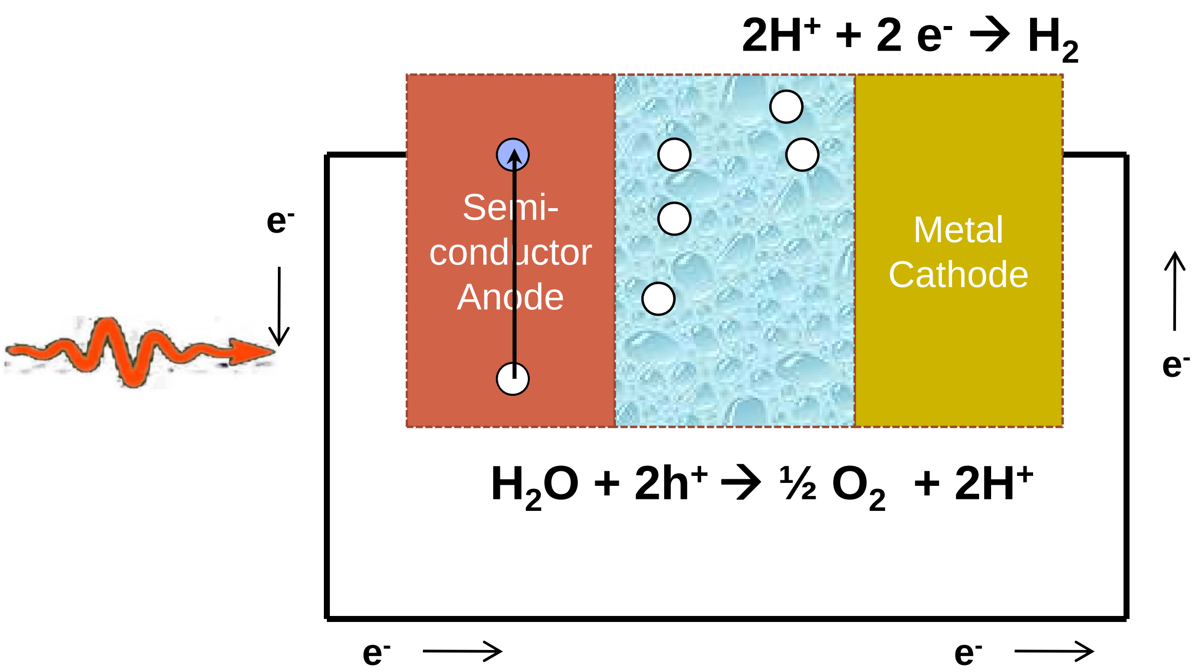
- Photovoltaic devices convert light into electrical energy
- Typically consist of semiconductor materials
  - Light is absorbed
  - Charge carriers (electrons and holes) are created
  - Charge carriers are separated
  - Current flows in a circuit



Photoelectrocatalysts do the same

Photoelectrocatalysts convert light energy into chemical energy

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



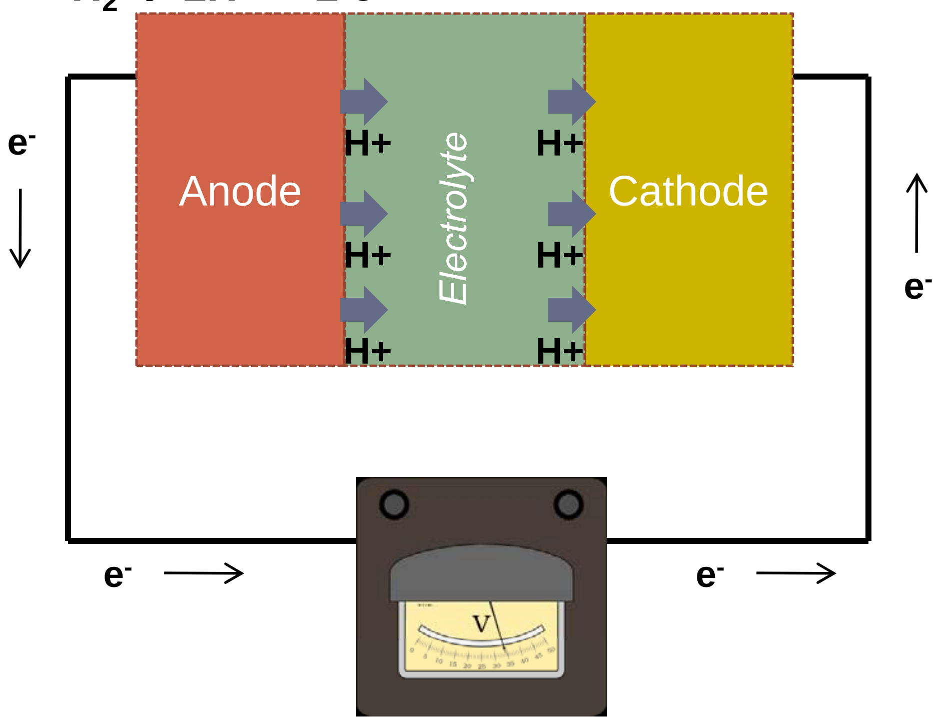
Fuel cells do the same

Fuel cells are devices that convert chemical energy into electrical energy

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

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

$2H^+ + \frac{1}{2} O_2 + 2e^- \rightarrow H_2O$

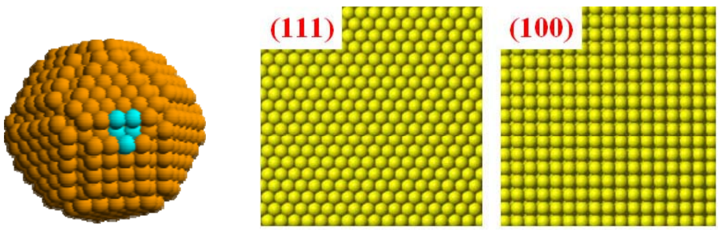


How can we improve this process?

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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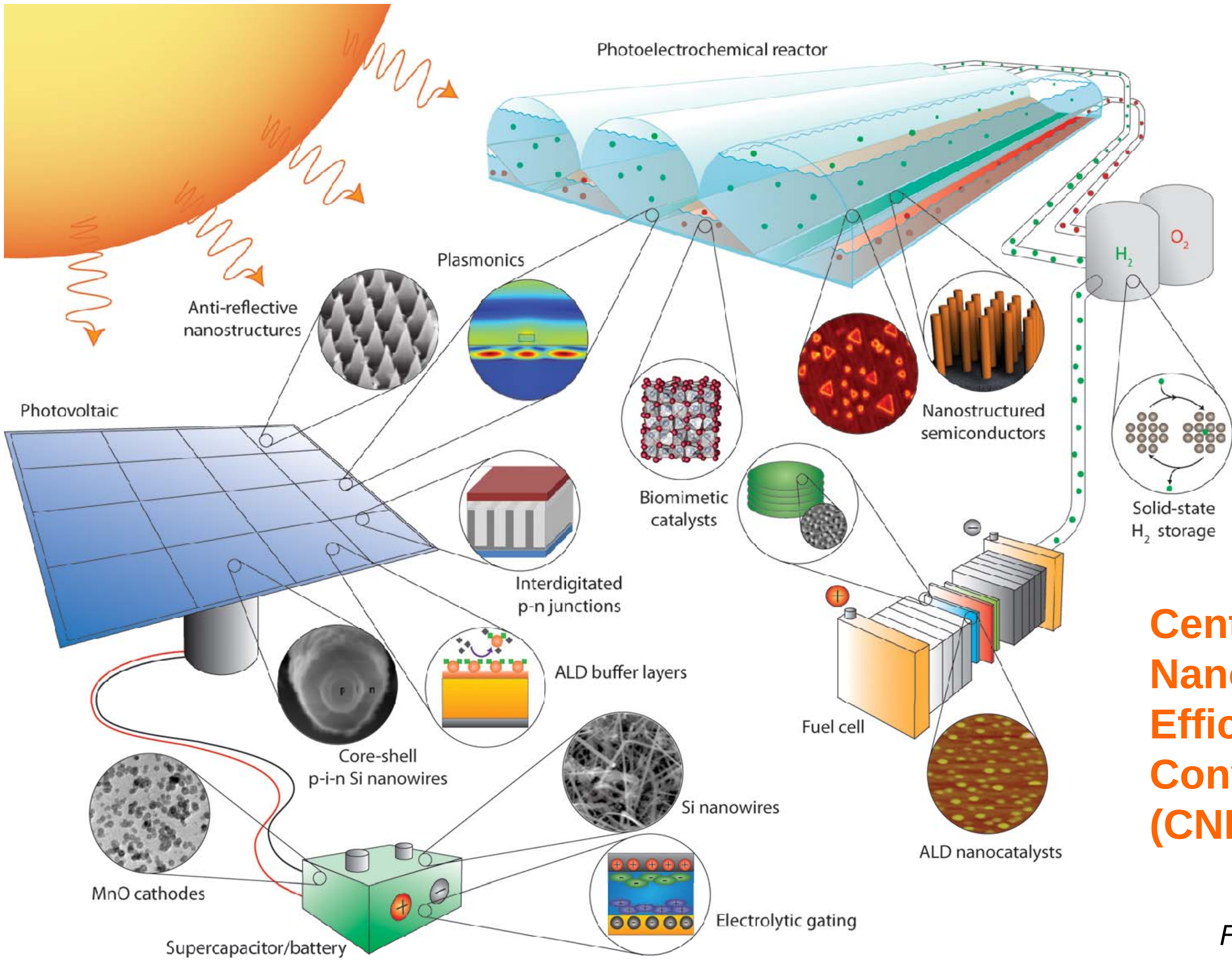
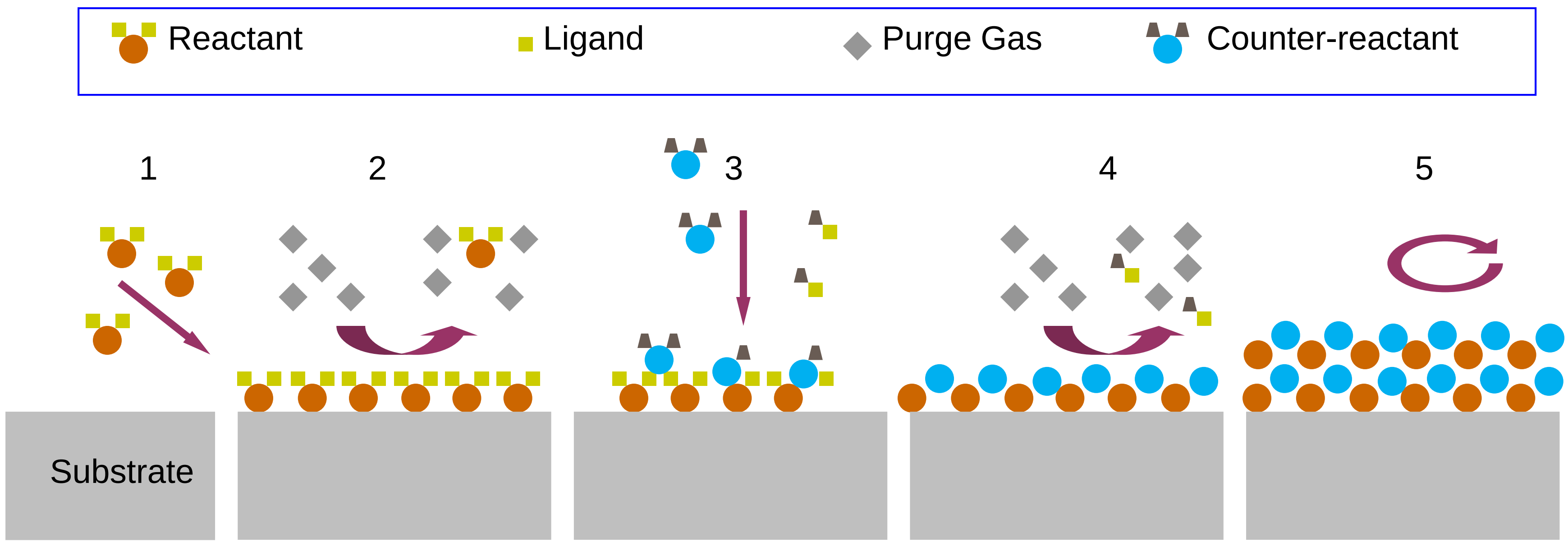


Center on Nanostructuring for Efficient Energy Conversion (CNEEC)

Figure by Zhebo Chen

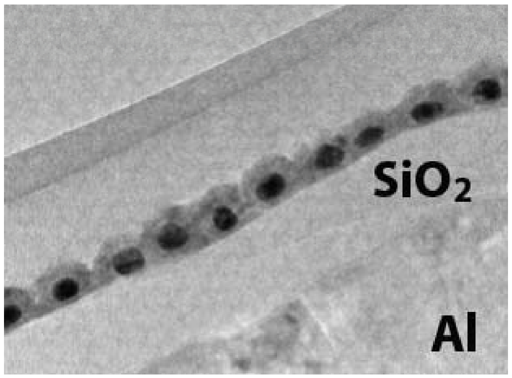
Atomic Layer Deposition (ALD)

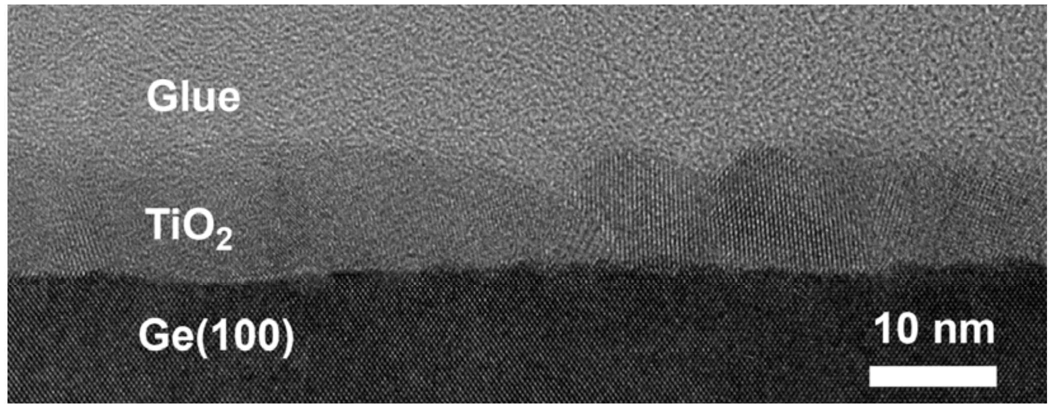
1) Pulse reactant into the reactor
2) Purge to remove excess reactant
3) Pulse counter-reactant
4) Purge to remove products/excess counter-reactant
5) Repeat 1-4 as many times as desired

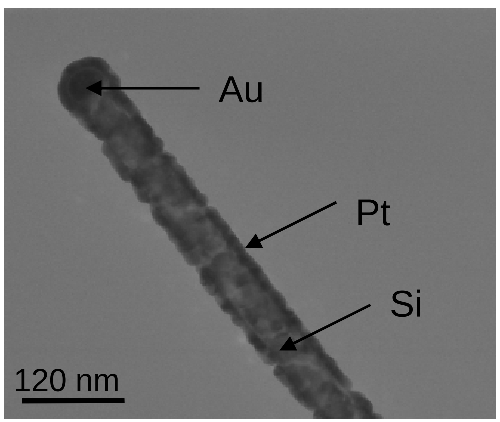


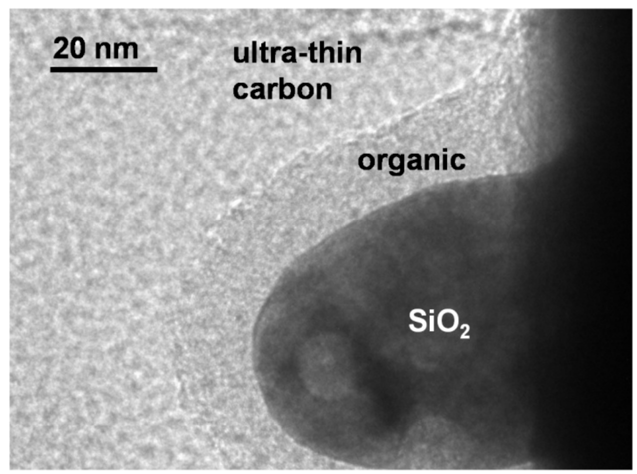
Atomic Layer Deposition

Excellent thickness control and conformality









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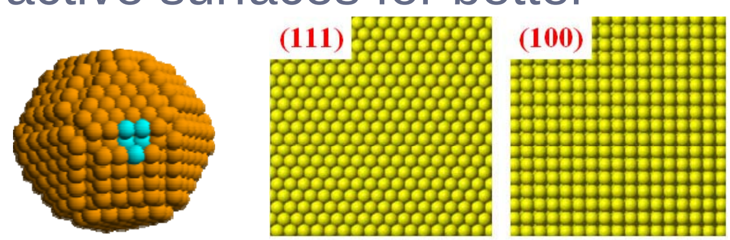
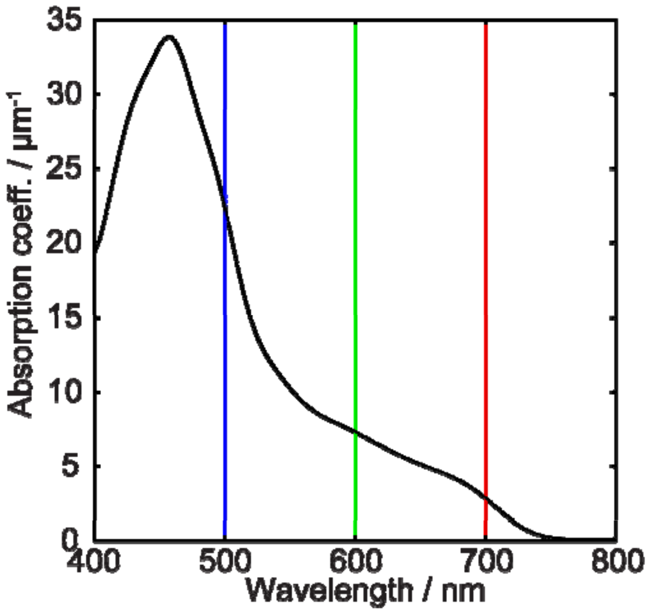
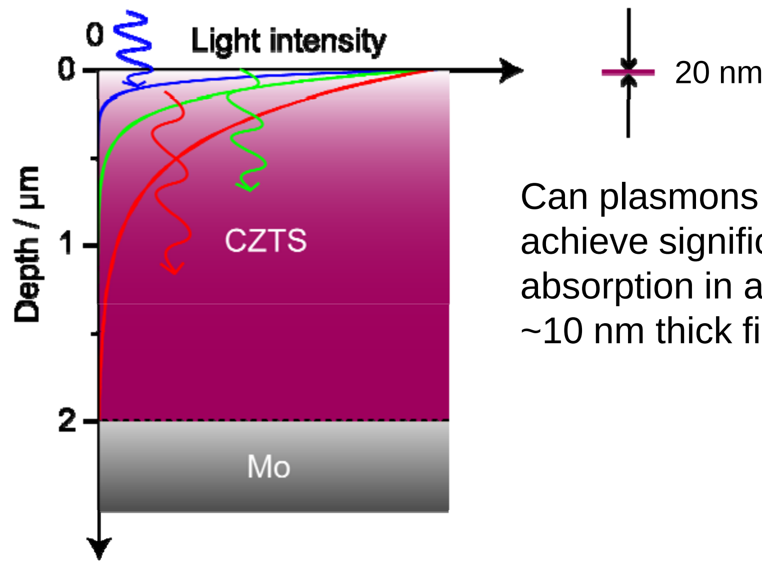


Thin film solar cell absorption:

Example of Cu_2ZnSnS_4 (CZTS)





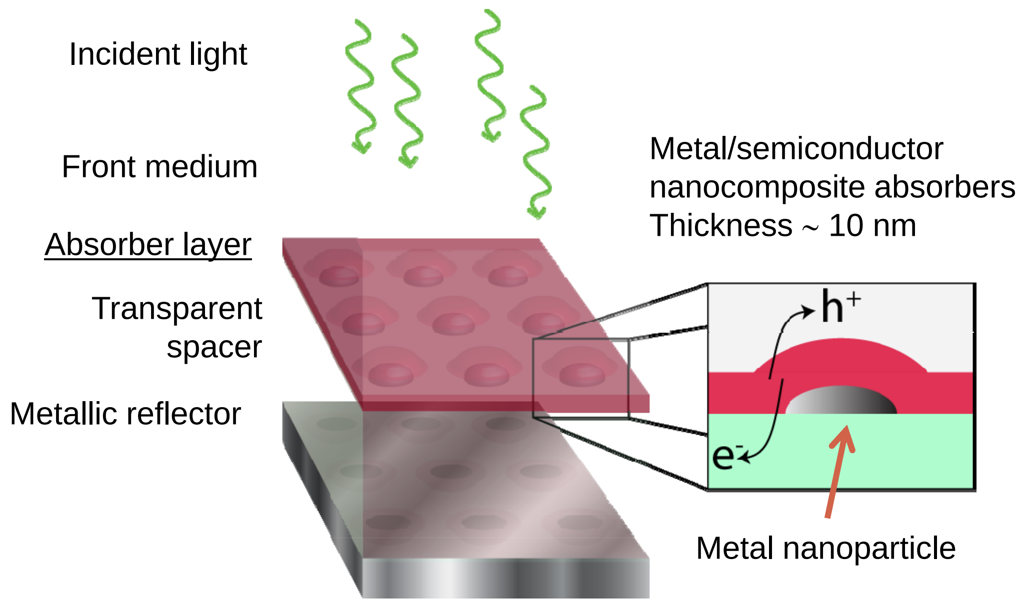
Can plasmons help achieve significant absorption in a ~10 nm thick film?

- 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

Optical constants of kesterite CZTS from Persson, C., Electronic and Optical Properties of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$. *J. Appl. Phys.* ***2010, 107, 053710.***

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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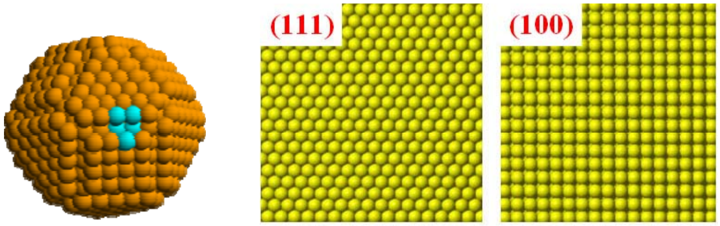
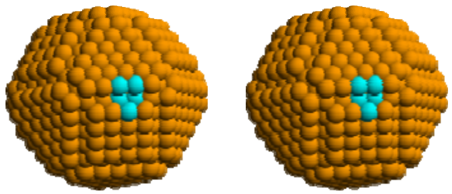


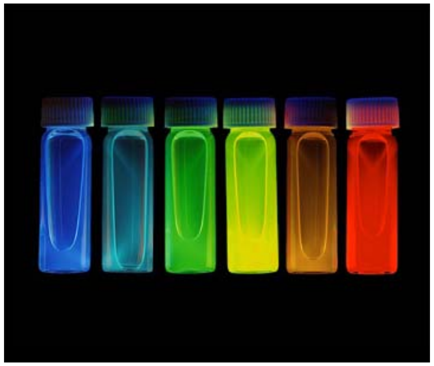
Quantum Dots



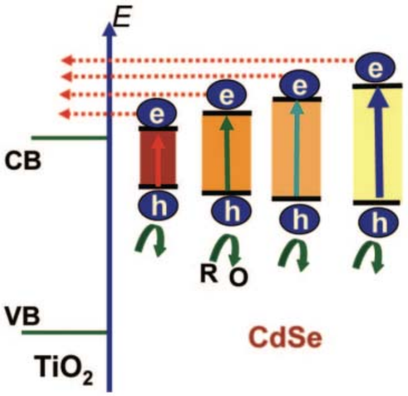
Semiconductor particles a few nanometers in size

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
  - *Nozik, A. J., Inorg. Chem., 2005 (44), 6893*

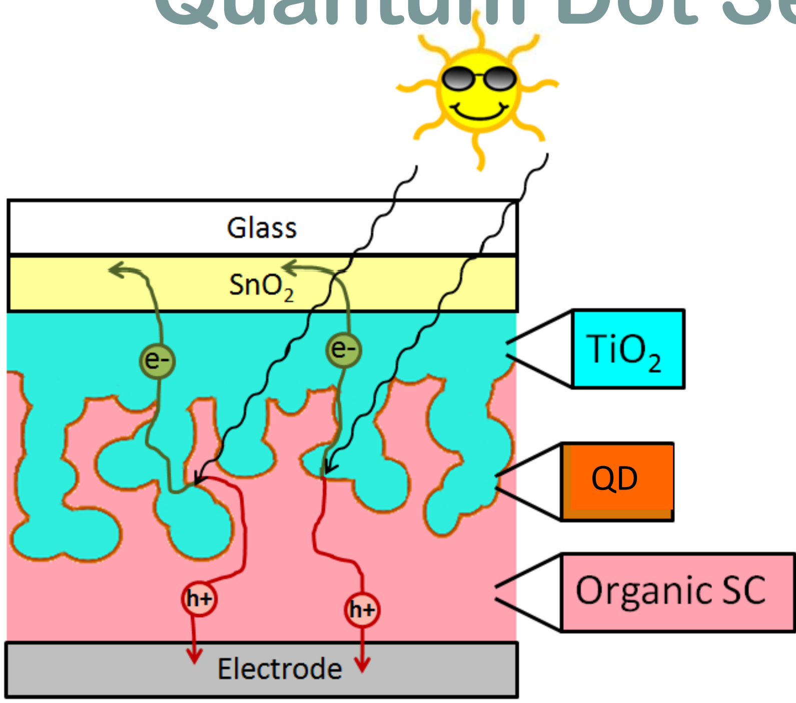


nanoe.ece.drexel.edu



Kamat, P. J. Phys. Chem. C, 2008, 112 (48), 18737

Quantum Dot Sensitized Solar Cells



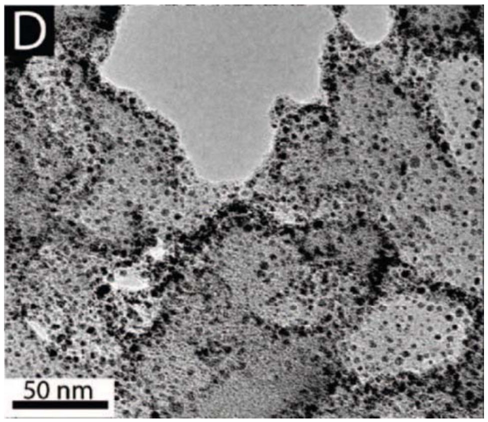
[1]: O'Regan & Grätzel. *Nature*. 335, (1991)

- 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

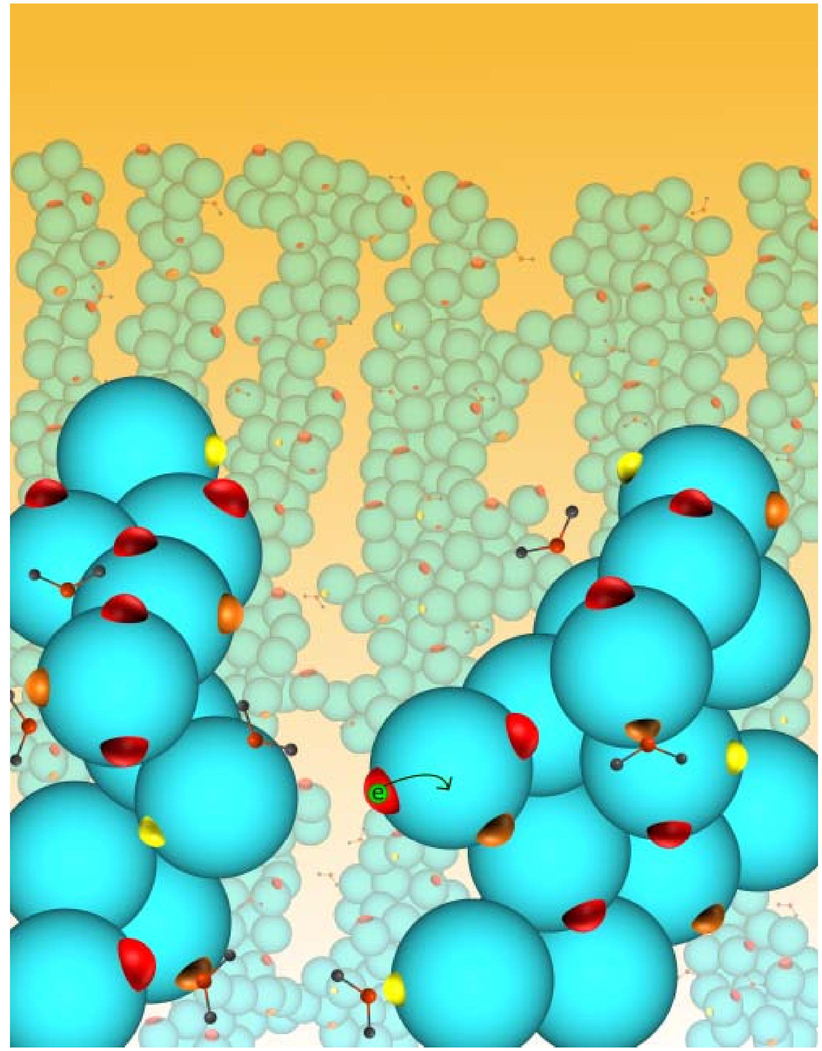
Low cost, third generation type solar cell

Can ALD be used to make the sensitizer?

- ALD can grow nanoparticles



Pt nanoparticles in a C matrix

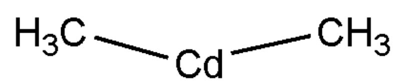


⇒ Deposit quantum dots for the sensitizer!

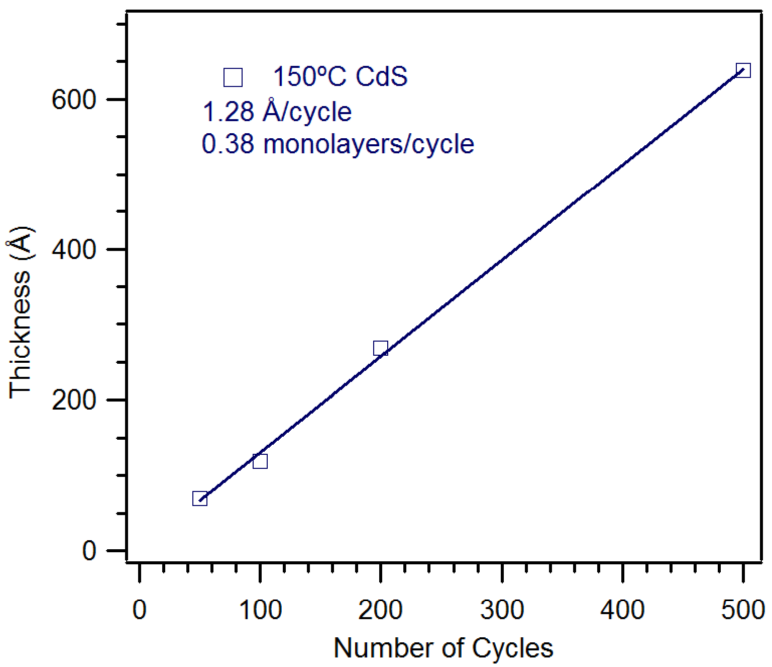
J. S. King, A. Wittstock, J. Biener, S. O. Kucheyev, Y. M. Wang, T. F. Baumann, S. Giri, A. V. Hamza, M. Baeumer, and S. F. Bent, *Nano Letters* **8** (2008) 2405-2409.

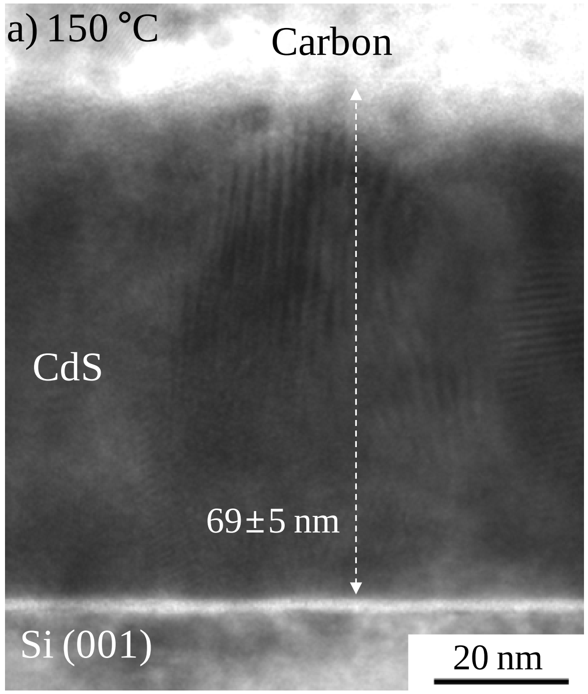
ALD of CdS Films

- Atomic layer deposition (ALD) of CdS by dimethylcadmium and H_2S
- CdS films are stoichiometric without contaminants
  - Substrate T :150 ˚C
  - Precursors: dimethyl cadmium, H_2S
  - 0.4 sec. pulse length, 20 sec. purge length
  - H_2S generated *in situ* from thioacetamide



TEM

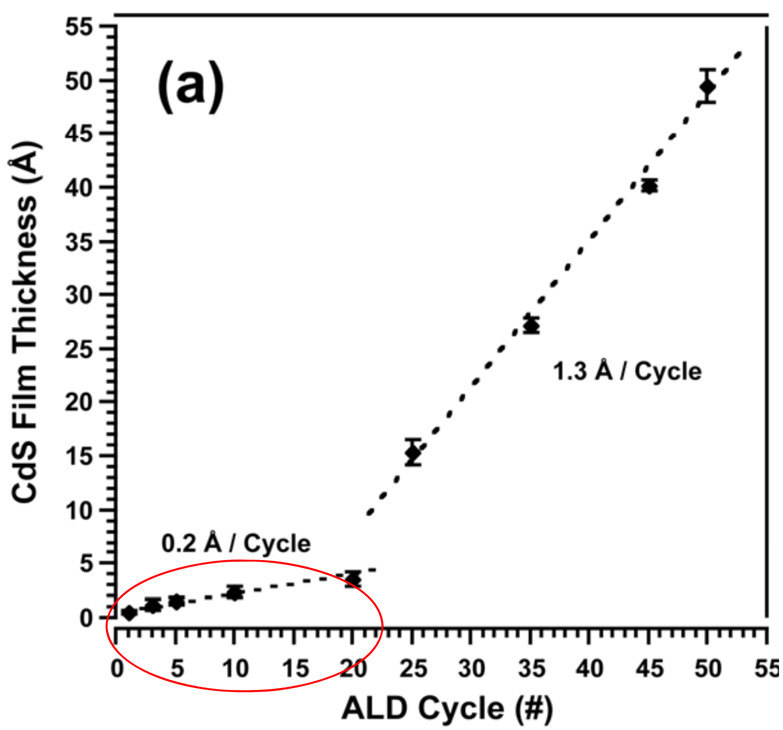


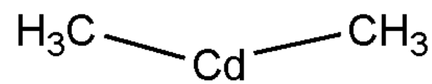


J. R. Bakke, H. J. Jung, J. T. Tanskanen, R. Sinclair and S, F. Bent, *Chem. Mat.,* 22 (2010) 4669-4678

ALD for QD synthesis

- Atomic layer deposition (ALD) can be used to deposit CdS QDs by operating in the "incubation regime"

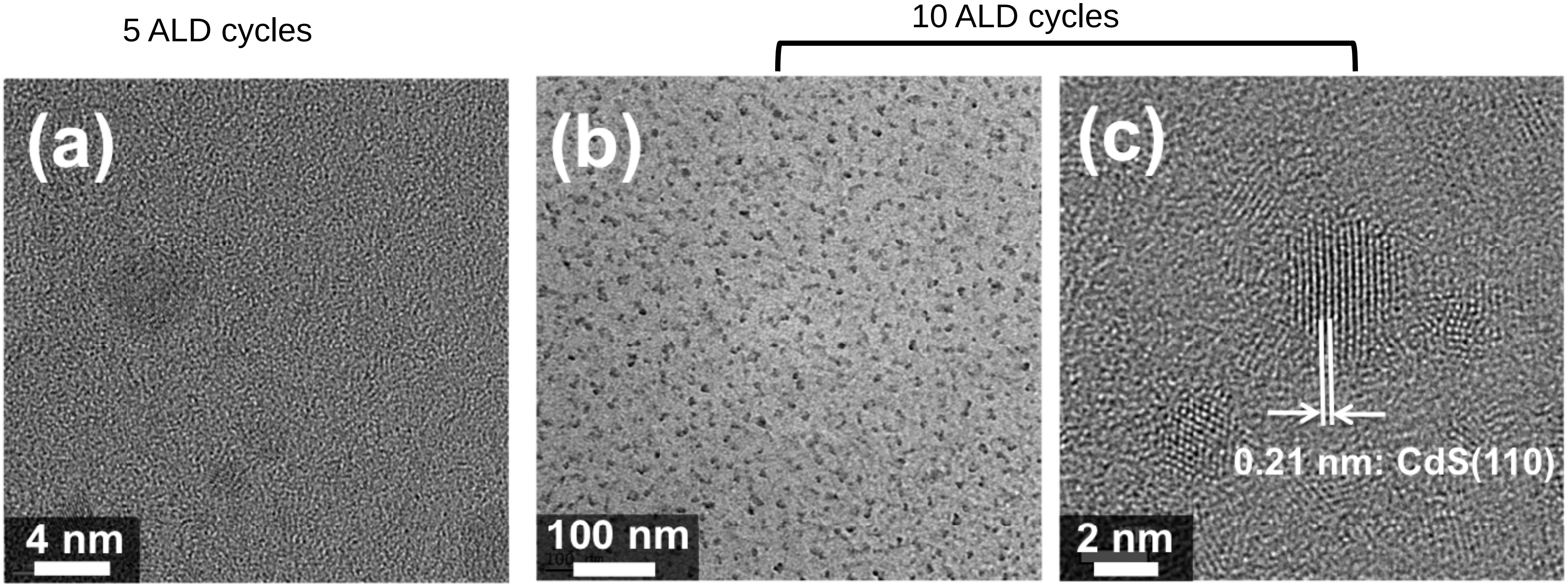




T. P. Brennan, P. Ardalan, H. B. R. Lee, J. R. Bakke, I.-K. Ding, M. D. McGehee, S. F. Bent, *Adv. Energy Mat.*, 2011, 1, 1169–1175

TEM of ALD CdS on planar substrate

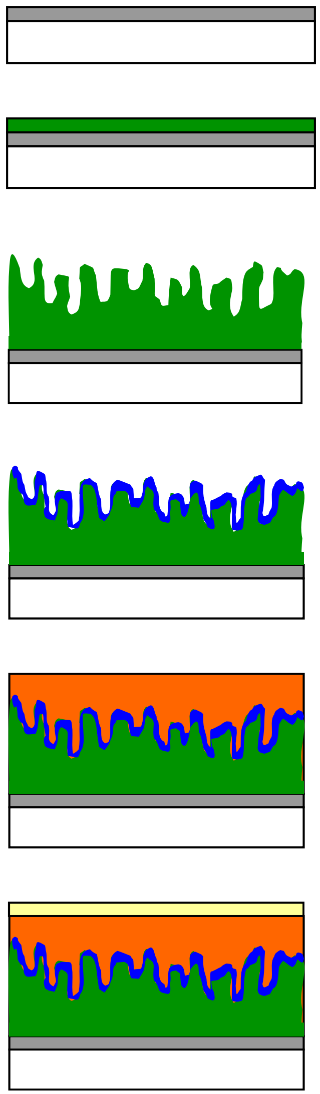
- CdS quantum dots of few nm diameter are deposited by ALD



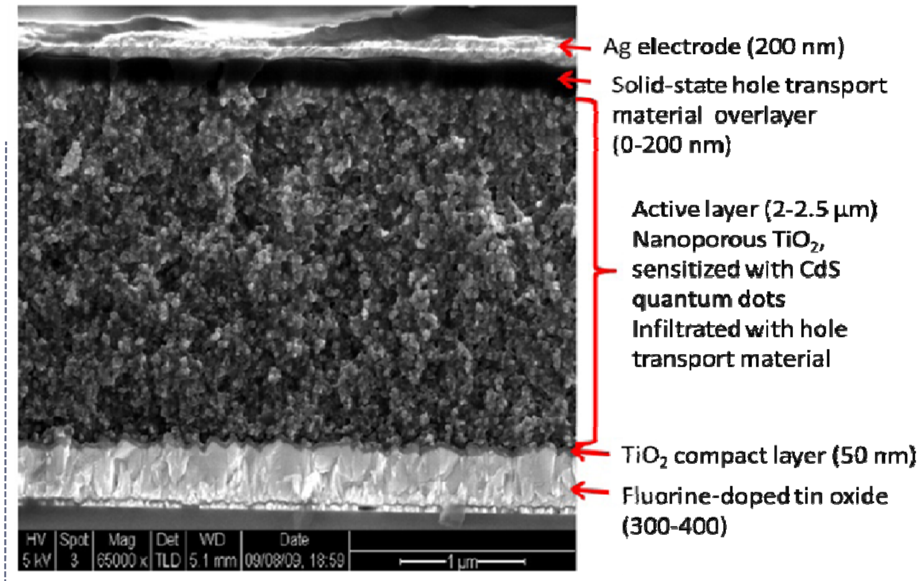
Plan-view TEM images of ALD CdS deposited for (a) 5 and (b)(c) 10 cycles on ALD TiO_2 surface on a Cu mesh TEM grid.

T. P. Brennan, P. Ardalan, H. B. R. Lee, J. R. Bakke, I.-K. Ding, M. D. McGehee, S. F. Bent, *Adv. Energy Mat.*, 2011, 1, 1169–1175

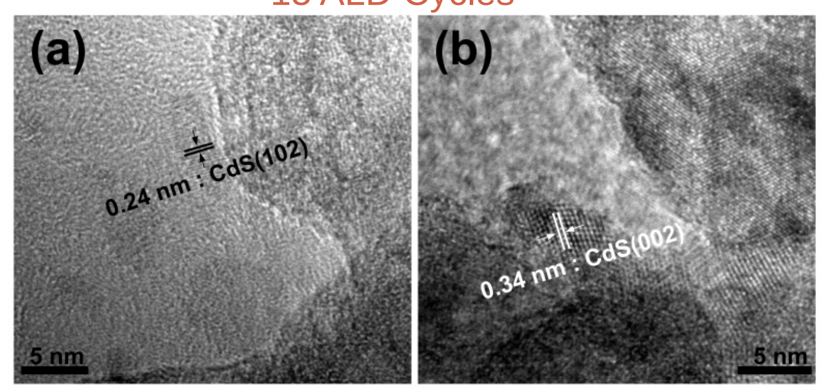
Fabrication of QDSSC



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



15 ALD Cycles



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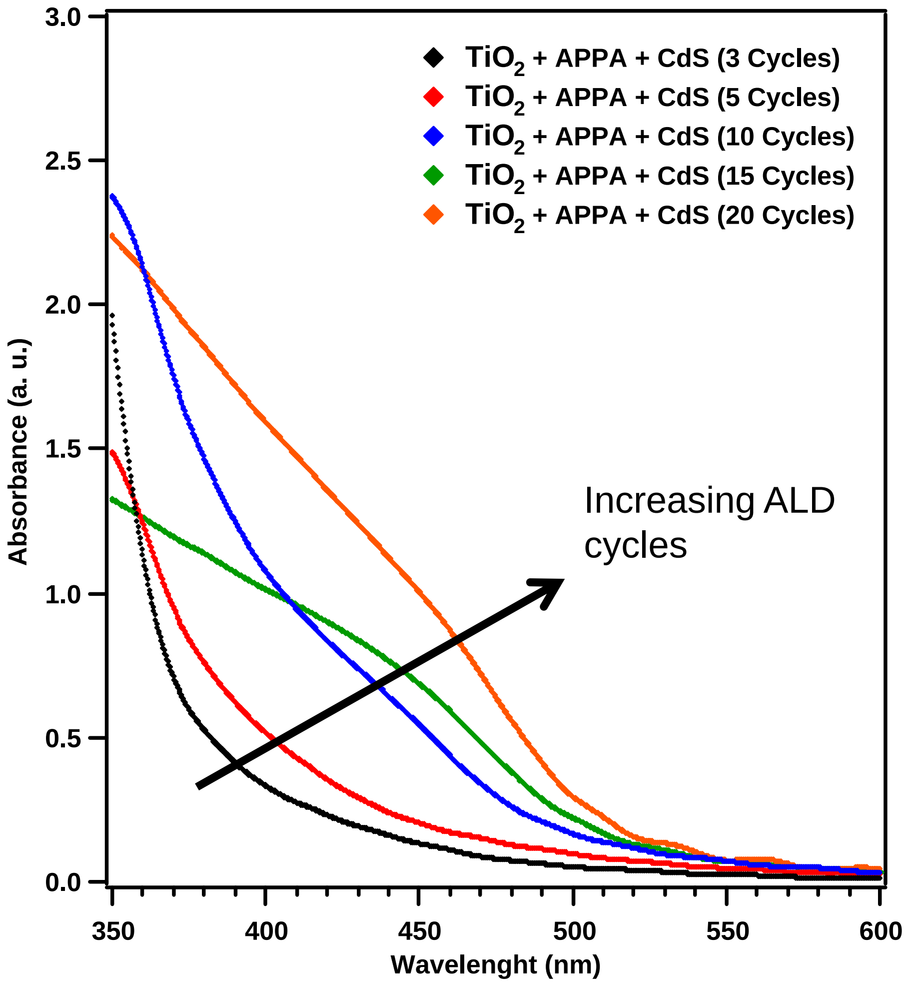
CdS Quantum Dots by ALD

Increasing ALD cycles

ALD Produces CdS Quantum Dots

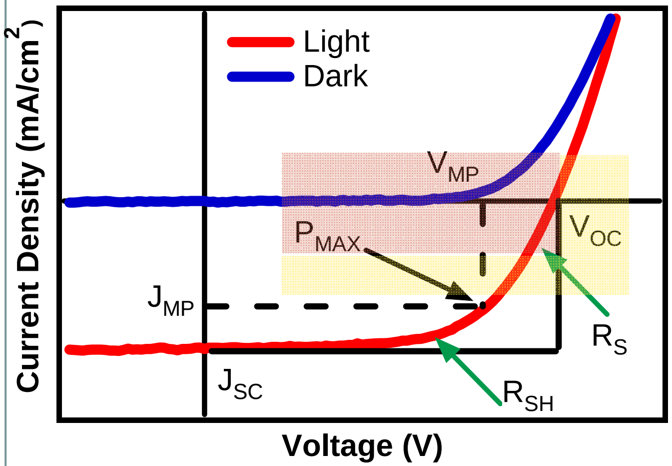


- Size quantization effects observed in materials grown by ALD
- QD sizes are ~2-6 nm according to UV-Vis bandgap

Sample	Bandgap (eV)
3 cycles ALD CdS	3.1
5 cycles ALD CdS	3.0
10 cycles ALD CdS	2.7
15 cycles ALD CdS	2.5
20 cycles ALD CdS	2.4

TiO_2 bandgap: 3.2 eV

PV Device Measurement



	ALD Cycle (#)	J_{SC} (mA/cm²)	V_{OC} (V)	FF	Efficiency (%)
CdS QDs	3	0.46	0.49	0.61	0.15
	5	0.38	0.53	0.56	0.13
	10	0.21	0.60	0.68	0.09
	15	0.14	0.58	0.77	0.07
	20	0.09	0.67	0.76	0.05
Spiro Only	0	0.34	0.45	0.45	0.05

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

T. P. Brennan, P. Ardalan, H. B. R. Lee, J. R. Bakke, I.-K. Ding, M. D. McGehee, S. F. Bent, *Adv. Energy Mat.*, 2011, 1, 1169–1175

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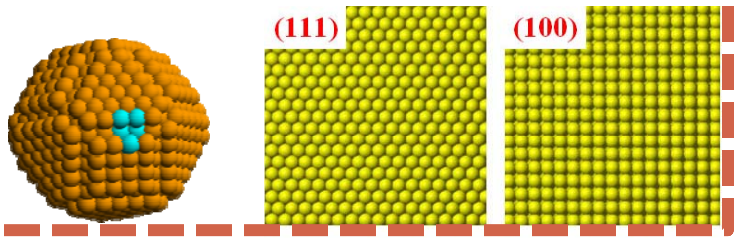
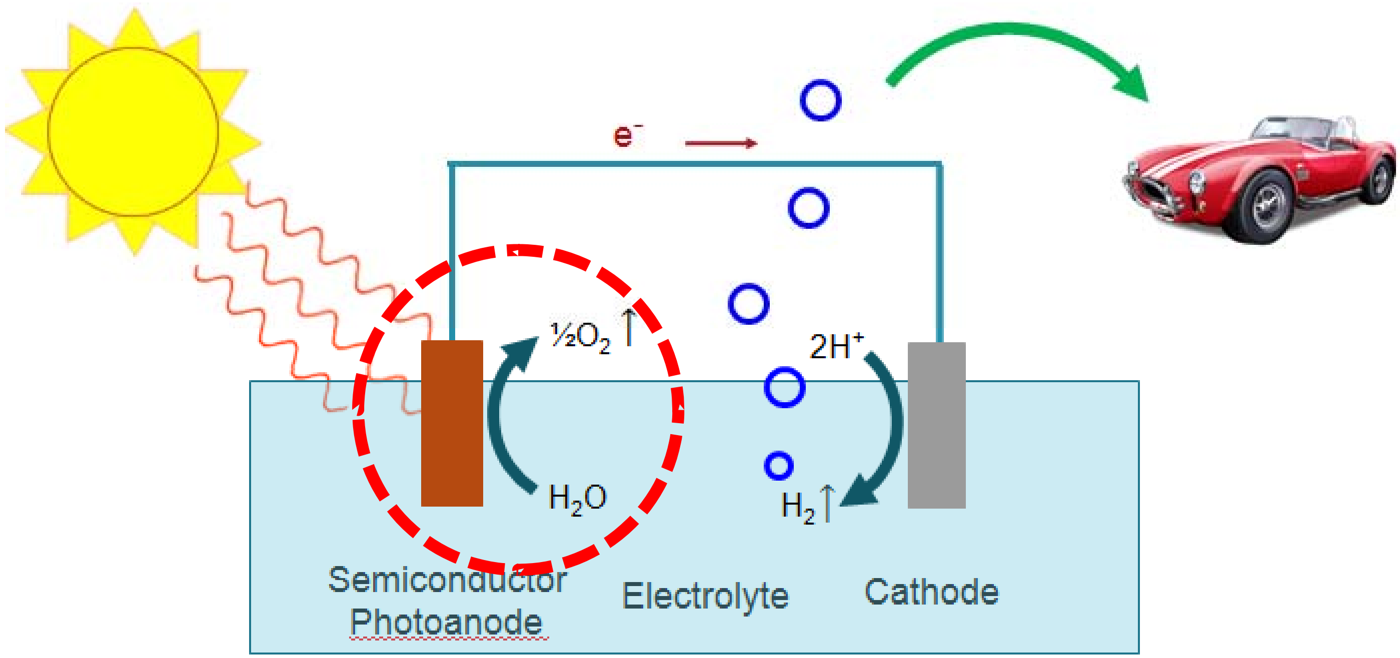


Photoelectrochemical Splitting of Water

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

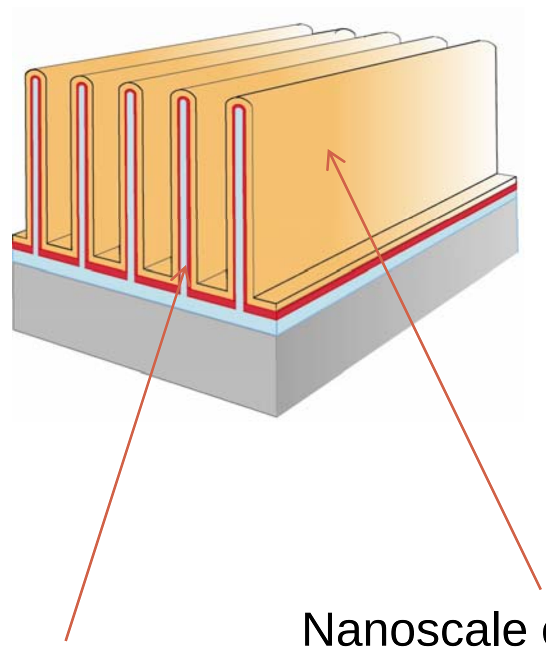
$$H_2O \rightarrow H_2 + \frac{1}{2} O_2$$



- 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

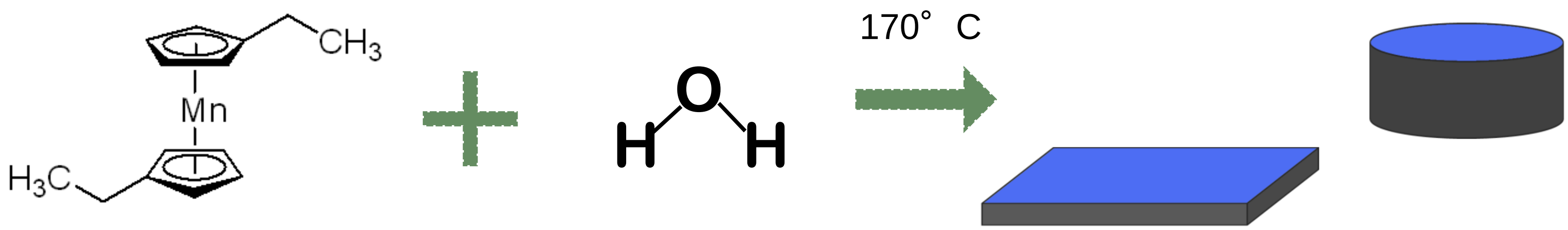


Nanostructured semiconductor for light absorption, high surface area

Nanoscale coating for stability and catalysis

Synthesis of MnO_x Catalyst

ALD procedure:

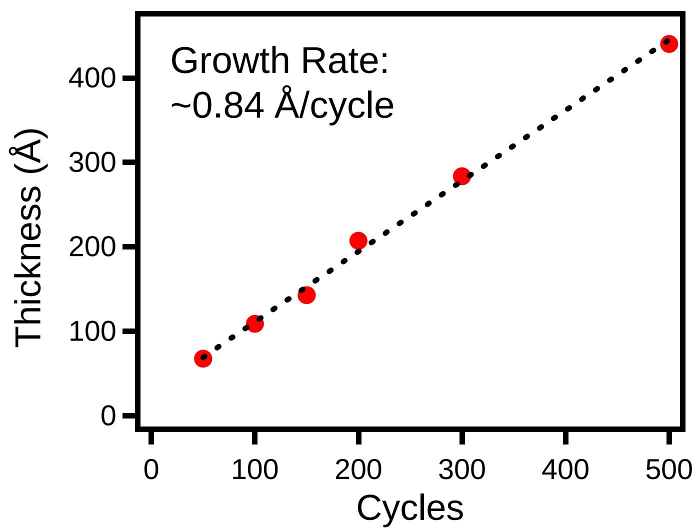


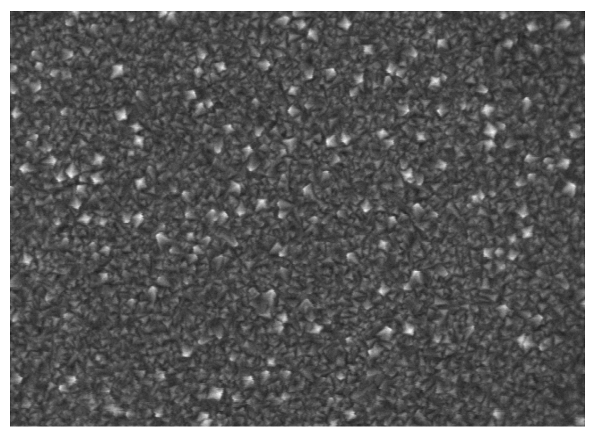
Bis(ethylcyclopentadienyl) manganese

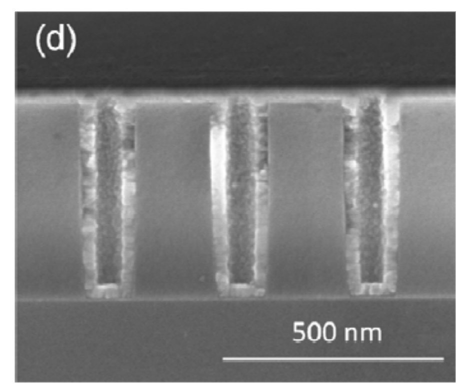
Water

MnO

Burton, B.B. et al. *Thin Solid Films,* 2009

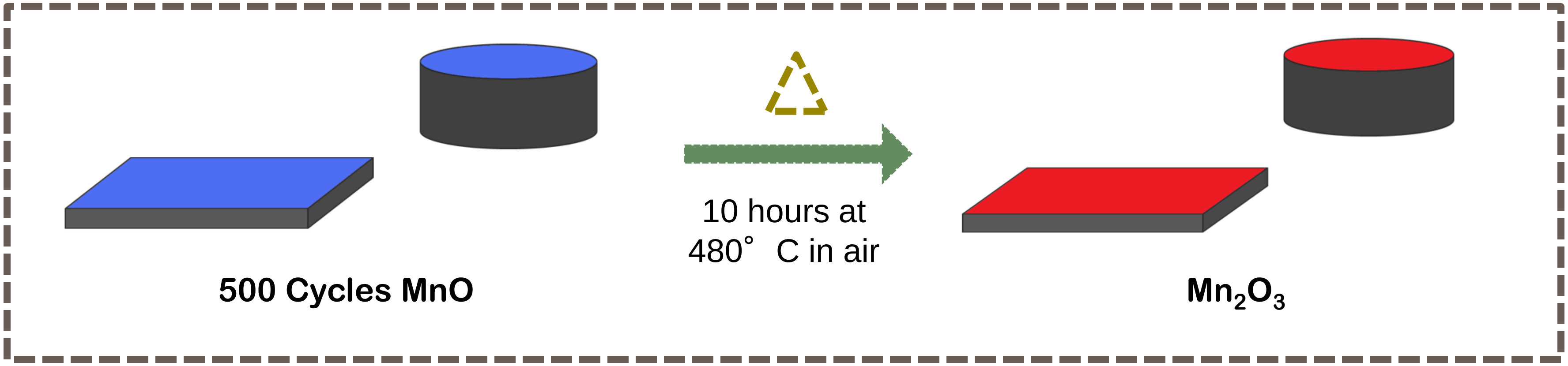


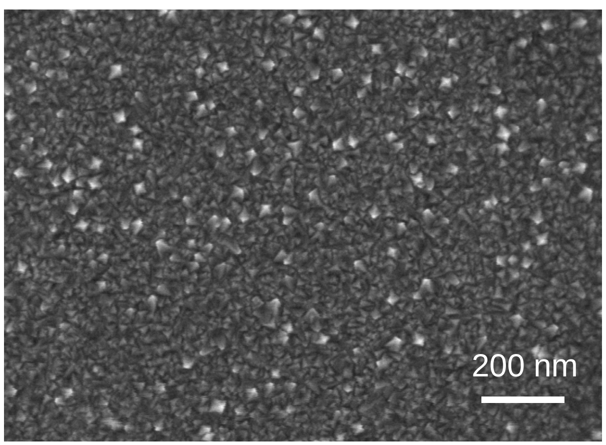




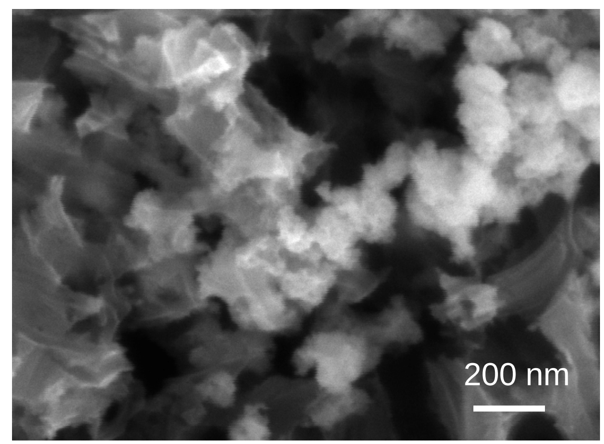
Synthesis of MnO_x Catalyst

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





MnO on GC Before Anneal

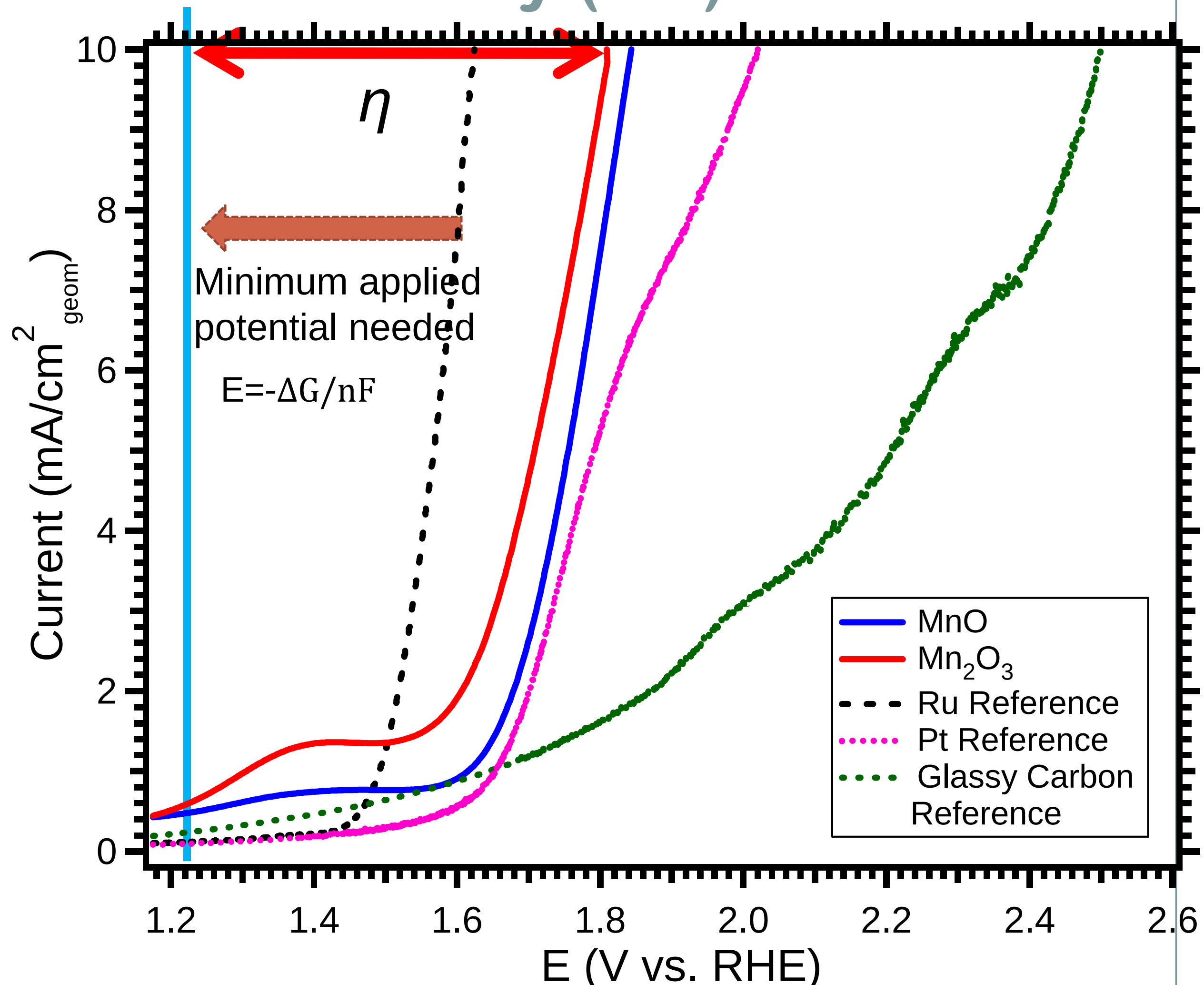


Mn_2O_3 on GC After Anneal

Testing MnO_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_2 saturated
- Rotation Speed : 1600 rpm
- Room temperature
- Hg/HgO reference electrode
- Platinum wire counter-electrode



K. L. Pickrahn, S. W. Park* Y. Gorlin, H. B. R. Lee, T. F. Jaramillo, and S. F. Bent, Adv. Energy Mat., 2 (2012) 1269–1277

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