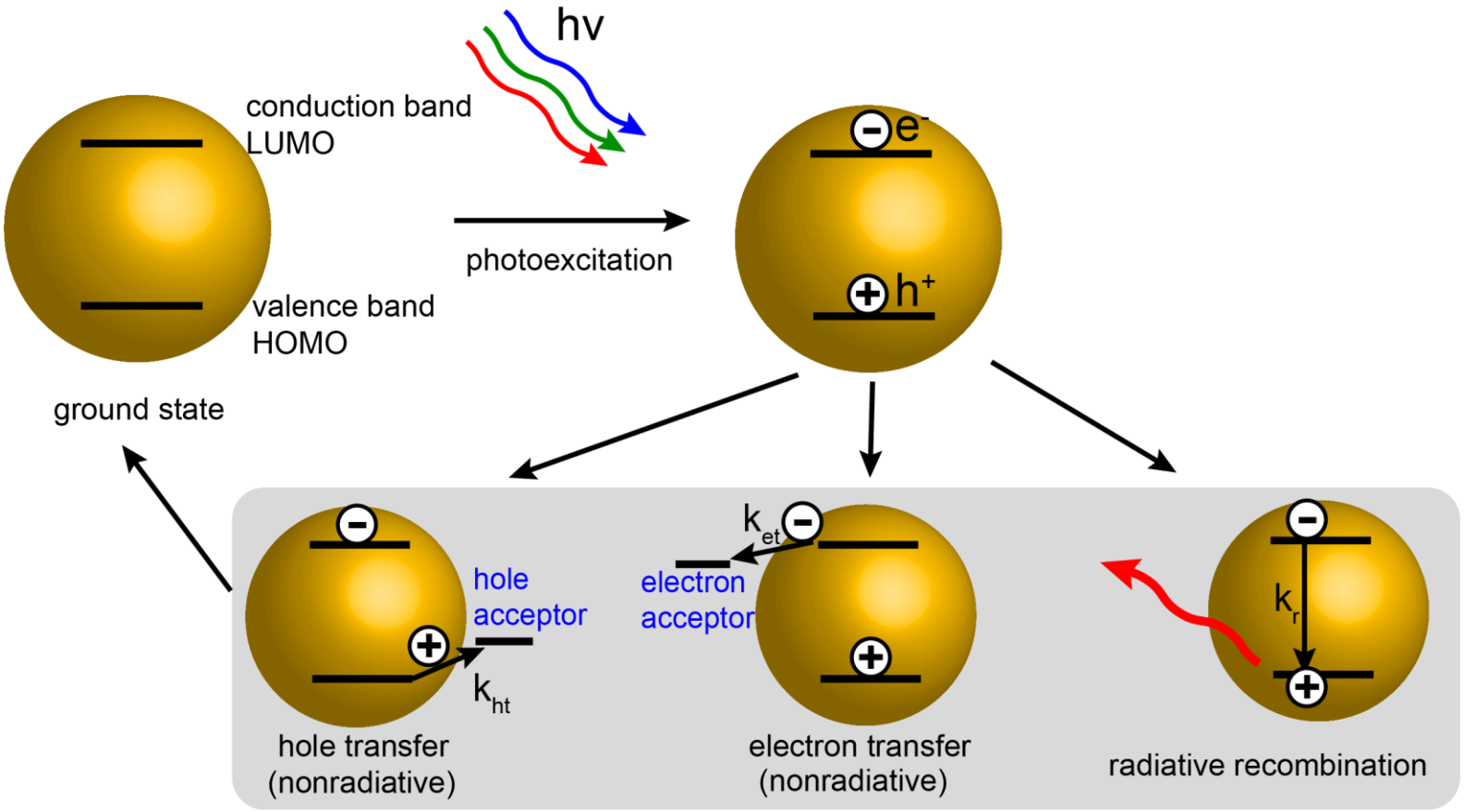
Quantum dot photophysics

Upon photoexcitation, a QD can undergo a variety of relaxation processes. The rate at which these processes occur is critical to understanding the photophysics ("photophysics" simply means light-initiated processes that do not involve bond-breaking or making, essentially limited to charge and energy transfer processes). Each process is denoted by a rate constant (k), which will have units of inverse time.



k_r = radiative rate constant (light emission via photoluminescence)

k_{et} = electron transfer rate constant

an electron acceptor will typically have a LUMO within the band gap of the QD

k_{ht} = hole transfer rate constant

a hole acceptor will typically have a HOMO within the band gap of the QD

k_{nr} = non-radiative rate constant = sum of all non-radiative rates (typically also including electron and hole transfer)

Electron or hole transfer to a charge acceptor will typically be a non-radiative process since the extracted charge (hole or electron), will eventually recombine with the charge left behind (electron or hole) in the QD (without emitting light). However, it is possible for the transferred charge to return to the band from which it came if the energy difference between the charge acceptor and band edge are similar. This will allow for radiative recombination to re-commence, resulting in "delayed fluorescence". When these electron and hole acceptors are poorly defined states that are accidentally present on the QDs, they are called "traps". Electron traps accept electrons and hole traps accept holes. "Shallow traps" have energies close to the band edges (i.e. shallow hole traps are near the valence band edge) and can lead to de-trapping and delayed fluorescence. Deep traps are typically non-radiative and exist deep in the band gap.

Quantum yield and core/shell QDs

Quantum yield is a measure of efficiency of light emission, and can be expressed in a few ways:

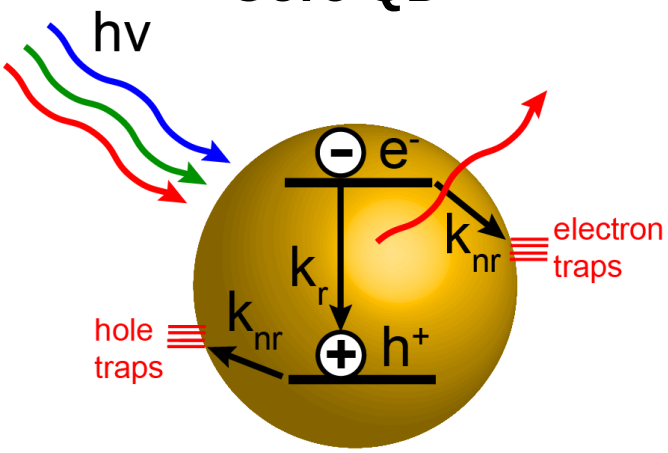
Quantum Yield = (# photons emitted)/(# photons absorbed)

$$QY = \frac{k_r}{k_r + k_{nr}}$$

CdSe core QDs have QY = 1-10%

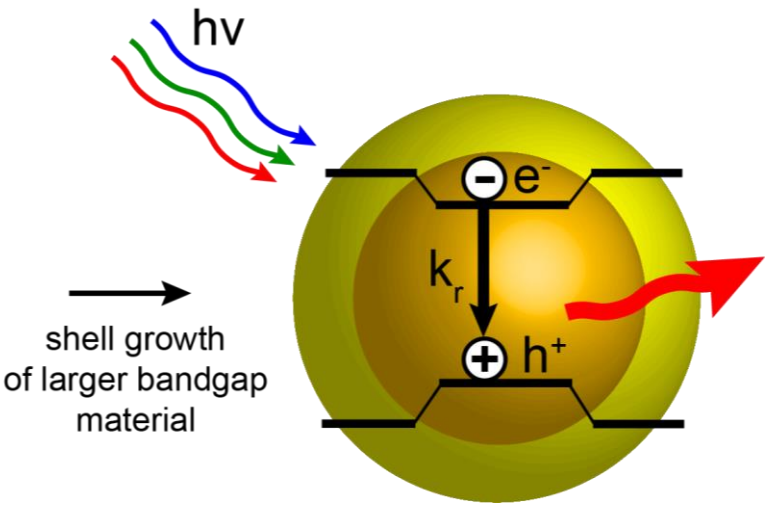
CdSe/ZnS core/shell QDs have QY = 30-100%

Core QD



e.g. CdSe

Core/Shell QD



e.g. CdSe/CdS or CdSe/ZnS

Concept check: if the radiative rate is 100 times larger than the non-radiative rate, then will the QDs be bright? What is the QY?
If the nonradiative rate is 100 times larger than the radiative rate, will the QDs be bright? What will be their QY?

Note again the importance of traps here. Electron and hole traps are molecular-like surface species that are intrinsic to QDs. These could include undercoordinated surface atoms, or odd bonding geometries which create molecular-like states with frontier orbital energies within the band gap of the QD. Traps predominantly exist at the surface of the QD, at the semiconductor – ligand interface, since it is very hard to make this interface perfectly passivated. Therefore, in core QDs, the electron and hole are very easily transferred to traps which leads to non-radiative recombination and thus low quantum yields.

An epitaxially grown shell of a larger band gap material, however, can eliminate the influence of these traps. (Epitaxial means that the crystal structure of one component seamlessly transitions to the next component with no defects). The shell essentially allows for the photoexcited charges to stay in the core of the QD, and acts a physical barrier, insulating the charges from surface traps. As trapping decreases, so does the non-radiative rate constant, therefore the QY is enhanced in core/shell QDs.

Photoluminescence lifetime measurements

Recording the time-resolved photoluminescence can give clues about the various rate constants discussed above.
This technique records the light emitted by a sample of QDs right after a very short laser excitation pulse (a few picoseconds). In this process, a population of QDs are put into the excited state and we observe them returning to the ground state by recording the light they emit as a function of time. It is important to realize that the intensity of light being emitted at a given time will be proportional to the remaining population of QDs in the excited state.

In the simple case that the QD excited state (QD*) decays via a radiative process and a sum of non-radiative processes (i.e. no delayed fluorescence from detrapping), then the excited state population vs. time will look like this:

$$QD^*(t) = QD_0^* \exp(-(k_r + k_{nr})\mathrm{t})$$

Where QD^*_0 is the initial population of excited QDs. Since the population of excited QDs will be proportional to intensity of photons emitted at a given time, the recorded time-resolved photoluminescence will follow this form:

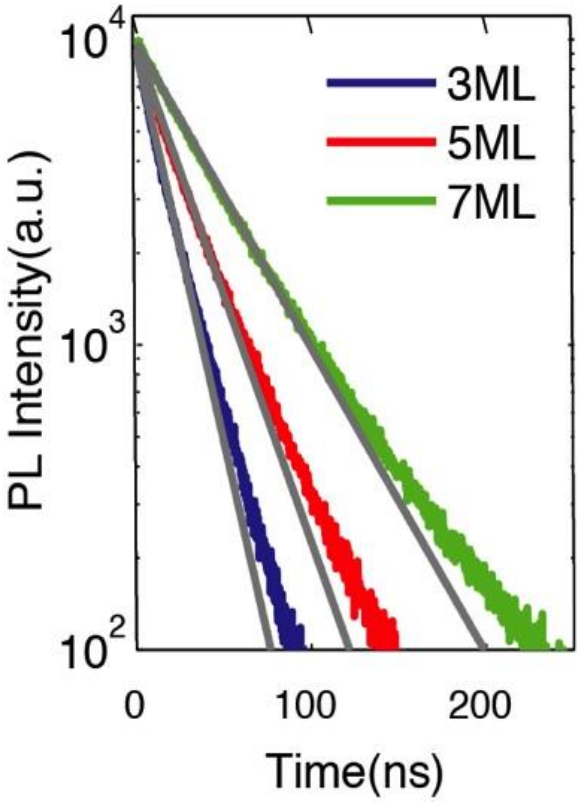
$$I(t) = I_0 \exp\left(-(k_r + k_{nr})t\right)$$

Alternatively, this can be written in terms of a "lifetime", tau.

$$I(t) = I_0 \exp(-\mathrm{t}/\tau)$$

In the simplest case (i.e. no delayed fluorescence), mono-exponential fits of photoluminescence lifetime data (see graph at right) can be performed to yield a "lifetime", τ. Coupling this value with an independent measure of the photoluminescence quantum yield can give you both the radiative and non-radiative rate constants using the following relations (check them for yourself!):

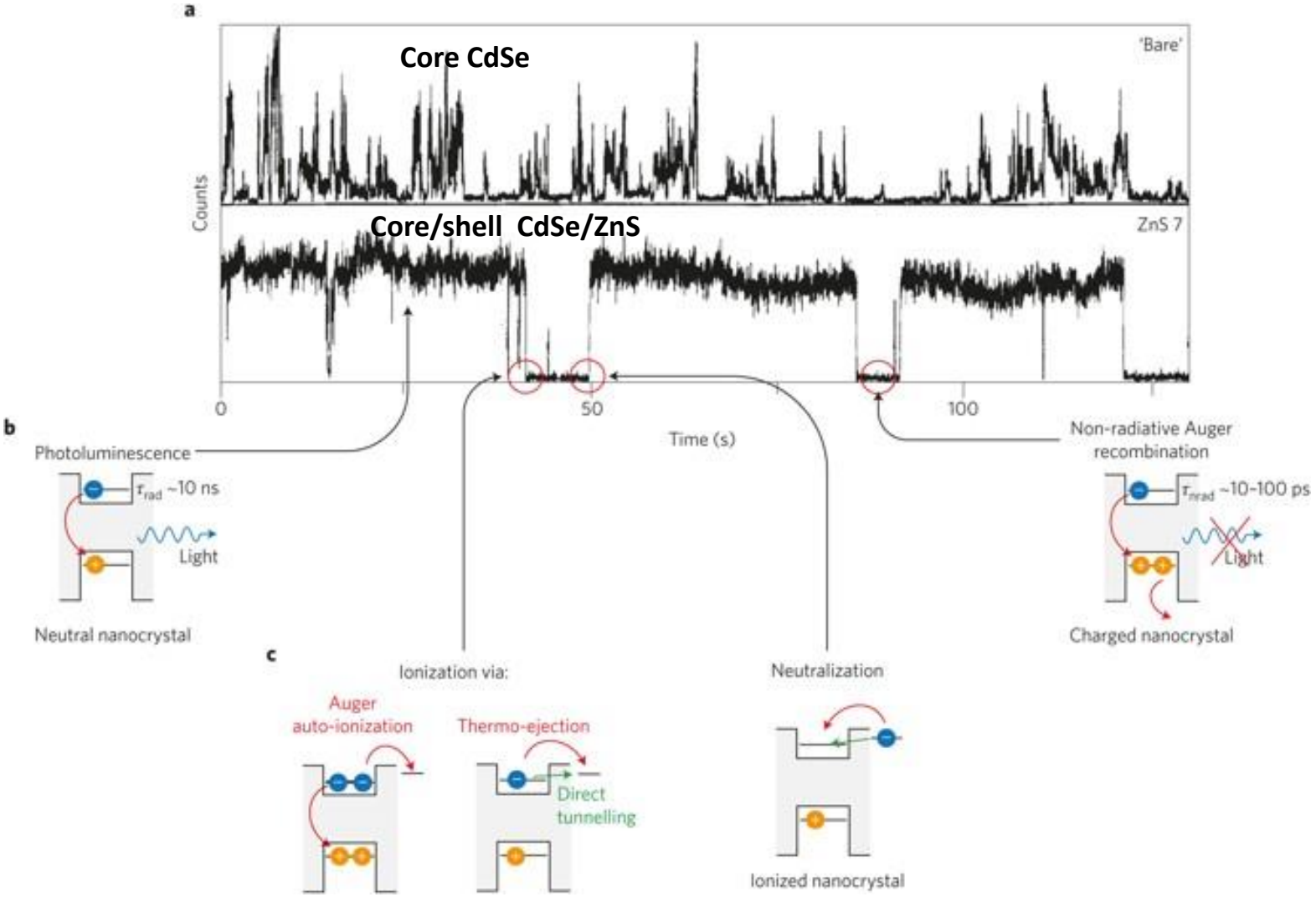
$$k_r = \frac{QY}{\tau} \qquad k_{nr} = \frac{1 - QY}{\tau}$$



The plot at right shows core/shell CdSe/CdS QDs with either 3 , 5 , or 7 monolayers of CdS as the shell (i.e. progressively thicker shells). You'll notice that thicker shells cause longer lifetimes. This is because the photoexcited electrons and holes have more space to spread out in the QD, thus reducing the chance that they can run into each other to radiatively recombine in a given timeframe. For the more advanced QD scientist, they can understand this effect as a result of electron and hole wavefunction overlap.

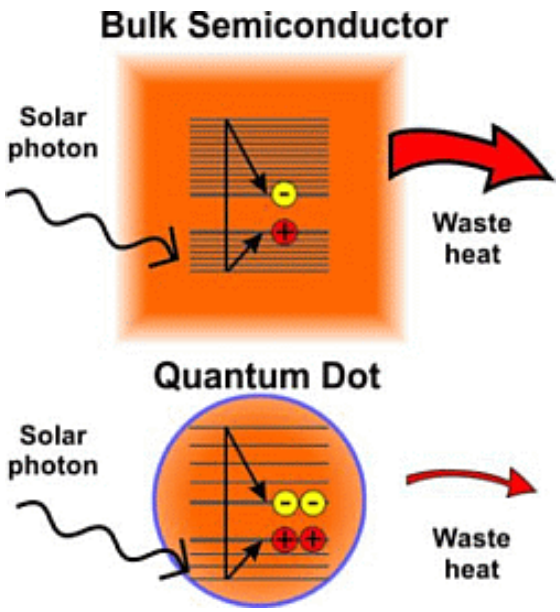
Odd features of QD photophysics

QD blinking: Individual QD photoluminescence as viewed in a fluorescence microscope will fluctuate. The QDs "blink" on and off on long time scales. Core QDs (with their lower QYs) tend to spend more time in the off state. Long lived charge traps are hypothesized to dictate this blinking behavior.



https://www.nature.com/articles/nnano.2016.140

Multi-exciton generation: QDs, unlike bulk semiconductors, can support the generation of two excitons (two electron-hole pairs) from only one high energy photon. If the efficiency of this process were improved, it would be a route to harness more energy in solar to electricity applications.



Resources

Description of time-correlated single photon counting:
https://www.picoquant.com/images/uploads/page/files/7253/technote_tcspc.pdf