# Introduction to Quantum Dot Nanocrystals and Nanocrystal Solids

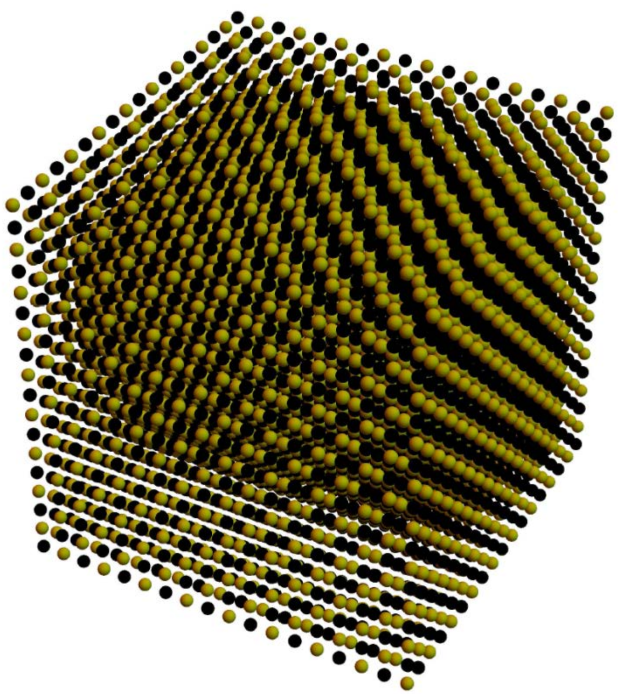
Nuri Yazdani, 10.03.15

# What is a QD Nanocrystal

Time: ~15m

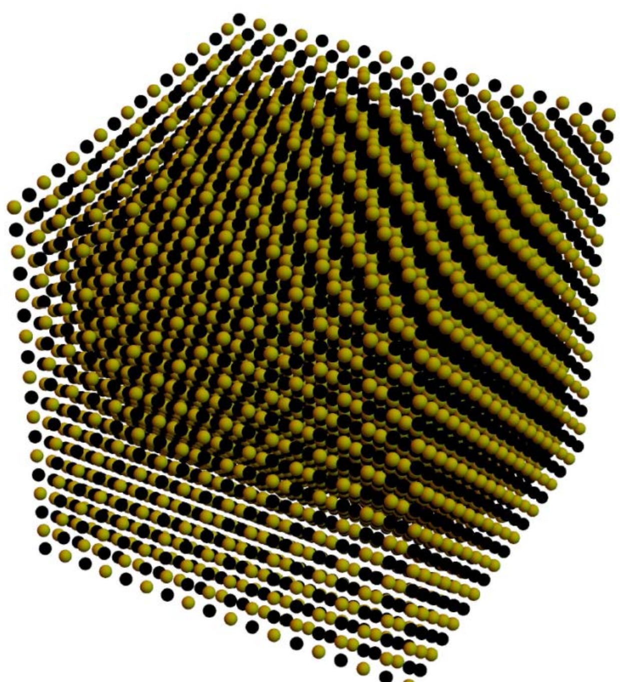
# What is a QD nanocrystal?

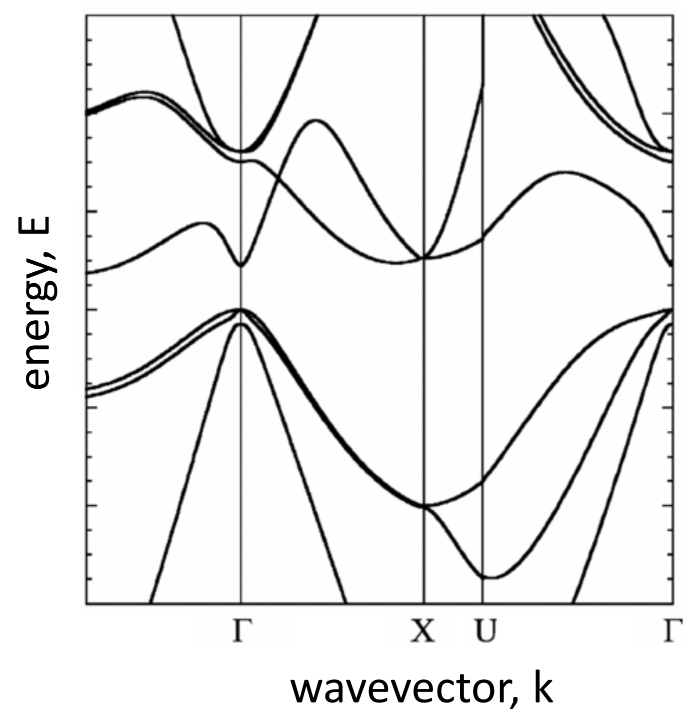
- Bulk Crystal
  - Periodic lattice of atoms which extends to infinity
  - Infinite crystal can be represented by finite amount of information → lattice vectors and constituent atoms



# What is a QD nanocrystal?

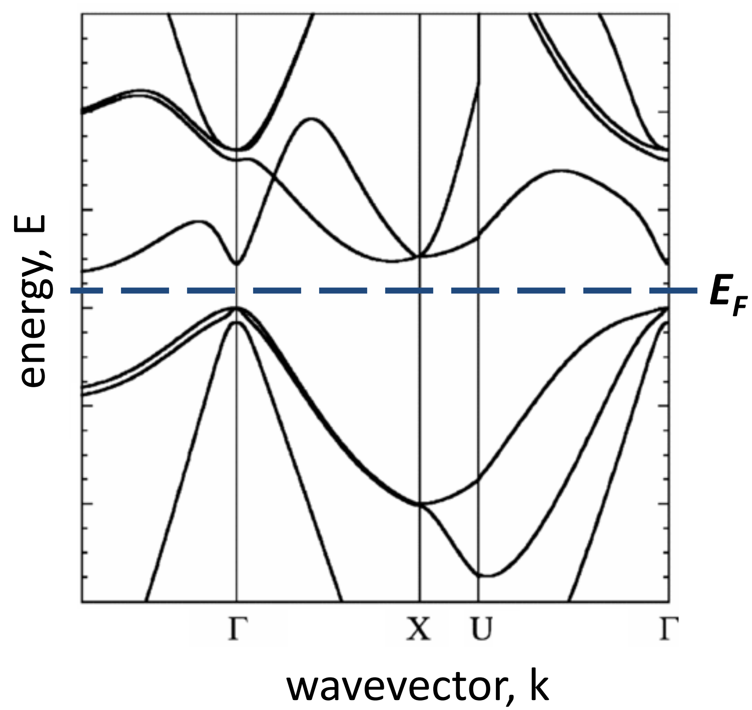
- Bulk Crystal
  - Bloch theorem: Define eigenstates with wavevector ***k*** and energy $\boldsymbol{E_k}$
  - Basic form of band structure can be obtained by crystal lattice
  - Considering constituent atoms further refines band structure





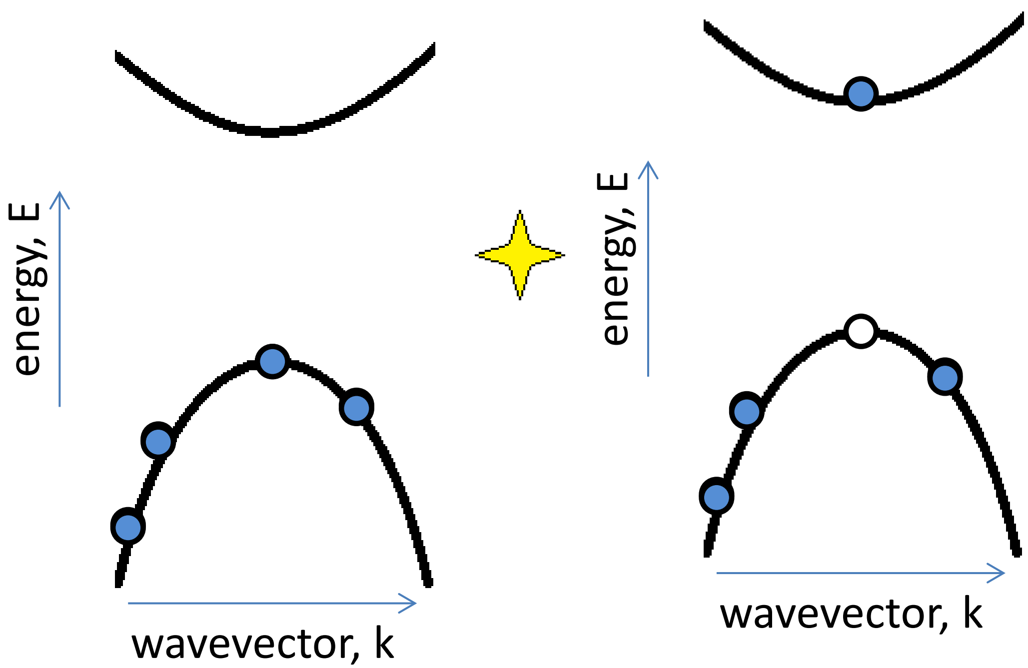
# What is a QD nanocrystal?

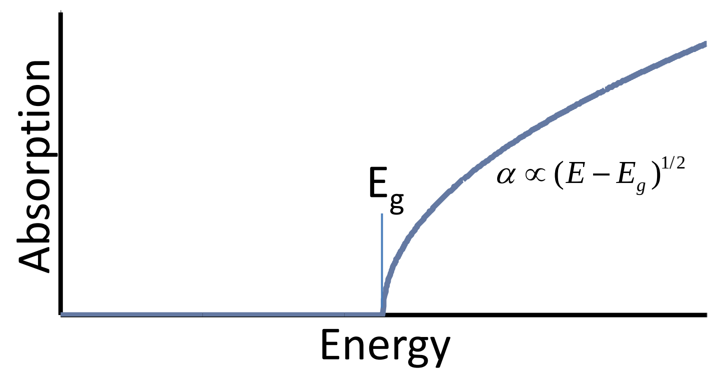
- Bulk Semiconductor
  - Fermi energy, $\boldsymbol{E_F}$, is the energy up to which all of the states below are filled with electrons at 0K
  - $\boldsymbol{E_F}$ for a semiconductor lies in a band-gap; a region in energy in which there are no available states



# What is a QD nanocrystal?

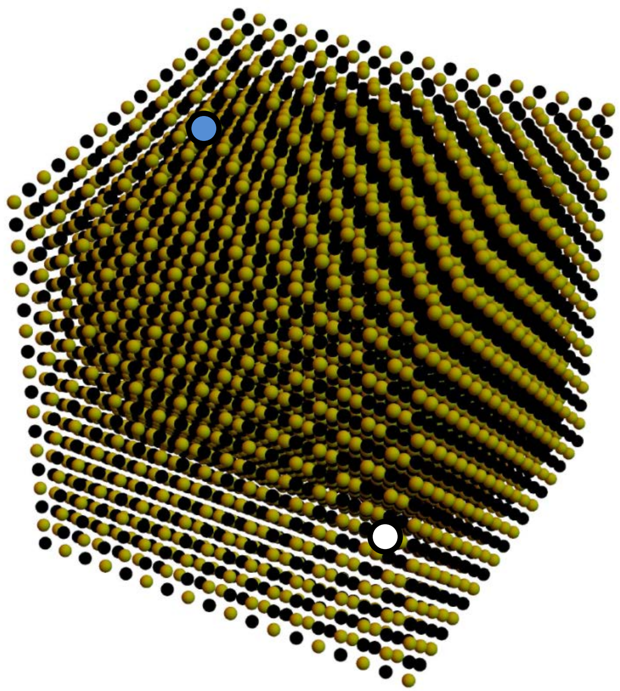
- Electron-Hole creation
  - A photon with energy larger than or equal to the bandgap can be absorbed, generating an electron in the conduction band and a hole in the valence band
  - Energy and momentum are both conserved



# What is a QD nanocrystal?

- Free electron and holes
  - In most semiconductors at room temperature, once generated, conduction band electrons and valence band holes are free to diffuse and drift in the crystal



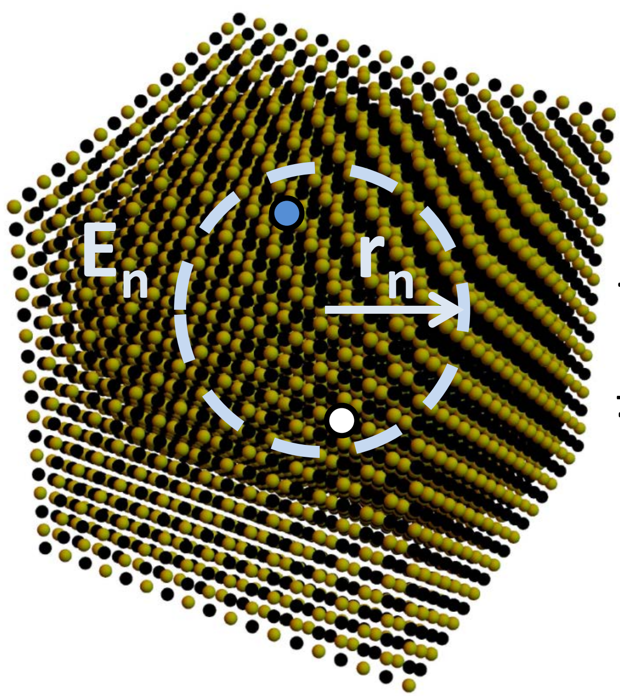
# What is a QD nanocrystal?

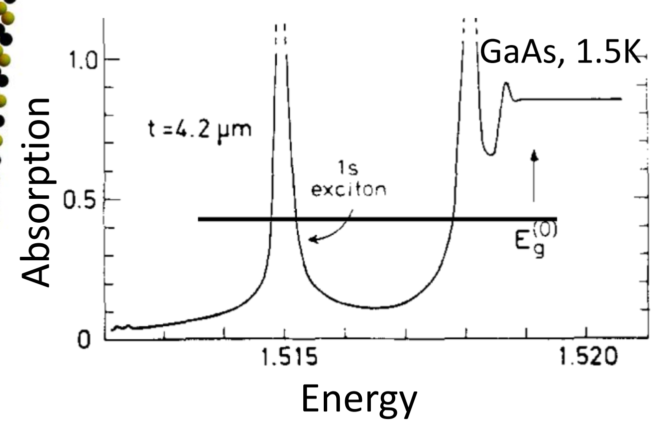
- Free electron and holes
  - In most semiconductors at room temperature, once generated, conduction band electrons and valence band holes are free to diffuse and drift in the crystal
  - At low temperatures, Coulomb attraction between the electron and hole can remain bound as an *exciton*

$$E_n = -\frac{\mu R_H}{m_0 \epsilon_r n^2}$$

$$r_n = \frac{m_0 \epsilon_r n^2 a_H}{\mu}$$

$\epsilon_r, \mu$ Material dependent

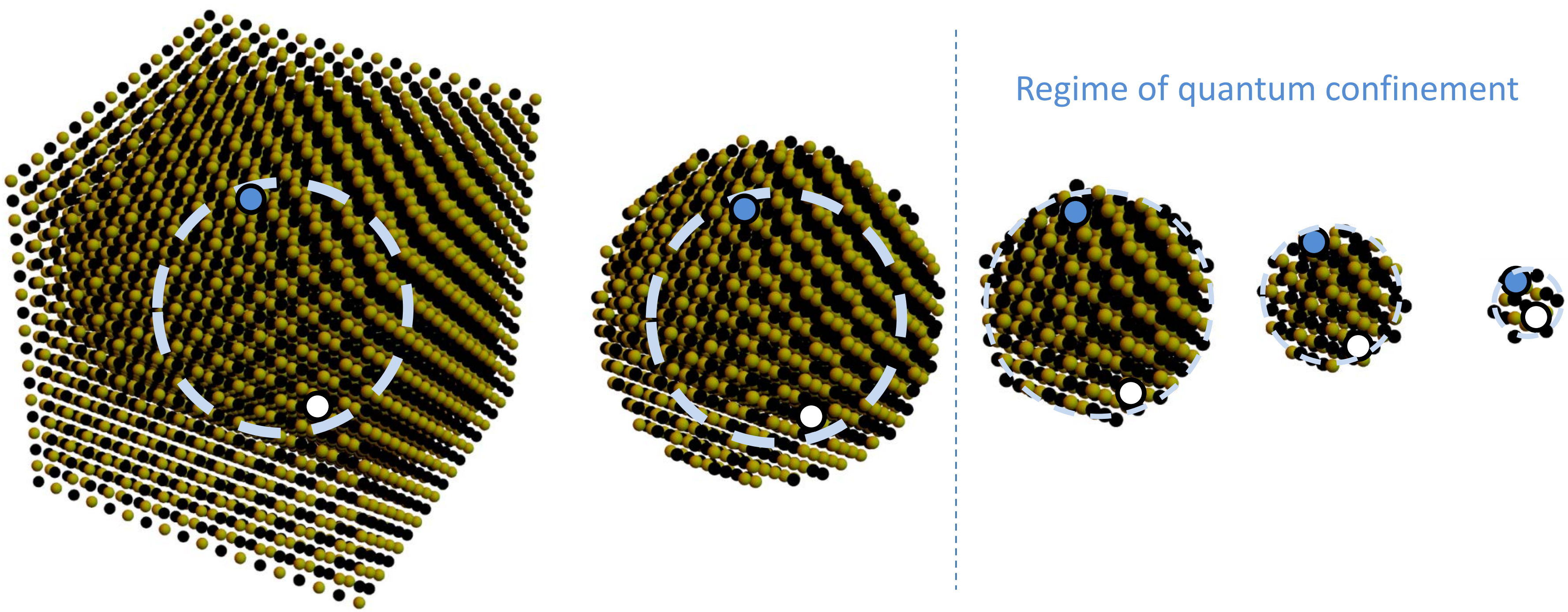



Fehrenbach, G. W., W. Schafer, and R. G. Ulbrich. *HESPP,* 30.1-4 (2012): 154.

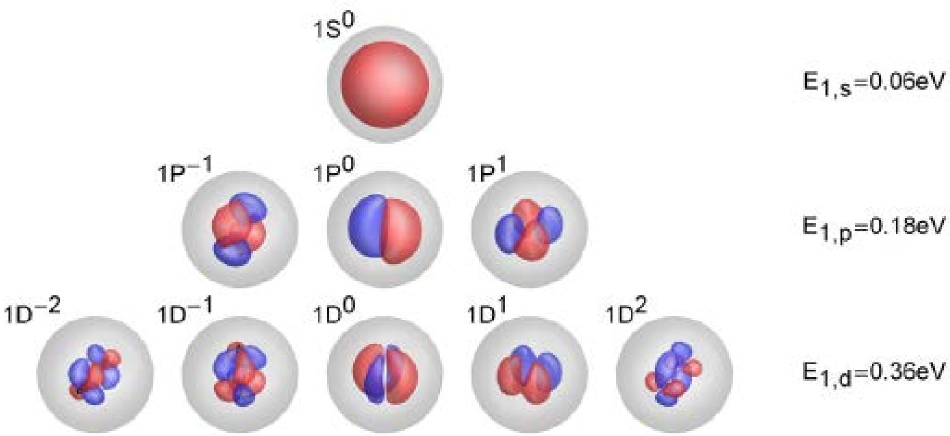
# What is a QD nanocrystal?

- Size scale:
  - For crystals of size considerably larger than the exciton radius $r_0$ can be considered as bulk
  - As the crystal size shrinks below the size of $r_0$, excitons become increasingly more confined
  - Coulomb energy of the exciton also increases

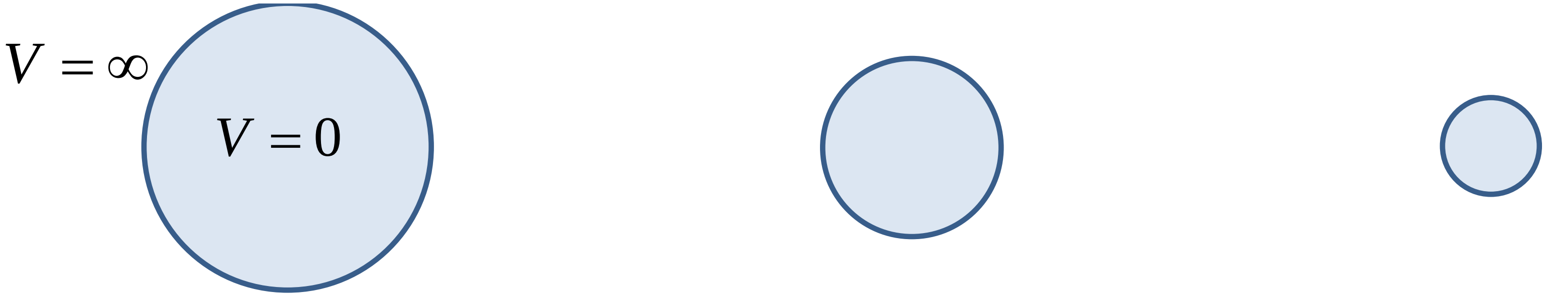


# Quantum Confinement

- Simplest model: Ignore constituent material, treat NCs as infinite quantum wells




$$E_{n,l} = \frac{\hbar^2 \alpha_{n,l}^2}{2 m_e r^2}$$



# Quantum Confinement

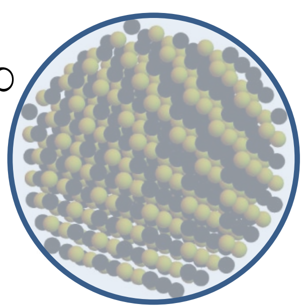
- Next level of sophistication: Envelope Approximation
- Carrier maintain effective mass from bulk band structure

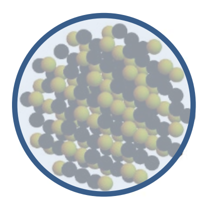
$$E_k^c = \frac{\hbar^2 k^2}{2\, m_{eff}^c} + E_g$$

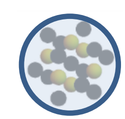
$$E_k^v = \frac{-\hbar^2 k^2}{2\, m_{eff}^v}$$

$$E_{ehp}(n_h L_h n_e L_e) = E_g + \frac{\hbar^2}{2\, a^2} \left\{ \frac{\alpha^2_{n_h, L_h}}{m_{eff}^v} + \frac{\alpha^2_{n_e, L_e}}{m_{eff}^c} \right\}$$

$V = \infty$

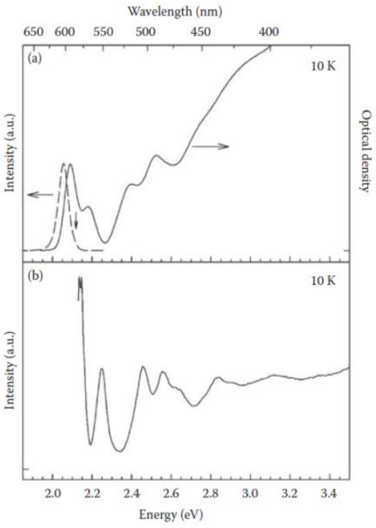


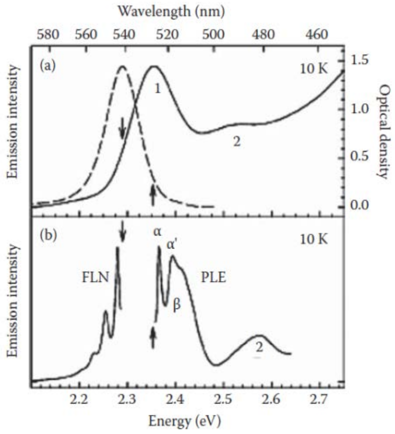




# Quantum Confinement

- Additional Corrections
  - Coulomb interaction energy of electron and hole
  - Degeneracy of bands in constituent material
  - Interactions between degenerate bands
  - Nonparabolicities of bands
  - Finite potential outside of NCs
- Spectroscopic methods
  - Absorption and Luminescence
  - PLE spectroscopy
  - FLN spectroscopy




Nanocrystal Quantum Dots, Klimov, V. I., et al. CRC Press, 2010

# Case Study: PbS

$$E_{g,QD} \sim E_{g,bulk} + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{1.8e^2}{\epsilon_r R}$$

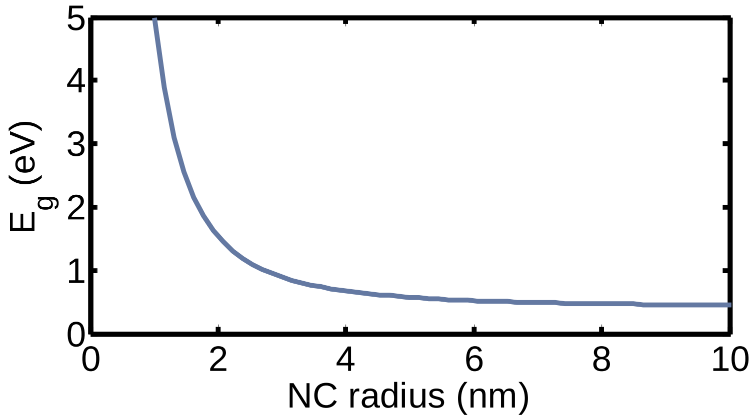
$$\epsilon_r = 169$$

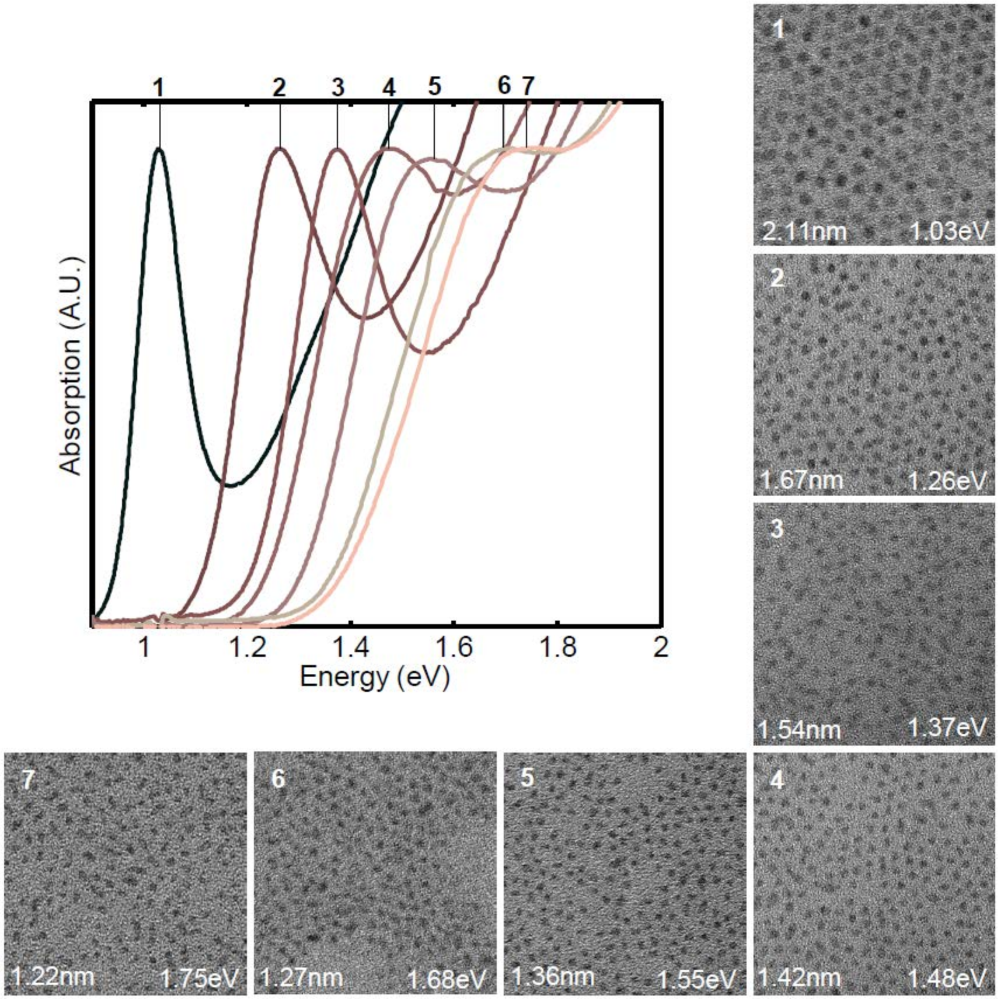
$$E_{g,bulk} = 0.42eV$$

$$m_c \sim 0.116 m_0$$

$$m_v \sim 0.121 m_0$$

$$\mu = 0.058 m_0$$





Preier, H. (1979). Recent advances in lead-chalcogenide diode lasers. *Applied physics*, *20*, 189–206.

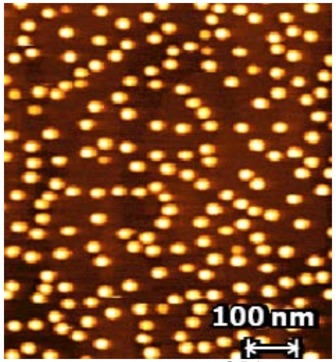
Yazdani, N. A., et al. (2014). Hole Mobility in Nanocrystal Solids as a Function of Constituent Nanocrystal Size. *The Journal of Physical Chemistry Letters*, (5), 3522–3527.

# Colloidal Synthesis

Time: ~10m

# NC Syntheses

| **Self Assembled Quantum Dots** | **Colloidal Quantum Dots** |
|---|---|
| Molecular Beam Epitaxy | Solution processed |
| Grown directly on substrate | Dispersion of NCs in Solution |
| Poor size distribution and therefore optical properties | Monodisperse |
| Materials & size well suited to IR | Tunable |

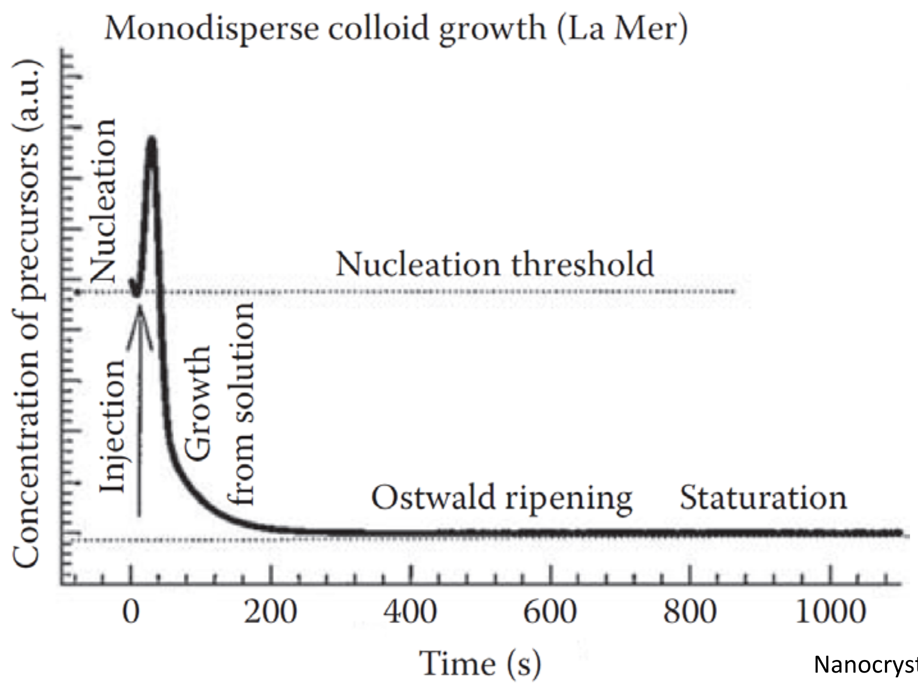



QDLaser

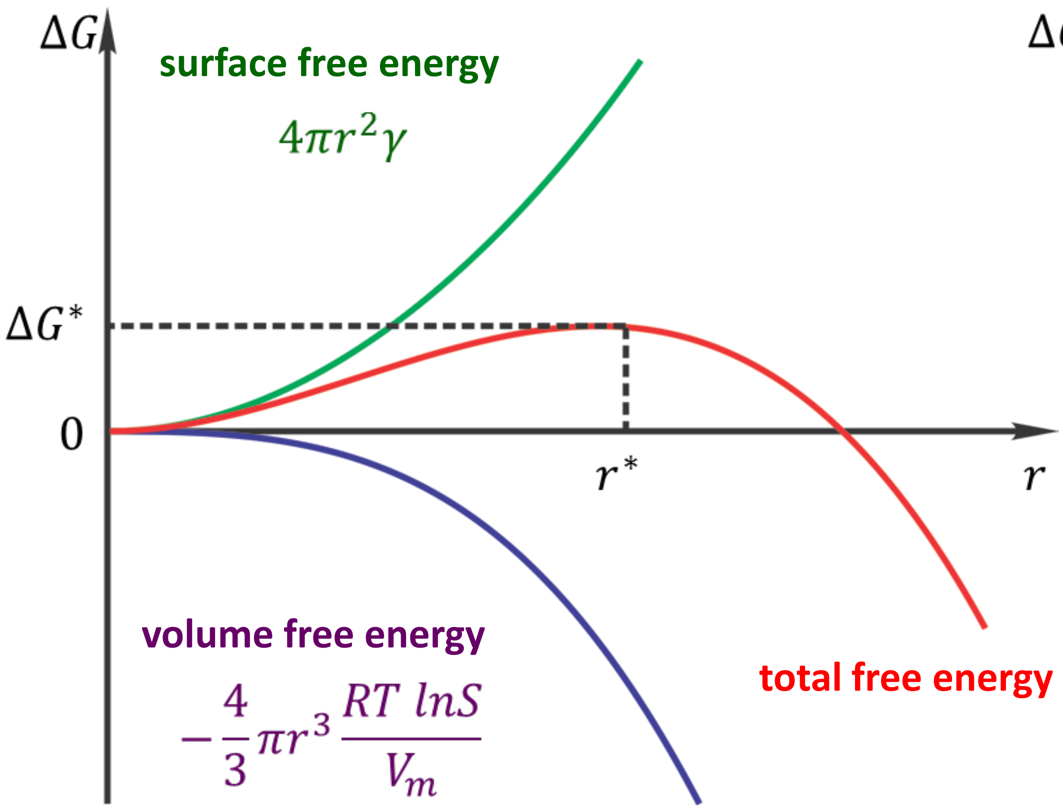
# Hot Injection Method

$$A + B \longrightarrow AB$$

- When the solution is supersaturated, nucleation of NCs occur
- Below supersaturation, monomers attach to nucleated NCs
- With sufficient time, the larger NCs eat up the smaller ones




Nanocrystal Quantum Dots, Klimov V., CRC Press 2010




surface tension on crystal|solution

$$\Delta G(r) = 4\pi r^2\gamma + \frac{4}{3}\pi r^3 \Delta G_V$$

$\Delta G_S$

$\Delta\mu$

$$\Delta G_V = -\frac{RT\ lnS}{V_m}$$

molar volume of bulk crystal

**Critical radius and total free energy**

$$r^* = \frac{2\gamma V_m}{RT\ lnS}$$

$$\Delta G^* = \frac{16\pi\gamma^3 V_m^2}{3(RT\ lnS)^2}$$

**Nucleation rate**

$$\frac{dN}{dt} = A\exp\left[\frac{-\Delta G^*}{RT}\right]$$

Kwon et al. Small 2011, 7, 2685

concentration of monomers in solution

diffusion coefficient

concentration of monomers on the surface

**Growth rate** $$\frac{dr}{dt} = \frac{DV_m([A]_{sol} - [A]_{surf})}{r - \frac{D}{k}}$$

reaction rate constant

$D \ll kr$ $\qquad$ $D \gg kr$

$$\frac{dr}{dt} = \frac{DV_m([A]_{sol} - [A]_{surf})}{r}$$

**diffusion controlled growth**

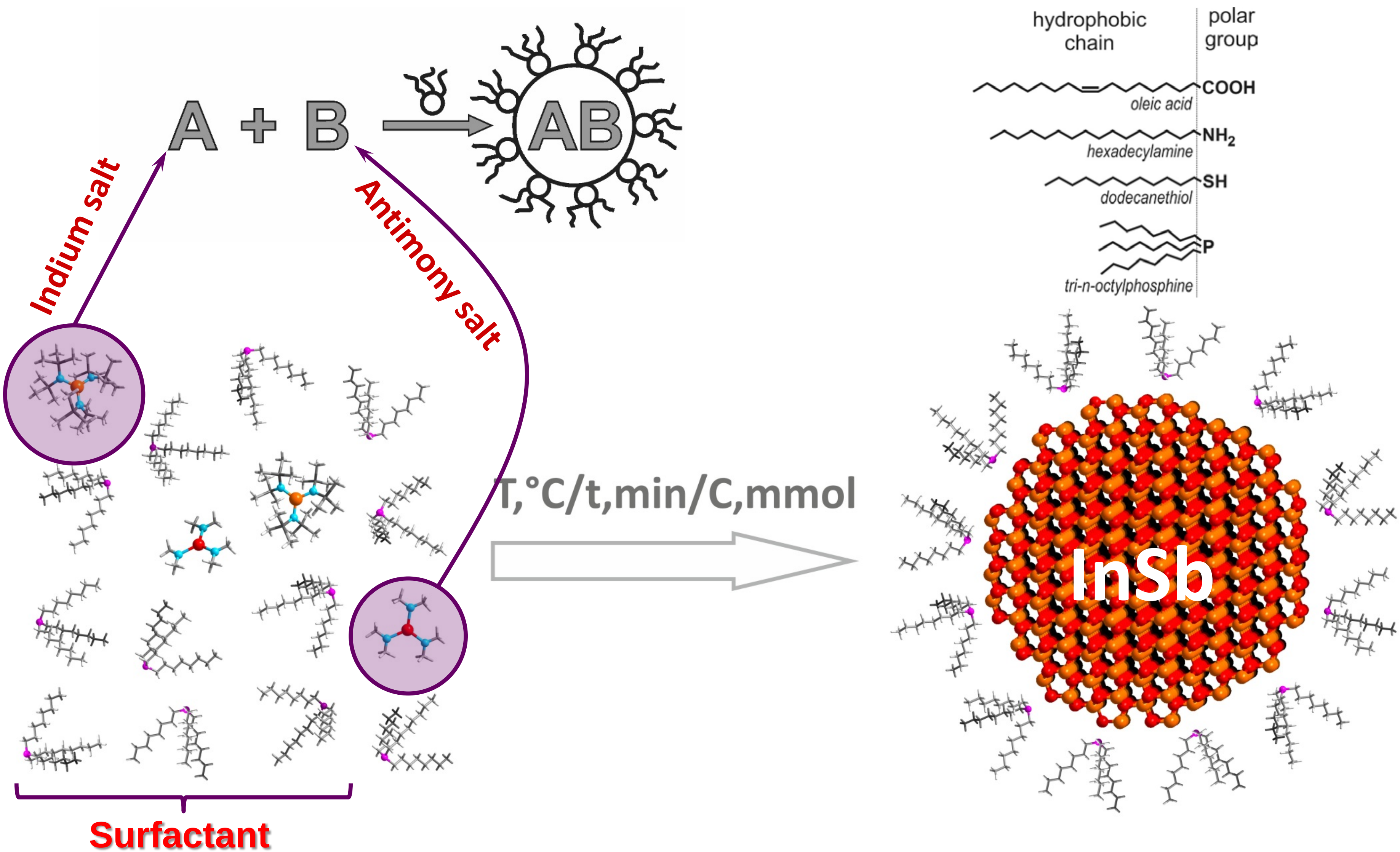
$$\frac{dr}{dt} = kV_m([A]_{sol} - [A]_{surf})$$

**reaction controlled growth**

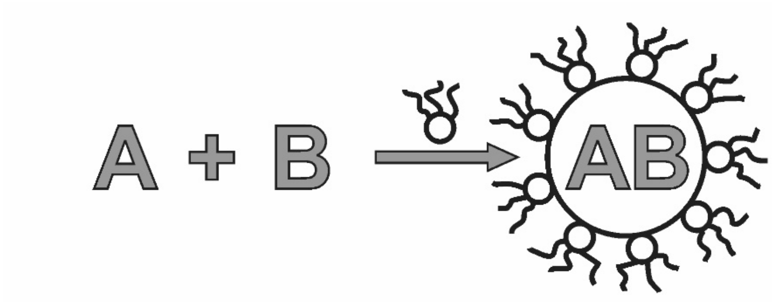
**Most of real systems are in the mixed growth regime**

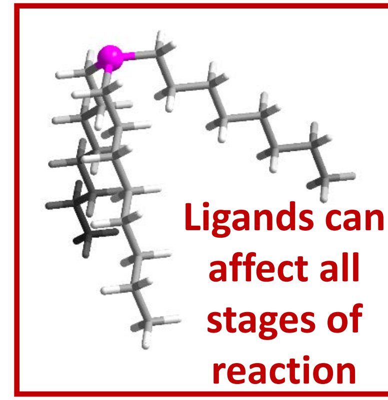
Kwon et al. Small 2011, 7, 2685

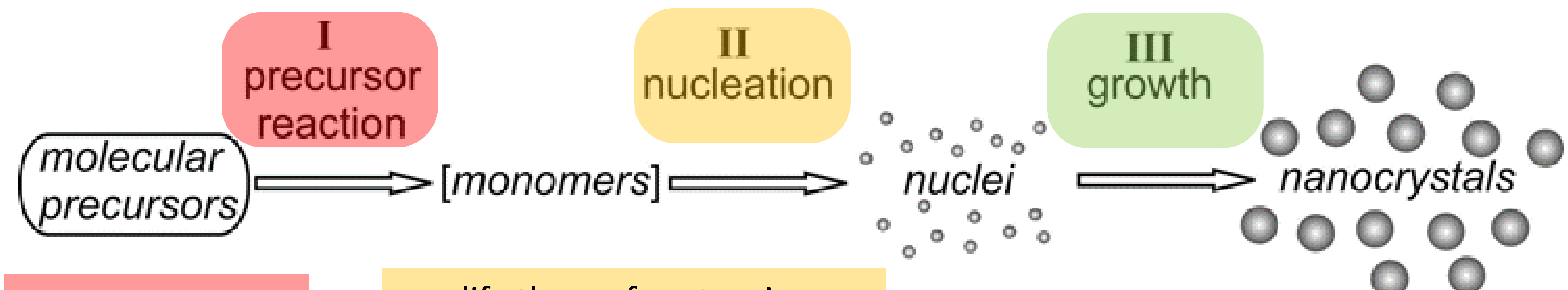
# Colloidal Synthesis



# Colloidal Synthesis




can be a part of monomers or intermediates

participate in redox processes or metathetic reactions

modify the surface tension on crystal-solution interface

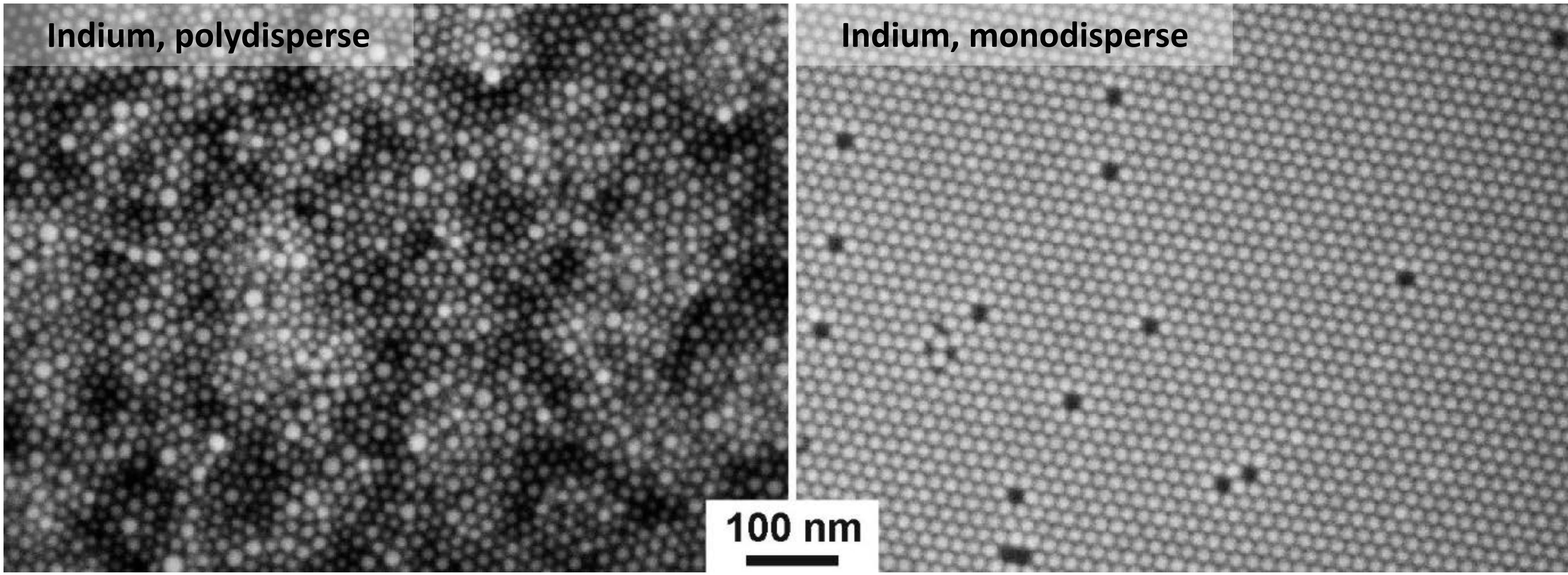
define solubility of monomers and nanocrystals

affect the diffusion coefficient

change the reaction rate constant

determine a shape of nanocrystals

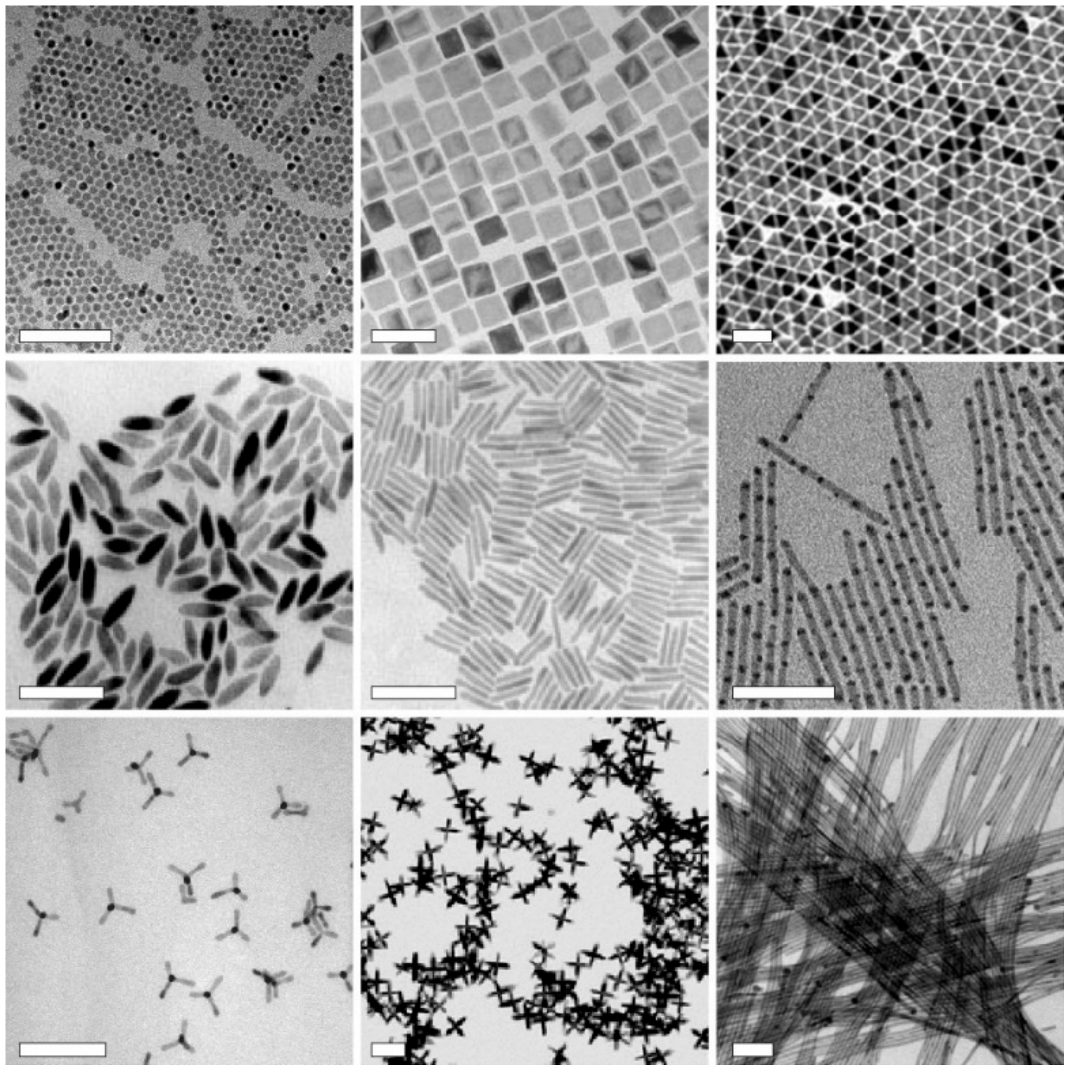
# Colloidal Synthesis




- Synthesis Optimization
  - Hard to predict a priory

Yarema et al. ACS Nano, 2012, 6, 4113

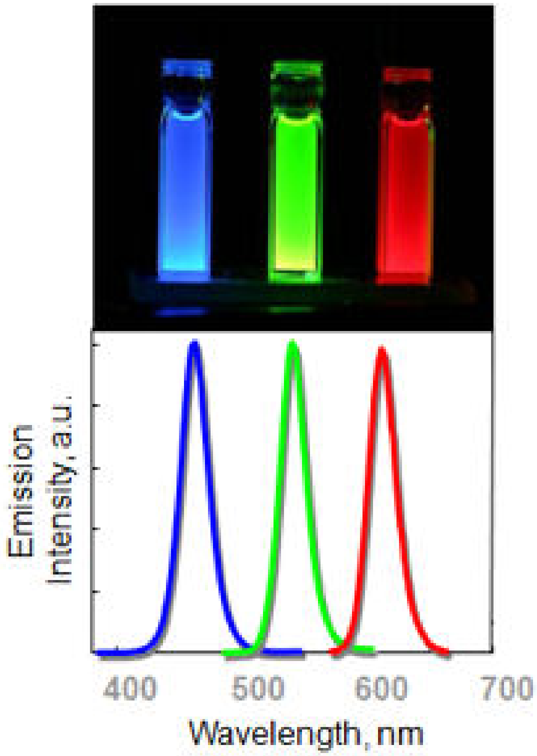
# Colloidal Synthesis



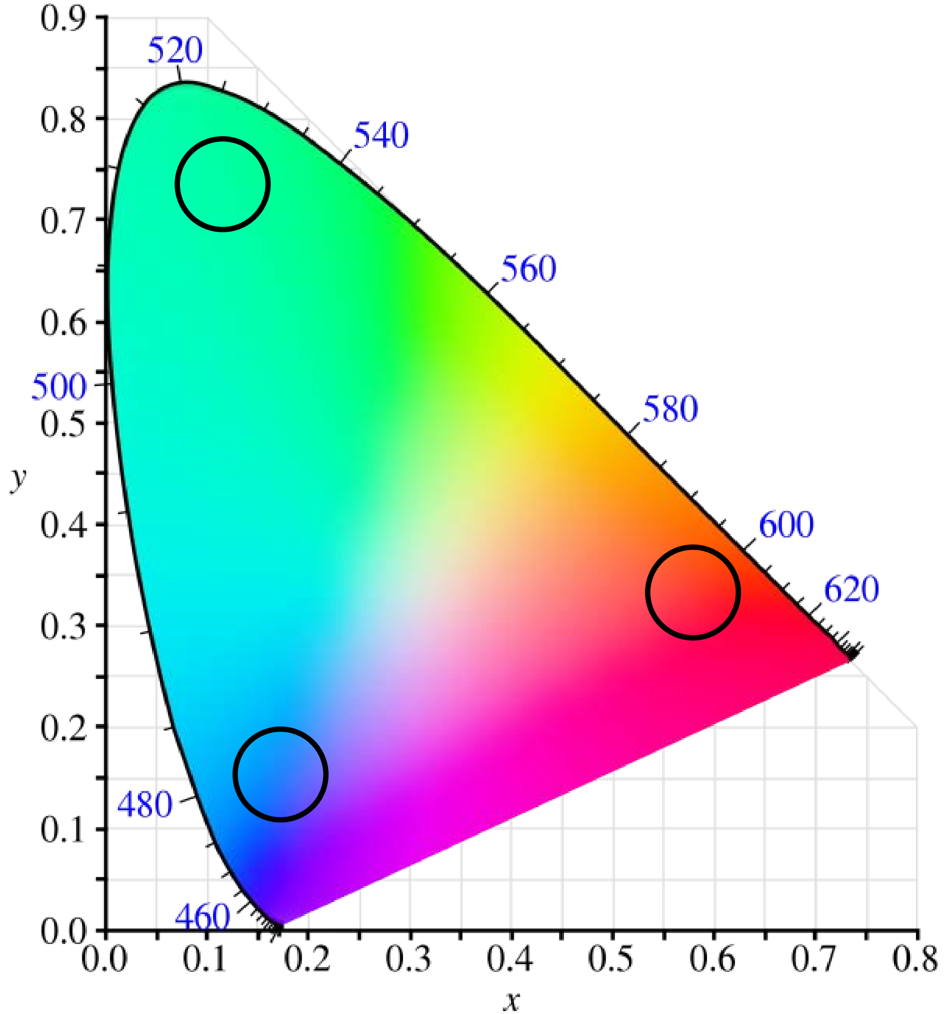
# Optical Applications

# Optical Applications

- Colloidal QD-NCs offer:
  - Easy tunability of luminescence color
  - Very narrow spectral distributions
- Filters/downconverters
- LEDs




# Generating the Visible Spectrum

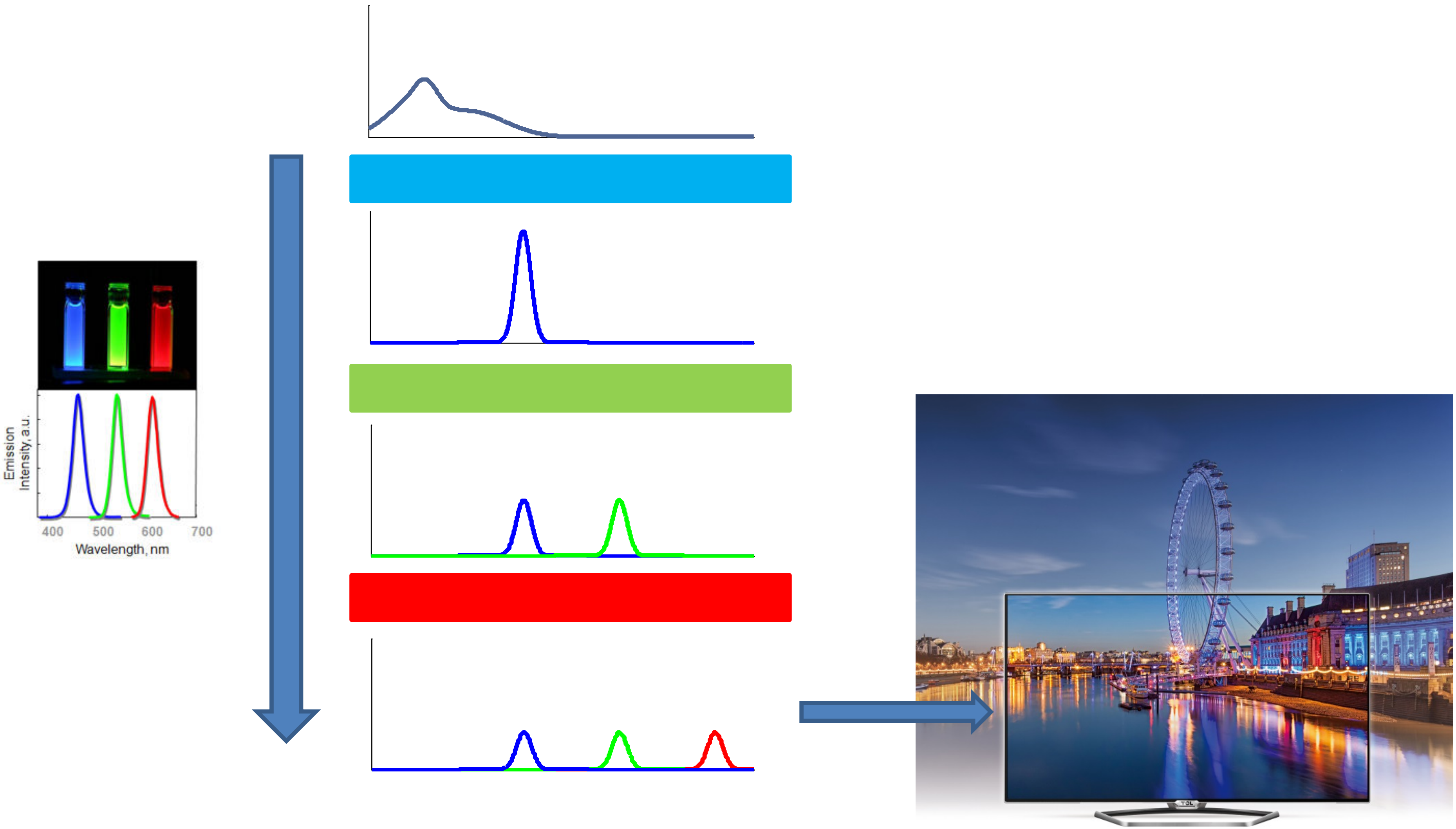



en.wikipedia.org/wiki/CIE_1931_color_space

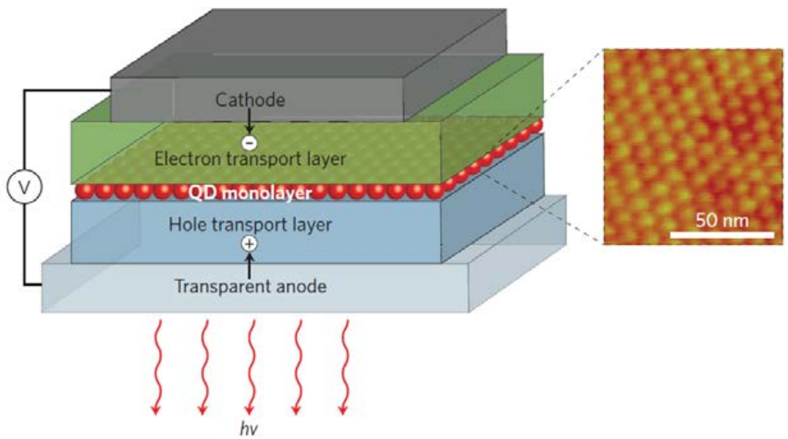
- A set of three colors can be mixed to generate any color enclosed by the triangle formed between the three points
- The sharpness of the initial colors determine the sharpness of the final mixed color

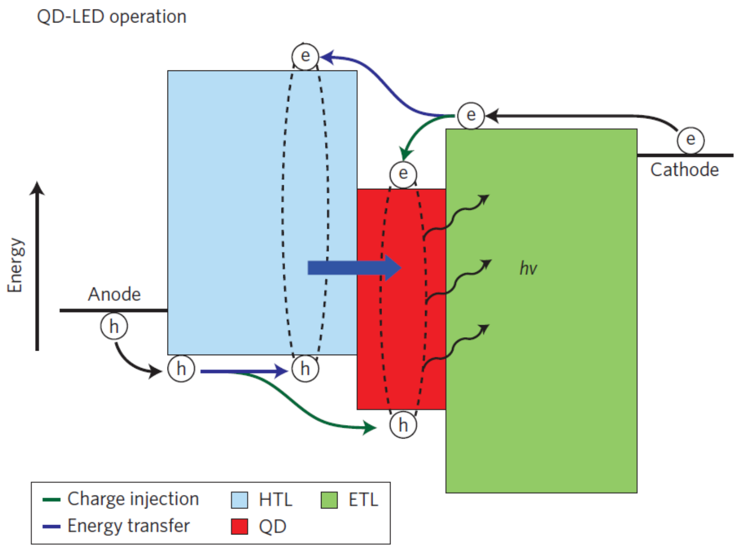
**LCD Displays and Television!**

# Generating the Visible Spectrum



# LEDs



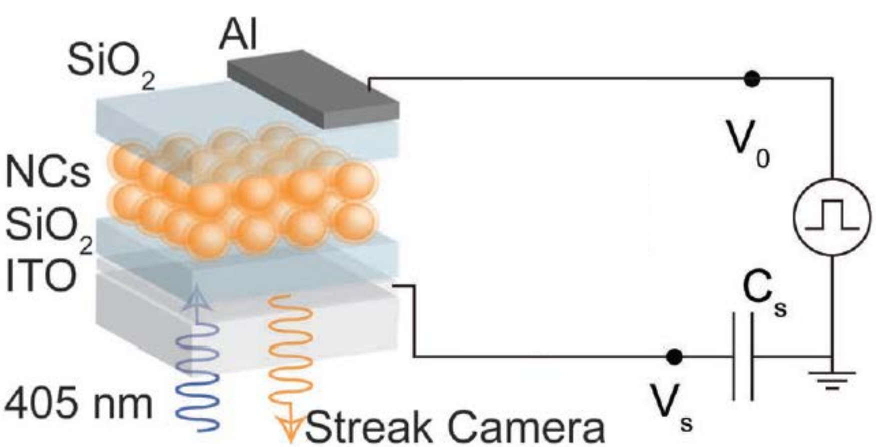



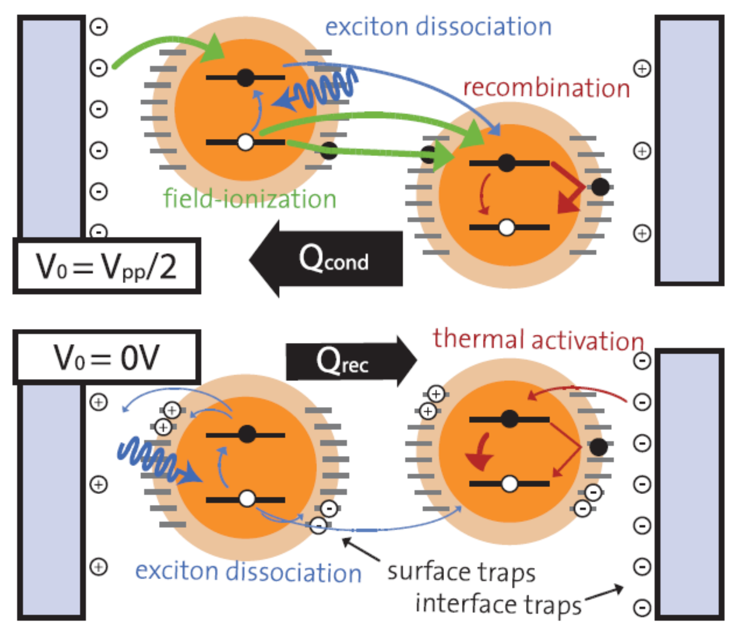

- Solution processable
- Compatible with flexible substrates
- Good efficiencies (~20%)
- Air Stability


Shirasaki, Y., Supran, G., Bawendi, M., & Bulović, V. (2013). Emergence of colloidal quantum-dot light-emitting technologies. *Nature Photonics*, *7* (December 2012).

# Field driven LEDs

- Driven with AC voltage
- Helped with fundamental research
- Very high power consumption / low efficiency

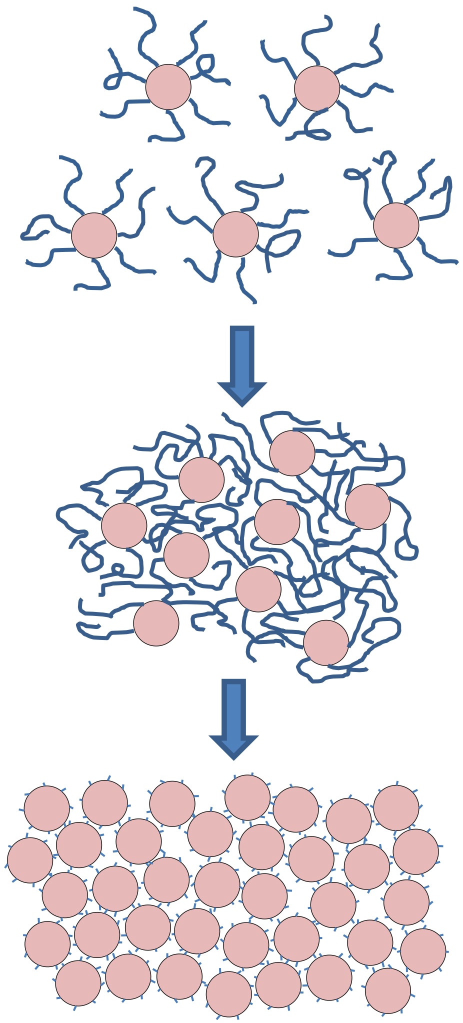



Bozyigit, D., Wood, V., Shirasaki, Y., & Bulovic, V. (2012). Study of field driven electroluminescence in colloidal quantum dot solids. *Journal of Applied Physics*, *111*(11)

# NC-Solids, Processing and Applications

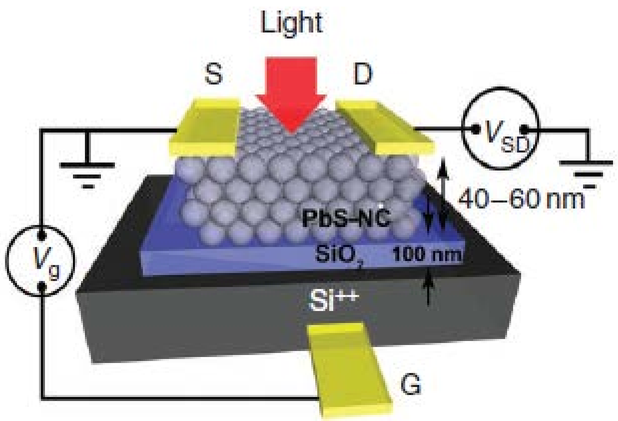
# NC-Solids

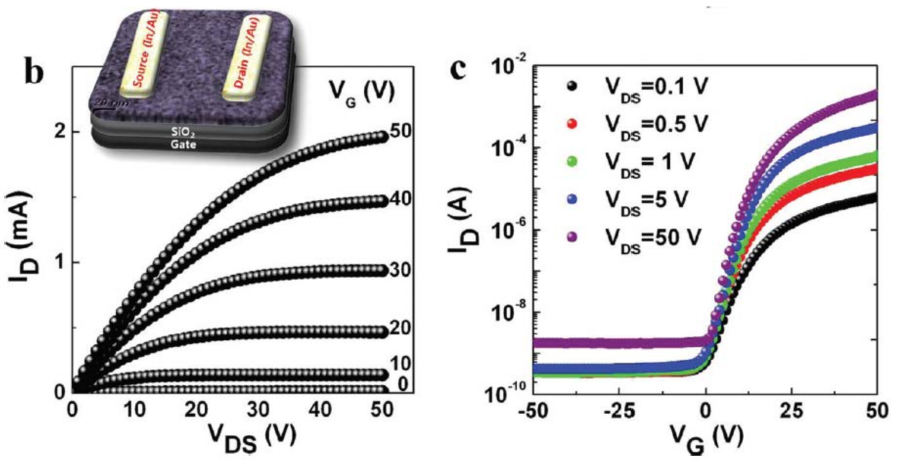


- Synthesis → NCs terminated with long, insulating ligands, suspended in solution
- Spin-coating, dip-coating, drop casting onto substrate
- Insulating ligands
  - poor charge transfer between NCs
  - insulating film
- Strategy: Ligand Exchange
  - Drastically enhance coupling between NCs
  - Semiconducting, and metallic films
  - → FETs, Solar Cells, photo-detectors …

**Lead Chalcogenides (PbS, PbSe) dominate for applications in electronics**

# NC FETs

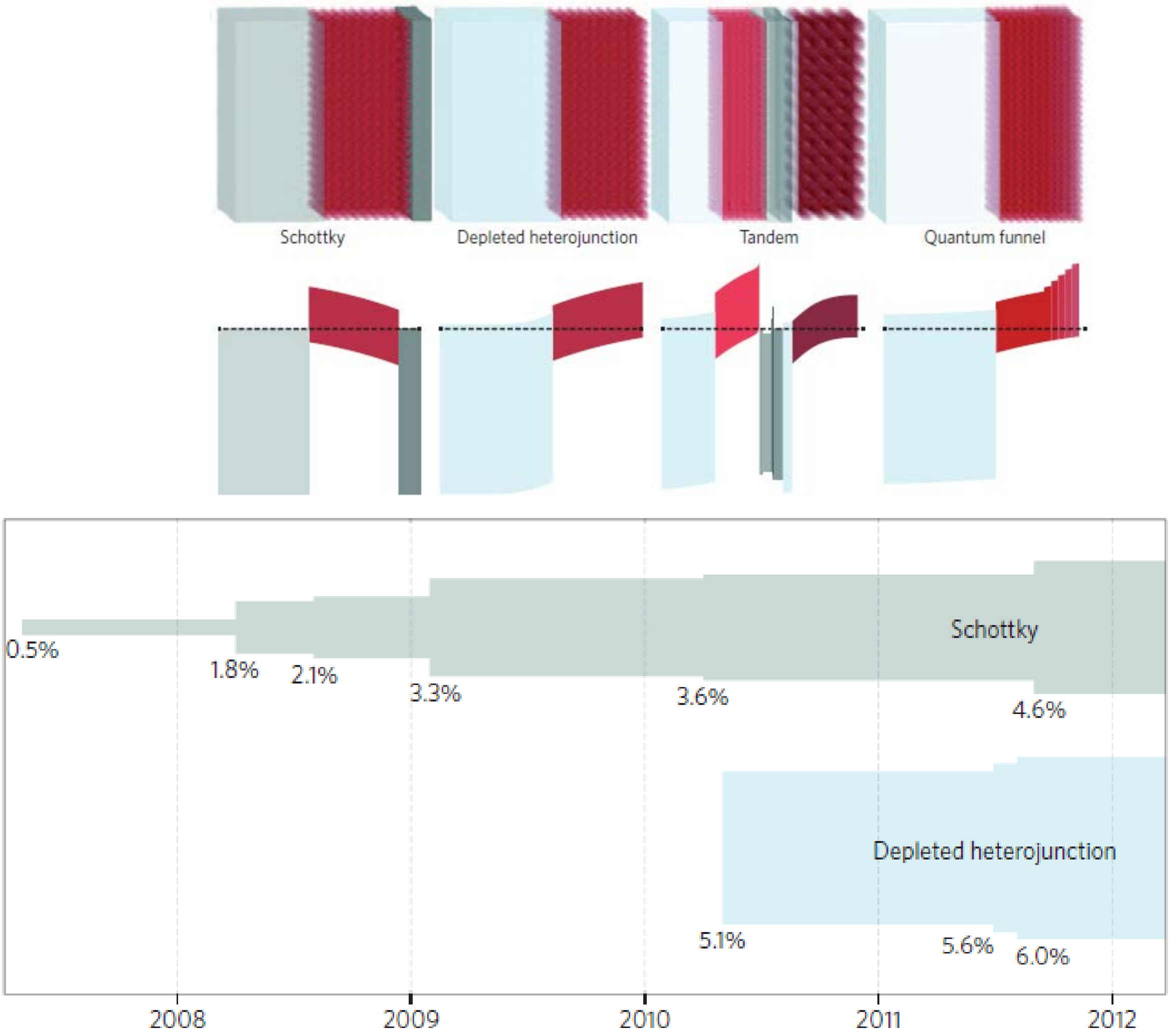



Nagpal, P., & Klimov, V. I. (2011). Role of mid-gap states in charge transport and photoconductivity in semiconductor nanocrystal films. *Nature communications*, *2*, 486.

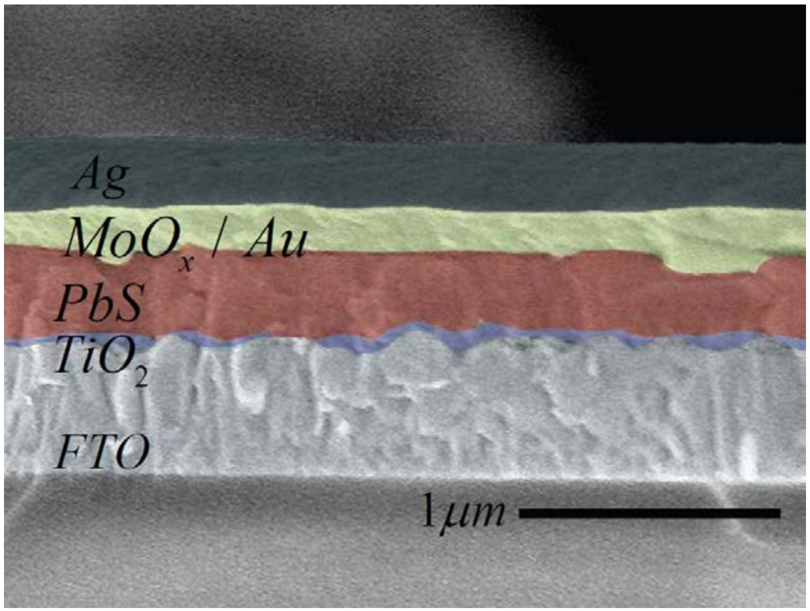
Choi, J.-H., Fafarman, A. T., Oh, S. J., Ko, D.-K., Kim, D. K., Diroll, B. T., Muramoto, S., et al. (2012). Bandlike transport in strongly coupled and doped quantum dot solids: a route to high-performance thin-film electronics. *Nano letters*, *12*(5), 2631–8.

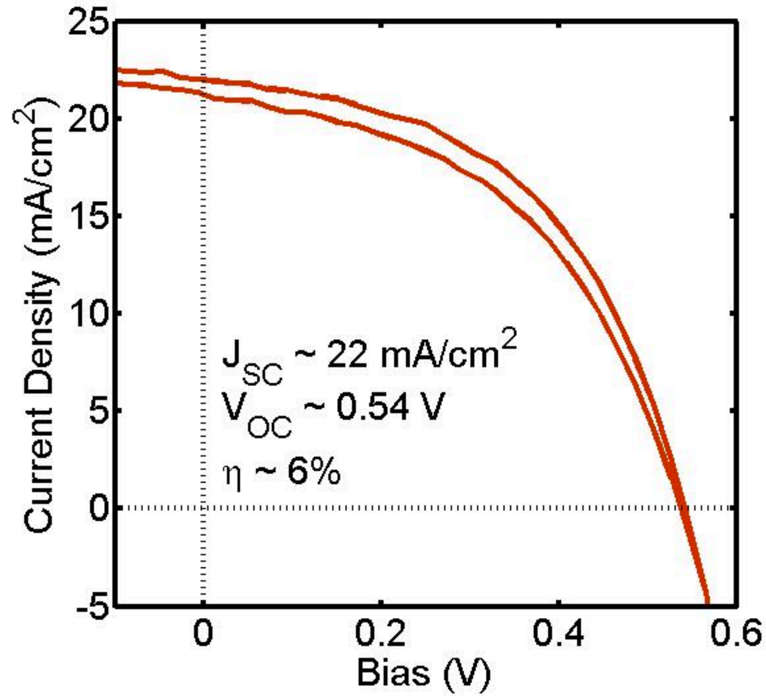
# NC Solar Cells




Sargent, E. H. (2012). Colloidal quantum dot solar cells. *Nature Photonics*, *6*(3), 133–135.

# NC Solar Cells

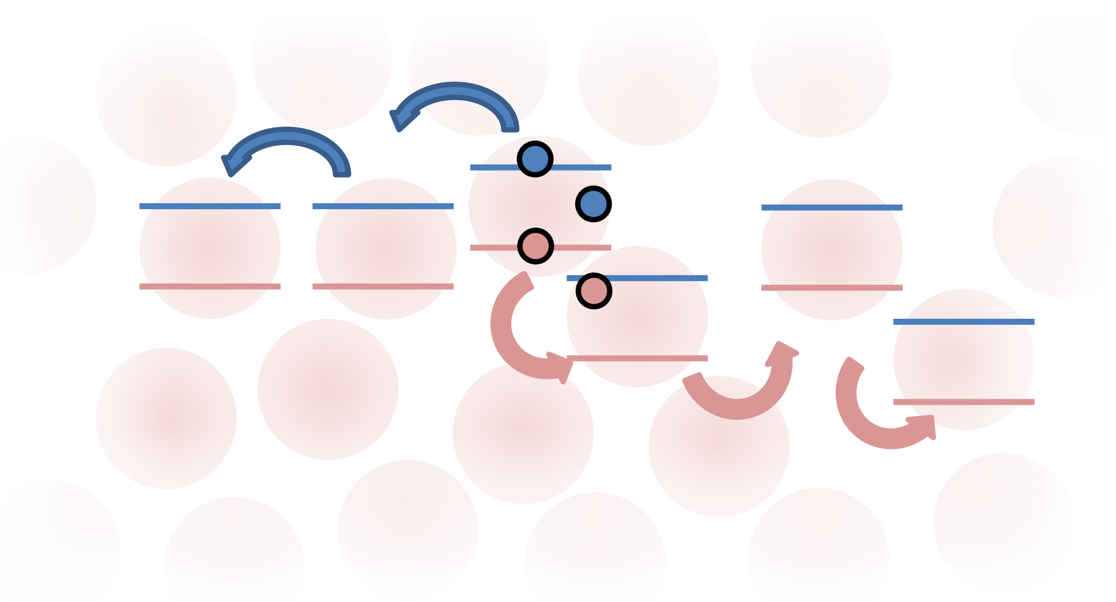



- Heterojunction solar cell architecture
  - Electron extraction from the $TiO_2$/FTO, hole extraction from the $MoO_x$/Au

# Transport in NC-Solids

- Nature of charge transport is densely packed NC solids is still under debate
- Transport is considered to occur prodominately through the first excited electron and hole states
- Transport is likely via variable range hopping between neighboring NCs
- It has been argued that in some cases coupling between the dots is large enough to form Bands that extend through the solid



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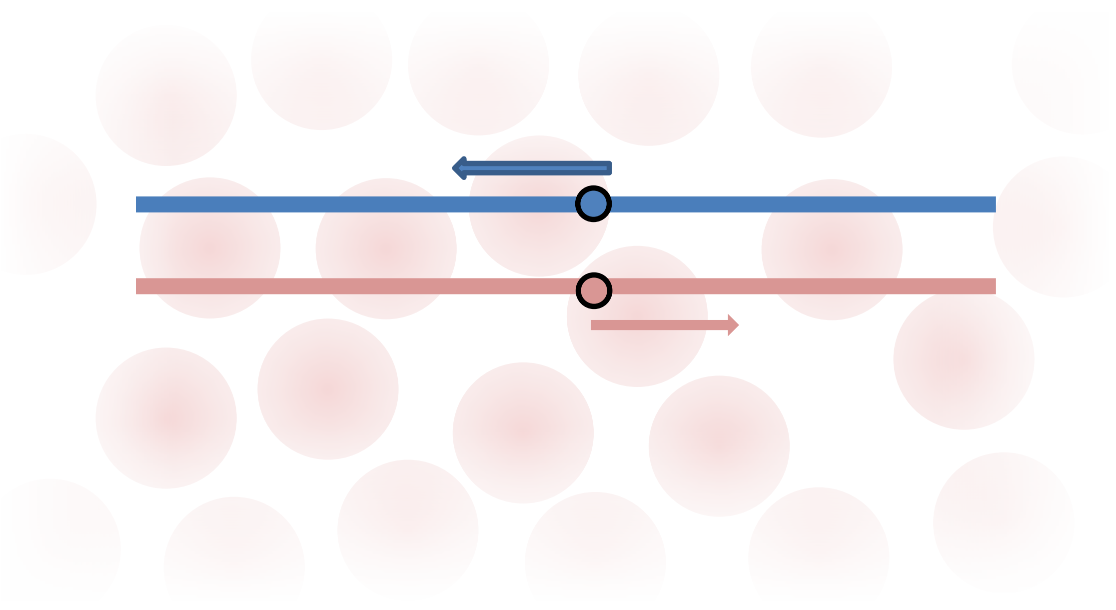


# Transport in NC-Solids

NCs
- Material and Size

$E_g$ $\mu$

NC-NC separation
- Coupling between NCs

$\mu$

Choice of Ligands
- Dielectric environment

$E_f$ $E_C$ $E_V$ $\mu$

Surface Chemistry
- Dielectric environment
- Fermi-level modification

$E_f$ $\mu$

Size Distribution
- Disorder in band gap

$\mu_{eff}$ $\eta$

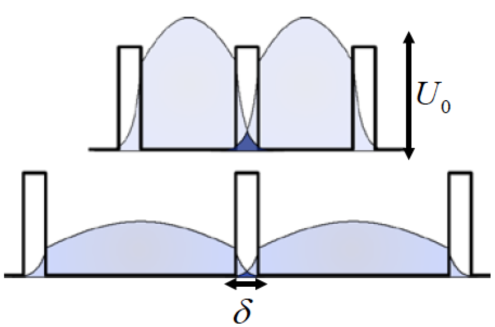
# Transport in NC Solids

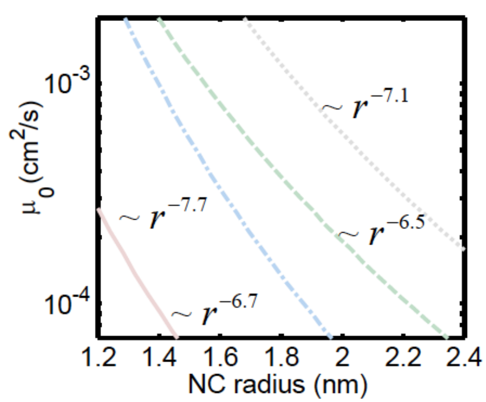
NCs
- Material and Size

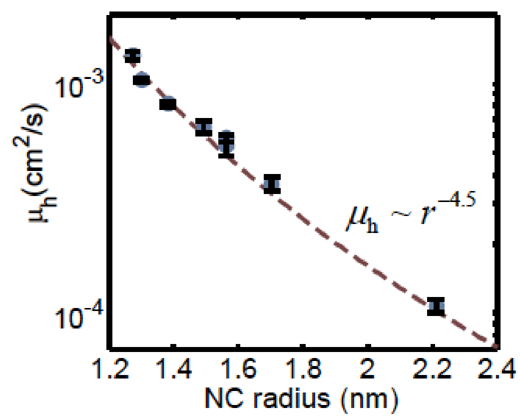
$E_g$ $\mu$

- Size plays an important role in determining the bandgap of the NC solid
- NC size also influences the carrier mobility through the **NC-NC coupling**

- Carrier mobility is dependent on the extent of the wavefunction overlap (**coupling**) between neighboring NCs, which depends on:
  - NC-NC separation
  - Energetic barrier between NCs
  - NC size
- Smaller NCs ➔ higher $E_k$ of carrier on the NC ➔ enhanced leakage of the wavefunction outside of the NC





Yazdani, N. A., Bozyigit, D., Yarema, O., Yarema, M., & Wood, V. (2014). *The Journal of Physical Chemistry Letters*, (5), 3522–3527.

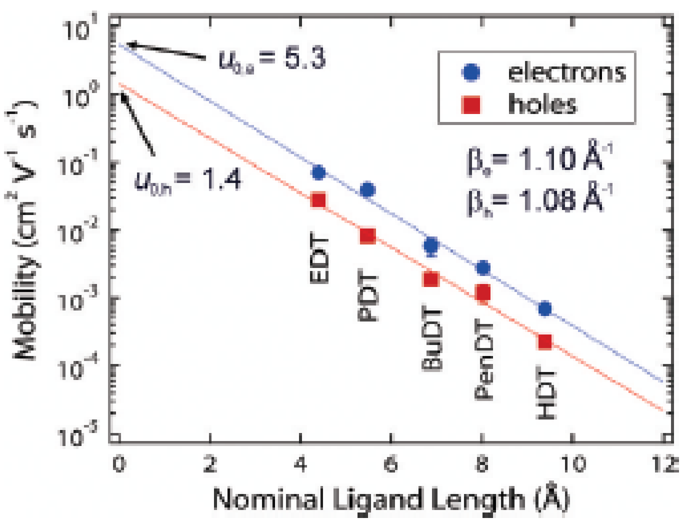
# Transport in NC Solids

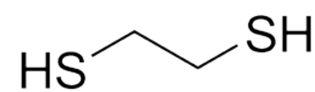
NC-NC separation

- Coupling between NCs

$\mu$

- Following the same line of argument on the **NC-NC coupling**, the NC-NC seperation also strongly affects the carrier mobility
- Shorter Ligand → increased coupling and higher mobilities

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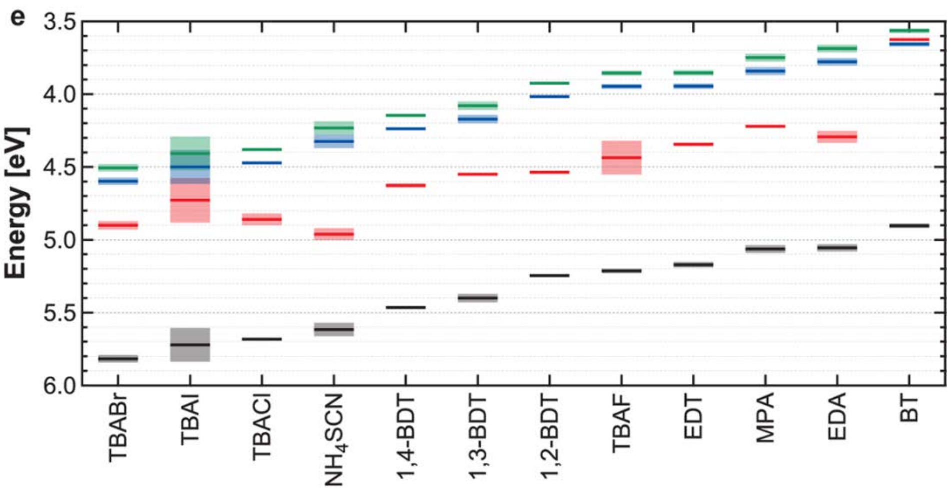
# Transport in NC Solids

Choice of Ligands
- Dielectric environment

$E_f \quad E_C \quad E_V \quad \mu$

- Affect of the surface terminating ligand is crucial!
- NC-NC separation
- Energetic barrier seen by charges between NCs
- Through surface dipoles: modifies the absolute position of the conduction and valence band in the NCs

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# Transport in NC Solids

Surface Chemistry
- Dielectric environment
- Fermi-level modification

$E_f \quad \mu$

- The largest challenge in NC-solids!
- Huge surface area available for reactions!
- Oxidation and reduction of the surface can modify Fermi level in the NC solid

- For PbS FETs, **!!NO AIR EXPOSURE!!**
- For PbS Solar Cells, **!!NEED AIR EXPOSURE!!**

???

If surface chemistry can be tamed → control of the fermi-level in the NC solid

# Transport in NC Solids

Size Distribution
- Disorder in band gap

$\mu_{eff}$ $\eta$

- Topic of current research