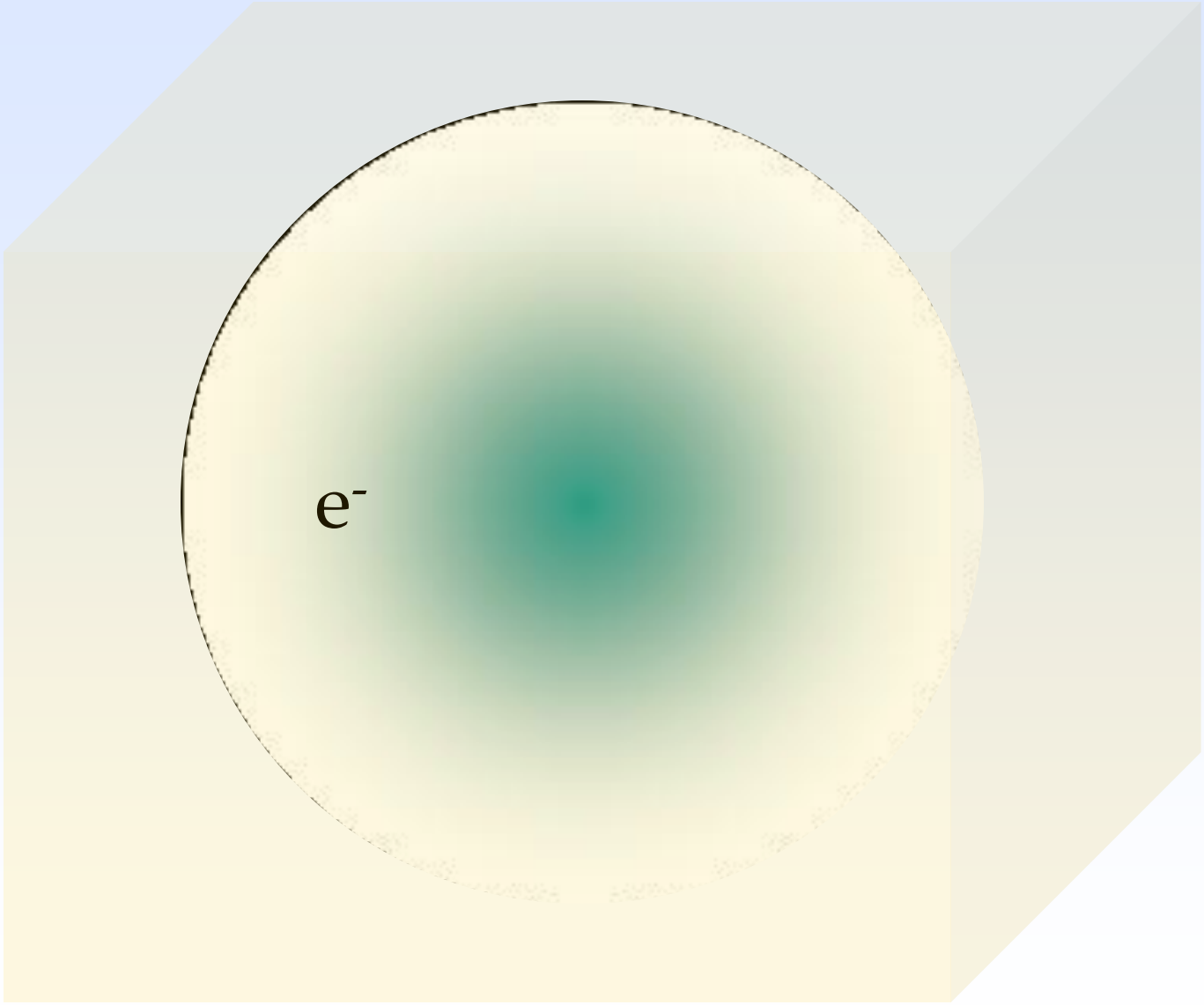
Nanostructured Semiconductor Crystals -- Building Blocks for Solar Cells: Shapes, Syntheses, Surface Chemistry, Quantum Confinement Effects

April 1,2014

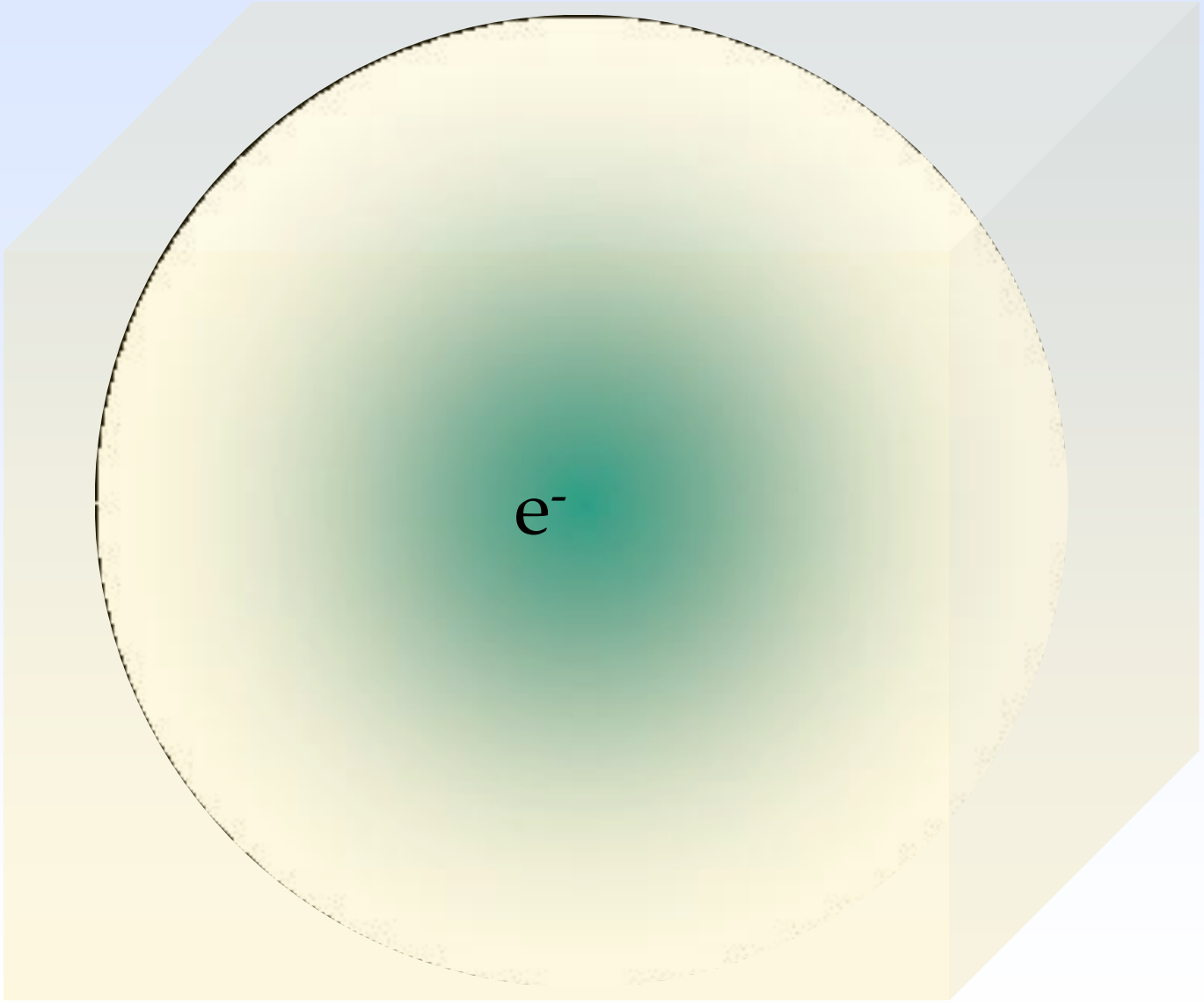
The University of Toledo, Department of Physics and Astronomy

Principles and Varieties of Solar Energy (PHYS 4400)

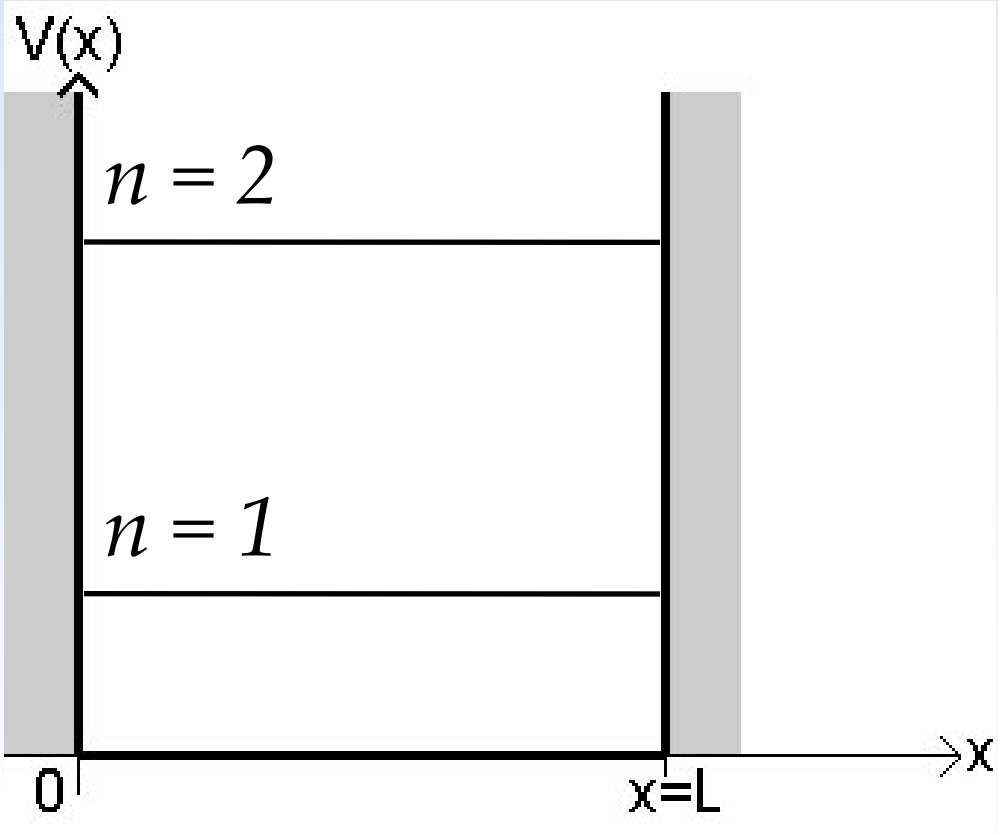
Quantum confinement effect



Quantum confinement effect (2)



Particle in a box (quantum well)



$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

The Potential, V(x), is 0 inside the box, and infinite elsewhere (infinite barriers)

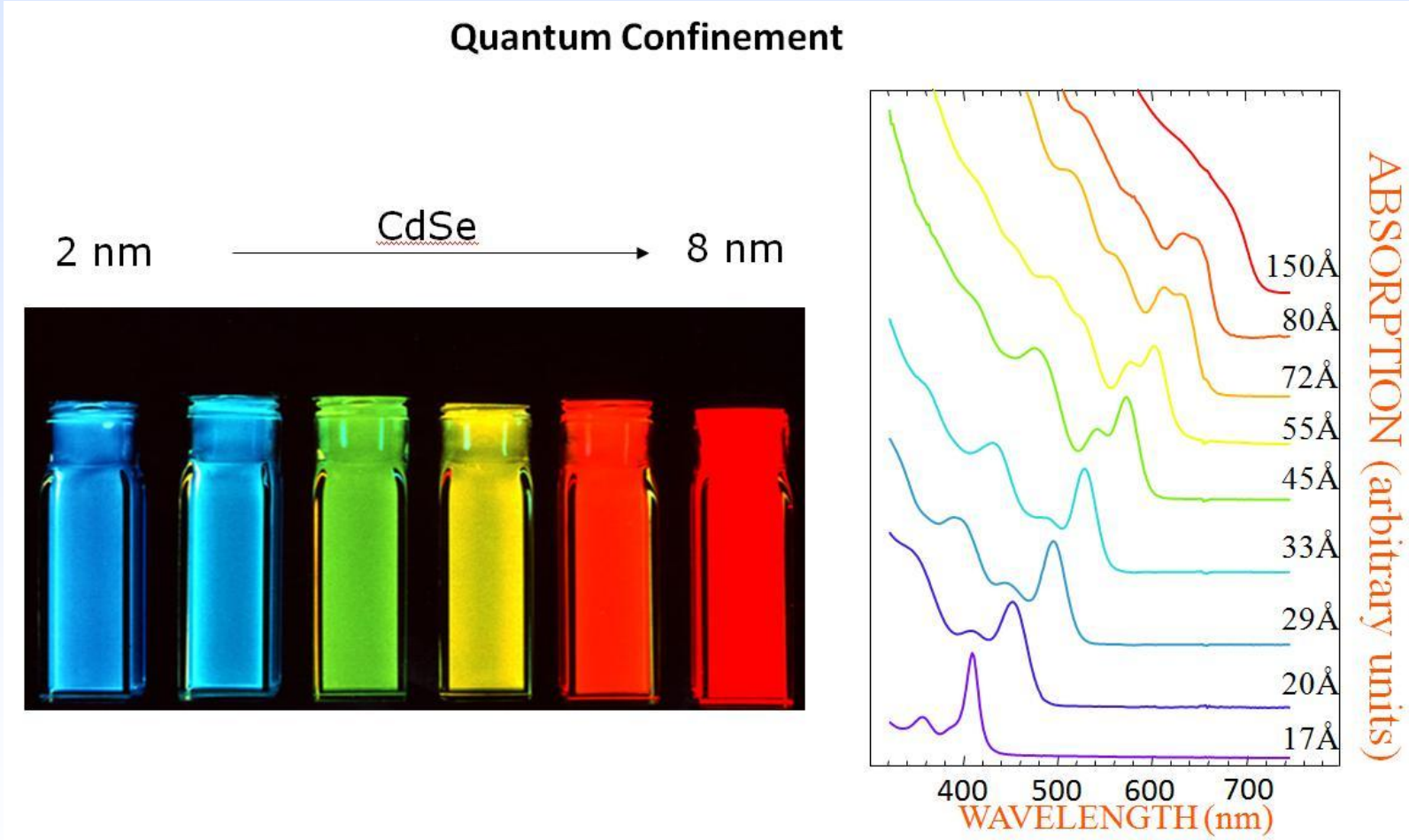
Nanomaterials for solar energy conversion

- Enable high surface area devices →
  - strong light absorption (dye-sensitized nanostructured TiO_2)
  - facilitates fast charge separation (proximity of photoexcited carriers to charge-separating interface)
- Customizable properties enable unique designs →
  - Engineerable (size-dependent) absorption spectrum
  - Varying geometries – e.g., efficient charge transport in quantum rods, nanotubes
  - Controlled chemical functionalization to direct charge separation
- Efficient multiple exciton generation

Consequences of Quantization

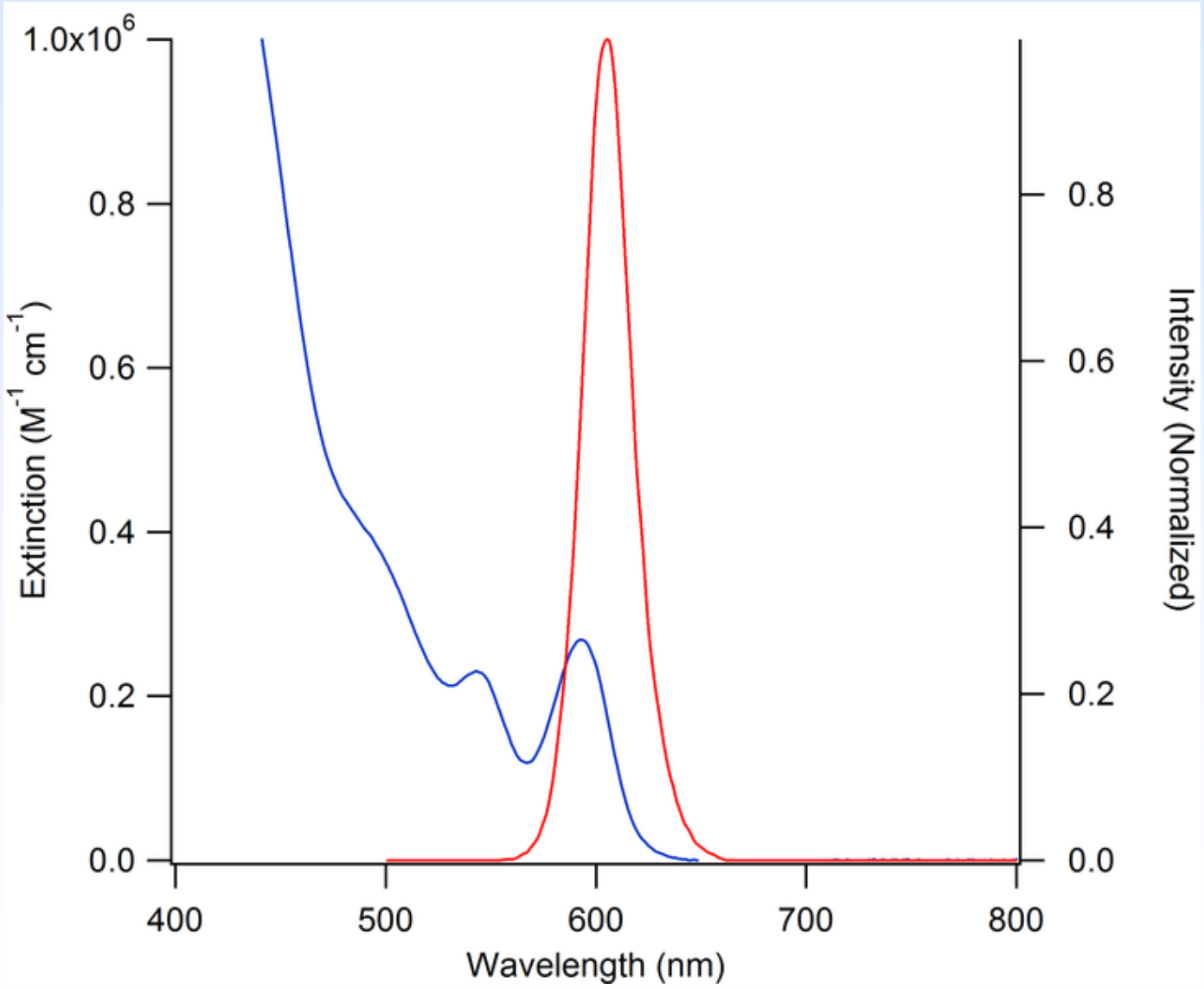
- *Dramatic variation of optical and electronic properties*
- *Large blue shift of absorption edge*
- *Discrete energy levels/structured absorption and photoluminescence spectra*
- *Enhanced photoredox properties for photogenerated electrons and holes*
- *Enhanced Inverse Auger (impact ionization, or multiple exciton generation)*
- *Slowed relaxation and cooling of photogenerated hot electrons and holes (controversial)*
- *PL blinking in single QDs*
- *Conversion of indirect semiconductors to direct semiconductors or vice versa*
- *Greatly enhanced non-linear optical properties*
- *Greatly modified pressure dependence of phase changes and direct to indirect transitions*
- *Efficient anti-Stokes luminescence*

Size-dependent optical properties



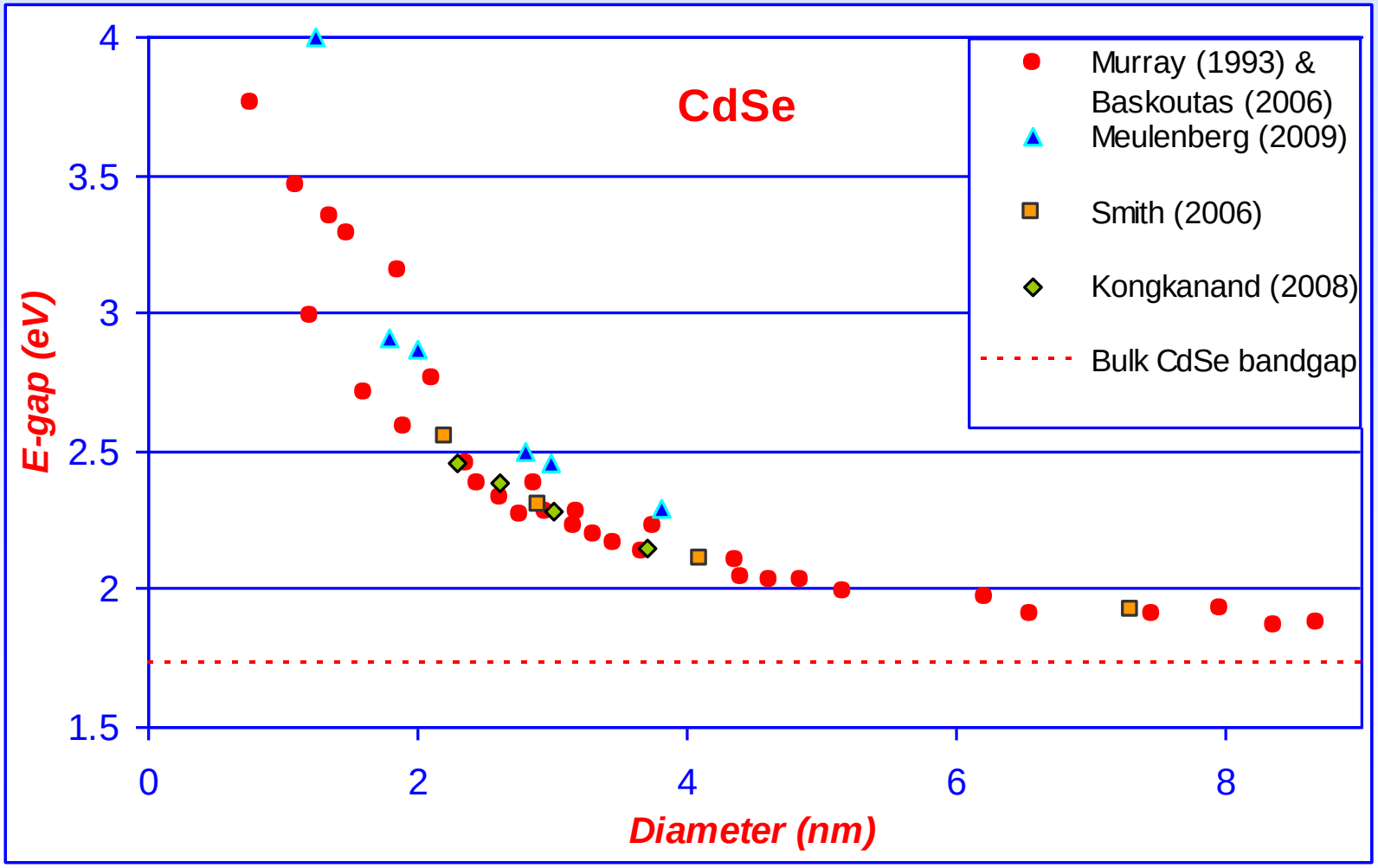
http://nanocluster.mit.edu/research.php

Absorption and emission (CdSe nanocrystals)



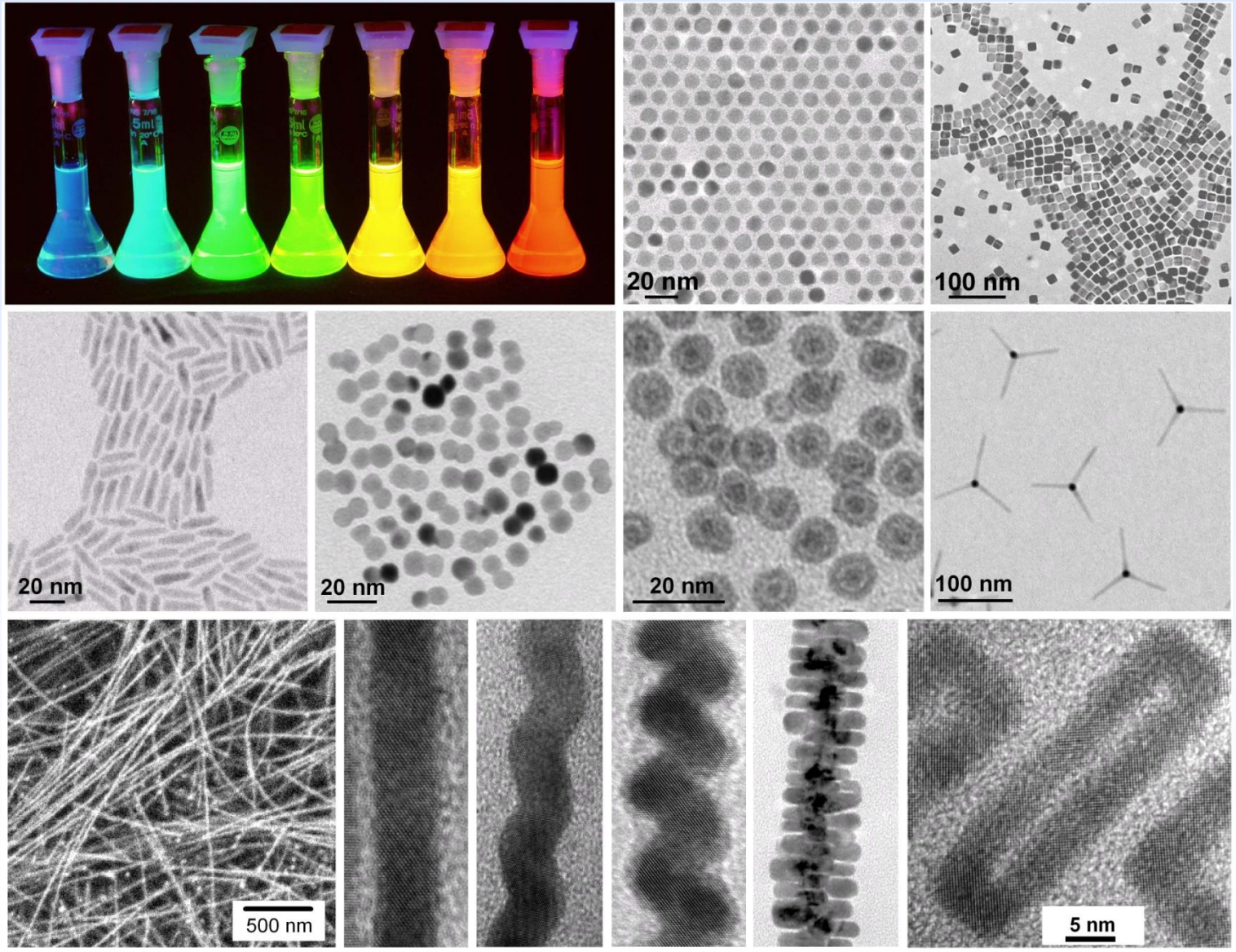
http://en.wikipedia.org/wiki/File:EF_605_spectra.png

Size-dependent bandgap of CdSe NCs



From *"Physical and Optical Properties of Colloidal Semiconducting Nanocrystals for Solar Absorption"*, by Abdel Ibdah (UT)

Colloidal nanostructures (crystalline)



http://talapinlab.uchicago.edu

Quantum Confined Structures – Density of States

The number of states between k and k + dk in 3, 2, and 1 dimensions:

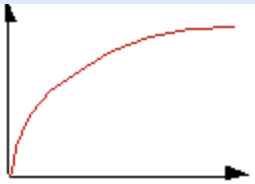
$$\frac{dN_{3D}}{dk} = 2\left(\frac{L}{2\pi}\right)^3 4\pi k^2, \quad \frac{dN_{2D}}{dk} = 2\left(\frac{L}{2\pi}\right)^2 2\pi k, \quad \frac{dN_{1D}}{dk} = 2\left(\frac{L}{2\pi}\right)$$

$$g_{c,3D} = \frac{8\pi\sqrt{2}}{h^3} m_{eff}^{3/2} \sqrt{E - E_{\min}}$$

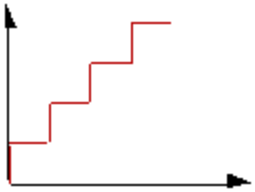
$$g_{c,2D} = \frac{4\pi m_{eff}}{h^2}$$

$$g_{c,1D} = \sqrt{\frac{2\pi m_{eff}}{h^2}} \frac{1}{\sqrt{E - E_{\min}}}$$

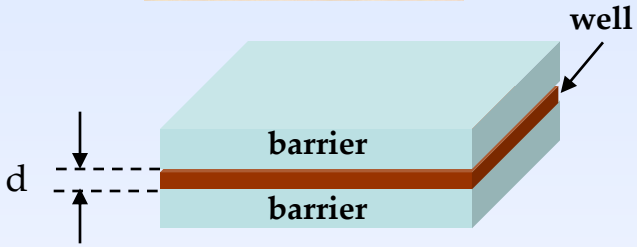
Quantum confinement effect on density of electronic states



Bulk Semiconductor

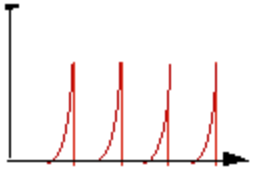


Quantum Well

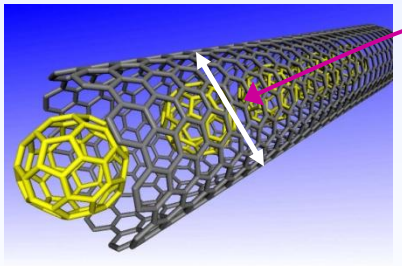


$d < a_B$ (Bohr exciton size)

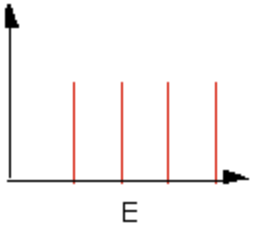
N(E)



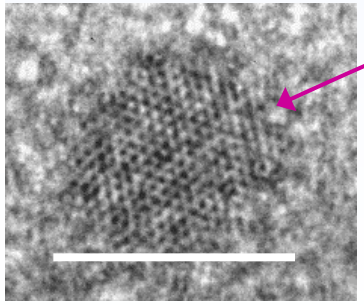
Quantum Wire



~1 nm



Quantum Dot
(or Nanocrystal)



~6 nm dia.

60 Å InP QD

Dimensionality

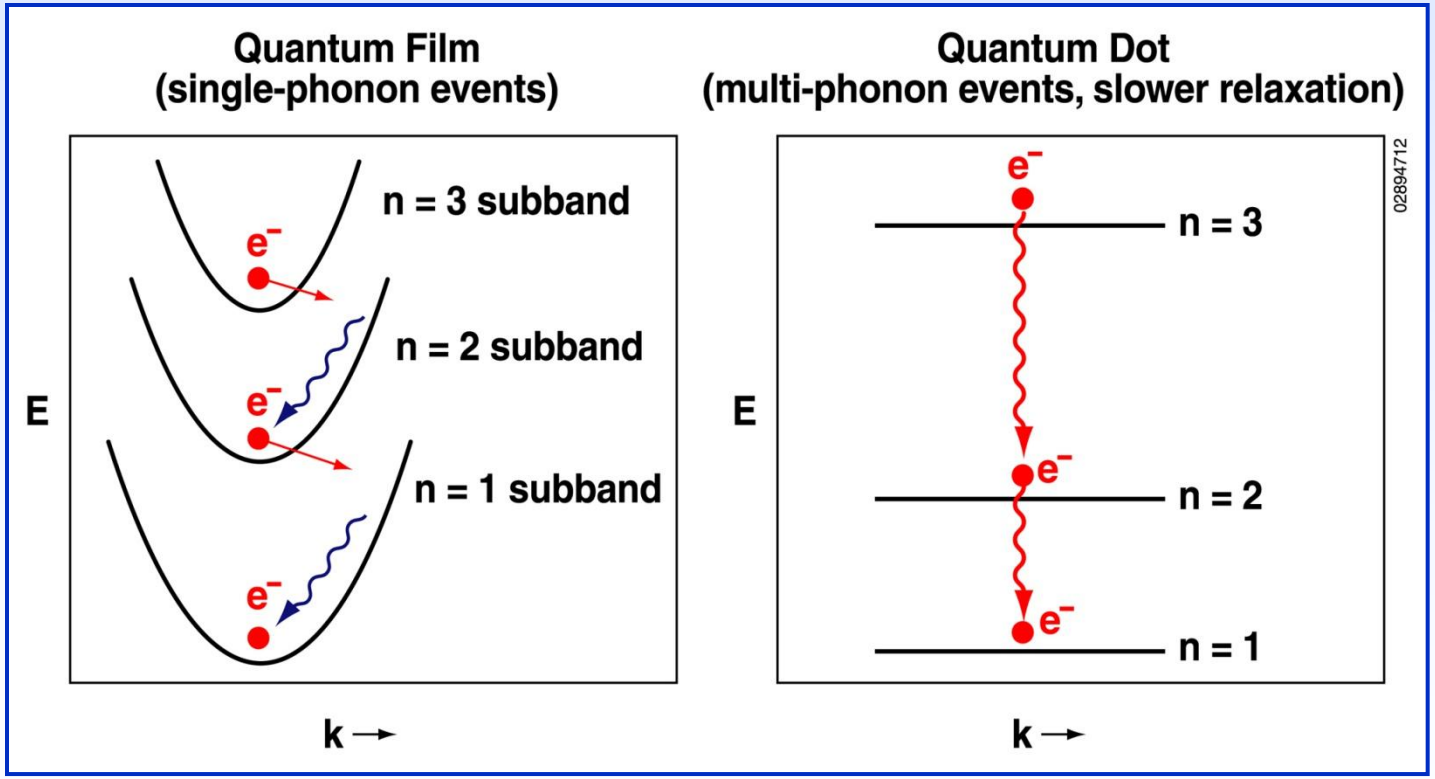
3D

2D

1D

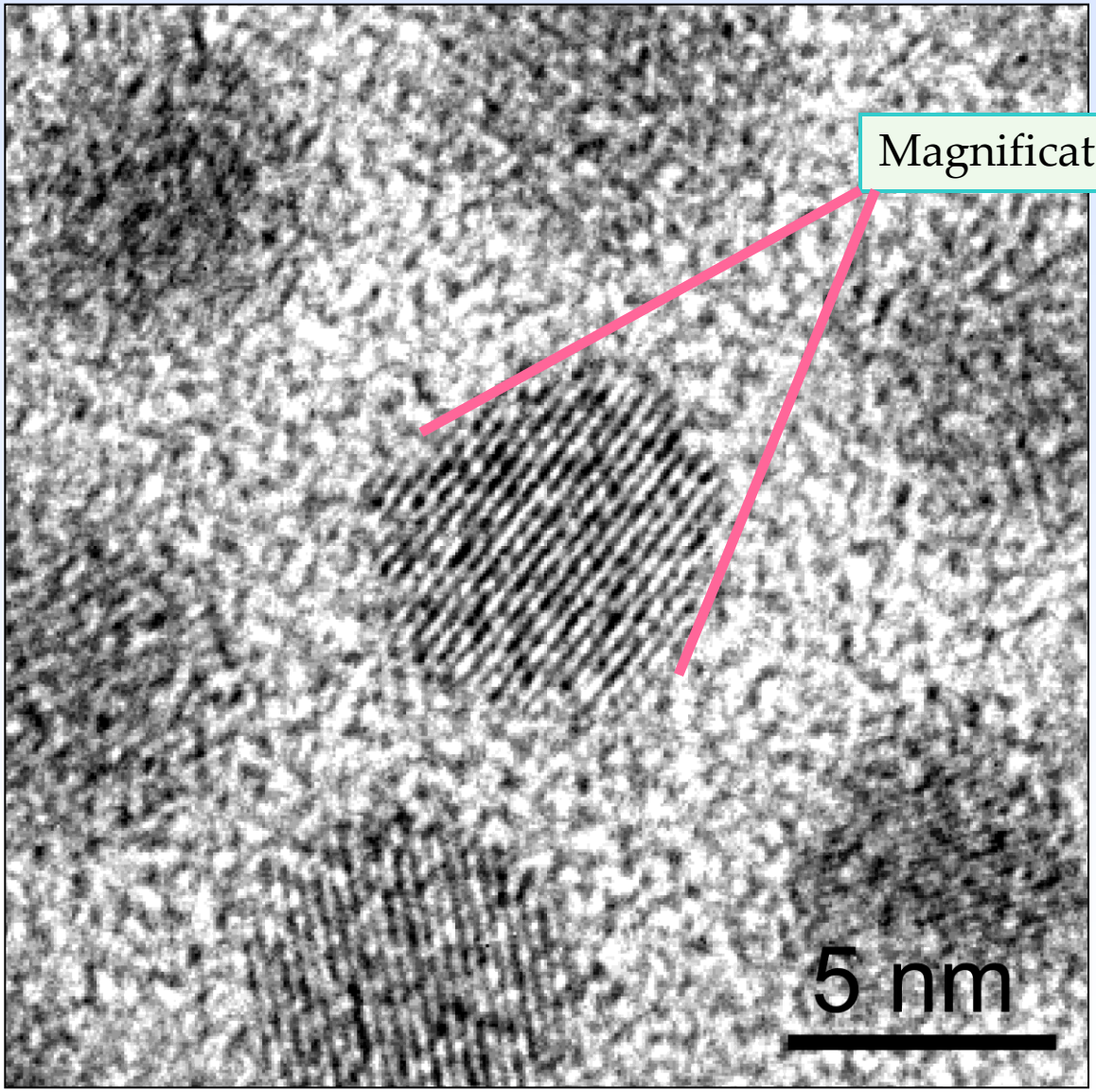
0D

Quantum Films vs Quantum Dots



phonon bottleneck

Transmission electron micrograph (TEM) of Lead Selenide NCs



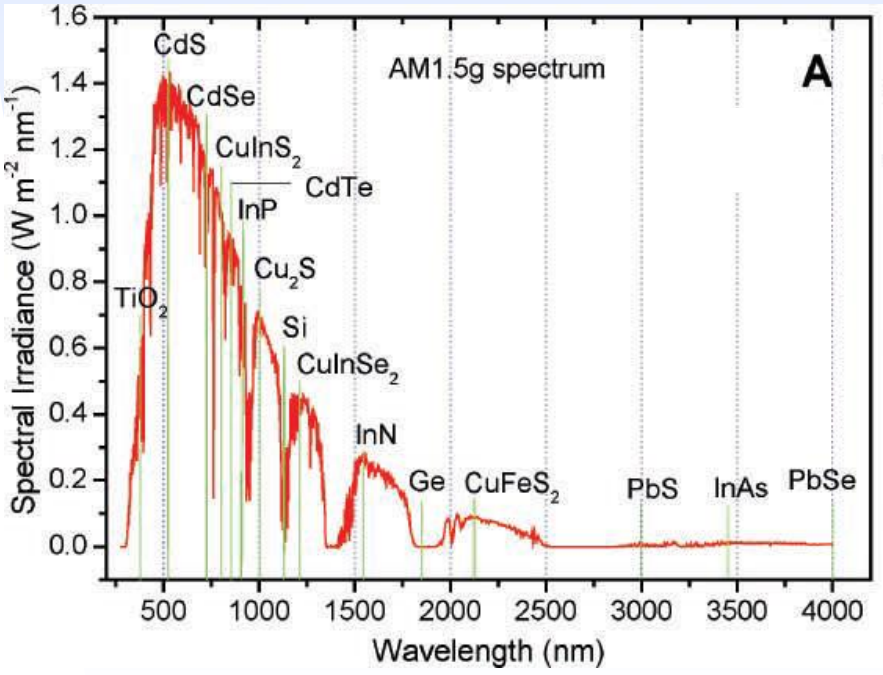
PbSe

Synthesis of colloidal nanocrystals

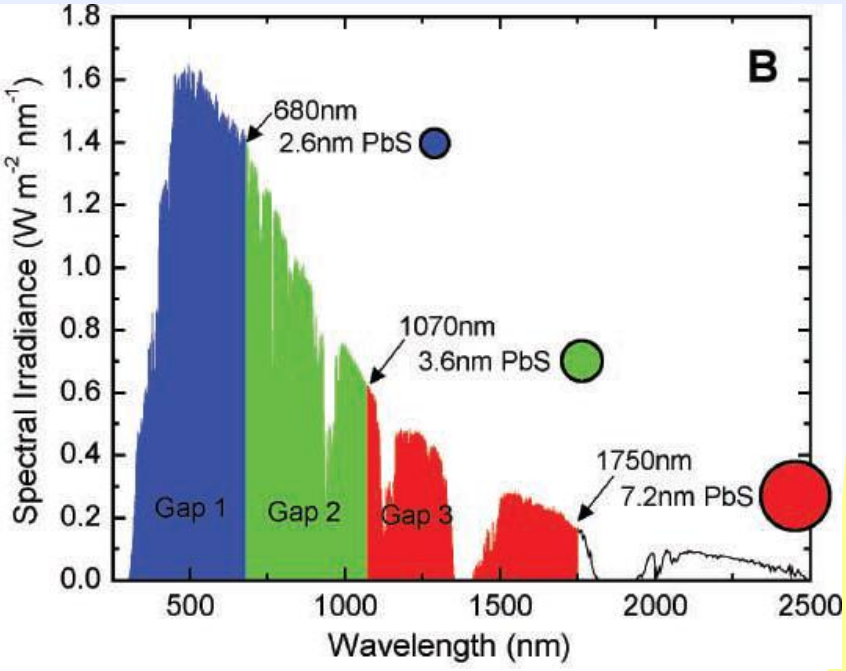
Typical three-headed flask set up. The middle head is connected to the Schlenk line's glass manifold. The left head is covered with a septum pierced by the thermocouple. The right head is for injection. Photo and caption courtesy of T. Kinner (UT).

Why pursue QD solar cells?

1. Colloidal synthesis produces high-quality nanocrystals
2. Solution processed, tunable band-gap
3. Potentially easy to process (room temperature, ambient air)
4. Scientifically interesting: balance quantum confinement w/ transport
5. Flexibility (?)



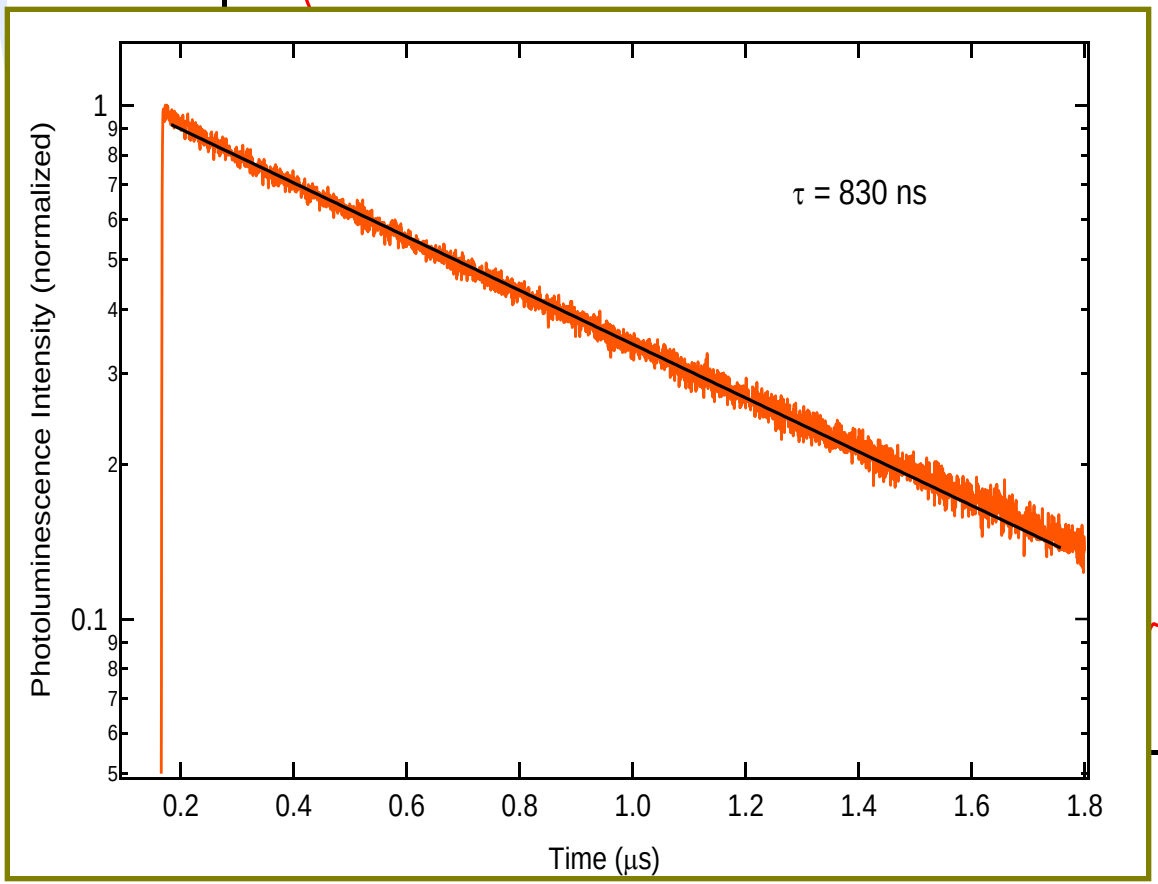
AM1.5G solar spectrum along with some common bulk semiconductors band-gaps



Triple junction PbS dot size

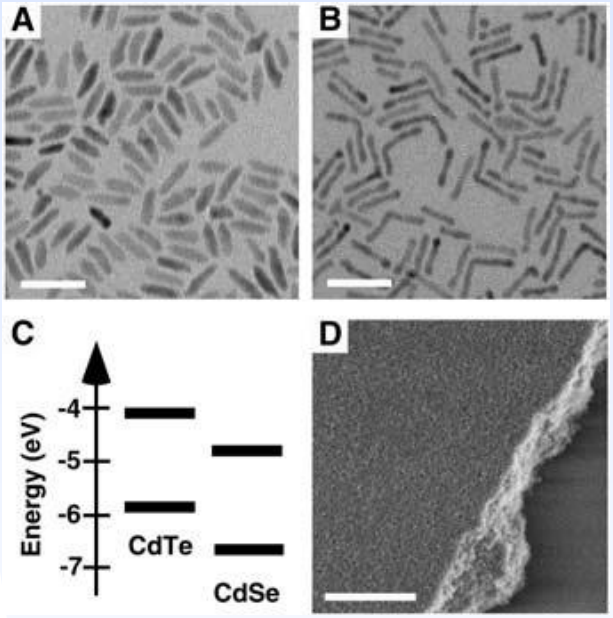
J. Tang, *et al.*, ***Adv. Mater***. *22,1(2010)*

Colloidal PbSe QDs in tetrachloroethylene (TCE)

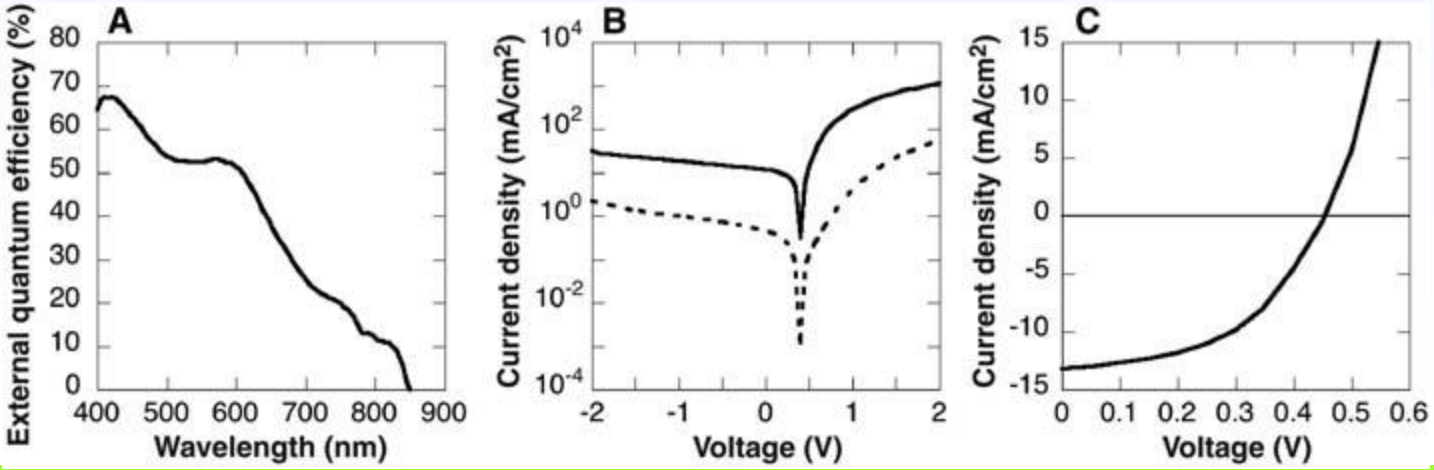


Annealed NC-based solar cell

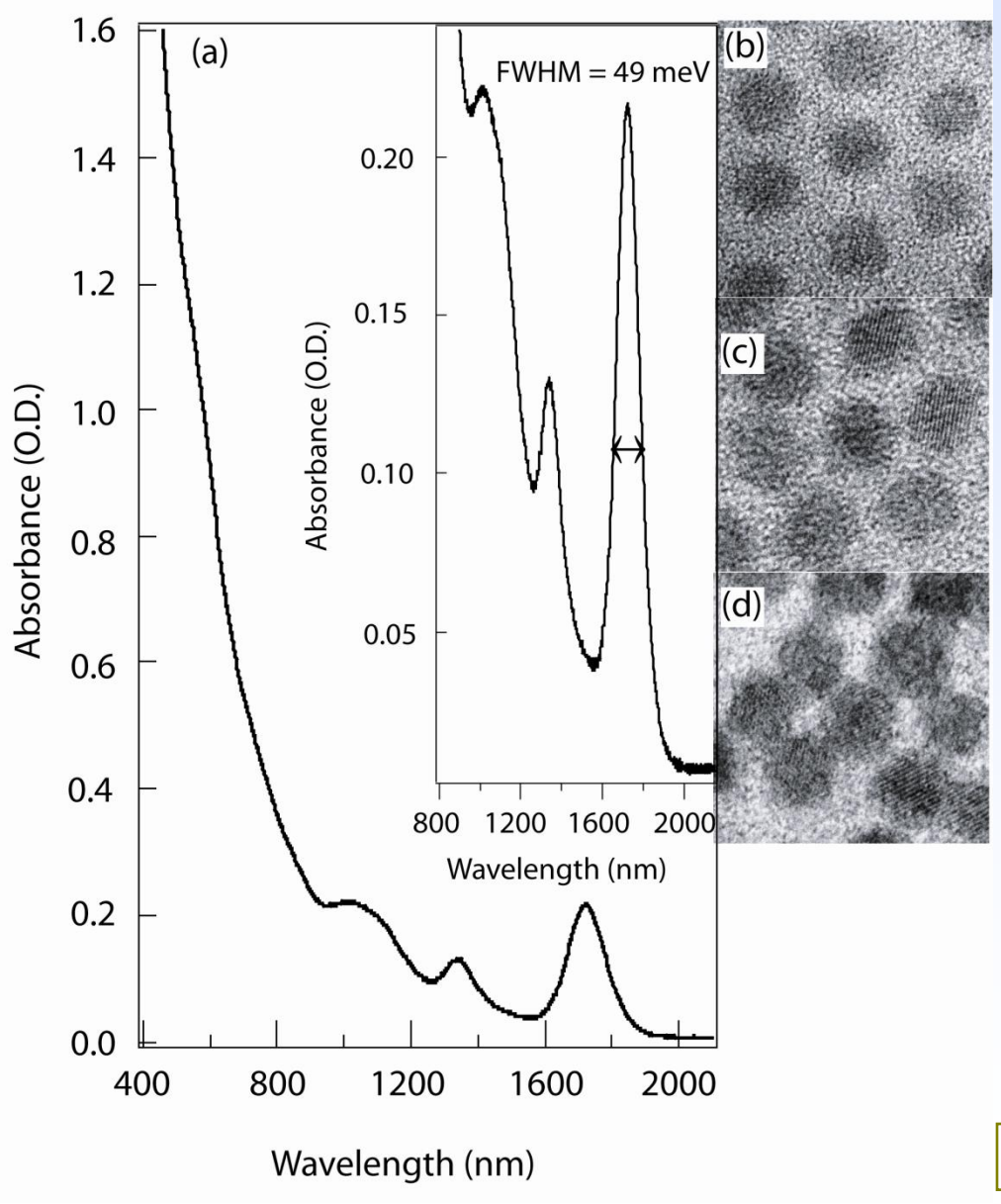
Air-Stable All-Inorganic Nanocrystal Solar Cells Processed from Solution
Ilan Gur, Neil A. Fromer, Michael L. Geier, A. Paul Alivisatos
21 OCTOBER 2005 VOL 310 SCIENCE



Transmission electron micrographs of (A) CdSe and (B) CdTe NCs used in this investigation. Scale bar, 40 nm. (C) An energy diagram of valence and conduction band levels for CdTe and CdSe illustrates the type II charge-transfer junction formed between the two materials…



Drop-cast films of 5.7 nm dia. PbSe NCs



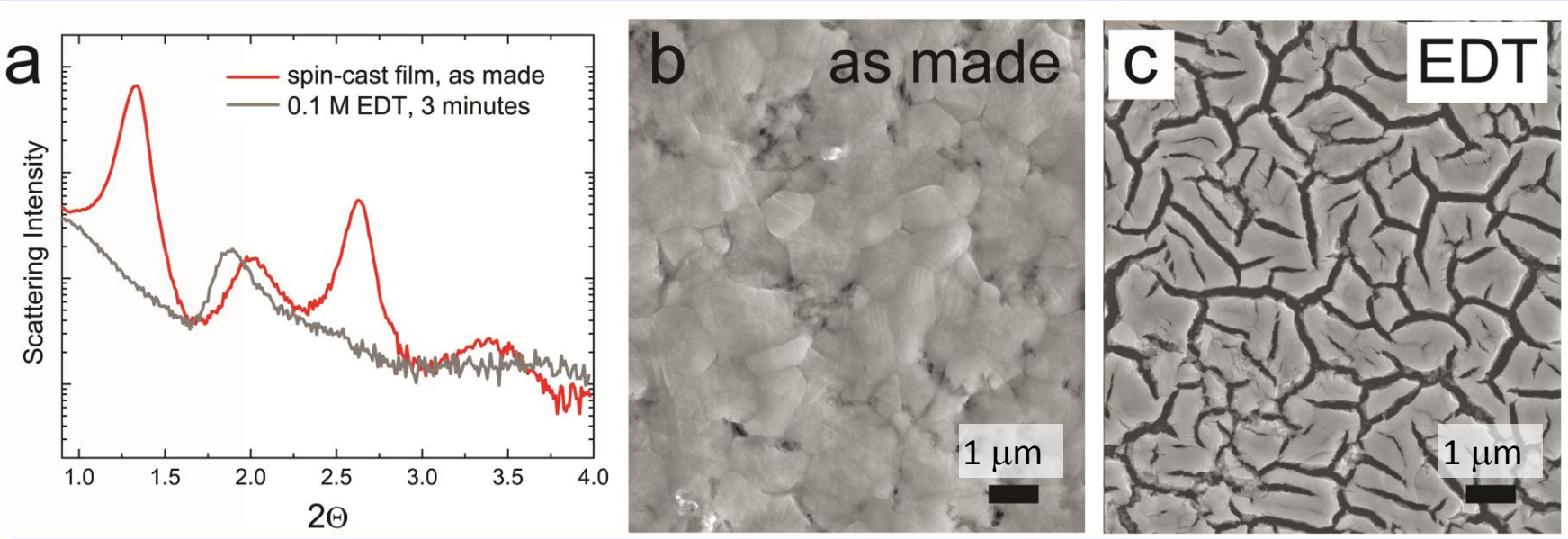
oleic acid (1.8 nm)

aniline (0.8 nm)

ethylenediamine (0.4 nm)

J. E. Murphy *et al.*, JACS **128**, 3241 (2006).

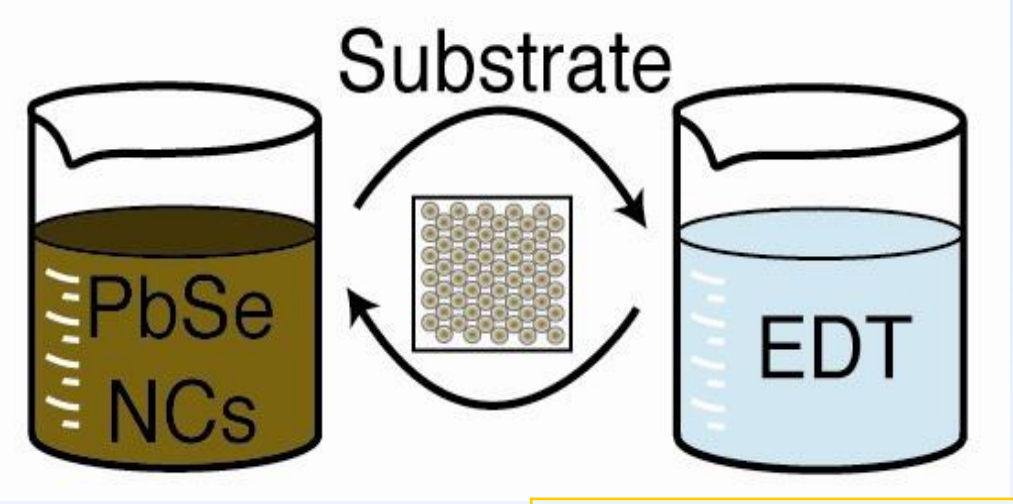
Post-casting treatment of spin-cast films of PbSe NCs



"Microstructure of the spin-cast NC films before and after EDT treatment. (a) SAXS data, showing a ~16 Å decrease in the spacing between the NCs and a dramatic loss of superlattice order upon EDT treatment. Measurements were taken in air. (b, c) Plan-view SEM images of (b) an untreated film and (c) a treated film."

J. Luther, M. Law et al., ACS Nano 2, 271 (2008).

Layer-by-layer fabrication of PbSe NC films

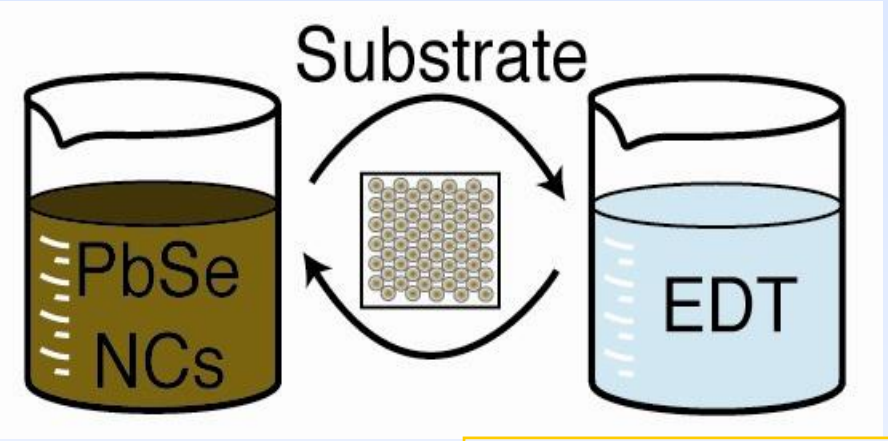


EDT = 1,2-ethanedithiol

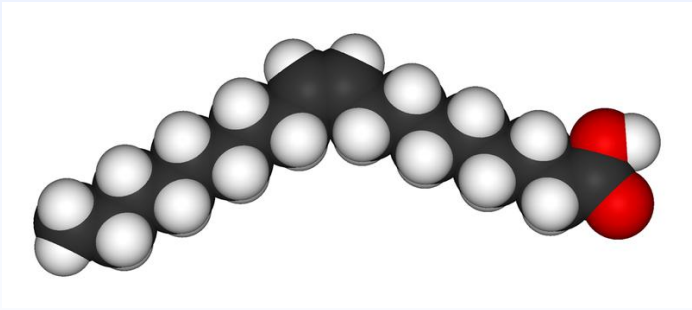
Layer by layer (LbL) fabrication of PbSe nanocrystal (NC) films. Nanocrystal films prepared by dip-coating, alternating between (1) PbSe NCs in hexane and (2) 0.1 M EDT in anhydrous acetonitrile, allowing the film to dry between each layer.

J. M. Luther, M. Law *et al.*, "Structural, Optical, and Electrical Properties of Self-Assembled Films of PbSe Nanocrystals Treated with 1,2-Ethanedithiol", *ACS Nano* **2**, 271 (2008).

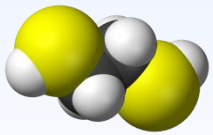
Ligand exchange in PbX NC films



EDT = 1,2-ethanedithiol

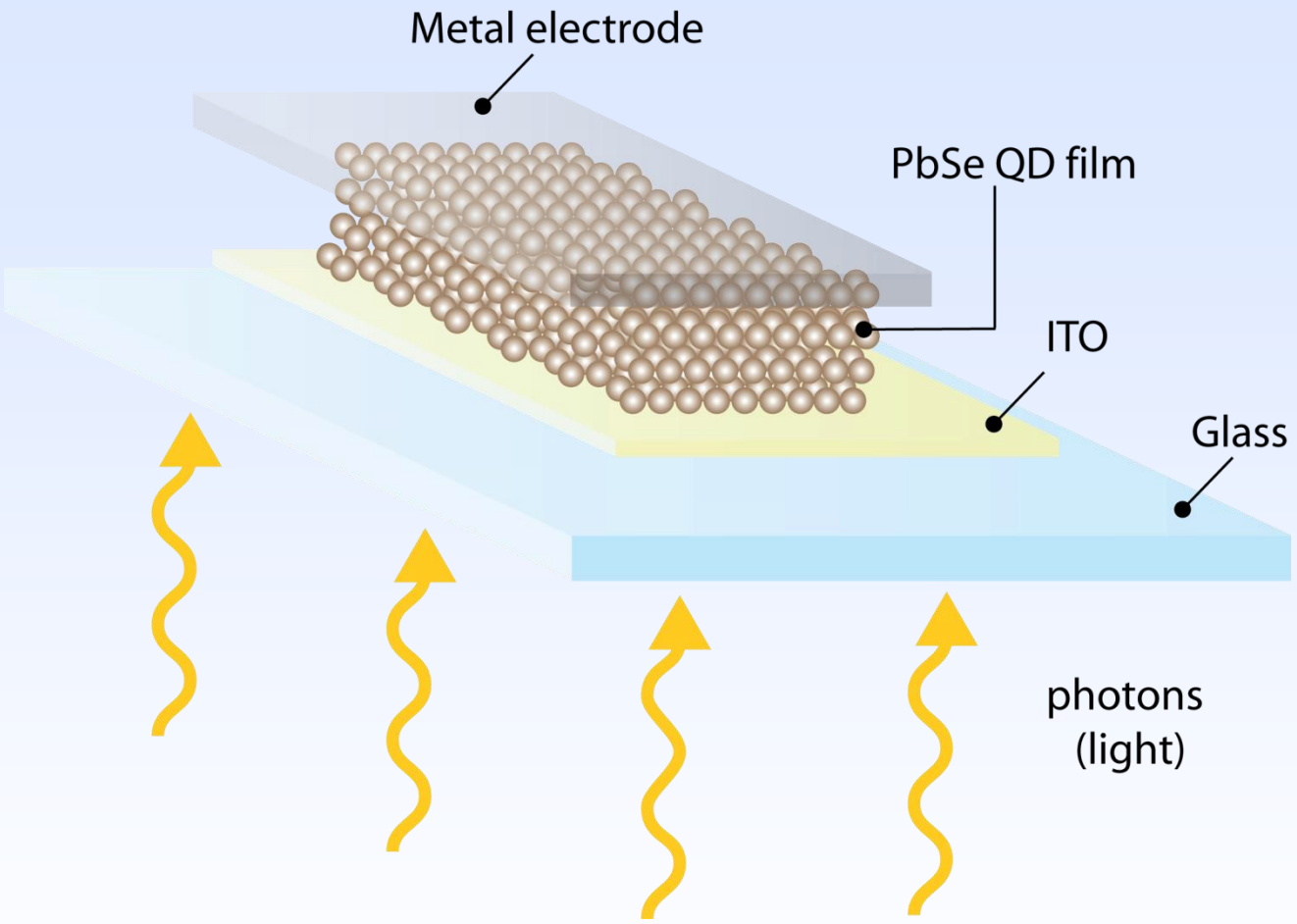


Oleic acid, $C_{18}H_{34}O_2$
L ≈ 20 Å



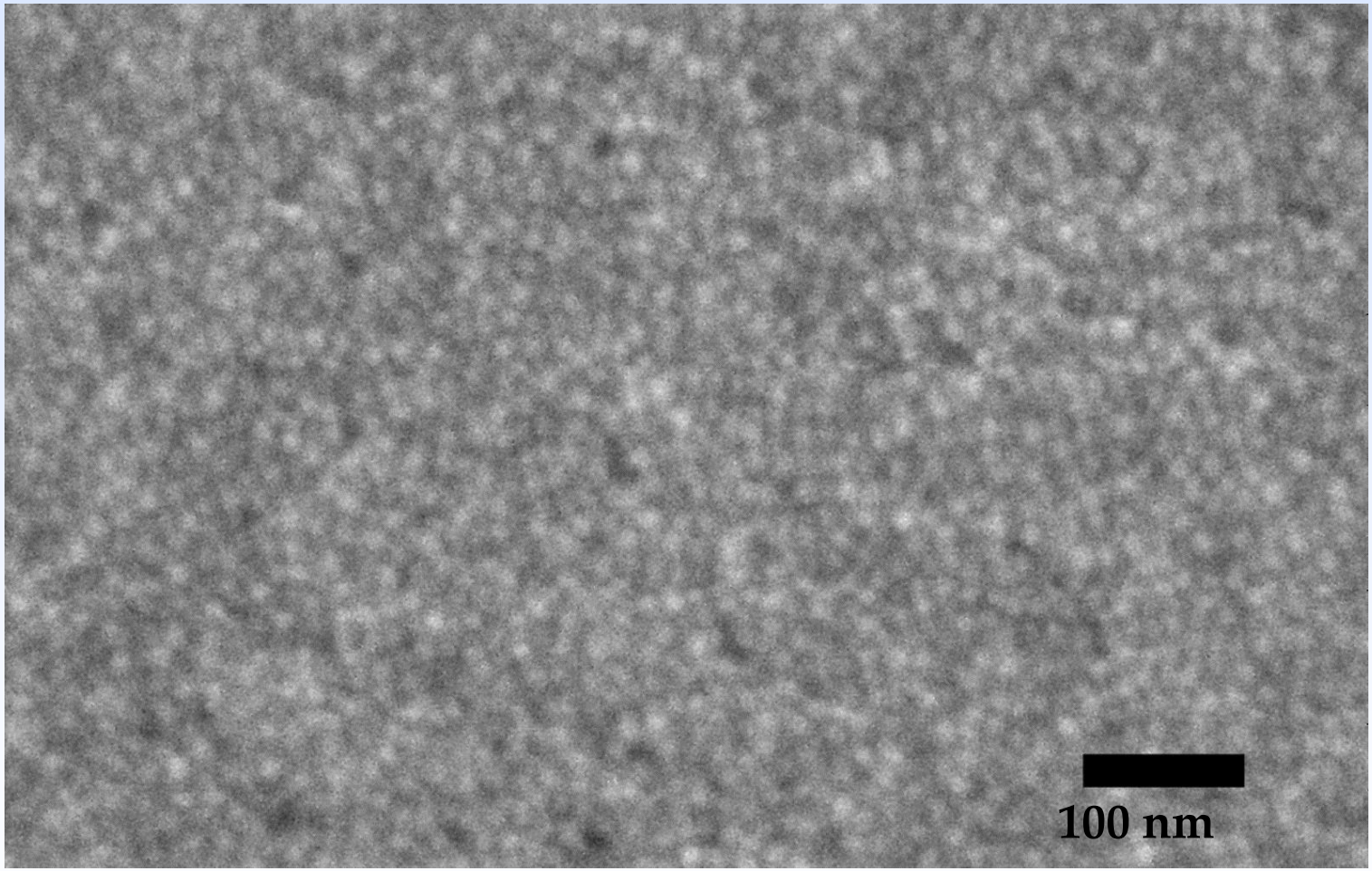
1,2-ethanedithiol
$C_2H_6S_2$
L ≈ 6 Å

Schottky barrier nanocrystal-based solar cell



- For MEG: Auger recombination typically occurs on $\lesssim$ 100 ps timescale (need fast exciton dissociation and/or diffusion to low density)
- High long-range mobility desired
- EQE > 100% would provide MEG process/concept confirmation

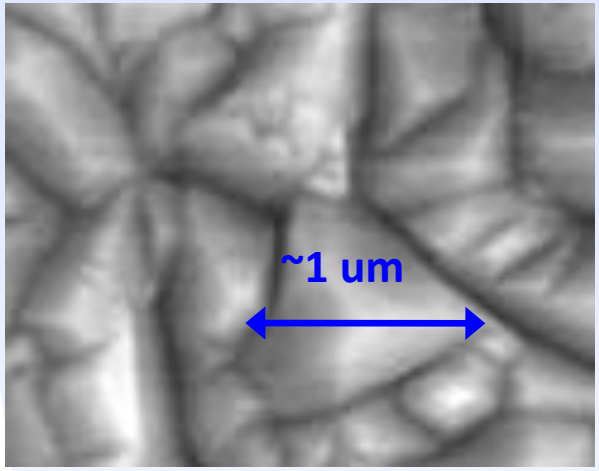
Layer-by-layer dip-coated PbSe films



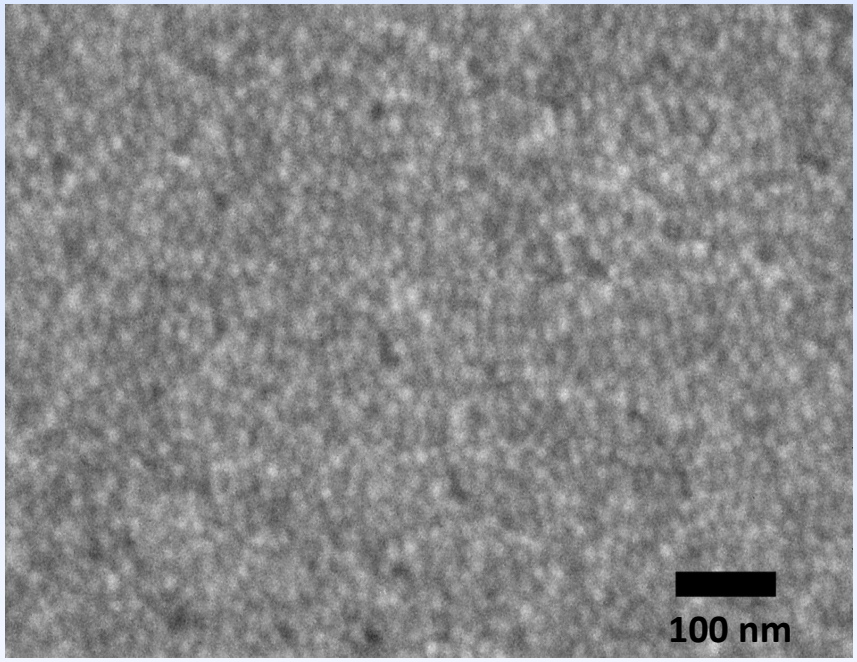
Plan view SEM image of PbSe NC films prepared by layer-by-layer dip coating onto ITO substrate. LbL film shown was produced using 10-20 dip coating cycles.

J. Luther, M. Law *et al.*, *ACS Nano* **2**, 271 (2008).

“Grain boundary” density considerations



e.g. CdTe



Estimating effective “grain boundary densities” (boundary area / layer area)

CdTe: ~1 μm grain size (assumed cubic grains, ~ 1 μm thick layer):

3 ($\mu m^2/ \mu m^2$)

PbSe QD film: ~5 nm “grain size” (assumed cubic grains 5 nm on a side, 1 μm thick film):

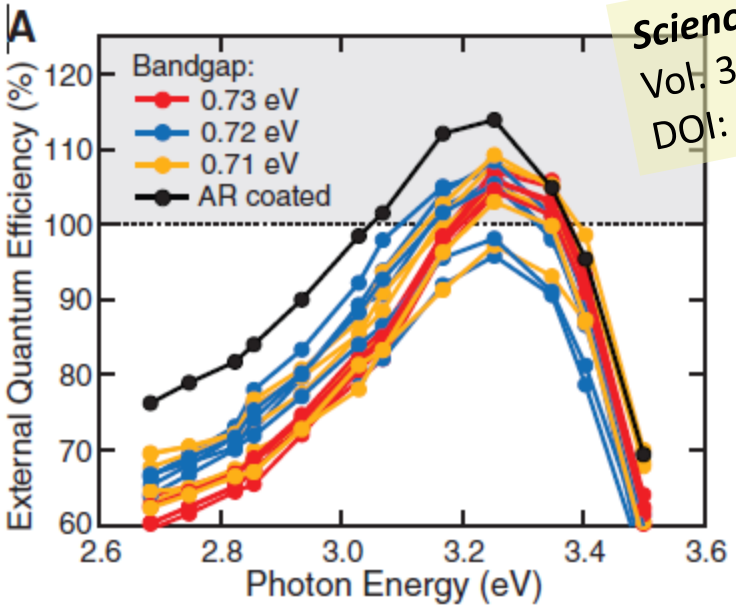
600 ($\mu m^2/ \mu m^2$)

$S/V \propto 1/r$

Directions in QD-based solar cell research

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]*



Science 16 December 2011:
Vol. 334 no. 6062 pp. 1530-1533
DOI: 10.1126/science.1209845

Roll-to-roll processing from solution source (e.g., Nanosolar CIGS)

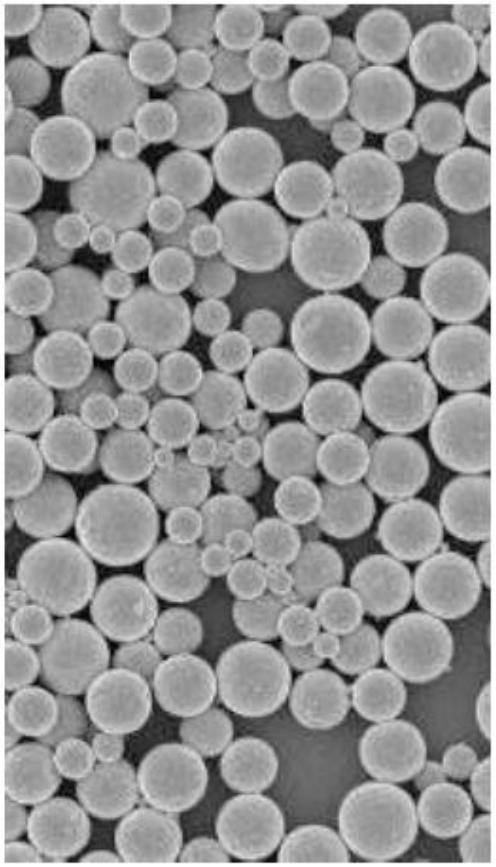


Figure 6 and 7: A laboratory sample of our nanoparticle ink. Nanoparticles shown to the right are an average of 20nm in diameter.

from NanoSolar white paper

Good solar cells from nanoparticle inks (CIGS)

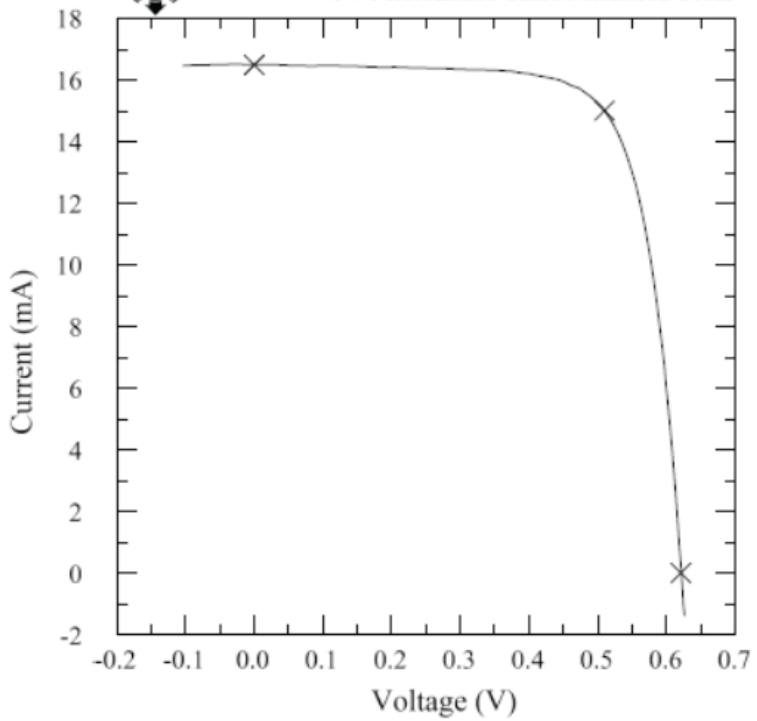
Nanosolar

$CdS/Cu(In,Ga)Se_2$ Cell

Device ID: H09B071-01C #2
Apr 09, 2009 12:31
Spectrum: ASTM G173 global

Device Temperature: 24.0
Device Area: 0.5000 cm^2
Irradiance: 1000.0 W/m^2

NREL X25 IV System Confidential
PV Performance Characterization Team



V_{oc} = 0.6214 V	I_{max} = 15.010 mA
I_{sc} = 16.490 mA	V_{max} = 0.5101 V
J_{sc} = 32.980 mA/cm^2	P_{max} = 7.6540 mW
Fill Factor = 74.70 %	Efficiency = 15.31 %

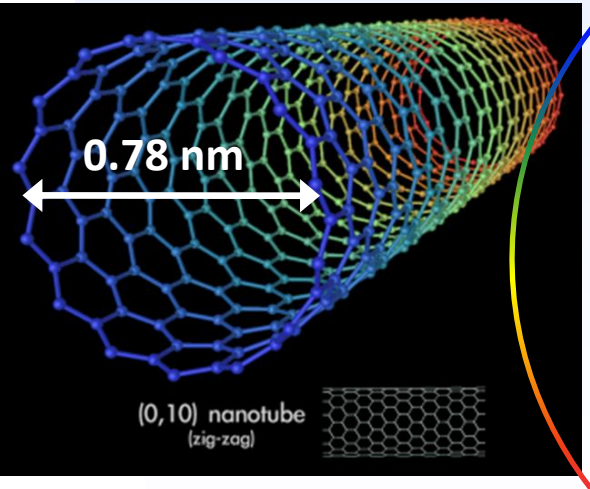
from NanoSolar white paper

Colloidal semiconductor nanocrystals

- Solution synthesis, typically at elevated temperature
- Inorganic crystalline core surrounded by organic capping molecules
- Most frequently suspended in organic solvents
- Can be stored stably either in powder or solution form

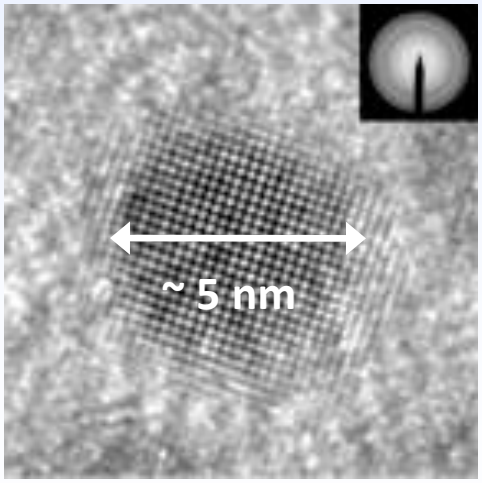
Colloidal semiconductor NCs have typical diameters of 1 nm to 10 nm

SWNT (10,0)



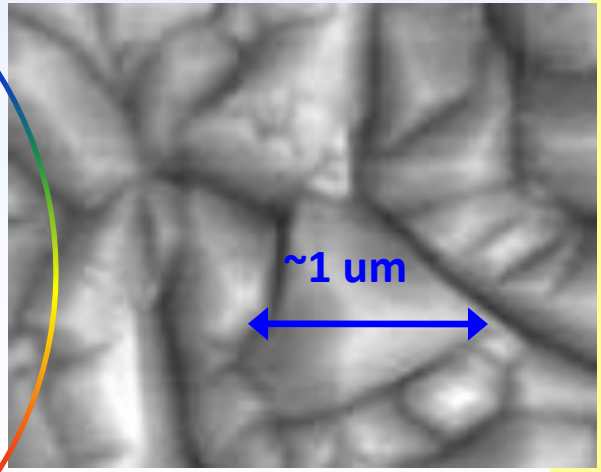
http://commons.wikimedia.org/wiki/Main_Page

PbS NC



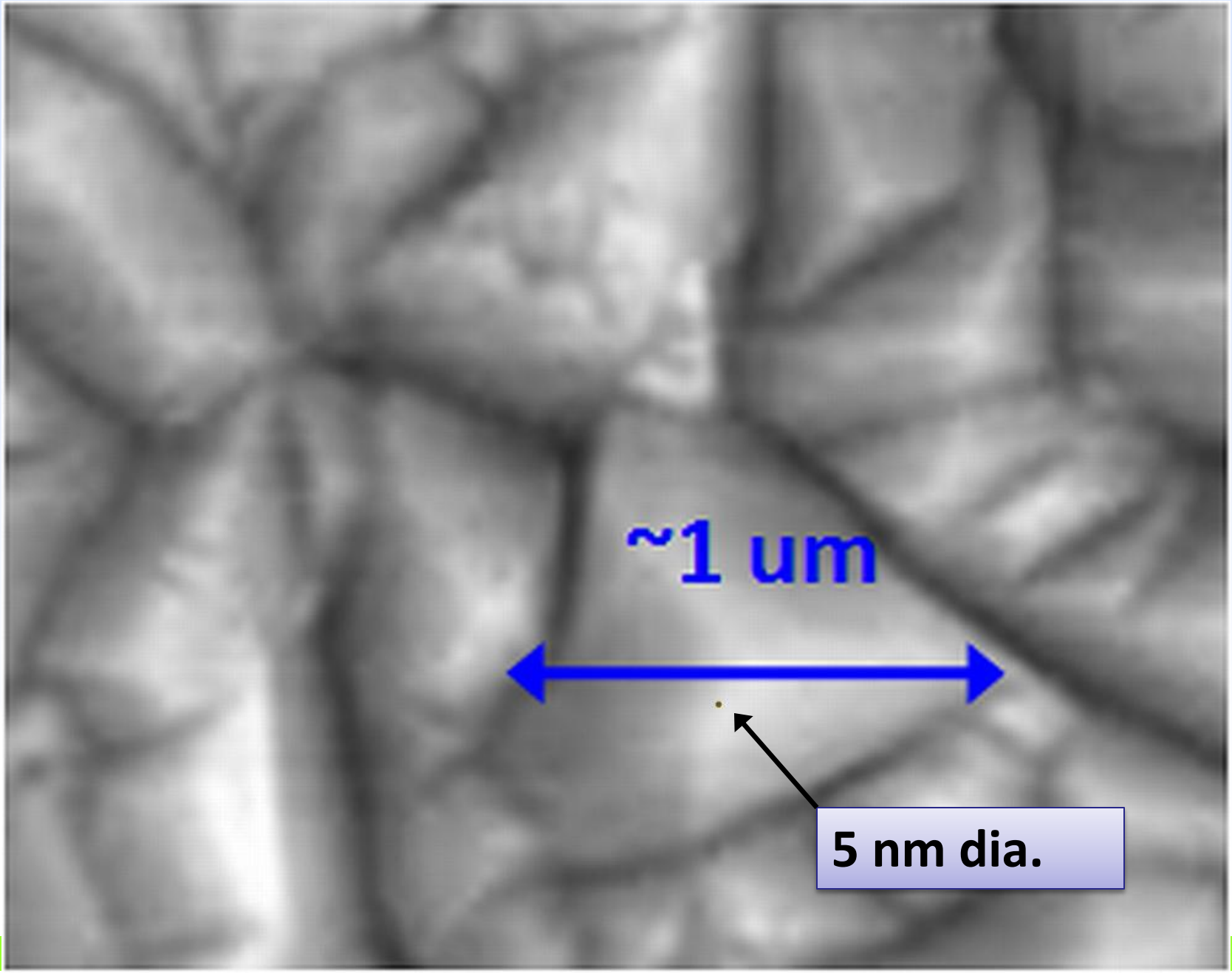
Sargent, Adv. Mat. (2005), 515-522.

CdTe grain size (CSS)

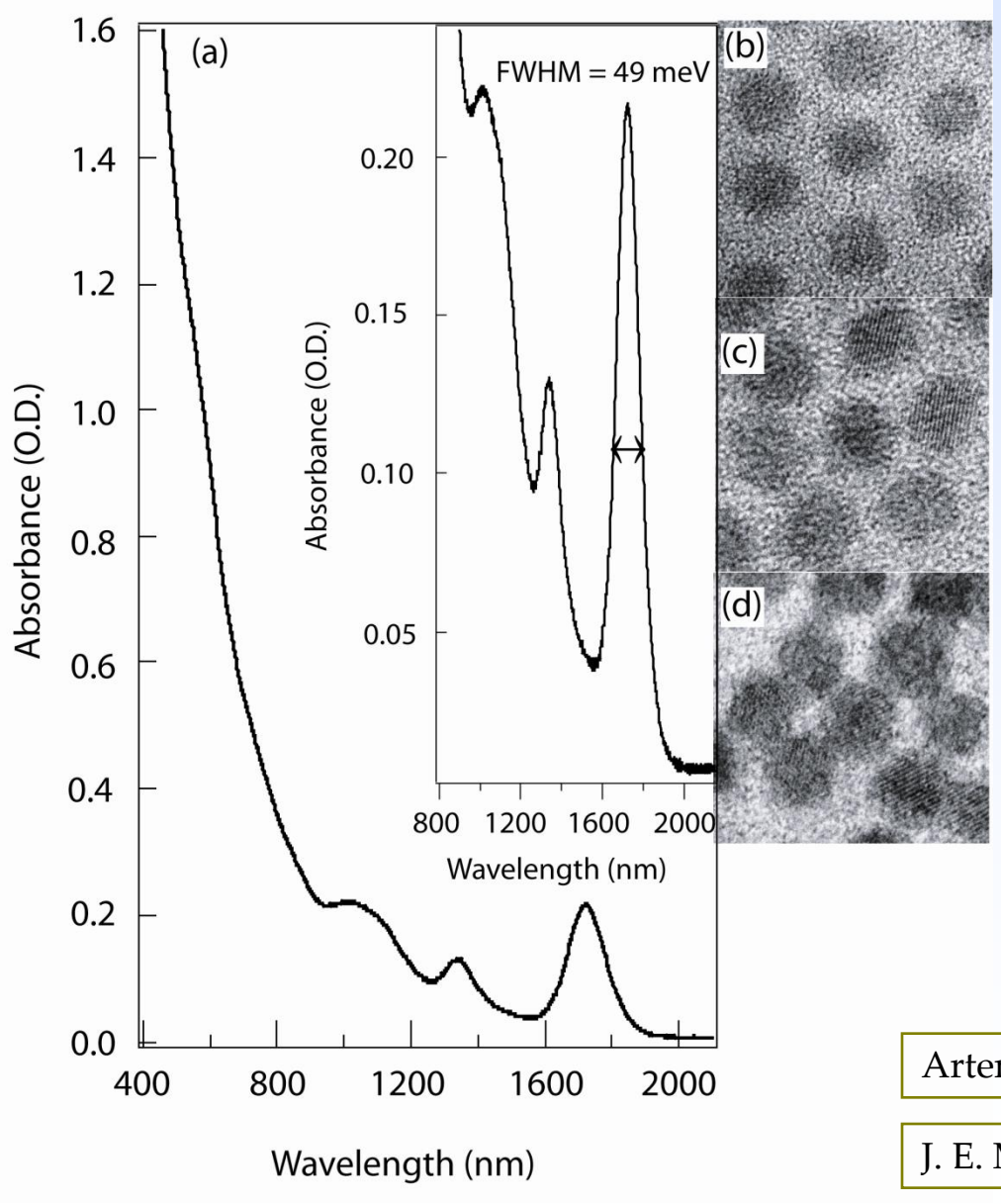


Quiñones et al., J. Mater. Sci: Mat. Electron (2007), 1085–1091

Colloidal quantum dot – scale



Post-deposition treatment of drop-cast films of 5.7 nm dia. PbSe QDs



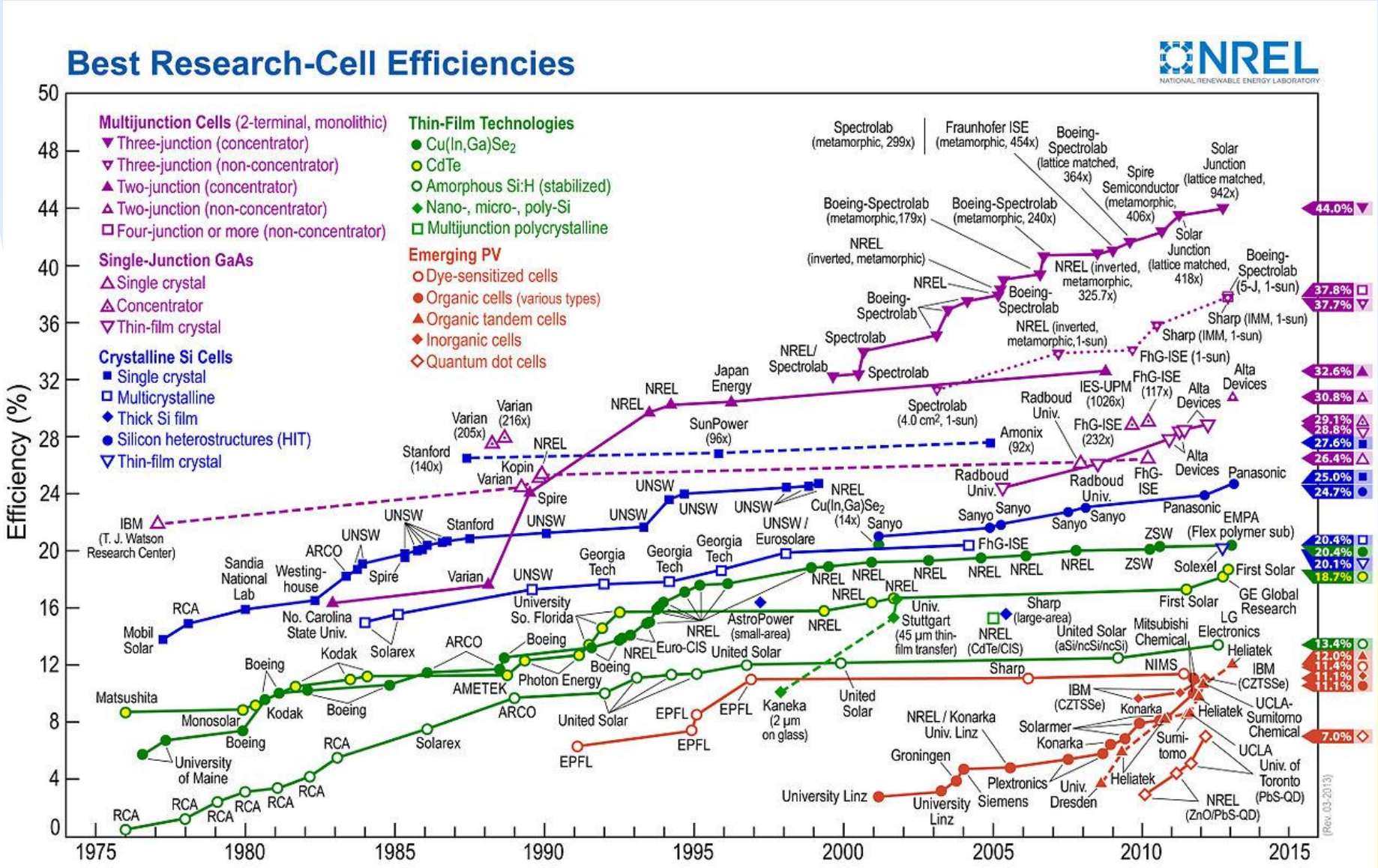
oleic acid (1.8 nm)

aniline (0.8 nm)

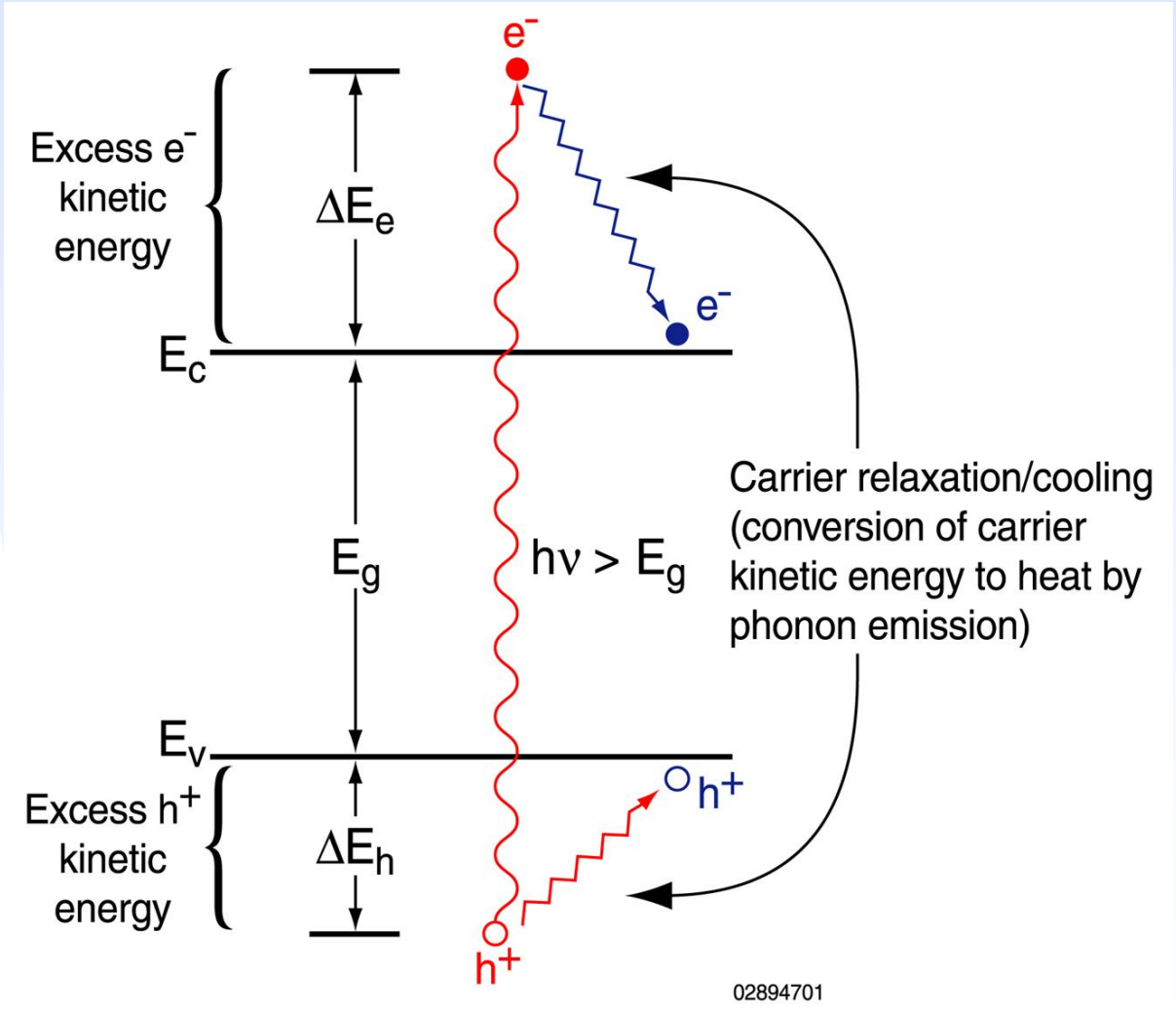
ethylenediamine (0.4 nm)

Artemyev *et al.*, J. Phys. Chem. B 2000, 11617.

J. E. Murphy *et al.*, J. Phys. Chem. B 2006, 25455.


Best Research-Cell Efficiencies
NREL
NATIONAL RENEWABLE ENERGY LABORATORY
Multijunction Cells (2-terminal, monolithic)
Three-junction (concentrator)
Three-junction (non-concentrator)
Two-junction (concentrator)
Two-junction (non-concentrator)
Four-junction or more (non-concentrator)
Single-Junction GaAs
Single crystal
Concentrator
Thin-film crystal
Crystalline Si Cells
Single crystal
Multicrystalline
Thick Si film
Silicon heterostructures (HIT)
Thin-film crystal
Thin-Film Technologies
Cu(In,Ga)Se2
CdTe
Amorphous Si:H (stabilized)
Nano-, micro-, poly-Si
Multijunction polycrystalline
Emerging PV
Dye-sensitized cells
Organic cells (various types)
Organic tandem cells
Inorganic cells
Quantum dot cells
Efficiency (%)
0
4
8
12
16
20
24
28
32
36
40
44
48
50
1975
1980
1985
1990
1995
2000
2005
2010
2015
44.0%
37.8%
37.7%
32.6%
30.8%
29.1%
28.8%
27.6%
26.4%
25.0%
24.7%
20.4%
20.4%
20.1%
18.7%
13.4%
12.0%
11.4%
11.1%
11.1%
7.0%
(Rev. 03-2013)

Thermalization losses



For *c*-Si (E_g = 1.1 eV)
at T = 300 K, AM1.5G

η_{max} = 32.9%

Losses

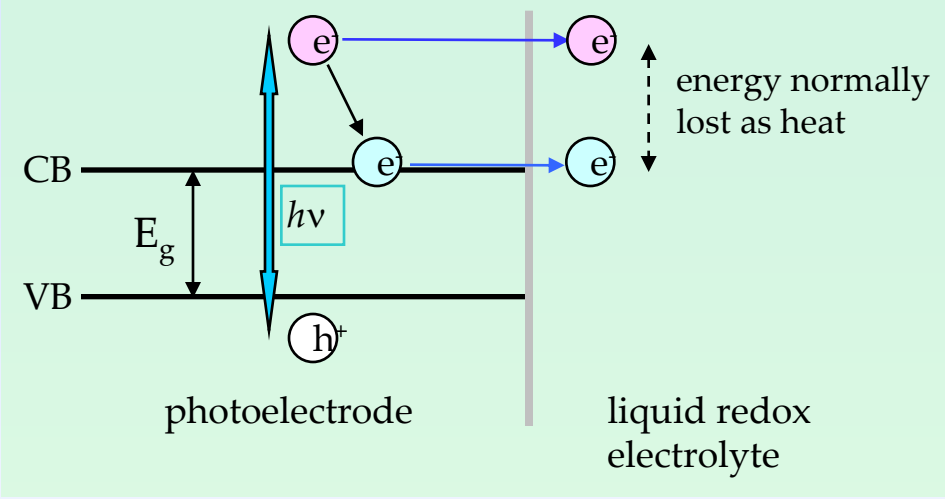
transmission = 18.7%

radiative em. = 1.6%

heat = 46.8%

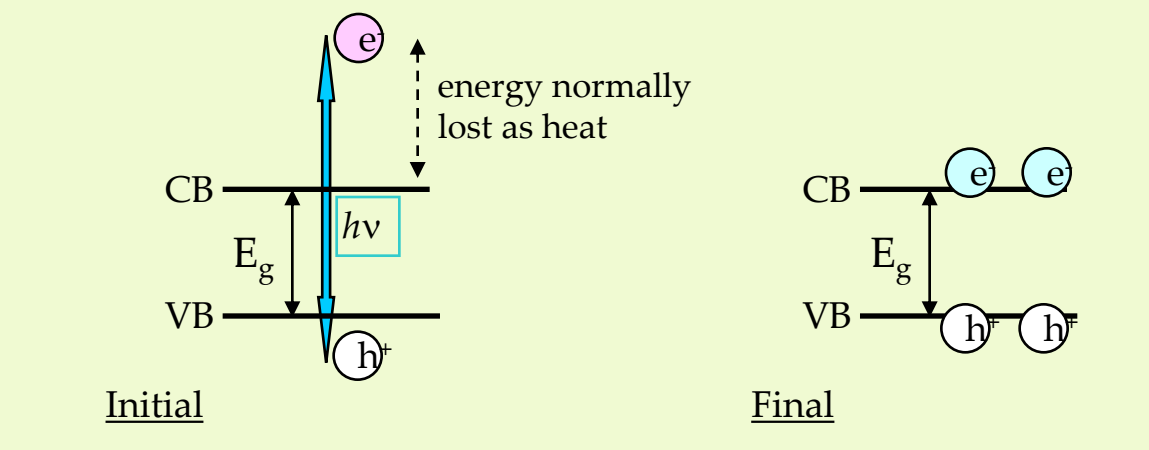
Utilize photogenerated hot electrons to increase efficiency

1. ***Higher photovoltage:*** *extract and utilize hot electrons*



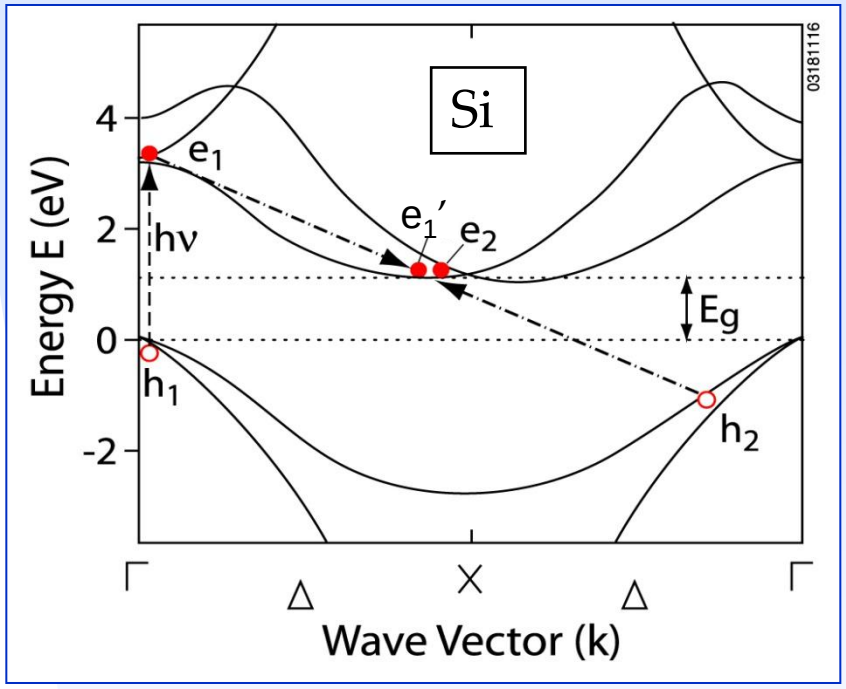
1 photon → 1 hot electron

2. ***Higher photocurrent:*** *carrier multiplication through impact ionization (inverse Auger process)*

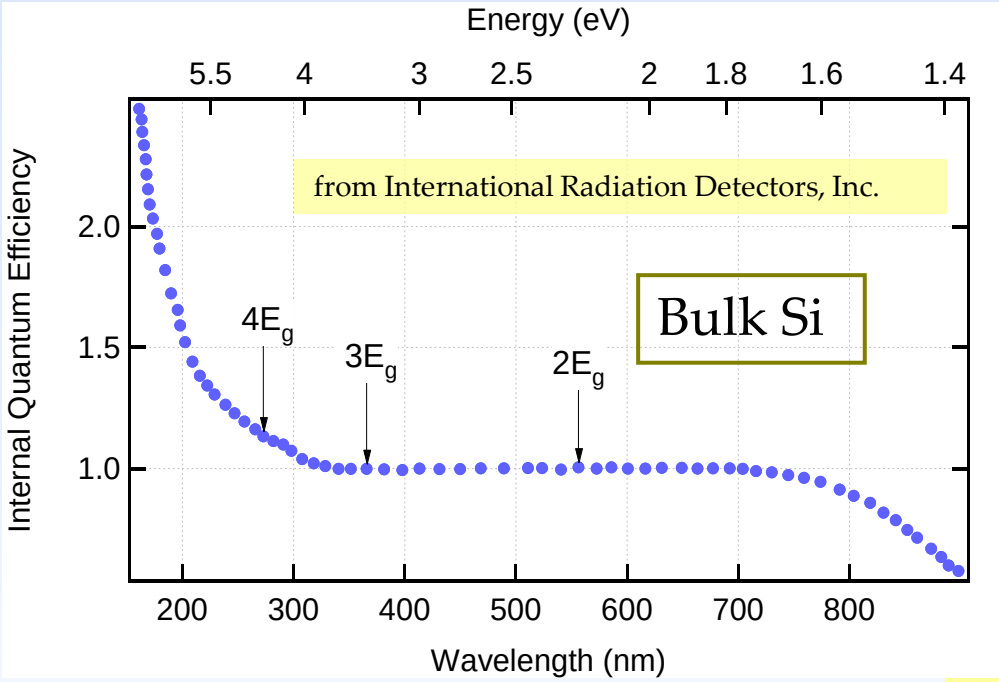


1 photon → 2 (or more) cooled electrons

Impact ionization in bulk semiconductors



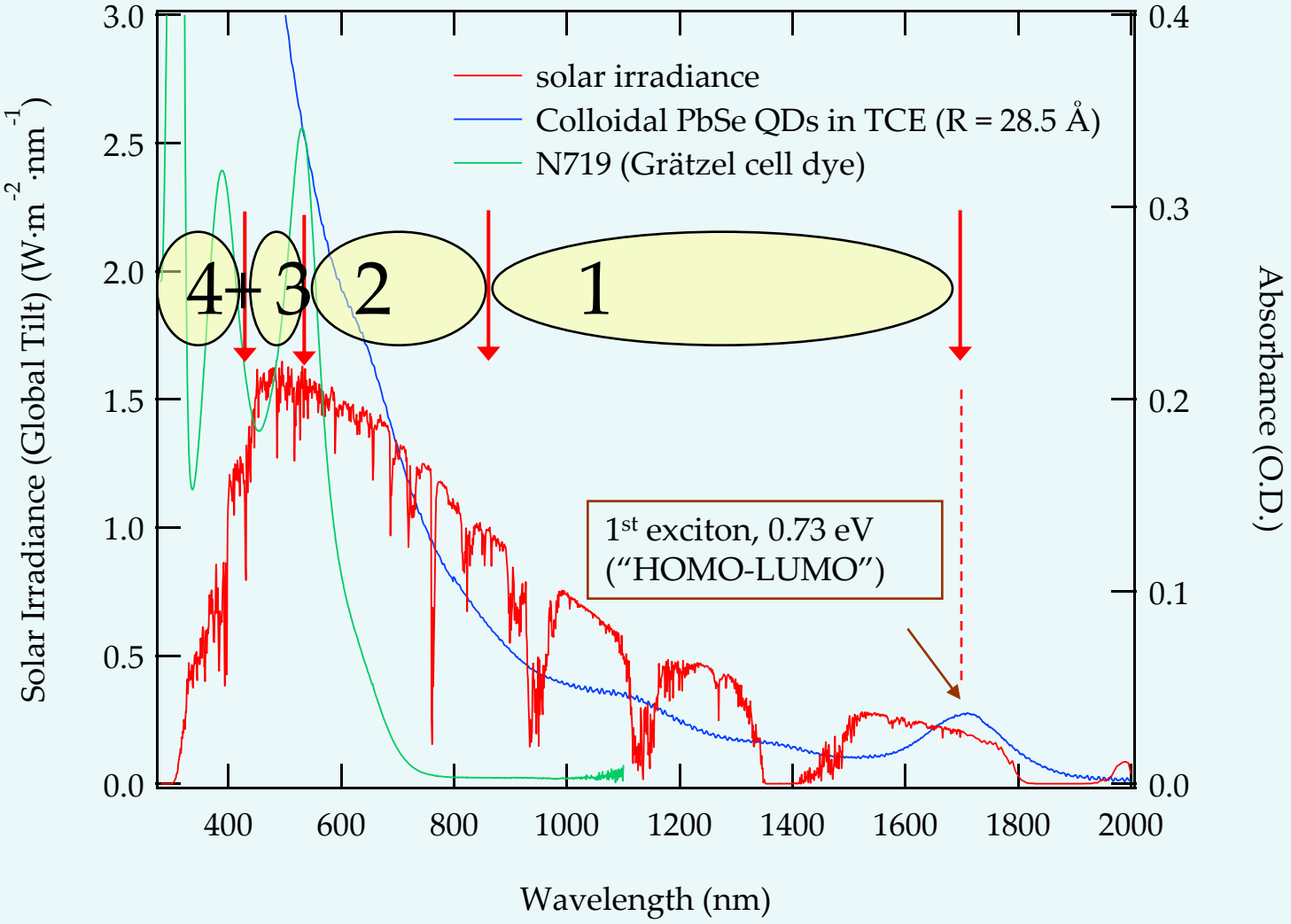
From Quiesser *et al.*, Appl. Phys. Lett. (1993).



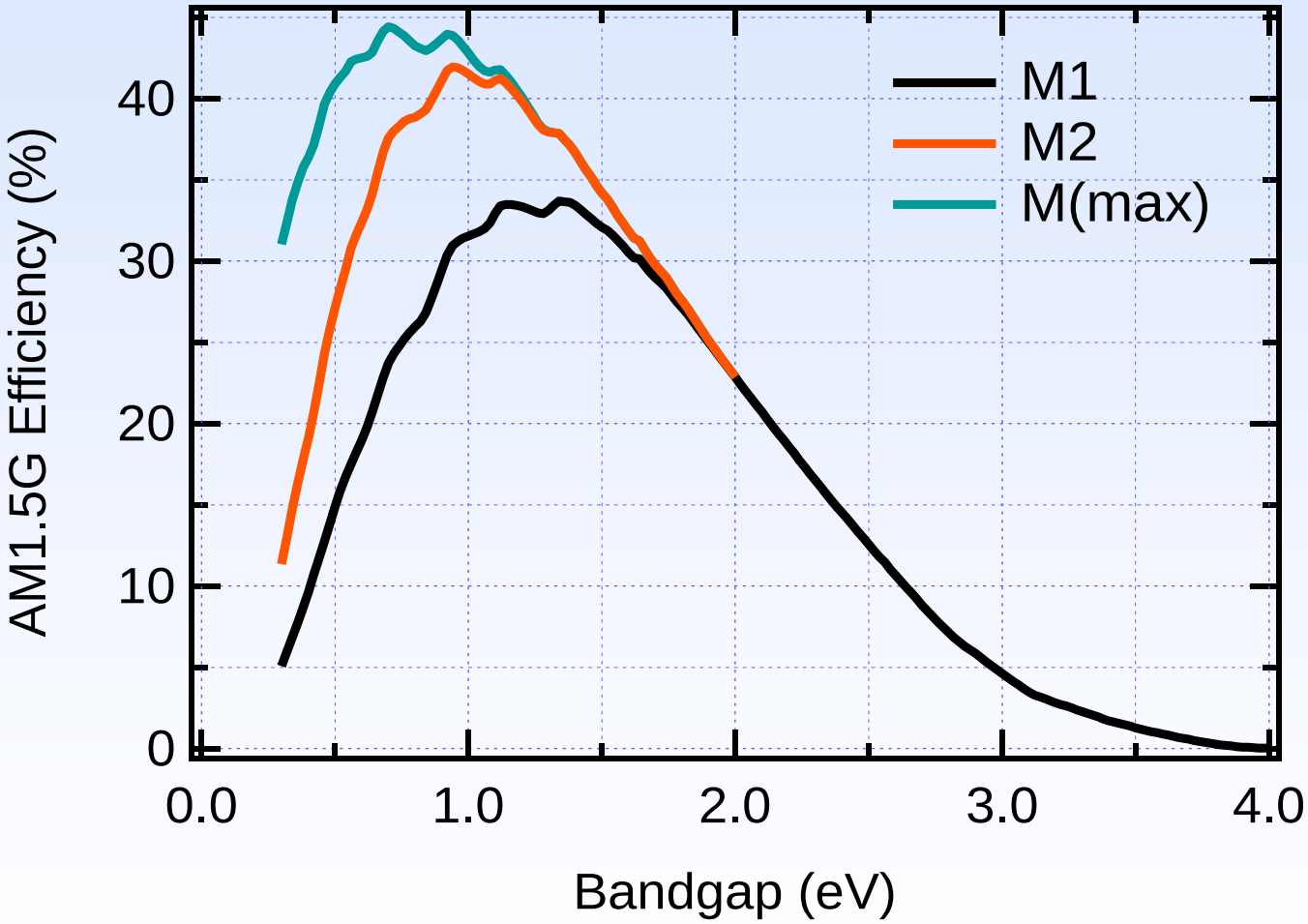
- Bulk Silicon ($E_g \approx 1.1$ eV) exhibits an I.I. QY of just 1.2 e^--h^+ pairs per photon absorbed at 4.5 eV ($\lambda = 275$ nm, $hc/\lambda > 4\ E_g$).
- Electron-phonon scattering dominates over I. I. up to very high photon energies.
- Nanocrystals exhibit a *reduced* momentum conservation requirement (NC surface can supply or absorb momentum during scattering processes).

Enhancing conversion efficiency using NCs & MEG

Matching absorption to solar irradiance spectrum

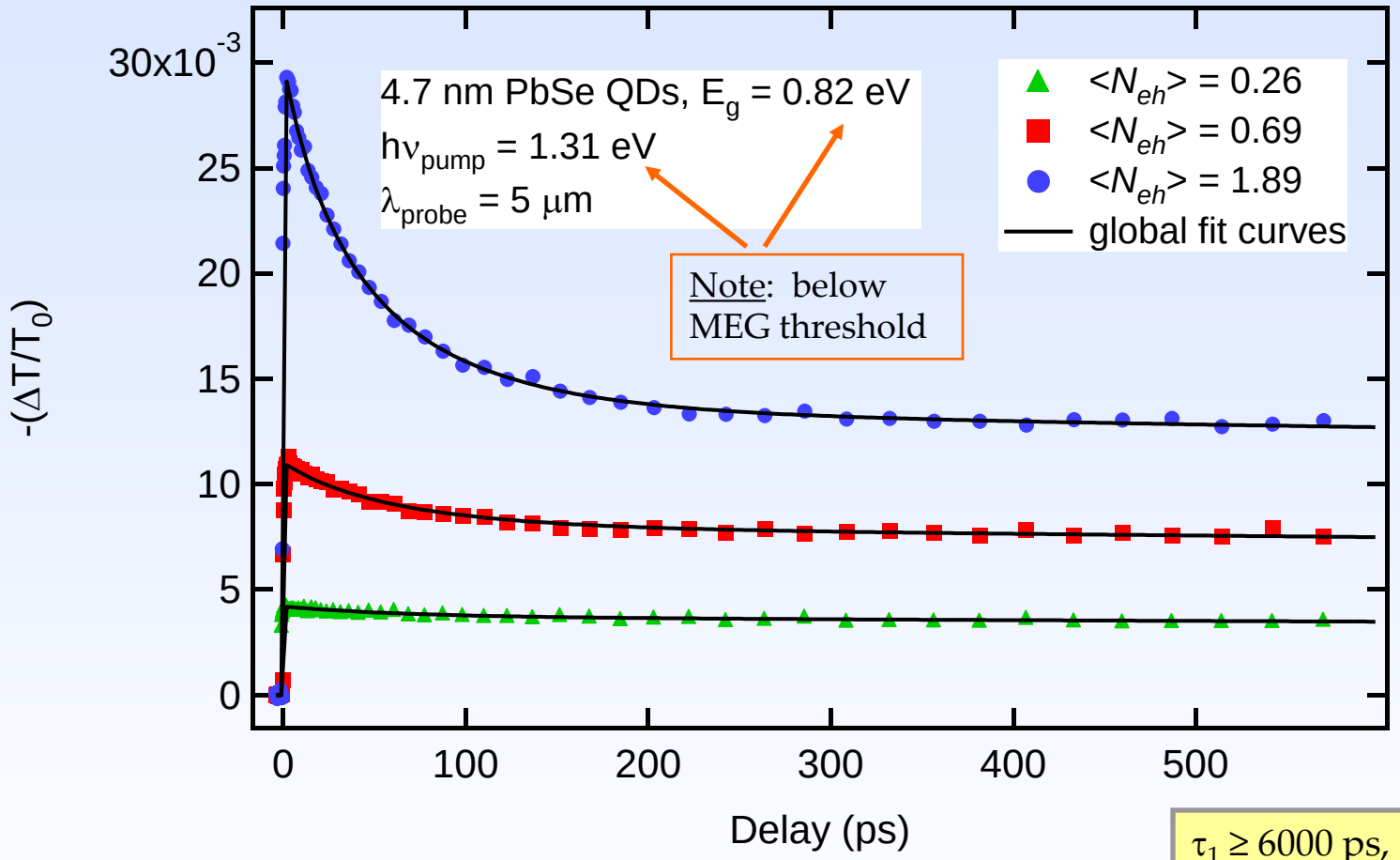


MEG-active solar cells – efficiency limitations



from Mark Hanna, NREL

Signature of multiple excitons: Auger recombination



Global fit for three intensities; excitation *below* the MEG threshold energy:

$$\Delta\alpha(t) \propto A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) + \ldots$$

$$\text{where the pre-exponential factors } A_i = \sum_{m=i}^{\infty} P(m)$$

How efficiently is excess energy converted to excitons?