Coming attractions for semiconductor quantum dots

Applications of colloidal semiconductor quantum dots (QDs) have recently begun to move from the laboratory into the commercial sector. This article provides a brief description of QDs and their associated optical properties, highlighting the concept that QD size is now a parameter used to tune photophysical properties. Additionally, three major applications of QDs are discussed: biological imaging, photovoltaic devices, and light-emitting devices. Progress in each area is highlighted, as well as potential advantages over existing technologies when QD products are realized. Finally, some of the challenges to the further development of QDs for each respective application and in the field overall are addressed.

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The term "nanotechnology" still conjures up many popular cultural depictions related to science fiction, such as tiny robots from *Star Trek*, or the miniaturized people in *Fantastic Voyage*, who are able to cure disease inside the body of a patient. But nanoscale materials are very real to the scientists and engineers who work on them, and in the case of colloidal semiconductor nanocrystals, or quantum dots, beginning to be very real to the general public as well. In this article, we hope to address a few fundamental questions about quantum dots: What are they? What makes them so potentially transformative? How can they be useful?

What are they?

In order to understand the photophysics of quantum dots, first consider any semiconductor with a bandgap of E_g between its conduction and valence bands. If this material absorbs a photon, an electron can be promoted into the conduction band, leaving behind a hole in the valence band (as shown in Fig. 1). Together, the two charge carriers can form a quasi-particle called an exciton, held together by Coulombic forces, similar to the hydrogen atom. The exciton can either recombine through fluorescence, reemitting a photon with energy approximately E_g, or through nonradiative processes (simply put, creating heat). Taking a simple Bohr model picture of the exciton, the electron and hole orbit each other at a distance known as the Bohr radius, which varies depending on the material, ranging from a few to tens of nanometers (10^{-9} m).

The difference between a bulk semiconductor and a semiconductor quantum dot is one of size, but how small is small enough? In simple bulk semiconductors, an exciton is rarely observed at room temperature because the energy binding the electron to the hole is smaller than the thermal "bath" of the crystal lattice; carriers are
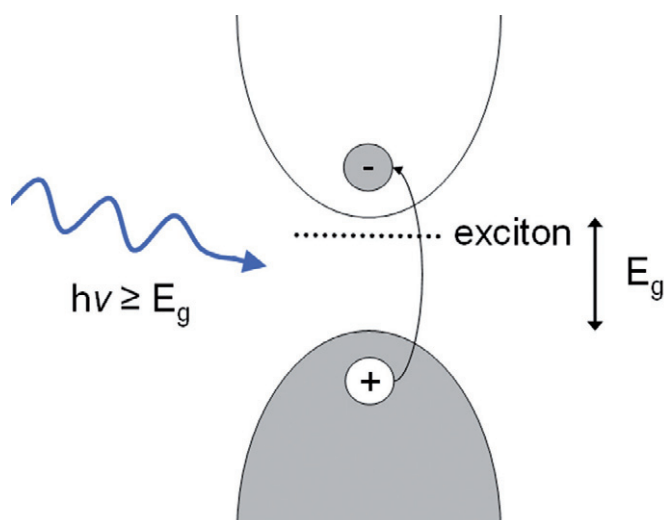
Fig. 1 A photon absorbed by a semiconducting material promotes an electron to the conduction band, leaving a hole in the valence band. An exciton has an energy state in the semiconductor band gap due to the Coulomb attraction between the electron and hole.

typically free. However, consider a situation where the electrons and holes are restricted by the physical dimensions of the material. In a semiconductor quantum dot (QD), the crystallite is so small that the excited electron and hole are physically confined to a separation smaller than their "natural" Bohr radius, providing a real materials system for the quantum mechanical "particle-in-a-box" potential energy function model[1-3]. Squashing the exciton into a smaller space makes it more energetic through what is known as quantum confinement[2,4-6] so with smaller and smaller nanocrystals, higher and higher energy excitons are produced. This phenomenon is illustrated in Fig. 2, which shows a rainbow of fluorescent colors all produced by CdSe QDs of various sizes. In addition to energy gap changes, the energy band structure of QDs also alters from the continuous nature of bulk semiconductors, to being quantized at the band edge similar

to molecular energy levels[3,7], as shown by the distinct sharp peaks in the absorption spectrum shown in Fig. 3. Thus, by reducing the size of semiconductor materials to the nanometer scale one can directly tune the electronic states and associated optical properties.

In several respects, quantum dots can potentially combine the best properties of small molecule chromophores and bulk semiconductors. As fluorophores, high quality QDs are extremely bright, with fluorescence efficiencies or quantum yields (QYs) approaching unity[8-10], meaning that nearly every absorbed photon results in an emitted fluorescence photon. In terms of photostability, individual organic molecules tend to photobleach on the timescale of seconds or minutes while QDs can last significantly longer, up to hours under constant excitation[11,12]. To draw another parallel to organic dyes, compare the absorption spectrum of CdSe QDs to that of Rhodamine 640 (a high QY dye) also shown in Fig. 3. Any given dye only absorbs light in a very narrow spectral window, while QDs absorb any photons higher in energy than their bandgap. Dyes also tend to have modest Stokes shifts, meaning that the wavelengths they emit are spectrally close to where they absorb, requiring high quality spectral filters to remove excitation light in applications such as fluorescence microscopy. While QDs also have small Stokes shifts, they can be excited at energies far above their bandgap, which makes them much more versatile for some applications. Arguably even more important is that multiple QD emission wavelengths can be collected from the same excitation wavelength. For someone with a mind to make a QD sensor (and, as will be addressed below, that is a lot of someones), QDs allow the possibility of simultaneous multiple analyte detection with one excitation wavelength[13].

In the last two decades, QDs have been made from a variety of semiconductor materials and are optically active from the ultraviolet to the near infrared portions of the electromagnetic spectrum. CdSe and CdTe, QDs, which emit largely in the visible region, are joined by CdS, ZnSe, and ZnS QDs in the ultraviolet, PbSe, PbTe, and PbS QDs in the near infrared. Cadmium and lead-free visible and near infrared emitting
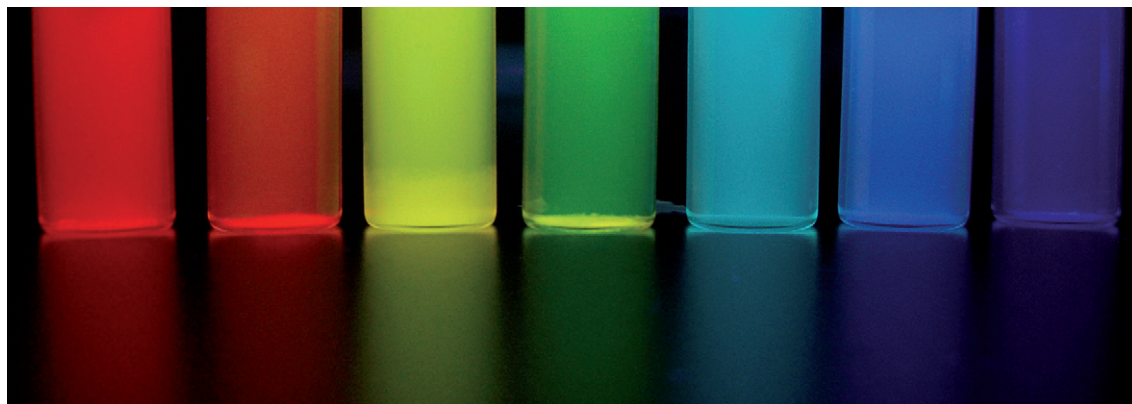

Fig. 2 Colloidal CdSe QDs with a range of fluorescent colors based only on variations in particle size, excited by an ultraviolet lamp. The QD size decreases from the red (about 6 nm in diameter) to the blue QDs (about 2 nm).
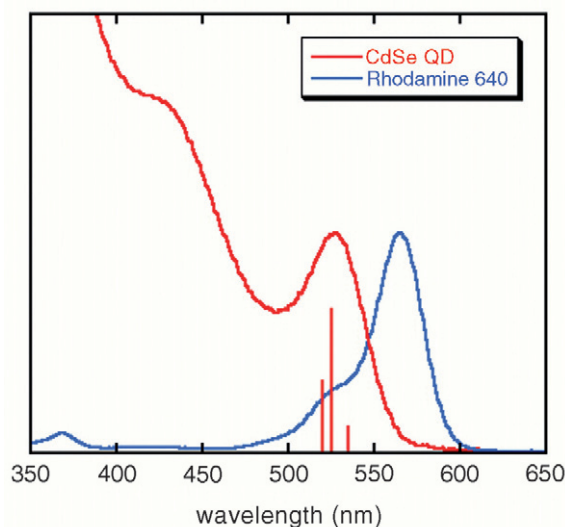
Fig. 3 Absorption spectrum of CdSe QDs (red) and the organic dye Rhodamine 640 (blue). The QD exhibits well defined first and second exciton peaks around 525 and 425 nm, respectively. The individual "molecular" like QD energy levels that contribute to the first exciton peak are shown as bars.

QDs are also being studied, such as InP, InAs[14], (though the tradeoff is lower toxicity for higher expense considering the rarity of indium), and GaP[15]. Generally, III-V colloidal particles are challenging to synthesize and less extensively studied than II-VI or IV-VI materials. Despite their indirect bandgaps in the bulk material, Si and Ge nanoparticles exhibit reasonably strong light emission as well. Si QDs emit in the visible (QYs up to 20 %), and Ge QDs in the near infrared (QYs under 10 %), although the mechanism for light emission in these nanoparticles is still not well understood[16].

One common method for growing QDs involves combining highly reactive and air-sensitive organometallic precursors at high temperatures, which, with the right equipment, is merely all in day's work to an experienced synthetic materials chemist[17]. QD size is dictated by how long the reaction mixture is heated (the longer the heating time, the larger the QDs), so a range of sizes can be produced in one synthesis by pulling successive aliquots out of the reaction vessel. Reactant to product chemical conversion yields tend to be low, though recent work has shown significant improvement in that metric[18]. The final product of the synthesis reaction is a liquid, but QDs are actually in a colloidal suspension rather than a solution, much like the protein and fat molecules in a glass of milk. The outermost atoms of the nanocrystal are coordinated to organic ligand molecules, which allow the QDs to interact with the solvent without precipitating. However, new progress has been made on development of inorganic capping ligands as well[19]. With the right chemistry, ligands can be changed, like a set of clothes, to suit the environment[20,21]. If you would like your QDs in water rather than an organic solvent, protocols exist to exchange from hydrophobic to hydrophilic ligands (Fig. 4). Ligands also allow you to perform chemistry with the QD, as chemical reactions on the outer ligand chemical groups can facilitate attachment
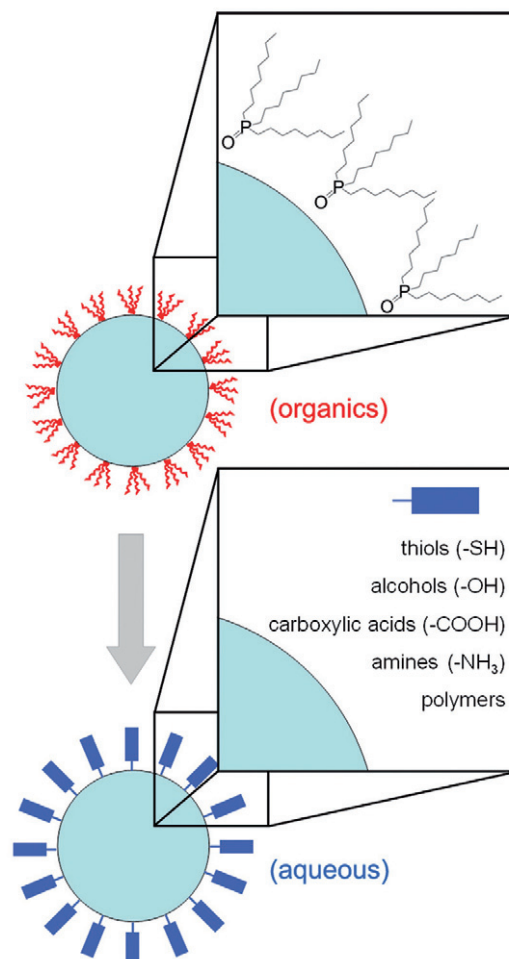

Fig. 4 Cartoon showing (top) a typical QD with hydrophobic surface capping ligands (tri-octylphosphine oxide) and (bottom) a QD after a ligand exchange to a hydrophilic ligand.

of various chemical and biochemical recognition elements such as antibodies or fluorescent species[22].

In the last decade, the simple core QD particle has given way to studies of more highly engineered structures. QDs are frequently overcoated with an outer layer, or shell, of another semiconductor material, a few atoms thick, much like the candy coating on an M&M[8,9]. This shell serves to passivate any dangling bonds on the core QD surface and prevents the inner QD core from photo-degradation processes such as reaction with oxygen. Using a higher bandgap semiconductor as the shell in core/shell particles can also improve the optical properties of a QD by causing tighter confinement and localization of the exciton in the QD core, offering dramatically increased QY and improved photostability. Alternately, "type-II" core/shell structures promote carrier separation by engineering band offsets to necessitate charge transfer at the core/shell interface[23]. This structure creates tunable infrared emission even when both components are visible emitting materials, while the ability to direct carriers is beneficial for device applications.

How are they useful?

Biology

One place you might encounter QDs is a biomedical research laboratory at a hospital. QDs have been used for a wide variety[24-26] of biological applications, such as staining and lighting up cells for visualization[11,20] or detecting a specific analyte[20,22]. QD bioconjugates can specifically bind to cancer cells[27] or tag bacteria such as *E. coli* and accurately differentiate between pathogenic and harmless strains[28]. Biologists who want to make use of the excellent fluorescent properties of QDs have no need to brush up on their synthetic chemistry skills though, as QDs are available for purchase from companies such as Invitrogen, suspended in water and capped in several kinds of ligand chemistries, ready for functionalization. QDs can even come already coated with proteins such as streptavidin, or some common antibodies, enabling attachment to a protein coated substrate, an antigen, or simple conjugation to a biomolecule of your choice.

For the short term, QDs will be found only under the microscope or on the bench-top rather than in the patient. *In vivo* imaging is being vigorously pursued[29,30], especially for particles with near infrared emission wavelengths which have good transmission through tissue and are well separated spectrally from background autofluorescence[31]. However, questions of cytotoxicity still remain unresolved, and conclusions about the relative harmful effects of QDs vary greatly depending on specific QD surface coatings[32,33]. Studies with animal models suggest that particles around 5 nm in diameter (and smaller) are able to pass quickly out of the body in the urine[34]. But most QDs suspended in water, considering their ligands and protective inorganic shells (which help prevent the leeching of QD core metals into the body in addition to protecting the QD)[35], tend to be bulkier than this. The ideal particle for *in vivo* applications, therefore, is extremely small, emits between 700 and 1000 nm, and is either exceptionally stable or made of non-toxic elements. For example, InAs/ZnSe, core/shell particles[36], InAs/InP/ZnSe core/shell/shell particles[37], PbSe nanoclusters[38] and CuInSe ternary particles[39] show promise in fulfilling some of these parameters.

A major breakthrough in biomedical imaging would come from the ability to follow single proteins inside a live cell in real time, for minutes to hours[40]. In principle, QD fluorescence is bright and robust enough to potentially make this long standing biological "holy grail" a reality. However, individual QDs exhibit fluorescence intermittency, or "blinking," a feature common to most single fluorophore molecules. Under constant excitation, a single QD will switch between a bright "on" state and a dark "off" period, as shown in Fig. 5. Early on, it was hypothesized that trapped surface charges could play a role in the blinking[41]. Indeed, single charges on QDs as observed through electrostatic force microscopy also exhibited blinking behavior, suggesting that surface charge traps may play a role in creating the off state[42]. However, the observation of fluorescence from charged QDs complicates matters[43], and the complexity of blinking
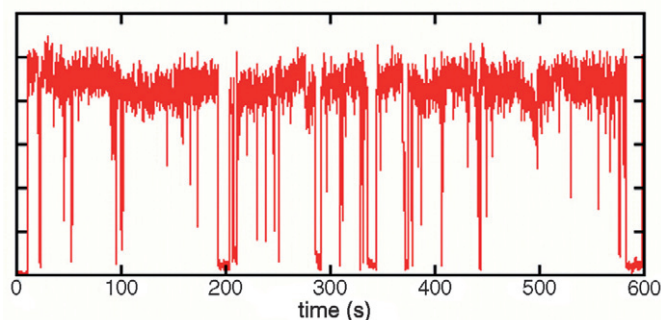

Fig. 5 Fluorescence intensity over time of a single CdSe QD (Invitrogen Qdot 585 ITK organic) under 488 nm excitation. Note that the QD fluorescence seems to "blink" between a bright "on" state and a dark "off" state.

statistics necessitates dynamic models to approximate experimental observations[44]. While blinking is a significant hurdle to overcome in order for QDs to be useful as single photon emitters and single particle trackers, recent results show that it can be suppressed both by growing an extremely thick CdS shell on CdSe[45,46], and by creating "alloy" QDs, where the core and shell materials make a gradual transition rather than having an abrupt boundary[47]. However, these steady emitting particles are still the exception rather than the rule[48].

Devices

Light in, electricity out

With the recent push for carbon-free energy sources and an ever increasing energy demand, all eyes are on ways to produce greener power. Indeed, novel materials for solar energy production have seen renewed interest, and following the example set by plants to harvest our energy from sunlight is as green as it gets. The theoretical upper limit (i.e., Shockley-Queisser limit) for the energy conversion efficiency of a Si photovoltaic cell is about 30 %[49]. In practice, the best Si devices have efficiencies around 25 %. Additional efficiency can be gained by using layers of different materials tailored to absorb different parts of the solar spectrum in multi-junction cells, with three junction cells exceeding 40 % efficiency[50]. So why haven't solar cells sprouted up on every rooftop yet? In part, it comes down to expense. Semiconductor photovoltaics capable of those high efficiencies are fairly costly to produce and install[51]. For an example of how this trickles down to the consumer, a pocket-sized solar cell that can charge your cell phone or MP3 player in a few hours retails for around $40: not a bad investment (and particularly attractive if you intend to be without access to an outlet on a long hike or camping trip) but considering the current cost of electricity, it would take over 4000 charges to break even compared to plugging in!

Fortunately there are potentially more inexpensive options in development, like a dye-sensitized TiO_2 nanoparticle based Graetzel cell[52] which boasts a very respectable 11 % energy conversion efficiency and easy, inexpensive solution-phase processing. Since colloidal QDs share the advantage of easy processing with dyes, their
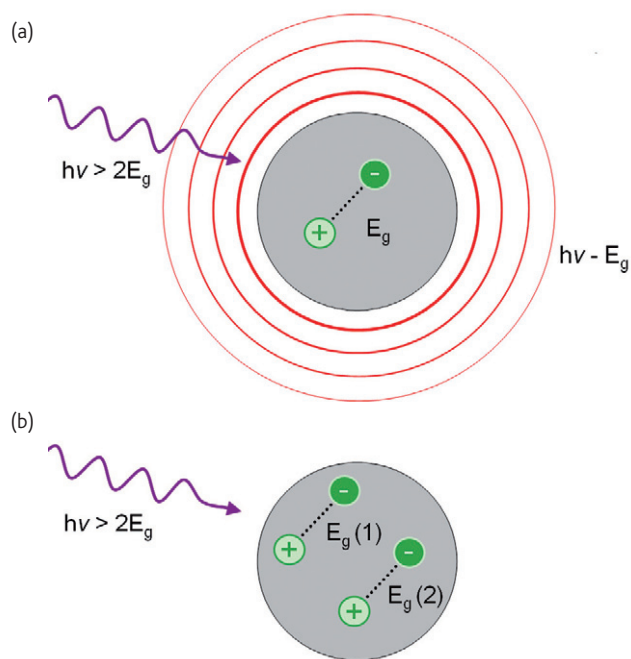
Fig. 6 (a) A high energy photon is absorbed by a QD, creating one exciton while excess energy is lost to fast phonon relaxation as heat. (b) A high energy photon is absorbed by a QD, creating two excitons through the MEG process.

broadband absorption properties (recall that instead of the tiny window of the solar spectrum accessible to a dye, QDs gobble up any photons higher in energy than their bandgap) can be harnessed[53] with Graetzel cell-type architectures. "Rainbow cells" use a variety of QD sizes, taking advantage of the fact that while larger QDs have a better match to the solar spectrum and can collect more light, for smaller QDs energy bands line up better to transfer that energy to the wide bandgap TiO_2[54]. Close packed films of QDs can be used as the basis for a solar cell on their own[55-57], though overall device efficiencies remain quite low. Additionally, photovoltaics can be made by incorporating QDs into conducting polymer matrices[58,59]. Quantum rods, the elongated relatives of the QD, may prove to be a superior choice for these types of devices due to improved charge separation along the long axis of the particle[58].

A factor that could help overcome the fundamental Shockley-Queisser limit is the phenomenon of multiple exciton generation (MEG), or carrier multiplication. When a very high energy photon is absorbed, an electron is created with large kinetic energy. Usually this electron will rapidly drop down to the conduction band edge, losing all its extra energy in phonon relaxation processes, i.e., the creation of heat. What if, instead, an electron with a kinetic energy greater than twice the energy gap could generate two carriers (see Fig. 6) with minimal heat generated? You could have twice the electrons per photon absorbed, resulting in a higher photocurrent, and giving your overall device efficiency quite a boost. A MEG type process can occur in bulk semiconductors (referred to as impact ionization)[60], though

with low efficiencies due to competition with those very fast cooling processes, and at energy thresholds inaccessible for the majority of the solar spectrum. It remains a matter of some debate[61,62] whether quantum confinement effects cause an enhancement of MEG efficiency such that it will have considerable impact on practical applications. However, recent prospects look fairly positive since a PbS-sensitized photovoltaic device has been shown to produce photocurrents corresponding to greater than one electron created per high energy photon absorbed[63]. At any rate, even those skeptical of MEG can agree that QDs have the potential to improve solar cells, if not through increased photocurrents due to enhanced MEG processes compared to bulk, then at least by the ability to better match the solar spectrum due to QD bandgap tunability.

Electricity in, light out

Once the sun goes down, attention turns to conserving energy, and one way to do that is with efficient light sources. Light-emitting diodes (LED) are superior to both incandescent and fluorescent bulbs in terms of energy efficiency, lifetime, and robustness (as anyone who has dropped an incandescent bulb or a mercury compact fluorescent bulb is bound to appreciate). Since LEDs are semiconductor devices, the color of light produced is characteristic of the bandgap of the material, and (similar to QDs) spectrally narrow. Much in the same way that fluorescent light bulbs convert ultraviolet radiation into visible light, blue or ultraviolet LED bulbs can be coated with phosphors for white light emission. White LED lamps and bulbs currently on the market have at least four times the luminous efficacy (lumens/watt) of incandescent bulbs[64]. However, the clear advantage in the efficiency arena is counterbalanced by a deficiency in the color quality of most white LEDs. Based on the color rendering index (CRI) scale, typical white light LEDs only score about 75 out of 100[65]; and their light appears cold and harsh. One method to improve the CRI score employs multiple sizes of QDs as phosphors to produce white light[66]. These downconversion (high energy light to lower energy light) devices have even made it out of the lab: currently there are QD-LED lamps for sale commercially with a CRI of 90[65]. Similar to QD photovoltaics, QD films for downconversion devices are easily made with solution processing.

While direct electroluminescence from QDs is certainly possible[67-69] and a hot area for research[70], device efficiencies have not yet reached a point where they are viably competitive with existing bulk semiconductor or organic LED technologies. In addition to efficient solid-state lighting, QD emission can be applied to the production of QD-LED displays. For these full color organic/nanoparticle hybrid devices, QD films can be created by inkjet printing (exactly what it sounds like) for a downconversion device[71], or by solvent free ink/stamp transfer for direct QD electroluminescence with a pixel size comparable to existing high definition displays[72]. Both displays have been successfully created on flexible substrates. The former features color saturation and purity comparable to the International

Telecommunications Union HDTV standard, though QDs have the potential to exceed that standard[65].

Conclusion and future challenges

While we have focused here on the prospects for someday having QD-related products throughout your home, it is clear that several significant remaining challenges must be first addressed before QDs will be decorating the shelves of your local department store. Though protocols for synthesizing QDs are well established, reproducibility is often poor due to the influence of impurities which may or may not be present in a given reagent batch[18]. With regard to biological applications, toxicity, as mentioned earlier, remains a complicated question. Additionally, cellular uptake of QDs is extremely complex, varying not only with size but with QD surface properties as well as

cell type[73]. For device applications, wide bandgap capping strategies used to protect QDs from oxidation result in poorer QD film conductivity for charge transport applications. Non-isovalent doping, which provides free charge carriers and thus is essential for forming *p-n* junctions and associated transistors in bulk semiconductors, is difficult to achieve in QDs[74,75]. Nonetheless, whether they are helping doctors make a diagnosis, helping engineers to build a better solar cell, or improving the light quality of energy efficient LEDs, the future of quantum dots is decidedly bright. mt

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