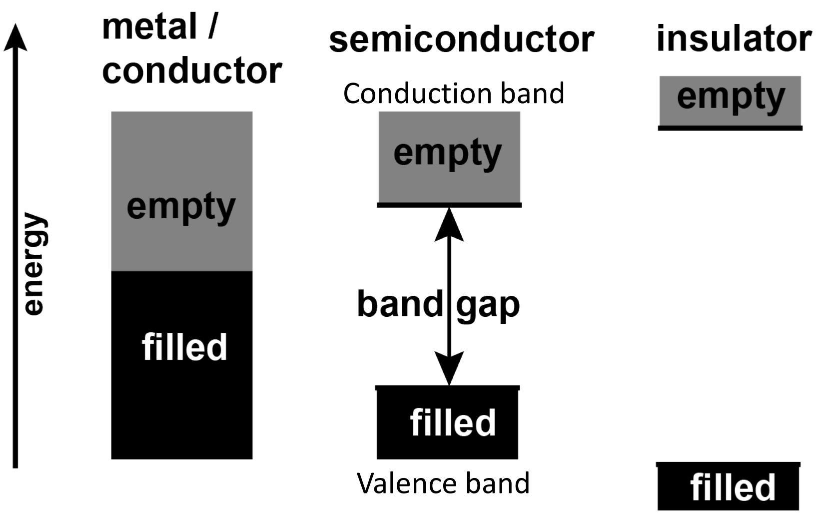
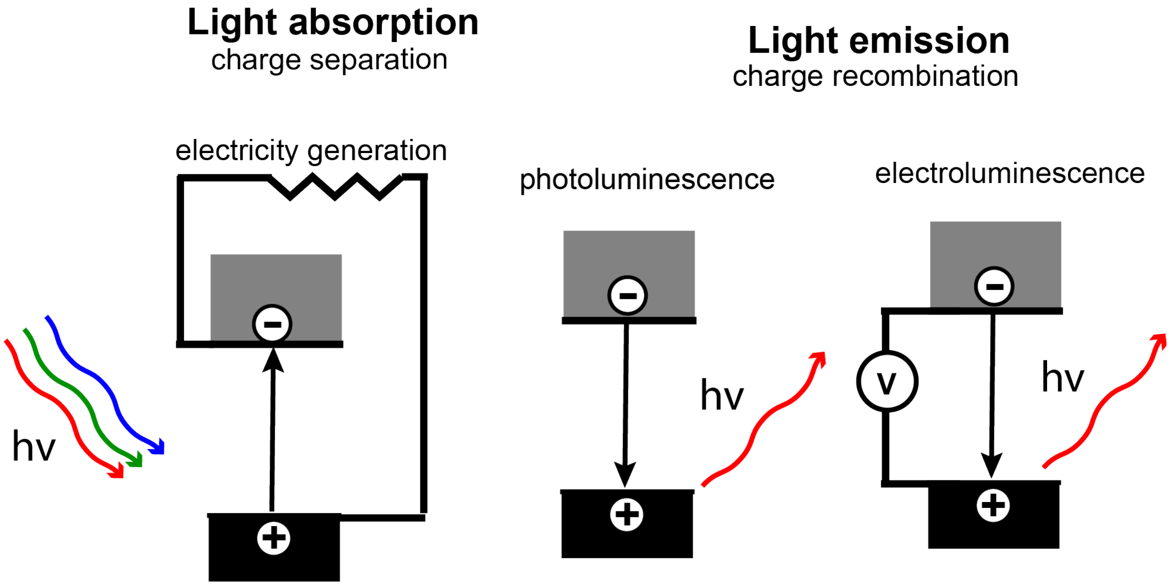
What are Quantum Dots? semiconducting nanocrystals with quantum confined charges

Part I. What is a semiconductor?



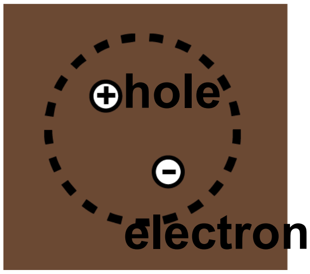
Semiconductors are materials that are characterized by intermediate electrical conductivity (between that of a metal and an insulator). From an energy level point of view, a metal has no gap between filled and empty electronic states, while an insulator has a large gap. A semiconductor has a gap close to the energy of visible light (1-3 eV). Semiconductors' unique properties have made them ubiquitous in technology: such as the transistors in all computers, the diodes in our LEDs, and as the material of solar panels. The archetypal semiconductor material is Silicon. Others include CdSe, CdS, ZnS, ZnSe.

Light-matter interactions in semiconductors



Semiconductors can absorb and emit light with energies equal to the **band gap** (the gap in energy between the valence band and conduction band). Light absorption creates an excited electron in the conduction band and the lack of an electron in the valence band (a hole). These excited charges can be used to generate electricity. They can also recombine to emit light.

An exciton is a bound electron-hole pair

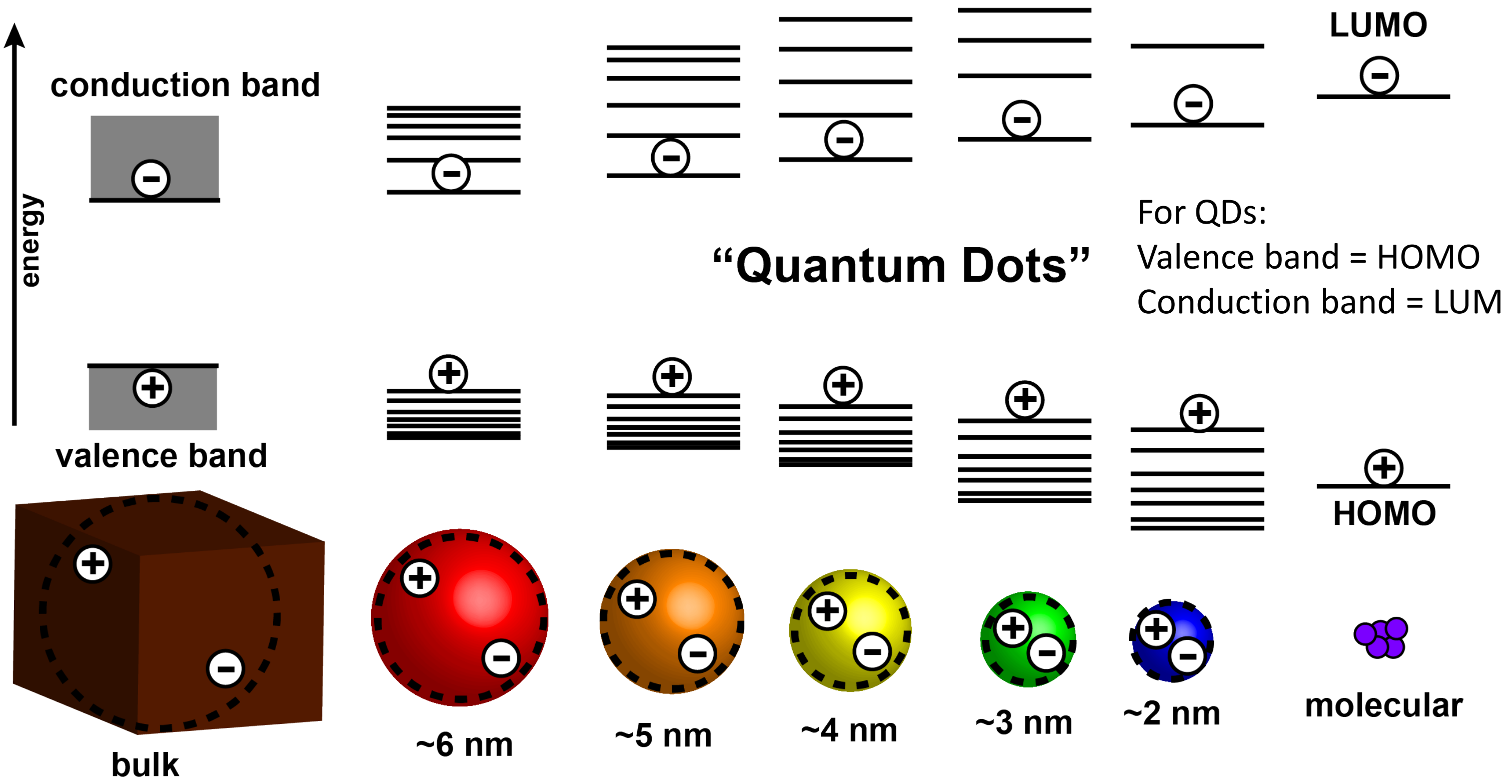


Upon photoexcitation, the excited electron is still attracted to the positively charged hole (Coulomb force). This interaction can be modeled in the same way as the hydrogen atom (i.e. an electron orbiting a positive charge). You may recall the Bohr radius being derived for the hydrogen atom. An analogous exciton Bohr radius can be derived (last page).

When a semiconductor is so small that is close to the size of the exciton Bohr radius, then the charges exhibit quantum confinement, and size dependent band gaps. This is a hallmark of quantum dots.

Part II. Nanocrystals can host quantum confinement

Quantum dots are semiconductor nanocrystals with quantum confined charges. They span the intermediate regime between bulk and molecular materials. Between continuous and discrete energy levels

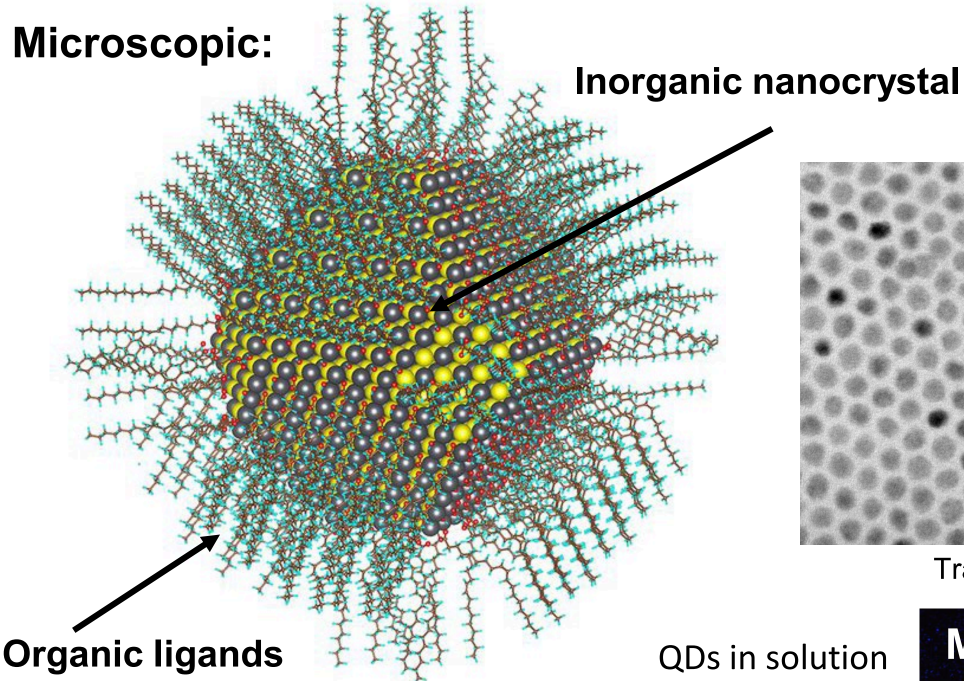


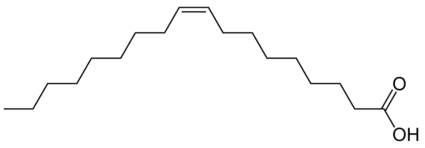
For QDs:
Valence band = HOMO
Conduction band = LUMO

What do quantum dots look like?

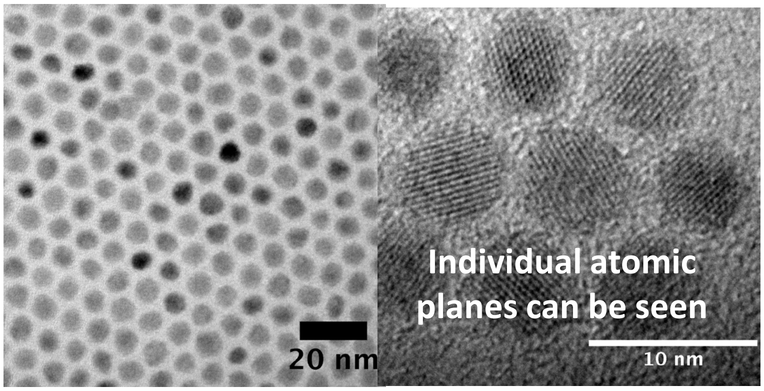
Colloidal QDs are much bigger than molecules, but can still be dissolved in a variety of solvents. This is made possible by coating them with ligands.

Microscopic:





Oleic acid is a common ligand



Transmission electron microscopy images

QDs in solution can possess a variety of colors and are often beautifully fluorescent.

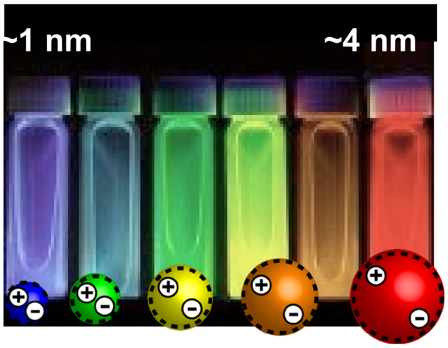
Image from phys.org

Zherebetskyy, D; Alivisatos, A. P, *et al.* *Science* **2014**, *6190*, 1380-1384.

Part III. Properties of Quantum Dots

Quantum dots possess a variety of unique and technologically useful properties. Notably, they exhibit high fluorescence since the photoexcited charges have to stay near each other (confined to the dot).

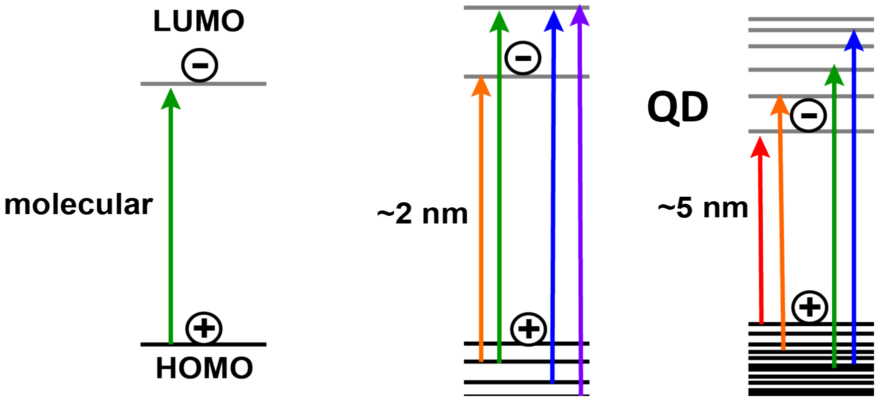
Size-dependent emission

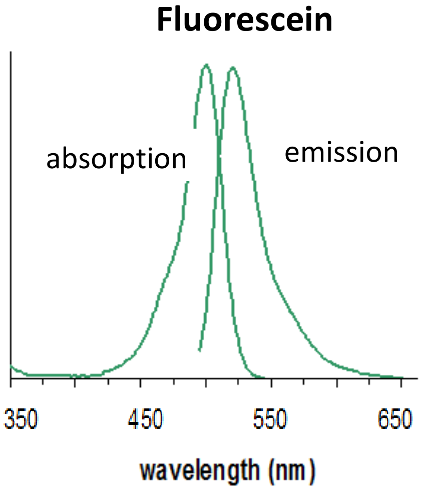


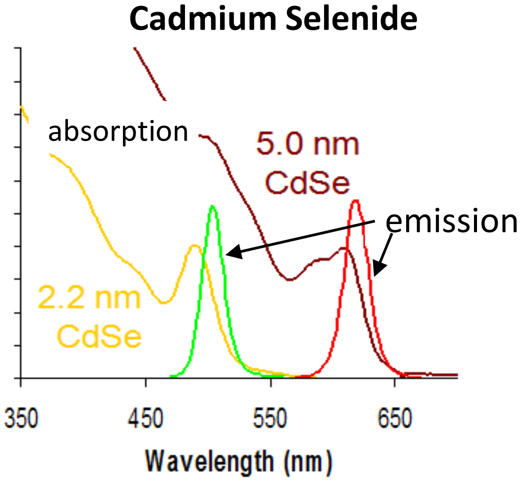
Since changing the QD size, changes the QD band gap, it also changes the fluorescence wavelength. CdSe QDs can be tuned to emit across the entire visible spectrum (just based on size). Another feature of QDs that makes them unique compared to molecular dyes is their broad absorption, across wavelengths bluer (higher energies) than their band gap. This is a result of their higher density of states above the band gap. Importantly, electron-hole pairs photogenerated with energies above the band gap quickly (a few picoseconds) relax the QD band edge from where they emit (10-30 nanoseconds).

Broad absorption and narrow emission

(compared to molecular dyes)



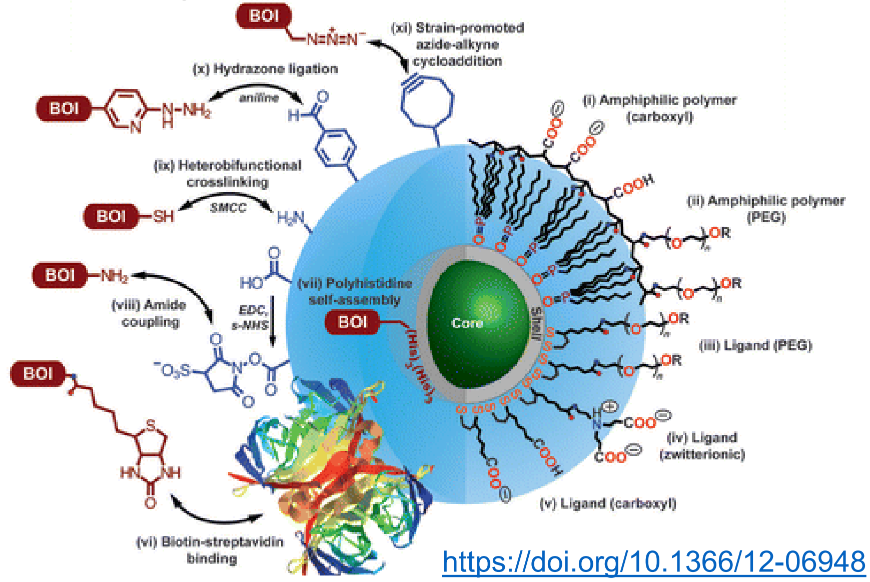




Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P., *Science* **1998**, *281*, 2013-2016.

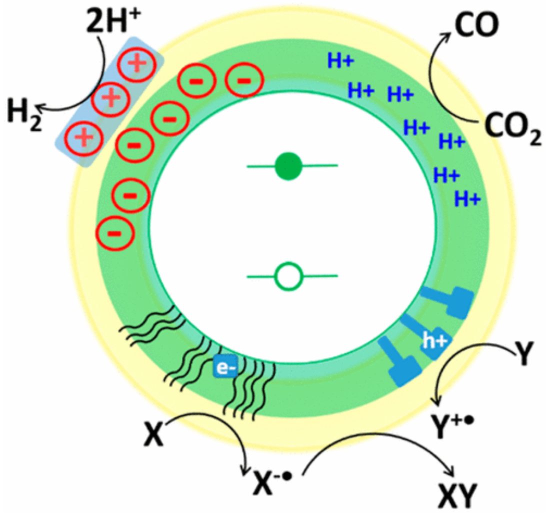
Functionalizable surface: the QD surface can be modified in numerous ways.

For biological applications



https://doi.org/10.1366/12-06948

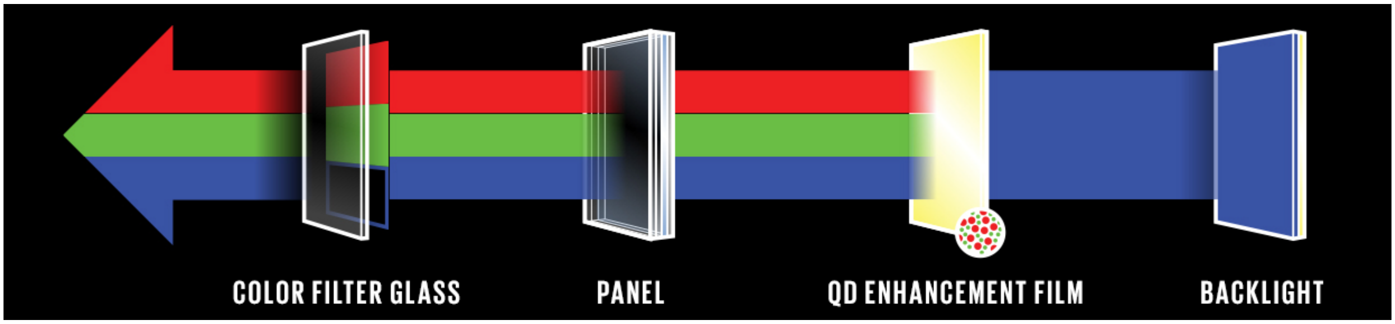
For energy/catalysis applications



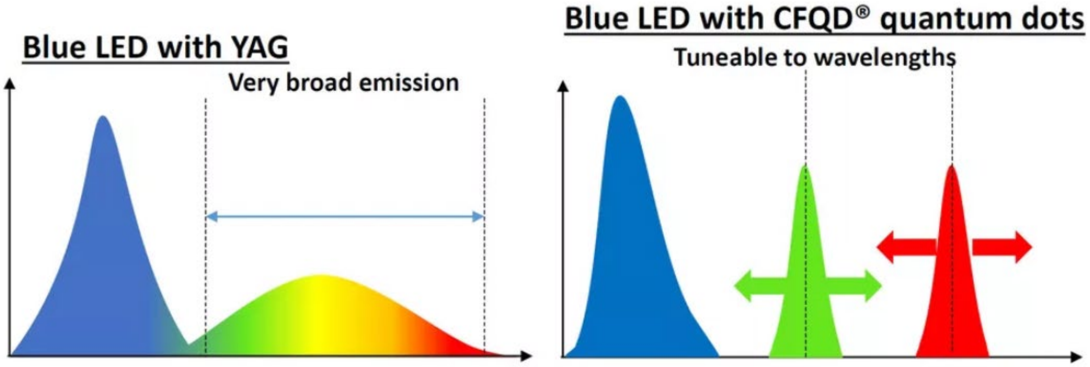
ACS Energy Lett. 2017, 2, 5, 1005−1013

Part III. Applications of Quantum Dots

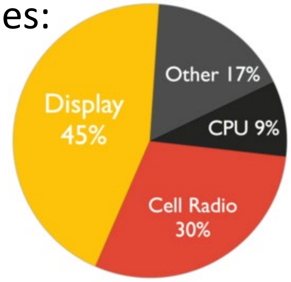
Displays: e.g. Amazon Kindle or Samsung QLED TV



nanosysinc.com nanoco



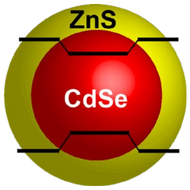
Power consumption of phones:



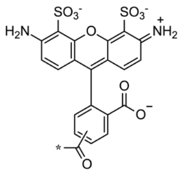
QD Displays are 20% more efficient!

Using red and green QDs as the red and green pixels in displays not only provides better color purity, but they are also more energy efficient. Less light is wasted by filters. Currently QDs act as "phosphors", which mean they absorb blue light and re-emit as green or red. However, work is ongoing to make electroluminescent QD devices in which electricity creates the excited electron- hole pair.

Bioimaging: QDs are bright and photostable emitters

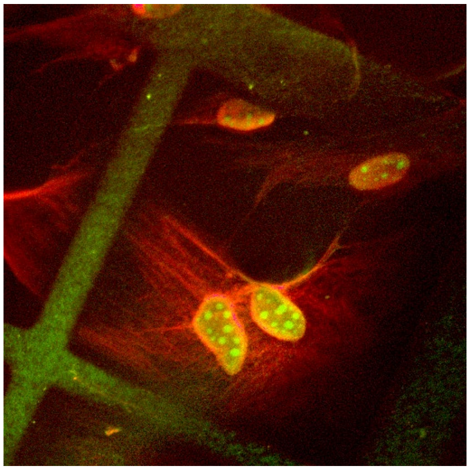


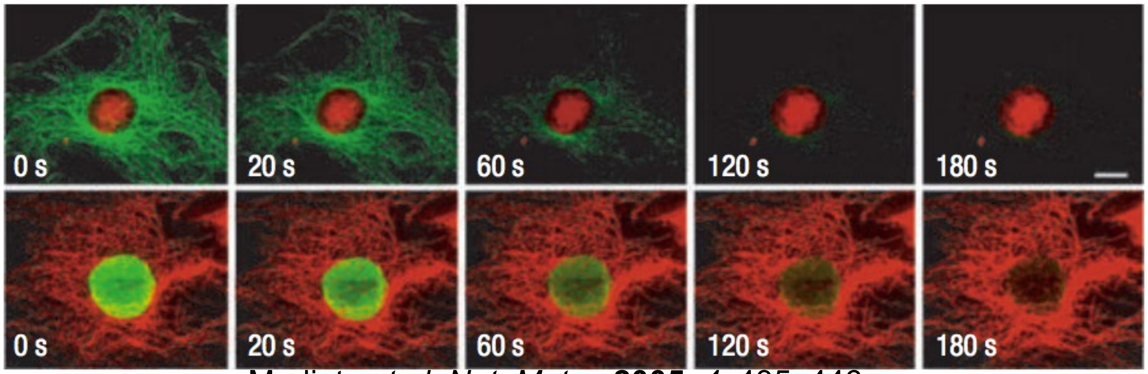
QD630



AlexaFluor488

Different parts of a cell can be functionalized with either a dye (green) or a QD (red). The QD is clearly more stable. This is because photoexcitation is delocalized across more atoms in a QD.





Medintz *et al*. *Nat. Mater.* **2005**, *4*, 435–446.

Beyond just imaging, QDs can act as fluorescent sensors in a variety of biological systems. See resources at end of this document.

Coming soon: ambient lighting?

Derivation of the Bohr radius, and examples

To solve for the radius of orbit of one charge around another, we typically start by equating the Coulombic force to the centripetal force (this is also how you solve for the speed of satellites and moons orbiting around planets, just replace the Coulombic force with the gravitational force):

$$\frac{mv^2}{r} = \frac{q^2}{4\pi\epsilon_0 r^2}$$

m is mass, v is velocity, q is elementary charge, ϵ_0 is the vacuum permittivity. However, quantum mechanical objects, like electrons, are better described by their momentum than their velocity, so we will try to rearrange to solve for velocity.

Now we assume the circumference of orbit can support only an integer number of wavelengths of the particle-wave electron: $2\pi r = n\lambda$

Now apply the deBroglie relation: $\lambda = \frac{h}{p}$ And solve for velocity: $v = \frac{n\hbar}{mr}$

Putting this all together, you should find that the Bohr radius is: $r_B = \frac{4\pi\epsilon_0 n^2\hbar^2}{mq^2}$

For n = 1, you should be able to show that the Bohr radius is 53 picometers.

Now that was all for hydrogen, which aside from the electron and proton exists in vacuum. In a semiconductor, the electron and hole are in a solid medium and therefore feel an effective permittivity and have effective masses. The modified Bohr exciton radius is then given by:

$$r_B = \frac{4\pi\epsilon_0\epsilon\hbar^2}{m_{eff}q^2}$$

Where the reduced effective mass comes from the effective mass of the electron and the hole:

$$\frac{1}{m_{eff}} = \frac{1}{m_e} + \frac{1}{m_h}$$

Try solving the exciton Bohr radius of CdSe and CdS given the following information:

CdSe	**CdS**
$m_e = 0.13\, m_0$	$m_e = 0.2\, m_0$
$m_h = 0.45\, m_0$	$m_h = 0.7\, m_0$
$\epsilon = 9.4$	$\epsilon = 8.6$

m_0 is the mass of an electron

Resources

Some introductory descriptions of quantum dots:

https://www.sigmaaldrich.com/technical-documents/articles/material-matters/quantum-dots-an-emerging.html

https://nanohub.org/resources/22265/download/NACK_U3__Maeder_Quantum_Dots.pdf

https://www.ocf.berkeley.edu/~jmlvll/lab-reports/quantumDots/quantumDots.pdf.

MIT, Bawendi Group, video of QD synthesis
https://www.youtube.com/watch?v=MLJJkztIWfg

Quantum dots as explained by nanosys.inc
https://www.nanosysinc.com/quantum-dot-basics/

Reviews of QD for bio applications
A review of using QDs for biological applications
https://doi.org/10.1366/12-06948

Quantum dots for charge transfer bio-sensing
https://pubs.rsc.org/en/content/articlehtml/2014/tb/c4tb00985a

Reviews of QDs for solar energy applications

General review and band gap engineering
https://pubs.acs.org/doi/pdf/10.1021/ar9001069

Colloidal photocatalysis review
https://pubs.acs.org/doi/pdf/10.1021/acs.inorgchem.7b03182

Building devices with QDs
https://science.sciencemag.org/content/353/6302/aac5523/tab-pdf

Colloidal QD Solar Cells
https://pubs.acs.org/doi/10.1021/acs.chemrev.5b00063

Review of QDs for Display Applications
https://onlinelibrary.wiley.com/doi/abs/10.1002/anie.202004857