Nanotechnology

Quantum dots realize their potential

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Scientists have engineered semiconducting nanocrystals called quantum dots that lack toxic heavy metals and are highly efficient light emitters. These nanostructures might be used in displays, solar cells and light-emitting diodes. **See p.634**

Tiny semiconductor crystals dubbed quantum dots (QDs) are one of the biggest nanotechnology success stories so far. Since their first synthesis[1,2] in the 1980s, QDs have featured in a wide range of optoelectronic devices, and QDs suspended in solution have been used in many *in vivo* and *in vitro* imaging, labelling and sensing techniques. However, two technical problems need to be resolved before their potential can be fully realized. First, QDs based on cadmium must be replaced by ones that are highly efficient light emitters and that do not contain such toxic heavy metals. And second, QD phosphors (substances that exhibit luminescence) in televisions must be replaced by QD light-emitting diodes (LEDs), to reduce power consumption. On page 634, Won *et al.*[3] report QDs that address both issues.

The absorption spectra of nanocrystal QDs depend on their size. This property was discovered independently for QDs in glass[1] and in aqueous solution[2] and was first described quantitatively[4,5] in the early 1980s. For practical applications, such a feature should be converted into size-dependent photoluminescence. In this process, an electron in the valence energy band of a QD absorbs a photon and moves to the conduction energy band, leaving behind a hole (electron vacancy). The photoexcited electron and hole then recombine (merge), releasing a photon (Fig. 1a).

Photoluminescence was achieved initially by coating QD surfaces with organic molecules[6] and later by using QDs that comprise a semiconductor core surrounded by a shell of a semiconductor that has a large bandgap[7] – the energy difference between the valence and conduction bands. In the latter case, the offset in energy between the bands of the shell and those of the semiconductor core prevents electrons and holes from the core escaping to the external surface and enables intrinsic photoluminescence. In cadmium selenide QDs, the size-dependent absorption and photoluminescence spectra cover the entire range of visible wavelengths from red to deep green[8].

For QDs grown using current techniques, the photoluminescence quantum yield (the number of photons emitted by the QD divided by the number of photons absorbed) can be quite high. However, this high quantum yield is still not good enough for some applications. For instance, a quantum yield of less than 100% is associated with blinking[9] – a phenomenon observed in single-QD experiments, in which the photoluminescence intensity varies under constant illumination. This blinking is linked to random processes in which QDs become charged and are subsequently neutralized.

An electron–hole pair that is photoexcited in a neutral QD can recombine only by emitting a photon – in other words, by photoluminescence. However, photoexcitation in a charged QD triggers another recombination process, which is known as non-radiative Auger recombination. In this process, the energy of the photoexcited electron–hole pair is transferred to another electron or hole and a photon is not emitted (Fig. 1b). For commonly used QDs that comprise a core surrounded by a thin shell, the rate of Auger recombination is usually much higher than that of photoluminescence. As a result, the former process completely quenches the latter process in most charged QDs.

To achieve a photoluminescence quantum yield that is close to 100%, Auger recombination needs to be suppressed. One approach is to prevent the optically produced electrons and holes from escaping to the QD surface, to avoid charging of the QD. This can be realized, for example, by using QDs that have a thick shell[9]. In the case of QD-LEDs, QD neutrality can be controlled by ensuring that electron and hole conductivities are similar.

A complementary approach is to engineer the QDs to have a soft confinement potential – a potential-energy profile that gently increases at the QD surface and so reduces the rate of Auger recombination[10]. This potential can be produced by forming an alloy of the core and shell materials at the core–shell interface of QDs, or by using multi-shell QDs in which each subsequent shell has a larger bandgap than the preceding one. Successful efforts to engineer such QDs were reported last year[11]. However, despite the outstanding optical properties of the cadmium selenide-based QD structures that were attained in that work, the photoluminescence quantum yield did not reach 100%.

Won and colleagues have developed an innovative method for synthesizing heavy-metal-free QDs that consist of a uniform indium phosphide core, a thick inner shell of zinc selenide and a thin outer shell of zinc sulfide (Fig. 1c). The technique involves two consecutive steps for the growth of the

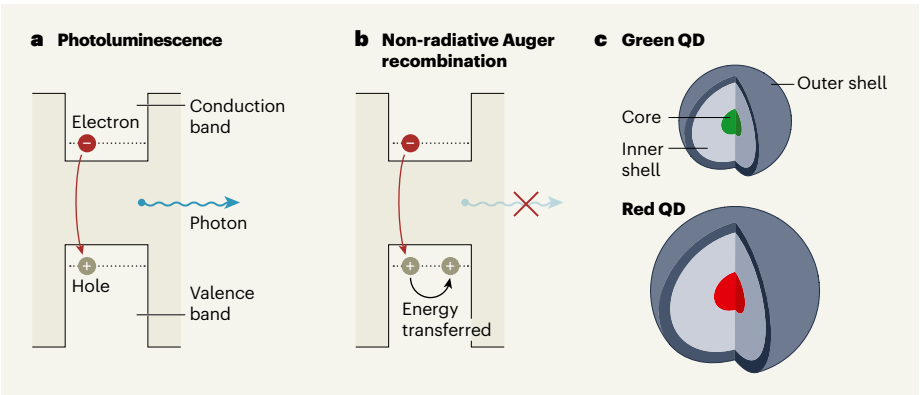

Figure 1 | Efficient light emission from quantum dots. a, Semiconducting nanocrystals known as quantum dots (QDs) can produce light through photoluminescence. In this process, there is a negatively charged electron in the conduction energy band of the QD and a positively charged hole (electron vacancy) in the valence energy band. The electron moves to the valence band and merges with the hole, releasing a photon. **b**, However, a process called non-radiative Auger recombination can instead occur. In this process, the energy generated by the electron–hole merger is transferred to another charge carrier, and a photon is not emitted. **c**, Won *et al.*[3] demonstrate QDs that are highly efficient light emitters, because Auger recombination is suppressed. The QDs consist of a uniform indium phosphide core, a thick inner shell of zinc selenide and a thin outer shell of zinc sulfide. The colour of the light produced by the core depends on its size.

core: the addition of hydrofluoric acid to etch off the oxidized core surface during the growth of the initial zinc selenide shell, and high-temperature zinc selenide growth at 340 °C.

The resulting QDs have a highly symmetrical spherical shape, which is one of the conditions for realizing a soft confinement potential. Any cavity or sharp corner on the surface or at the core–shell interface would enhance the rate of non-radiative Auger recombination. Charged or deep-level defects would also lead to such enhancement. The authors found that the thick zinc selenide shell suppresses Auger recombination, suggesting that the interface is of extremely high quality and that there are no crystal defects called stacking faults in the zinc selenide shell. The intrinsic photoluminescence quantum yield of these QDs is 100%.

Won *et al.* used their QDs to make LED devices in which electrons and holes are injected into the QDs instead of being photoexcited. To maintain QD neutrality during such injection, and to improve the transport of electrons and holes in the LEDs, the authors replaced long-chain ligand molecules at the QD surface with short-chain ones. The QD-LEDs achieve an external quantum efficiency (the number of photons that leave the LED divided by the number of charges injected into it) of 21.4%, which is the theoretical maximum. The improved injection and transport of charges reduces accumulated electrical resistance during operation, lowers power consumption and increases the lifetime of the LED device.

This work shows that the detailed understanding of the physical properties of QDs that has accumulated over more than 30 years should now allow us to engineer QDs for multiple and diverse applications. These could include televisions and displays, LEDs and solar cells.

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