Nanostructured Semiconductor Crystals -- Building Blocks for Solar Cells: Shapes, Syntheses, Surface Chemistry, Quantum Confinement Effects
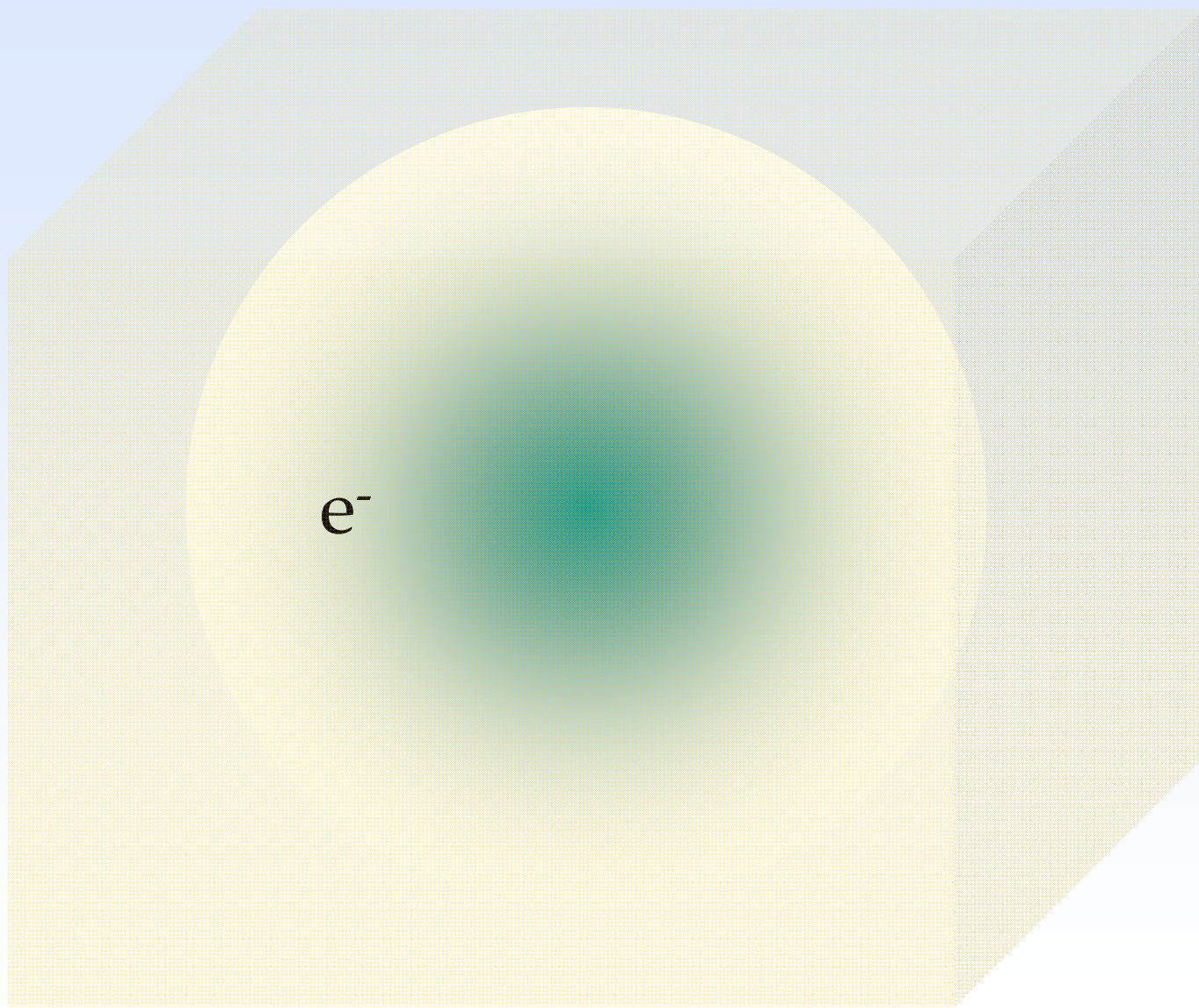
April 12, 2012

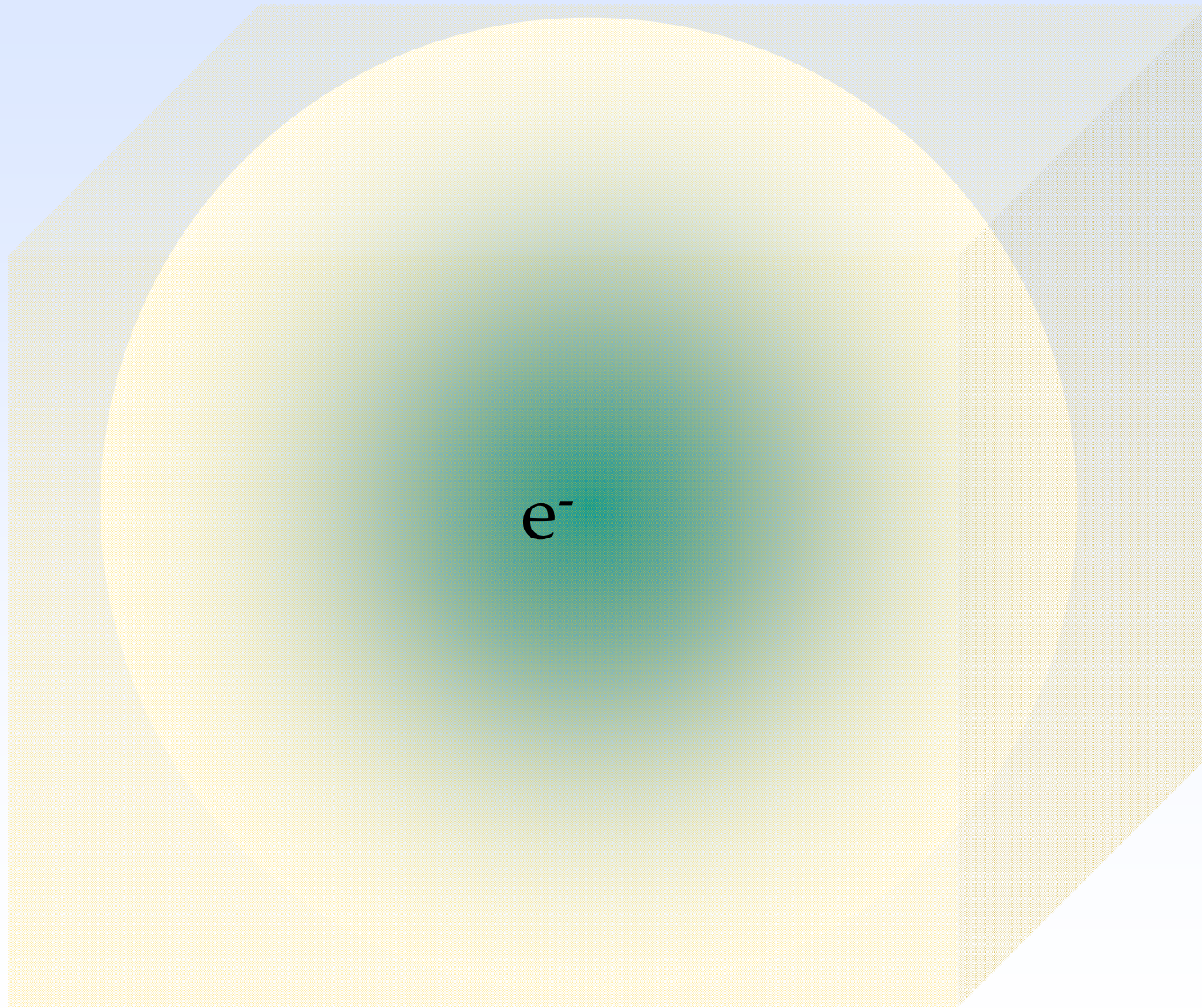The University of Toledo, Department of Physics and Astronomy
SSARE, PVIC

Principles and Varieties of Solar Energy (PHYS 4400)
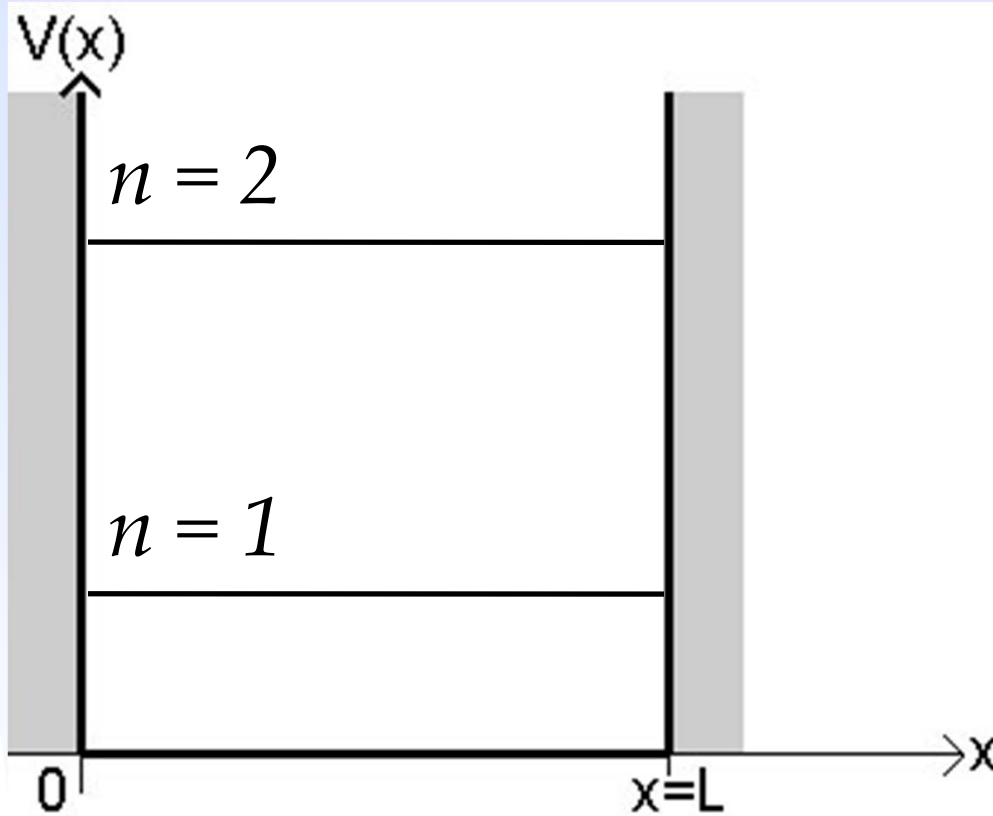and
Fundamentals of Solar Cells (PHYS 6980)

.... energizing Ohio for the 21st Century

Quantum confinement effect

e⁻

Particle in a box (quantum well)

$V(x)$

$n = 2$

$n = 1$

0 $x=L$ $\rightarrow x$

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

The Potential, V(x), is 0 inside the box, and infinite elsewhere (infinite barriers)
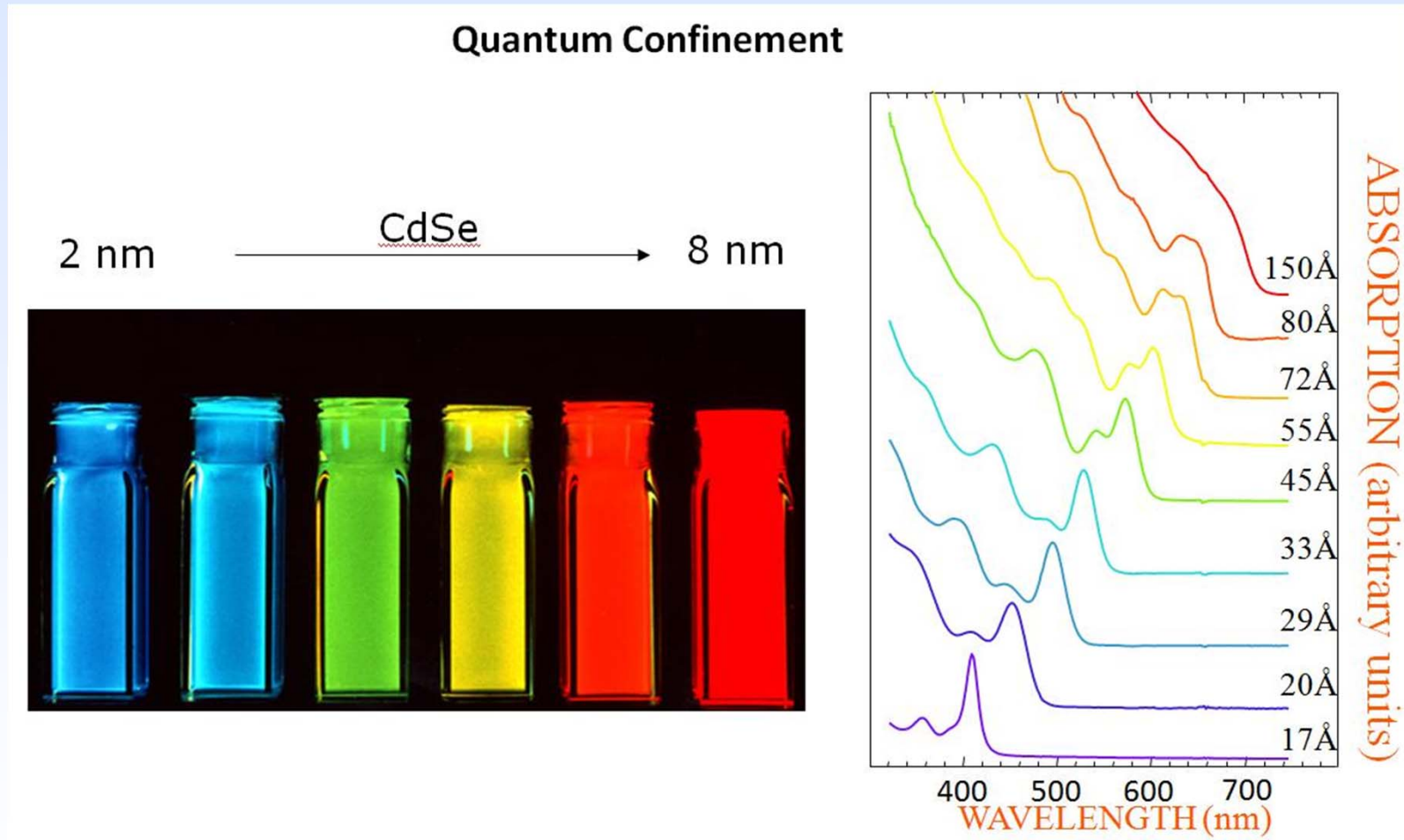
Nanomaterials for solar energy conversion

- 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*
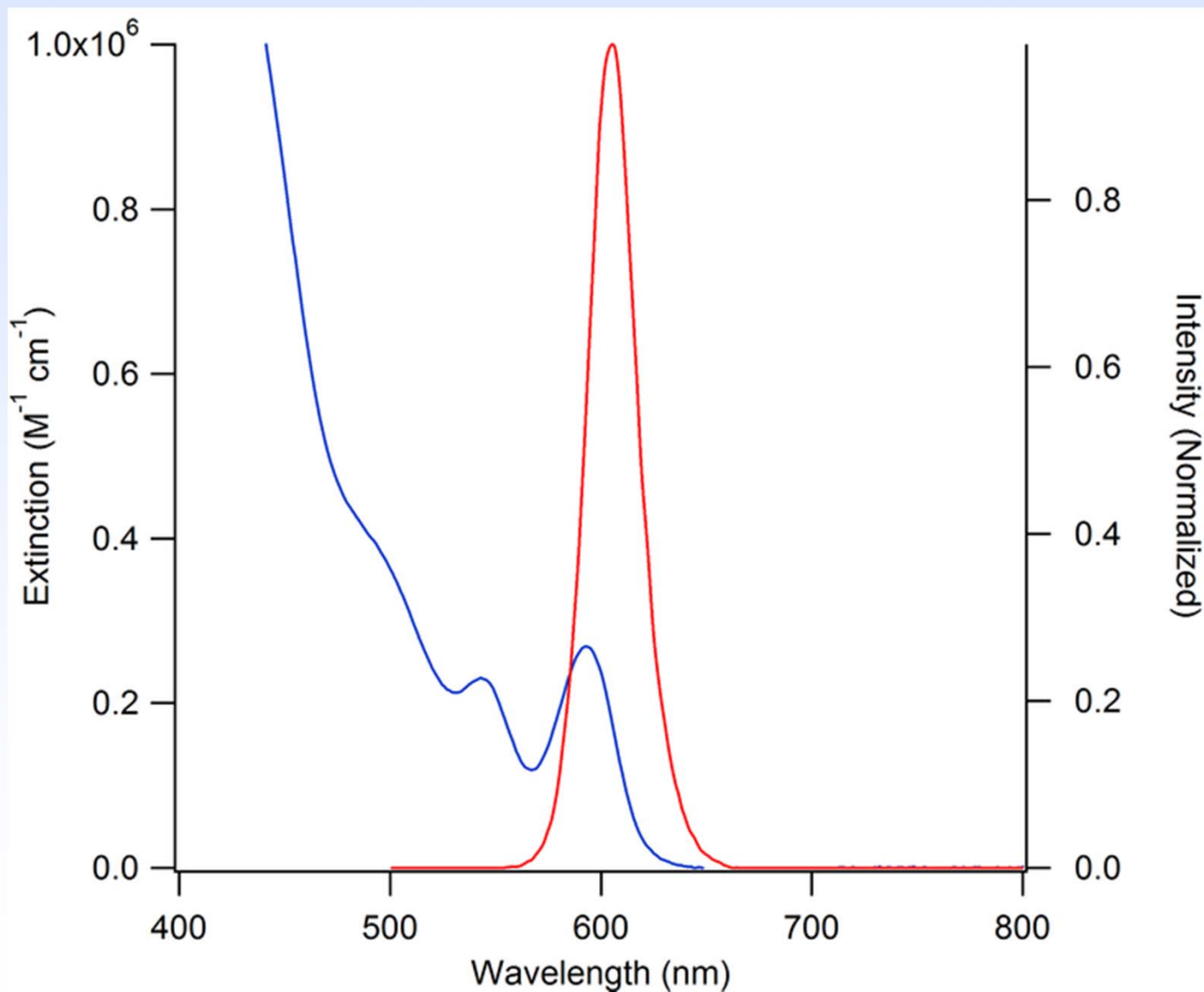- *Efficient anti-Stokes luminescence*

Size-dependent optical properties

Quantum Confinement

2 nm → CdSe → 8 nm

150Å
80Å
72Å
55Å
45Å
33Å
29Å
20Å
17Å

ABSORPTION (arbitrary units)

WAVELENGTH (nm)

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

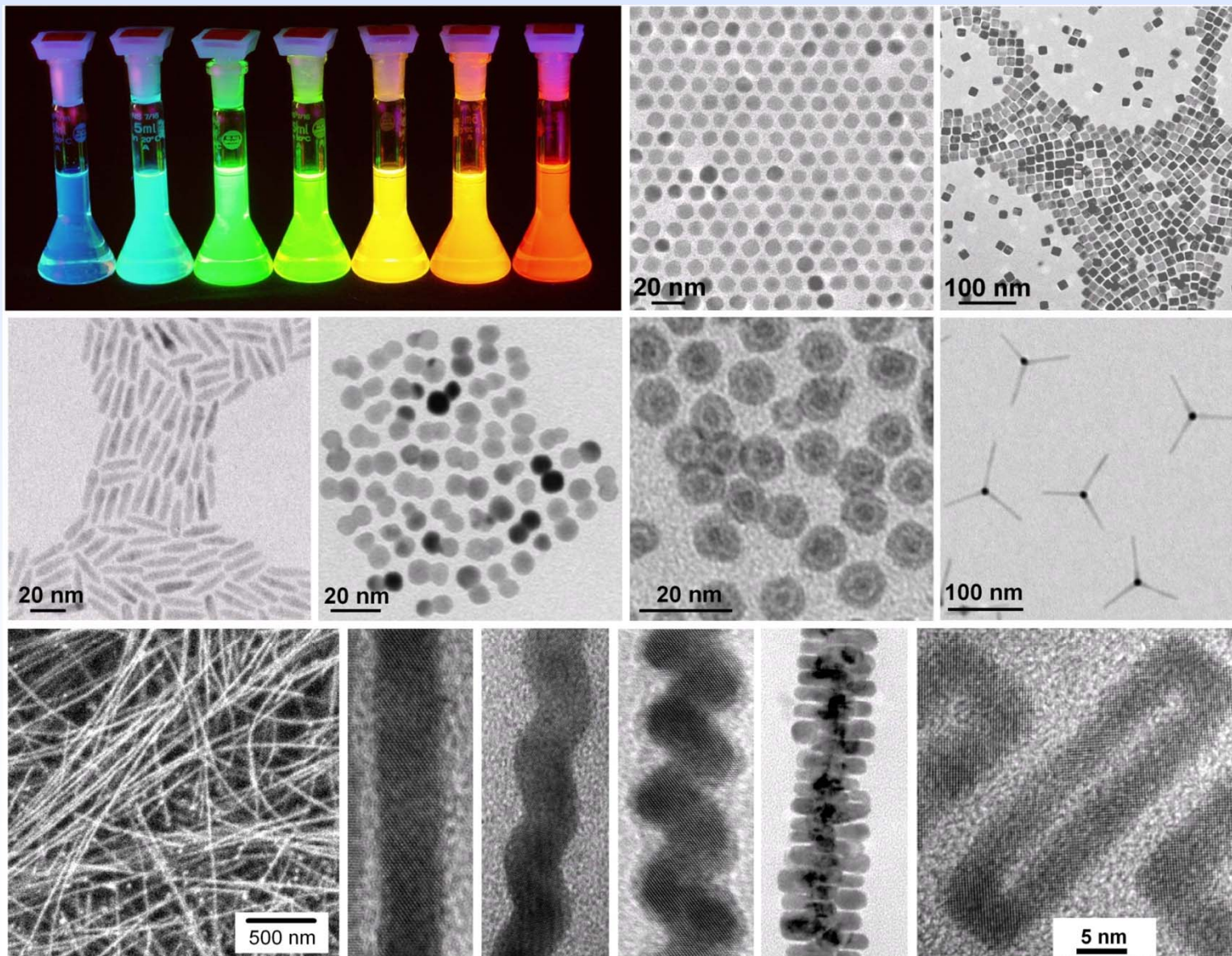# Absorption and emission (CdSe nanocrystals)

Size-dependent bandgap of CdSe NCs
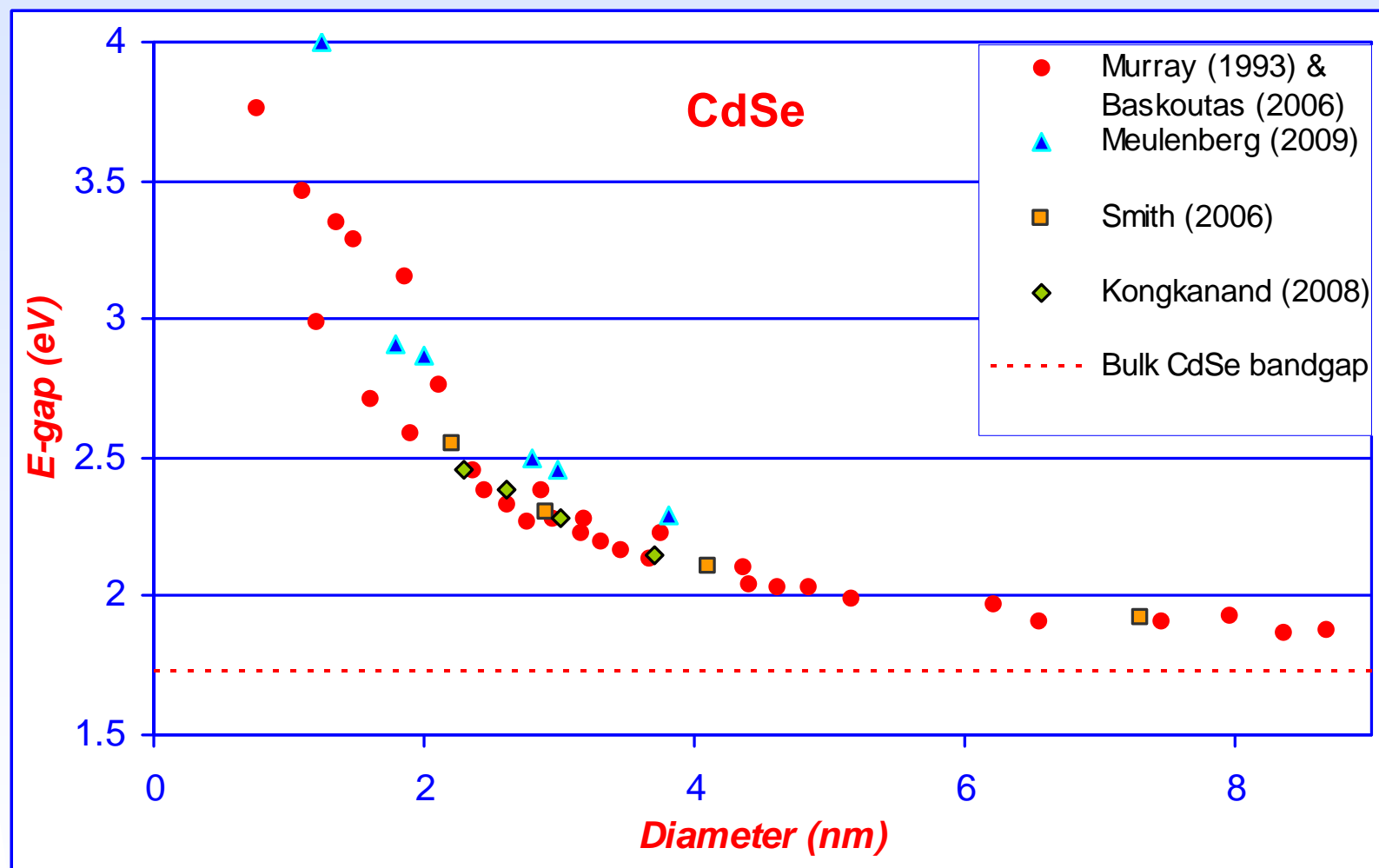
From *"Physical and Optical Properties of Colloidal Semiconducting Nanocrystals for Solar Absorption"*, by Abdel Ibdah (UT)

Colloidal nanostructures (crystalline)

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

$$\frac{dN_{3D}}{dk} = 2\left(\frac{L}{2\pi}\right)^3 4\pi k^2, \ \frac{dN_{2D}}{dk} = 2\left(\frac{L}{2\pi}\right)^2 2\pi k, \ \frac{dN_{1D}}{dk} = 2\left(\frac{L}{2\pi}\right)$$
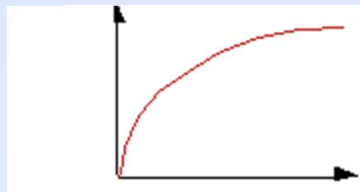
$$g_{c,3D} = \frac{8\pi\sqrt{2}}{h^3} m_{eff}^{3/2} \sqrt{E - E_{min}}$$
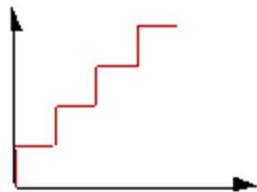
$$g_{c,2D} = \frac{4\pi m_{eff}}{h^2}$$

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

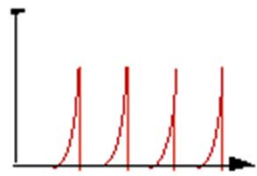# Quantum confinement effect on density of electronic states

N(E)

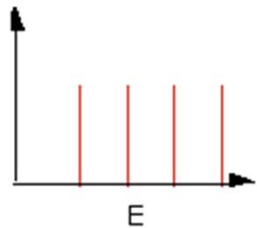Bulk Semiconductor

Quantum Well
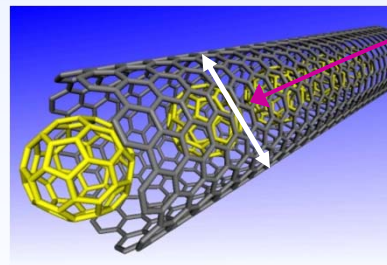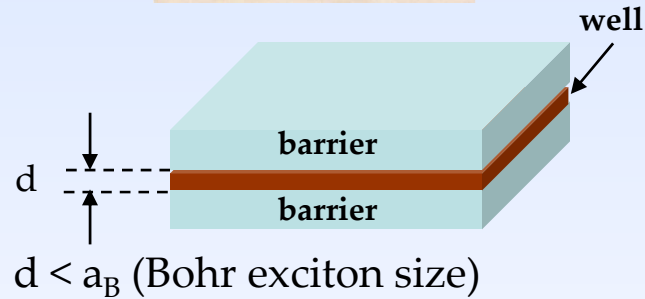
d < a$_B$ (Bohr exciton size)

well

barrier

barrier

d

Quantum Wire

~1 nm

Quantum Dot
(or Nanocrystal)

~6 nm dia.

E
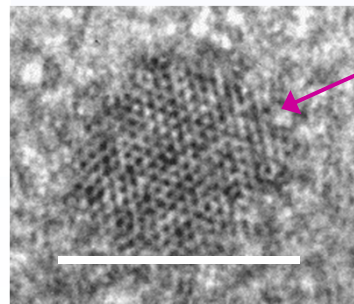
60 Å InP QD

Dimensionality

3D

2D

1D

0D

Quantum Films vs Quantum Dots
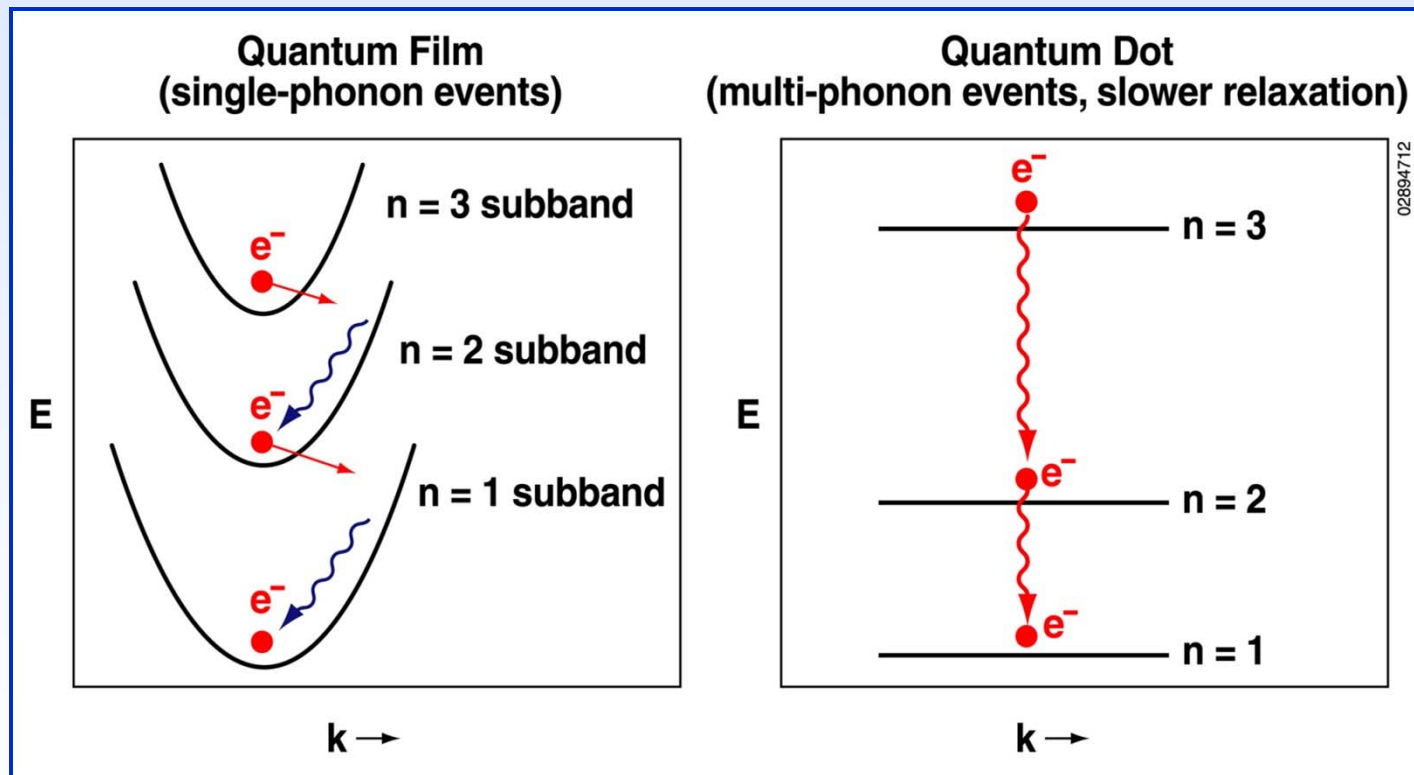
phonon bottleneck

Excitonic energies are calculated using the atomistic pseudopotential method (APM). Two steps are involved:

1. single-particle orbital energies and wavefunctions are computed by solving the Schrödinger equation; $v_\alpha(\mathbf{r} - \mathbf{R}_n - \tau_\alpha)$ is the screened, nonlocal pseudopotential for the atom of type α located at site τ_α in cell $\mathbf{R}_n$ and ε_i is the single particle orbital energy.

$$\left\{ -\frac{1}{2}\nabla^2 + \sum_{R_n}\sum_{\tau_\alpha} v_\alpha(\mathbf{r} - \mathbf{R}_n - \tau_\alpha) \right\}\psi_i = \varepsilon_i\psi_i$$

2. excitonic energy levels and wavefunctions are calculated using the configuration interaction (CI) approach.

Calculated energy levels in 42 Å InP QD

(a) Valence States — Character of Wavefunction

State Index	Energy (eV)	S	P	D	F
1	-6.0303	76.9	9.5	8.0	1.7
2	-6.0303	76.9	9.5	8.0	1.7
3	-6.0679	2.7	84.9	5.7	2.6
4	-6.0679	2.7	84.9	5.7	2.6
5	-6.1268	0.2	84.2	6.0	4.5
6	-6.1275	69.8	4.8	17.7	2.1
7	-6.1386	2.0	60.5	11.5	16.1
8	-6.1386	2.0	60.5	11.5	16.1
9	-6.1403	0.4	5.3	77.5	5.7
10	-6.1403	0.4	5.3	77.5	5.7
11	-6.1542	0.0	2.9	80.9	4.5
12	-6.1834	40.2	4.2	37.4	3.6
13	-6.1835	40.2	4.1	37.3	3.7
14	-6.1961	0.5	2.2	0.7	82.5
15	-6.2261	37.3	2.1	33.4	5.8
16	-6.2473	0.9	25.4	11	36.9
17	-6.2496	3.0	21.8	14.8	35.2
18	-6.2544	5.1	21.3	7.2	47.3
19	-6.2549	3.5	23.1	16.5	36.4
20	-6.2552	1.9	25.9	18.8	27.5
21	-6.2641	2.0	35.8	21.1	21.1
22	-6.2657	1.5	33.1	14.6	30.5
23	-6.2665	5.3	38.3	8.6	29.1
24	-6.2880	1.6	32.7	15.2	19.3
25	-6.2852	1.9	26.1	20.4	20.9

(b) Conduction States — Character of Wavefunction

State Index	Energy (eV)	S	P	D	F
1	-4.0608	82.5	10.6	1.5	1.4
2	-3.7855	5.7	73.2	10.5	2.6
3	-3.7855	5.7	73.2	10.5	2.6
4	-3.7771	5.3	73.1	10.5	2.9
5	-3.7019	0.8	1.2	6.3	0.8
6	-3.7017	0.7	1.1	6.4	0.8
7	-3.7017	0.7	1.1	6.4	0.8
8	-3.6994	2.7	0.3	3.7	0.8
9	-3.6324	1.3	3.3	1.3	16.5
10	-3.6312	0.1	6.1	1.0	9.6
11	-3.6298	0.1	6.3	0.9	9.3
12	-3.6298	0.1	6.3	0.9	9.3
13	-3.5879	4.6	0.9	5.6	5.0
14	-3.5599	1.9	9.0	58.5	12
15	-3.5568	1.8	5.7	39.1	7.5
16	-3.5540	1.6	2.6	22.3	3.9

Valence (a) and conduction (b) single-particle states for a 41.8 Å diameter InP quantum dot. Columns 3-6 indicate the percentage distribution of envelope angular momentum components for each single-particle level. Energies are relative to vacuum.
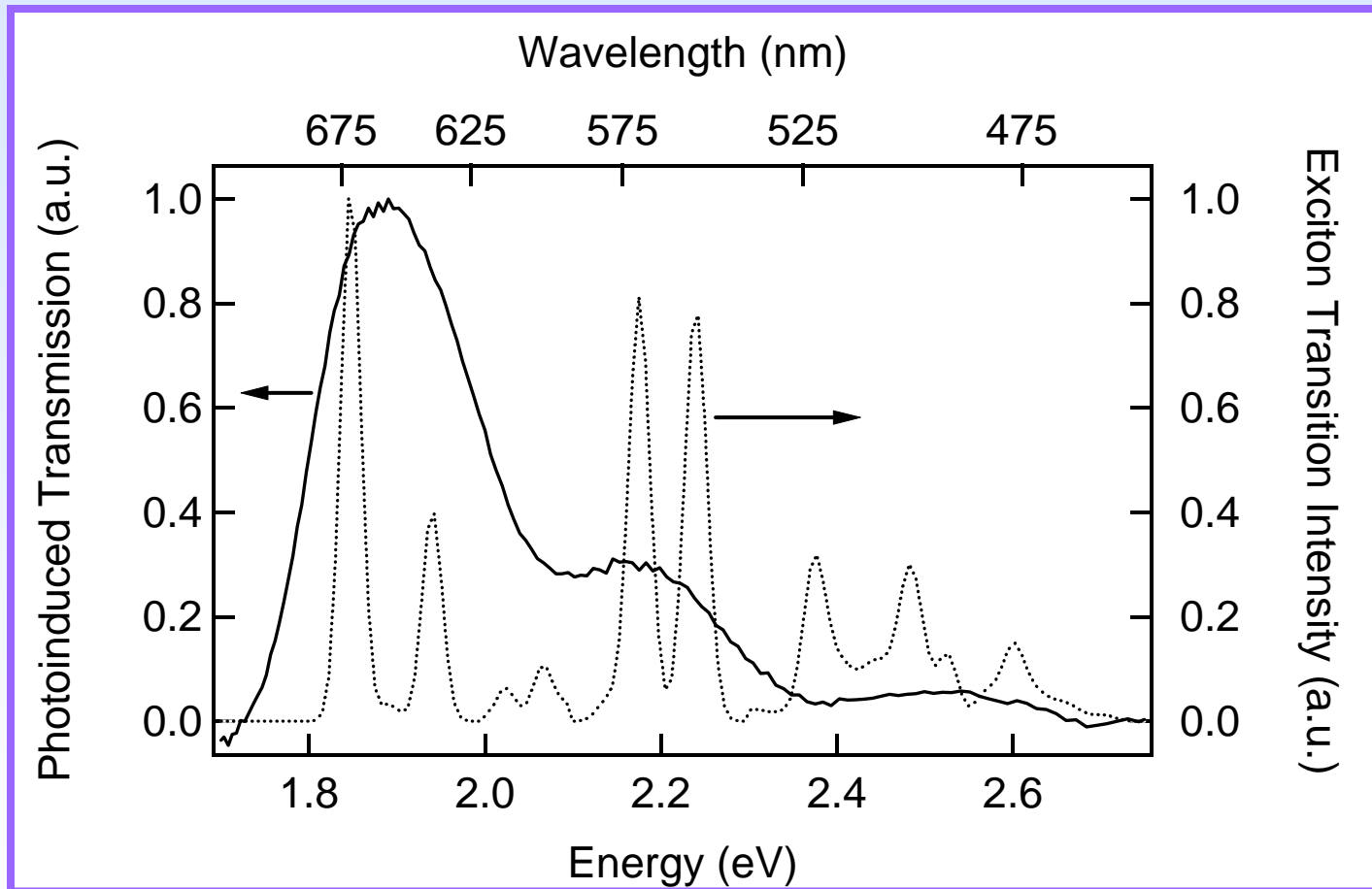
Calculated *excitonic* transitions in 42 Å InP QD

| PEAK POSITION (EV)	INITIAL VALENCE STATES	FINAL CONDUCTION STATES
1.84	1, 2	1
1.94	6	1
2.18	3, 4	2, 3, 4
2.24	5	4
2.24	7, 8	2, 3
2.38	17-25	2, 3, 4
2.48	9, 10, 11	14, 15
2.60	17, 19, 21, 22, 24, 25	14

Excitonic spectrum for 42 Å InP QD

Theoretical excitonic spectrum (dashed line) for a sample of 41.8 Å diameter InP quantum dots. The transition intensity is proportional to the absorption coefficient, and consists of a sum of the oscillator strengths for various excitonic transitions. The solid line shows the measured photoinduced bleach spectrum, at a delay of 1.0 ps, for a sample with average size of ~42 Å diameter. Theoretical transition peaks correspond to those listed at left. The two small peaks between 2.0 and 2.1 eV originate from transitions between valence states 12, 13, and 15, and conduction state 1.

Transmission electron micrograph (TEM) of Lead Selenide NCs
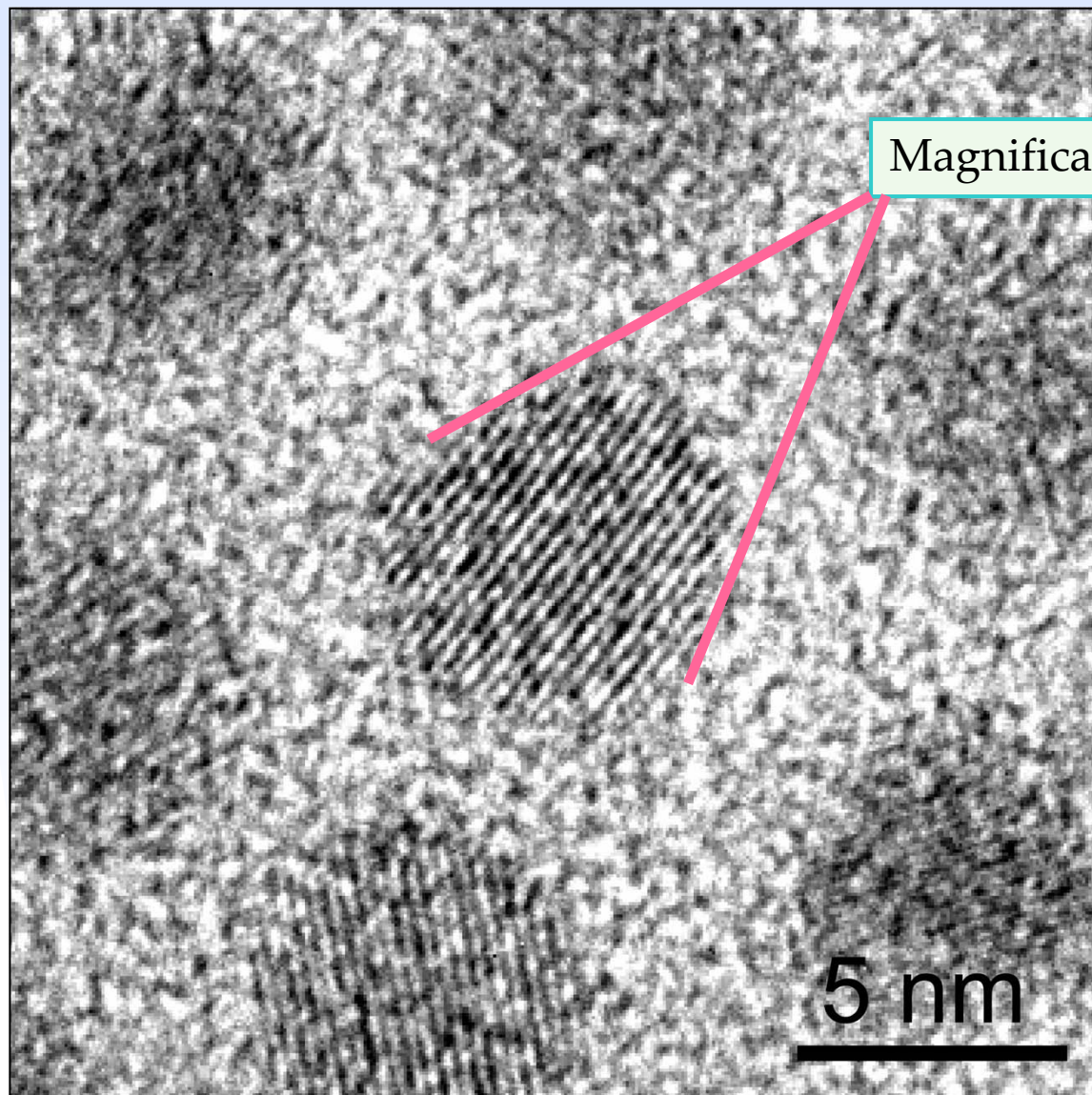
PbSe

Magnification ~ 2,000,000x

5 nm

Colloidal quantum dots
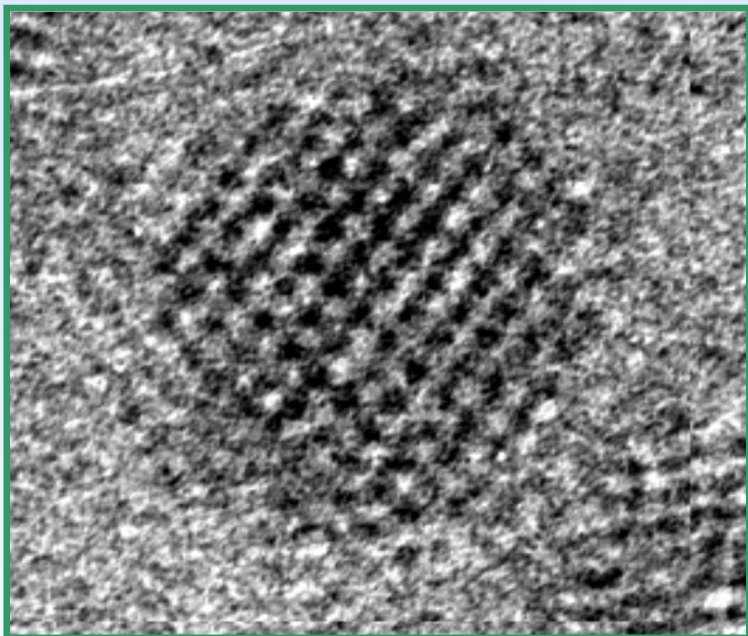
TEM image of 60-Å InP QD
(K.Jones, NREL)

Colloidal synthesis
InP QDs synthesized by colloidal methods starting with $InCl_3$ and tris(trimethylsilyl)phosphine in presence of TOP/TOPO

Small size – strong confinement regime
small size (15 Å - 80 Å diameter), spherical shape, many confined valence and conduction states [compare to epitaxial SK dots typically > 100 Å, with potential barriers confining ~ 6 conduction and valence states]

Variable surface chemistry
as-prepared dots are capped with organic stabilizer (TOP/TOPO) $\Rightarrow$ surface chemistry alters electrical and optical (emission) properties (pyridine, Na^+ - biphenyl[(-)], etched QDs)

High ratio of atoms on surface
e.g., for 35 Å dots, ~30% of atoms reside on surface $\Rightarrow$ importance of surface effects

Synthesis of colloidal nanocrystals

http://nanocluster.mit.edu/research.php
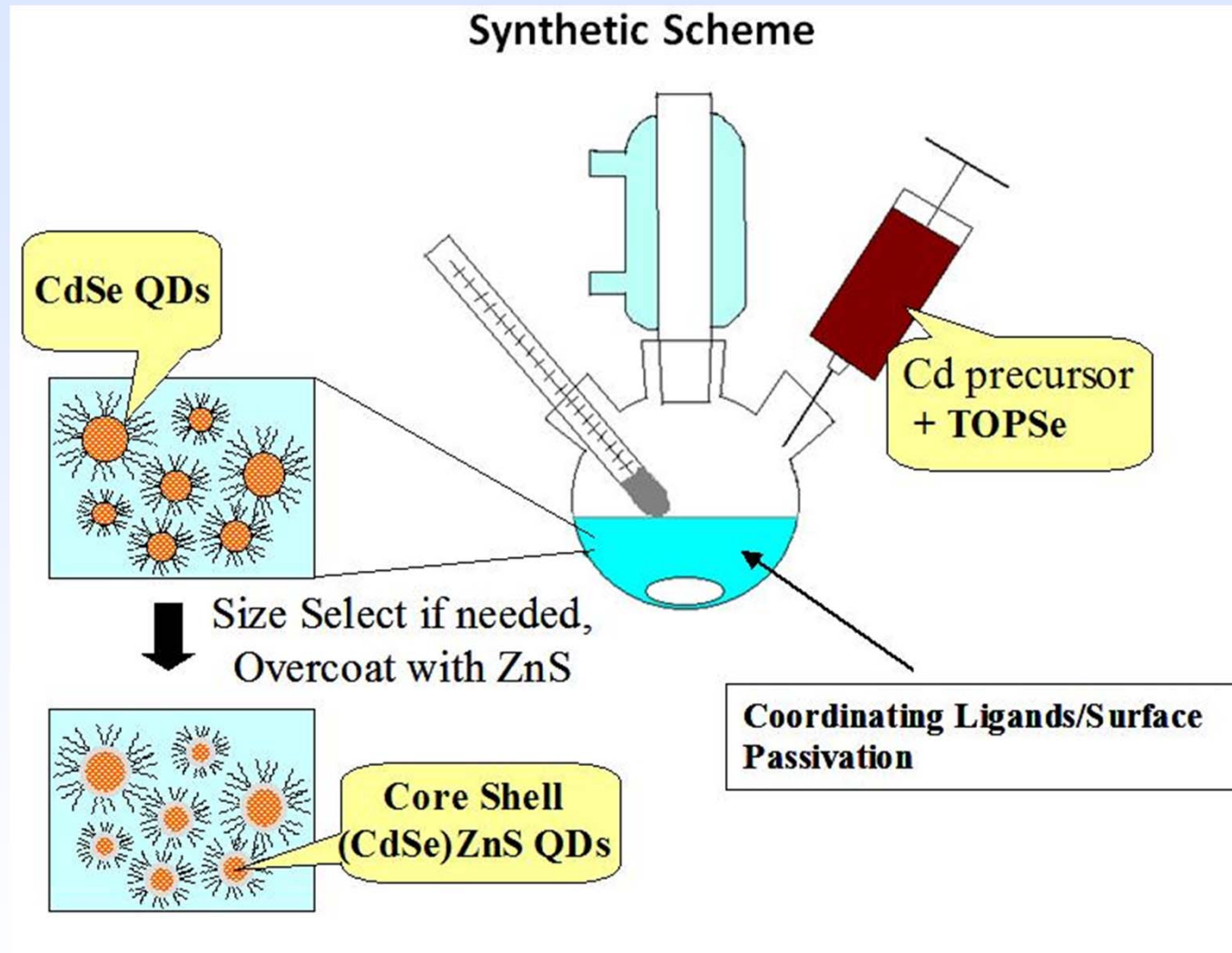
# Synthesis of colloidal nanocrystals

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).
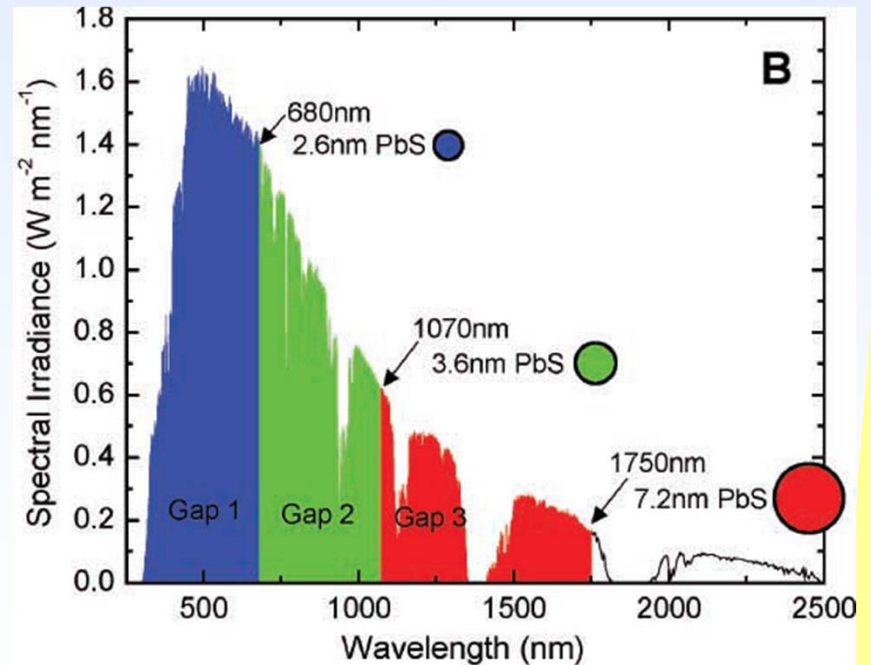
Why pursue QD solar cells?

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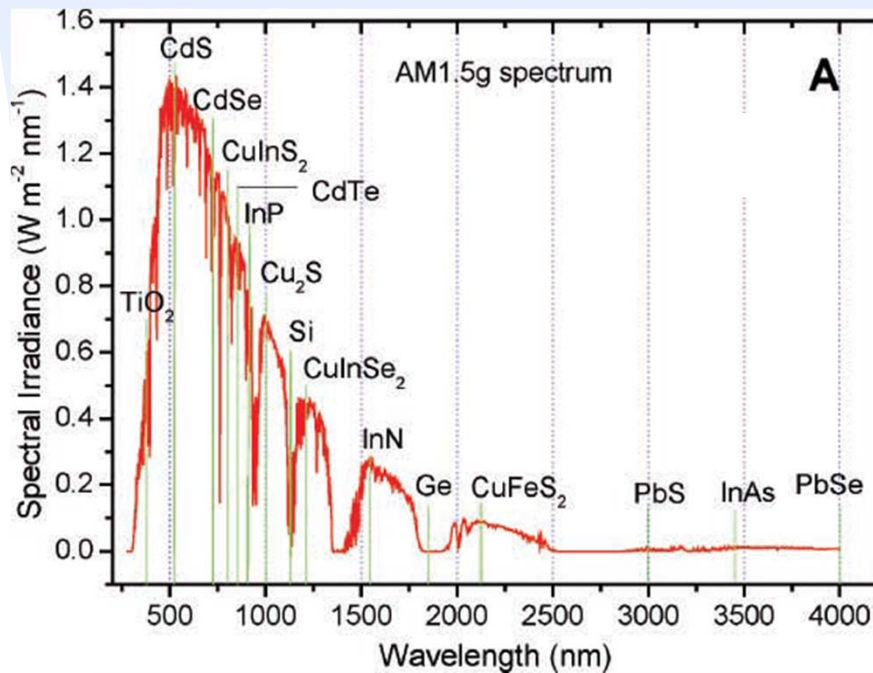
AM1.5G solar spectrum along with some common bulk semiconductors band-gaps

Triple junction PbS dot size

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

Colloidal PbSe QDs in tetrachloroethylene (TCE)

Oleic acid-capped PbSe QDs (R = 2.7 nm) in tetrachloroethylene

$E_g = 0.76$ eV

$\tau = 830$ ns

Photoluminescence Intensity (normalized)

Time (μs)

1600   1800   2000
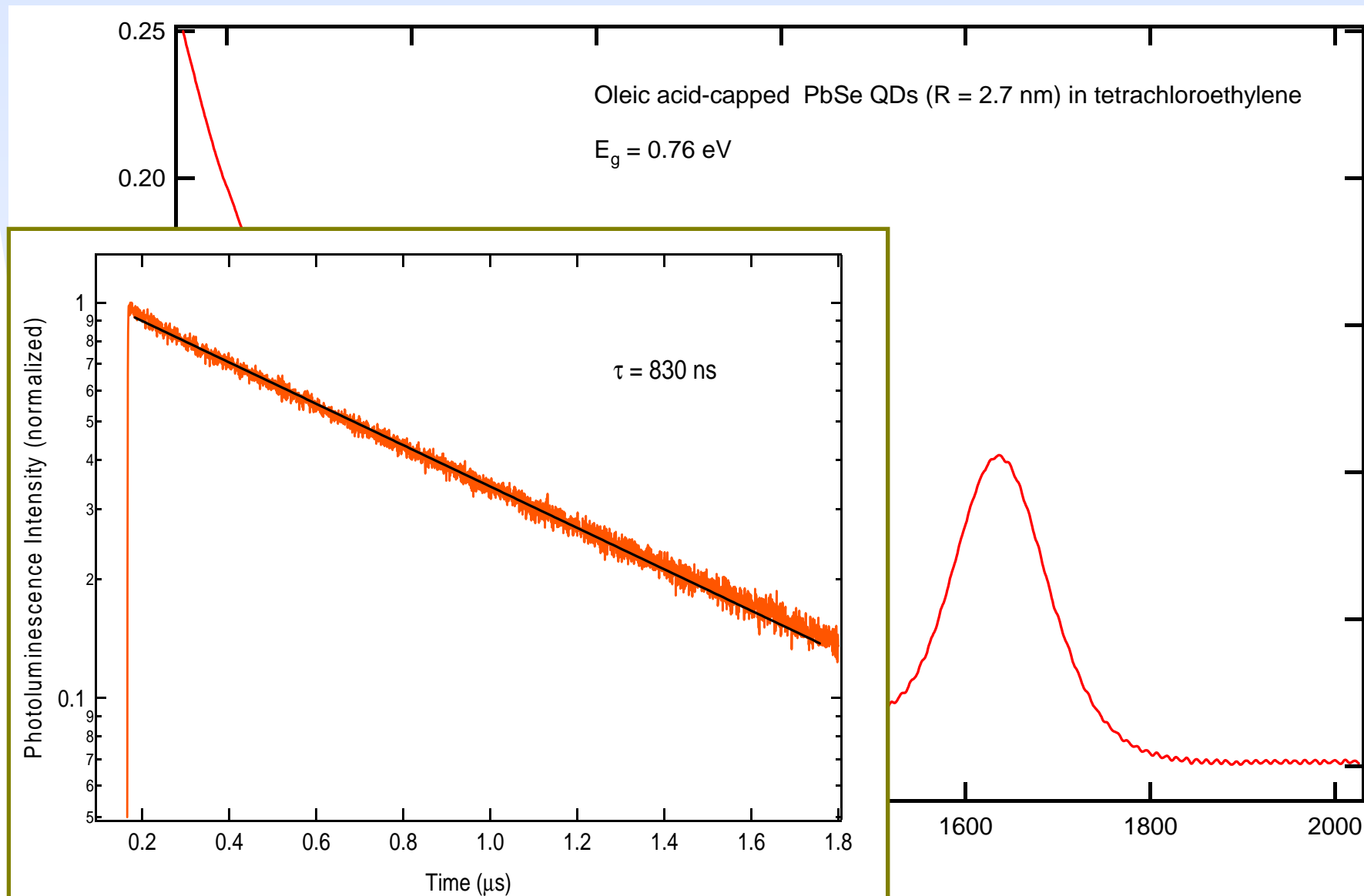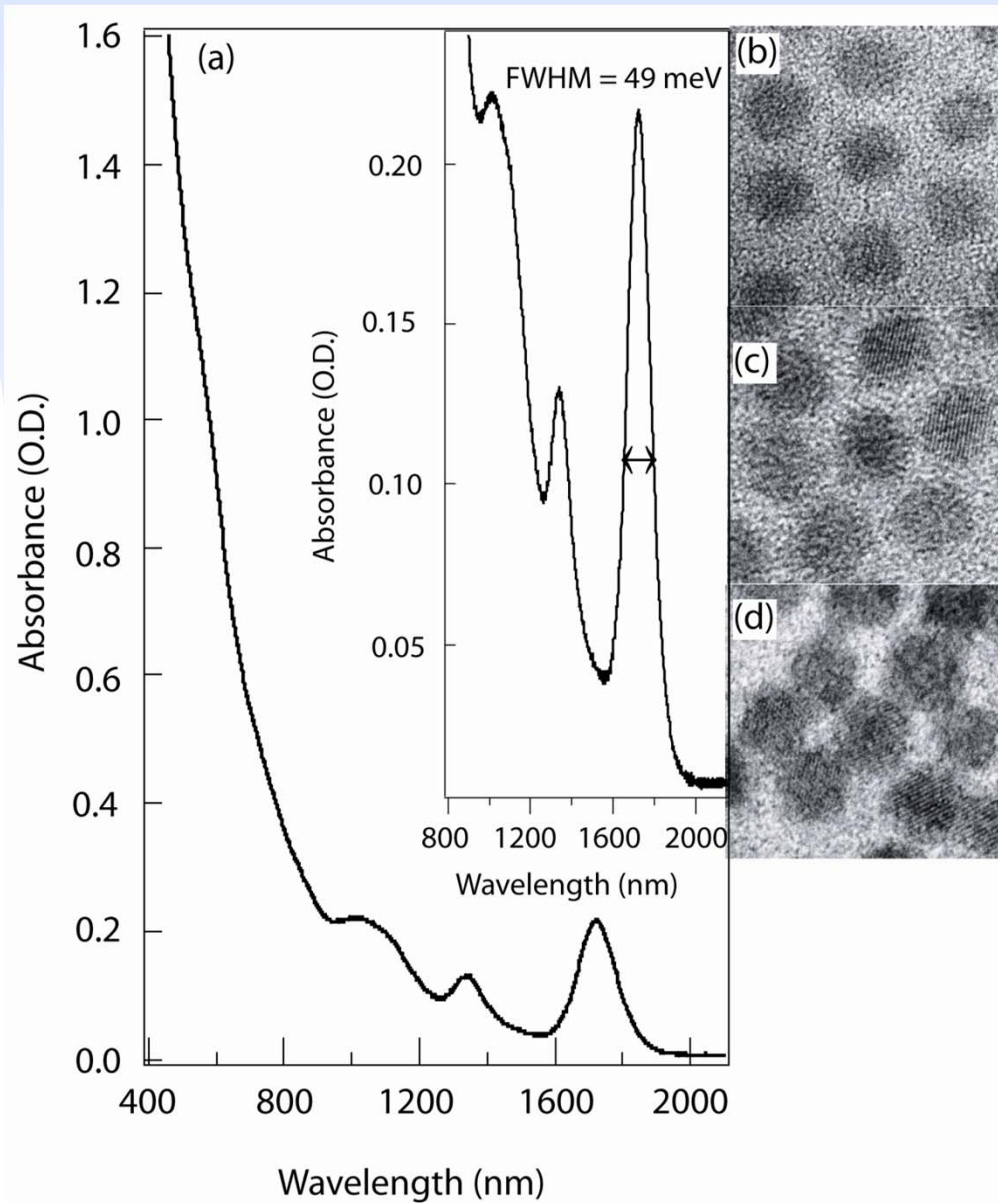
Annealed NC-based solar cell
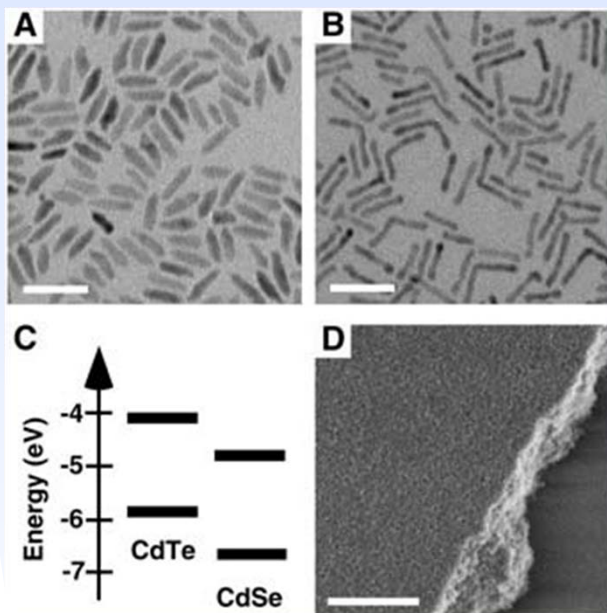
Transmission electron micrographs of (A) CdSe and (B) CdTe NCs used in this investigation. Scale bar, 40 nm. (C) An energy diagram of valence and conduction band levels for CdTe and CdSe illustrates the type II charge-transfer junction formed between the two materials…

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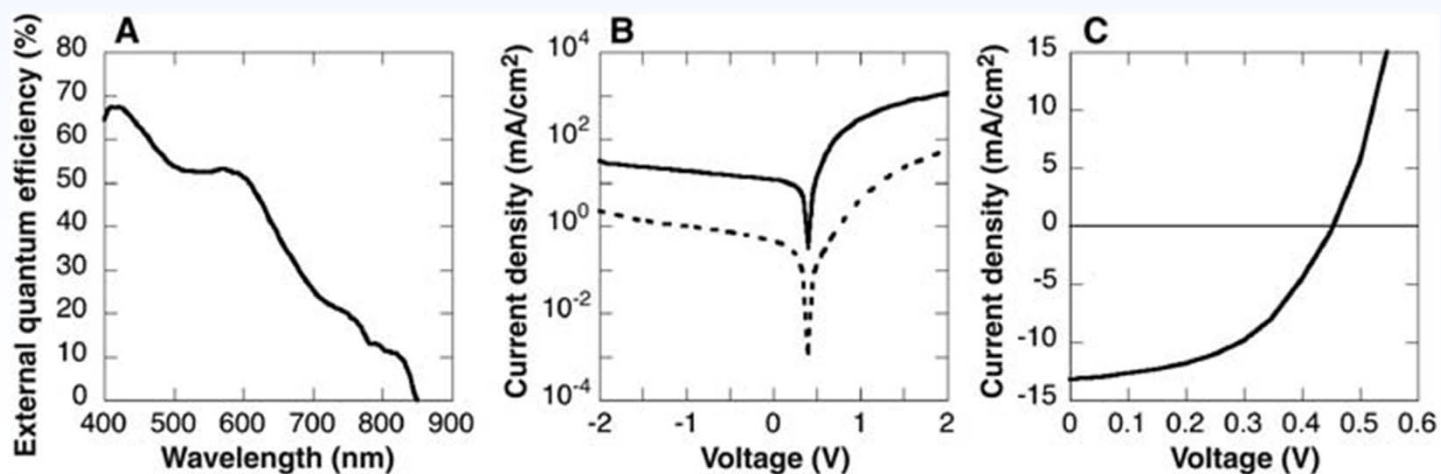
Drop-cast films of 5.7 nm dia. PbSe NCs

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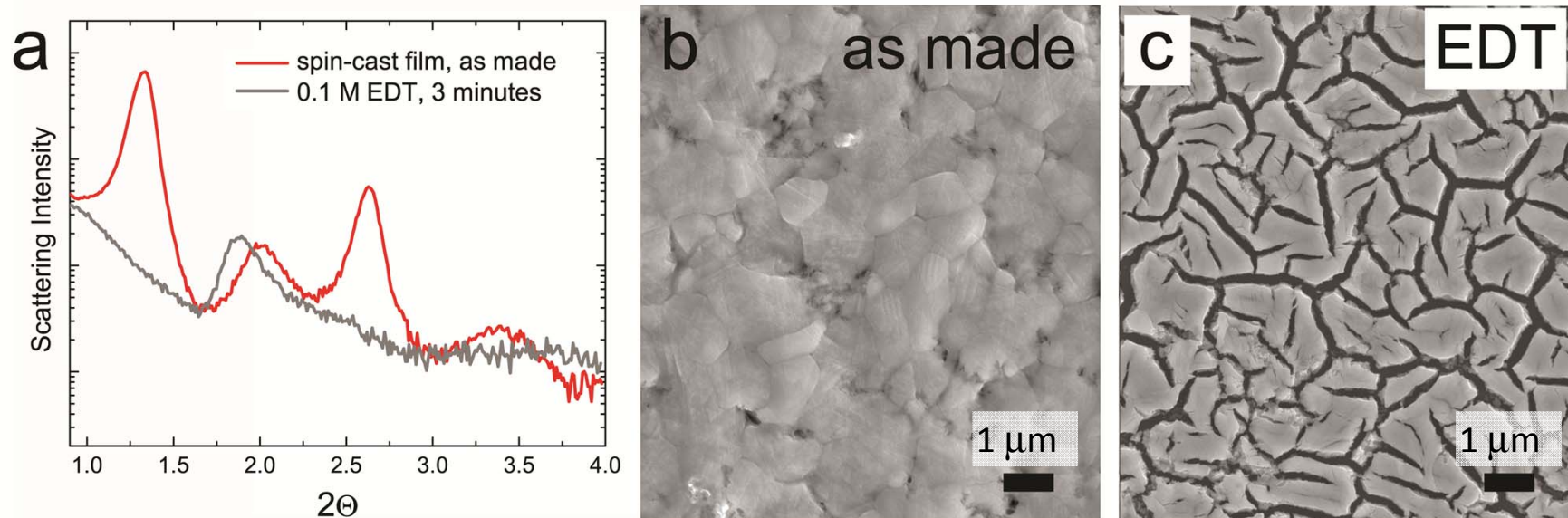
"Microstructure of the spin-cast NC films before and after EDT treatment. (a) SAXS data, showing a ~16 Å decrease in the spacing between the NCs and a dramatic loss of superlattice order upon EDT treatment. Measurements were taken in air. (b, c) Plan-view SEM images of (b) an untreated film and (c) a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

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

Layer-by-layer fabrication of PbSe NC films
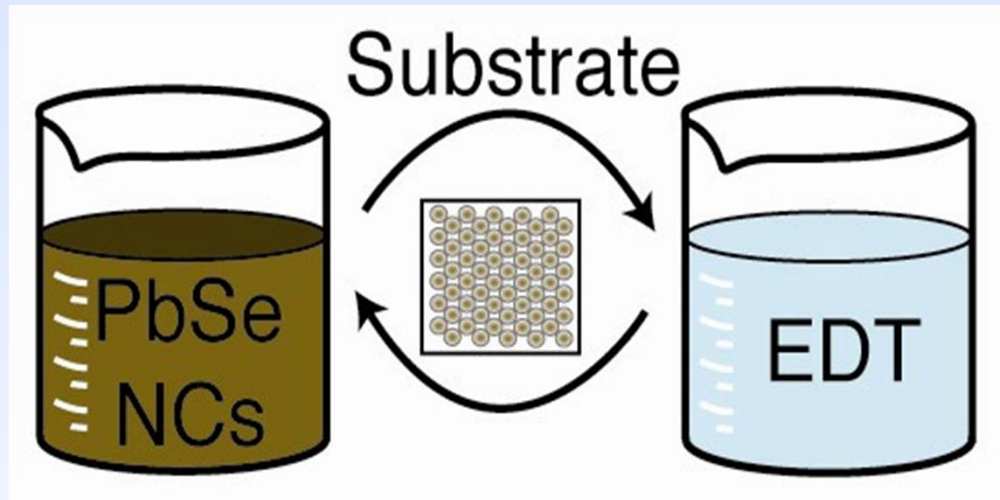
EDT = 1,2-ethanedithiol

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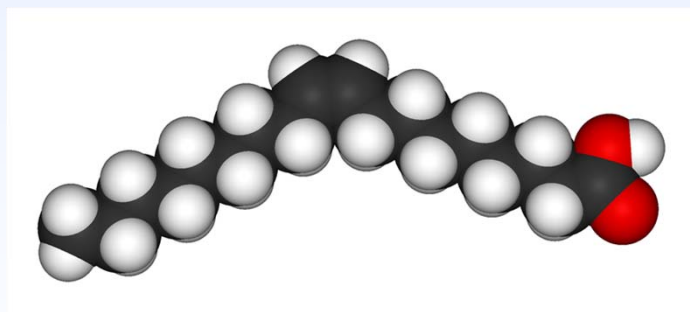
J. M. Luther, M. Law *et al.*, "Structural, Optical, and Electrical Properties of Self-Assembled Films of PbSe Nanocrystals Treated with 1,2-Ethanedithiol", *ACS Nano* **2**, 271 (2008).

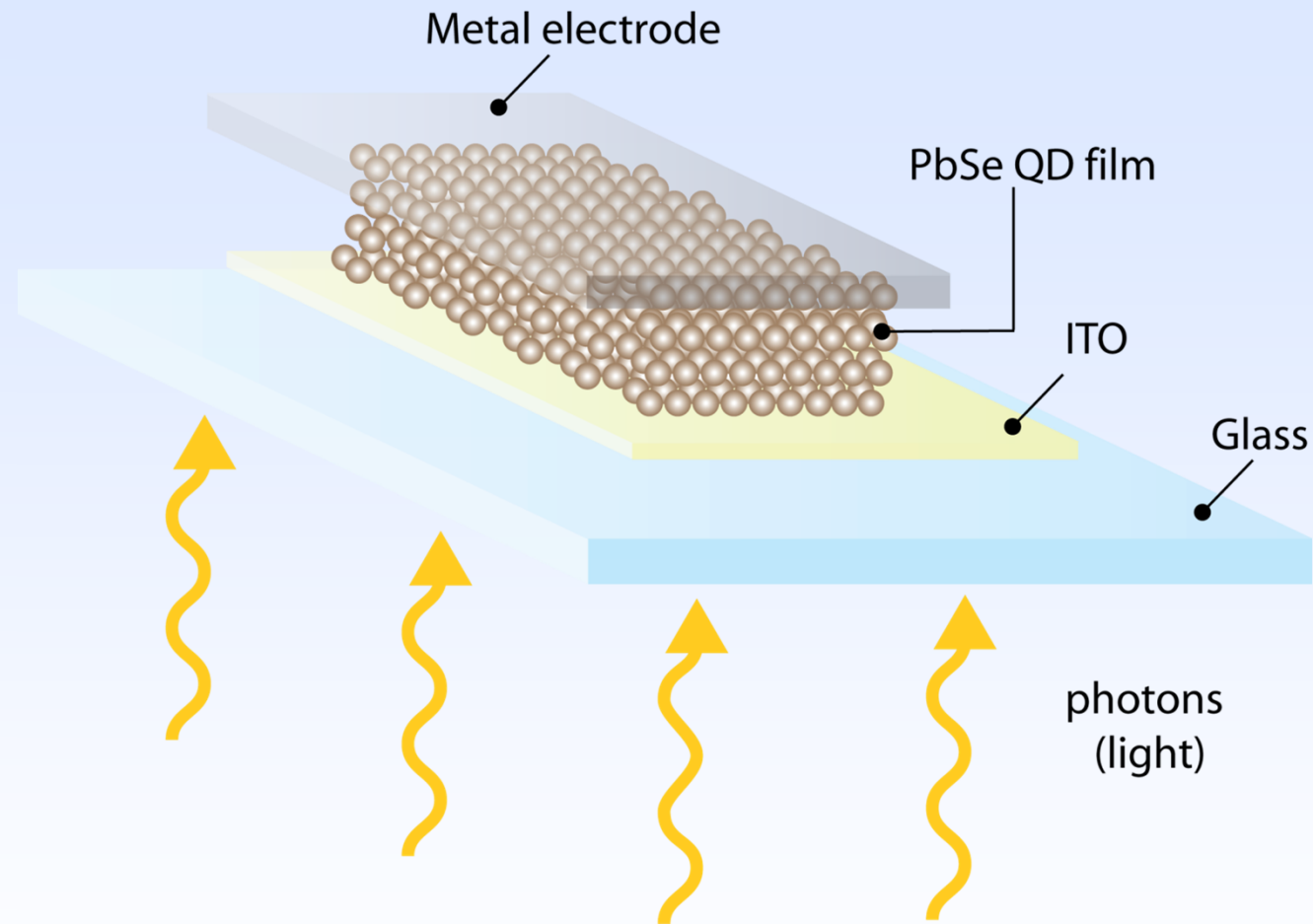# Ligand exchange in PbX NC films
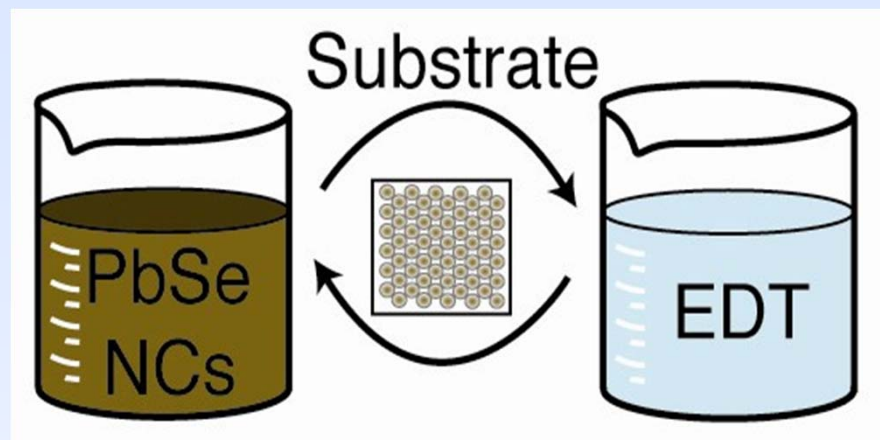
EDT = 1,2-ethanedithiol

Oleic acid, $C_{18}H_{34}O_2$
$L \approx 20 \text{ Å}$
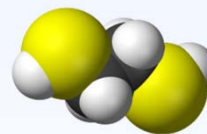
1,2-ethanedithiol
$C_2H_6S_2$
$L \approx 6 \text{ Å}$

Schottky barrier nanocrystal-based solar cell

Metal electrode

PbSe QD film

ITO

Glass

photons
(light)

- 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

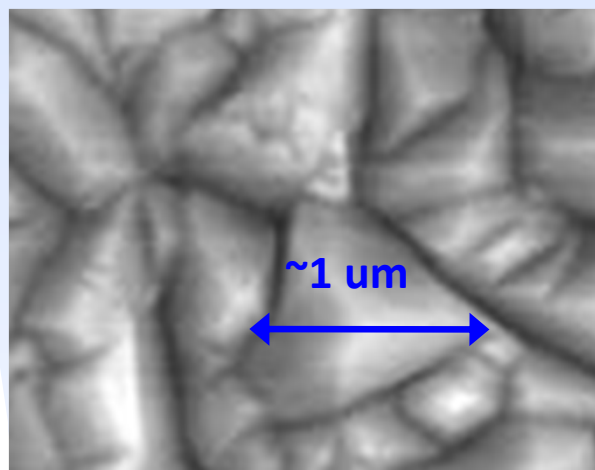# Layer-by-layer dip-coated PbSe films

100 nm
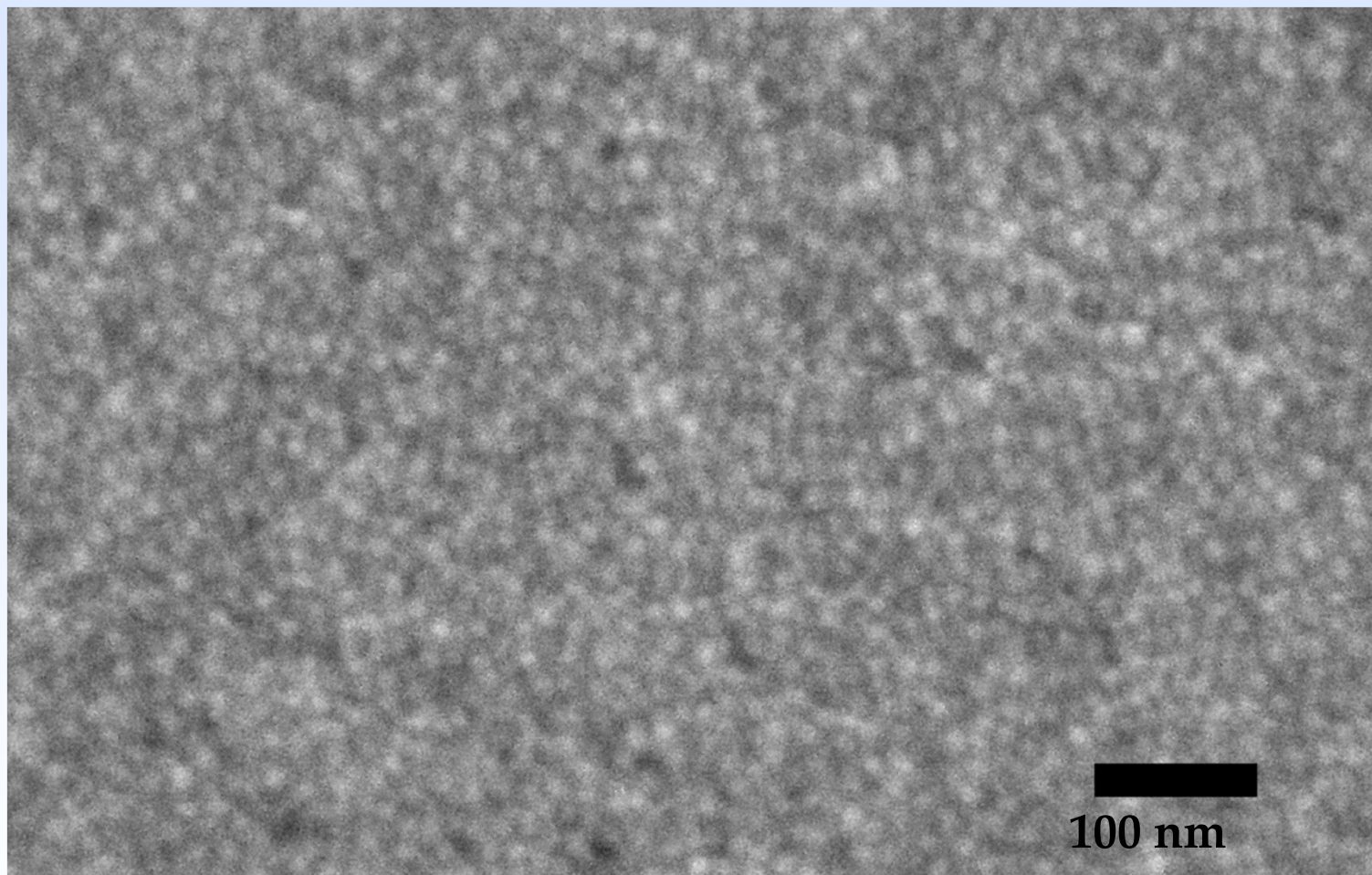
Plan view SEM image of PbSe NC films prepared by layer-by-layer dip coating onto ITO substrate. LbL film shown was produced using 10-20 dip coating cycles.
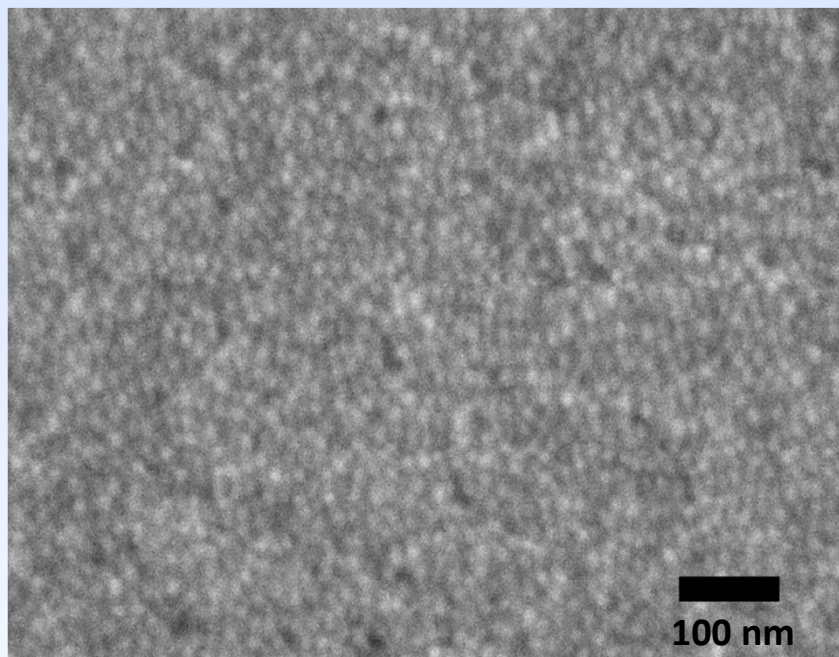
J. Luther, M. Law *et al.*, *ACS Nano* **2**, 271 (2008).

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"Grain boundary" density considerations

e.g. CdTe

100 nm

Estimating effective "grain boundary densities" (boundary area / layer area)

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

3 (µm²/ µm²)

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

600 (µm²/ µm²)

$$S/V \propto 1/r$$

Directions in QD-based solar cell research

Nozik, 2002
Schaller, 2004

Gur, 2005

Luther, 2008

Choi, 2009

Leschkies, 2009

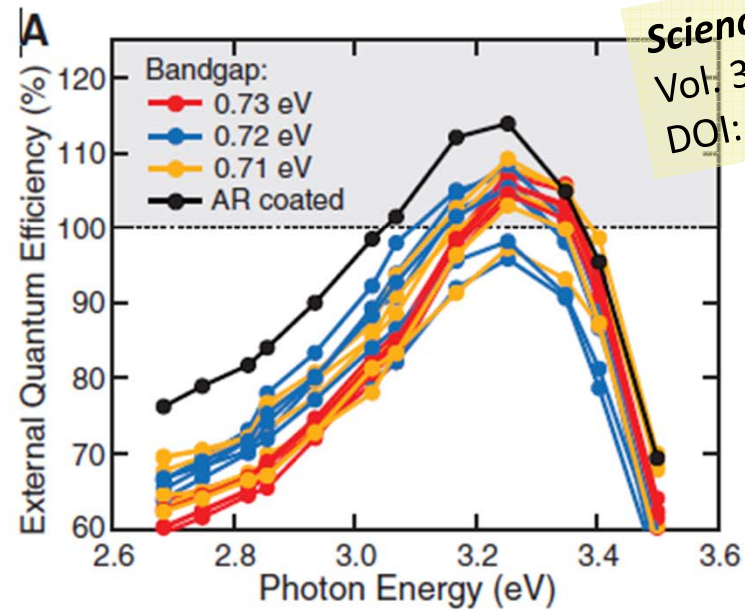Luther, 2010, 2.9%

Gao, 2011

Gao, 2011, 4.4%

Tang, 2011, 5.1%

Directions in QD-based solar cell research
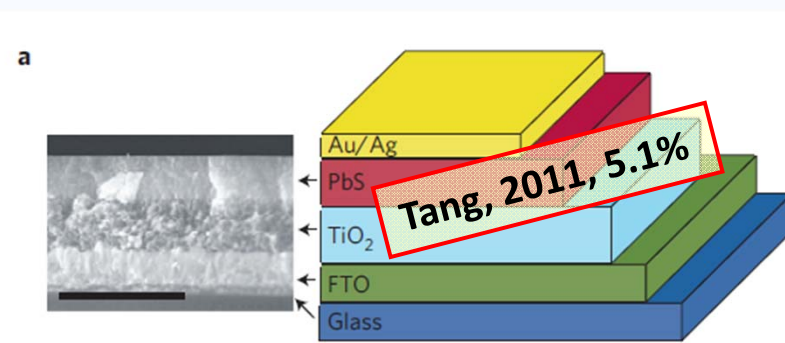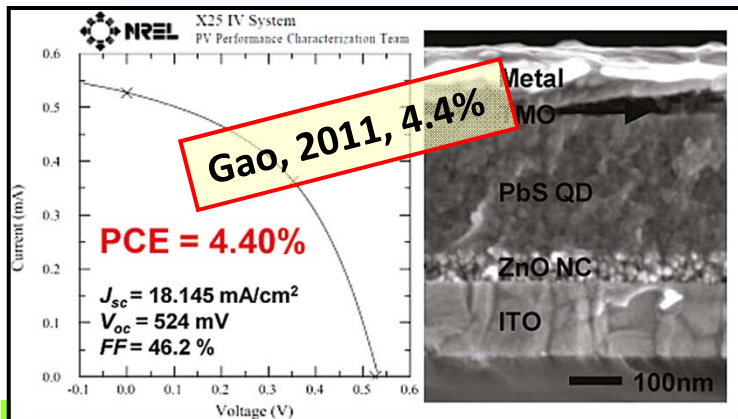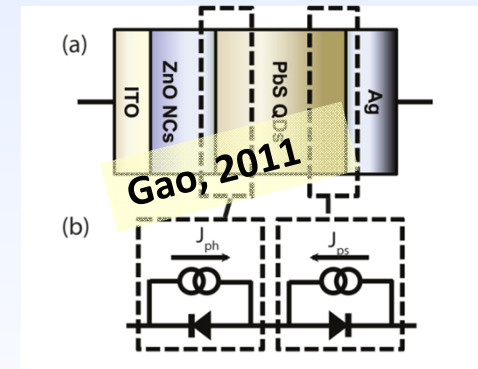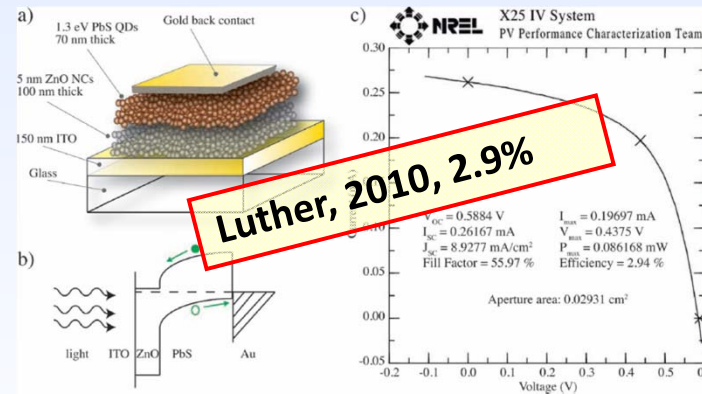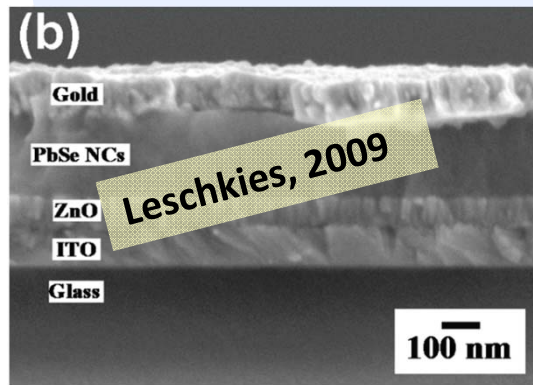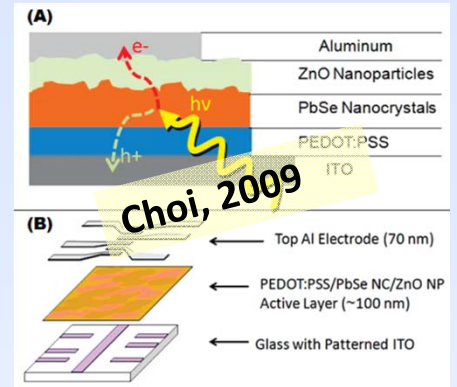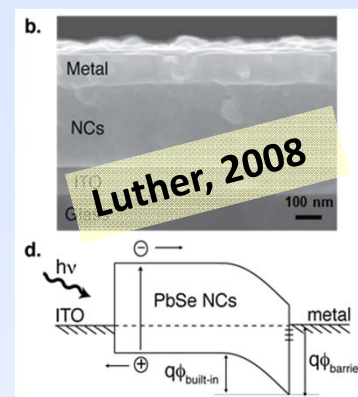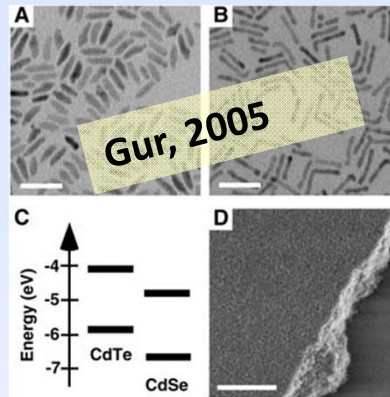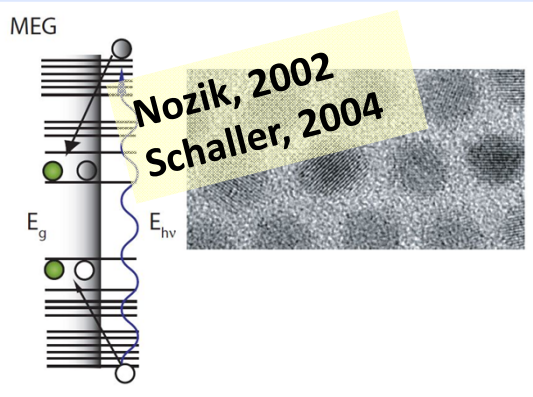
Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell

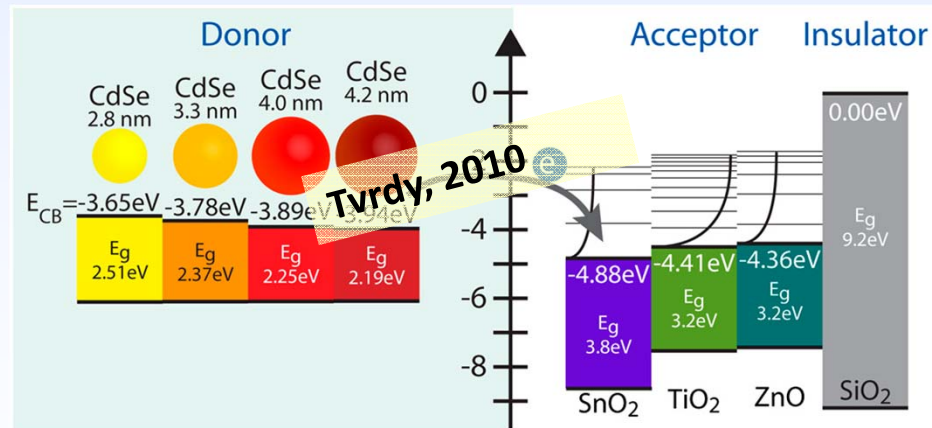Octavi E. Semonin,[1,2] Joseph M. Luther,[1] Sukgeun Choi,[1] Hsiang-Yu Chen,[1] Jianbo Gao,[1,3] Arthur J. Nozik,[1,4]* Matthew C. Beard[1]*

Directions in QD-based solar cell research

Ju, 2010

Kang, 2011

Fu, 2011

Tvrdy, 2010
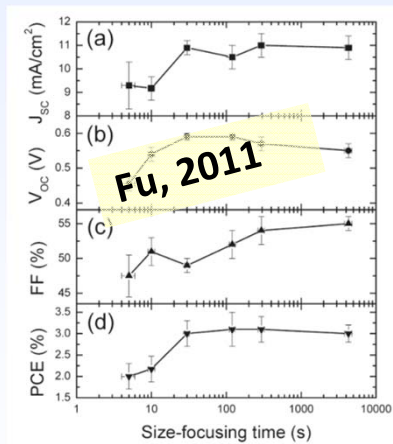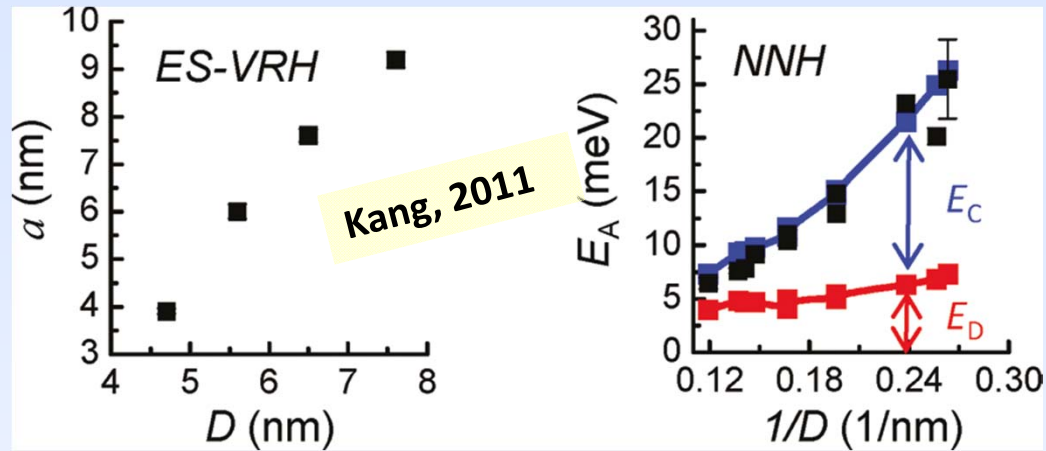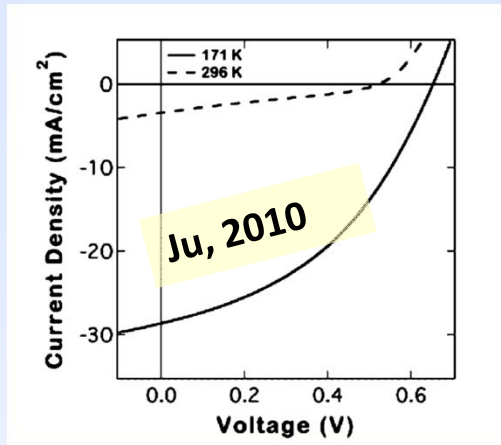
Many others
2002-2012

Roll-to-roll processing from solution source (e.g., Nanosolar CIGS)
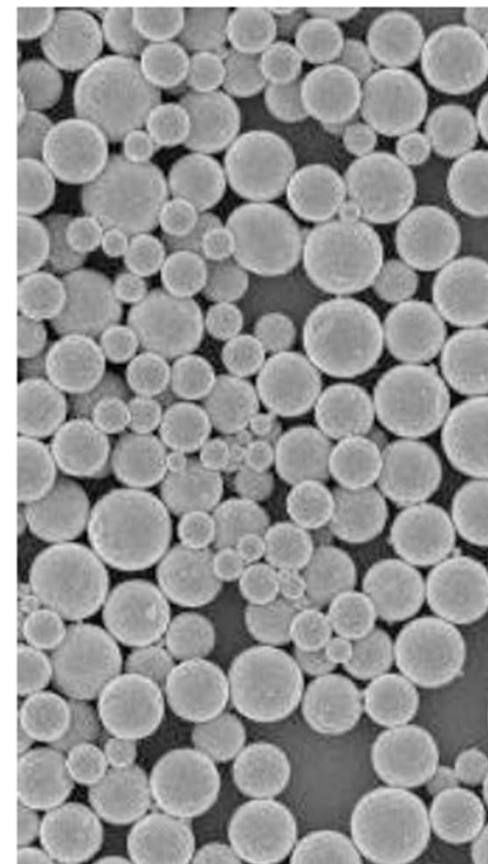
Figure 6 and 7: A laboratory sample of our nanoparticle ink. Nanoparticles shown to the right are an average of 20nm in diameter.

from NanoSolar white paper

Good solar cells from nanoparticle inks (CIGS)

Nanosolar
CdS/Cu(In,Ga)Se$_2$ Cell

Device ID: H09B071-01C #2   Device Temperature: 24.0

Apr 09, 2009 12:31   Device Area: 0.5000 cm^2

Spectrum: ASTM G173 global   Irradiance: 1000.0 W/m^2

NREL X25 IV System   Confidential
PV Performance Characterization Team
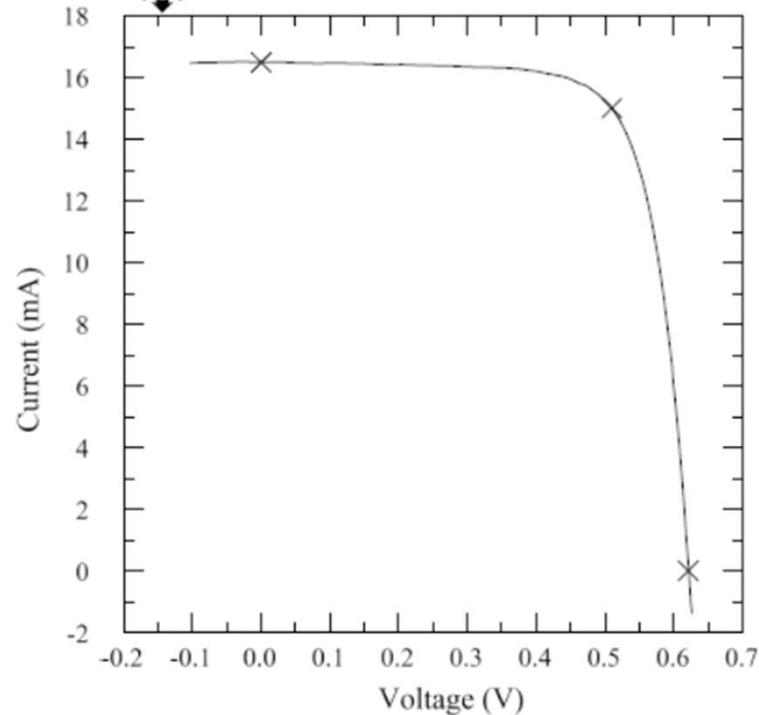
V_{oc} = 0.6214 V I_{max} = 15.010 mA

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

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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)

0.78 nm

(0,10) nanotube
(zig-zag)
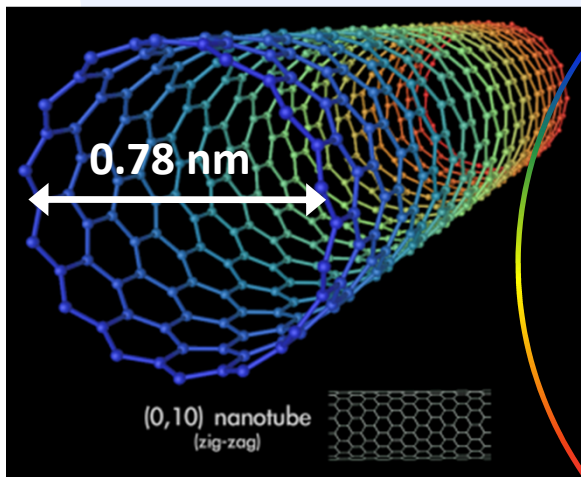
http://commons.wikimedia.org/
wiki/Main_Page

PbS NC

~ 5 nm
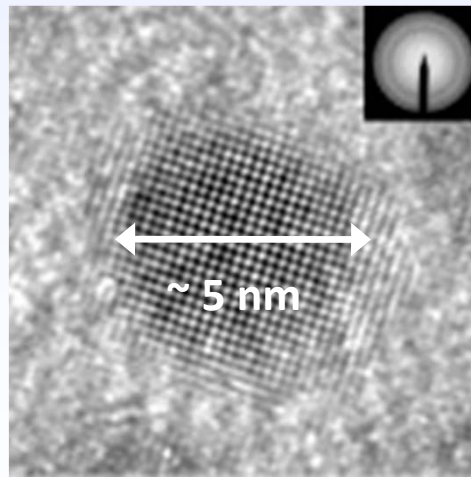
Sargent, Adv. Mat. (2005),
515-522.

CdTe grain size (CSS)

~1 um
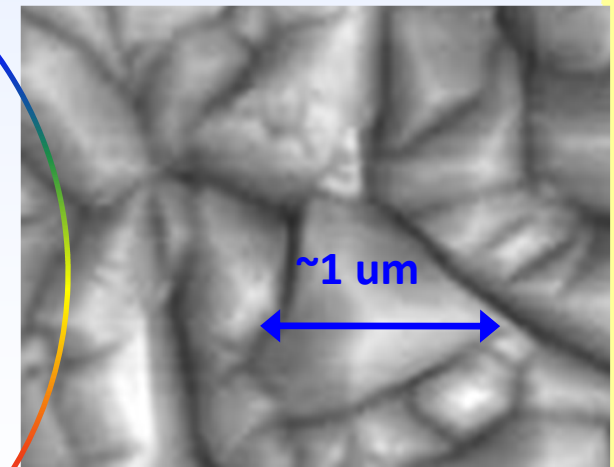
Quiñones et al., J. Mater. Sci: Mat.
Electron (2007), 1085–1091

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Colloidal quantum dot – scale

~1 um

5 nm dia.
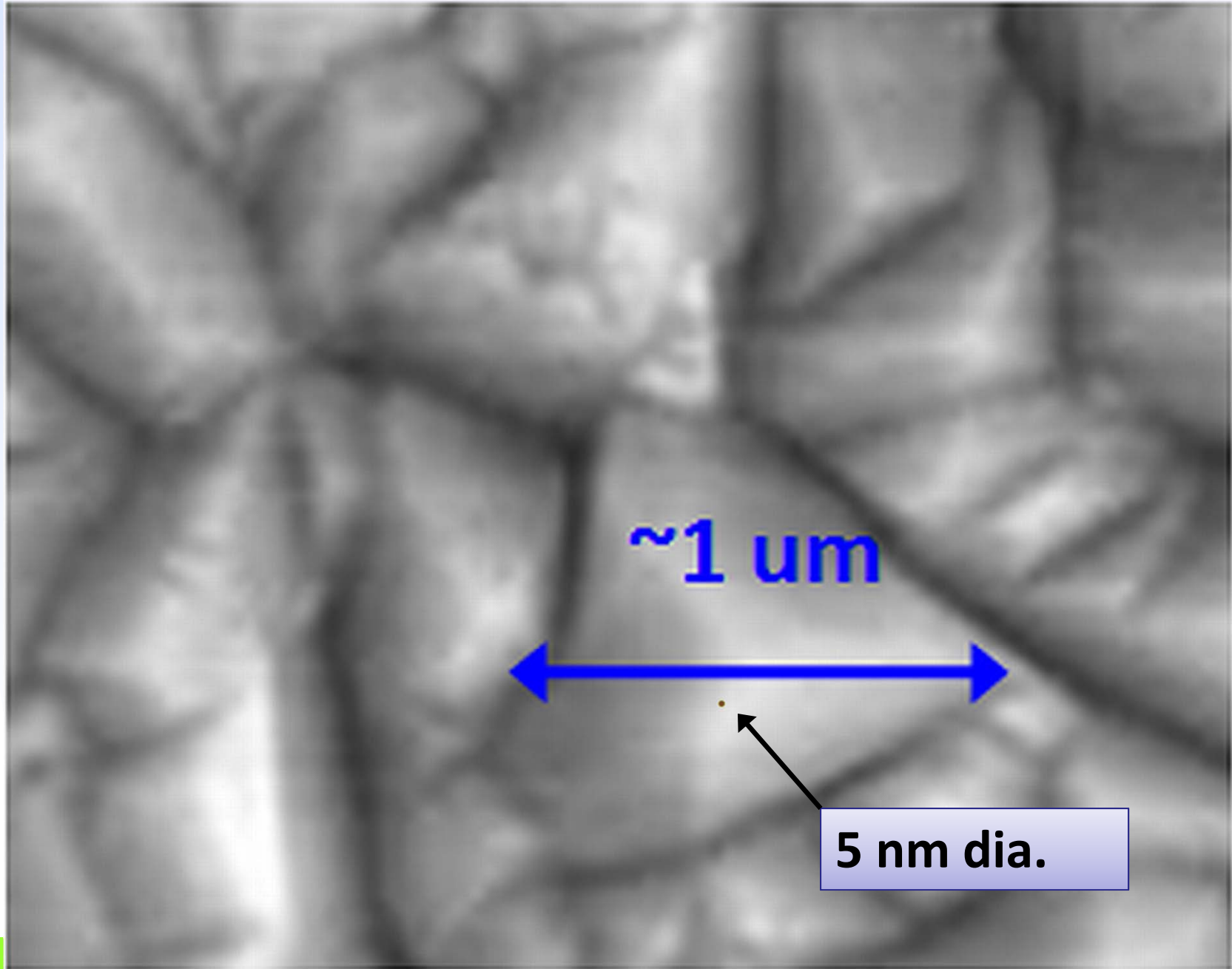
Coupling QDs within a film (or array)

Figure 6. Absorption and luminescence spectra (λ_{exc} = 500 nm) of InP QDs in dilute colloidal solution and in close-packed films for 45- and 35-Å diameter QDs.

Optical, Electronic, and Structural Properties of Uncoupled and Close-Packed Arrays of InP Quantum Dots
Olga I. Mic´ic´ et al., 1998.

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Coupling mechanisms

What could cause a decrease in QD-QD spacing to red-shift the exciton transition?

"This can cause (i) an increase in the average dielectric constant of the film, (ii) an increase in the inter-QD radiative coupling, and (iii) an increase in the inter-QD electronic coupling."

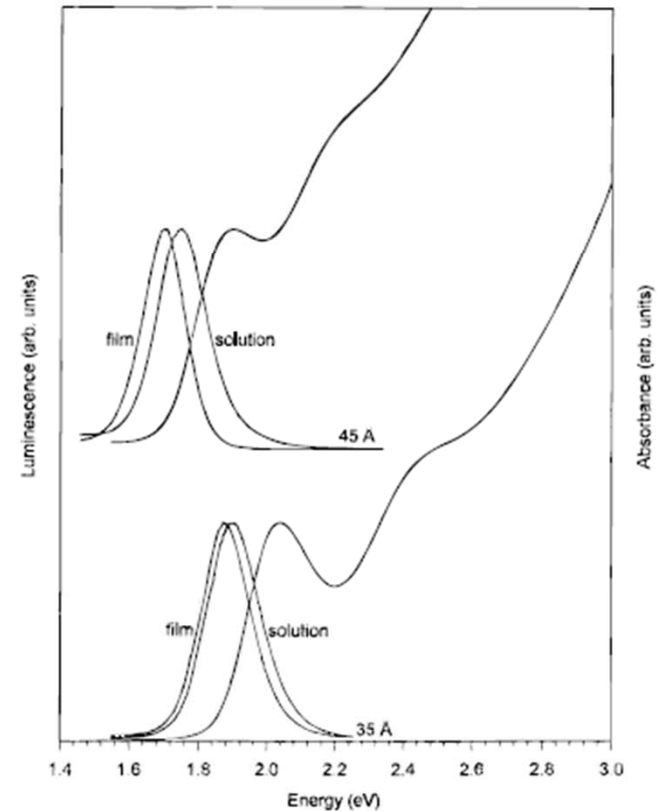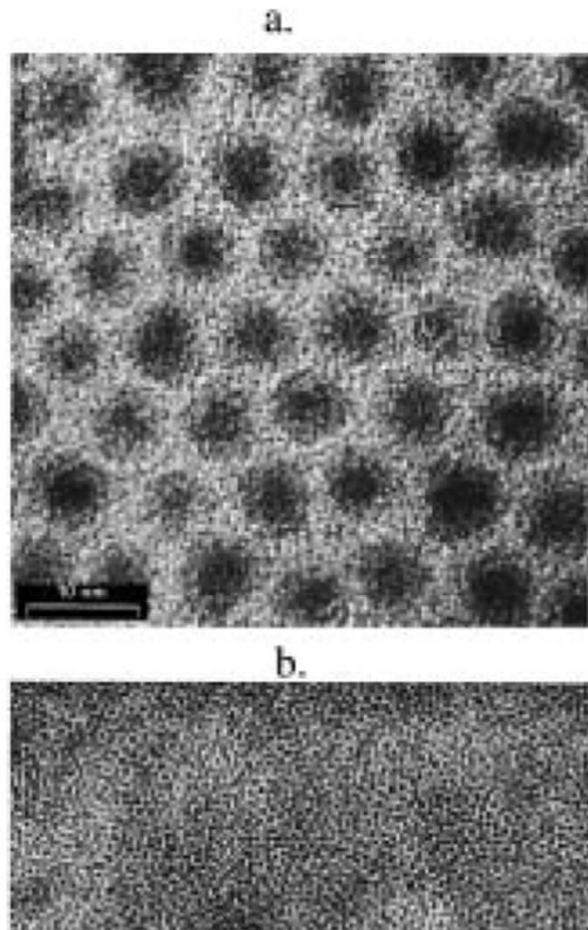> *Strong Electronic Coupling in Two-Dimensional Assemblies of Colloidal PbSe Quantum Dots*, Williams et al., ACS Nano (2009)

i)   Increased wavefunction extension

ii) Increased FRET

iii) Reduced barrier width for tunneling/hopping transport

$$a_B^* = \left(\frac{\varepsilon m_e}{\varepsilon_0 m_r^*} \right) 0.053 nm$$

Kopf, R. F., E. F. Schubert, et al. (1993). "Modification of GaAs/AlGaAs growth-interrupted interfaces through changes in ambient conditions during growth." Journal of Applied Physics 74(10): 6139-6145.

Energy/charge transport mechanisms

Energy transfer (FRET):

$$E = \cfrac{1}{1 + \left(\cfrac{r}{R_0} \right)^6}$$

$\Rightarrow R_0 \approx$ 8-9 nm for ~3 nm InP QDs

*J. Phys. Chem. B **1998, 102, 9791-9796***

Hopping/tunneling transport:

$$\Gamma_{ij} = \Gamma_0 \exp(-\beta d) \begin{cases} \exp\left[-\dfrac{E_j - E_i}{kT} \right] & E_j > E_i \\ 1 & E_i > E_j \end{cases}$$

Miller, Abrahams, Phys. Rev. 120, 745–755 (1960)

Liu, Hillhouse, Law, Nano Lett. (2010), 10, 1960.

Post-deposition treatment of drop-cast films of 5.7 nm dia. PbSe QDs
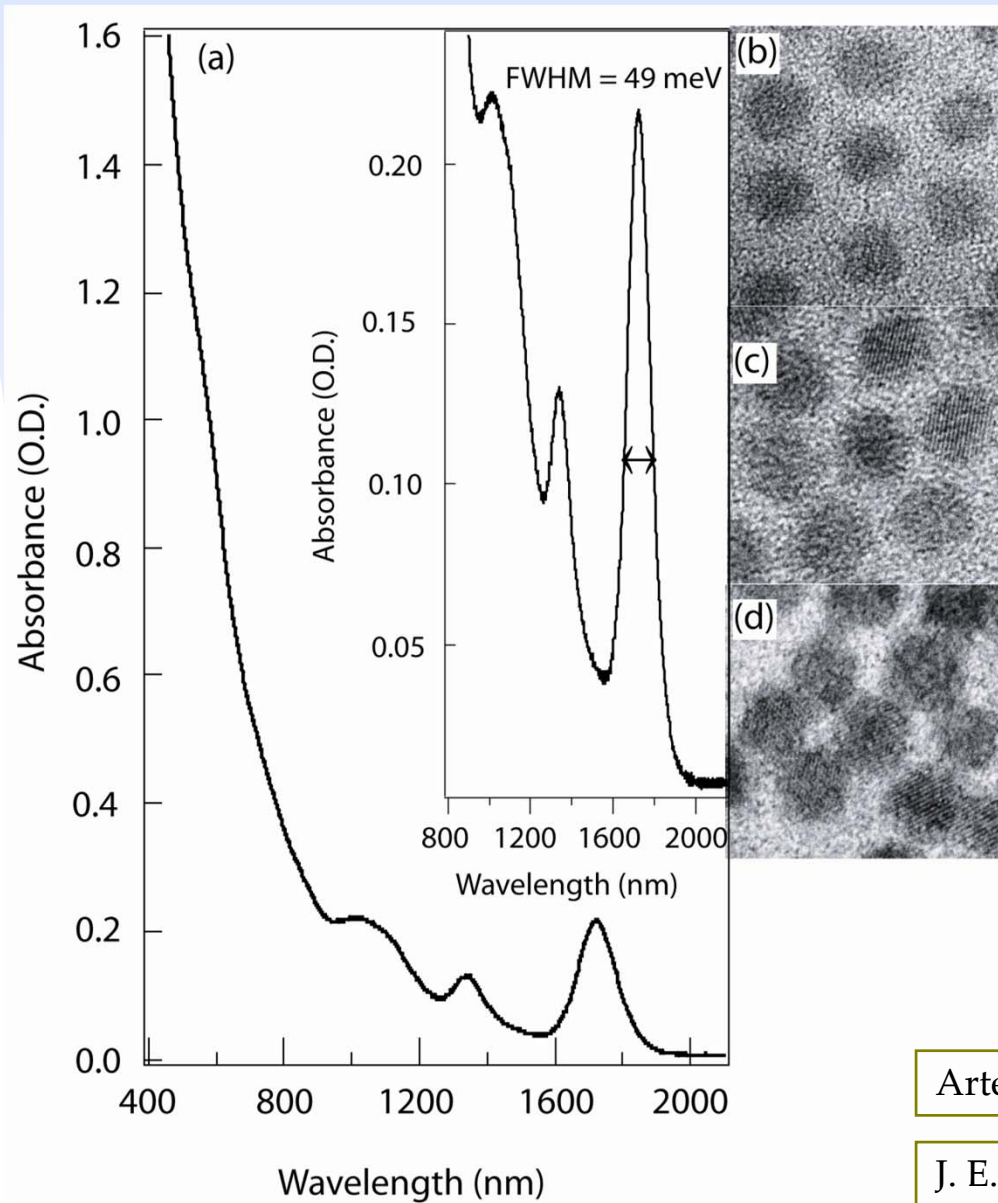
oleic acid (1.8 nm)

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.

Absorption spectra: spincast films of 1310 nm PbSe NCs

Steady-state photoluminescence (1310 nm NCs)
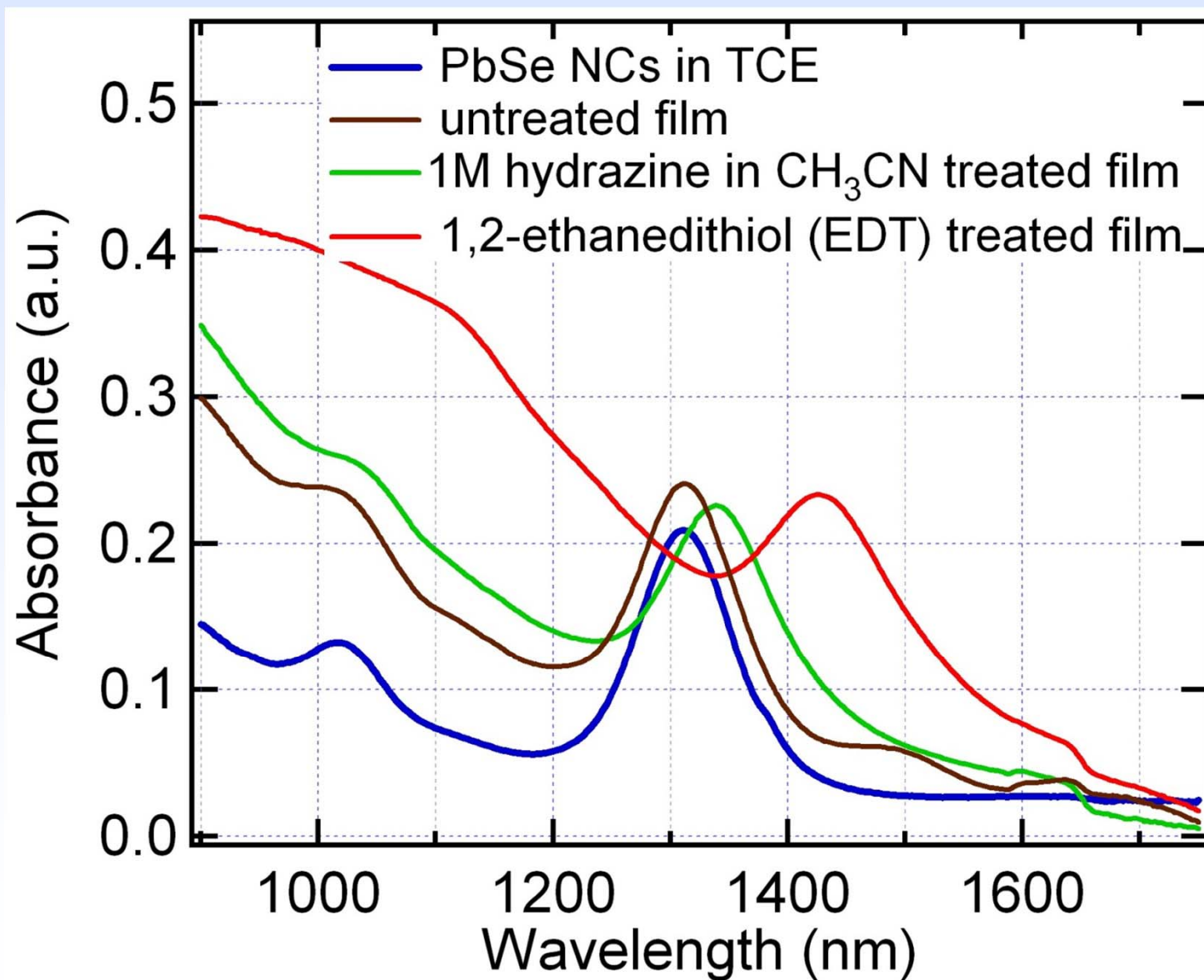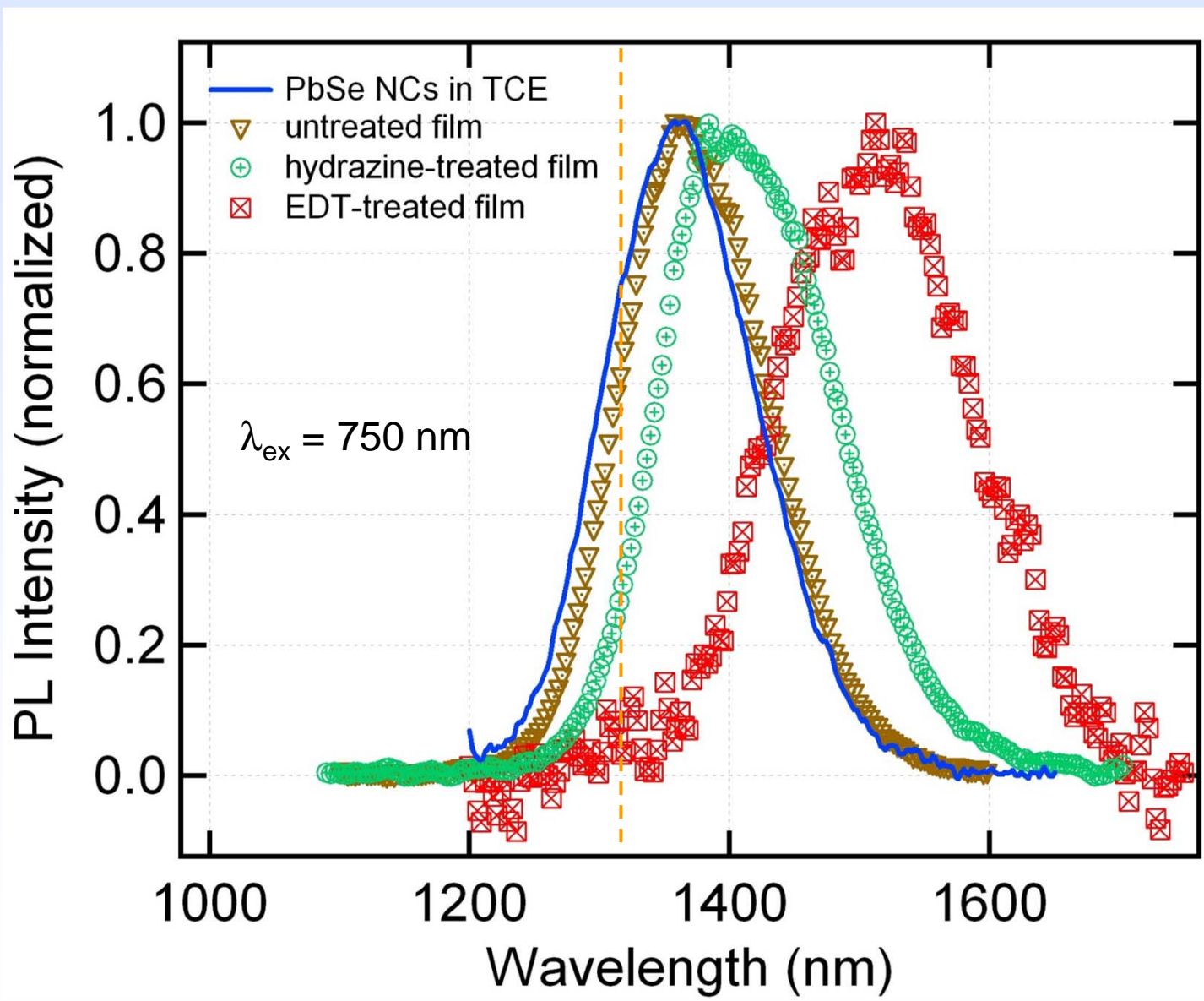
Time-resolved photoluminescence spectra

1310 nm (1st exciton) PbSe NCs (solution and films), λ_{ex} = 750 nm

⊠ PbSe NCs in TCE, τ_1 = 1.2 µs (λ_{PL} = 1362 nm)

● aged untreated film, τ_1 = 550 ns, τ_2 = 270 ns (λ_{PL} = 1364 nm)

◆ fresh untreated film, τ_1 = 750 ns, τ_2 = 380 ns (λ_{PL} = 1364 nm)

▲ hydrazine treated film, τ_1 = 80 ns (λ_{PL} = 1400 nm)
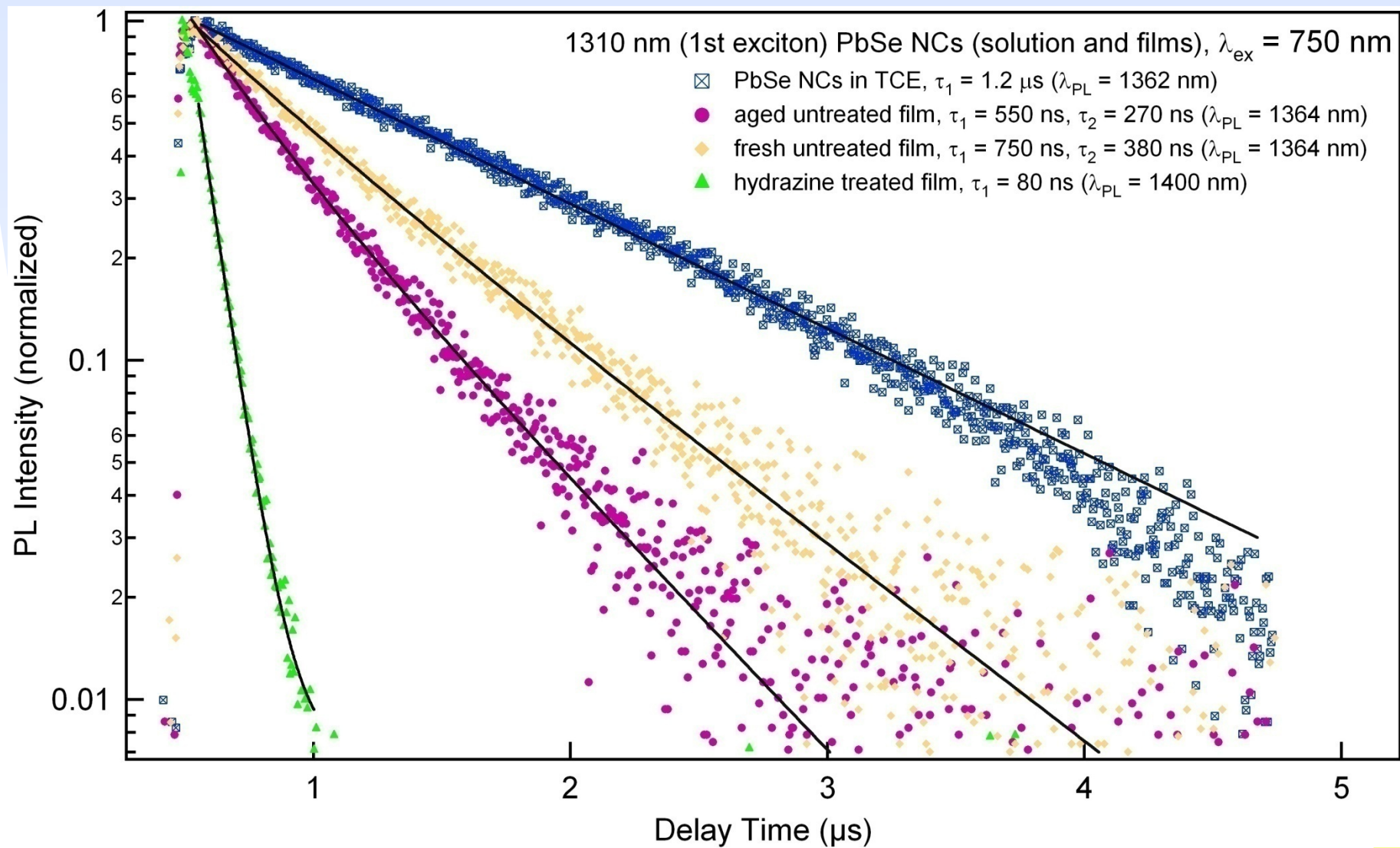
PL lifetime for EDT-treated PbSe NC film

Figure legend:
⊕ EDT treated film
τ_1 = 0.30 ns (λ_{PL} = 1530 nm)
- - - instrument response function (IR26 dye)
—— single exp fitting

Axis labels:
PL Intensity (normalized)
Delay Time (ns)
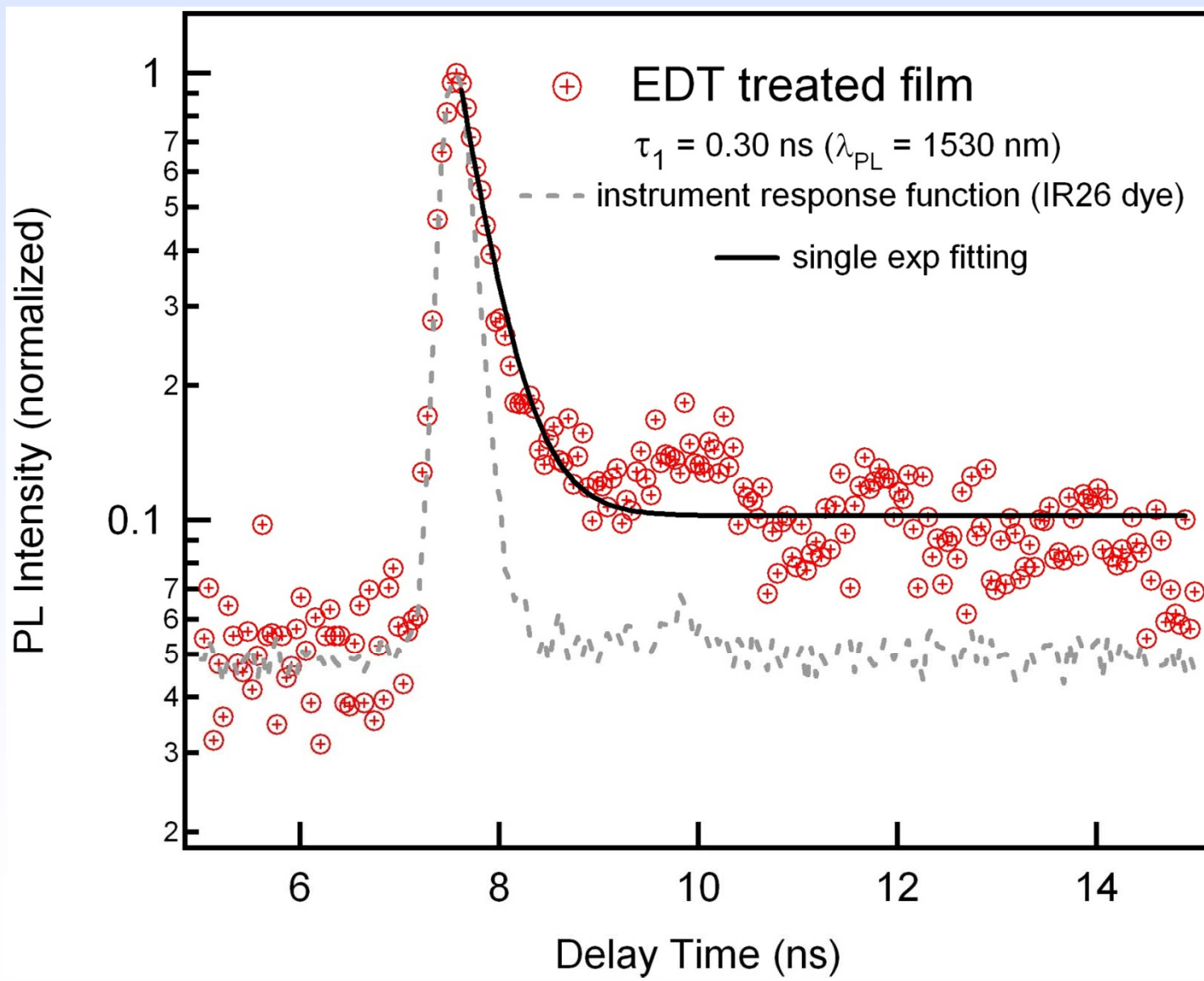
Depletion width and doping density

a.

0.72 eV PbSe NCs
- □ 400 nm
- ○ 65 nm

y-axis: $1/C^2$ (F^{-2}), from 0.0 to 1.0×10^{17}

x-axis: Voltage (V), from -0.8 to 0.4

Inset:
- y-axis: Carrier Density (cm^{-3}), 10^{15} to 10^{18}
- x-axis: Depletion width (µm), 0.1 to 0.4
- -2 V, 0 V labels
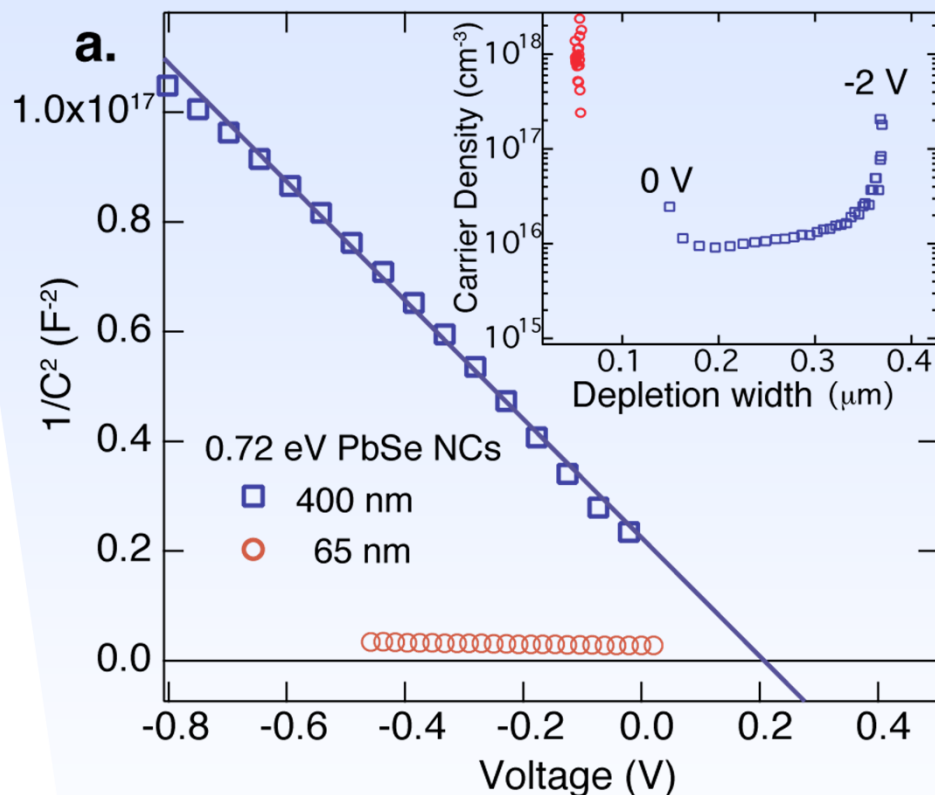
"Mott-Schottky plots at 1 kHz for devices with a thin (65 nm, red) and thick (400 nm, blue) NC layer. The thick device has an equilibrium depletion width of ~150 nm, while the thin device is fully depleted."
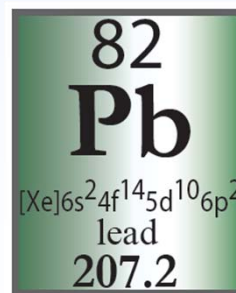
Relation between doping density and QD density? QD size ~ 6 nm dia., add 1 ligand ~0.5 nm, so V(QD) = $(4\pi/3)(3.2 \text{ nm})^3 = 1.3 \times 10^{-19} \text{ cm}^3$

Random packing of spheres → ~ 0.64

→ Vol. density of QDs ~ 5×10^{18} cm^{-3}
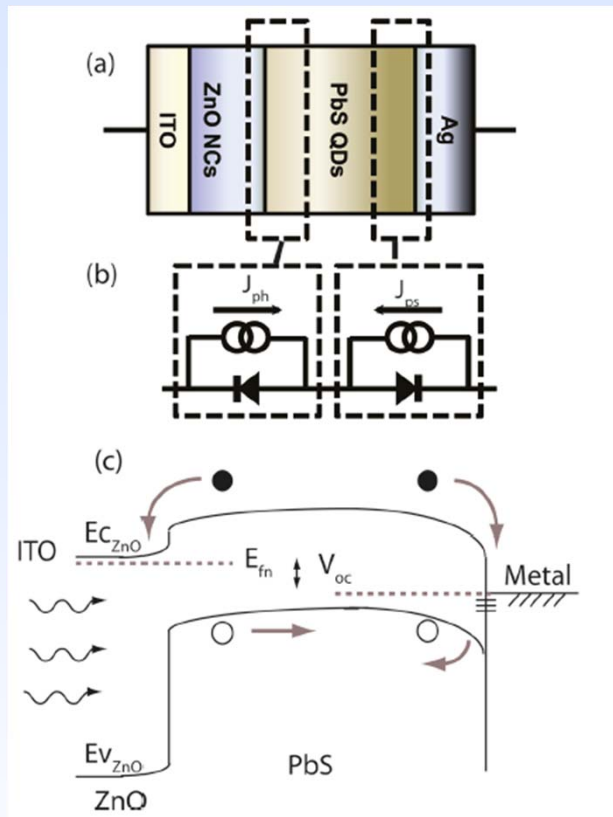
→ **~1 free carrier per 500 QDs**

How/why?

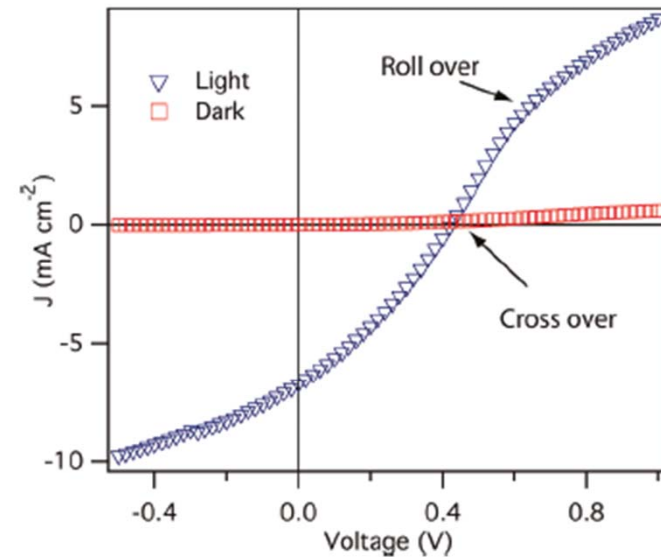| 82	16
Pb	**S**
[Xe]6s^{2}4f^{14}5d^{10}6p^2	[Ne]3s^{2}3p^4
lead	sulfur
207.2	32.07

Pb-rich → n-type

S-rich → p-type

Two-diode model for PbS/ZnO heterojunction device

(a) ITO | ZnO NCs | PbS QDs | Ag

(b) J_{ph} ... J_{ps}

(c) ITO Ec_{ZnO} ... E_{fn} ... V_{oc} ... Metal

Ev_{ZnO} ... PbS

ZnO

Figure 1. Typical characteristics of $J-V$ in the dark and under 1 sun illumination, which shows the crossover and roll-over effects. The device structure is ITO/ZnO NC/PbS QD/Ag with PbS layer thickness of ∼550 nm.

Two-diode model equivalent circuit including a main diode between ZnO QD film with PbS QD film, and a Schottky-diode between PbS QD film with top contact Au or Ag.

1. **Roll-over effect**, a fact of current limiting at positive voltage, is due to a hole transport barrier at Schottky-junction formed by PbS QD film with metal contact .
2. **Cross-over effect:** low forward current due to Schottky barrier at metal contact (hole transfer barrier).

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Best Research-Cell Efficiencies
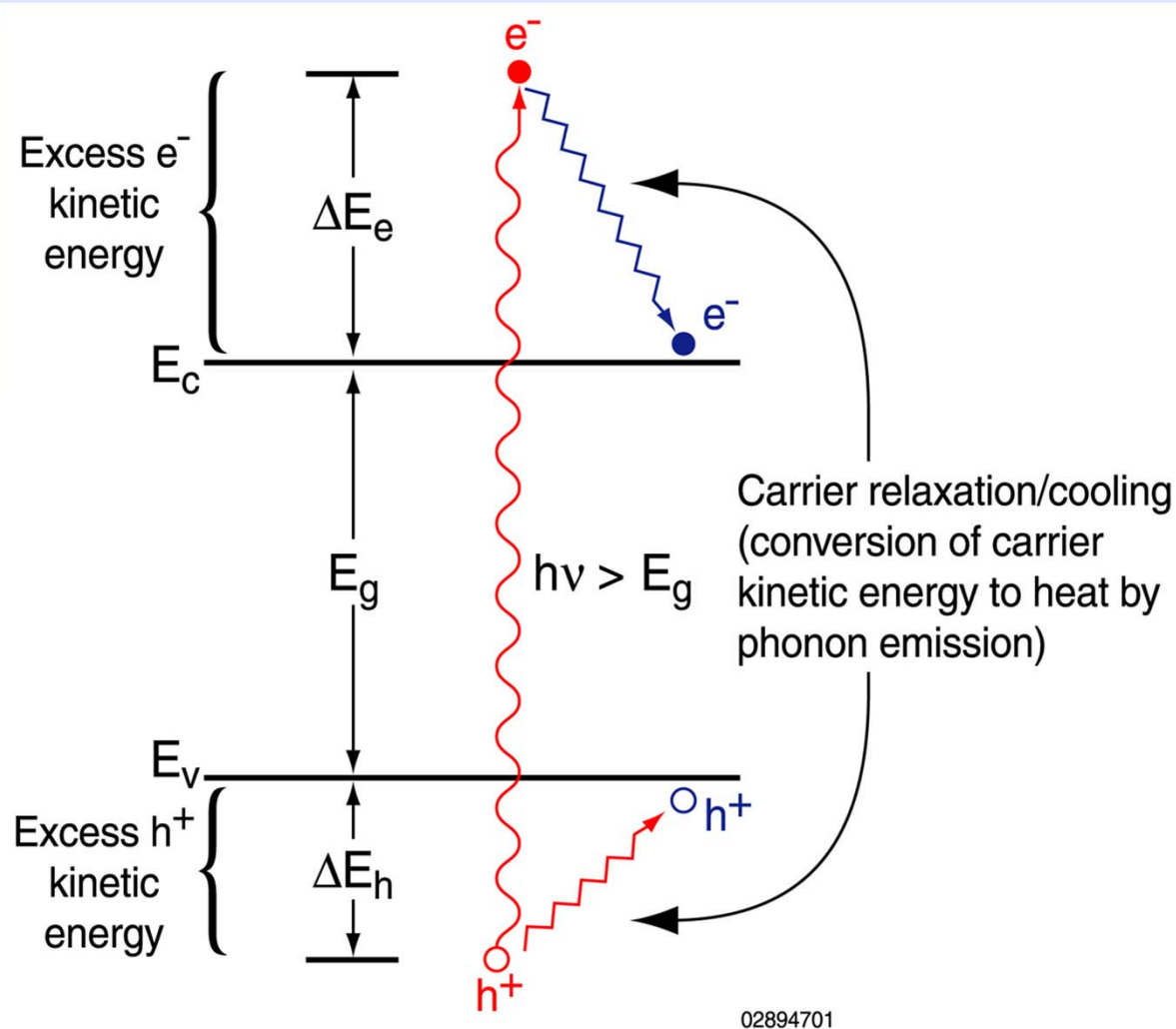
.... energizing Ohio for the 21st Century
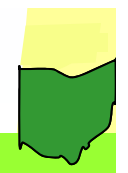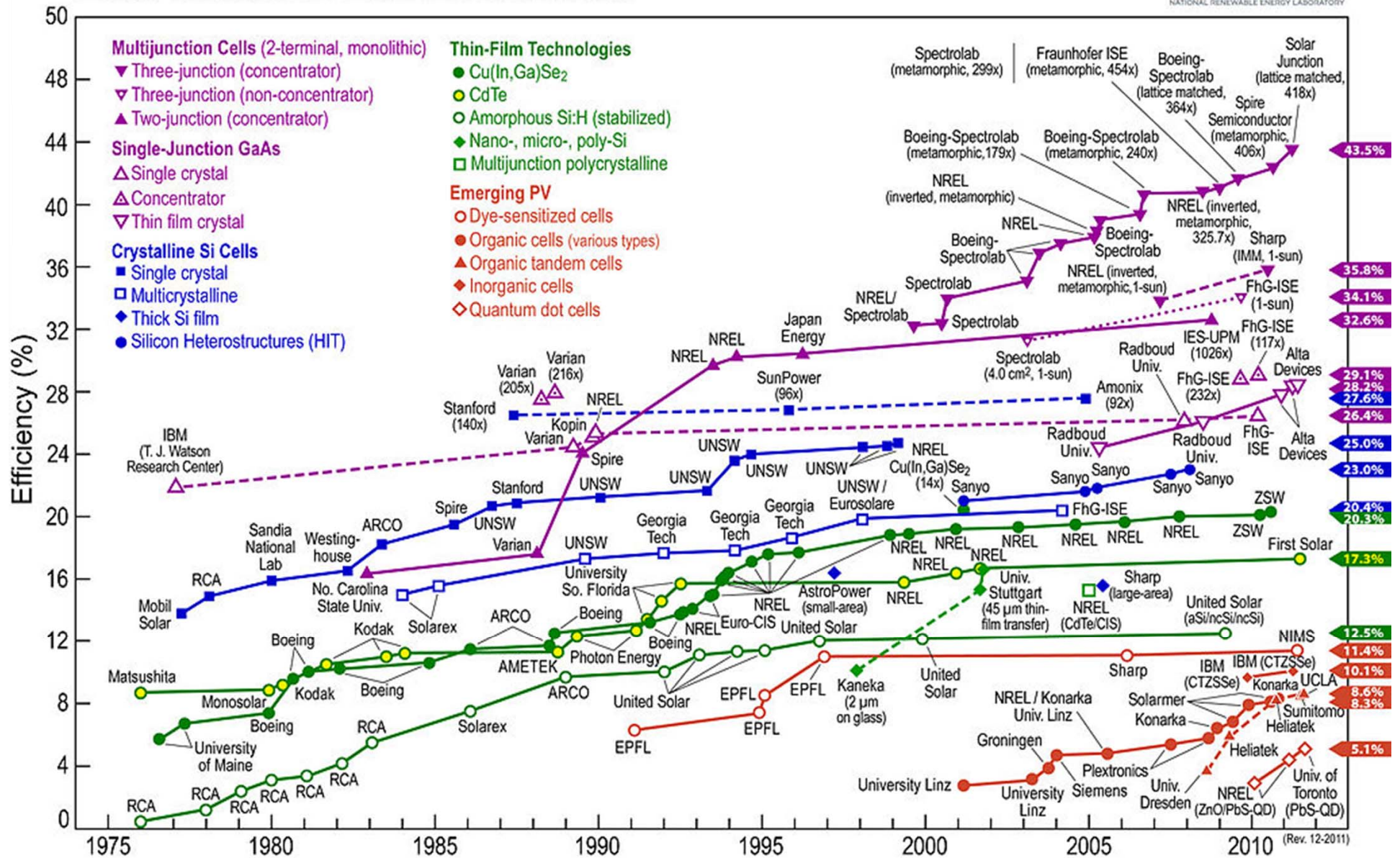
Issues of interest for QD-based thin film PV

- Energy intensity of materials and deposition
- Doping control within films
- Air/moisture tolerance (deposition and operation)

Thermalization losses

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

$\eta_{max} = 32.9\%$

Losses

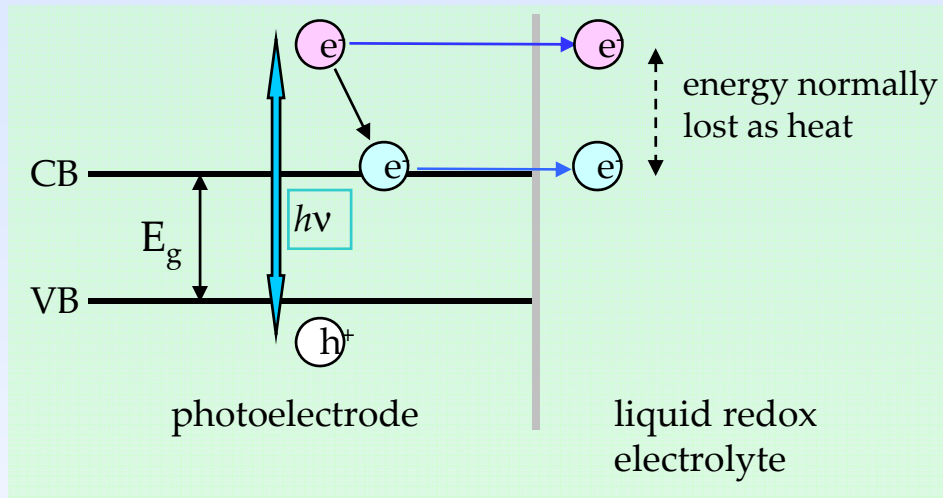transmission = 18.7%
radiative em. = 1.6%
heat   = 46.8%

Utilize photogenerated hot electrons to increase efficiency

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

CB

VB

E_g

$h\nu$

e

e

e

e

h+

energy normally lost as heat

photoelectrode

liquid redox electrolyte

1 photon →
1 hot electron

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

CB

VB

E_g

$h\nu$

e

h+

energy normally lost as heat

Initial

CB

VB

E_g

e   e

h+   h+

Final
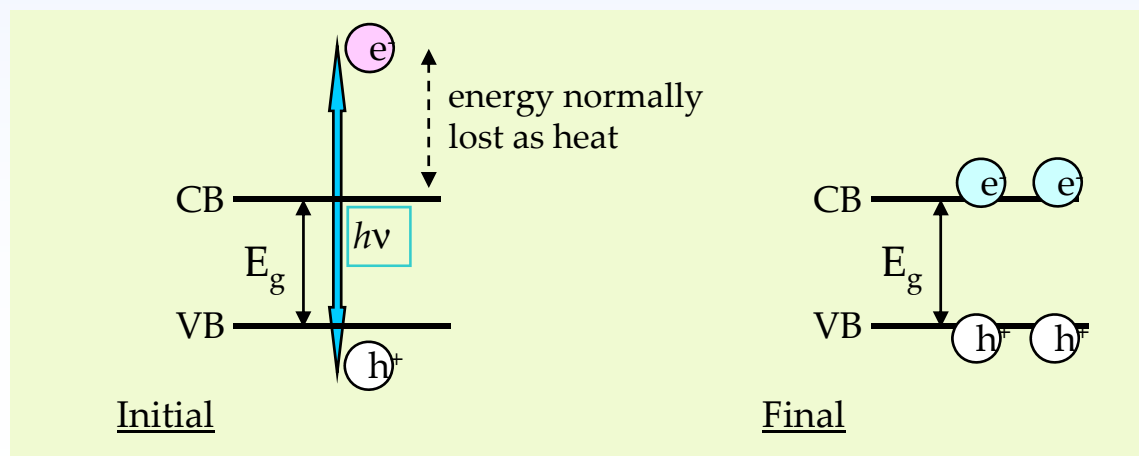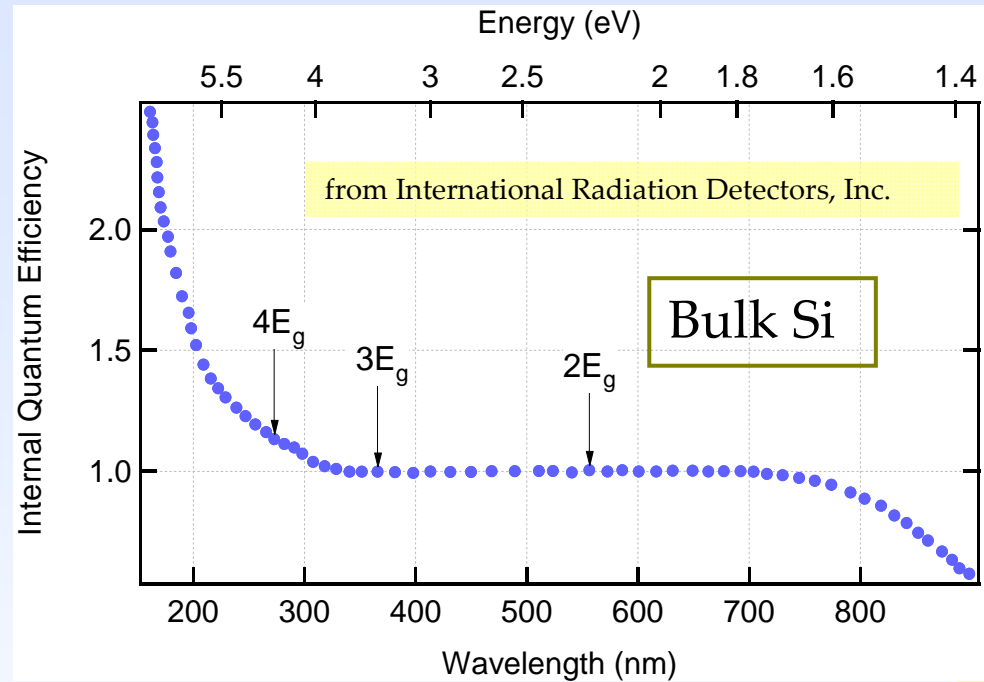
1 photon →
2 (or more) cooled electrons

# Impact ionization in bulk semiconductors
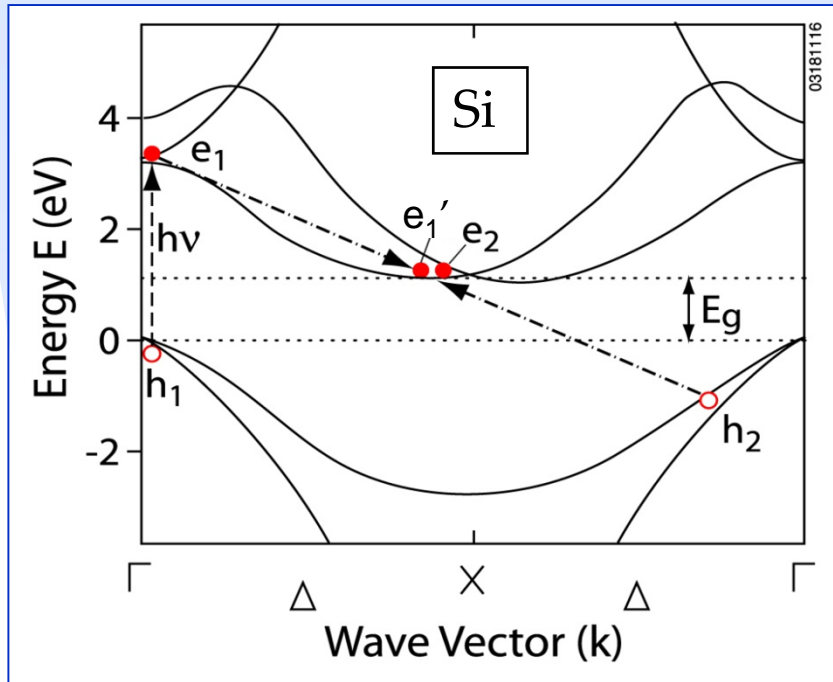

From Quiesser *et al.*, Appl. Phys. Lett. (1993).

- <u>Bulk Silicon</u> ($E_g \approx 1.1$ 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.

- <u>Nanocrystals</u> exhibit a *reduced* momentum conservation requirement (NC surface can supply or absorb momentum during scattering processes).

Enhancing conversion efficiency using NCs & MEG
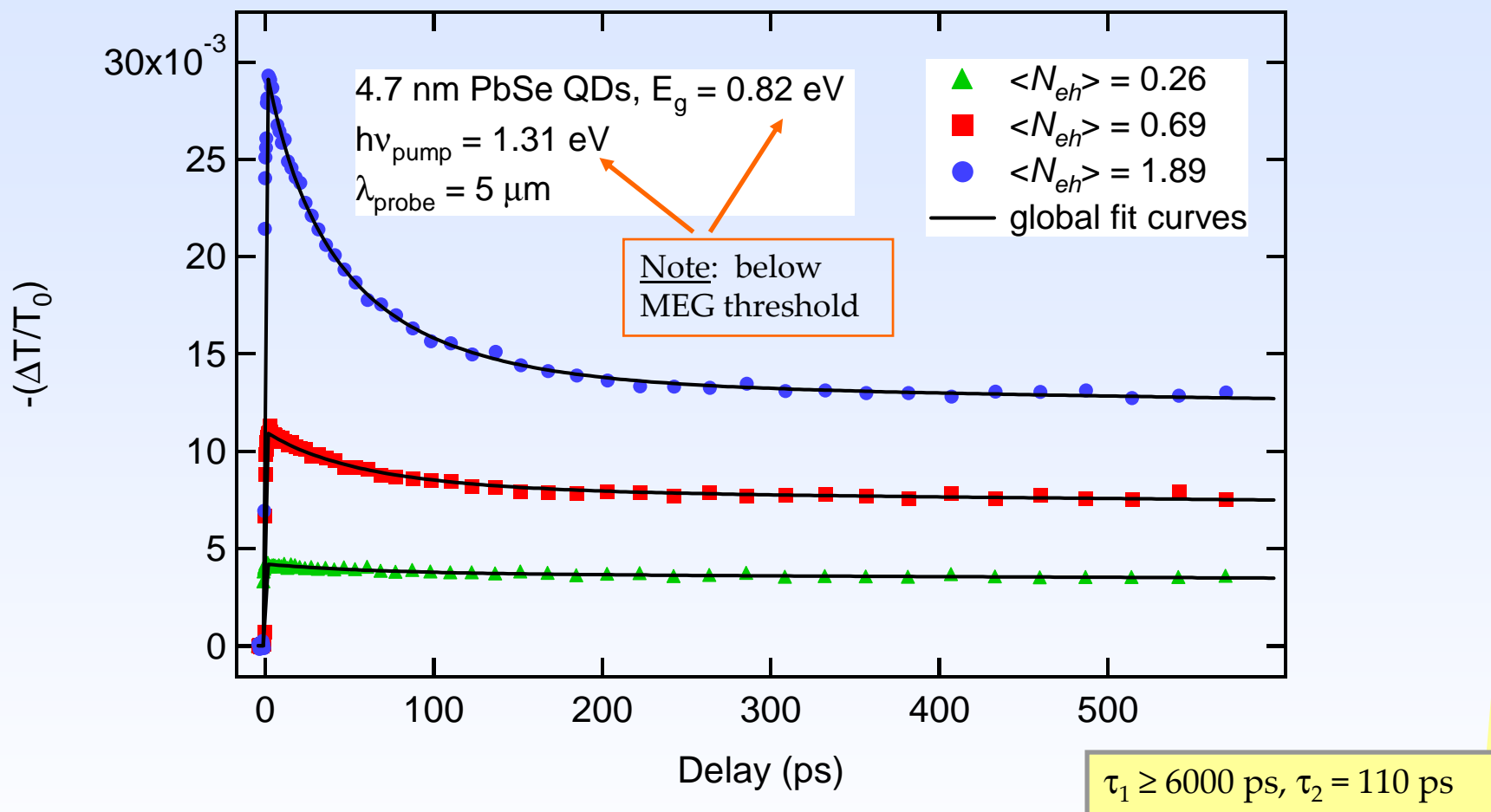

Matching absorption to solar irradiance spectrum
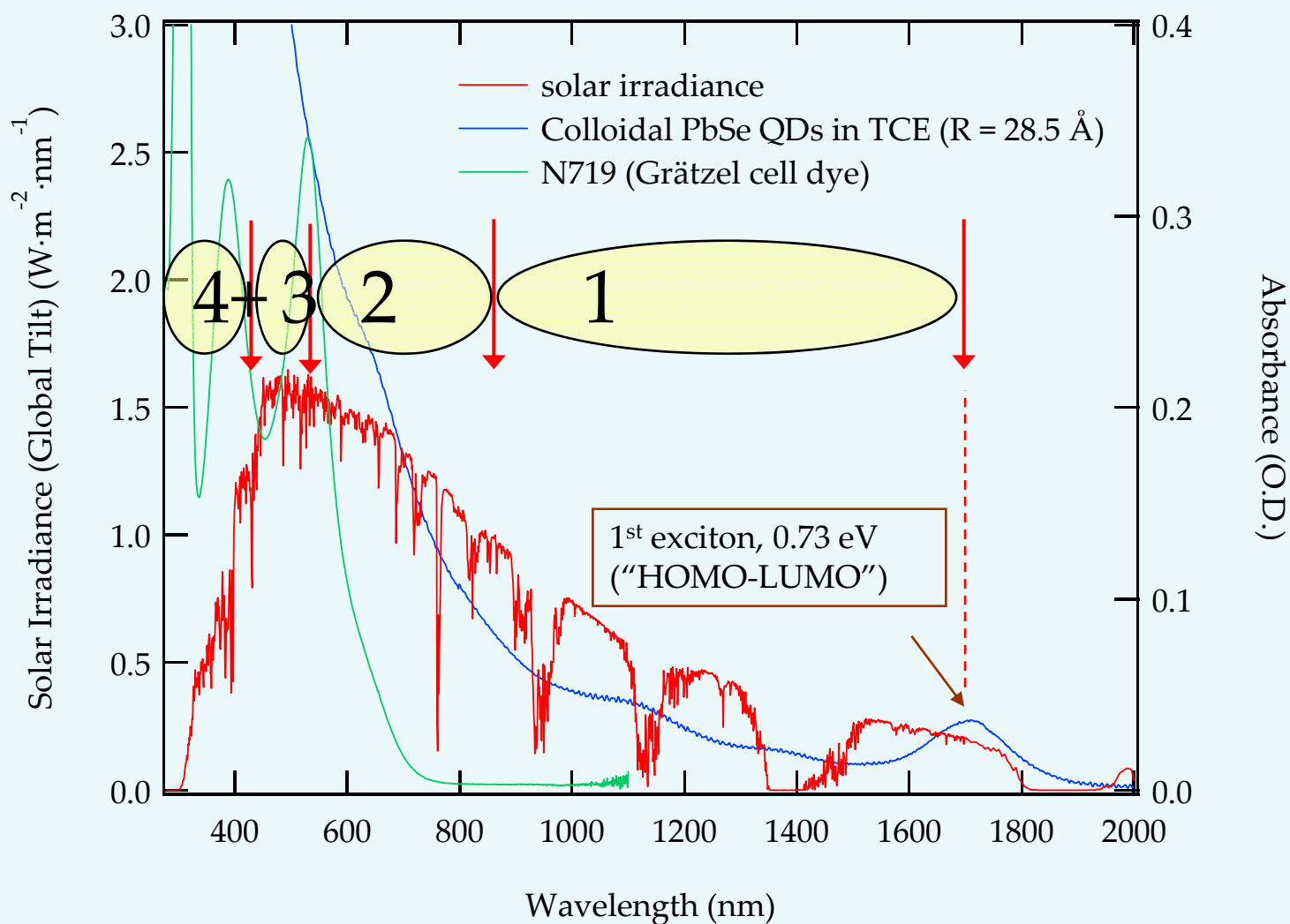
MEG-active solar cells – efficiency limitations
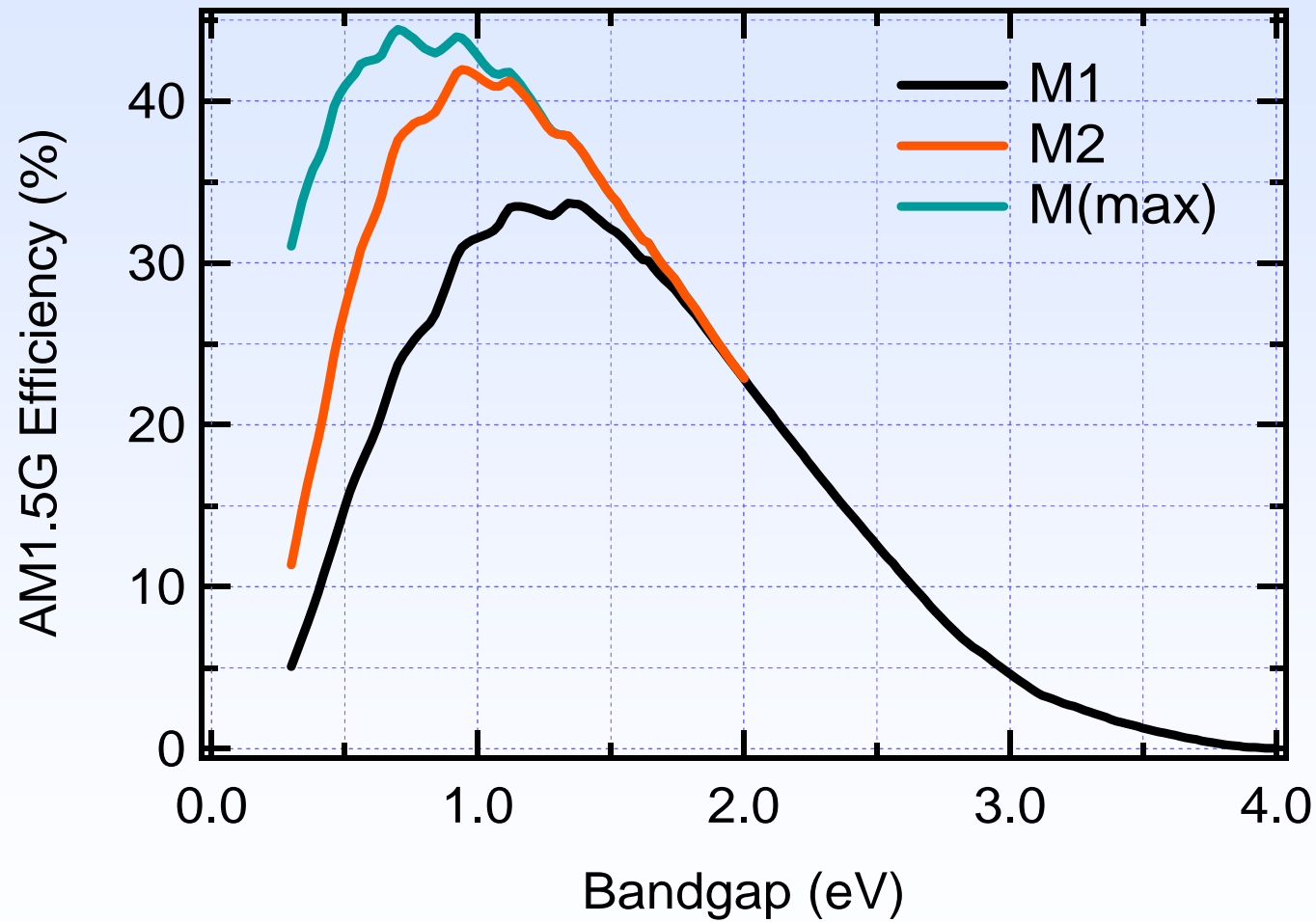
from Mark Hanna, NREL

Signature of multiple excitons: Auger recombination

4.7 nm PbSe QDs, E_g = 0.82 eV

$h\nu_{pump}$ = 1.31 eV

λ_{probe} = 5 µm

Note: below MEG threshold

- ▲ $\langle N_{eh} \rangle$ = 0.26
- ■ $\langle N_{eh} \rangle$ = 0.69
- ● $\langle N_{eh} \rangle$ = 1.89
- — global fit curves

y-axis: $-(\Delta T / T_0)$

x-axis: Delay (ps)

$\tau_1 \geq 6000$ ps, $\tau_2 = 110$ ps

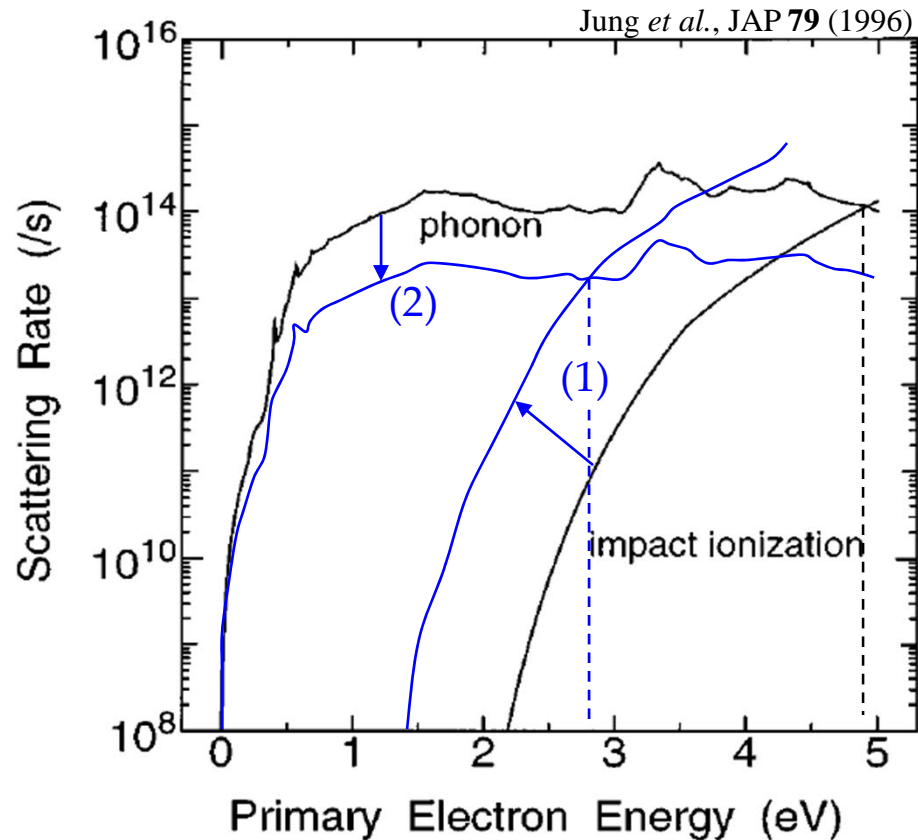Global fit for three intensities; excitation *below* the MEG threshold energy:

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

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

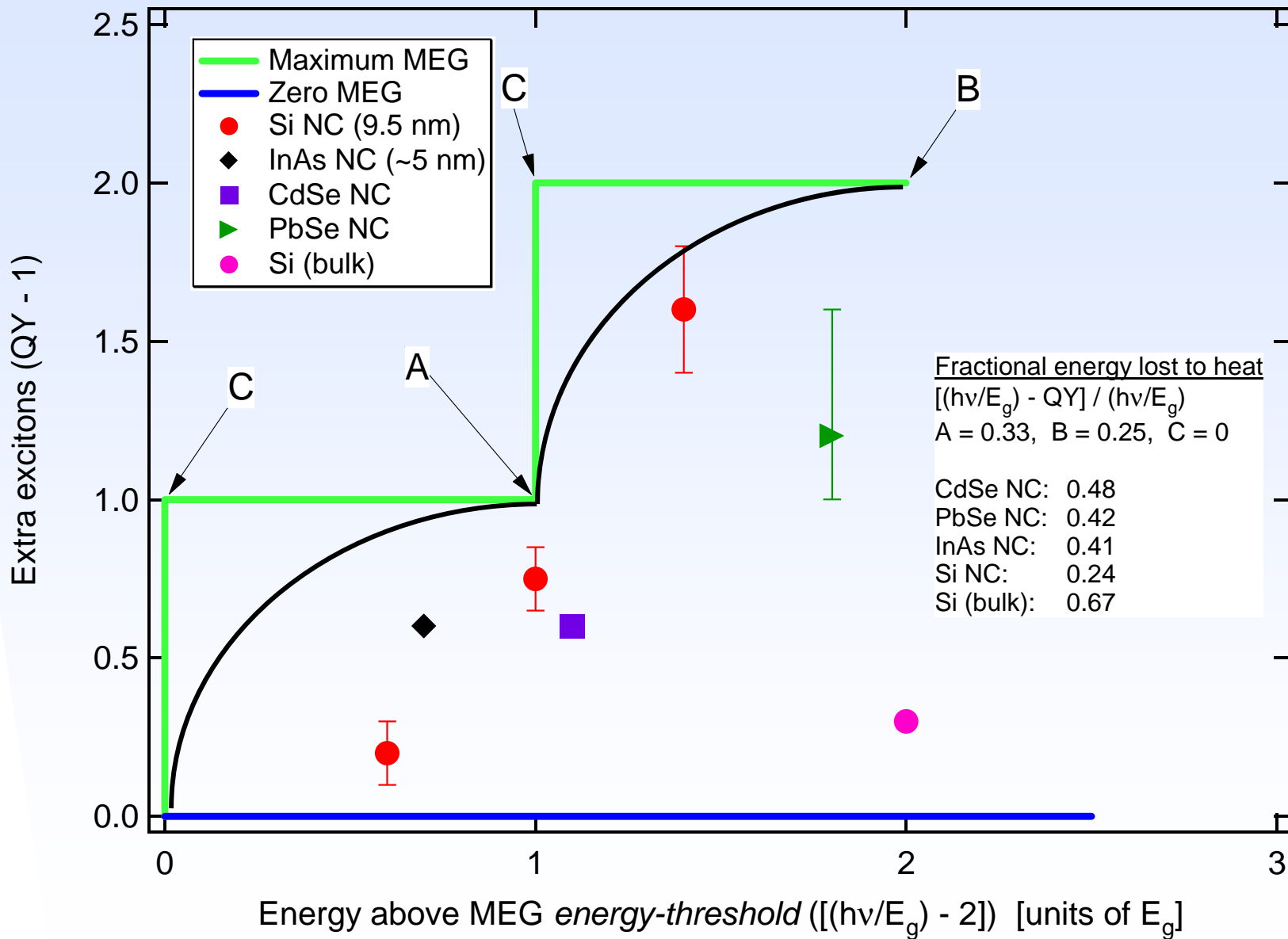# Scattering rates for impact ionization and phonons in bulk GaAs

Jung *et al.*, JAP **79** (1996)

In NCs:

(1) Auger processes increase as: $1/(NC\ dia)^3$;

(2) electron cooling by phonon scattering can be significantly reduced (10X) because of a "partial" phonon bottleneck if Auger cooling can be inhibited.

How efficiently is excess energy converted to excitons?

Analytical form of intensity-dependent ratio: early/late populations

$$R_{\text{pop}} = \frac{\alpha_{\text{photoinduced}}(t = \tau')}{\alpha_{\text{photoinduced}}(t = \tau'')} = \frac{J_0 \cdot \sigma_p \cdot \text{QY} \cdot \delta}{1 - \exp(-J_0 \cdot \sigma_p)}$$

τ' = short delay (indicates initial exciton density)

τ'' = long delay (indicates fractional exciton population remaining after Auger recombination (max. 1 exciton/NC))

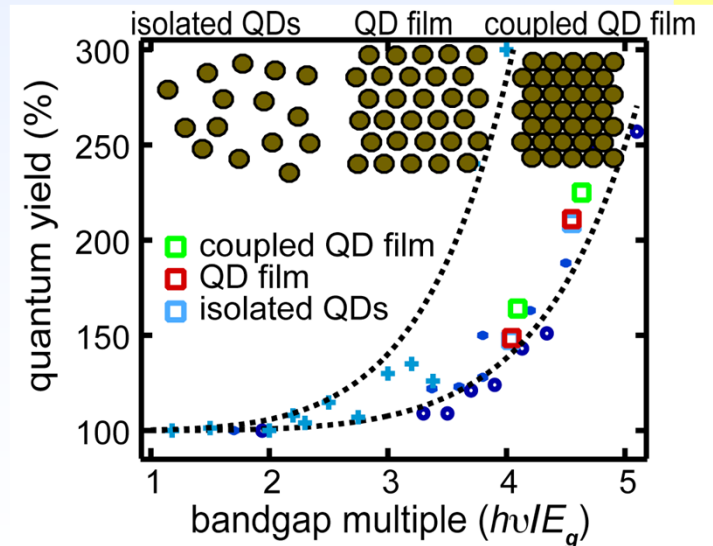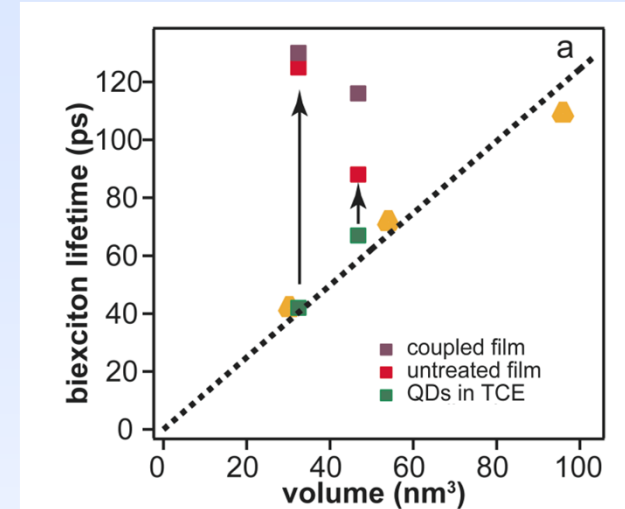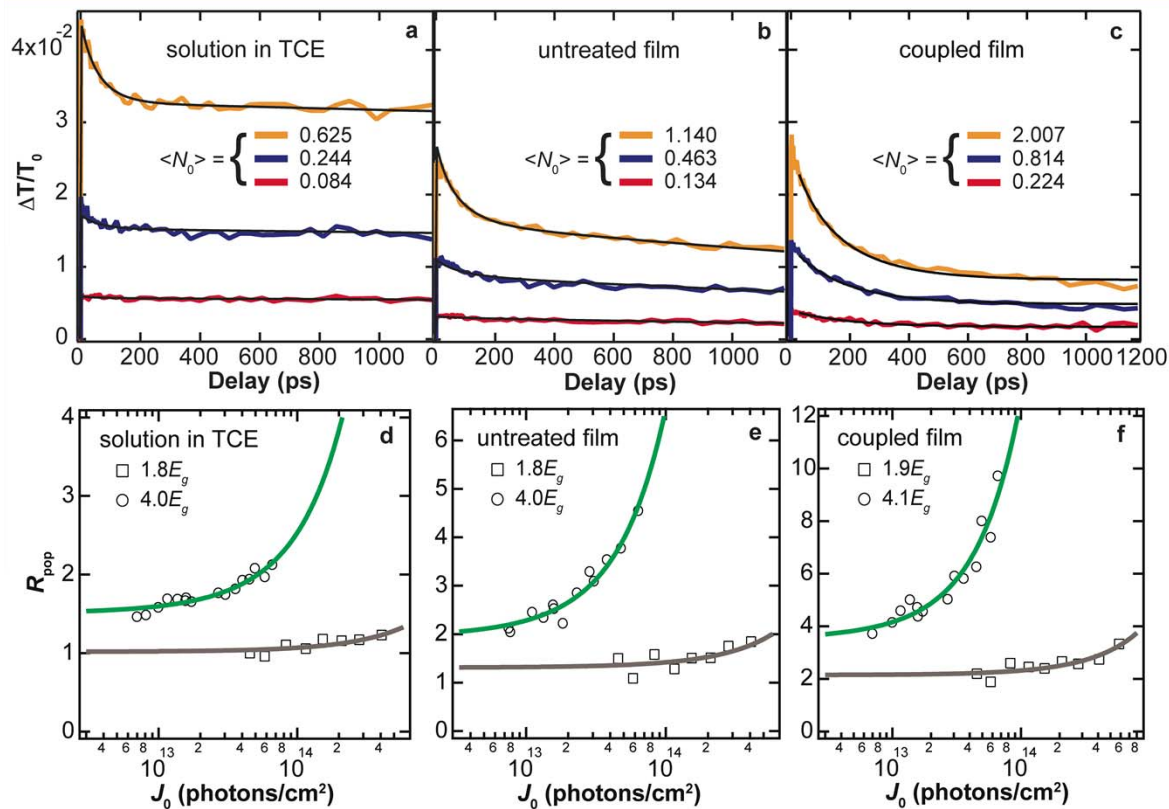J_0 = pump photon fluence (photons $\cdot$ cm^{-2} $\cdot$ pulse^{-1})

σ_p = pump photon energy absorption cross section (cm^2)

QY = exciton yield (excitons/absorbed photon)

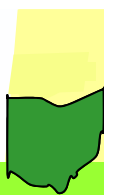δ^1 = single exciton fractional decay between τ' and τ''
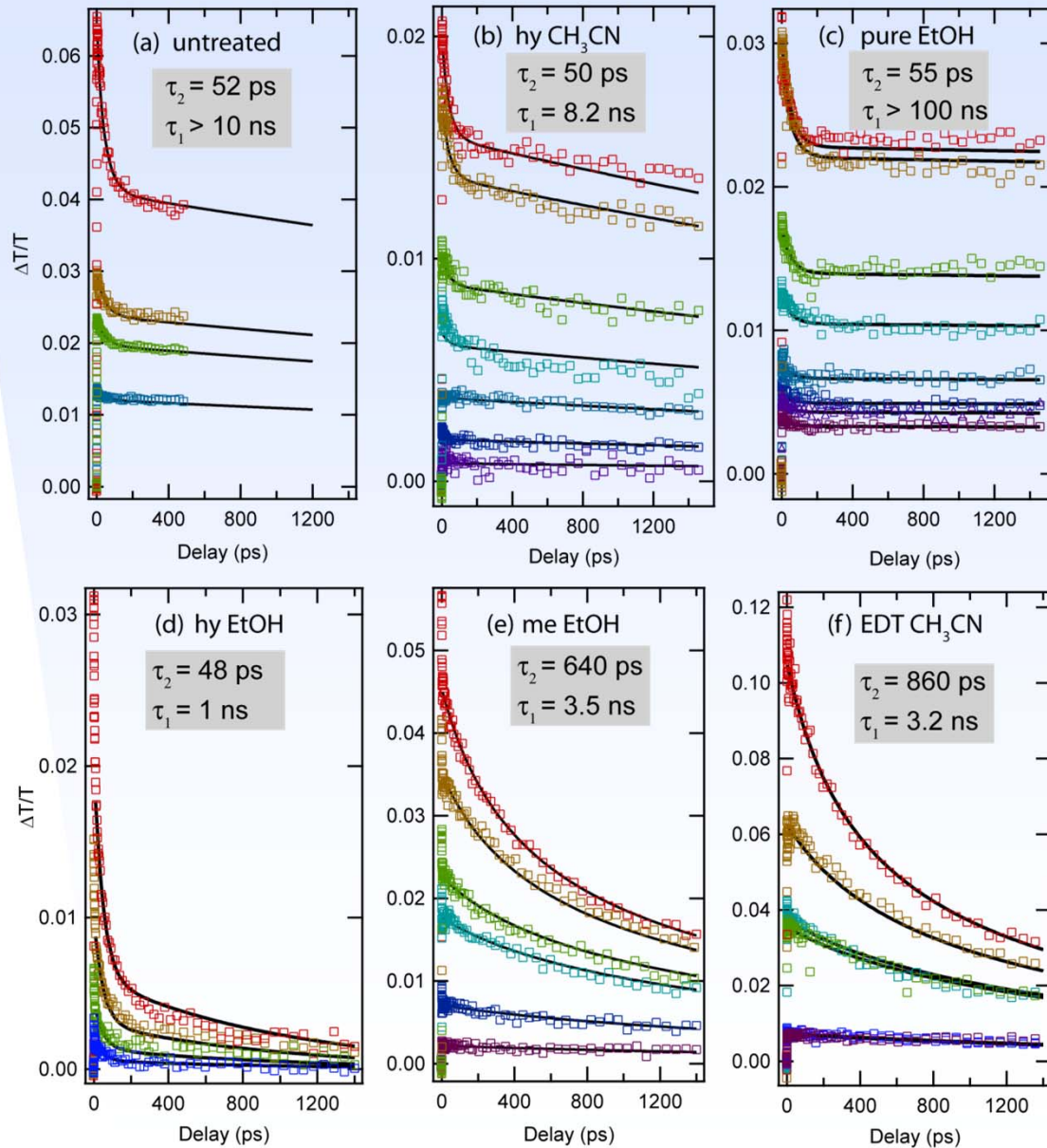
MEG in arrays of PbSe NCs

- MEG occurs in these coupled films
- Coupling allows longer time to extract MEG carriers

J. Luther *et al.*, Nano Lett. **7**, 1779-1784 (2007).

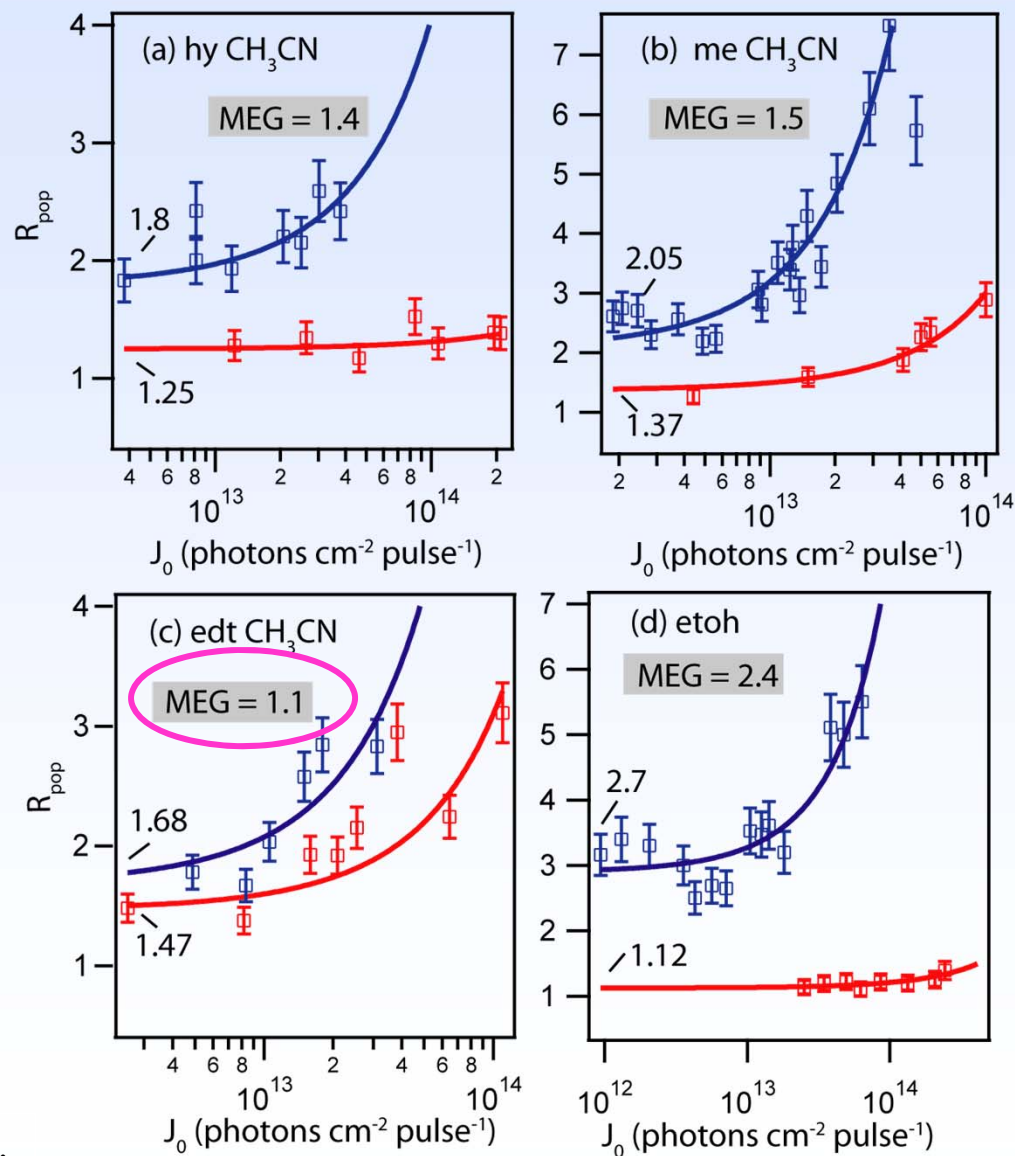# PbSe NC films: Biexciton lifetime dependence on chemical treatment

NC size = 3.7 nm

M. C. Beard *et al., Nano Lett.* **2009,** *9* (2), pp 836–845.

PbSe NC films: MEG QY dependence on chemical treatment

NC size = 3.7 nm

M. C. Beard *et al.*, *Nano Lett*. 9, 836–845 (2009).

Future directions for NC solar cells

Opportunities

- low-cost solution-based processing and fabrication techniques

- size-engineered absorption spectra; enhanced IR absorption

- improved efficiency through MEG

- low toxicity NC materials (e.g., Si, Ge)

Challenges

- efficient charge collection -- record efficiency with semiconductor NCs ~ 3 %

- materials design and development – control of surface/interface properties

- defect tolerance (e.g., Grätzel cell behavior)

Recent MEG review:

Beard, M. C., and Ellingson, R. J., *Laser & Photon. Rev.* **2,** 377-399 (2008).