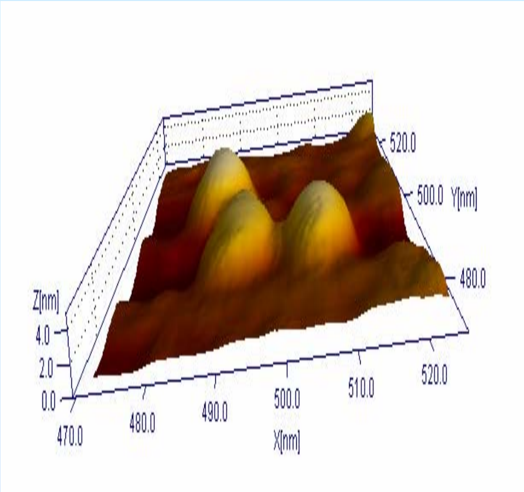
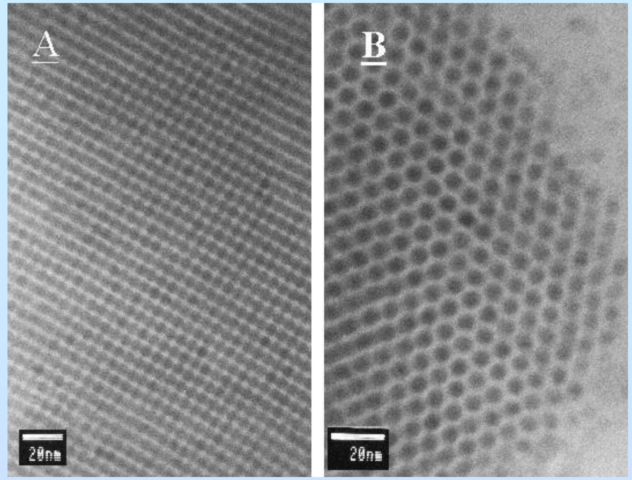
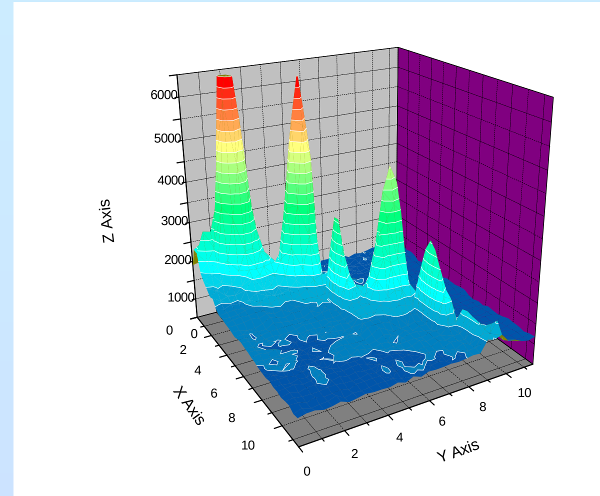






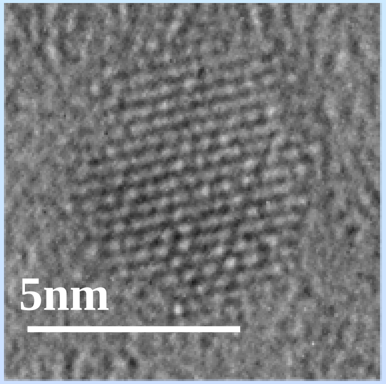
Single and multi-excitons in core-shell semiconductor nanocrystals

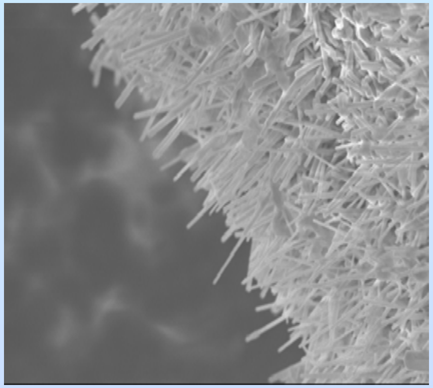
Prof. Efrat Lifshitz

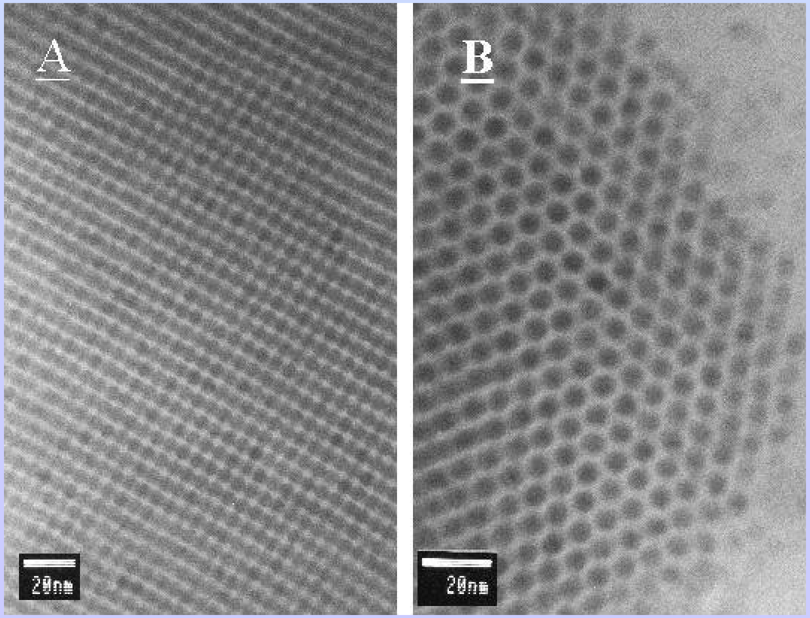
Dept. of Chemistry, Solid State Institute and the Russell Berrie Nanotechnology Institute, Technion, Haifa, Israel

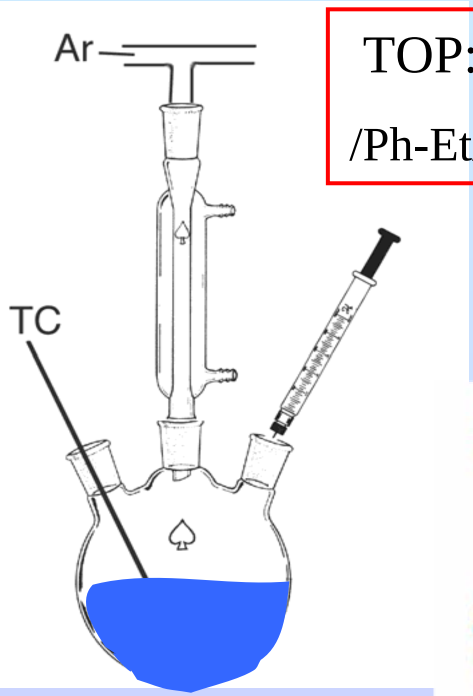
RBNI TECHNION

Synthesis of PbSe nanocrystals quantum dots









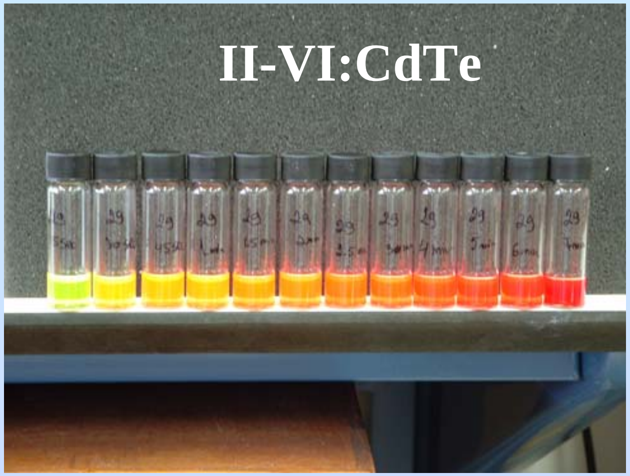
TOP:Se + Pb-Ac

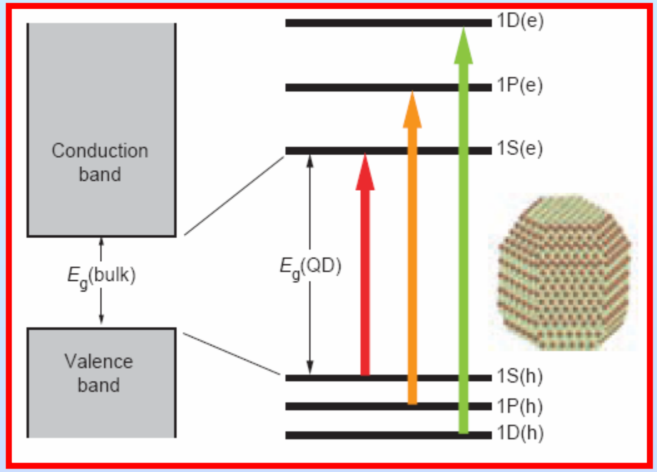
/Ph-Et/OA/TOP (**130 ^{o}C)**

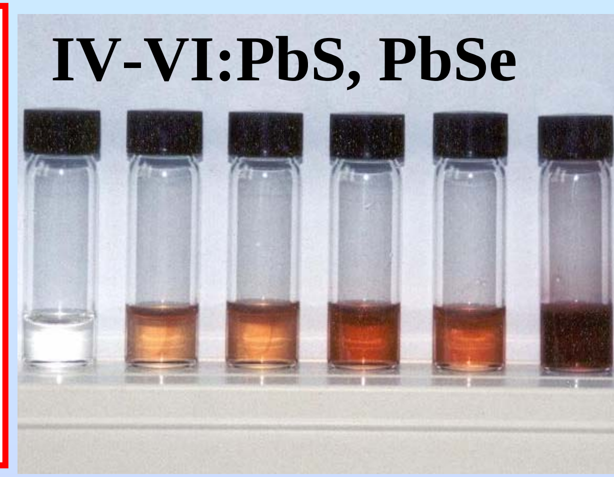
Lifshitz et al., Adv. Fn. Mat., 05,

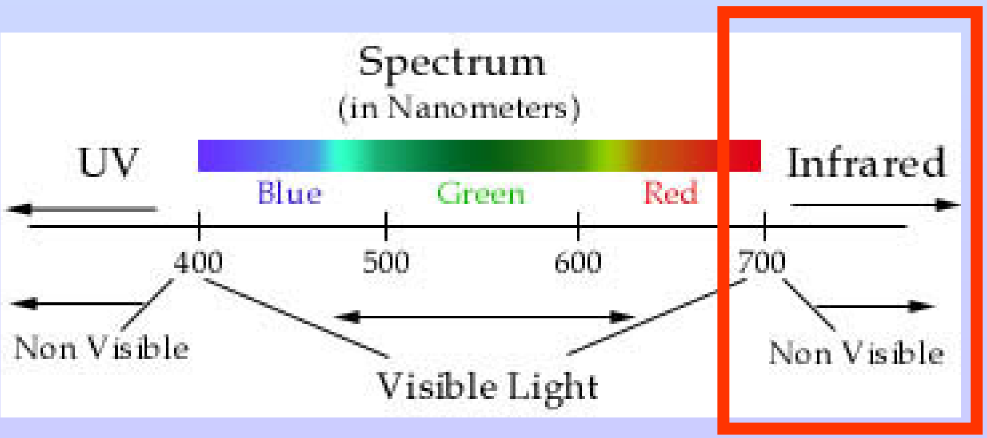
J. Phys. Chem. B, 06, Inorg. Chem., 07

Nanocyrstals quantum dots (NQDs) active in the near infra-red





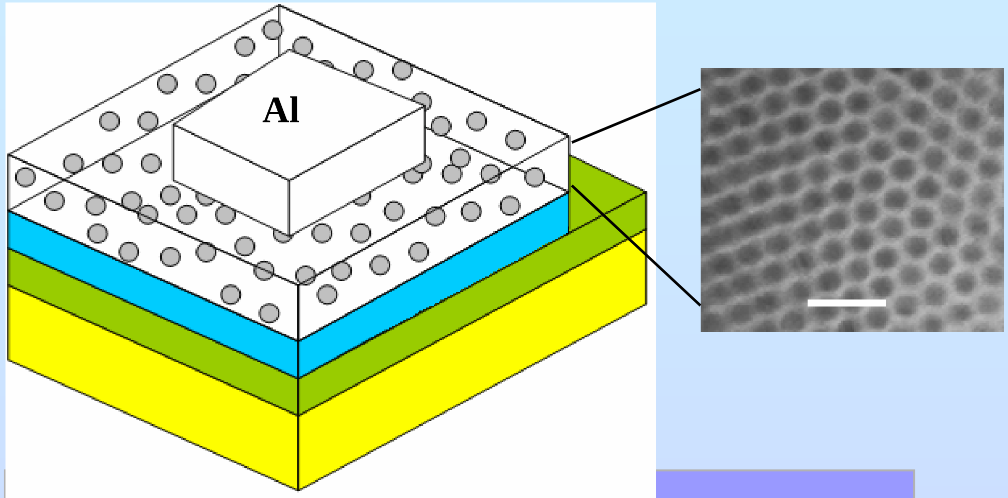


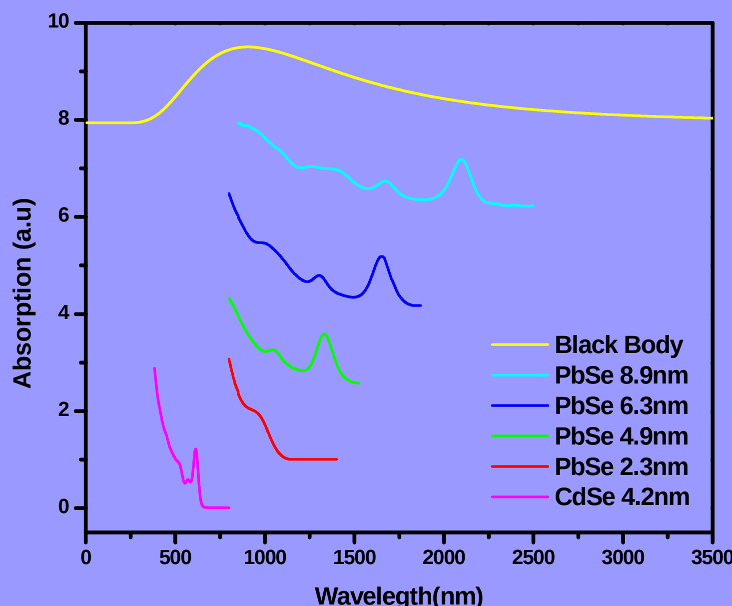


Novel Physics,

Applications

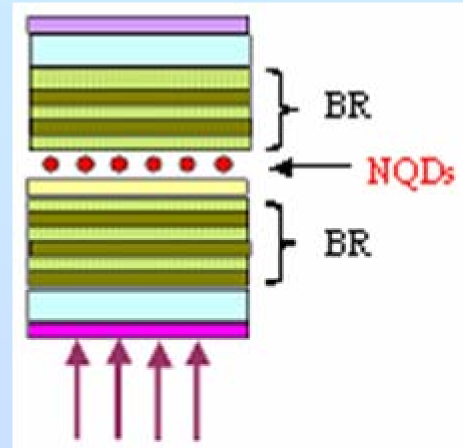
Photovoltaic cells

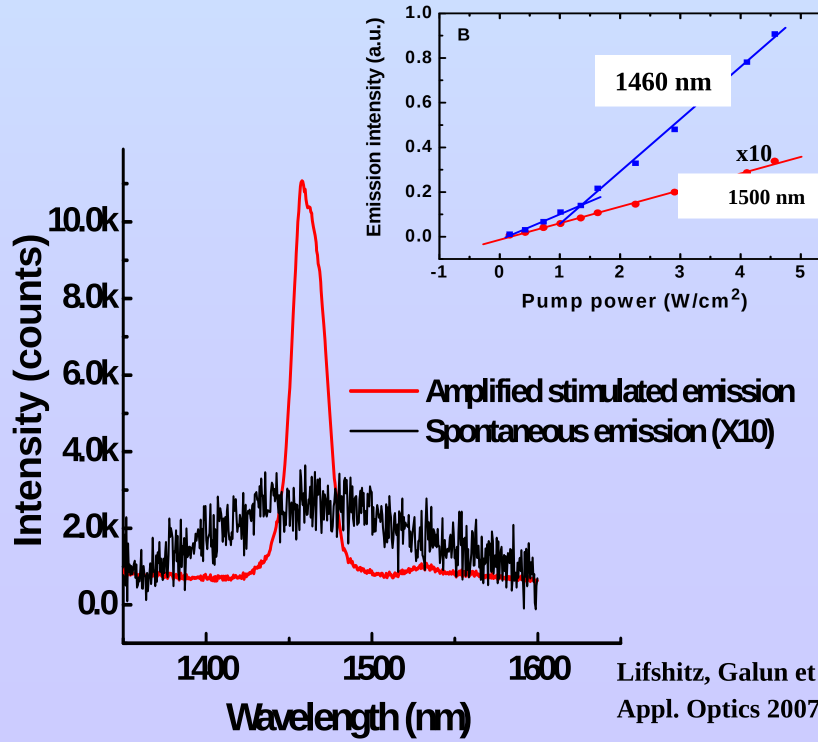




Tessler, Lifshitz et al. Appl. Phys. Lett., 2006

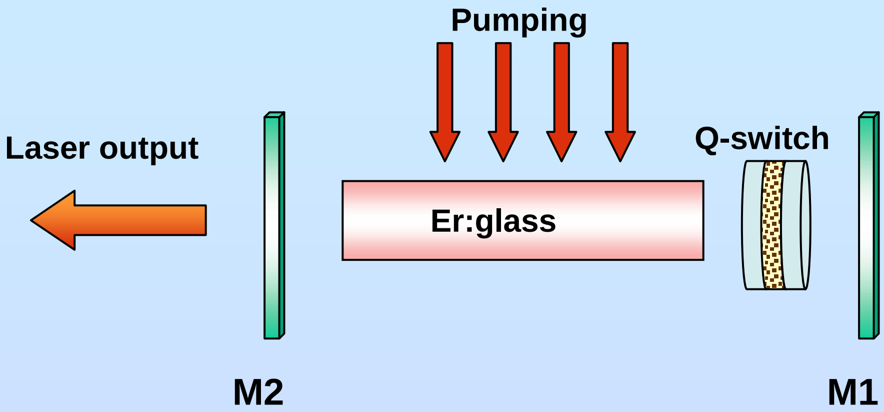
Gain devices

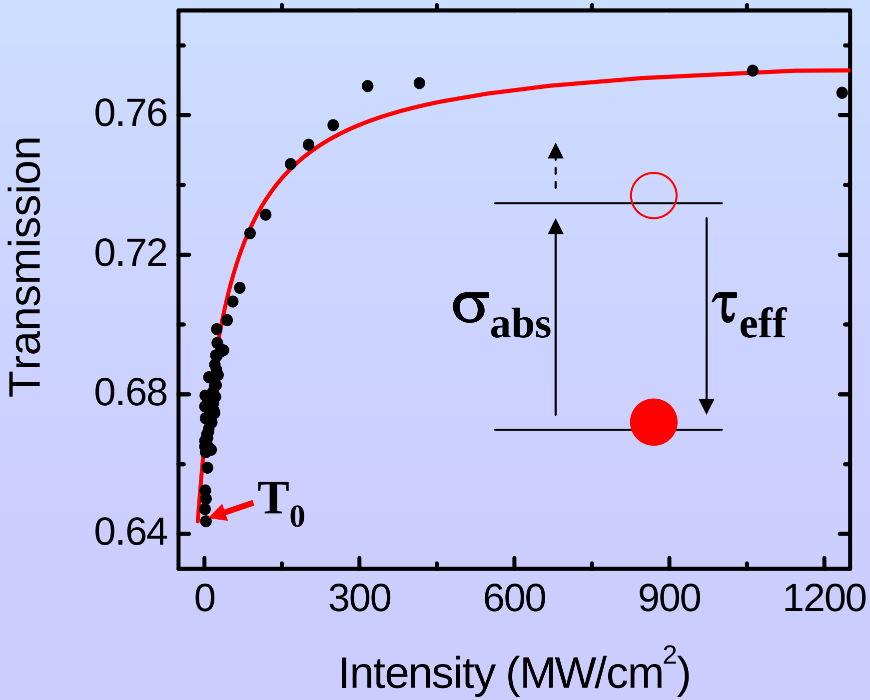




Lifshitz, Galun et al., Appl. Optics 2007

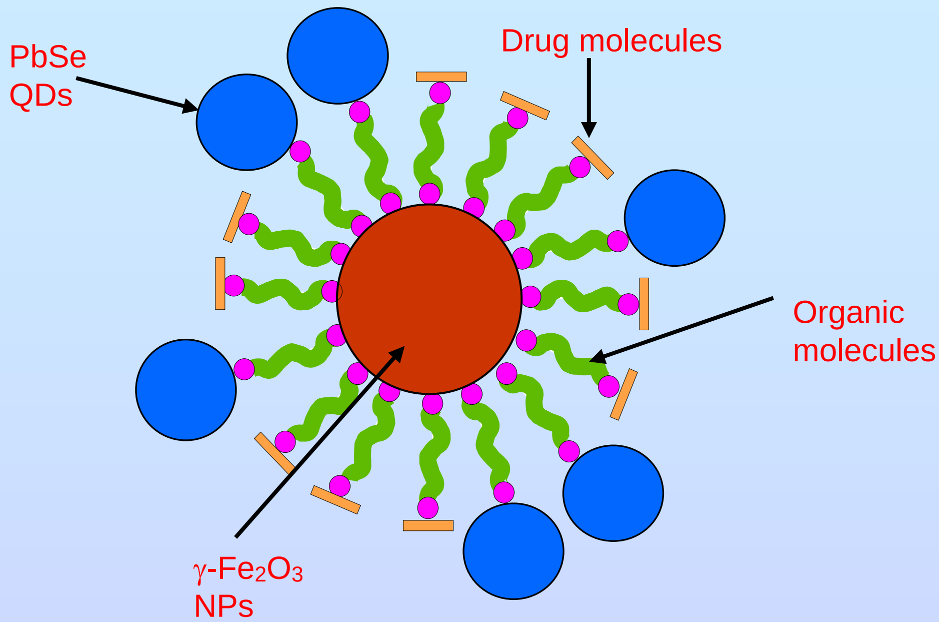
Optical switches



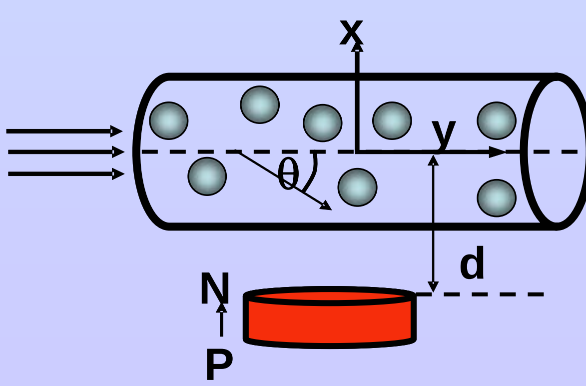


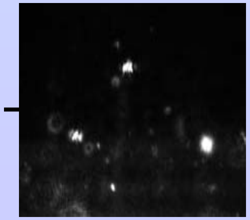
Lifshitz, Tannenbaum et al, Appl. Optics 2006

Medical platform



Lifshitz, Tannenbaum et al., J.Phys. Chem. C. 2007





Lifshitz, Tannenbaum et al., PRL, submitted

SINGLE & MULTIEXCITONS

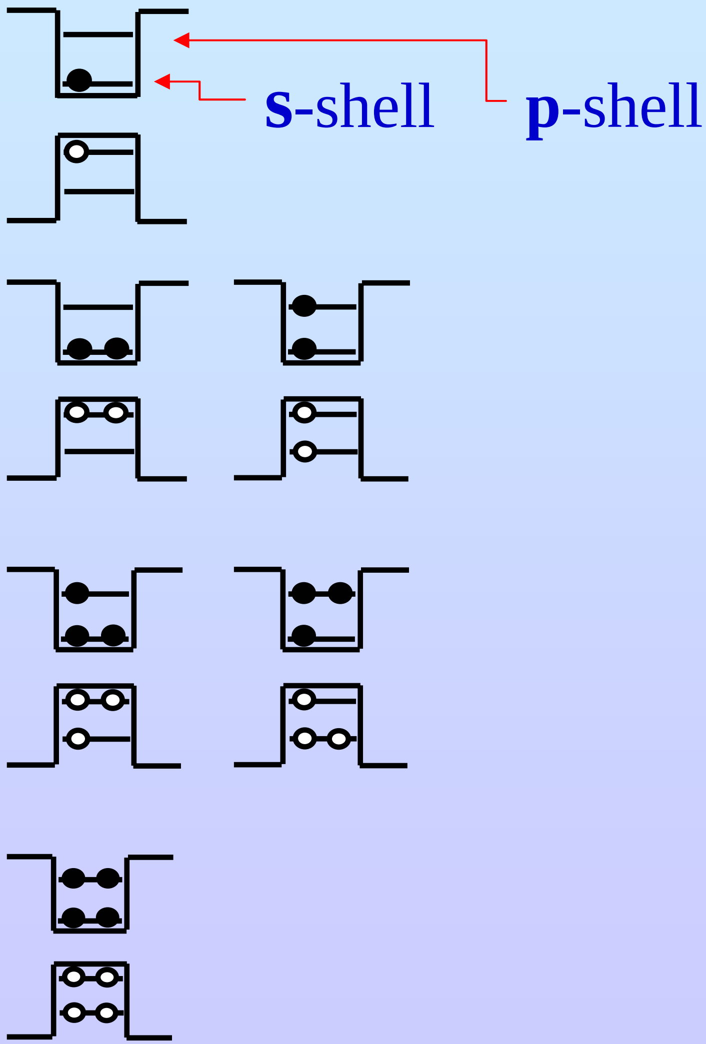
(gain device, solar energy, optical switch, single-photon light source)

A single exciton (X)

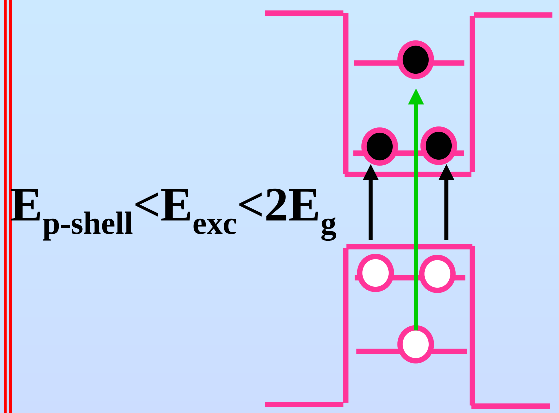
Biexciton (2X)

Triexciton (3X)

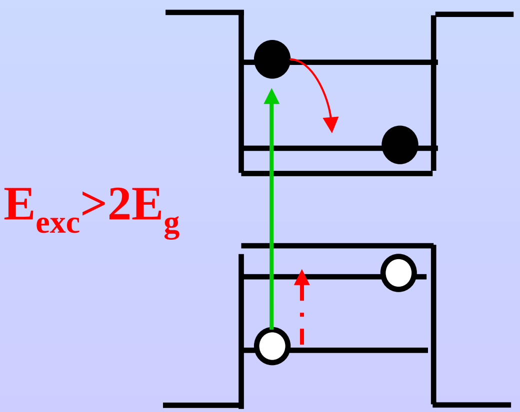
Tetraexciton (4X)



Generation



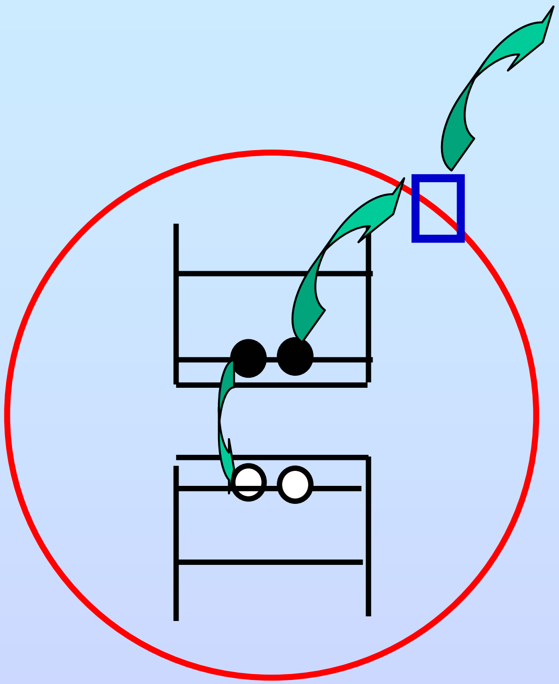
Sequential Filling



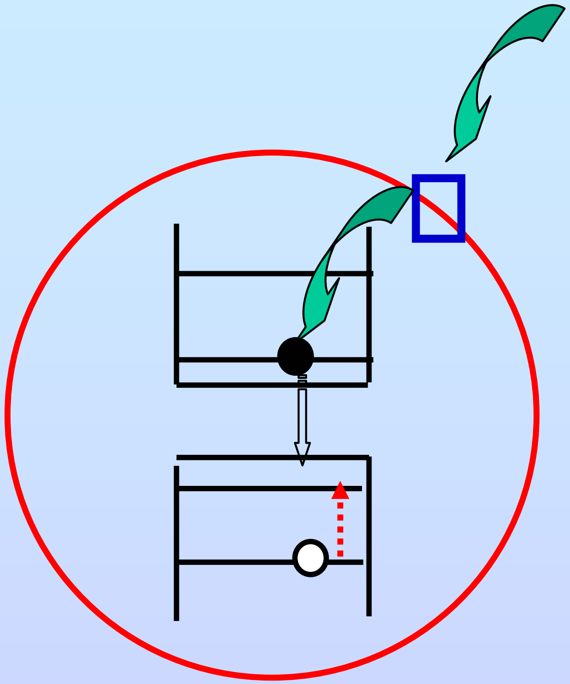
Impact Ionization

[Klimov (04), Nozik&Efros (05), Bawendi, Banin (08)]

Auger Relaxation



“Off”

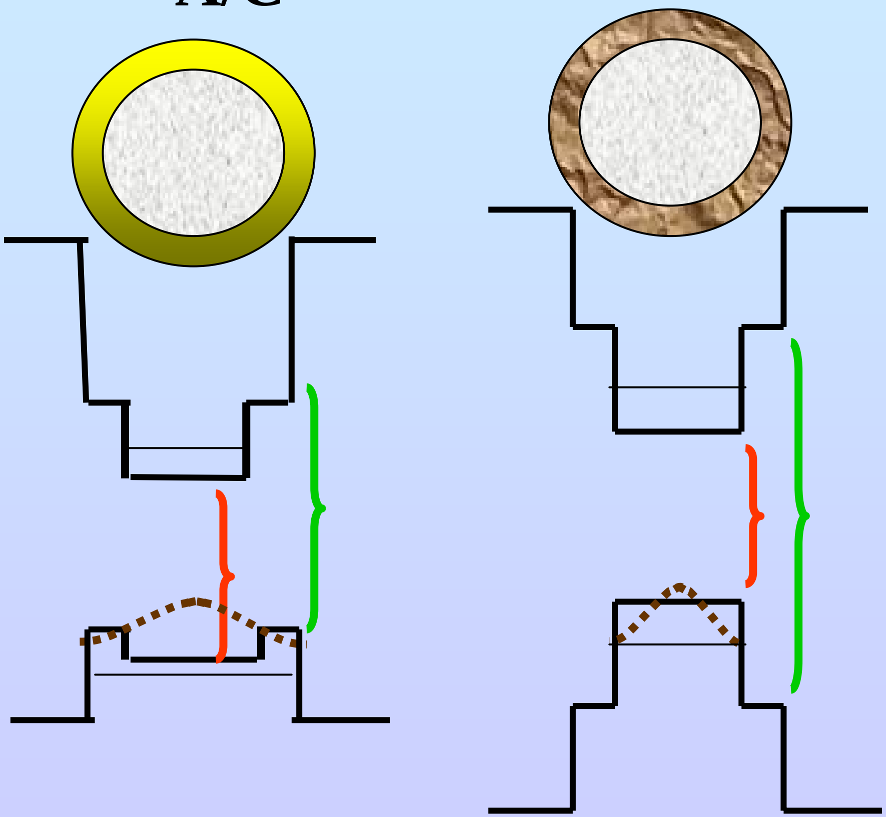


“On”

1. Fluorescence intermittency (Blinking)
2. Intermediate charge species ($2X \rightarrow 2X^{+} + e$, $2X \rightarrow X^{+} + X$)
3. Requires transient measurements

Looking for a solution

A/C A/B



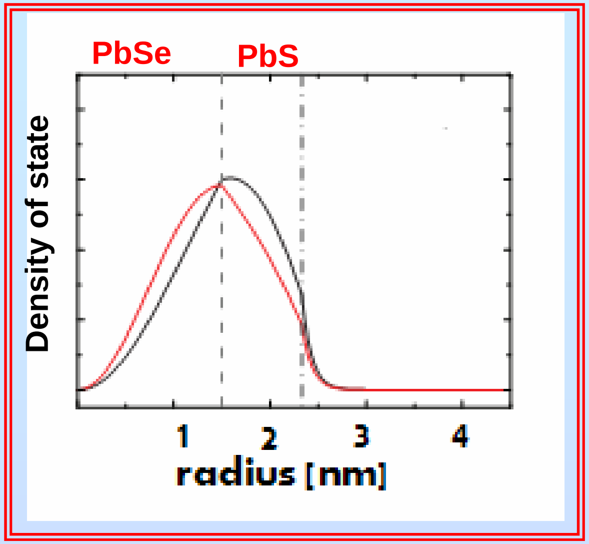
Core-Shell Structures

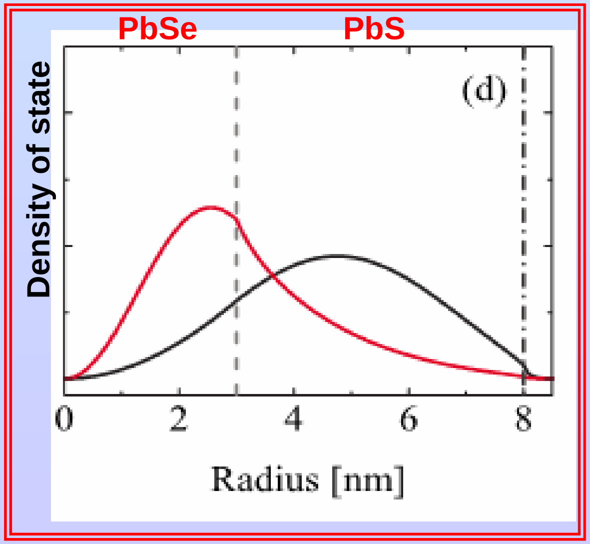
- Increase of the effective size
- Improved surface quality
- A better match of dielectric const. at the core/shell interface
- Carriers' distribution between the core and the shell

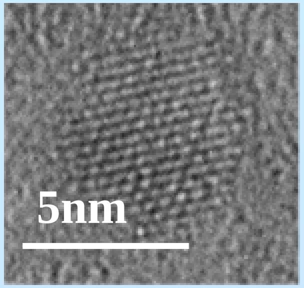
Type II ↔ Type I

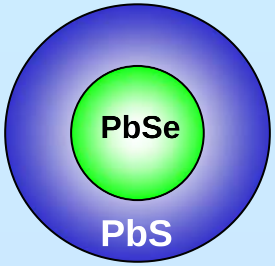
Q-Type II

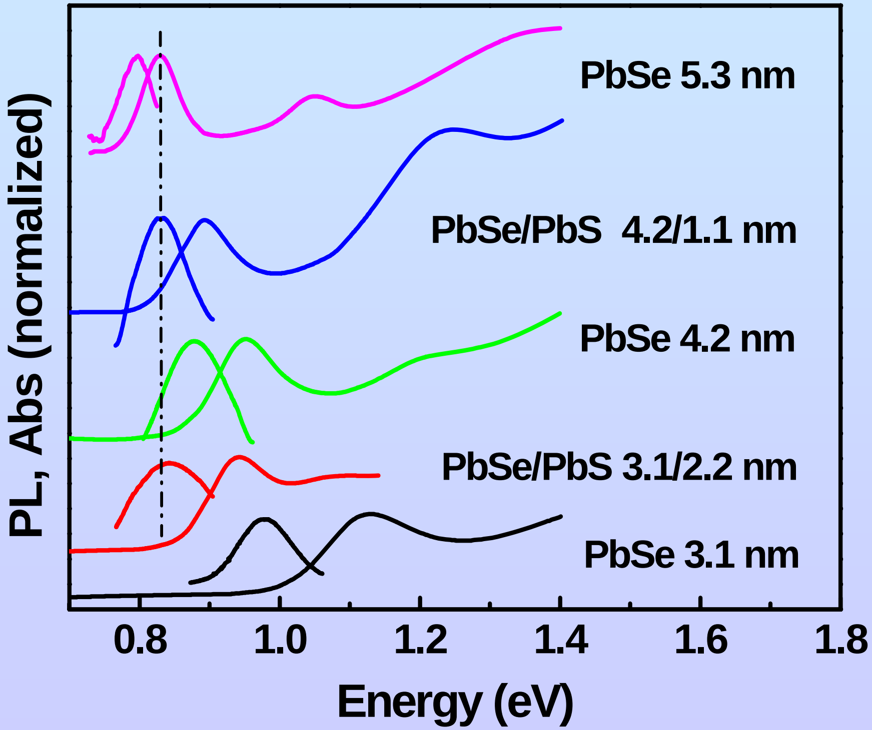
Core-shell-shell











Wise, Lifshitz et al., P RB (07)

Lifshitz et al., Adv. Fn. Mat.,(05),

J.Phys. Chem. B (06), Nano Lett.l, submitted (08)

$$E_g(T) = E_g(0) + \frac{\alpha T^2 (1 - A_1 x)}{T + \beta} + A_2 x$$

α_{core}=dE$_g$/dT=0.20 (core),

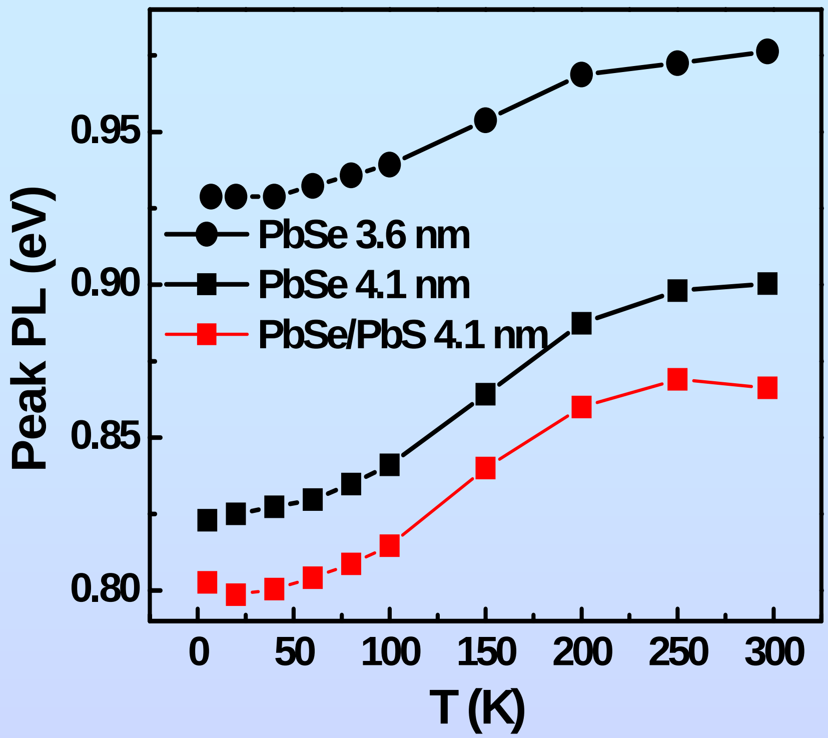
0.42 (core-shell) meV/K

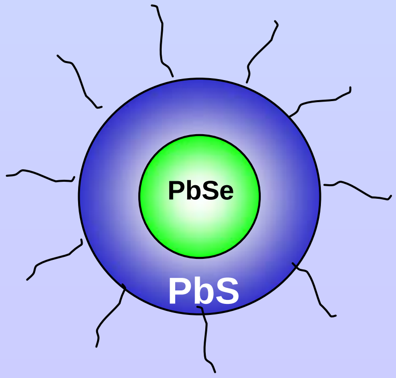
$\alpha_{PbSe\text{-}bulk}$= 0.38 meV/K

$\alpha_{PbS\text{-}bulk}$= 0.50 meV/K

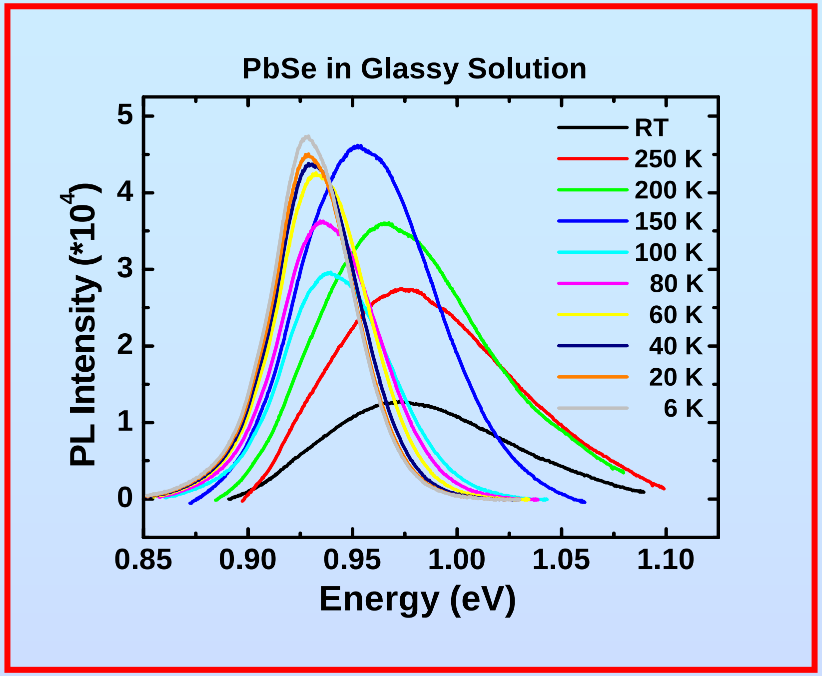
=====================

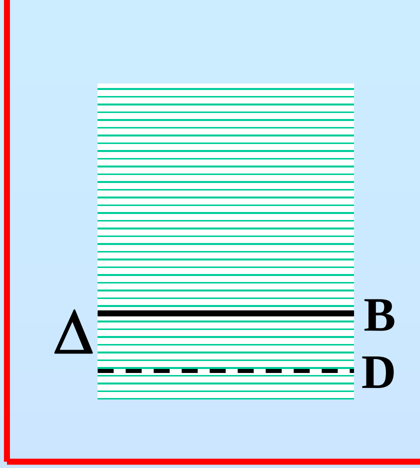
- **Lattice dilation**
- **Surface tension**
- **Electron-phonon coupling**

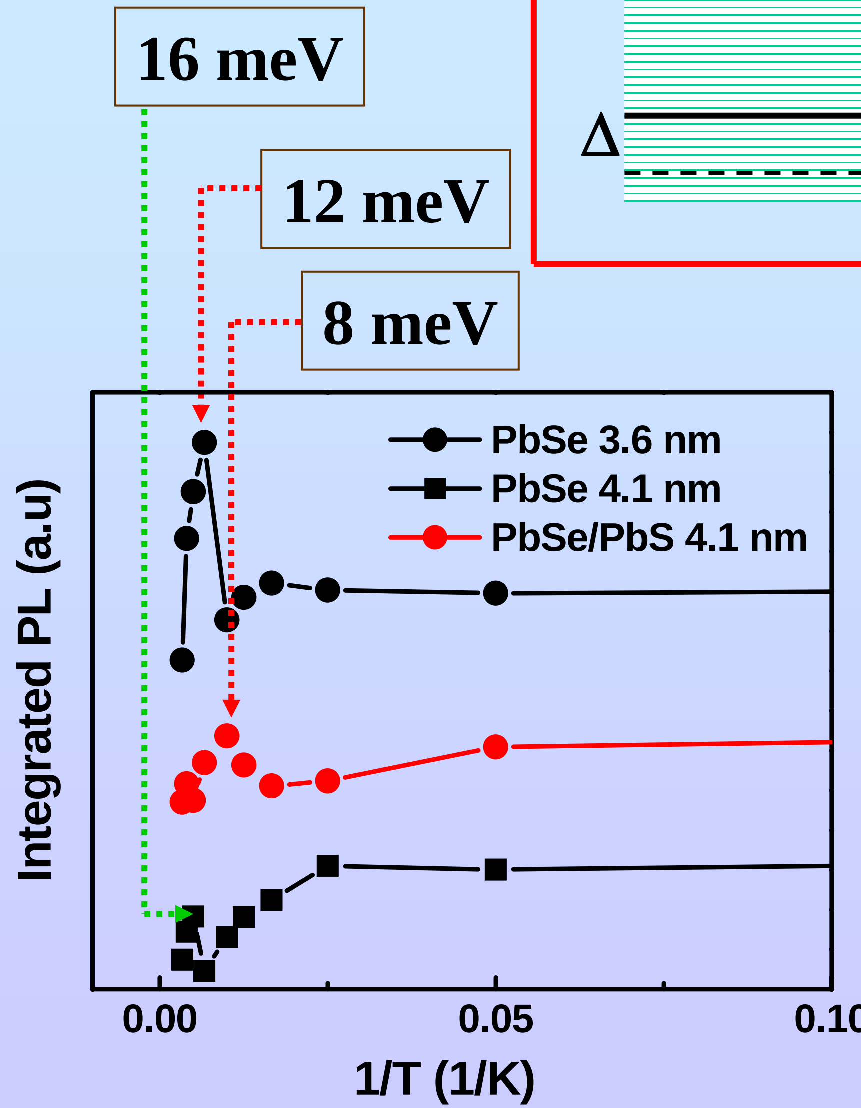




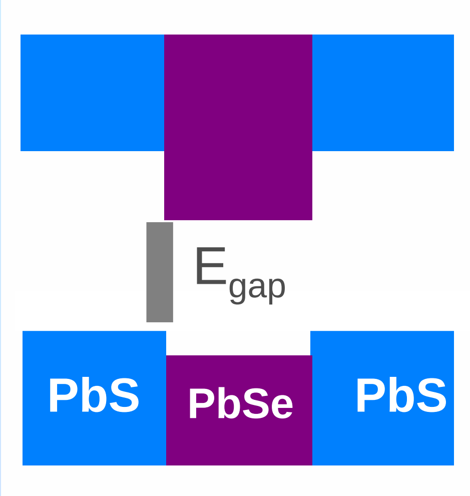
E. Lifshitz *et al.*, submitted (08)



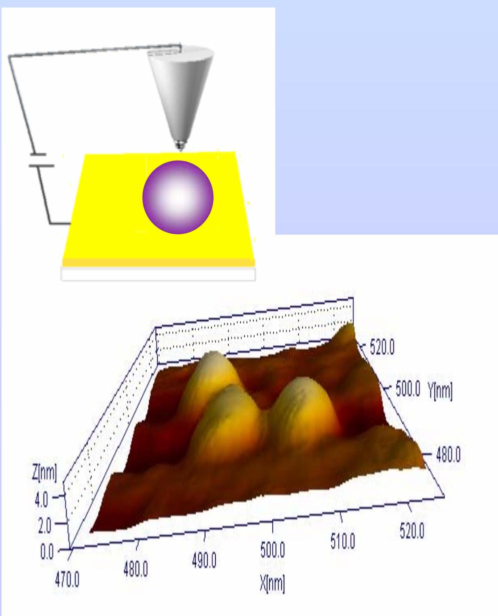


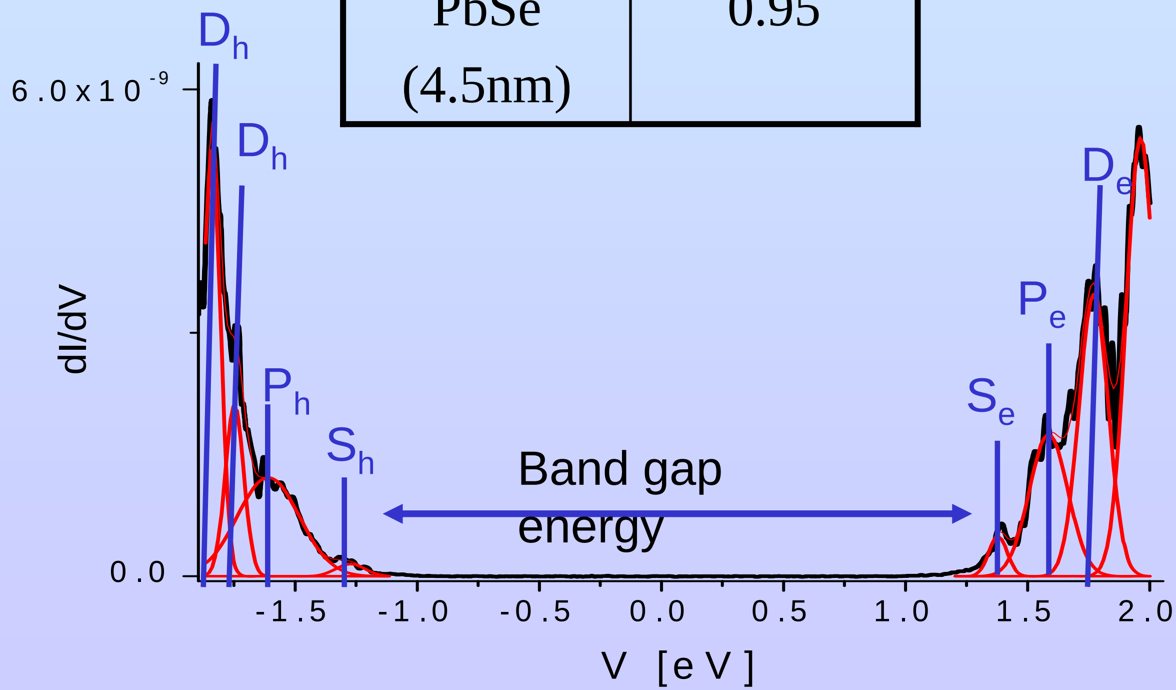


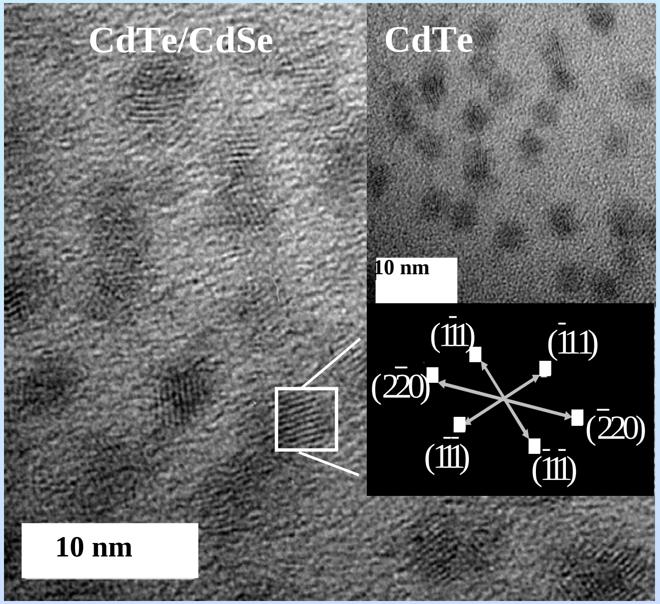
$$I_{PL}(T) = \frac{I_0}{1 + a\exp(-\frac{\Delta}{k_B T}) + b\exp(\frac{E_{ph}}{k_B T} - 1)^{-m}}$$

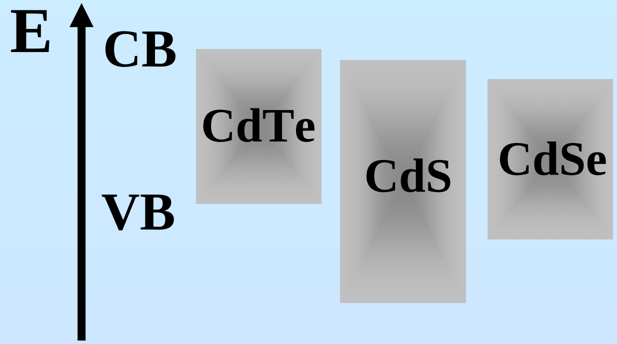


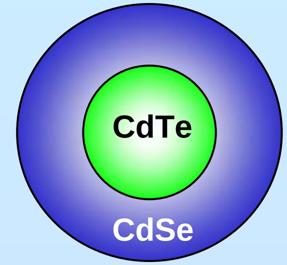
NQD (D_{total})	E_{gap}^{QD} (eV)
PbSe (3nm)	1.25
PbSe/PbS (4.5nm)	1.19
PbSe (4.5nm)	0.95

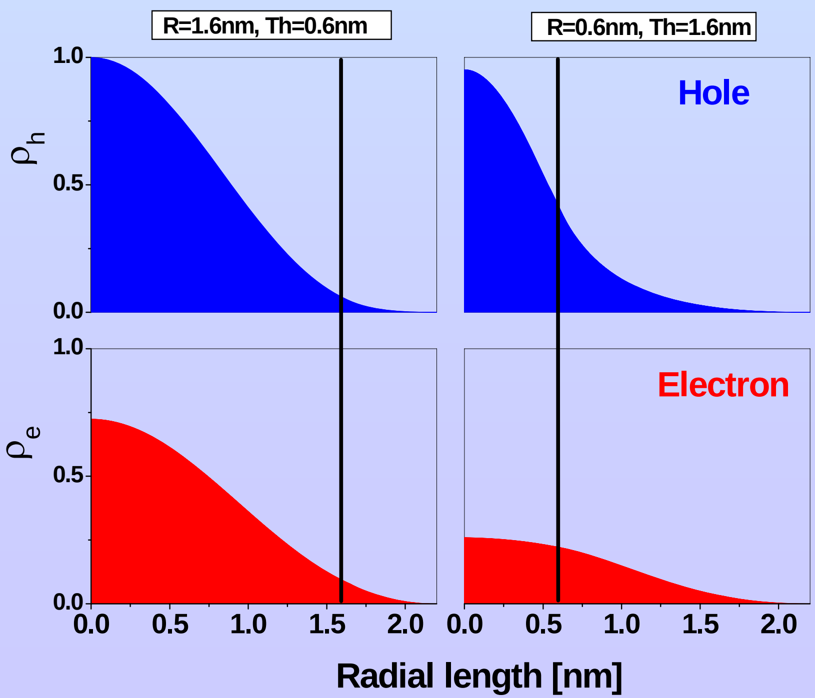


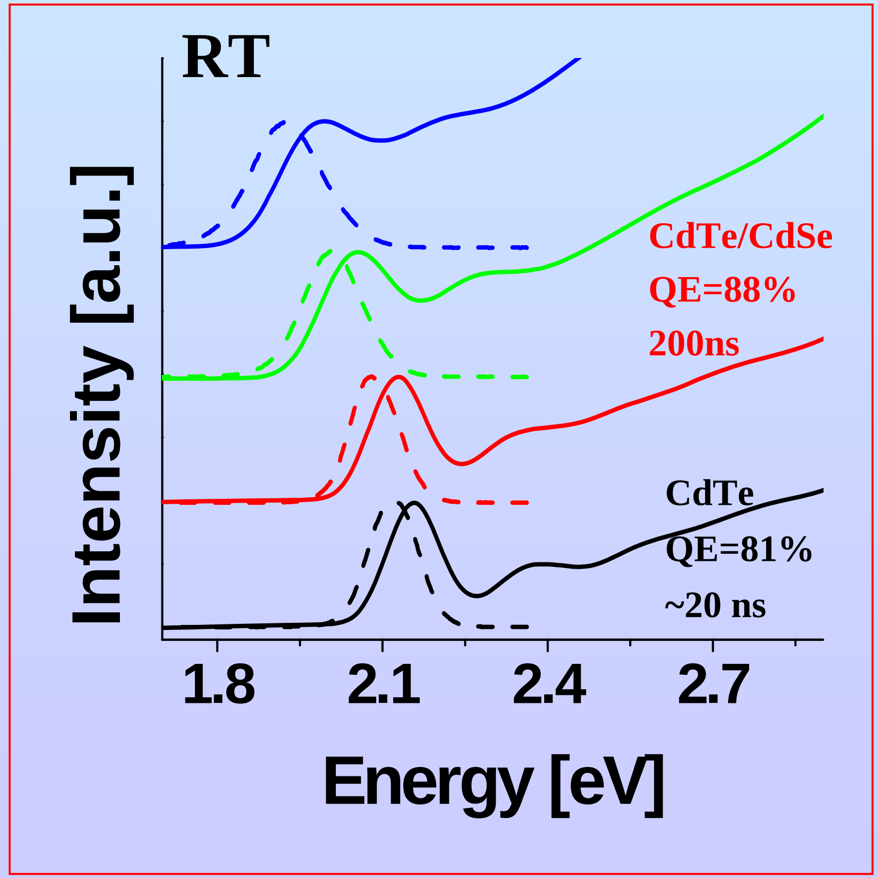



CdTe/CdSe
CdTe
10 nm
(1̄11)
(1̄11)
(2̄20)
(2̄20)
(1̄1̄1)
(1̄1̄1)
10 nm

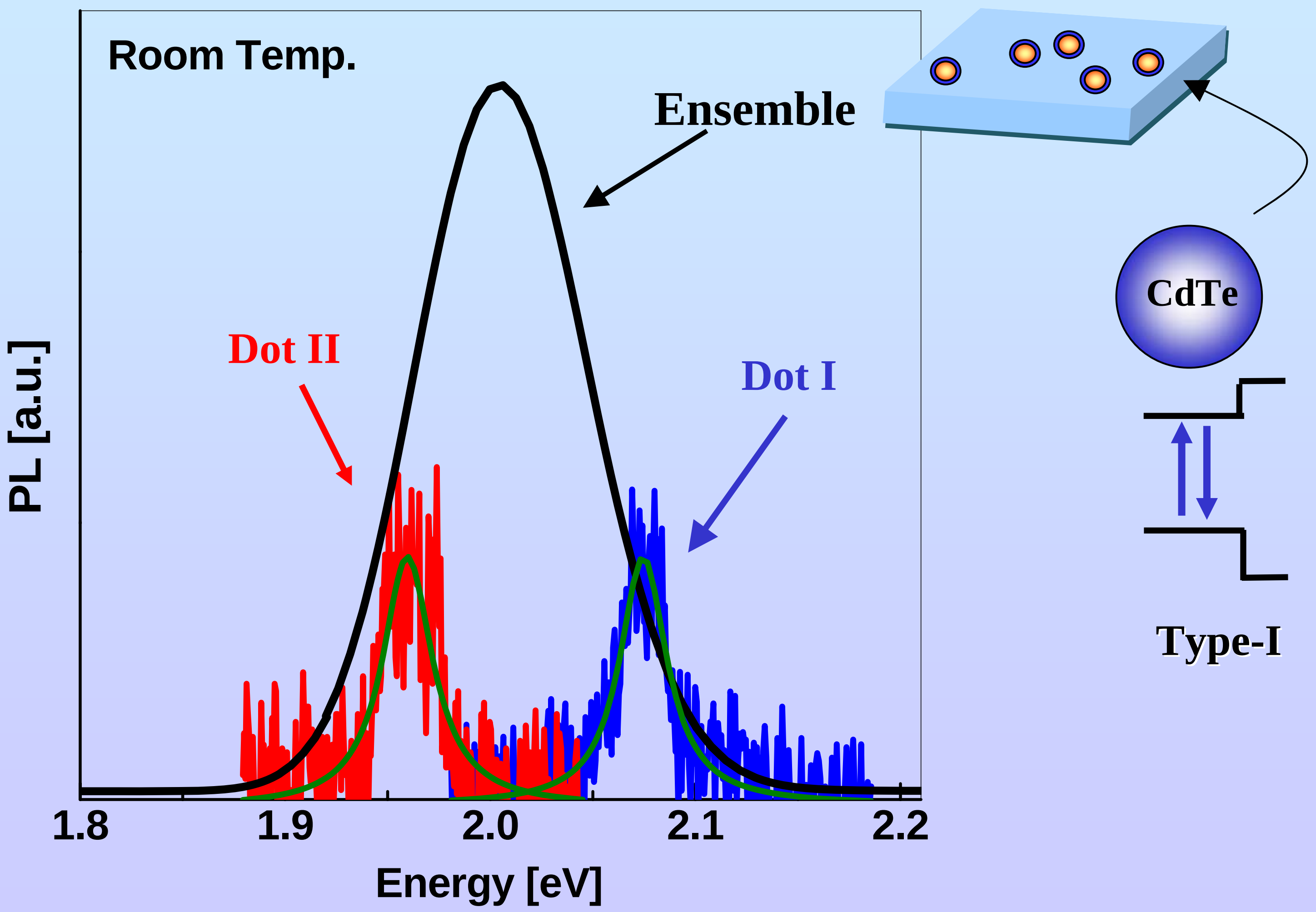

E
CB
VB
CdTe
CdS
CdSe


CdTe
CdSe


R=1.6nm, Th=0.6nm
R=0.6nm, Th=1.6nm
Hole
Electron
ρ_h
ρ_e
1.0
0.5
0.0
0.0 0.5 1.0 1.5 2.0
Radial length [nm]

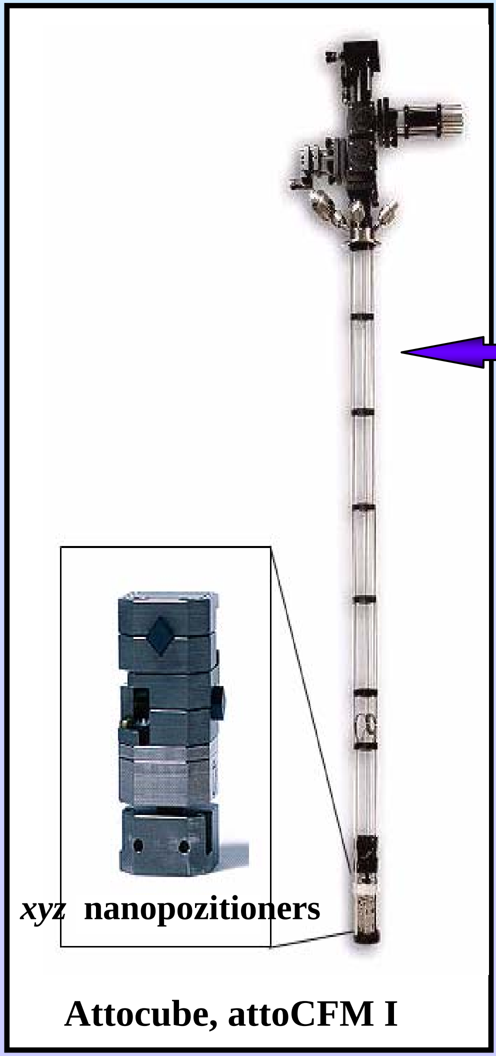

RT
CdTe/CdSe
QE=88%
200ns
CdTe
QE=81%
~20 ns
Intensity [a.u.]
1.8 2.1 2.4 2.7
Energy [eV]

Single dot spectroscopy of Type-I NQDs

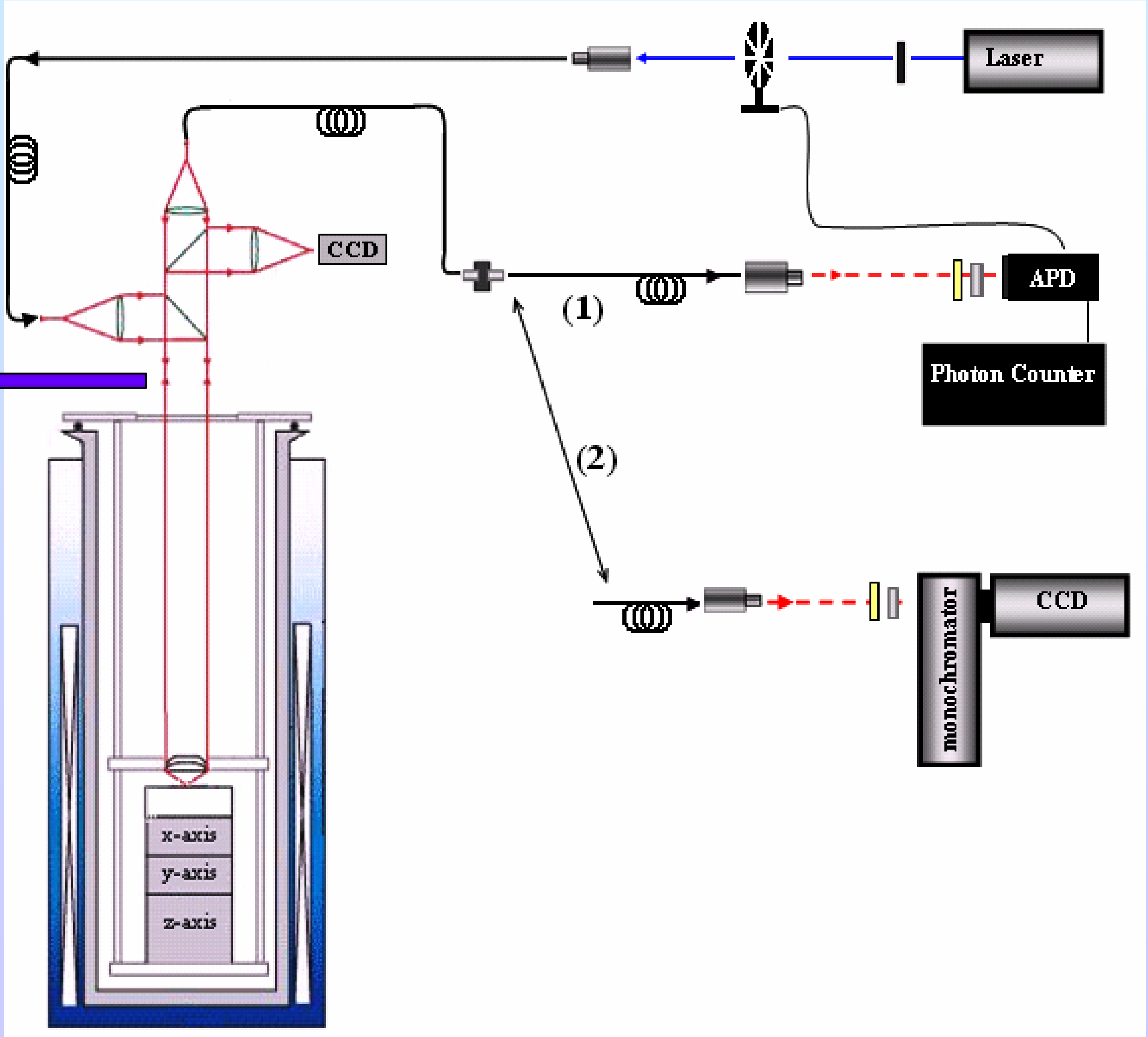


FIBER-BASED micro-photoluminescence (μ-PL) setup

for single dot spectroscopy at RT and 4.2 K with magnetic field up to 12 T



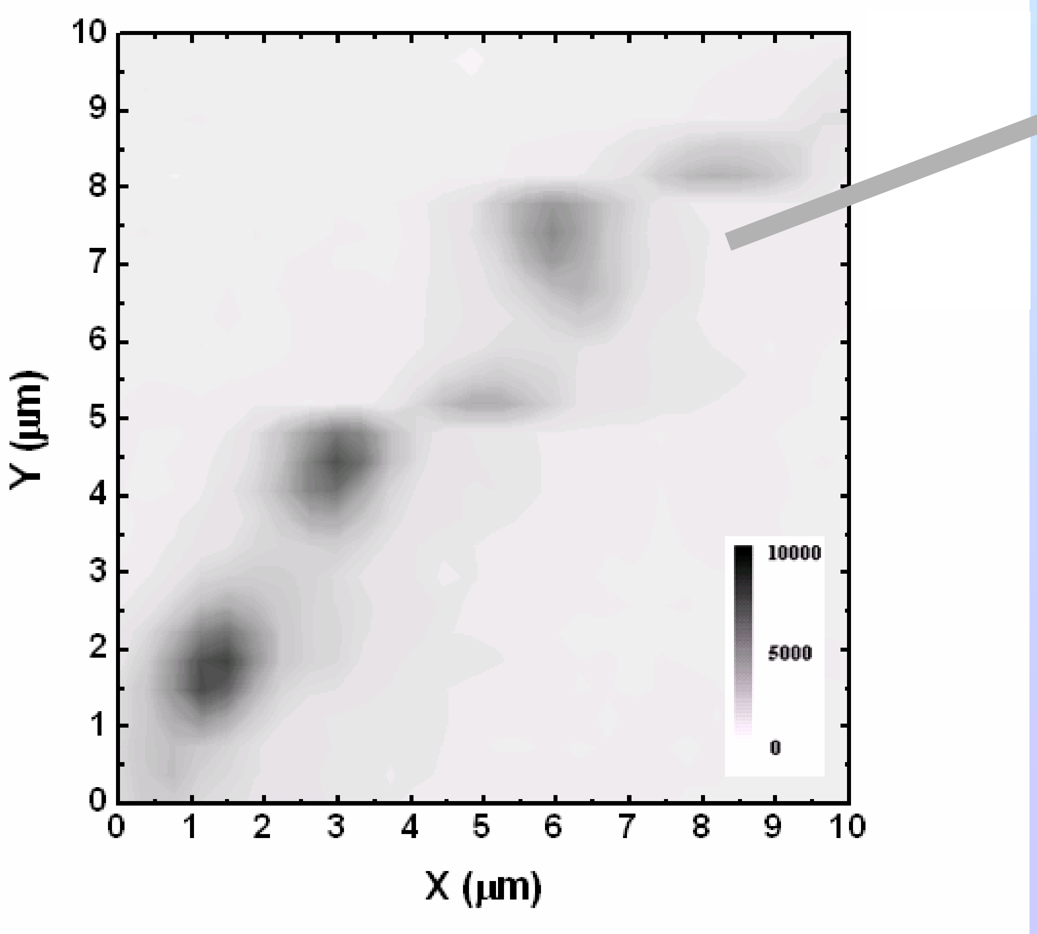
Attocube, attoCFM I

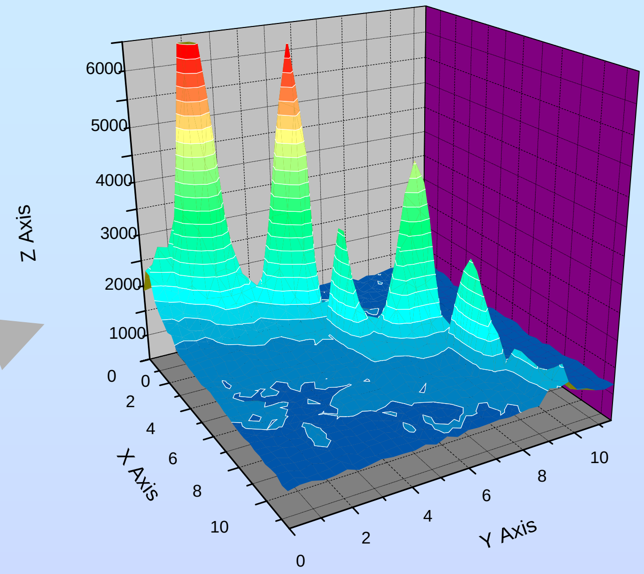


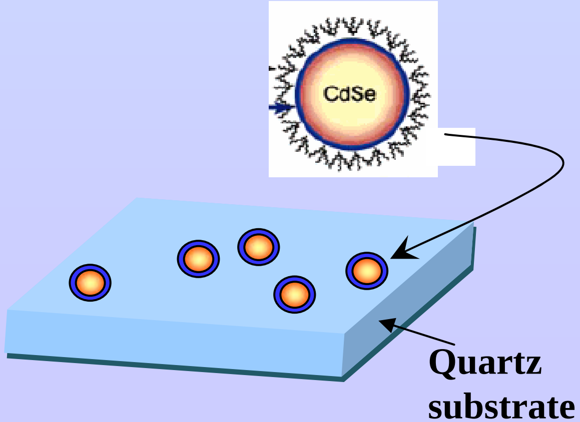
Fluorescence Imaging of individual NQDs

$$\langle N_x \rangle = \frac{\sigma_a \lambda j_p \tau_R}{hc} = 12$$

Spatial resolution <1 μm

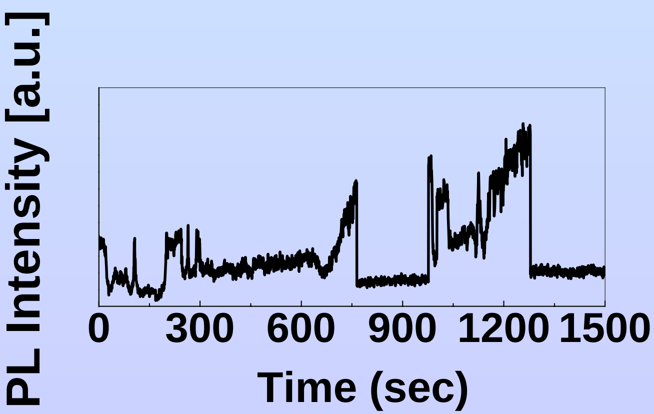




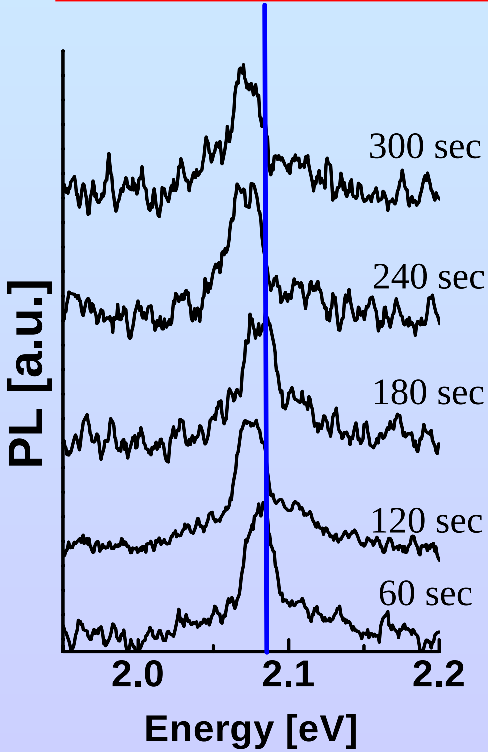


Typical phenomena in single NQDs: Spectral Diffusion (shifting) and Fluorescence Intermittency (blinking).

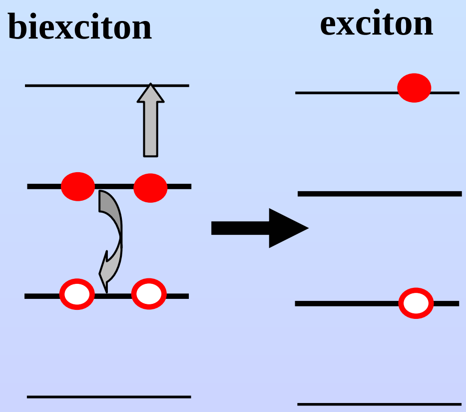
Fluorescence Intermittency



Spectral Diffusion

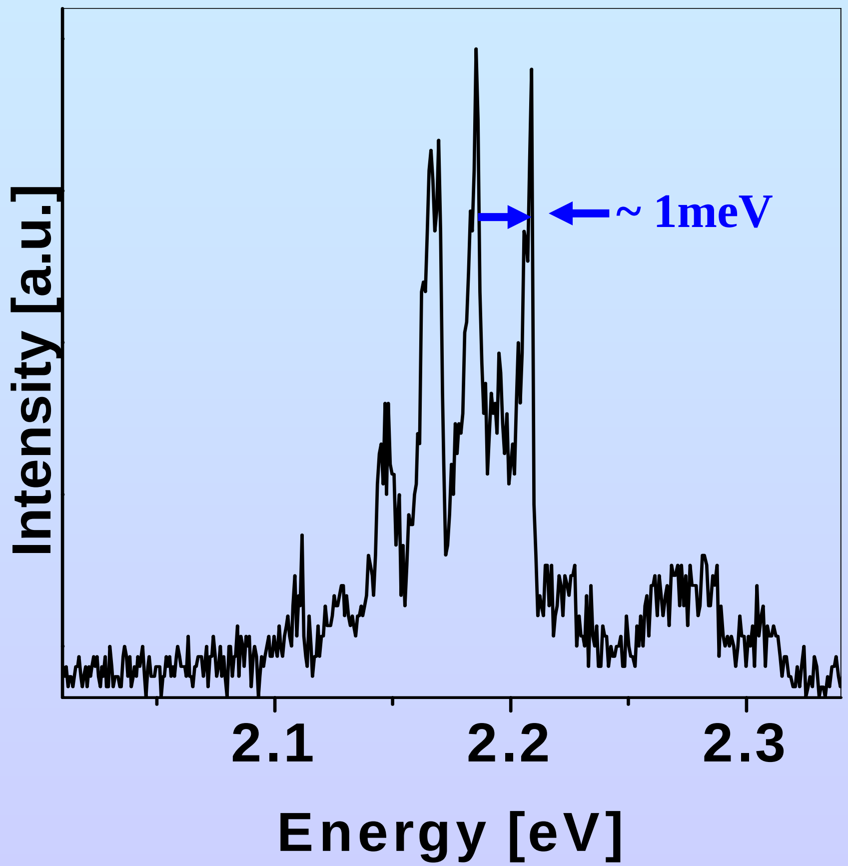


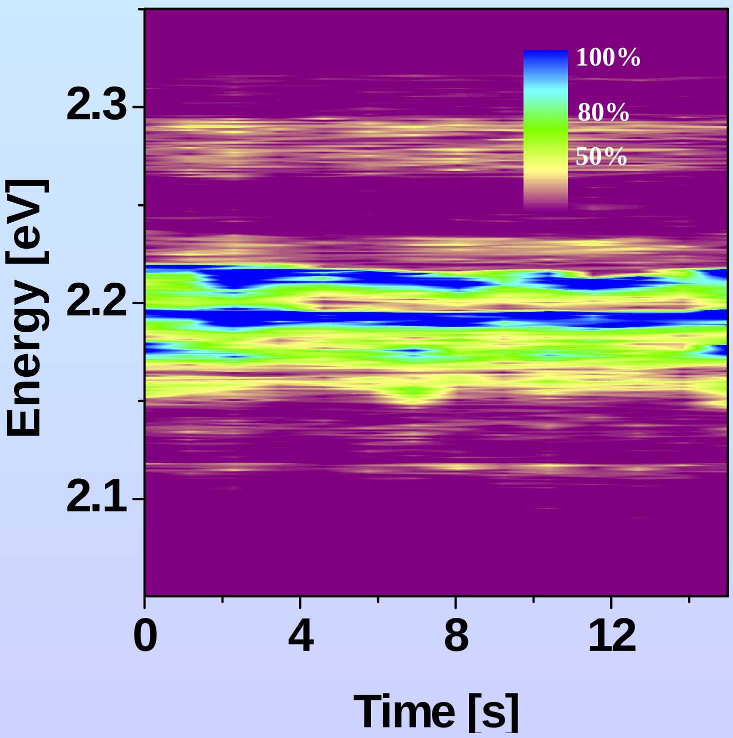
Auger Process



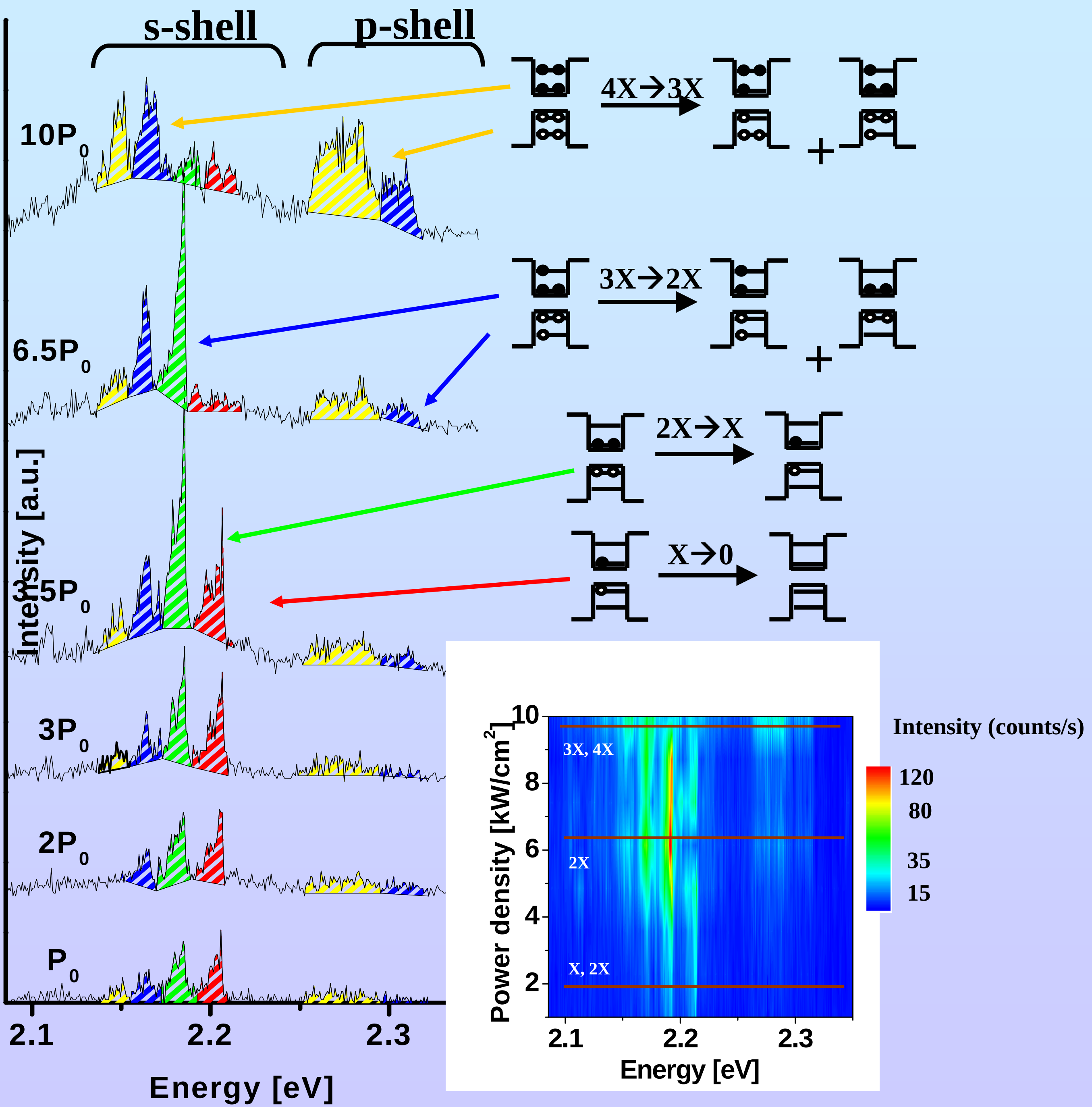
Auger recombination process is extremely efficient in NQD cores

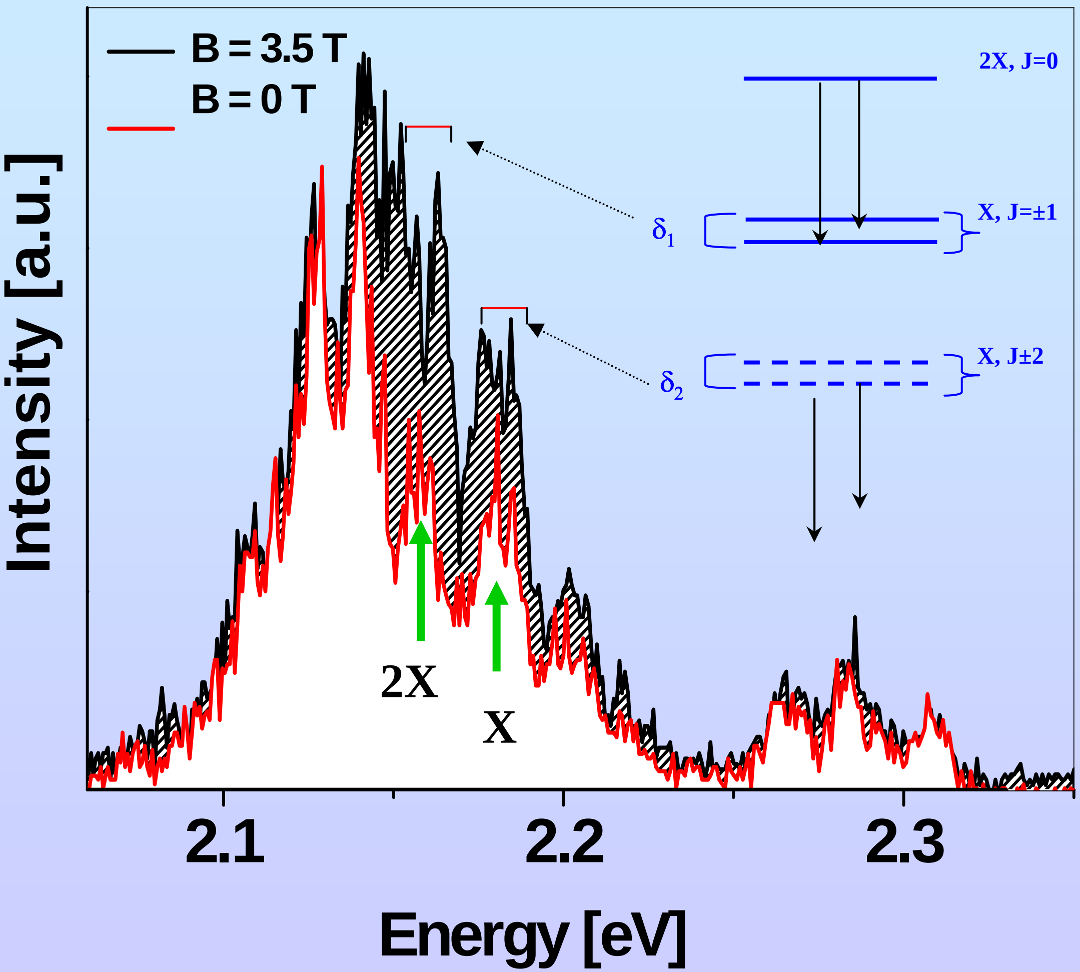
CdTe/CdSe





Blinking Free


s-shell
p-shell
10P0
6.5P0
3.5P0
3P0
2P0
P0
Intensity [a.u.]
2.1
2.2
2.3
Energy [eV]
4X→3X
+
3X→2X
+
2X→X
X→0
10
8
6
4
2
Power density [kW/cm2]
3X, 4X
2X
X, 2X
2.1
2.2
2.3
Energy [eV]
Intensity (counts/s)
120
80
35
15


B = 3.5 T
B = 0 T
2X, J=0
X, J=±1
X, J±2
δ1
δ2
2X
X
Intensity [a.u.]
2.1
2.2
2.3
Energy [eV]

Summary

Applications: Gain devices, optical switches, solar energy and medical platforms, based on single and multiexcitons in NIR active semiconductor NQDs, requiring:

- Preparation of high quality core-shell NQDs with high QE and chemical robustness,
- The ground-state exciton of core-shell structures showed a red-shift of the optical transitions, longer lifetime, narrower energy-gap at the STS spectrum, reduced surface strain [see dE_g/dT], effective increase of the NQD's volume,
- On top of all, BLINKING FREE process, enabled the detection of MULTIEXCITONS (including **s**- and **p**-shell recombination) in the μ-PL of a single core-shell NQD, generated by mild conditions (cw-laser)

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Dr. L. Fradkin
Dr. D. Cheskis
Dr. A. Saschiuk

Collaborators

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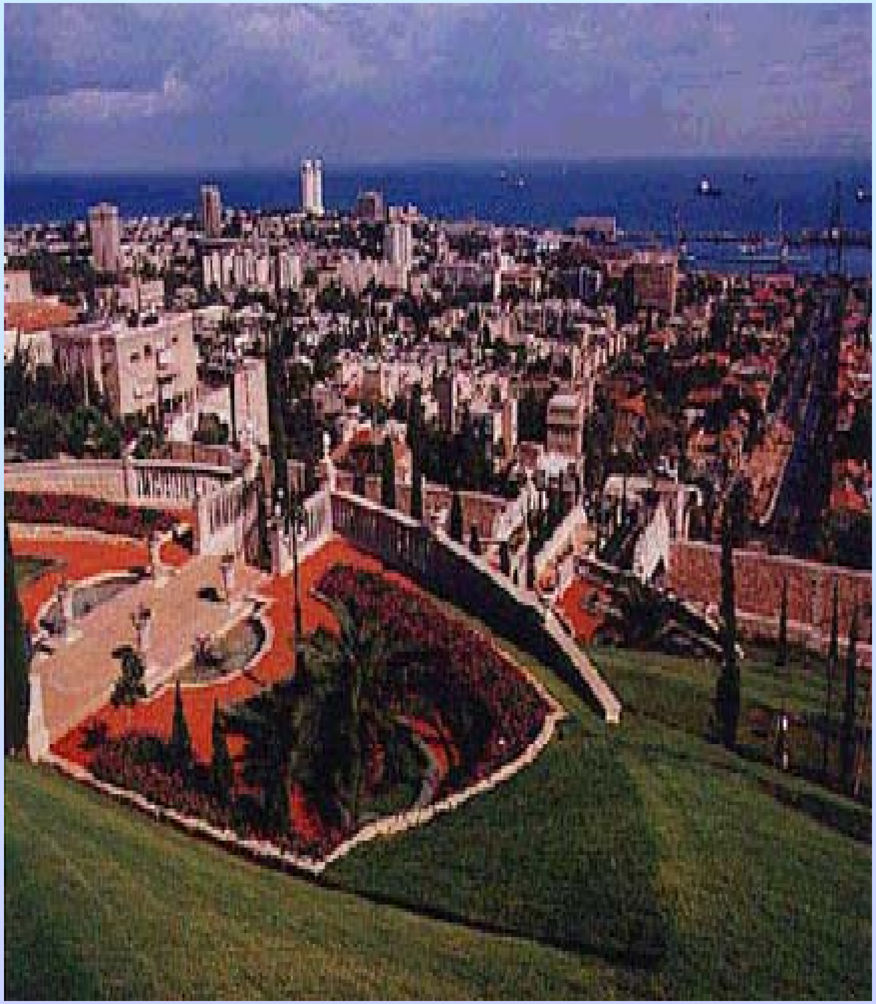
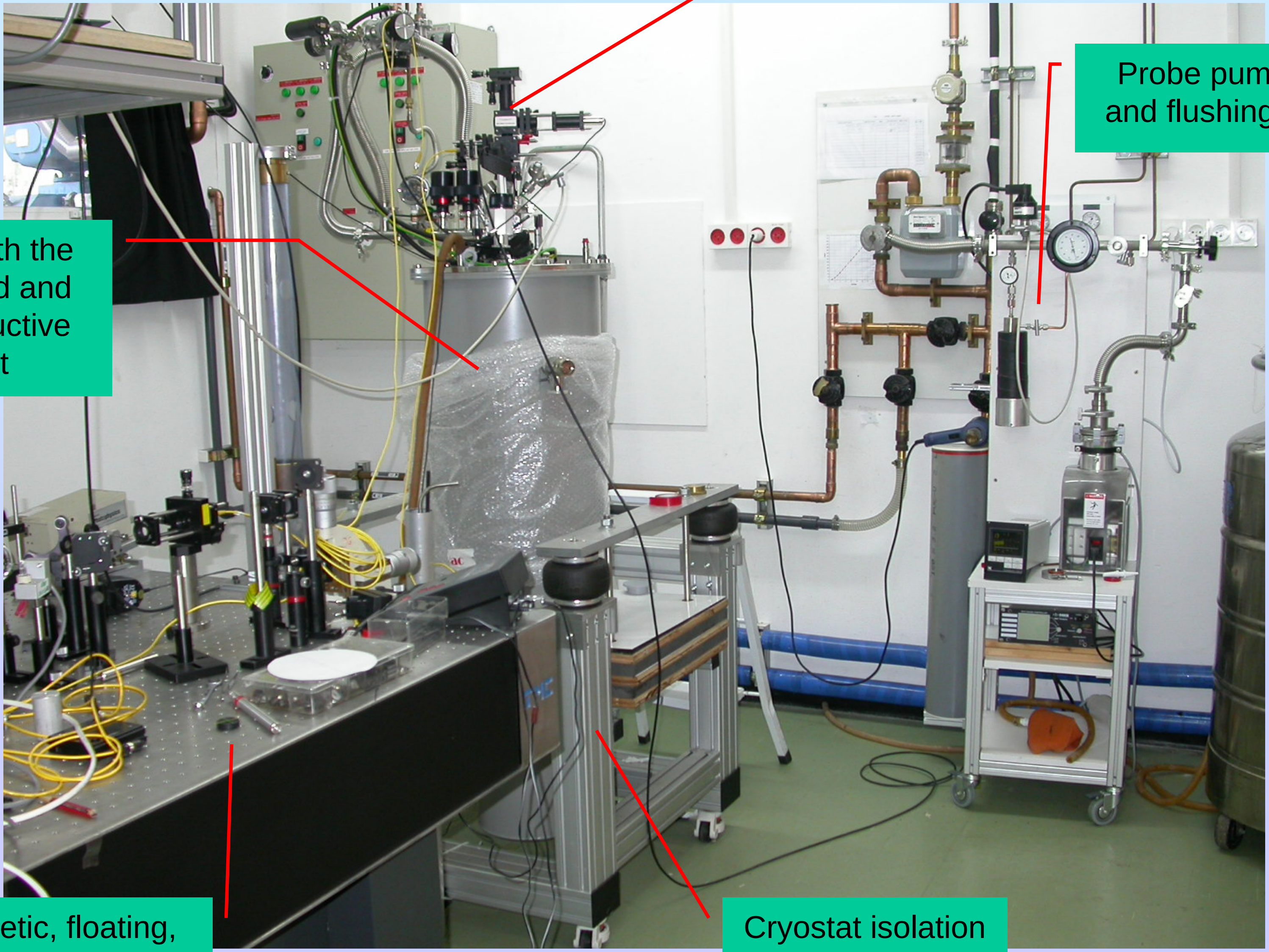
Funding of this work

BSF, ISF, Nofar, Bikura (ISF), Niedersachsen

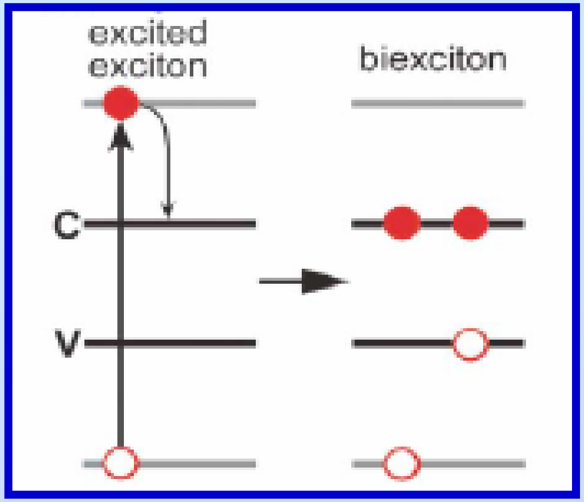


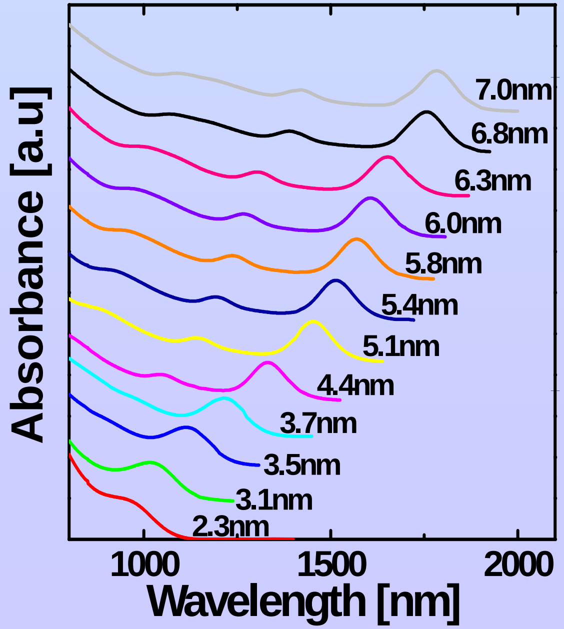
Thank you for your attention !

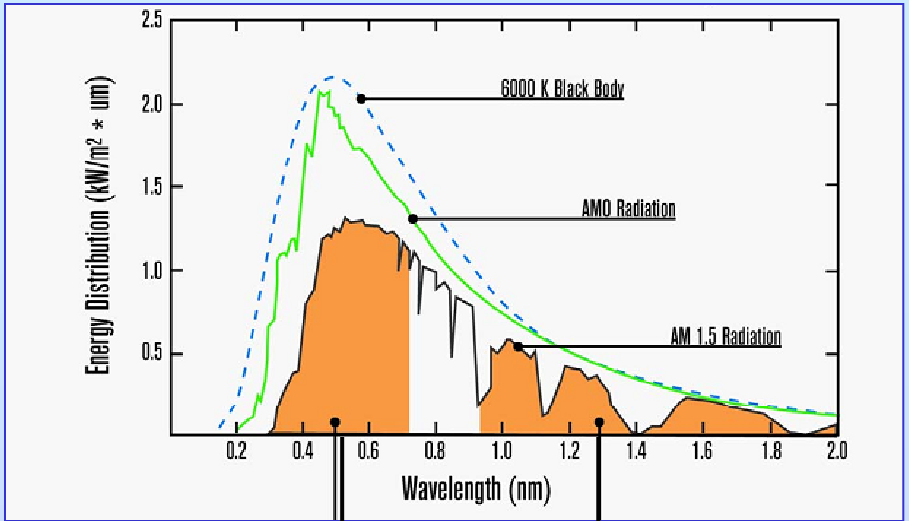

Optical head
Probe pumping and flushing spot
Cryostat with the optical head and superconductive magnet
Nonmagnetic, floating, optical table
Cryostat isolation stage

Technion - Projects

1. Semiconductor nanocrystals quantum dots (NQDs), active in the NIR

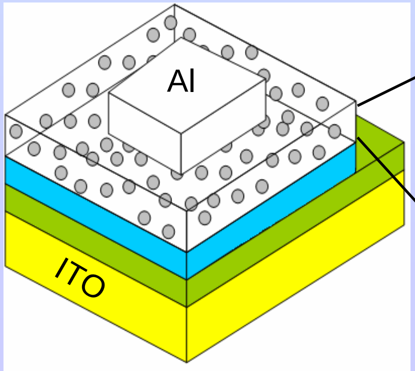


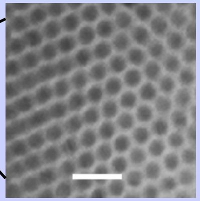




Impact ionization

Band-edge absorption

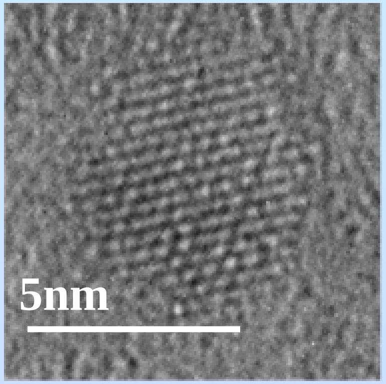


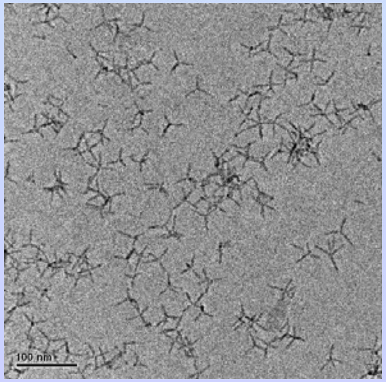


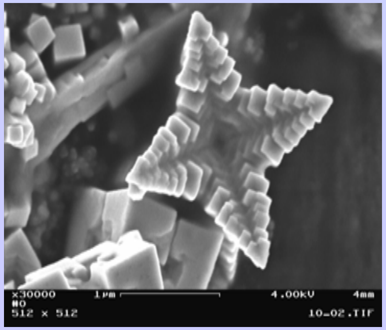
Thin film or a blend of NQDs/polymer

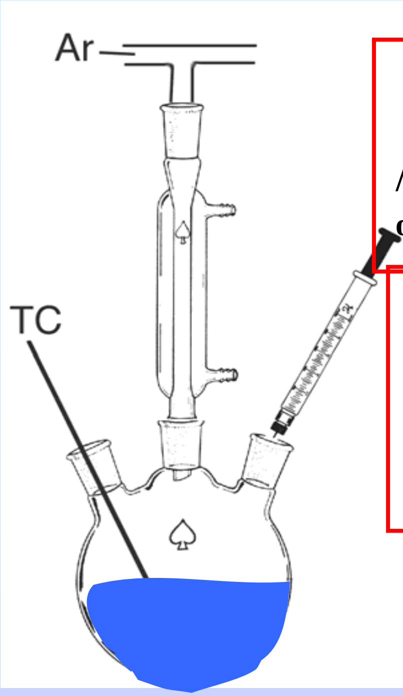
Efrat Lifshitz (Chemistry) and Nir Tessler (EE)

Synthesis of PbSe nanocrystals (NCs): Dots, Rods, Wires & Multipods









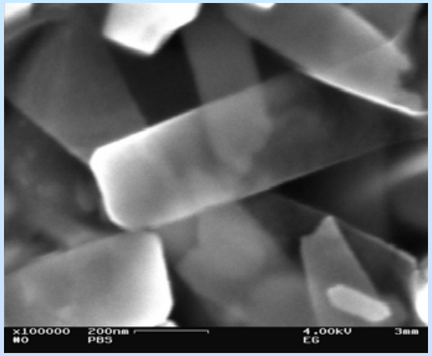
TOP:Se + Pb-Ac

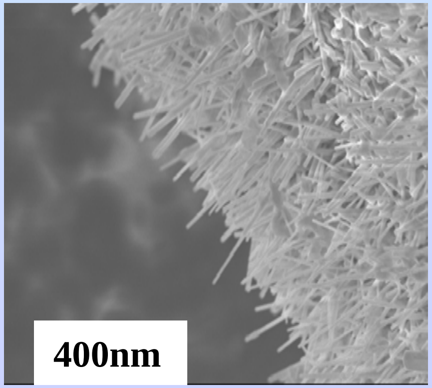
/Ph-Et/OA/TOP (**130 ºC)**

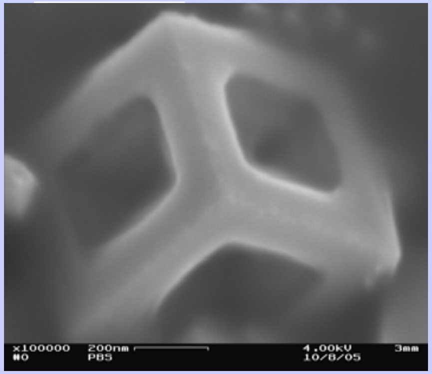
Ethylene-diamine/glycol

[templating ligands]

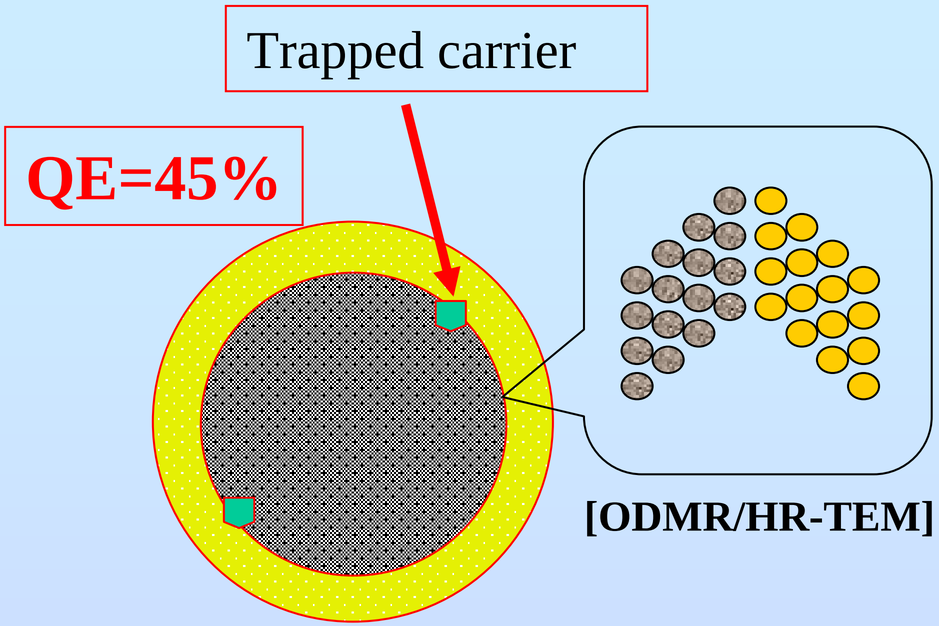
(10°-120°C);

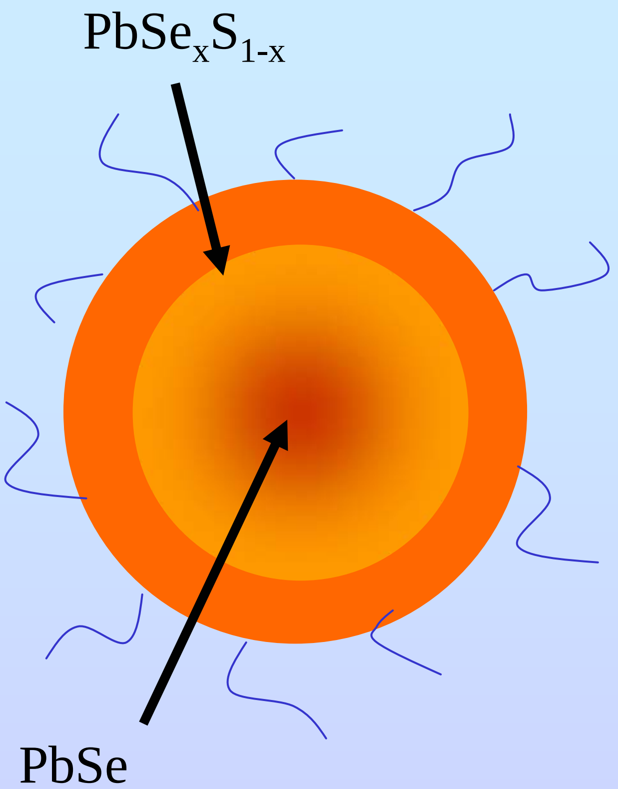




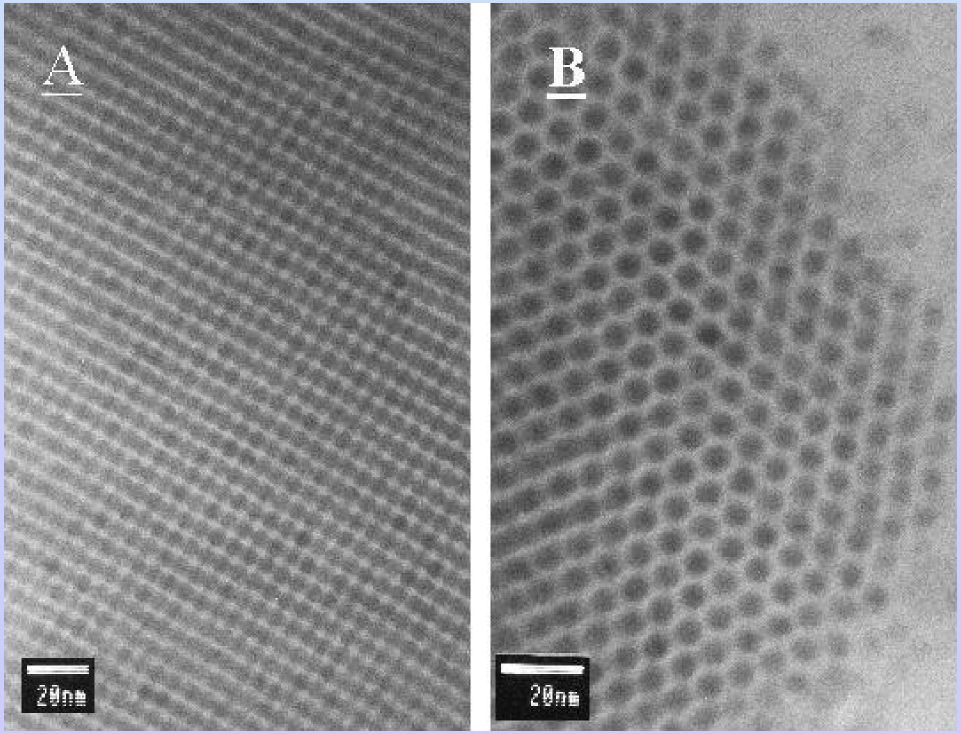


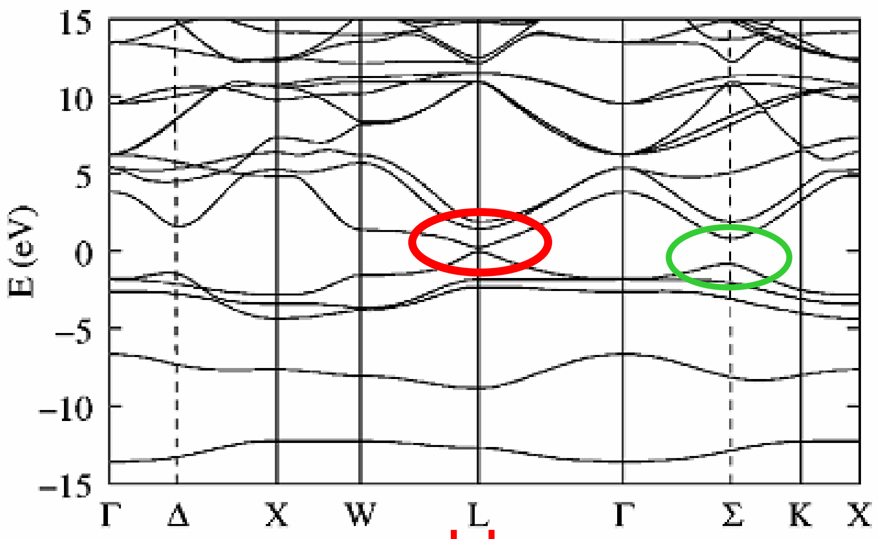
Lifshitz et al.,
Adv. Fn. Mat., 05,
J. Phys. Chem. B, 06,
Inorg. Chem., 07

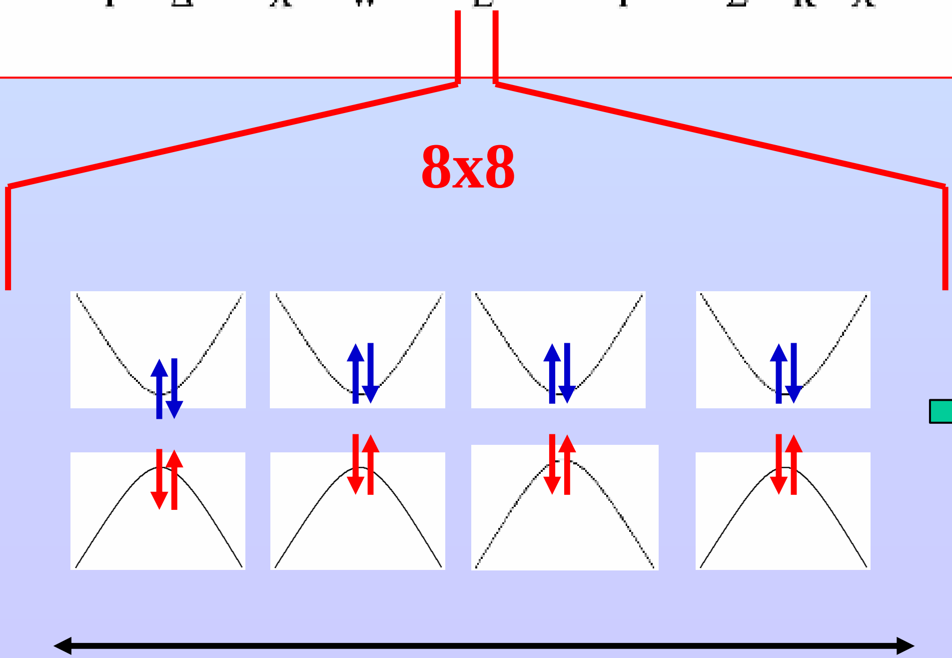




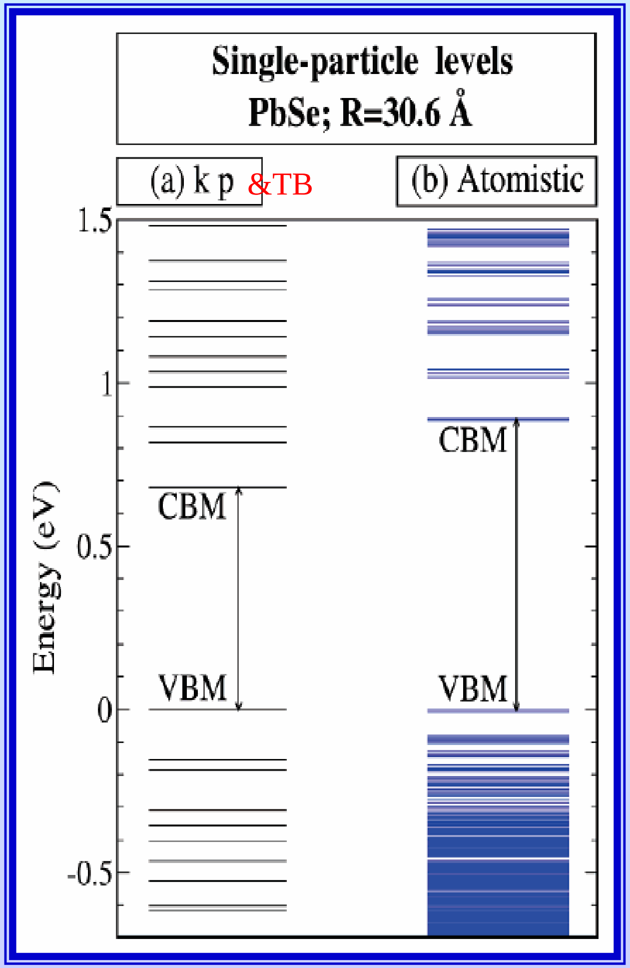
QE=80%







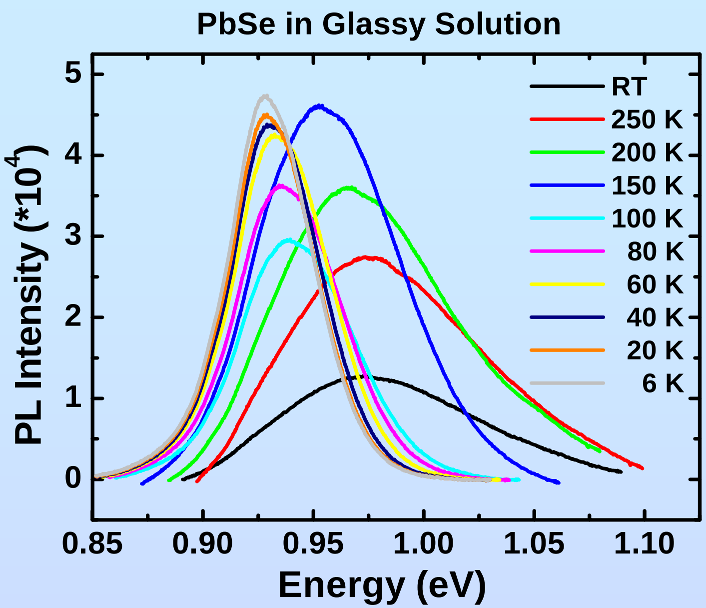
Inter-valley interaction

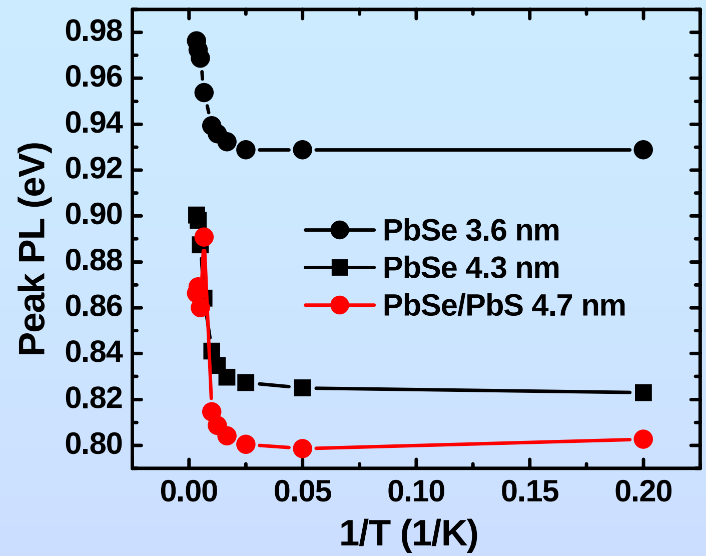


Efros Al. (2005), Wise (1997),

Allen and Deleru, (2004, 2008),

Zunger (2006)



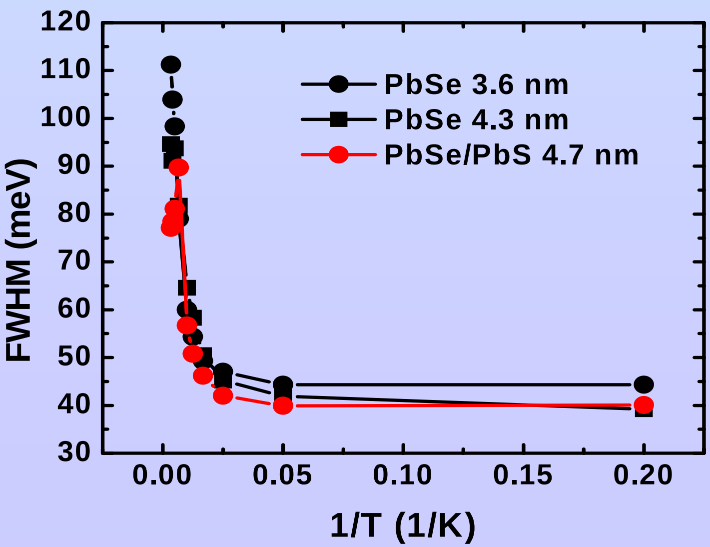


$$E_g(T)=E_g(T) - \alpha(T^2/(T+\beta))$$

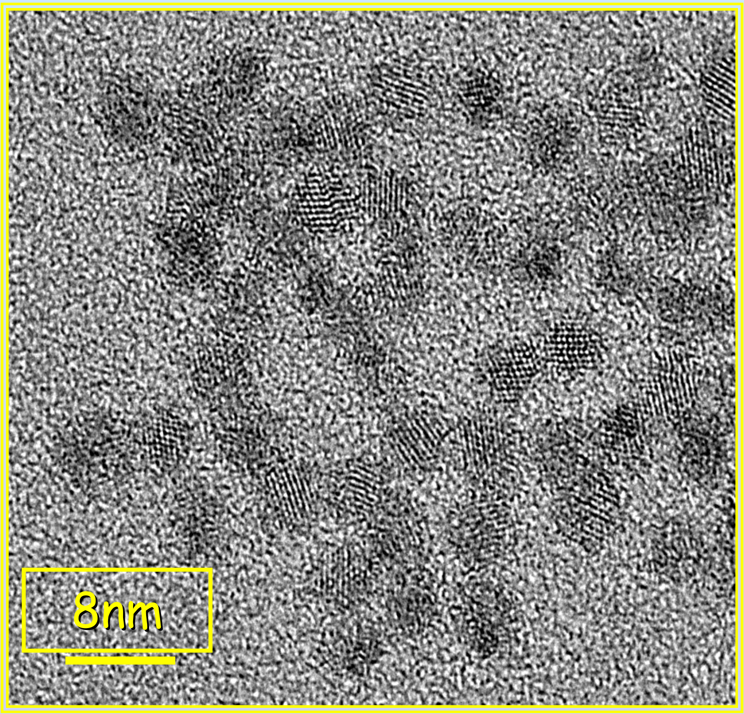
$\alpha = dE_{g/}dT = 0.15\text{-}0.20$ meV/K

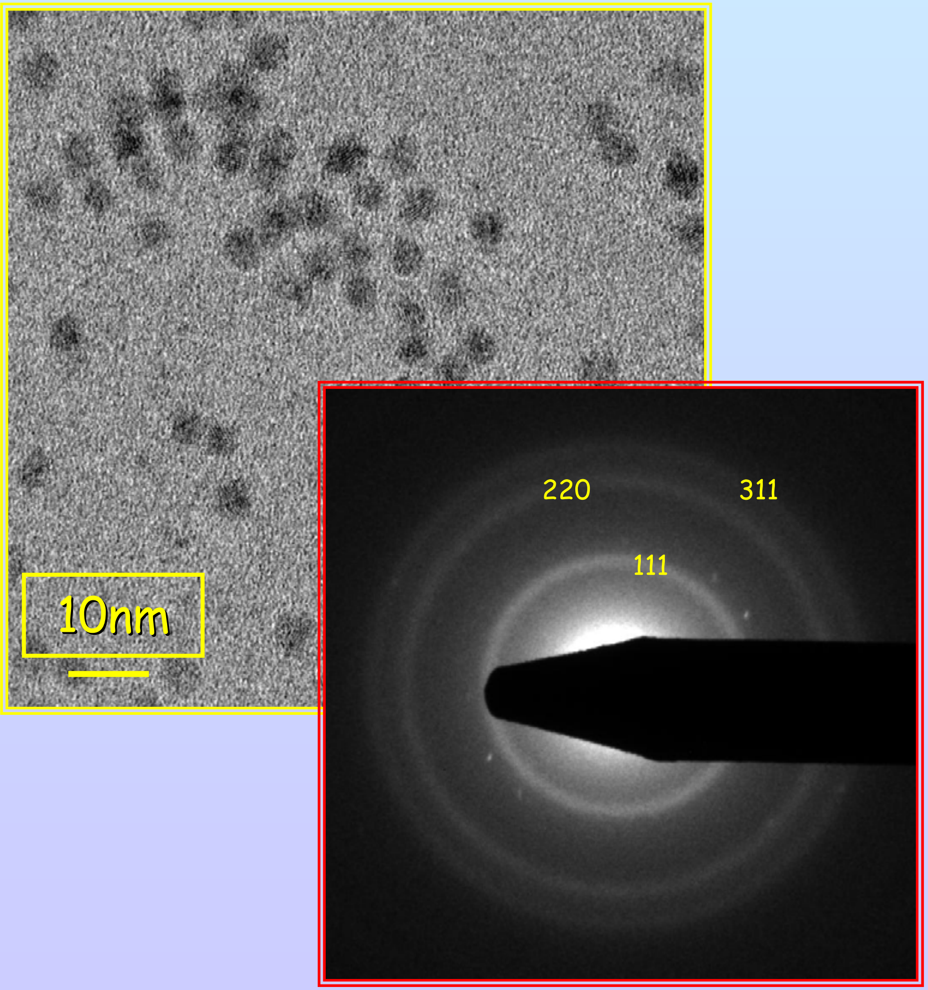
(0.28 meV/K-bulk)

[lattice, strain, el-ph]



$$\Gamma(T) = \Gamma_{inh} + \sigma T + \Gamma_{LO}(e^{E_{LO}/k_B T} - 1)^{-1}$$


8nm


10nm
220
311
111

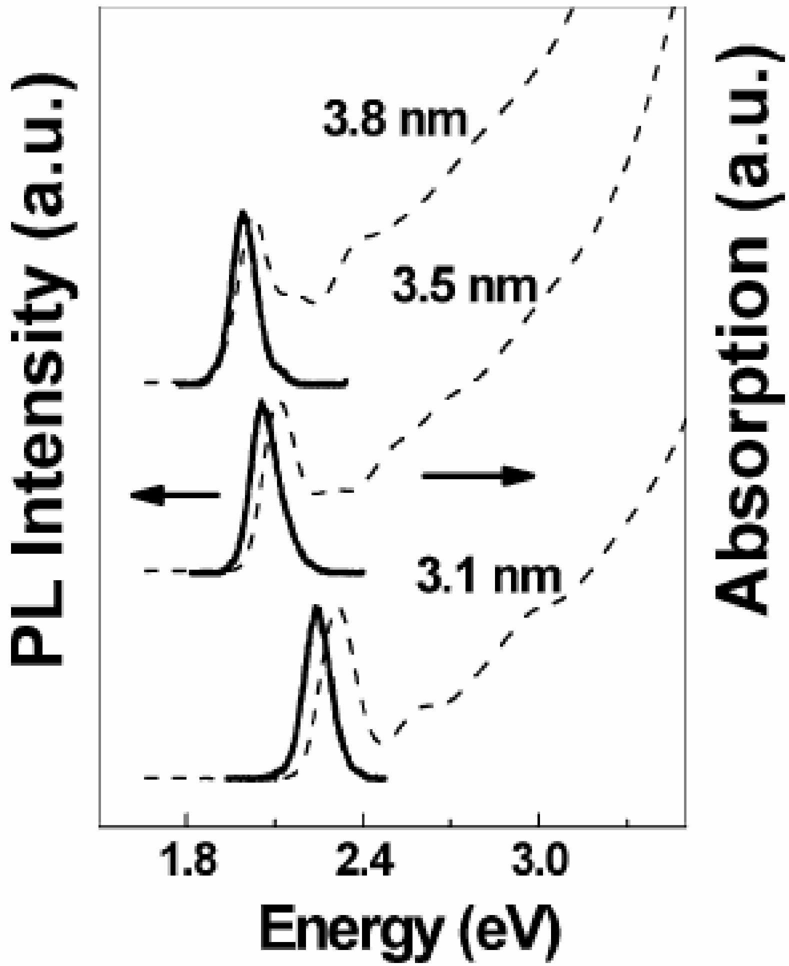
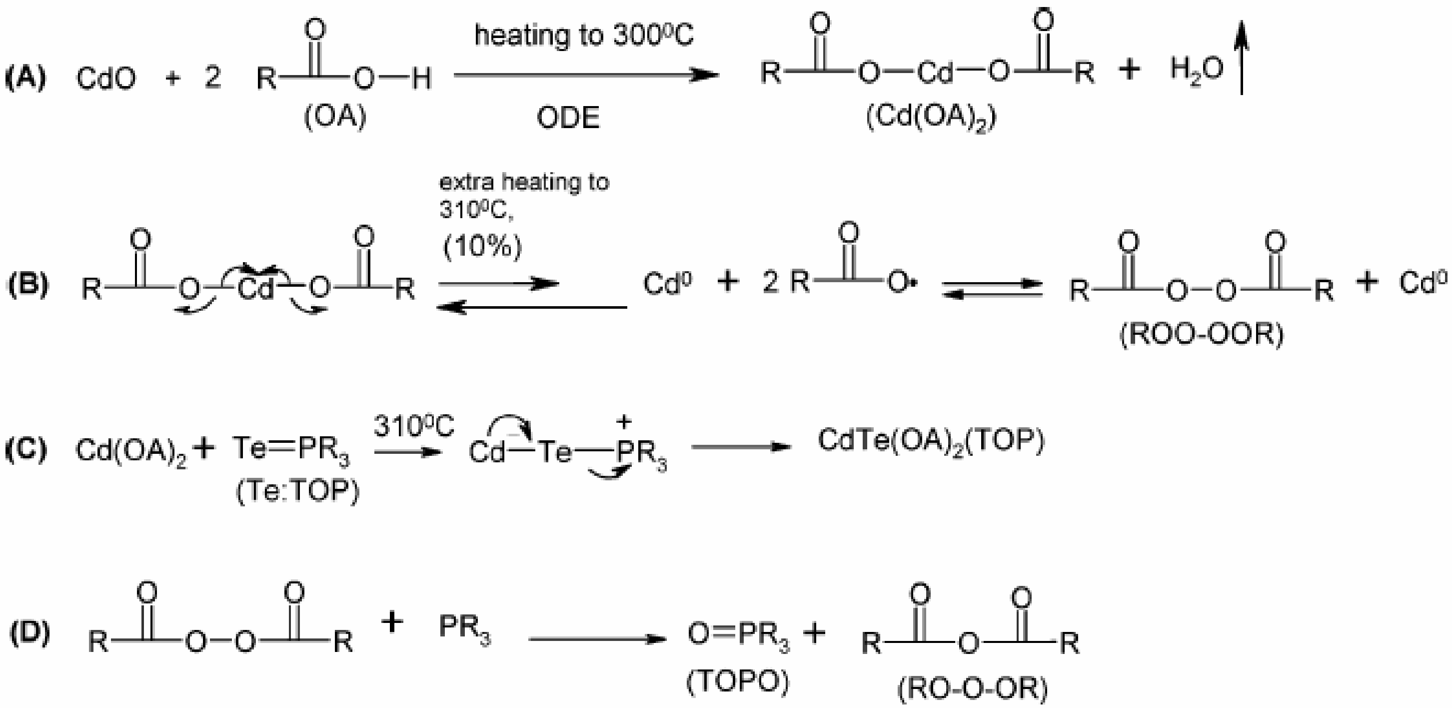
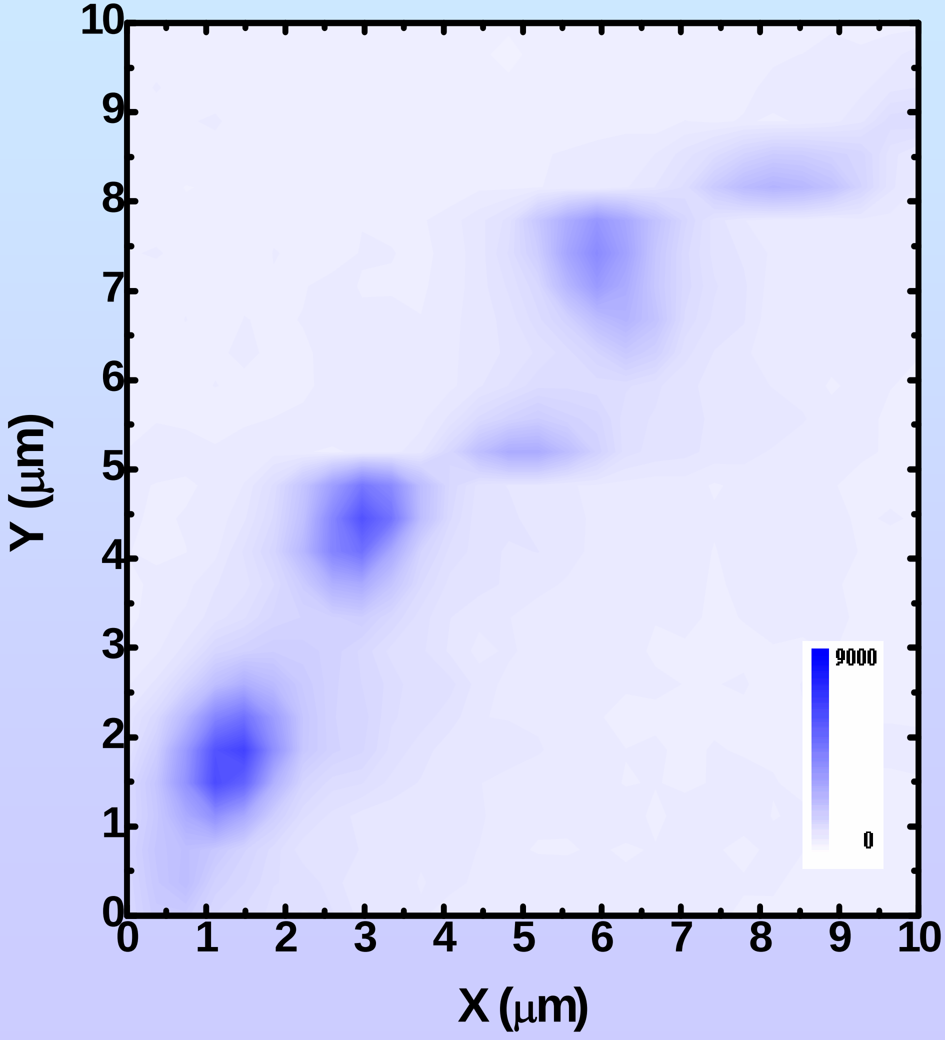


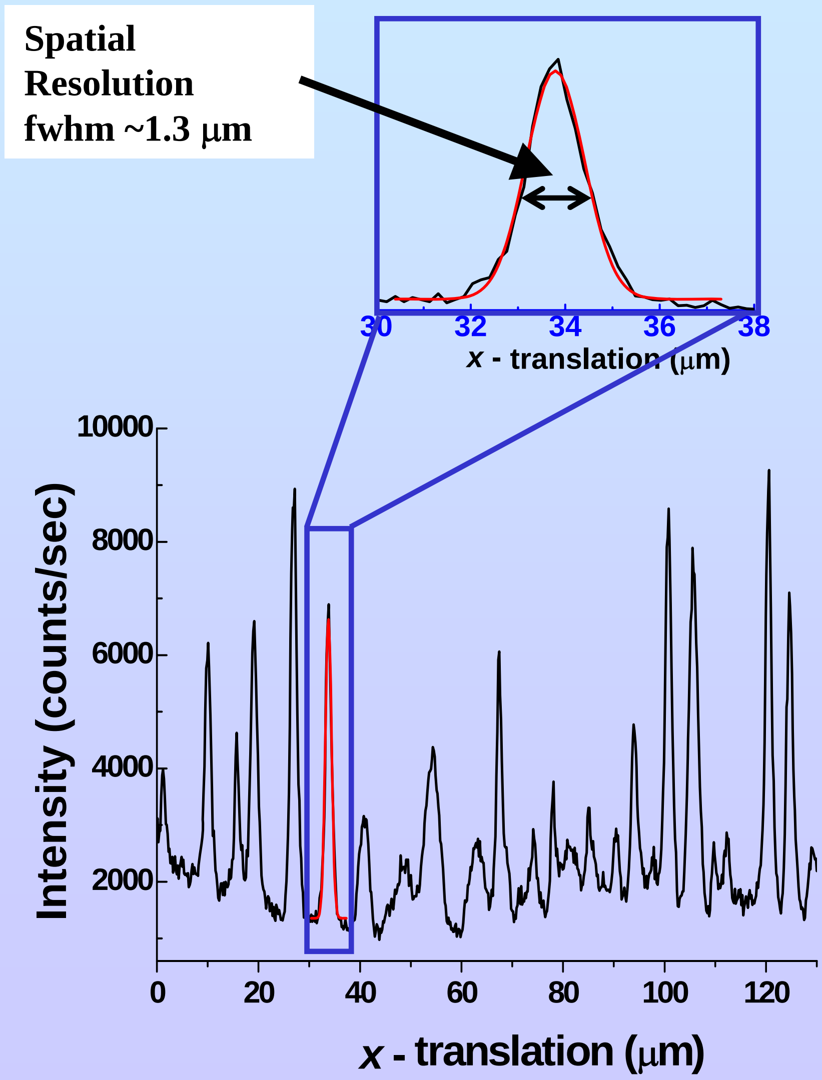
Figure 7. Absorbance spectra (dashed line) and PL spectra (solid line) of CdTe NQDs with diameters between 3.1 and 3.8 nm.

SCHEME 1: Proposed Synthesis Mechanism



Fluorescence imaging of individual fluorescing NQDs



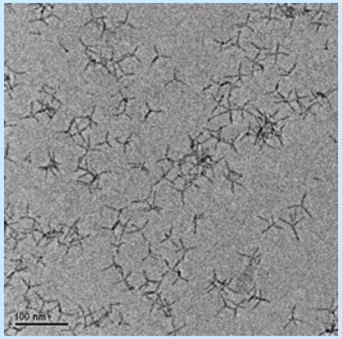


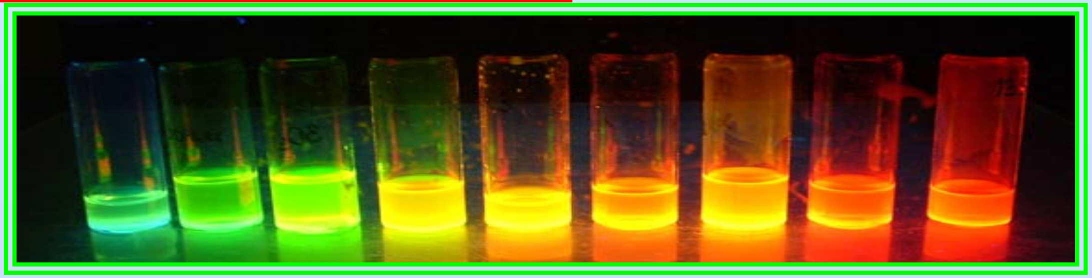
Multiexciton: Historical Background

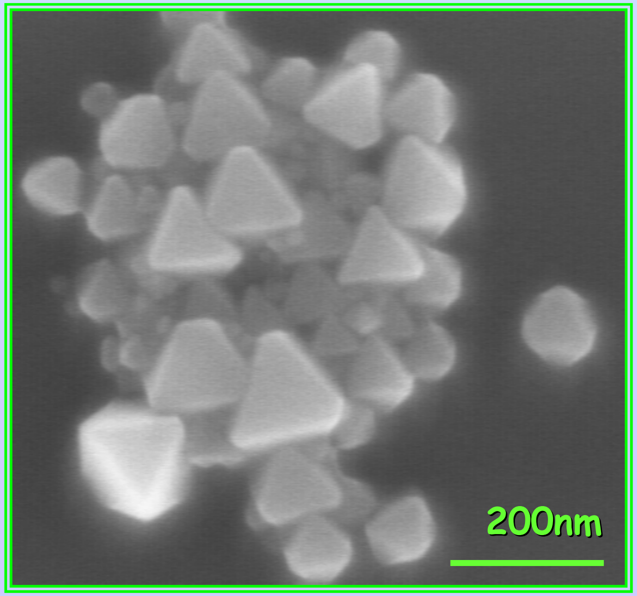
	Self assembled QDs	Colloidal NQDs
Shape/ Typical size	Pyramid/drop 20 nm*5 nm	Spherical/rods 3-4 nm
Surrounding	Wetting & cladding layers (ε_∞= 8-16)	Organic surfactants ($\varepsilon_\infty \cong 2$)
Generation	cw- or pulse- laser (E_{exc}<$2E_g$)	Pulse- or q-cw laser (E_{exc}>$2E_g$)
Lifetime	0.5-1 nsec	1-100 psec

CdTe/CdSe

Time

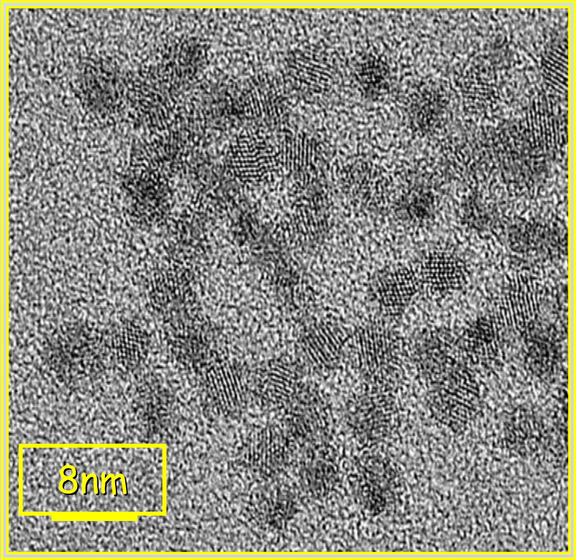






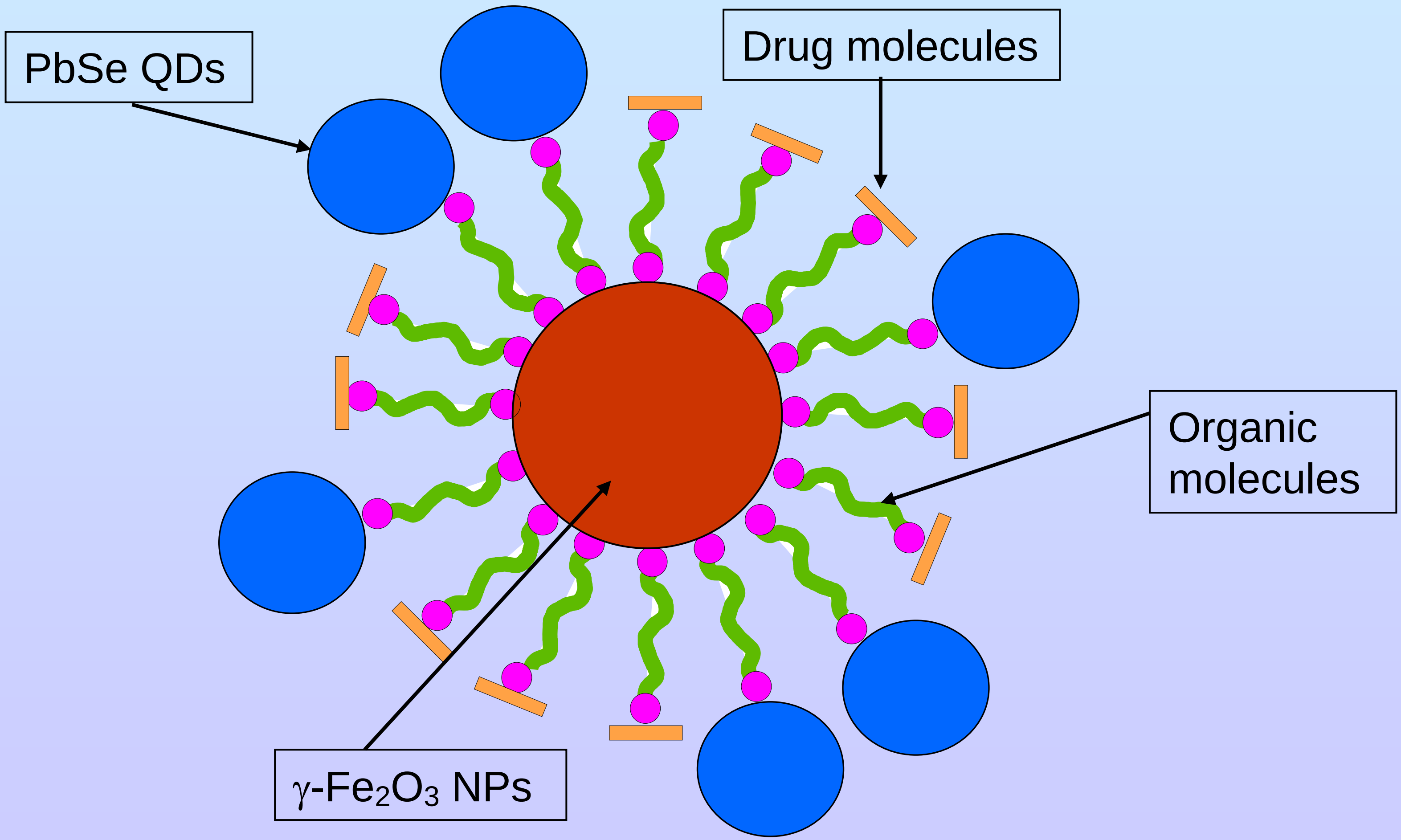
Cd^0 ← → Cd^{+2}

(NPs ← → monomers)

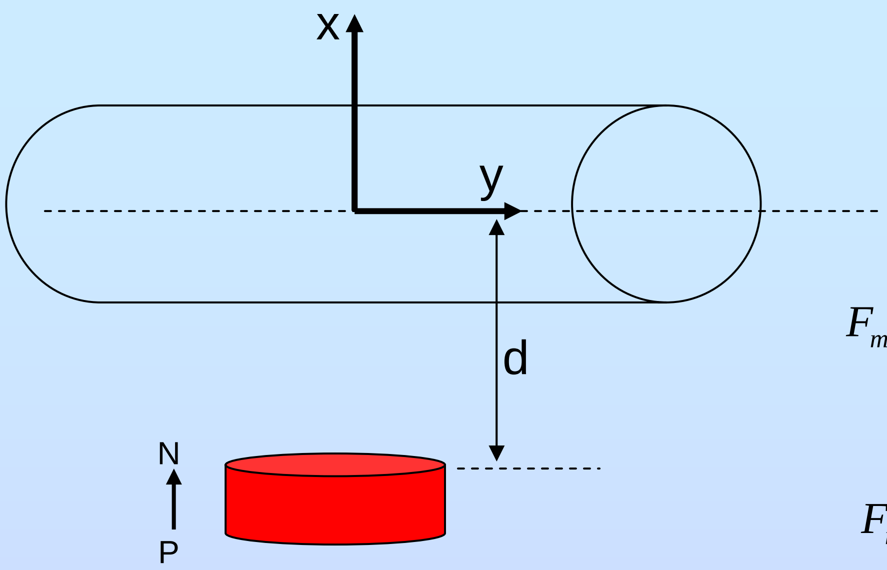


J. Konly-Olesiak *et al*. Surface Science (07), Lifshitz *et al*., J.Phys. Chem C, (07), and J.Phys. Chem. C. (08)

How do we create functionalized conjugate structures?



Etgar L.; Lifshitz E.; Tannenbaum R. J. Phys. Chem C, (07)

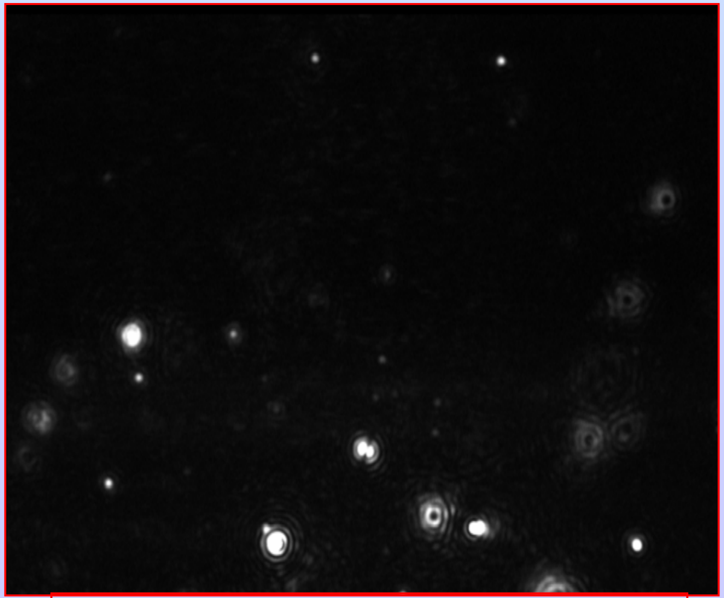


$$F_{fy} = -6\pi\eta R_p (v_{py} - v_{fy})$$

$$F_{fx} = -6\pi\eta R_p v_{px} \qquad (v_{fx} = 0)$$

$$F_{mx} = -\frac{3\mu_0 N_{mp} V_{mp} \chi_{mp} M_s^2 R_{mag}^4}{\chi_{mp} + 3} \frac{(x+d)}{2((x+d)^2 + y^2)^3}$$

$$F_{my} = -\frac{3\mu_0 N_{mp} V_{mp} \chi_{mp} M_s^2 R_{mag}^4}{\chi_{mp} + 3} \frac{y}{2((x+d)^2 + y^2)^3}$$



Conjugate structure flow at 0.05ml/hr in 3.71cP fluid viscosity