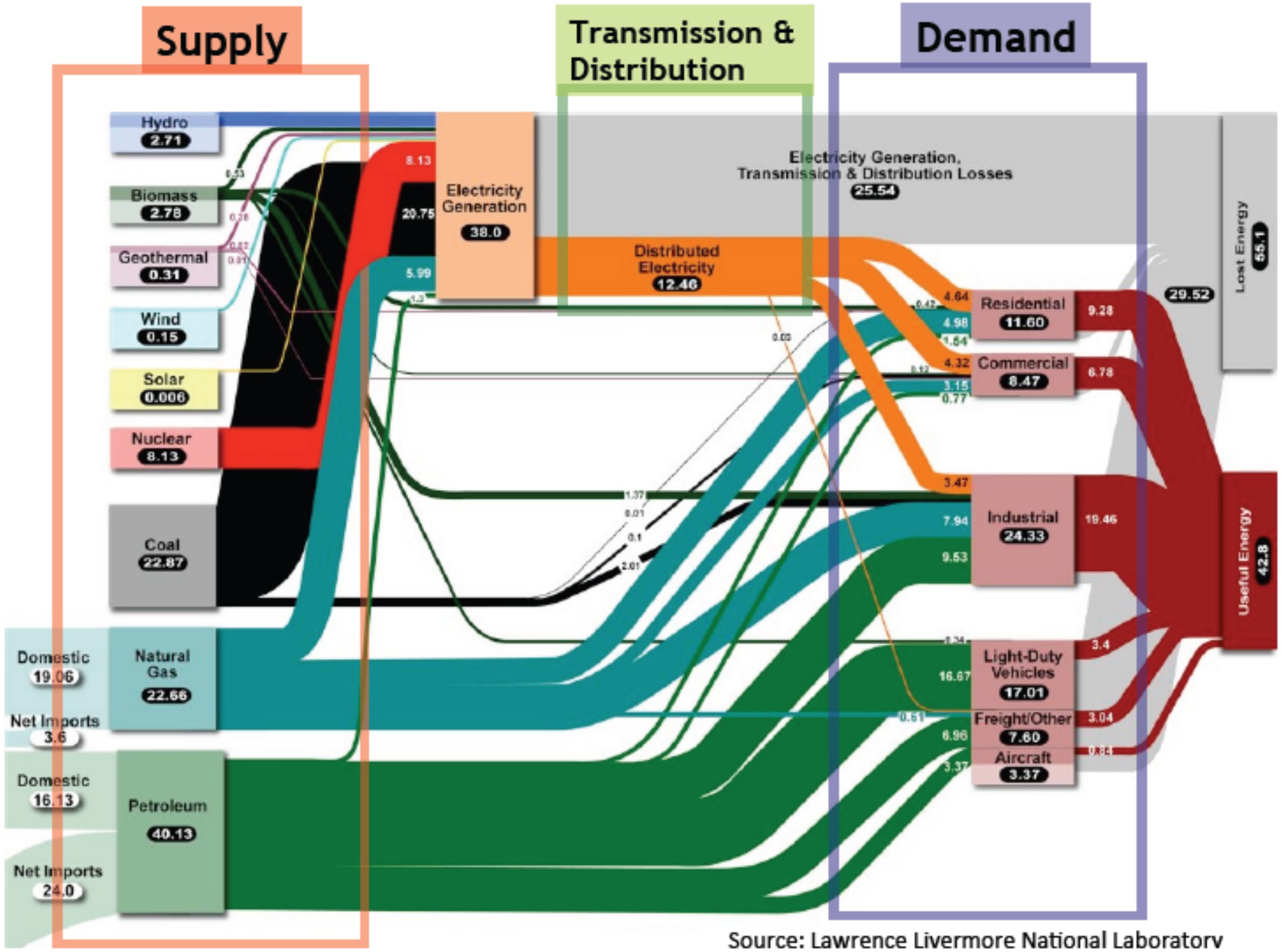
Energy and Environment: the Challenge of Our Times



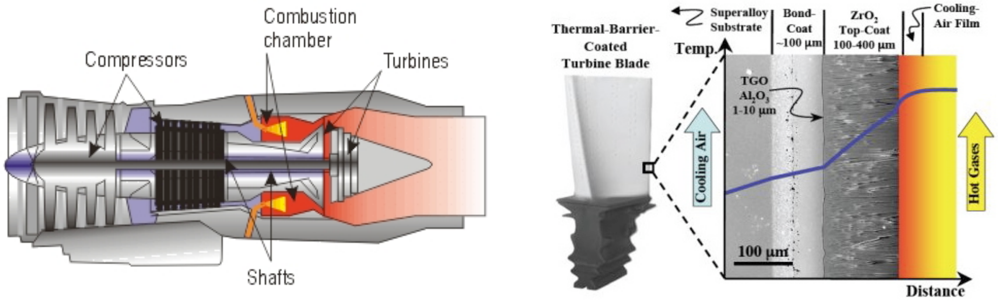
Source: Lawrence Livermore National Laboratorv

85% comes from non-renewable fossil fuels that warm the Earth, distort our foreign policy, and damage our economy

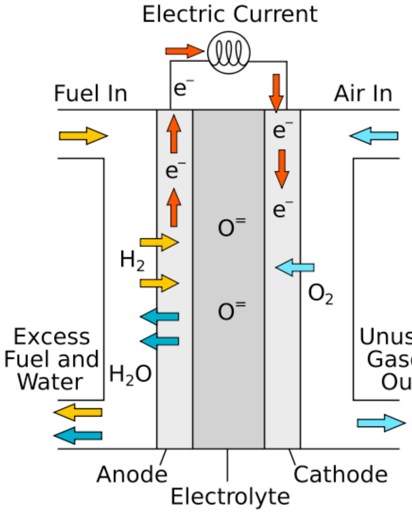
New Ideas for Green Energy Solutions (from Computer Simulations)

Emily A. Carter
Princeton University
http://carter.princeton.edu

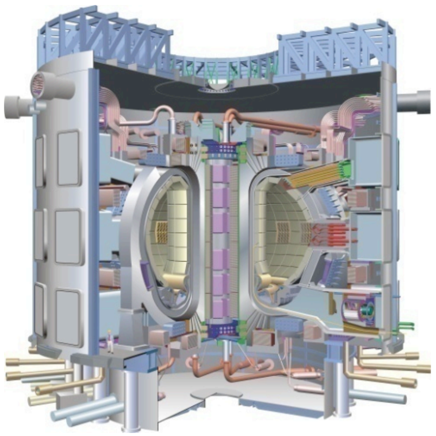
Combustion of Biofuels



Jet Turbine Engines



Solid Oxide Fuel Cells



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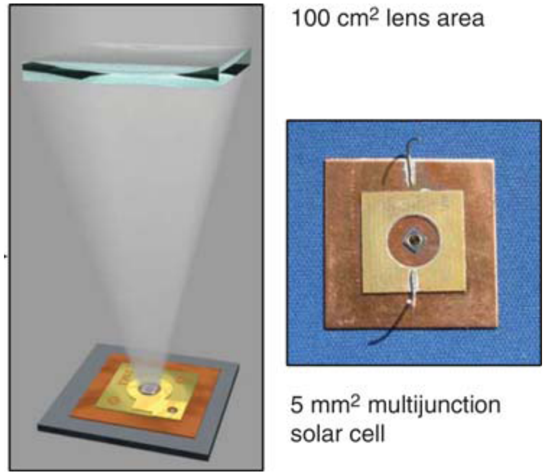
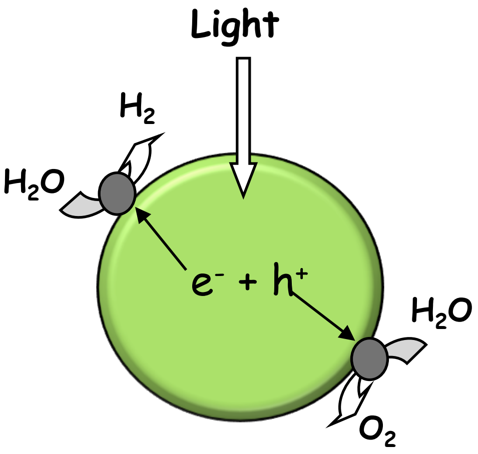
Lightweight vehicles



Photovoltaics

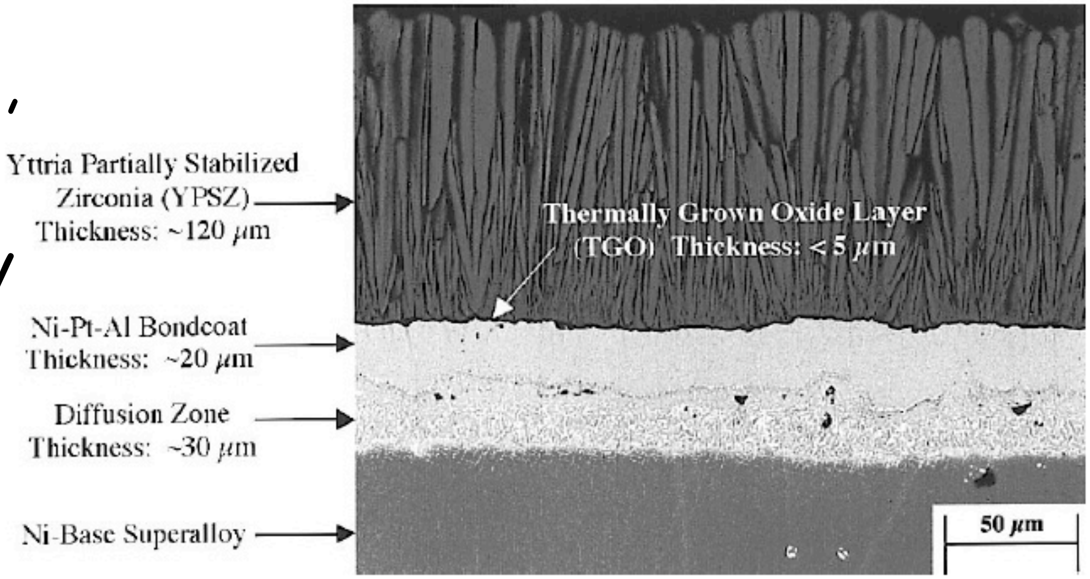


Photocatalysts

Why Computation?

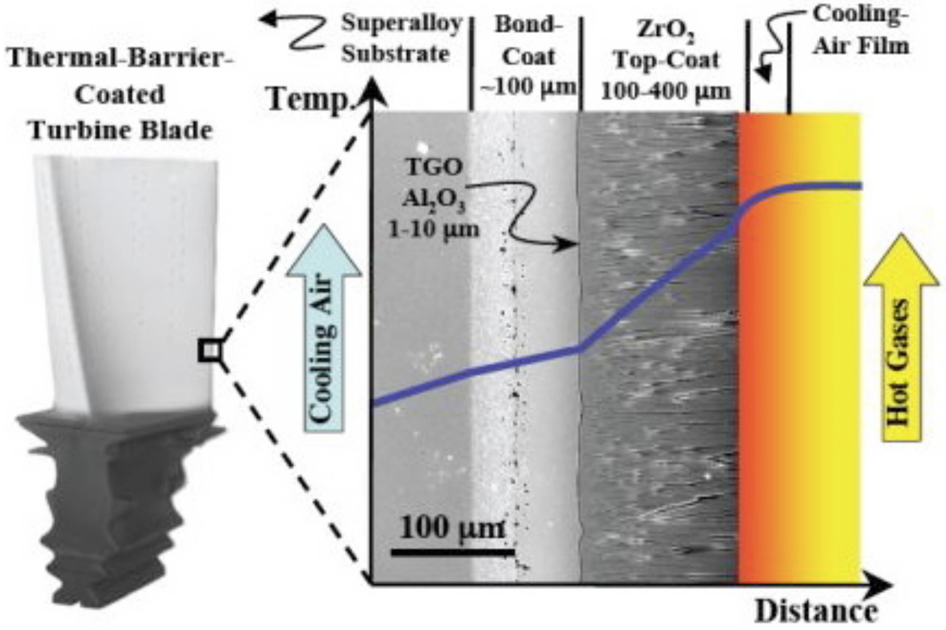
- Lab measurements provide incomplete picture
- Computer simulations can:
  - Fill information gaps
  - Offer interpretations
  - Suggest new targets
- What physics to include?

- Independence crucial.
- For molecules/materials, fundamental physical interactions governed by electron distribution => quantum mechanics.



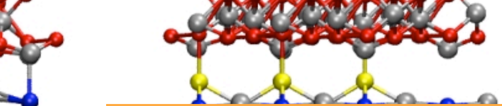
E. A. Carter, *Science*, **321**, 800 (2008).

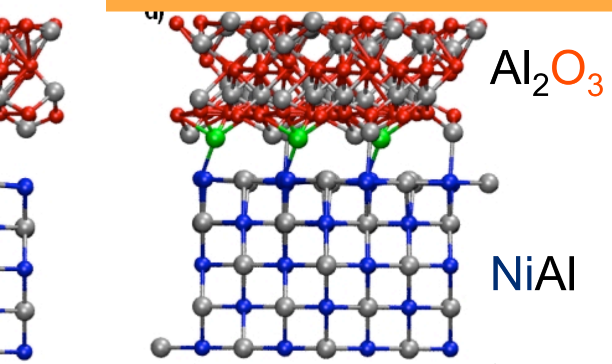
Jet Turbine Engine Thermal Barrier Coating (TBC) Design: Improved Fuel Efficiency for Airplanes and Power Plants



- Coating fails after high T cycling at metal-oxide interface (TGO growth).
- Adding Hf, Y, Pt to NiAl bond coat helps for unclear reasons
- Quantum mechanics calculations reveal roles of each => design insights
- New NiAl alloy composition for higher T operation (patent pending)
- => More energy efficient planes and electricity production

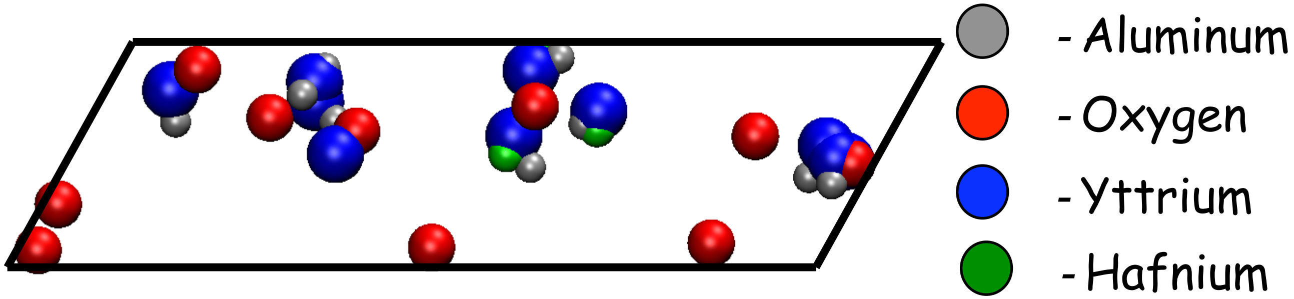
Discovered Roles of Hf and Y in TBCs => Suggest New Additive to Increase TBC Stability





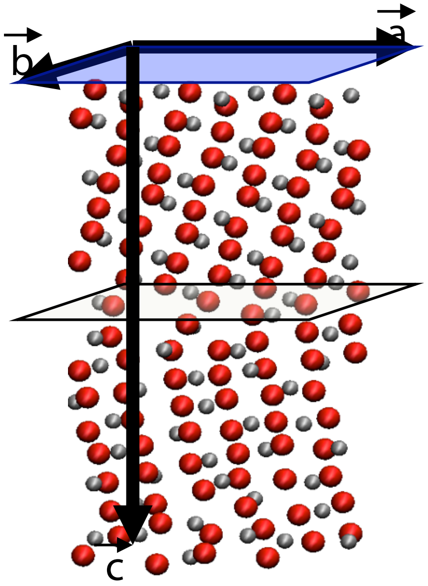
Hf increases adhesion >3x, forming many strong M-O bonds.

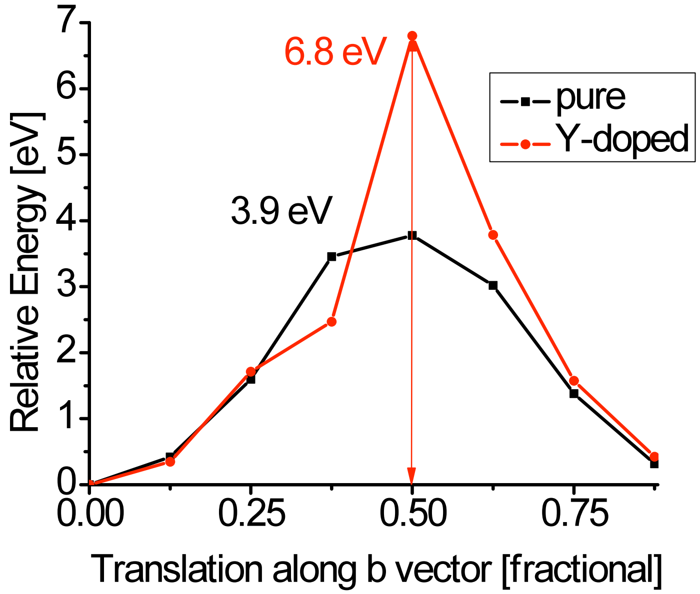
K. Carling & EAC, Acta Materialia **55**, 2791 (2007)



Y and Hf block diffusion of Al in alumina grain boundaries, slowing alumina growth and creep.

I. Milas, B. Hinnemann, & EAC, J. Mat. Res. **23**, 1494 (2008)





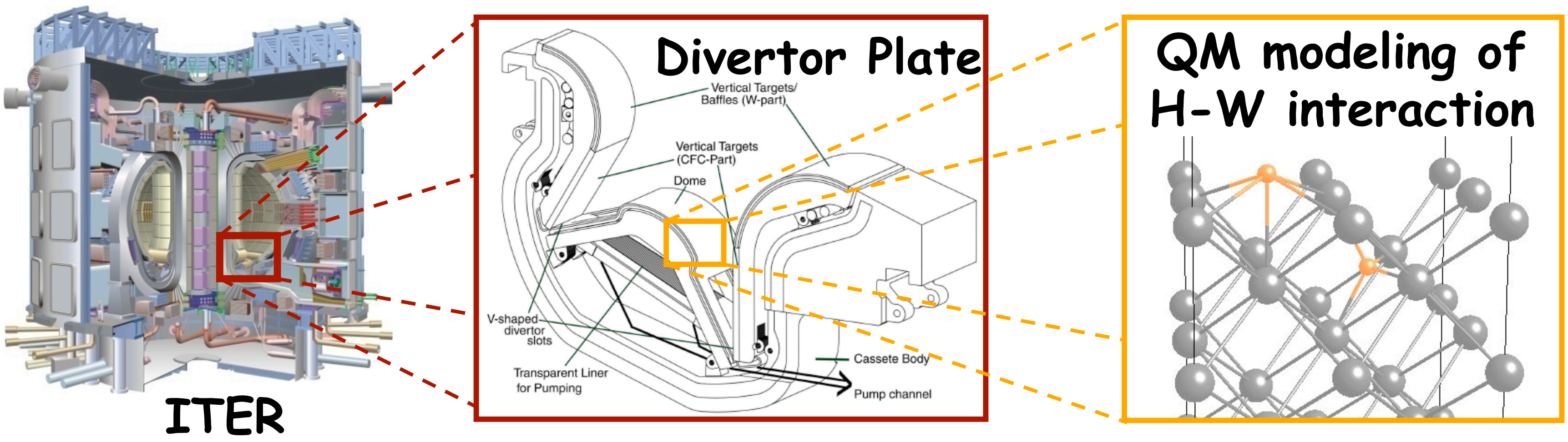
Small Y additions increase barrier to GB sliding, inhibiting creep, due to strong M-O bonds

⇒ predict Ba increases barrier most

(proposed new additive)

I. Milas & EAC, J. Mat. Sci. **44**, 1741 (2009)

New Materials for Fusion Reactor Walls



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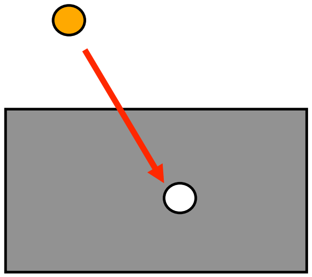
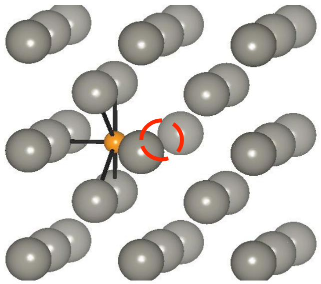
Divertor Plate

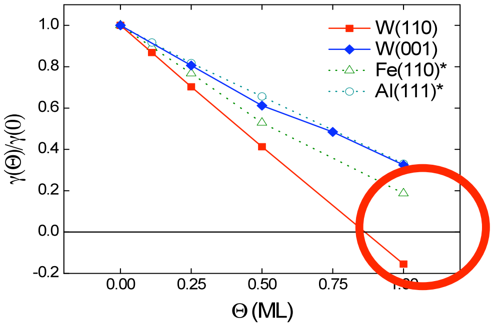
QM modeling of H-W interaction

e.g., Tungsten

- High m.p. (3695 K), good neutron absorber, high thermal conductivity, H/D/T?







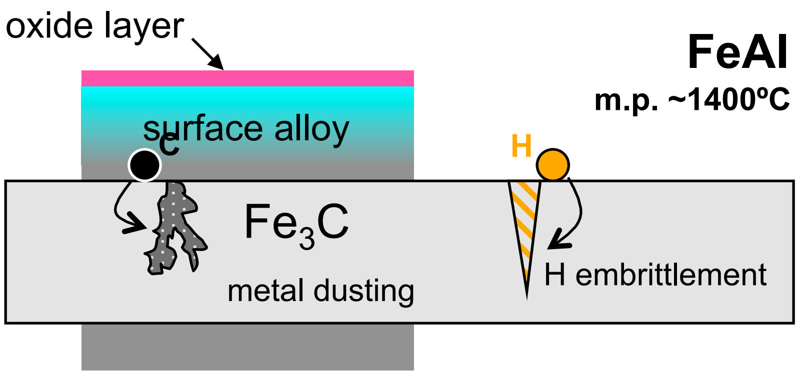
Neutrons produce vacancies → Predict D/T bind to vacancies → Fracture

- Optimize alloy composition to inhibit D/T incorporation (cf. steel)

D. Johnson and EAC, J. Mater. Res., **25**, 315 (2010)

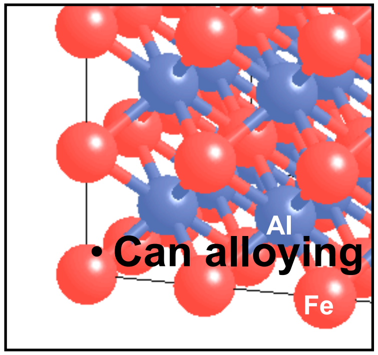
Designing Iron (Fe) Alloys to Protect Steel

D. F. Johnson and EAC, Acta Materialia, 58, 638 (2010); J. Phys. Chem. C, 114, 4436 (2010)



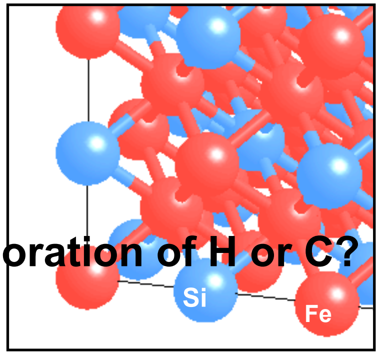
FeAl

m.p. ~1400ºC



Fe_3Si

m.p. ~1250ºC



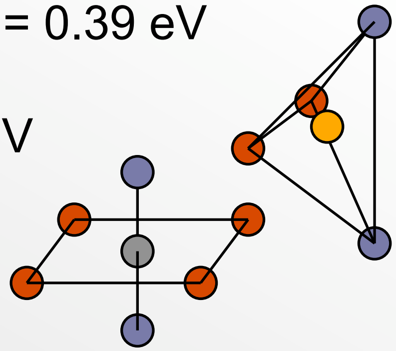
- **Can alloying Fe limit incorporation of H or C?**

Both form stable oxides/withstand high T

FeAl

$E_{dissolution}$ (H) = 0.39 eV

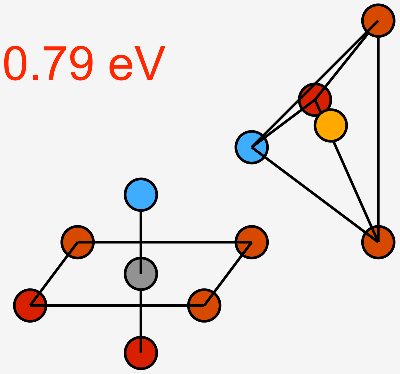
$E_{dissolution}$ (C) = 1.26 eV



Fe_3Si

$E_{dissolution}$ (H)= 0.79 eV

$E_{dissolution}$ (C)= 1.65 eV



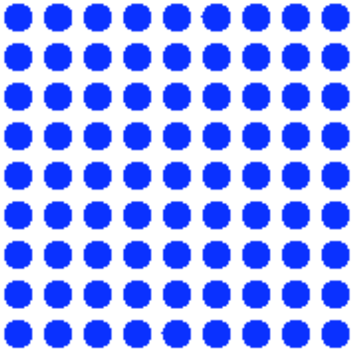
Predict 2-4x more unfavorable E_{diss} in Fe_3Si than in steel (Fe)

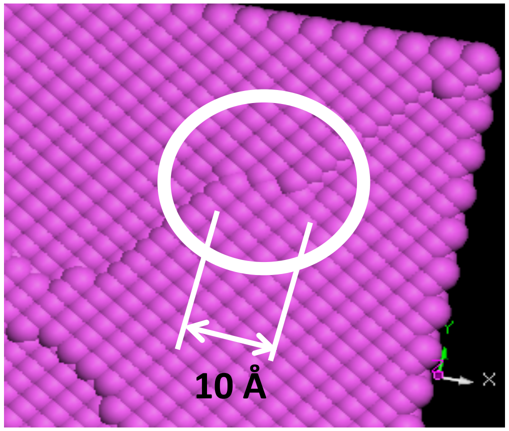
⇒ Use thin film of Fe_3Si to keep H and C out of steel.

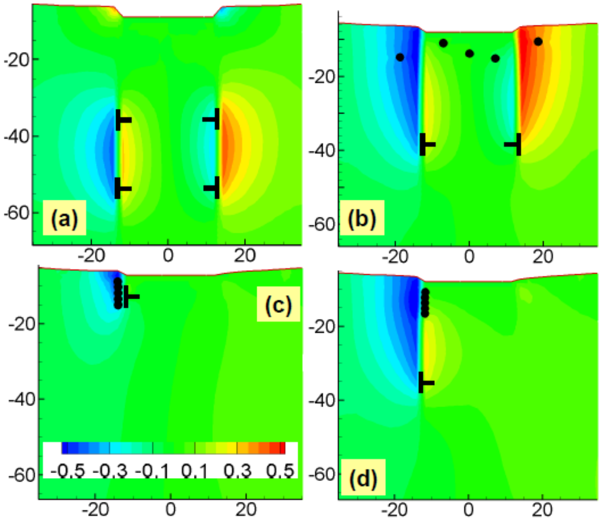
Lightweight Alloys for Improved Vehicle Fuel Efficiency

- Optimize alloy mechanical properties (ductility, strength)
- Controlled by microstructure (grain boundaries, dislocations)
- Expts post-mortem; classical, empirical simulations till now
- Parallel, linear quantum mechanics code for up to 10^6 atoms

(L. Hung and EAC, Chem. Phys. Lett. 475, 163 (2009))



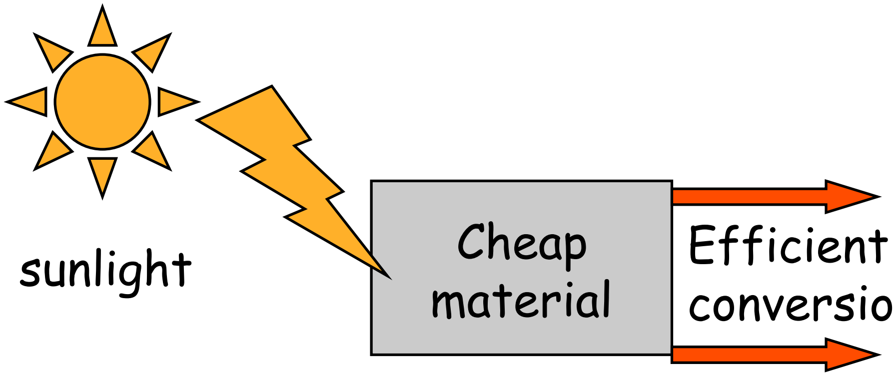




Predict structure and motion of dislocations as metal deforms
Use to design Al, Mg alloys (additives, microstructure) with optimal strength and ductility to manufacture strong lightweight vehicles

I. Shin, A. Ramasubramaniam, C. Huang, L. Hung, and EAC, Phil. Mag. **89**, 3195 (2009)
Q. Peng, X. Zhang, C. Huang, EAC, and G. Lu, submitted (2010)

Photovoltaic and Photocatalyst Design Concepts from Molecular Biology and Quantum Mechanics



sunlight

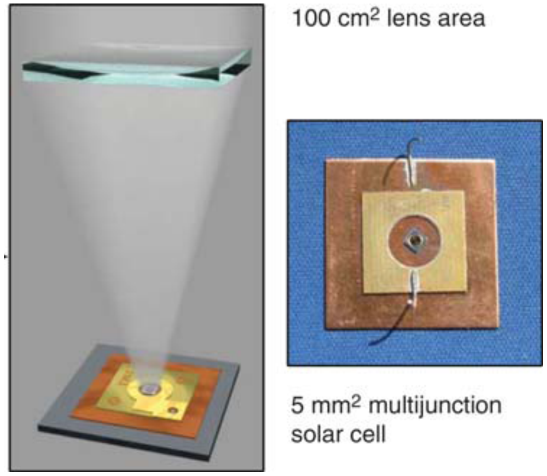
Cheap material

Efficient conversion

Electricity

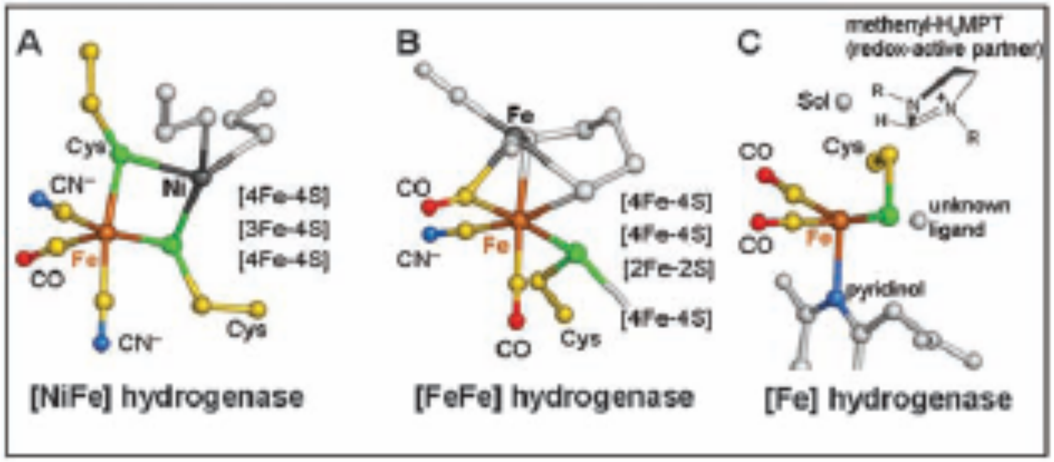
Fuels (hydrogen, natural gas,…)

State-of-the-art design for PV



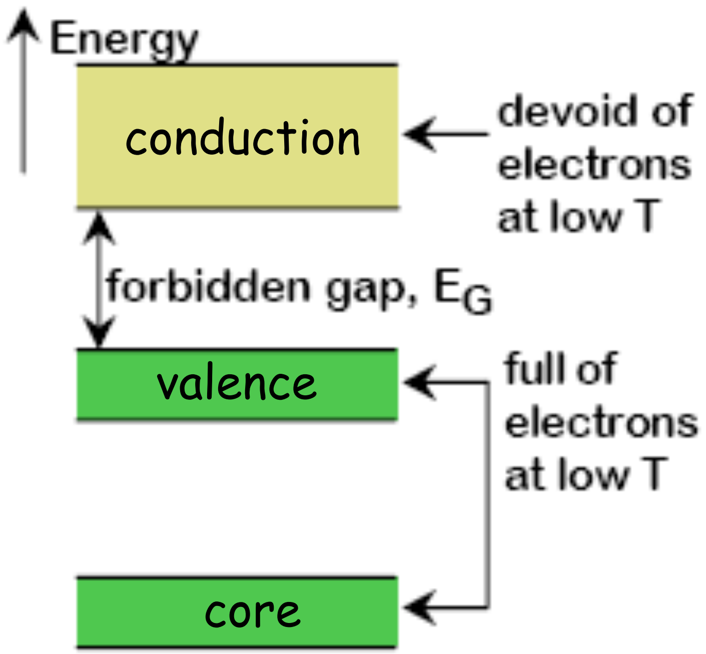
Problems: Efficiency, Cost, Toxicity

Bio-inspired design with quantum constraints



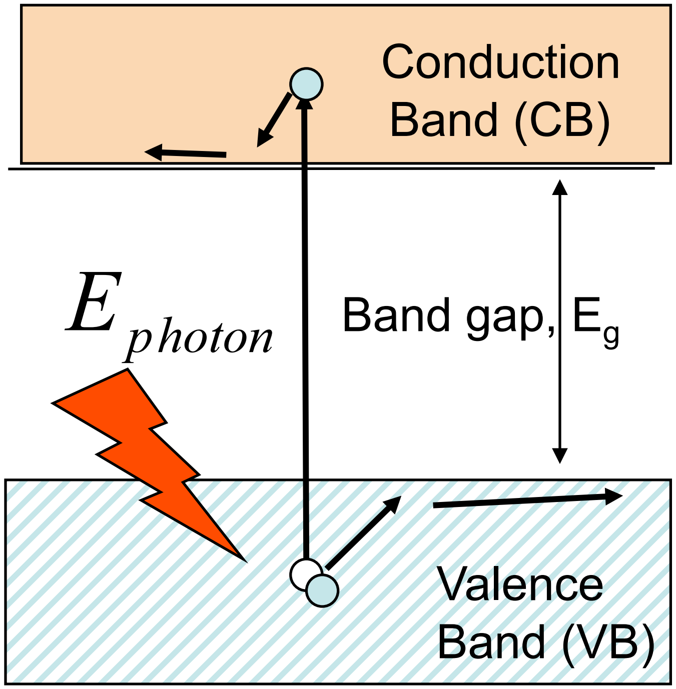
Key Actors: Electrons

- Key to creating electricity & fuels
- Electrons distributed in both space and energy
- Tightly bound "core and valence bands"
- "Excite" electrons to loosely bound "conduction band" to harvest electricity or catalyze chemistry



Key Concept: Conservation of Energy

Convert "photon" energy:
excite electron, leave "hole"



Graphic: Courtesy of Dick Swanson

Light absorbed only if $E_{photon} > E_g$

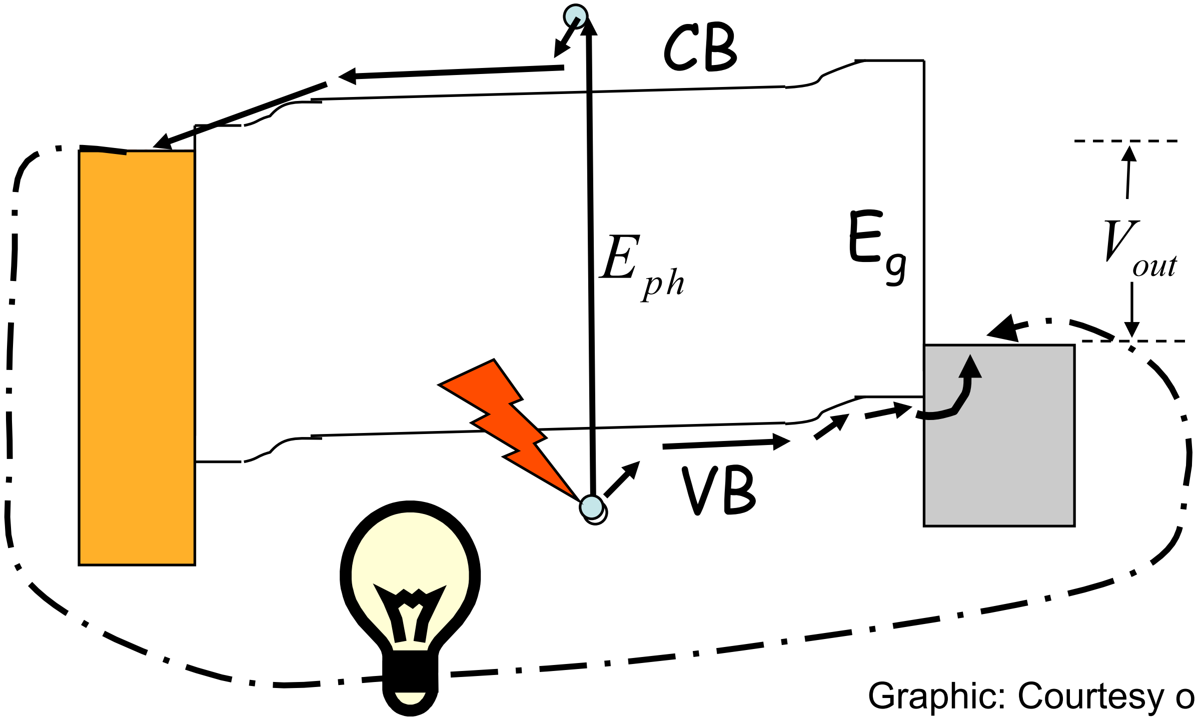
Solar Cell Operation

1: Absorb photons => create (e-h) current, I_{out}

2: Electrons flow to external circuit

3: Power = $I_{out}V_{out}$ where voltage $V_{out} < E_g$

Max power: max e-h generation and separation I_{out} at max V_{out}



Graphic: Courtesy of Dick Swanson

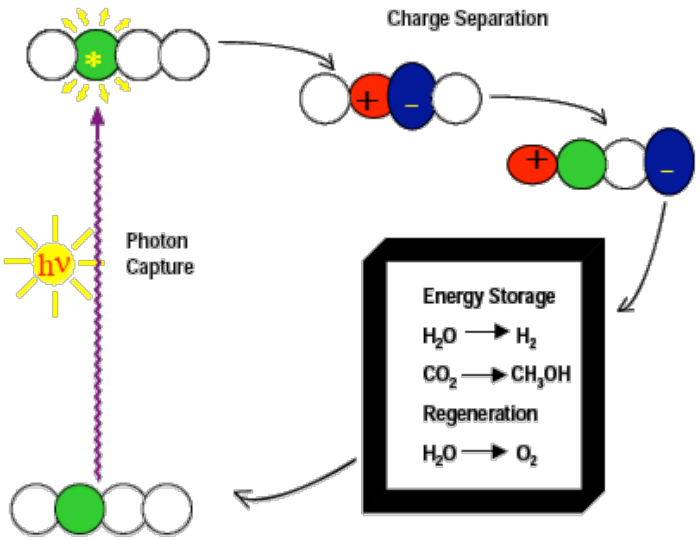
Silicon: must be ultrapure for max I_{out} and has non-optimal E_g

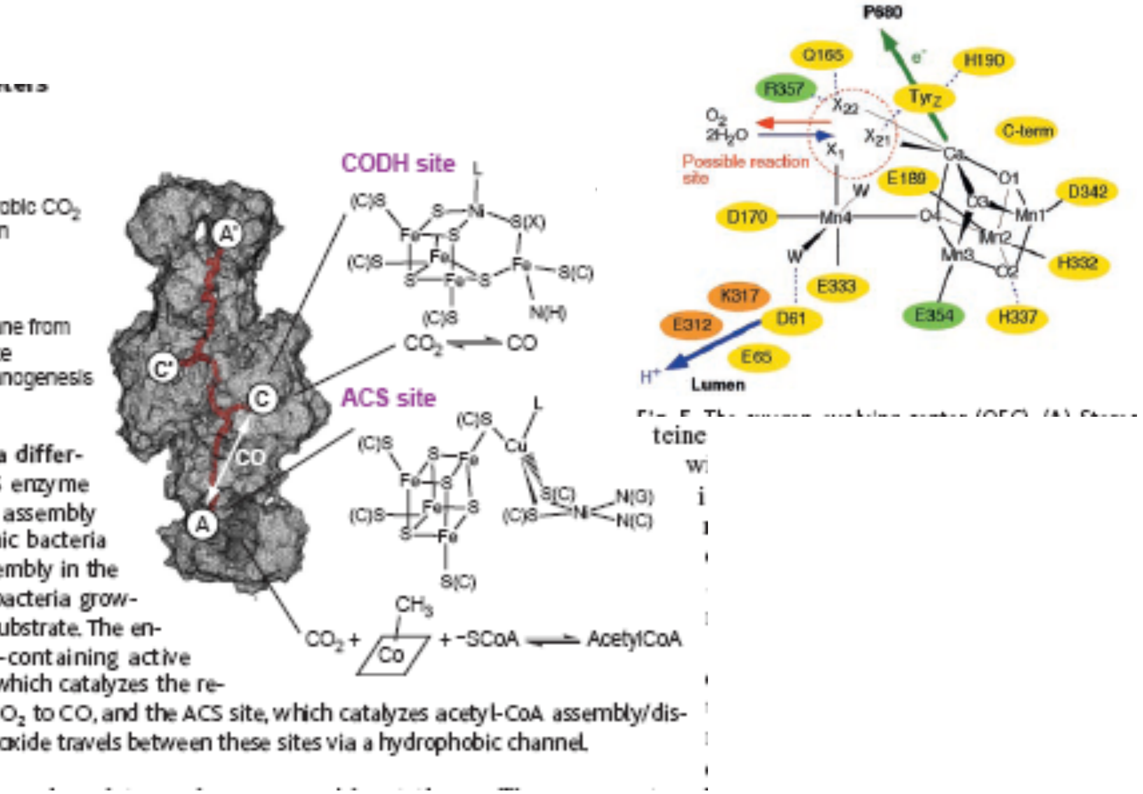
=> increases cost, limits power

New Materials: Cues from Nature

How does Nature:
- separate charge?
- transport electrons?
- make fuel?

Plants, algae, & bacteria use: metal oxides & sulfides



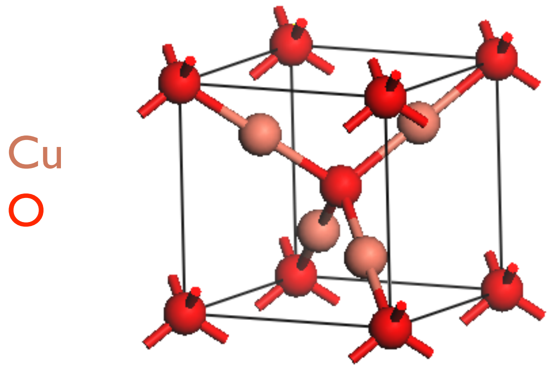


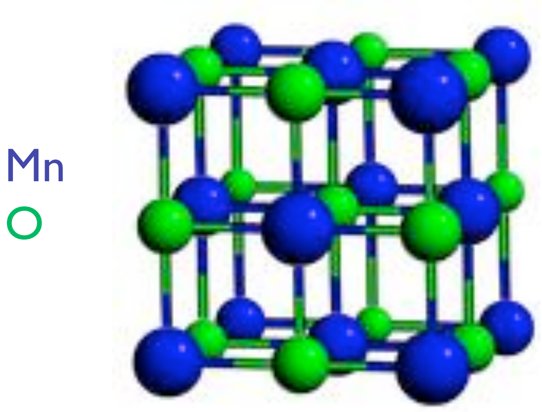
a differ-
enzyme
assembly
ic bacteria
embly in the
acteria grow-
ubstrate. The en-
-containing active
which catalyzes the re-
O_2 to CO, and the ACS site, which catalyzes acetyl-CoA assembly/dis-
oxide travels between these sites via a hydrophobic channel.

Our Strategy:
Exploit evolution
without its constraints (of early Earth environment or keeping plants alive!)

Cues from Nature

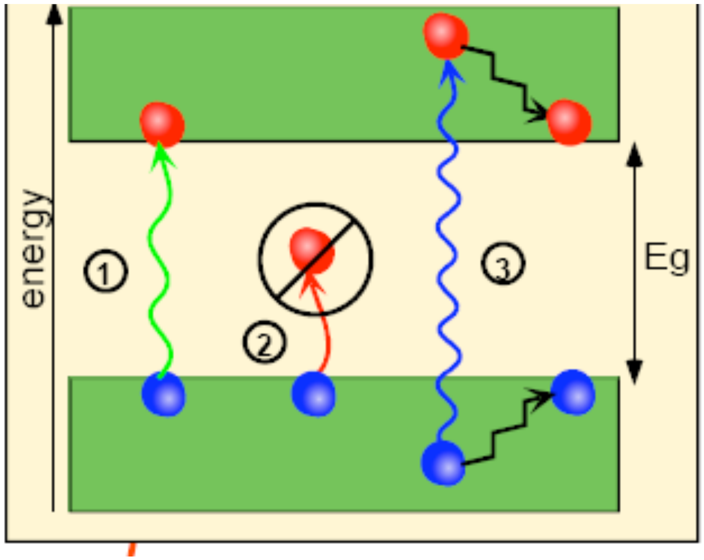
- Use cheap metals: manganese, calcium, iron, nickel, and copper
- Use in cheapest form (oxides)

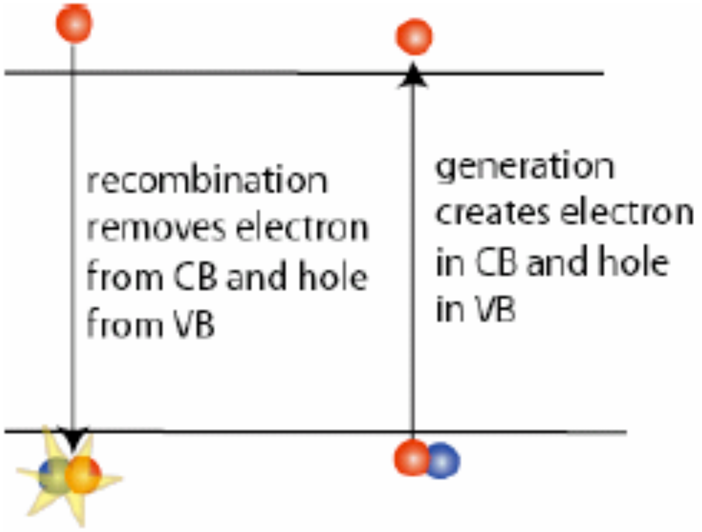




- Optimize composition and nanostructure
- What to optimize? Back to physics…

Optimize Band Gap and Avoid Recombination





- Small E_g absorbs most sunlight -> maximizes current I
- Large E_g maximizes voltage V

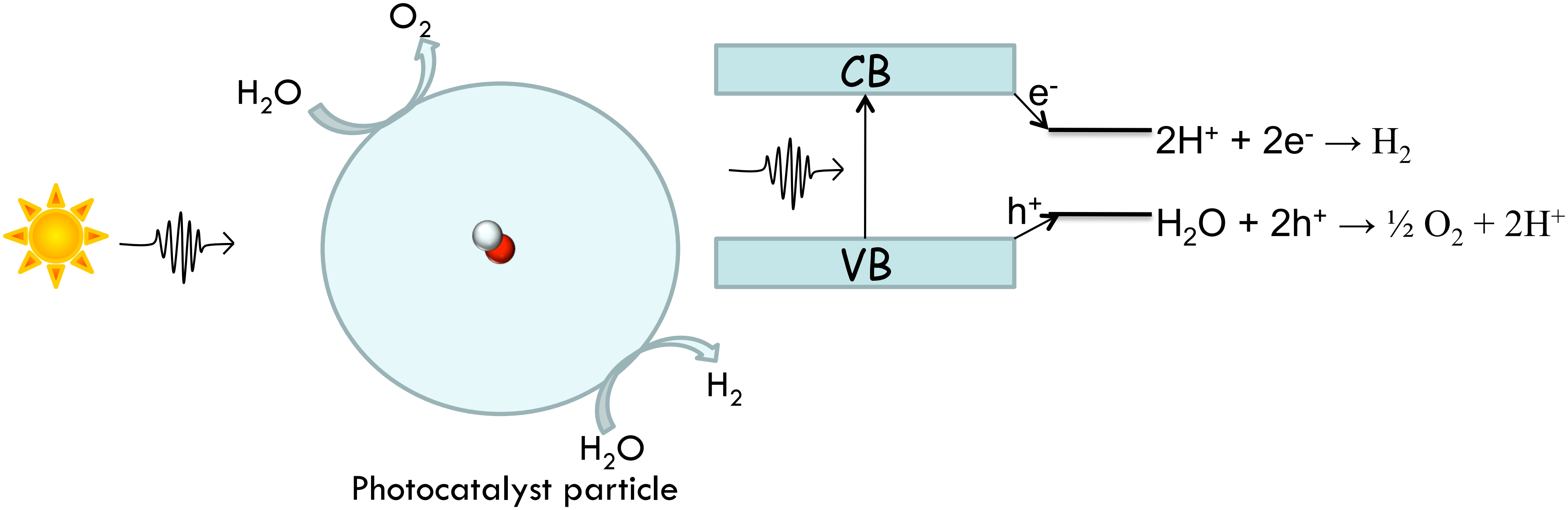
Electron-hole recombination -> reduces external current or electron-hole chemistry to fuels

New Materials Design Strategies:

- Max power (IV) at intermediate E_g => optimize E_g by alloying oxides
- Avoid recombination by maximizing e-h pair lifetime

=> alloy oxides to exploit quantum spin manipulation

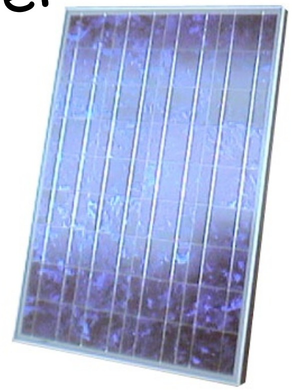
Photocatalysts a Step Beyond Photovoltaics: Further Constraints



- Thermodynamics of, e.g., water splitting places lower bound on $E_g \Rightarrow$ only visible/UV light absorbers $\Rightarrow$ visible light absorber for max absorption
- Positions of VB and CB must straddle energy required to split water
- Best catalyst now at most few % efficient and requires additives…
- Design metal oxide alloy catalysts with proper E_g, CB/VB placement, max e-h lifetime, fast surface chemical kinetics
  => produce hydrogen, natural gas, methanol from sunlight, H_2O, and CO_2

Clean Energy Future

Daytime:



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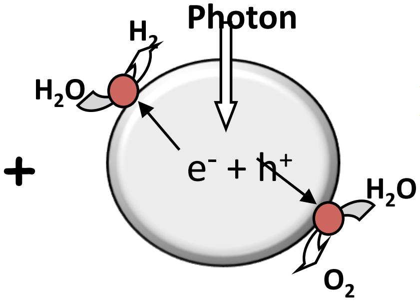
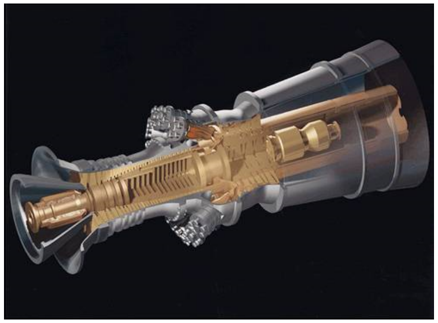
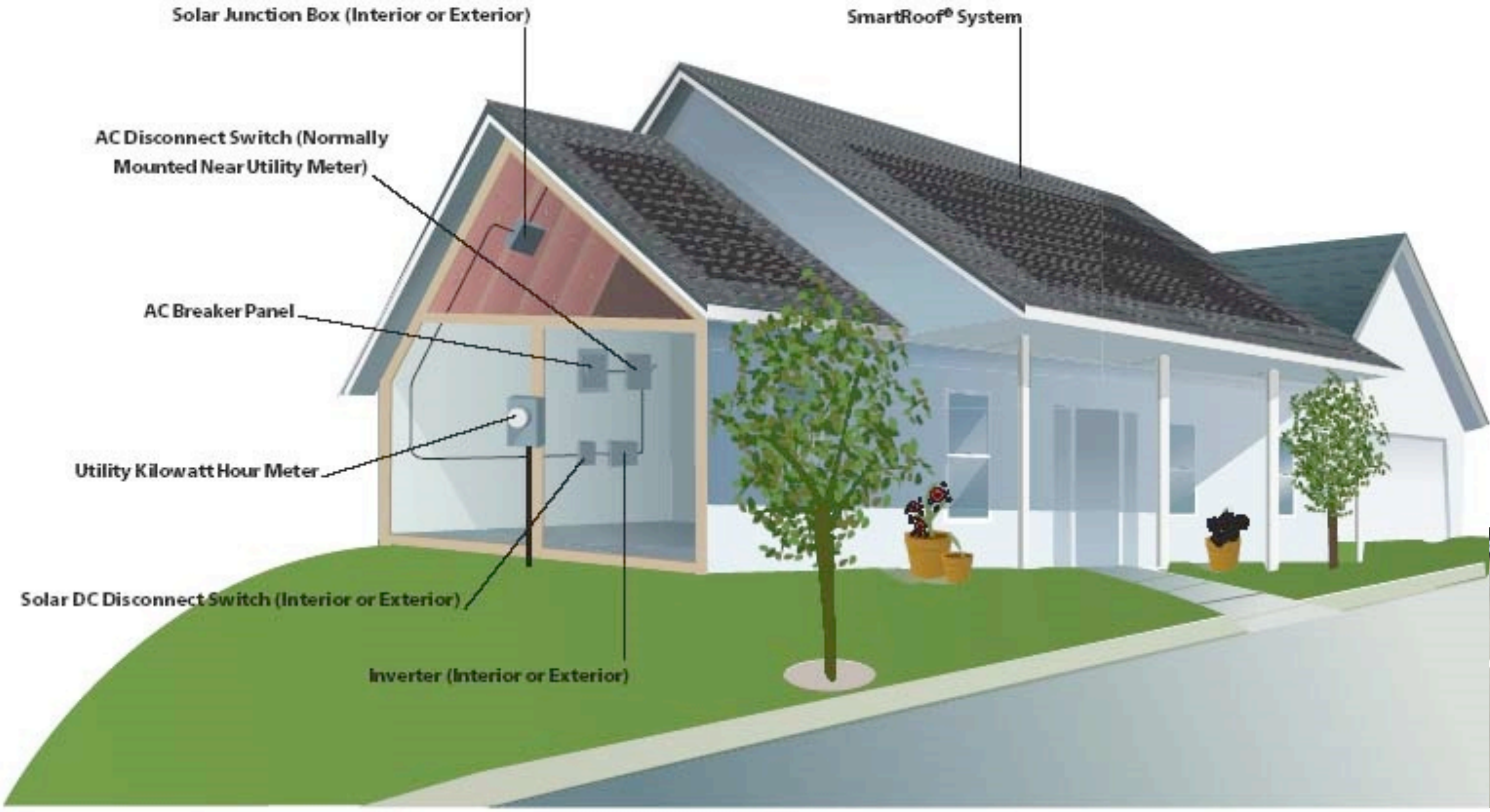


Nighttime:





Thanks


Maytal Toroker


Karin Carling


Nima Alidoust


Berit Hinnemann

$: NSF, AFOSR, DOE-BES, ARO, ONR, Princeton University (GCI/SEAS), PPPL

Team on work presented: Don Johnson (H-W/ITER & H,C/Steel); Ivan Milas, Berit Hinnemann, Karin Carling (TBCs); Isaac Shin, Ashwin Ramasubramaniam, Chen Huang, Linda Hung, Qing Peng, Xu Zhang, Gang Lu (lightweight alloys); Dalal Kanan, Leah Isseroff, Peilin Liao, Nima Alidoust, and Maytal Toroker (solar materials).

Other group members not pictured: Victor Oyeyemi, Andrew Ritzmann, David Krisiloff, Ting Tan, Junchao Xia