The Full spectrum boost project in nanoparticle solar cells: Downconversion, Upconversion, Transport

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UC Santa Cruz: S.Carter, C.Church, I.Carbone
UC Irvine: Matt Law

Chicago:
G.Galli

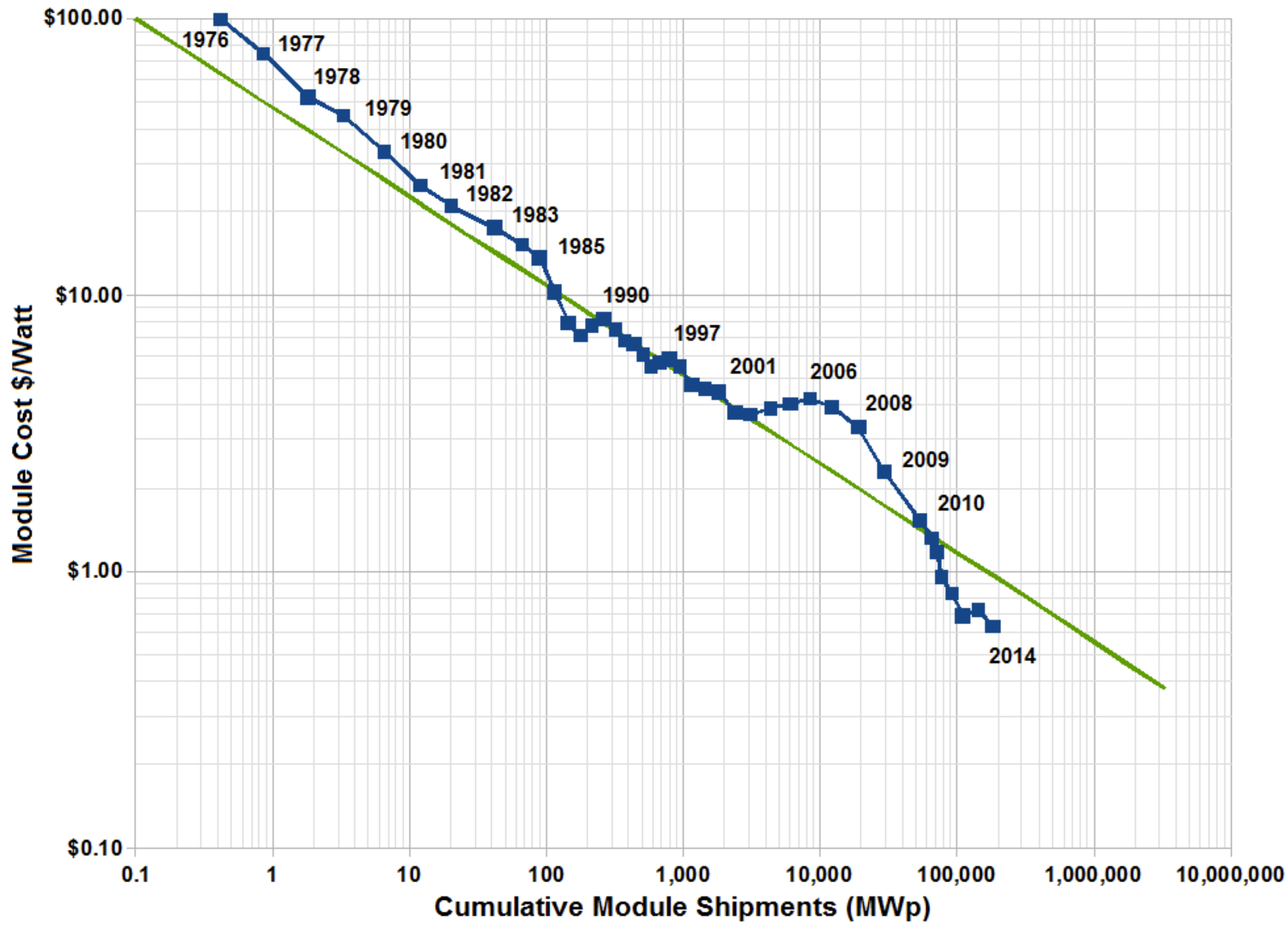
Budapest:
A. Gali

Harvard:
T.Kaxiras

Max Planck:
S.Wippermann

DOE Sunshot Goal - Reach grid parity at 1$/W

Swanson's Law/Solar Moore's Law



Present Day

Present status: 0.5-0.7 $/W: SunShot goal achieved!

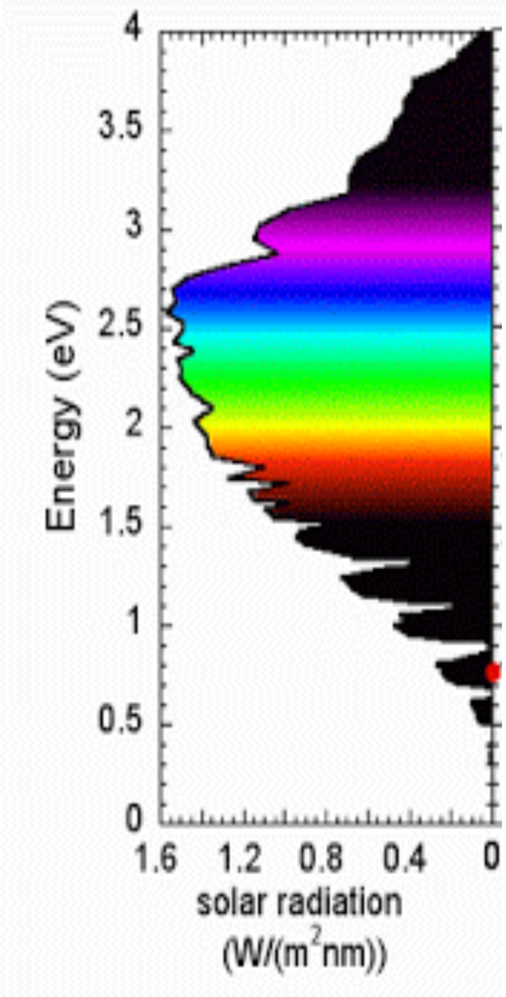
Present records:

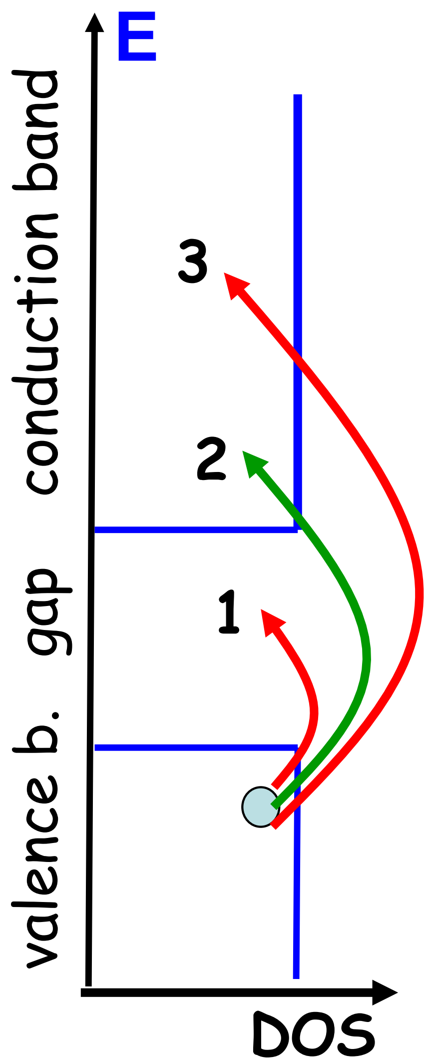
GaAs	29%	Alta Devices
HIT c-Si/a-Si cell	25.6%	Panasonic, SunPower
Perovskites	22	EPFL, Korea, Oxford
Thin film CdTe	20%	First Solar
Organic solar cells	12%	Sumitomo

BUT fracking moved grid parity to ~0.3$/W

So, the energy challenge needs pursuing all promising ideas

Solar energy conversion is inefficient at low and high end of spectrum





1. No absorption below gap:
   photon wasted

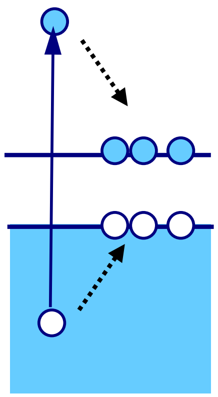
2. Absorption to bottom of
   conduction band: optimal

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

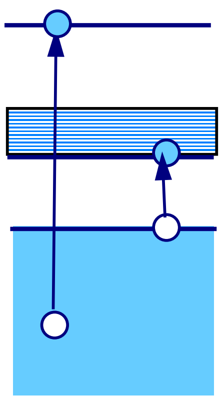
Optimization of gap:
   max efficiency: **31%**

New physics needed: **3rd generation PV**

Adapt 3rd generation up-conversion and down-conversion channels to provide Full Spectrum Boost

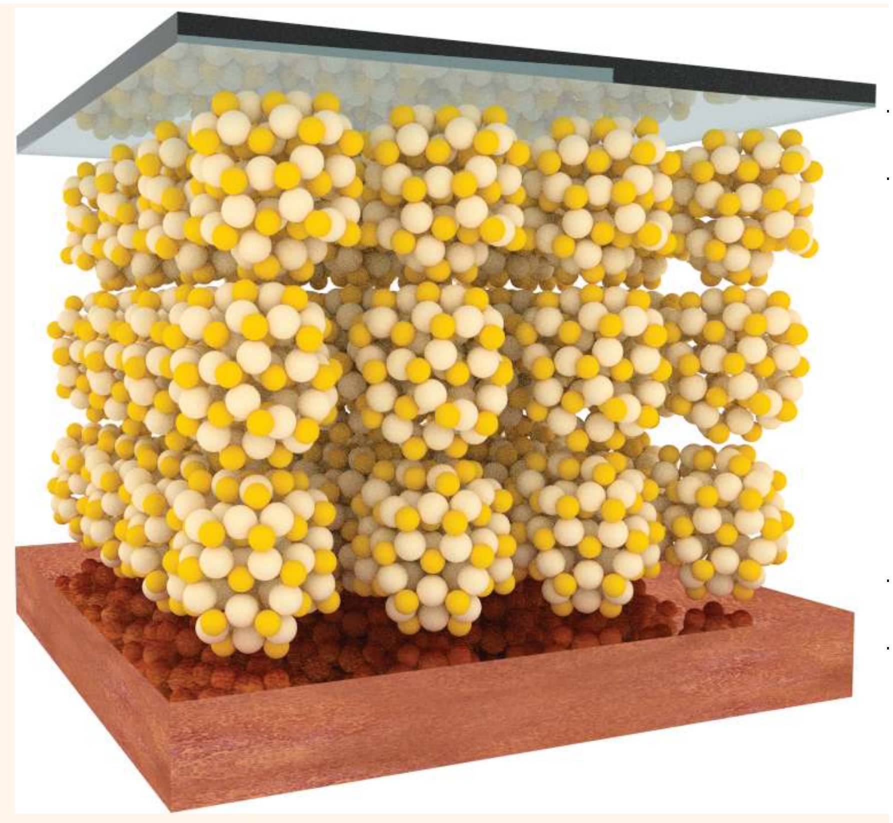


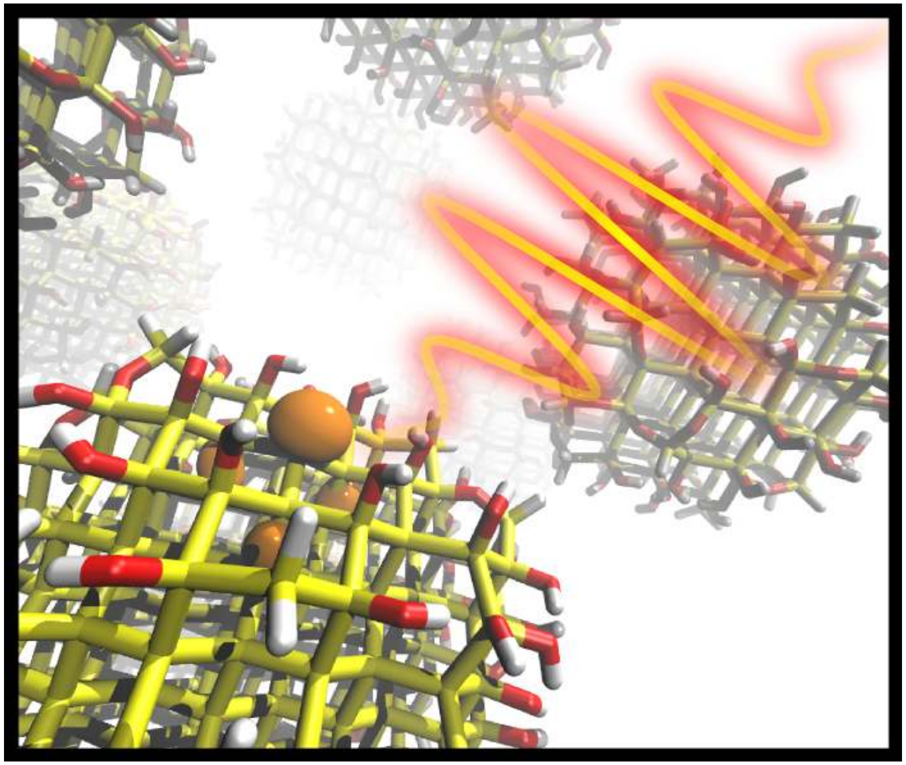
Carrier Multiplication (CM): high-above gap photon excites electron that relaxes by exciting 2nd electron
CM boosts absorption at high energies



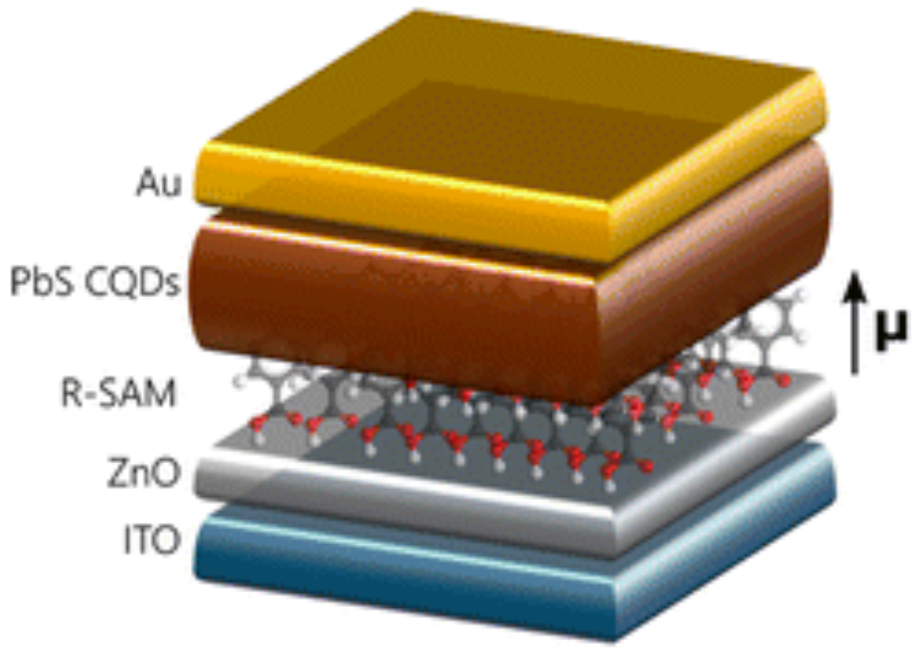
Intermediate Band (IB): below-gap photon excites electron from an intra-gap band to conduction band
IB boosts absorption at low energies

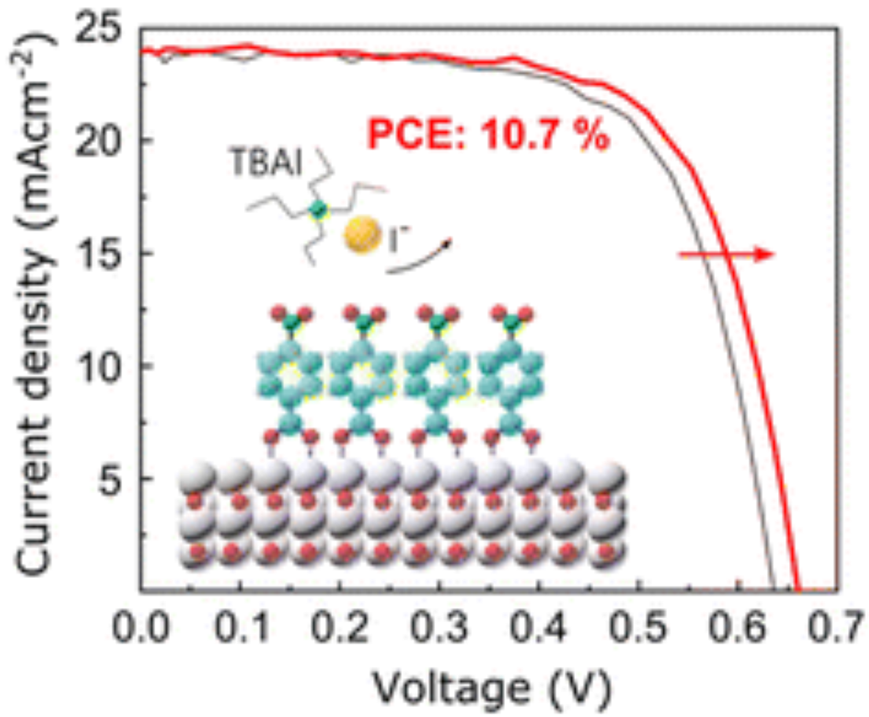
Colloidal Nanoparticle Solar Cells are promising platform for the Full Spectrum Boost Project





A. Colloidal Nanoparticle Solar Cells Broke 10% Psychological Barrier in 2015

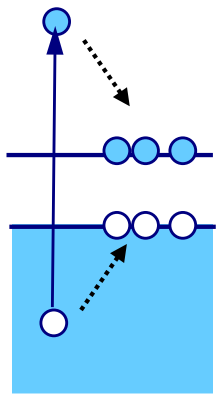




PbS CNPs

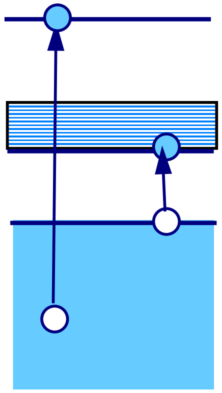
Sargent group
Nano Lett, **15**, 7691 (2015)

B. Colloidal Nanoparticles are promising platform to implement Carrier Multiplication and Intermediate Bands



CM boosts absorption at high energies

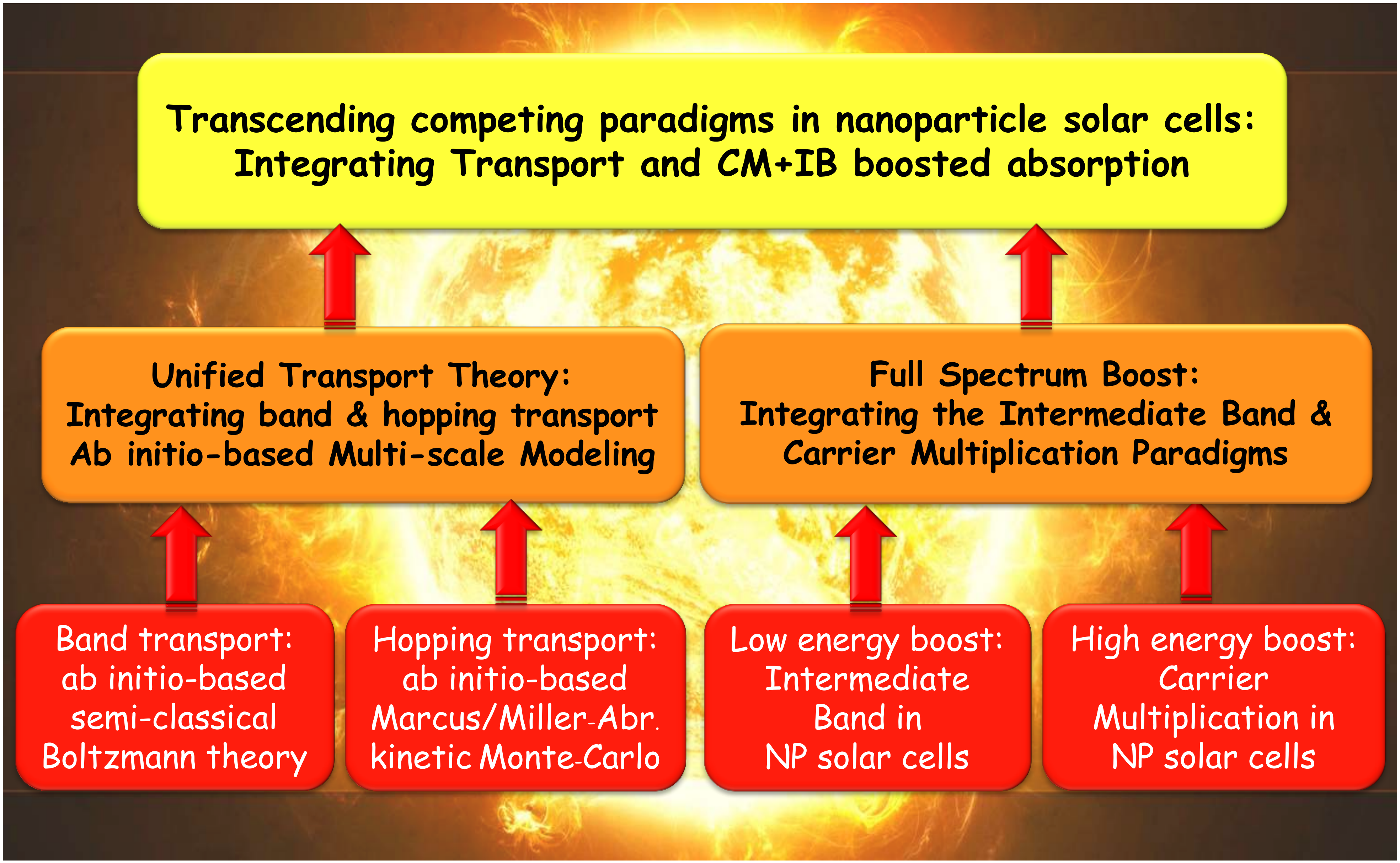
CM can be enhanced in Nanoparticles because Quantum Confinement enhances Coulomb interaction



IB boosts absorption at low energies

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

The Full Spectrum Boost Project



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

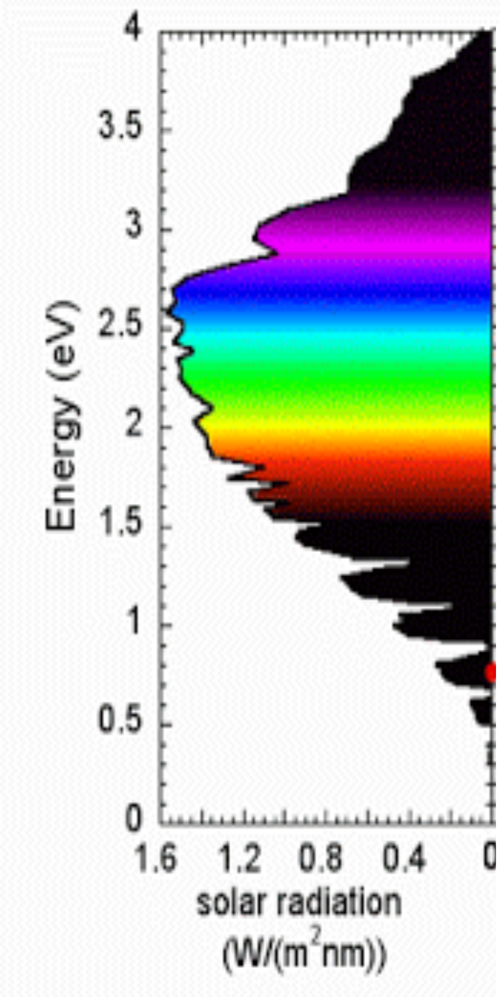
Band formation, Lifetime for Boltzmann transport

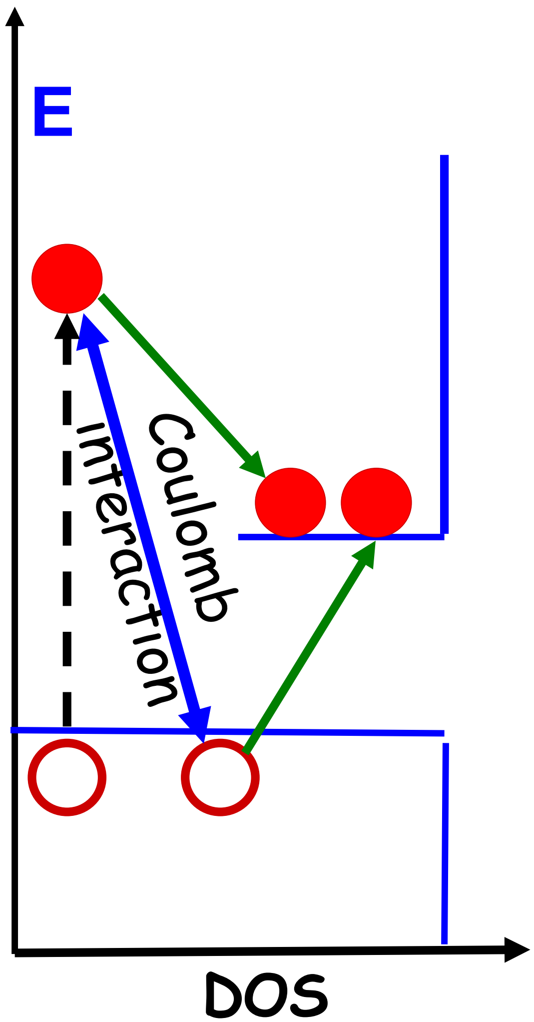
Ab-initio compute of E_{1p}, E_c, τ for Marcus/Miller-A. hopping transport

Intermediate Band: VB/IB, VB/CB rates

Carrier Multiplication: X->XX rate

1. Down-conversion by Carrier Multiplication





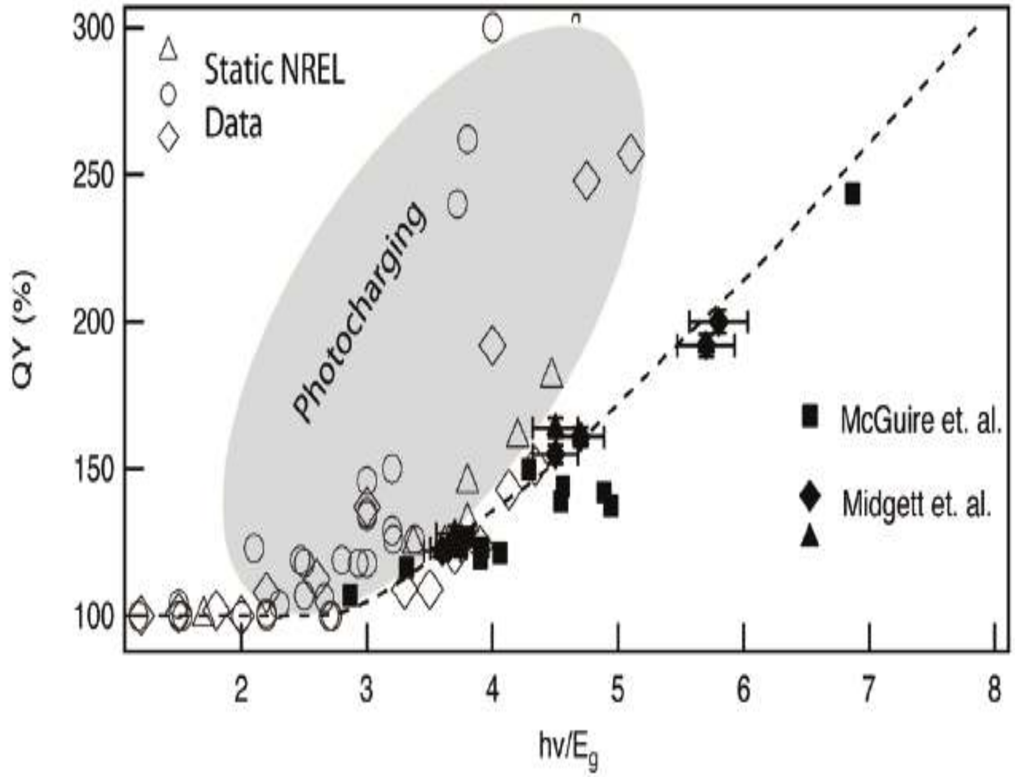
Keep energy of high energy photons in electronic sector:

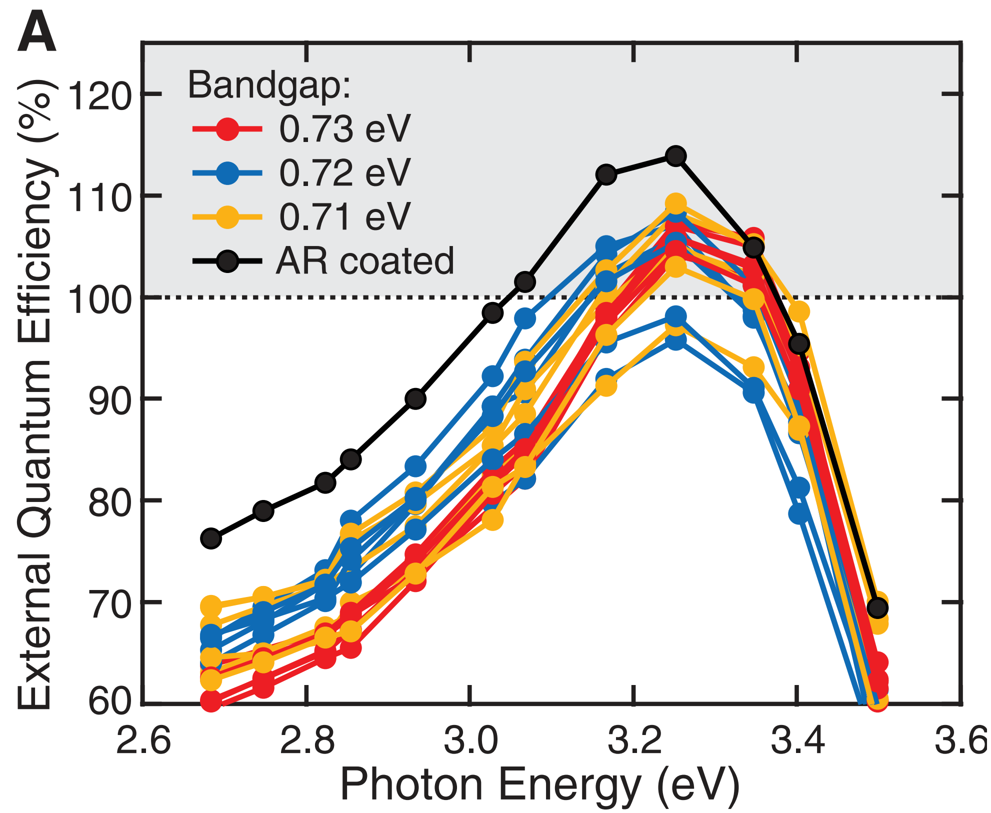
Electron relaxation by Carrier Multiplication:

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

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

CM in Nanoparticles: Discovery, Status





Klimov (2004): Presence of CM in Nanoparticles proven Beard (2011) Nanoparticles in solution

Semonin et al (2012): First working CM/MEG solar cell

QCD - The Quantum Confinement Dilemma in Nanoparticle Solar Cells

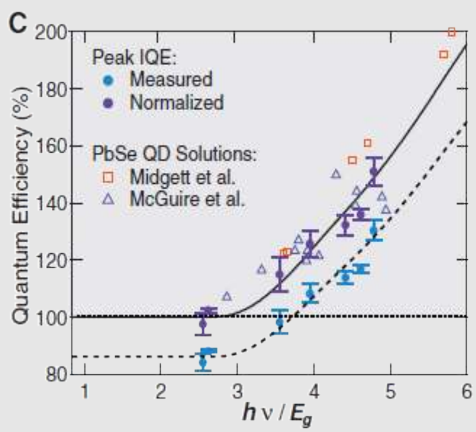
Positives of QC

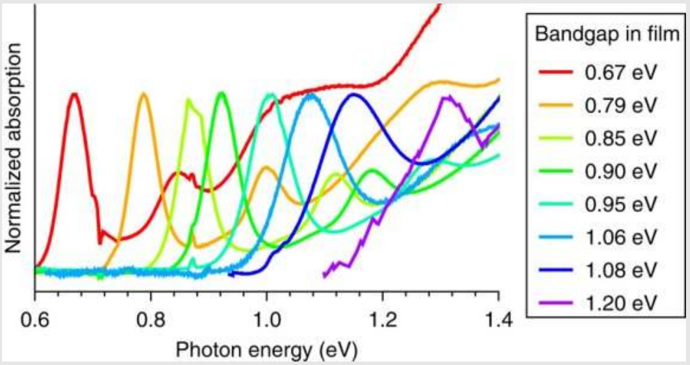
Negatives of QC

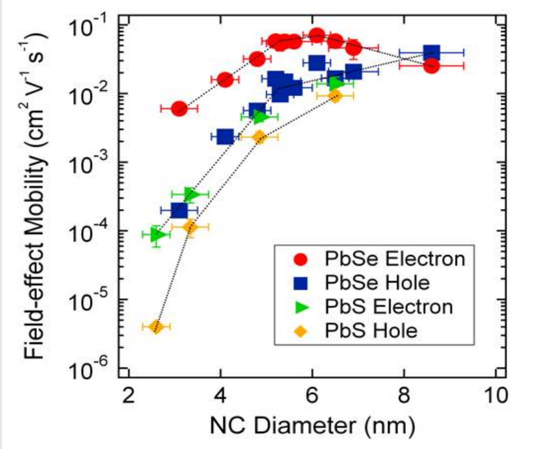
Enhances Coulomb interaction: Enhances CM

Widens gap: Absorption is pushed out of solar spectrum

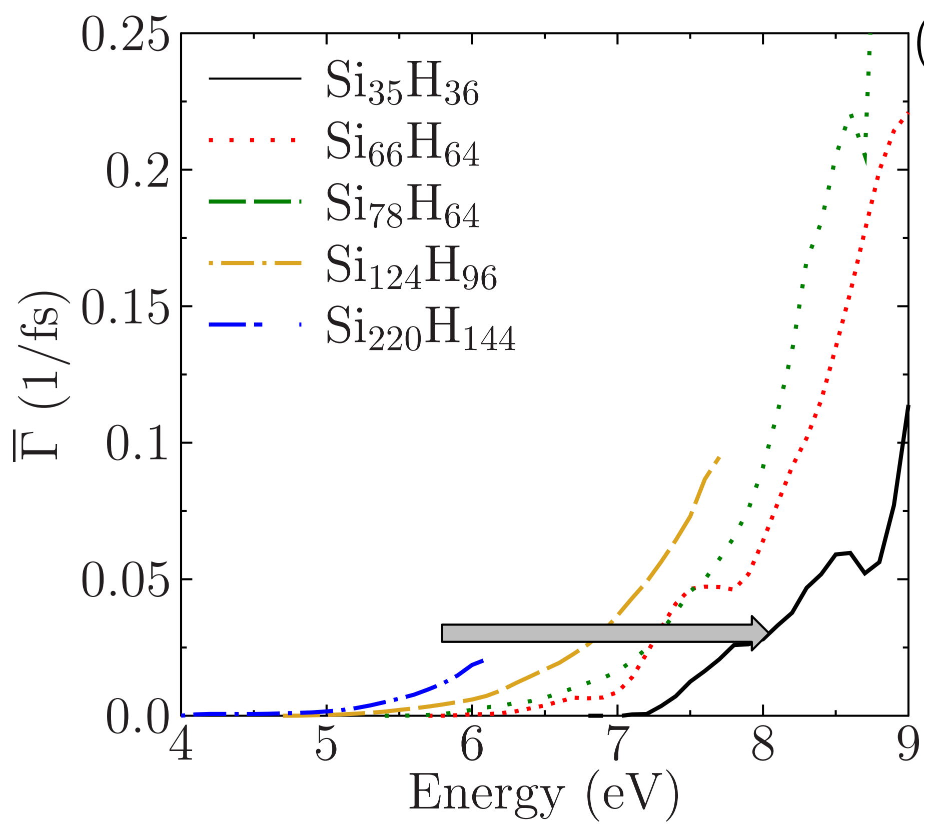
Localizes charges: Hinders transport

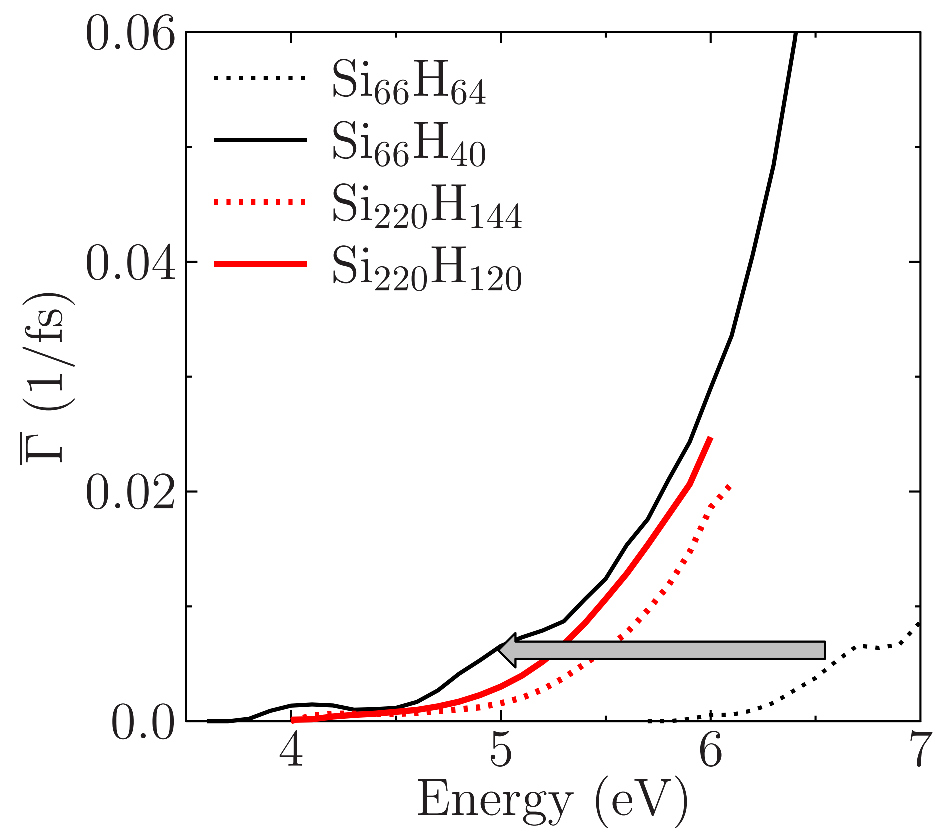






1a. Reconstruction Compensates Gap-Enhancement without Reducing Coulomb Strength/CM



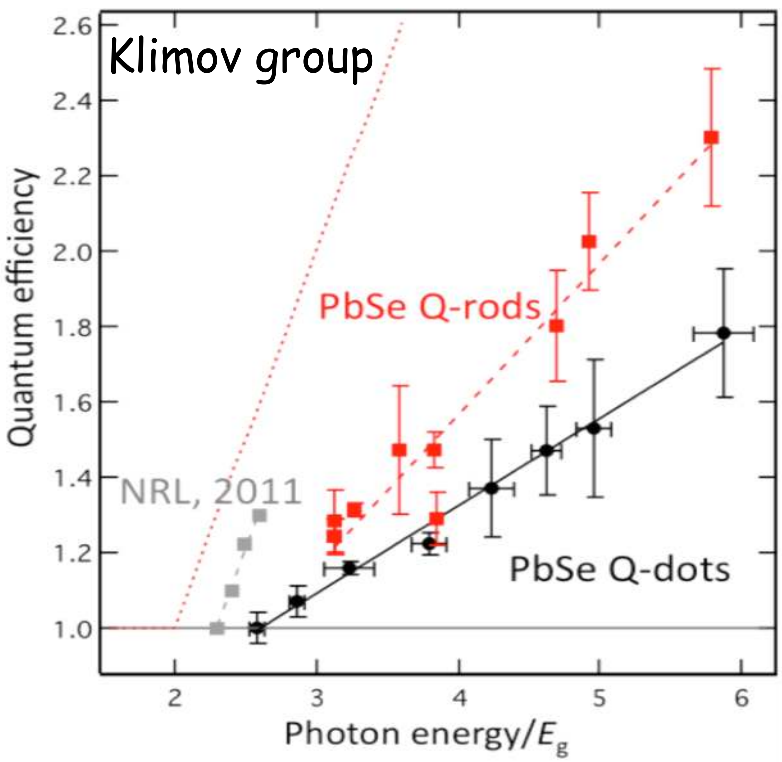


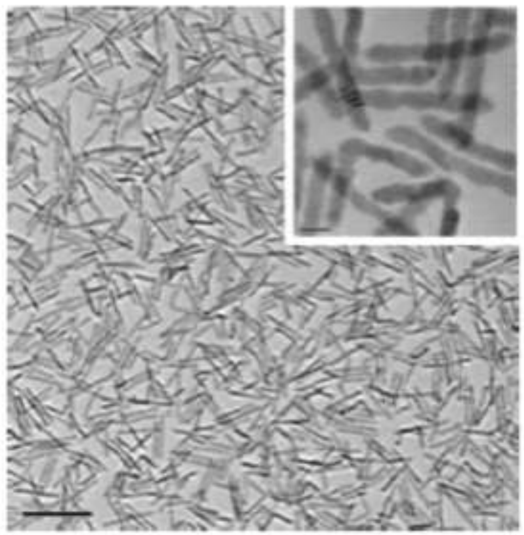
Quantum confinement enhances the gap in unreconstructed NPs

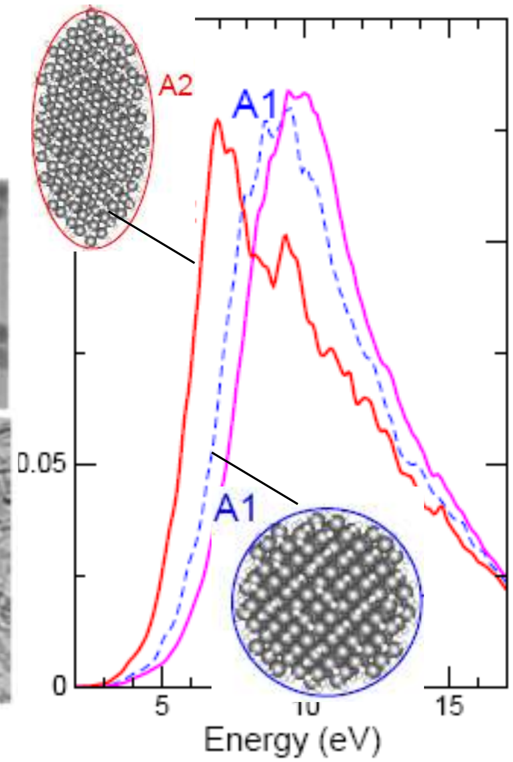
Reconstruction
- compensates gap enhancement
- preserves enhanced Coulomb/CM

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

1b. Lowered Symmetry: Gap Reduction, More Allowed Transitions





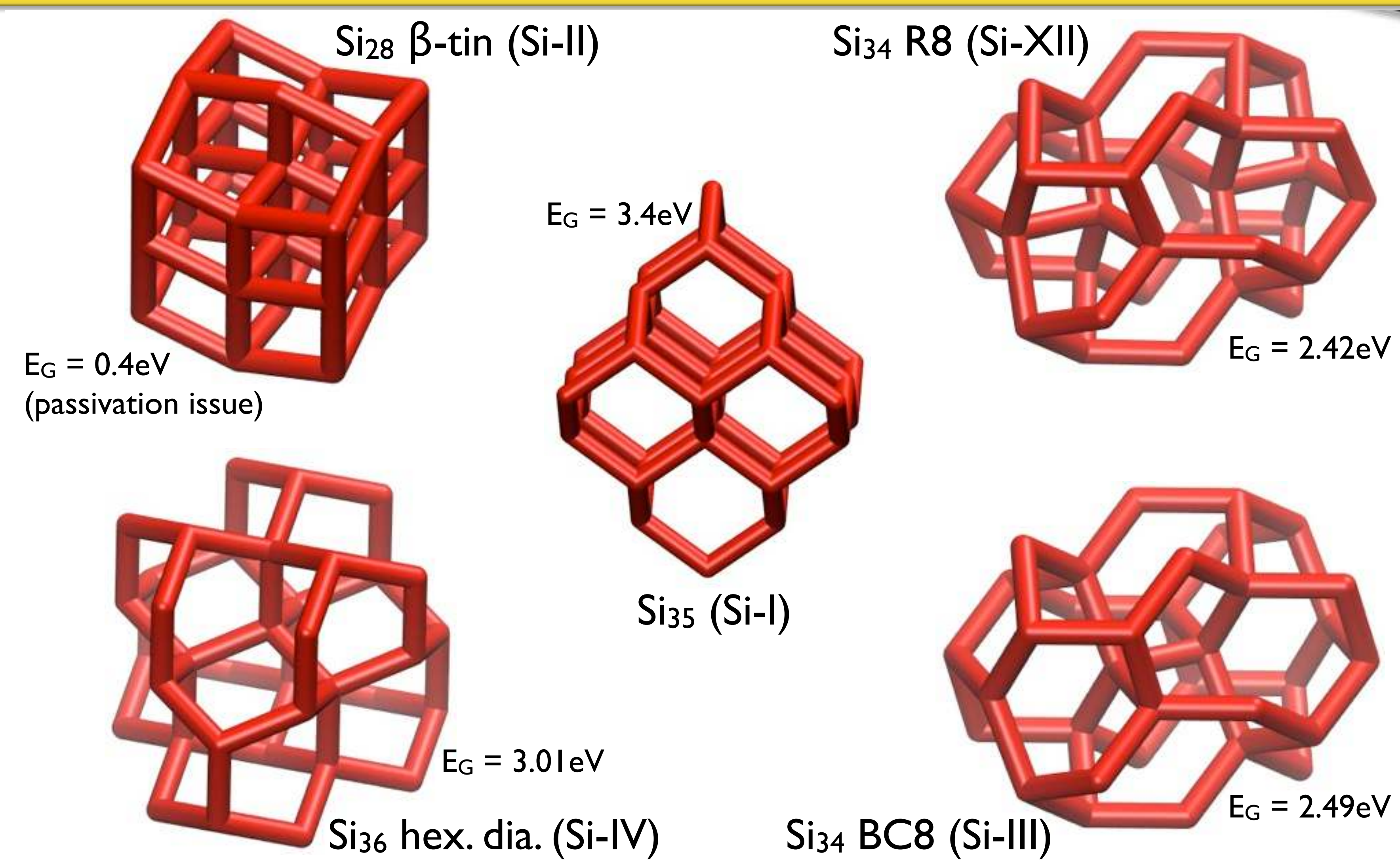


Many transitions forbidden by symmetry-driven selection rules
Lowering symmetry of nanoparticles allows more transitions:

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

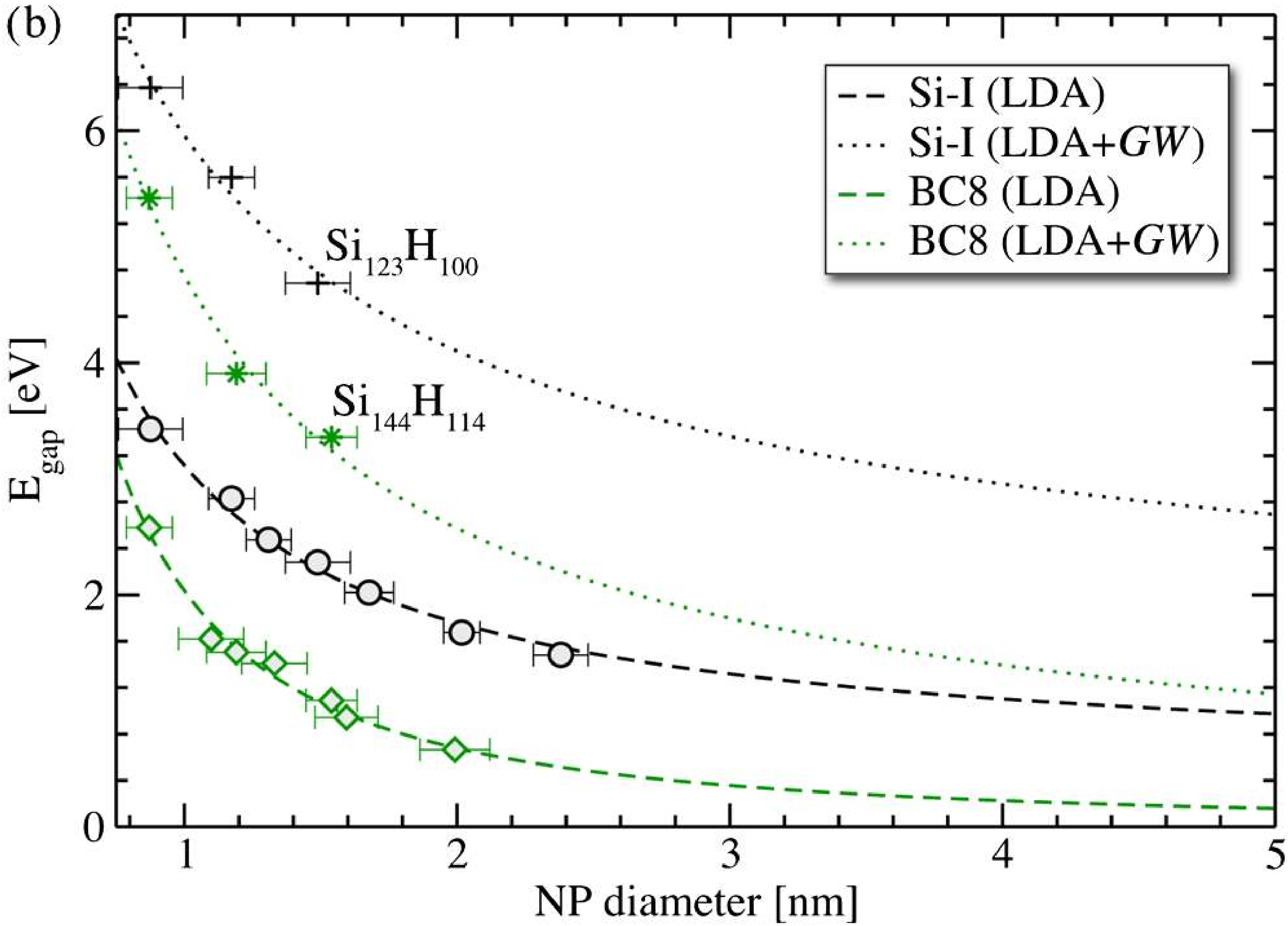
Gali, Kaxiras, Zimanyi, Meng, Phys. Rev. B 2010

1c. Exotic Core Phase Si/Ge NPs: Reduce Gap by using Bulk-Gapless Phases

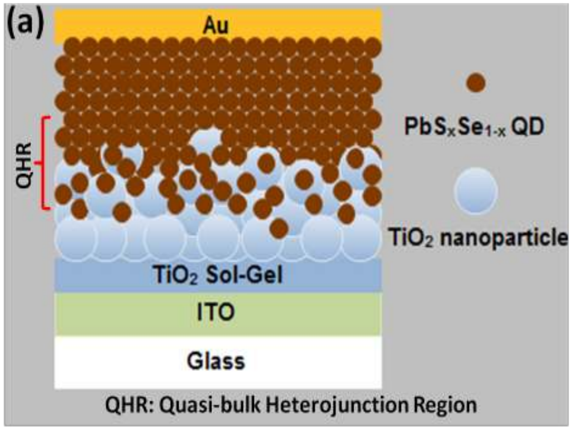


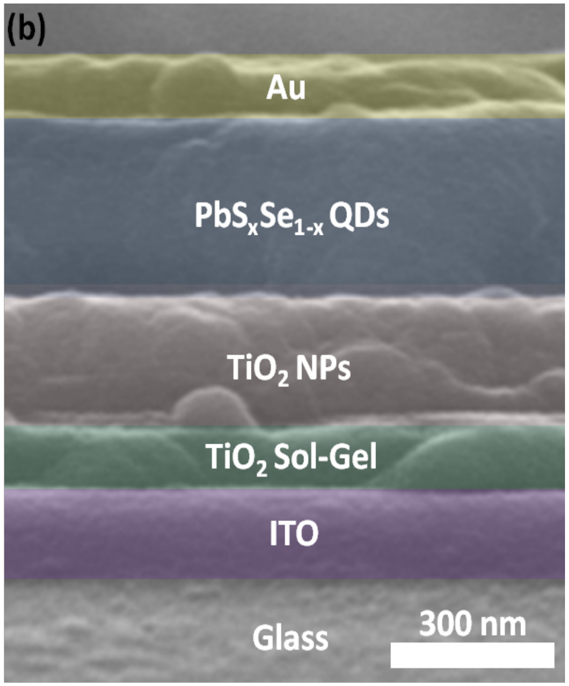
Wippermann, Voros, Gali, Rocca, Zimanyi, Galli Phys. Rev. Lett. **110**, 046804 (2013)

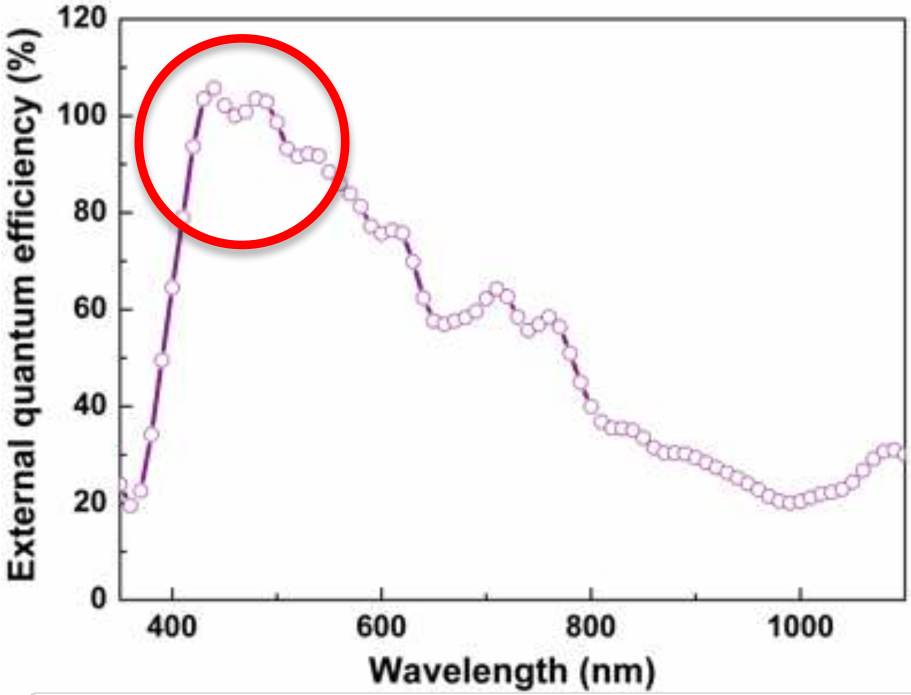
1c. Comparison of LDA and GW



1d. Demonstration of Carrier Multiplication in a Functioning Solar Cell







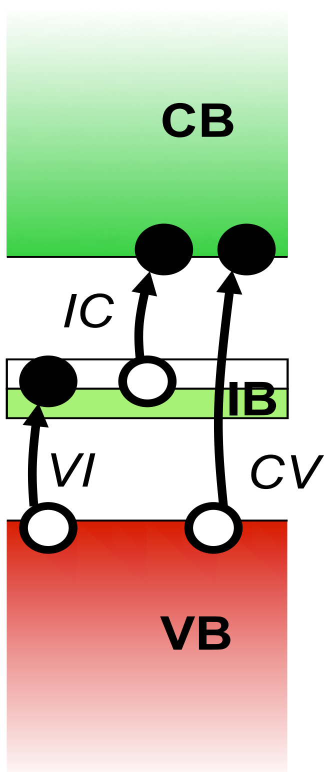
Semonin (2012): CM in working solar cell.
Used hydrazine: combustible

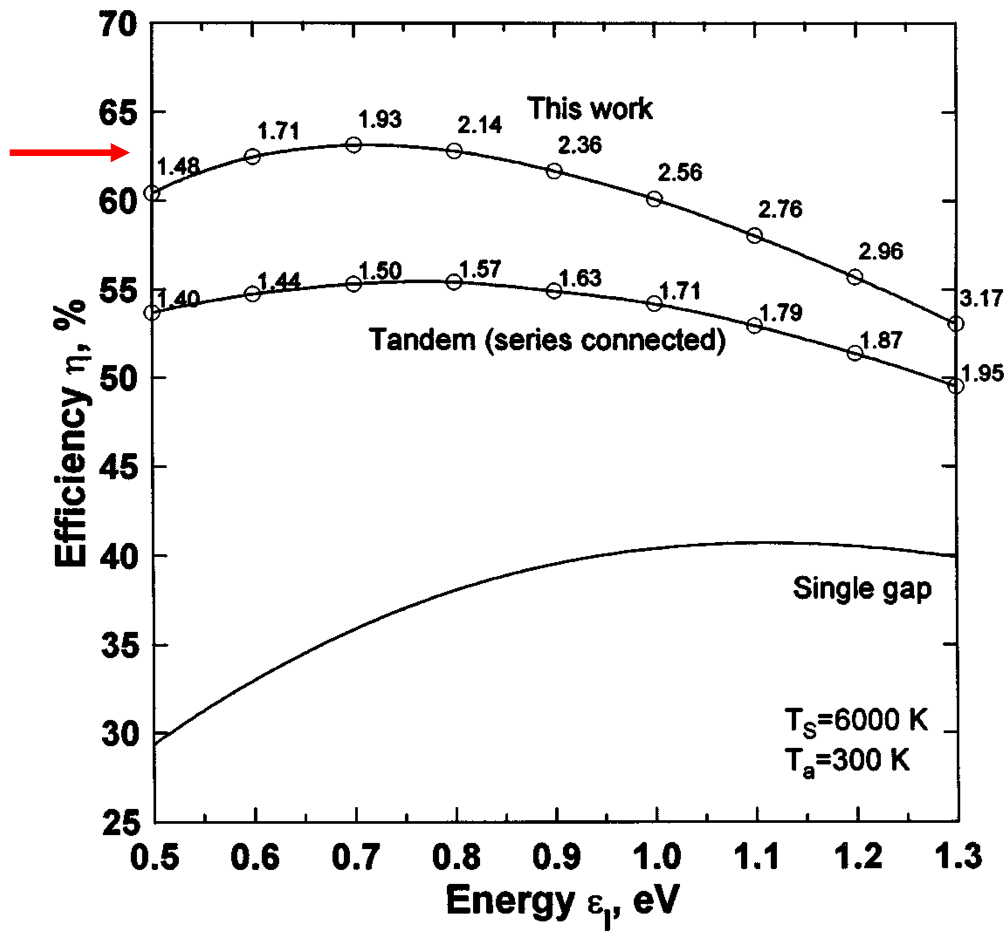
Carter lab: EQE>100% in working solar cell

(a) Optimized cell performance by varying the composition PbS_xSe_{1-x}.
(b) Avoided using hydrazine

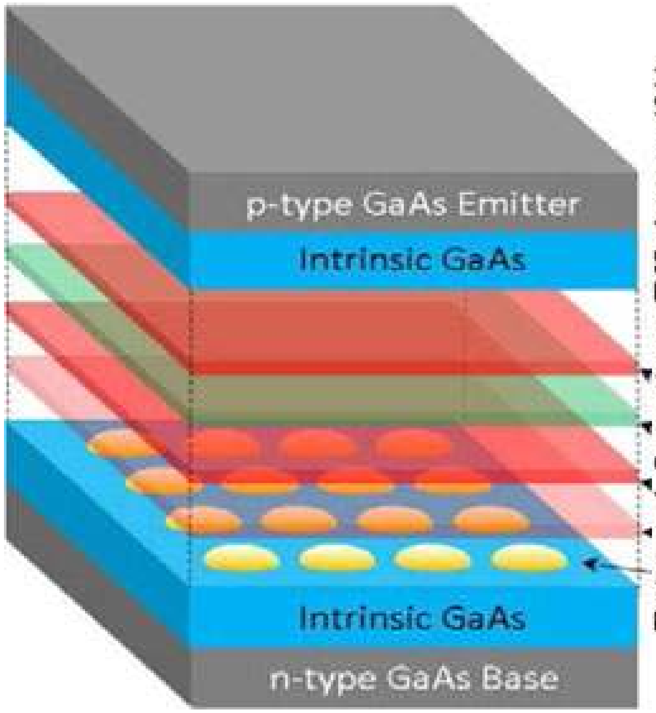
2. Up-conversion with Intermediate Band Solar Cells

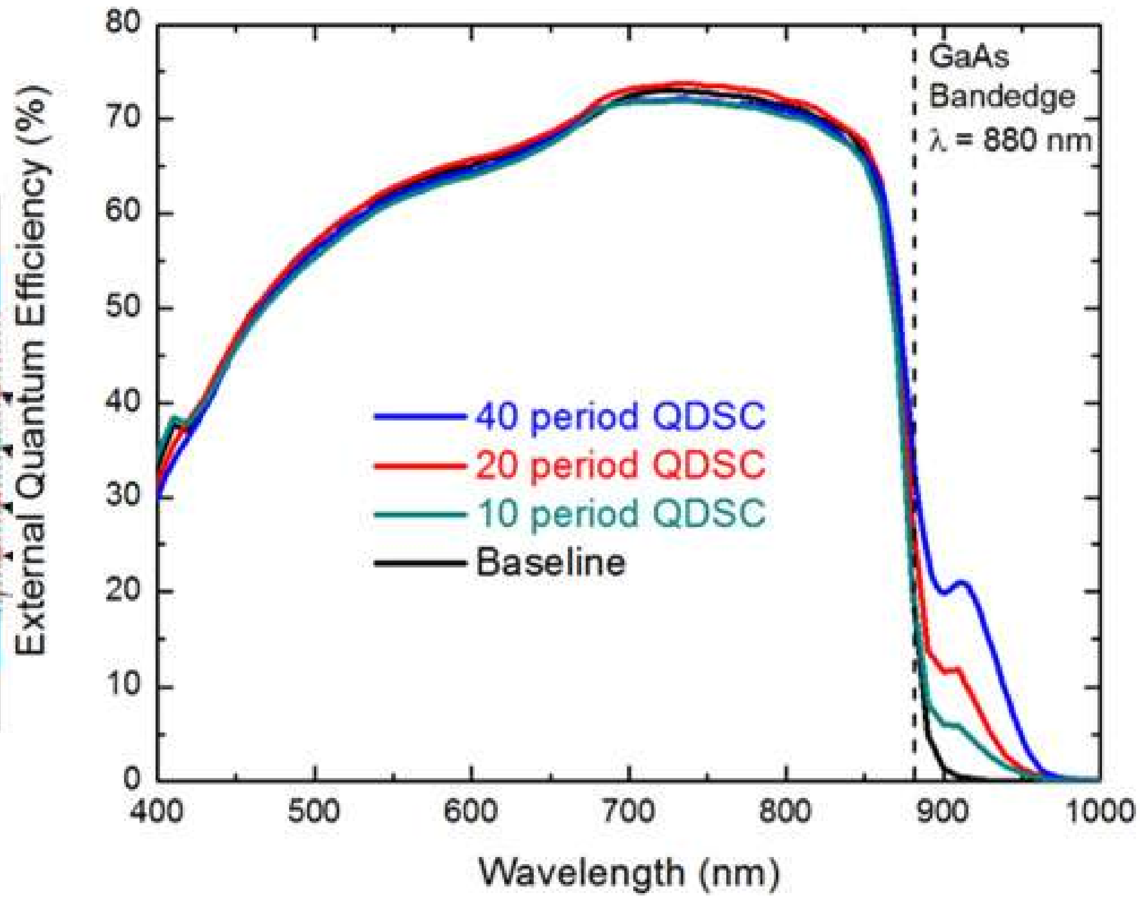
1. Absorb photon with sub-gap energy: electron IB->CB & VB->IB
2. Fill IB by chemical doping or by photo-doping





Intermediate Band PV: Epitaxial Design

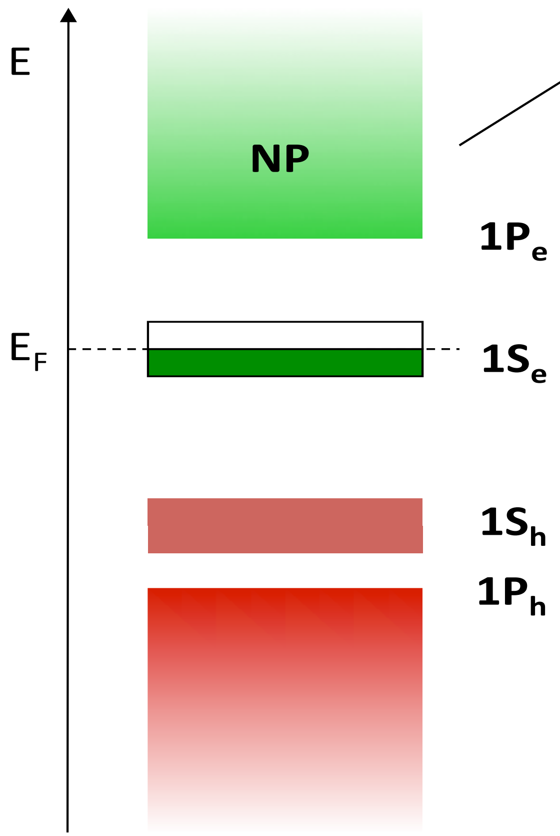




(1) Process steps increase from ~10 to 50-100

(2) Efficiency increase minimal: Great chance for nanoparticles

Intermediate Band PV: Colloidal Nanoparticle Platform



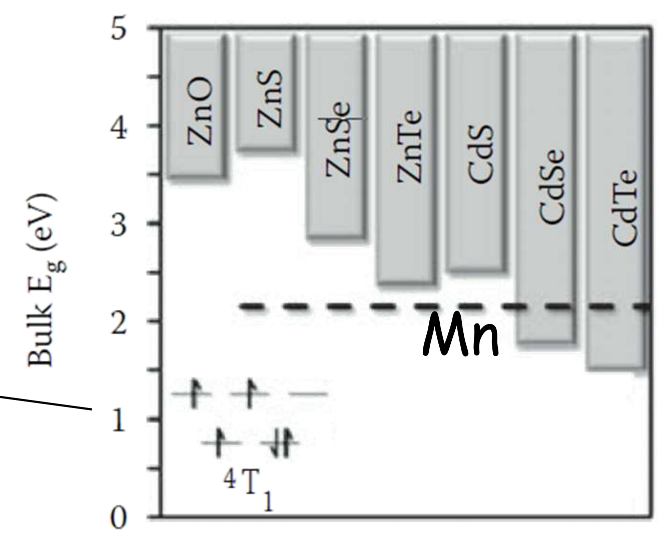
Quantum confinement

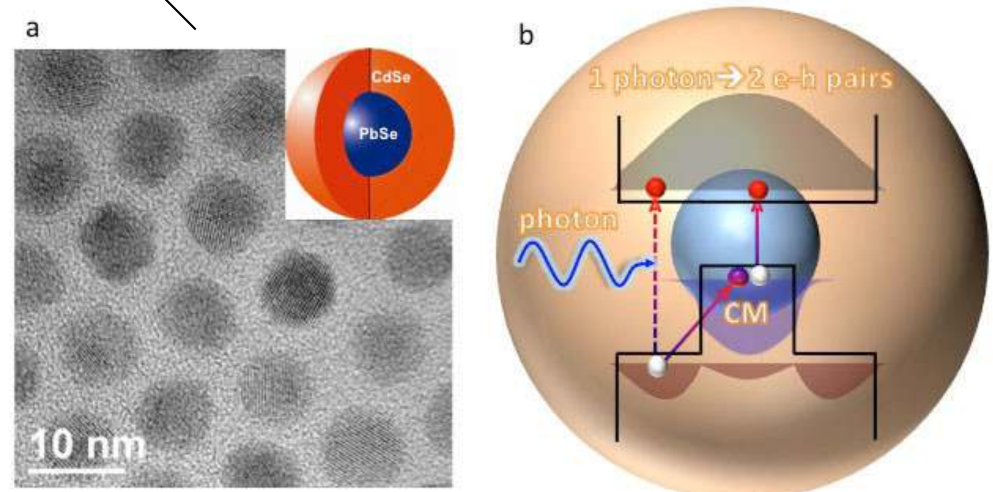
Surface relaxation

Surface doping

Core doping

Core-shell NPs

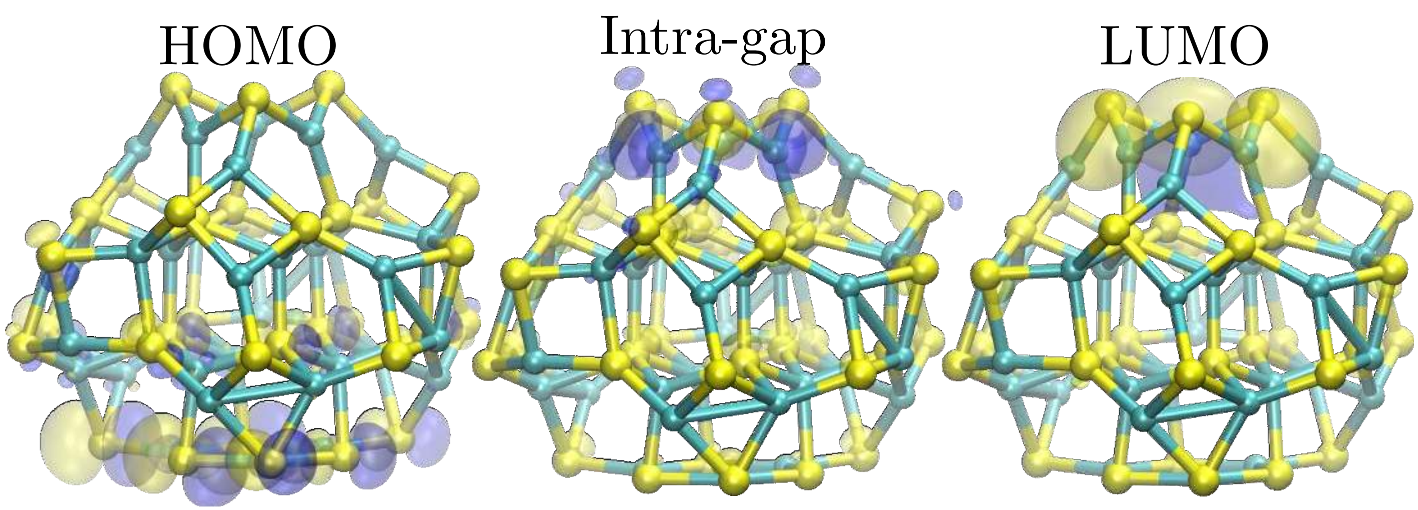




Intermediate Band from surface relaxation

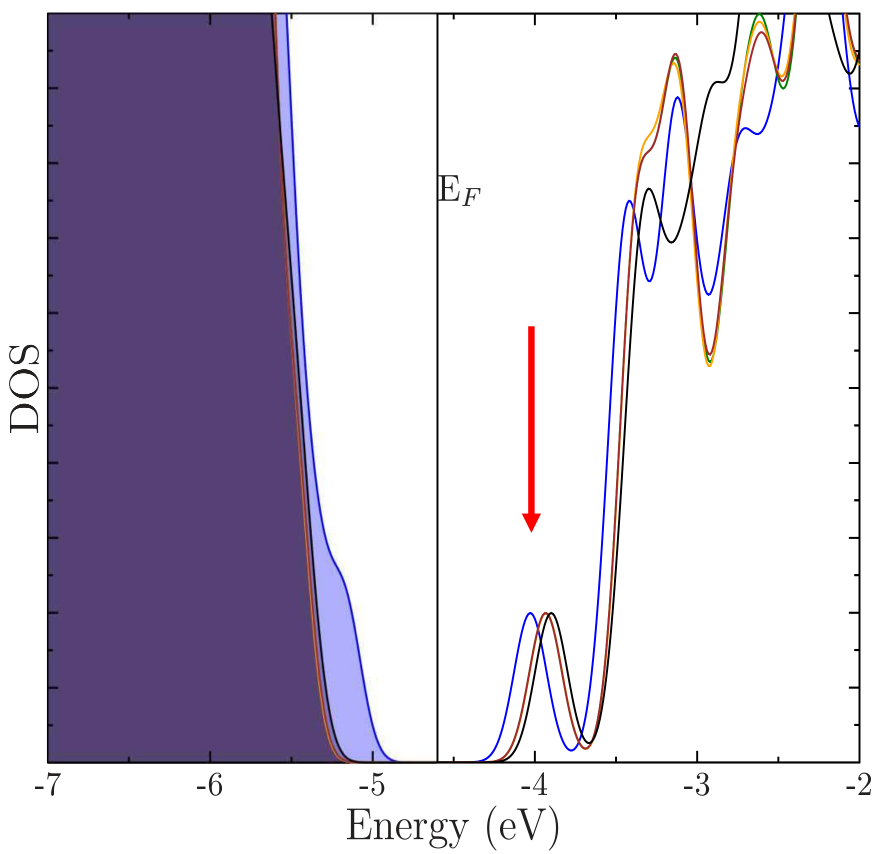
Intermediate band from surface relaxation

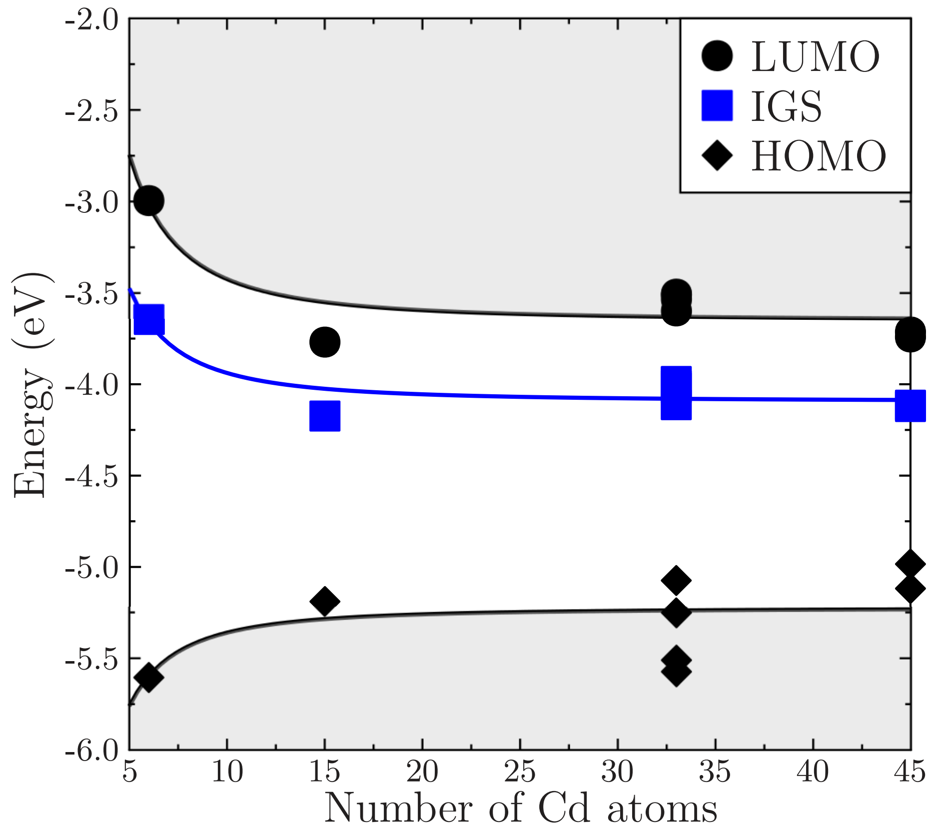
$Cd_{33}Se_{33}$ NP



Intra-gap State from NP Surface Relaxation

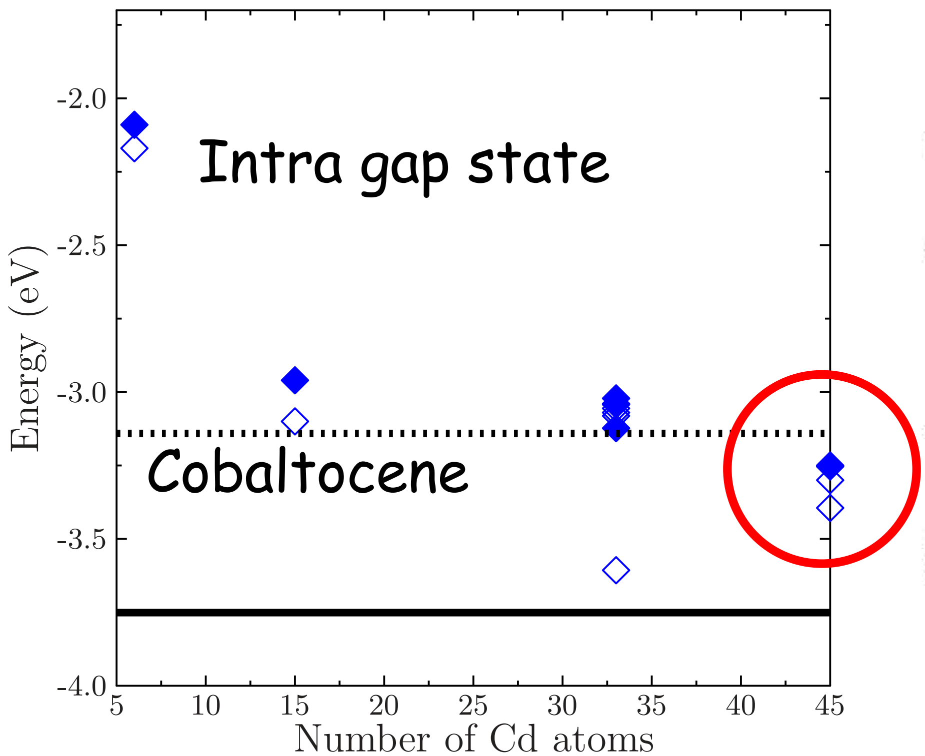
$Cd_{33}Se_{33}$ NP: An intra-gap state is formed by NP relaxation



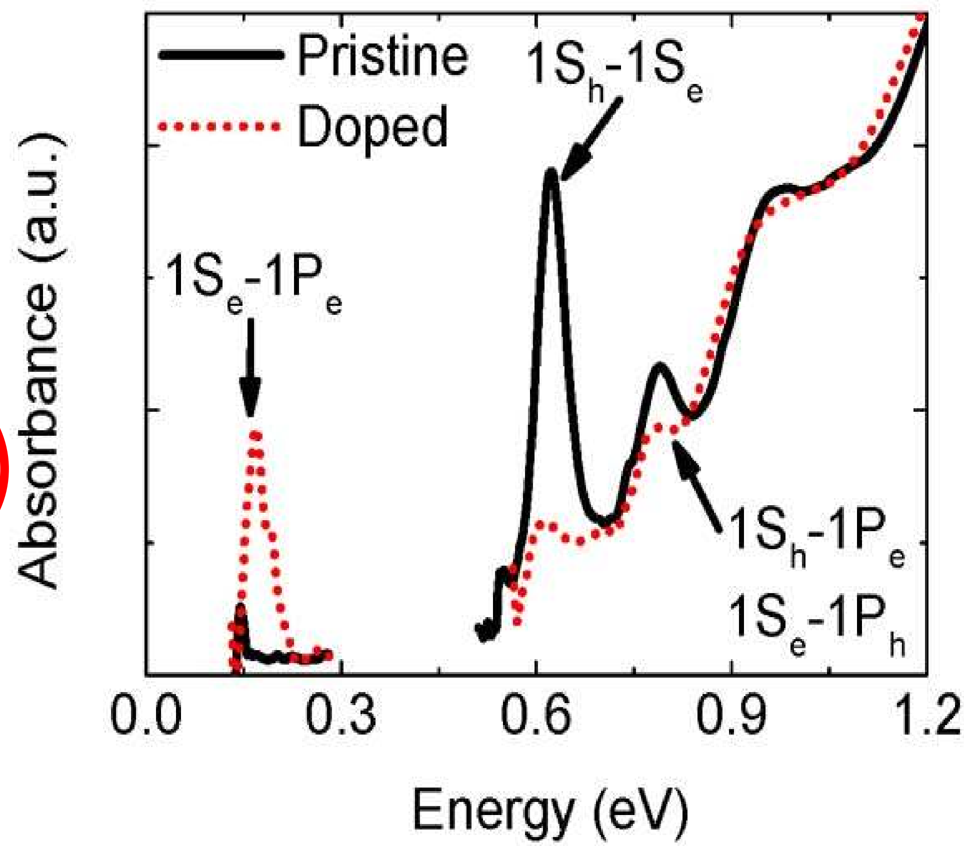


Intra-gap State Filling by Chemical Doping

Intra-gap state filled by cobaltocene doping



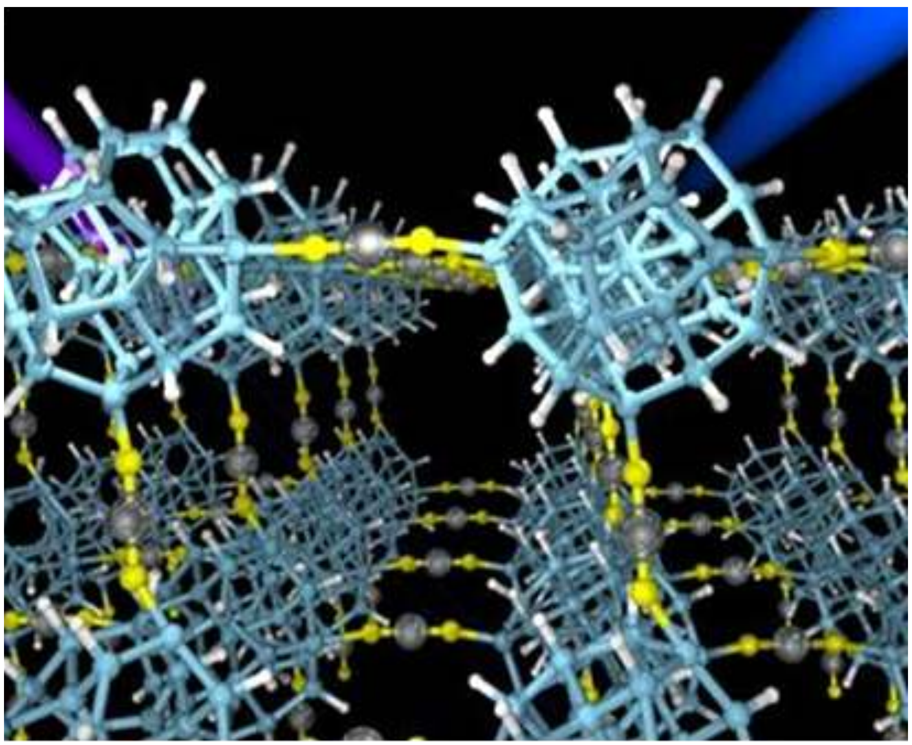
Voros, Galli, GTZ 2014

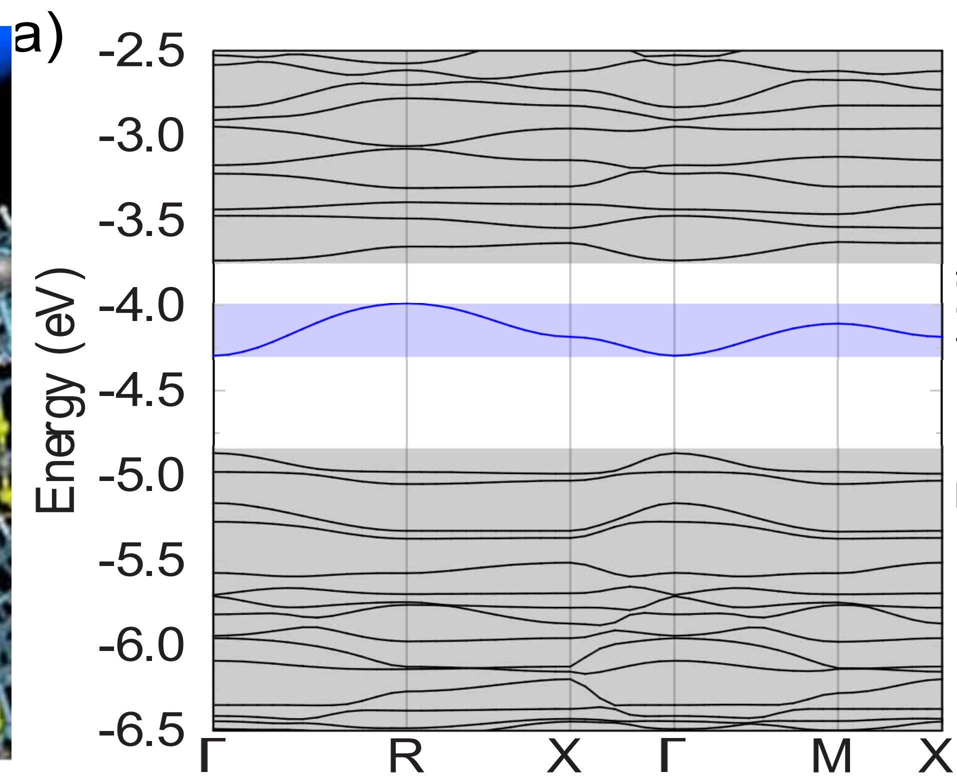


Klimov 2014

Intermediate Band Formed in NP Array

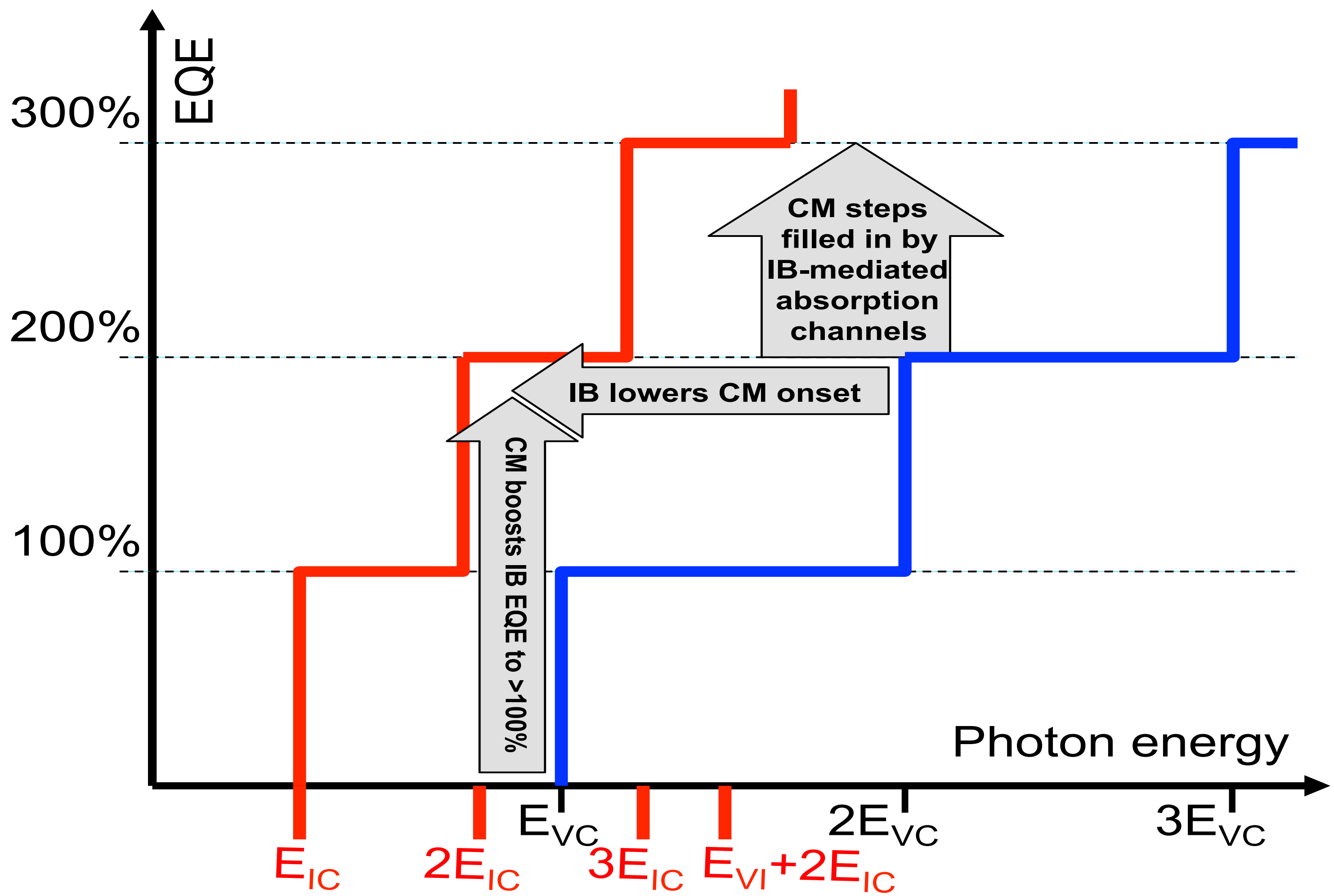
Intra-Gap states combine into Intermediate Band in Simple Cubic nanoparticle array: **Proof of concept**





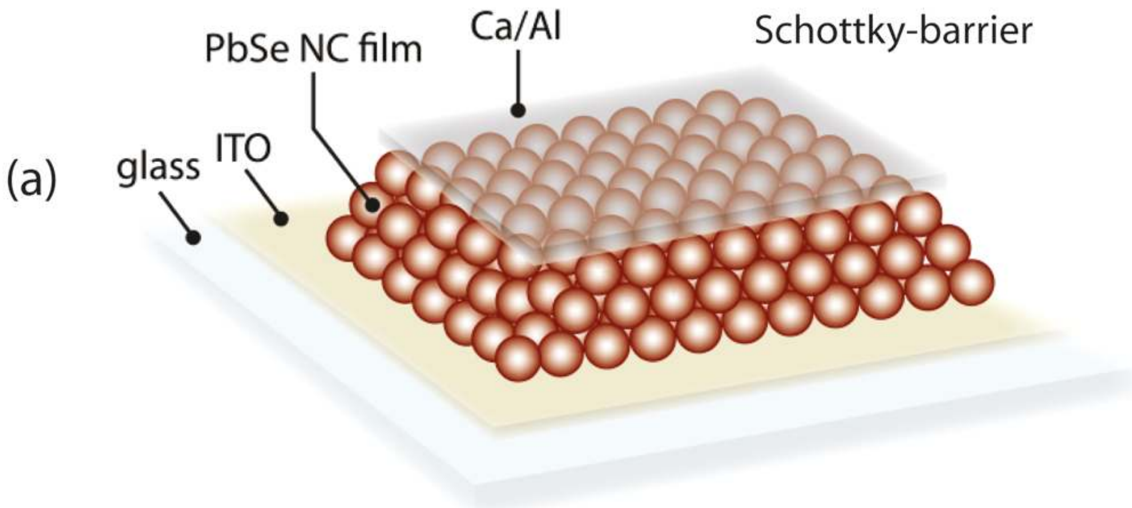
Voros, Galli, GTZ ACS Nano 9, 6882 (2015)

Synergy between Intermediate Band absorption and Carrier Multiplication channels

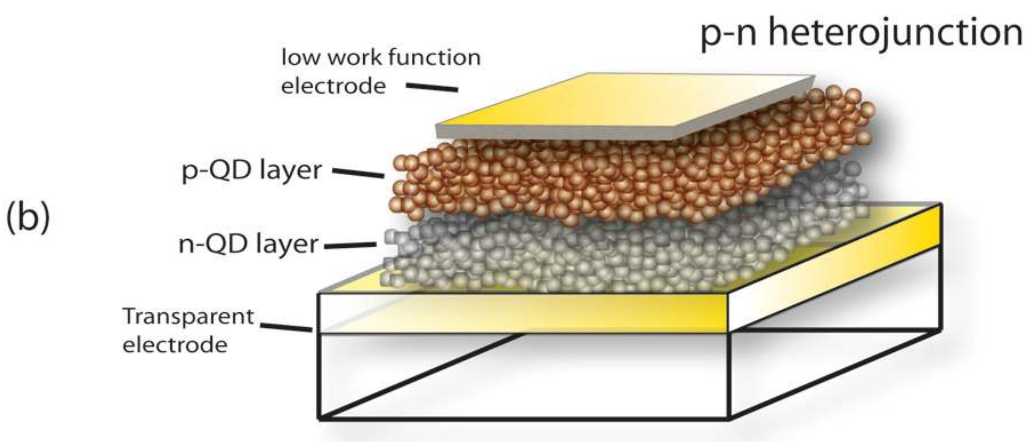


Theoretical maximum: 55% at one-sun, 72% at full concentration

3. Transport bosted in Nanoparticle Solar Cells

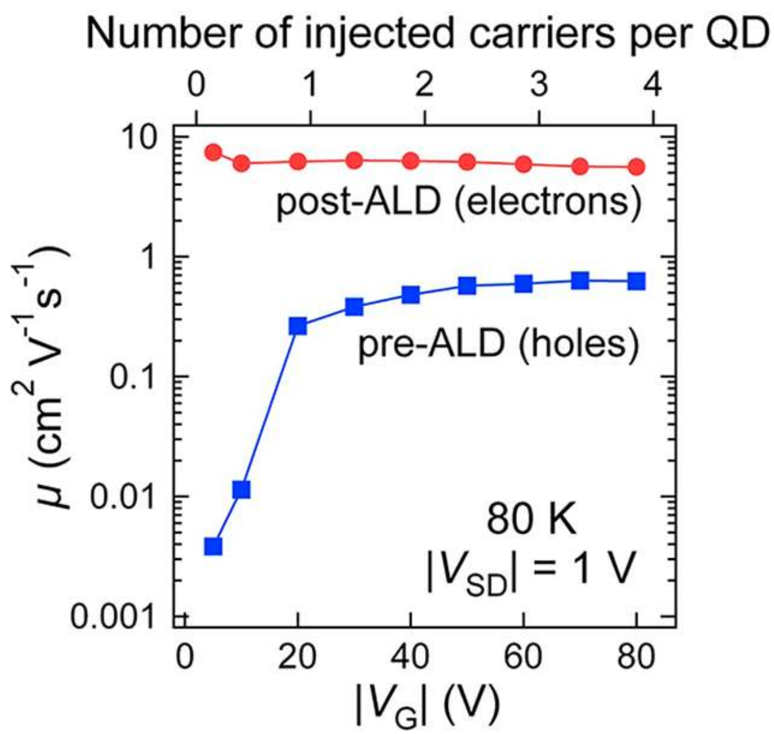


Built-in field generated by difference of electrode work functions



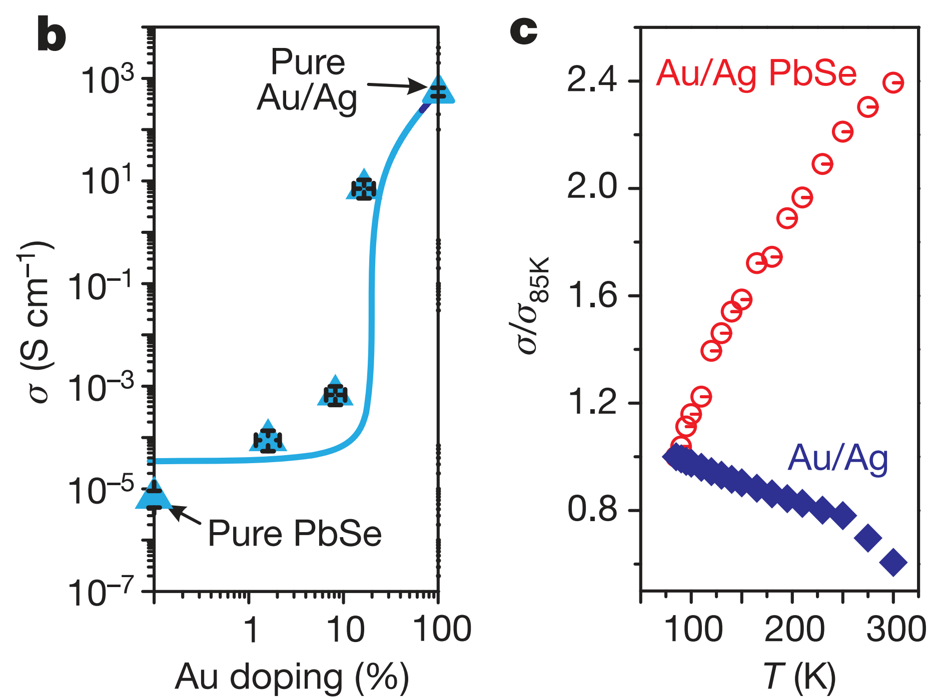
Built-in field generated by forming p- and n-doped nanoparticle layers

Transport boosted through Metal-Insulator-Transition in CNP solids



PbSe NP film - Atomic Layer Deposition:
Mobility exhibits MIT

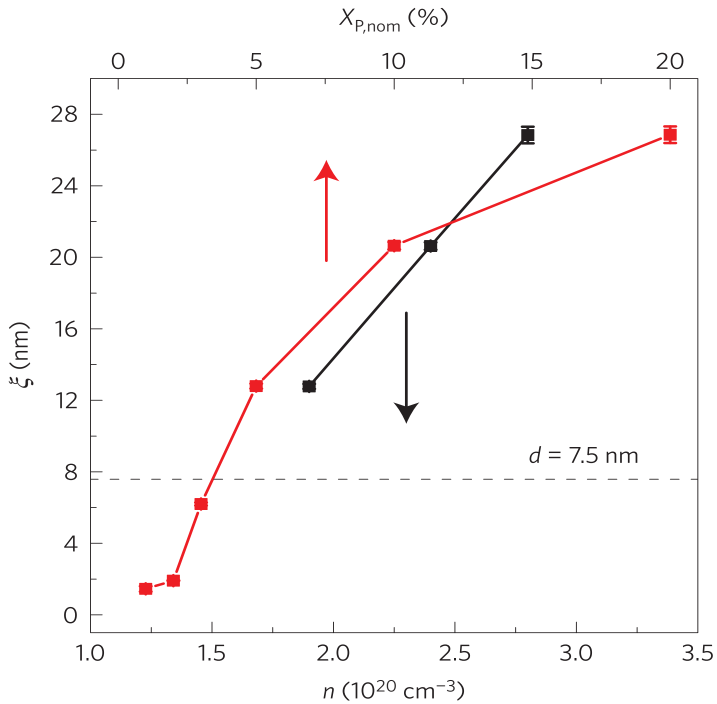
Law group
Nature, **524**, 450 (2015)

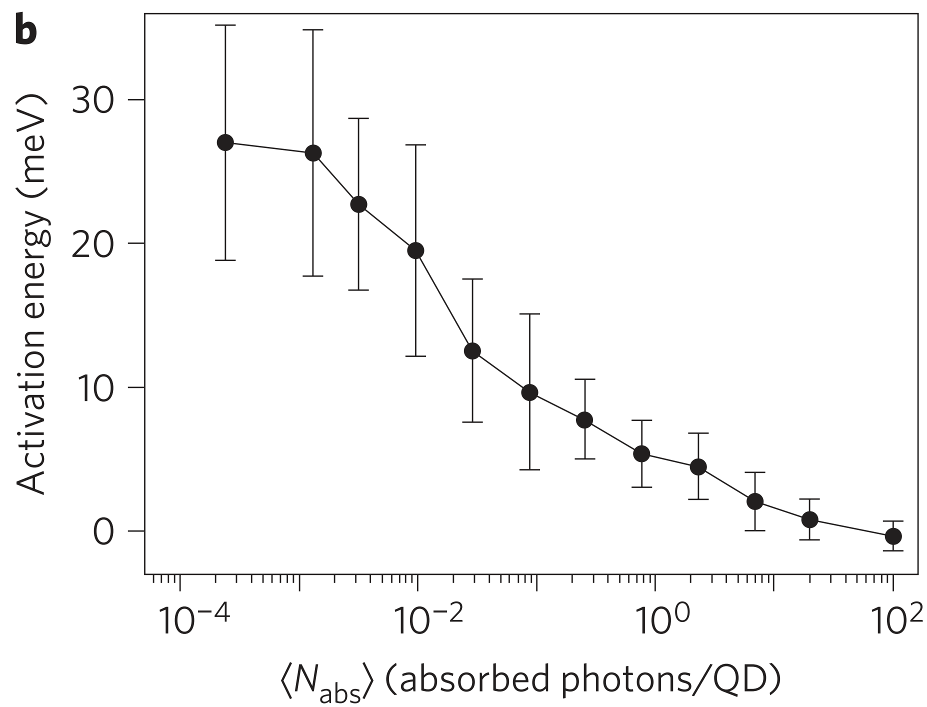


PbSe NP film - Au/Ag CNPs substitution:
Mobility exhibits MIT

Kagan, Murray group
Nature, **524**, 450 (2015)

Metal-Insulator-Transition in CNP solids





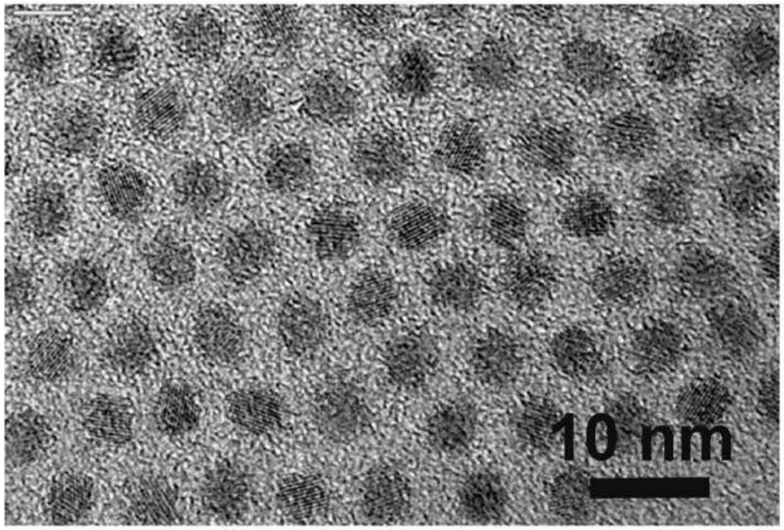
P doping of Si NPs: Localization length exceeds CNP diameter

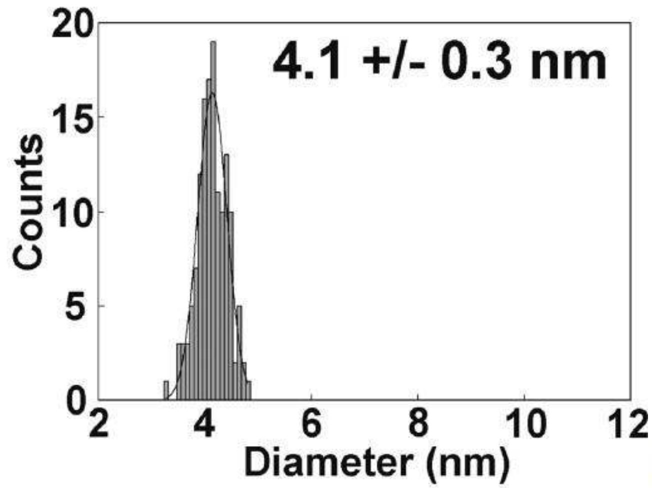
Kortshagen, Shklovski
Nature Materials, **11**, 299 (2015)

Photo-doping of PbSe CNPs: Activation energy goes to zero

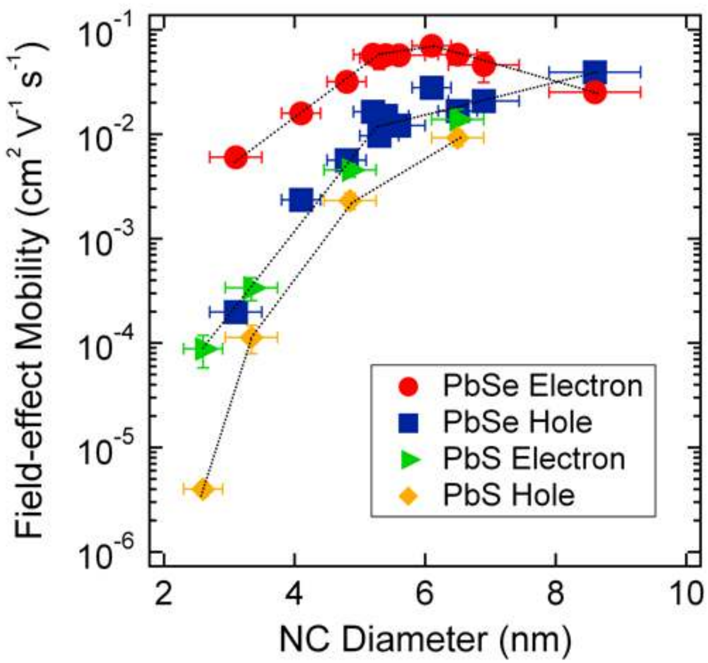
Van der Zant, Siebbeles group
Nature Nanotech, **6**, 733 (2011)

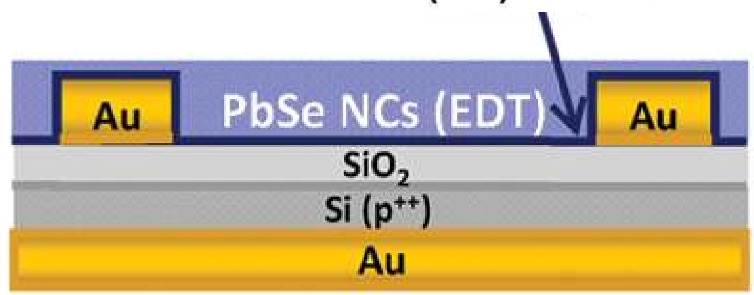
FET mobility in PbS and PbSe Nanoparticle films





M. Law (2010)





Mobility(diameter D): rise->maximum

Mobility μ~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

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

↓ ↓

Kinetic Monte Carlo of device transport

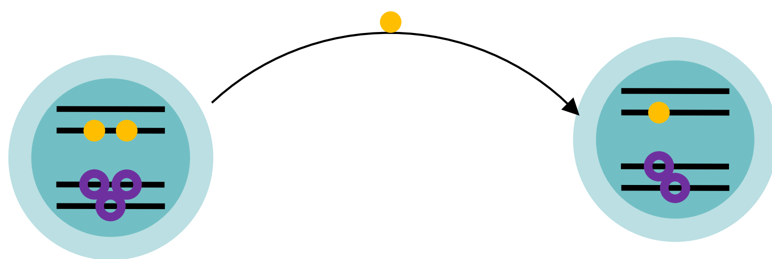
Current-current correlation and response function

I. Carbone, S. Carter and GTZ J. Appl. Phys. 114, 193709 (2013)
M. Voros, G. Galli and GTZ ACS Nano (2015)

3a. Towards ab initio-based transport modeling: nanoparticle energetics

Input to transport: energy differences from ab initio

n_a before
n_a-1 after



n_b before
n_b+1 after

$$\Delta E_{ab} = \Delta E_{ab}^{kin} + \Delta E_{ab}^{C} + \Delta E_{ab}^{V}$$

Confined kinetic energy (~1/R²)

$$\Delta E_{ab}^{kin} = E_b^{kin} - E_a^{kin}$$

Long range Coulomb interaction (~1/d)

Coulomb

$$\Delta E_{ab}^{C} = \Sigma_b + n_b E_b^{e-e} - (\Sigma_a + (n_a - 1) E_a^{e-e}) + \frac{1}{2} V_{ab}$$

External field

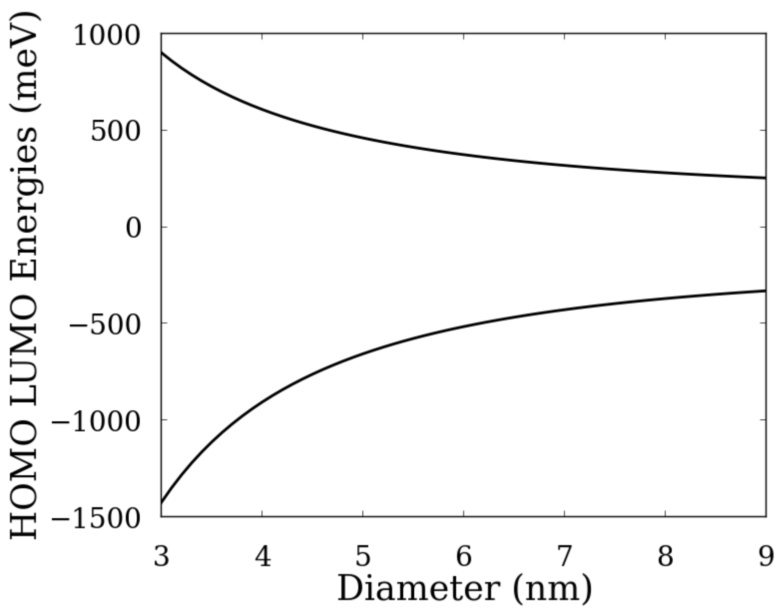
$$\Delta E_{ab}^{V} = q \frac{V}{L_z} (z_b - z_a)$$

On-site Coulomb (~1/R)

Towards ab initio nanoparticle energetics

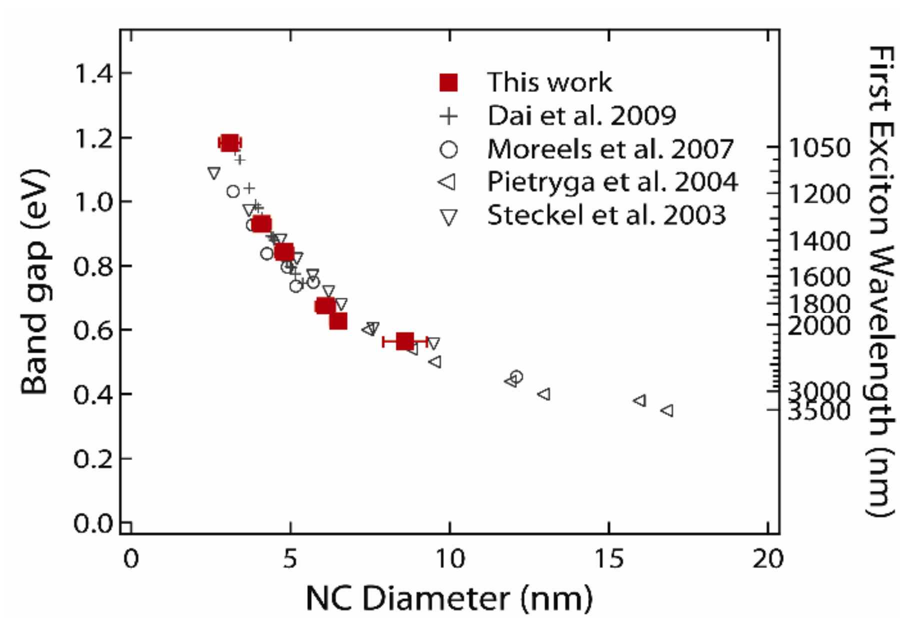
Kinetic energy E^{kin}
Sophisticated k.p calculation

Kang and Wise J. Opt. Soc. Am. B, 14, 1632 (1997)



Validate by comparison to experiment

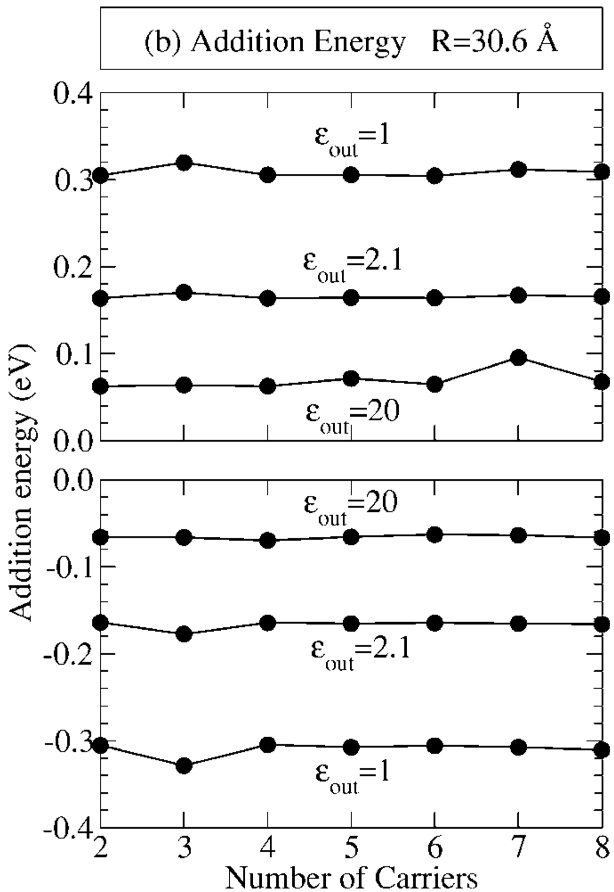
Law group Nano Letters 10, 960 (2010)



Towards ab initio nanoparticle energetics

On site charging energy E^C
Configuration
Interaction

An, Franceschetti, Zunger,
PRB 76, 045401 (2007)

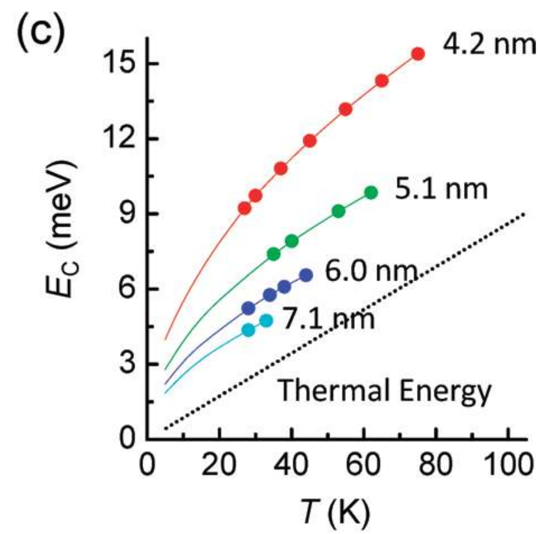


Substantial screening of charging energy E^C in NP layers

D. Norris Nano Letters 11, 3887 (2011)

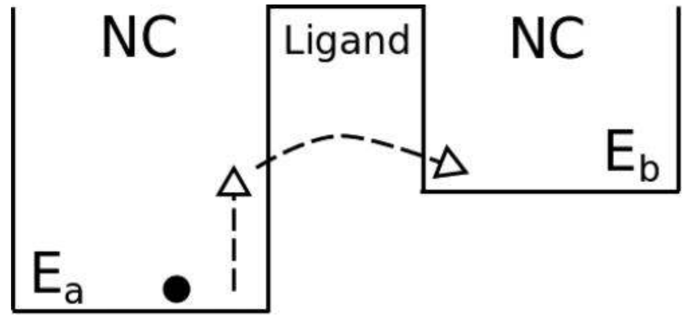
Table 1.

D (nm)	E_C (meV)
3.8	19.0
3.9	18.0
4.2	**15.2**
5.1	**9.7**
5.1	9.7
6.0	**6.7**
6.0	6.7
6.8	5.1
7.1	**4.8**
7.3	4.5
8.4	3.3



Dynamics: 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

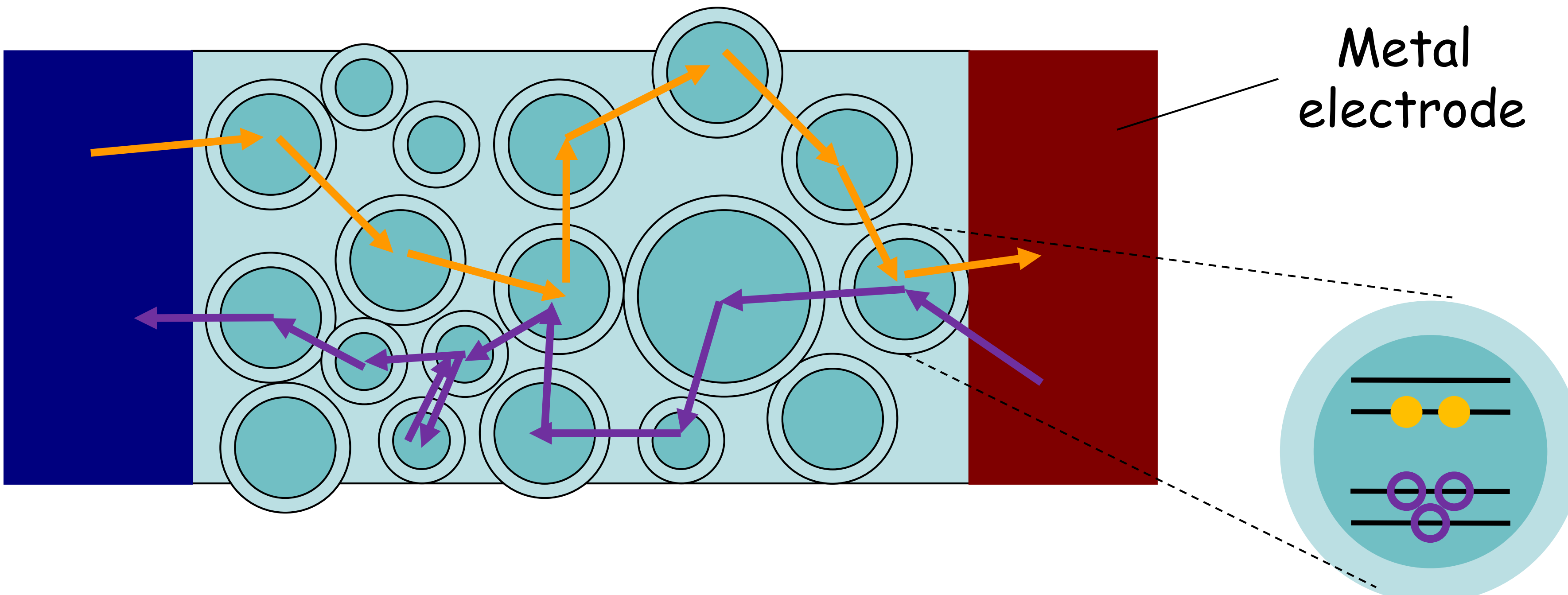
$$\Gamma_{a\to b} = \frac{2\pi}{\hbar}|H_{ab}|^2 \frac{1}{\sqrt{4\pi\lambda_{ab}kT}} \exp - \frac{(\lambda_{ab} + E_b - E_a)^2}{4\lambda_{ab}kT}$$

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

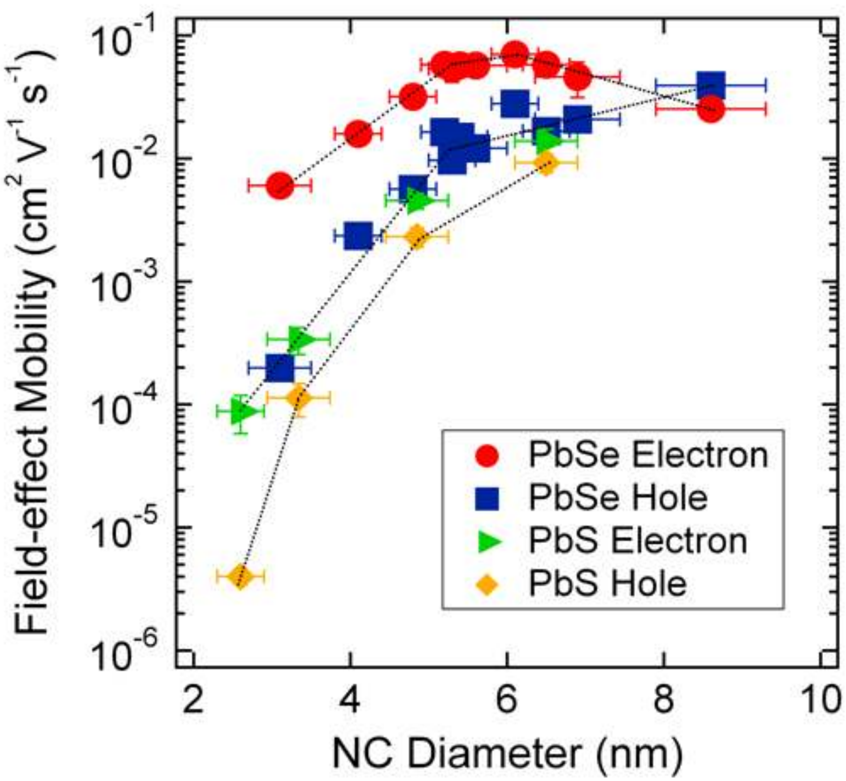
λ: reorganization energy
H: "electronic coupling"

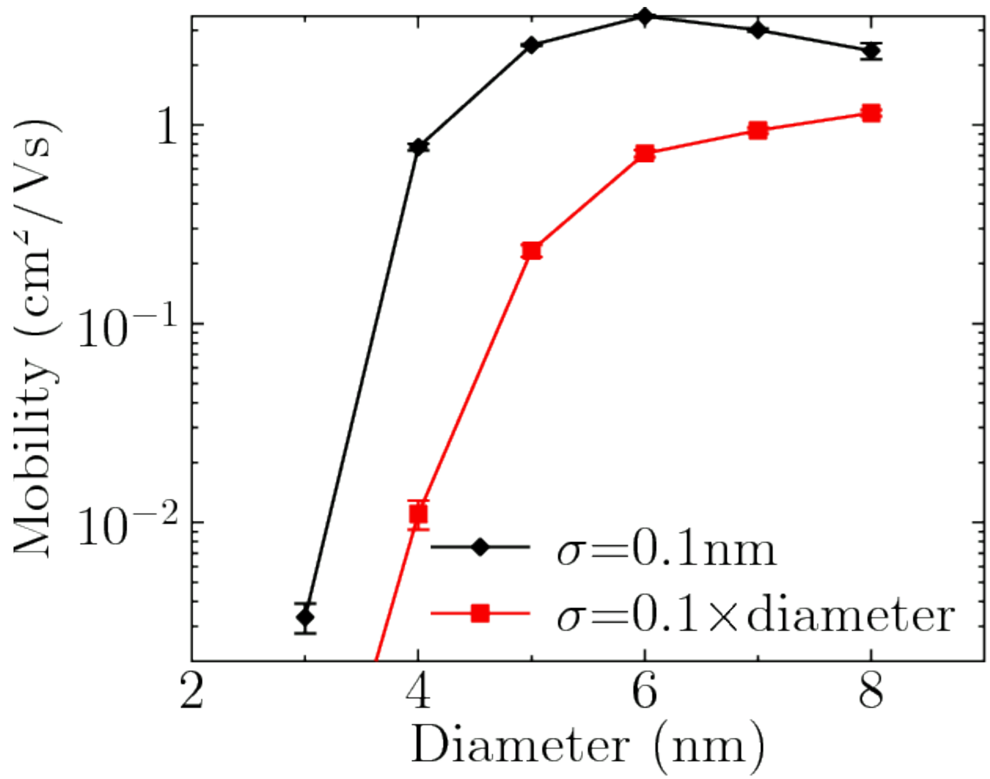
Transport simulation: Kinetic Monte Carlo

BKL, Gillespie, N-fold way, Residence time method:
J. of Comp. Phys. 17, 10 (1975)



Diameter dependence of mobility



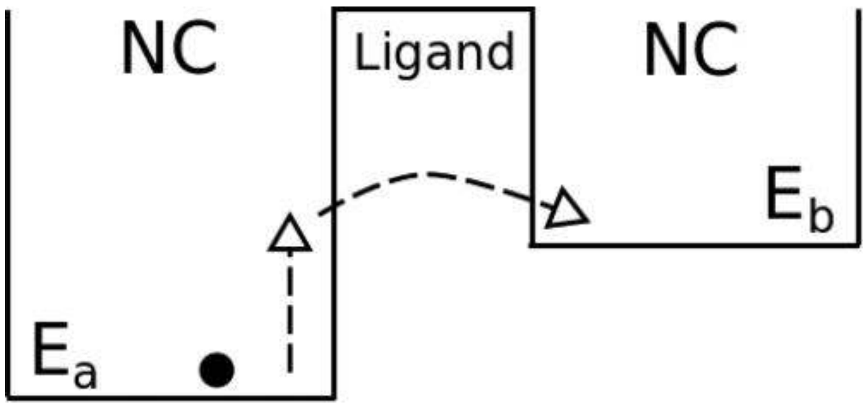


M. Law group
Nano Letters, 10, 1960 (2010)

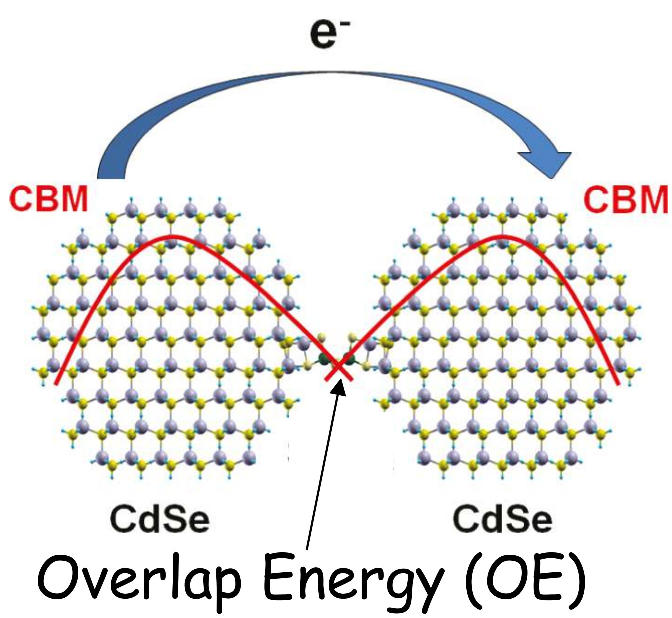
I. Carbone, S. Carter and GTZ
J. Appl. Phys. 114, 193709 (2013)

Compelling evidence for veracity of code

Approaching the Metal-Insulator Transition from the Hopping regime: "Overlap Energy"



$(E_b\text{-}E_a) > $ Overlap Energy (OE):
Thermally activated hopping transition

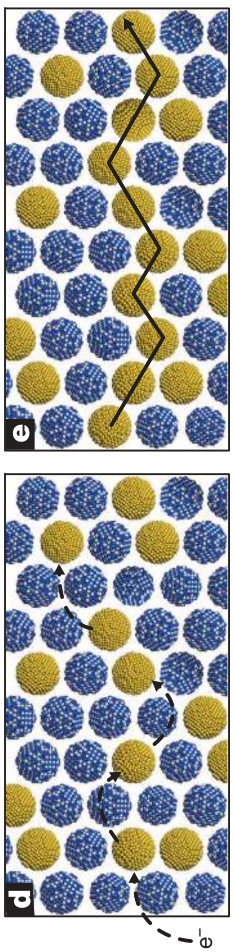


$(E_b\text{-}E_a) < $ Overlap Energy (OE):
Metallic, non-activated quantum transition

Metal-Insulator-Transition: Nanoparticles with metallic couplings percolate

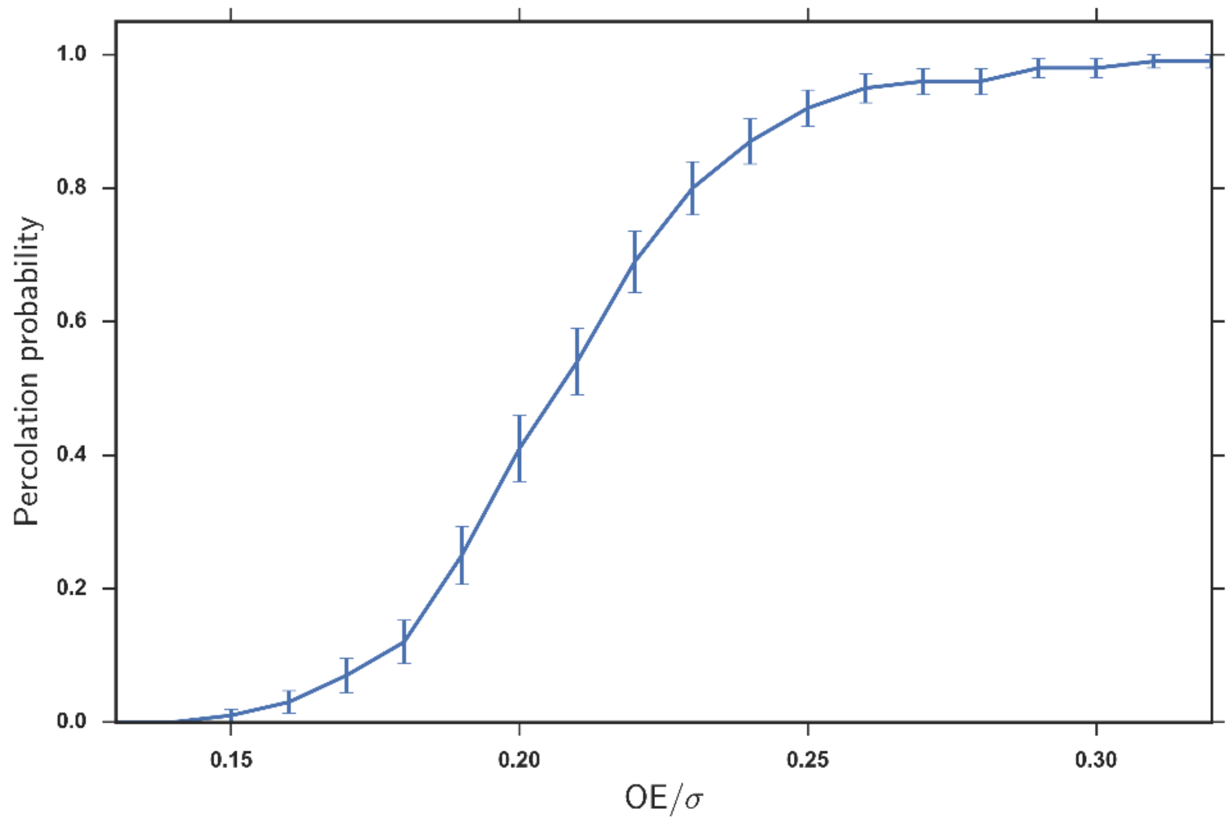
PbSe NP film: Au/Ag CNPs substituted

Kagan, Murray group
Nature, **524**, 450 (2015)

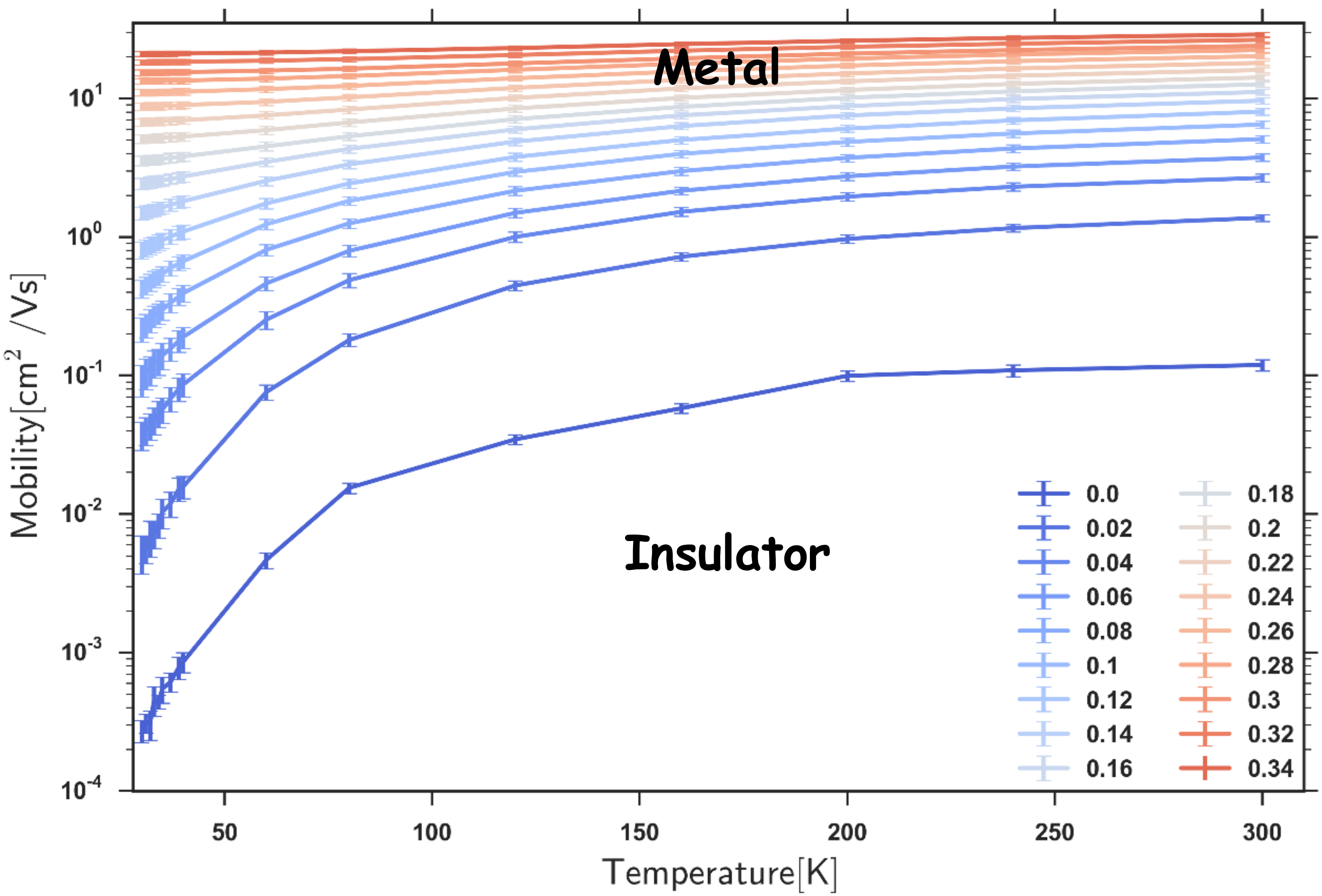


CNPs connected by metallic transitions percolate

Percolation probability as the function of OE/σ

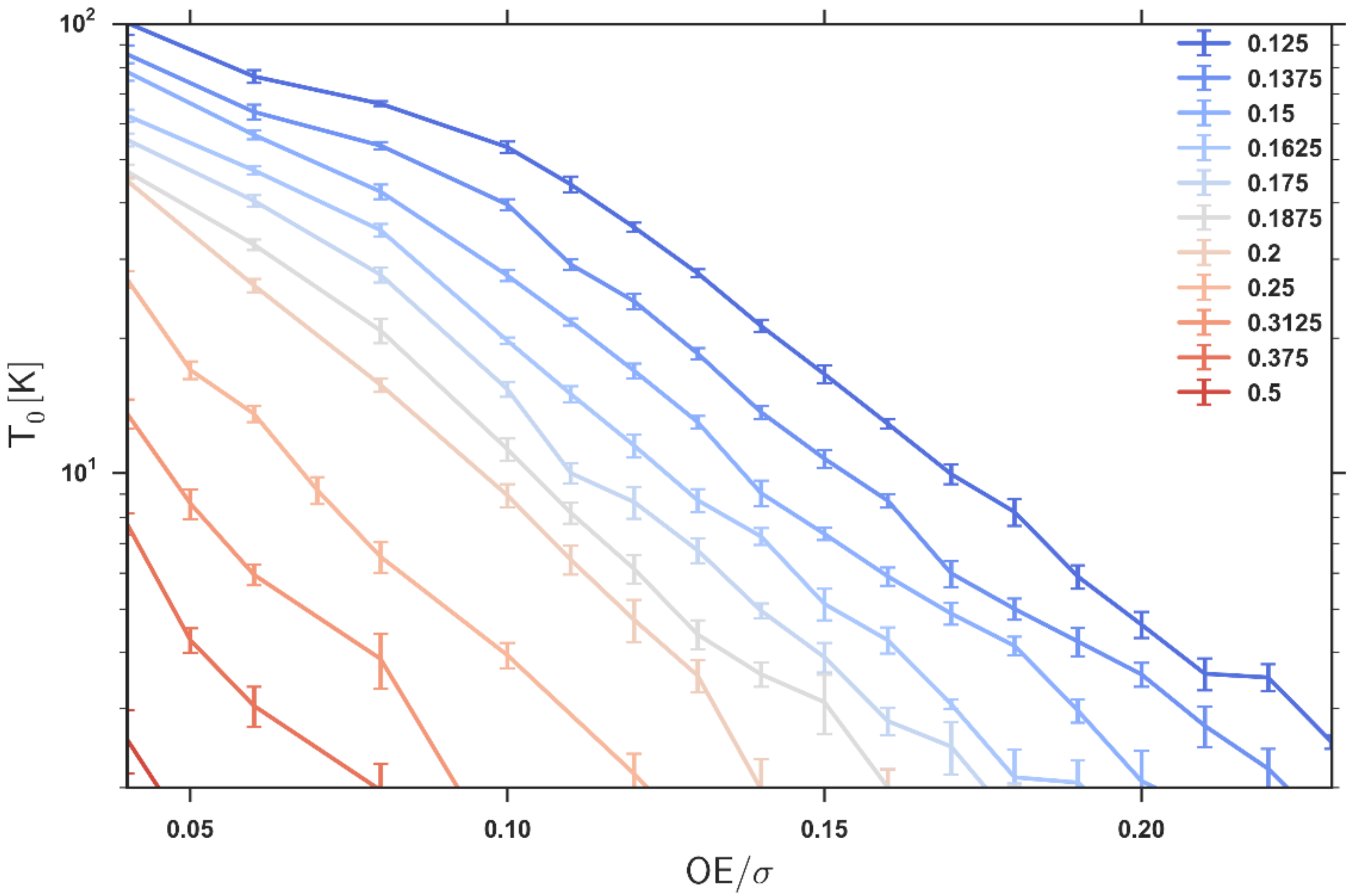


Mobility exhibits Metal-insulator Transition

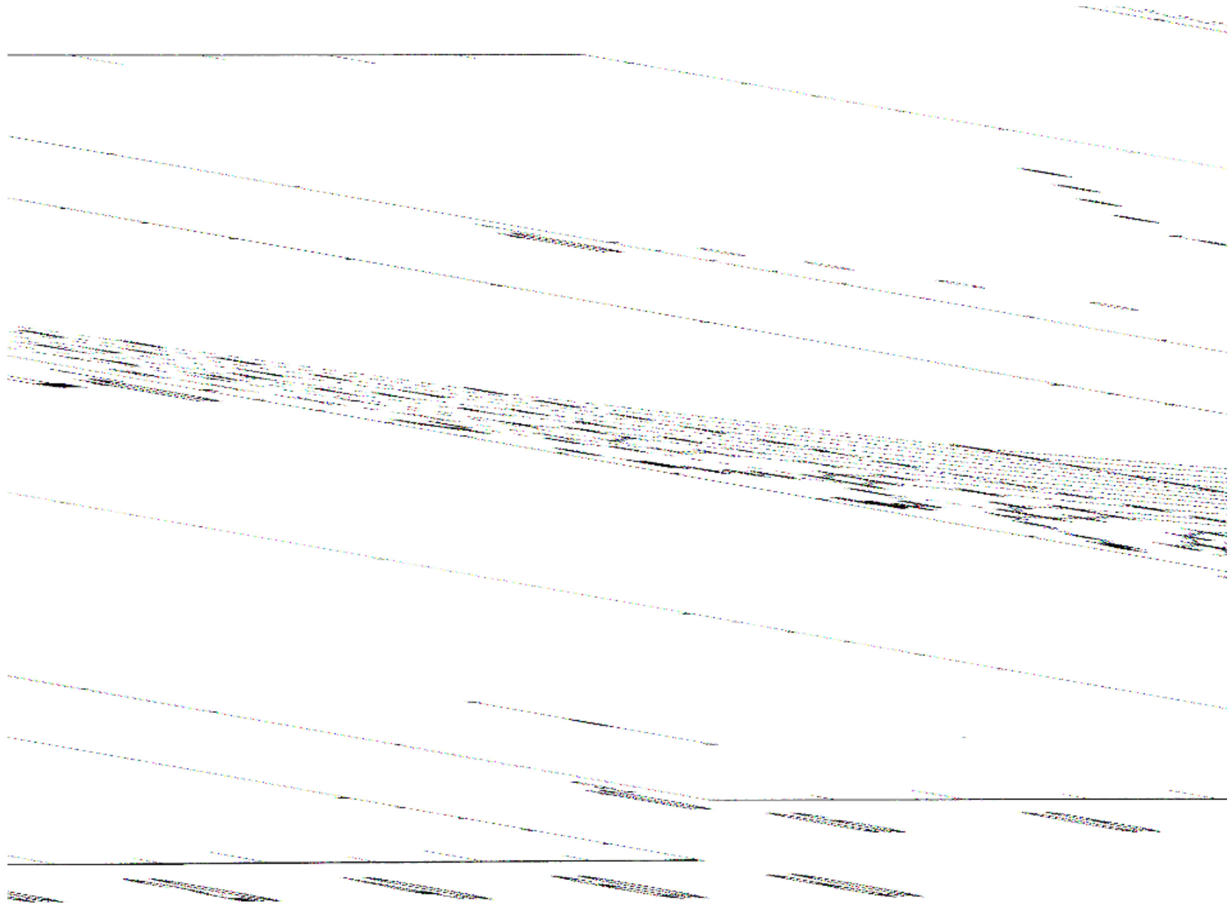


Collapse of effective gap T_0 indicates MIT

Effective gap T_0 as as function of OE/σ (Overlap energy/width of site energy distribution)



Two possible interpretations:
a. MIT as a Quantum phase transition



$\sigma(T) \sim \exp(-T_0/T)$

Gap T_0 is critical:

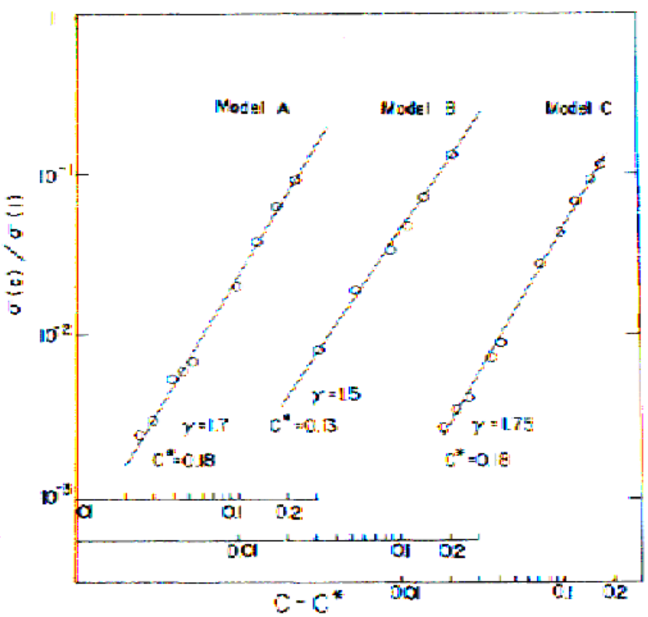
$T_0 \sim (n-n_c)^\beta$

MPA Fisher

A. Goldman

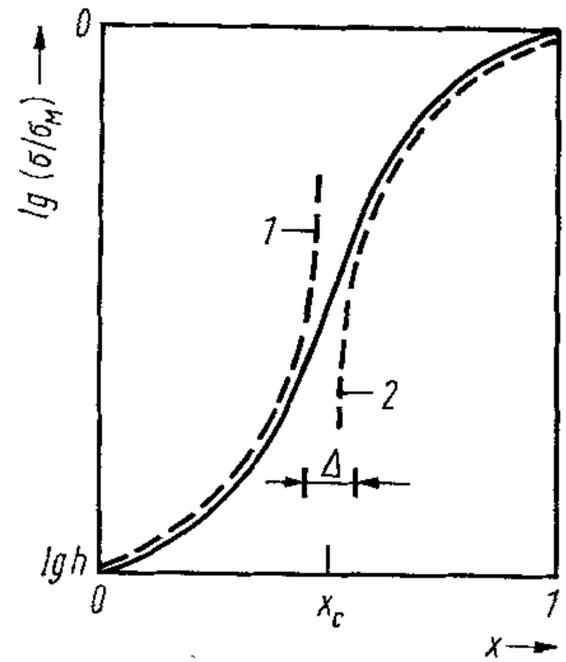
S. Sachdev

b. MIT as a Percolation transition



One component system
Mobility σ is critical:
$\sigma \sim (c-c^*)^{\gamma}$

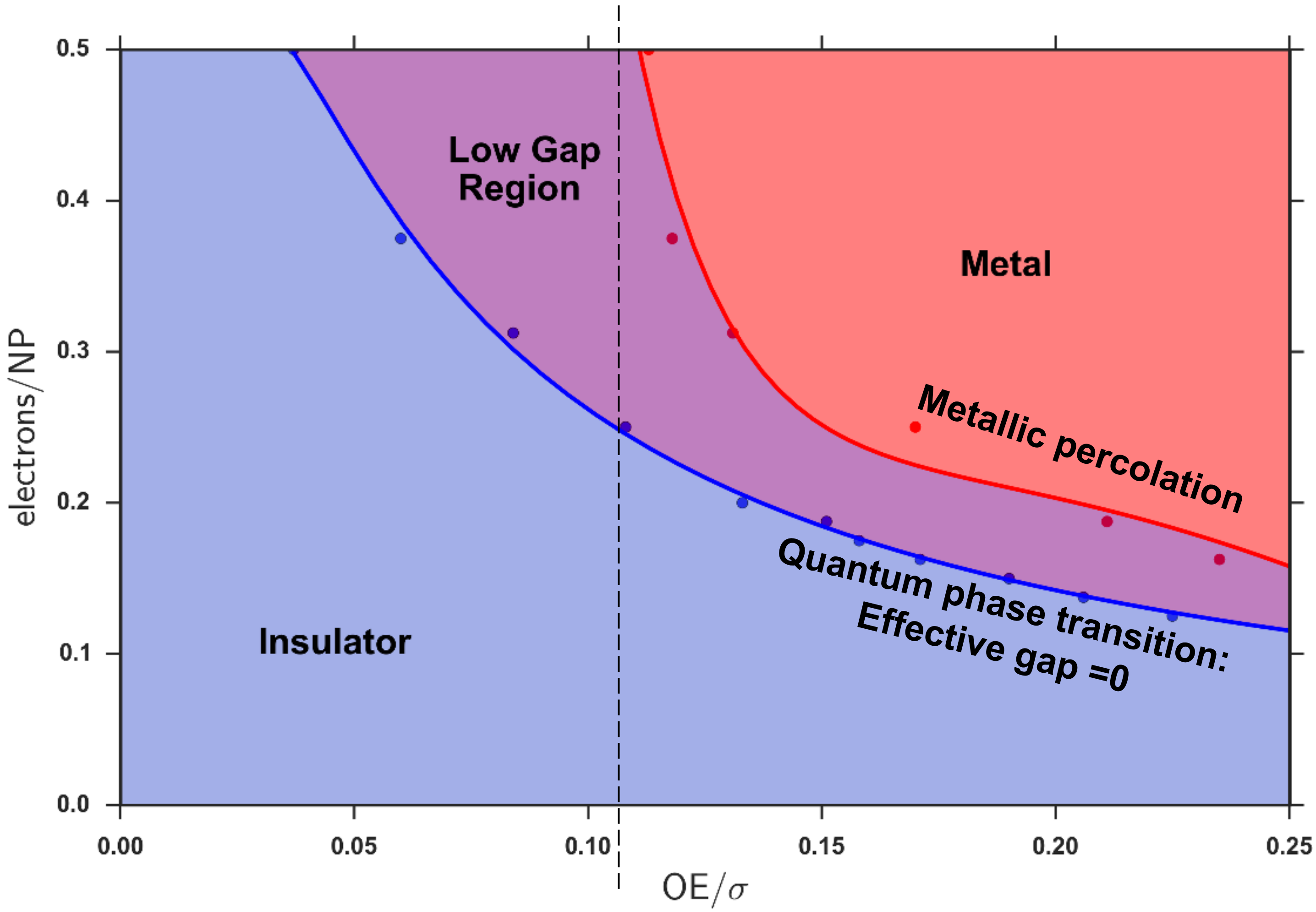
Webman et al, PRB, 11, 2885 (1975)



Two component system:
Mobility has critical crossover:
$\sigma \sim (\sigma_i/\sigma_m)^s \, \phi[(x-x_c)(\sigma_i/\sigma_m)^m]$

Efros, Shklovskii, Phys.Stat.Sol. 76,475 (1976)

MIT: Quantum vs. Percolation



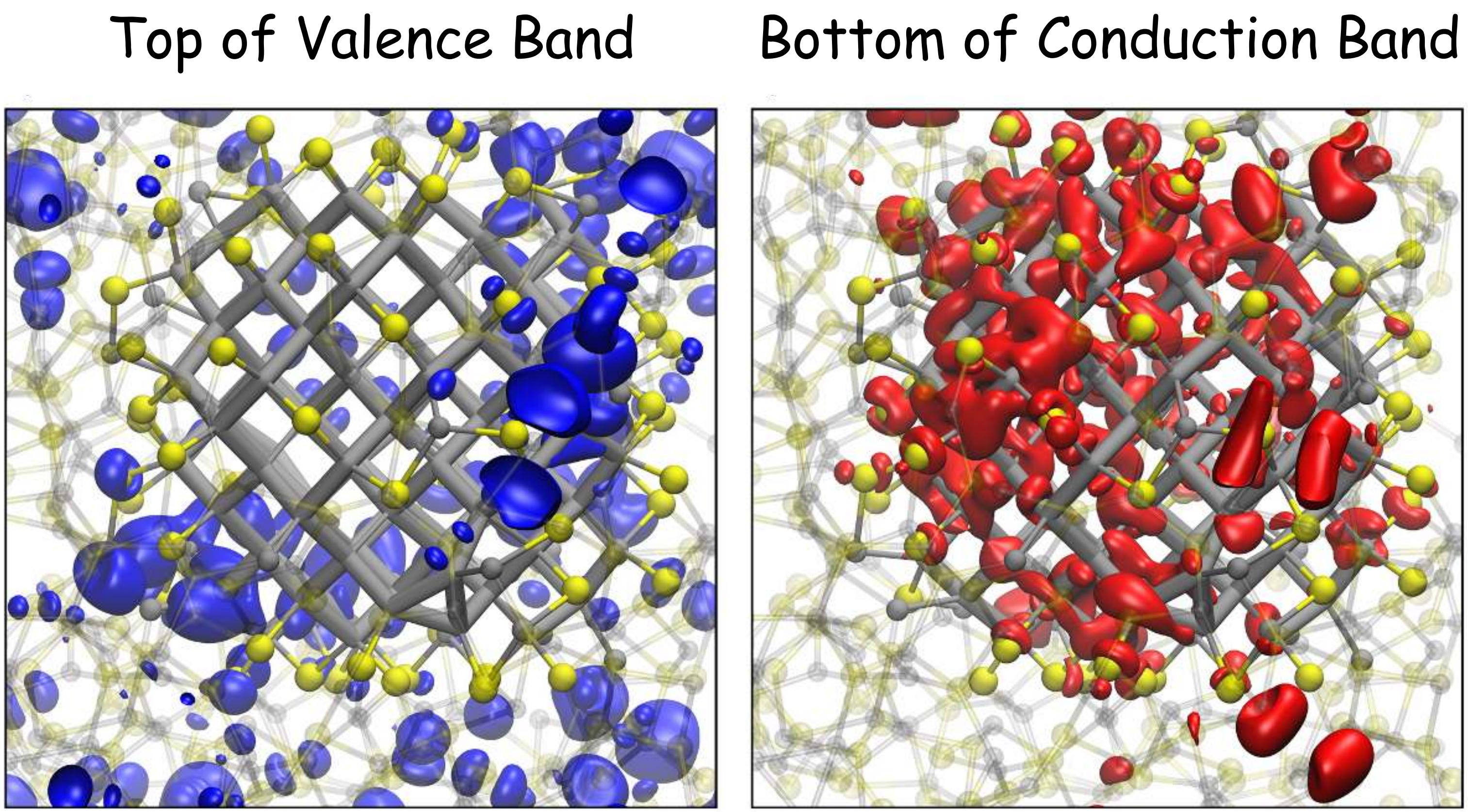
Percolation transition onset

The quantum phase transition & the percolation transition theories yield different phase boundaries!

We adopt the percolation picture as otherwise the metal phase would extend in the non-percolated region.

Data should be analyzed according to both theories to determine most appropriate theory

3b. Complementary Charge Transport Channels



ZnS NPs: Electron transport: NP-NP transition

Hole transport: in host matrix

Complementary transport channels **reduce recombination**

Wippermann, Voros, Galli, GTZ, PRL 2014

Summary of Full Spectrum Boost project

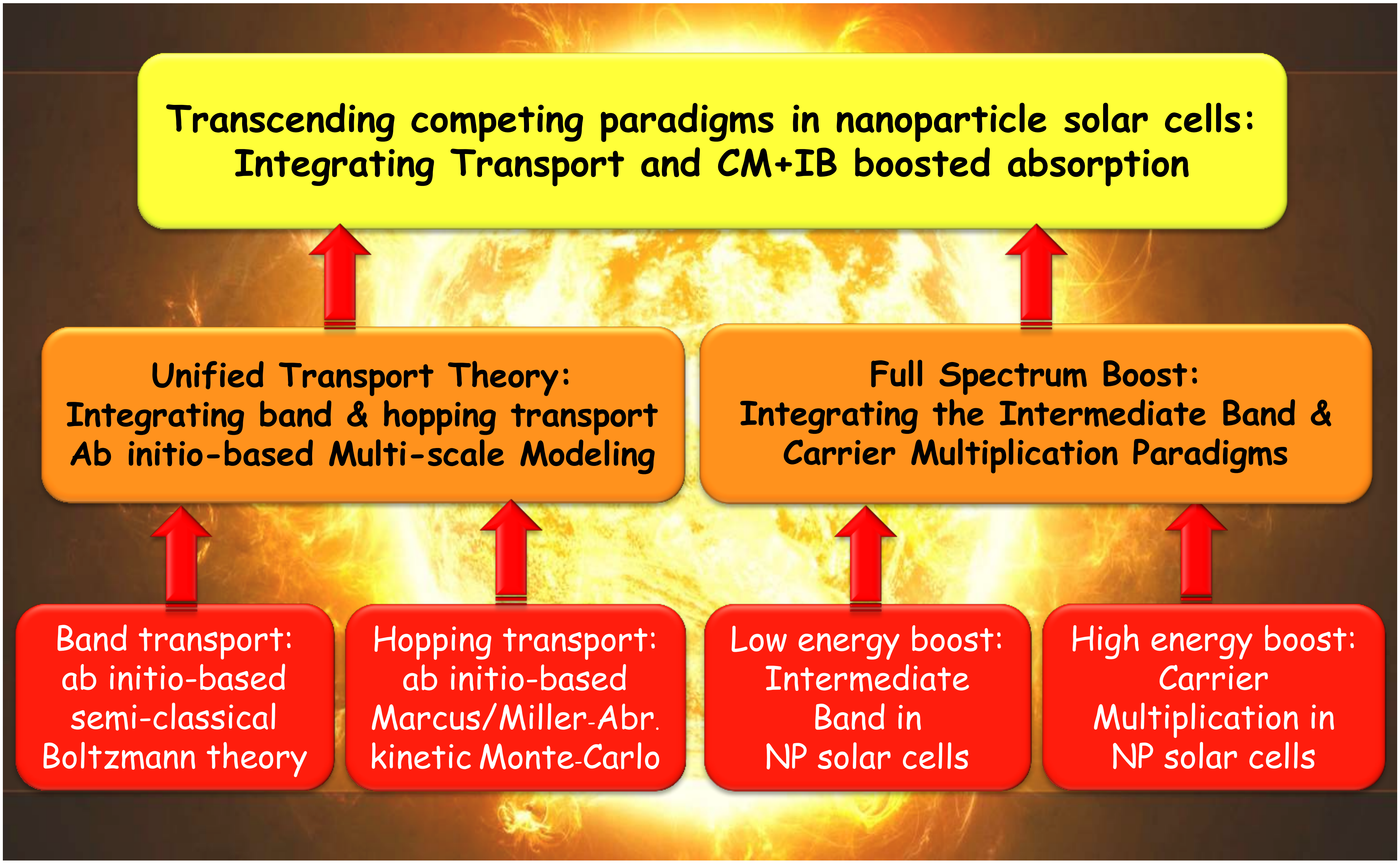
Colloidal Nanoparticles are promising platforms for 3rd generation solar cells

Boosting efficiency at high energies with down-conversion: Quantum Confinement Dilemma can be overcome, Carrier Multiplication can be efficiently implemented

Boosting efficiency at low energies with up-conversion: Intermediate Band solar cells can be implemented in Colloidal Nanoparticles; Strong synergies with CM

Transport can be boosted through Metal-Insulator Transition, Percolative quantum critical framework can describe transition

The Full Spectrum Boost Project

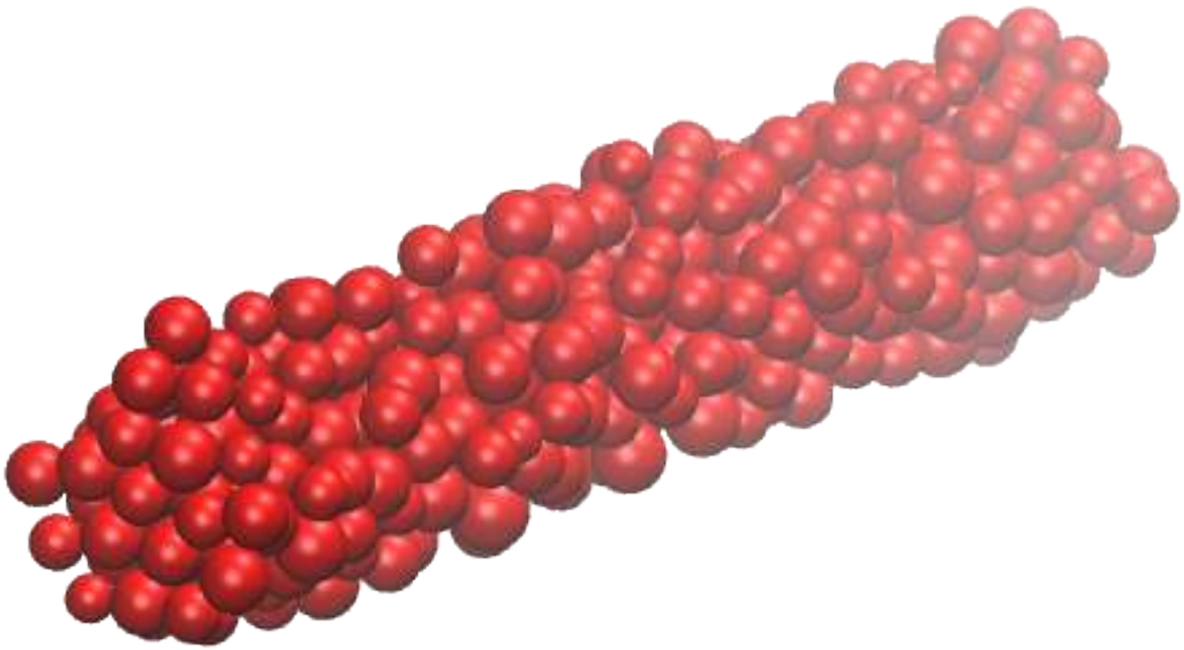


Nanoparticle array:
Size and positional disorder

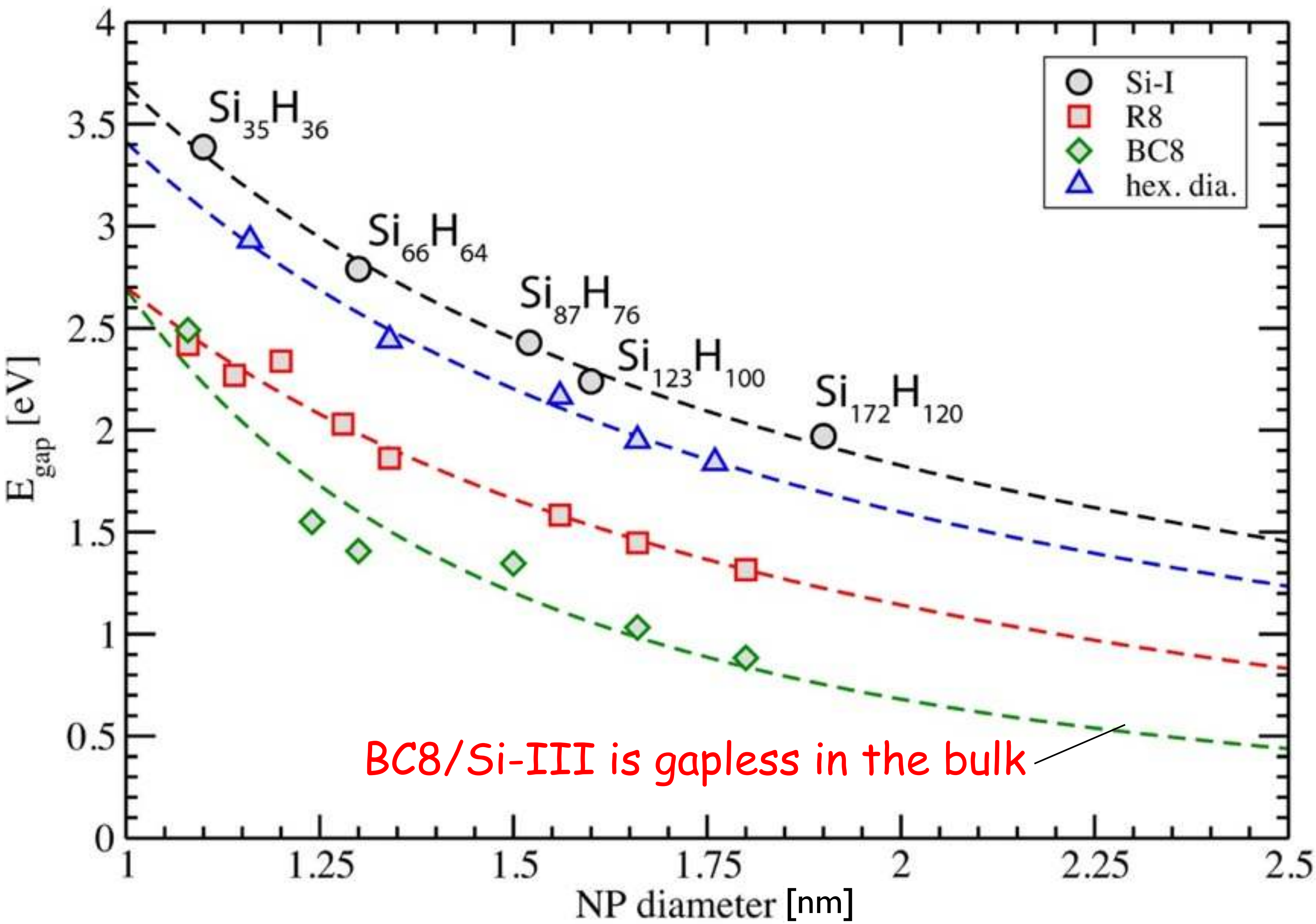
Collision Driven Molecular Dynamics (PackLSD):

Generate disordered jammed packing,
density: ρ=0.62-0.63 (monodisperse max.: ρ=0.634)

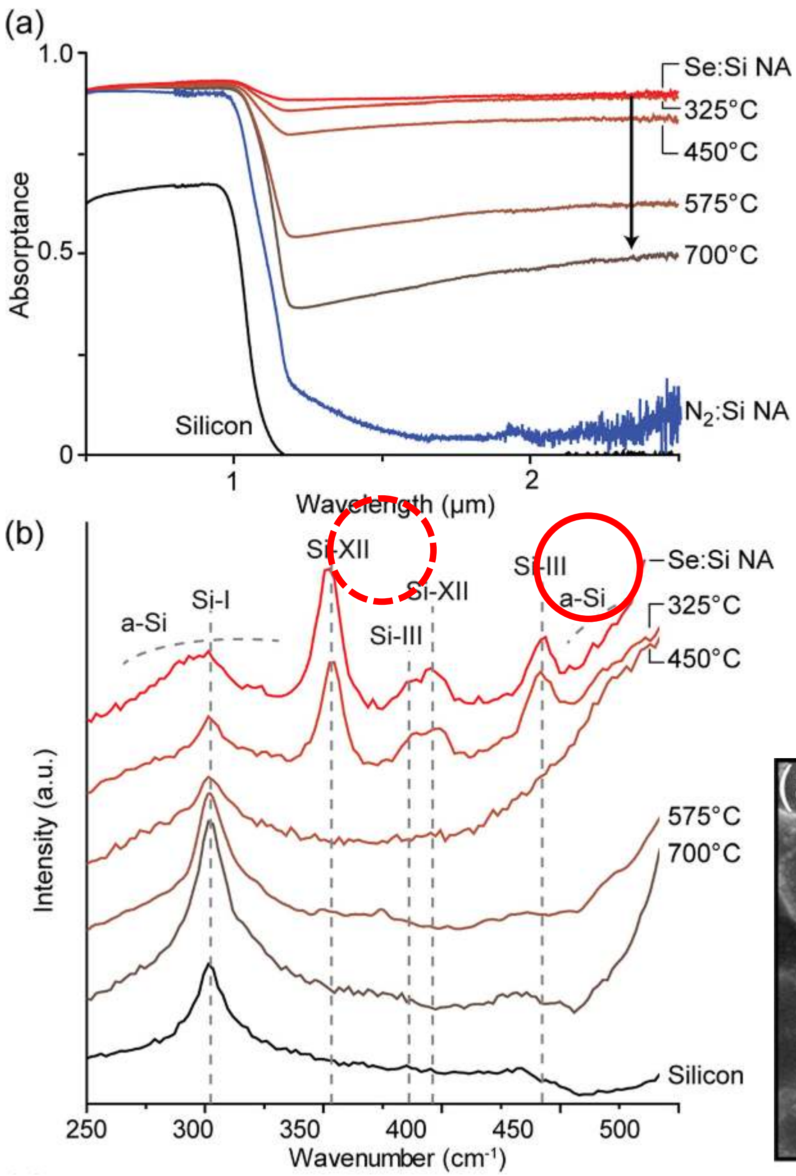
A.Donev, F. Stillinger, and S. Torquato, J. Comp. Phys, **202**, 737 (2005)



1c. Gap reduction in BC8/Si-III



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