Full Spectrum Boost in Nanoparticle Solar Cells

UC Davis/Theory: F.Gygi, M.Voros, GTZ
UC Davis/Expt: S.Kauzlarich, E.Muthuswamy
UC Santa Cruz: S.Carter, C.Church, I.Carbone

Chicago:
G.Galli

Harvard:
T.Kaxiras

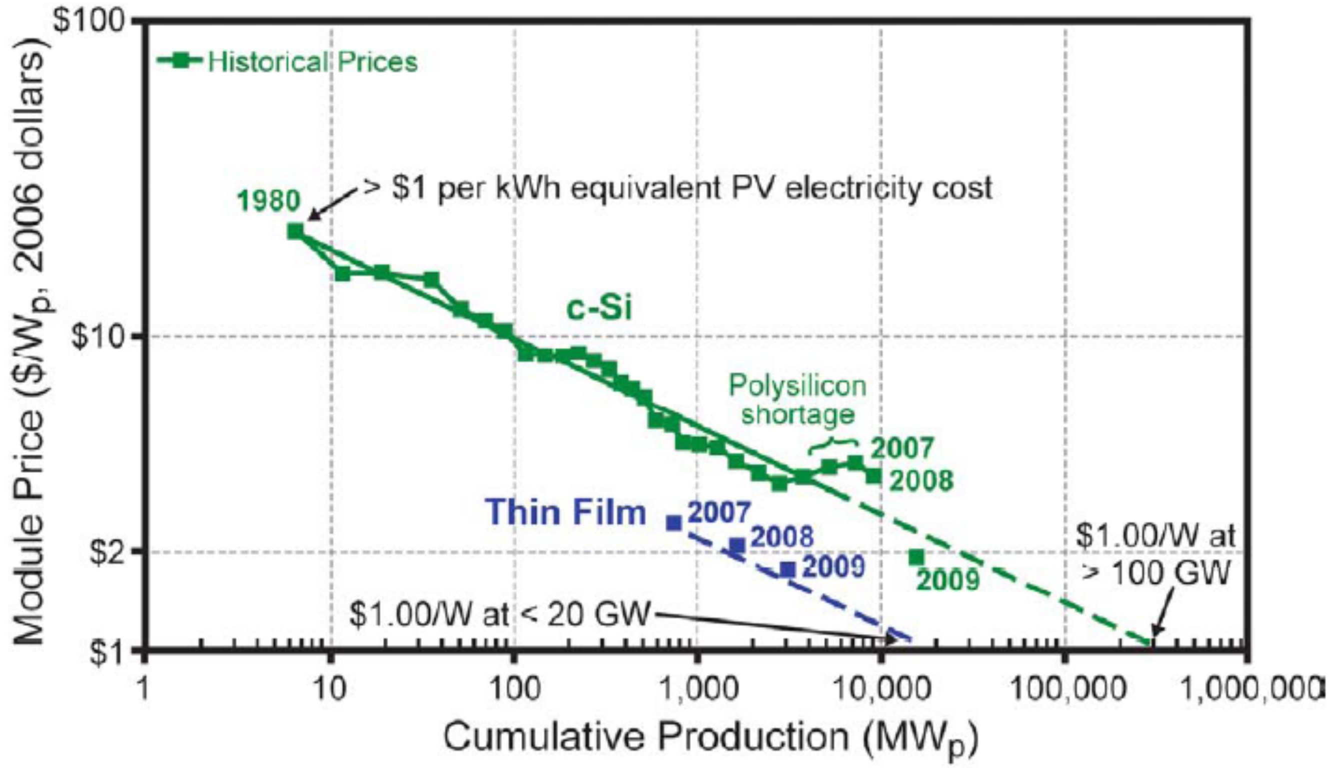
Nancy:
D.Rocca

Max Planck:
S.Wippermann

I do as I preach

Our “Solar Snow Koan” camp at Burning Man

DOE Goal - Reach grid parity at 1$/W



The Solar Moore's Law:
Price drops by 20% for every doubling of production
No doubling per 18 months: area is not scaled down as in chips
DOE Sunshot initiative: Reach grid parity at 1$/W!

Present Day

Present status: 0.53-0.72 $/W: Economy of scales, strong production in China: DOE's SunShot goal achieved early!

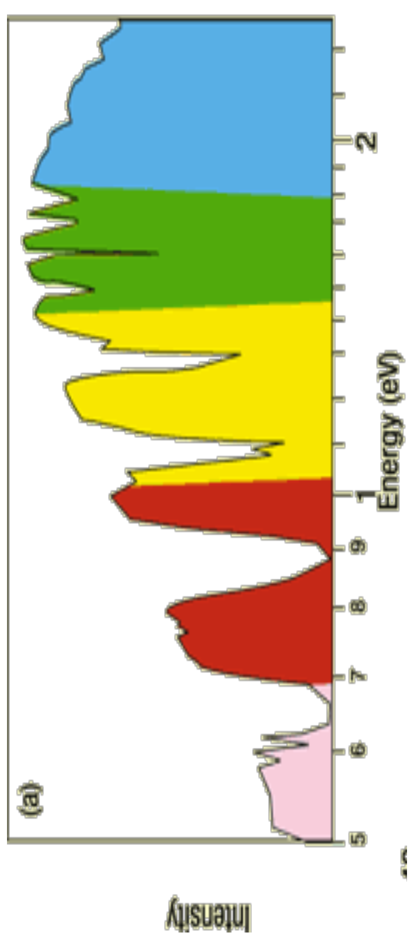
Present records:

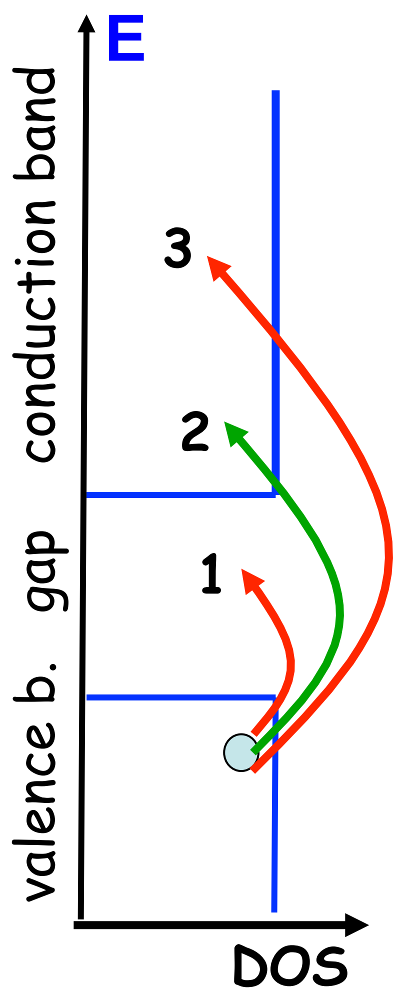
GaAs	29%	Alta Devices
HIT c-Si cell	26%	Panasonic, SunPower
Thin film CdTe	20%	First Solar
Organic solar cells	12%	Sumitomo

BUT: (1) Fracking moved grid parity to ~0.3$/W
(2) Energy problem needs pursuing all promising ideas

Bold & Innovative PV designs are needed

Solar Energy Conversion: Basics





1. No absorption below gap:
   photon wasted

2. Absorption to bottom of
   conduction band: optimal

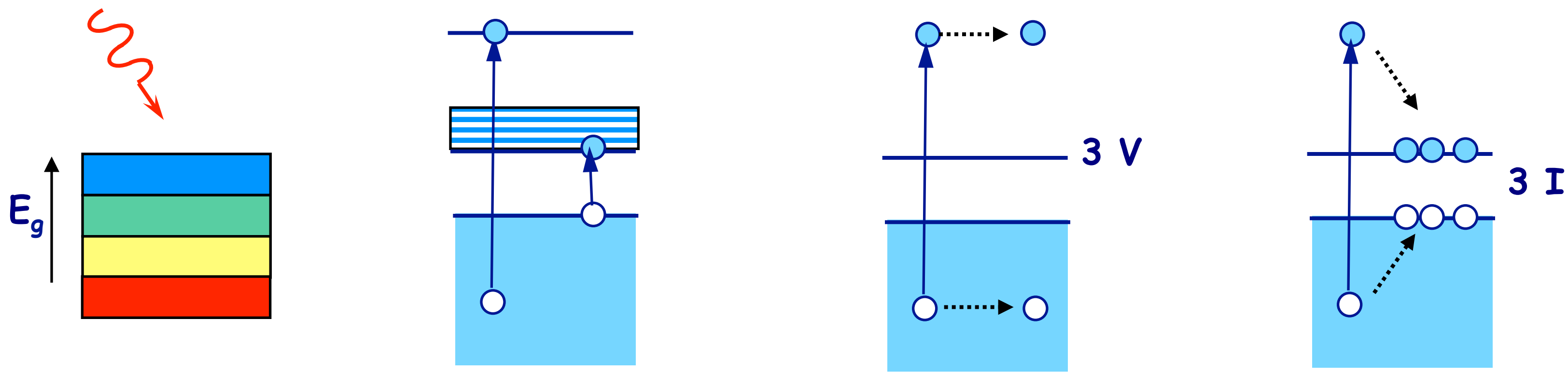
3. Absorption high into band:
   excess energy to phonons heats cell

Optimization of gap:
   max efficiency: **31%**

(Shockley Queisser 1961)

In real PV cells ~80% of incident solar energy is lost!

Examples of Innovative PV Designs



Multiple junctions

Intermediate Band absorbs IR photons: Boosts absorption at low energies. Max eff: 49%

Hot carriers

Multiple excitons generated by high energy photon: Boosts absorption at high energies. Max eff: 44%

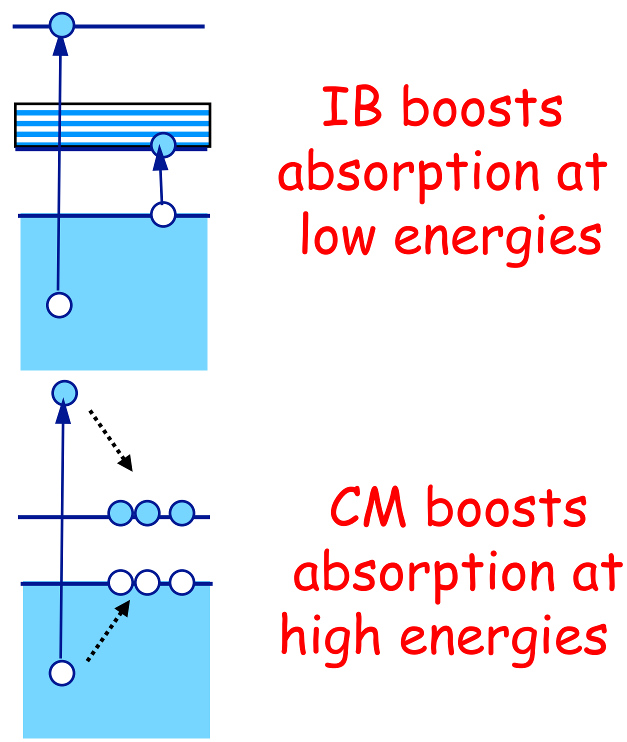
Measured efficiency increases not close to theoretical maxima

Selection of Innovative PV Designs

Efficiency of colloidal nanoparticle solar cells rapidly grew to 9.2% by 2014 from 4% a few years ago.
Organic PV(McGehee): 9%-2011, 12%-2014

In the 17 years since its invention, IB was only tried in epitaxial solar cell structures, with limited success. IB was never tried in colloidal NPs

CM can be enhanced by
(a) optimizing NP design, and
(b) implementing IB at the same time to pursue CM-IB synergies

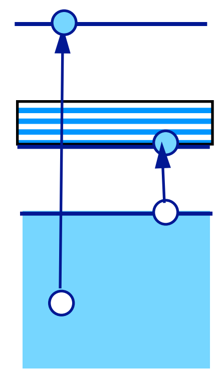


The Full Spectrum Boost Project

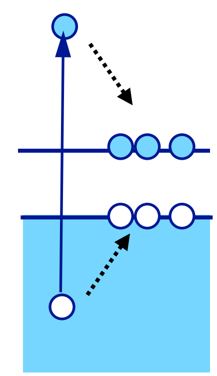
Focus on colloidal nanoparticle solar cells

Implement the Intermediate Band mechanism in colloidal NP solar cells

(a) Optimize NP design for CM
(b) Implement CM and IB to **boost absorption at low & high E**

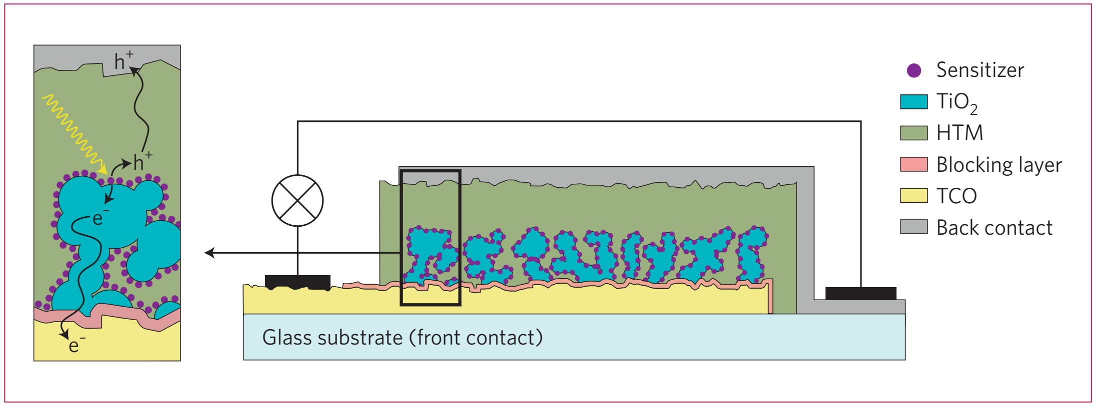


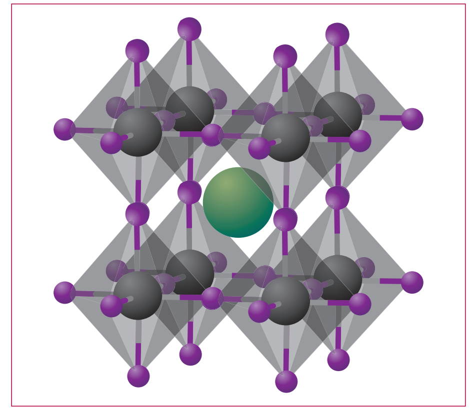
IB boosts absorption at low energies

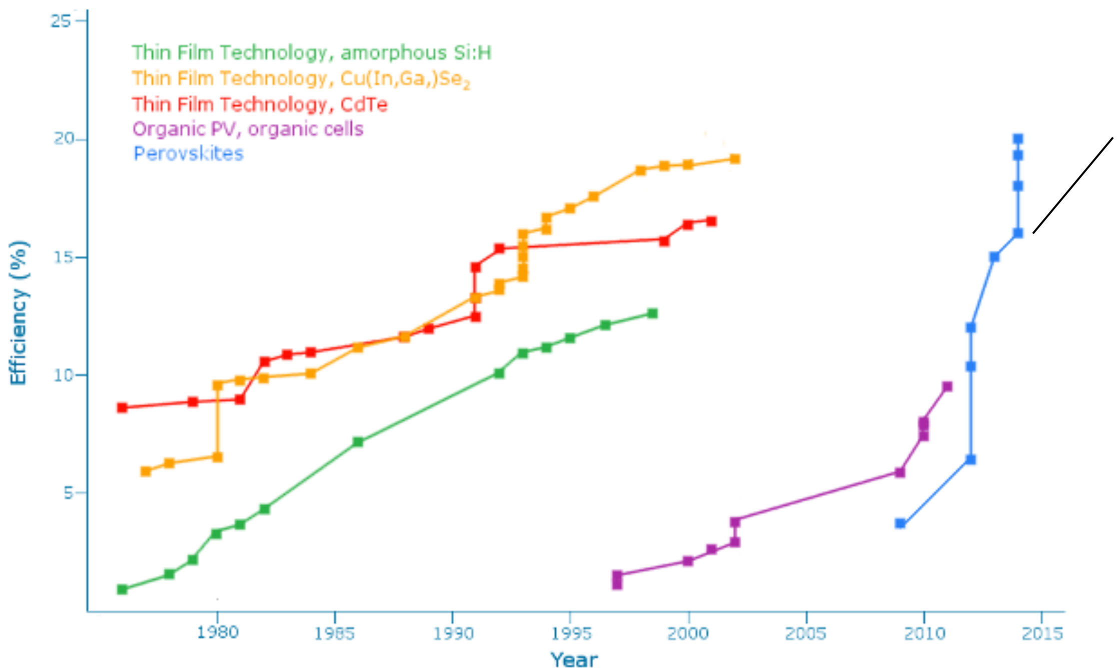


CM boosts absorption at high energies

The Perovskite Revolution Started in Nanoparticle Solar Cells too







Perovskite: $CH_3NH_3PbI_3$

"High Tc-like" explosion

Simple, low temperature solution-based fabrication

Lifetime ~ hours

Top cell for Si?

Full Spectrum Boost: Theory Infrastructure

Nanoparticle Structure: ab-initio-driven structural relaxation

One particle energies: DFT, GW, Quantum Espresso ,PBE, PBE0

Transport:
Parameter & lifetime calculation

Optical absorption:
TDDFT

Band formation, Lifetime for Boltzmann transport

Ab-initio compute of E_{1p}, E_c, τ for Marcus/Miller-A. hopping transport

Intermediate Band: VB/IB, VB/CB rates

Carrier Multiplication: X->XX rate

Plan of the Talk

Carrier Multiplication Boost at high energies

Intermediate Band boost at low energies

Transport to extract photo-induced charge carriers

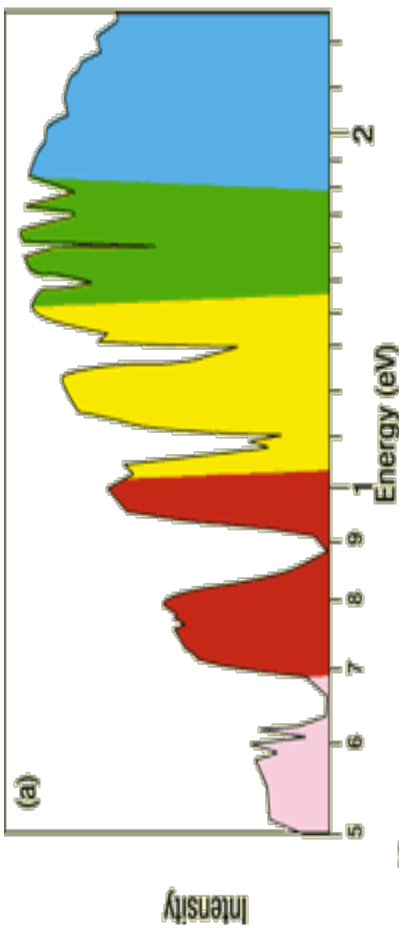
Plan of the Talk

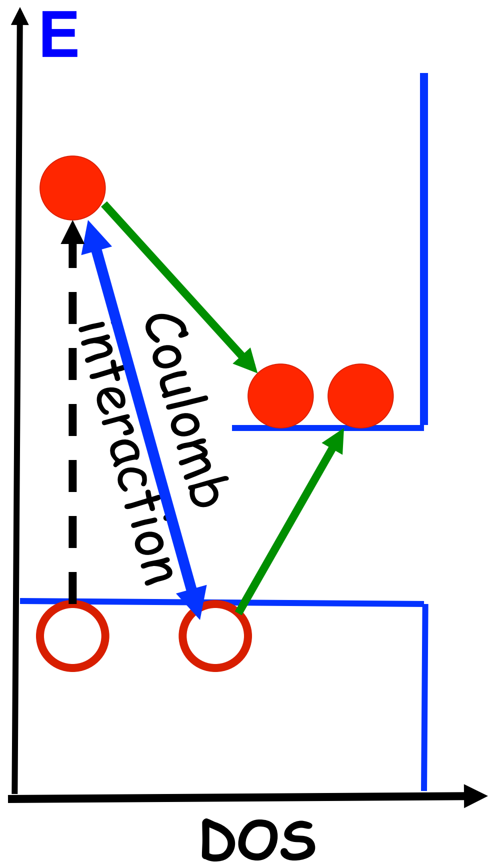
Carrier Multiplication Boost at high energies

Intermediate Band boost at low energies

Transport to extract photo-induced charge carriers

Down-conversion by Carrier Multiplication





Keep energy of high energy photons in electronic sector:

Electron relaxation by Carrier Multiplication:

Photo-excited first exciton relaxes by exciting second exciton instead of phonons

Max efficiency:
44% 1 Sun (Klimov 2005)
70% 1000 Sun (Nozik 2013)

13

Carrier Multiplication - 1957

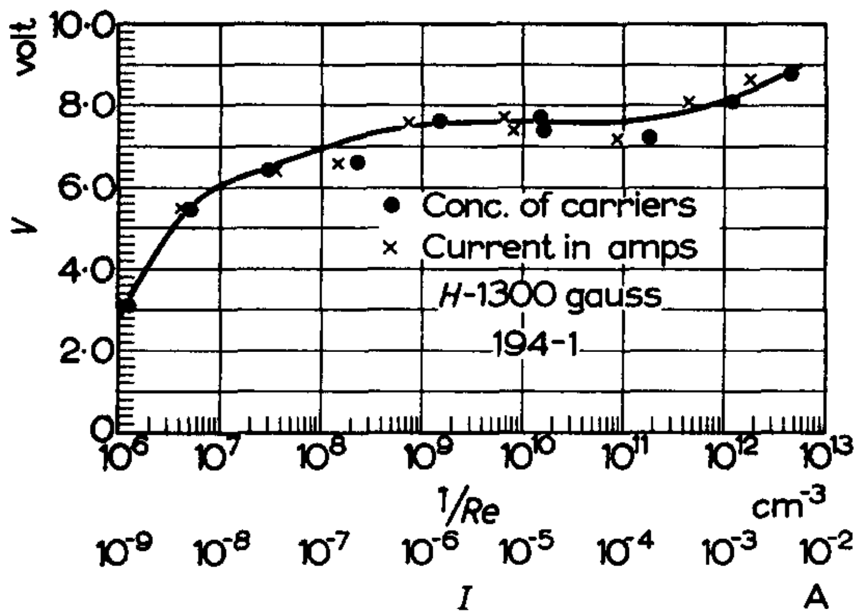
J. Phys. Chem. Solids. Pergamon Press 1957. Vol. 2. pp. 1–23.

IMPACT IONIZATION OF IMPURITIES IN GERMANIUM*

N. SCLAR† AND E. BURSTEIN

United States Naval Research Laboratory, Washington, D.C.

(*Received* 16 *September* 1956)



"Impact Ionization" (=CM) has a 1% efficiency in bulk

Sclar (1957)

Carrier Multiplication

Save the exciton generation from jaws of electron-phonon interaction:

"We gonna need a bigger Coulomb interaction"

Carrier Multiplication

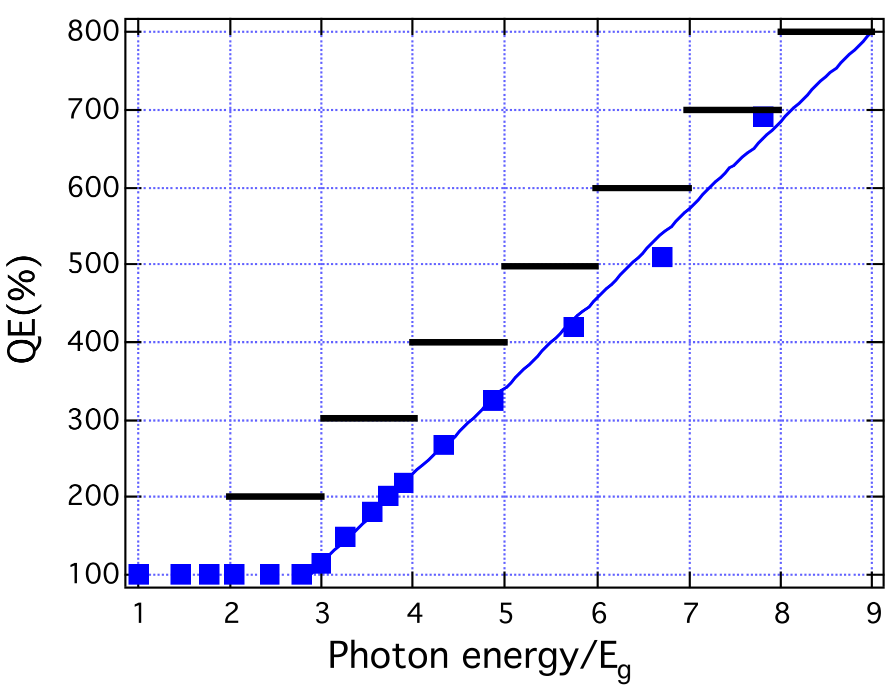
Save the exciton generation from jaws of electron-phonon interaction:

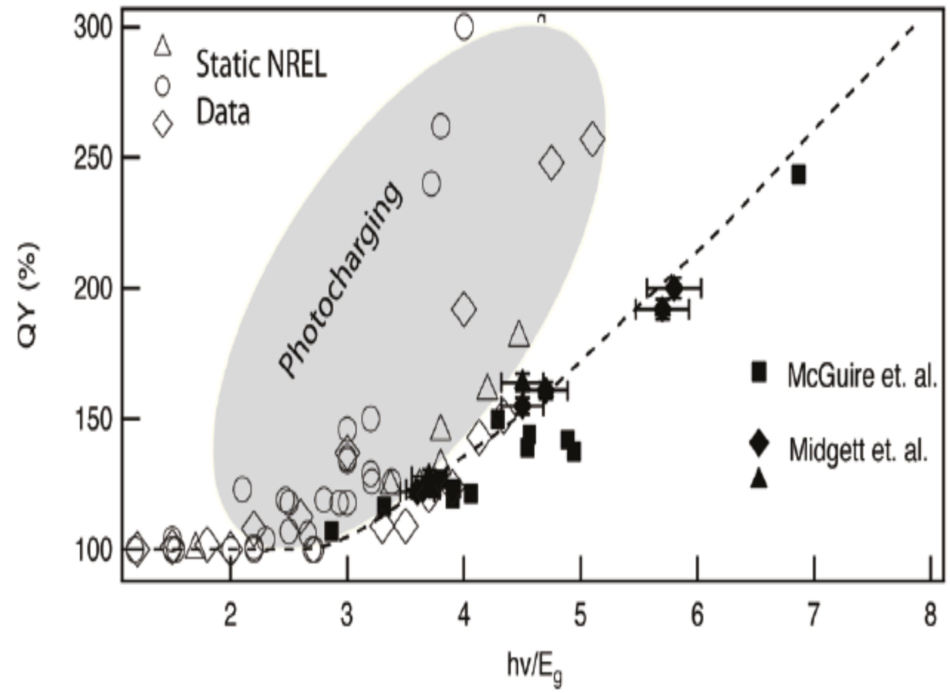
"We gonna need a bigger Coulomb interaction"

1. In nanoparticles electrons cannot avoid each other: screening is reduced, Coulomb interaction enhanced (Nozik 2001)

2. Use Mott insulators/perovskites! U large in bulk (Manousakis 2010)

CM in Nanoparticles: Discovery, Status





Klimov, Schaller (2004) quantum yield (=#electrons/photon) up to 700%

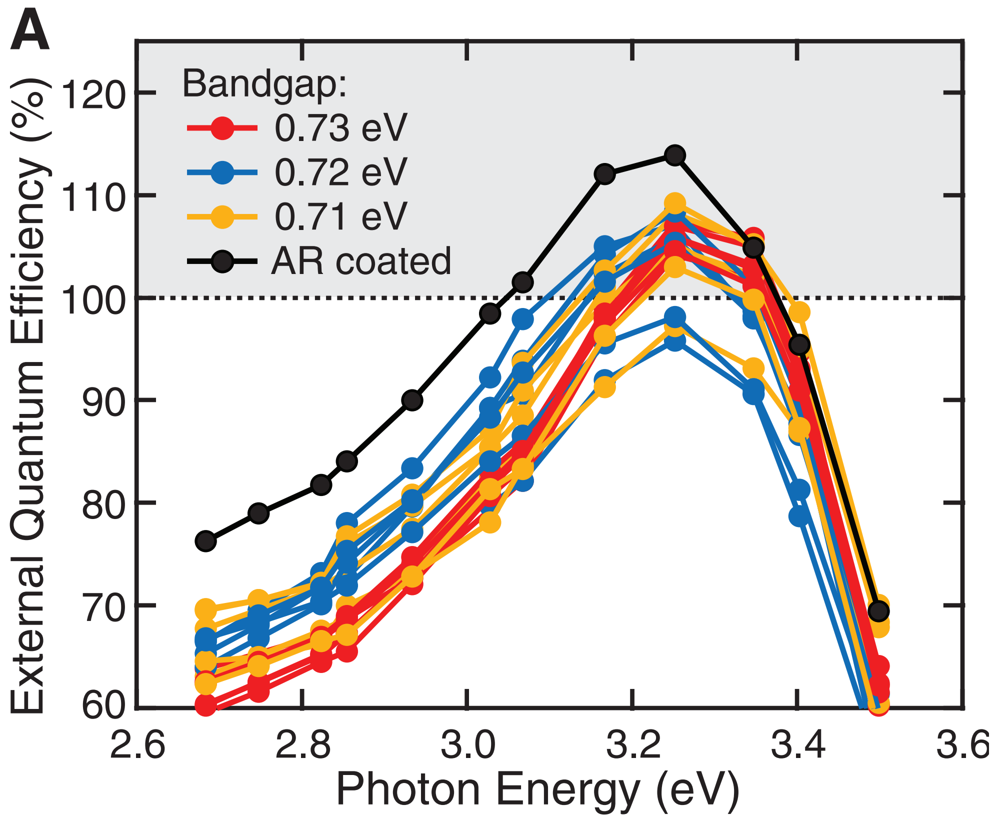
Beard (2011): CM present, with lower efficiency

Nanoparticles in solution, not in solar cell

First working CM/MEG solar cell: Dec. 2011

Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell

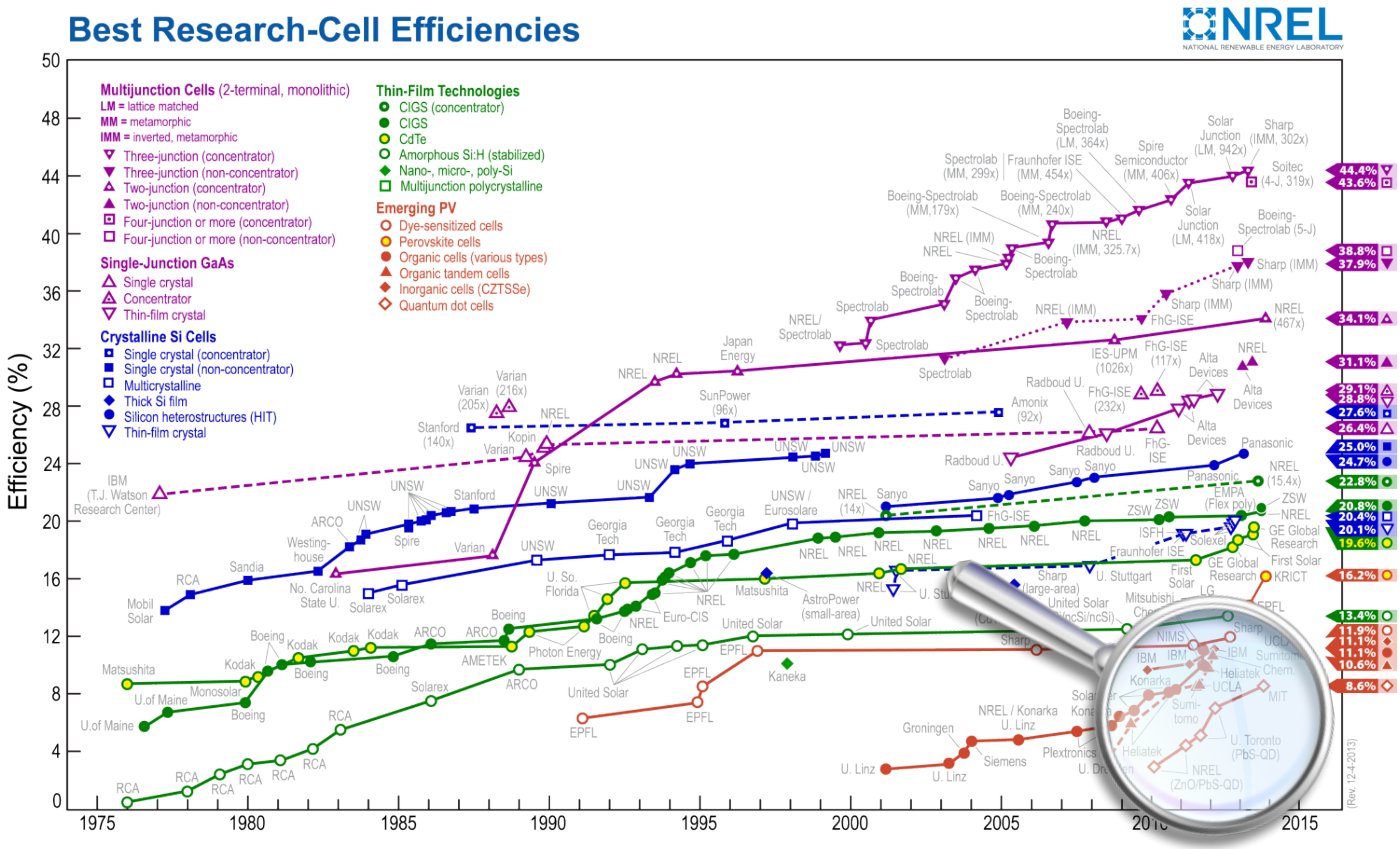
Octavi E. Semonin,[1,2] Joseph M. Luther,[1] Sukgeun Choi,[1] Hsiang-Yu Chen,[1] Jianbo Gao,[1,3] Arthur J. Nozik,[1,4]* Matthew C. Beard[1]*



EQE>100%:

Proves presence of CM

Nanoparticle solar cells appeared on the NREL efficiency chart in 2010



QCD - The Quantum Confinement Dilemma in Nanoparticle Solar Cells

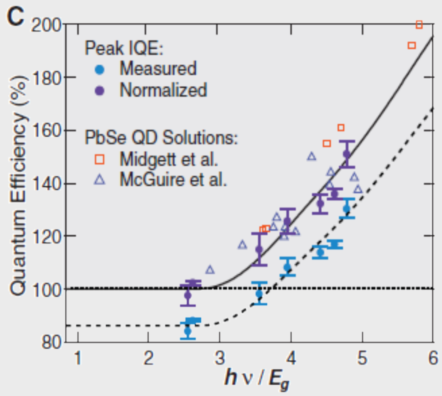
Positives

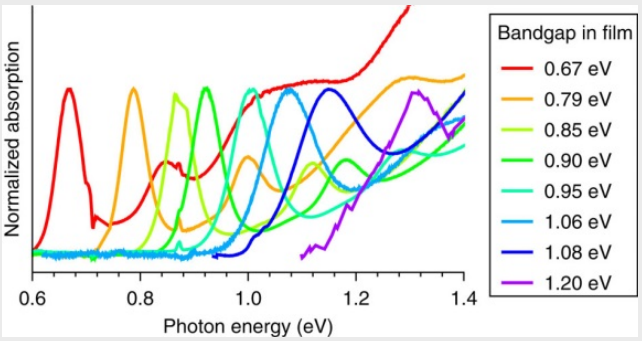
Negatives

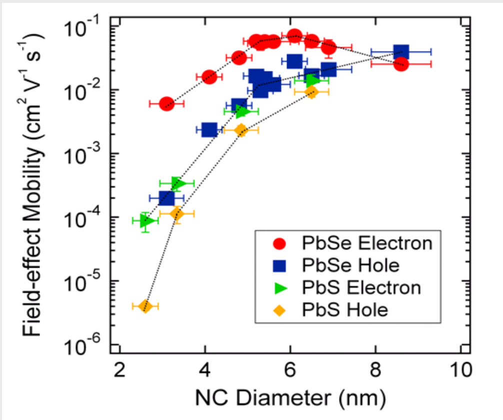
Enhances Coulomb interaction: Enhances CM

Widens gap: Absorption is pushed out of solar spectrum

Localizes charges: Hinders transport

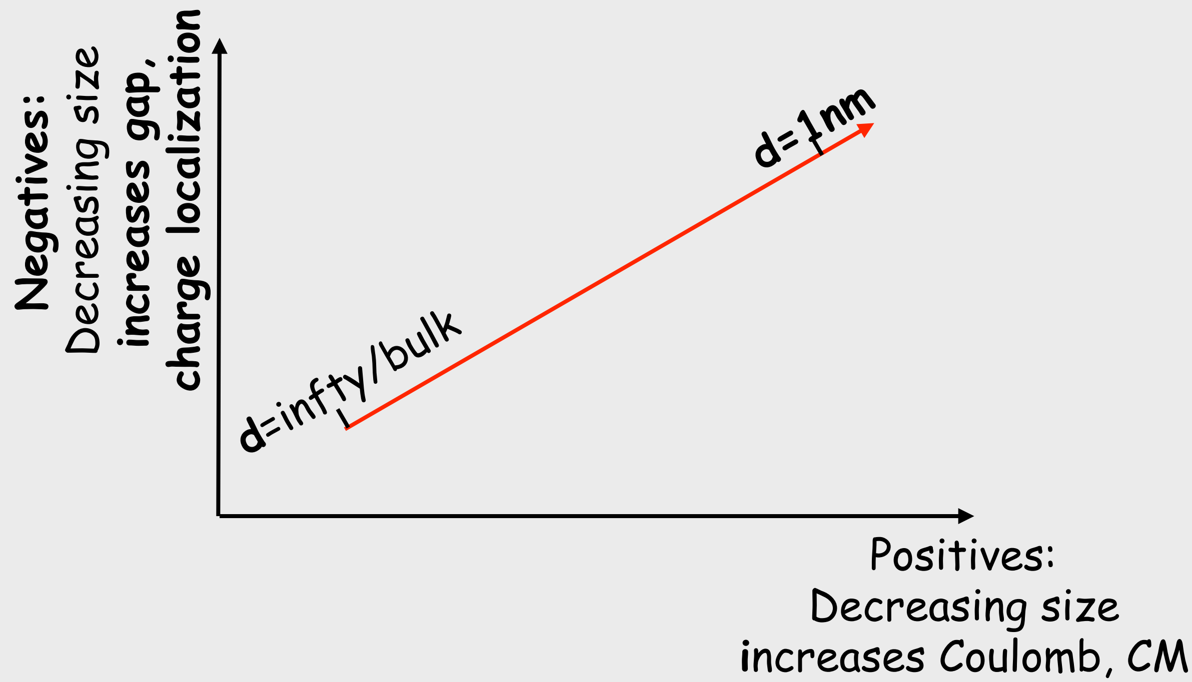






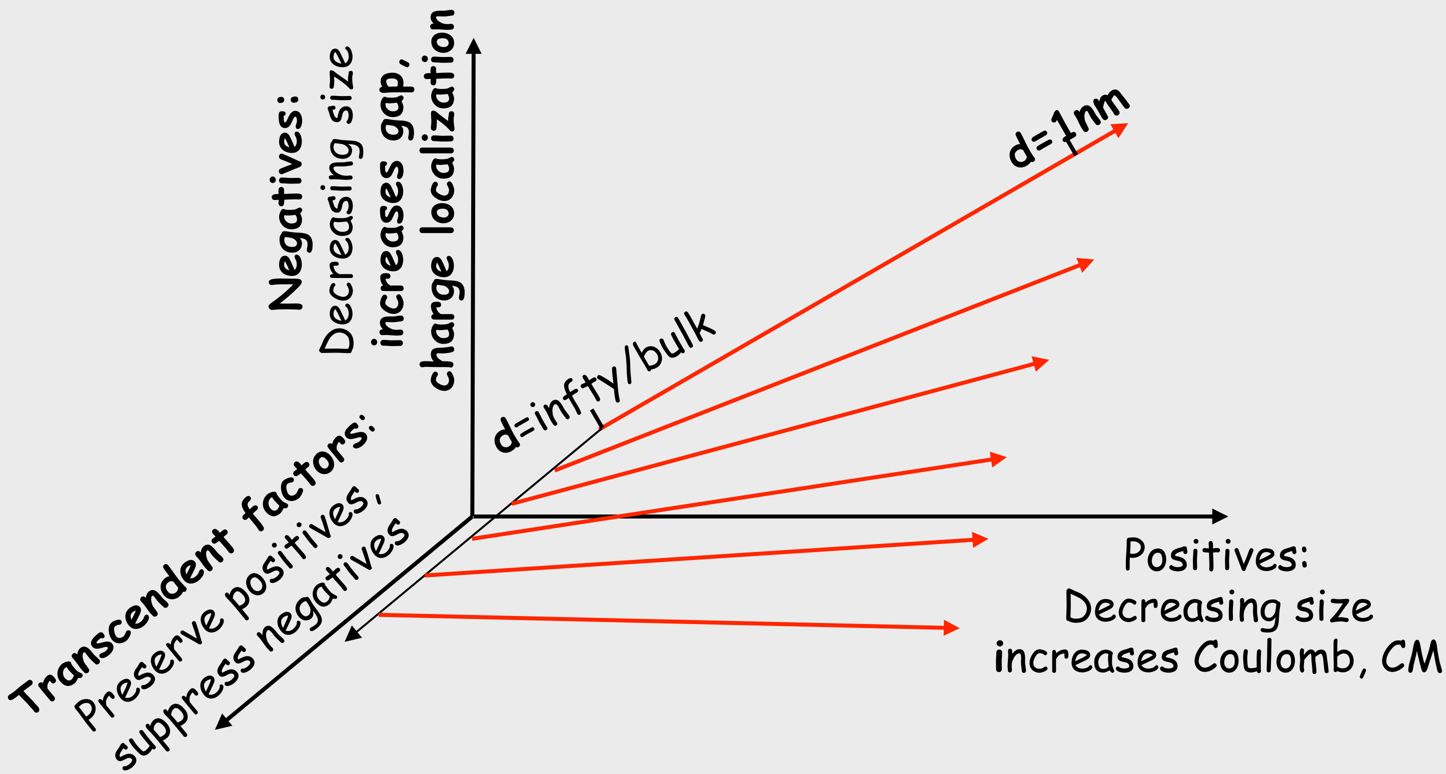
QCD - The Quantum Confinement Dilemma in Nanoparticle Solar Cells

Decreasing size enhances CM but introduces negatives



Transcending QCD in Nanoparticle Solar Cells

Transcendent factors: Preserve positives, suppress negatives



Transcending QCD in Nanoparticle Solar Cells

Transcendent factors:
preserve positives, suppress negatives

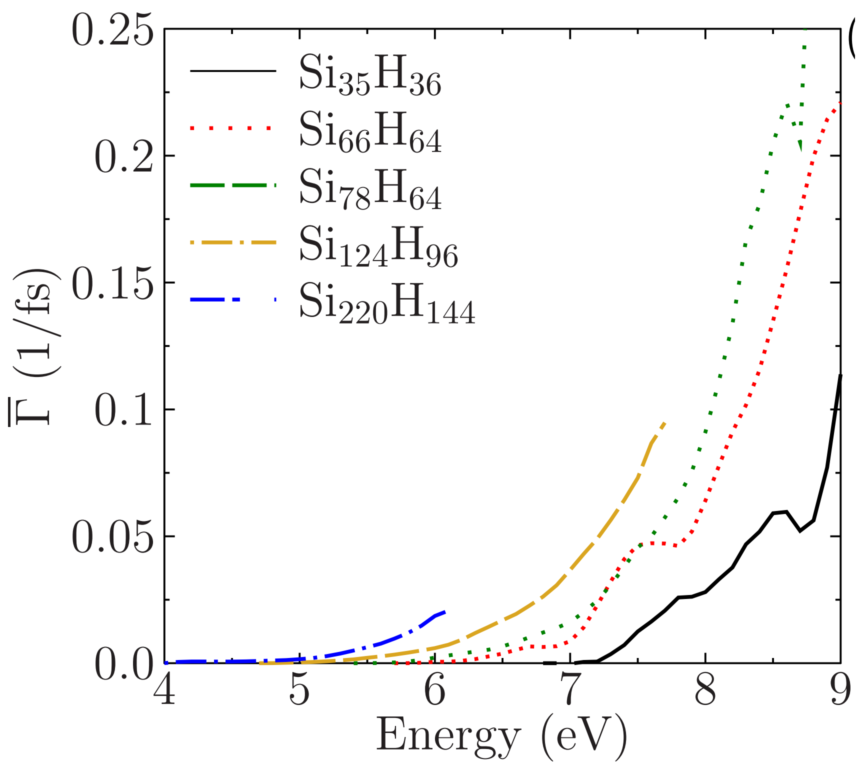
1. Surface reconstruction of nanoparticles

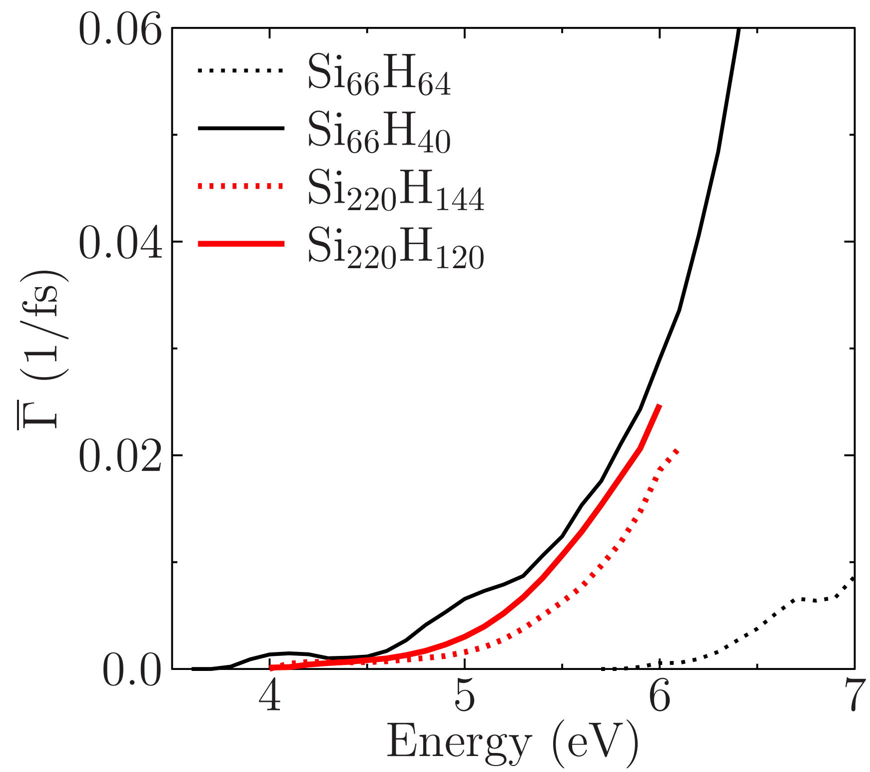
2. Shape engineering of nanoparticles: from dots to rods

3. Exotic core phase nanoparticles

4. Charge separation, transport and extraction

Reconstruction Compensates Gap-Enhancement without Reducing Coulomb Strength/CM



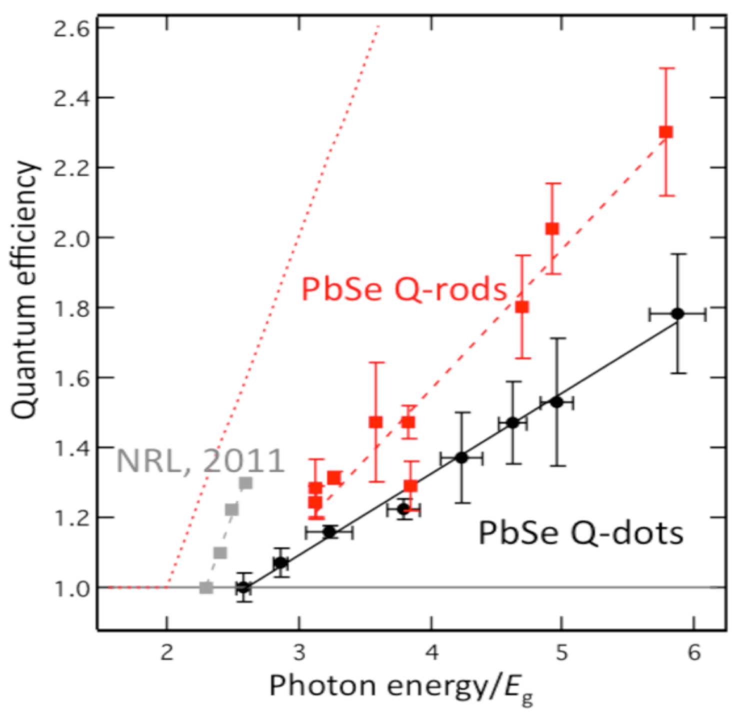


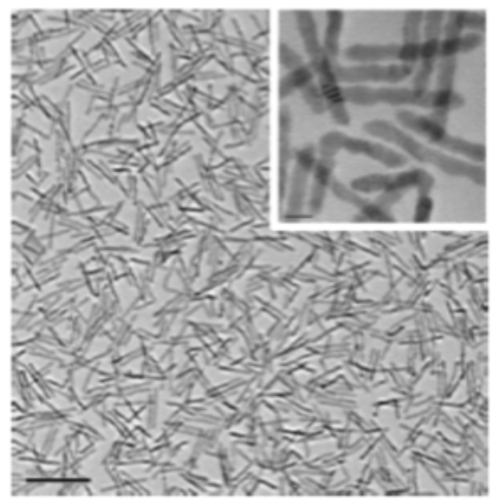
Quantum confinement enhances the gap in unreconstructed NPs

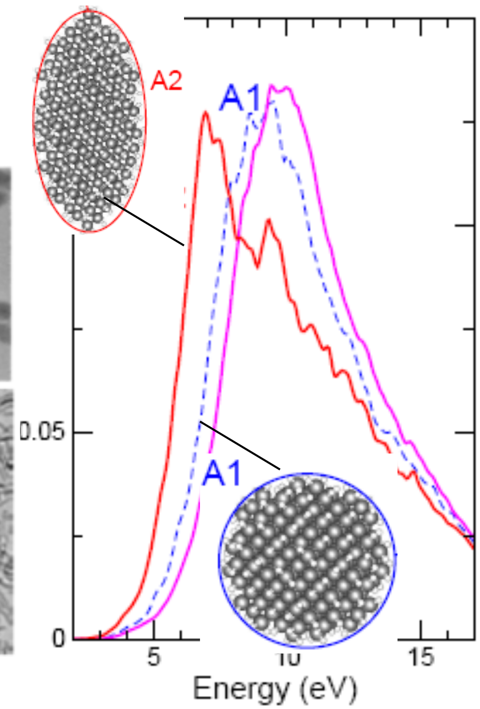
Reconstruction
- compensates gap enhancement
- preserves enhanced Coulomb/CM

Voros, Galli, Zimanyi Phys. Rev. B, 2013

2. Lowered Symmetry: Gap Reduction, More Allowed Transitions







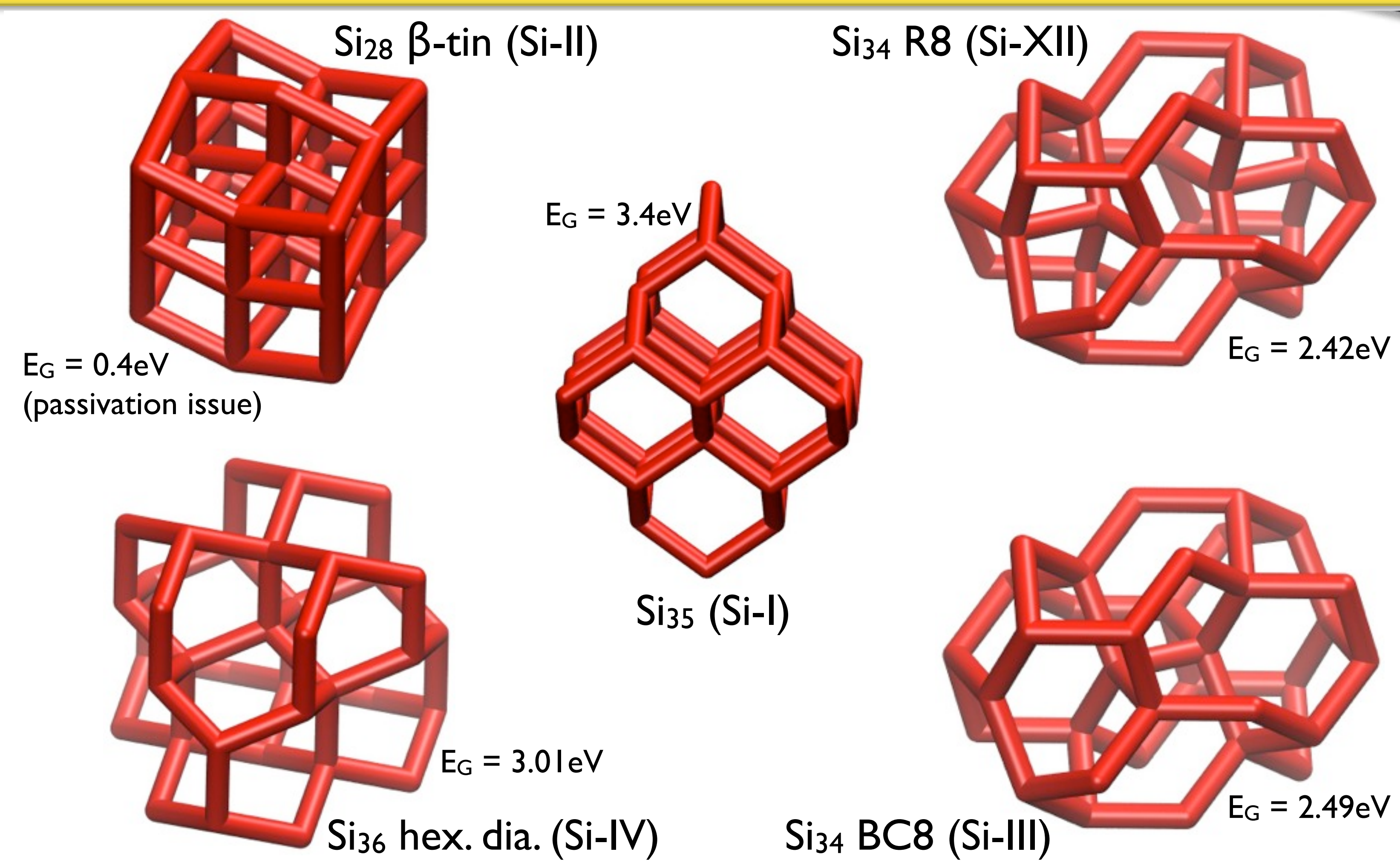
Many transitions forbidden by symmetry-driven selection rules
Lowering symmetry of nanoparticles allows more transitions:

Nanorods: lower CM onset energy; enhanced CM at higher energy

Nanowires: Cui group

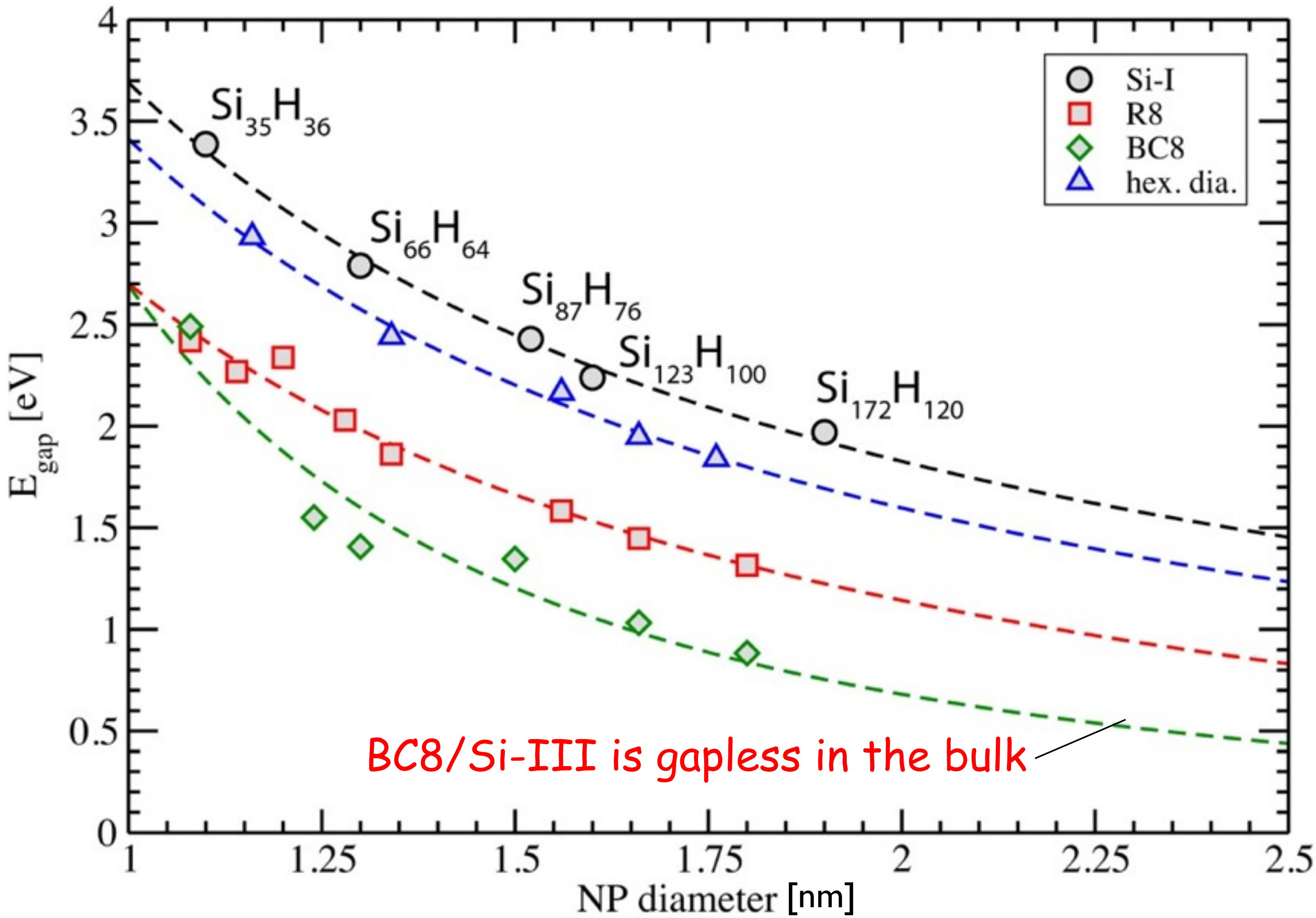
Gali, Kaxiras, Zimanyi, Meng, Phys. Rev. B 2010

3. Exotic Core Phase Si/Ge NPs:
3.1. Reduce Gap by using Bulk-Gapless Phases

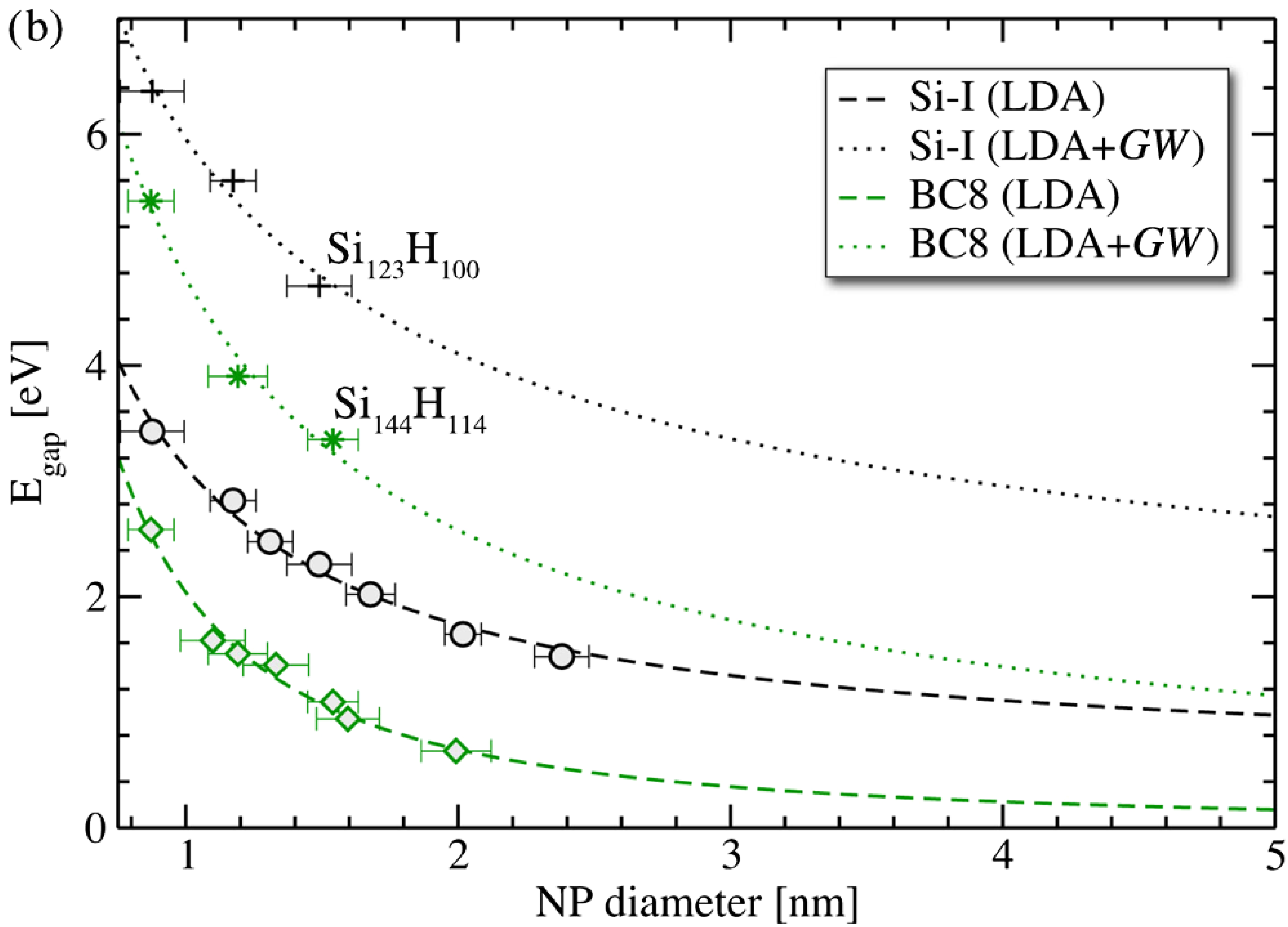


Wippermann, Voros, Gali, Rocca, Zimanyi, Galli Phys. Rev. Lett. **110**, 046804 (2013)

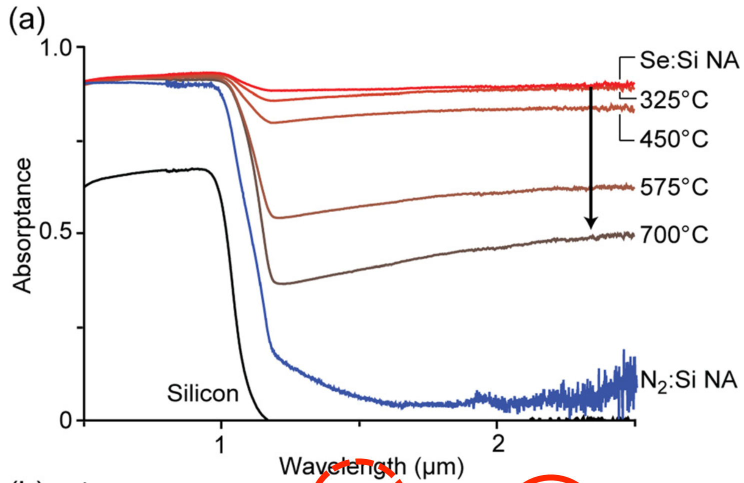
3.1. Gap reduction in BC8/Si-III

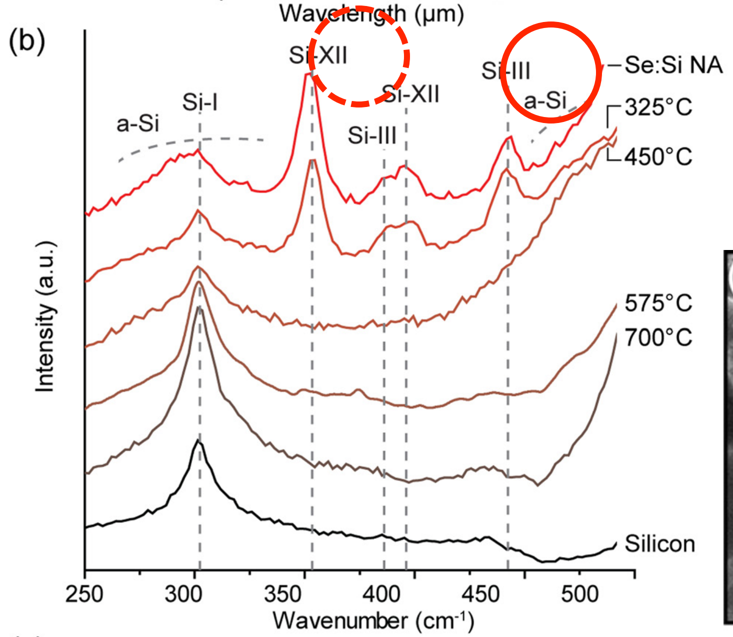


3.1. Comparison of LDA and GW

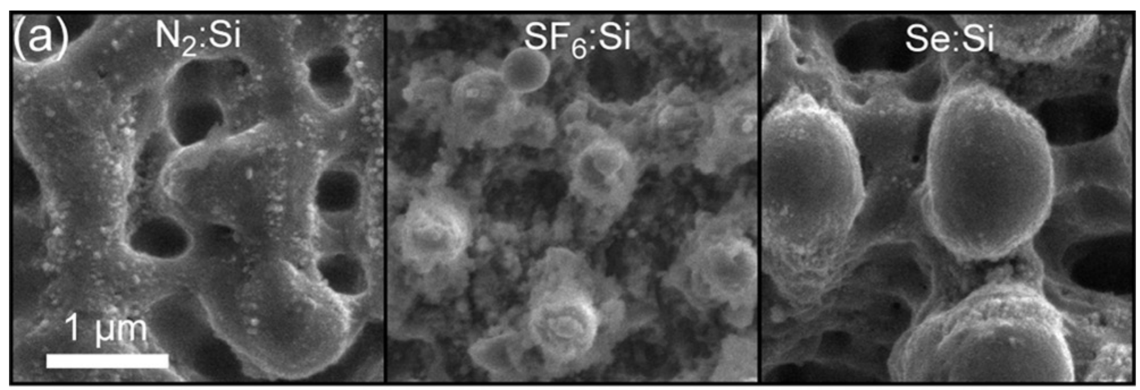


3.2. High Pressure Polymorphs in Black Si

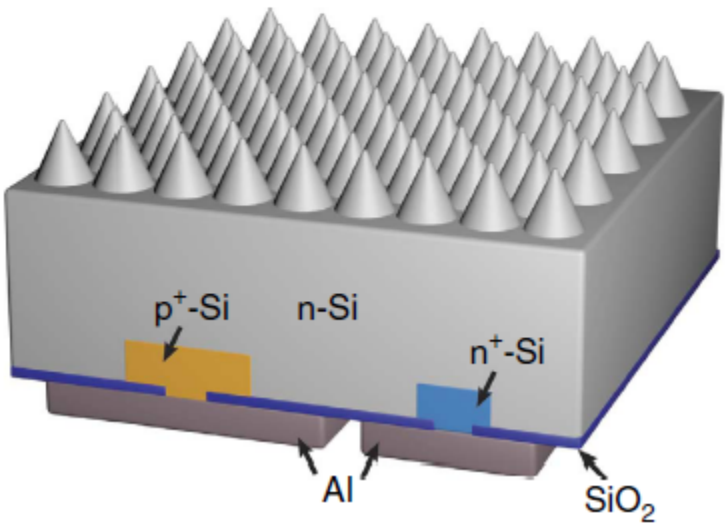


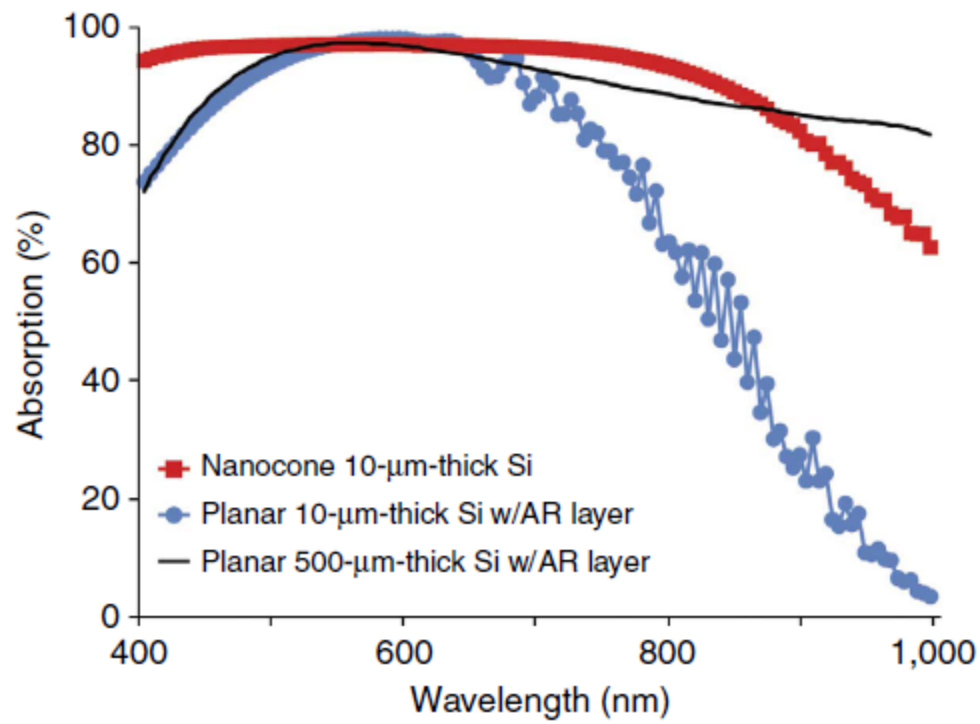


1. Top layer of PV cell transformed by high energy laser pulses (Mazur 2013)
2. Observed large enhancement of sub-gap absorption
3. Observed the formation of BC8/Si-III phase by Raman scattering
4. When BC8/Si-III phase was annealed away, sub-gap absorption greatly reduced



Using nanocones to enable complete light absorption in thin Si

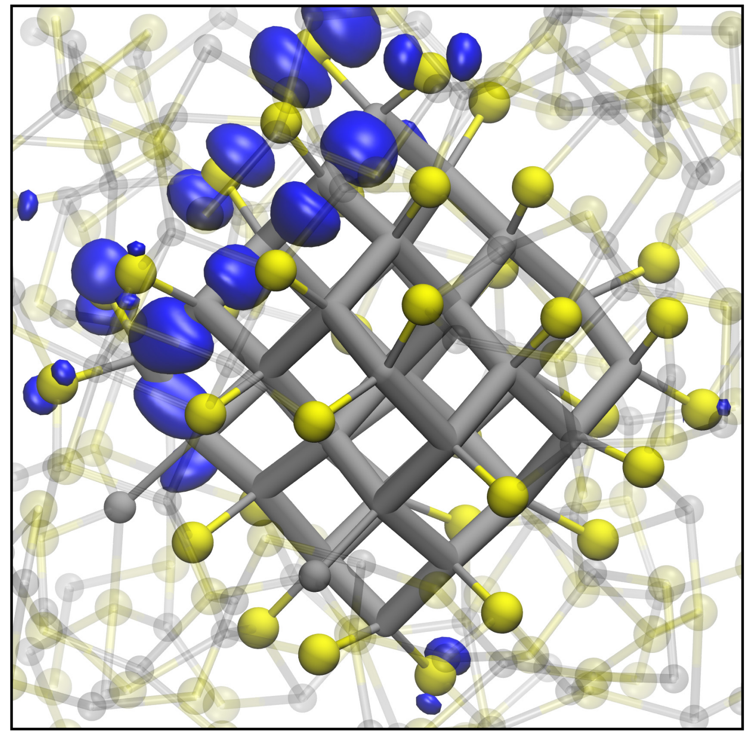




Sangmoo Jeung, Mike McGehee, Yi Cui, *Nature Comm*.

4. Charge Separation and Extraction:
4.1. Si NP in ZnS

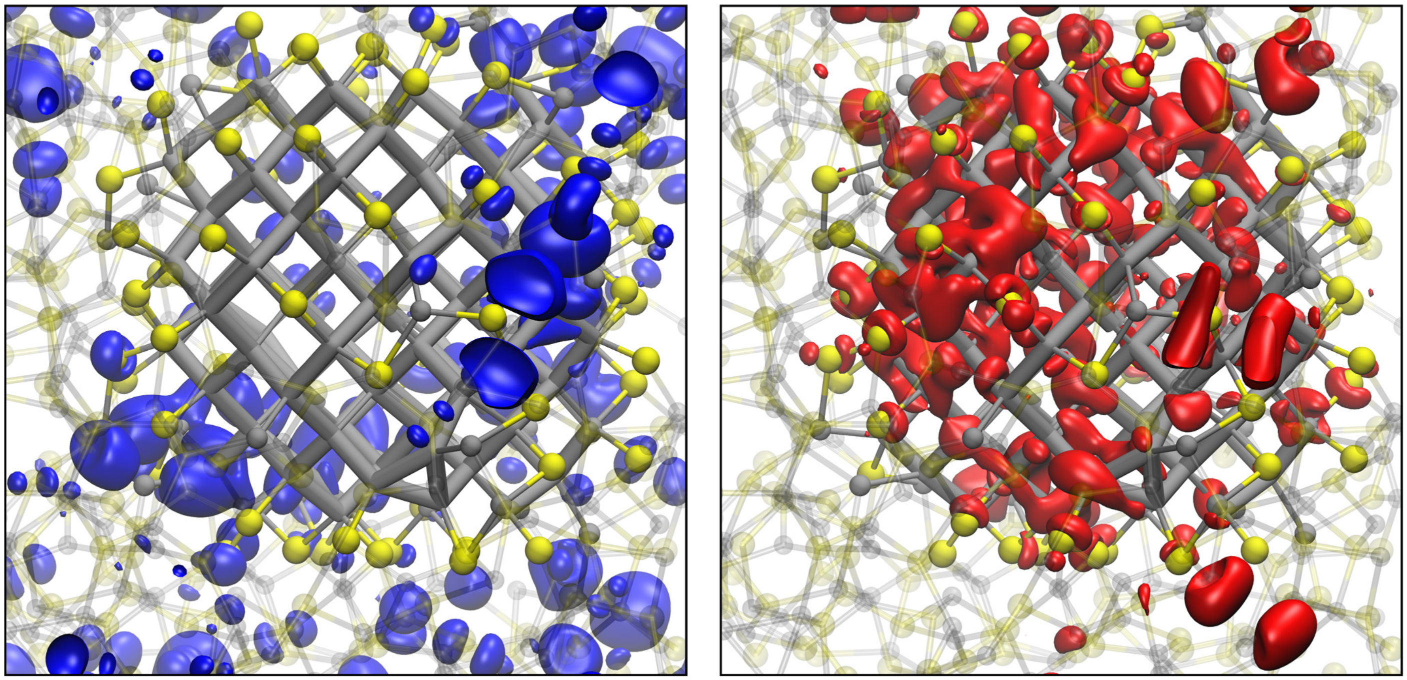
1. Create ZnS matrix with 512 atoms
2. Replace 35-172 Zn/S atoms
   with Si atoms
3. Relax structure with Qbox package
   T(anneal) upto 1,000K
4. Calculate energy



Cover of PRL, March 14, 2014

4.2. Complementary Charge Transport Channels

Top of Valence Band | Bottom of Conduction Band

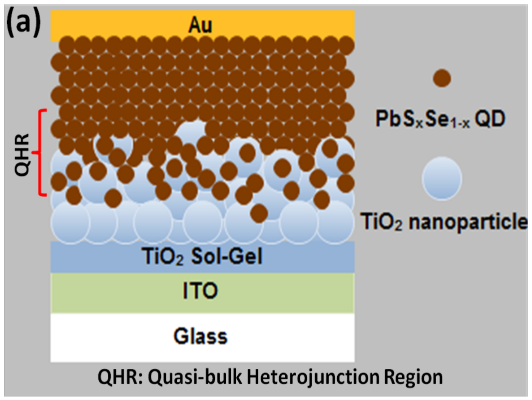


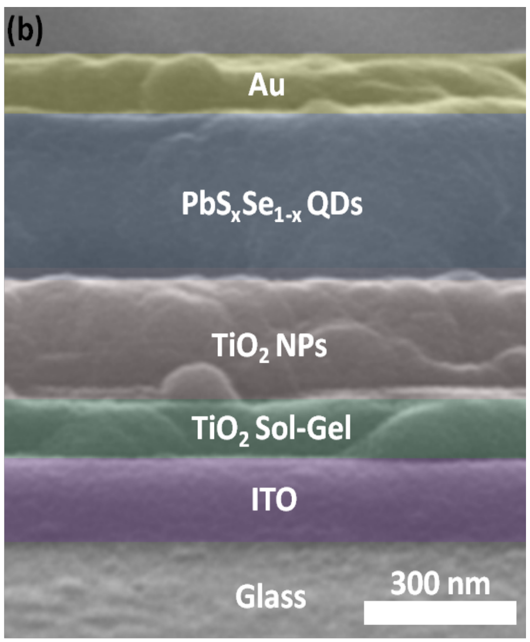
Electron transport: NP-NP transition

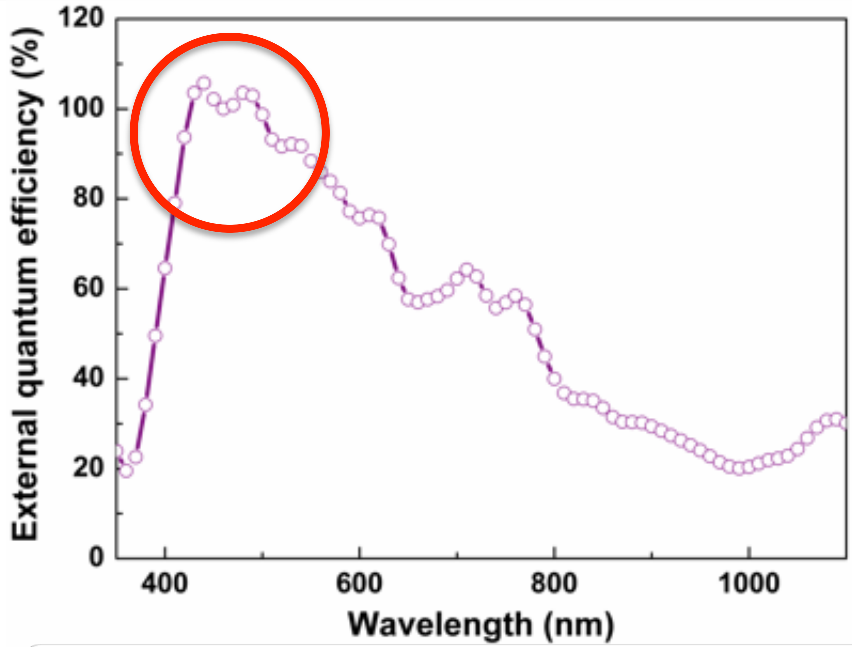
Hole transport: in host matrix

Complementary charge transport channels – **recombination reduced**

Demonstration of Carrier Multiplication in a Functioning Solar Cell







Beard & Nozik (2011):
CM in working solar cell.
Used hydrazine: combustible

Carter lab: EQE>100% in working solar cell

Optimized cell performance by varying the composition PbS_xSe_{1-x}.

Carrier Multiplication Summary

Carrier Multiplication is a promising solar paradigm

Quantum Confinement Dilemma: QC enhances Coulomb/CM, but enhances the gap and makes charge extraction harder

Transcending QCD possible:

1. Surface reconstruction of NPs: decreases gap, preserves MEG

2. Shape engineering of NPs (from dots to rods): decreases gap, increases number of allowed transitions

3. Exotic core phase NPs: decrease gap, increase Coulomb/CM

4. Embedding NPs in host matrix: interface changes type I -> type II: complementary charge transport channels form, reduce recombination

Plan of the Talk

Carrier Multiplication Boost at high energies

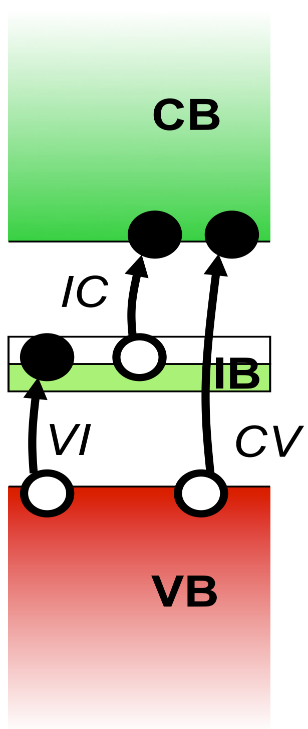
Intermediate Band boost at low energies

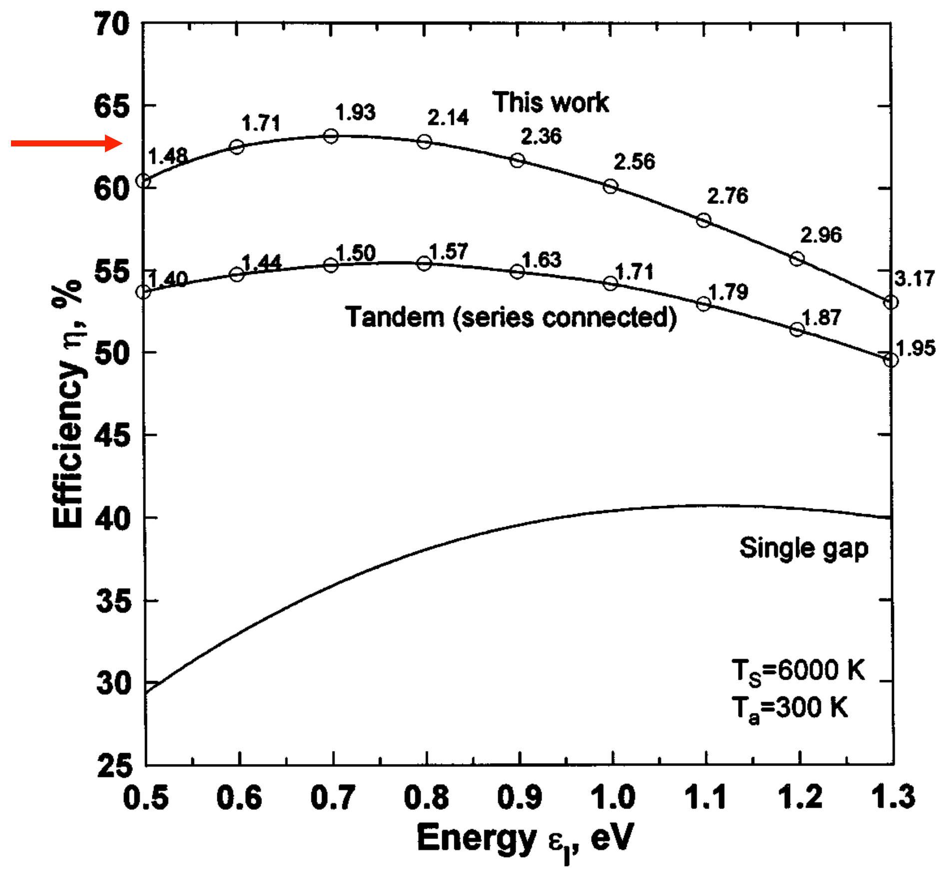
Transport to extract photo-induced charge carriers

Up-conversion with Intermediate Band Solar Cells

1. Absorb photon with sub-gap energy: electron IB->CB & VB->IB

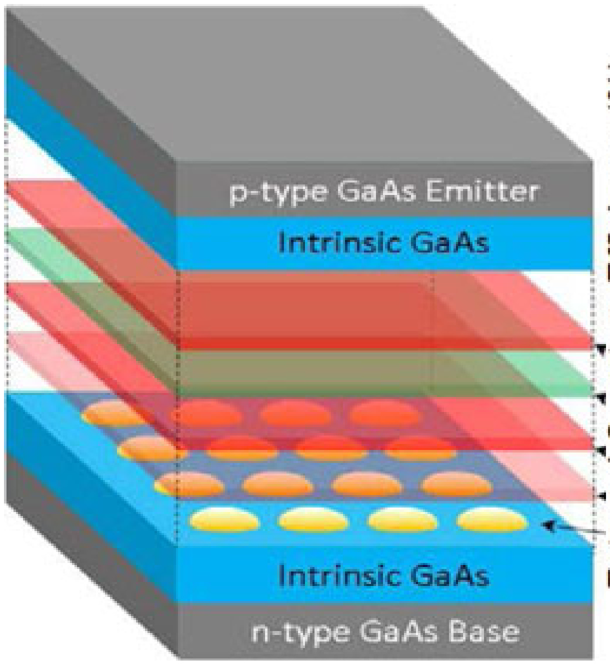
2. Fill IB by chemical doping or by photo-doping

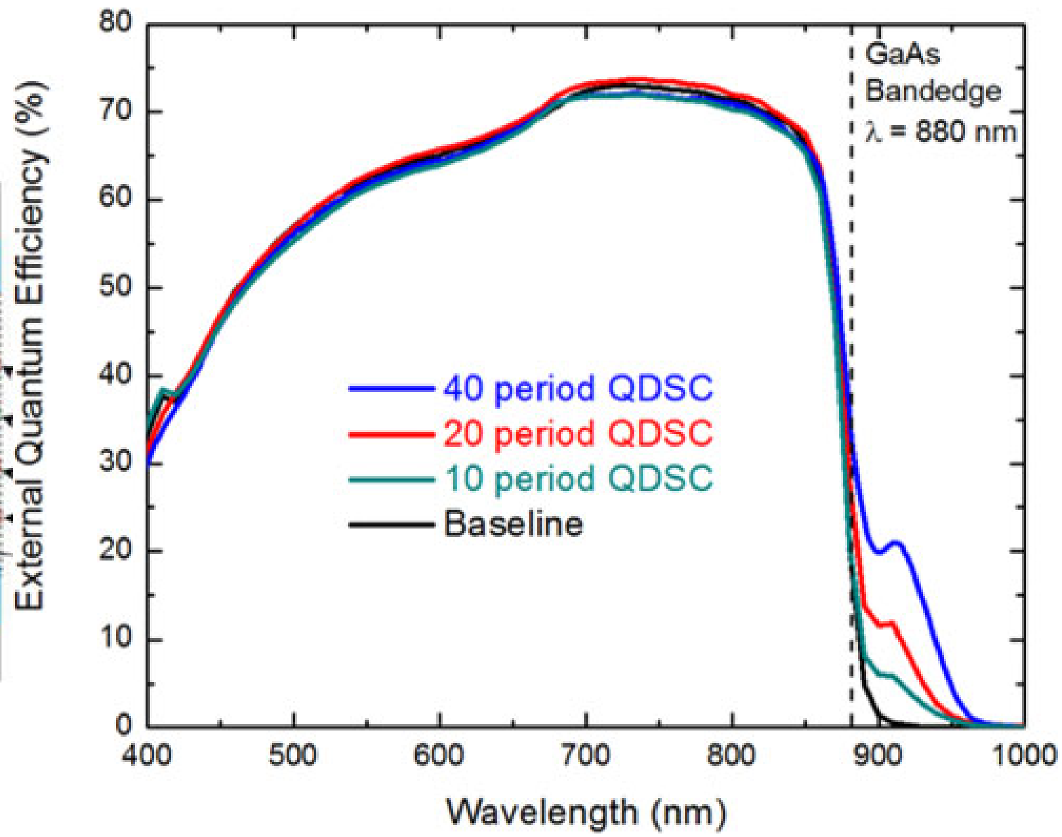




Up-conversion: Dionne group

Intermediate Band: Epitaxial Design

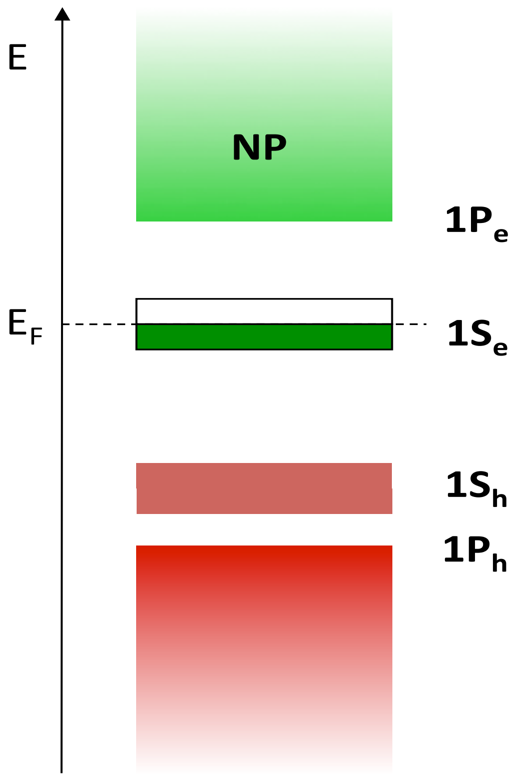




(1) Process steps increase from ~10 to 50-100

(2) Efficiency increase minimal

Intermediate Band: Colloidal Nanoparticle Design



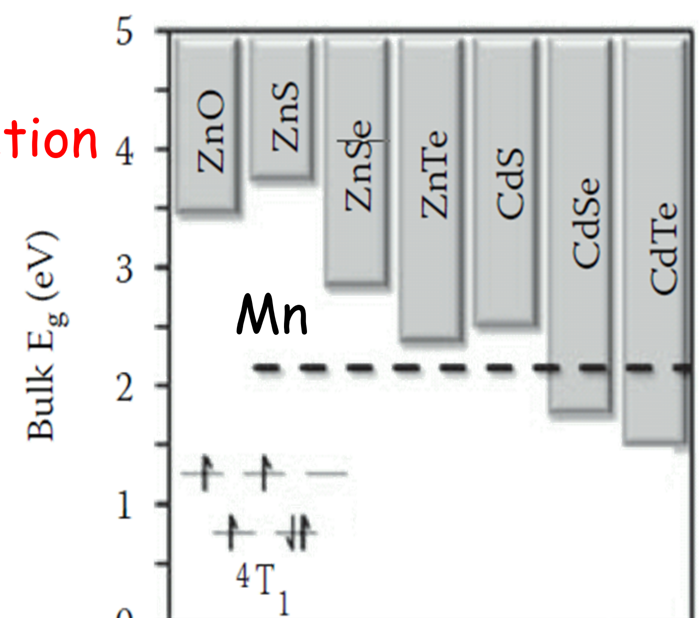
Core-shell NPs

Structural reconstruction

Quantum confinement

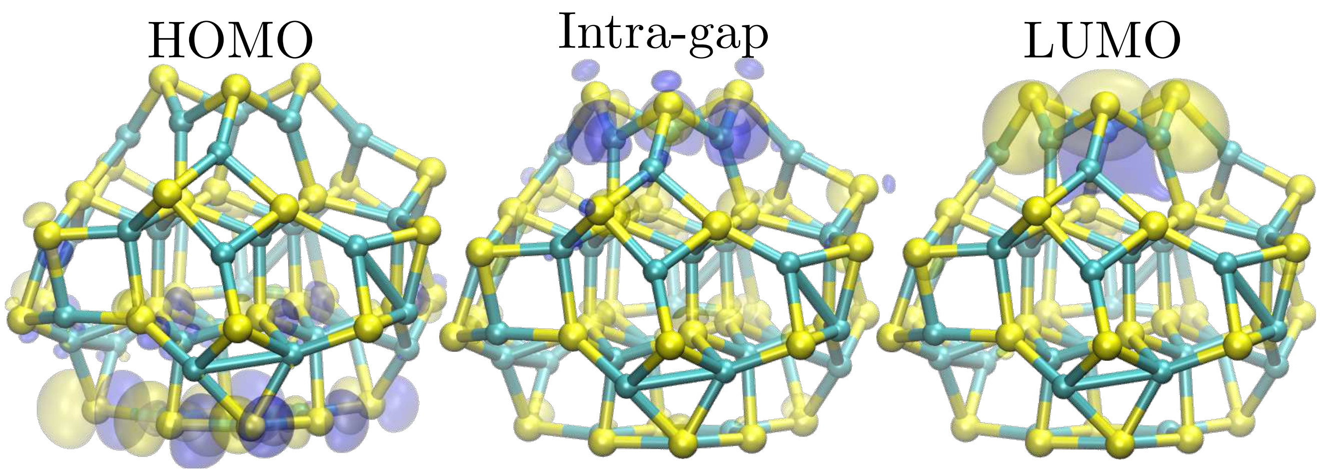
Surface doping

Core doping



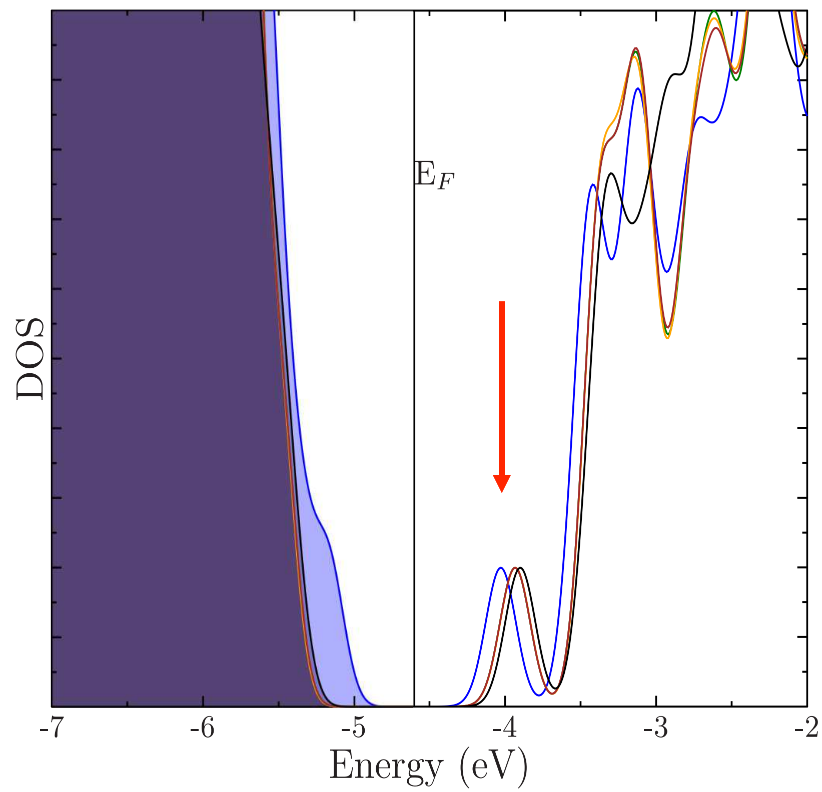
Intermediate Band from NP Surface Relaxation

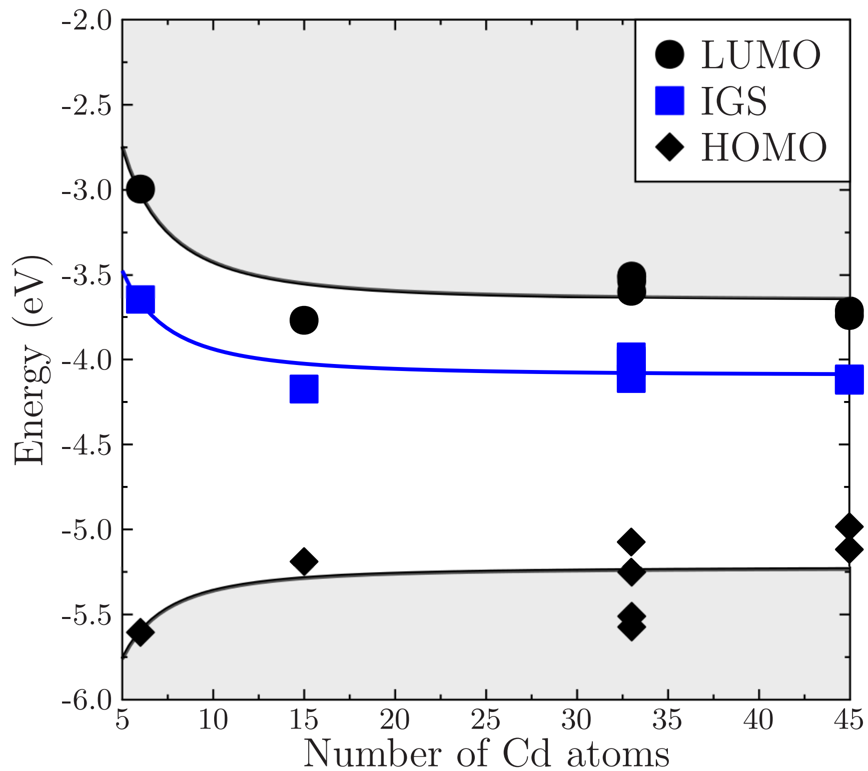
Cd33Se33 NP



Intra-gap State from NP Surface Relaxation

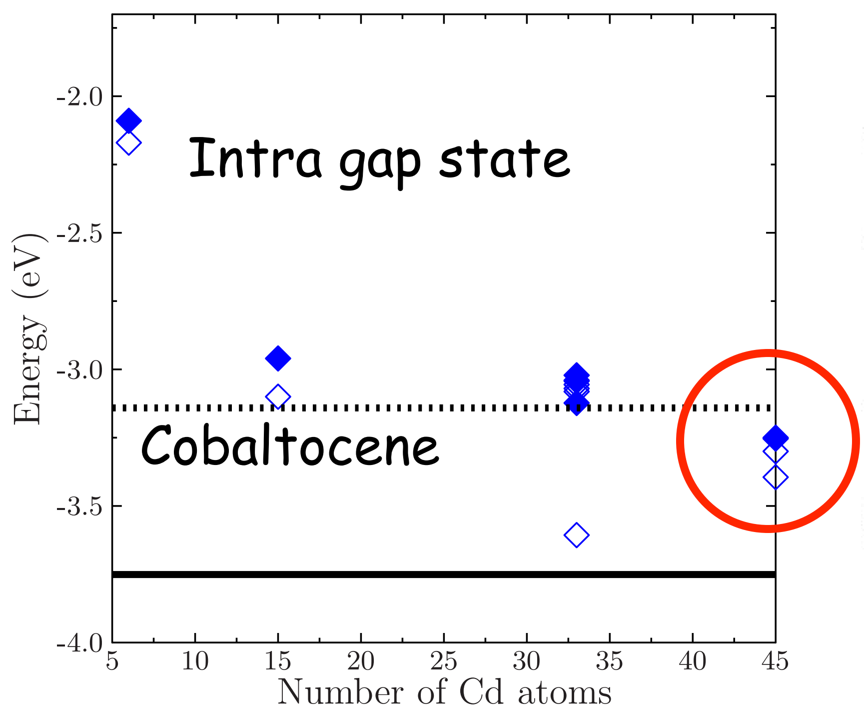
Cd33Se33 NP: An intra-gap state is formed by NP relaxation

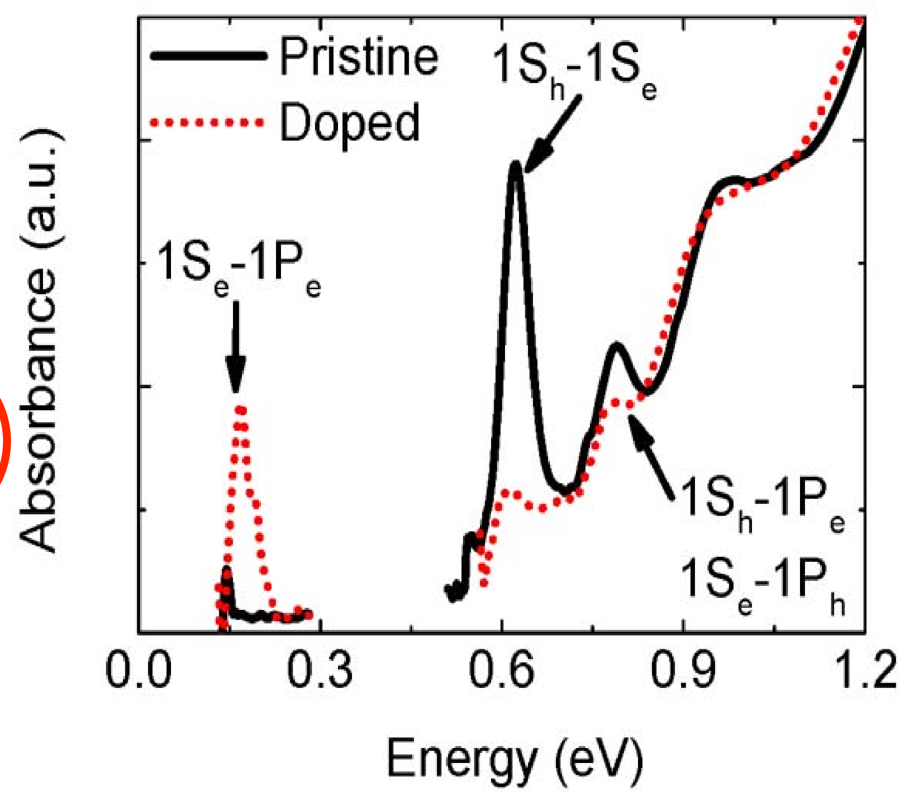




Intra-gap State Filling by Chemical Doping

Intra-gap state filled by cobaltocene doping



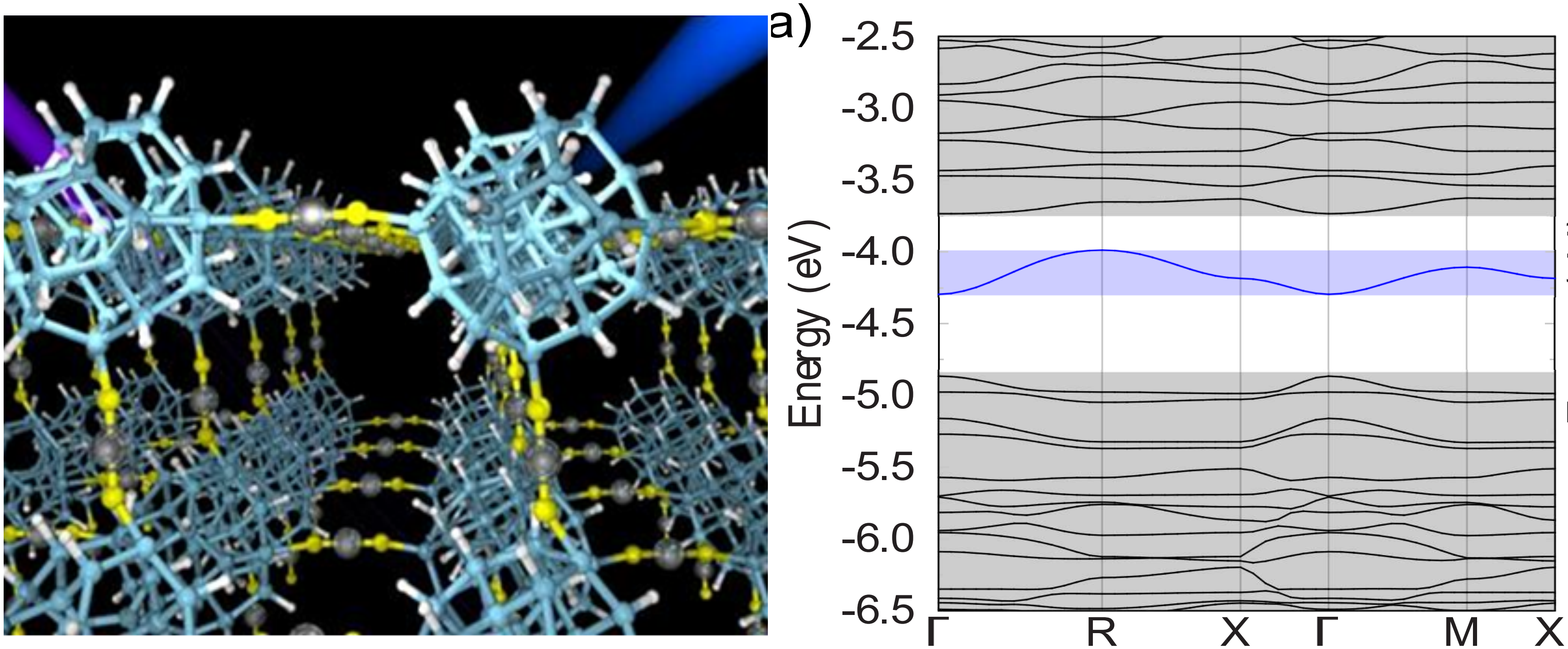


Voros, Galli, GTZ 2014

Klimov 2014

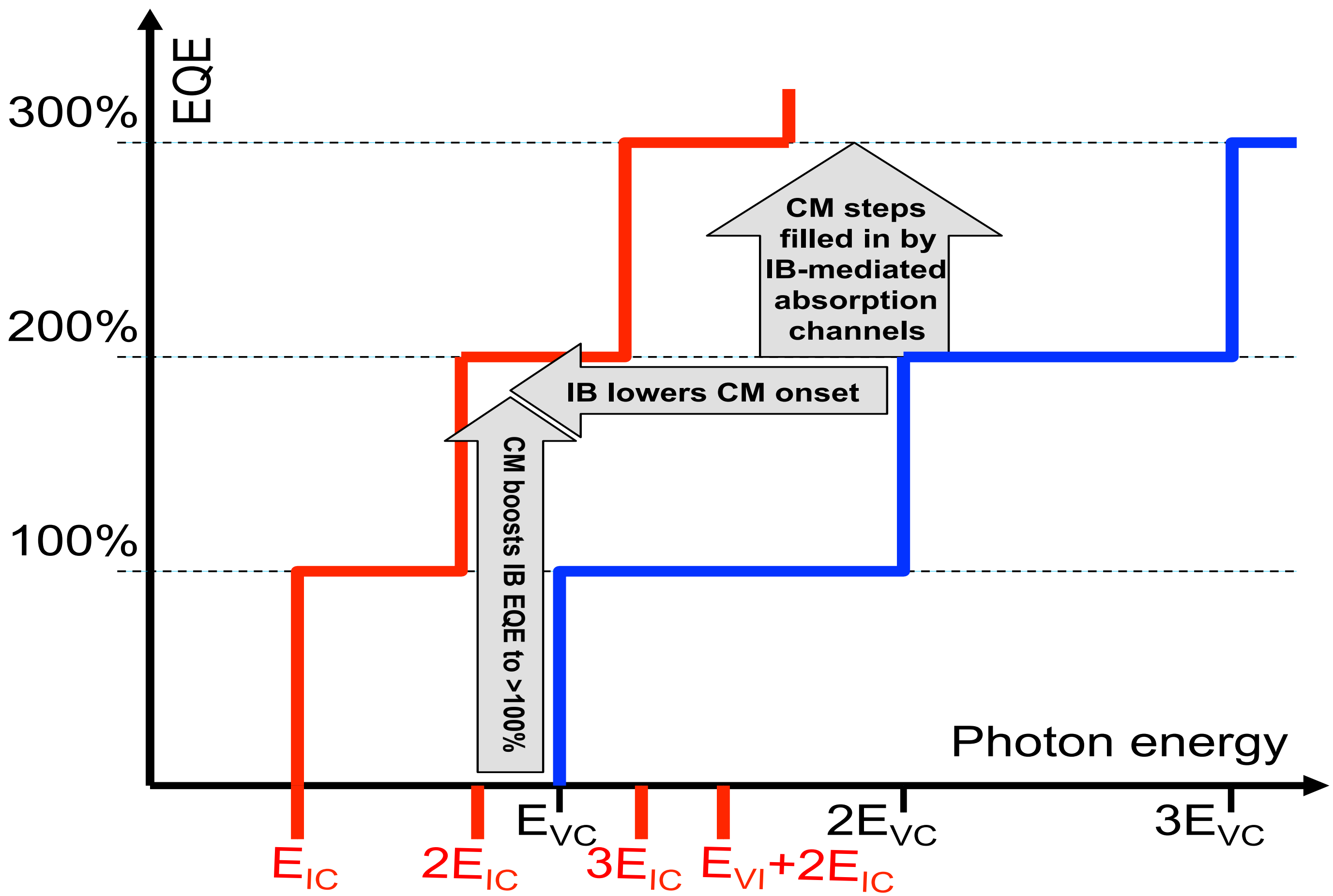
Intermediate Band Formed in NP Array

Intra-Gap states combine into Intermediate Band in Simple Cubic nanoparticle array



Voros, Galli, GTZ 2014

Synergy between Intermediate Band absorption and Carrier Multiplication



Theoretical maximum: 55% at one-sun, 72% at full concentration

Intermediate Band Summary

- IB is the most promising paradigm to boost sub-gap absorption
- Epitaxial implementation yet to fulfill its promise
- **Proposed to use Colloidal Nanoparticles to implement IB**
- **Several designs to form intra-gap states**
- **Proof of Concept: Intra-gap state by NP relaxation**
- **Chemical doping of intra-gap state by cobaltocene**
- **Demonstrated formation of intermediate band in NP arrays**

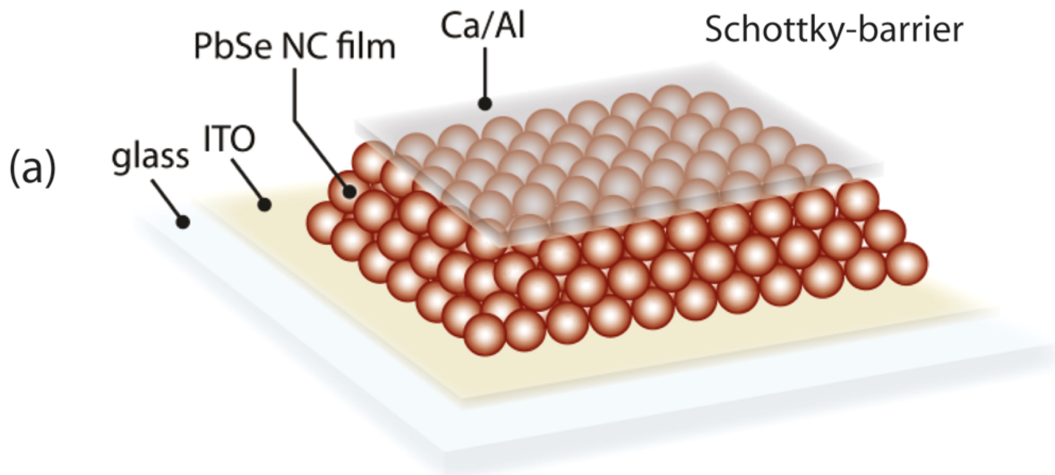
Plan of the Talk

Carrier Multiplication Boost at high energies

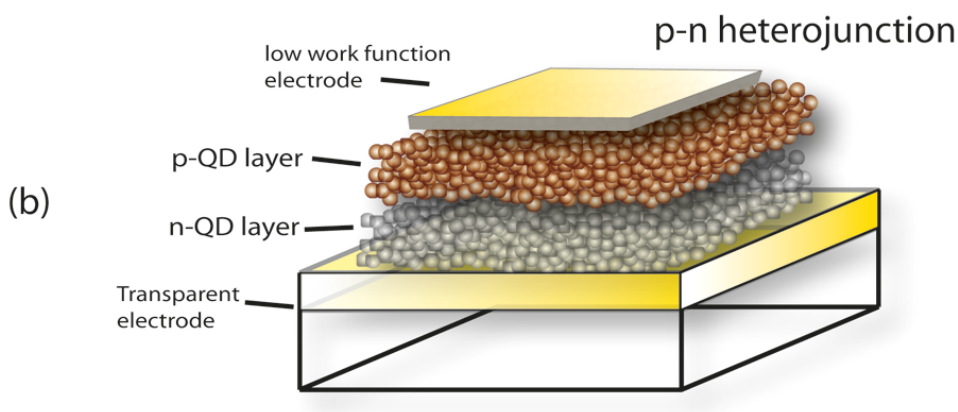
Intermediate Band boost at low energies

Transport to extract photo-induced charge carriers

Transport in Nanoparticle Solar Cells

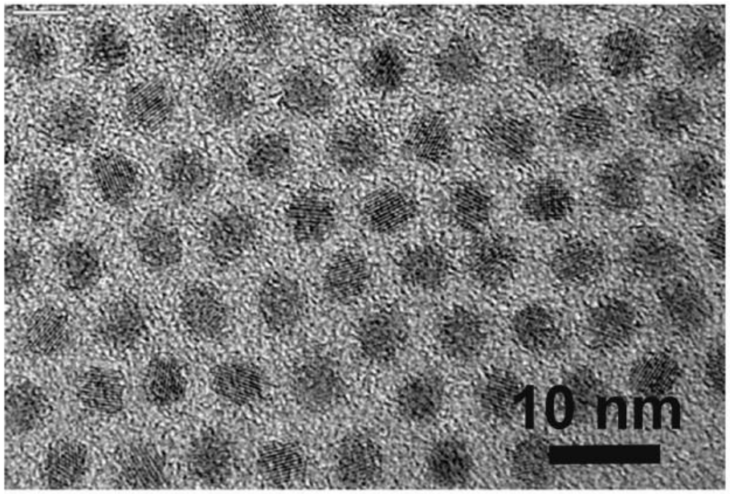


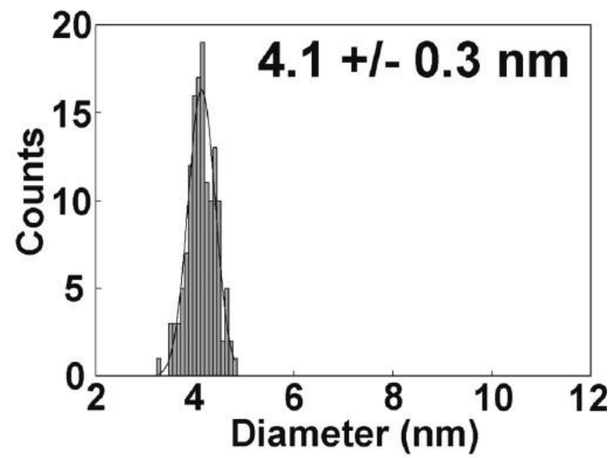
Built-in field generated by difference of electrode work functions



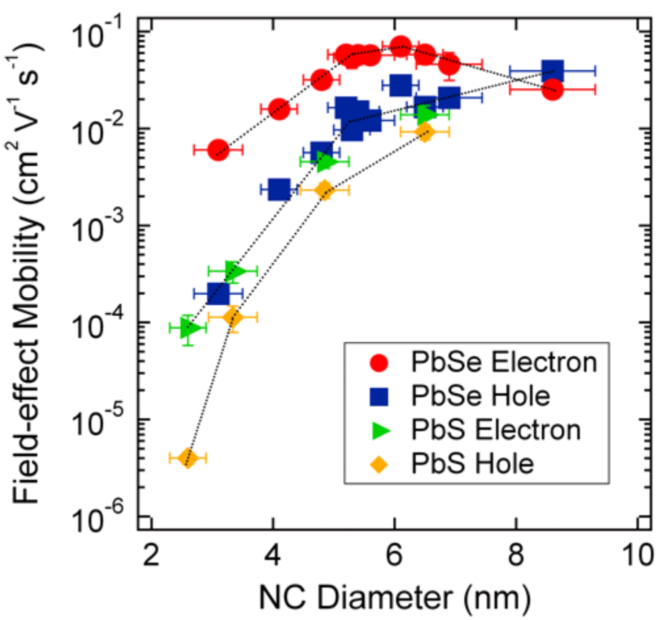
Built-in field generated by forming p- and n-doped nanoparticle layers

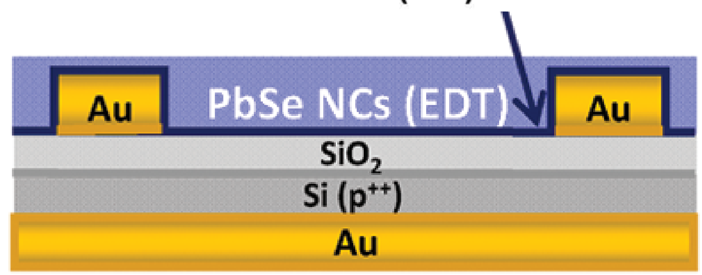
FET mobility in PbS and PbSe Nanoparticle films





M. Law (2010)





Mobility(diameter D): rise->maximum

Mobility $\mu \sim 10^{-3}$-10^{-2} v. 10^3 cm^2/Vs bulk Si

Hierarchical transport studies based on electron energy calculations

Energetics of coupled nanoparticles/nanostructures

↓

Extraction of representative parameters

↓

Hopping limit: Marcus, Miller-Abrahams: E_c, E_{kin}, τ

↓

Kinetic Monte Carlo of device transport

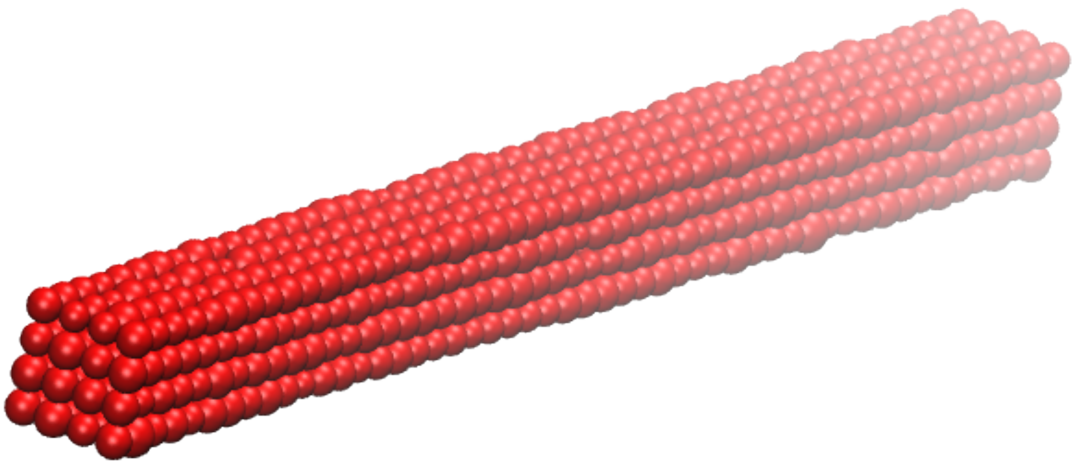
Band limit: Band formation, Boltzmann transport: W, m_{eff}, τ

↓

Current-current correlation and response function

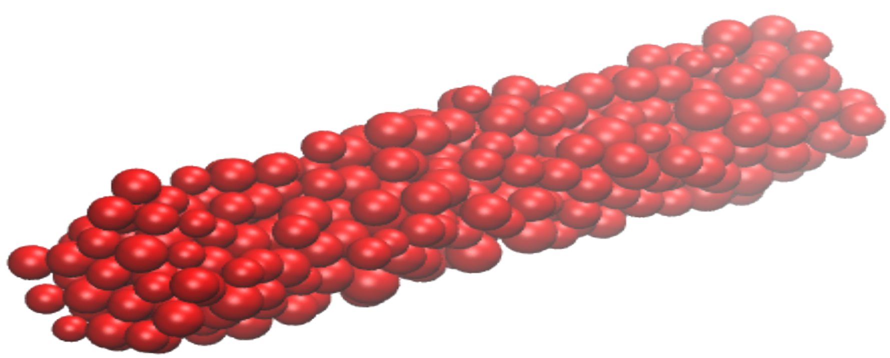
I. Carbone, S. Carter and GTZ J. Appl. Phys. 114, 193709 (2013)
M. Voros, I. Carbone, S. Carter, G. Galli and GTZ submitted

1. Define nanoparticle lattice



Nanoparticle radius selected with Gaussian distribution

Always six nearest neighbors, packing density ~ ρ=0.52



PackLSD: collision driven molecular dynamics

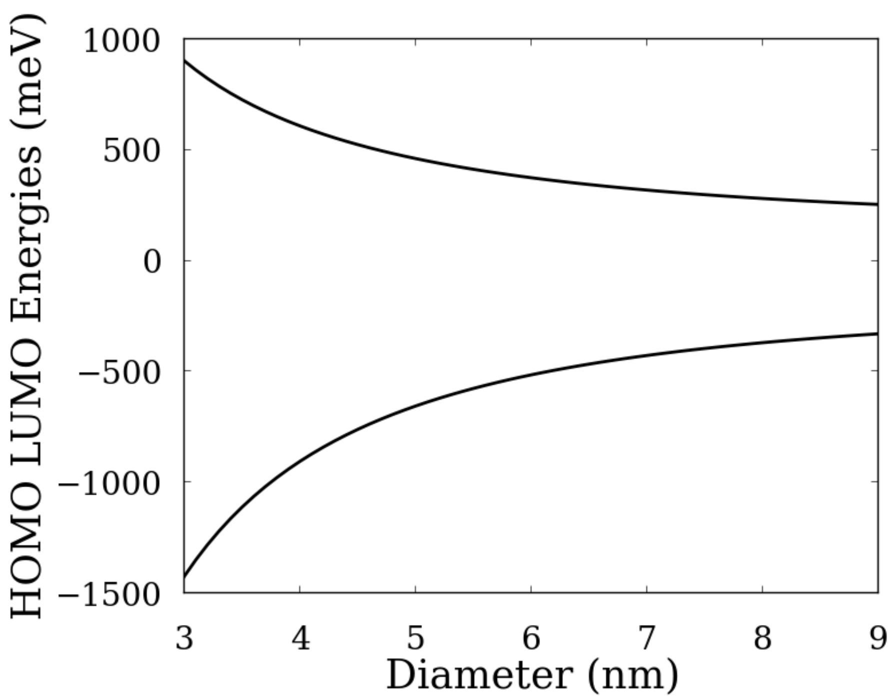
Generate disordered jammed packing, density: ρ=0.62-0.63

Donev et al, (2005)

2. Ab Initio Nanoparticle energetics

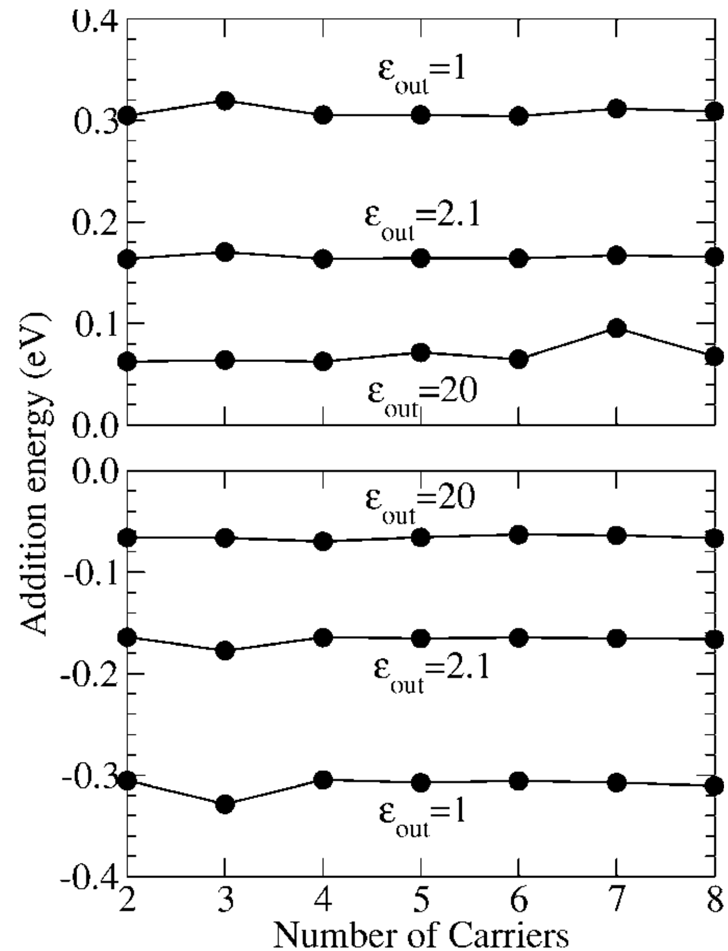
One-particle energy E^{1p}

Kang and Wise (1997)



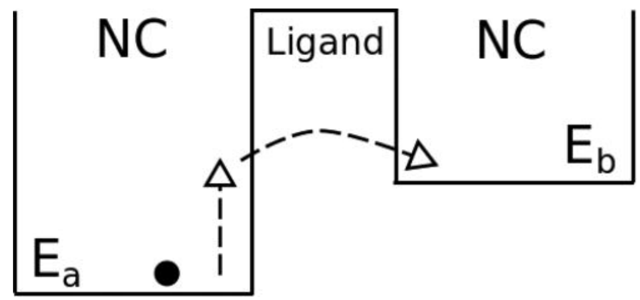
Addition/charging energy E^c

An, Franceschetti, Zunger (2007)



3. Dynamics: NP-NP Transition rates

Thermally activated
nearest-neighbor hopping



Miller-Abrahams: low T single phonon

$$\Gamma_{a\to b} = \Gamma_0 \exp(-2\beta\Delta x) \begin{cases} \exp\left(-\frac{E_b - E_a}{kT}\right) & (E_b > E_a), \\ 1 & (E_b \leq E_a). \end{cases}$$

$$\beta = \sqrt{\frac{2m^*(E_{vac} - E_{barrier})}{\hbar^2}}$$

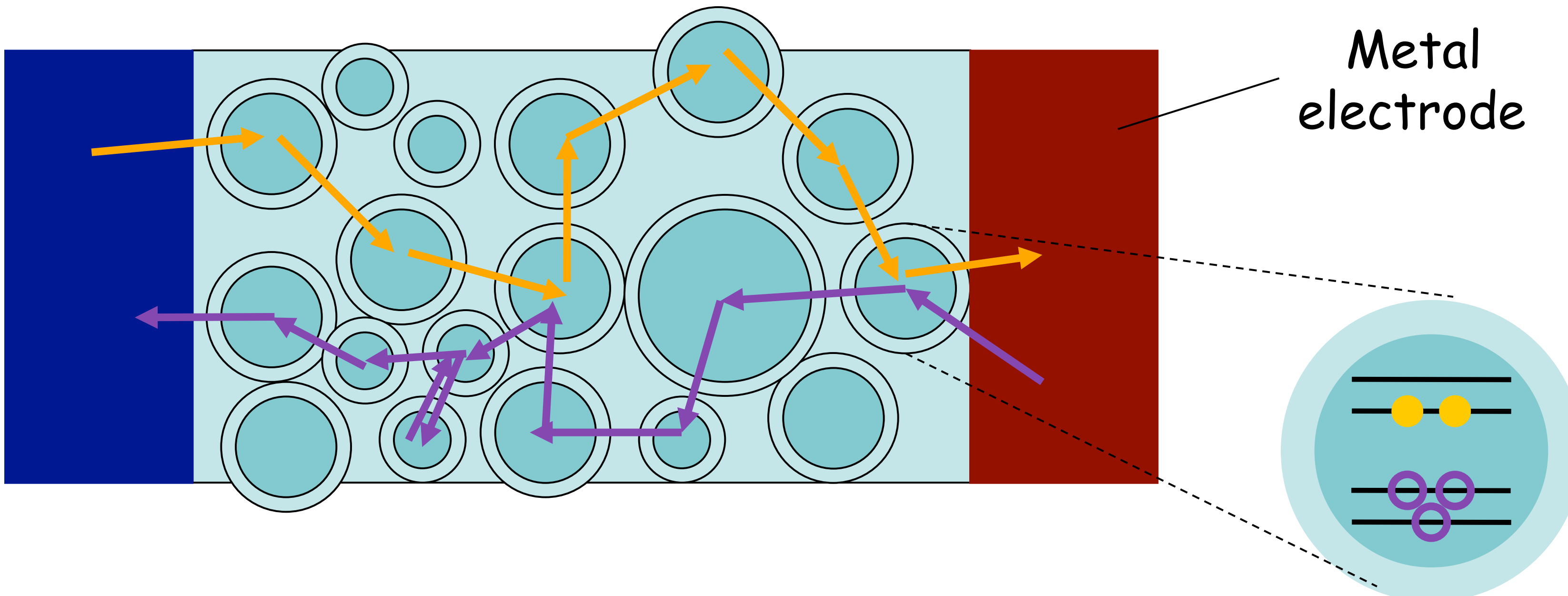
Marcus: high T "multi phonon"/polaronic

$$\Gamma_{a\to b} = \frac{2\pi}{\hbar}|H_{ab}|^2 \frac{1}{\sqrt{4\pi\lambda_{ab}kT}} \exp - \frac{(\lambda_{ab} + E_b - E_a)^2}{4\lambda_{ab}kT}$$

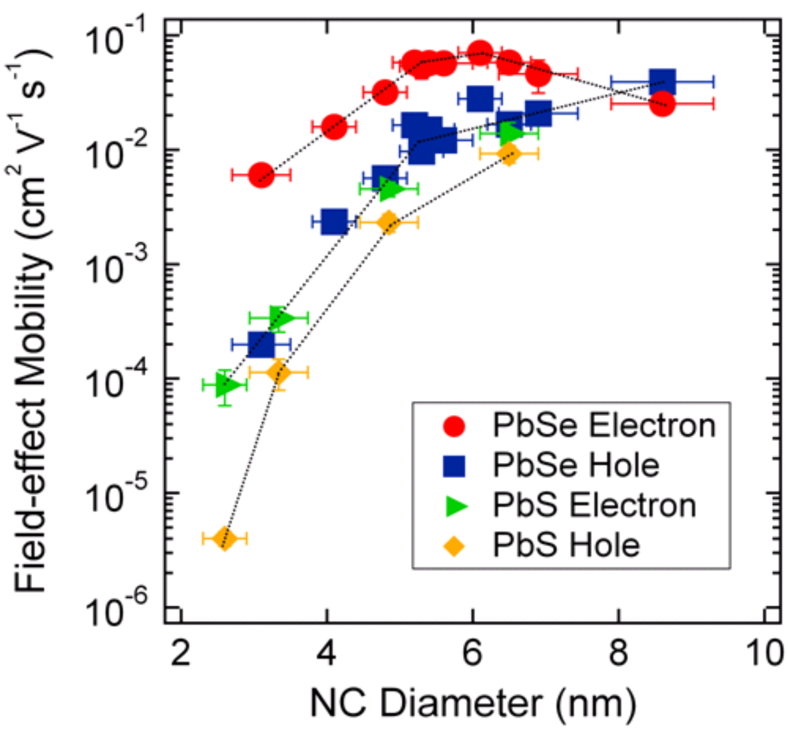
$$|H_{ab}|^2 \approx |H_0|^2 \exp(-2\beta\Delta x)$$

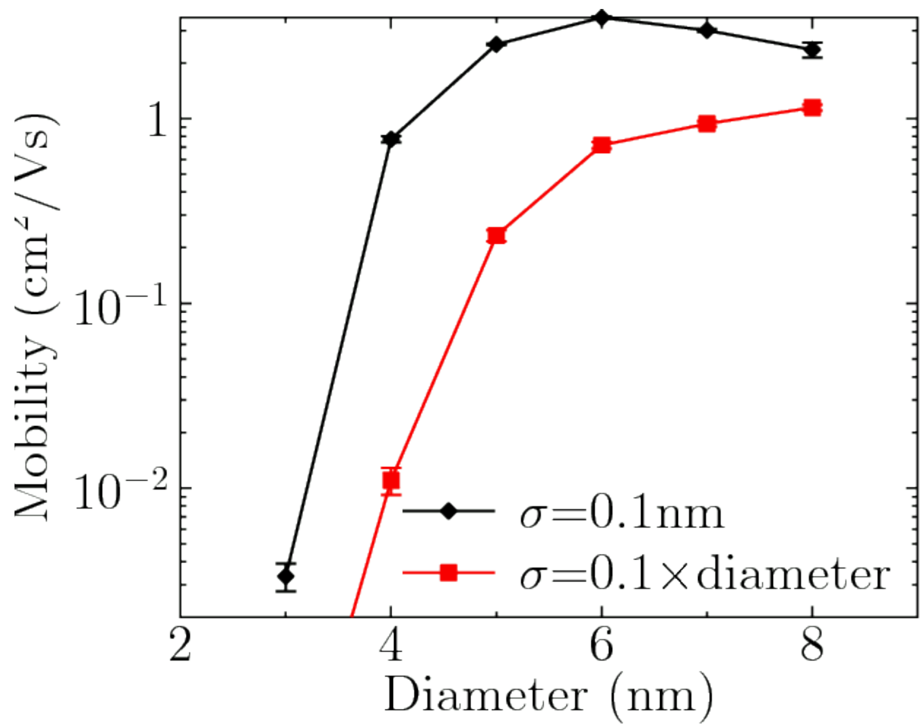
λ: reorganization energy
H: "electronic coupling"

3. Dynamics: Device level modeling



RESULTS: Diameter dependence of μ





Small D: steep rise
Large D: plateau/decrease

σ = width of NP size distribution

RESULTS: Diameter dependence of μ – Physics

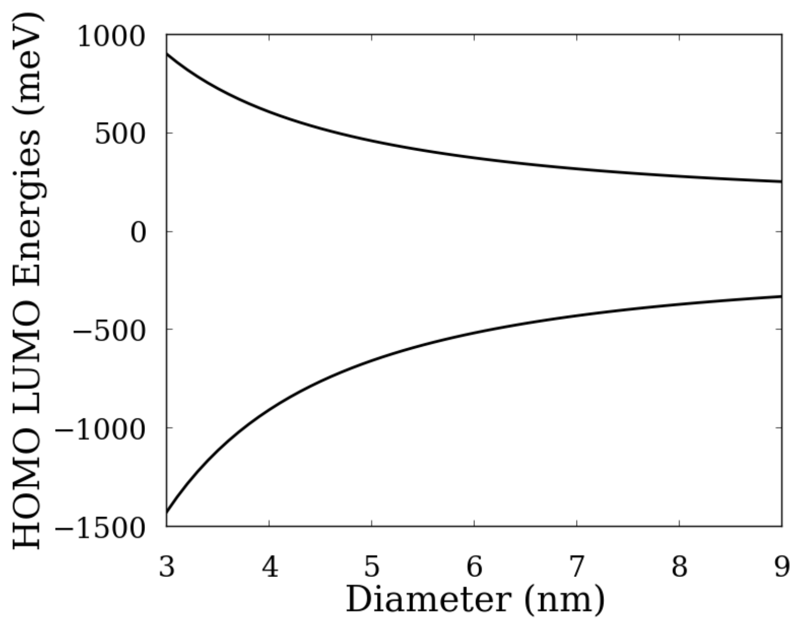
Small D: steep rise

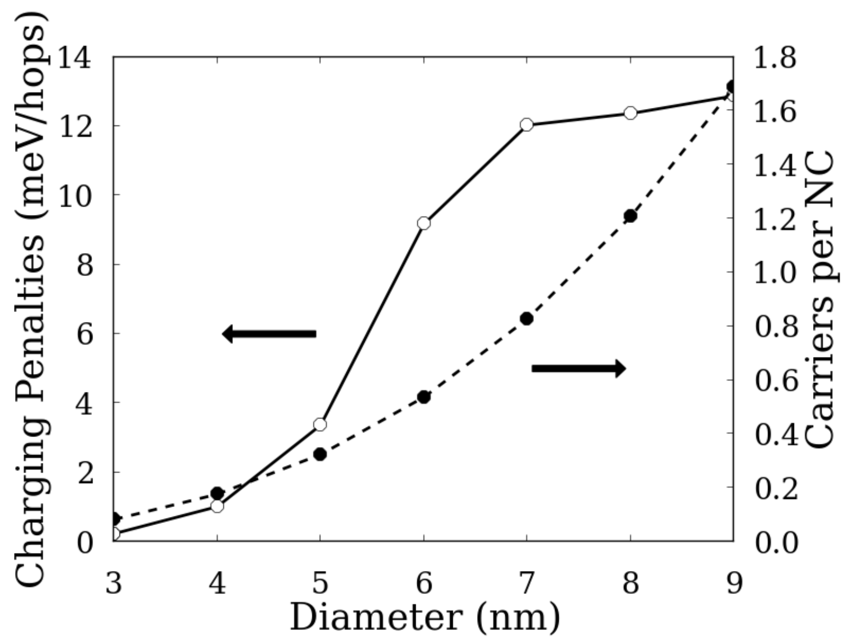
1. For increasing D less hops are enough to cross sample

2. $E^{1p}(D)$ less steep for increasing D, energy disorder is decreases with D

Large D: plateau/decrease

The electron density (#/unit volume) is kept constant, for increasing D the electron #/ nanoparticle increases, increasingly blocking transport by Coulomb blockade/charging energy E^C

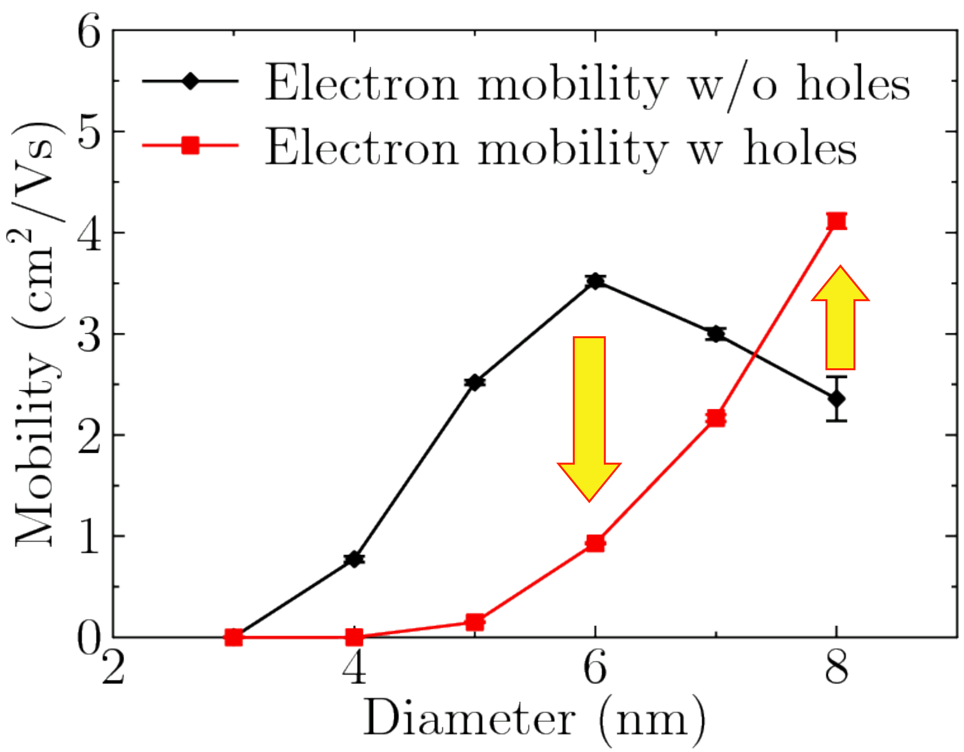




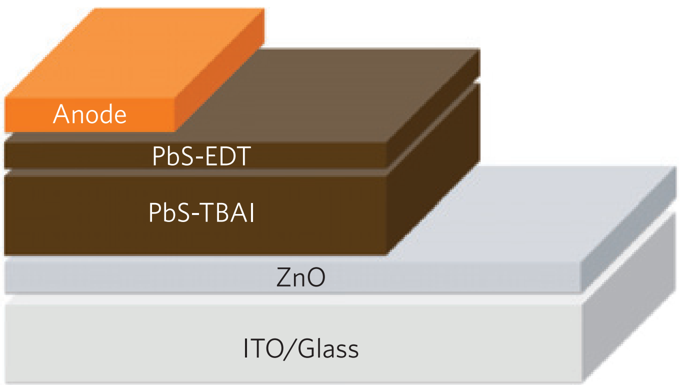
RESULTS: Verifying Electron-hole effects

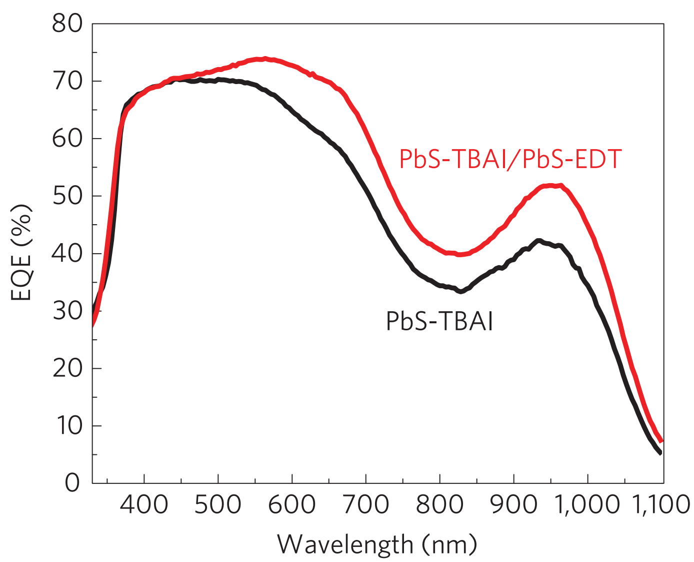
Simulated equal electron and hole densities

Presence of holes neutralizes the Coulomb barrier: conductivity grows instead of peaking



Transport optimization leads to 9% efficiency





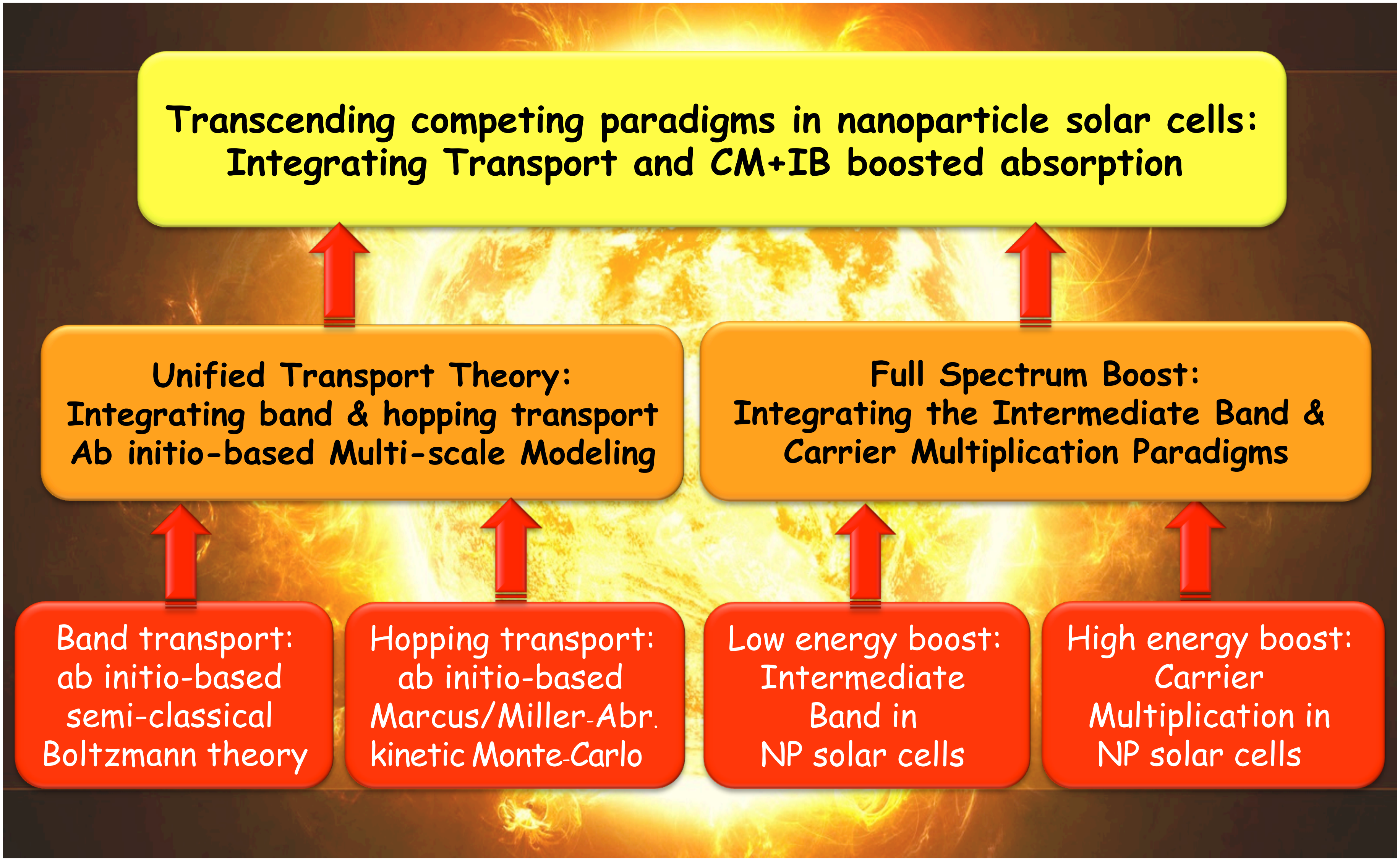
Transport optimization by strategic
- ligand-exchange processes
- bandgap-engineering
- surface passivation and
- atomic layer deposition infilling

9.2% efficiency was reached in PbS-TBAI nanoparticle solar cells

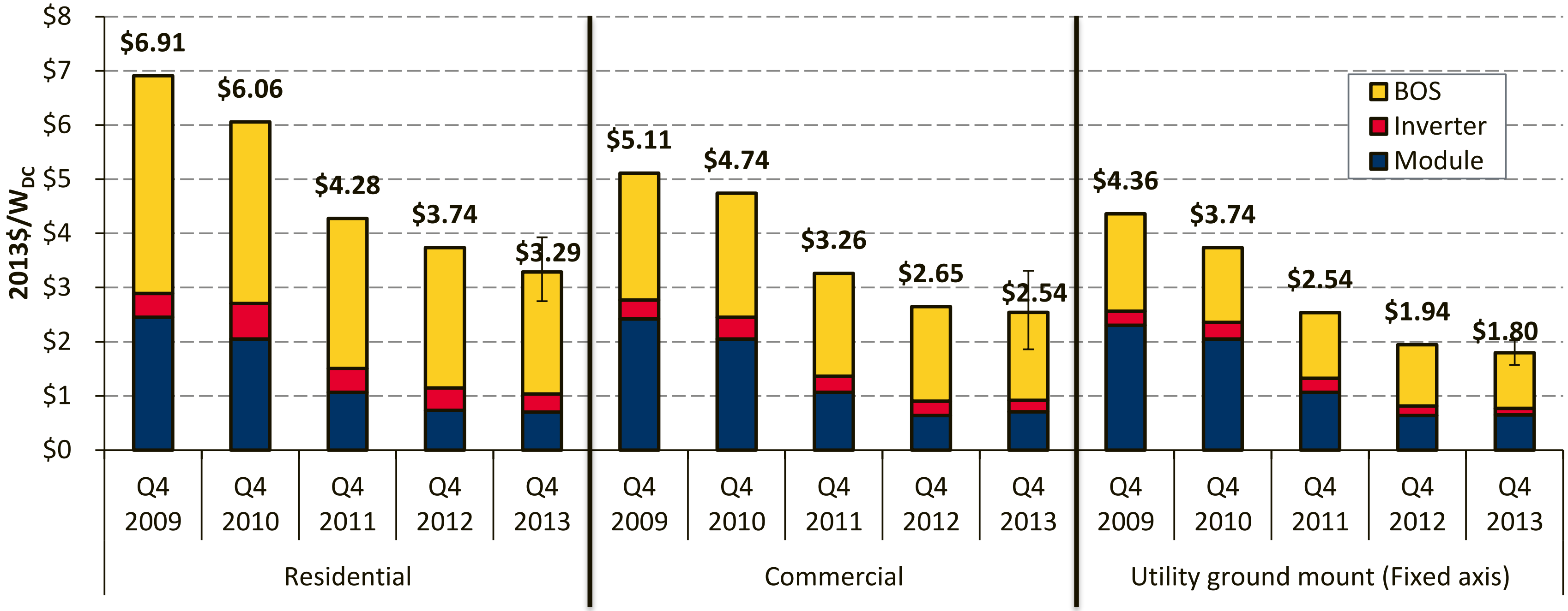
Bawendi (2014)

2015: The year nanoparticle solar cells break 10% ?!

The Full Spectrum Boost Project



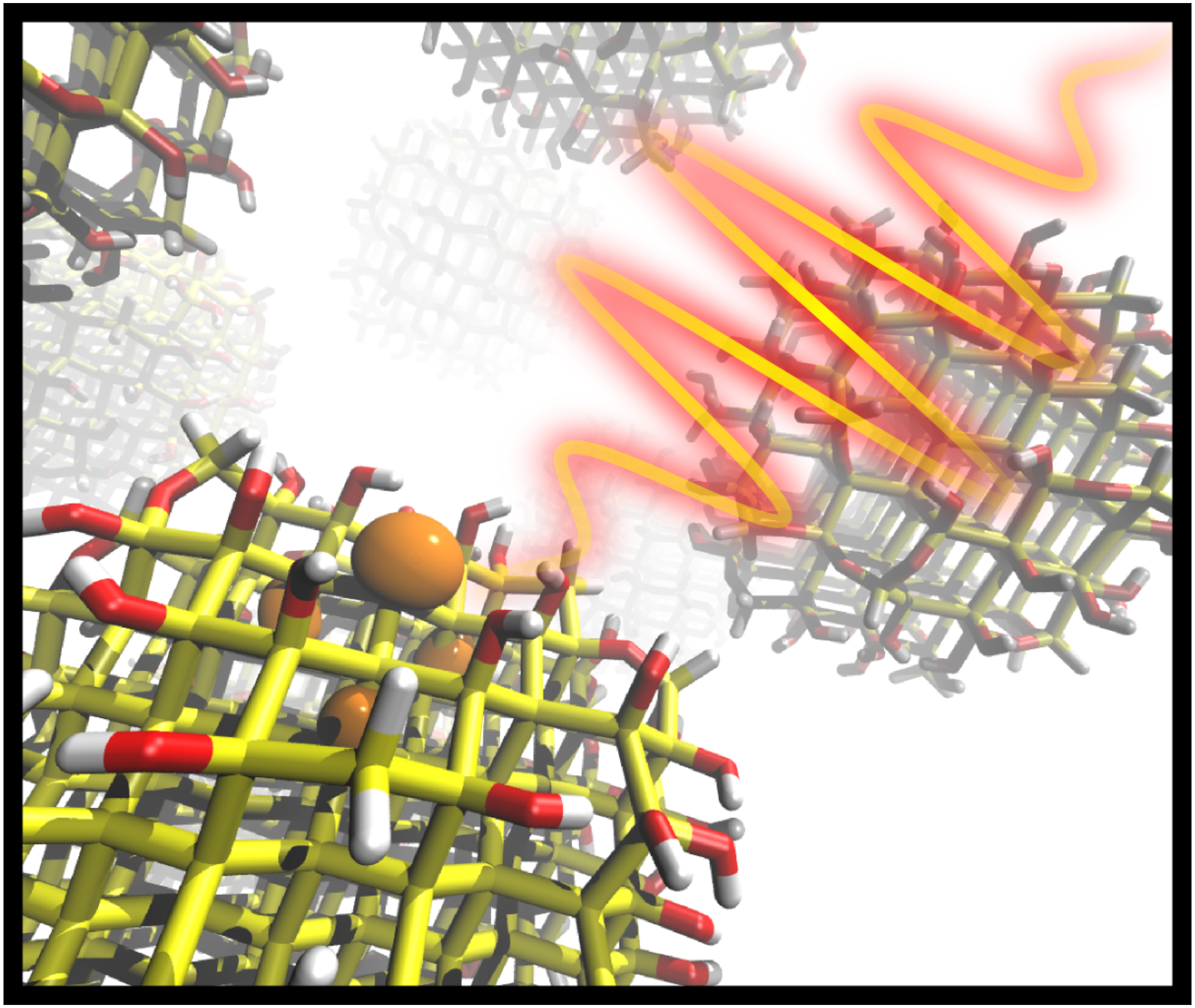
PV System Price, 2009-2013



- Since Q4 2009, modeled system prices fell between 16% – 19% per year
  - 1/2 - 2/3 of reduction attributed to module price reductions
- From Q4 '12 to Q4 '13, modeled system prices fell between $0.07/W - $0.44/W, or 3-12%
- Q4 2013 bottom-up modeled residential system price of $3.29/W is consistent with leading residential installers' pricing, such as SolarCity's reported Q2 2014 costs ($3.03/W), plus a reasonable operating profit margin.

Note: Standard crystalline silicon modules (13.5% efficiency in Q4 2009 to 15.0% in Q4 2013). System sizes: residential: 5 kW in Q4 2009 through Q4 2013; commercial: 202 kW in Q4 2009 to 223 kW in Q4 2012 (200 kW in Q4 2013); utility-scale: 175 MW in Q4 2009 to 185 MW to Q4 2013). Modeled system sizes in the residential and commercial rooftop sectors were chosen based on typical system sizes, then adjusted for optimal inverter configuration. System sizing for utility-scale benchmarks were chosen for comparison purposes against pricing reported from DOE's Energy Information Administration (2010).
Source: SolarCity. (2014). "Cost Calculation Methodology." Accessed September 2, 2014: http://investors.solarcity.com/events.cfm.

Reduction of Nonradiative Recombination by Strain in Nanoparticle Arrays



Reduction of Nonradiative Recombination by Strain in Nanoparticle Arrays

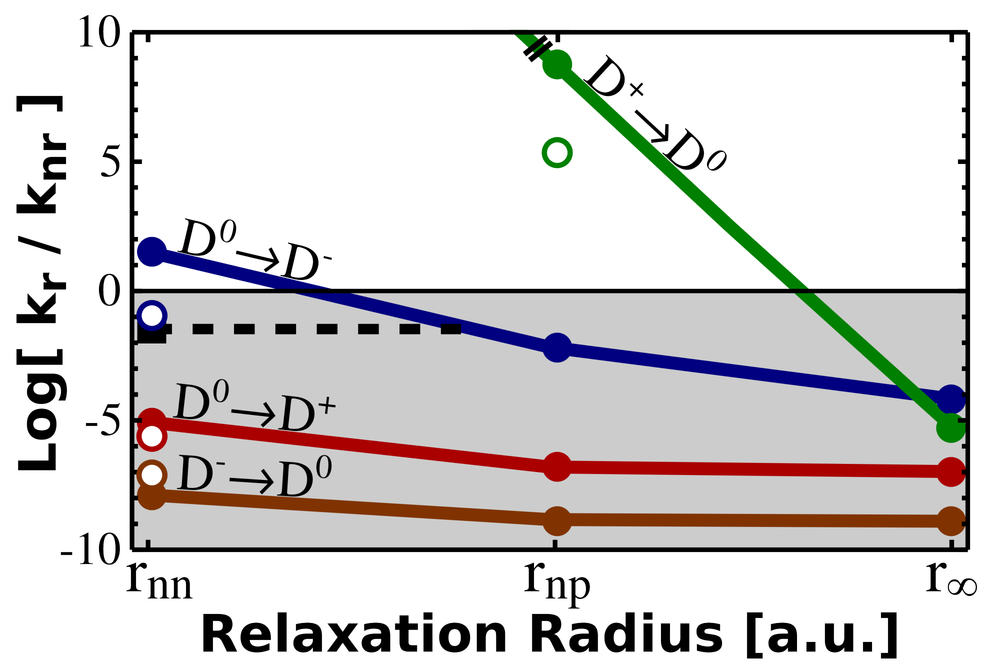


Figure 5: The logarithm of the ratio between radiative (k_r) and nonradiative (k_{nr}) decay rates for the four capture processes outlined in Figure 4, as a function of decreasing strain on the NP (see text), for a P_b defect at the surface of a 1.3 nm Si NP terminated by an oxide layer. The black horizontal line represents the boundary between radiative (white area) and nonradiative (gray area) recombination processes. Configurations representing different relaxation schemes around the defect (and hence different amount of strain) are shown on the x axis: r_{nn} (nearest neighbor), r_{np} (Si NP and first layer of oxygen) and r_∞ (all atoms in the system). Nonradiative rates given by Equation 7 and 3 are indicated by the dots and open circles respectively.

4.2. Projected DOS

Projected states to atomic orbitals to determine character of states

$$EDOS_{\text{region}}(E) = \sum_j \sum_{i \in \text{region}} |\langle \phi_i | \psi_j \rangle|^2 \, \delta(E_j - E)$$