6. Quantum nanostructures

6.1 Quantum wells

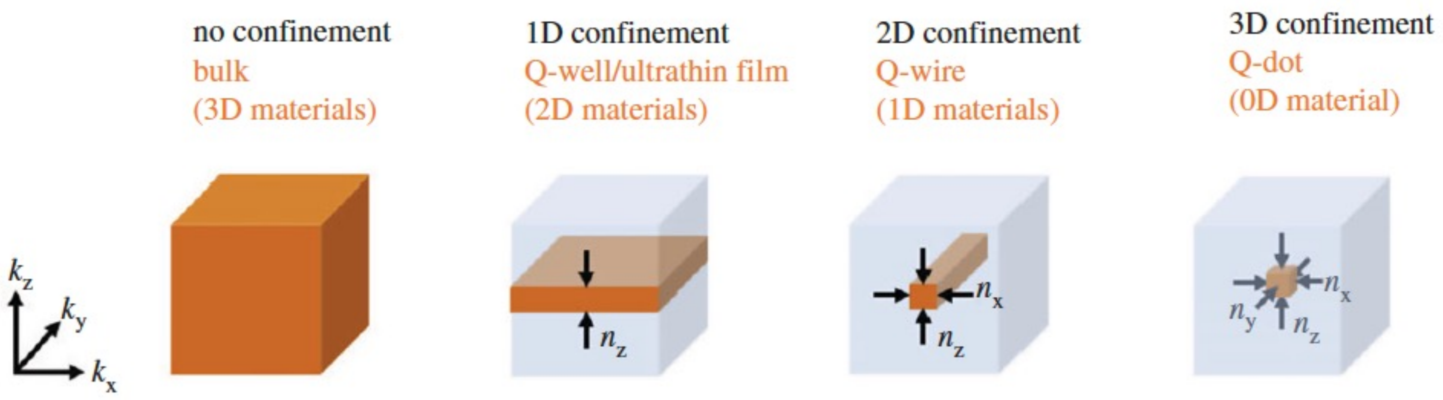
Topics of this lecture:

- Quantum confinement
- Quantum wells
- Absorption in quantum wells
- Applications of quantum wells

- Quantum dots
- Absorption in quantum dots
- Applications of quantum dots, part I

Quantum confinement

Edvinsson T. 2018,. R. Soc. open sci. 5: 180387



- In general, optical/electronic properties of solids do not depend on size

Ex: Ruby will be red for small (micrometer) or large crystals!

- However, when **one** or **more** dimensions are reduced down to the scale of the De Broglie wavelength of the carriers (e^- or h^+) in artificial structures, quantum confinement occurs

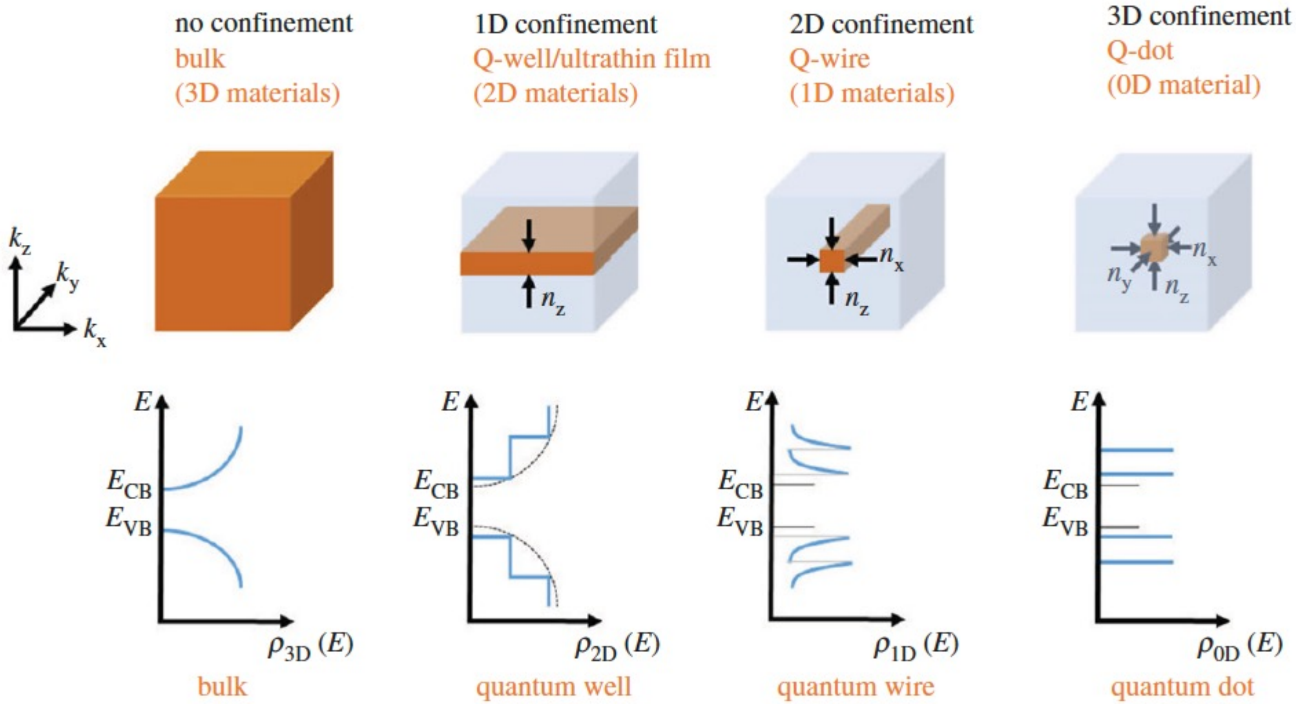
- De Broglie wavelength: $\lambda = \frac{h}{p}$

- A material can be considered a nanostructured material if some of the dimensions are less than 500 nm

Quantum confinement

- As a consequence of the low dimensions, higher surface areas are obtained but also introduce new physics and increased tunability of the electronic states

  → ***Discrete energy levels can appear***



Edvinsson T. 2018,. R. Soc. open sci. 5: 180387

Structure	Quantum confinement	Number of free dimensions	Electron density of states
Bulk	none	3	$E^{1/2}$
Quantum well/superlattice	1-D	2	E^0
Quantum wire	2-D	1	$E^{-1/2}$
Quantum dot/box	3-D	0	discrete

Fox, Mark. Optical Properties of Solids

Quantum confinement

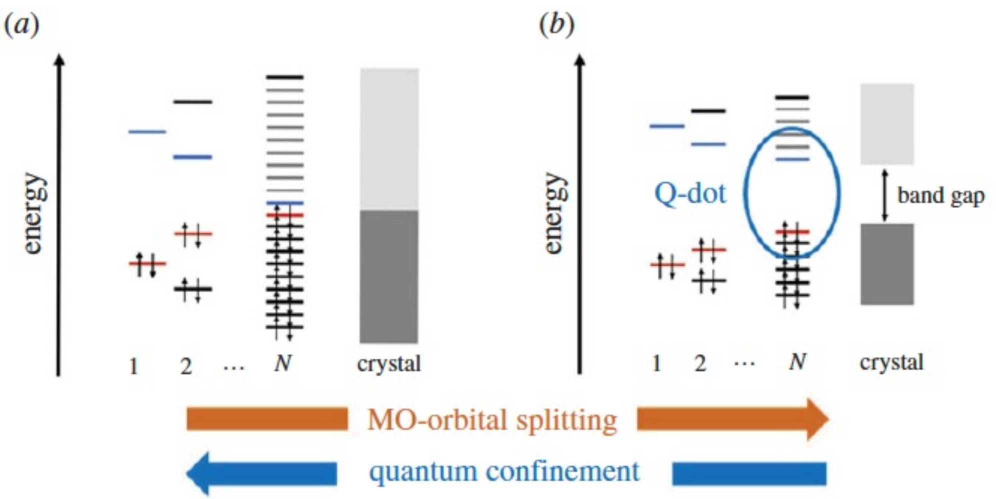
- Heisenberg principle: $\Delta p_x \sim \frac{\hbar}{\Delta x}$
- Confinement gives an additional kinetic energy (*which increases the total E of the particle at rest*):
- This is equivalent to saying that Δx must be comparable to or smaller than the de Broglie wavelength $\lambda = \frac{h}{p}$ for the thermal motion
- At **RT**, we find that we must have $\boldsymbol{\Delta x}$ **< 5 nm** for an electron in a typical semiconductor
- Thus a "thin" semiconductor layer of 1 µm is not "thin" by the standards of the electrons -→ It a bulk crystal without any quantum size effects except **at extremely low T**

In the quantum world…
…metals can become semiconductors!

- Striking effects in quantum-confined materials: Size dependence of the electronic states and thus also of the optical properties

- **Ex:** When a metal particle decreases in size and eventually becomes a cluster, discrete states are formed, with remarkable effects on the IR absorption for these structures
  → Require a quantum mechanical description that goes beyond the Drude model

- Sufficiently small metallic clusters more or less behave as semiconductors



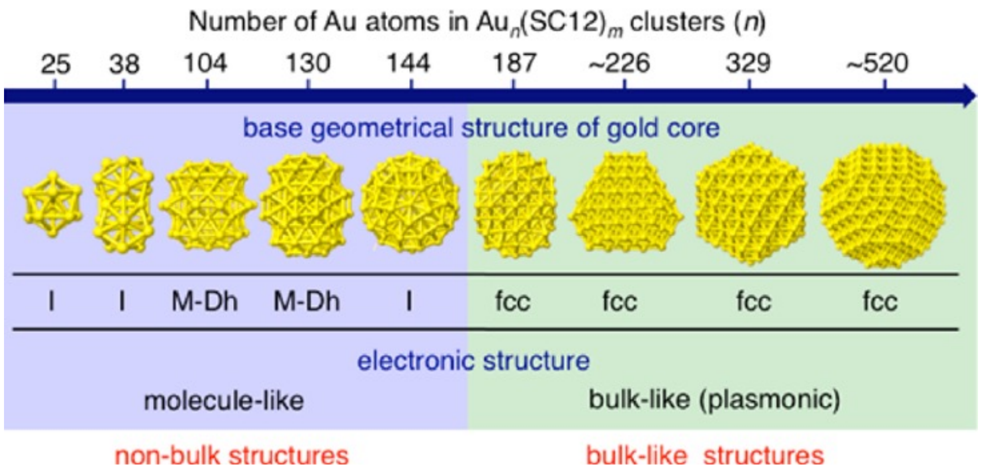
Schematic image of the quantum confinement effect in a metal (*a*) and a semiconductor (*b*).

Edvinsson T. 2018,. R. Soc. open sci. 5: 180387

In the quantum world…
…metals can become semiconductors!

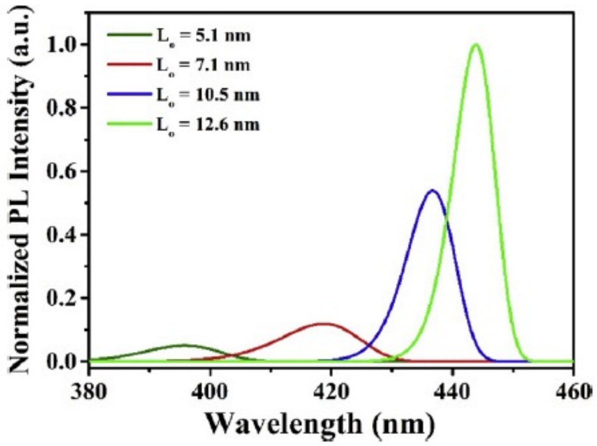
Ex: Gold nanoclusters

Transition between 144 and 187 atoms



Negishi et al., *JACS,* **2015**, *137*, 1206–1212

Photoluminescence can arise even in gold (but mechanism is not clear yet)



Alluhaybi et al., Optik – Int. J. Light and Electron Opt. 192 (2019) 162936

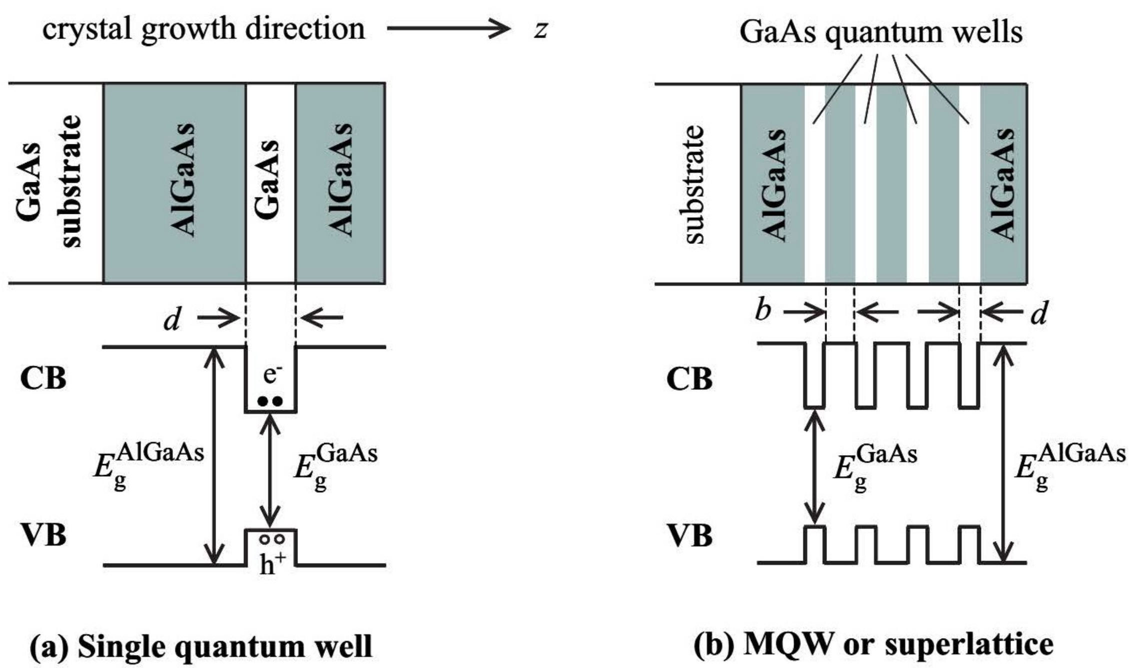
Quantum wells

- Widely used in commercial opto-electronic devices (mainly electroluminescent devices)

- Heterostructure crystals made by techniques of advanced epitaxial crystal growth
→Molecular beam epitaxy (MBE) or metal–organic chemical vapor deposition (MOCVD)

- Layer thickness can be controlled with atomic precision (possibility of multiple quantum wells, MQW)

Free motion in x,y planes Trapped in z by potential barrier

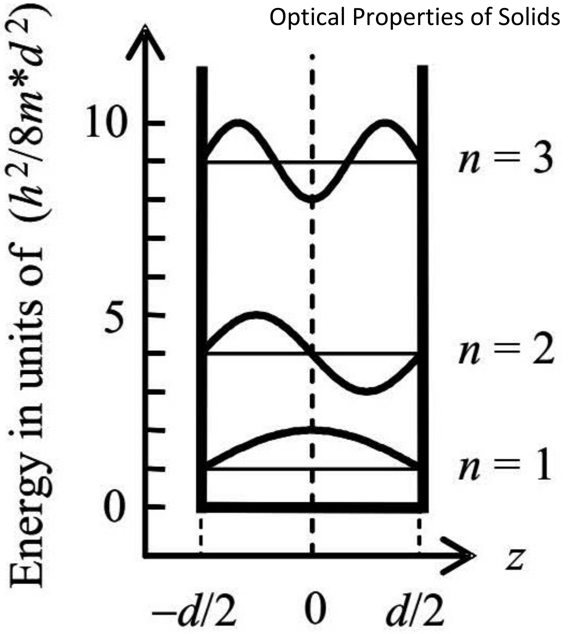


Large b: MQW
Small b: Superlattice, tunneling through the barrier possible

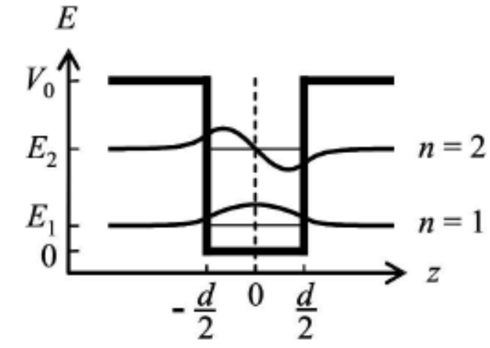
Used for optical applications:
Sizeable absorption

Particle in a box model

Fox, Mark.
Optical Properties of Solids



In reality:



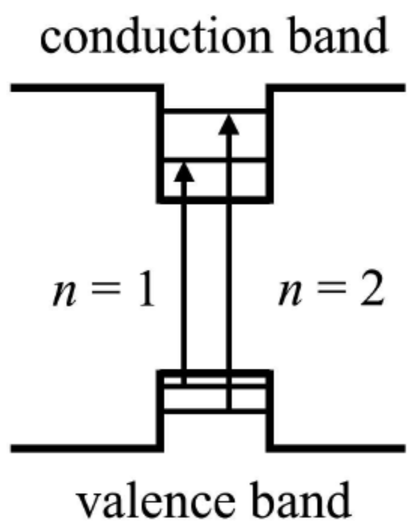
Particle in a box model

- **The energy of the levels is inversely proportional to the effective mass and the square of the well width!**

→ Low mass particles in narrow quantum wells have the highest energies

- Since the energy depends on the effective mass, the electrons, heavy holes, and light holes will all have different quantization energies

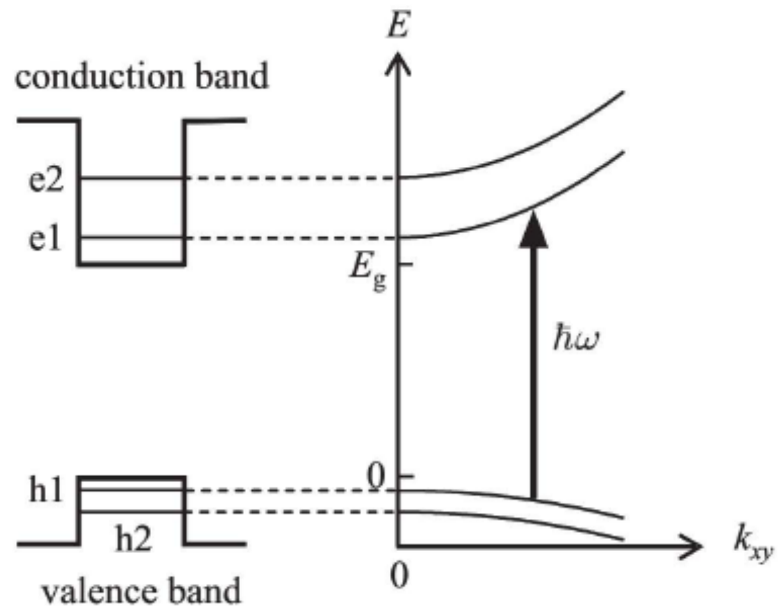
The QW will look like:



- In the valence band, the heavy holes will have the lowest energy, and are **dominant** in most situations because they form the ground-state level

Absorption in quantum wells

- Transition possible when exciting electrons from the ground state of the valence band (n = 1 heavy-hole level) to the lowest conduction band state (the n’ = 1 electron level) ($\Delta n = 0$)



$$\hbar\omega = E_g + E_{hh1} + \frac{\hbar^2 k_{xy}^2}{2m_{hh}^*} + E_{e1} + \frac{\hbar^2 k_{xy}^2}{2m_e^*}$$

$$= E_g + E_{hh1} + E_{e1} + \frac{\hbar^2 k_{xy}^2}{2\mu}$$

- For $k_{xy} = 0$ (analogous to the center of the Brillouin zone where $\boldsymbol{k}$= 0 in direct SC)

$$\hbar\omega = E_g + E_{hh1} + E_{e1}$$

- The optical absorption edge of the quantum well has been shifted by $E_{hh1} + E_{e1}$ compared to the bulk semiconductor

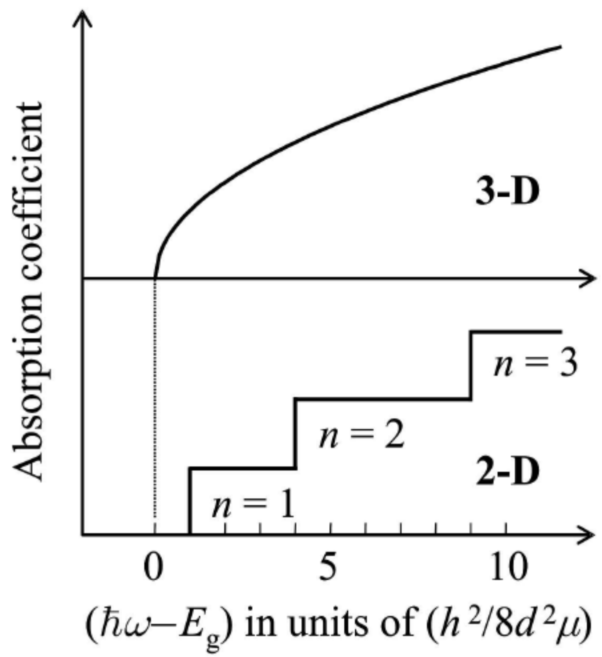
Absorption in quantum wells

- **Since the confinement energies can be varied by choice of the well width, this gives a way to tune the frequency of the absorption edge!**

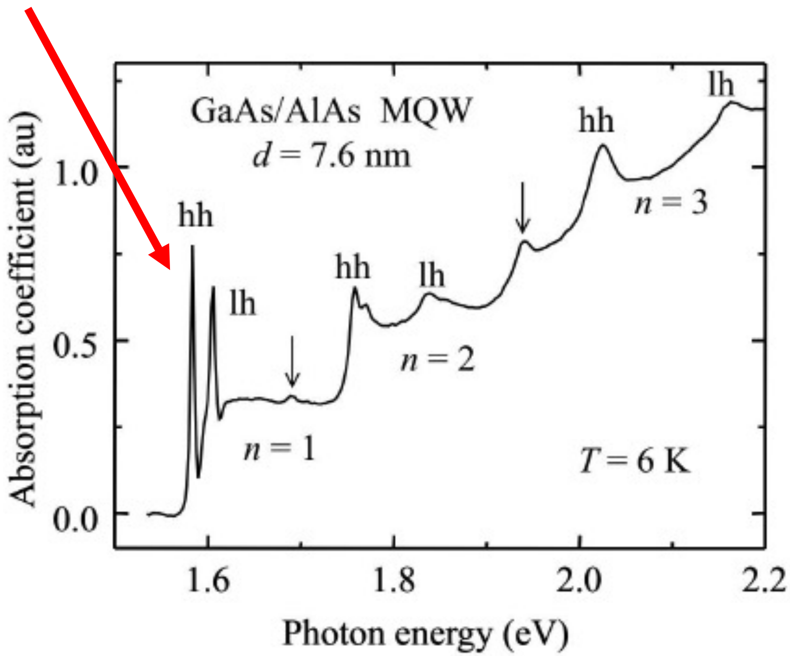
- The argument can be repeated for the other allowed optical transitions in the QW

→ The next $\Delta n = 0$ transition for the heavy-hole states occurs at an energy of:

$$\hbar\omega = E_g + E_{hh2} + E_{e2}$$

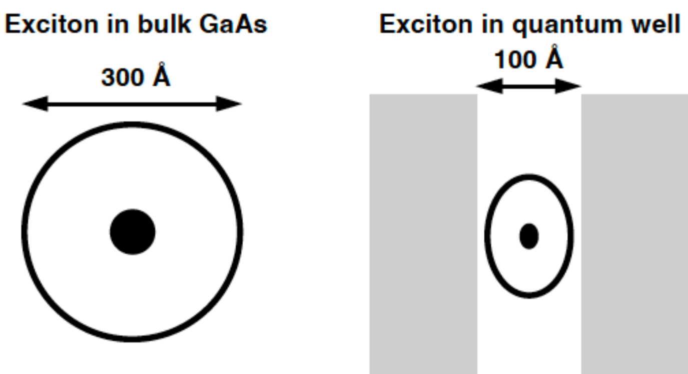


Excitonic effects

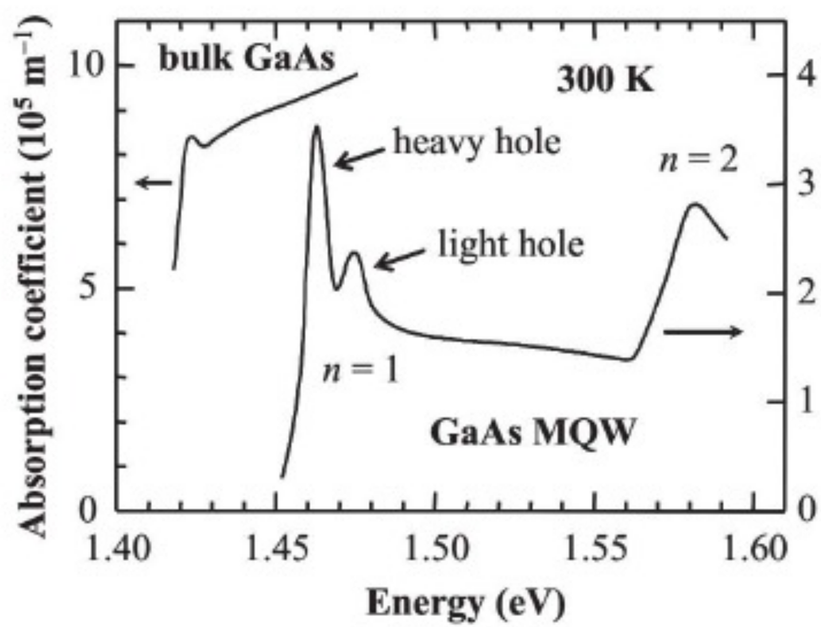


Excitons in quantum wells

- Reminder: We saw that usually excitons are delocalized in bulk SC and with low E
- Confined excitons are strong, can be stable at RT!
- The practical consequence is that in QW we may be able to make some use of the excitonic peaks at RT: Remarkable difference between bulk and confined!



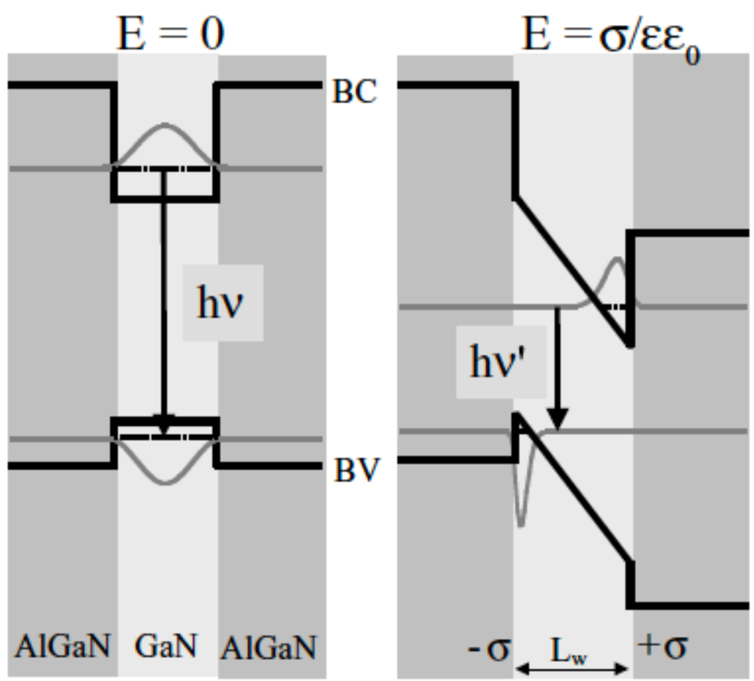
Miller, D., Optical Physics of Quantum Wells



Quantum-confined Stark effect

- In some materials, polarization linked to hexagonal structure (ex: wurtzite, GaN/AlN and InN/GaN) can generate very strong E fields up to 10-15 MV/cm
- When the field (external or due to polarization) is applied along confinement direction (z), it pushes e- and h^+ in opposite directions, but the barriers prevent the exciton from breaking apart

→ The excitons are stable up to very high field strengths



Quantum-confined excitons interact with the field and shift to lower energy!

From: Les nitrures d'éléments III : des semiconducteurs III-V singuliers ?

Application: Laser diodes

- Nitrides have remarkable properties and can cover the visible spectrum and UV!
- Bandgap: 1.9 eV for InN, 3.4 eV for GaN, 6.2 eV for AlN
- High stability for GaN
- Very good for blue LEDs and laser diodes (after solving the p-doping problem in the 1990s)

Laser diode material (active region / sub-strate)	**Typical emission wavelengths**	**Typical application**
InGaN / GaN, SiC	380, 405, 450, 470 nm	data storage
AlGaInP / GaAs	635, 650, 670 nm	laser pointers, DVD players
AlGaAs / GaAs	720–850 nm	CD players, laser printers, pumping solid-state lasers
InGaAs / GaAs	900–1100 nm	pumping EDFAs and other fiber ampli-fiers; high-power VECSELs
InGaAsP / InP	1.2–2.0 μm	optical fiber communications, sensing, spectroscopy
AlGaAsSb / GaSb	1.8–3.4 μm	defense, sensing, spectroscopy

Table 1: Emission wavelengths of various common types of laser diodes.

https://www.rp-photonics.com/laser_diodes.html

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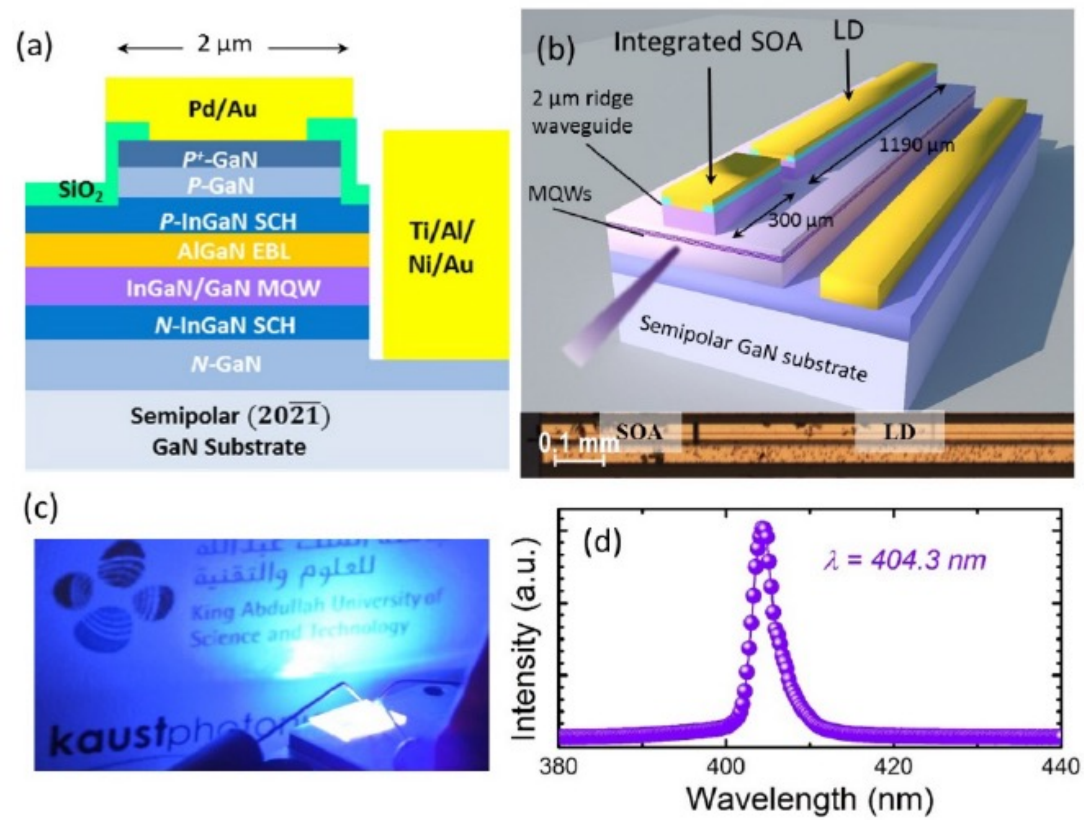


Shen et al., *Optics Express*, **2016**, Vol. 26, pp. A219-A226

6.2 Quantum dots
(also called semiconductor nanocrystals)

Size matters, again!

CdSe-CdS core-shell nanoparticles with various diameters

$$E_{nl} = \frac{\hbar^2}{2m^*}\frac{C_{nl}\pi^2}{R_0^2}$$

Particle diameter

1.7 nm → 6 nm

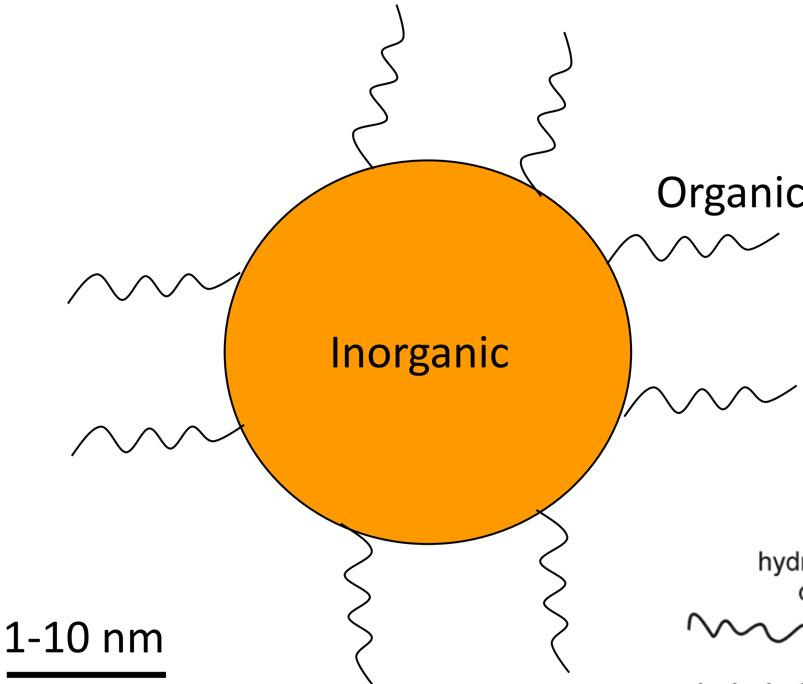
E. Roduner, *Size matters: why nanomaterials are different* , Chem. Soc. Rev., 2006,35, 583–592

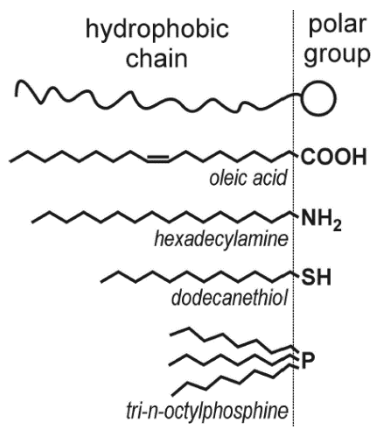
- Quantum dots can be made by lithographic patterning of quantum wells

OR

- Colloidal synthesis of quantum dots or nanoplatelets using organic precursors, surfactants and solvents

QDs : Inorganic Nanocrystals





Inorganic:
MX
where M: Pb, Cd and X: S, Se

Like **PbS, CdS or PbSe**
… and many more possibilities!

Around 200 – 10000 atoms

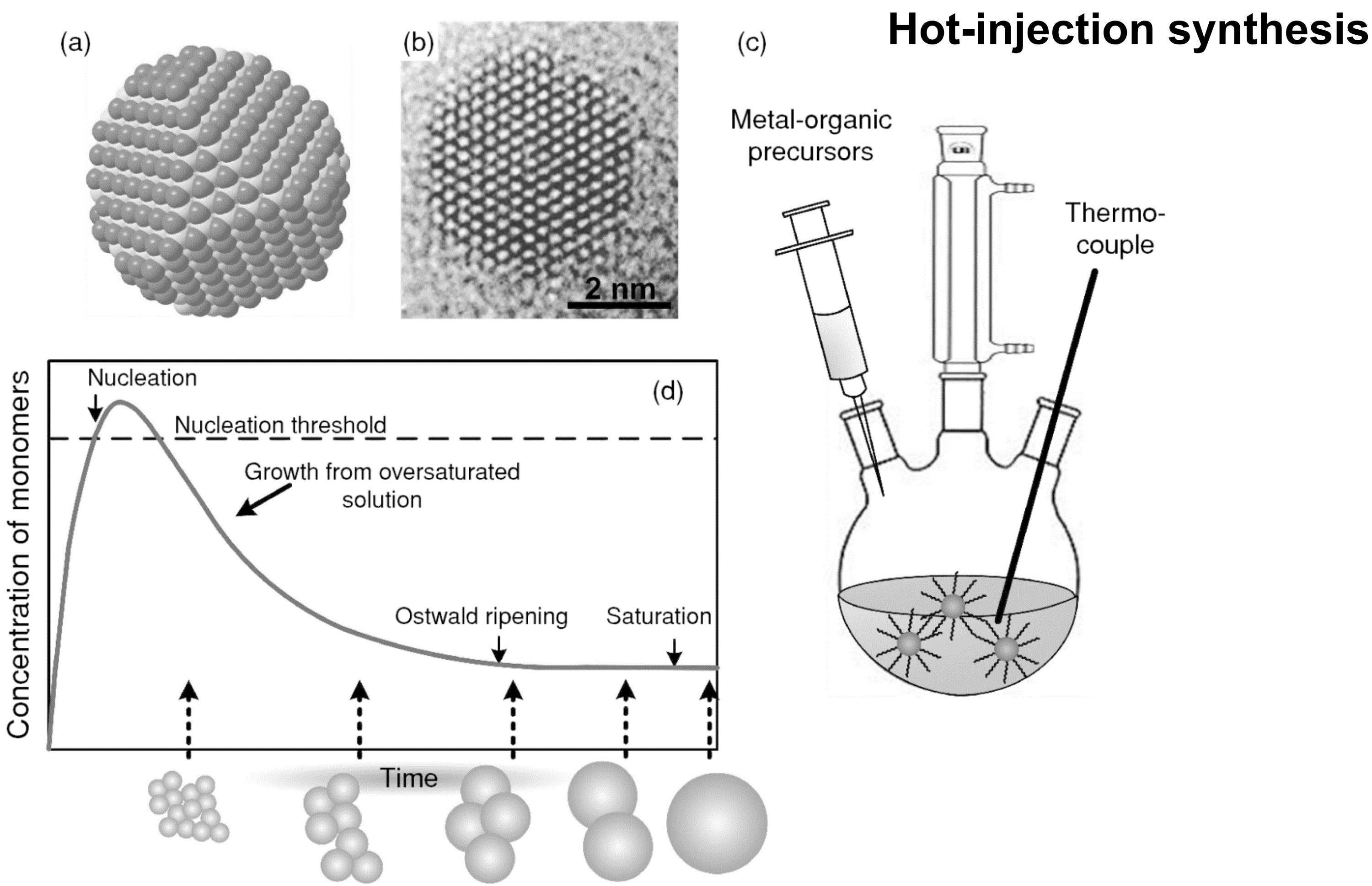
Organic:

Surfactant monolayer (or ligands)

- Anchoring part
- Hydrophobic part

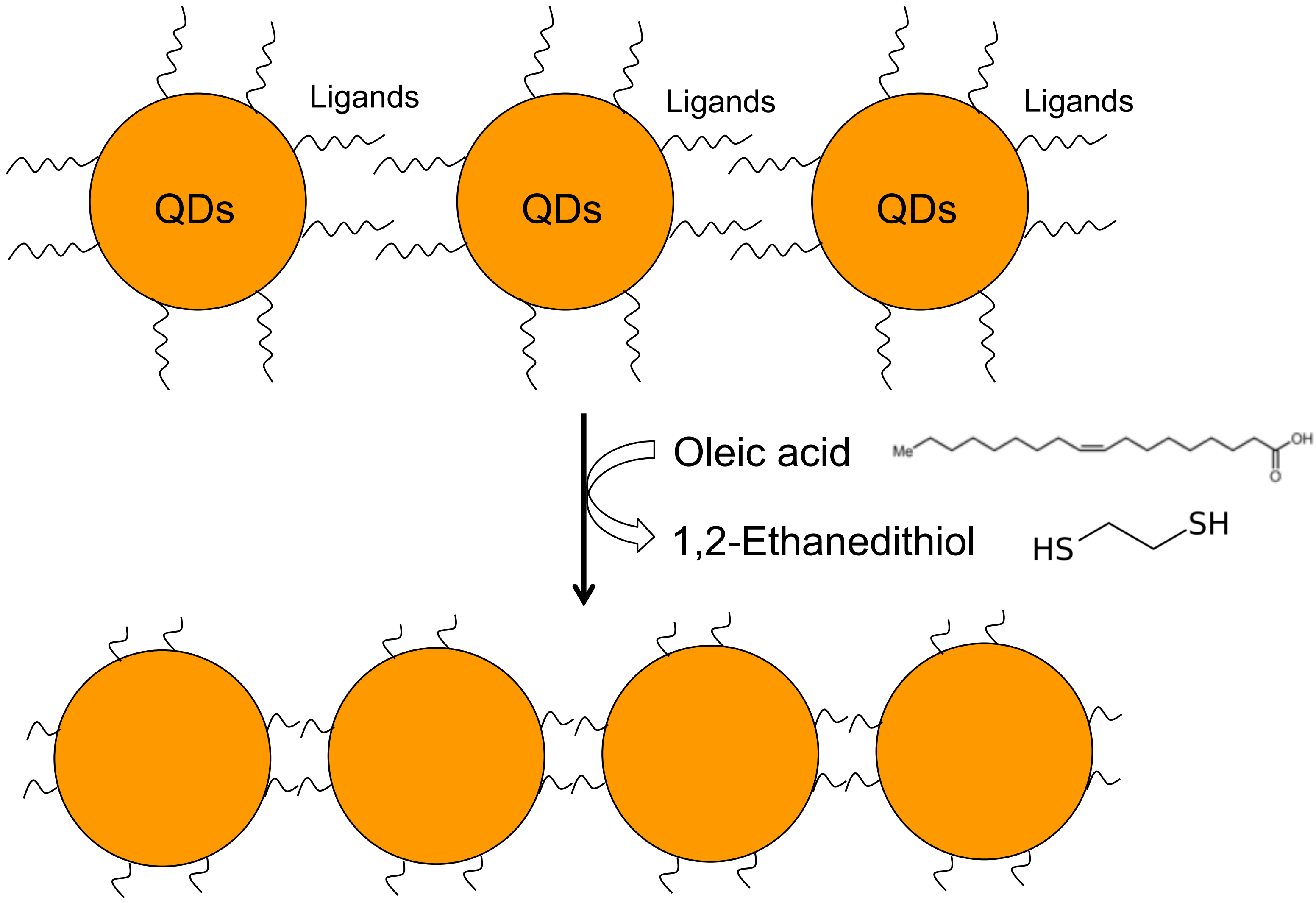
Role of ligands:
(1) Monodispersity of QDs (2) Preventing agglomeration (3) Defect passivation
Alternative to ligands: Inorganic shells (but less flexibility in design)

QDs synthesis



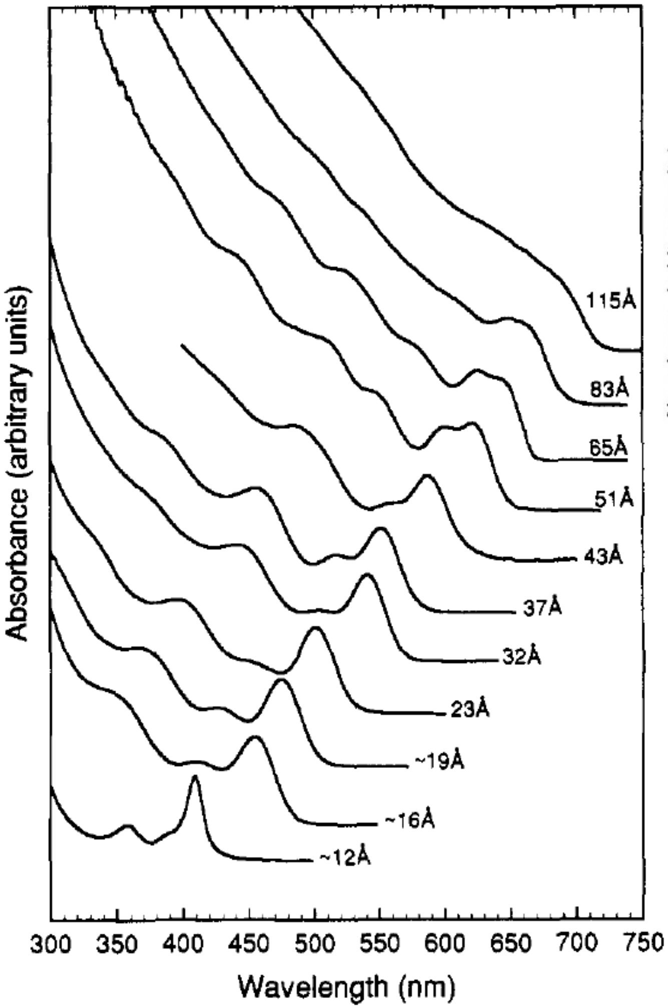
Bodnarchuk, M., & Kovalenko, M. (2013). *Colloidal Quantum Dot Optoelectronics and Photovoltaics* (pp. 1-29). Cambridge University Press.

Ligand exchange: Functionalization

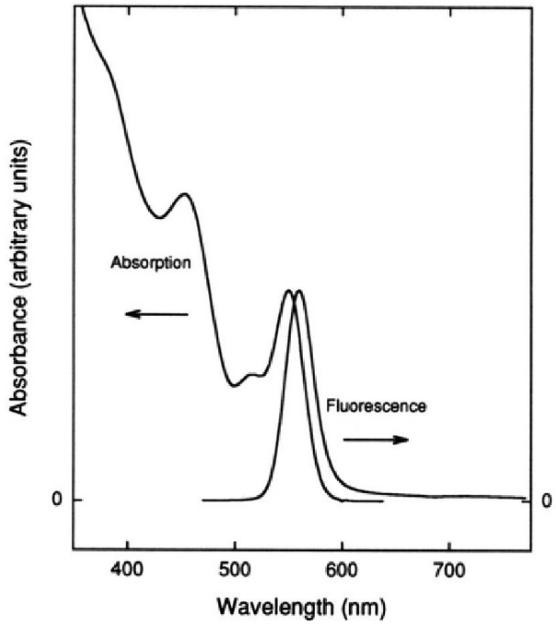


Potential of QDs

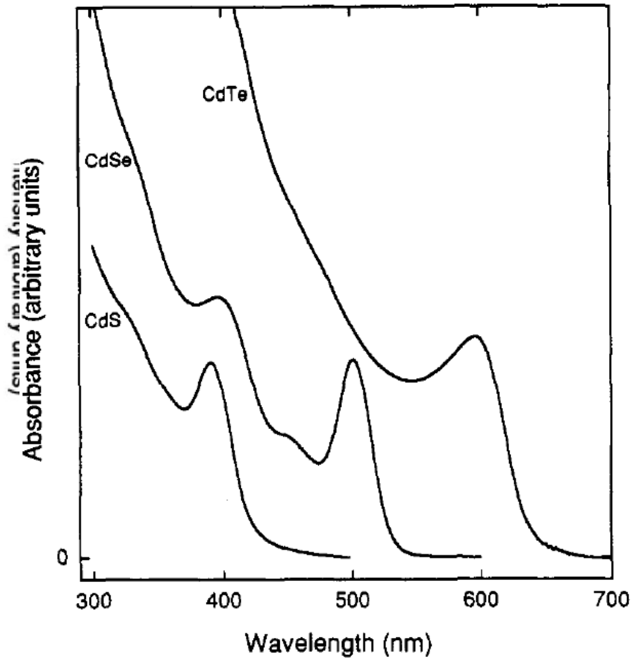
Size effect (CdSe)



Narrow PL

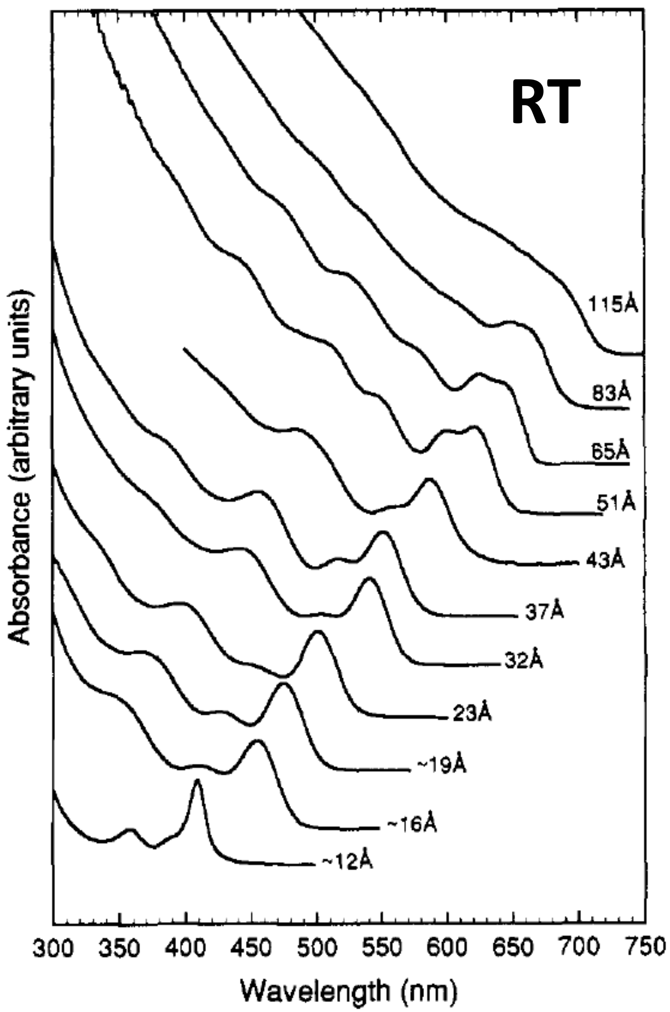


Band edge tunability



Murray, Norris and Bawendi, *JACS* **115**, 8706 (1993)

Absorption in QDs: Size effect



CdSe QDs dispersed in hexane

$$\hbar\omega = E_g + E_{nl} - E_{ex}$$

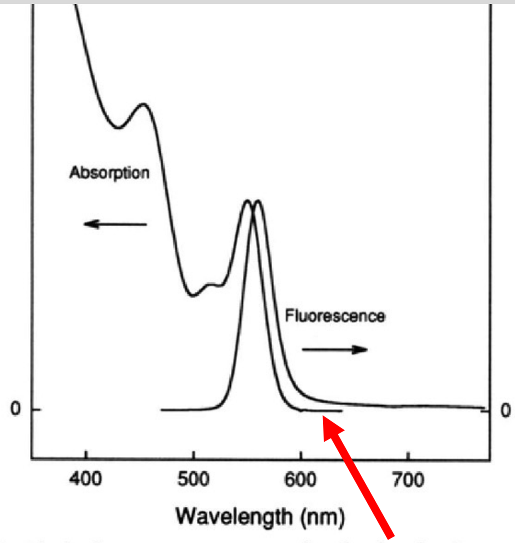
$$= E_g + \frac{2\hbar^2}{\mu}\frac{\pi^2}{R_0^2} - E_{ex}$$

- A large part of the "art" of making colloidal quantum dots is obtaining a good size distribution
- Usually, the standard deviation of the diameters of the dots can be < 5%

Absorption in QDs: Narrow PL

- By confining the carriers in 3D, we increase the e-/h+ overlap and increase the radiative quantum efficiency → **very high QY can be achieved!!**
- The discrete nature of the density of states reduces the thermal spread of the carriers

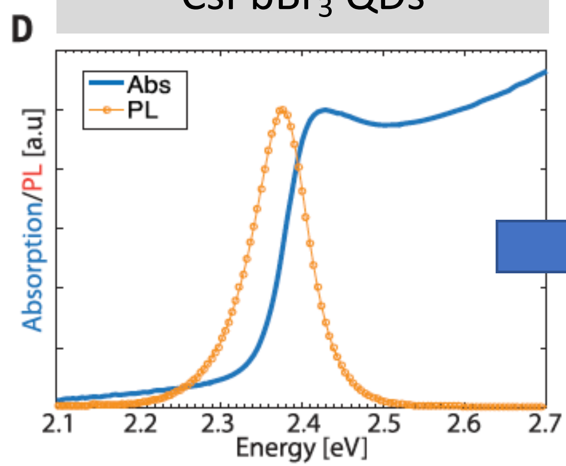
RT band edge luminescence for d = 35 Å CdSe crystallites



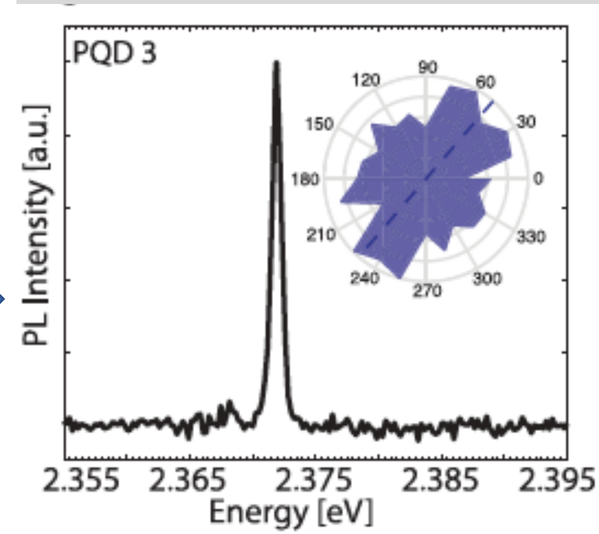
No deep trap luminescence detected!

And obviously… Perovskite make great QDs emitters!

Ensemble spectra of $CsPbBr_3$ QDs



As a **single particle**: No broadening from inhomogenous size distribution



Utzat et al., Science 363, 1068–1072 (2019)

Murray, Norris and Bawendi, *JACS* **115**, 8706 (1993)

Absorption in QDs: Narrow PL

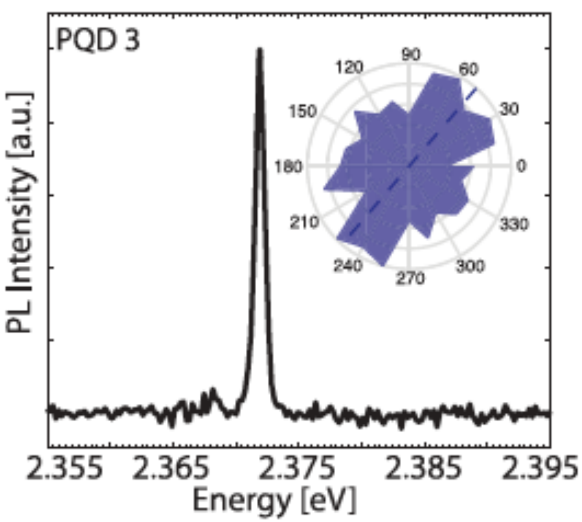
- By confining the carriers in 3D, we increase the e-/h⁺ overlap and increase the radiative quantum efficiency
- The discrete nature of the density of states reduces the thermal spread of the carriers

As a single particle: No broadening from inhomogenous size distribution

- The width of the exciton line from a single quantum dot is ultimately limited by the radiative lifetime!

$$\Delta E \Delta \tau \geq \frac{\hbar}{2}$$

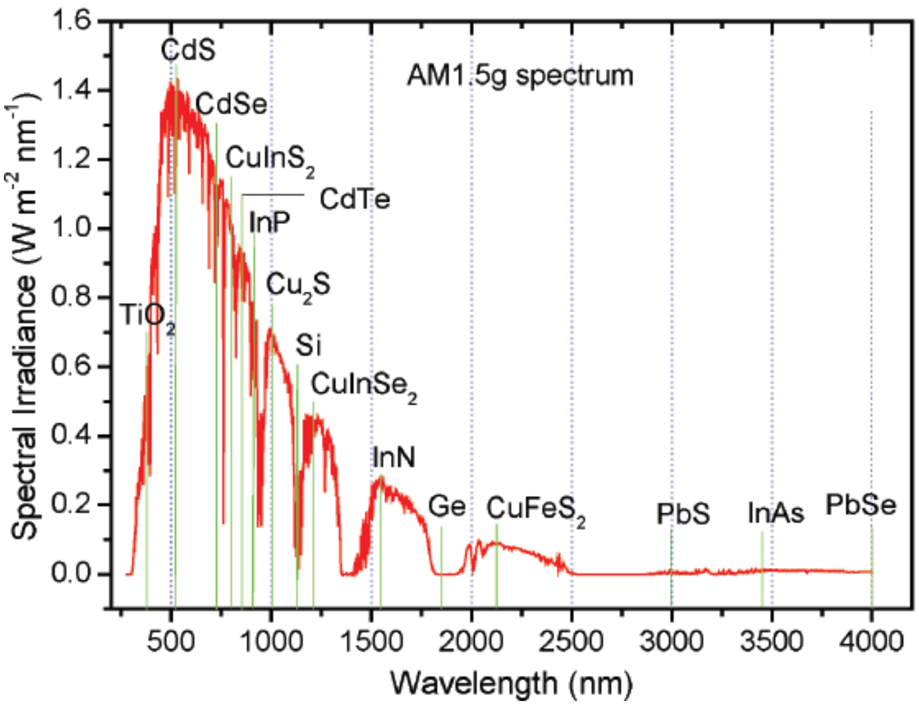
- With typical values of radiative lifetimes ~1ns, linewidths as small as a few μeV have been observed



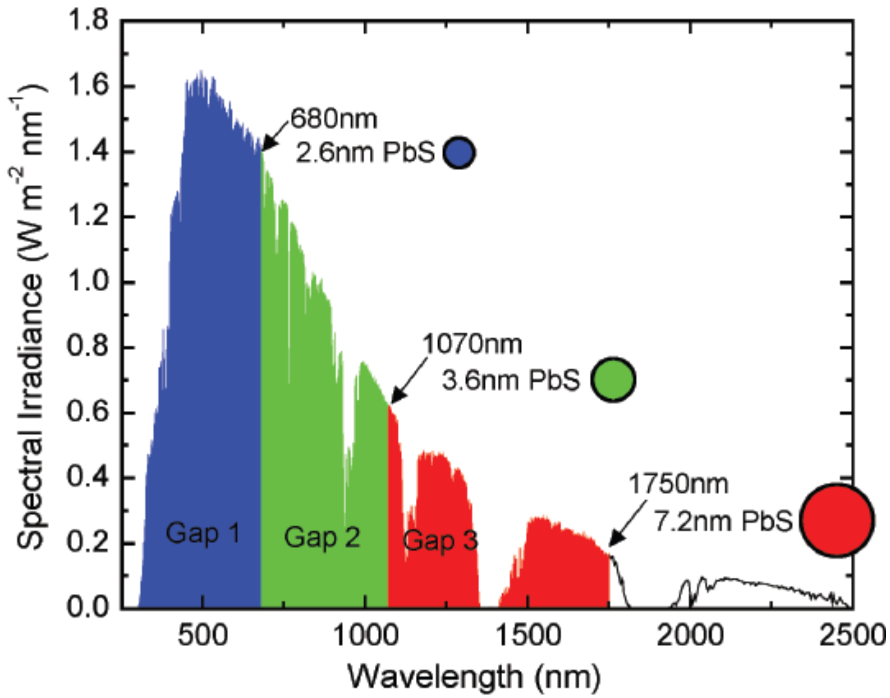
Utzat et al., Science 363, 1068–1072 (2019)

Absorption in QDs: Band gap tunability

Changing the material of NCs

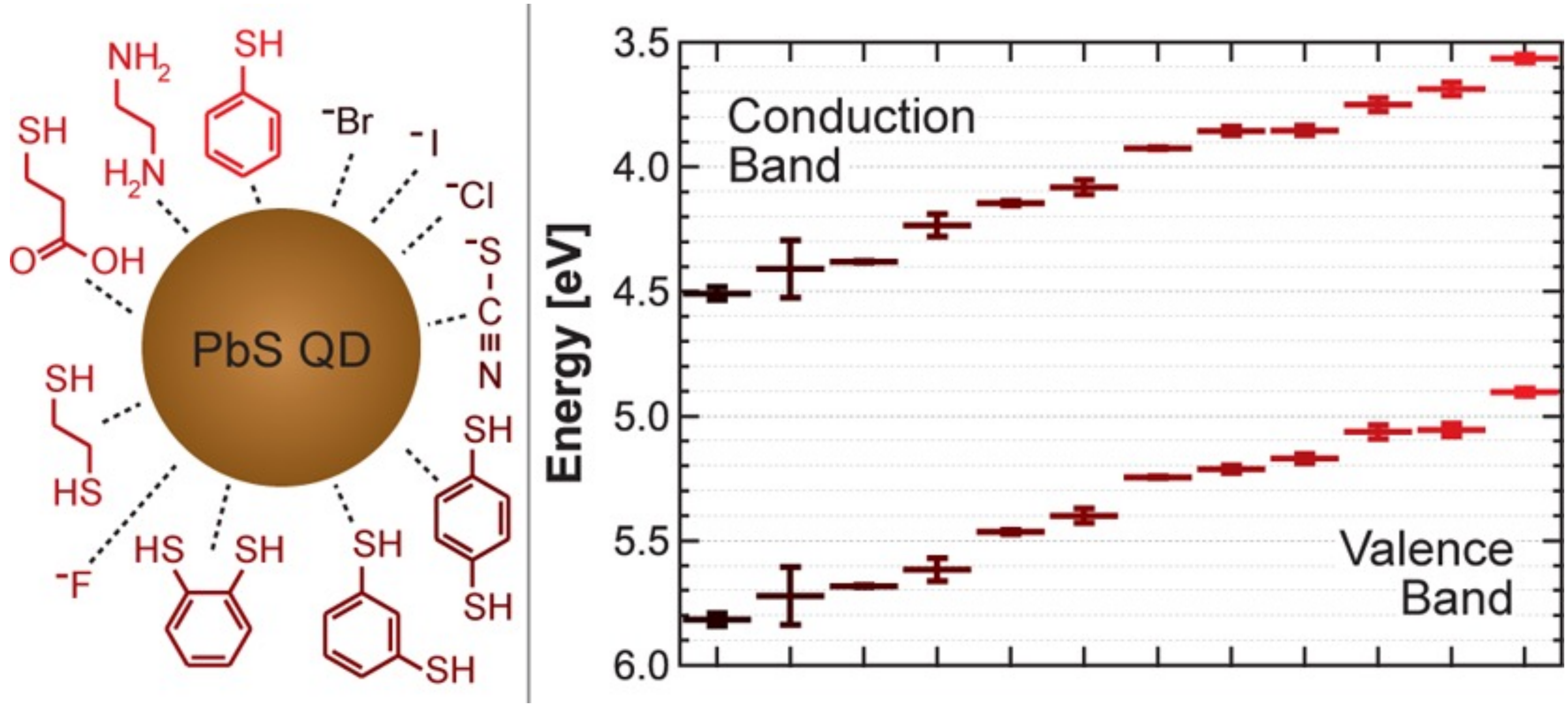


Changing the radius of NCs



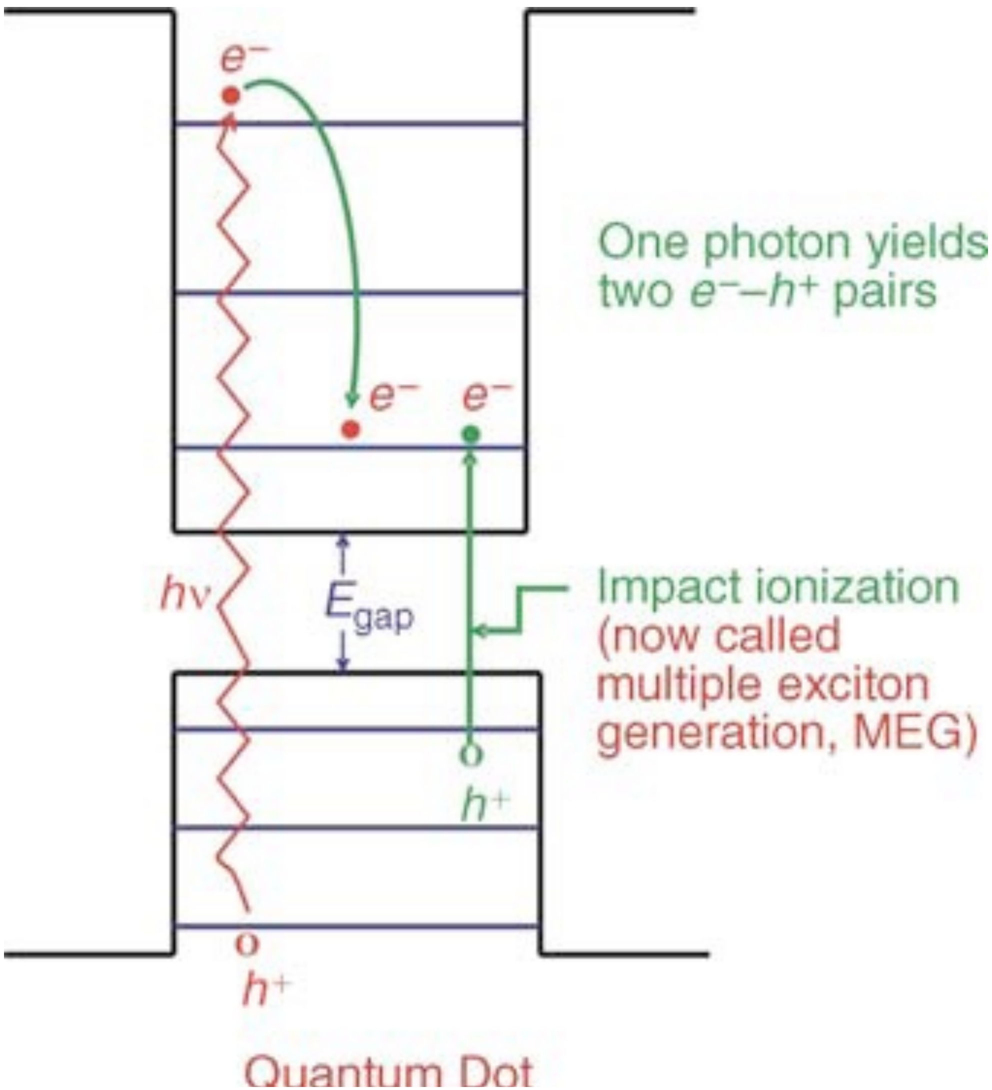
J. Tang, E.H. Sargent, *Adv. Mater.* **13**, 12 (2011)

Absorption in QDs:
Energy level alignment from ligand exchange



Brown et al. *ACS Nano* **8**, 5863 (2014)

Multiple-exciton generation in QDs



Released excess energy does not go into a phonon but excites another electron across the bandgap!

One photon creates
2, 3, or more e-/h^+ pairs

→ Quantum efficiency of 200-300-400% possible!

Luque et al, MRS Bulletin 2007

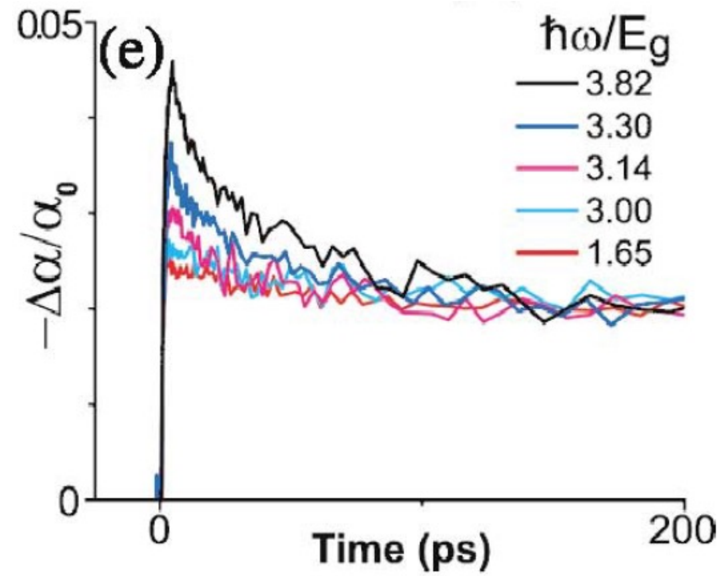
Probing MEG with TA

- Colloidal PbSe NC samples with absorption maxima at 0.86 eV (~ 1400 nm) for the lowest transition

- Normalized pump-induced bleaching of the lowest transition

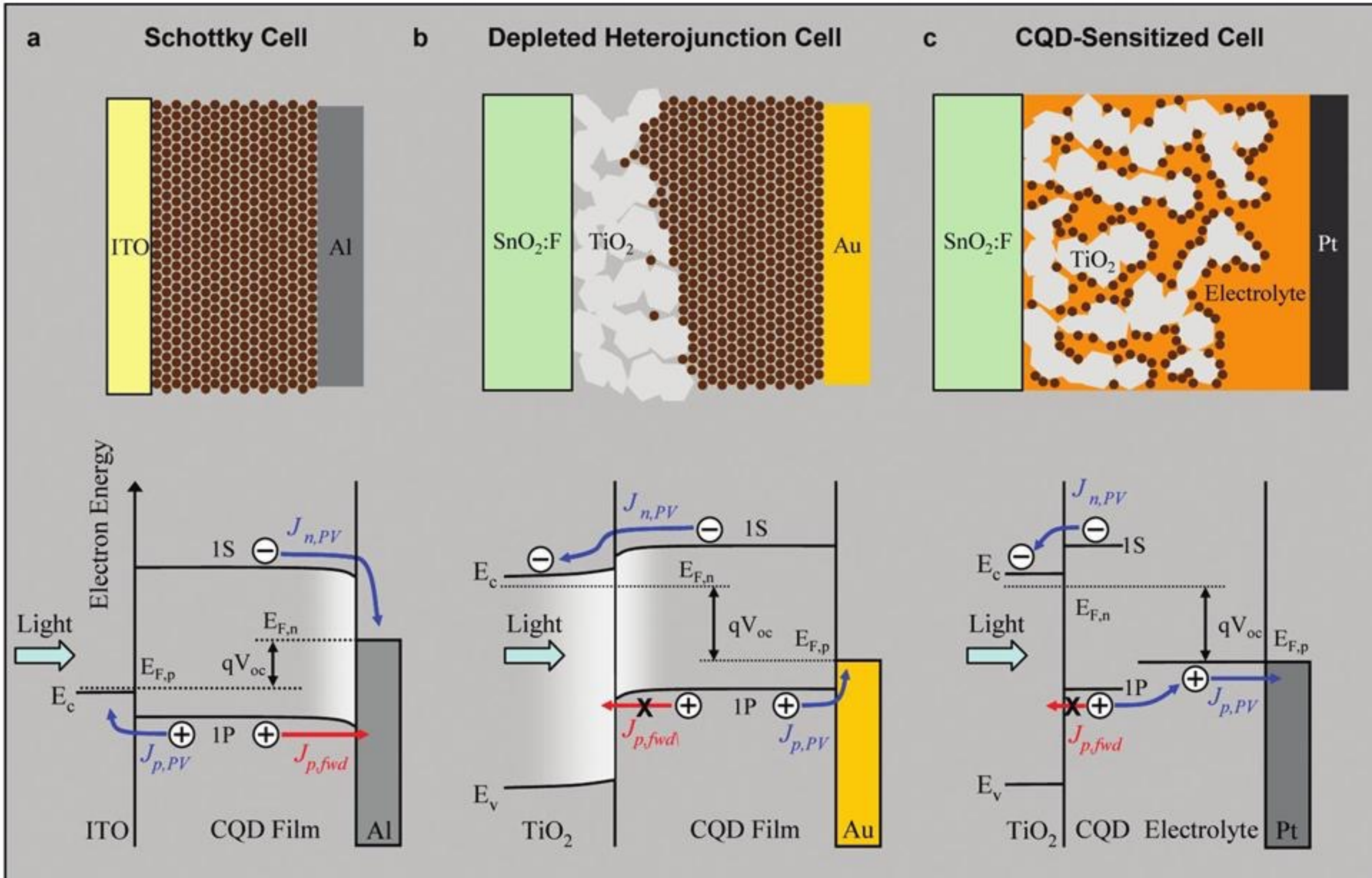
- Bleaching has an additional component at higher energies above the bandgap: MEG takes place on an ultrafast (picosecond) time scale

- Even with only ~10-100 ps lifetime of biexcitons observed here, MEG can still be useful for solar power generation!



Schaller, Klimov, *Phys. Rev. Lett*. **2004**, *92*, 186601

Design of „real“ QD solar cells



Pattantyus-Abraham et al., *ACS Nano*, **2010**, *4*, 3374-3380