14. Semiconductor Nanocrystals

14.1. Structure, preparation, size effects, applications

Semiconductor crystals present a band gap, i.e. a forbidden energy zone between a full valence band and an empty conduction band. This gap is responsible for the luminescence properties of these materials: in first approximation, the first optically excited state of the semiconductor is an electron at the bottom of the conduction band and a hole at the top of the valence band. They can recombine with emission of one photon (radiative recombination). In metals, or for excitations within the bands, nonradiative recombination can proceed via emission of low-frequency vibrations (phonons) to intermediate states, and is therefore much faster than the radiative channel. The gap of semiconductors allows the radiative channel to compete efficiently with internal conversion. In a crystal, emission of a photon must also conserve the wavevector (see Fig. 14.1). From the lowest excited state, the emission is wavevector-allowed only in the case of direct-gap semiconductors, which is the case of many II-VI (ACh, with A= Zn, Cd, Hg,… and Ch= O, S, Se, Te,…) and III-V (AB, A= Al, Ga, In,… and B= N, P, As, Sb…), but not of Si or Ge, which are indirect band gap semiconductors.
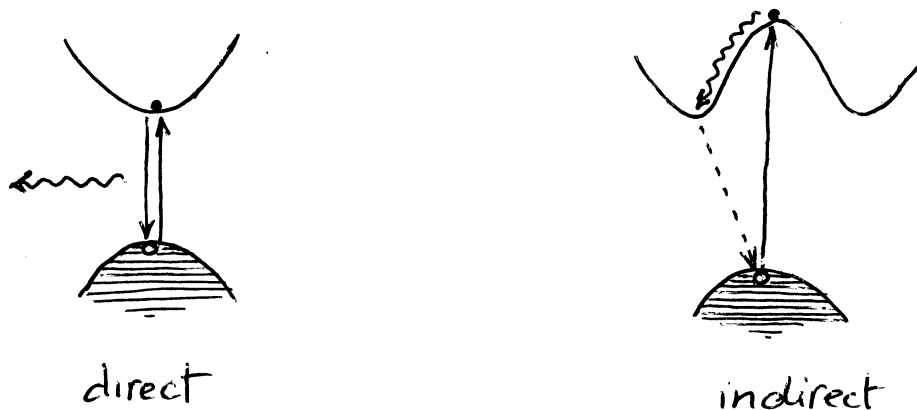

Figure 14.1: Energy-wavevector diagram (dispersion curve) for direct and indirect semiconductors. Because the wavelength of light is large, optical transitions are nearly vertical in the diagram, and are therefore forbidden for the relaxed state in indirect gap semiconductors such as Si and Ge.

Being charged, electron and hole can form a bound state, a hydrogenoid atom called exciton. The optical transition to the exciton concentrates an important part of the oscillator strength and is a central feature in the optical spectroscopy of

semiconductors. In a continuous homogeneous model for the material, the Bohr radius of the exciton is:

$$a_{exc.} = \frac{\hbar^2}{m_{exc.}} \frac{4\pi\varepsilon_0\varepsilon_r}{e^2} \, ,$$

$m_{exc.}$ being the reduced mass of the electron-hole system (involving effective masses of electron and hole), and ε_r the relative dielectric permittivity of the material, which reduces electrostatic interactions with respect to vacuum. The values of $a_{exc.}$ are about 100 Å for GaAs, 56 Å for CdSe, and 7 Å for CuCl,. The exciton is a mobile quasiparticle (a Wannier exciton). The eigenstates in the perfect crystal are k-states delocalized over many lattice sites, and can be combined to form wave packets.

Nanocrystals of semiconductor materials can be prepared in several ways. The most ancient one is precipitation by cooling from molten glass. It was already used in the Middle Ages to stain glass, and is still employed today for some fluorescence cutoff filters. Nanocrystals with definite sizes can also be grown in inverted micelles. The most current preparation now is a high-temperature synthesis from solutions of organo-metallics in tri-octyl-phosphine and its oxide (TOP, TOPO) at 300 °C. Another route at lower temperature uses oleic acid and oleates as organic solvent and surfactants. After a fast nucleation step, Ostwald ripening leads to larger and larger crystals. A careful control of this step leads to highly monodisperse particles, with less than 10% size dispersion. Their structure can be monitored by electron microscopy, and shows much less defects than bulk materials (being small, nanocrystals easily eject defects through their surfaces).

In semiconductor nanocrystals, the reduced size leads to two effects:

i) the discretization of all states at the bottom of conduction and top of valence bands (quantized electron-in-a-box states),

ii) a blue shift of the optical transitions, which increases with confinement (approximately as $\hbar^2\Delta K^2/2M$, where M is an effective mass and ΔK is the extension in K-space of the wavepacket due to the finite size D of the crystal $\Delta K \approx 1/D$; for example, in CdSe, the band gap shifts from 1.7 eV to 2.4 eV when the crystal diameter passes from 20 nm to 2 nm).

In small nanocrystals (NC's), a few nanometers in diameter, up to half of the atoms can be at the surface of the particle! This means that surface effects become extremely

important. Surface defects can trap charges, or cause nonradiative recombination. Bare NC's are usually nonfluorescent, and when capped with organic surfactants such as TOP/TOPO or oleate salts layer, they fluoresce with yields of up to a few %. In order to achieve a better emission yield, one "caps" NC's with a protecting layer of a different semiconductor, which has the effect of pushing the traps at a larger distance, while still confining the exciton in the core of the NC. NC's capped with a few monolayers of a higher-gap semiconductor have quantum yields of typically 20-50 %, up to 80 %. A usual combination is CdSe/ZnS. The quantum yield given here is an average value including the effect of blinking (see below); the fluorescence yield during the on-times is in fact close to 100 %. Unless the core is small enough, increasing the shell thickness beyond a few monolayers does not improve the yield, because lattice mismatch leads to strains and cracks (which again allow access of traps to the core) or because the shell does not grow on the whole surface of the core. Several features of nanocrystal luminescence are very attractive for labeling in molecular biophysics:

i) Their fluorescence lifetimes are considerably longer than that of organic fluorophores, typically 30 nanoseconds at room temperature. This means that their luminescence can be separated temporally from the autofluorescence of a cell. They can thus be detected on lower background.

ii) Their broad excitation spectrum and their tunability mean that only one laser can excite labels of various colors. Besides its non-negligible economic aspect, this feature automatically solves the problem of chromatic aberration for the excitation.

iii) They are considerably more photostable than molecules (but they slowly photooxidize, and eventually bleach).

Their main disadvantages are:

i) their larger size, particularly when they are capped, and conjugated to biomolecules.

ii) the difficulty to couple them in a one-to-one way to biomolecules.

iii) the near-impossibility to use them as acceptors in FRET schemes, because the acceptor would absorb the donor excitation wavelength (this is the downside of a broad excitation spectrum). However, they can serve as donors.

14.2. Luminescence properties

The absorption spectra of an ensemble and of a single nanocrystal are depicted schematically on Figure 14.2. The emission of a bulk crystal usually arises from traps. That of an ensemble of nanocrystals is inhomogeneously broadened, mostly by the size distribution. Single NC's emit a single narrow line, with a weak phonon sideband. This means that it is rather difficult to observe the ZPL in a luminescence excitation spectrum, in contrast to molecules, because the intensity of the red-shifted photoluminescence is low. Therefore, the luminescence line is usually observed through a spectrograph under excitation at higher energy of phonon sidebands or higher electronic excited states. Therefore, the linewidth is limited by the spectral resolution of the spectrograph used for recording. The following questions are still largely open: Can the linewidth reach the radiative limit at low temperature? What is the influence of spectral diffusion? How do dephasing and linewidth depend on temperature? For single molecules, the answers to all these questions are well known.
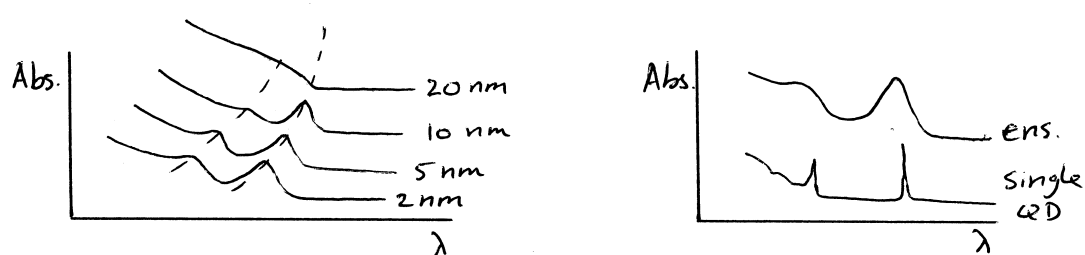

Figure 14.2: Left: Shift of the lowest optical transition of nanocrystals with crystal diameter. Right: comparison of spectra from an ensemble of nanocrystals or quantum dots (top) with the spectrum of a single dot. The excited state of the exciton can be detected in self-assembled quantum dots, but usually not in II-VI nanocrystals.

The Stark effect of NC's is very strong and interesting. The difference of static dipoles between excited and ground states reaches tens, sometimes hundreds of Debye, about two orders of magnitude larger than for molecules. This is due to their large size and to the polar (non-centrosymmetric) structure of many II-VI semiconductors. Stark shifts are caused not only by external fields, but also by charges in the environment of the NC. Rearrangements of these charges lead to

spectral diffusion, and are observed to occur dominantly upon changes in luminescence brightness (i.e. upon transitions between on- and off-times, see below). L. Brus and colleagues have observed single NC's with an electric force microscope (T. D. Krauss, S. O'Brien, L. E. Brus, J. Phys. Chem. B 105 (2001) 1725). Under illumination, NC's undergo occasional transitions from their neutral (initial) state, to a state where they are positively charged, with one, rarely two, elementary charges. This picture suggests that excited NC's can transfer an electron (sometimes two) to acceptor sites in their surroundings. The fact that charging stops after the first electron is ejected may indicate that the Coulomb energy necessary to abstract a second charge would exceed that of the excitation (a similar phenomenon in the microlithographic structures of solid state physics is called Coulomb blockade).

Single semiconductor NC's are similar in many ways to large organic molecules. In particular, just as molecules, they show strong photon antibunching. Although the absorption of the NC is barely changed by the presence of an exciton (particularly in the broad absorption continuum), no or weak emission is seen from the bi-exciton state. Even a single charge in the NC is enough to quench luminescence efficiently. This is in strong contrast to the self-assembled quantum dots discussed in the second part of this lecture. The absence of luminescence from a bi-exciton state can be understood easily with the following model (see Fig. 14.3):

A single charge in the quantum dot opens new non-radiative relaxation channels, which completely dominate radiative recombination. The optical energy may easily be dissipated by successive one-phonon processes, lifting a deep electron of the valence band to the empty hole level, or lifting the free electron to an empty higher level in the conduction band. These processes are still largely active if the charges are combined as an exciton in the NC. On the other hand, for the neutral dot, non-radiative recombination across the gap requires a one-step multi-photon process, whose probability is very low. This self-quenching of the bi-exciton is very similar to the relaxation of higher singlet states, or to singlet-singlet annihilation in organic materials.
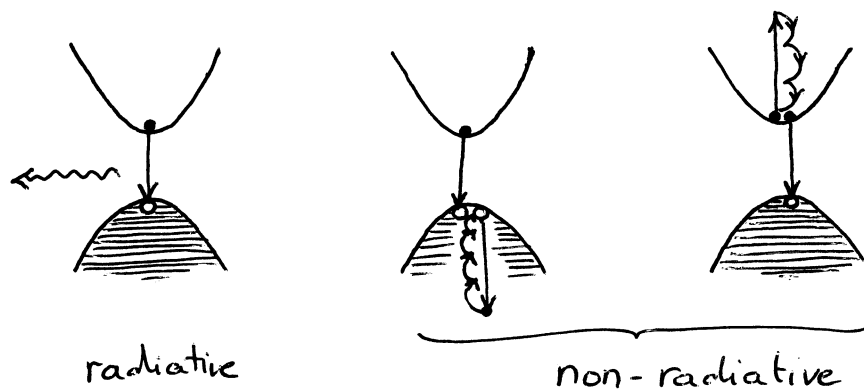
Figure 14.3: A single exciton (left) can relax only via radiative recombination (neglecting multiphonon processes). If a charge is already present in the dot, either an electron (right) or a hole (center), it can be promoted to a higher energy level, from which it relaxes very quickly via a cascade of efficient one-phonon processes.

14.3. Blinking

The preceding remarks allow us to propose a model for the on-off blinking of single quantum dots, which is one of the most striking features of these systems. Let us first summarize blinking observations, mostly made on capped NC's. The luminescence intensity of a single NC is seen to fluctuate on a very wide range of times (Kuno et al., J. Chem. Phys. 115 (2001) 1028). When plotted with log-log axes, the histograms of on- and off- times τ are seen to obey power-laws τ^{-m} over several decades of times, indeed over the whole interval of times accessible to experiment, from microseconds to minutes. The exponent m lies between 1 and 2 (often between 1.4 and 1.8). Neither the qualitative appearance of the blinking, nor the exponent seem to depend significantly on temperature. Similar laws are found for the distributions of on- and off-times.

In the following, we discuss a model proposed by our group for uncapped NC's. We assume that the off-times correspond to a charged state of the NC. The NC has transferred an electron to a trap. As long as the dot is charged, it remains dark, and it lights up again when the electron hops back to the dot. Electron jumps occur via (incoherent) tunneling through the barrier of the matrix. Trapping times can be as long as several seconds, which means that the corresponding traps have to be relatively far away from the dot (tunneling probabilities decrease roughly by a factor e per 0.1 nm).

Let us assume a random distribution of traps around the dot, which we replace by a uniform distribution. The rate of transfer to a trap at distance r varies as $e^{-\alpha r}$, where α characterizes the decay of the electron wavefunction through the matrix. The rate of the back reaction (i.e., the off-time τ) varies as $e^{-\beta r}$, where β is now the tunneling coefficient for the wavefunction of the trapped electron. Therefore, $\beta > \alpha$ because a deeper electron is more localized. The probability of an off-time $\tau = \tau_0 e^{\beta r}$ corresponding to trapping at a distance r is thus proportional to $e^{-\alpha r}$. With these simple assumptions, the distribution of off-times is found to obey a power-law with exponent $m = 1 + \alpha / \beta$. From the inequality $\beta > \alpha$, we find that $1 < m < 2$, as experimentally observed. Moreover, incoherent tunneling to a much lower state being nearly independent of temperature, we conclude that the power-law and the exponent do not depend strongly on temperature. A consequence of the model is that the luminescence intensity traces are self-similar on all timescales: they show long off-times on all timescales, and are therefore non-stationary on all timescales. Therefore average times cannot be defined.

In this model, however, we expect the distribution of on-times to be single-exponential (the rate being the sum of all trapping rates), which is indeed consistent with observations of uncapped NC's, but not with those of capped ones. A slightly modified model can explain the observed power-law distribution of on-times in capped NC's. For a more extended discussion, in particular of the nature of the dark states as self-trapped states, see the review by Cichos et al. (Curr. Opin. Coll. Interf. Sci. **12** (2007) 272).

14.4 <u>Self-assembled quantum dots</u>

i) Structure, preparation, uses

Quantum wells and quantum dots are much studied because of their uses as solid-state laser sources and in opto-electronic devices. Much effort has been devoted to their preparation and characterization. The most reliable method to build quantum-well structures is molecular beam epitaxy (MBE; a quantum well is a layer of semiconductor B in a crystal of semiconductor A, for example, GaAs in (Al,Ga)As). If the lattice mismatch between materials A and B is too large, after one or two

'wetting' monolayers, material B prefers to grow in three-dimensional islands (which can also follow Ostwald ripening). This is called Stranski-Krastanov growth. For well-controlled conditions, it leads to islands of material B on a surface of A. These islands can then be 'buried' in a further thick layer of A (see Fig. 14.4), which protects them from traps and impurities (in contrast to the loose NC's of the preceding section). The islands often have a pyramidal or hill-form, but such exotic shapes as doughnuts can also be obtained. In some cases, an incomplete monolayer formed by MBE spontaneously creates monolayer islands, by a similar mechanism. The islands act as traps for the exciton in the quantum well, yielding again self-assembled quantum dots (cf Gammon et al., Science 273 (1996) 87).
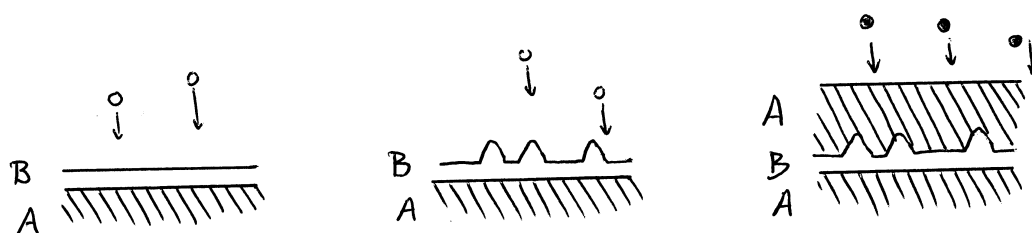

Figure 14.4: Schematic growth of self-assembled quantum dots. When material B is deposited on A, after a first few wetting layers, 3D growth of small self-assembled islands starts. If the growth of A then resumes, the islands of B remain isolated in the A matrix. Note, however, that the B monolayers play the role of a quantum well, and can permanently feed excitations to the dots.

Single quantum dots can be isolated from an ensemble by several different methods, using the microlithographic techniques of the electronic industry. For example, one can cover the QD sample with a metal (Al) layer with small holes in it. Observing a single hole, only the few QD's in the hole will contribute to the optical signal. Another method is to etch 'mesa' structures of a few microns in size, again selecting the QD(s) remaining in the mesa.

ii) Luminescence properties

The main difference with the isolated nanocrystals, is that self-assembled QD's are resting on a quantum well, or on a few monolayers of B material (perturbed by the vicinity of A on both sides). These extended structures have a large oscillator strength. They act as funnels, filling in the dots with new excitons all the time. Therefore, self-assembled quantum dots are much brighter than nanocrystals. This is presumably also one of the reasons why bi- and multi-exciton states, as well as

charged excitons can be observed optically in self-assembled dots, while only the single-exciton state is observed in nanocrystals. The other possible reasons for this difference are the much higher material quality and purity of self-assembled dots, and their larger sizes. Thanks to their brighter luminescence, self-assembled QD's can be detected with much less numerical aperture, i.e., with optics outside the cryostat. The photoluminescence spectrum shows a single line, with a width of a few tens of μeV at low temperature. The temperature dependence of the linewidth is much reduced (as compared to the bulk) because of the quantization of exciton states. Since the splitting to the next exciton state increases with confinement, it becomes more and more difficult for phonons to couple the two states.

Self-assembled QD's in general do not blink, at least in high-quality samples. This may be attributed either to their higher purity (no organic ligands, no traps), or to the absence of disorder and therefore of possible initial sites for self-trapping in their neighborhood.

Localized excitons in QD's are found to be sensitive to nuclear spins, and to shift according to their polarization (this is an Overhauser effect due to the polarization of nuclear spins under repeated optical pumping). A "resonance Raman" signal can also be detected by exciting at the exciton energy plus the energy of an optical phonon (see Fig. 14.5, from D. Gammon et al., Science **277** (1997) 85).
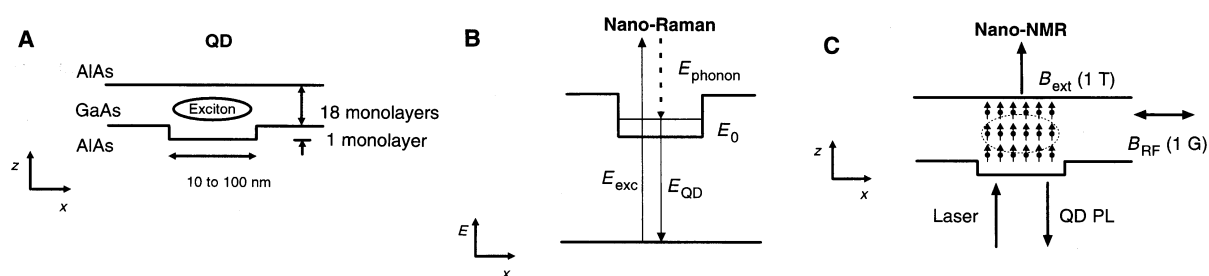

Figure 14.5: Illustration of a quantum dot (left), and the two processes observed. Center : an absorbed photon gives rise to a photon emitted by the dot and to an acoustic phonon. This process is enhanced by resonance with the well. Right: Nuclear spin polarization induced by optical pumping of the dot with circularly polarized light. The induced polarization leads to shifts of the optical transition. Reprinted from Gammon et al. Science277:85 (1997). Copyright 1997 AAAS.

14.5 Semiconductor nanowires

Nanowires from Si, AsGa, GaN, etc. can be grown from the gas phase. The growth often proceeds from a nanoparticle of a catalyst, often a noble metal such as gold. In some cases (GaN) nanowires can grow spontaneously under precise conditions. The composition of nanowires can be changed during the growth, which can give rise to quantum dots included in a one-dimensional pillar. Nanowires can be broken off their substrate and can be interesting single nano-objects for spectroscopy (cf. work of E. Bakkers and V. Zwiller at TU Delft).

Exercise 14.1: *The regime of strong confinement in semiconductor quantum dots is reached when the dot diameter is lower than the exciton Bohr radius.*
i) Explain why, in that case, the Coulomb interaction between electron and hole can be considered as constant, so that the QD potential for electron and hole can be replaced by a spherical box with a flat bottom (pill box potential).
ii) The leading contributions in the Hamiltonian of the electron and hole are therefore their kinetic energies. m_e and m_h being the effective masses of these quasi-particles, and assuming the semiconductor gap to be direct, calculate the energy corrections to the two lowest levels (ground and excited) by taking the expectation value of the kinetic energy (first order perturbation).
iii) Deduce from this model that the exciton energy shift scales as the inverse square of the dot diameter.

Exercise 14.2: *In the blinking model given above, the excited QD transfers an electron to a nearby electron trap with a rate scaling as $\exp(-\alpha r)$, where r is the distance between the QD and the trap. Once the electron is trapped, the QD is positively charged and becomes dark. It stays dark until the electron is transferred back to the a QD and photoluminescence resumes. The rate of back-transfer scales as $\exp(-\beta r)$, where the characteristic length $1/\beta$ is shorter than $1/\alpha$.*
i) Give the distribution of dark times in this model. What can you say about the distribution of bright times? Explain why the assumption $\alpha > \beta$ is reasonable.

ii) We now assume that the QD is surrounded by a distribution of similar traps, placed at different distances r from the QD. Explain qualitatively the kind of photoluminescence time trace that will be observed while trapping can occur towards different traps at different distances.

iii) To estimate the distribution of dark times, look for the probability to trap the electron at distance r. Once this happens, what will be the average duration of the dark time? Assuming the relation between dark time duration and distance to be deterministic (instead of Poisson distributed), relate the distribution of dark times to the spatial distribution of traps $p_s(r)$, and the probability to trap at distance r. For a uniform $p_s(r) = p_0$, prove that the dark time distribution is a power law of their duration. What can you tell about the distribution of bright times?

iv) Explain qualitatively why the above approximations of a deterministic relation between distance and trapping time, and of a constant spatial distribution of traps are not critical in this model.