Multiple Exciton Generation in Quantum Dots

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Materials 265
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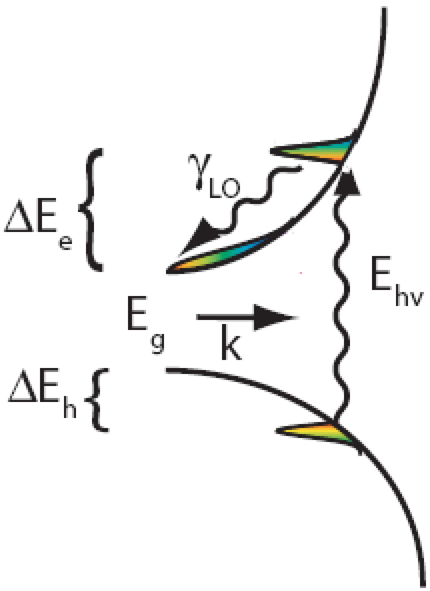
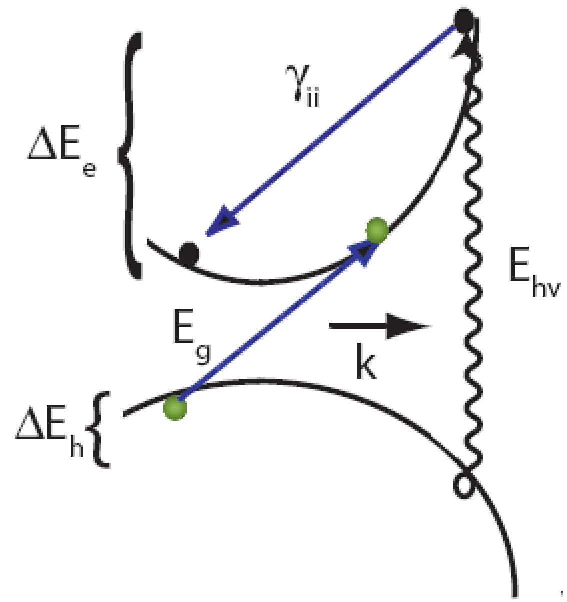
Exciton Generation

Single Exciton Generation in Bulk Semiconductors



$E_g < E_{h\nu} < 2E_g$

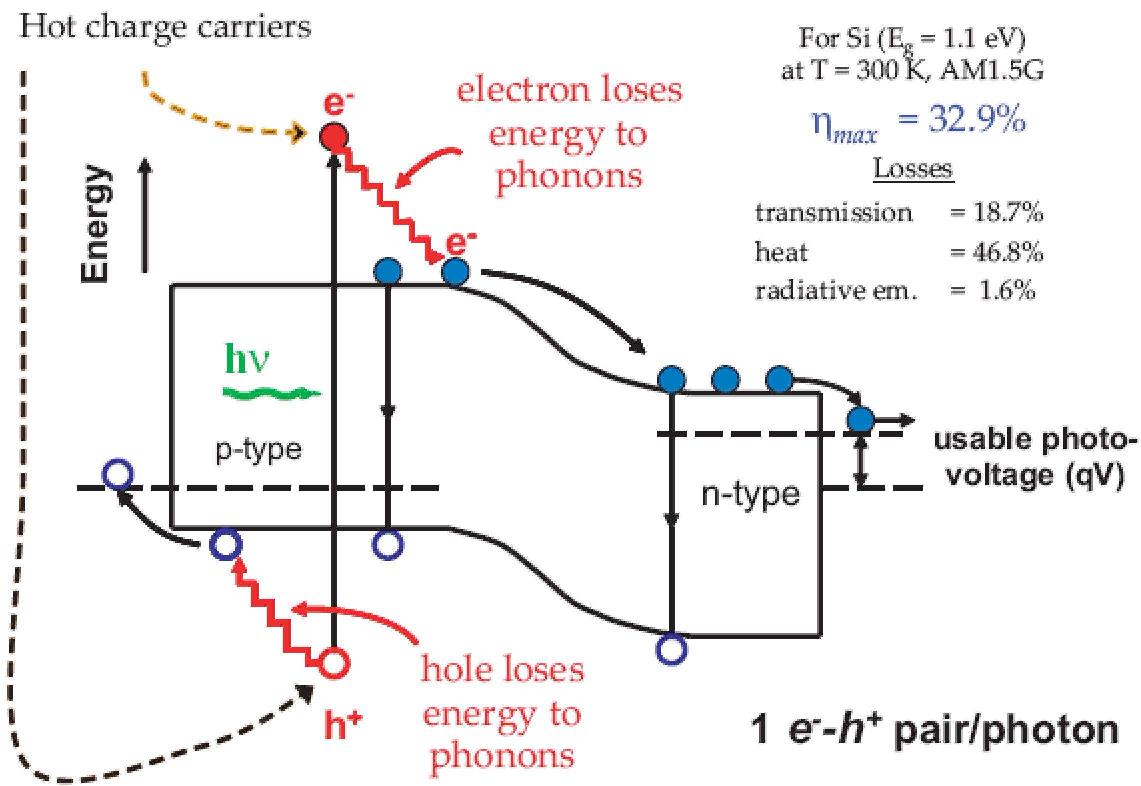
Multiple Exciton Generation in Bulk Semiconductors



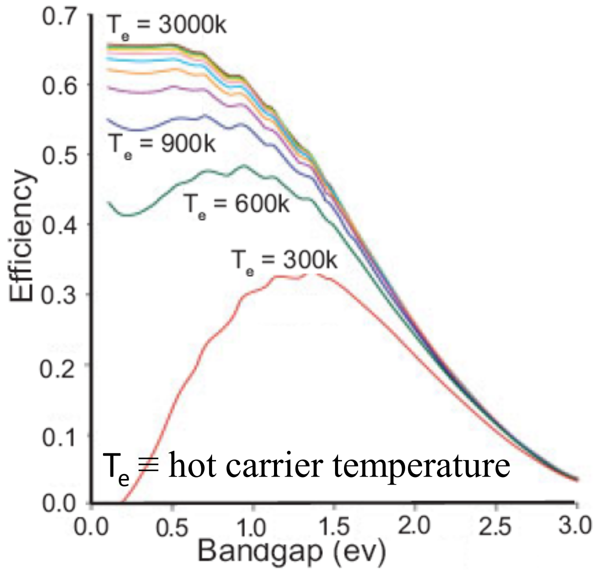
$E_{h\nu} > 2E_g$

Singe exciton efficiency limits

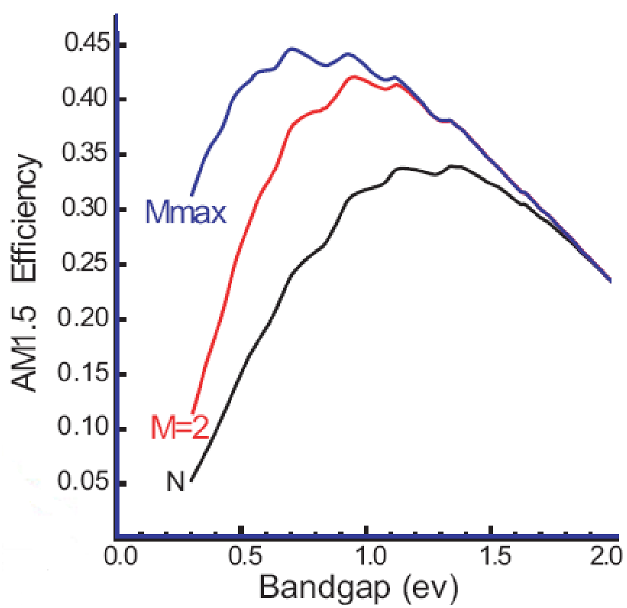
- Record Laboratory efficiency for crystalline silicon under solar irradiation: **24.7%**
- Thermodynamic limit for one photon-one exciton generation under solar irradiation: **33%**
- Amount of incident energy lost as heat: **47%**



Multiple exciton efficiency limits



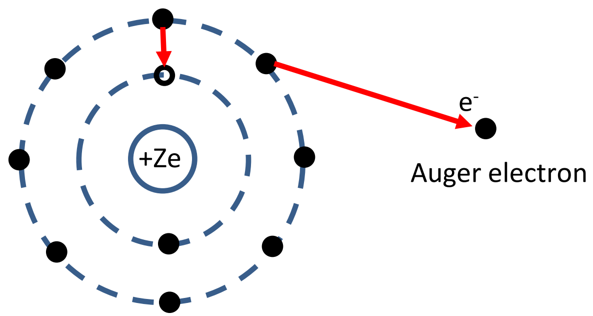
- Theoretical efficiency if carriers are extracted prior to cooling: **67%**



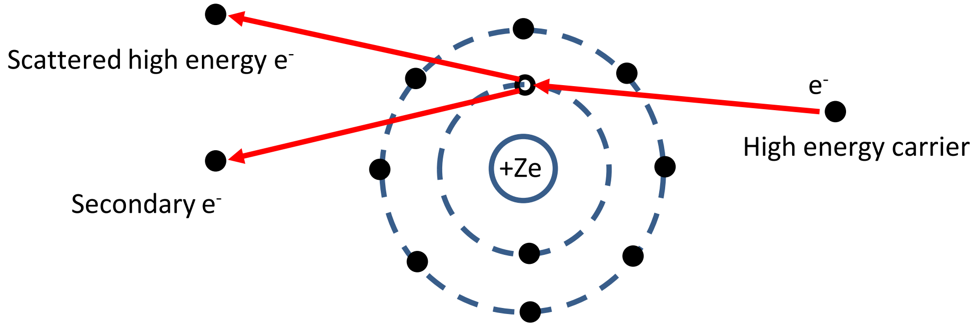
- For $E_{hv} > 2 \cdot E_g$ we consider three possibilities
  - 1 e^-h^+ pair per photon
  - 2 e^-h^+ pairs per photon
  - M e^-h^+ pairs per photon
- Theoretical efficiency achieved through MEG: **43%**

How does MEG occur?

- Impact ionization
  - Consider the familiar auger recombination process:



  - Consider the inverse of this process:



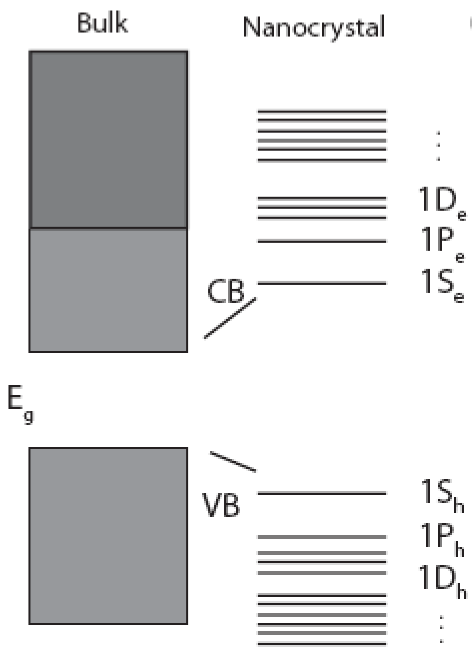
Impact Ionization (I.I.)

MEG is an unlikely process

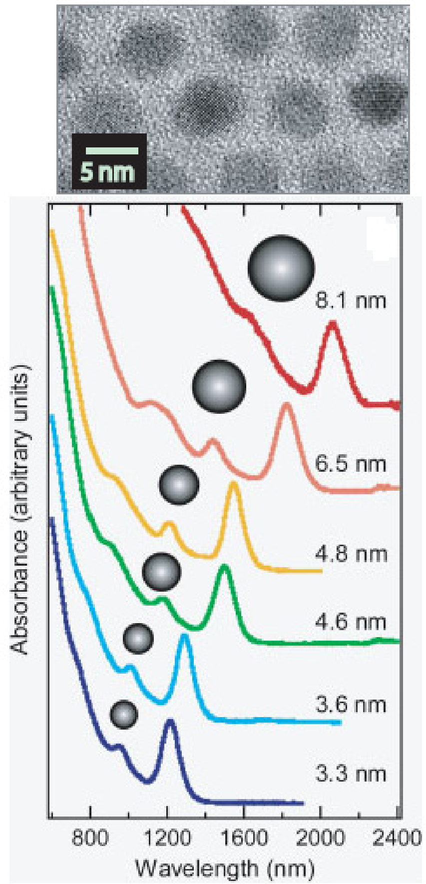
- Competing processes
  - Inelastic carrier-carrier scattering (10^{13} sec^{-1})
    - Dependent on carrier concentration
  - Phonon scattering (10^{12} sec^{-1})
    - Independent of carrier concentration
  - Auger recombination
  - Exciton-exciton annihilation (10-100 ps)
    - Exciton concentration dependent

Impact ionization rates in bulk semiconductors surpass phonon scattering rates only when the electron kinetic energy exceeds ~5ev

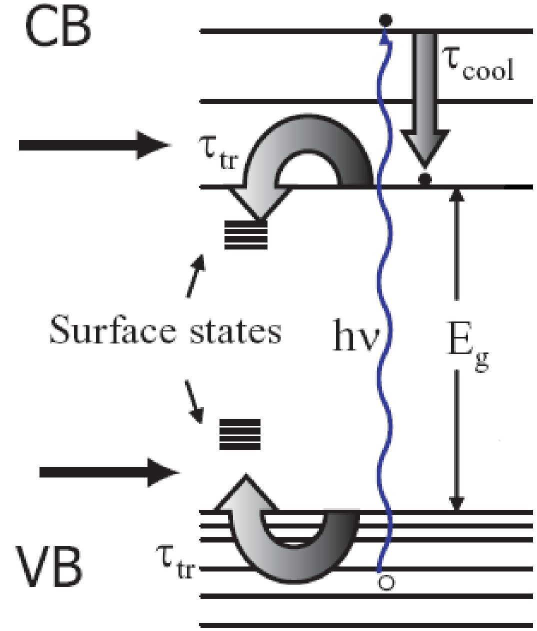
Effects of quantum confinement



Discretization of electronic structure

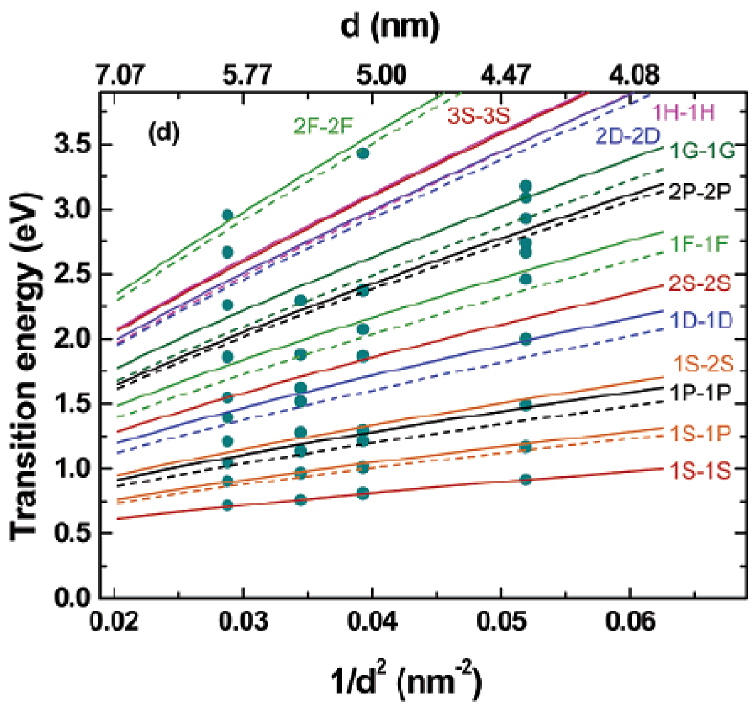


Change in bandgap energy

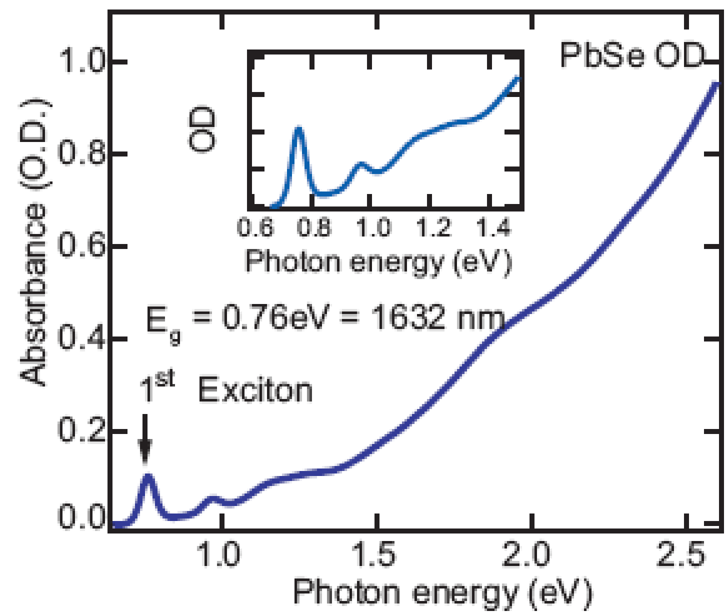


Importance of Surface States

Effect of particle size on band structure

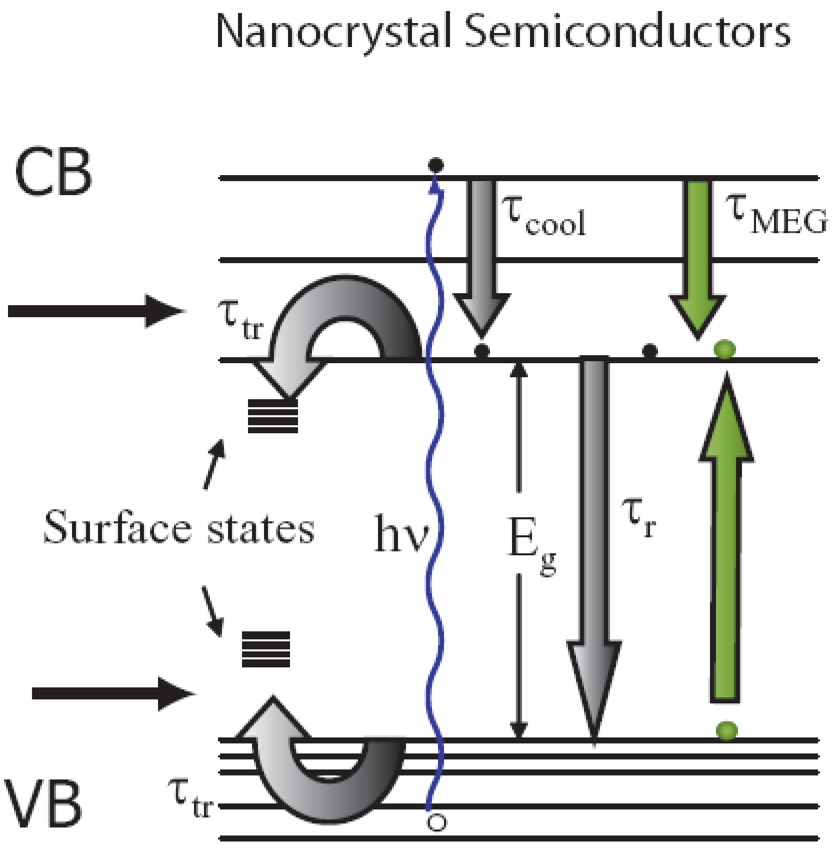


Theoretical transitions for four PbSe QD sizes with experimental transitions superimposed.



Observable size effects on particle absorbance

MEG in semiconductor nanocrystals



- Tunable bandgap
- Phonon bottleneck
- Surface traps

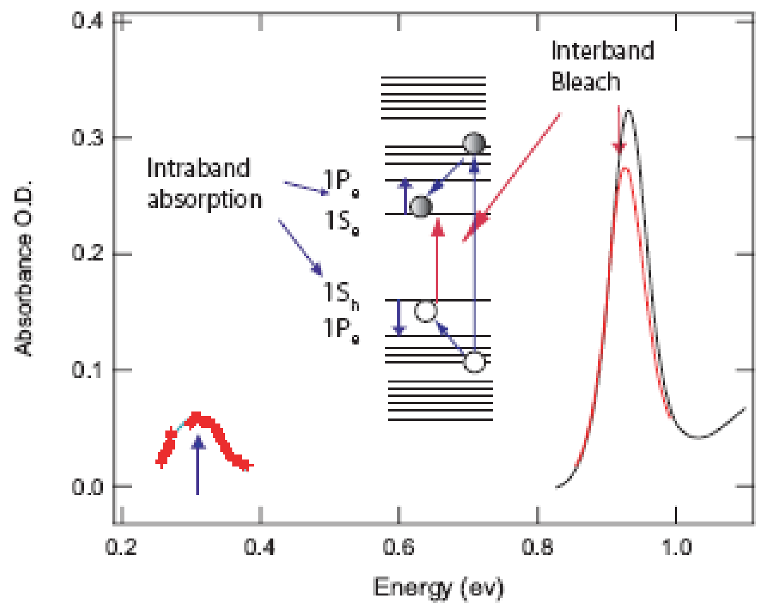
Femtosecond (fs) transient absorption spectroscopy

Step 1:

- Expose particle to short pulse (~200 fs) with $E_{hv} > E_g$
- Measure absorbance

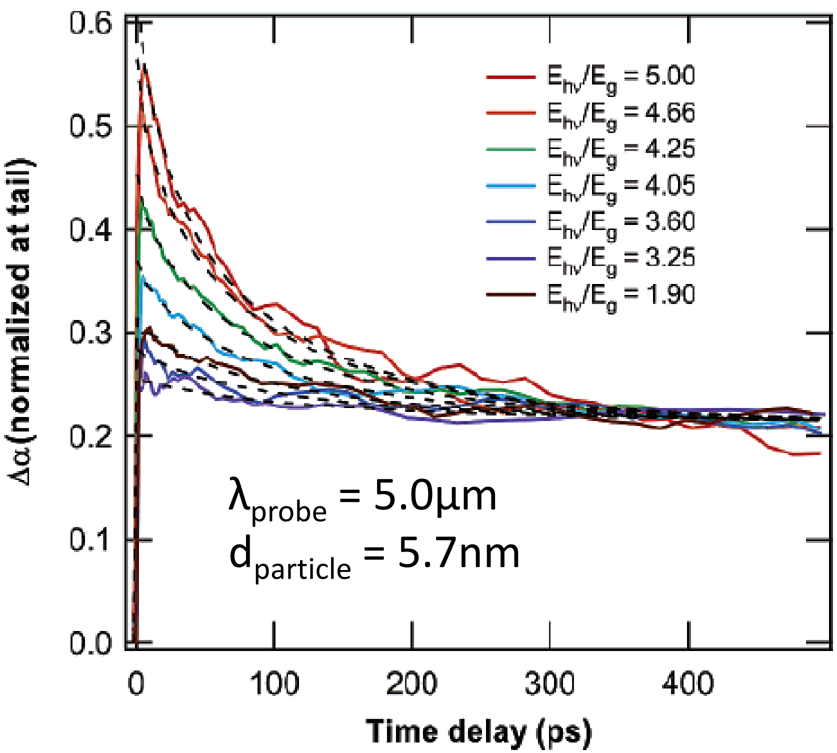
Step 2:

- Expose particle to short pulse (~1 ps) with $E_{hv} << E_g$
- Measure absorbance

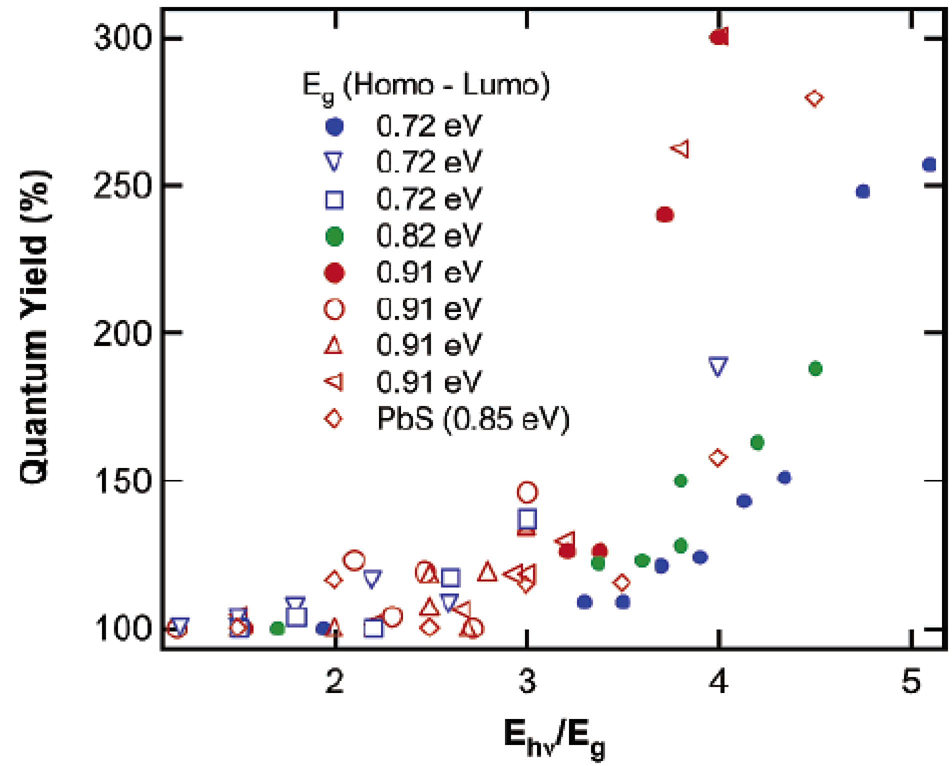


Experimental observation of pulse and probe absorbance

Exciton generation vs. E_g



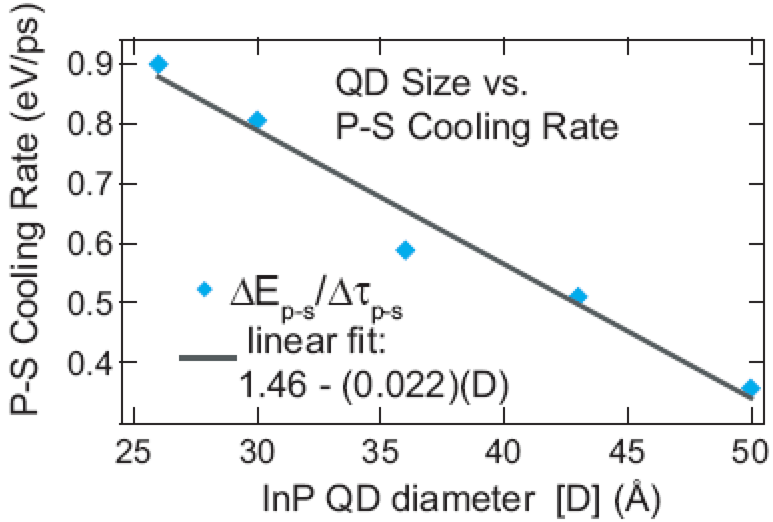
Exciton population decay dynamics obtained by probing intraband transitions



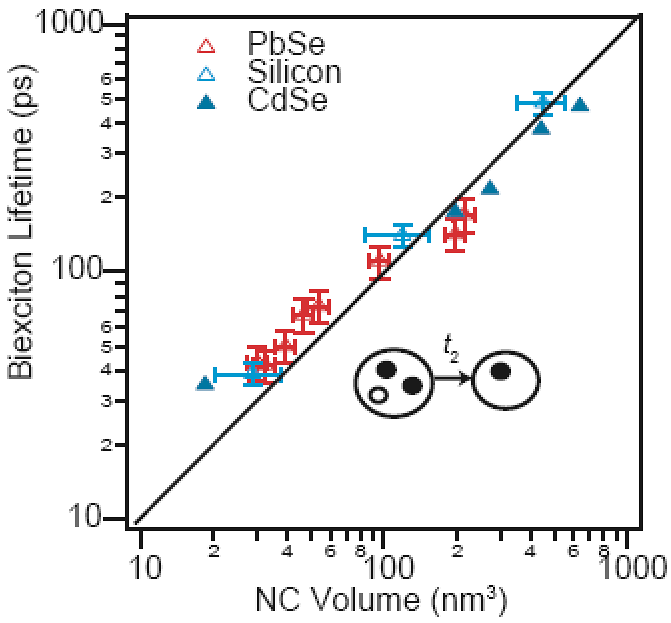
Quantum yield (QY) for exciton formation from a single photon vs. E_{hv}

Competing effects:
Cooling rate vs. particle diameter

– Electron cooling rate increases as size decreases

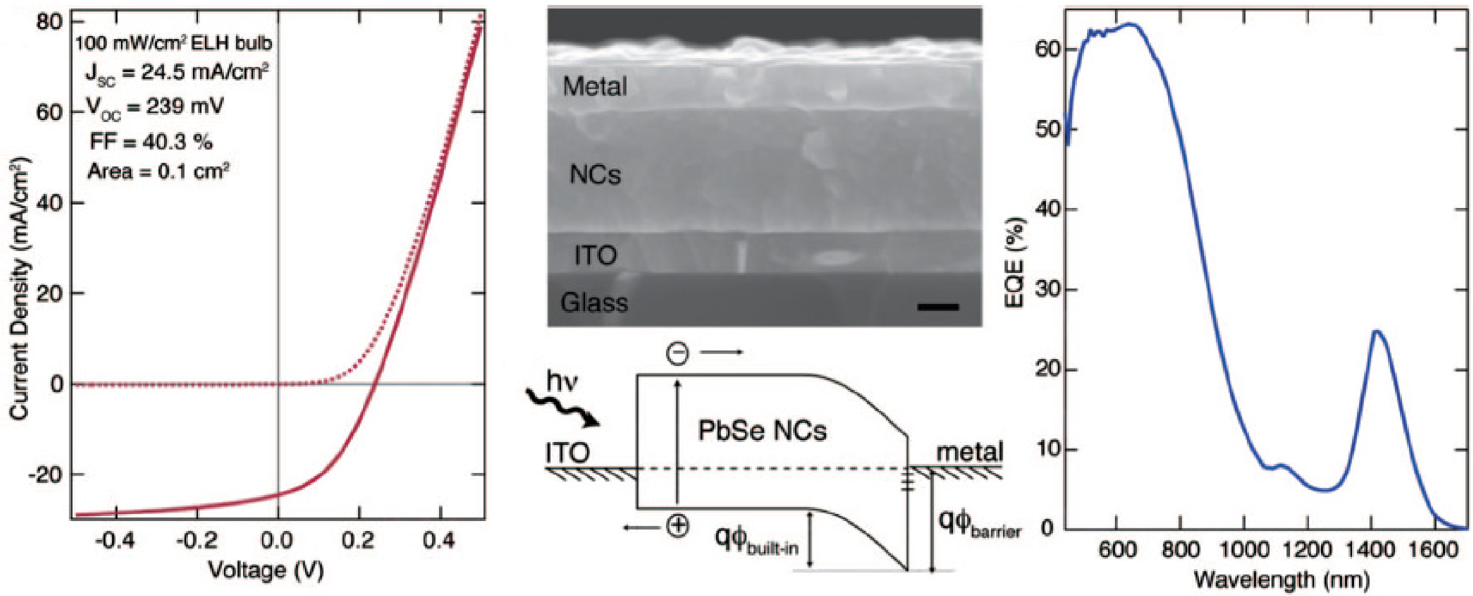


– Exciton lifetime decreases as size decreases



- State of current research
  - Multiple exciton generation has been measured
  - Carrier cooling rate has been slowed
- Toward potential applications
  - Must electronically couple NCs to their environment
  - High collection efficiencies must be achieved

Schottky solar cells from NC films



- Simple device architecture (ITO/NC/Metal)
- High external quantum yields (EQE > 65%)
- Record short circuit currents ($J_{SC} > 21$ mA·cm^{-2})
- Efficiency under solar illumination: 2.1%

Conclusion

- Semiconductor NCs are an inexpensive alterative to silicon devices which have the potential to achieve EQEs greater than 100%
- Particle size and composition precisely determine both MEG rate and cooling rate
- Practical application of this technology will require better electronic coupling and more efficient charge capture

References

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