



UNIVERSITÀ  
DEGLI STUDI DI TRIESTE

# Engineering (with) Nanoparticles

*Ljubljana – February 5<sup>th</sup>, 2020*

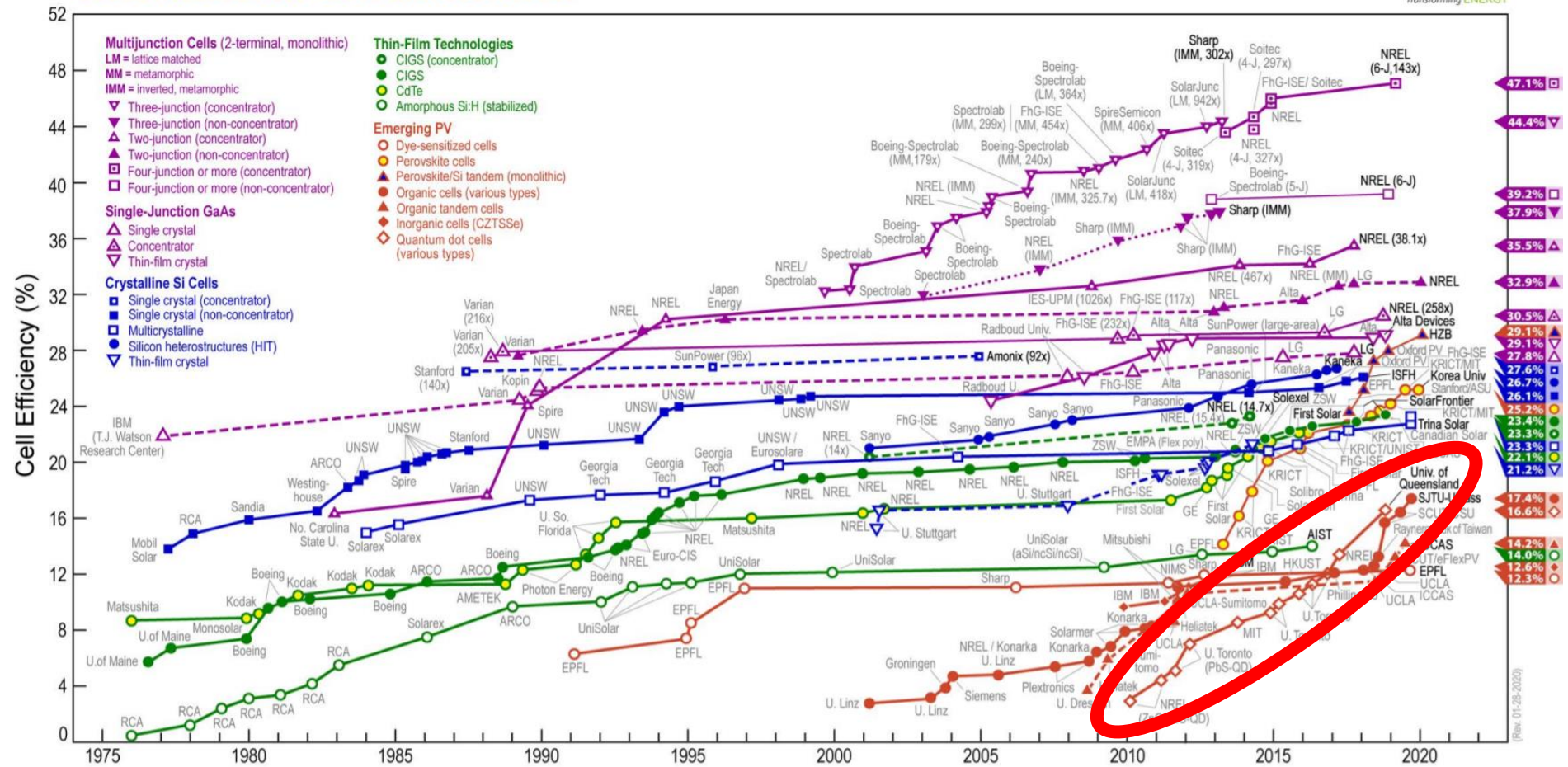
Vanni Lughi

*DIA – Department of Engineering and Architecture, University of Trieste*

[vlughi@units.it](mailto:vlughi@units.it)

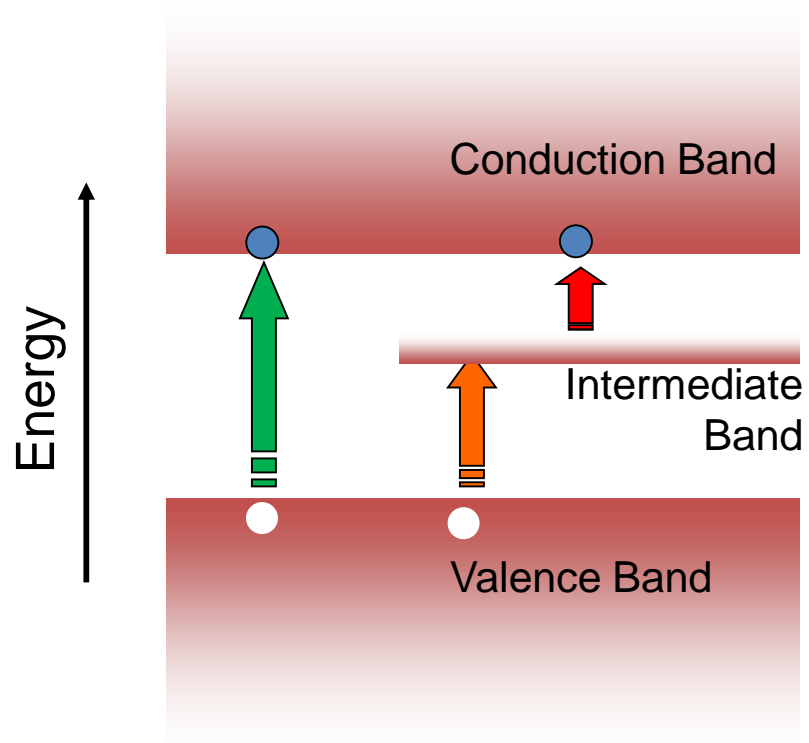
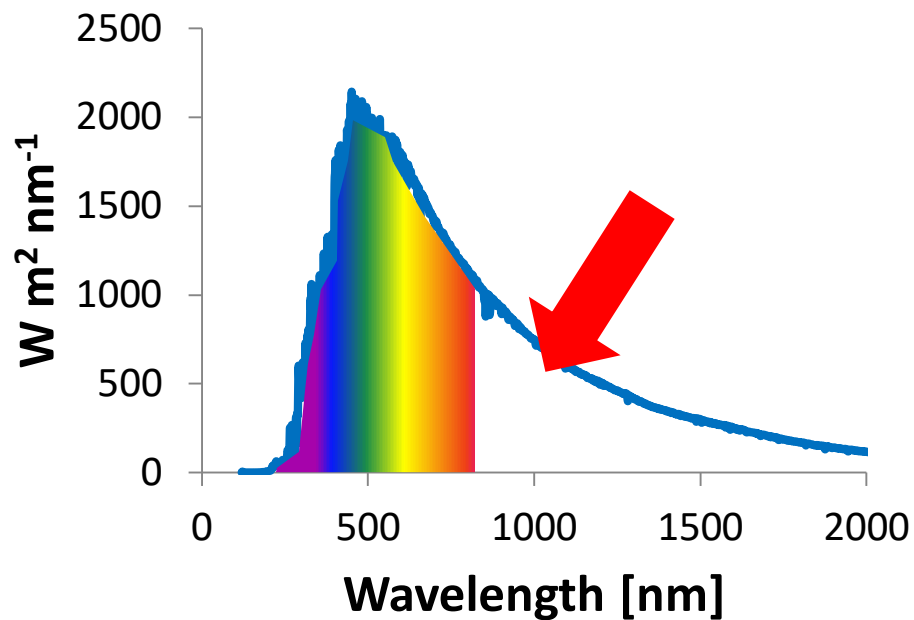
# Nanotechnology in photovoltaics

## Best Research-Cell Efficiencies



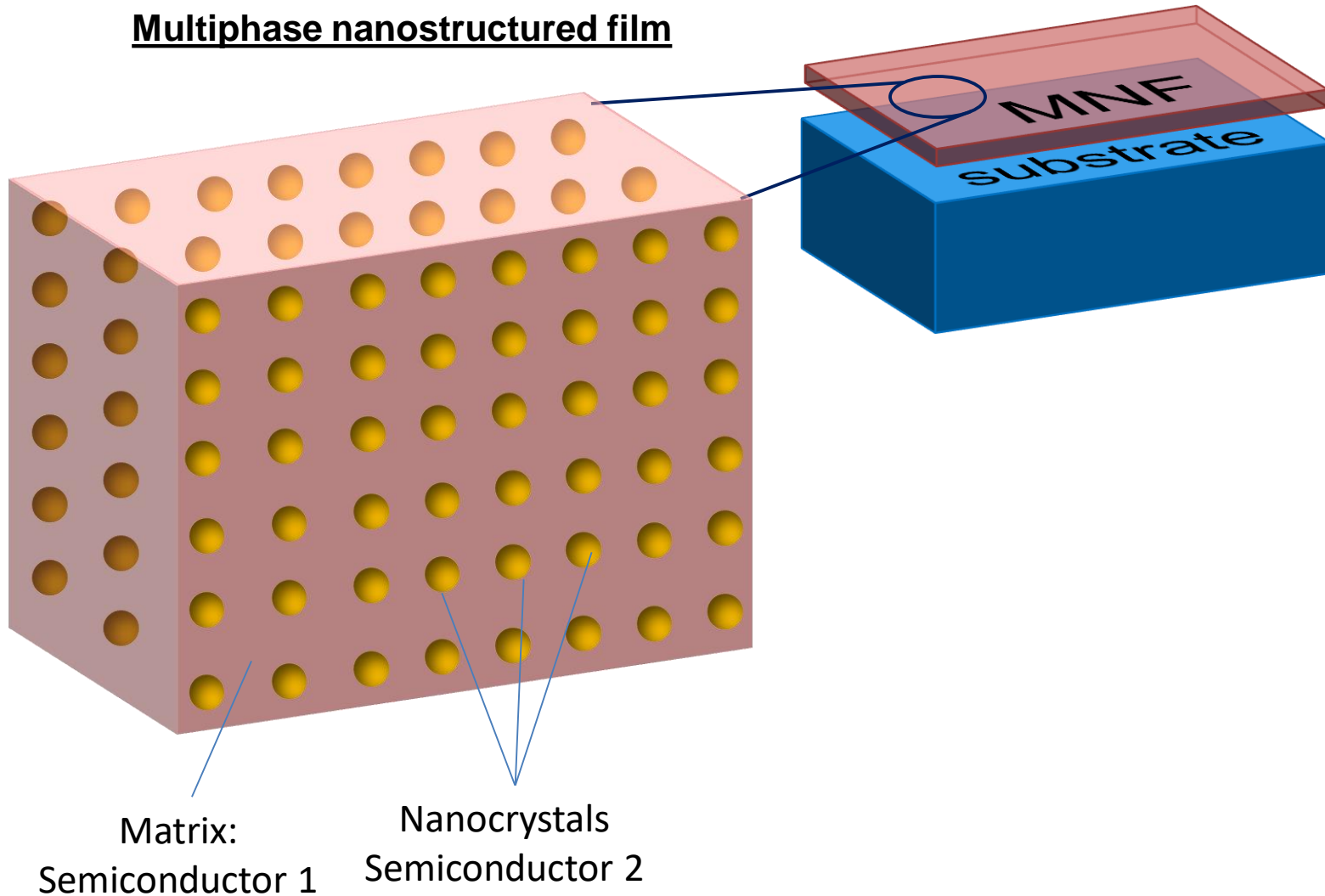
# Beyond the single junction limit

- Using Low Energy Photons

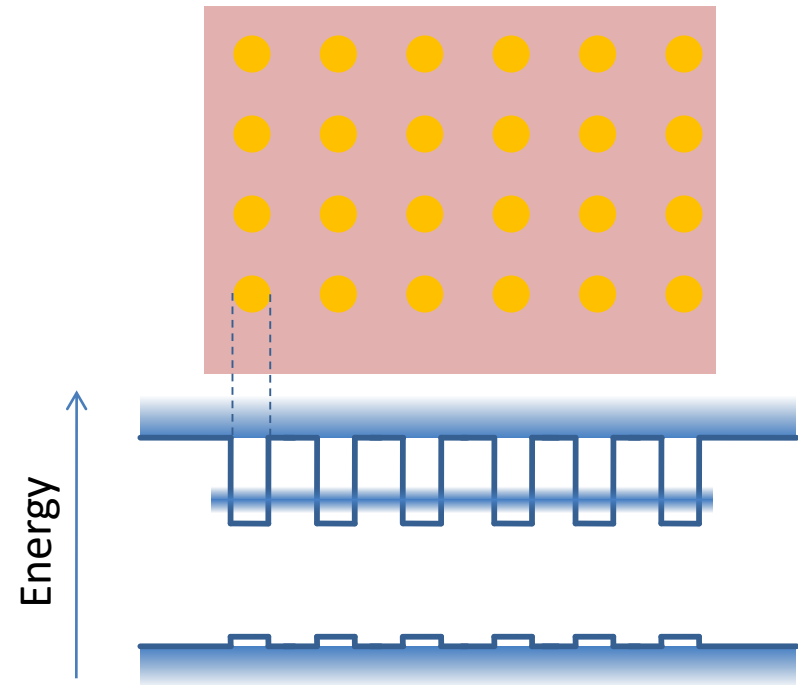
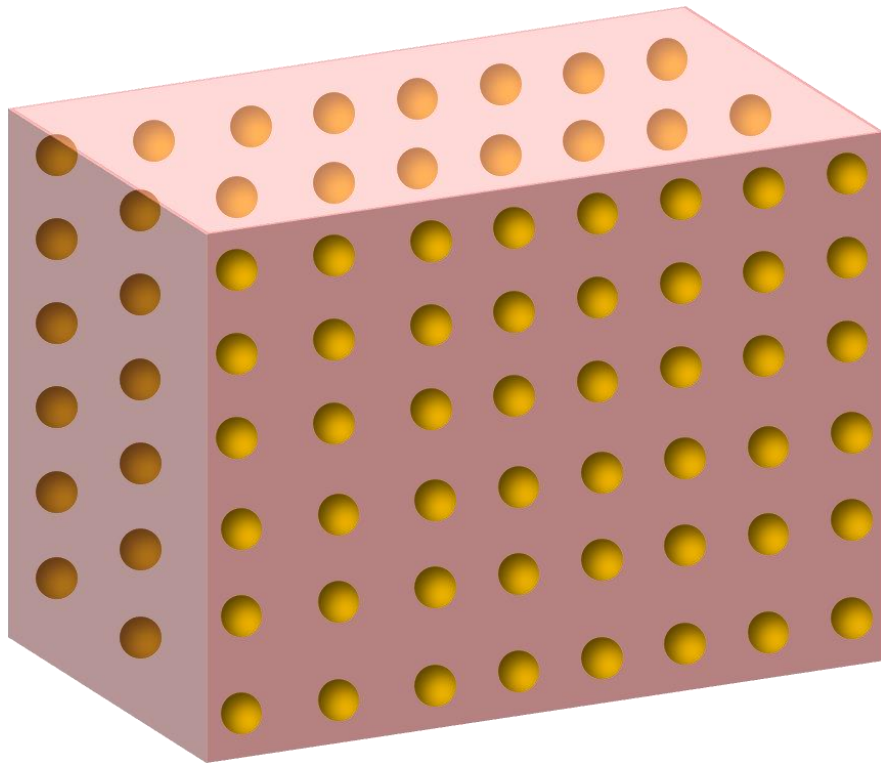


# Intermediate Band Materials

## Multiphase nanostructured film



# Intermediate Band Materials

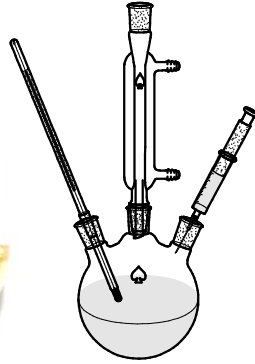


# Multiphase Nanostructured Films

## - Our Approach to Fabrication -

Synthesis of **nanocrystals**  
in colloidal suspension  
(building blocks)

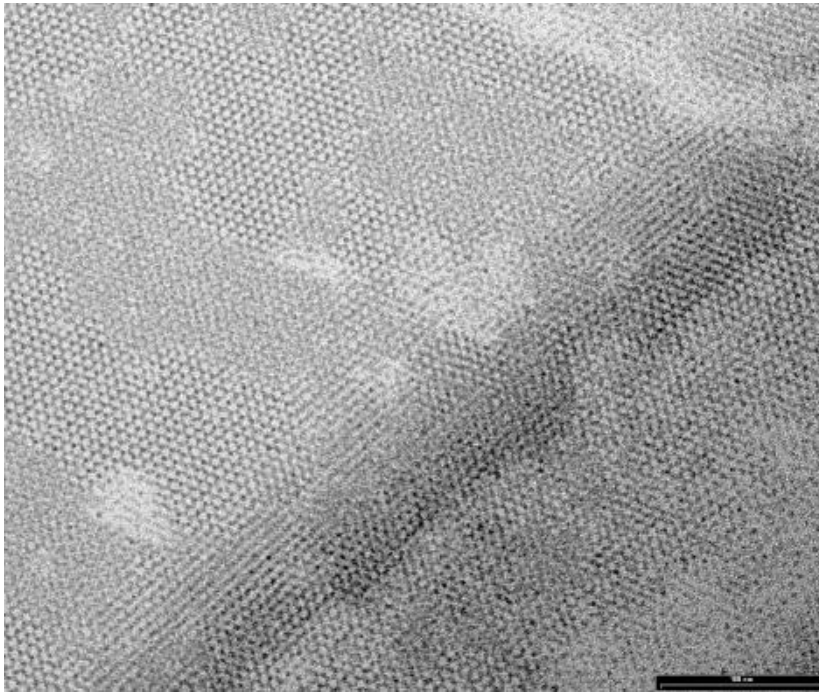
1



- Bottom Up -> Fully Tunable
- Colloidal Chemistry -> Inexpensive

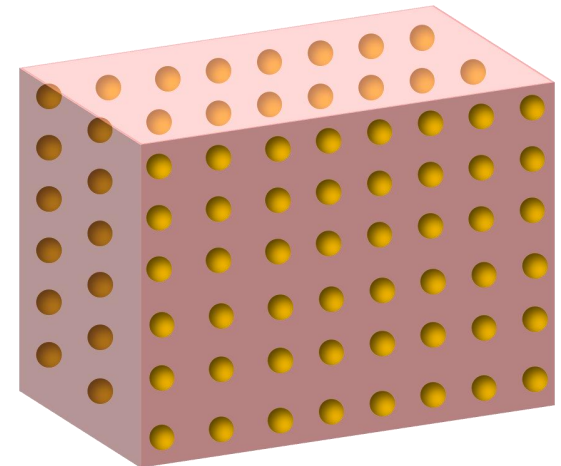
Assembly of close-packed nanocrystal arrays

2



3

Obtain a fully dense  
**nanostructured film**  
(inorganic)



# Contents

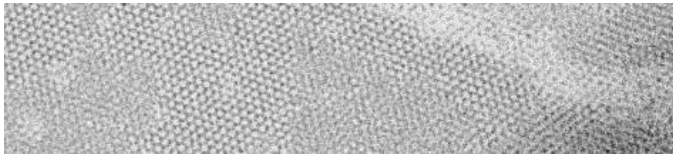
- Motivation: fabricating a QD-based material for upconversion

- What we learned from:

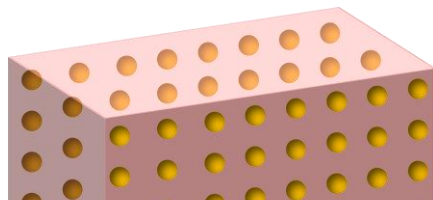
1. Synthesis of nanocrystals



2. Surface chemistry and assembly



3. Obtaining the *QD array-in-a-matrix* architecture



- Control of optical properties
- QD synthesis at full yield
- Nucleation and growth model in closed systems
- Precise engineering of heterostructures

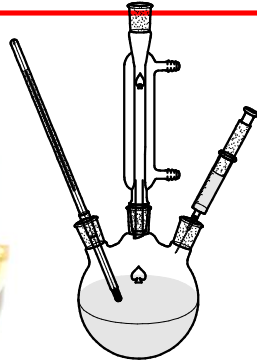
- Large scale ordered assembly
- Assembly with inorganic capping
- Supramolecular assembly

- Quantification of interdiffusion in model systems
- First evidence of upconversion

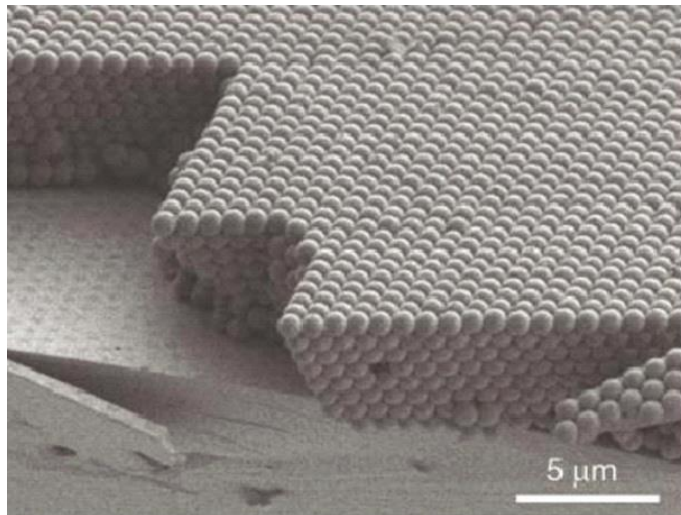
# Multiphase Nanostructured Films

## - Our Approach to Fabrication -

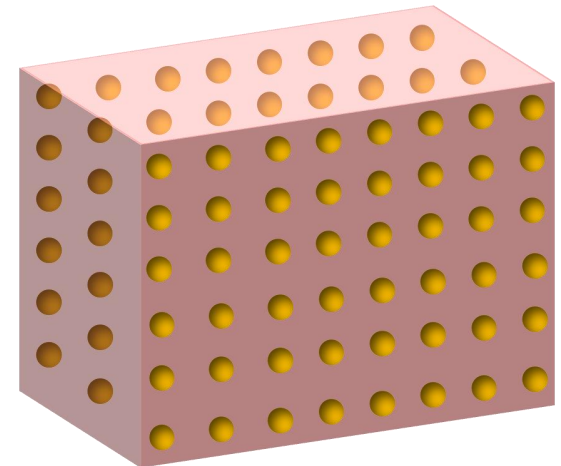
1 Synthesis of **nanocrystals**  
in colloidal suspension  
(building blocks)



2 Assembly of close-packed nanocrystal  
arrays in the form of thin films  
(colloidal thin film solids)

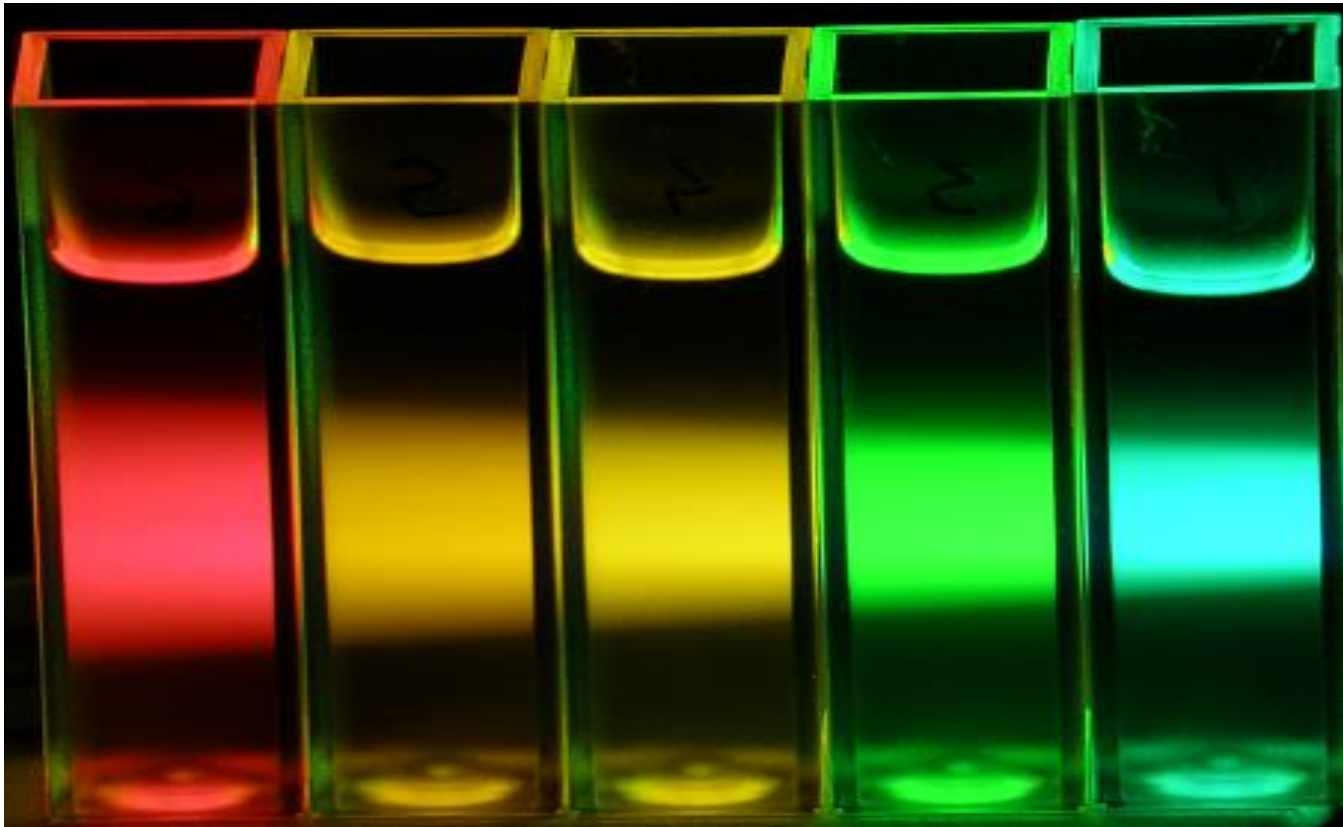


3 Obtain a fully dense  
**nanostructured film**  
(inorganic)

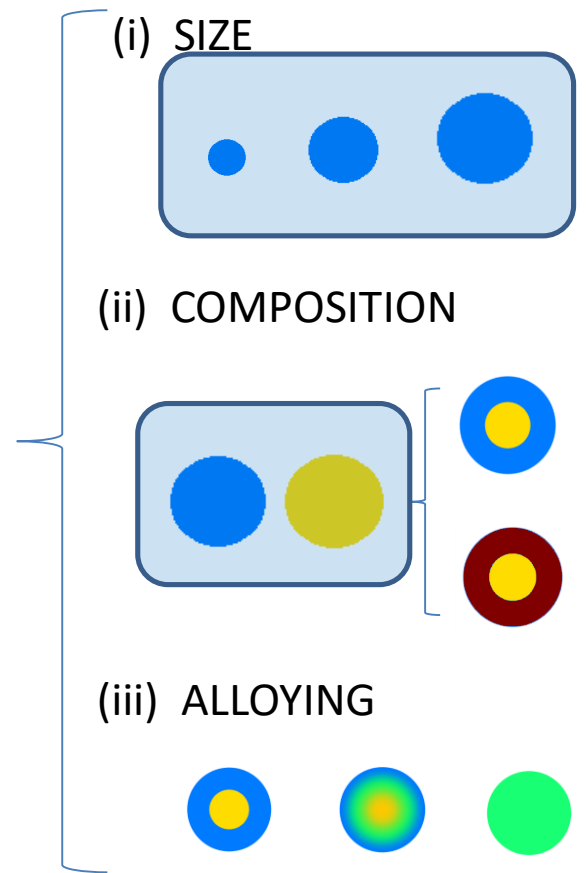
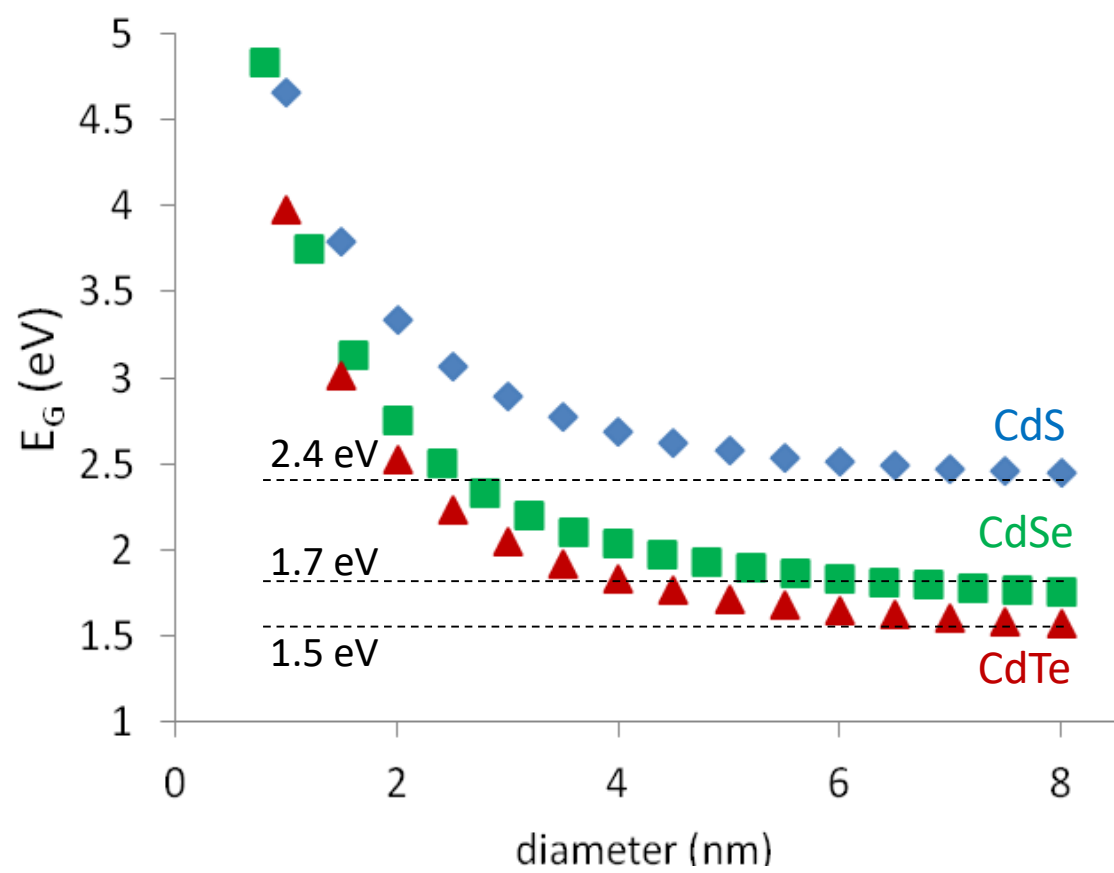




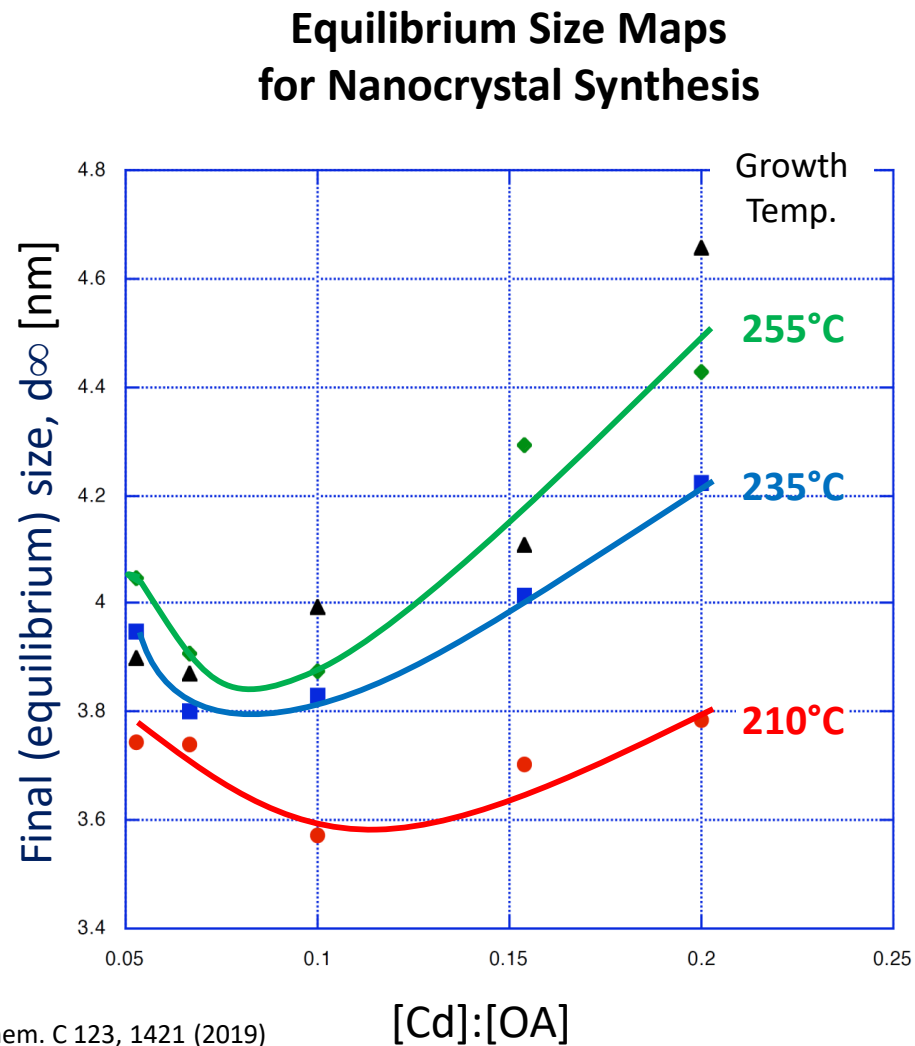
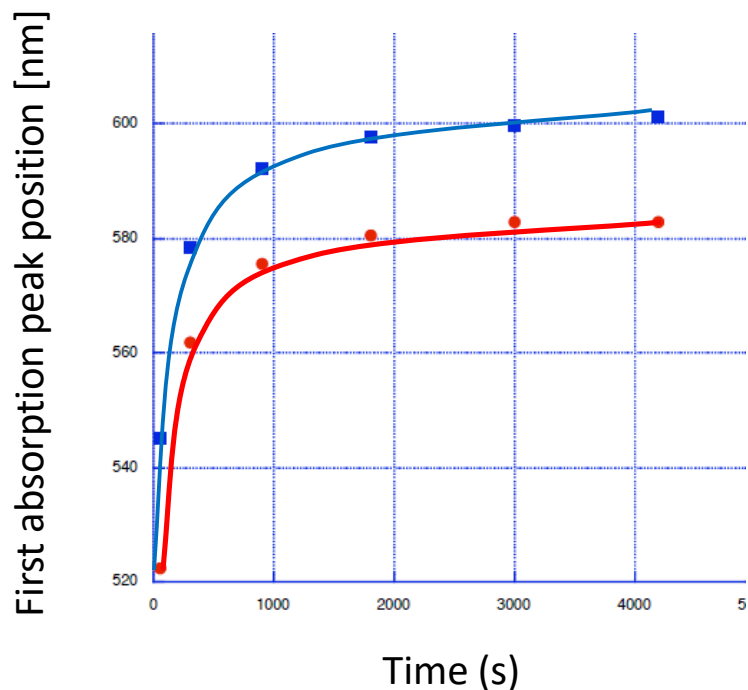
# Quantum Dot Engineering



# Tuning the Optical Properties: Size and Composition



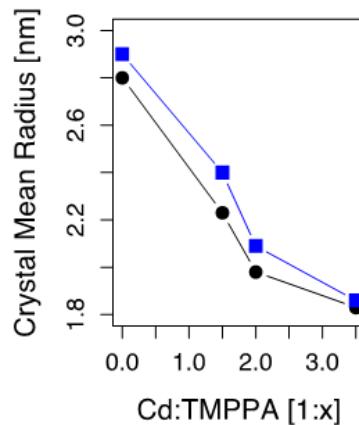
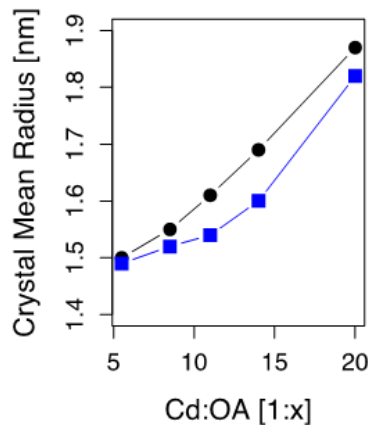
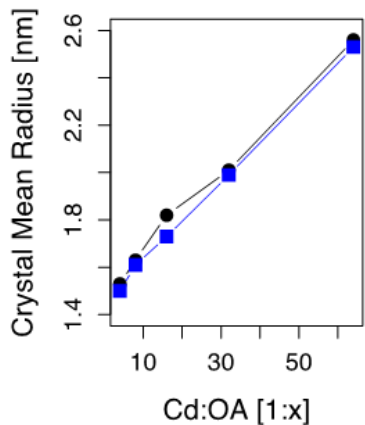
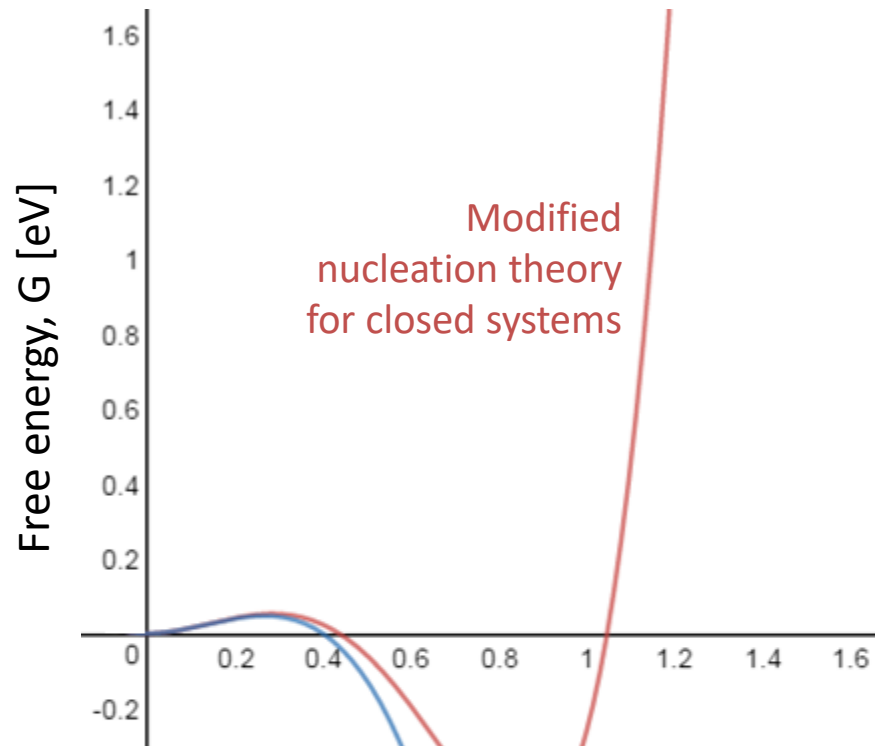
# Synthesis of Quantum Dots at Maximum Yield



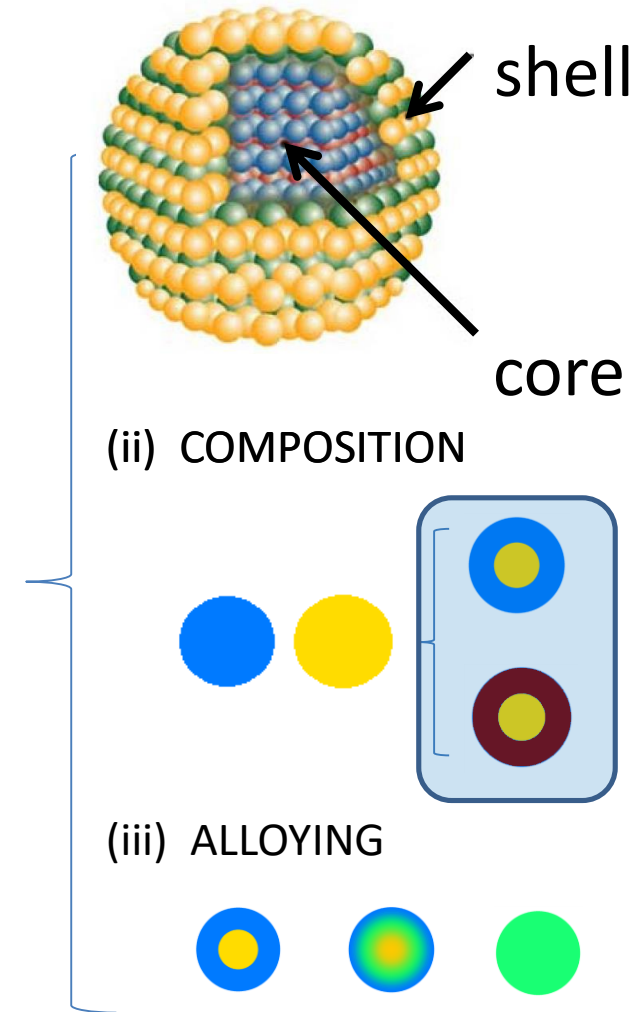
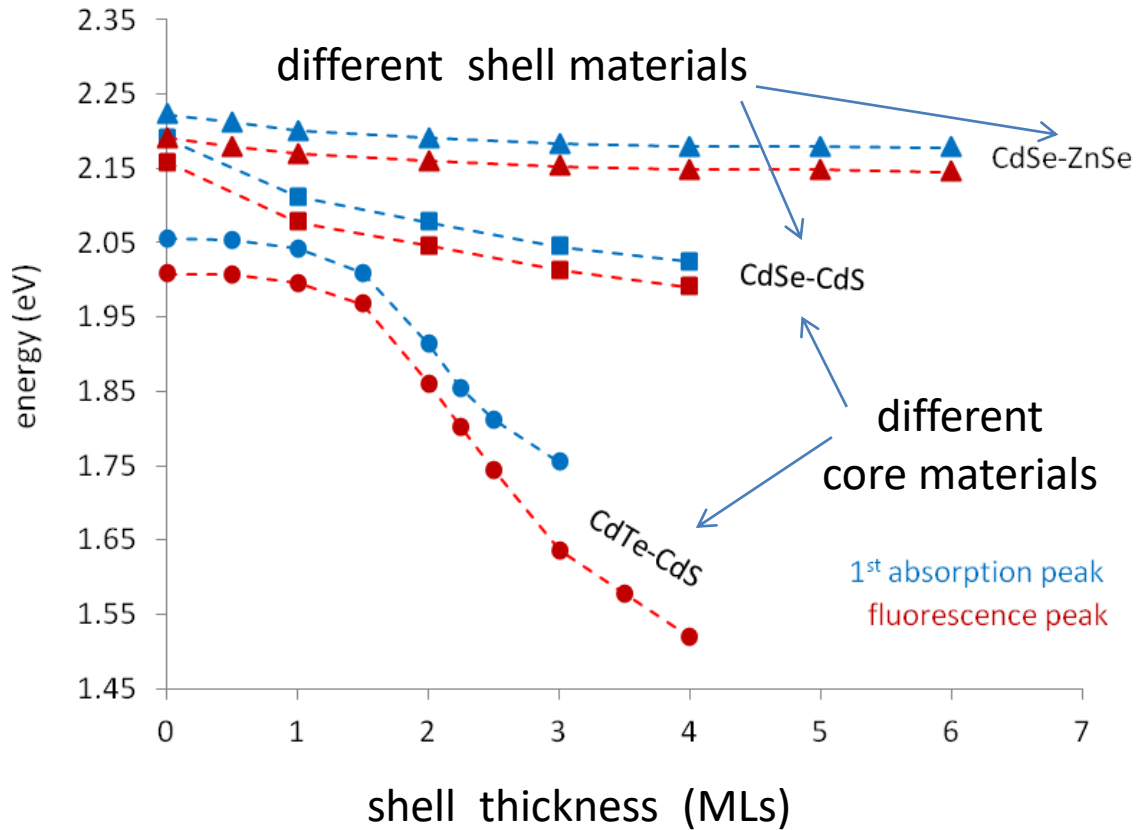
# Maximum Yield Synthesis in a Closed System



$$G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \left[ RT \ln \left( S_0 - \left( \frac{4}{3} \pi r^3 \right) \frac{C_{np}}{v_0 C_s} \right) \right]$$

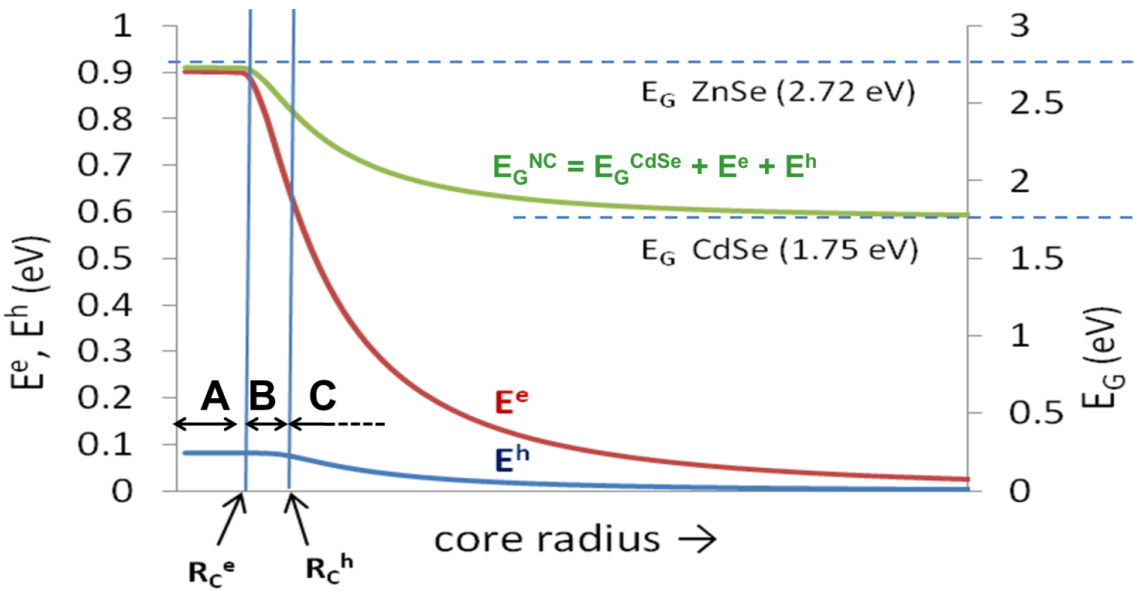
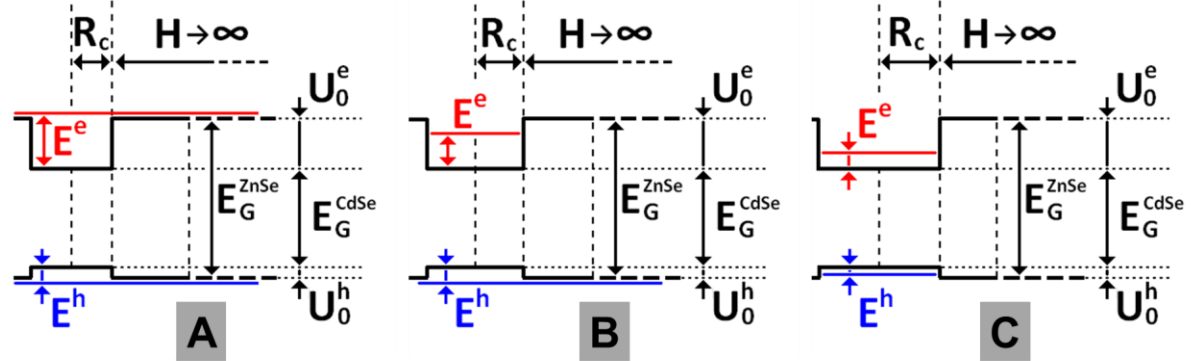
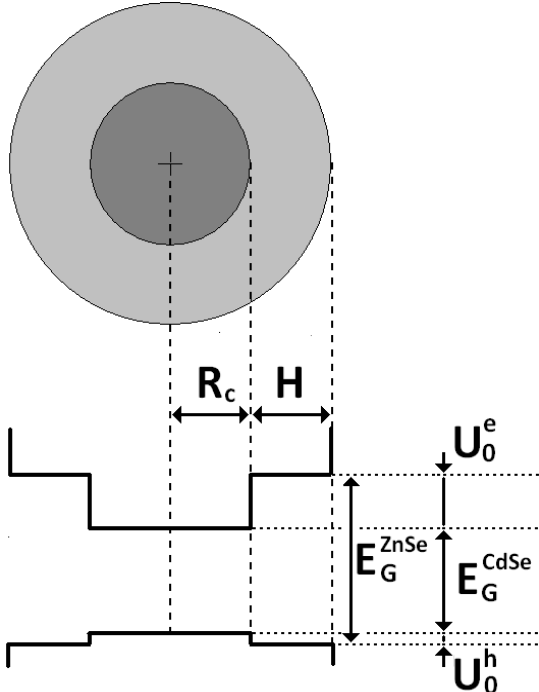


# Tuning the Optical Properties: Shell

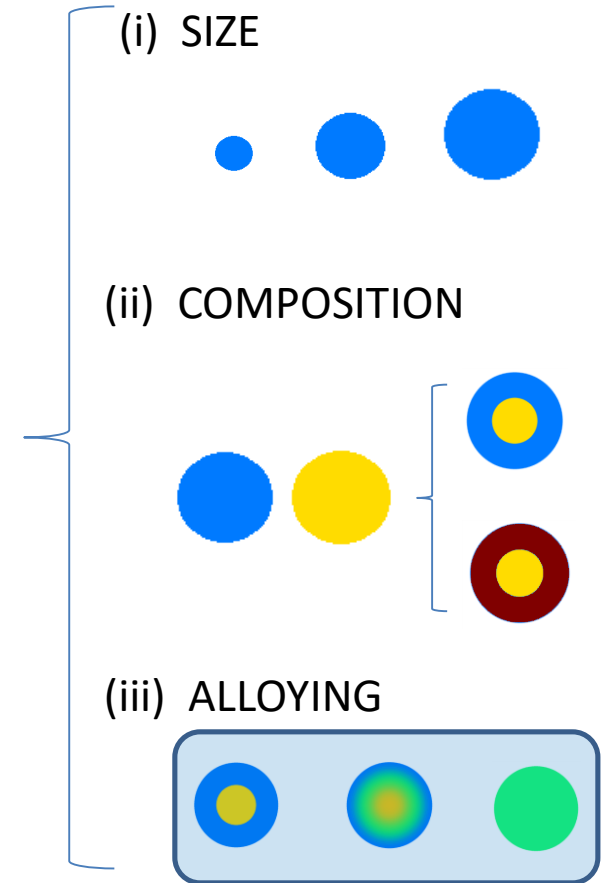
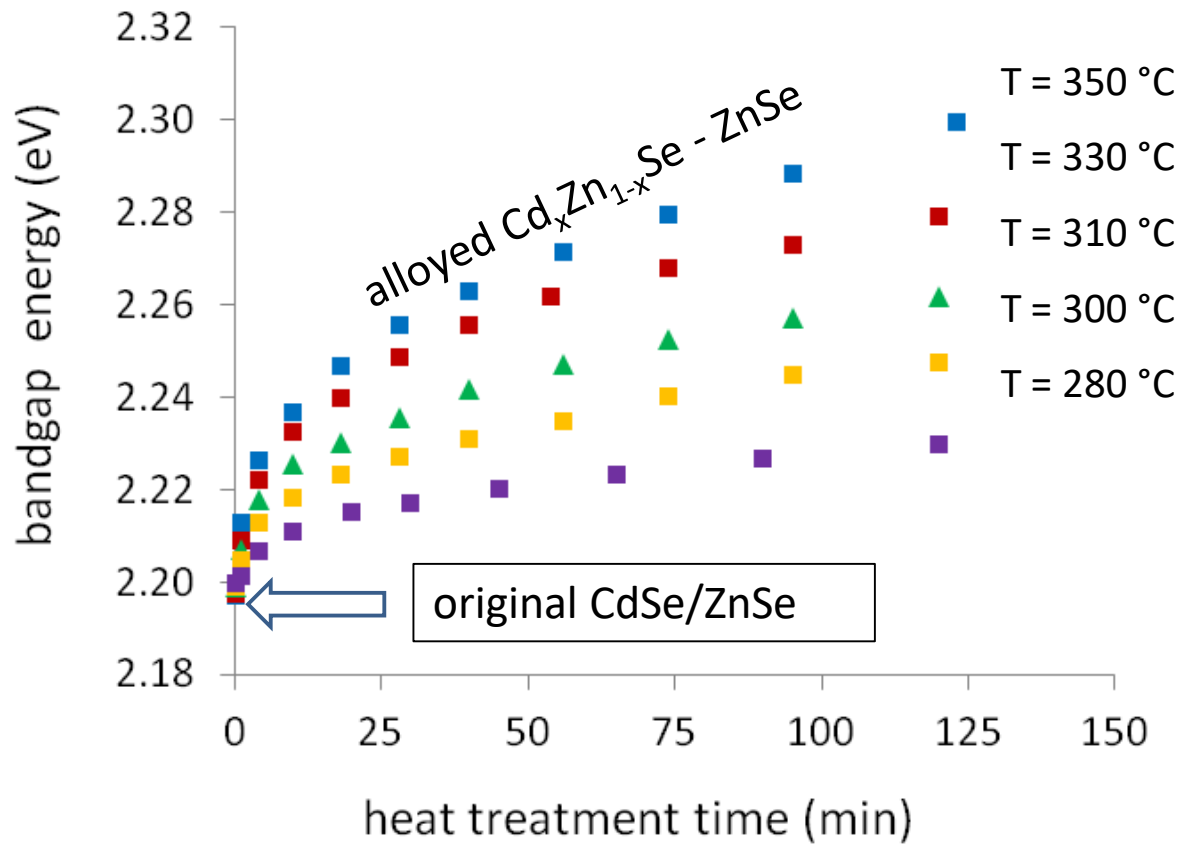


# Modeling the Optical Properties of Nanoheterostructures

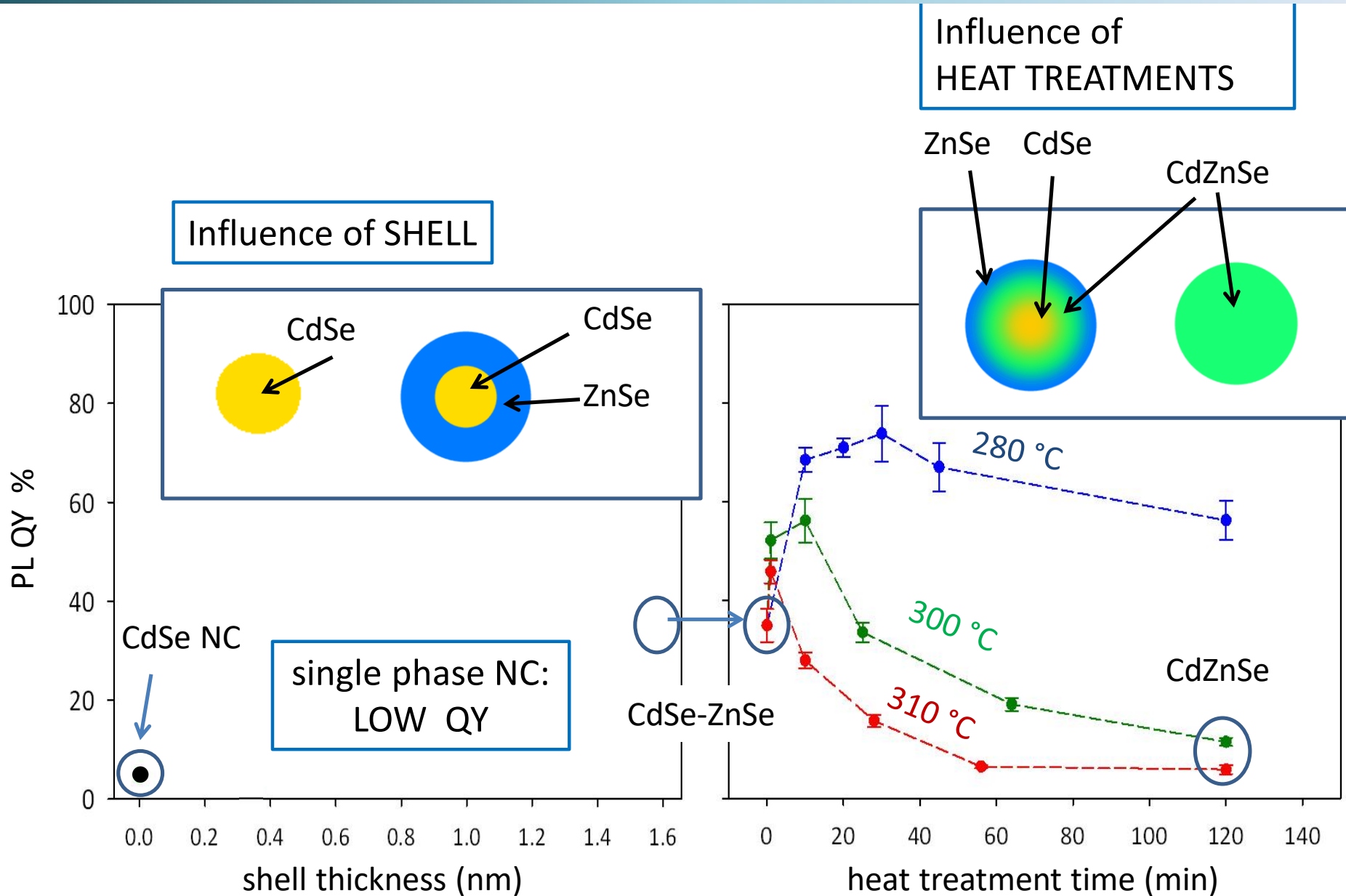
## Effective mass model



# Tuning the Optical Properties: Interdiffusion

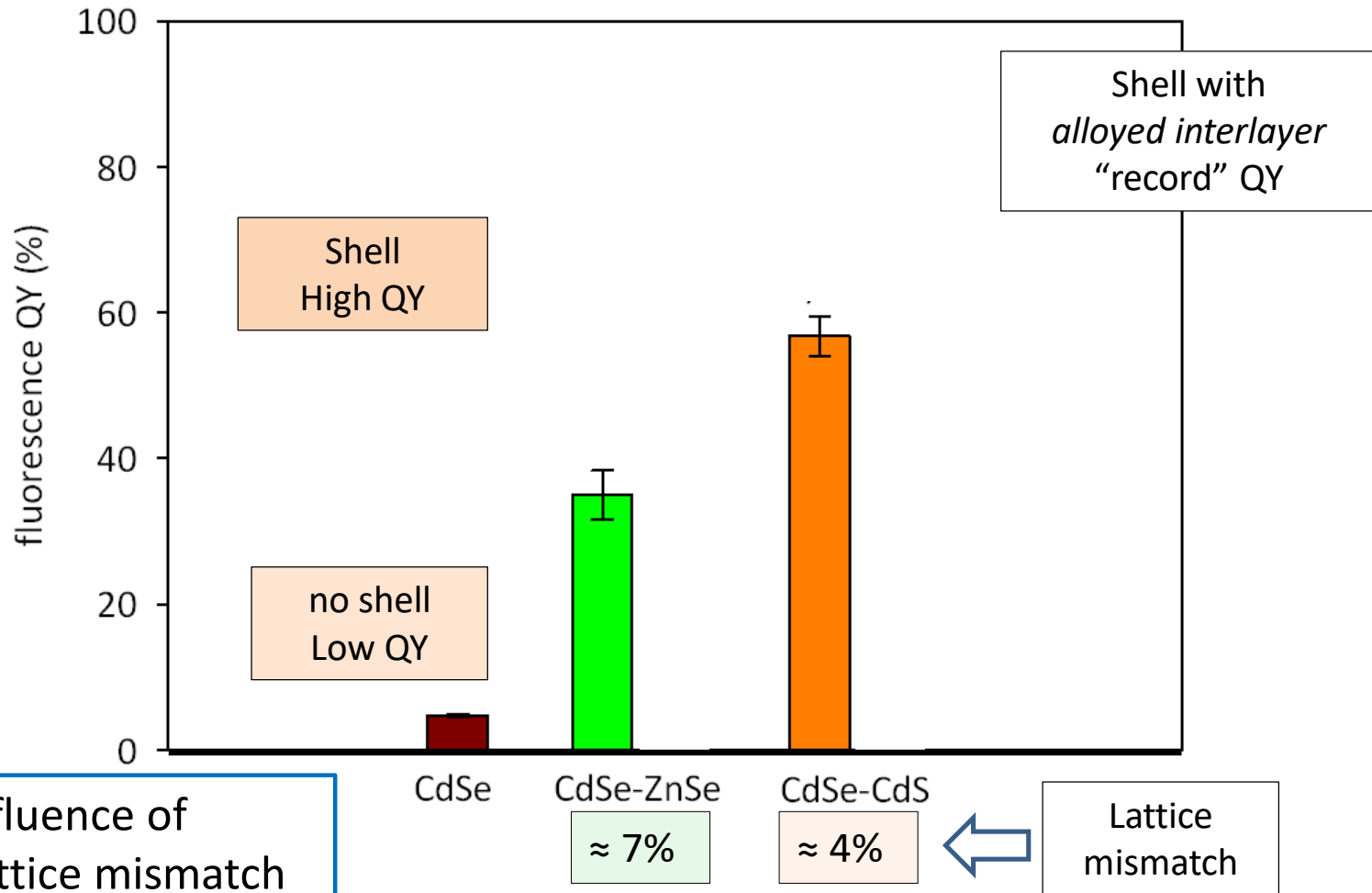


# Optimizing the Quantum Yield





# Optimizing the Quantum Yield

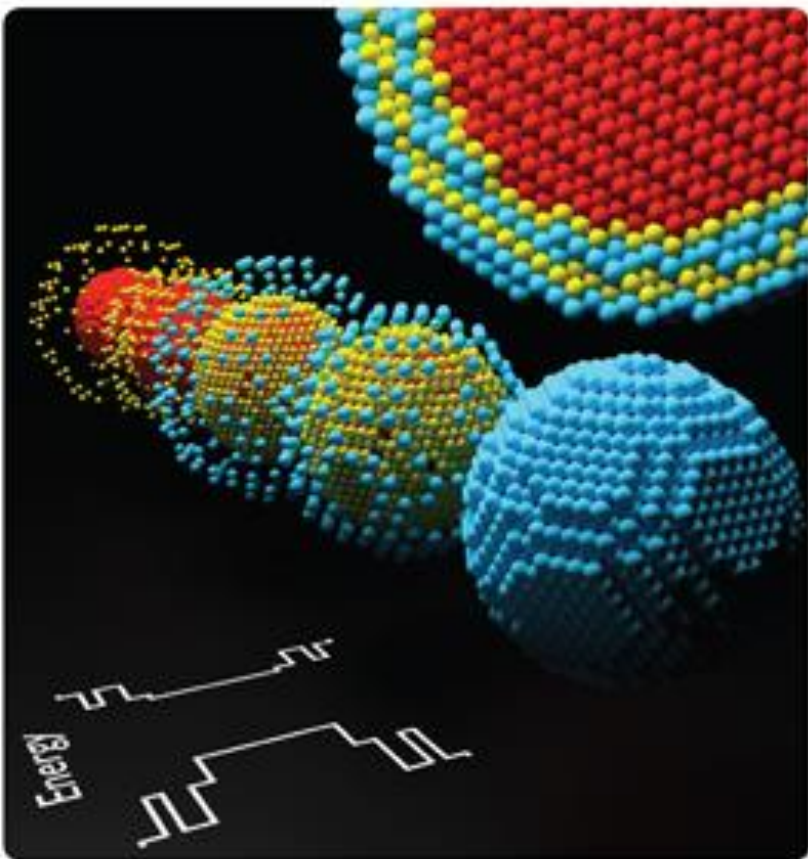


# Precise Engineering of Semiconductor Core-Shell Structures

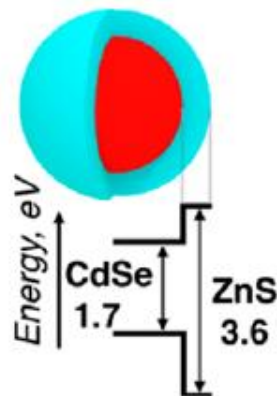
via Colloidal Atomic Layer Deposition (cALD)

**cm** CHEMISTRY OF MATERIALS

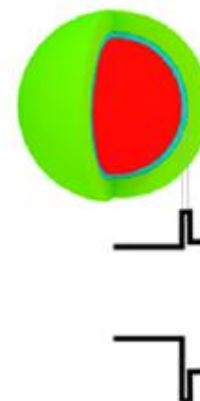
OCTOBER 18, 2017 | VOLUME 29 | NUMBER 28 | pubs.acs.org/cm



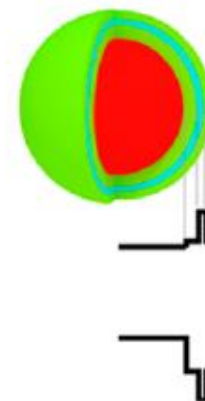
CdSe/ZnS4



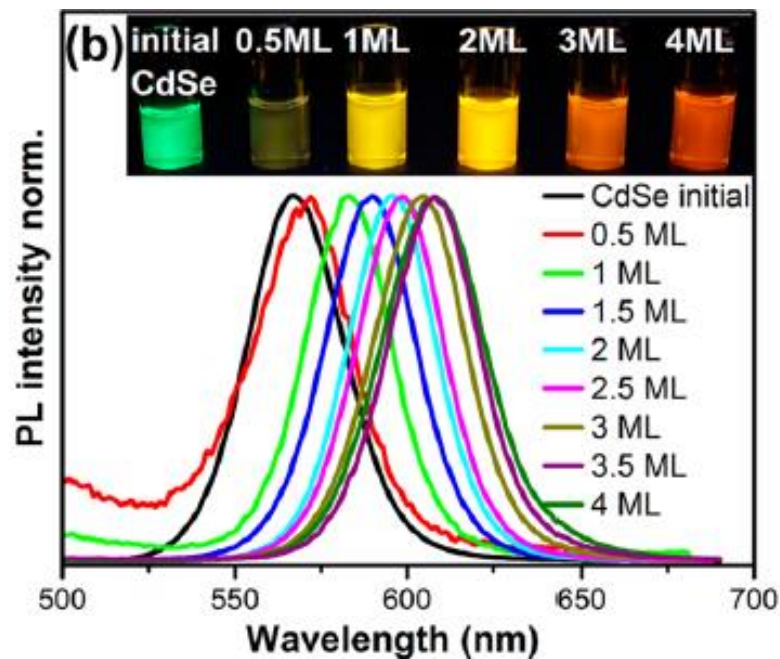
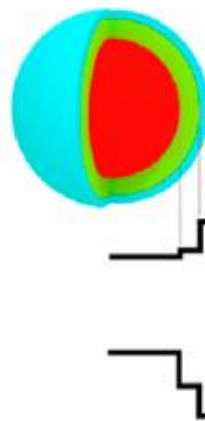
CdSe/ZnS/CdS3



CdSe/CdS2/ZnS/CdS



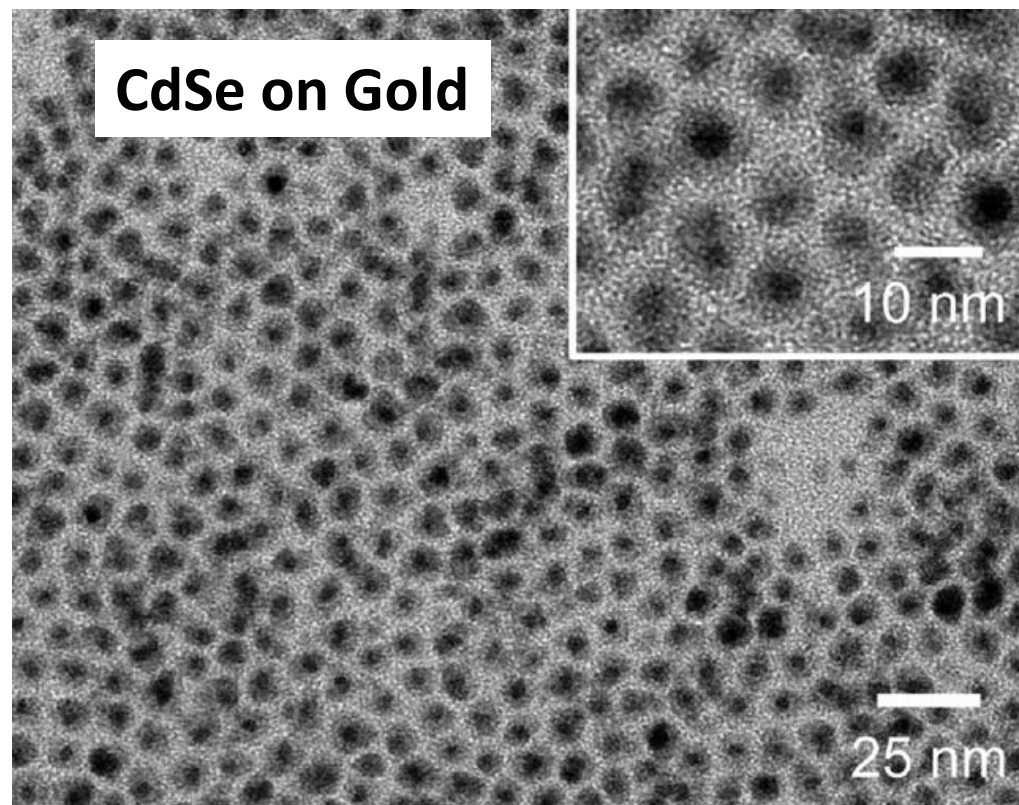
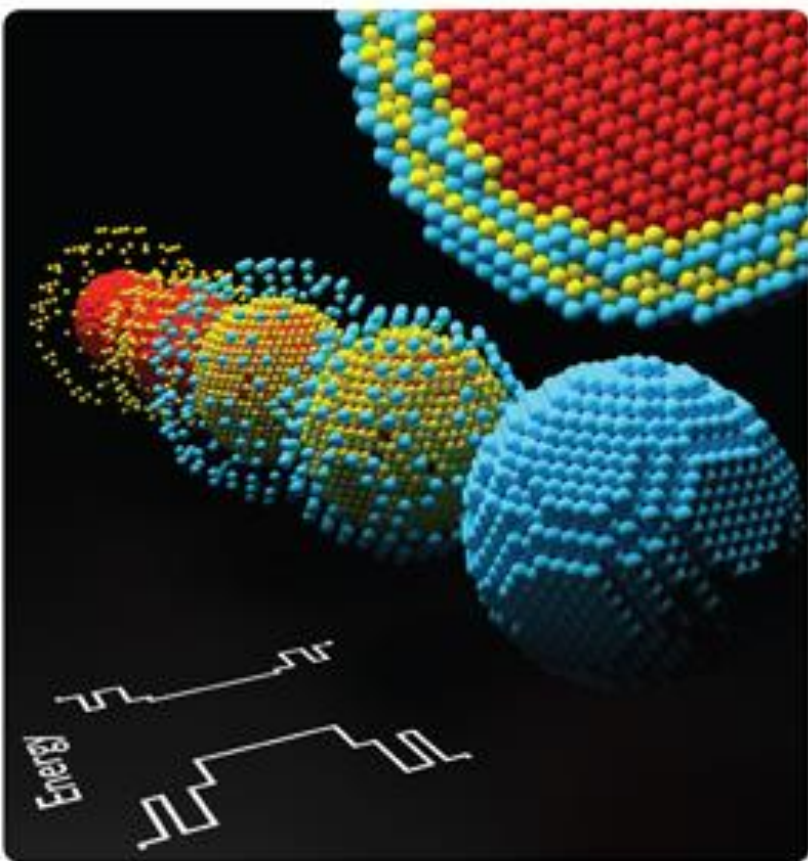
CdSe/CdS3/ZnS



# Precise Engineering of Hybrid Core-Shell Structures

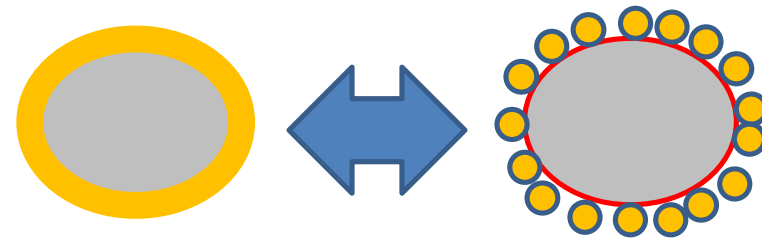
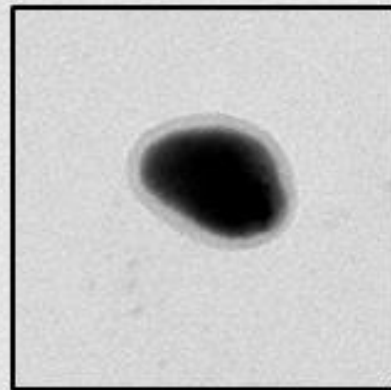
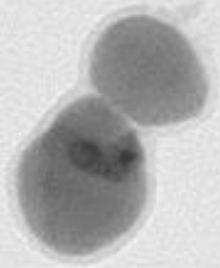
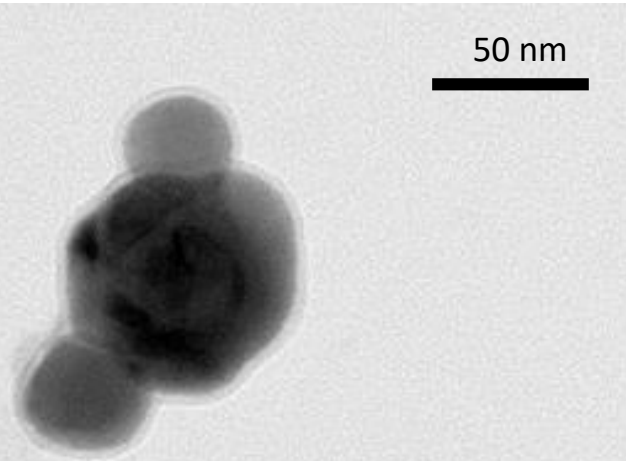
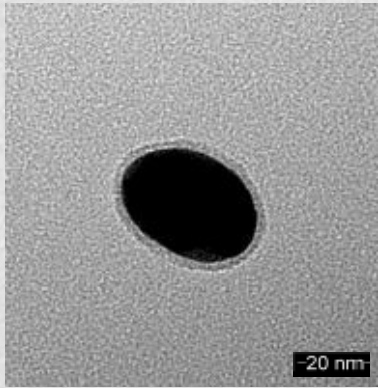
via Colloidal Atomic Layer Deposition (cALD)

**cm** CHEMISTRY OF MATERIALS  
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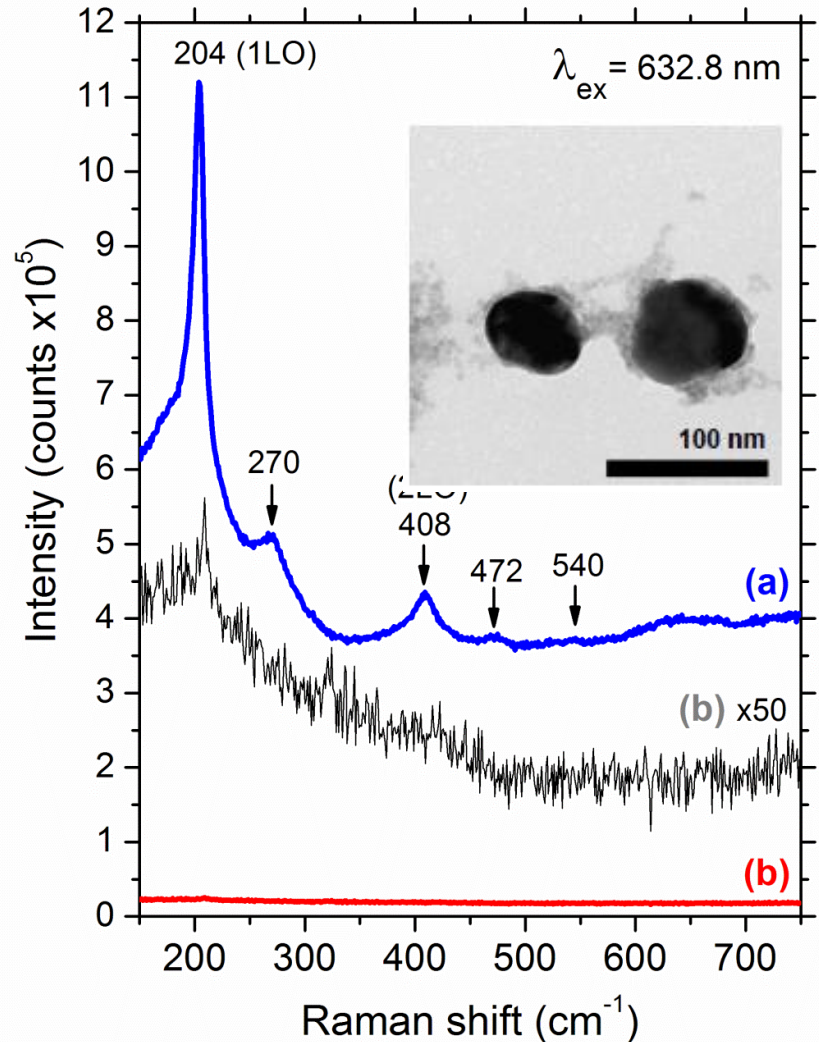
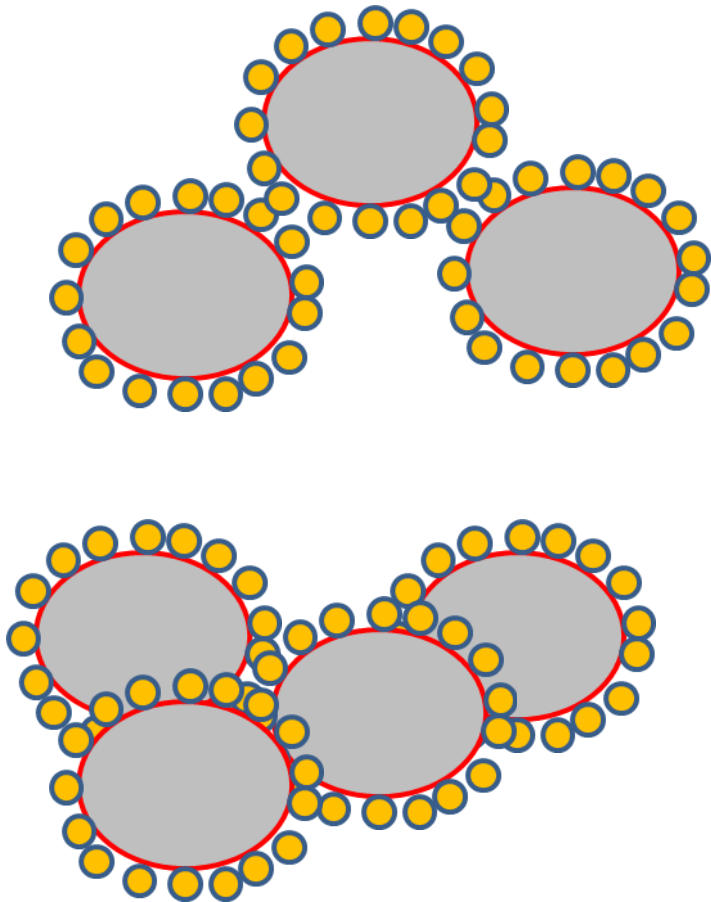


# Hybrid Core-Shell Structures

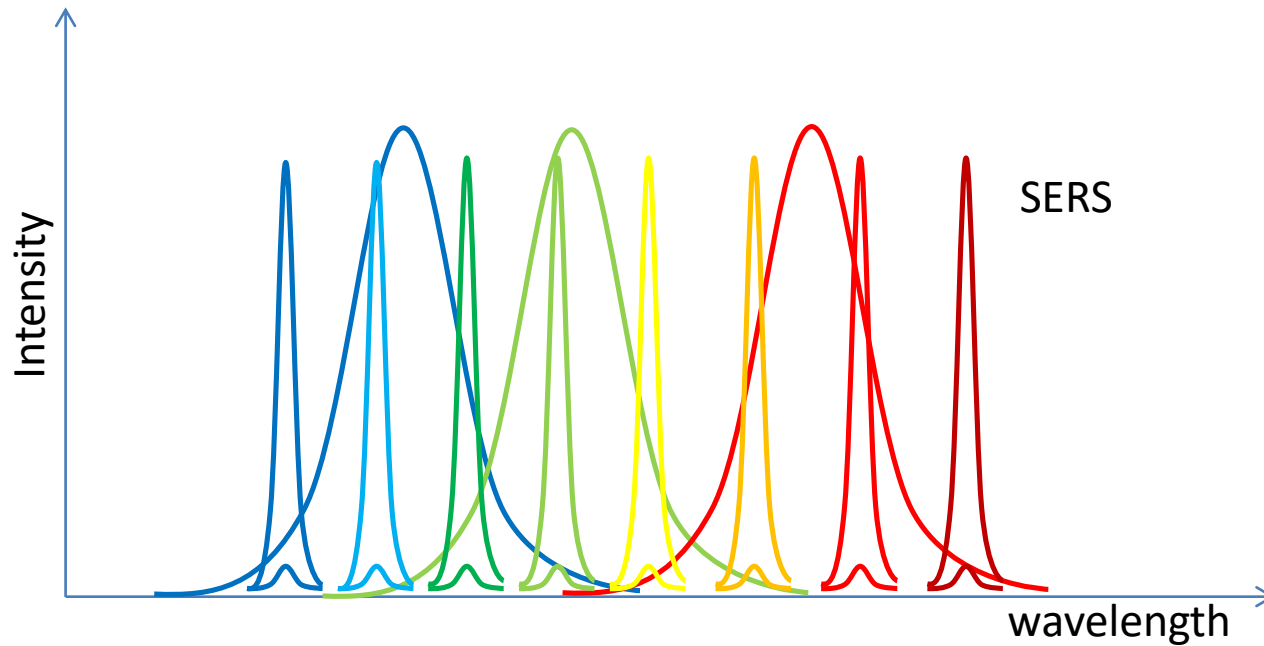
via Chemical Bath NanoDeposition



# Nano-hybrid particles as SERS-based optical biomarkers



# Raman vs Photoluminescence



# QD as Phosphors in Solid Materials

NCs / polymer composite material

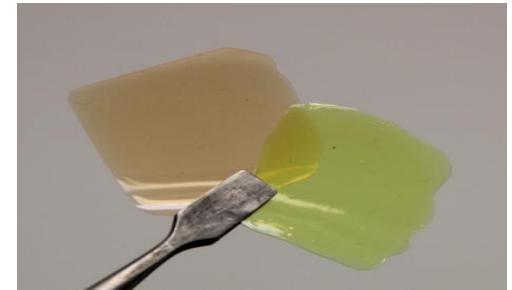
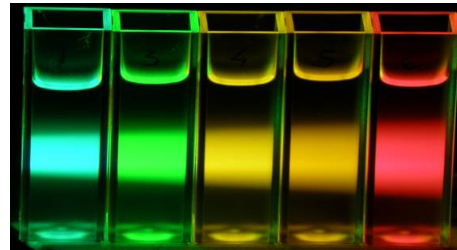
LIQUID



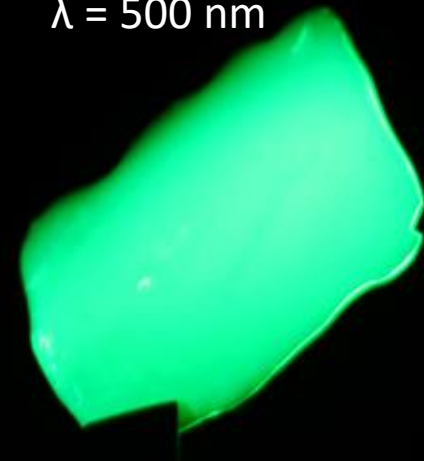
SOLID

BLEND in PMMA

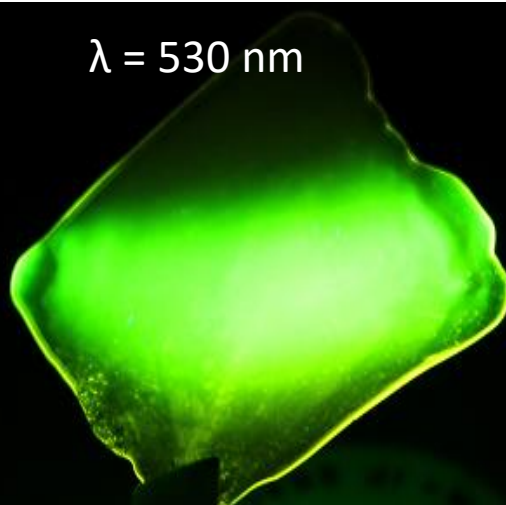
$\text{CdSe}_x\text{S}_{1-x}$ - CdS colloidal NCs



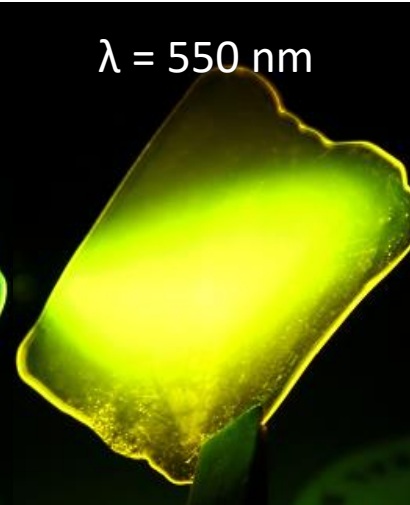
$\lambda = 500 \text{ nm}$



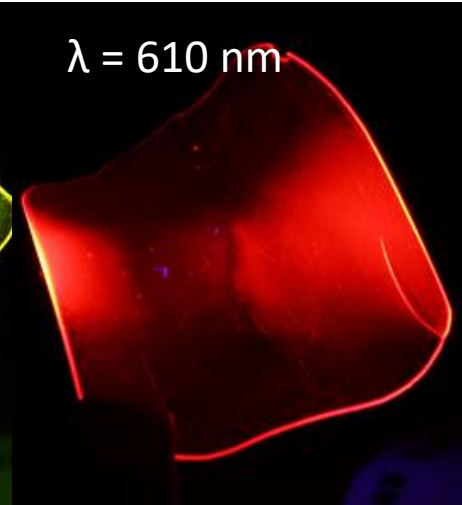
$\lambda = 530 \text{ nm}$



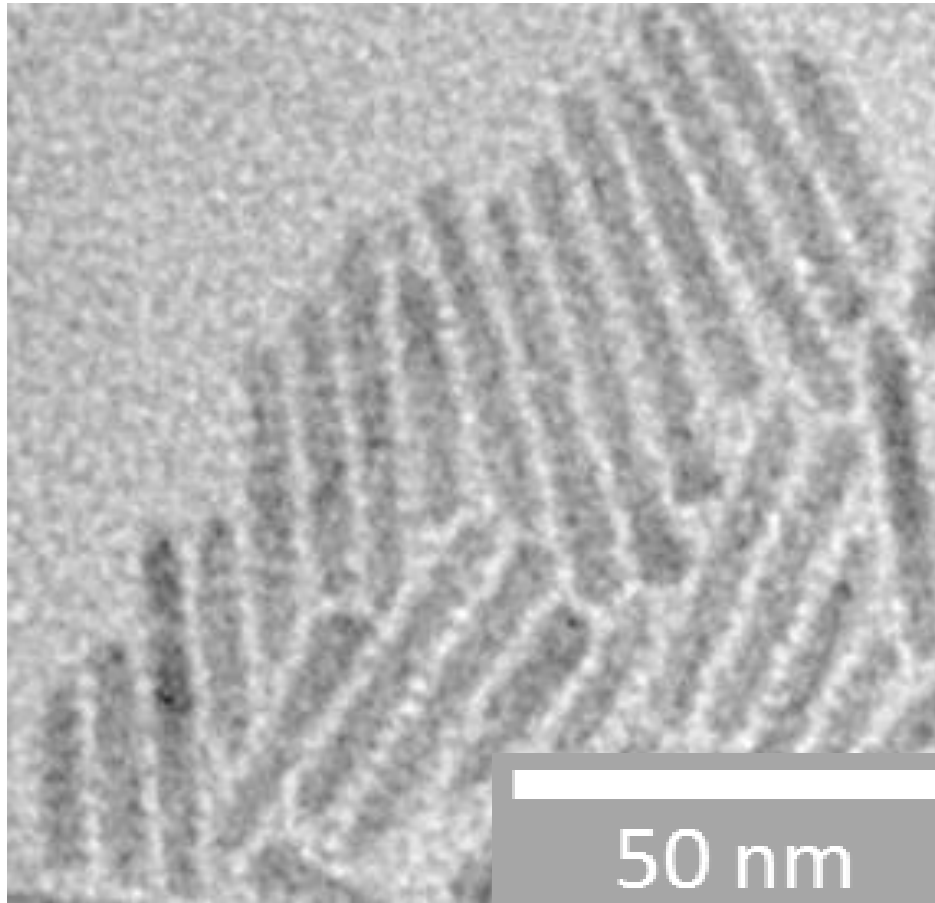
$\lambda = 550 \text{ nm}$



$\lambda = 610 \text{ nm}$

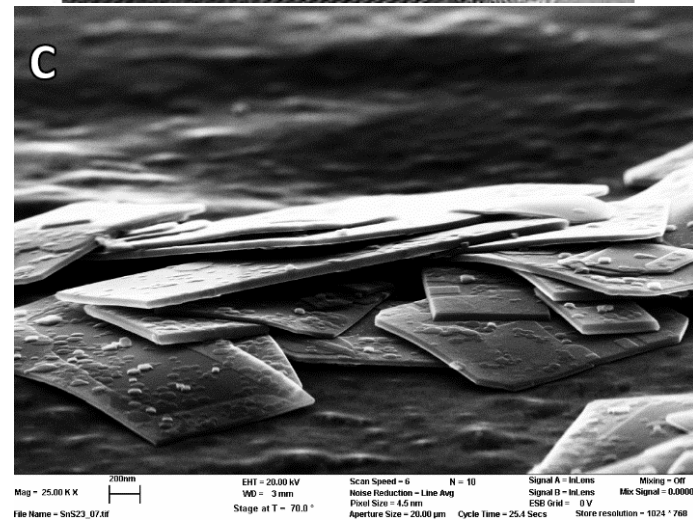
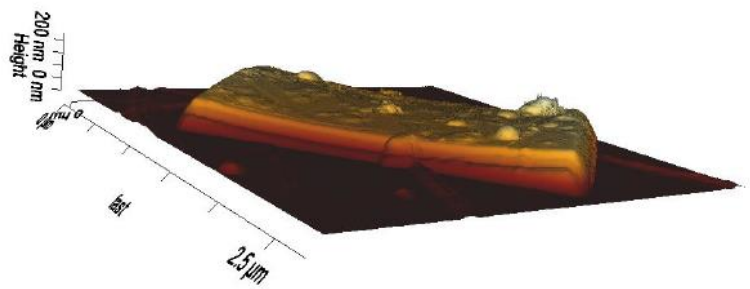
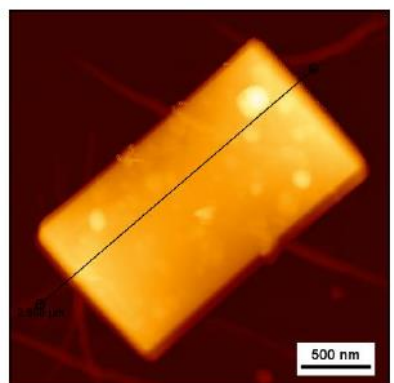
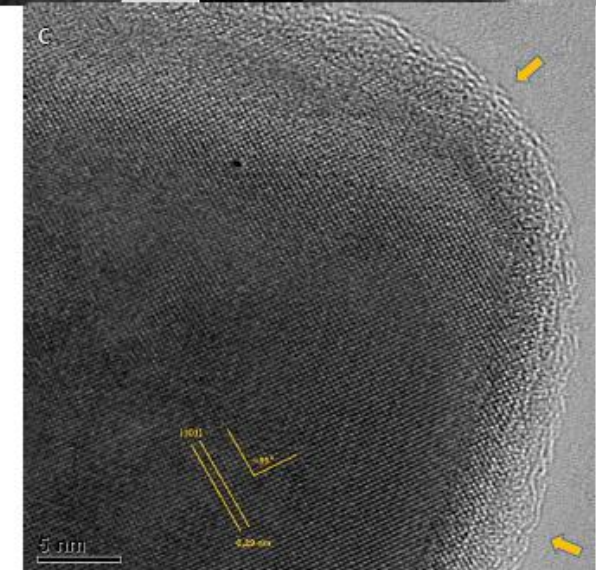
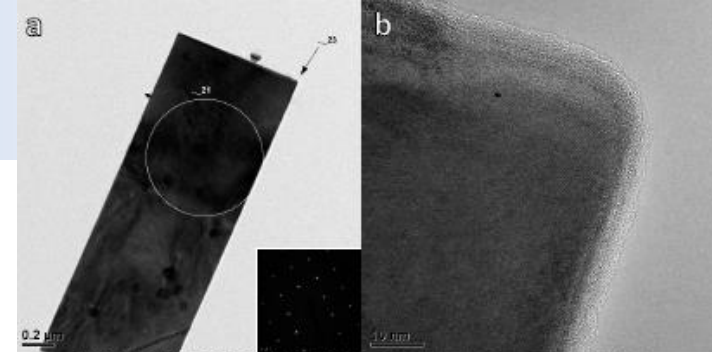
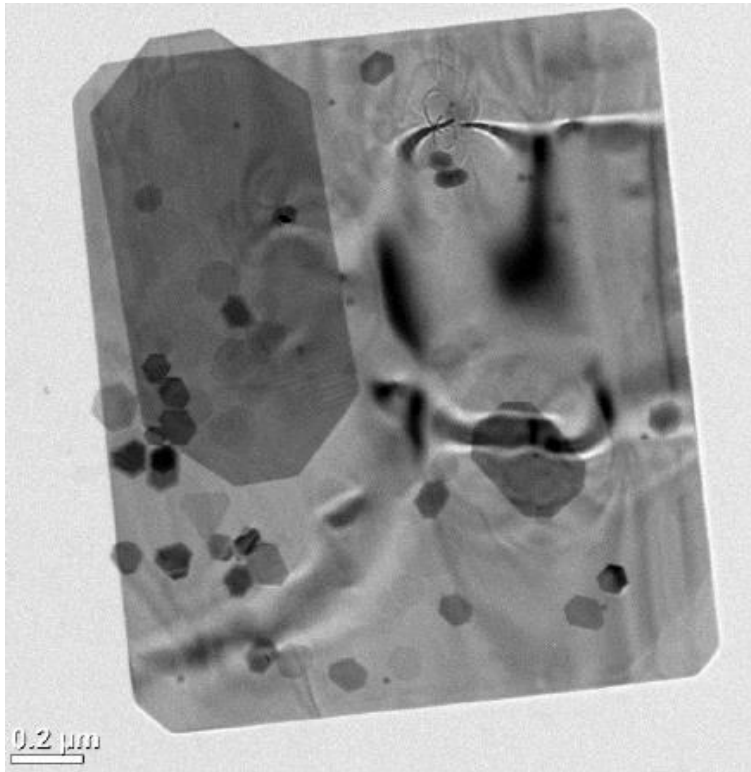


# Core-Shell Nanorods





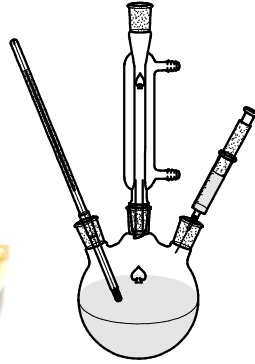
# Semiconductor Nanoplatelets



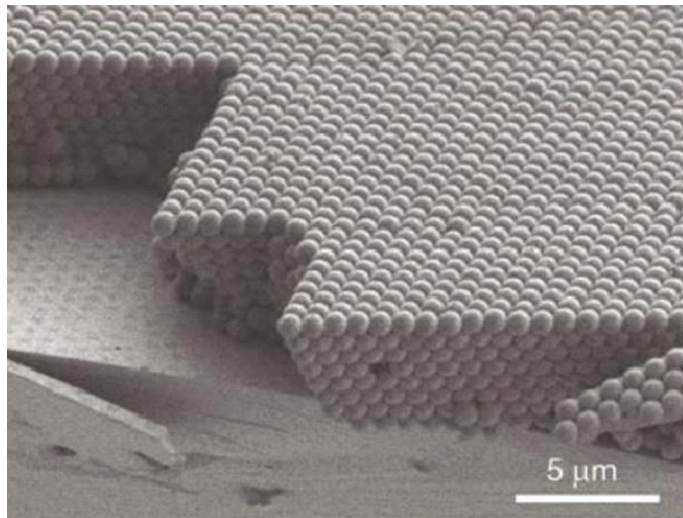
# Multiphase Nanostructured Films

## - Our Approach to Fabrication -

1 Synthesis of **nanocrystals**  
in colloidal suspension  
(building blocks)

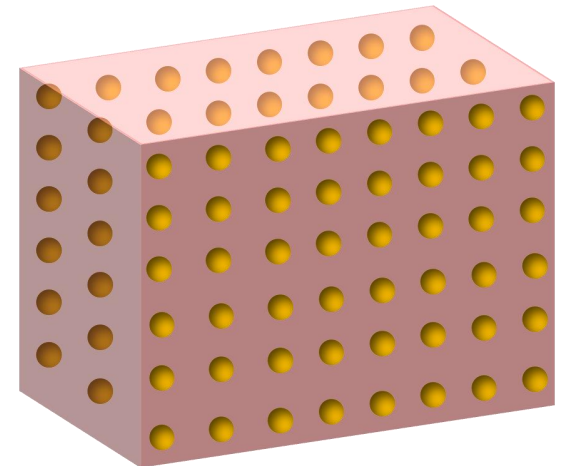


2 Assembly of close-packed nanocrystal  
arrays in the form of thin films  
(colloidal thin film solids)

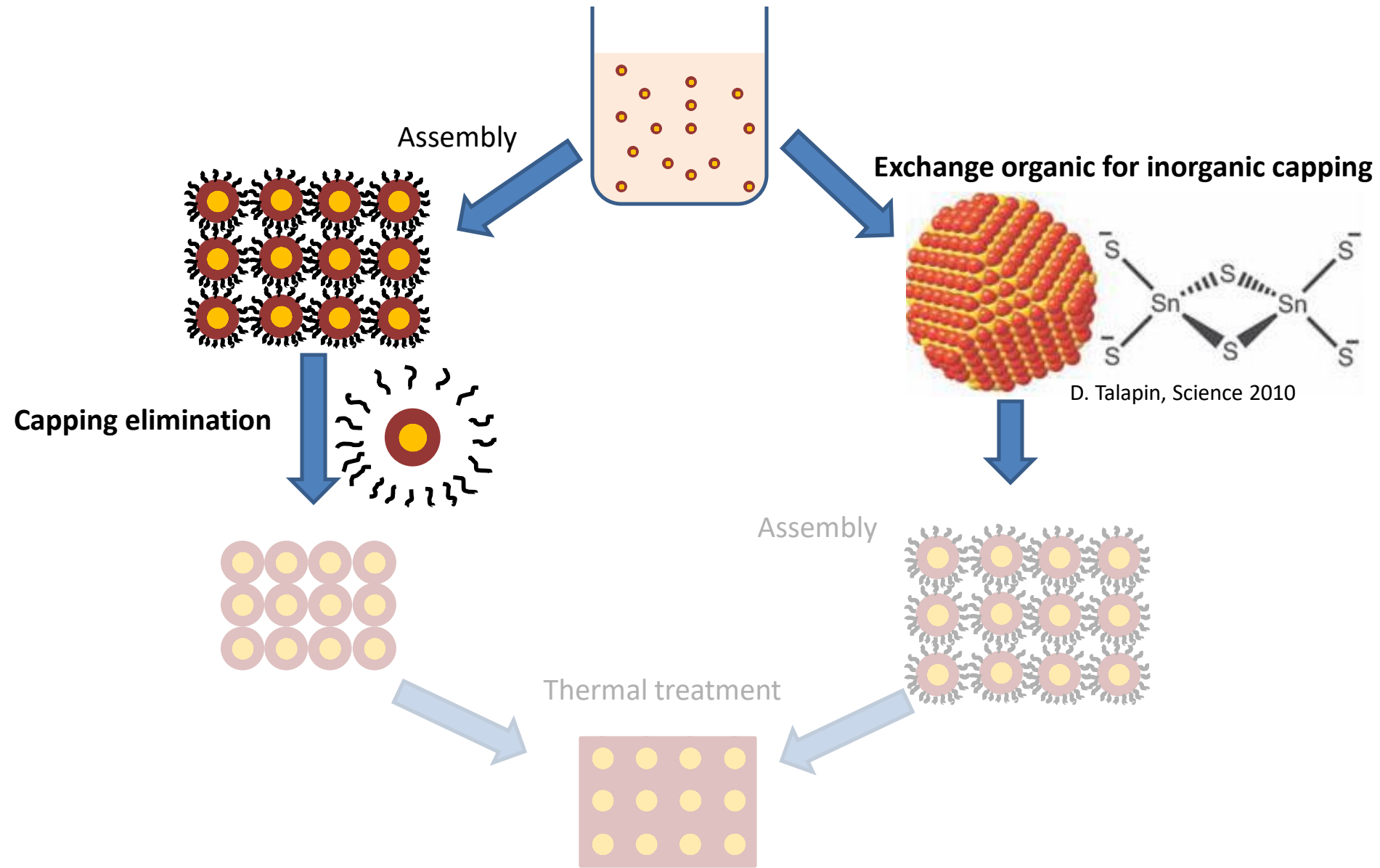


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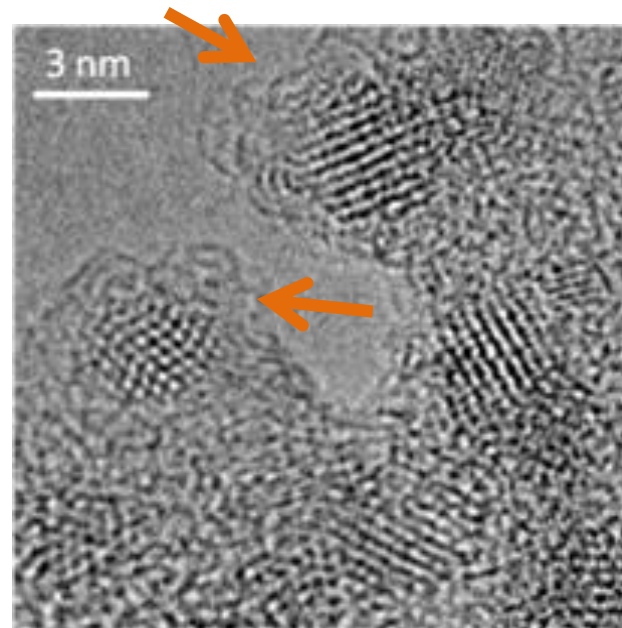
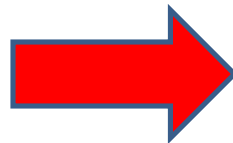
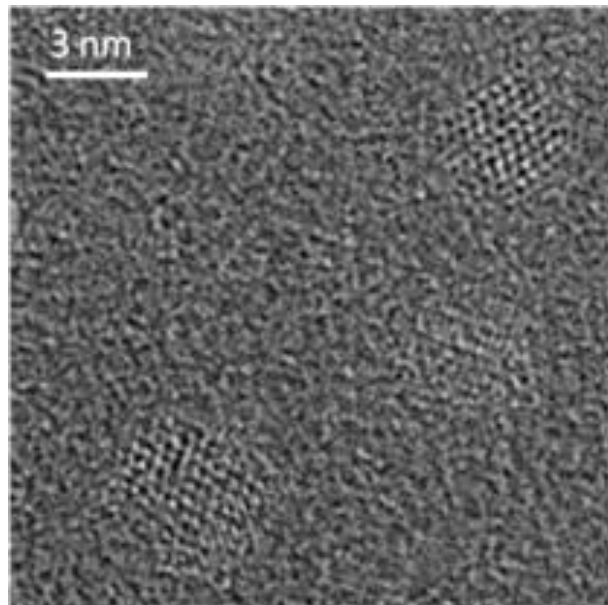
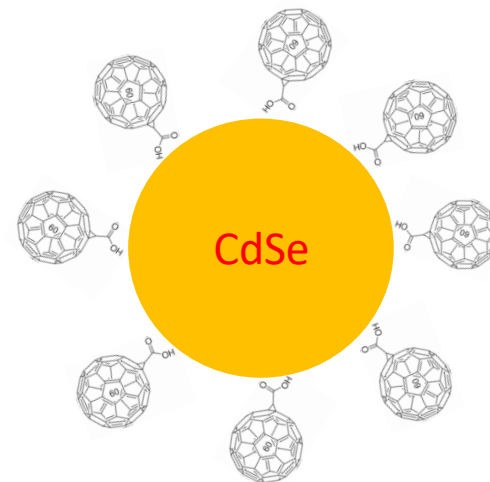
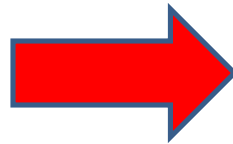
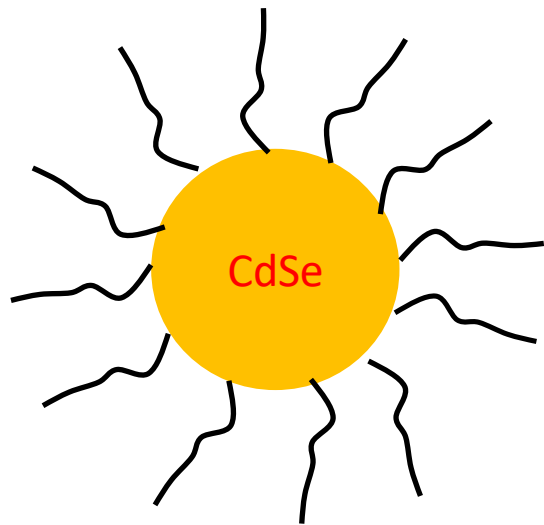
Obtain a fully dense  
**nanostructured film**  
(inorganic)



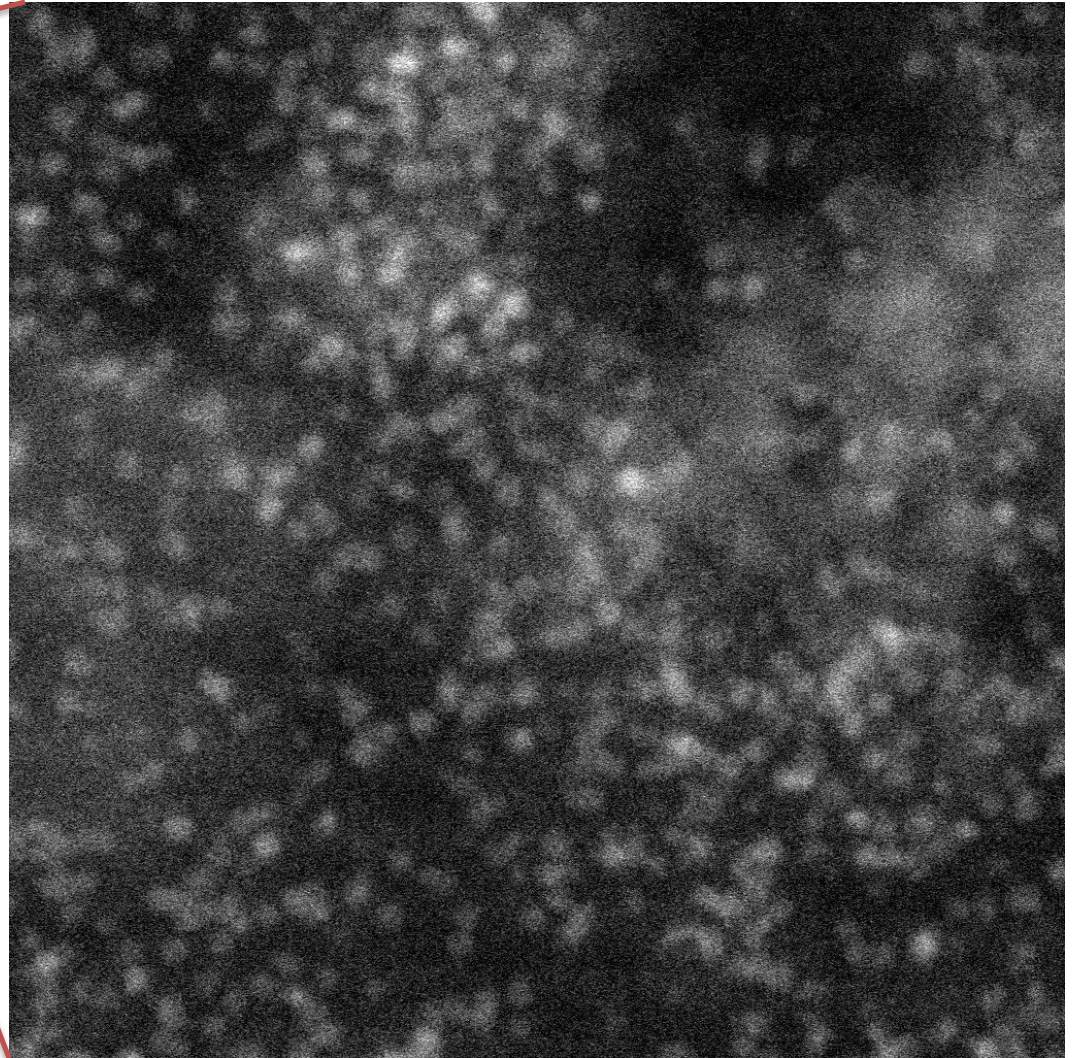
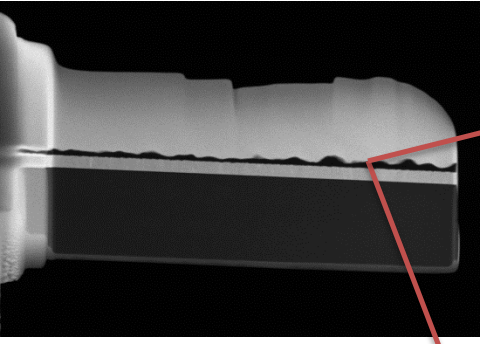
# Engineering Surface Chemistry



# CdSe@C6: Synthesis via Capping Exchange

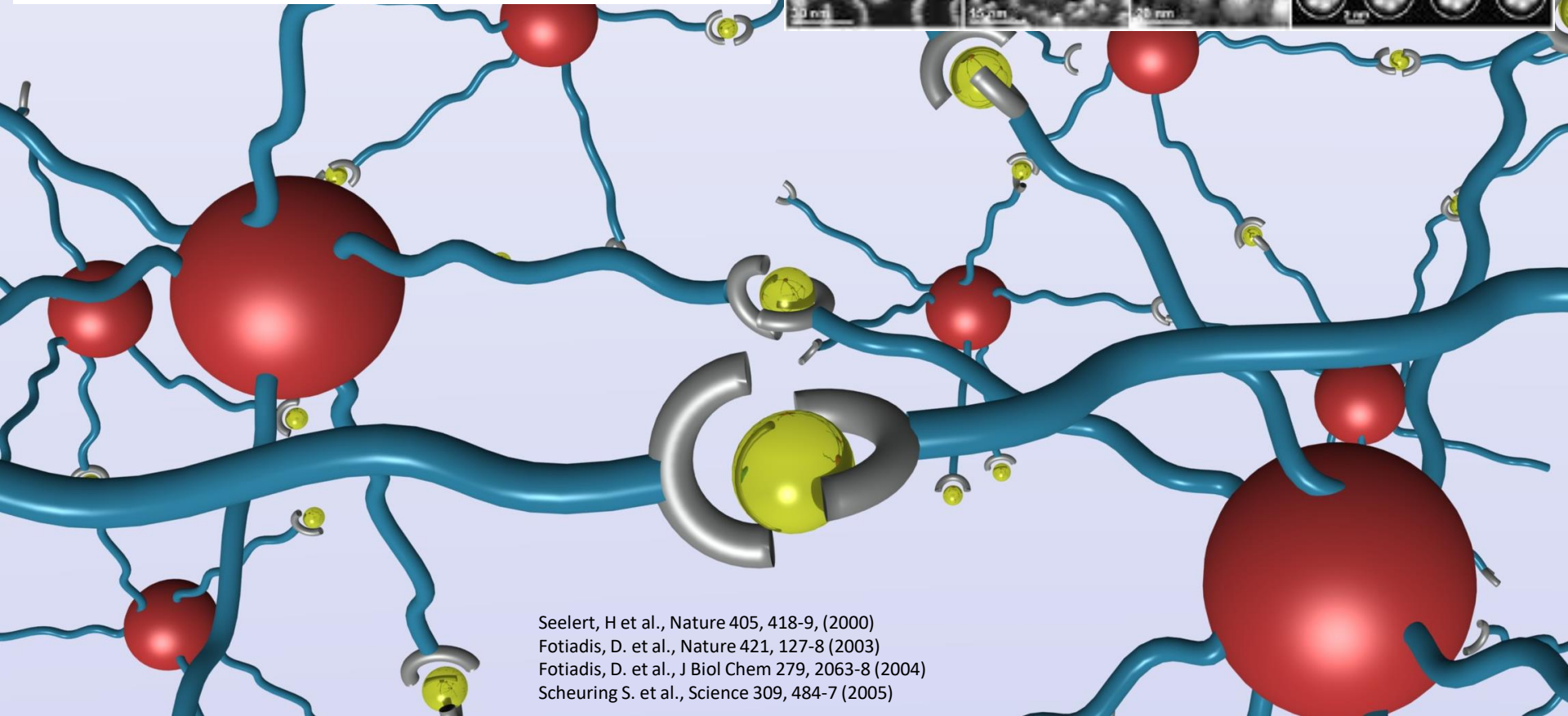
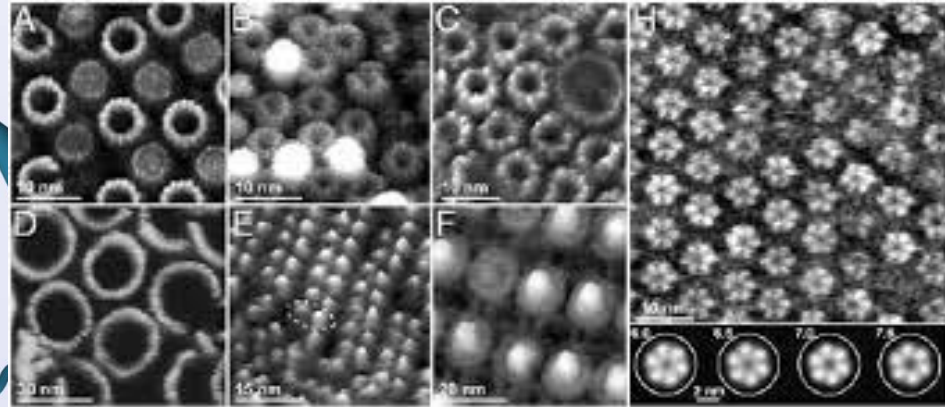


# P3HT:CdSe@C61 blend



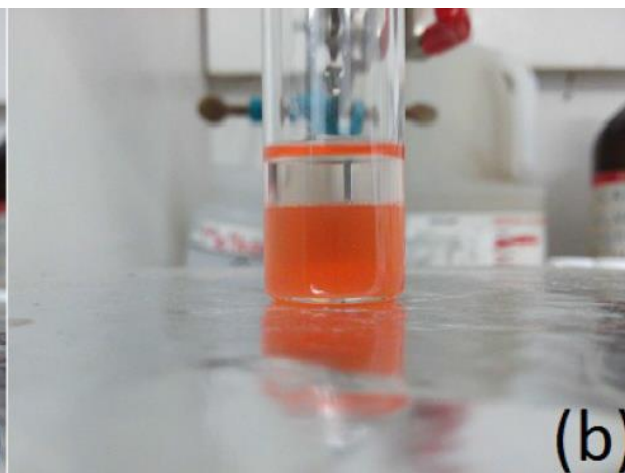
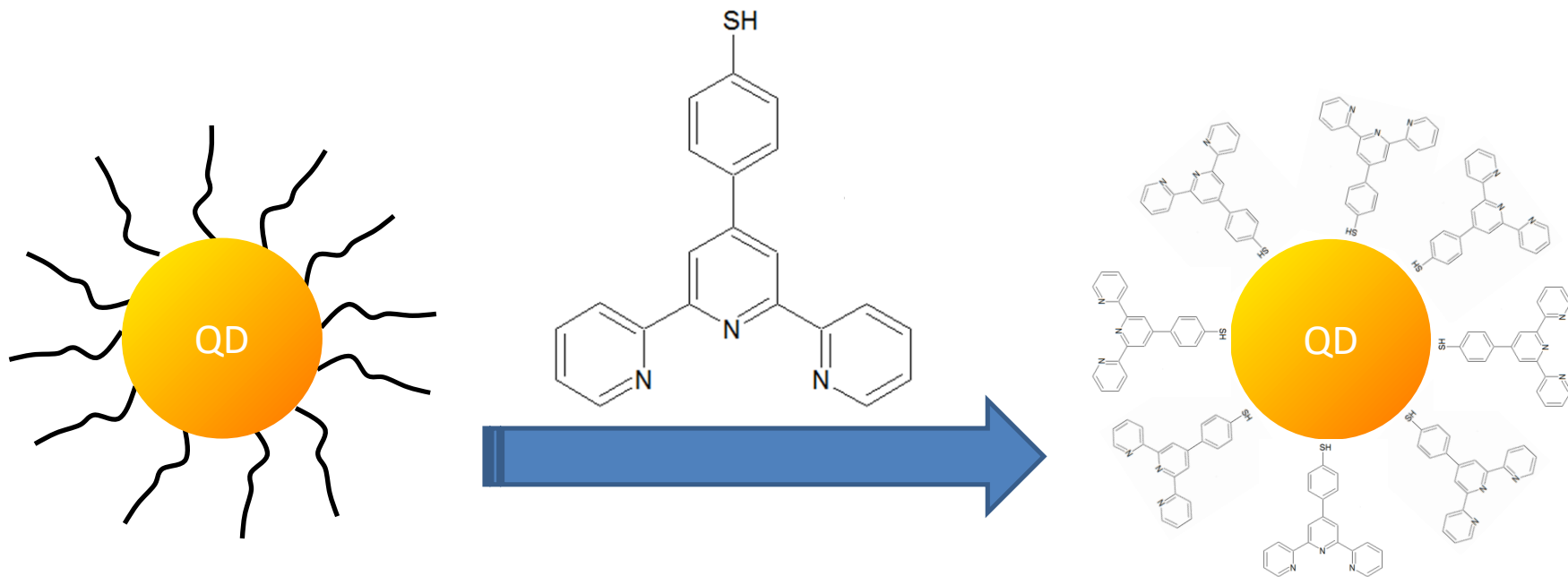
# Supramolecular Assembly

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



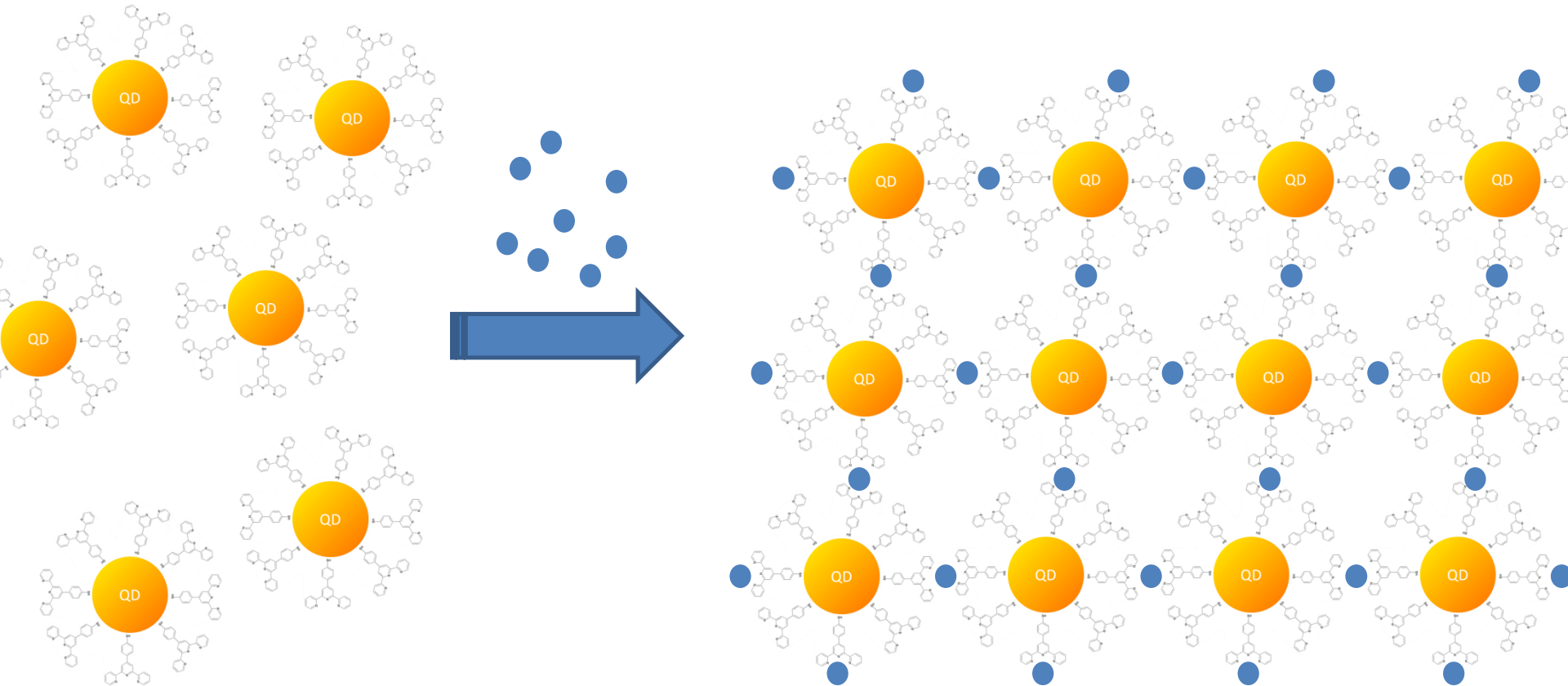
Seelert, H et al., Nature 405, 418-9, (2000)  
Fotiadis, D. et al., Nature 421, 127-8 (2003)  
Fotiadis, D. et al., J Biol Chem 279, 2063-8 (2004)  
Scheuring S. et al., Science 309, 484-7 (2005)

# Supramolecular Assembly Applied to Quantum Dots



# 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





# Control of QD-assembly morphologies

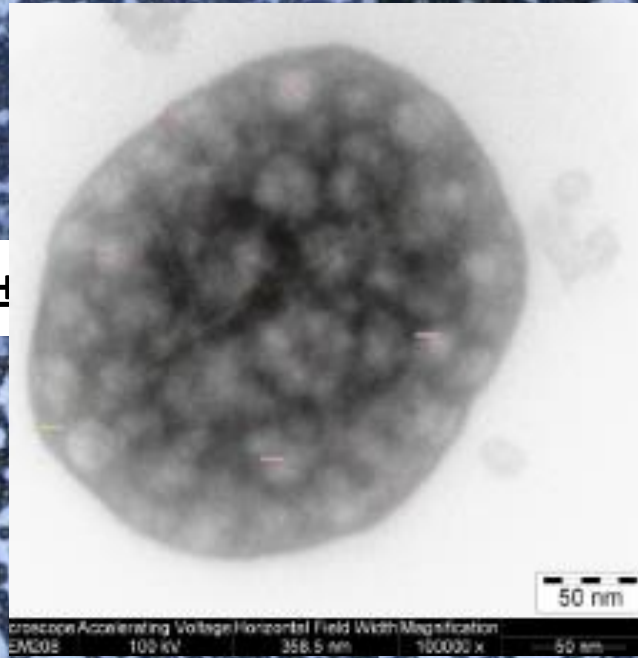
Quantum dot diameter: 2.8 nm  
Assembly time: 2 hrs

1:100  $\rightarrow$  1.2  $\mu\text{m} \pm 0.5$

1:10  $\rightarrow$  1.7  $\mu\text{m} \pm 0.5$

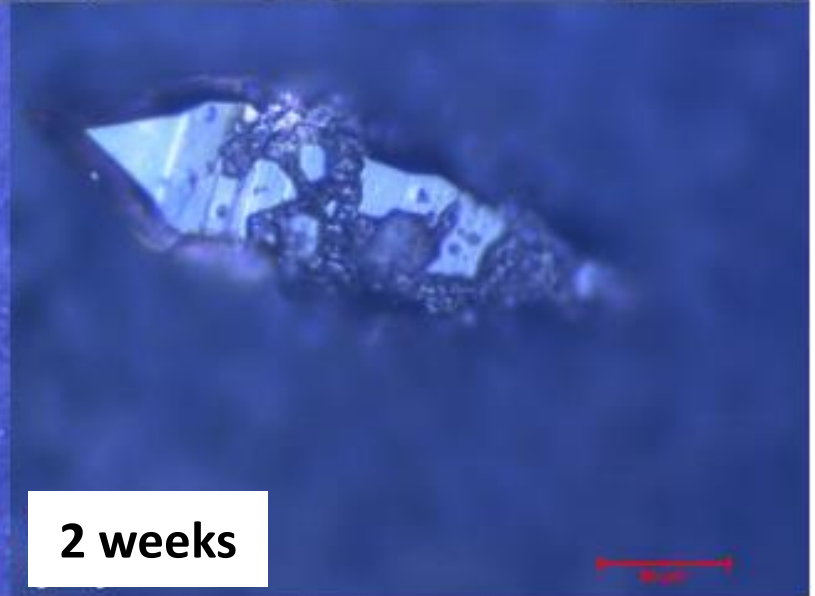
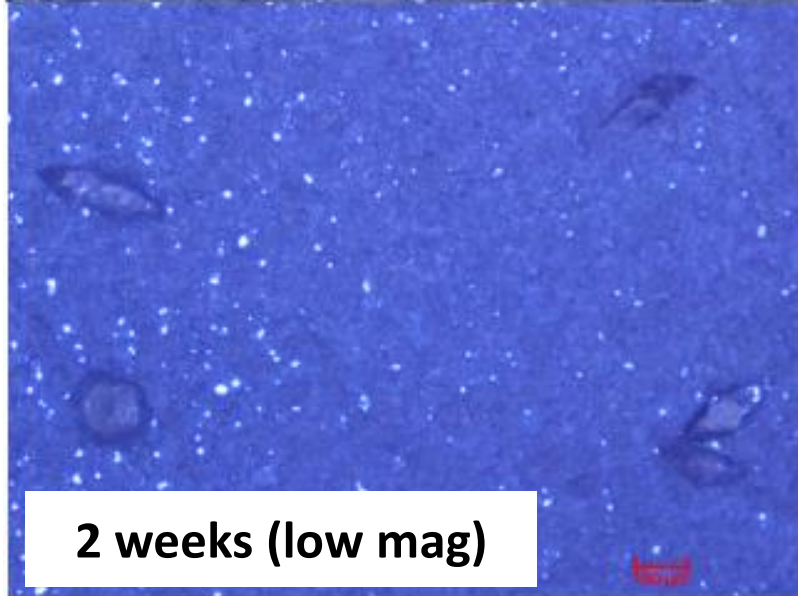
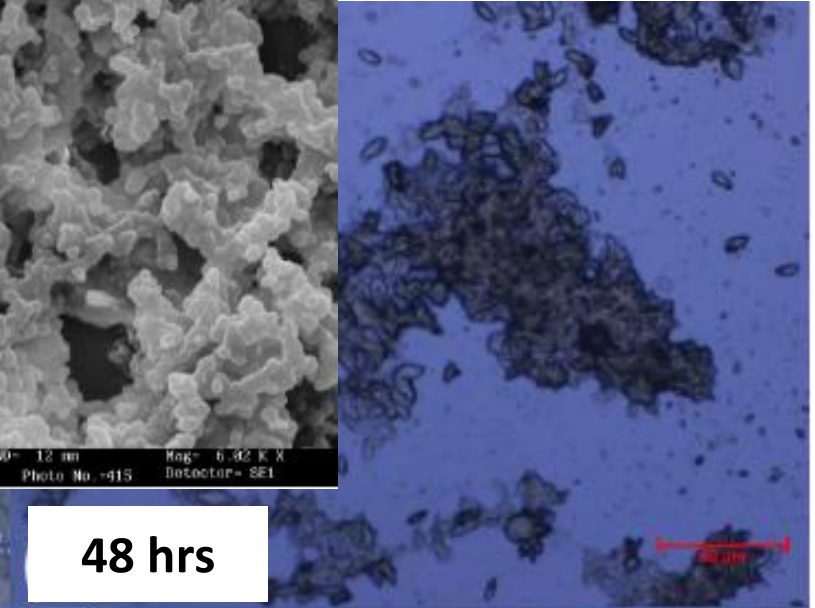
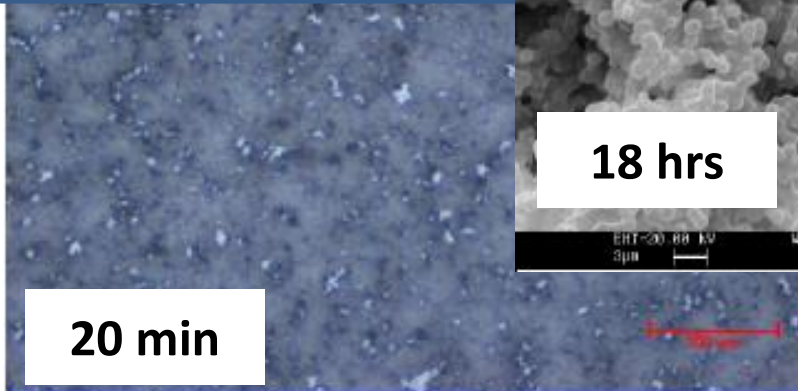
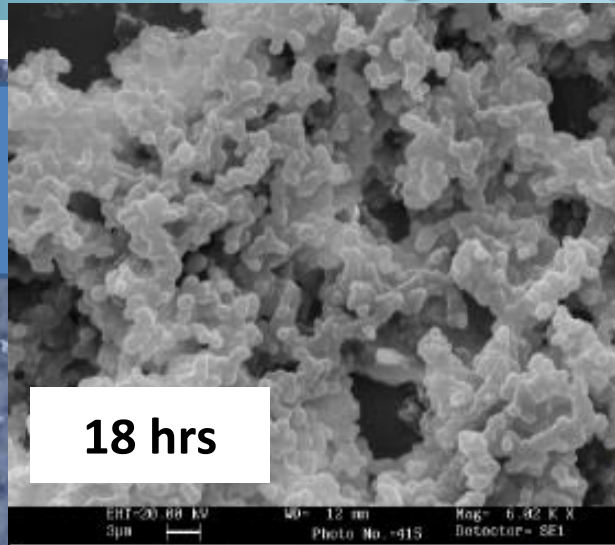
1:2  $\rightarrow$  2.9  $\mu\text{m} \pm 0.7$

1:12  $\rightarrow$  3.1  $\mu\text{m} \pm 0.8$



# Control of QD-assembly morphologies

Quantum dot diameter: 2.8 nm  
QD-MPT:Co(II) ratio: 1:15

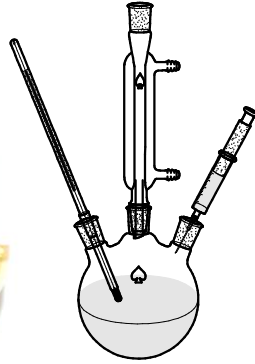


# Multiphase Nanostructured Films

## - Our Approach to Fabrication -

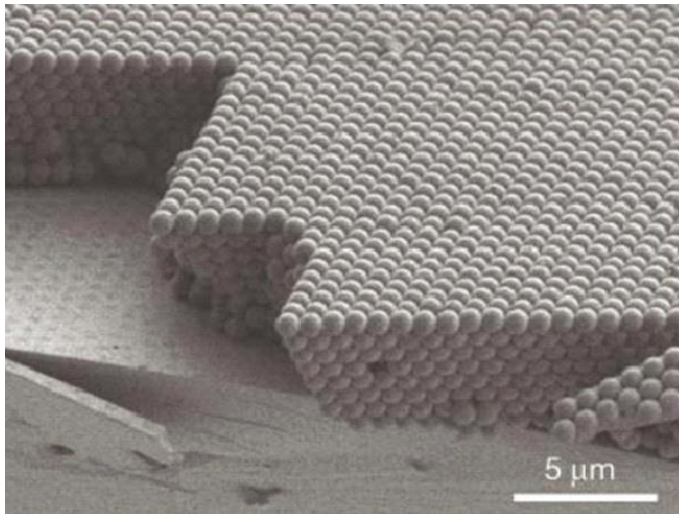
Synthesis of **nanocrystals**  
in colloidal suspension  
(building blocks)

1



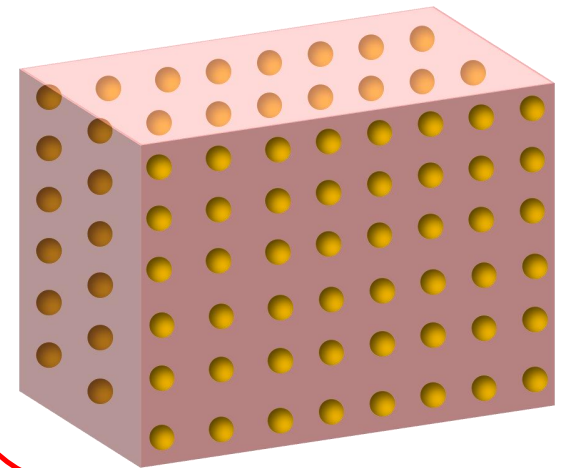
Assembly of close-packed nanocrystal  
arrays in the form of thin films  
(**colloidal thin film solids**)

2

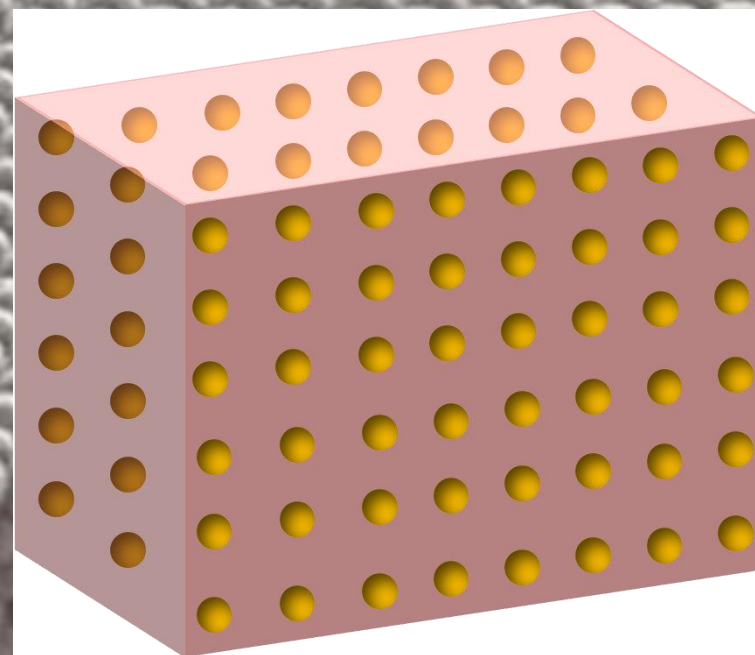
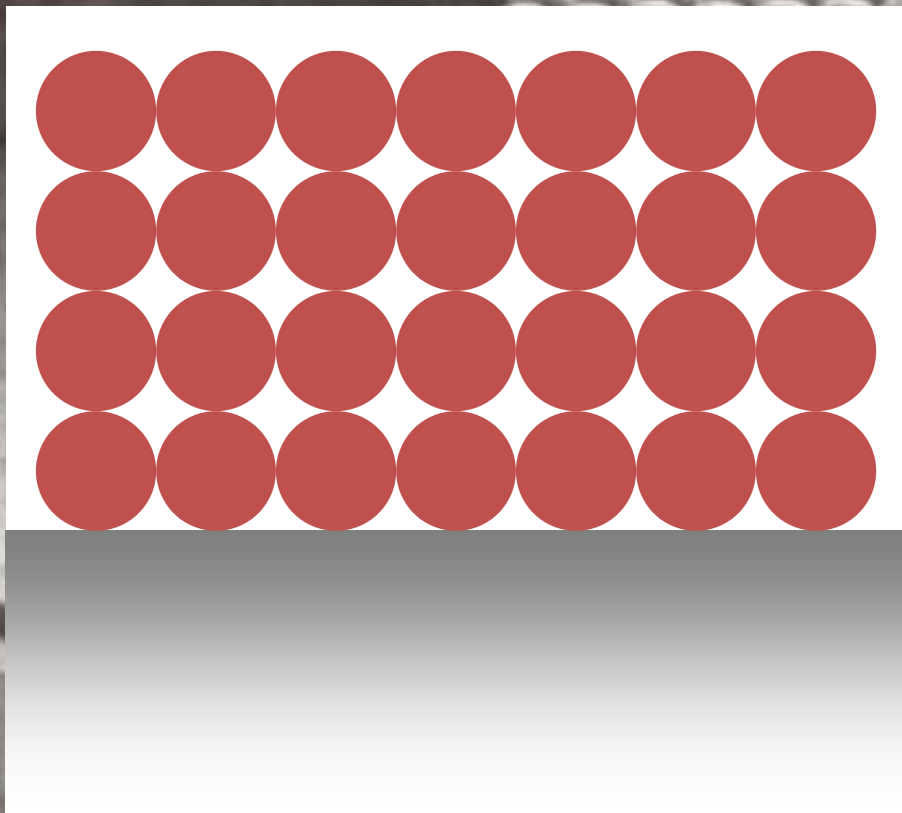


3

Obtain a fully dense  
**nanostructured film**  
(inorganic)



# From a Colloidal Solid to a Dense Nanostructured Film

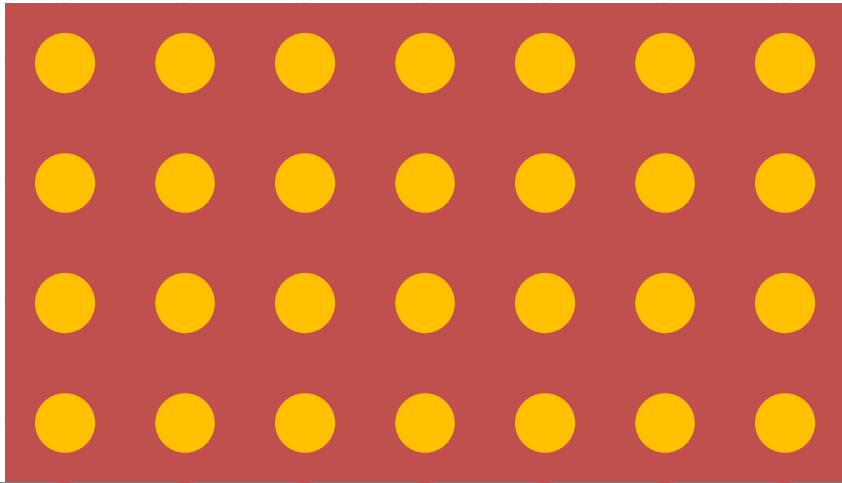


5  $\mu\text{m}$

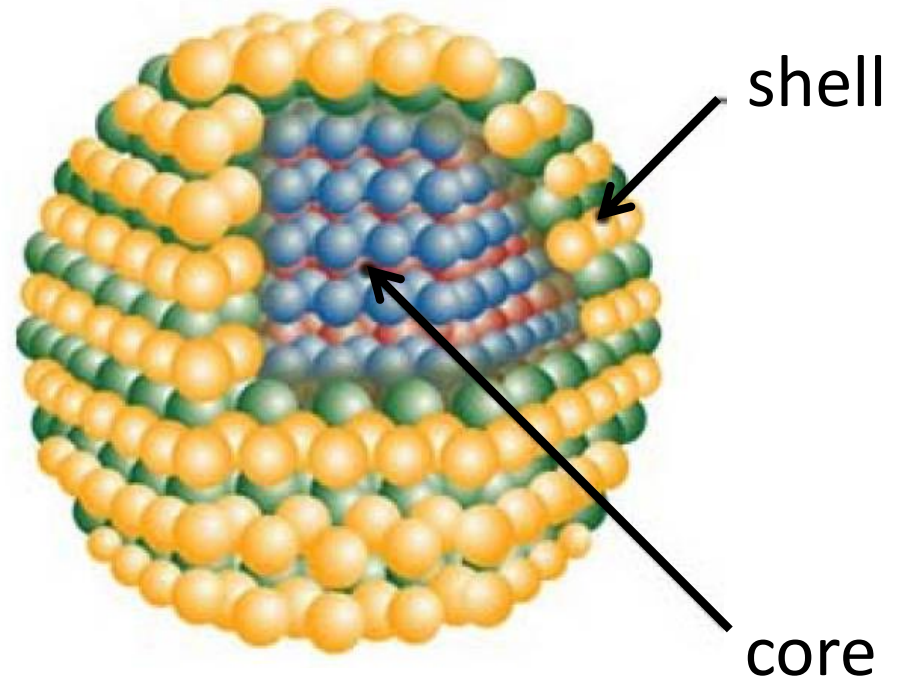


# From a Colloidal Solid to a Dense Nanostructured Film

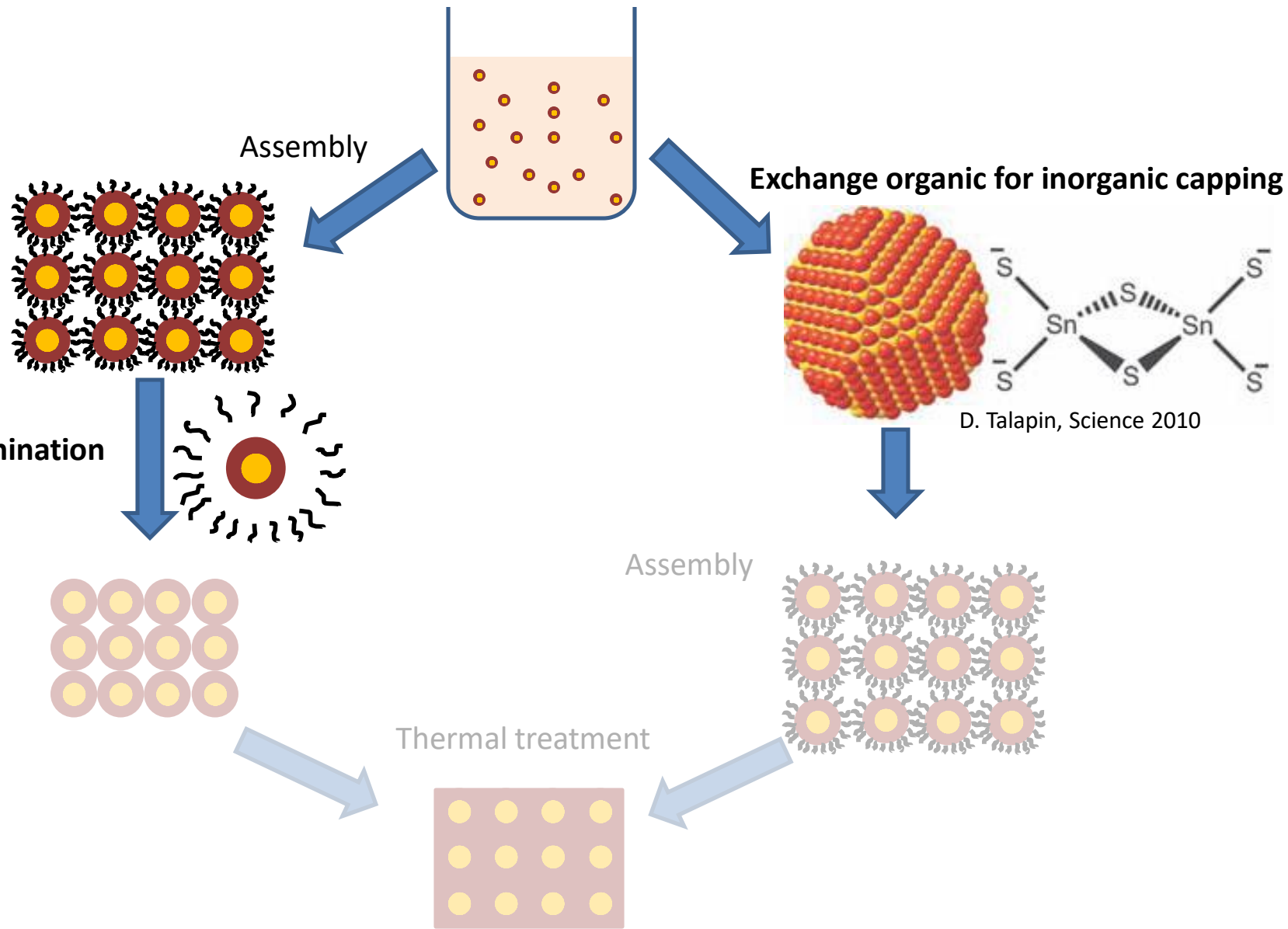
Use Core/Shell Nanocrystals



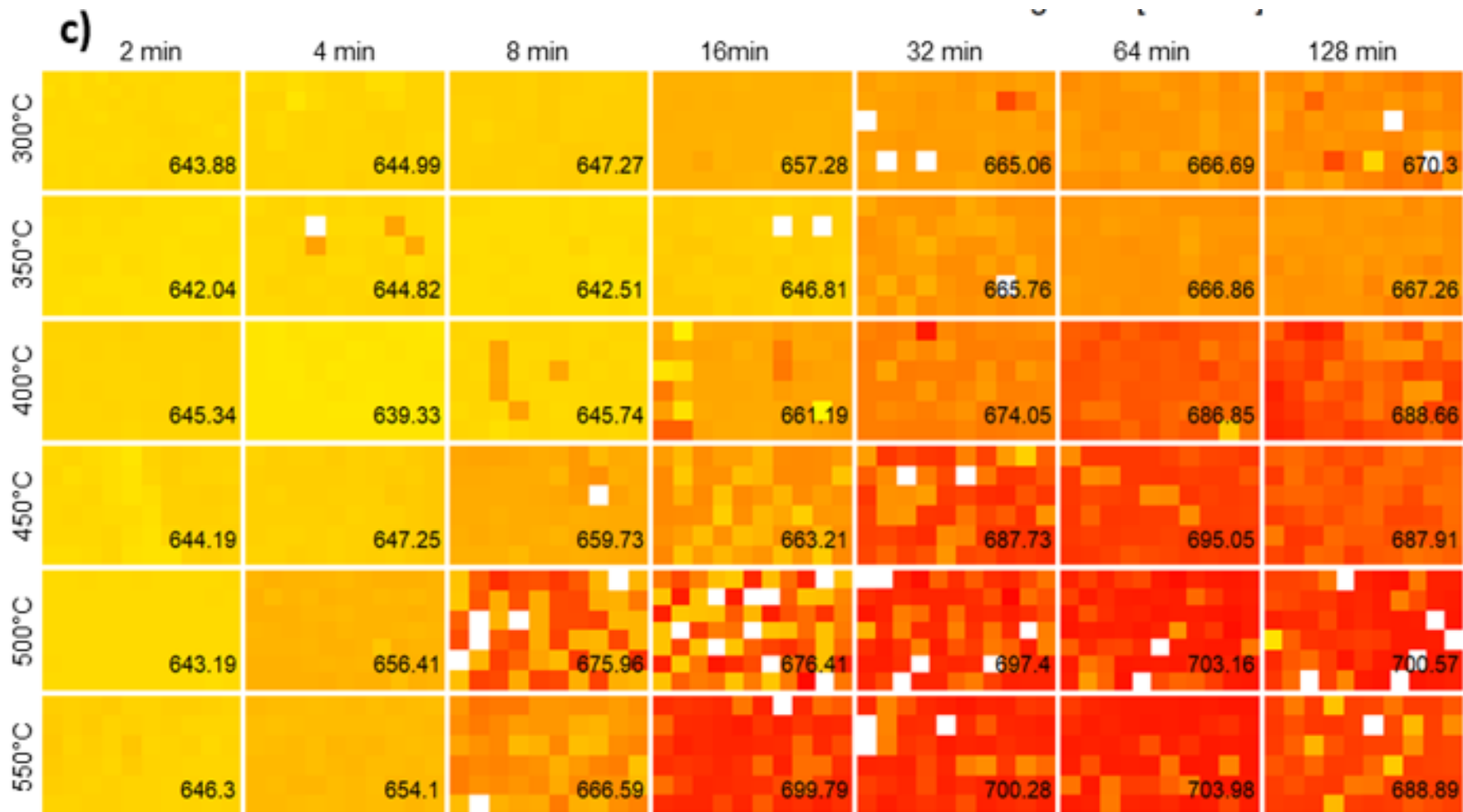
Thermal Treatment



# Engineering Surface Chemistry

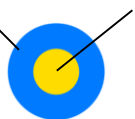


# Photolumuminescence Shift upon Heating

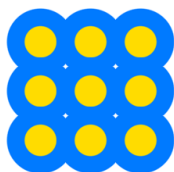
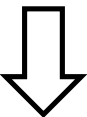


# Thermal Treatment

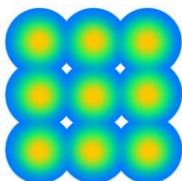
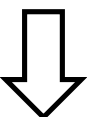
CdS CdSe



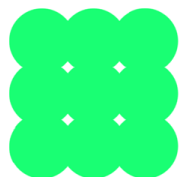
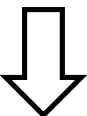
Thermal treatment



Thermal treatment



Thermal treatment

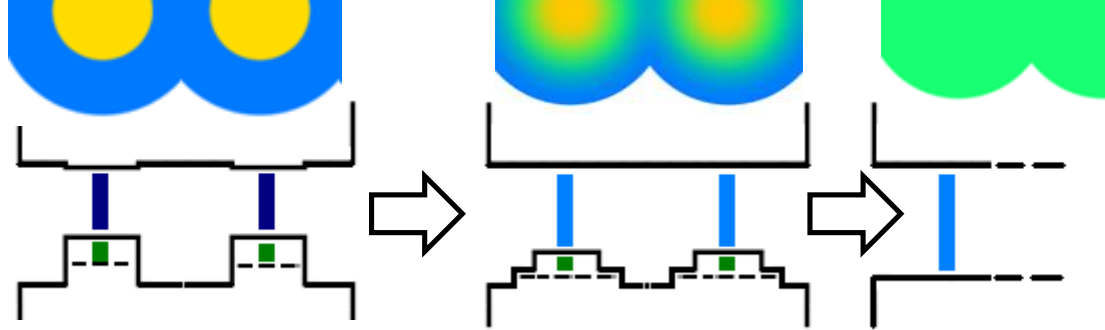


$E_G$  energy decreasing

BUT still higher than bulk CdSe (1.7 eV)

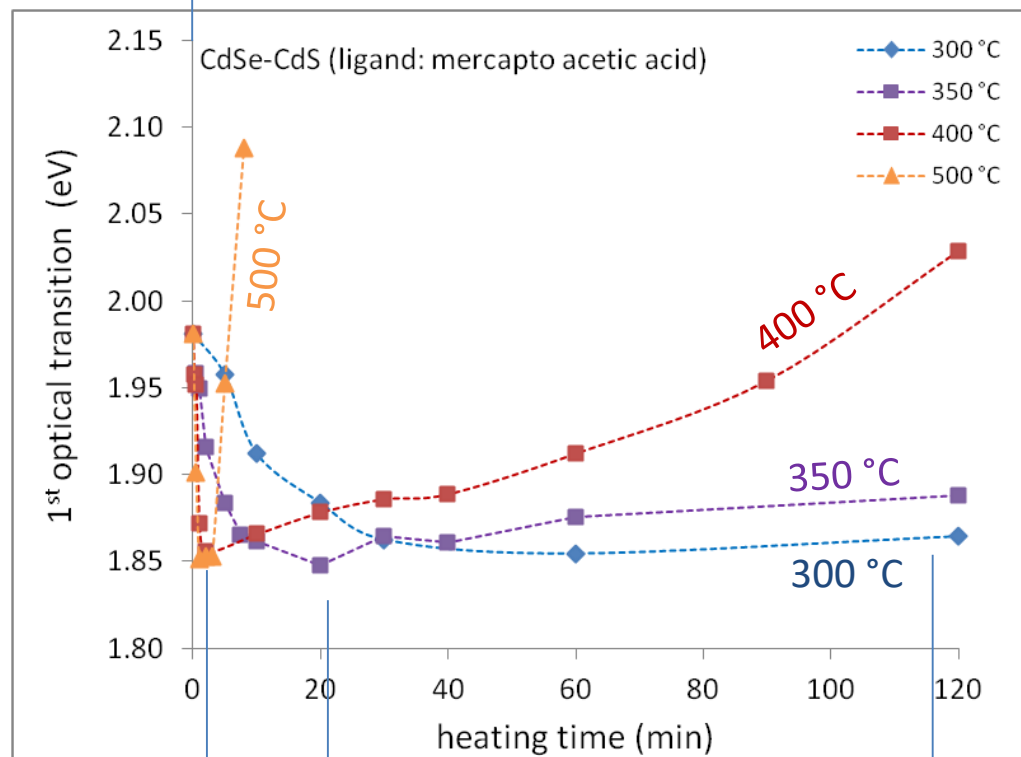
$E_G$  energy increasing

compatible with INTERDIFFUSION



CALCULATED ALLOY  $E_G$

$$E_G (\text{CdSe}_{0.3}\text{S}_{0.7}) = 2.2 \text{ eV}$$



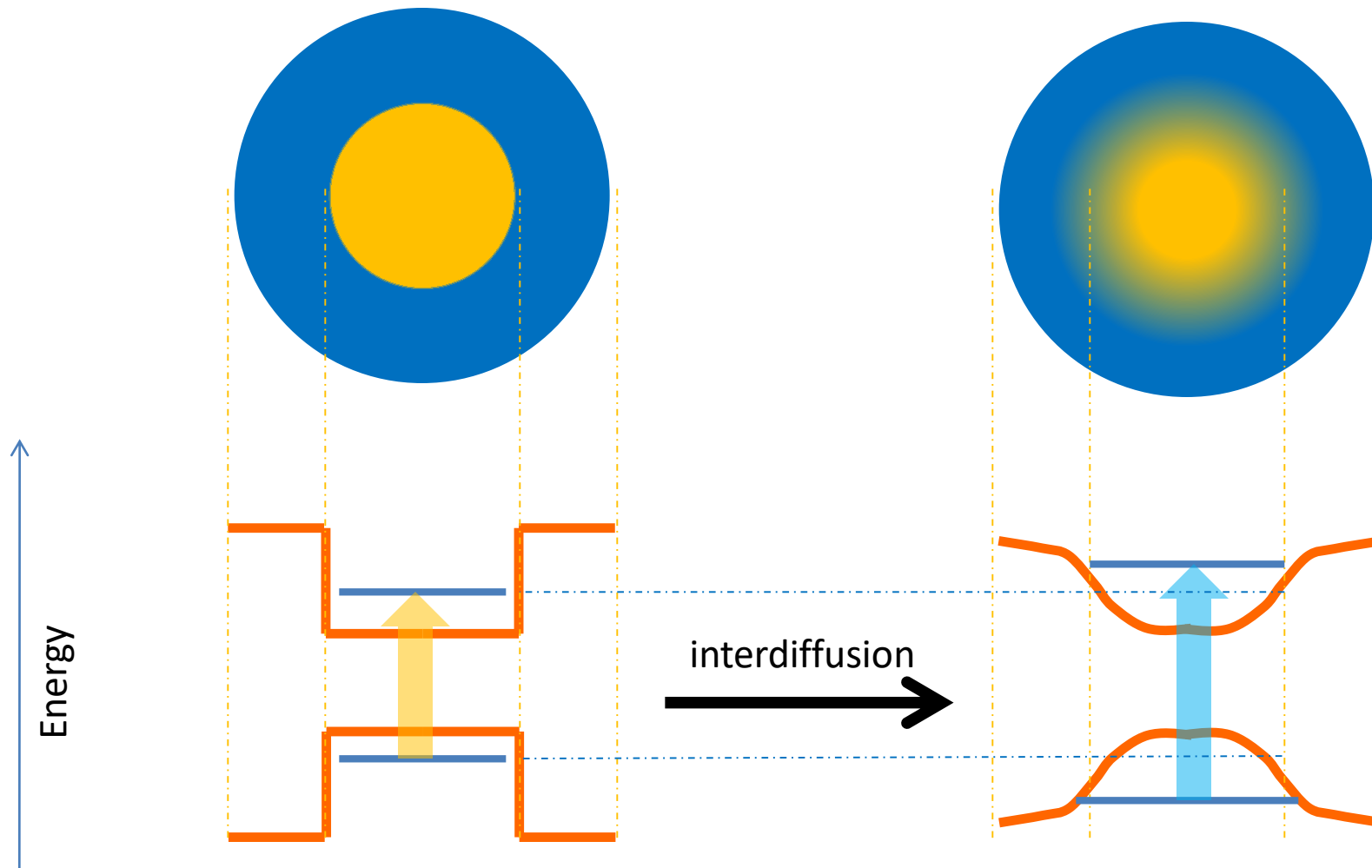
2 min ( $T = 400^\circ\text{C}$ )

20 min ( $T = 350^\circ\text{C}$ )

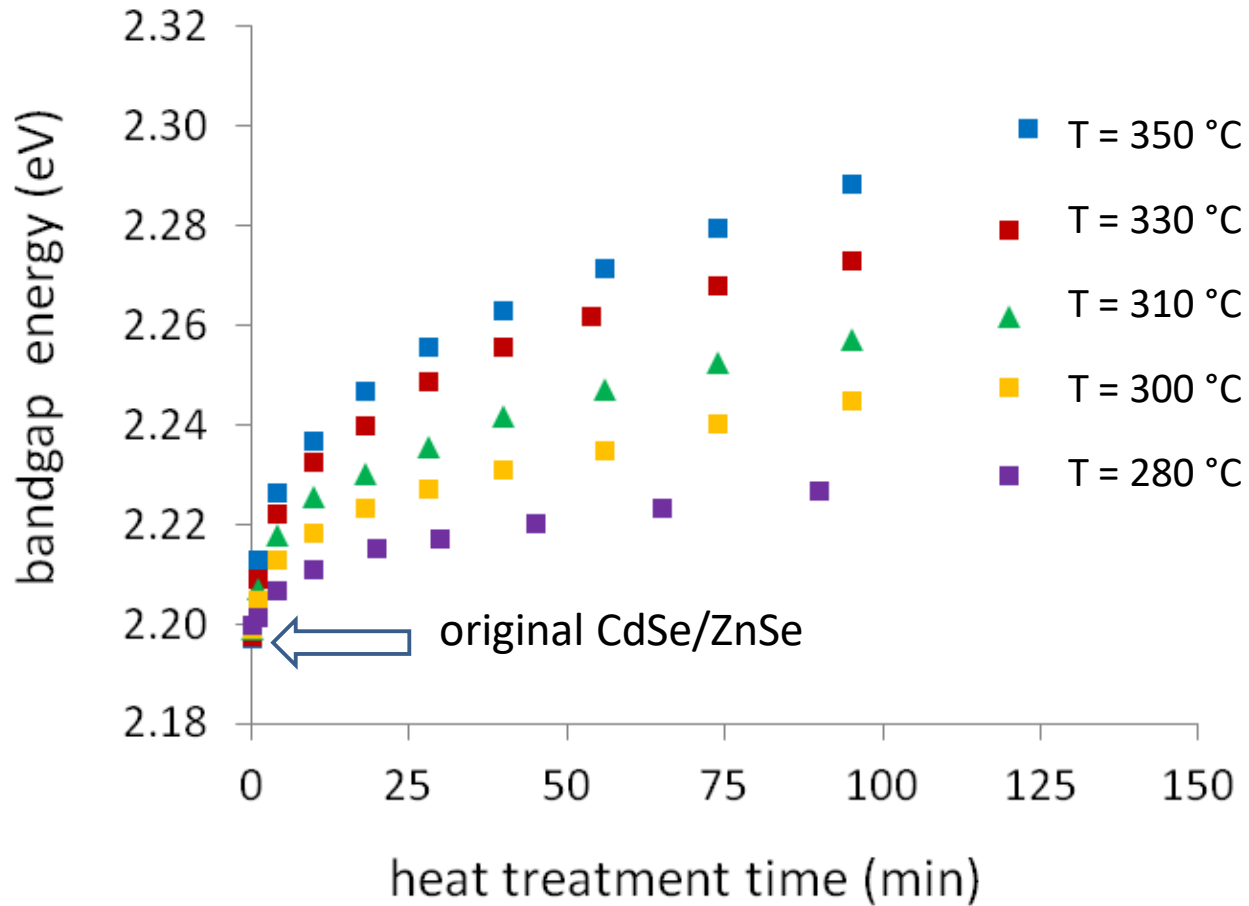
$t = \infty$  ( $T = 300^\circ\text{C}$ )



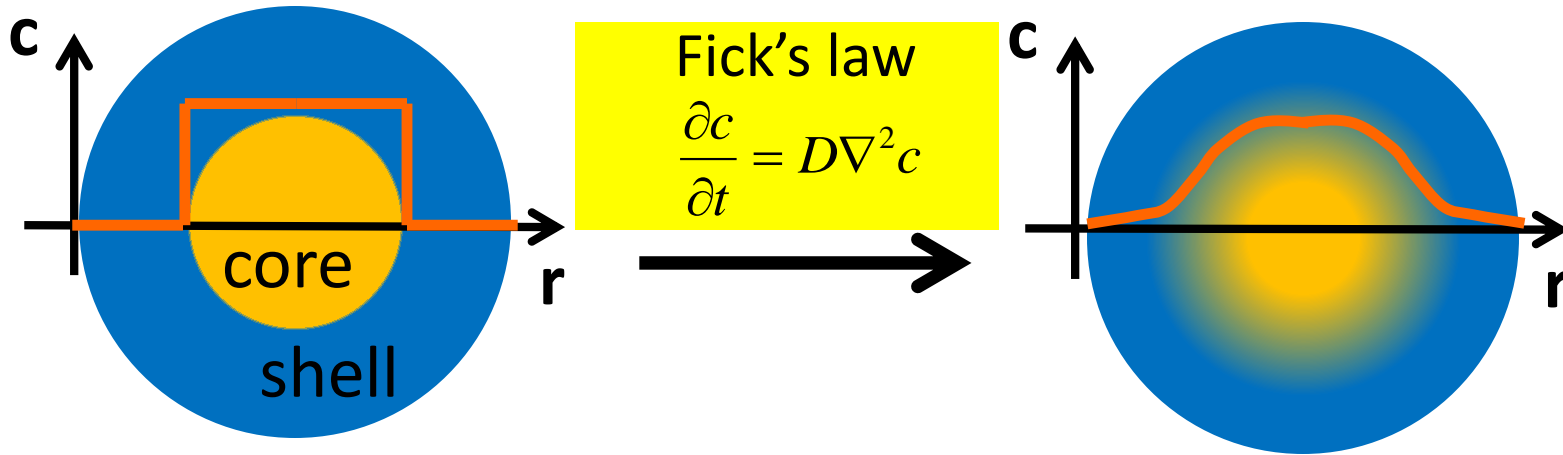
# Interdiffusion Kinetics at the Nanoscale



# Bandgap engineering through diffusion

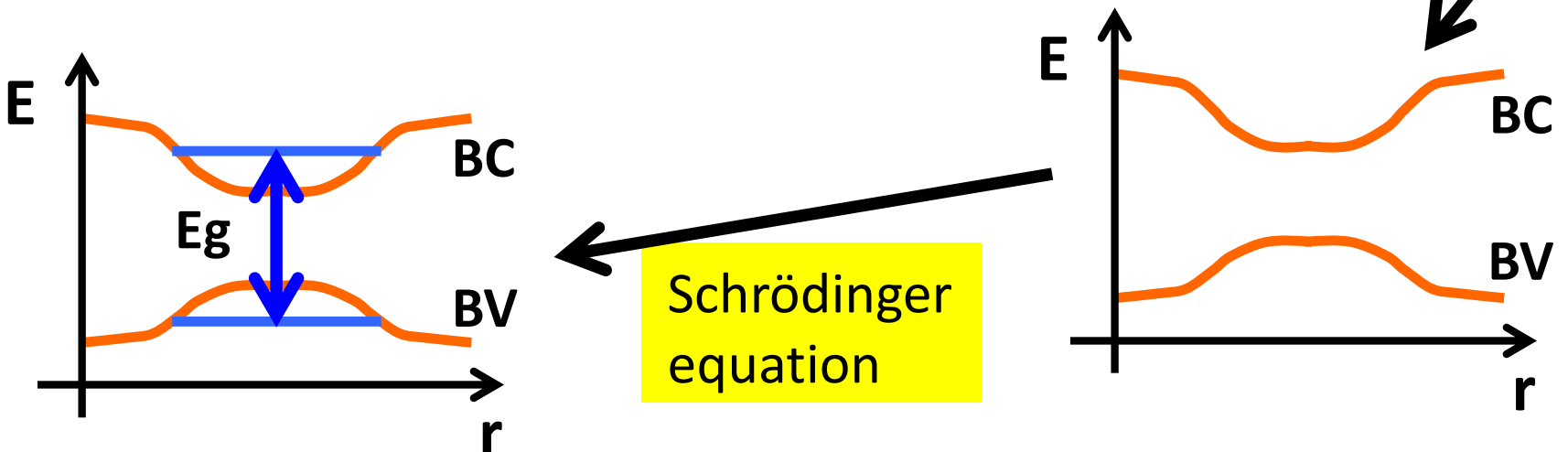


# Roadmap: From diffusion to optoelectronic properties

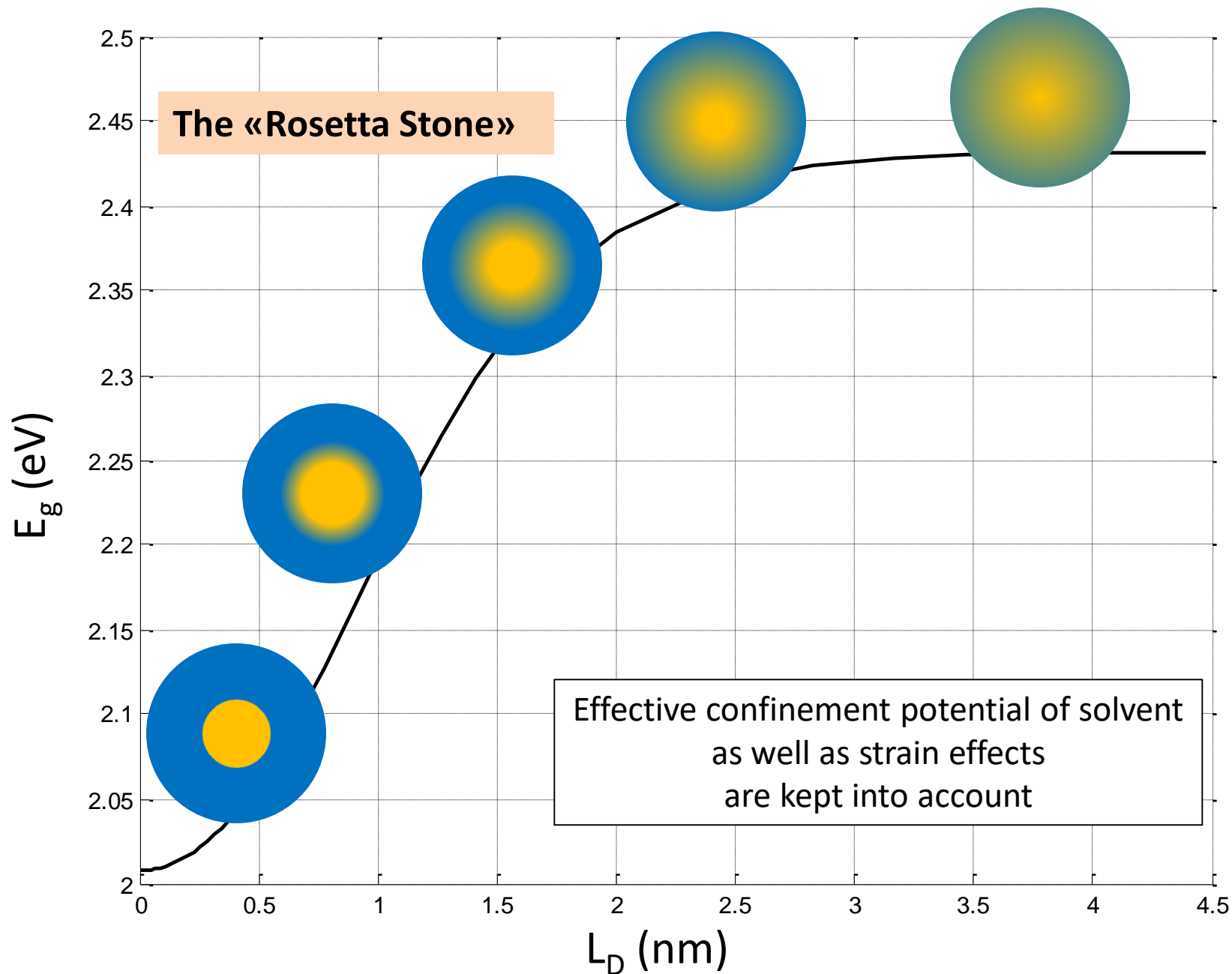


E.g.: **CdSe-CdS** → diffusion of anions in Cd lattice  
**CdSe-ZnSe** → diffusion of cations in Se lattice

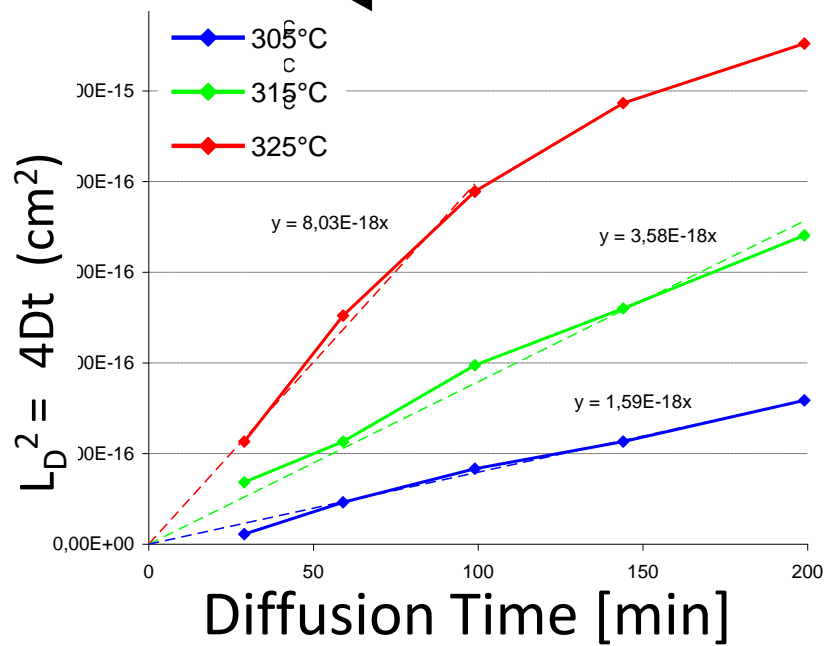
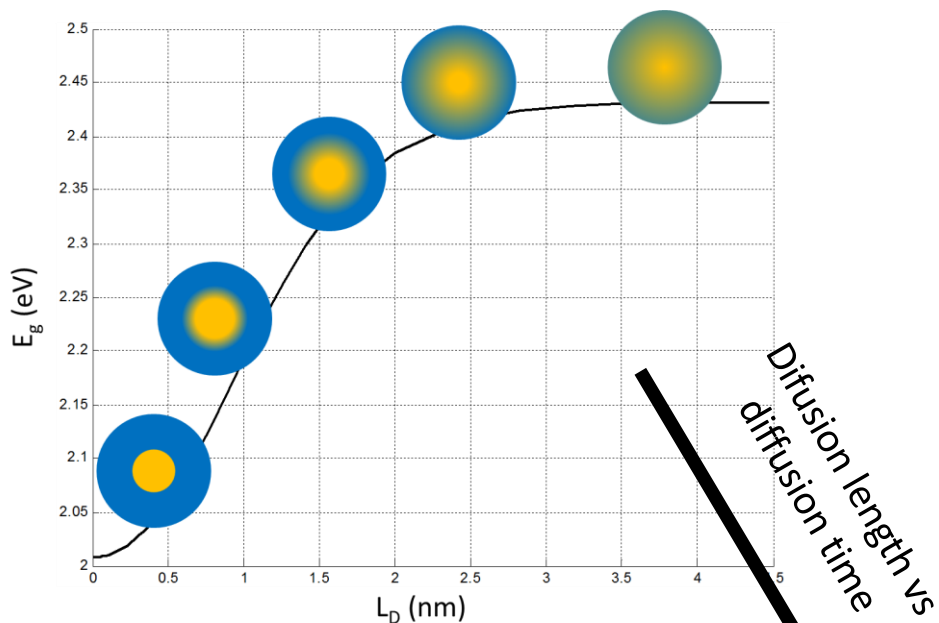
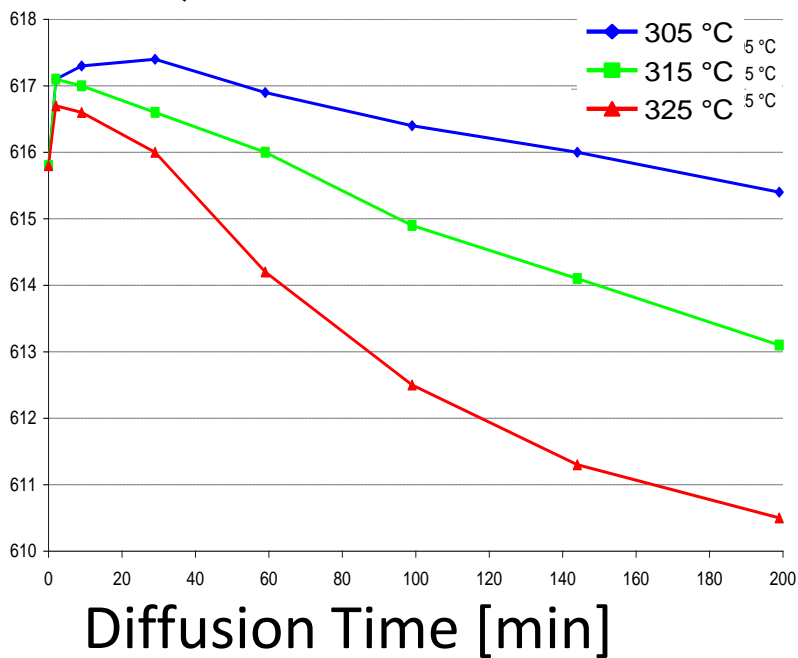
Electronic Structure  
vs. Composition



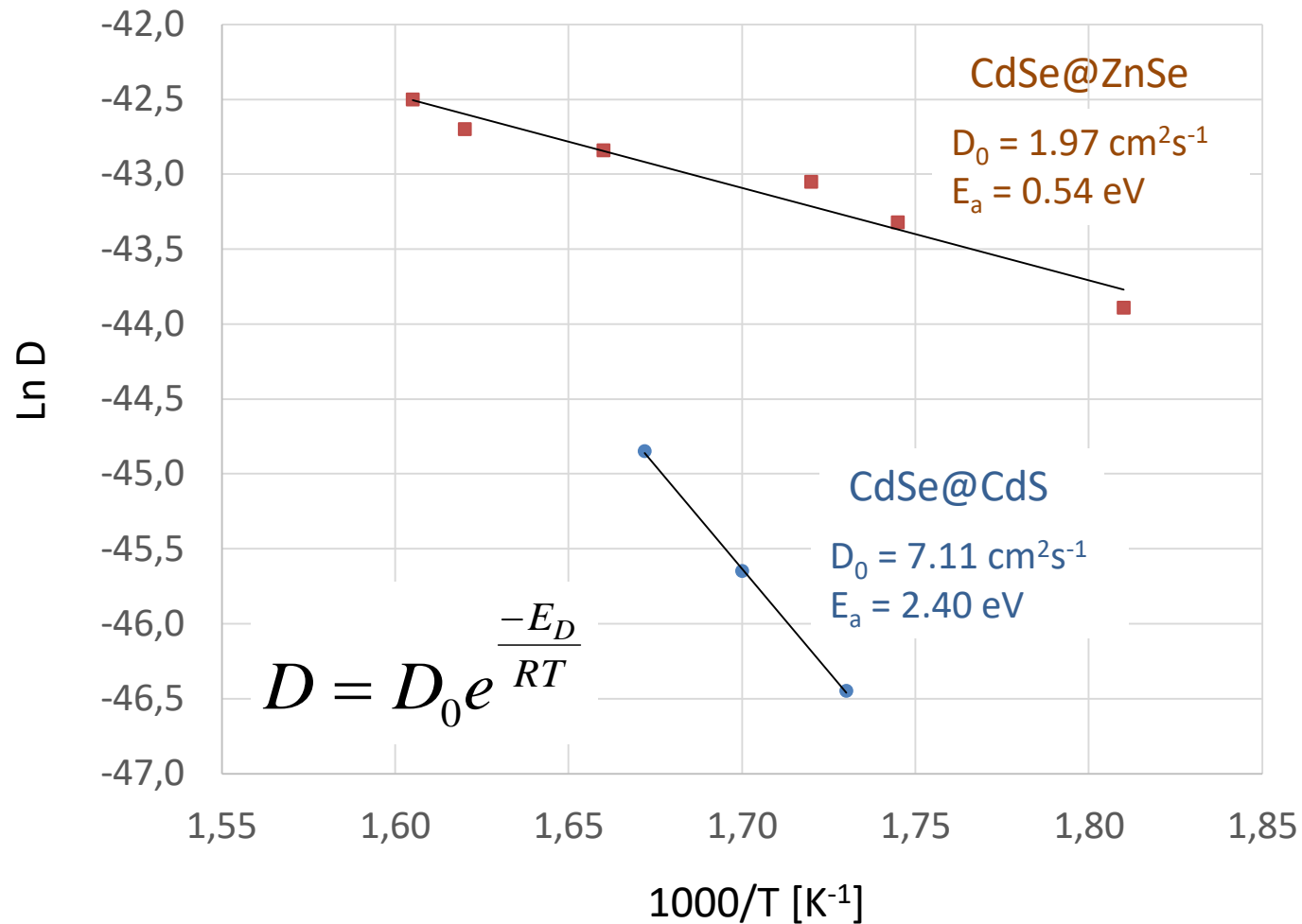
# Output of the model: $E_g$ vs. Diffusion Length



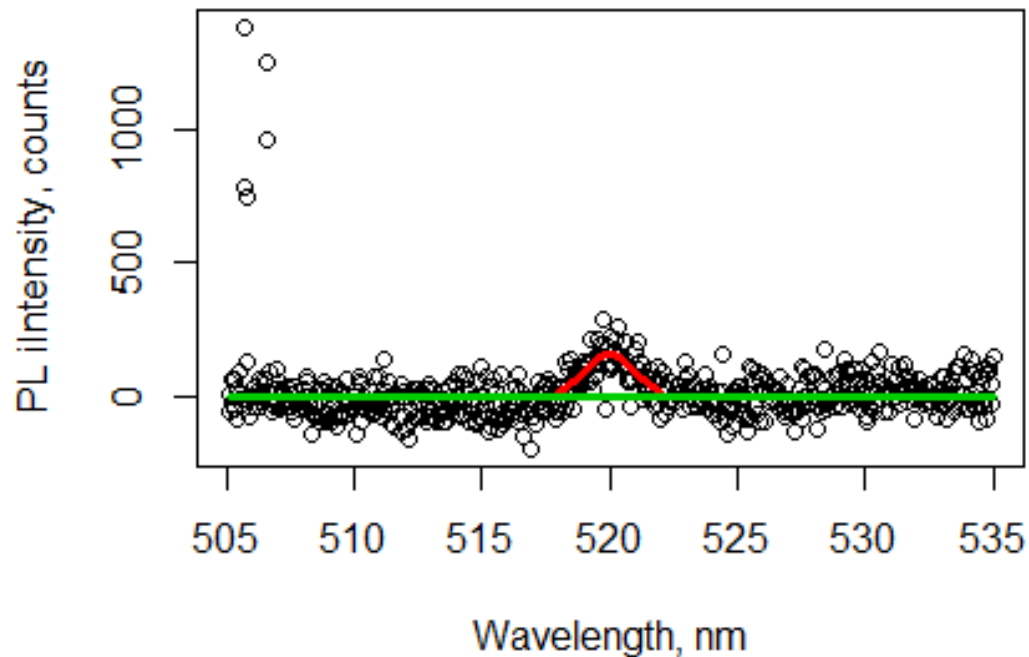
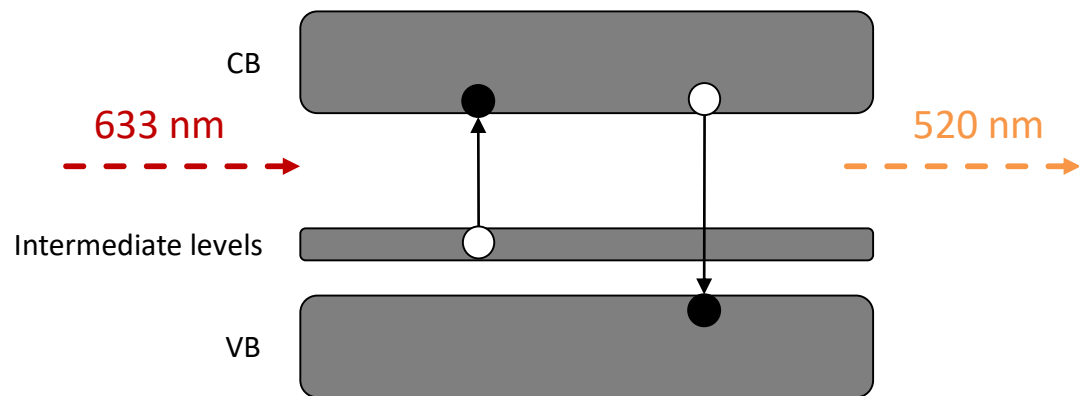
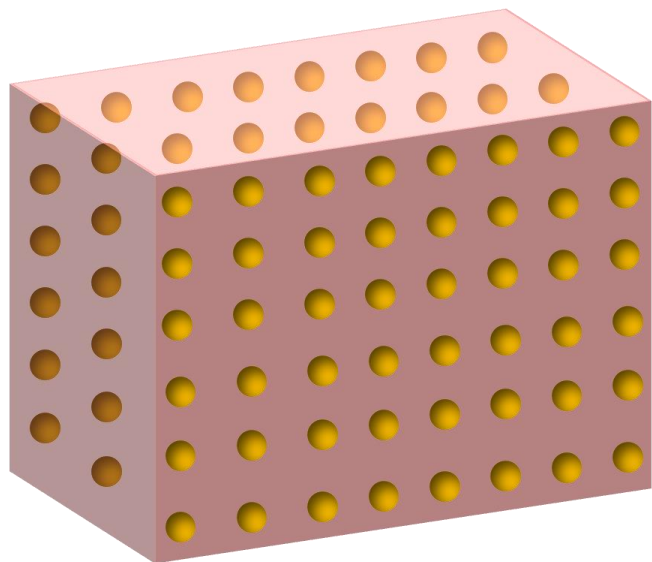
First absorption peak wavelength (nm)



# Diffusion Kinetics at the Nanoscale



# Intermediate Band Materials: Evidence of Upconversion



# Thank you!

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