

Nanostructured Semiconductor Crystals

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

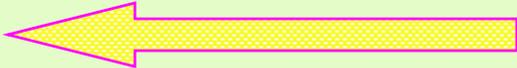
March 1, 2011

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)



Nanomaterials for solar energy conversion

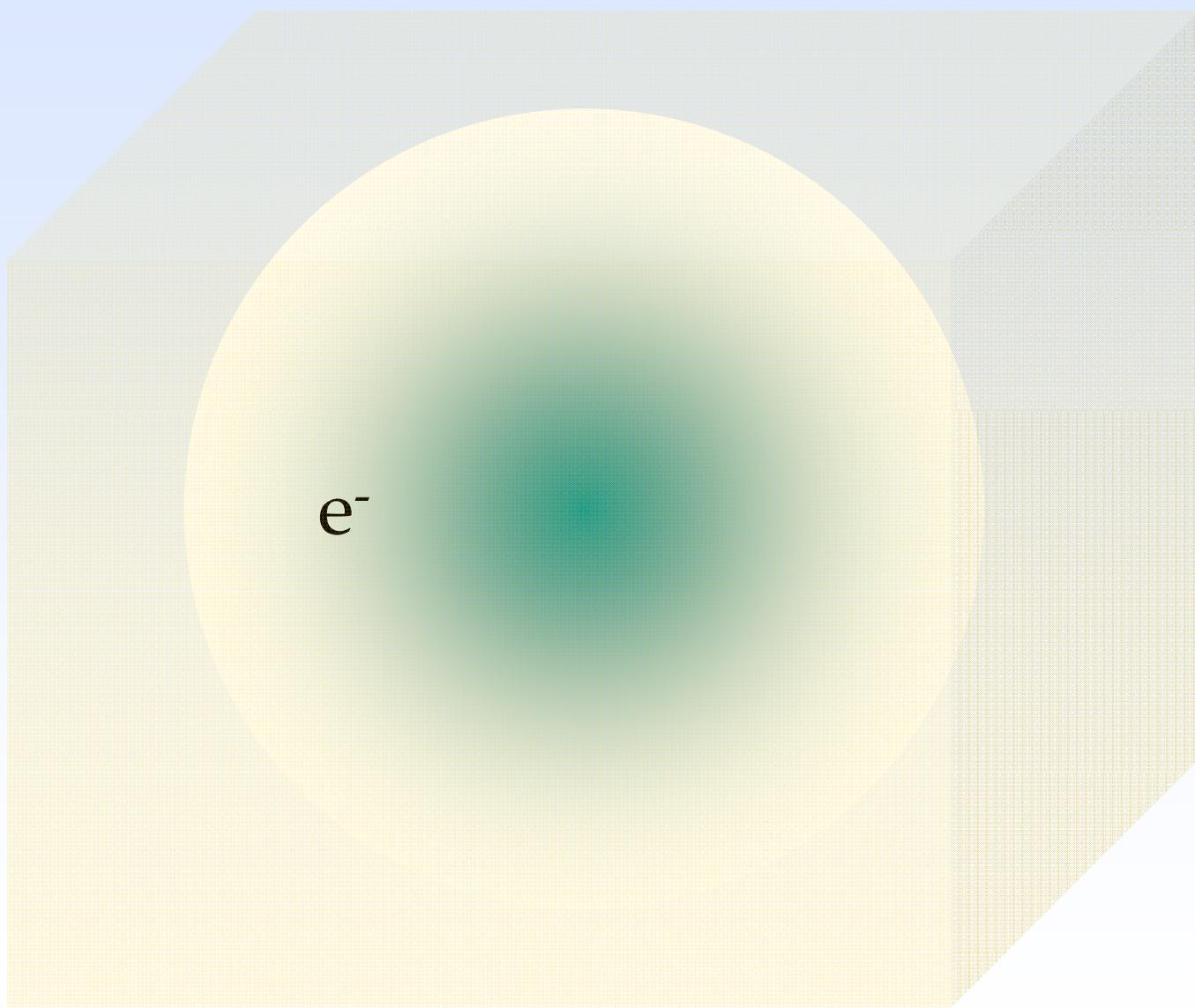
- Enable high surface area devices →
 - strong light absorption (dye-sensitized nanostructured TiO₂)
 - facilitates fast charge separation (proximity of photoexcited carriers to charge-separating interface)
- Customizable properties enable unique designs →
 - Engineerable (size-dependent) absorption 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

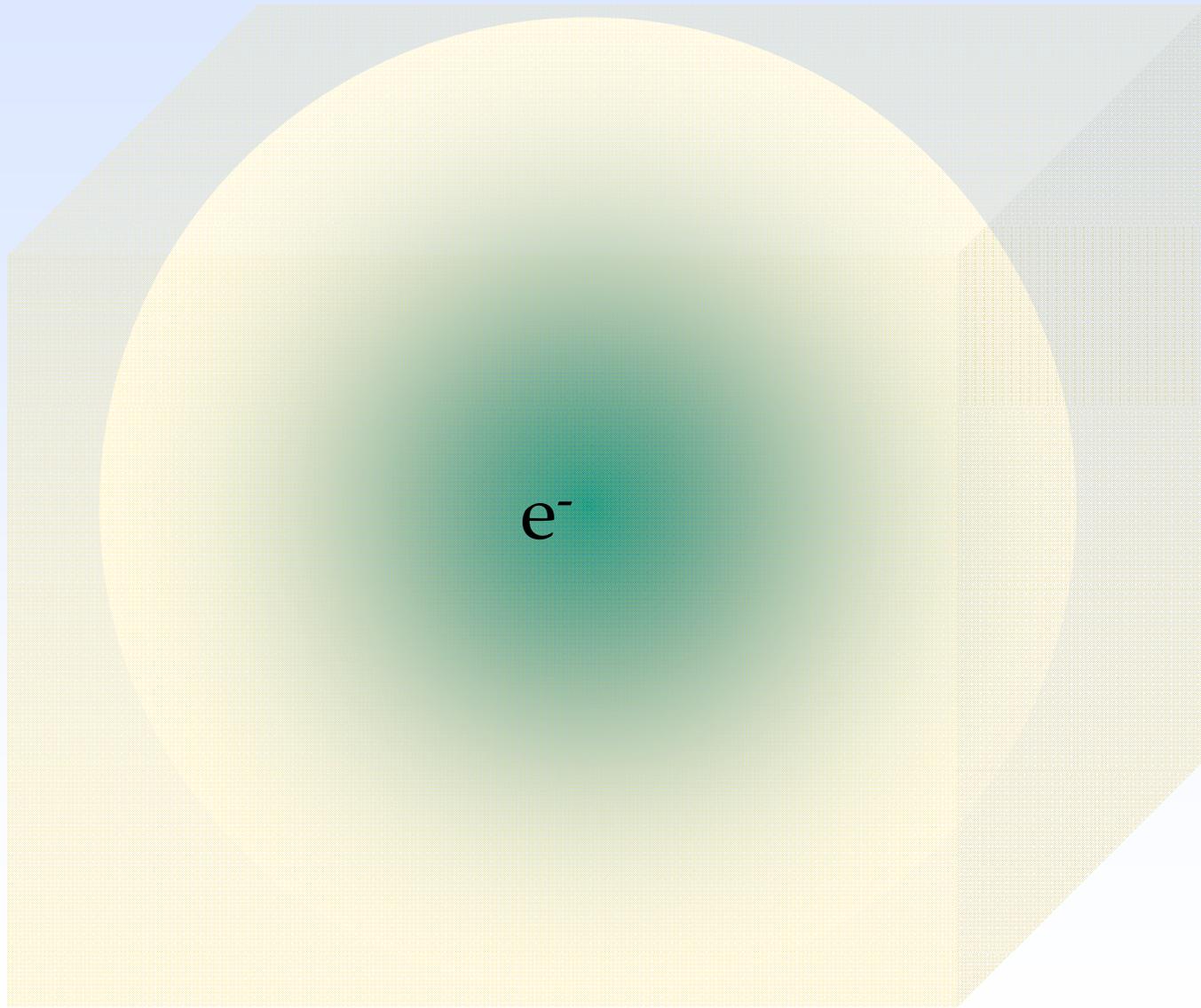
- *Dramatic variation of optical and electronic properties*
- *Large blue shift of absorption edge*
- *Discrete energy levels/structured absorption and photoluminescence spectra*
- *Enhanced photoredox properties for photogenerated electrons and holes*
- *Enhanced Inverse Auger (impact ionization)*
- *Greatly 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 exciton absorption at 300 K*
- *Greatly enhanced oscillator strength per unit volume (absorption coefficient)*
- *Greatly enhanced non-linear optical properties*
- *Greatly modified pressure dependence of phase changes and direct to indirect transitions*
- *Efficient anti-Stokes luminescence*



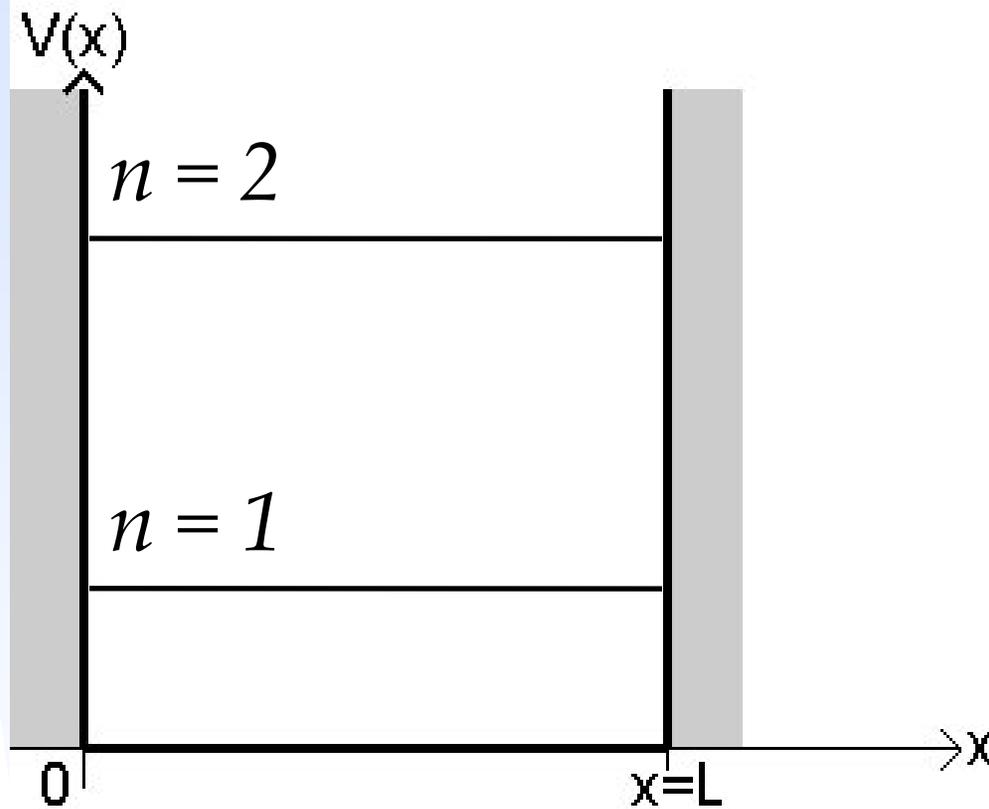
Quantum confinement effect



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)



Quantum Confined Structures – Density of States

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

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

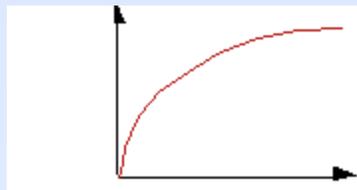
$$g_{c,3D} = \frac{8\pi\sqrt{2}}{h^3} m_{eff}^{3/2} \sqrt{E - E_{min}}$$

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

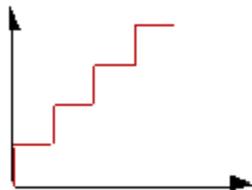
$$g_{c,1D} = \sqrt{\frac{2\pi m_{eff}}{h^2}} \frac{1}{\sqrt{E - E_{min}}}$$



Quantum confinement effect on density of electronic states

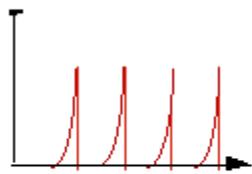


Bulk Semiconductor

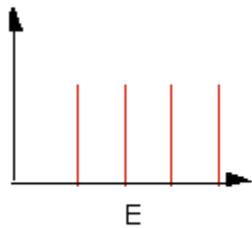


Quantum Well

$N(E)$

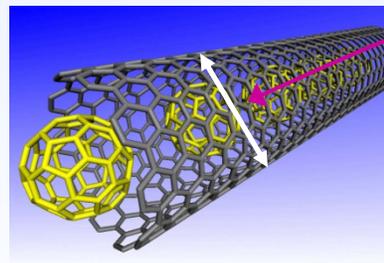
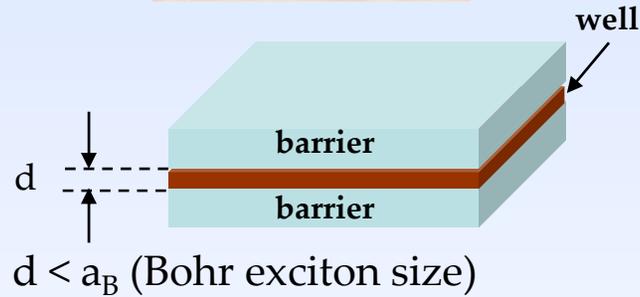


Quantum Wire

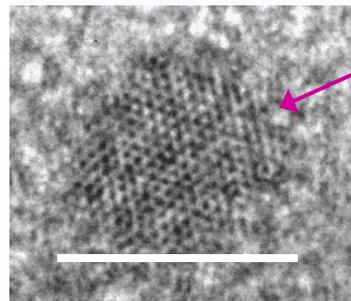


Quantum Dot
(or Nanocrystal)

E



~1 nm



~6 nm dia.

60 Å InP QD

Dimensionality

3D

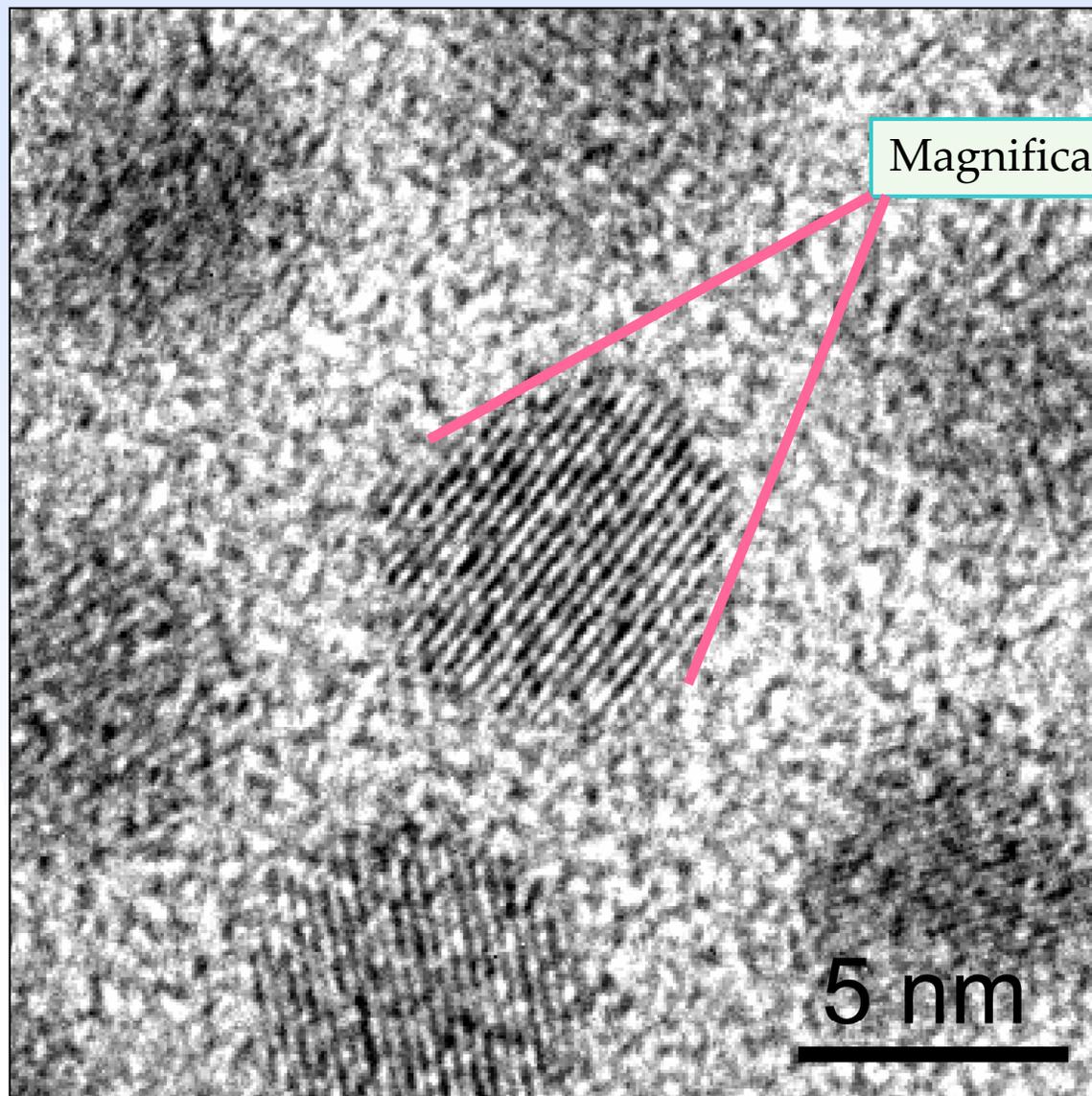
2D

1D

0D



Transmission electron micrograph (TEM) of Lead Selenide NCs

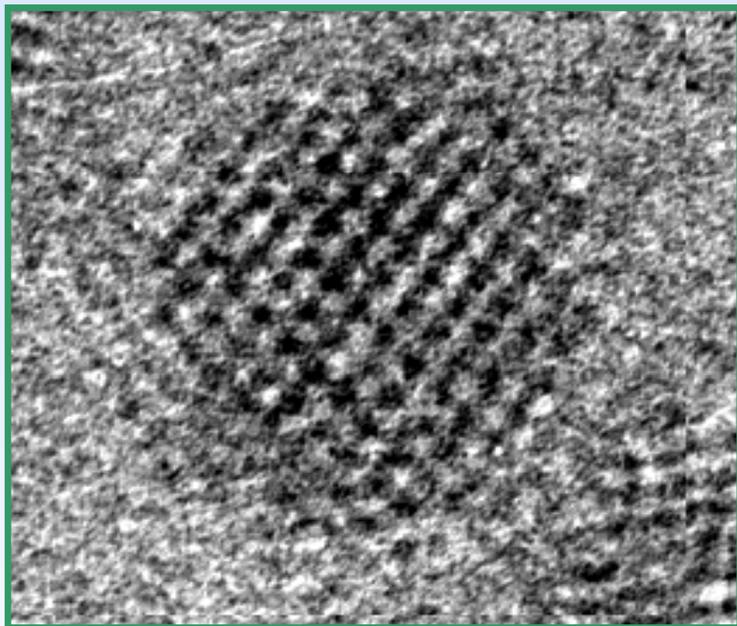


Magnification ~ 2,000,000x

PbSe



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

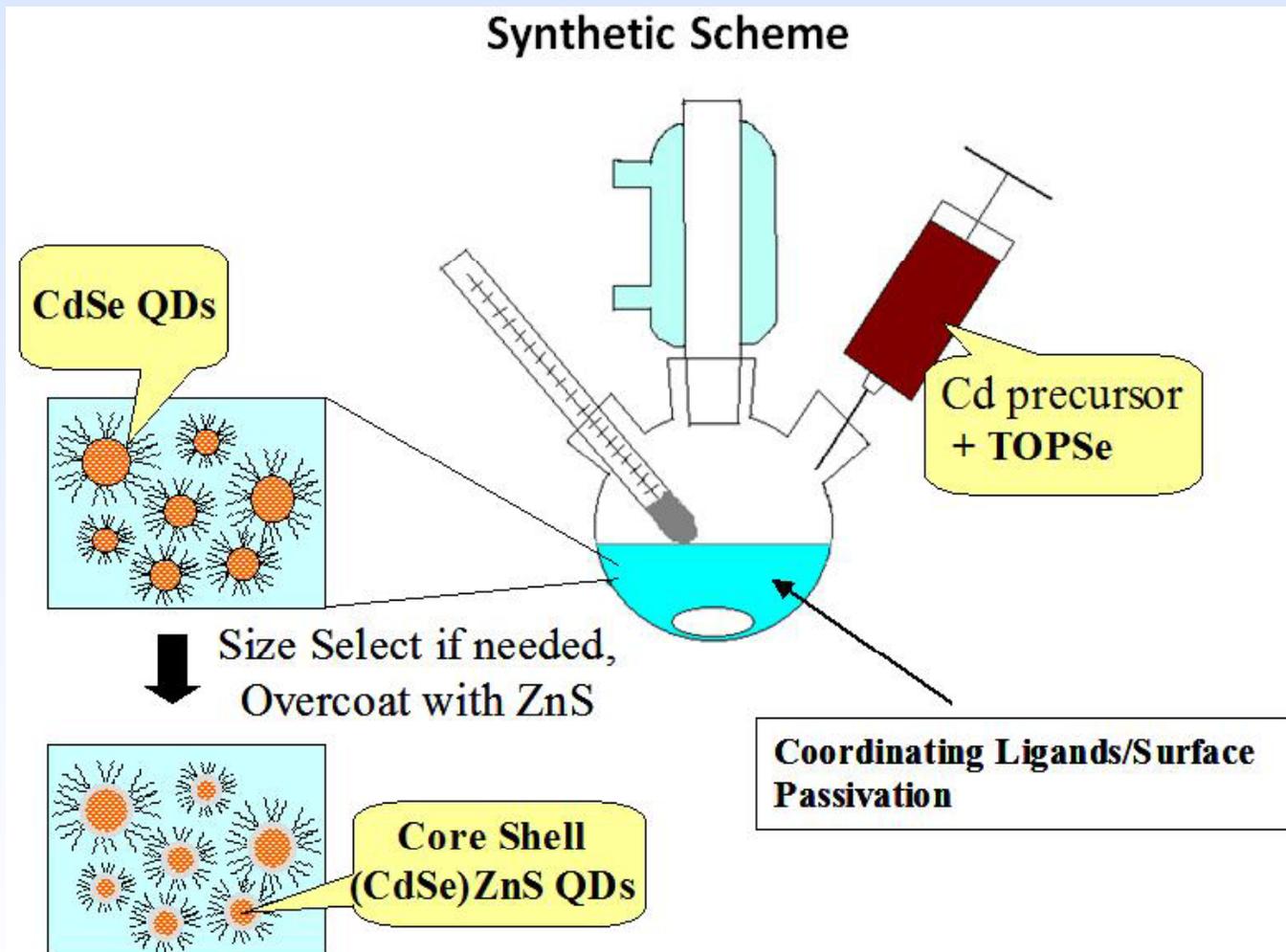
as-prepared dots are capped with organic stabilizer (TOP/TOPO) \Rightarrow surface chemistry alters electrical and optical (emission) properties (pyridine, Na^+ - biphenyl⁽⁻⁾, etched QDs)

High ratio of atoms on surface

e.g., for 35 Å dots, $\sim 30\%$ 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).



Nanostructures for PV

Solar Energy Technologies Program

National Solar Technology Road Nano-Architecture PV

Facilitator: *Yong Zhang*

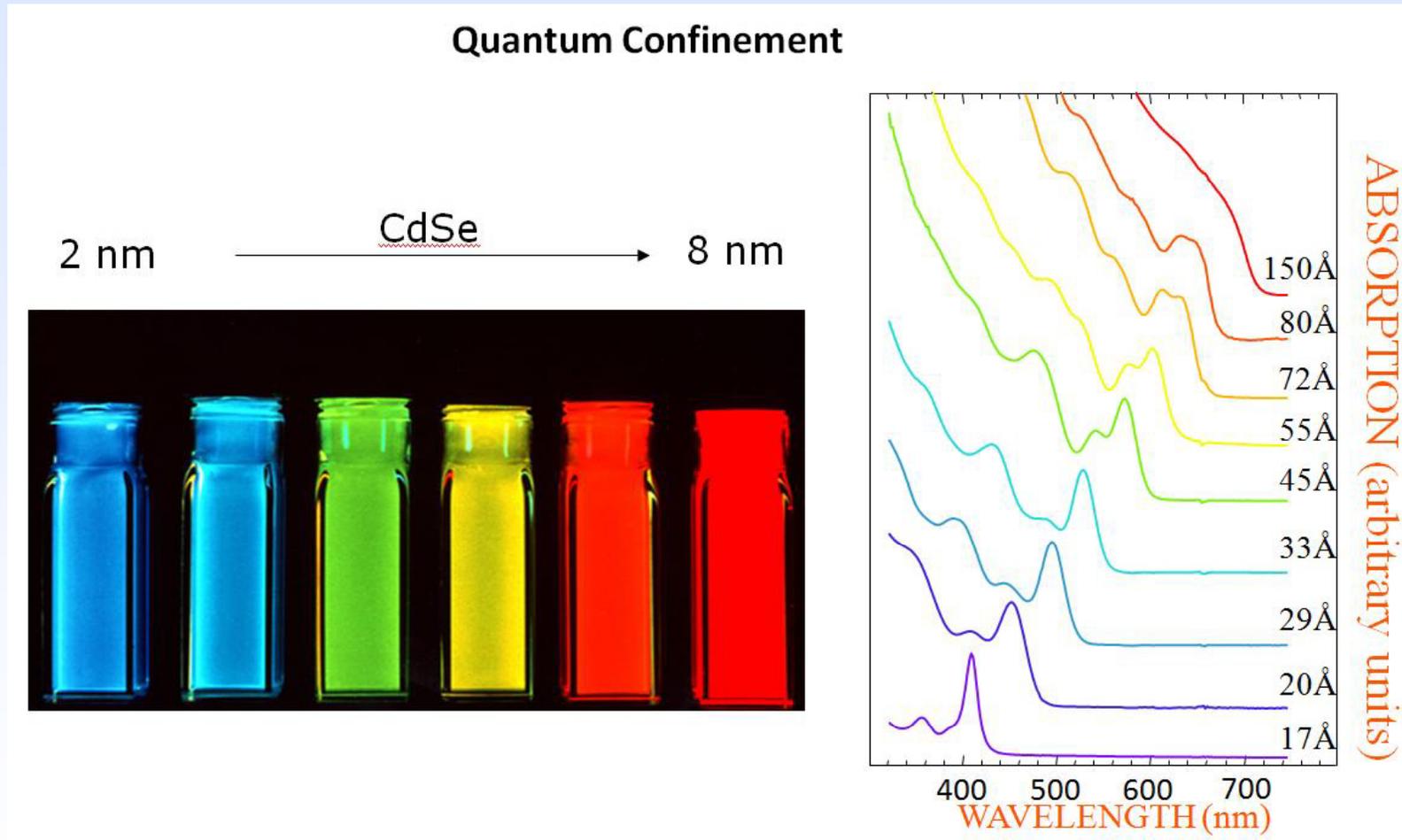
Participants included:
*National Renewable Energy Laboratory
Sandia National Laboratories
U.S. Department of Energy
University and private-industry experts*

Background

Quantum confinement allows more flexibility in electronic structure engineering than the conventional route of alloying bulk materials; but it also results in blocking the carrier transport in the confined dimension(s). Quantum dots could maximize the tunability, but suffer from the shortcoming of being fully confined structures that prevent the carrier transport critically needed for solar cells. A number of approaches have been suggested to restore the carrier transport: (1) forming a quantum-dot lattice that facilitates partial transport (similar to that in a molecular crystal), (2) using quasi-one-dimensional systems (nanowires or nanotubes) as the carrier transporter to extract the photogenerated carriers otherwise trapped in the nanocrystal, (3) using the nanowire or nanotube as absorber, as well as transporter. It is relatively straightforward using any of these approach to achieve the most basic goal—tuning the bandgap—but less trivial to also obtain a few other desirable properties specifically for the solar cell. Thus, major effort is required to develop conceptually sound and practical material systems from any of these general approaches.



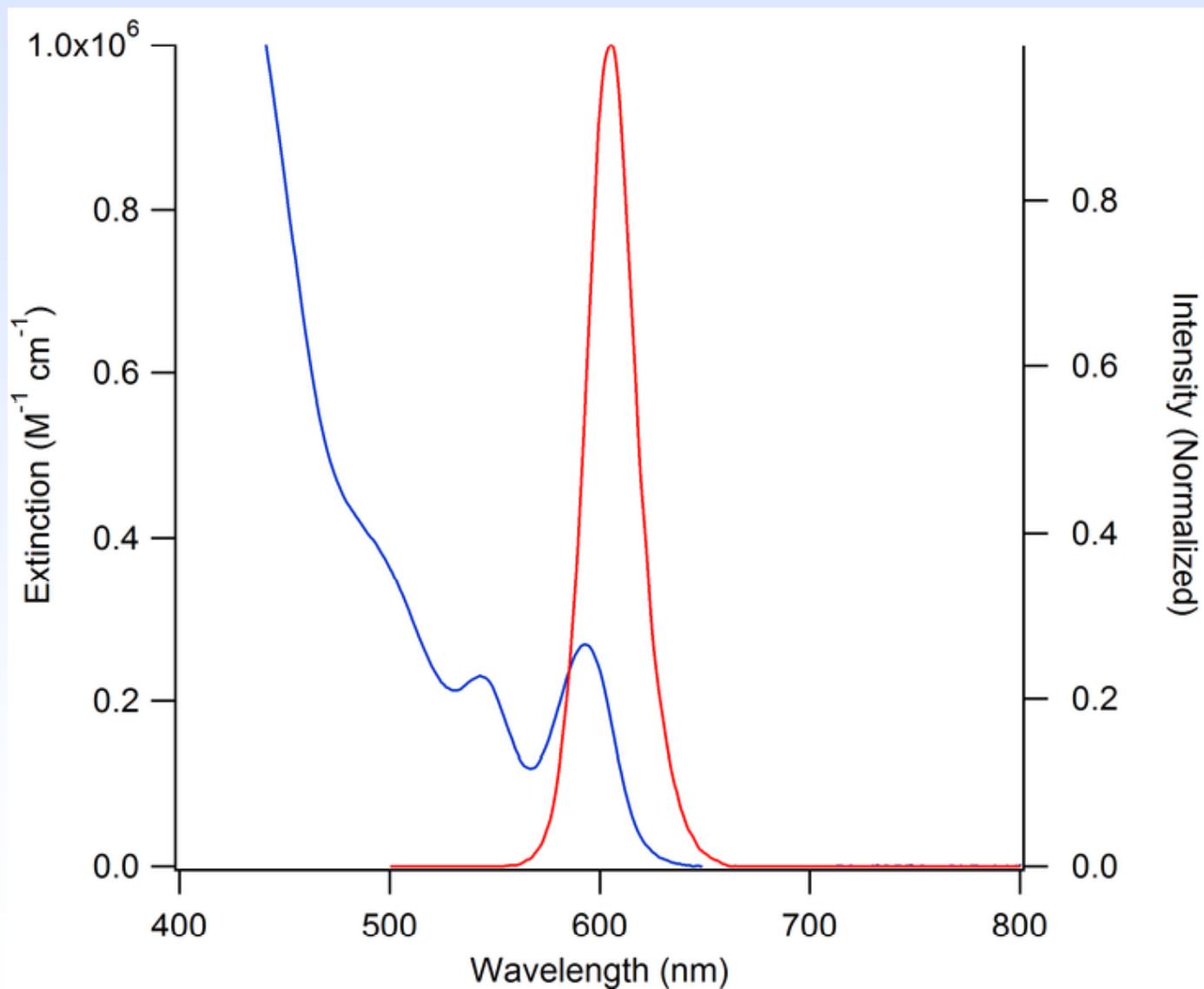
Size-dependent optical properties



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



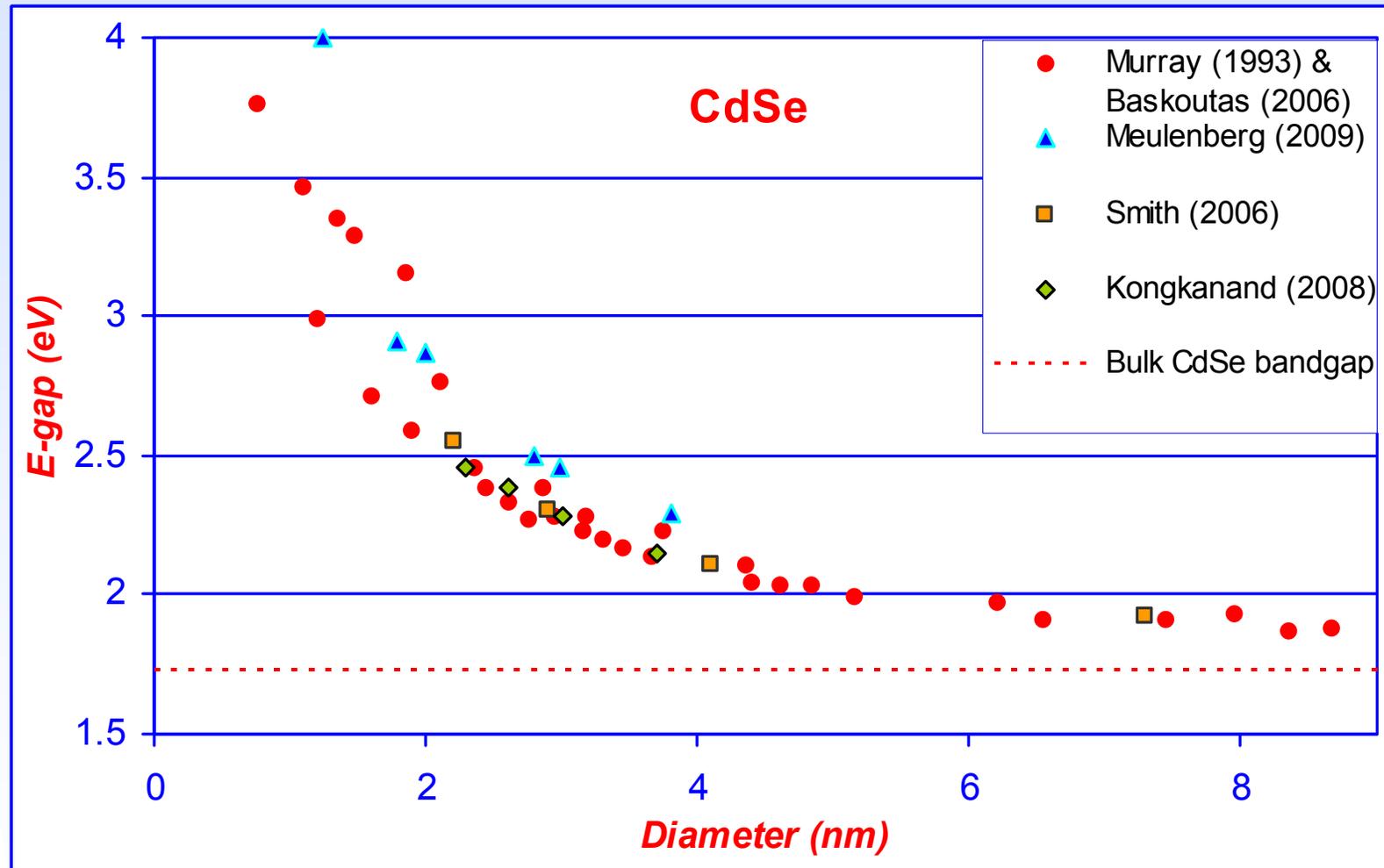
Absorption and emission (CdSe nanocrystals)



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



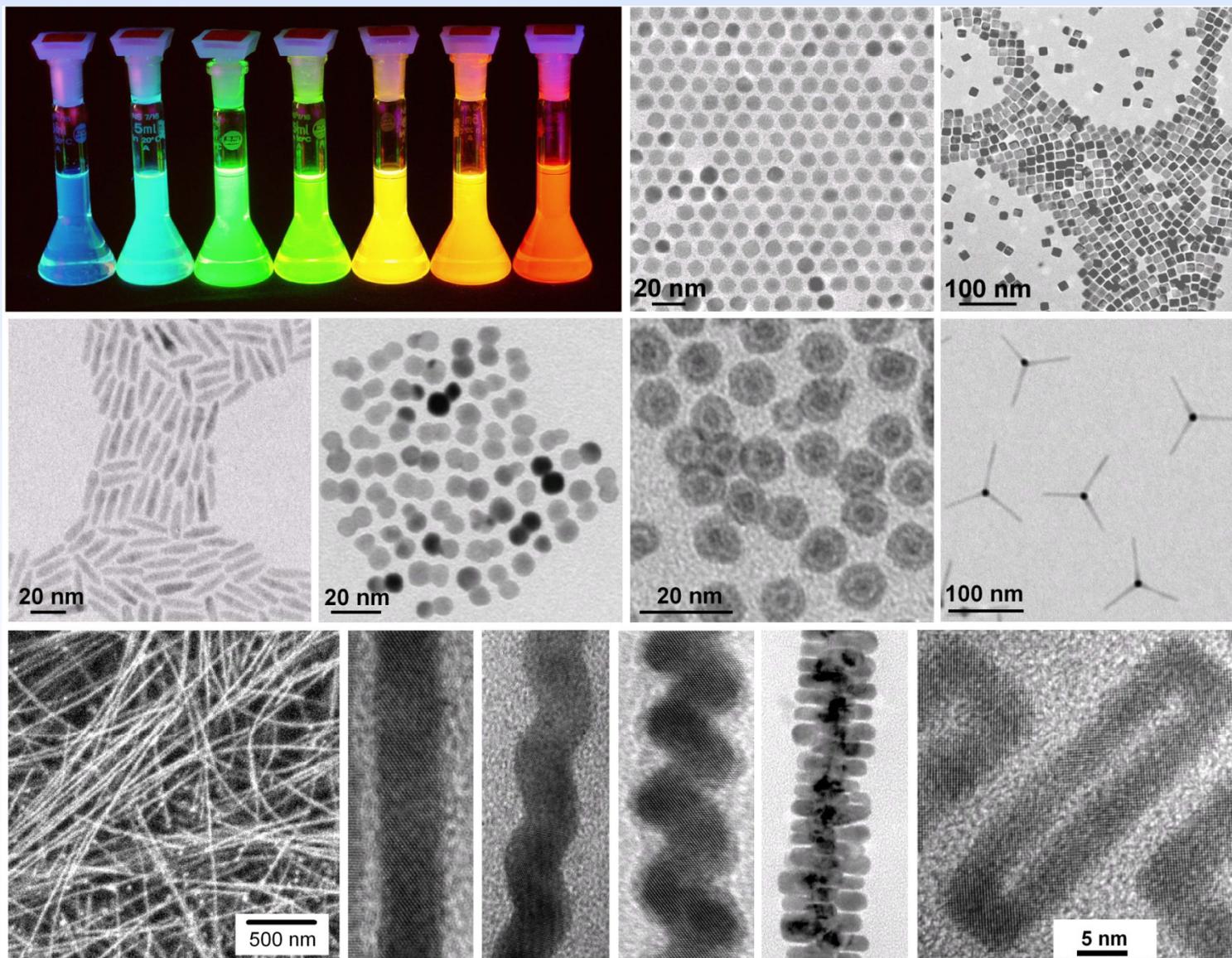
Size-dependent bandgap of CdSe NCs



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



Colloidal nanostructures (crystalline)

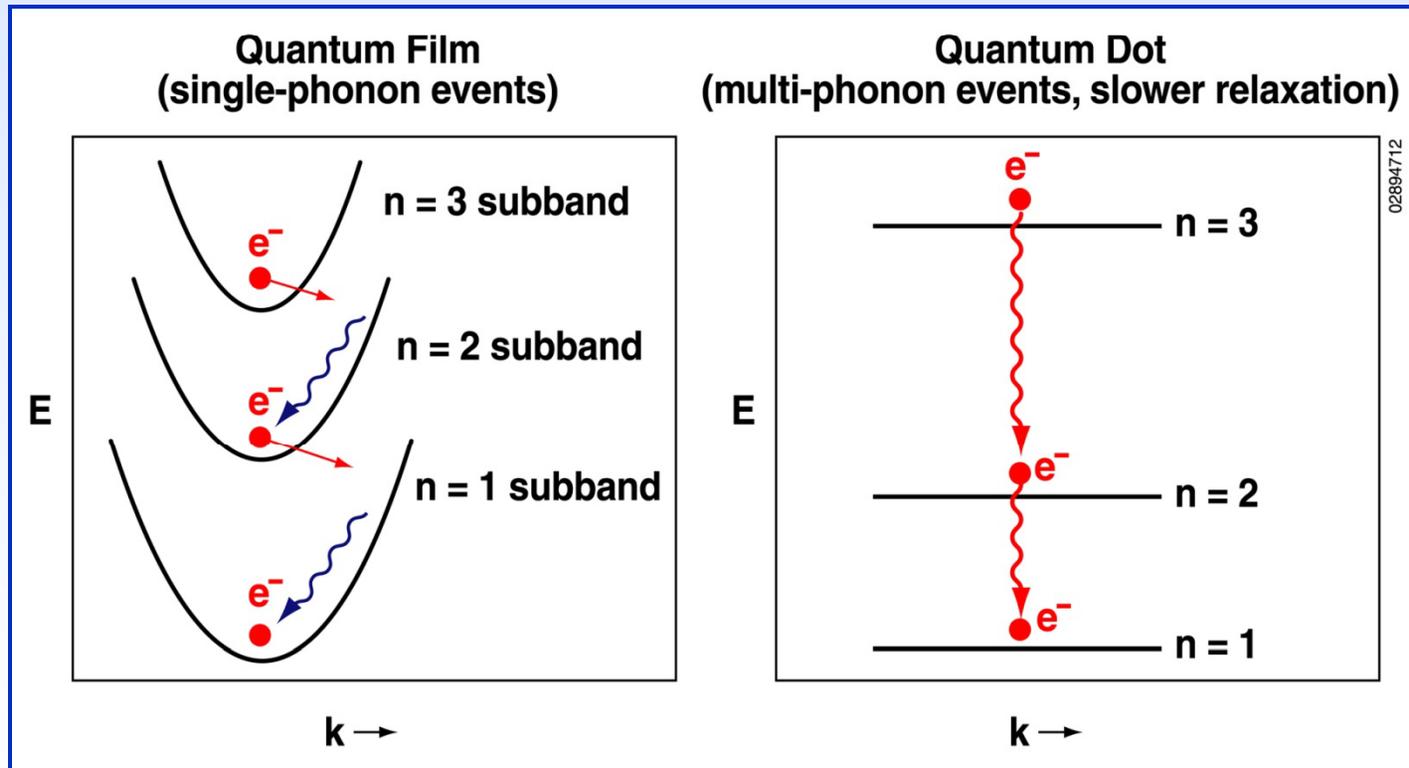


<http://talapinlab.uchicago.edu>



Hot electron relaxation pathways

Quantum Films vs Quantum Dots



phonon bottleneck



Electronic Structure Calculations for 41.8 Å InP QD

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.

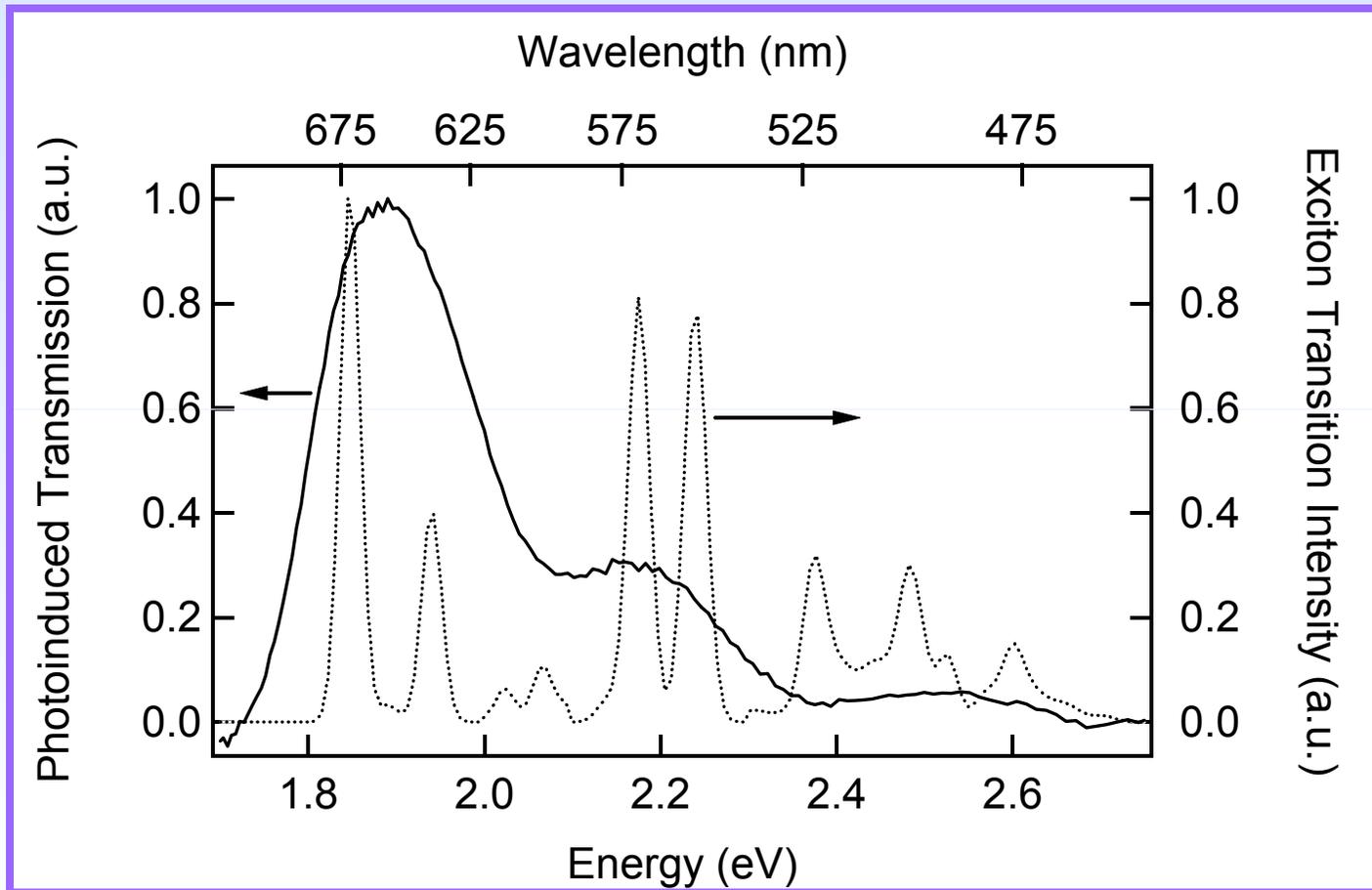


Calculated *excitonic* transitions in 42 Å InP QD

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

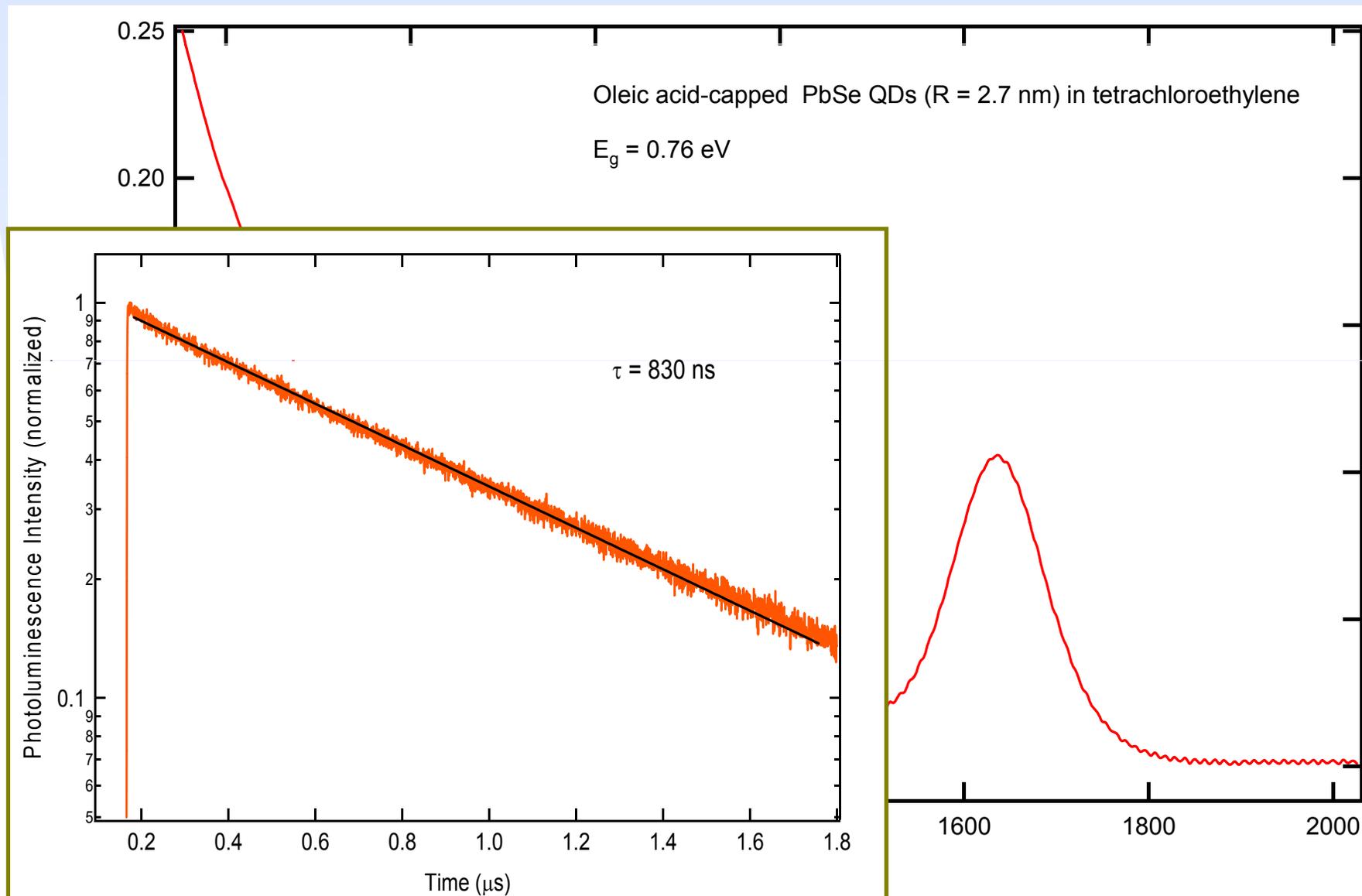


Excitonic spectrum for 42 Å InP QD

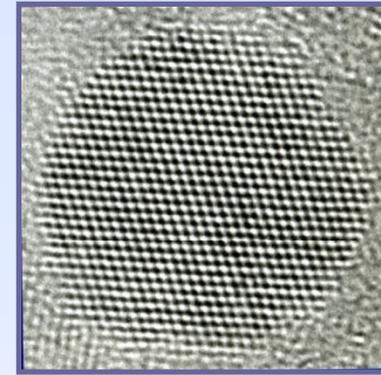
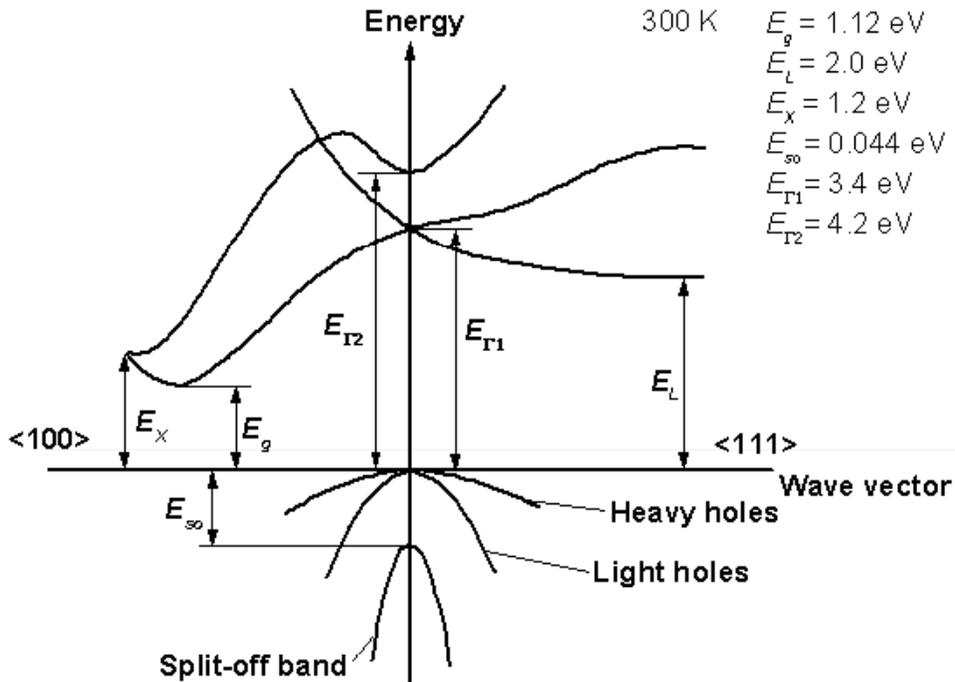


Theoretical excitonic spectrum (dashed line) for a sample of 41.8 Å diameter InP quantum dots. The transition intensity is proportional to the absorption coefficient, and consists of a sum of the oscillator strengths for various excitonic transitions. The solid line shows the measured photoinduced bleach 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.

Colloidal PbSe QDs in tetrachloroethylene (TCE)

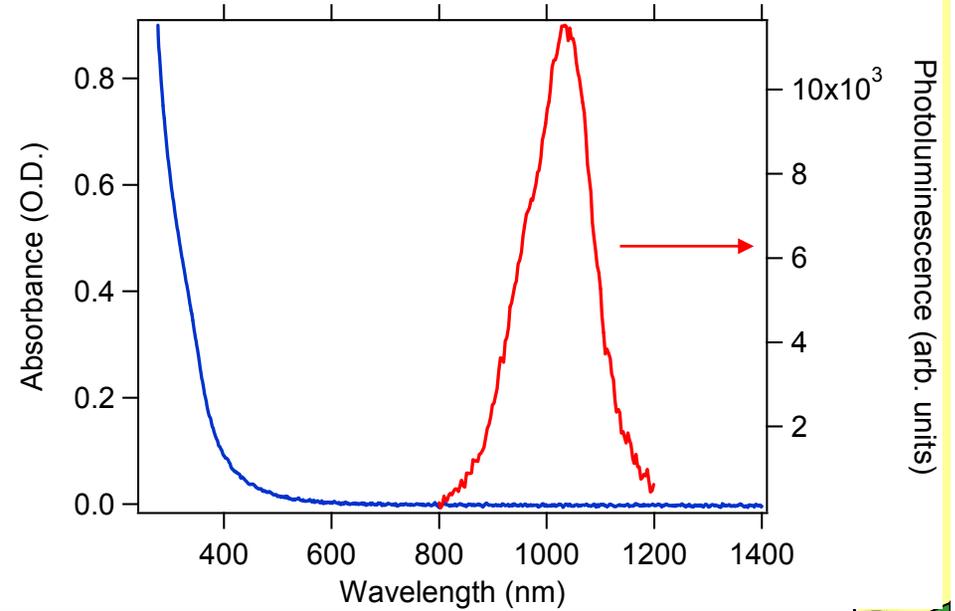
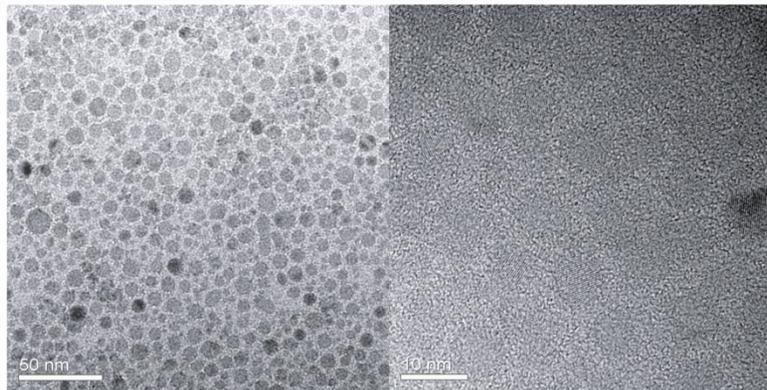


Silicon Nanocrystals



Silicon NC

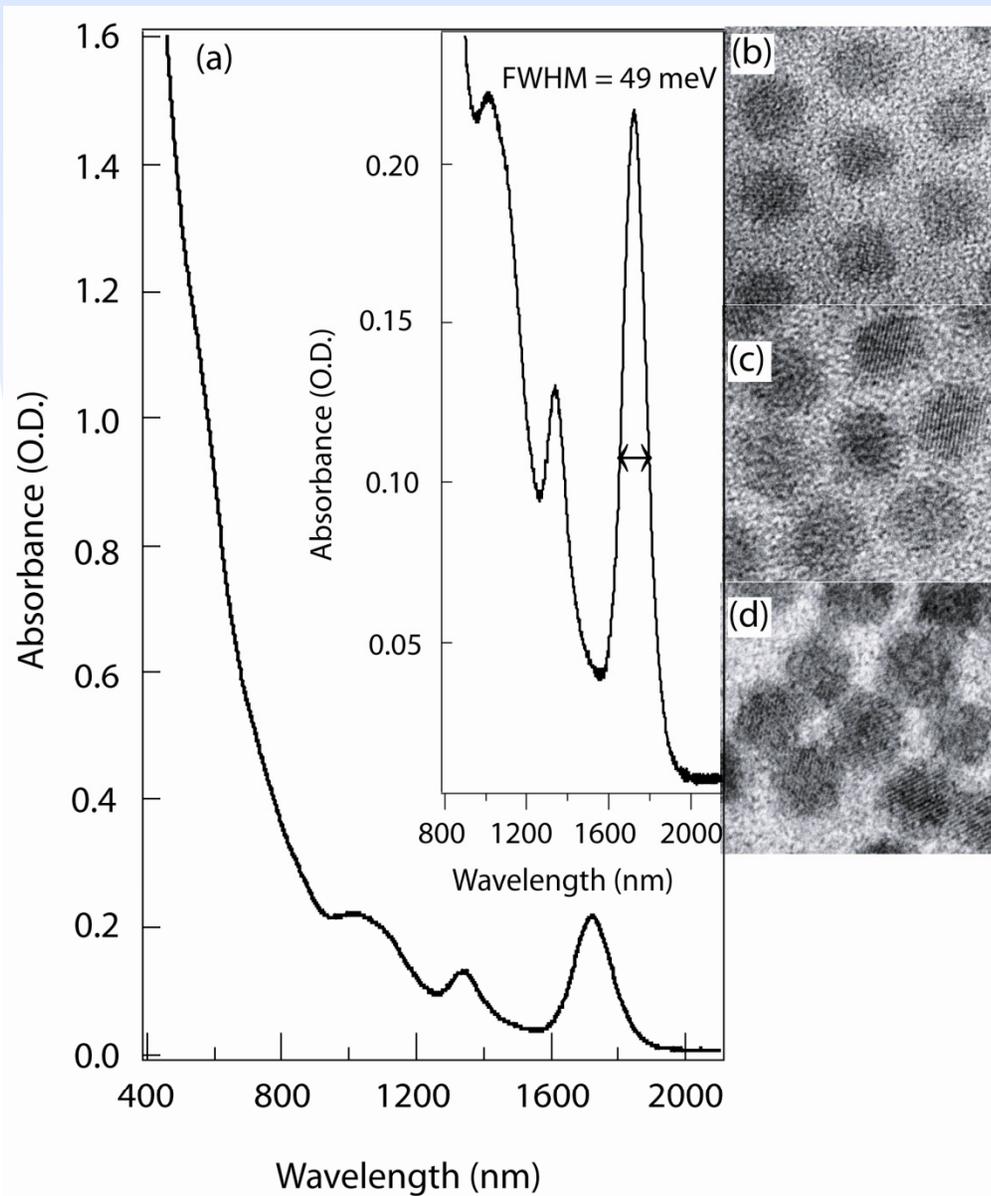
Silicon Nanocrystals ($D \approx 9$ nm)



L. Mangolini *et al.* *Nano Lett.* **5**, 655 (2005)



Drop-cast films of 5.7 nm dia. PbSe NCs



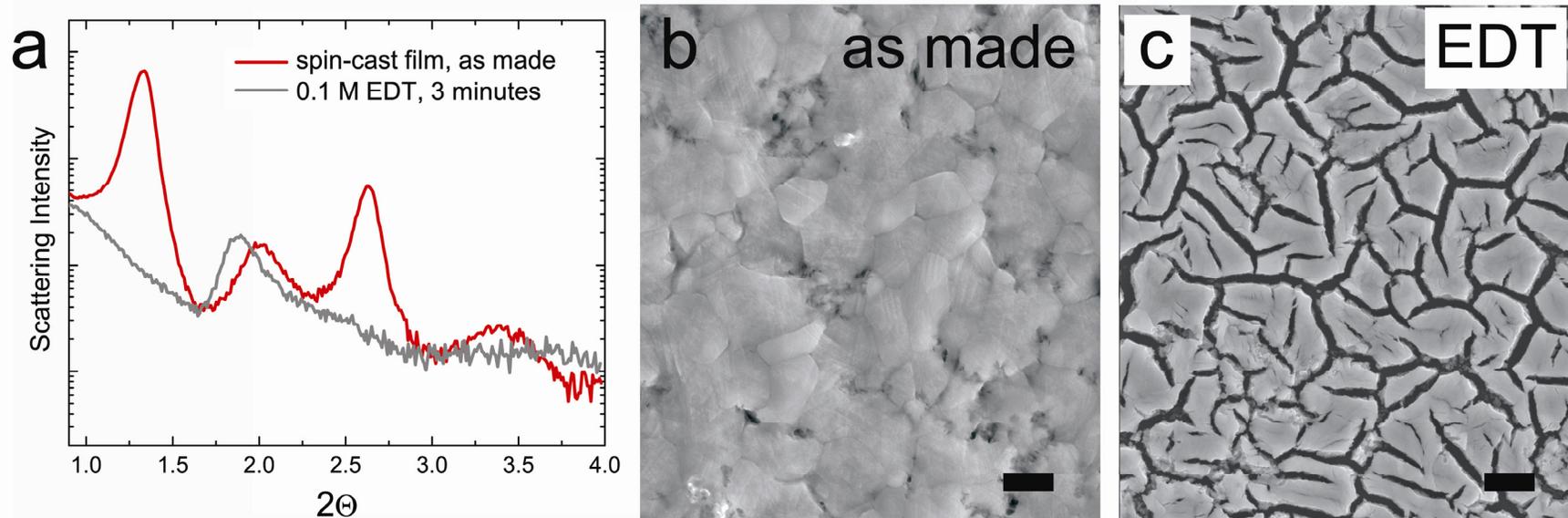
oleic acid (1.8 nm)

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

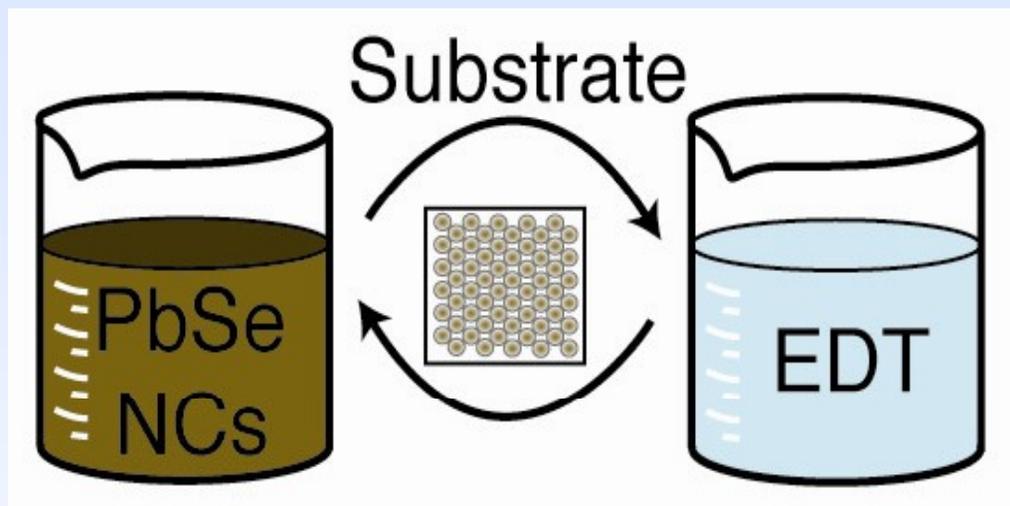


Microstructure of the spin-cast NC films before and after EDT treatment. (a) SAXS data, showing a ~ 16 Å decrease in the spacing between the NCs and a dramatic loss of superlattice order upon EDT treatment. Measurements were taken in air. (b, c) Plan-view SEM images of (b) an untreated film and (c) a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

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



Layer-by-layer fabrication of PbSe NC films



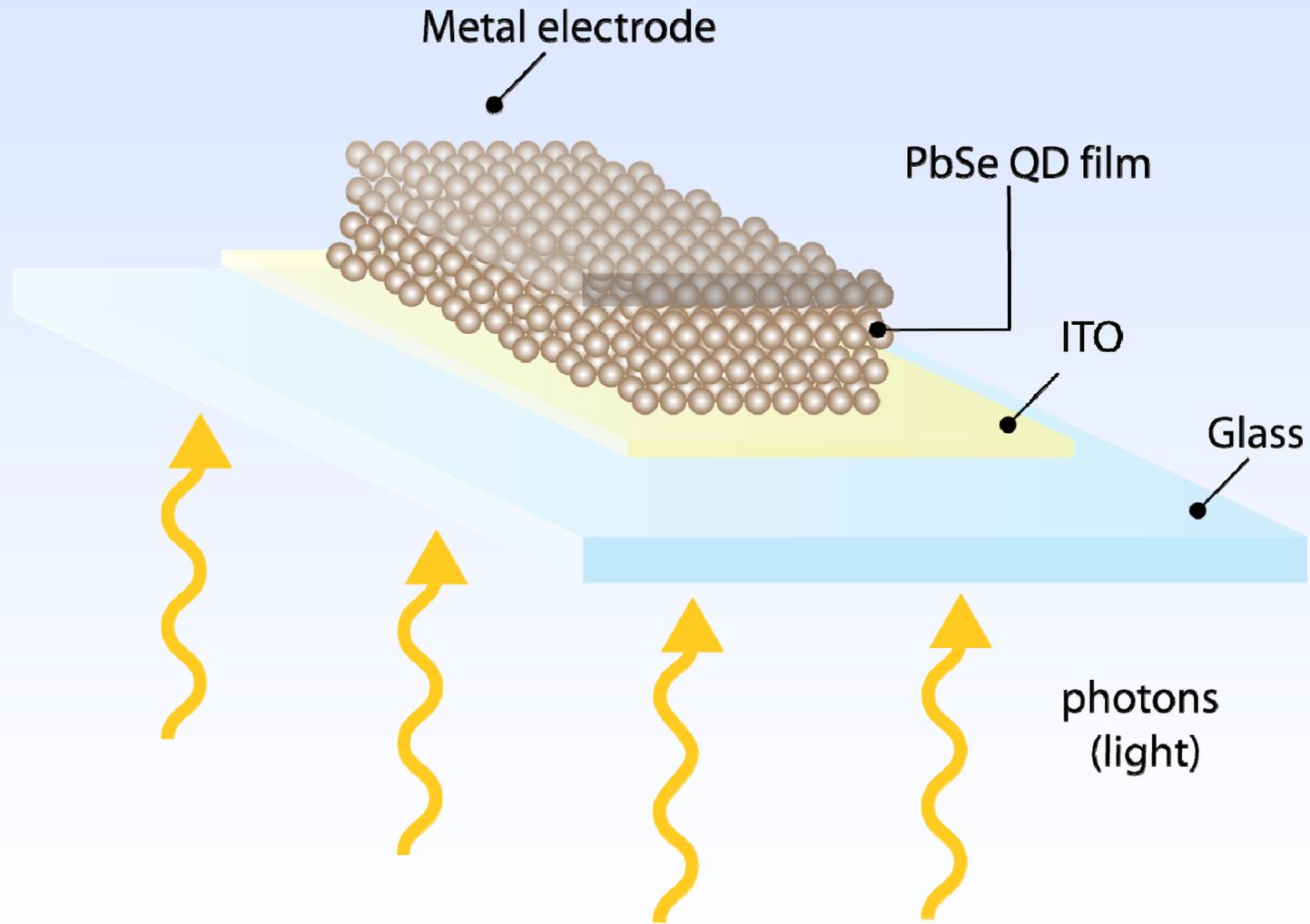
EDT = 1,2-ethanedithiol

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.

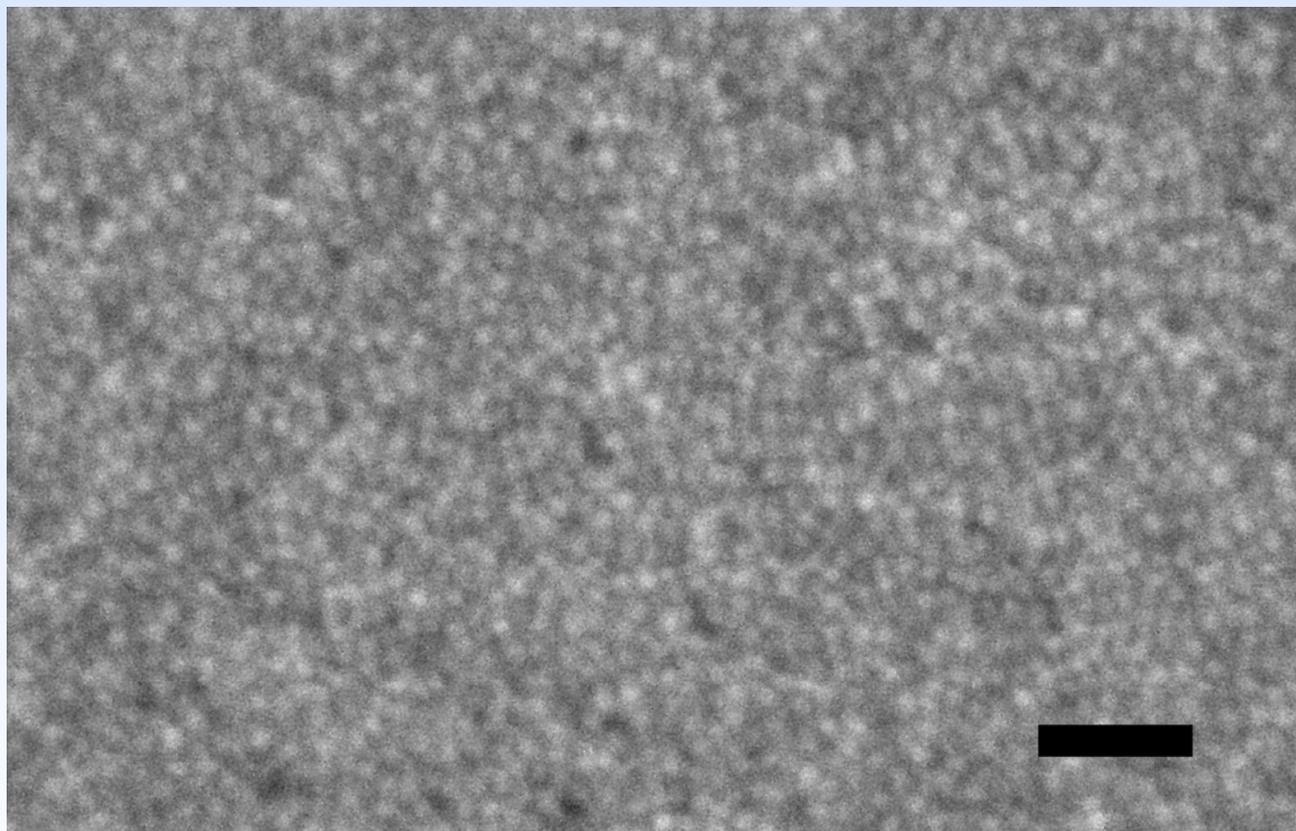
J. M. Luther, M. Law *et al.*, "Structural, Optical, and Electrical Properties of Self-Assembled Films of PbSe Nanocrystals Treated with 1,2-Ethanedithiol", *ACS Nano* **2**, 271 (2008).



Novel nanocrystal-based solar cell



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; scale bar equals 50 nm. The LbL film shown was produced using 10-20 dip coating cycles.

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



Post-casting treatment of spin-cast films of 7 nm dia. PbSe NCs

Characterization:

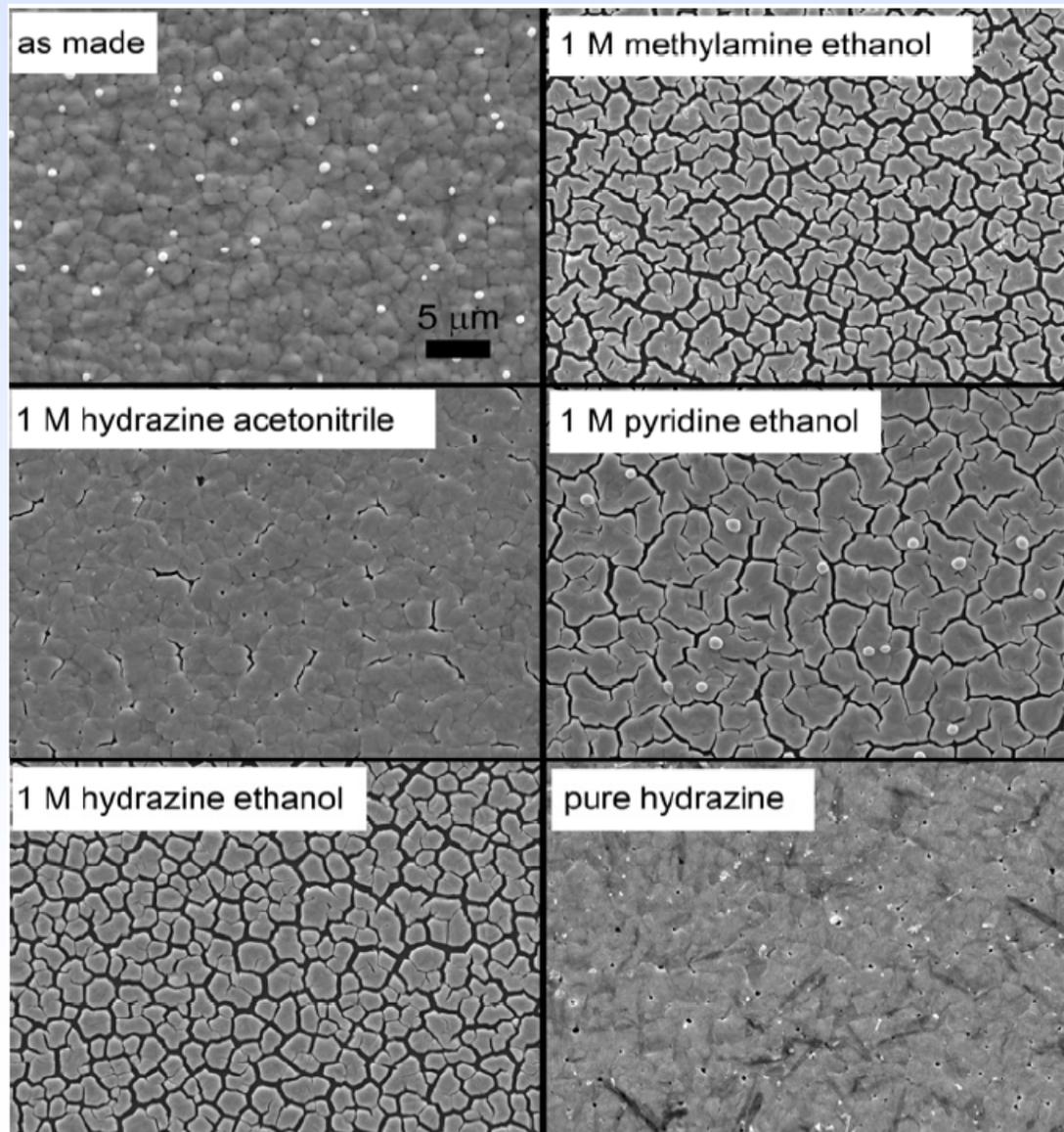
SEM

WAXS

SAXS

FTIR

UV-Vis-IR Absorbance

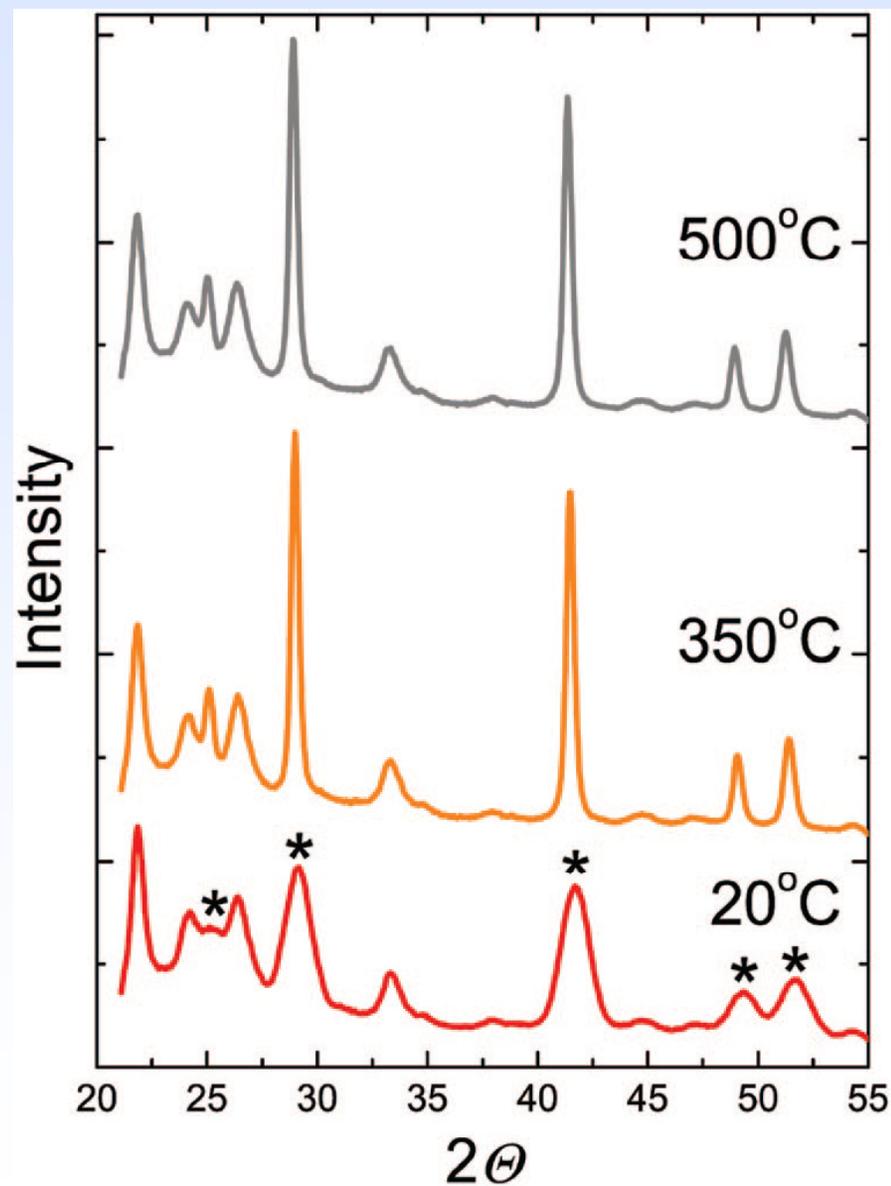


Films spun from octane solution.



Annealing NC-based films

“WAXS patterns of a PbSe NC sample at room temperature, 350, and 500 °C in a nitrogen atmosphere. PbSe peaks are labeled with asterisks...”



Law et al., J. AM. CHEM. SOC. 2008, 130, 5974–5985

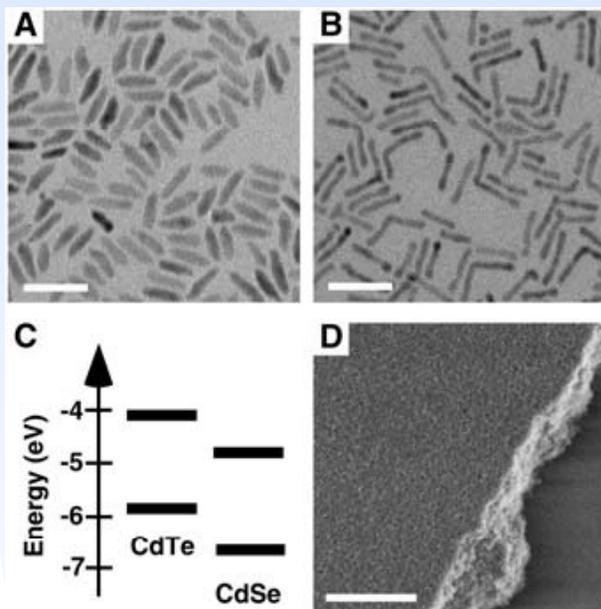


Annealed NC-based solar cell

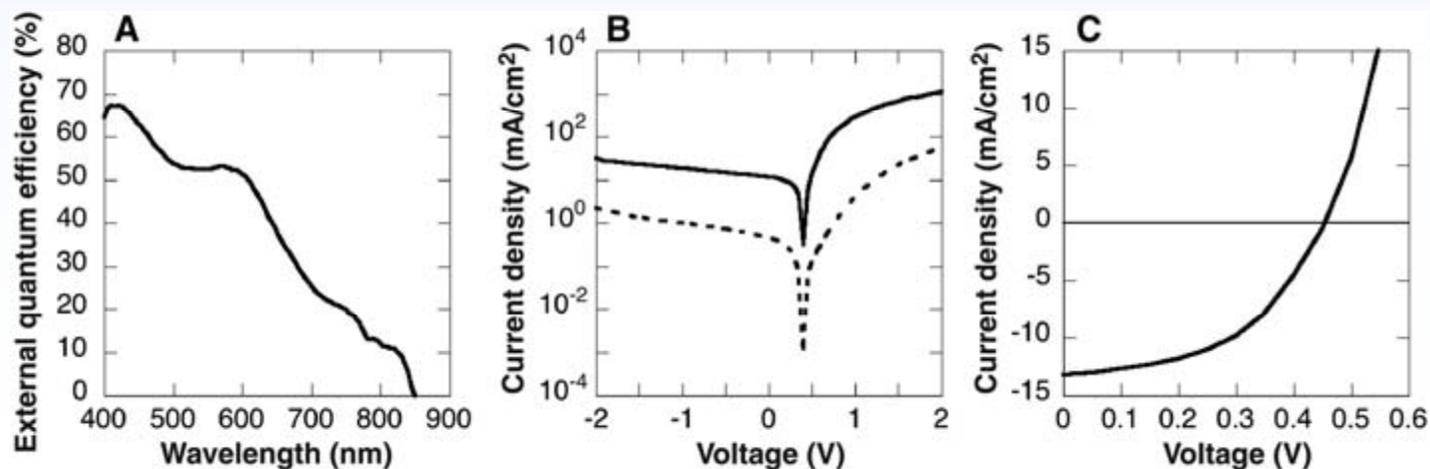
Air-Stable All-Inorganic Nanocrystal Solar Cells Processed from Solution

Ilan Gur, Neil A. Fromer, Michael L. Geier, A. Paul Alivisatos

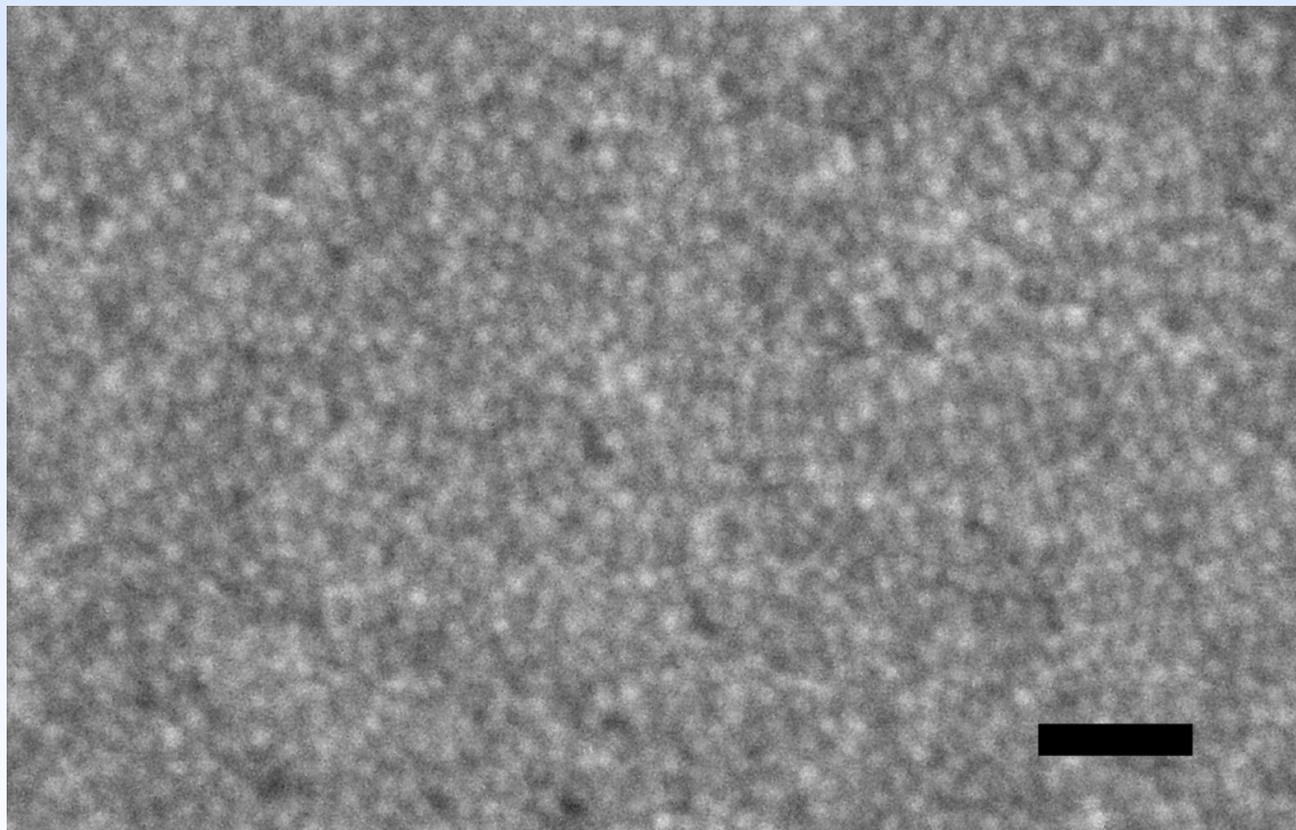
21 OCTOBER 2005 VOL 310 SCIENCE



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...



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; scale bar equals 50 nm. The LbL film shown was produced using 10-20 dip coating cycles.

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

