Multiexciton Generation at the Nanoscale

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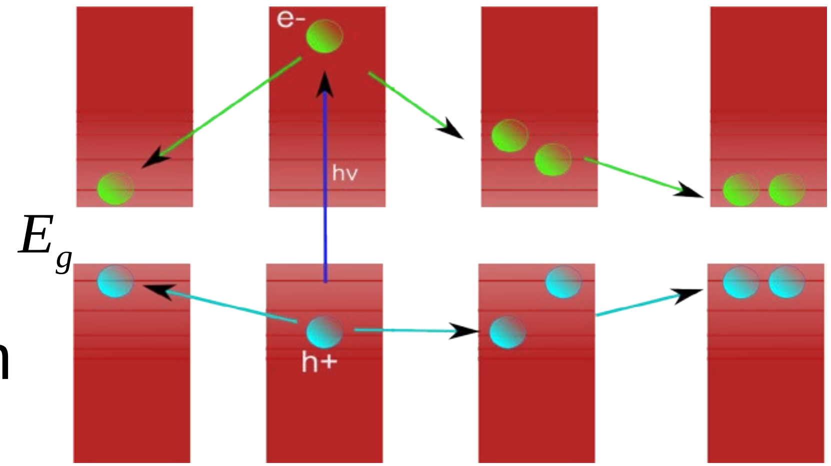
Outline / Acknowledgments

- Why MEG?
- MEG in NC – highly efficient or not?
- Surprising MEG in carbon nanotubes
- The future of MEG: Type II nanorods



- Acknowledgments: Dr. Hagai Eshet, Prof. Roi Baer (HUJI), Prof. Daniel Neuhauser (UCLA)
- Former support: ISF, EFRC (Columbia)

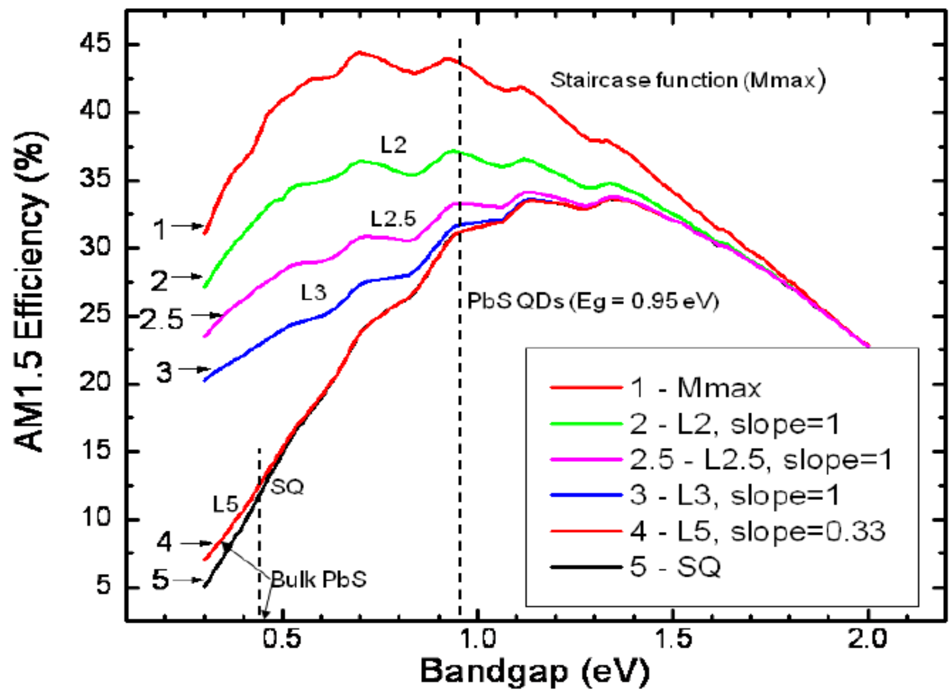
Background

The Shockley-Queisser limit

The Shockley-Queisser (1961) efficiency limit applies to single band gap semiconductor photovoltaic systems. It is assumed that one absorbed photon produces one electron-hole pair.

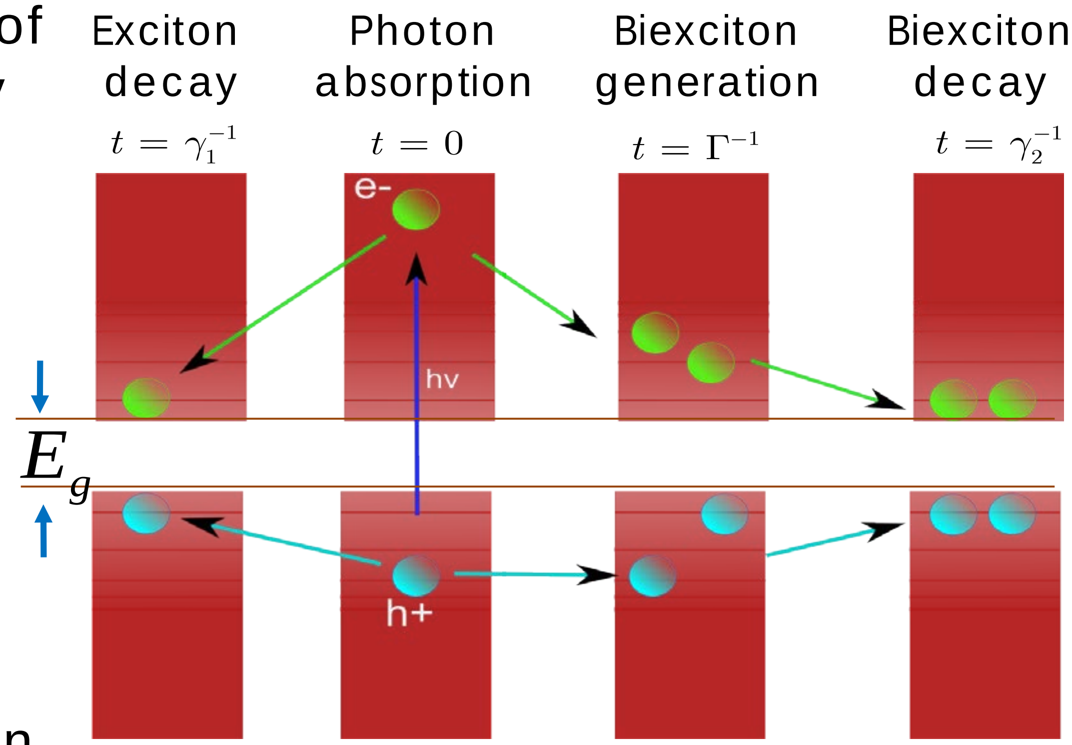
Limiting factors:

- The absorption of the solar spectrum at energies below the fundamental energy gap.
- Excess kinetic energy is lost to heat.
- The maximum efficiency is about 31% under one-sun illumination.



"Collecting" Hot Carriers

- Collecting hot carriers would have a potential of increasing the efficiency to 66%.
- Charge multiplication (CM) via multiexciton generation (MEG). This would lead to maximal efficiencies of 45%.
- Singlet fission at Northwestern: Marks, Ratner, Schatz, Seideman, Shiozaki, Wasielweski.



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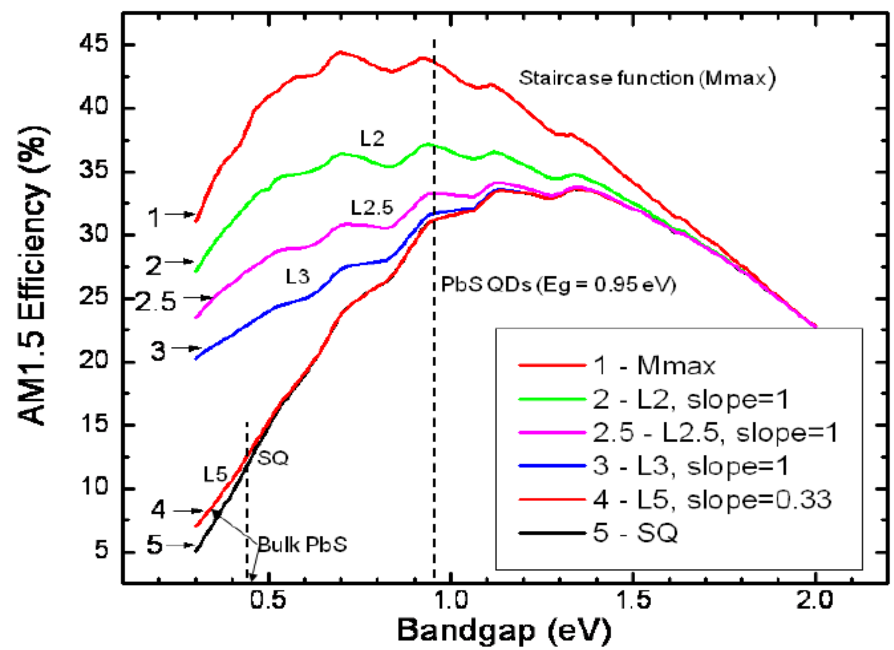
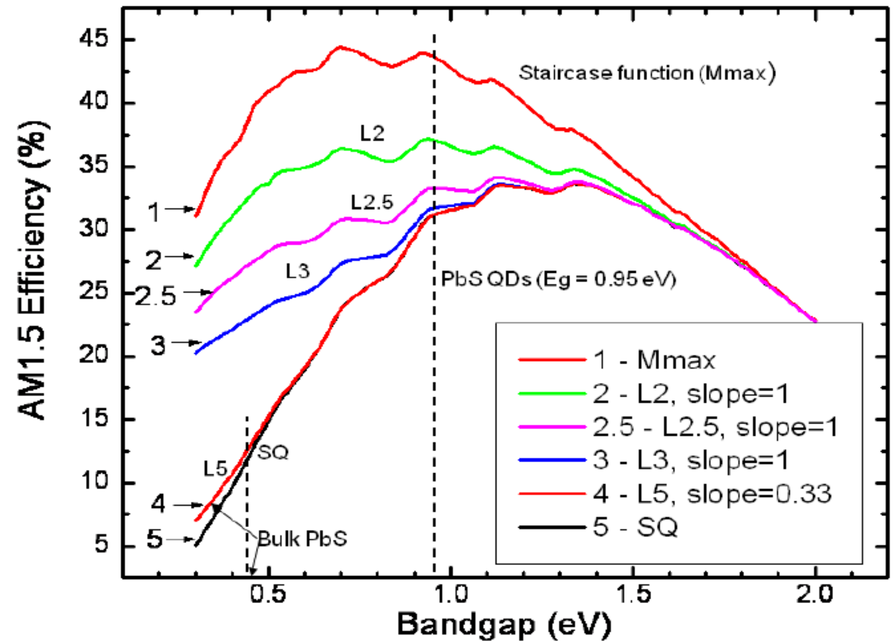


MEG in Bulk Semiconductors

Multiexciton generation (MEG) is a process where several excitons are generated upon the absorption of a single photon in semiconductors. J. Tauc, J. Phys. Chem. Solids 8, 219 (1959); L. Keldysh, Sov. Phys. JETP-USSR 10, 509 (1960).

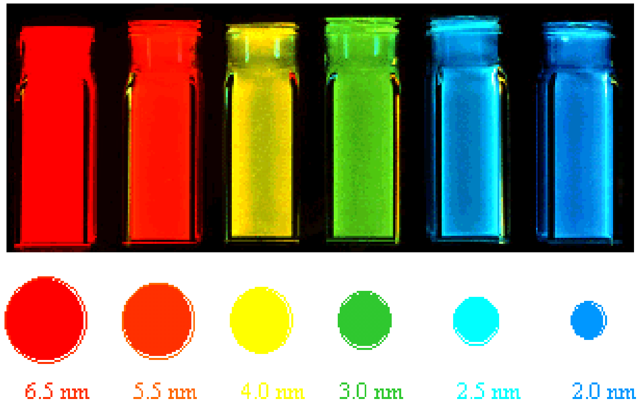
- Strict selection rules and competing processes in the bulk allow observation of MEG only at energies of 5E_g.
- Since the effect in bulk is similar to that of nanowires, it was suggested that NCs may exhibit MEG at lower values of photon energy (typically 2-3E_g).



MEG in Nanostructures

Why Nanostructures?

- Quantum confinement
- No strict selection rules
- Phonon bottleneck



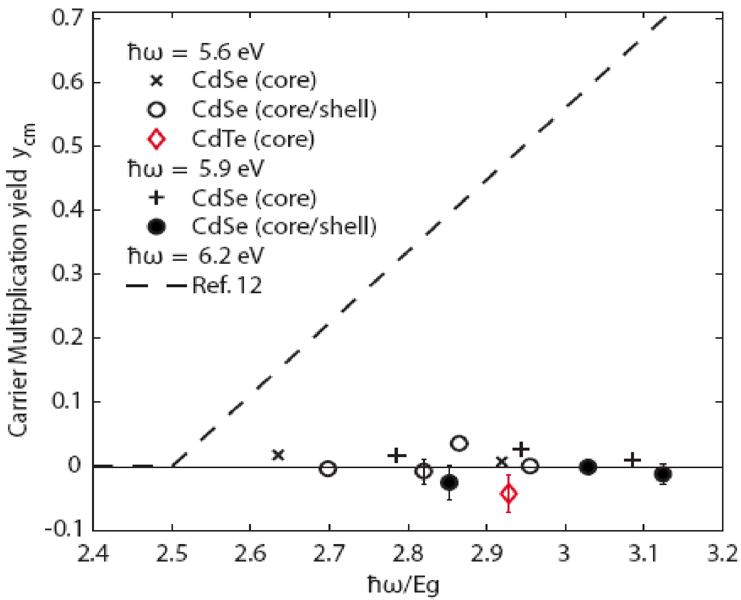
Experimental Results

Indeed, MEG in NCs has been reported recently for several systems below $3E_g$:

PbSe PbS	R.D. Schaller and V.I. Klimov, Phys. Rev. Lett. 92, 186601 (2004); R.J. Ellingson et al., Nano Lett. 5, 865 (2005); R.D. Schaller et al., Appl. Phys. Lett. 87, 253102 (2005); V. I. Klimov, J. Phys. Chem. B 110, 16827 (2006); R.D. Schaller et al., Nano Lett. 6, 424 (2006). B. Cho et al., Nano Lett. 10, 2498 (2010).
PbTe	J.E. Murphy et al., J. Am. Chem. Soc.128, 3241 (2006).
CdSe	R.D. Schaller et al., Appl. Phys. Lett. 87, 253102 (2005); R.D. Schaller et al., Nature Physics 1,189 (2005).
InAs	R.D. Schaller et al., Nano Lett. 7, 3469 (2007).
InP	S.K. Stubbs et al., Phys. Rev. B 81, 081303 (2010).
Silicon	M.C. Beard et al., Nano Lett. 7, 2506 (2007).

Pessimistic View

- G. Nair and M. G. Bawendi, Phys. Rev. B 76, 081304 (2007): “Carrier multiplication yields of CdSe and CdTe nanocrystals by transient photoluminescence spectroscopy”.
- Gautham Nair, Scott M Geyer, Liang-Yi Chang, and Moungi G Bawendi, Phys. Rev. B 78, 125325 (2008):“Carrier multiplication yields in PbS and PbSe nanocrystals measured by transient photoluminescence”.
- M. Ben-Lulu, D. Mocatta, M. Bonn, U. Banin, and S. Ruhman, Nano Lett. 8, 1207, 2008: “On the Absence of Detectable Carrier Multiplication in a Transient Absorption Study of InAs/CdSe/ZnSe Core/Shell1/Shell2 Quantum Dots”.
- J. J. H. Pijpers, R. Ulbricht, K. J. Tielrooij, A. Osherov, Y. Golan, C. Delerue, G. Allan & M. Bonn, Nature Physics 5, 811 (2009): “Assessment of carrier-multiplication efficiency in bulk PbSe and PbS”.

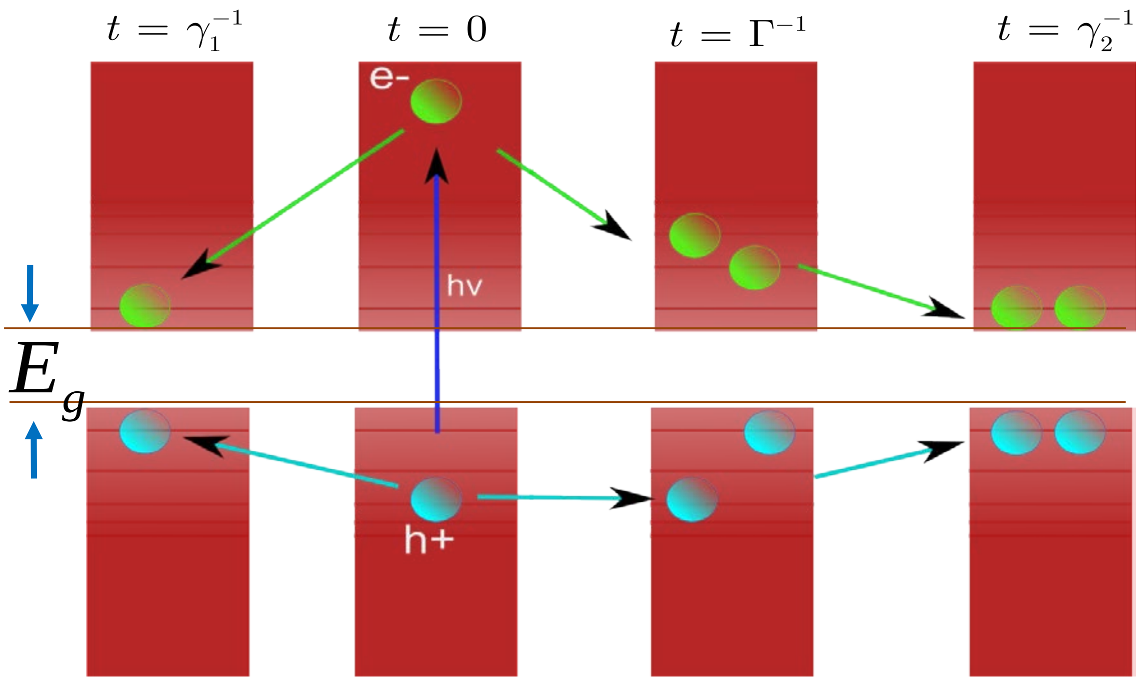


Theory

E. Rabani and R. Baer, Nano. Lett. 8, 4488 (2008).
E. Rabani and R. Baer, Chem. Phys. Lett. 496, 227 (2010).

Impact Excitation

$$\Gamma_S = 2\pi \sum_B \left|W_{SB}\right|^2 \delta\left(E - E_B\right)$$



$$n_{ex}\left(\omega\right) = \sum_S P_S(\omega) \frac{2\Gamma_S + \gamma}{\Gamma_S + \gamma}$$

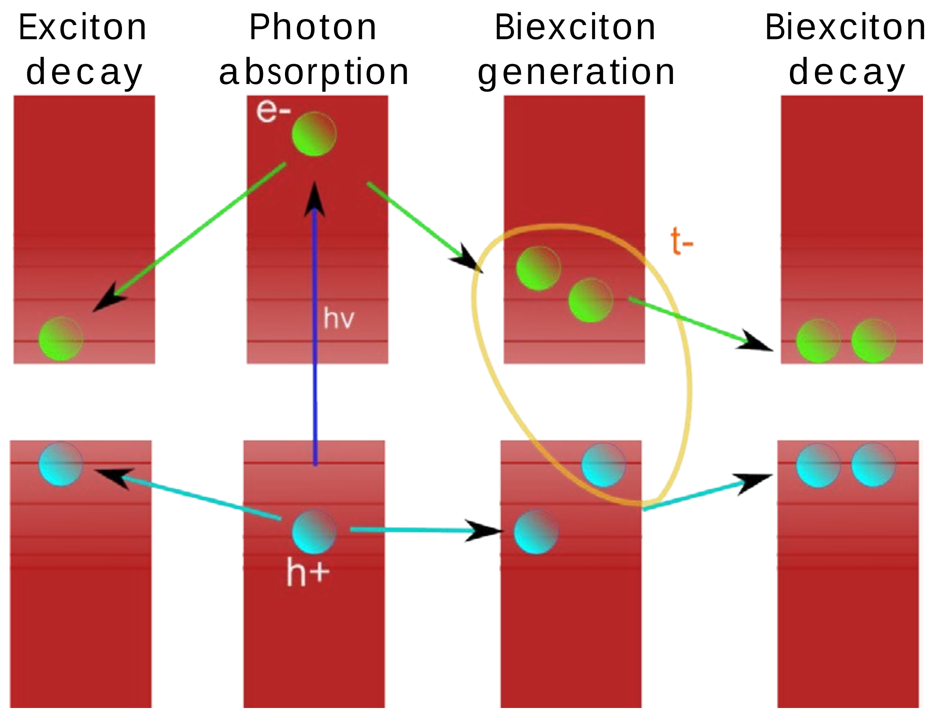
$$P_S(\omega) = \left|\mu_{0S}\right|^2 \Big/ \sum_S \left|\mu_{0S}\right|^2$$

Physical Picture

$$\left\langle S_{i\uparrow}^{a\uparrow} \middle| W \middle| B_{k\uparrow j\uparrow}^{b\uparrow c\uparrow} \right\rangle = \delta_{ac}\left(V_{jikb} - V_{kijb}\right) + \delta_{ab}\left(V_{kijc} - V_{jikc}\right) + \delta_{ij}\left(V_{kcab} - V_{ackb}\right) + \delta_{ki}\left(V_{acjb} - V_{jcab}\right)$$

$$\left\langle S_{i\uparrow}^{a\uparrow} \middle| W \middle| B_{k\uparrow j\downarrow}^{b\uparrow c\downarrow} \right\rangle = \delta_{ab} V_{kijc} - \delta_{ki} V_{jcab}$$

$$\left\langle S_{i\uparrow}^{a\uparrow} \middle| W \middle| B_{k\downarrow j\uparrow}^{b\downarrow c\uparrow} \right\rangle = \delta_{ac} V_{jikb} - \delta_{ji} V_{kbac}$$

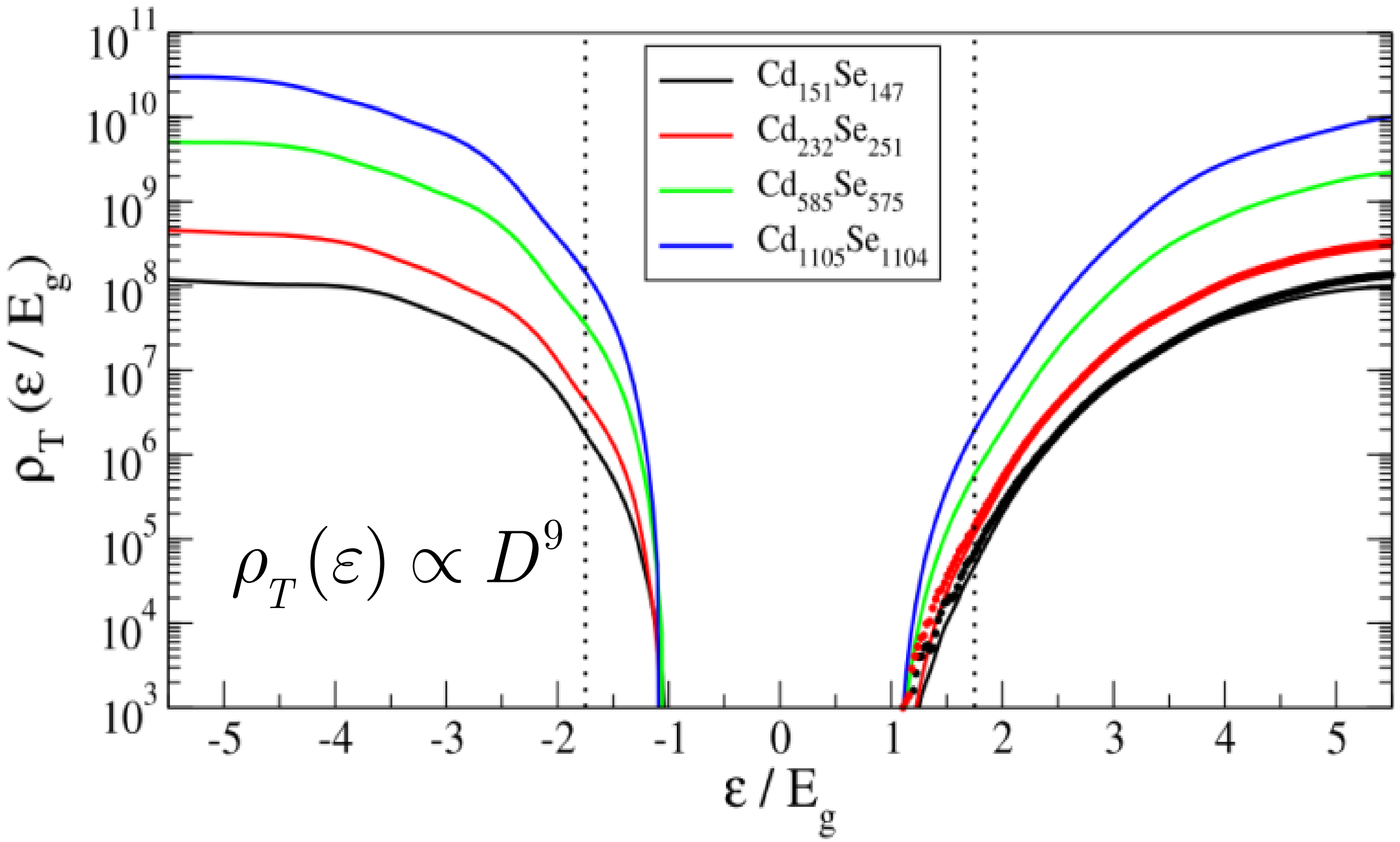


$$\Gamma_a^- = \frac{2\pi}{\hbar} \sum_{cbj} \left| W_{cbj} \right|^2 \delta\left(\varepsilon_a - \left(\varepsilon_b + \varepsilon_c - \varepsilon_j\right)\right)$$

Results for NC

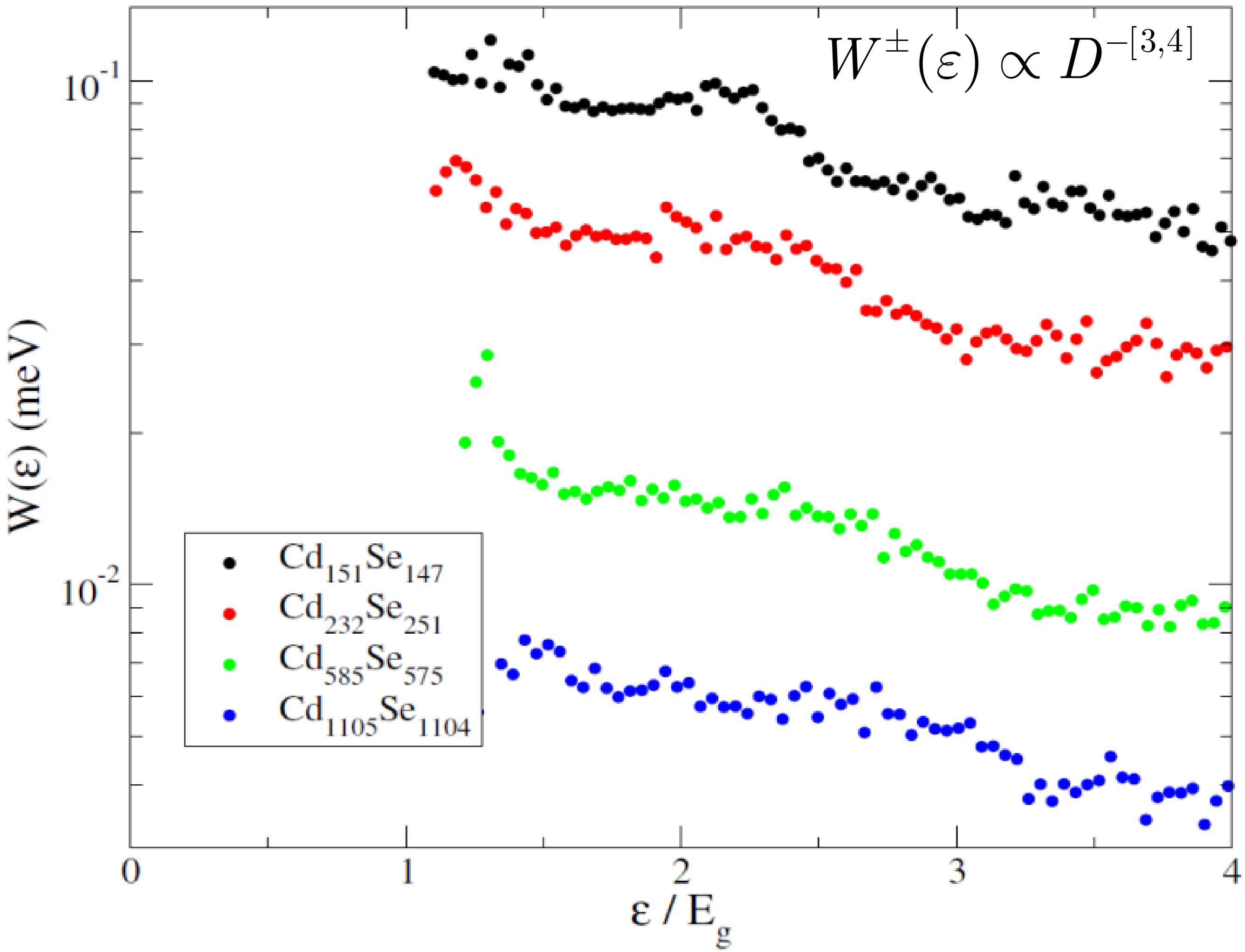
E. Rabani and R. Baer, Nano. Lett. 8, 4488 (2008).
E. Rabani and R. Baer, Chem. Phys. Lett. 496, 227 (2010).
R. Baer and E. Rabani, Nano Lett. 12, 2123 (2012).

DOTS in NCs



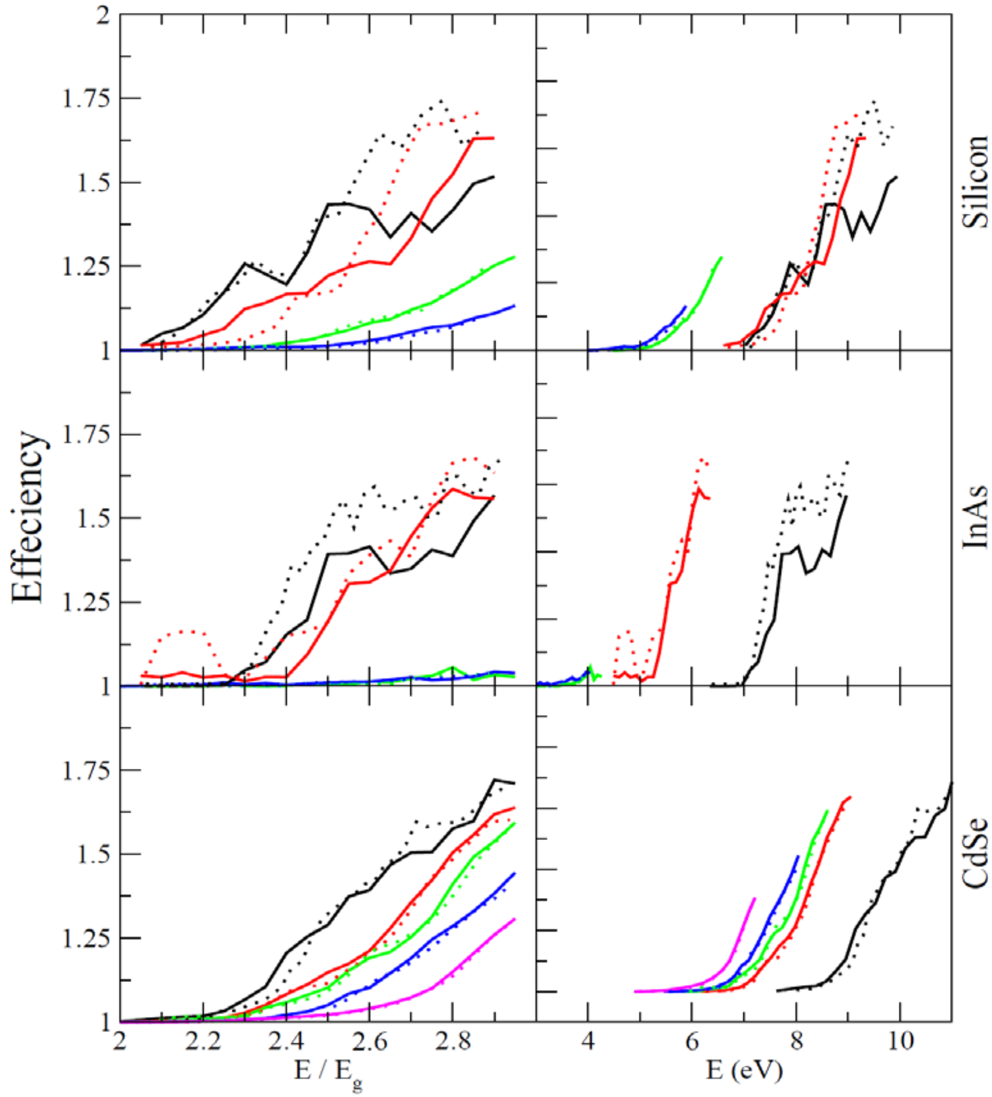
$$\rho(\varepsilon) = \sum_{cbj} \delta\left(\varepsilon - \left(\varepsilon_b + \varepsilon_c - \varepsilon_j\right)\right)$$

Coulomb Couplings in NCs



Average Number of Excitons

- Left: The average rate of exciton to biexciton transition in various silicon (upper), InAs (middle) and CdSe (lower) NCs vs. the photon energy.
- Right: Average number of excitons generated in various silicon (upper), InAs (middle) and CdSe (lower) NCs.
- Phonon self-energy 3ps^{-1}



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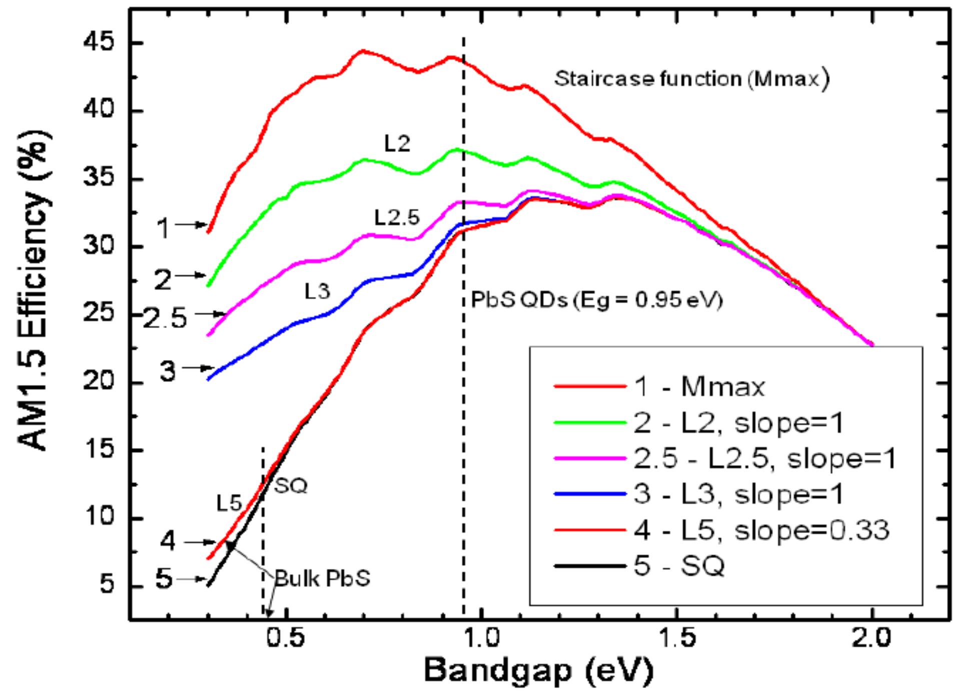
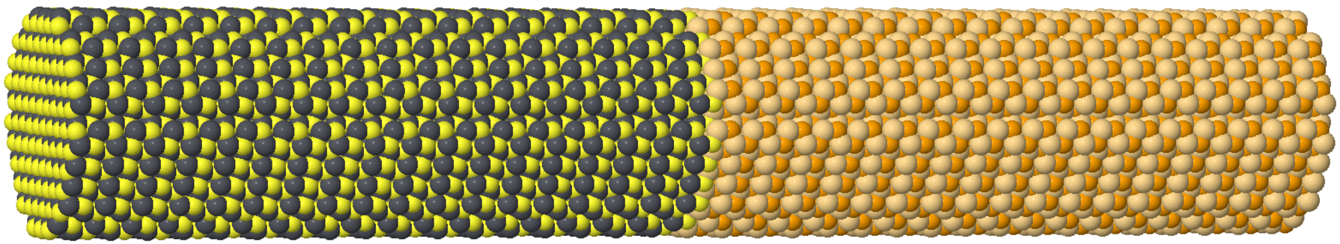
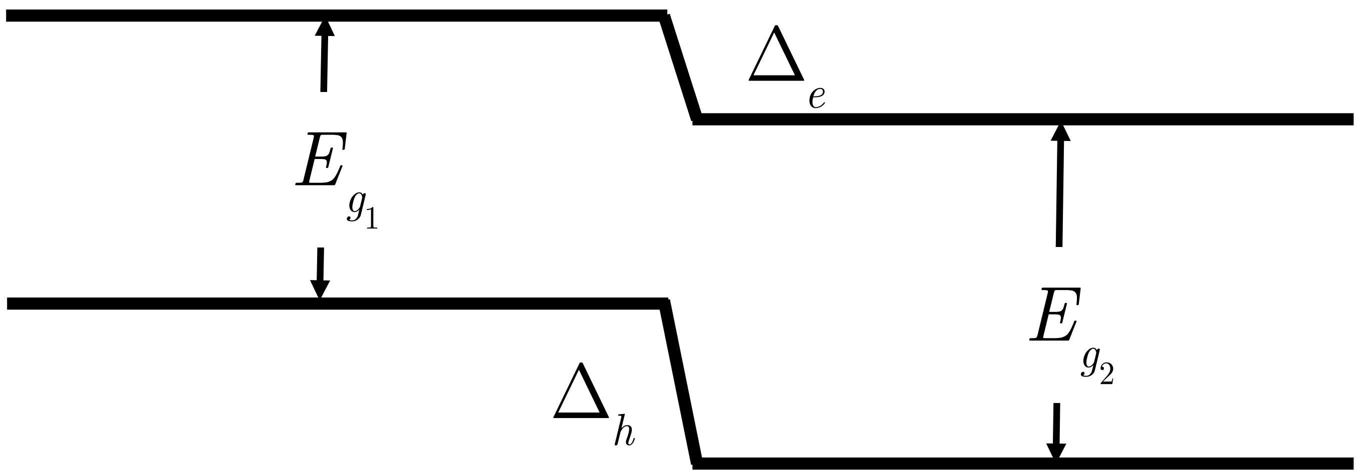


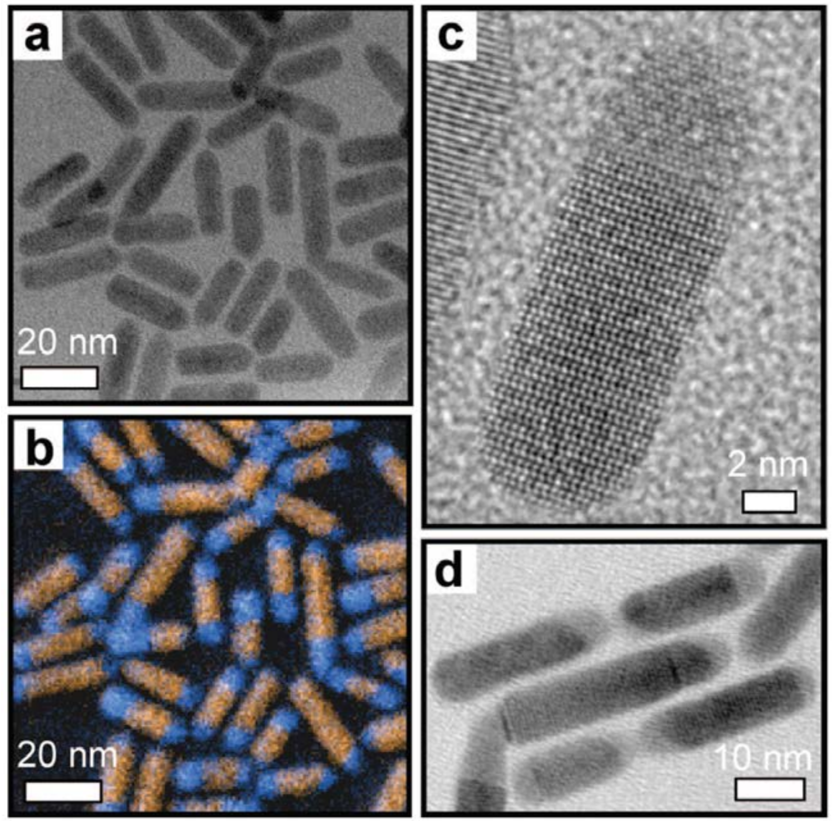
MEG in Type II Nanorods

What are Type II Nanorods?



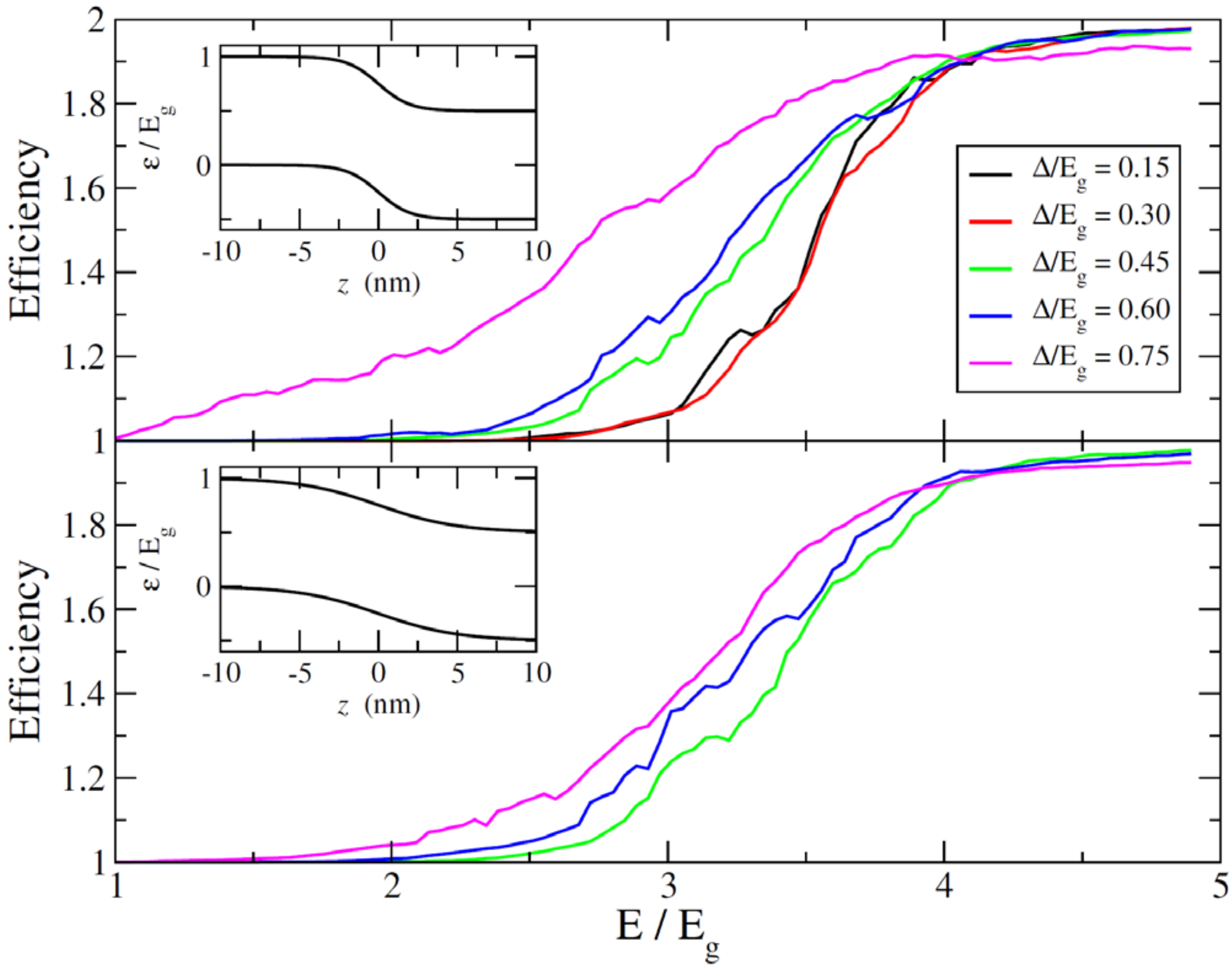


Cation Exchange

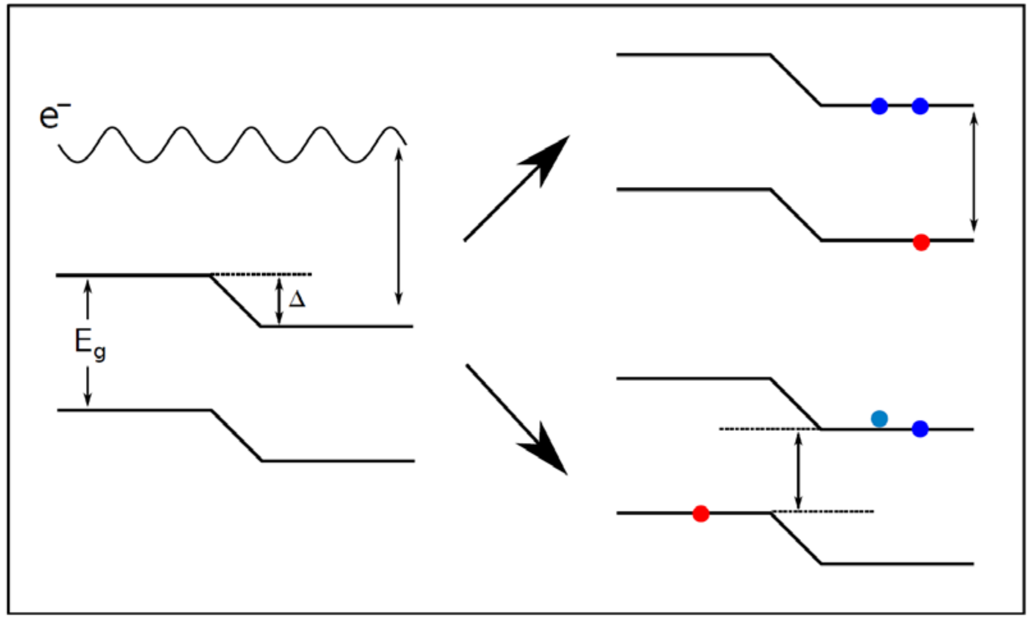


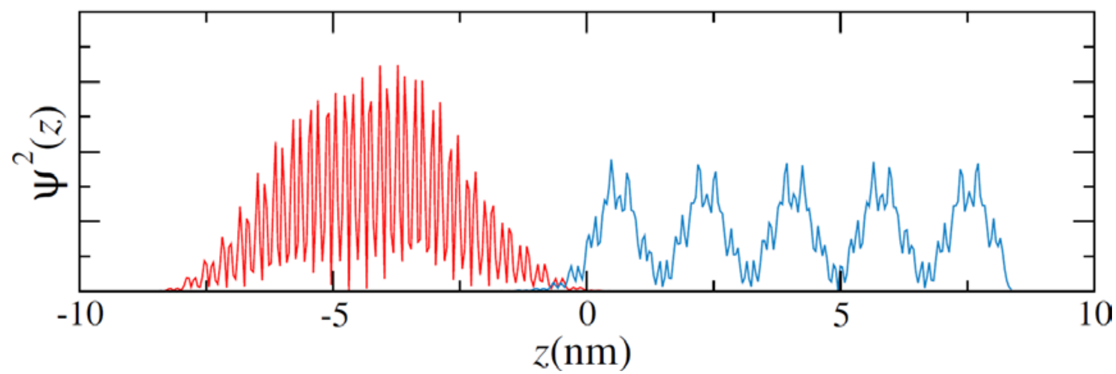
Sadtler, Demchenko, Zheng, Hughes, Merkle, Dahmen, Wang, Alivisatos, JACS 131, 5285 (2009).

MEG Efficiencies in Type II Rods

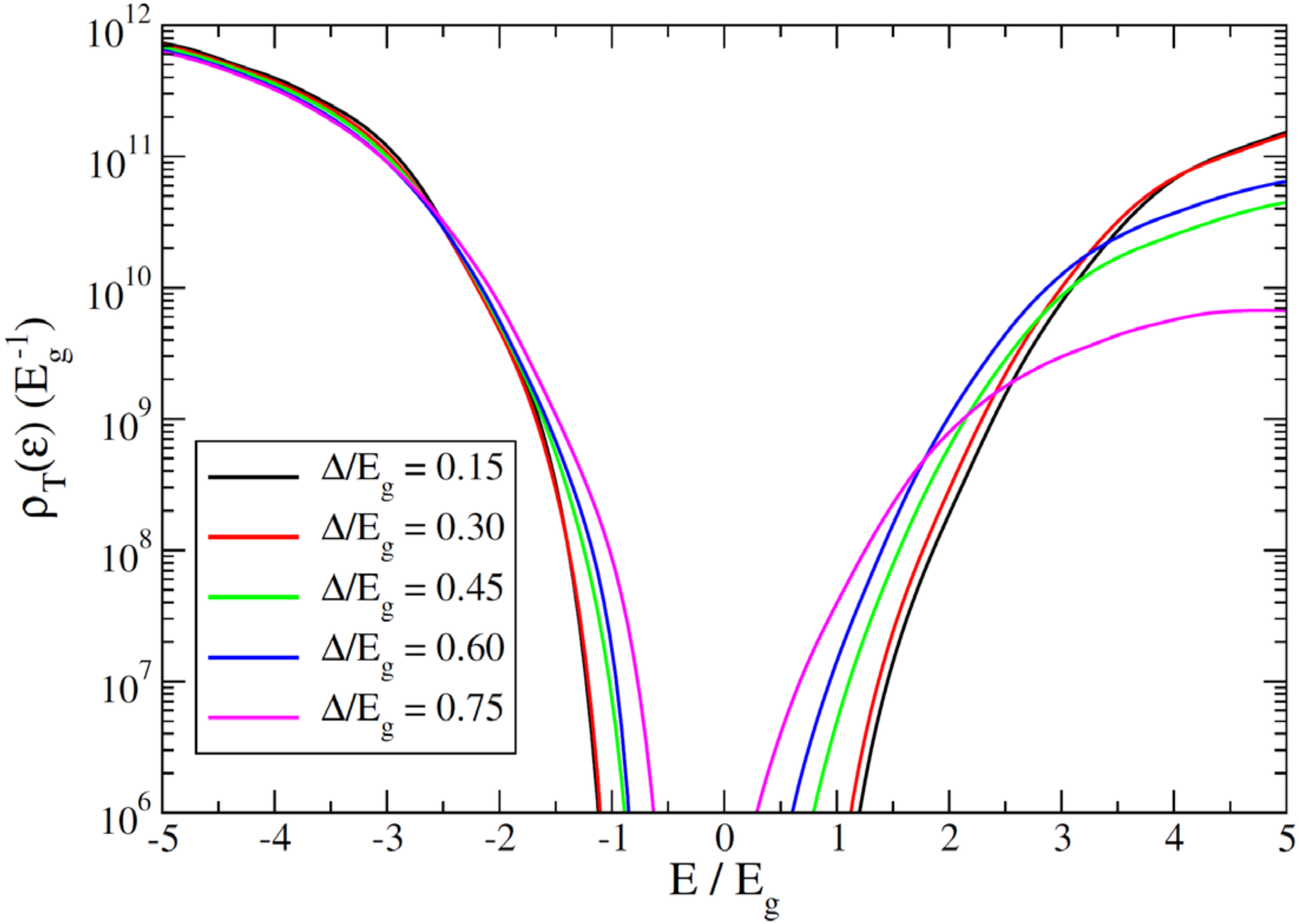


Physical Picture





DOTS in Type II Rods



Average Coupling in Type II Rods