Università degli Studi di Trieste
Dipartimento di Ingegneria e Architettura
A.A. 2021-2022

Scienza e Tecnologia dei Materiali Ceramici

Modulo 2: Materiali Nanostrutturati

- Lezione 5 -

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Università degli Studi di Trieste

Previous lecture: Review

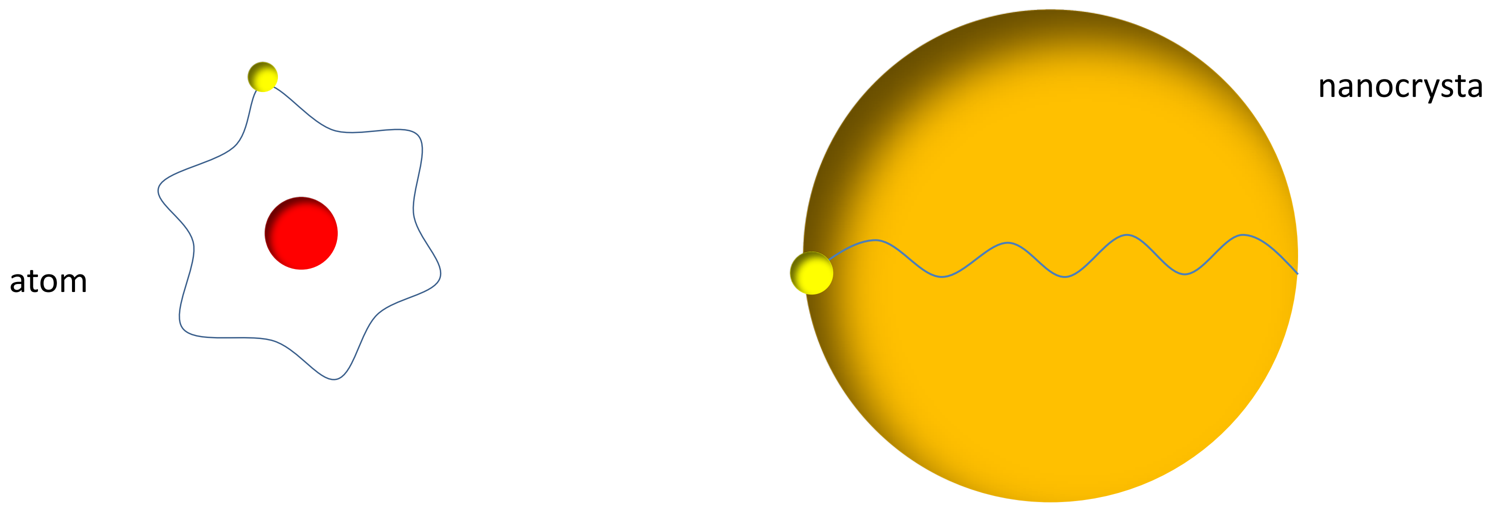
- Basic nanostructures: overview
- Nanoparticles
  - Growth kinetics

This lecture: Content

- Basic nanostructures: overview
- Nanoparticles
  - Steric stabilization approaches
  - Colloidal synthesis of nanocrystals of binary compounds
  - Colloidal synthesis of metal nanoparticles
  - Kinetics of nucleation and growth in colloidal suspensions
  - Optoelectronic properties
  - Applications

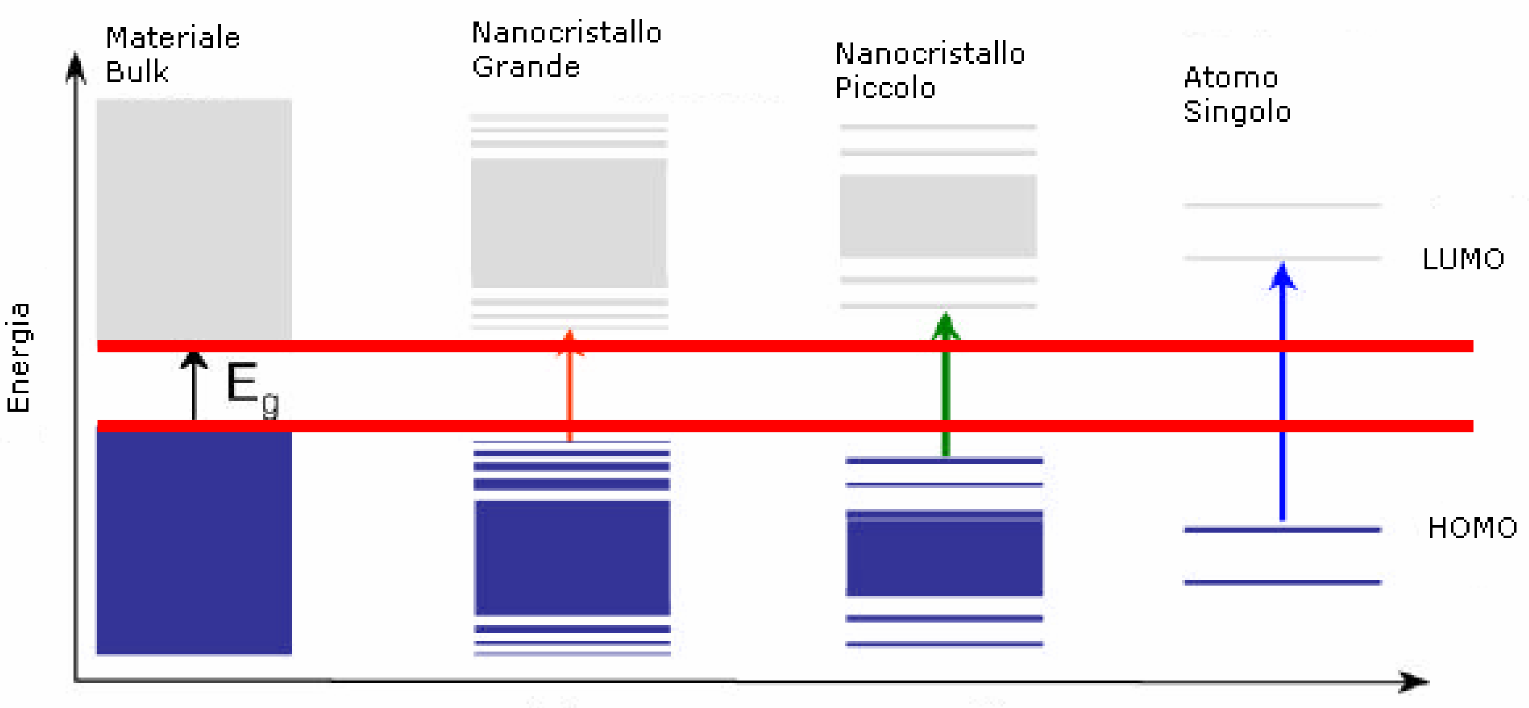
Optoelectronic properties of semiconductor nanocrystals

Artificial atoms

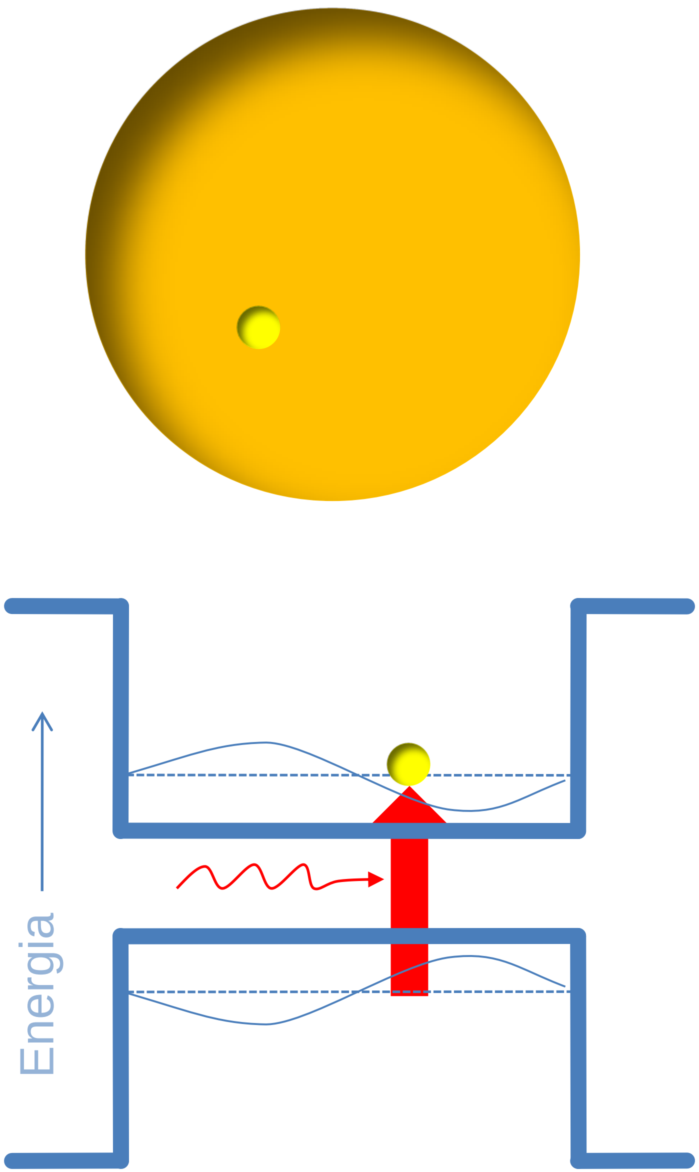


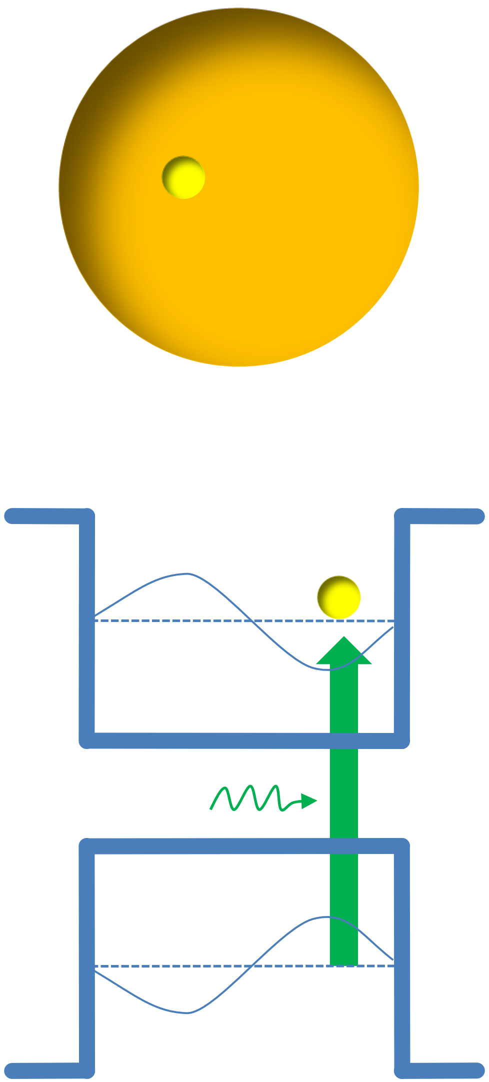
Quantum dots, just like atoms, have discrete energy levels

Artificial atoms

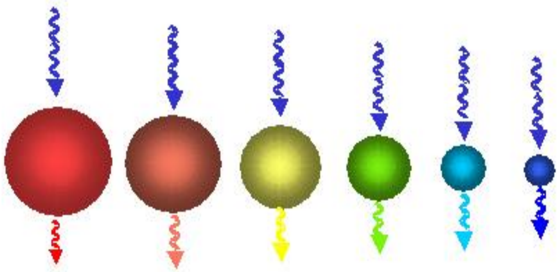


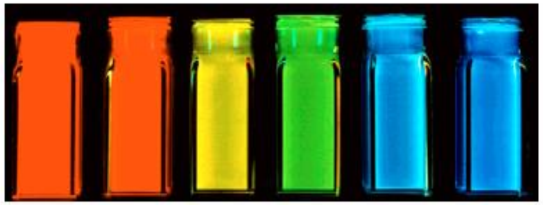
Absorption and emission in quantum dots



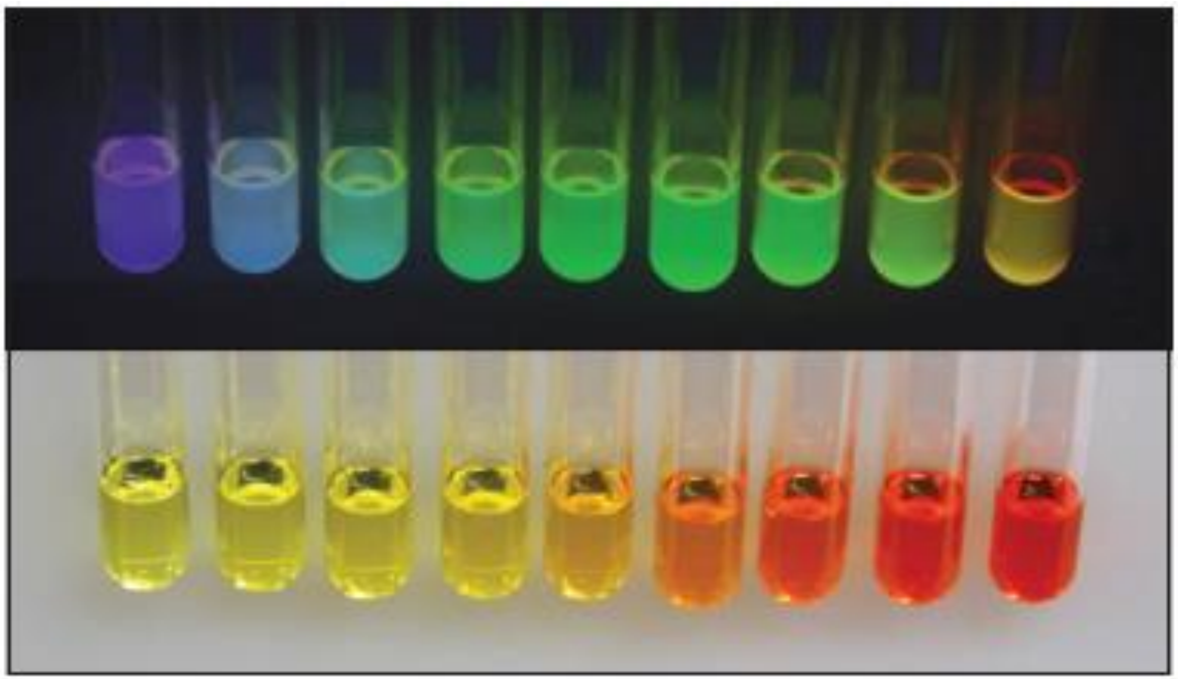


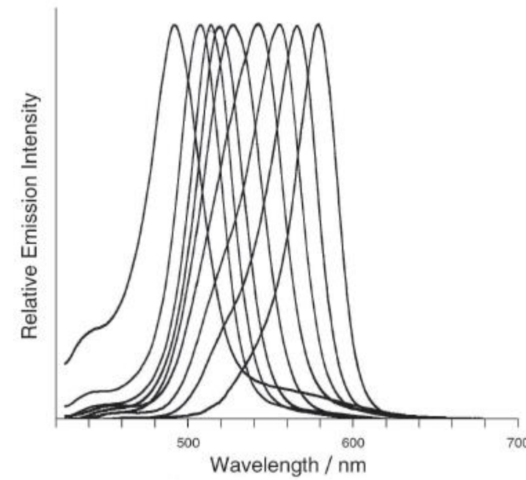
$$\hbar\omega = E_g + \frac{\hbar^2}{2m_e^* r^2}\pi^2$$

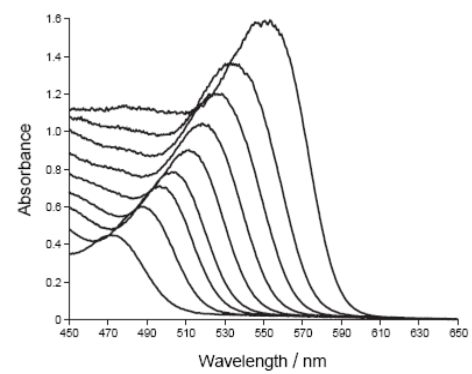




Absorption and emission in quantum dots







Absorption and emission in quantum dots

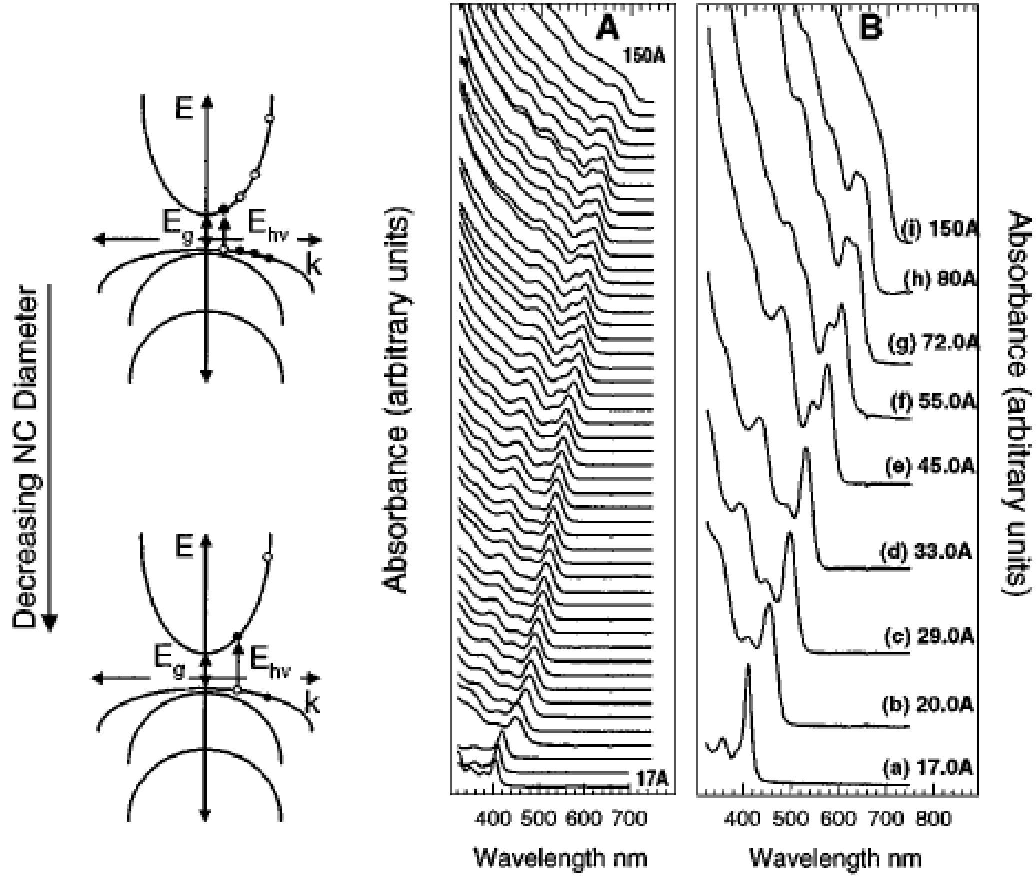
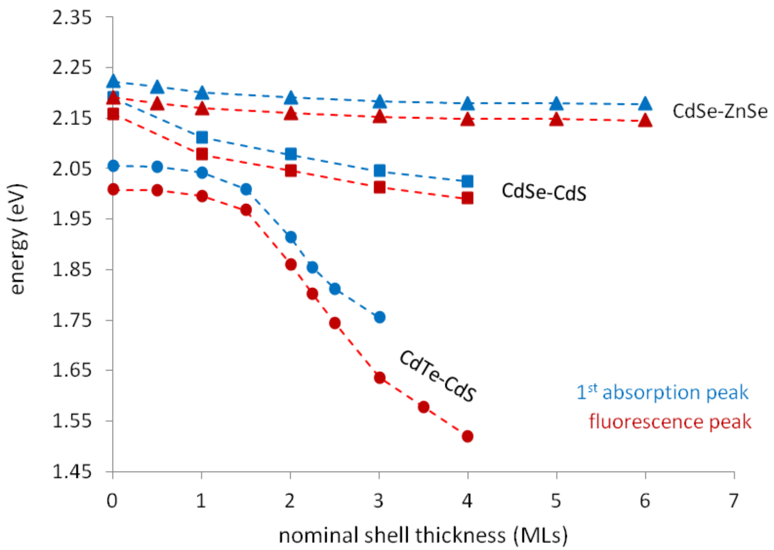
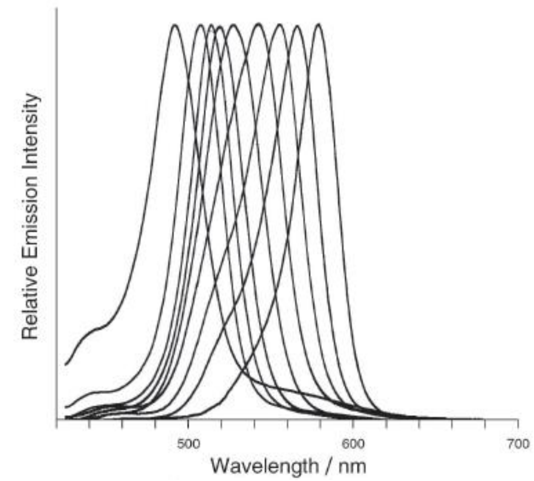
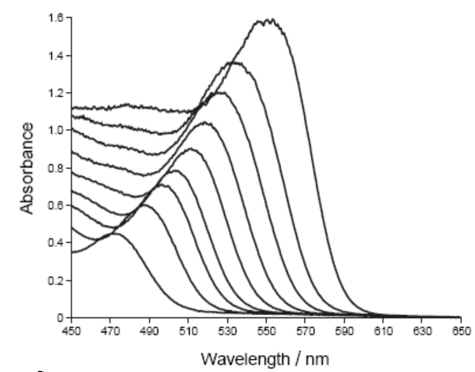


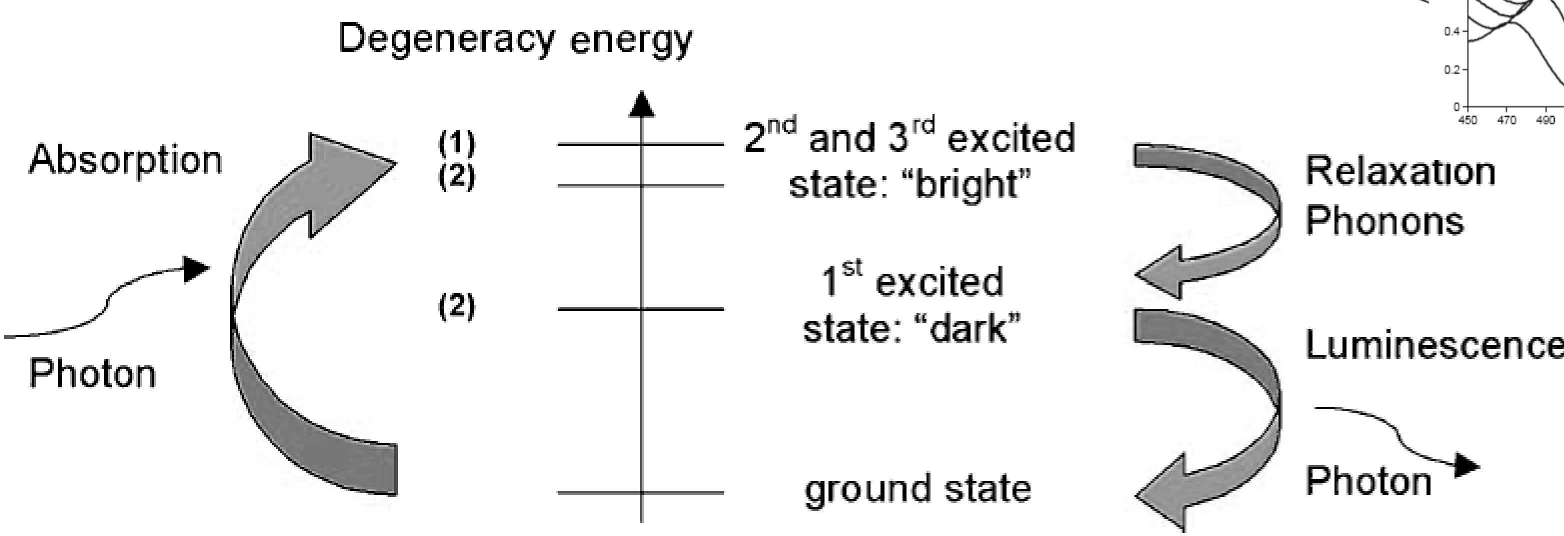
Figure 6 The bulk conduction and valence bands for semiconductors are assumed to be parabolic in the simple effective mass approximation. Energy diagrams (E versus k) show the complexity of the valence band for the example of CdSe, important in assigning NC electronic states. The finite size of the NC quantizes the allowed k values. Decreasing the NC diameter shifts the first state to larger values of k and increases the separation between states. (*a*) This is seen spectroscopically as a blue shift in the absorption edge and a larger separation between electronic transitions for a homologous size series of CdSe NC dispersions, collected at RT. (*b*) Observation of discrete electronic transitions in optical absorption is a measure of the wealth of spectroscopic information that can be uncovered in monodisperse NC samples ($\sigma \leq 5\%$).

Absorption and emission in quantum dots - Stokes shift

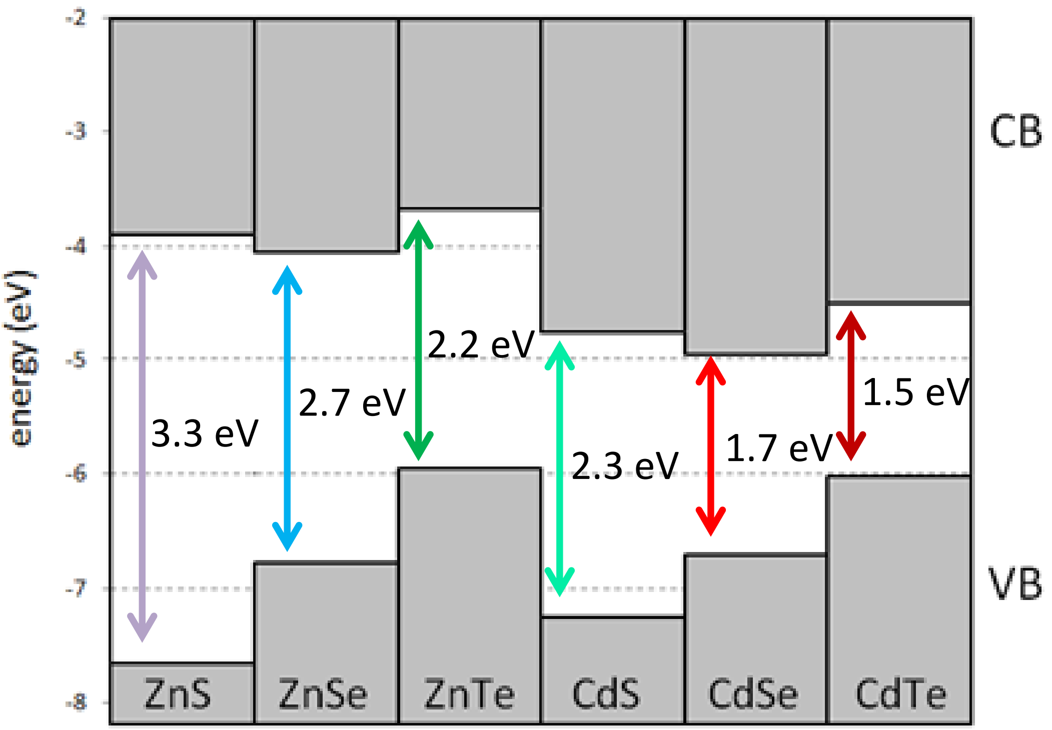


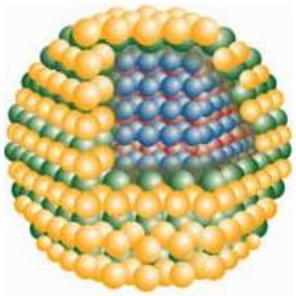




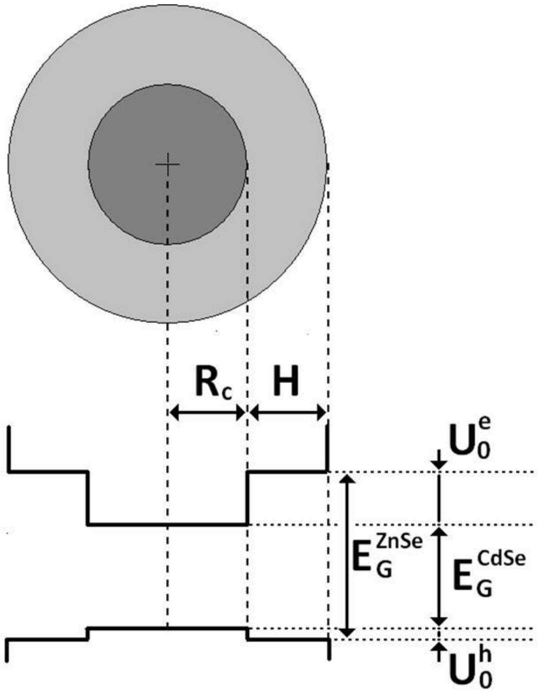


Core-shell nanocrystals



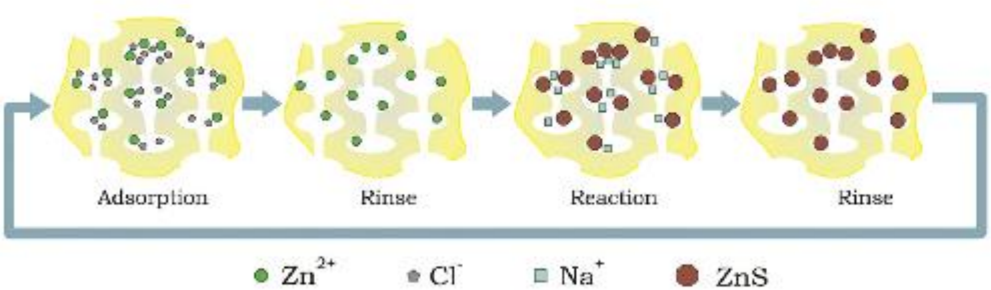


Core/shell Model

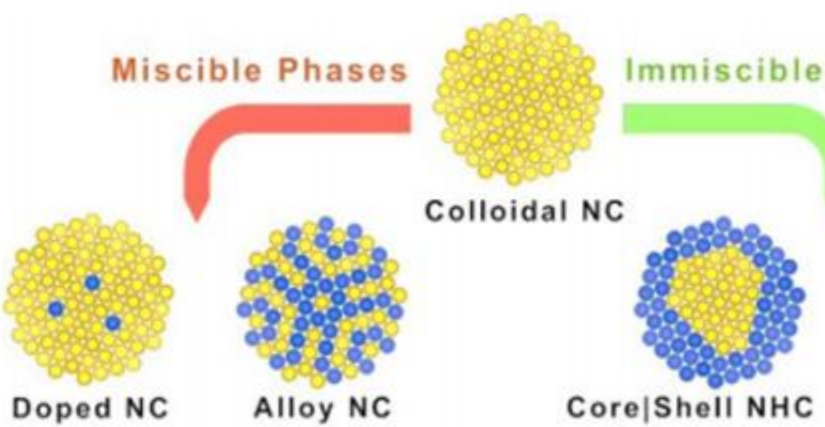


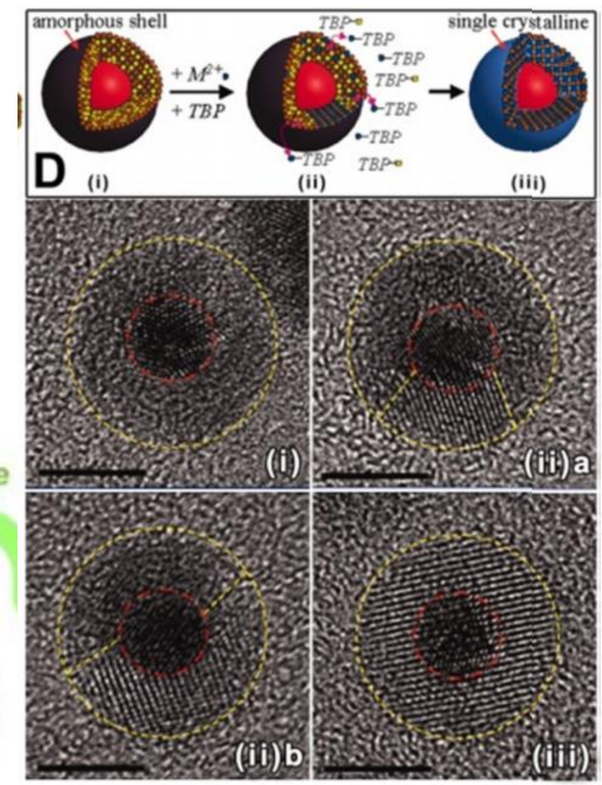
Core-shell nanocrystals
- Fabrication Methods -

SILAR
Successive Ion Layer Adsorption and Reaction



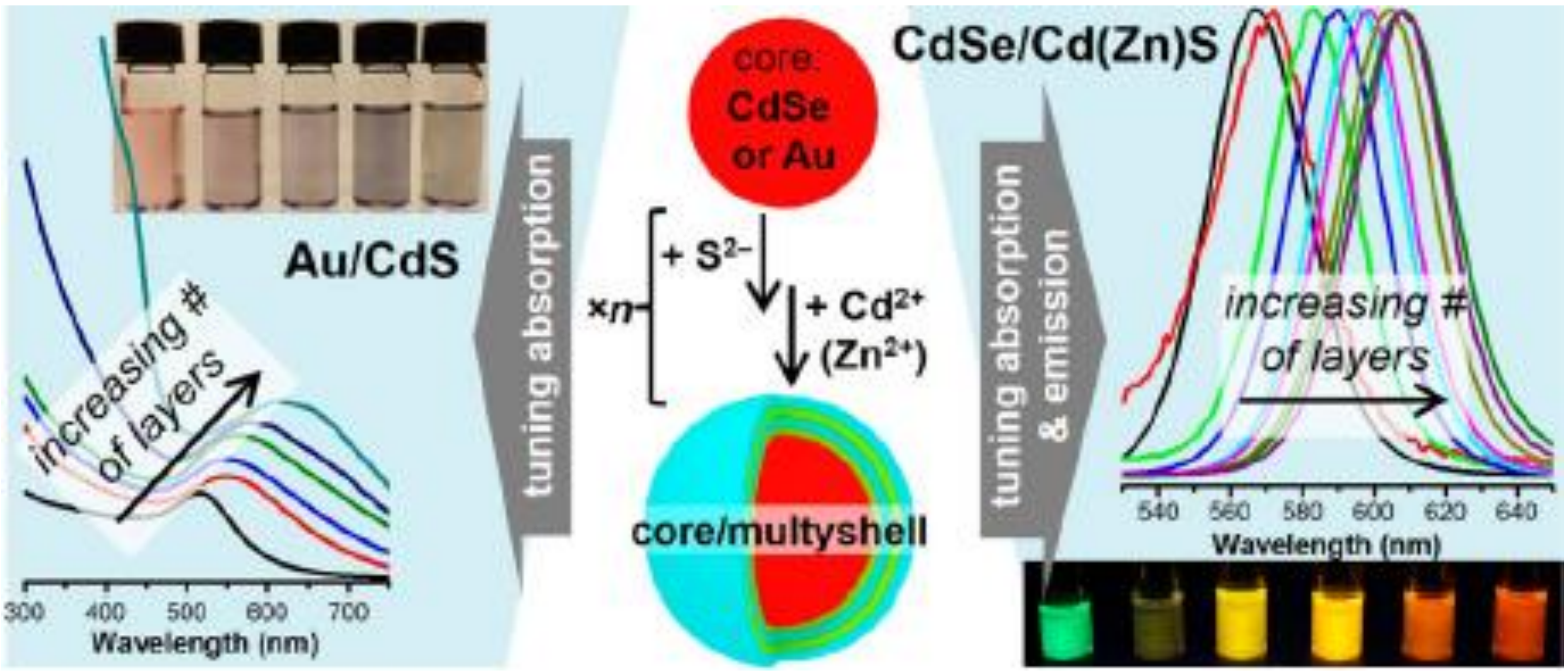
Cation Exchange





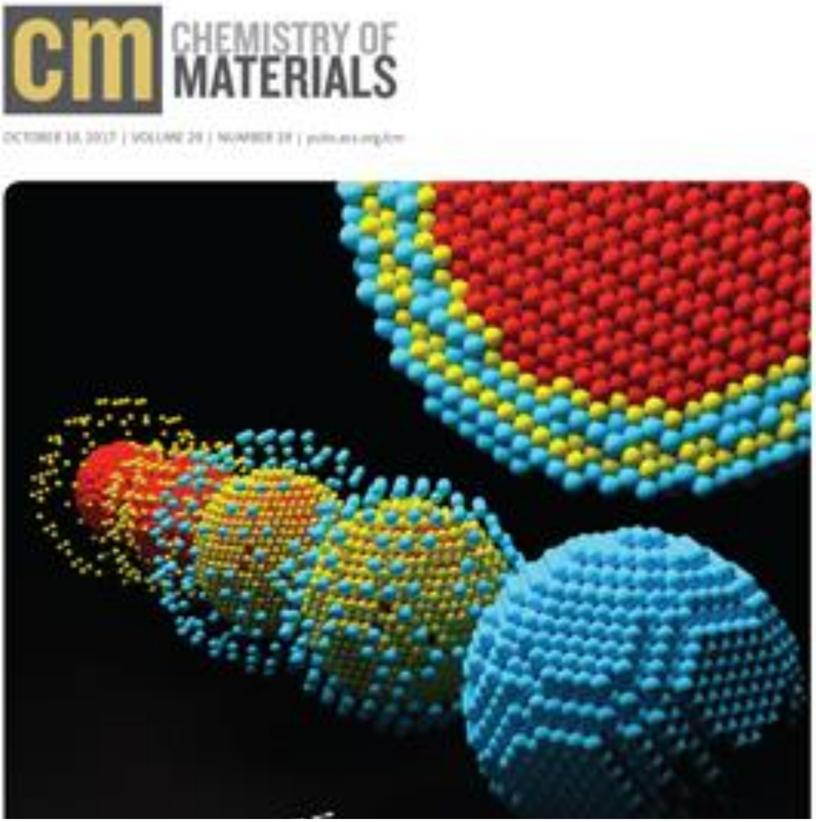
DOI: 10.1021/acs.chemrev.5b00739

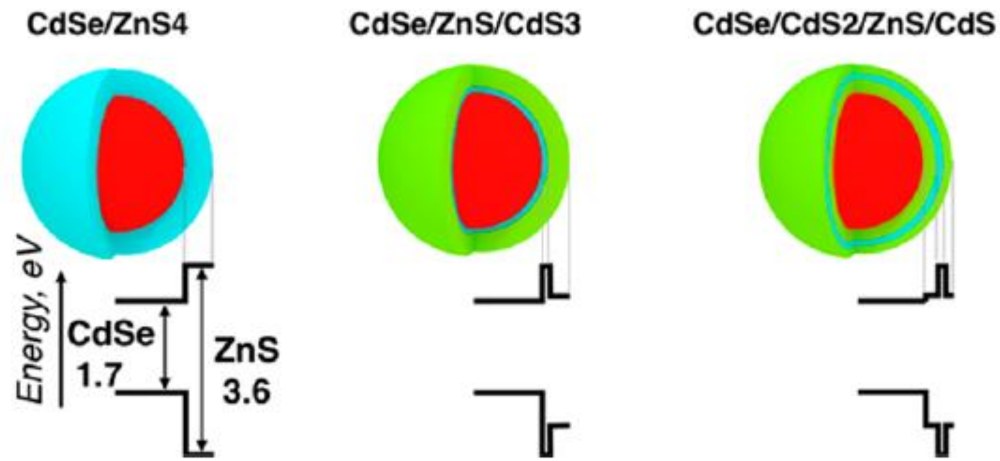
Core-shell nanocrystals - Fabrication Methods colloidal Atomic Layer Deposition (c-ALD)

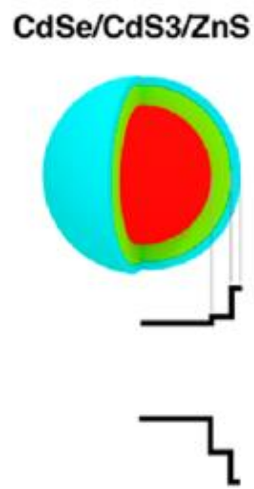


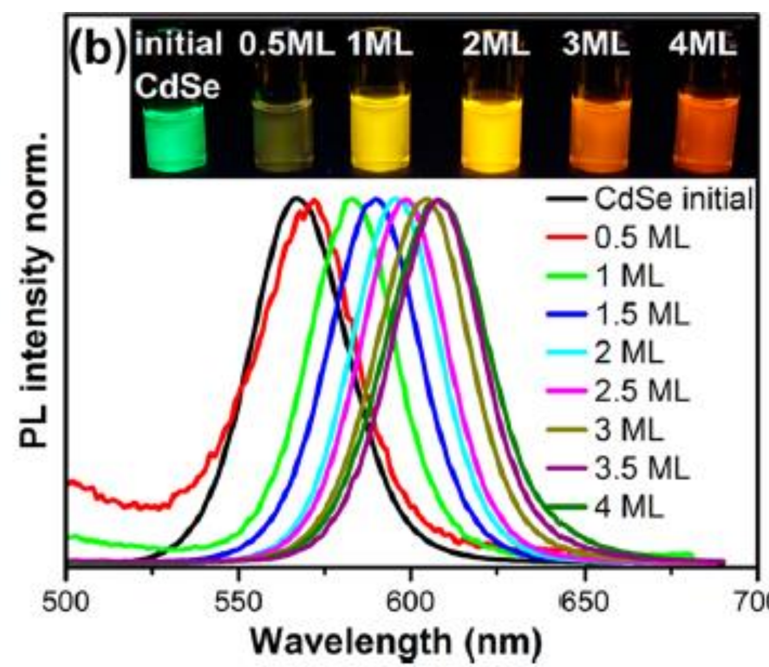
Core-shell nanocrystals - Fabrication Methods

colloidal Atomic Layer Deposition (c-ALD) for quantum dots









CHEMISTRY OF MATERIALS Article pubs.acs.org/cm

Precise Engineering of Nanocrystal Shells via Colloidal Atomic Layer Deposition

Emanuele A. Slejko,[†,‡,§] Vladimir Sayevich,[†,§] Bin Cai,[†] Nikolai Gaponik,[†] Vanni Lughi,[‡] Vladimir Lesnyak,[*,†] and Alexander Eychmüller[†]

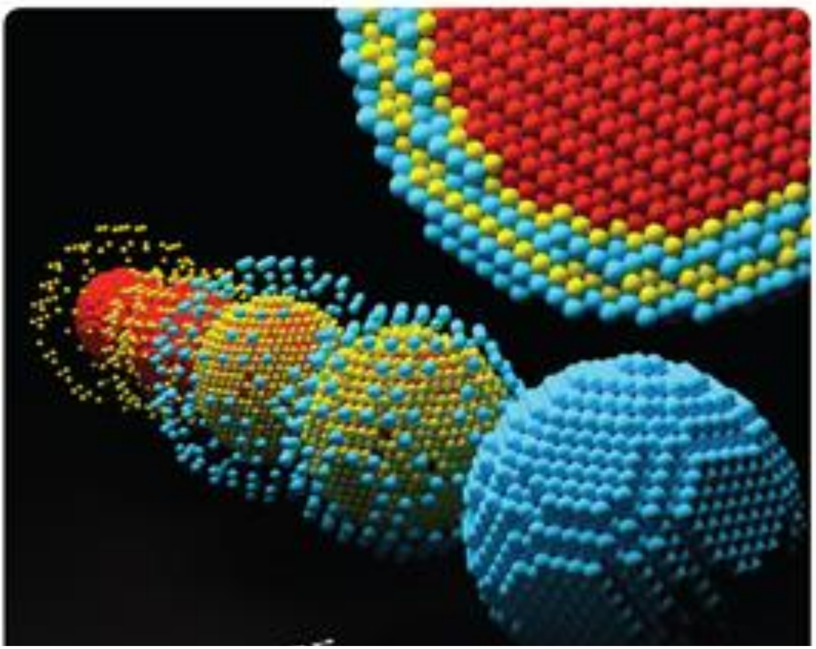
ACS Publications

EA. Slejko et al., "Precise Engineering of Nanocrystal Shells via Colloidal Atomic Layer Deposition" *Chem. Mater*. 29, **2017**

Core-shell nanocrystals - Fabrication Methods

colloidal Atomic Layer Deposition (c-ALD) for quantum metal nanoparticles

CHEMISTRY OF MATERIALS



CHEMISTRY OF MATERIALS

Article

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Precise Engineering of Nanocrystal Shells via Colloidal Atomic Layer Deposition

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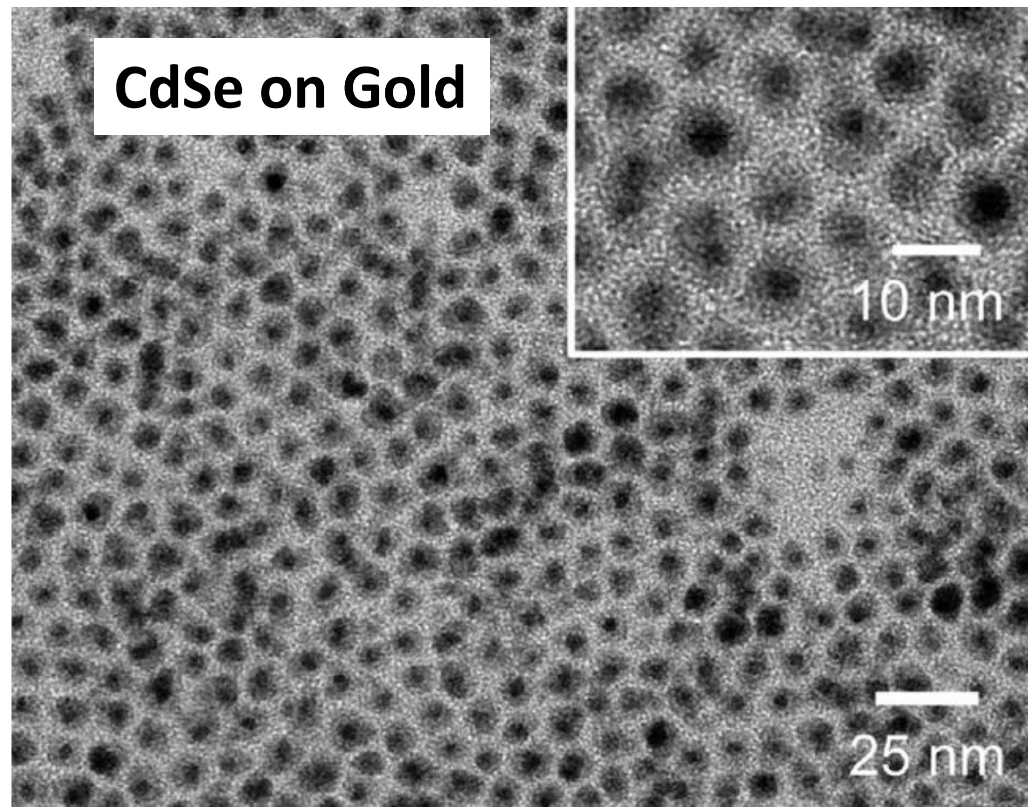
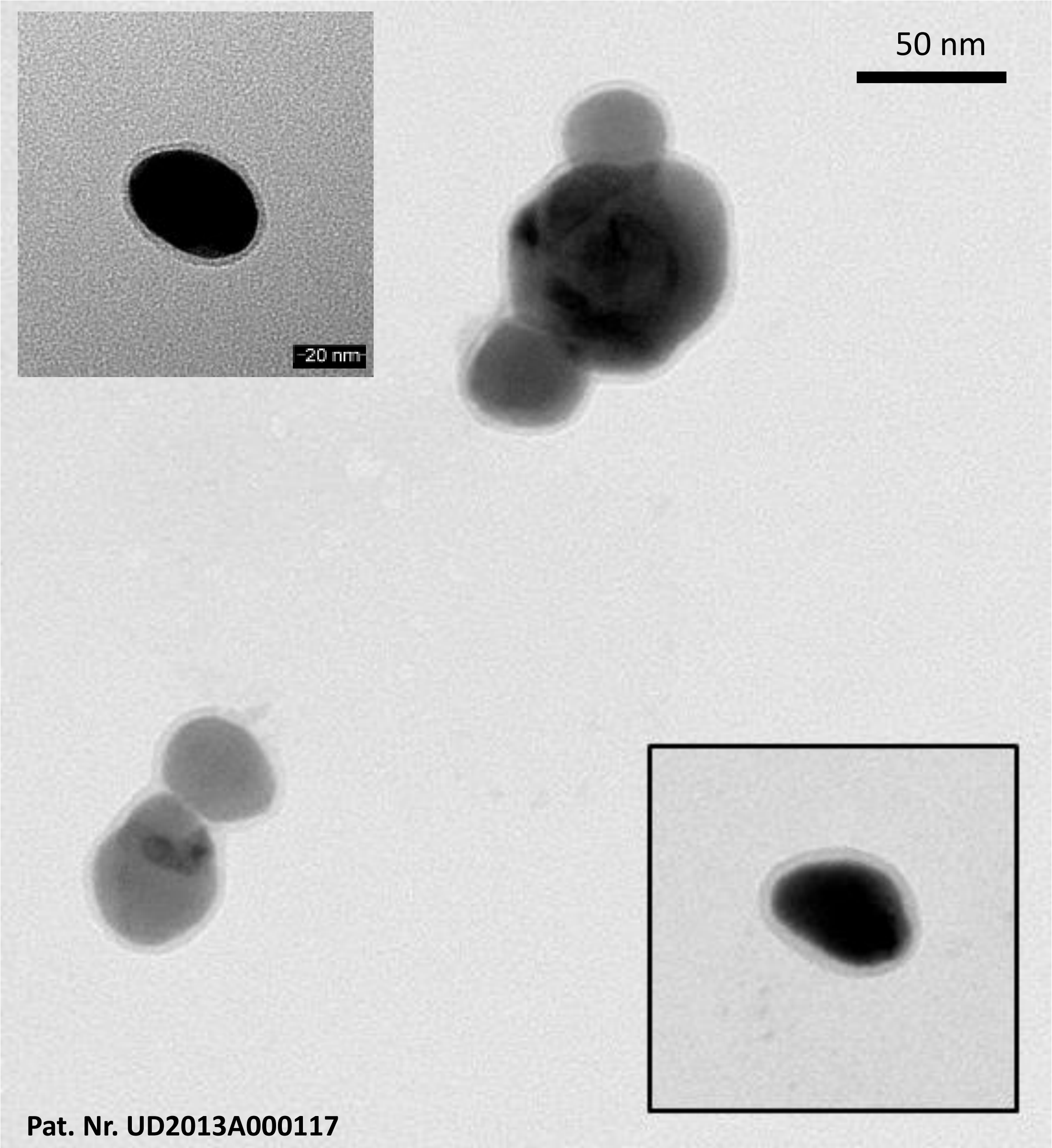
ACS Publications

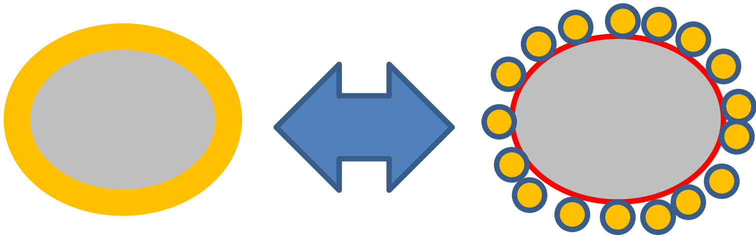


EA. Slejko et al., “Precise Engineering of Nanocrystal Shells via Colloidal Atomic Layer Deposition” *Chem. Mater*. 29, **2017**

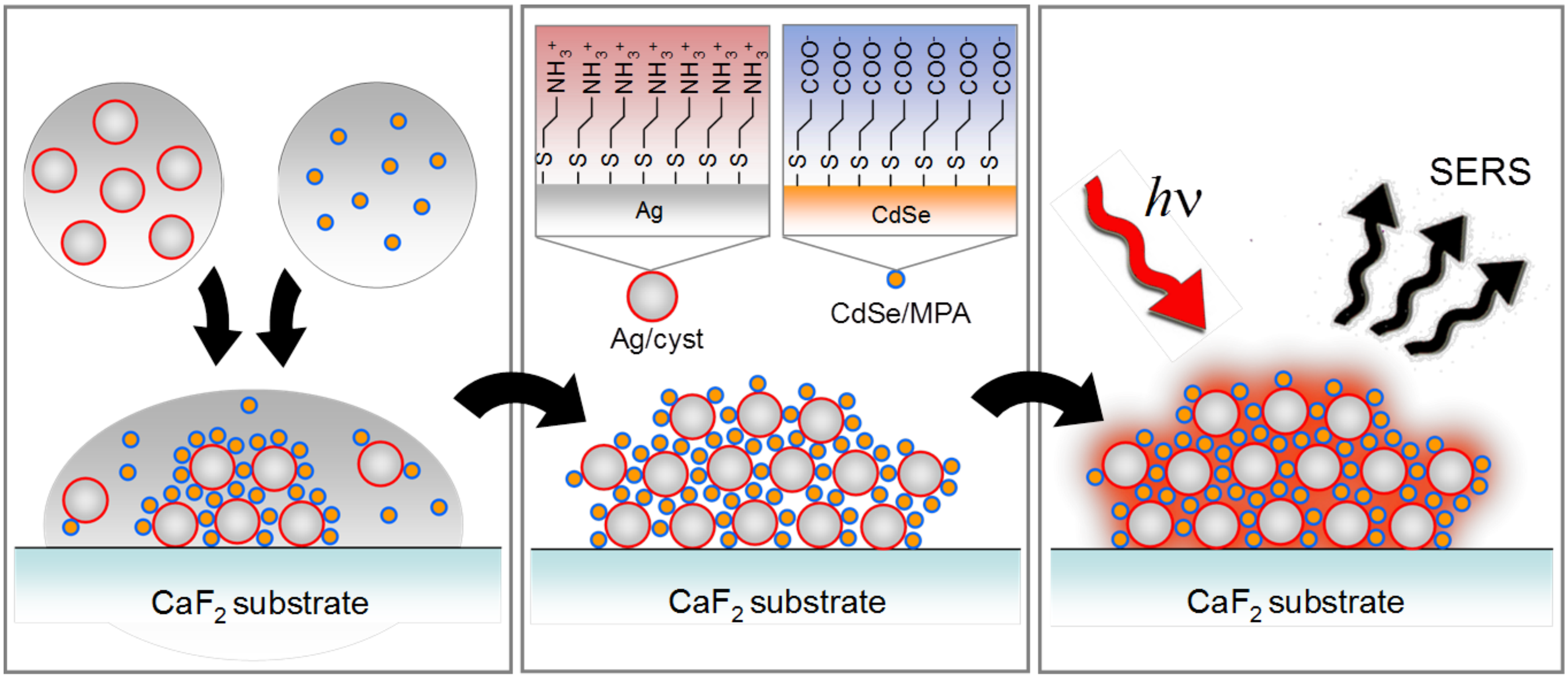
Hybrid Core-Shell Structures

via Chemical Bath NanoDeposition



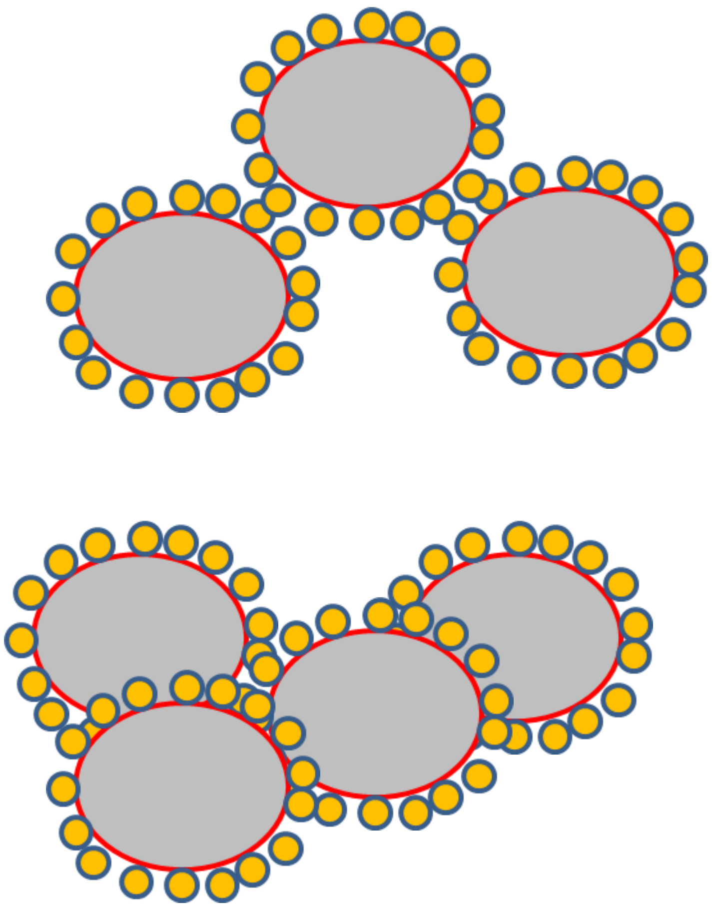


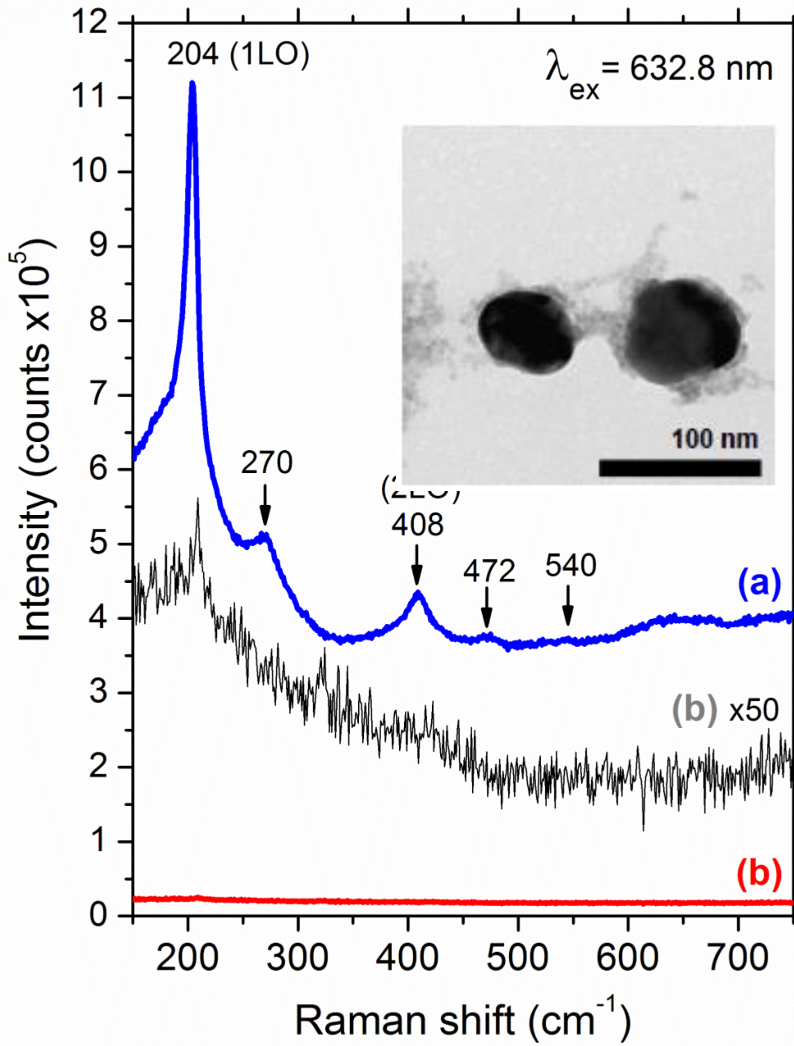
Nano-hybrid particles as SERS-based optical biomarkers



Lughi, Bonifacio et al. J Nanop Res 15, 1663 (2013)

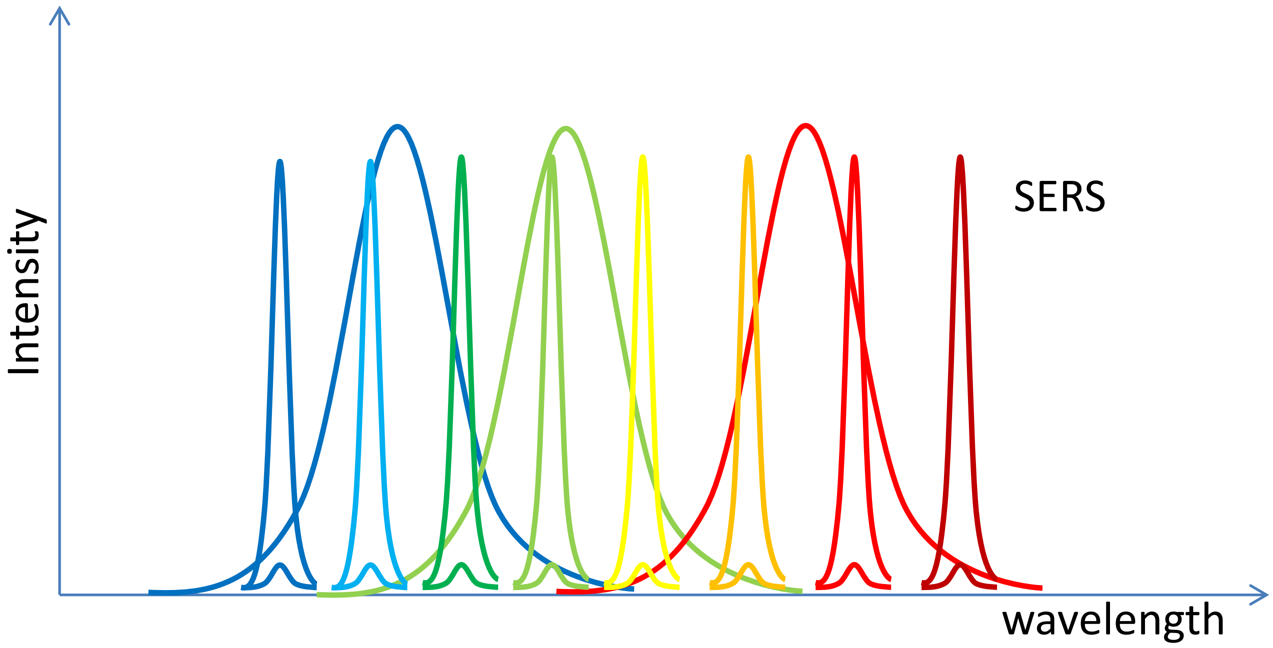
Nano-hybrid particles as SERS-based optical biomarkers



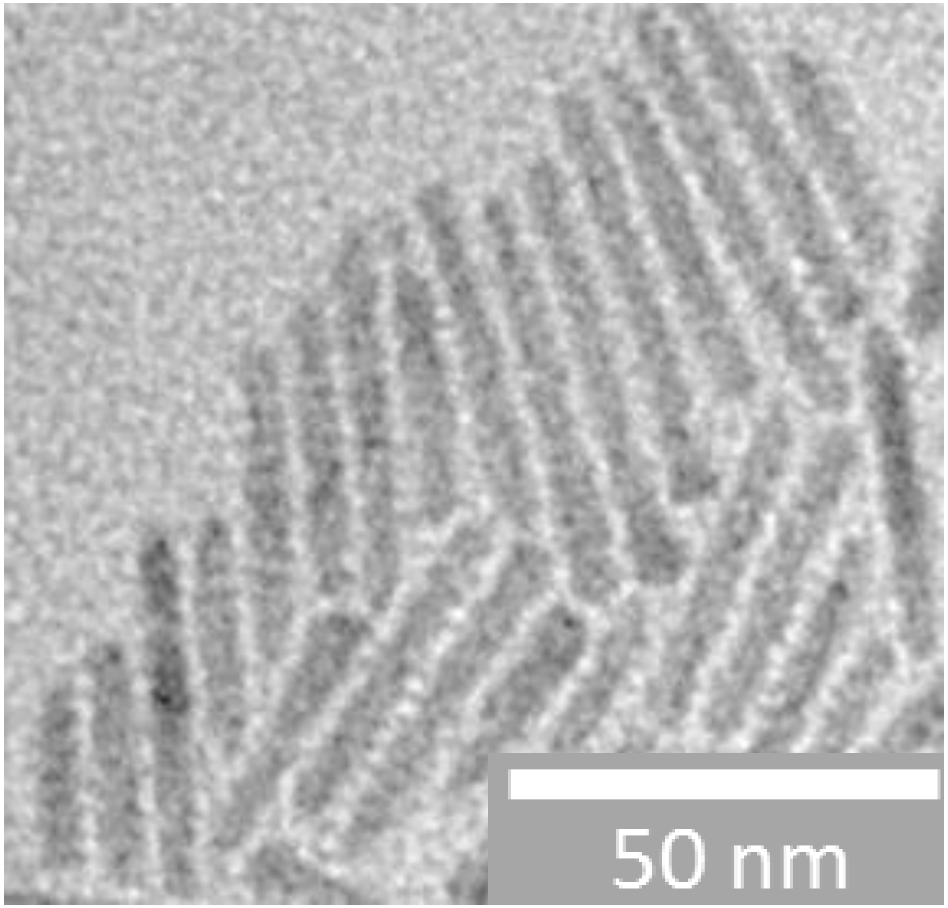


Lughi, Bonifacio et al. J Nanop Res 15, 1663 (2013)

Raman vs Photoluminescence



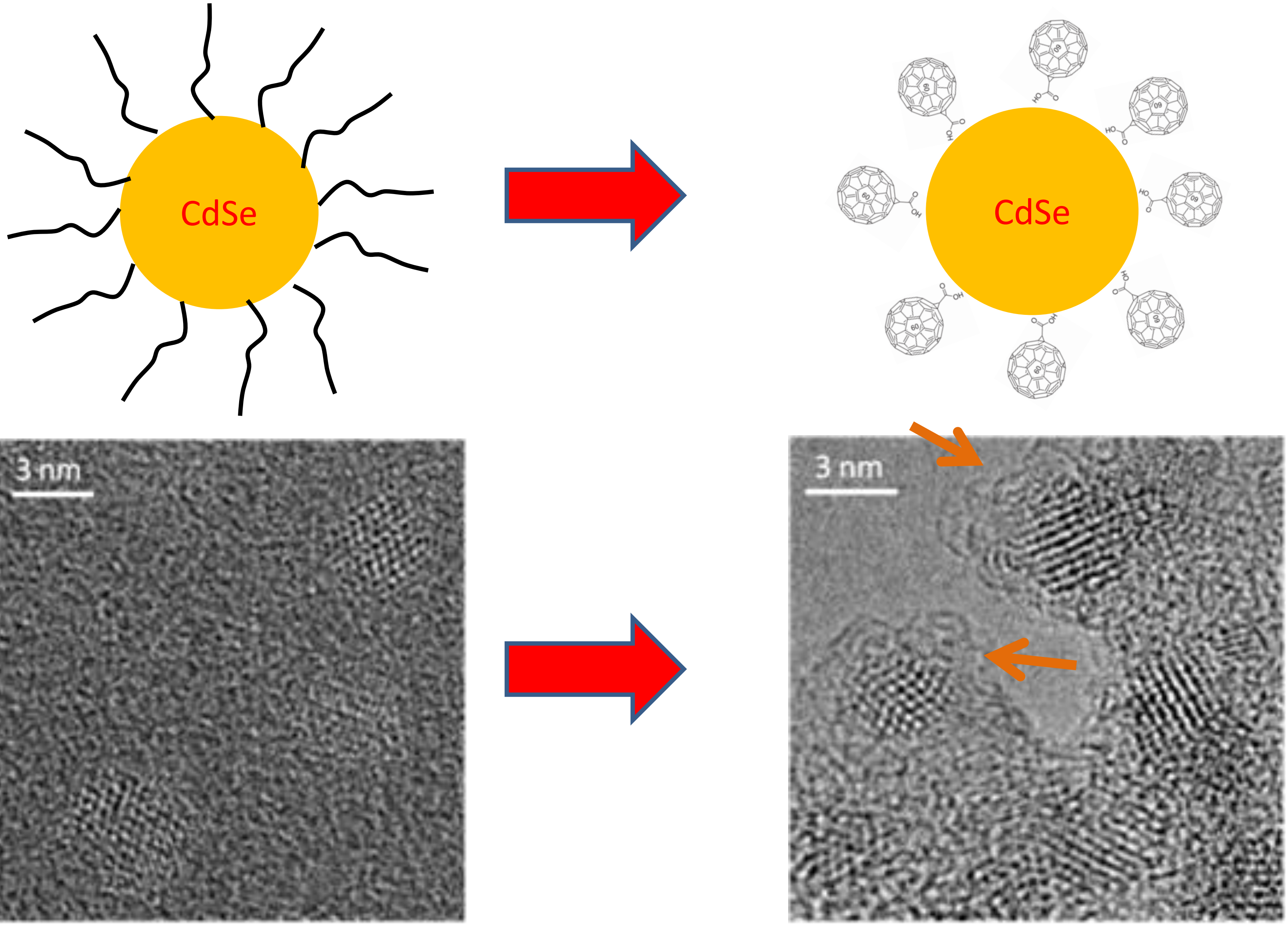
Playing with the shape: Core-Shell Nanorods



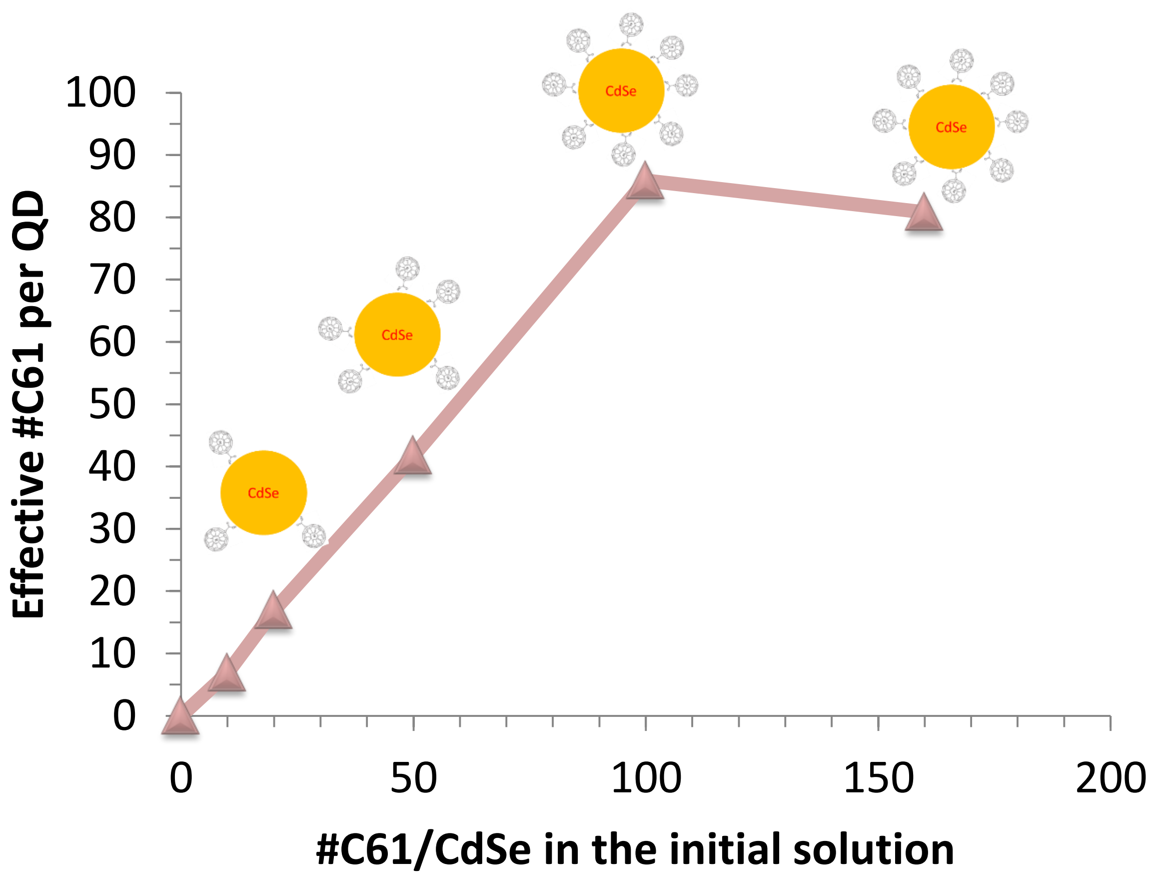
Courtesy Martina Segato, 2017

Playing with the surface chemistry:

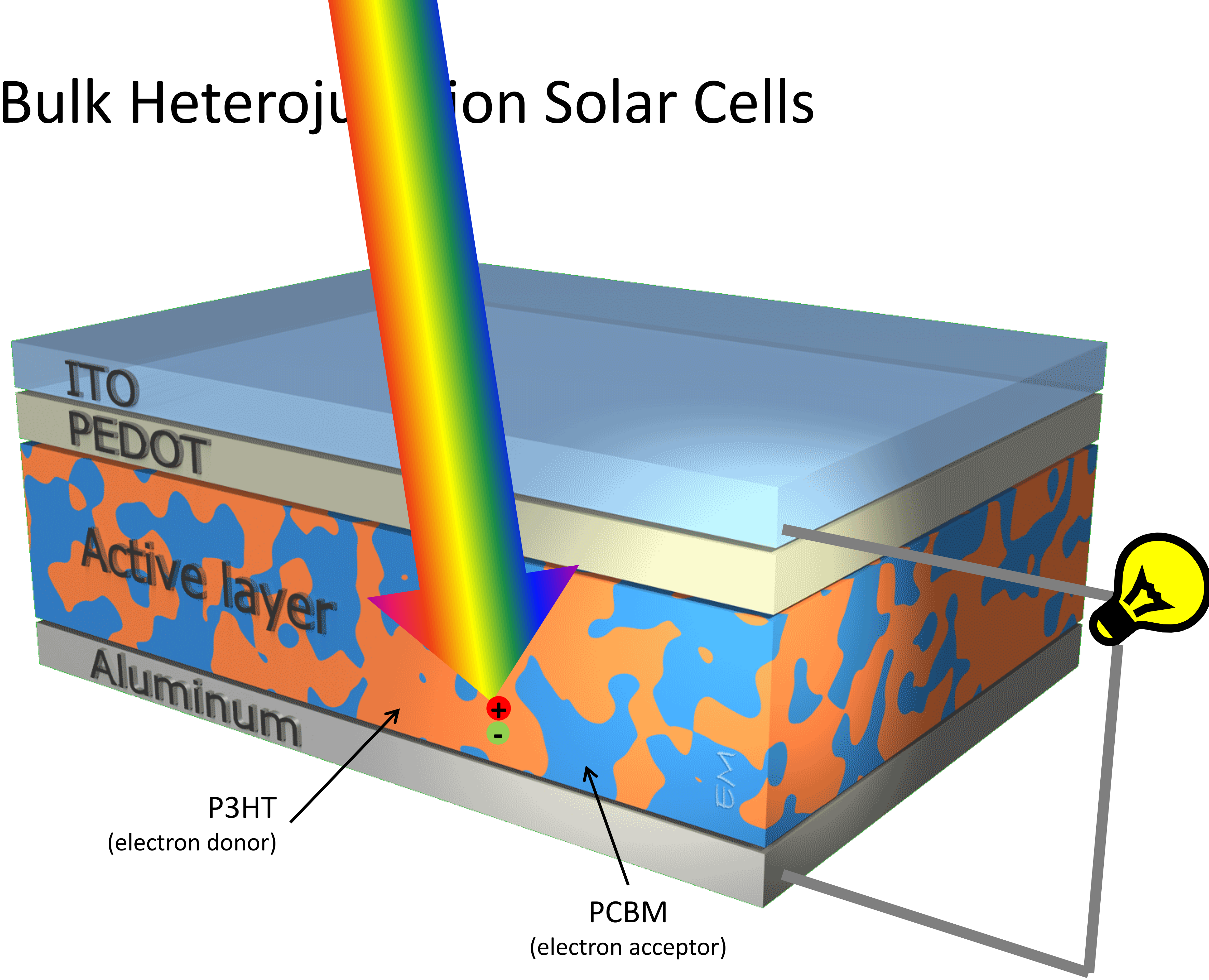
CdSe@C61: Synthesis via Capping Exchange



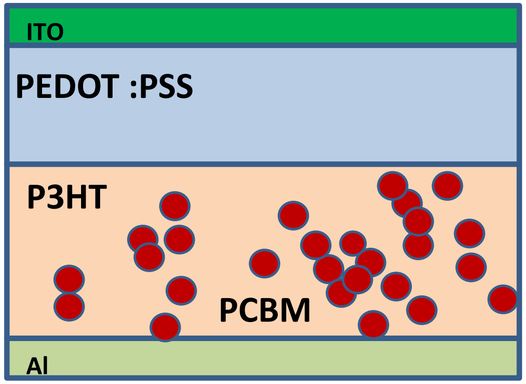
CdSe@C61: Synthesis via Capping Exchange
Control of the C61 coverage

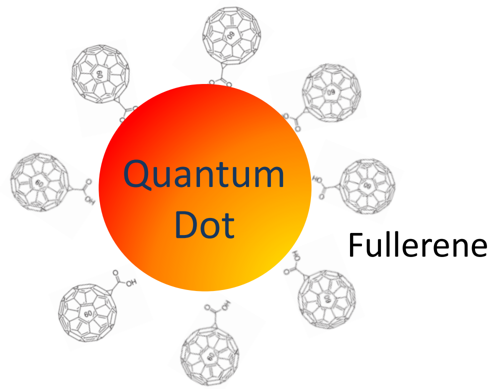


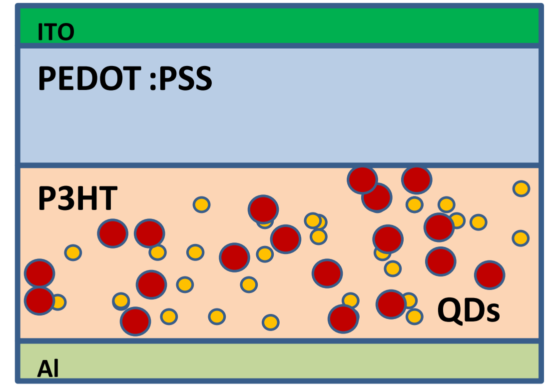
Bulk Heteroju ion Solar Cells



State of the Art and Founding Idea

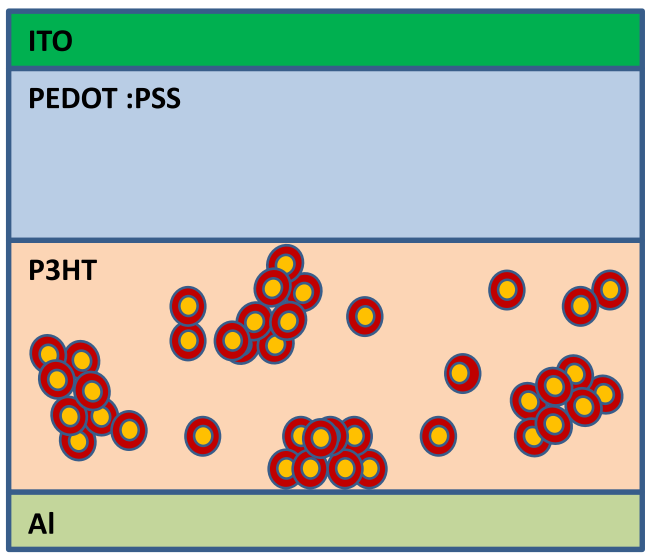




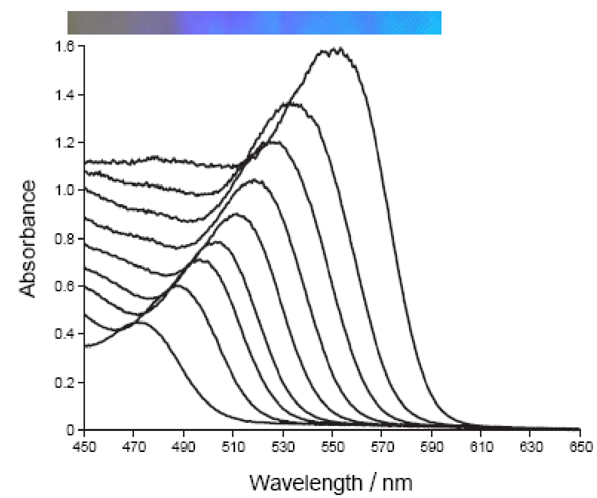


Fullerenes

(e.g. PCBM)



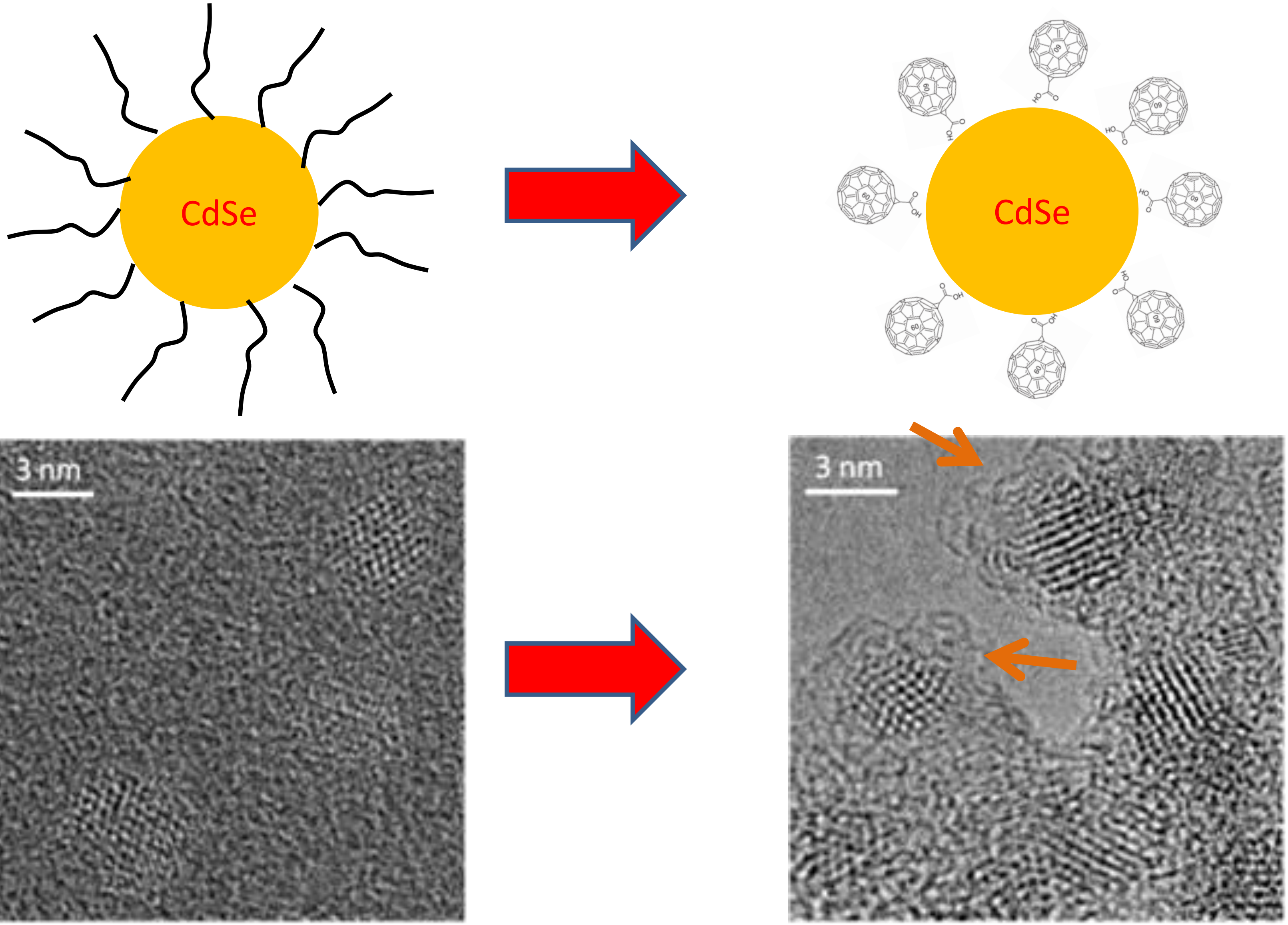
Quantum dots



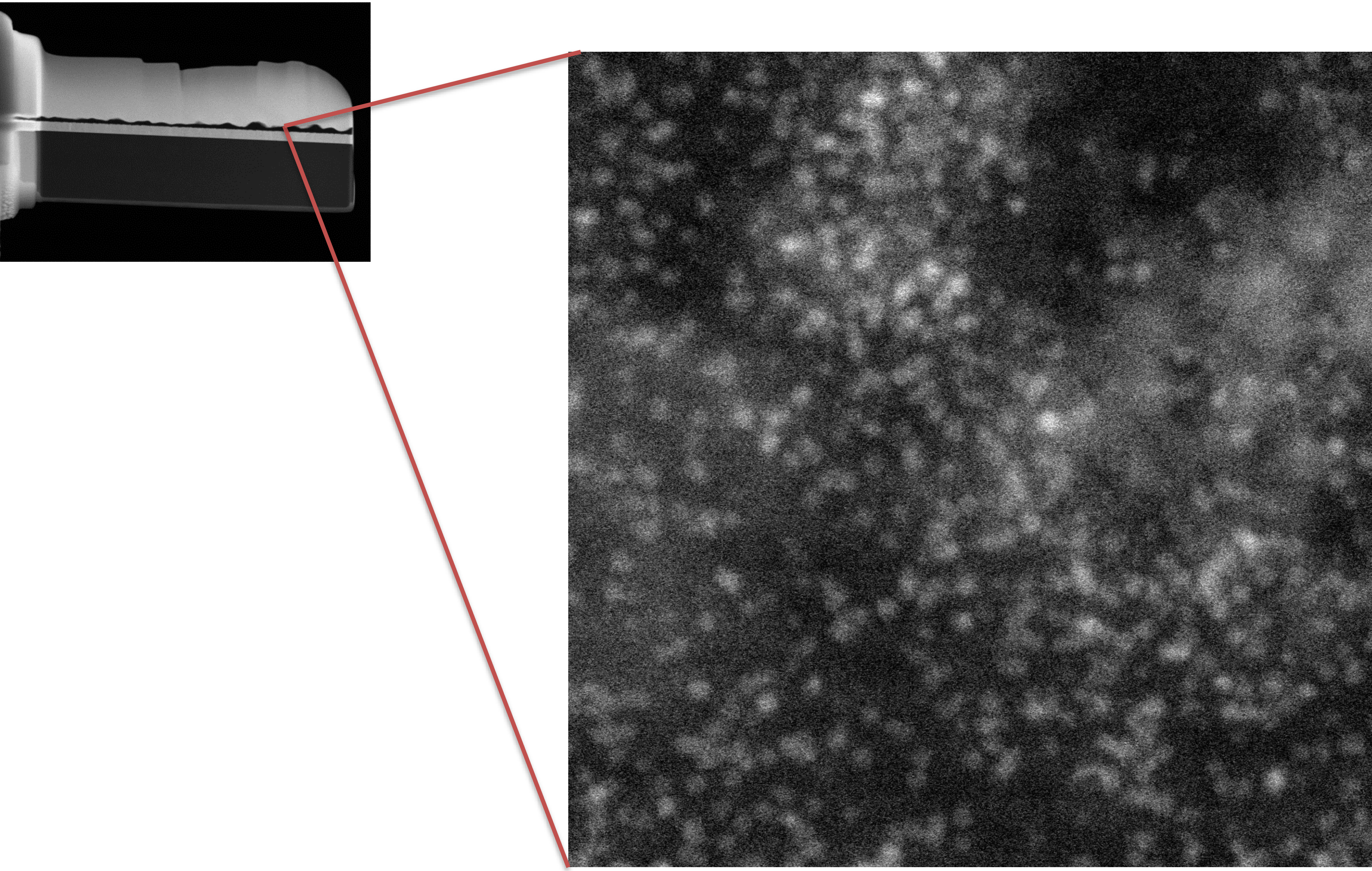
TRANSPORT

ABSORBANCE

CdSe@C6: Synthesis via Capping Exchange



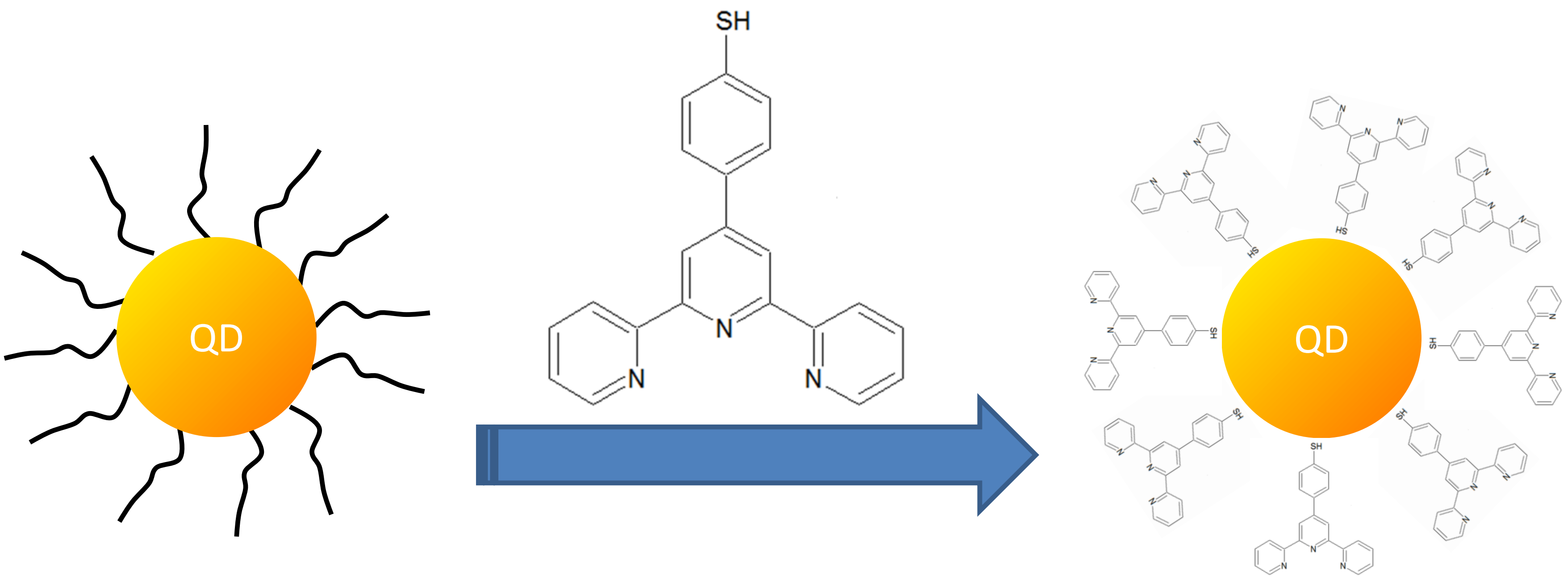
Use in photovoltaic cells: P3HT:CdSe@C61 blend

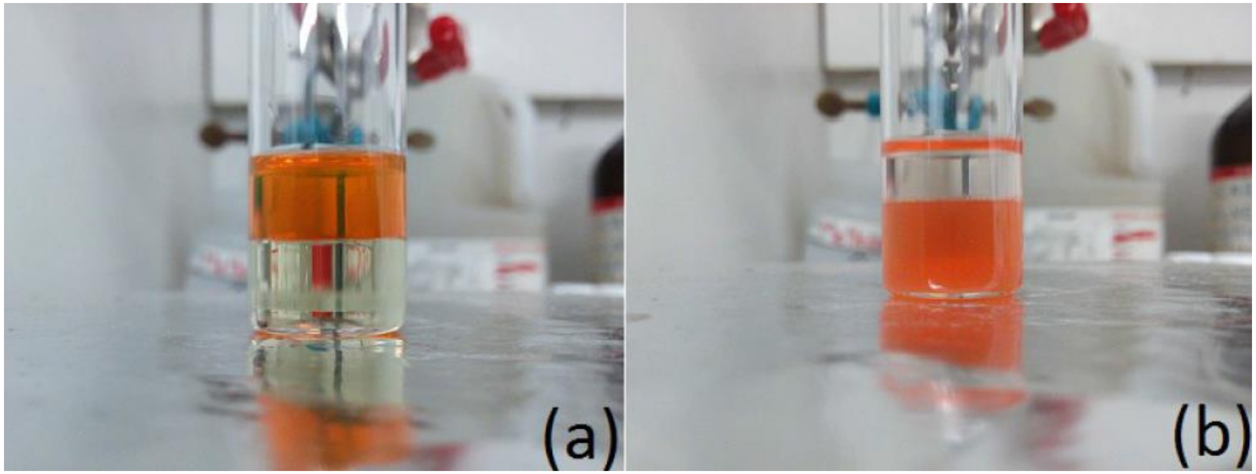


STEM analysis: excellent dispersion!

Playing with surface chemistry:

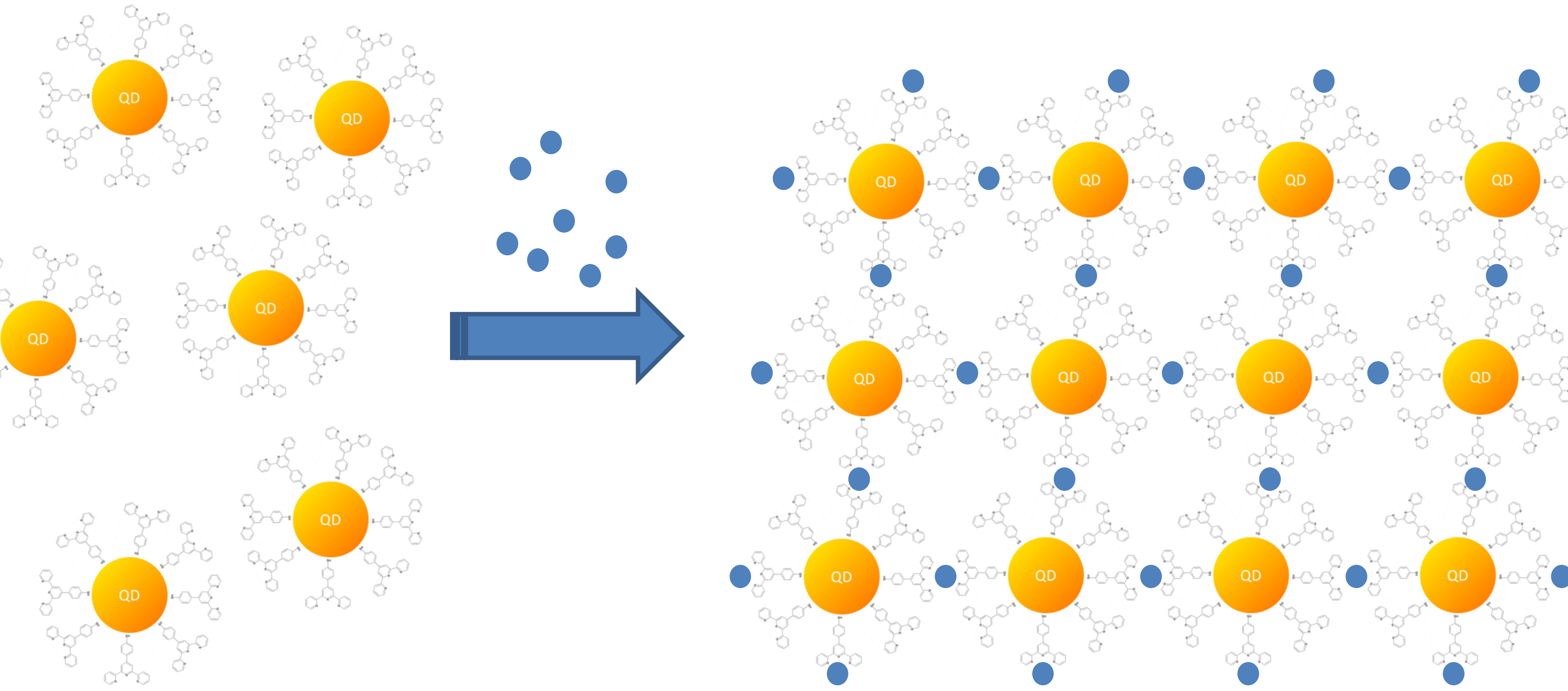
Terpiridine capping exchange on Quantum Dots for QD supramolecular assembly





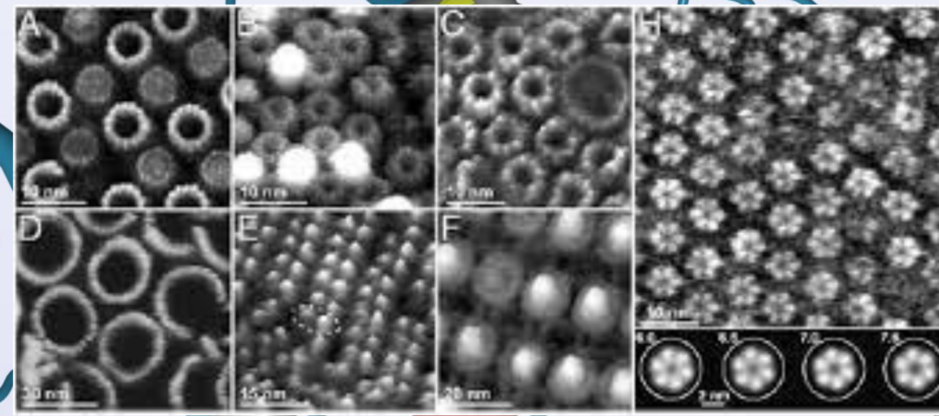
Supramolecular Assembly Applied to Quantum Dots

1. Synthesize functionalized quantum dots
2. Add mediating agent (e.g. metal ion)
3. Self assembly via coordinating bonds



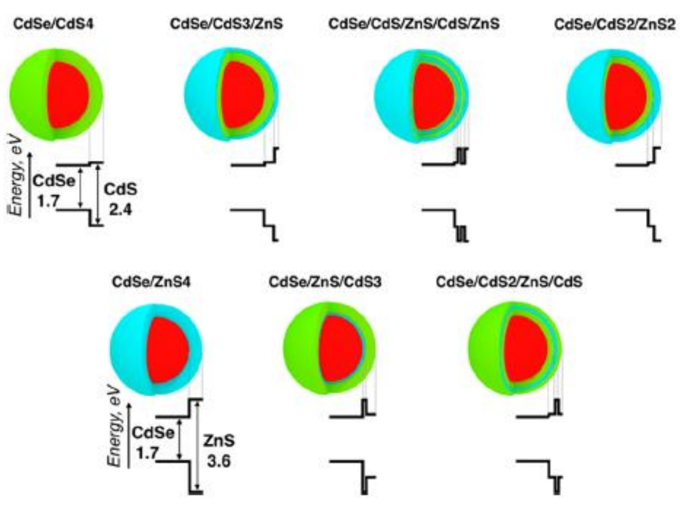
Supramolecular Assembly

- Access to **complex geometries**
- **Coordination bonds** (strongest among weak bonds, therefore **stable** but **easy to manipulate**)
- **Bond can be functionalized**



Seelert, H et al., Nature 405, 418-9, (2000)
Fotiadis, D. et al., Nature 421, 127-8 (2003)
Fotiadis, D. et al., J Biol Chem 279, 2063-8 (2004)
Scheuring S. et al., Science 309, 484-7 (2005)

Nanoparticle Engineering
Controlling the optical properties via bandgap engineering



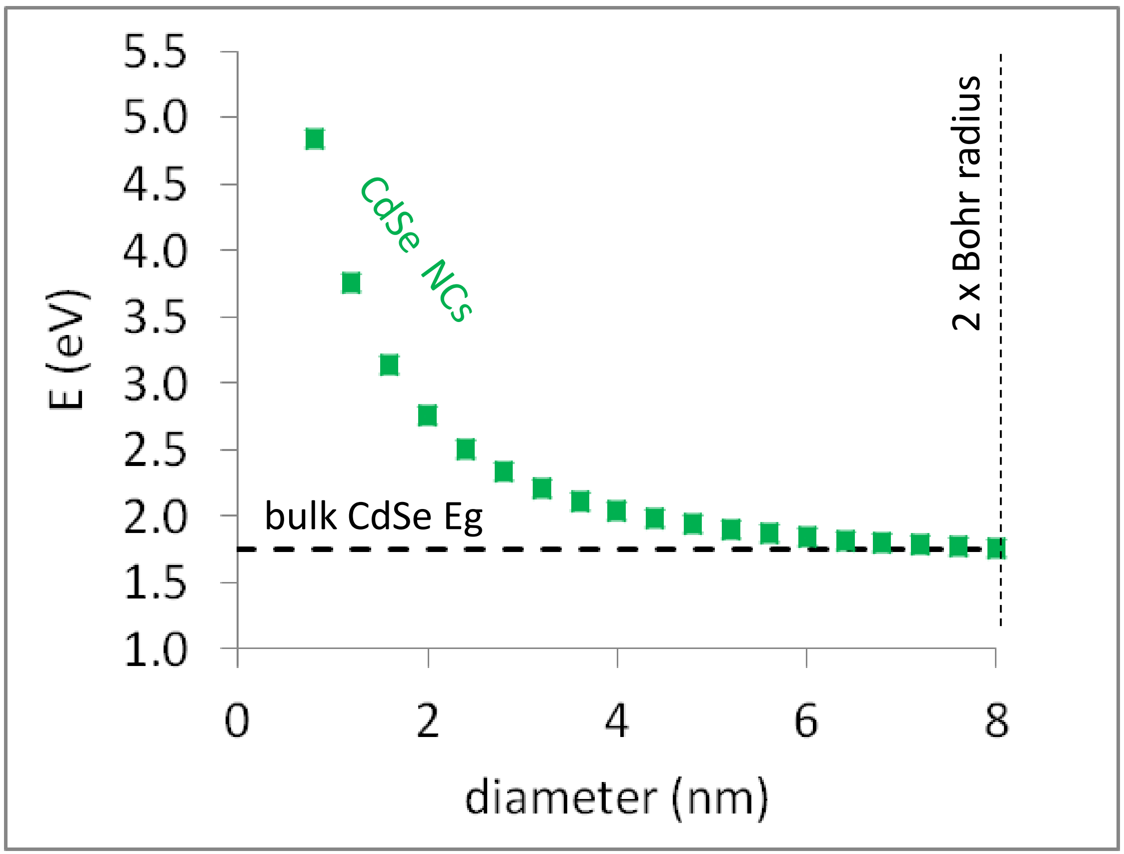
Nanoparticle Engineering
Controlling the optical properties

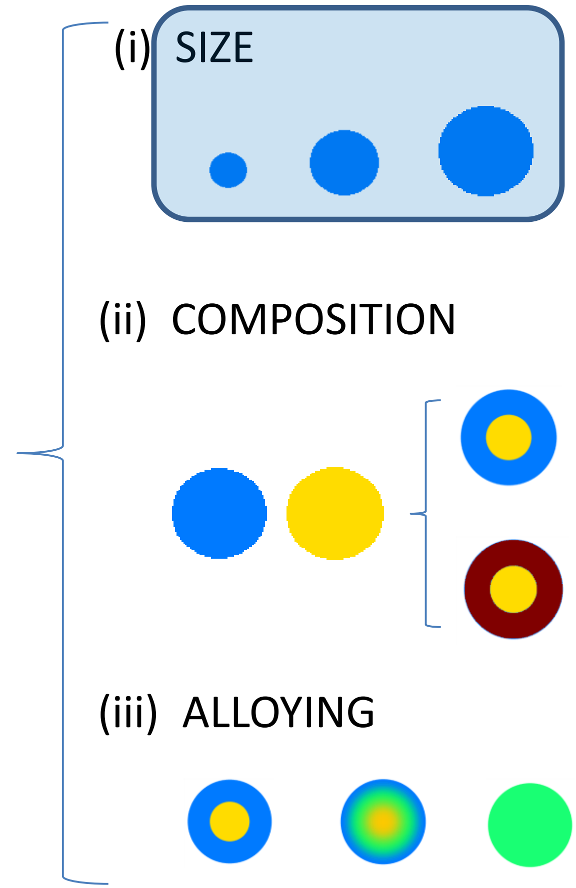
(1) NCs as PHOSPHORS

color = f (E_G)

(I) COLOR ENGINEERING

E_G can be easily tuned

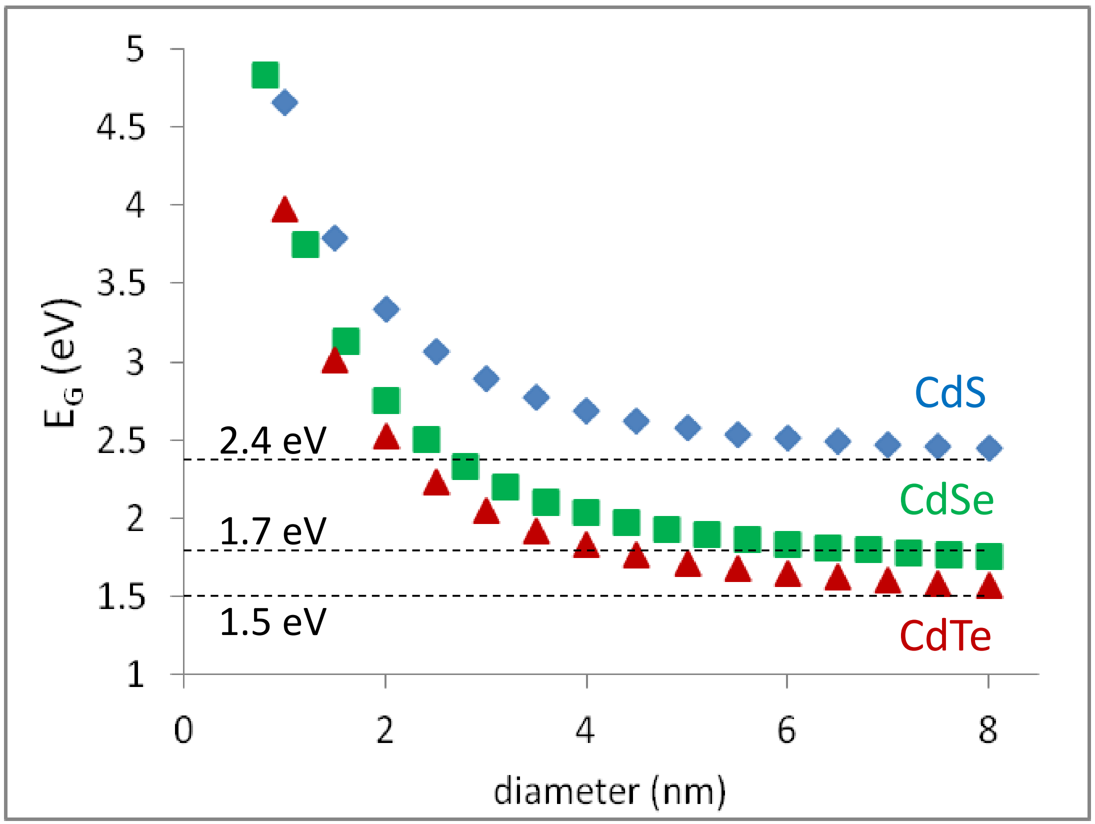


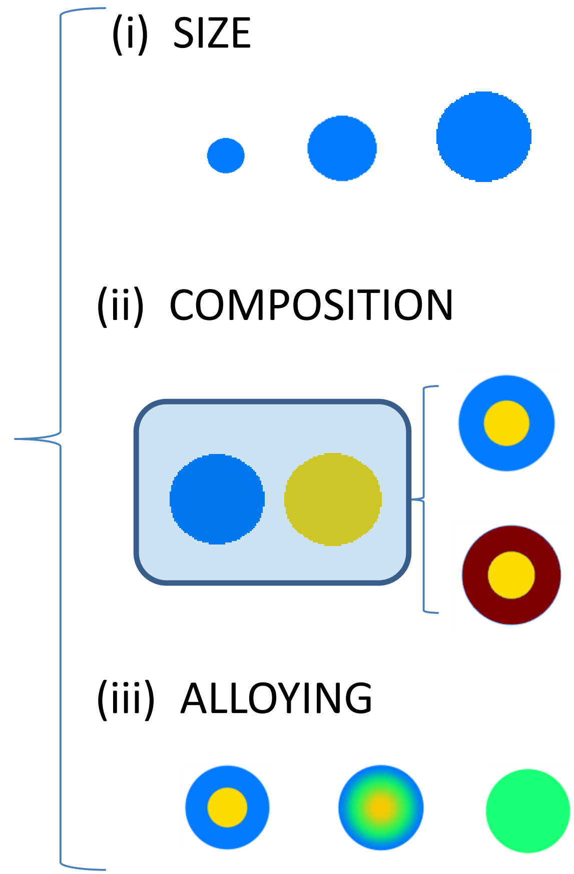


(1) NCs as PHOSPHORS

(I) COLOR ENGINEERING

Composition

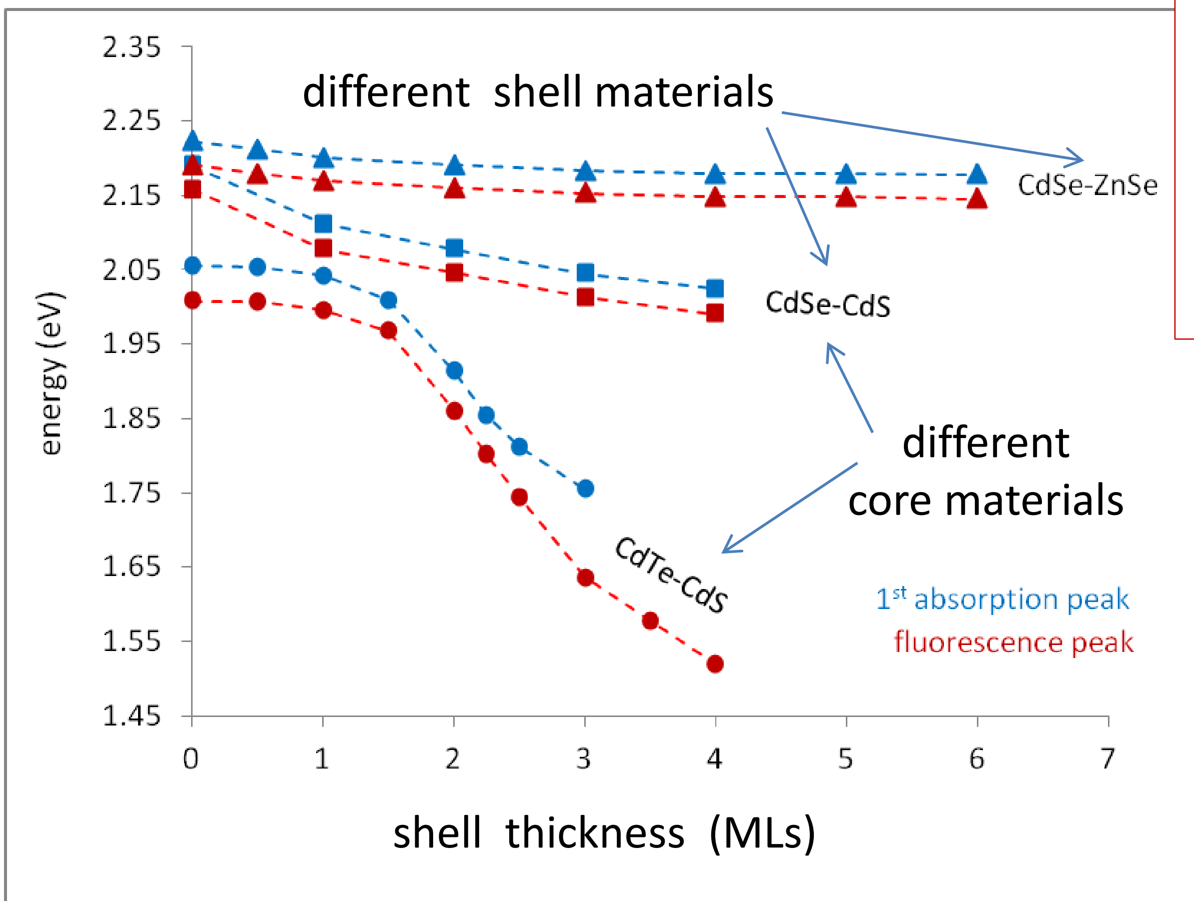




(1) NCs as PHOSPHORS

(I) COLOR ENGINEERING

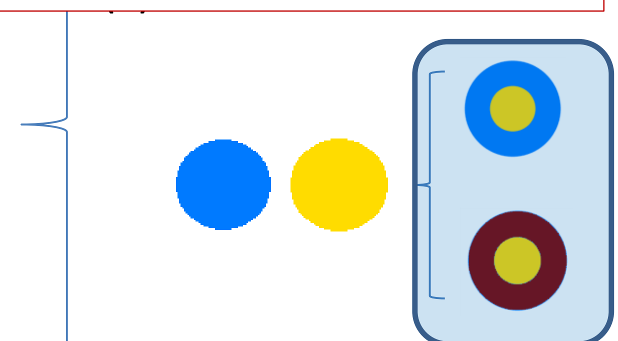
Shell



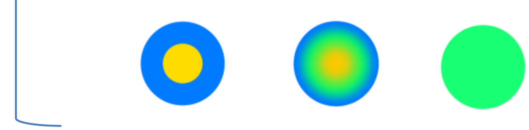
Shell growth increases overall size of the NC

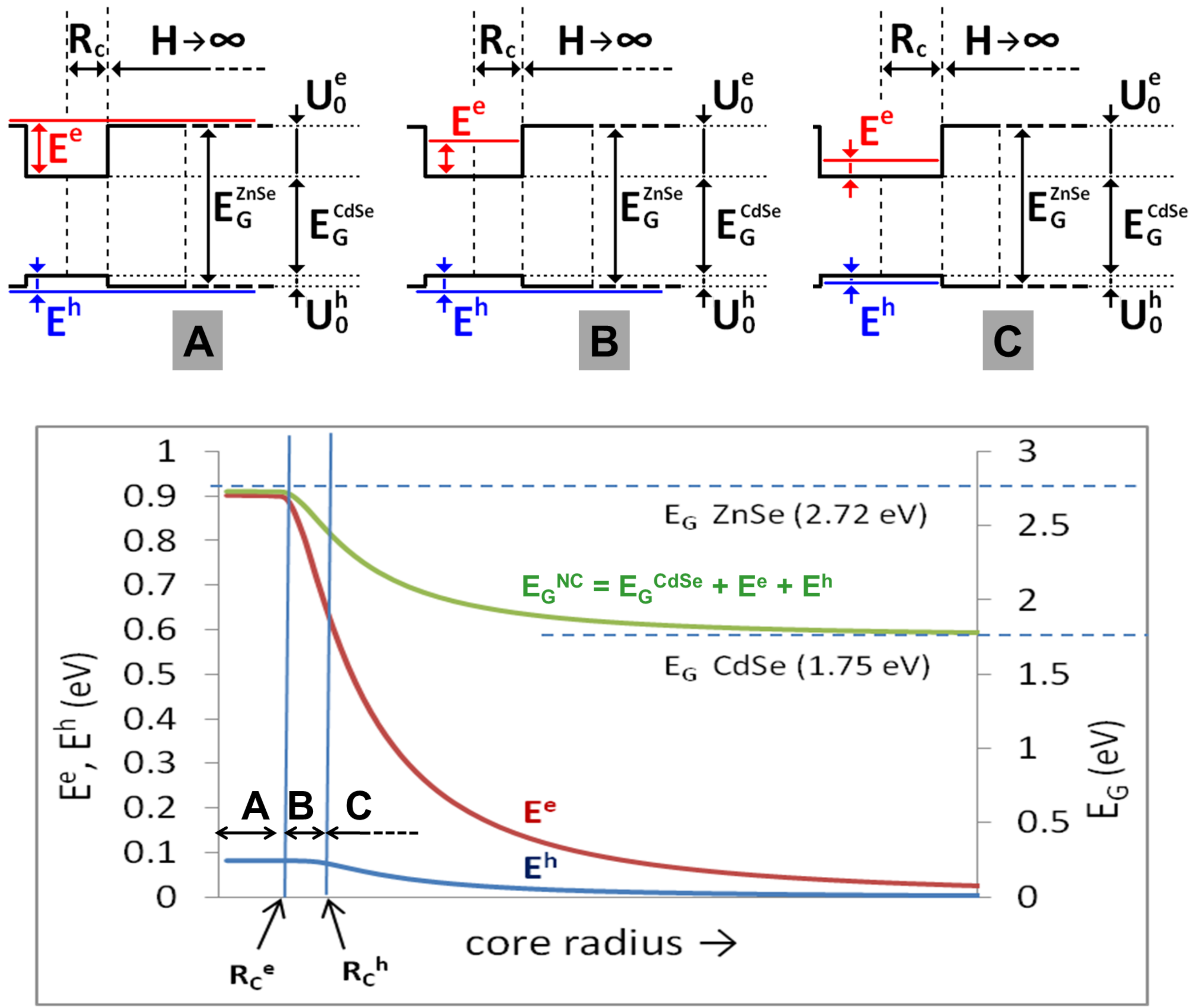
→ reduction of E_G according to:

- shell thickness
- shell composition
- original core size



(iii) ALLOYING





R_c
$H \to \infty$
U_0^e
E^e
E_G^{ZnSe}
E_G^{CdSe}
E^h
U_0^h
A
B
C
E_G ZnSe (2.72 eV)
$E_G^{NC} = E_G^{CdSe} + E^e + E^h$
E_G CdSe (1.75 eV)
E^e, E^h (eV)
E_G (eV)
E^e
E^h
R_C^e
R_C^h
core radius →

(1) NCs as PHOSPHORS

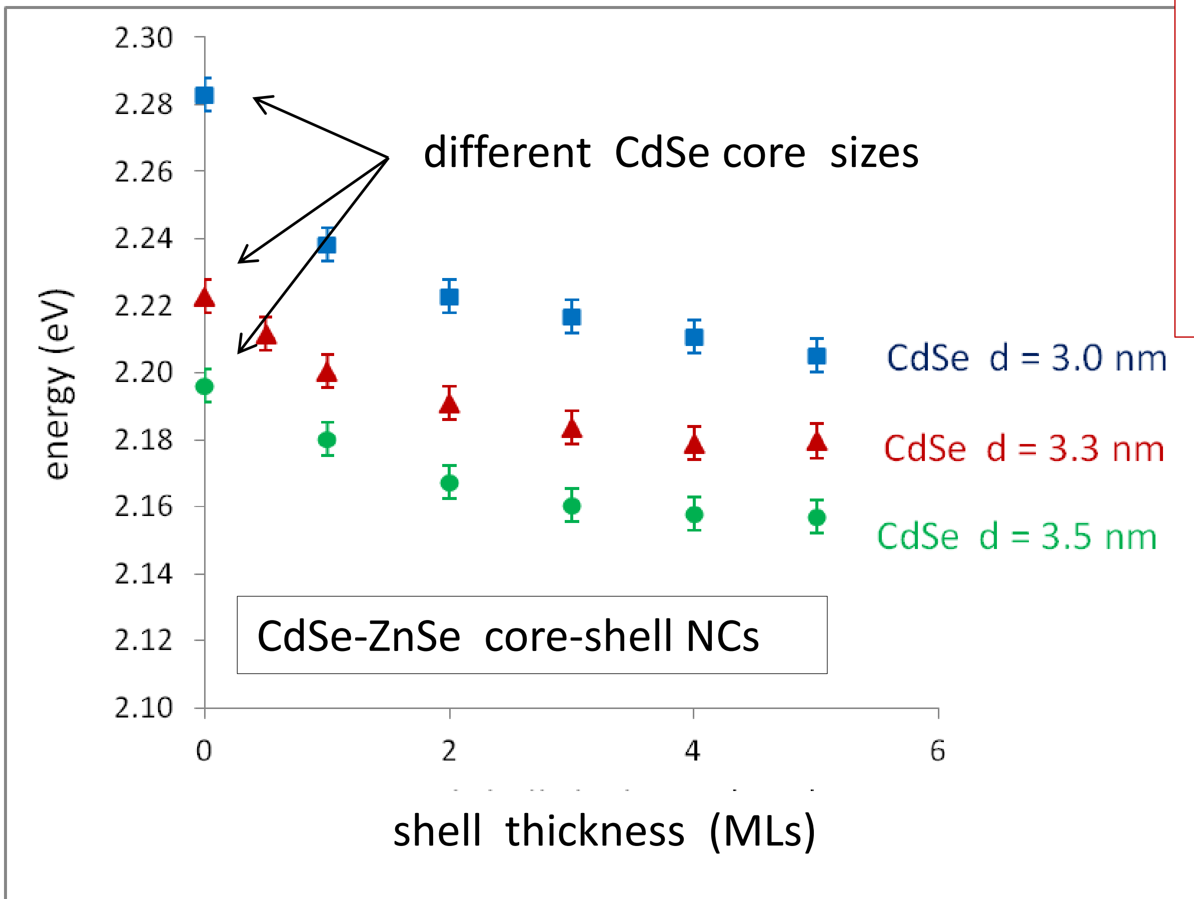
(I) COLOR ENGINEERING

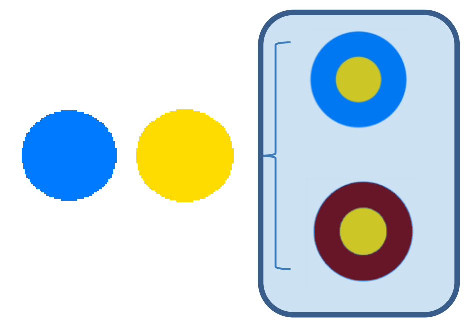
Shell

Shell growth increases overall size of the NC

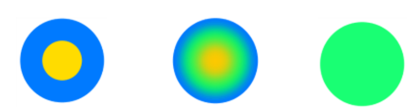
→ reduction of E_G according to:

- shell thickness
- shell composition
- original core size





(iii) ALLOYING



(1) NCs as PHOSPHORS

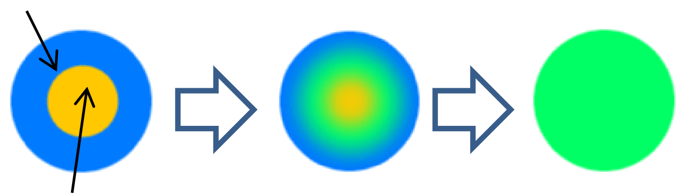
(I) COLOR ENGINEERING

alloying

DIFFUSION (alloying)
causes E_G to change
according to composition

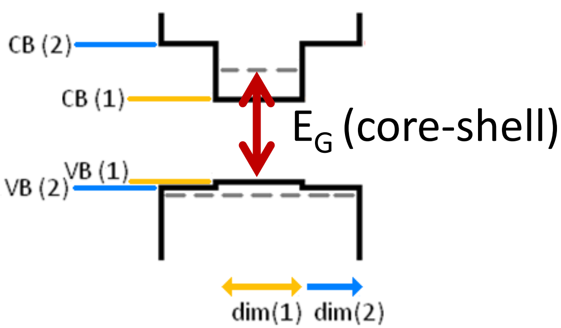
(in this system, increase of E_G)

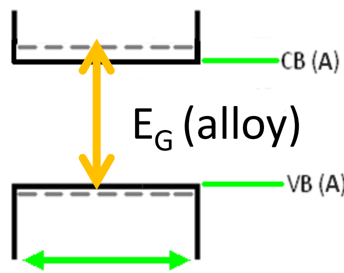
ZnSe (E_G = 2.7 eV)



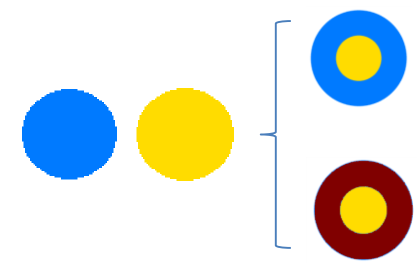
CdSe (E_G = 1.7 eV)

$Cd_xZn_{1-x}Se$

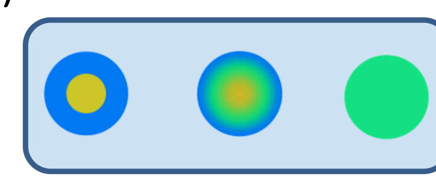




(ii) COMPOSITION



(iii) ALLOYING



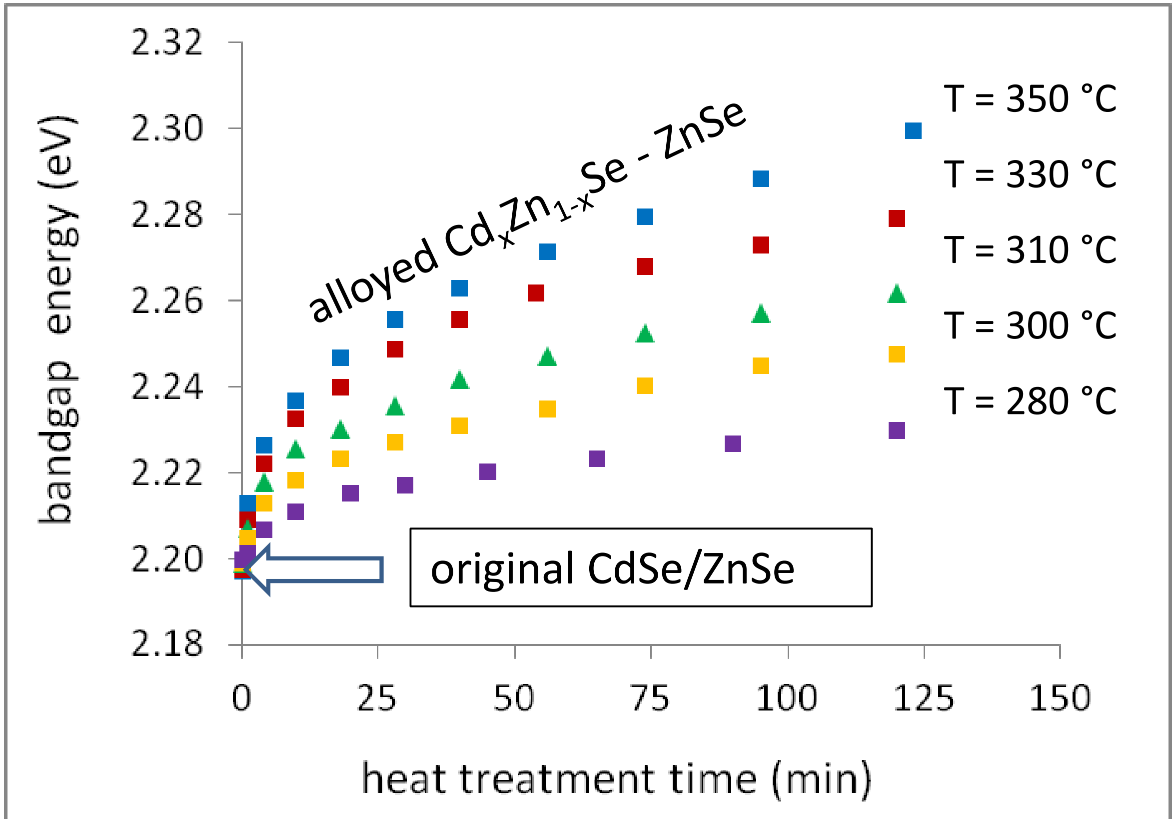
Vegard's Law

$$E_G(Cd_xZn_{1-x}Se) = x\,E_G(CdSe) + (1-x)\,E_G(ZnSe) + b(1-x)$$

(1) NCs as PHOSPHORS

(I) COLOR ENGINEERING

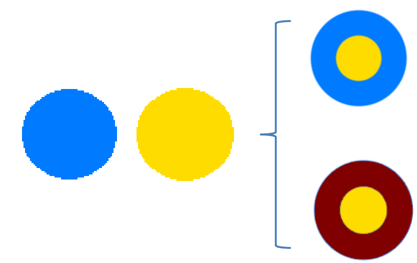
alloying



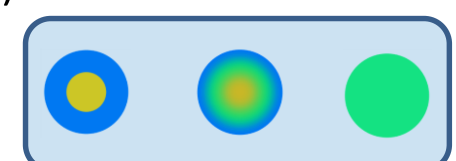
DIFFUSION (alloying)
causes E_G to change
according to composition

(in this system, increase of E_G)

(ii) COMPOSITION



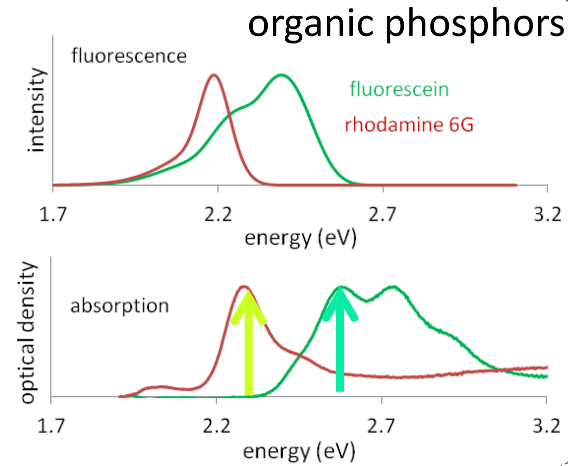
(iii) ALLOYING

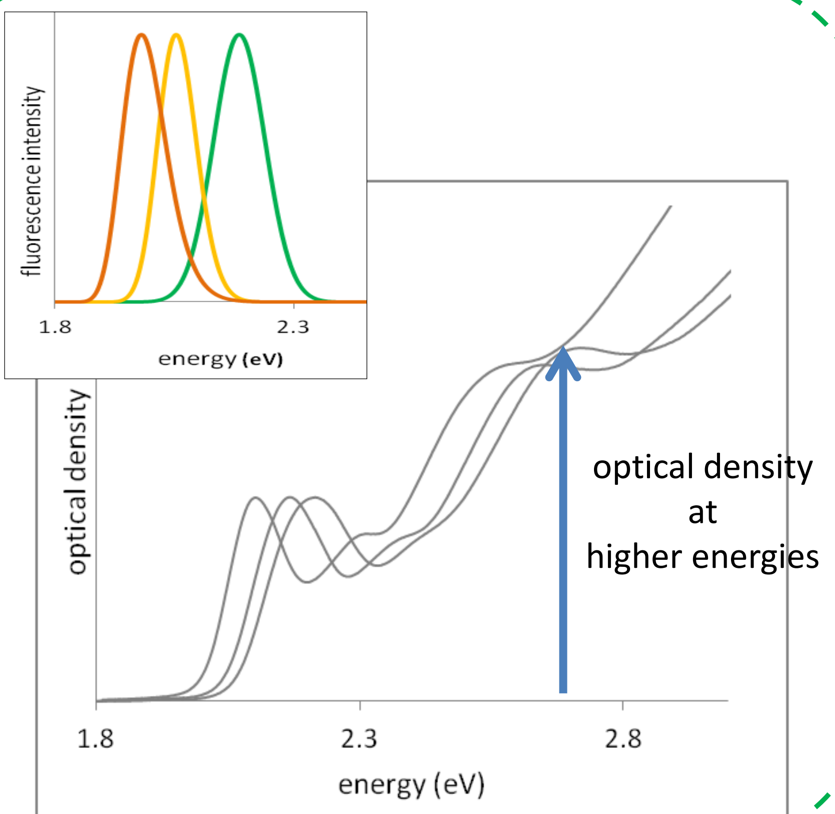


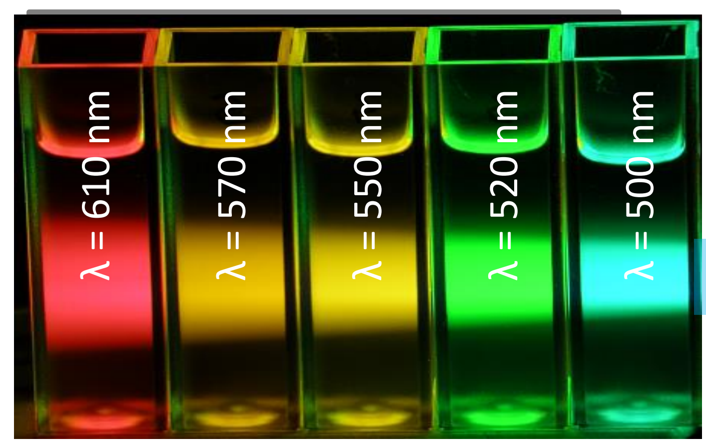
(1) NCs as PHOSPHORS

(II) SINGLE EXCITATION WAVELENGTH for different phosphors

different excitation wavelenghts







UV light

λ = 350 nm

(1) NCs as PHOSPHORS

(III) CONVERSION EFFICIENCY

Fluorescence QUANTUM YIELD

$$QY = \frac{nF_{PL}}{nF_{abs}}$$

f (Probability of BAND-EDGE radiative RECOMBINATION)

high QY (up to 85%)

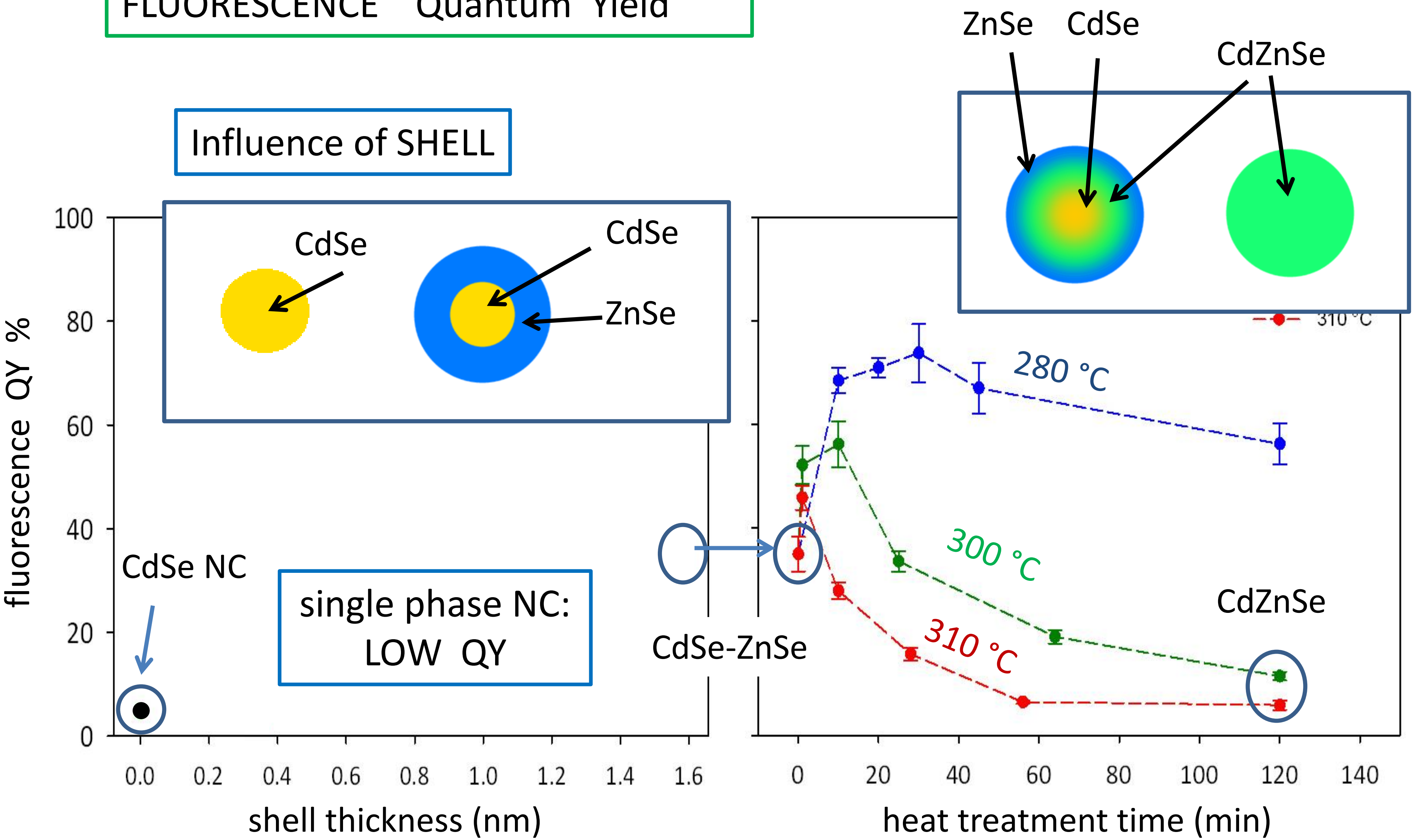
QY tunable; depends on:

- Single phase NCs: chemistry
- Multi phase NCs:
  - surface chemistry
  - lattice mismatch
  - VBO/CBO

(1) NCs as PHOSPHORS

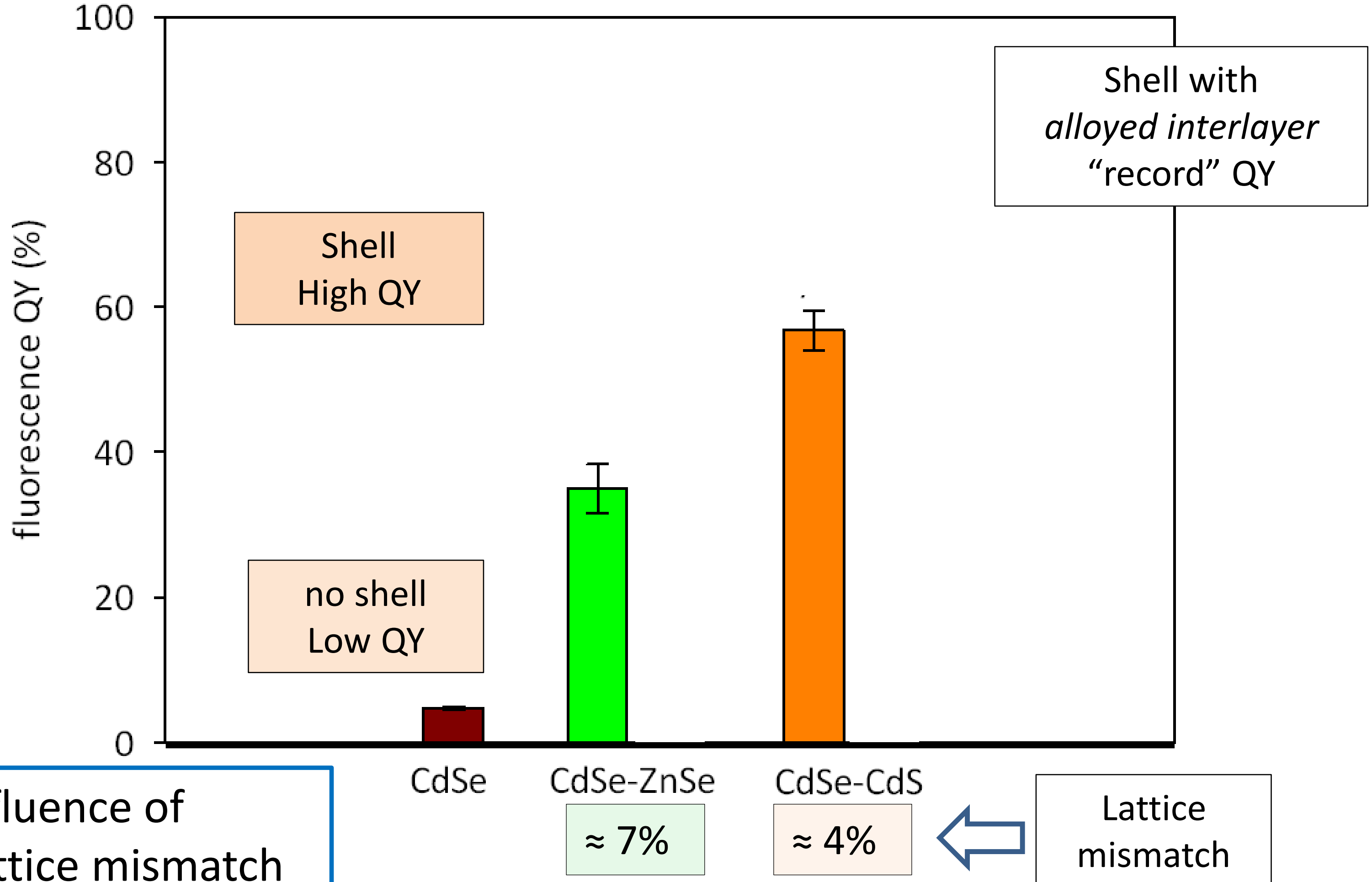
FLUORESCENCE Quantum Yield

Influence of HEAT TREATMENTS



(1) NCs as PHOSPHORS

FLUORESCENCE Quantum Yield



Influence of
Lattice mismatch

(1) NCs as PHOSPHORS

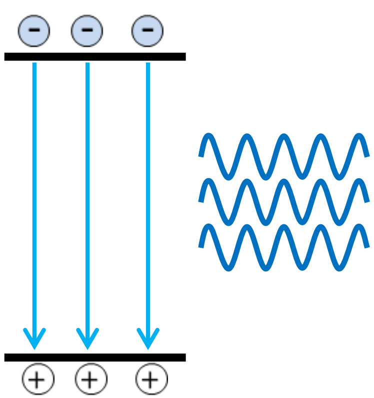
Ideal compromise of:
- Easy synthesis
- Color control
- High Conversion Efficiency

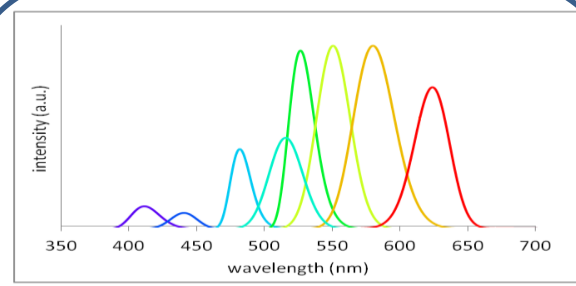
SOLID STATE LIGHTING

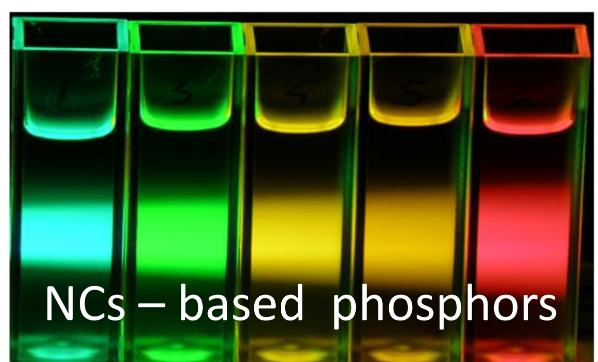
“pc-LED” system

LED
Light Emitting Diode

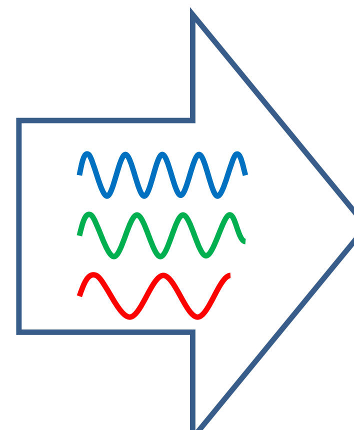
Emission of light
(electroluminesce)





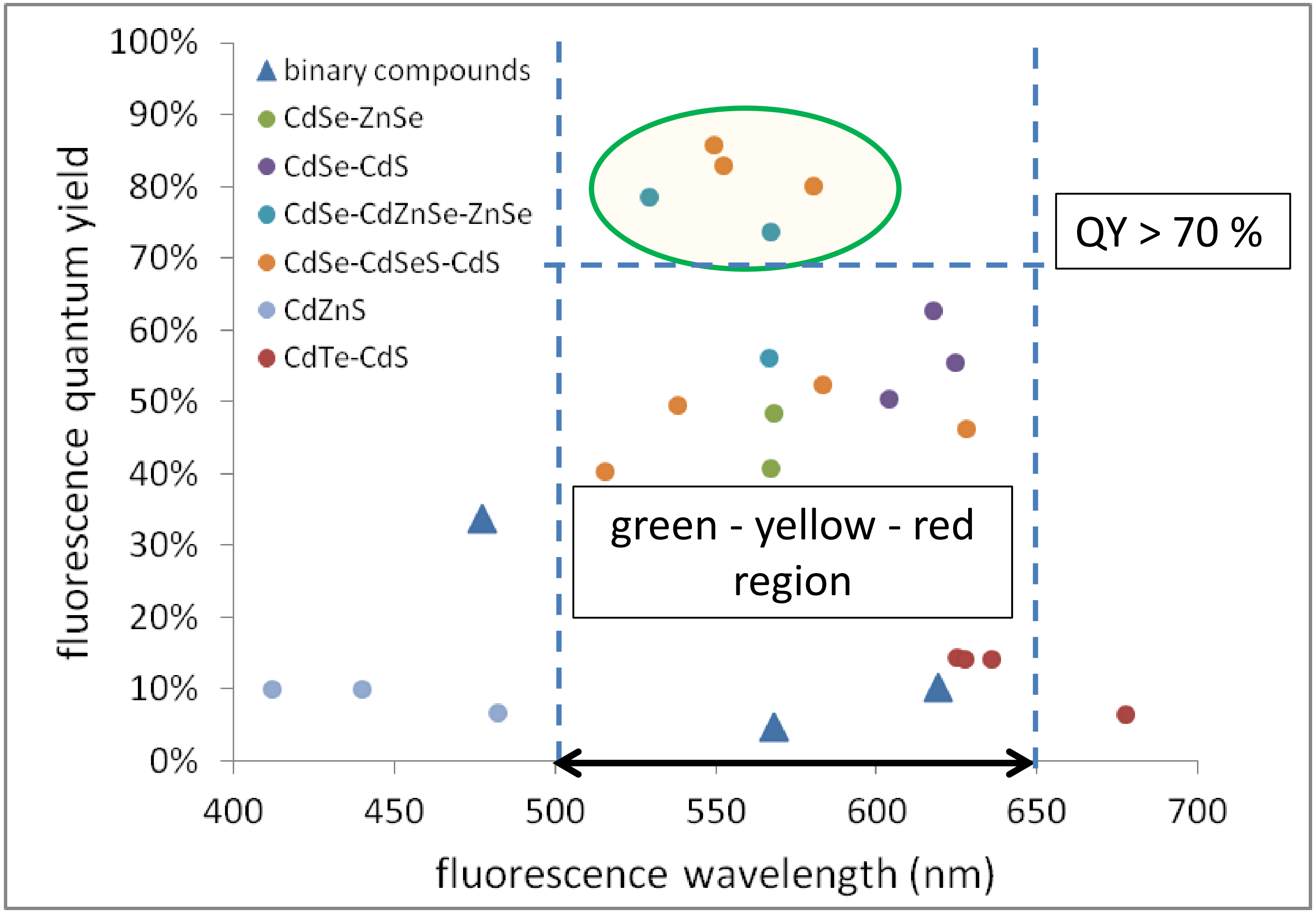


WHITE
(POLYCHROMATIC)



(1) NCs as PHOSPHORS

Available Nanocrystals



(1) NCs as PHOSPHORS

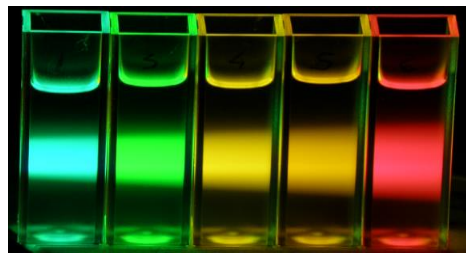
1.3 NCs / polymer composite material

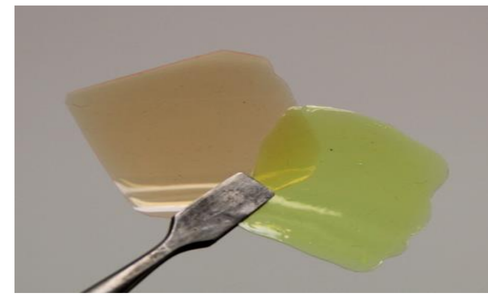
LIQUID

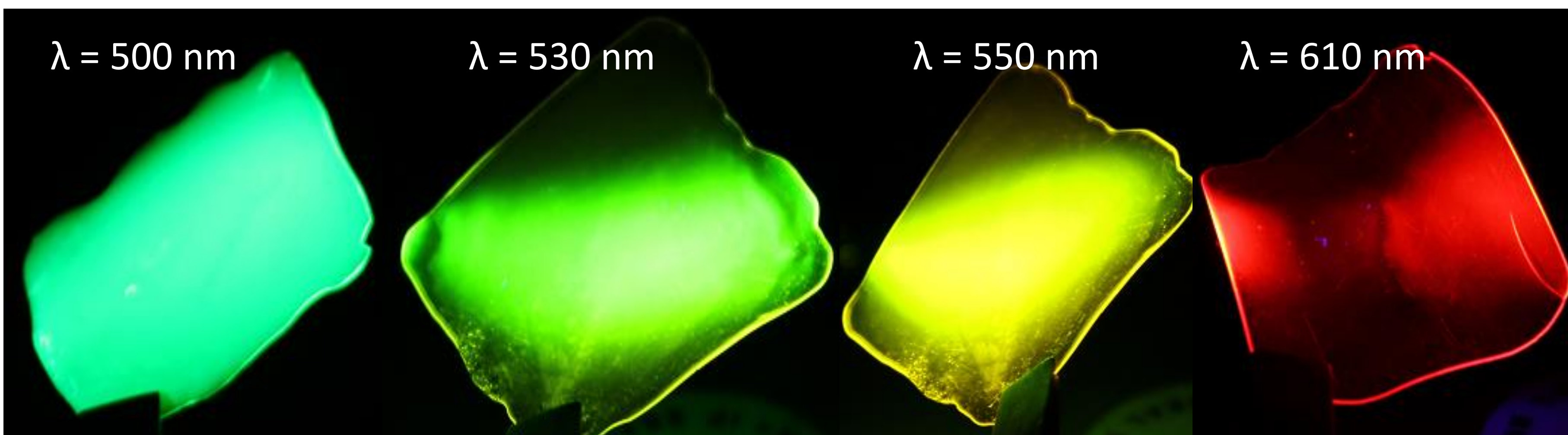
SOLID

BLEND in PMMA

$CdSe_xS_{1-x}$- CdS colloidal NCs







(1) NCs as PHOSPHORS

(still in development)

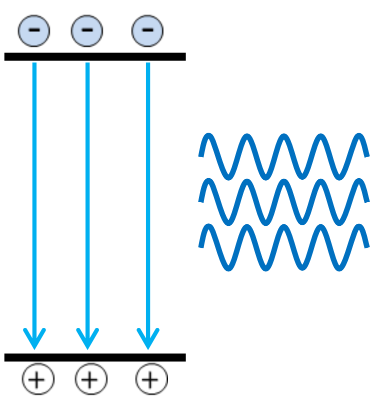
1.3 NCs / polymer composite material

COST-EFFECTIVE
white lighting device

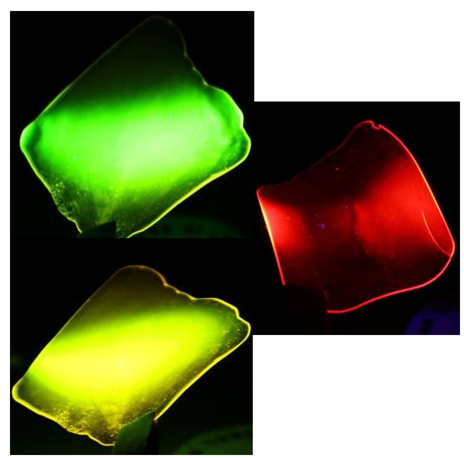
"pc-LED" system

LED
Light Emitting Diode

Emission of light
(electroluminesce)



NCs in polymeric lenses
as PHOSPHORS



WHITE
(POLYCHROMATIC)