Colloidal quantum dots (QDs) have been widely studied as absorbers for various solar technologies because of their excellent optoelectronic properties, such as a size-dependent absorption spectrum, efficient charge separation and transport, and good photostability. During the last decade, major research initiatives have been pursued to elucidate the structure-dominated optoelectronic properties with the goal of maximizing overall solar-device power-conversion efficiency. In this review, we discuss the chemical synthesis methods and the properties of these QDs and emphasize their applications in solar cells, solar-driven hydrogen production, and luminescent solar concentrator devices. We describe recent research advances in this rapidly growing field by highlighting various strategies developed for the synthesis of QDs with different structure and composition. We also describe available approaches for tuning charge dynamics in QDs and metal oxides. Finally, we introduce several types of solar devices based on QDs and discuss their fabrication and performance. We also discuss challenges to be addressed for the controlled synthesis of QDs.

INTRODUCTION

The efficient conversion of solar radiation into electrical or chemical energy is one of humanity’s greatest challenges in the 21st century, in view of the ever-growing global demand for renewable energy solutions. Current research directions in solar technologies investigate new methods and, in particular, new materials and processes that will render integrated, more efficient, and lower-cost power harvesters. From a technological point of view, low-cost fabrication processes using available, inexpensive, healthy, and environmentally friendly materials are required.

Materials that can harness and convert energy from the sun are by necessity semiconductors, because there is a need for a gap that will allow photons to be absorbed, convert them into excited states (excitons), split them into electron-hole pairs, and drive the resulting charges toward electrodes. Among various kinds of semiconductors, colloidal semiconductor quantum dots (QDs) have been studied extensively because of their excellent optoelectronic properties. QDs are fluorescent nanocrystals (NCs) with nanoscale dimensions, normally smaller than 20 nm in diameter. Typically, they are composed of an inorganic core, made of a few hundred to a few thousand atoms, surrounded by an organic outer layer of surfactant molecules (ligands). Semiconductor QDs exhibit dramatic quantization effects, defined by an increasing bandgap accompanied by quantization of the energy levels in discrete values, similar to atomic energy levels. In most semiconductors, once the size is reduced to a few nanometers, quantum confinement occurs, leading to size-dependent optoelectronic properties of QDs. Such size effects allow us to design and synthesize QDs with controllable size, shape, and chemical composition to precisely tune the optical transitions and the energy of discrete electronic energy states. Over the past two decades, various types of high-quality colloidal QDs, including bare and core-shell QDs, can be controllably synthesized via efficient and environmentally friendly synthetic routes for QDs with well-controlled size, crystalline phase, and chemical composition. We further discuss efficient approaches to improving charge separation and transport in the presence of electron-hole acceptors by tuning band alignment. This is achieved by controlling the structure of the core-shell materials. The architecture, performance, challenges, and recent progress of each type of solar device are discussed. Finally, we propose possible approaches to improving the efficiency of solar devices.
including bare and core-shell QDs (Figure 1), with strong absorption, size-tunable emission and absorption, high photoluminescence quantum yield (PLQY), and good photostability have been realized by various well-controlled synthetic approaches. Recent studies revealed that QDs show great potential in clean and renewable energy applications, such as photovoltaic devices, photocatalysts, luminescent solar concentrators (LSCs), etc., to address the grand challenges represented by the energy crisis and environmental pollution.

This review focuses on the synthesis of colloidal QDs and their integration in solar energy devices. We describe the synthetic routes, structure and property relationships, optoelectronic properties, device architecture, and performance of various kinds of QDs. We address the key challenges for energy applications: size monodispersity, tunable bandgap, and high PLQY, including different sizes and structures; tuning the photoinduced charge-transfer processes in QDs and metal oxides by controlling either band alignment or structure; and using these QDs in optoelectronic devices to maximize overall solar-device power-conversion efficiency (PCE).

Figure 1. Schematic Representation of the Synthesis of Colloidal QDs via Various Approaches and Their Emission Range
(A) A synthetic apparatus used in the preparation of various structured QDs. The bare QDs can be synthesized via a cation exchange approach. The core-shell structure can be obtained via both a cation exchange approach and SILAR approach.
(B) The emission range for representative QDs.
SYNTHESIS OF COLLOIDAL QDs

The development of simple, efficient, and environmentally friendly, large-scale synthetic routes for high-performance QDs with controlled size, crystalline phase, and chemical composition is crucial to exploit the relationship between their structure and properties. This section introduces several recently reported methods to grow colloidal semiconducting QDs. Synthetic routes for QDs have been explored since the 1990s4,23 and can be divided into two categories: wet-chemical synthesis and gas (or vapor) phase deposition.23,34,35

In this review, we focus on solution-based synthetic routes, which include various low-cost and simple approaches, such as hydro- and solvothermal synthesis, thermolysis method, co-precipitation synthesis, sol-gel method, continuous flow approach, etc.4,36–40 These methodologies are especially powerful for the convenient and reproducible synthesis of highly monodisperse colloidal QDs, including pure QDs, core-shell QDs, and core-multi-shell “giant” QDs, because they allow the size, structure, and chemical composition of the resulting NCs to be tuned, and they also deliver materials that are already well dispersed in a solvent, capped with various surface surfactants (ligands), ready for further applications.4,36–40 The typical reaction setup for the thermolysis method is shown in Figure 1A.

SYNTHESIS OF BARE COLLOIDAL QDs

The synthesis of colloidal QDs has been conducted in both organic and aqueous phases.23,34 QDs with different elemental composition, including II–VI (e.g., CdX, X = S, Se, Te), III–V (e.g., InP, InAs, GaAs), and IV–VI (e.g., PbX, X = S, Se, Te) semiconductors (Figure 1B), have been synthesized.4,36,39 Other types of group IV QDs, such as carbon, silicon, and germanium QDs with size- and chemical-composition-dependent emission properties, have also been realized via wet-chemical approaches.51–43 However, high-quality QDs with narrow size and size distribution, high PLOY, and good photo- and thermal stability have been synthesized almost exclusively via a high-temperature organometallic route by the hot-injection method.36,39

The organometallic precursor is mixed with the solvent in the presence of molecular surfactants. The mixture is then heated to a certain temperature (T1) in the range of 100°C–320°C under a gas flow (nitrogen or argon), which can prevent the oxidation of precursors. Subsequently, the non-metallic precursor is injected into the mixture at a much lower temperature (T2, usually at room temperature). As T1 is much higher than T2, after injection, the temperature of the mixture drops very quickly. Small nuclei are formed at higher temperature (T1) and grow further at a lower temperature, leading to separate stages of nucleation and growth of the NCs.44 The size, shape, and structure of QDs can be further controlled by varying parameters such as the type of precursors and surfactants, reaction temperature, molar ratios of precursors, precursor concentration, reaction time, etc.26,39,45 As an example of visible-emitting II–VI QD synthesis,45 cadmium oxide, hexylphosphonic acid trioctylphosphine oxide, and tetracycliphosphonic acid were loaded in a three-necked flask. At about 300°C, the reddish CdO powder was dissolved and generated a colorless homogeneous solution. After the formation of the complex, an injection of selenium dissolved in tributylphosphine at 250°C–300°C generated CdSe NCs. Tunable particle sizes of CdSe QDs in the range of 2–8 nm can be synthesized by changing the growth temperature and reaction time. The as-produced CdSe QDs exhibit a typical emission in the wavelength range 450–650 nm.
Another interesting example is the organometallic synthesis of near-infrared (NIR)-emitting PbS QDs with tunable size in the 2–8 nm range. Typically, a certain amount of PbO dissolved in oleic acid was purged with a nitrogen gas flow and heated in a reaction flask to 150°C. Stock solutions of bis(trimethylsilyl) sulfide and octadecene were then added to the flask and mixed under vigorous stirring. After injection, PbS NCs nucleated quickly. The temperature was maintained at 100°C for the growth of NCs. This synthetic approach is able to produce PbS NCs with a highly crystalline rock-salt structure with a narrow size distribution (SD, σ < 10%–15%) (Figures 2A and 2B). PbS NCs show a peak emission ranging from about 800 to 2000 nm, as well as a narrow emission peak with PLQY up to 20% (Figures 2C and 2D). The as-produced QDs capped with oleic acid ligands and large-scale synthesis can produce 1 g of NCs in one batch. Because of its effectiveness, the hot-injection method has also been applied for the preparation of binary semiconductor QDs, such as CdS, CdTe, ZnSe, HgS, InAs, PbSe, PbTe, and ternary semiconductor QDs, such as CdSxZnxCdx1-x, ZnxCdxS, and CuInSxSe2-x. The as-produced QDs exhibit high PLQYs in the range of 20%–90% with size distribution less than 10%. However, it is critical to control the reaction temperature because both nucleation and the growth rate are highly dependent on temperature. In addition, in this method, the injection temperature is generally higher than 150°C and up to 320°C.

Quite recently, high-quality perovskite CsPbX3 (X = Cl, Br, I) QDs were also synthesized via a hot-injection approach in order to control their size and size distribution. Typically, after injecting the Cs precursor into a mixture of PbX and oleylamine, growth occurs within the first 1–3 s. By tuning the reaction temperature (140°C–200°C), molar ratio of Cl/Br or Br/I, and reaction time, the as-obtained QDs exhibit size- and composition-tunable bandgap energies covering the entire visible spectral region (410–700 nm) with narrow and bright emission (Figures 3A–3C). The size of CsPbX3 QDs can be conveniently tuned in the 4–15 nm range with cubic shape and a cubic perovskite crystal structure. The perovskite QDs show narrow emission line widths of 12–42 nm, high PLQYs of 50%–90%, and short radiative lifetimes of 1–29 ns (Figures 3C and 3D). However, this type of perovskite QD is very sensitive to moisture, causing the photoluminescence signal to decrease gradually over time. After only a day, the photoluminescence intensity disappears totally. This is because of the degradation of perovskite materials after reacting with moisture, which causes them to rapidly change color. The product of PbX (X = Cl, Br, I) after reaction does not show any optical properties and leads to the disappearance of the photoluminescence signal in perovskite materials. Further improvement in stability might be achieved by improving our understanding of the degradation mechanism and by optimizing synthetic methods.

For example, a new surface technique in which the surface of CsPbBr3 QDs was capped with an inorganic-organic hybrid ion pair has been found to improve the air stability of perovskite materials. The formation of a protective layer enriched with sulfide endows perovskite QDs with unprecedented stability in air (60% ± 5% humidity) for at least 4 months and under high laser fluences, with samples showing no noticeable degradation after 34 hr. Other possible approaches to improving the stability of perovskite QDs could use an inorganic shell (e.g., PbS) via an overcoating approach to protect the core material.

A clear advantage of the hot-injection method is the simple control of the size and size distribution of QDs, within less than 10% because of the good separation of nucleation and growth at different temperatures by controlling the temperature of
the injected precursor solution. As the optical properties of QDs are size dependent, the narrow size distribution leads to very narrow emission spectra with photoluminescence width less than 100 meV. In addition, high-temperature growth yields highly crystalline structures, avoiding possible surface traps and defects and leading to a high PLQY.

This approach can also be applied to a variety of QDs, with emission ranging from UV to visible and the NIR range (400–2,000 nm). This approach can produce

Figure 2. Morphologies and Optical Spectra of Colloidal PbS NCs
(A) High-resolution transmission electron microscopy images of colloidal PbS NCs with an exciton absorption at 1,440 nm.
(B) The selected area electron diffraction spacing (inset on the single-particle close up on the right) correspond to bulk lattice parameters. Room temperature optical characterization of toluene solutions of PbS NCs.
(C) Absorption spectra spanning the range of tunable sizes.
(D) Band-edge absorption and photoluminescence peaks for a sample ~6.5 nm in diameter.
Adapted with permission from Hines et al. Copyright 2003 John Wiley and Sons.
high-quality QDs on a large scale with high yield and low cost. The disadvantage of the hot-injection method, similarly to other methods such as solvothermal synthesis and co-precipitation synthesis, is the use of toxic organic solvents and surfactants. In addition, the reaction temperature required to decompose the precursor species is often very high (up to 300°C). Aqueous colloidal synthesis is considered a “greener” approach for QD production. Because of the low synthetic temperature (<100°C), the as-obtained QDs in general exhibit low PLQY because of the presence of surface traps or defects. The traps and defects lead to charge trapping, inhibiting efficient charge separation and transfer, and worsen the performance of QD-based optoelectronic devices. It is still very challenging to produce high-quality colloidal aqueous QDs with outstanding optoelectronic proprieties. A further post-surface treatment approach, such as inorganic ligands or inorganic shell coating, might improve the surface passivation of QDs, as well as their optical and electronic properties.

Another well-established approach to synthesize high-quality QDs is through a cation-exchange reaction (Figure 1A). Pre-synthesized QDs with well-defined size and structure, such as CdS and CdSe QDs, can be used as an anion template for the synthesis of compositionally bare and alloyed NC structures. For example, Kim et al. developed a direct, cation-exchange-based procedure that produces PbSe from ZnSe QDs (Figure 4A). The Zn cations are replaced by Pb cations and form PbSe QDs capped with both halide anion and zinc cation passivation (Figure 4A). The typical reaction procedure consisted of first synthesizing ZnSe QDs via a hot-injection approach. Then PbX₂ (X = Cl, Br, I) precursors were mixed with oleylamine and heated to 140°C. Subsequently, the ZnSe QDs dispersed in octadecene at room temperature were injected into the PbX₂/oleylamine complex at injection temperatures ranging from 80°C to 200°C. Finally, oleic acid was injected into the final solution to exchange the native oleylamine ligands. After injection of the ZnSe QDs, as the reaction proceeds, the PbSe QDs continue to grow (Figure 4B, shaded traces). The final size of the PbSe QDs obtained can be effectively controlled.
by optimizing the QD injection temperature and reaction time (Figure 4C). With an initial seed of 3 nm in diameter (first excitonic absorption peak of 3.3 eV; Figure 4D) the diameter of the PbSe QDs can be tuned over a broad range (~1.8 to ~7 nm) (Figure 4C). Similar methods have been used to synthesize CuInSe NCs by partial cation exchange in Cu_{2-x}S NCs with the presence of In cations. Generally, the as-prepared PbSe or PbS QDs via cation exchange exhibit better air stability than directly synthesized QDs, benefiting from better surface halide passivation. Improving the air stability of cation-exchanged PbSe QDs enables us to fabricate solar energy devices with higher PCE.
On the other hand, the main drawback of this approach is that the reaction process is complicated, involving a seed-based QD synthesis. In addition, during cation exchange, a large amount of precursors was used to facilitate complete exchange (in general, the molar ratio of precursors and cation in QDs is >10). To address the limitations of this method, chemically active precursors could help to accelerate the degree of cation exchange to obtain completely exchanged QDs with a lower concentration of precursors.

**SYNTHESIS OF CORE-SHELL QDs**

The typical size of a QD is very small (less than 20 nm), leading to a very high surface-to-volume ratio. The co-ordination of surface organic ligands can stabilize colloidal QDs in solution and at the same time passivate dangling bonds at the QD surface. However, the interaction between the QD and surface organic ligand is weak. Therefore, the properties of bare QDs capped by organic ligands are very sensitive to changes in their surface conditions, especially after exposing the QDs to illumination. The surface-related traps and defects formed act as fast non-radiative de-excitation channels for photogenerated charge carriers, thereby reducing the PLQY and long-term photostability. Recent studies revealed that a core-shell structure is an efficient strategy to improve the surface passivation of QDs. As a result, a robust inorganic shell can protect the semiconductor core against surface defect states, trap sites, and environmental chemical status, improving both PLQY and stability. Furthermore, by the appropriate choice of core-shell materials, it is possible to tune the band alignment of the core and shell to improve the exciton separation and charge (electron-hole) transfer in the presence of electron or hole scavenger, which is a crucial factor for applications in photovoltaics.

As shown in Figure 5, the core-shell heterostructures are typically classified as type I and type II depending on the relative alignment of conduction- and valence-band edges of the elements that are combined at the heterointerface. In type-I-structured core-shell QDs, the bandgap of the core is smaller than that of the shell, and both band edges of the core are located in the band gap of the shell. Therefore, both electrons and holes are confined in the core region, leading to fewer
interactions of core-localized e-h pairs (excitons) with surface traps than with bare QDs and thus enhanced PLQY and photo- and thermal stability over that of pure QDs.\textsuperscript{23} In the type II structure, either the conduction-band edge or the valence-band edge of the shell is located in the bandgap of the core (Figure 5). The band alignment causes spatial separation of the electrons and holes into different regions of the core-shell structure.\textsuperscript{52,66} A special case is called quasi type II. In this case, only one type of carrier is delocalized over the entire core-shell structure, whereas the other type of carrier is confined in the core.\textsuperscript{59,65,67} For example, core-shell PbSe/CdSe QDs\textsuperscript{65} present the typical properties of quasi type II band alignment. The electron spreads over the entire core-shell structure, whereas the holes are still confined in the core region.

Core-shell QDs have most commonly been achieved through injection of the shell precursors into the core solution.\textsuperscript{4,23,52,68} Several approaches have been reported, including injection of a mixture of cationic and anionic precursors at the growth temperature or alternative injections of cationic and anionic precursors (also named a successive ion layer adsorption and reaction [SILAR] approach), etc.\textsuperscript{4,23,52,68,69} To prevent homogeneous nucleation of the shell material and uncontrolled ripening of the core NCs, the temperature for shell growth (\(T_2\)) is generally lower than that used for the core NC synthesis.\textsuperscript{4} For example, for the synthesis of CdSe/ZnS core-shell QDs,\textsuperscript{23} core QDs of CdSe were first synthesized via a hot-injection approach at 300°C–320°C. After purification, CdSe QDs were dispersed in octadecene and octadecylamine. The mixture was then heated to 240°C in N\textsubscript{2} for shell growth. Equimolar amounts of the Zn/S precursor mixture solution were slowly injected into the core mixture. The optimal thickness of the shell is less than 1.5 nm.\textsuperscript{23} Via an overgrowth approach, many core-shell QDs, such as CdSe/ZnS, CdSe/CdS, CdS/HgS, CdSe/ZnTe, InP/ZnS, and PbSe/PbS, have been synthesized with well-controlled shell thickness.\textsuperscript{52,58,68–70}

Core-shell QDs possess significantly enhanced PLQY and largely improved chemical, thermal, and photo-physical stability over pure QDs.\textsuperscript{23} For example, the PLQY increases from 5% to 15% for bare CdSe QDs to values ranging from 30% to 50% for CdSe/ZnS QDs;\textsuperscript{23} the PLQY of InP QDs increases from around 10%–22% to up to 60% with the deposition of a thin ZnS shell (~0.6 nm).\textsuperscript{70} The advantage of the SILAR approach is that the shell thickness can be effectively controlled within one monolayer. The main disadvantage of this method is the high overgrowth temperature of the shell elements, which requires good thermal stability of the core, limiting the selection of suitable materials in the core-shell architecture.

Among various types of core-shell systems, “giant” core-shell QDs (in which the shell is very thick, from several up to 20 nm, and the core exhibits quantum confinement behavior) have been widely studied because of their superior chemical and photo-stability over both pure QDs and thin-shell QDs.\textsuperscript{54,69,71} A thicker shell can efficiently protect the core material, insulating it from QD surface chemistry and the surrounding chemical environment. More importantly, for suitably tailored compositions and electronic band structures, the lifetime of excitons generated in the core can be significantly longer than pure and thin-shell QDs as a result of efficient leakage of the electrons in the shell, forming a quasi type II band alignment.\textsuperscript{54,69,71} For instance, in CdSe/CdS “giant” core-shell QDs, the electrons leak into the shell region, and the holes are still confined within the core. The decrease in spatial overlap between electron and hole wave functions leads to a reduced recombination probability, resulting in a prolonged lifetime, up to ~50–100 ns.\textsuperscript{72} Besides CdSe/CdS, CdSe/ZnS, ZnSe/CdS and ZnTe/ZnSe, “giant” core-shell QDs have also been synthesized via
the SILAR approach. The type II (or quasi type II) band alignment of these “giant” QDs makes them excellent candidates as building blocks for future solar technologies.

In the above-mentioned overcoating approach, the core size remains essentially constant during the process. Compared with high-temperature growth of shell materials via a SILAR approach, cation exchange has been reported for the growth of a wider-bandgap material onto lead chalcogenide QDs. The formation of PbSe/CdSe core-shell QDs by cation exchange was first demonstrated by Pietryga et al. As shown in Figure 1A, during the shell coating process, the overall size of the QDs does not change. Only the precursor of the cationic constituent of a shell material is introduced during the shell formation process, and shell growth proceeds through the gradual replacement of core cations by newly introduced cations in solution. For example, core-shell structured lead chalcogenide/cadmium chalcogenide core-shell QDs have been synthesized via a cation-exchange approach. In general, PbX (X = S, Se, Te) QDs were first synthesized. After purification, the PbX QDs were dispersed in toluene and heated to 100°C. In a separate flask, a Cd(oleic acid)2 mixture was heated to 155°C under N2 and then injected into the PbX QD dispersion. The core size of PbX QDs can be tuned by varying the reaction temperature and time. The as-synthesized QDs show a typical core-shell structure (Figures 6A and 6B). By controlling the reaction parameters, such as the starting core size of the QDs, the reaction temperature, the molar ratio of QD/precursor, and reaction time, the core size and structure of the QDs can be controlled, allowing us to study their optical and optoelectronic properties. As shown in Figure 6C, the as-synthesized PbS/CdS core-shell QDs show photoluminescence emission covering the whole NIR region with a quite narrow photoluminescence peak width. The shell can largely enhance the PLQY and stability of core QDs. For example, the PLQYs in PbS/CdS core-shell QDs are typically around 60%–70%, which is much higher than 20%–40% for bare QDs. A similar cation-exchange approach was also used to realize core-shell CuInSSe/ZnS QDs with typical PLQY of the order of 40%–50%.

The cation-exchange approach can be performed at relatively low temperature (20°C–150°C), which is in general lower than the seeded overgrowth approach (>200°C). The experimental setup is simple because only one precursor is used in the reaction. In addition, when the shell thickness exceeds a certain value (>1 nm), rather than forming concentric core-shell structures, it also often forms a non-concentric structure, leading to a non-uniform shell thickness distribution. Thicker shells often lead to surface defects as a result of interfacial strain. Thus, the PLQY is very low in thicker-shelled core-shell QDs. On the other hand, cation exchange is limited to some systems, and accurate control of the interfacial layer between the core and the shell and the thickness of the shell remains challenging. Colloidal atomic layer deposition is a self-limiting layer by layer growth method that has been developed to deposit CdS layers on PbS QDs to produce high-quality PbS/CdS core-shell QDs. This method allows for fine control of the CdS thickness, down to the monolayer, combined with room temperature conditions. This method could in principle be extended to the synthesis of other QDs systems, such as PbSe/CdSe, PbS/CdS/ZnS, HgSe/CdS, etc.

**CHARGE DYNAMICS IN COLLOIDAL QDs**

In QD-based optoelectronic devices, the PCE or solar to fuel conversion efficiency is critically related to the ability to generate excitons after photon absorption, electron injection from photoexcited QDs to the wide-bandgap semiconductor, as well as
carrier lifetime and mobility.\textsuperscript{77} In general, charge recombination is regarded as one of the most significant factors in limiting the performance of solar devices, such as solar cell or photoelectrochemical (PEC) devices.\textsuperscript{77} Charge recombination occurs mostly at photoanode-QD-electrolyte interfaces. Efficient charge injection, long-lifetime carriers, and high charge mobility can minimize charge recombination processes, thus increasing charge collection efficiency, improving the device performance.

In the solar cell, the valence- and conduction-band energy alignments of the donor and acceptor materials must facilitate charge separation at their interface.\textsuperscript{77,78} For example, in some QD solar cells, anodic charge transport is carried out by a wide-bandgap oxide semiconductor (Figure 7). Electrons are injected from the QDs to the oxide, generating a photocurrent. This is why one of the most important challenges to improve device efficiency is to understand and control fast exciton dissociation at the QD-oxide interface and charge injection into the anodic material. Exciton separation and charge injection are regulated by the general band-edge scheme of the whole system, including QDs, hole transporter, and metal oxide. It
is important to tune the band alignment of the core-shell structure to improve charge separation and transport in the presence of the electron-hole acceptor (Figure 7). The band energy alignment is strongly dependent on the structure of core and shell materials, core and shell size, and the chemical component.\(^7\)

In the bare QD system, the charge-transfer rate is strongly dependent on the size of the QDs, the type of carrier acceptor, and the distance between the QD and acceptor.\(^7,7^9\) For example, Hines et al.\(^7\) used transient absorption spectroscopy to monitor the electron transfer rate at the interface as a function of the bridge molecules that link QDs to TiO\(_2\). With the use of mercaptoacetic acid, 3-mercaptopropionic acid (3-MPA), 8-mercaptooctanoic acid (8-MOA), and 16-mercaptohexadecanoic acid (16-MHA), the distance between the QDs and TiO\(_2\) can be precisely varied (Figure 8A). The difference in absorption spectrum of CdSe QDs connected by various types of linker (Figure 8B, spectra b–e) is monitored over the course of \(\sim 1.6\) ns after excitation with a 387 nm pump pulse. Exponential attenuation of \(k_t\) with increasing linker length was observed and was attributed to the tunneling of electrons through the insulating linker molecule (Figures 8B and 8C). The observed decrease in lifetime is a consequence of the photoexcited electron transfer from the CdSe QDs to TiO\(_2\). \(k_t\) was then estimated by the following equation to provide a quantitative description of charge injection:

\[
k_t = \frac{1}{\langle \tau \rangle} - \frac{1}{\langle \tau \rangle_{\text{SiO}_2}}
\]

where \(\langle \tau \rangle\) and \(\langle \tau \rangle_{\text{SiO}_2}\) are the average lifetimes of QDs/TiO\(_2\) and QDs/SiO\(_2\), respectively. With an increase in barrier width, \(k_t\) decreases (Figure 8D). This demonstrates that electron transfer between CdSe and TiO\(_2\) can be viewed as electron tunneling through a layer of linking molecules and provides a useful method for predicting electron transfer rate constants. In general, \(k_t\) is around \(5.0 \times 10^8\) to \(2.2 \times 10^9\) s\(^{-1}\) (Figure 8D). Without any linker, the direct deposition of CdSe QDs on TiO\(_2\) can yield \(k_t\) as high as \(1.5 \times 10^{10}\) s\(^{-1}\).\(^7^9\)
Because of the small size of QDs, they are very sensitive to environmental conditions, such as light and moisture. A promising solution is to use core-shell QDs as light absorbers. In type I QDs, both electrons and holes are confined in the core region, which is not suitable for efficient charge transfer. On the other hand, in type II or quasi type II QDs, electrons can delocalize into the shell region and improve charge separation and transport in the presence of electron-hole acceptors. These observations provide important insights for the design of efficient core-shell QDs systems in which exciton dynamics can be controlled by means of a core-shell structure, core-shell materials and components, and their relative energy levels for efficient charge transfer.

It was recently shown that the charge-transfer rate in core-shell QDs can be largely improved by carefully engineering the core-shell structure. Zhao et al. synthesized PbS/CdS QDs with tunable core sizes and shell thickness and further investigated the photoelectron-transfer rate from core-shell QDs to wide-bandgap semiconducting mesoporous films by using transit photoluminescence spectroscopy. In all the experiments, the same linker (methyl methacrylate [MAA]) was used to connect the QDs with the oxide surface. The different electron affinity of the oxides (SiO₂, TiO₂, and SnO₂), the core size, and the shell thickness allow the electron injection rate.
to be fine-tuned by determining the width and height of the energy barrier for tunneling from the core to the oxide (Figure 9A). Electrons can still transfer into TiO$_2$ (Figures 9B and 9C) while $k_t$ decreases with the increase in both core size and shell thickness (Figure 9D). The results demonstrate the possibility of obtaining fast charge injection in NIR QDs stabilized by an external shell (injection rates as high as $8 \times 10^6$ s$^{-1}$ for TiO$_2$ films, comparable with that of pure PbS QDs; $k_0$, $1.2 \times 10^7$ s$^{-1}$), with the aim of providing viable solutions to the stability issues typical of NIR QDs capped with pure organic ligand shells.

Figure 9. Electron Dynamic in Core-Shell PbS/CdS QDs in the Presence of Metal Oxide
(A) Scheme of the PbS/CdS core-shell QDs bound to the TiO$_2$ or SnO$_2$ surface through mercaptoacetic acid ligand. The position of the electronic conduction bands is sketched (not to scale) as a function of core size, shell thickness, and QD-oxide distance. Electron injection rate is assumed to increase from 1 to 4, as confirmed by experimental findings and theoretical calculations.
(B and C) Fluorescence decays of PbS/CdS QDs grafted on silica, TiO$_2$, and SnO$_2$ for different PbS core diameters: (B) 3.0 nm and (C) 4.2 nm. The shell thickness is approximately 0.2–0.3 nm. The excitation wavelength is $\lambda_{ex} = 444$ nm. All measurements were carried out at ambient temperature.
(D–F) $k_t$ as a function of core diameter for three different shell thicknesses: (D) 0 nm; (E) 0.3 nm; (F) 0.6 nm.
(G) Tunneling rate $k_t$ as a function of shell thickness for a fixed core size of 3.0 nm. Black circles, TiO$_2$, experiment; red squares, TiO$_2$, theory; blue triangles, SnO$_2$, experiment.
Adapted with permission from Zhao et al.$^{78}$ Copyright 2014 Royal Society of Chemistry.
Typically, in PbS/CdS core-shell systems, the shell acts as a barrier to be overcome through tunneling for injection to take place, through leakage of electrons from core to shell (quasi type II band alignment). In some core-shell systems, such as CdSe/CdS (shell thickness less than 1 nm), the bulk band alignment is type I (Figure 10A). Adhikari et al. showed that $k_t$ of CdSe/CdS QDs with a radius of 1.65 nm and shell thickness of 4.3 nm is around 1.5–1.9 times lower after linking to TiO$_2$ than in pure QDs. The observed decrease in $k_t$ can be ascribed to a decrease in electron density at the surface of the QDs. The leaked electrons are long lived (up to 60 ns), which allows for efficient electron transfer from the...
QDs to the oxide. However, the hole is still confined mainly in the core region (Figure 10B). In general, with the increase in shell thickness, the physical barrier can slow down or even block hole transfer because the hole density at the QD surface is very low (close to 0). Recently, Alivisatos’ group synthesized CdSe QDs (R, 1.95 nm) with tunable CdS shell thickness (H, 0.35–2.45 nm) (Figures 10G and 10H). They further examined hole transfer from the CdSe core to acceptors covalently linked to the QD surface via the thiolate binding group (Figures 10C and 10D). As the band energy level of various molecules is favorable for hole transfer, the dominant pathway for quenching photoluminescence intensity and the decrease in photoluminescence lifetime is attributed to hole transfer from the CdSe core to ferrocene (Figure 10E). The PLQYs of core and shell QDs with different shell thickness decrease as a function of N (the average number of hole acceptor molecules). The acceptors are the high driving force (defined as the difference between the oxidation potential of the hole acceptor and the valence band of QDs) for the hole accepting ferrocene moiety and the low driving force thiol. In summary, it is still possible to achieve a high photostability core-shell system and high charge-transfer efficiency concurrently in core-ultra-thick-shell QDs. This finding suggests a promising approach to overcome current challenges in liquid-junction QD-based solar cells, by either modifying the surface capping ligands of QDs or adding efficient hole scavengers to the electrolyte to improve the hole transfer rate in “giant” core-thick-shell QDs. However, the combination of the shells and surface long-chain ligands on the QD cores still largely reduces carrier transport in comparison with a pure QD thin-film system. For example, in many optoelectronic devices, such as solid-state solar cells, the efficient coupling strength among core-shell QDs can be much less because of the presence of the shell. This situation is favorable for fabricating high-luminescent solar concentrators but not for transport of electrons and holes between QDs.

In addition, in solid-state QD solar cells, without the additional hole acceptor, even one type of carrier in core-thick-shell QDs can be transported efficiently, but another type of carrier is suppressed in the QDs. This occurrence hinders the use of “giant” QDs in solid-state solar cells. In this framework, engineering the interfacial composition of core-shell QDs could facilitate carrier transfer of both holes and electrons. In view of its significance, the core size, shell thickness, and shell composition need to be controlled at the atomic level.

APPLICATIONS IN SOLAR TECHNOLOGIES
QDs are considered particularly attractive for energy applications, such as photovoltaic devices, photo- and electrochemical catalysts for hydrogen and methanol production, as well as luminescent solar concentrators because of their tunable op-toelectronic properties. For instance, the spectral absorption of QDs can be tuned so as to significantly overlap the sun’s broad spectrum (300–1,800 nm), making them excellent sensitizers. In addition, they have a high absorption coefficient and tunable bandgap, can generate multiple excitons, can be processed in solution, and have a fairly easy and low-cost synthesis.

QD Solar Cells
QD solar cells (QDSCs) are a promising type of excitonic solar cells that produce electricity from solar energy through the creation of an “exciton,” which is an electron-hole pair. As a result of recent developments in the field, there are increasing
efforts to improve their performance. QDSCs are promising devices because of a series of critical properties and performance indicators such as low cost and high PCE as well as full-spectrum solar harvesting by tuning QD size. In addition, they present a theoretically predicted PCE of 45% in a single-junction QDSC and up to 66% in a multiple-junction QDSC as a result of efficient multiple-exciton generation and hot-electron extraction, with the potential to exceed the Shockley-Queisser limit. In addition, they can be fabricated through low-temperature processes, enabling solar cell fabrication on inexpensive, flexible substrates and large-scale roll-to-roll processing, involving continuous processing of a flexible substrate transferred between two moving rolls of material. Three types of configuration, including solid-state heterojunction QDSCs, hybrid QD-organic solar cells, and liquid-junction QDSCs, have emerged as excellent candidates. For example, colloidal liquid-junction QDSCs are at present one of the most promising technologies to obtain efficient and cost-effective solar energy conversion, with the highest certified PCE of ~12.07%.

The typical device architecture of a liquid-junction solar cell is shown in Figure 11A. The QDs are attached on a mesoporous n-type wide-bandgap semiconductor serving as light absorber. The presence of TiO₂ can improve charge separation and further transport. The QDs can be deposited in situ into mesoporous oxide films via SILAR. Alternatively, colloidal QDs can be first synthesized and then deposited into the film by a linker approach or electrophoretic methods. Generally, colloidal QD-based solar cells can have much better PCE than SILAR-deposited QD-based solar cells because the colloidal QDs have better size and structure control. For example, Du et al. synthesized Zn–Cu–In–Se (ZCISe) alloyed colloidal QDs with an absorption onset extending to ~1,000 nm as effective light harvesters to construct liquid-junction QDSCs. The current density-voltage (J-V) curves of champion ZCISe and CuInSe (CISe) QDSCs are shown in Figure 11B. An average PCE of 11.66% and a certified PCE of 11.61% have been demonstrated in QDSCs on the basis of these ZCISe QDs, which is better than the CISe-based solar cell under identical measurement conditions. The high photocurrent density in ZCISe QDSCs was further confirmed by the incident photon-to-electron efficiency (IPCE) spectra (Figure 11C). The improved photovoltaic performance for ZCISe QDSCs over that of CISe QDSCs (11.66% versus 9.54%, respectively, in PCE) is mainly a result of the higher conduction-band edge, which leads to a higher photocurrent, and the alloyed structure, which benefits suppression of charge recombination at the photoanode-electrolyte interfaces. The certified PCE was further improved from 11.66% to 12.07% simply by replacing the Cu₂S-based counter electrode with nitrogen-doped mesoporous carbon (N-MC)-based counter electrodes. The N-MC-based counter electrode exhibits much stronger activity in catalyzing the reduction of a polysulfide redox couple (S₄²⁻/S₈⁰⁻) with respect to counter electrodes based on Cu₂S.

The advantages of liquid-junction solar cells are the simple fabrication procedure and low cost. However, liquid-junction QDSCs obviously contain a liquid electrolyte and might leak during cell preparation and further use. Over the last 10 years, solid-state heterojunction QDSCs have been widely explored to overcome the drawback of liquid-junction QDSCs.

A typical architecture is illustrated in Figures 12A and 12C. Colloidal QDs are deposited on an electrode coated with a metal oxide layer (such as indium-doped tin oxide), which serves as electron acceptor. As colloidal QDs are often capped with long-chain ligands, which serve as insulator to block efficient charge transfer,
a layer by layer ligand-exchange approach is used to replace the surface long chains with shorter ligands, such as MAA, MPA, etc.\textsuperscript{31} An efficient ligand-exchange procedure is important to achieve high-efficiency QDSCs because this process involves surface modification, which leads to the formation of surface traps. Recently, Lan et al.\textsuperscript{31} used a new surface-ligand-exchange approach that enables increased passivation of QDs with the use of iodide anion. The approach allows the ionic molecule, methylammonium iodide (MAI), to access targeted non-polar-dispersed colloidal QDs by tuning the polarity of the dispersion medium. They first used MAI to replace the oleate ligands of PbS QDs in solution, followed by the solid-state ligand-exchange process using tetrabutylammonium iodide (TBAI). The enhanced passivation increases the photovoltaic performance up to a certified efficiency of 10.6\% (Figure 12B). The improvement comes mainly from the increase in short-circuit current density ($J_{sc}$) as a result of the improved passivation, which contributes to enhanced diffusion lengths and thus enables thicker devices.
Core-shell QDs have also been used for high-efficiency solid-state solar cells. Benefiting from the improved surface passivation, the QDs are very robust during cell fabrication and in operation. For example, Neo et al. used core-shell PbS/CdS for QDSCs. The architecture is shown in Figure 12C. They fabricated the solar cells in ambient conditions because of the superior air stability of core and shell QDs. Compared with bare QDs, the core-shell QDs show improved values for open circuit voltage (V_{oc}) and J_{sc} (Figure 12D). In particular, V_{oc} can increase from 0.42 to 0.66 V. This is attributed to a decrease in recombination events as a result of the passivating shell. With an optimal shell thickness of ~0.1 nm, a PCE of 5.6% ± 0.4% has been achieved with a simple heterojunction device architecture. These results indicate that the core-shell strategy has great potential for the realization of air-stable QDSCs.

Current research efforts still focus on improving the PCE by addressing the passivation and transport properties of QD films with the aid of organic, inorganic, or hybrid ligands, which have led to the rapid development of high-efficiency solar cells with PCE exceeding 10%, as summarized in Table 1.

Currently, QDSCs are still far from commercialization because of the small active area, limited PCE, and poor long-term stability. It is still very challenging to obtain...
high-efficiency QDSCs because of polydispersity, random packing, and inhomogeneous aggregation of QDs during the ligand-exchange process, leading to the inhomogeneous energy landscape present in QD solids. Various strategies have been developed to enhance the PCE of QDSCs, such as synthesis of high-quality QDs with respect to a trap-free surface, broad light-harvesting range, and narrow size distribution; use of plasmonic nanostructures to enhance the absorption of QD films; and use of a QDSCs tandem structure to improve IR absorption.

A most pressing challenge is to improve the long-term stability of QDSCs. Device stability depends on the interface and band alignment between the QDs and anodes, and also on the QD layer itself. To date, PbS QD-based solid-state QDSCs only retain 90% of their initial PCE (11.28%) after 1,000 hr of storage in air without encapsulation. This would be even worse if the QDSCs operate under sunlight. A greater understanding of the thermal and photostability of QDs, optoelectronic properties of QDSCs, and further progress in materials development and solar cell structure could potentially lead to a new generation of air-stable QDSCs.

**QD-Based Hydrogen Production**

In addition to solar cells for direct conversion of radiation into electrical power, QDs are also widely used as light harvesters in solar-driven water splitting, in which water is separated into oxygen and/or hydrogen with semiconductors as active photosensitized materials. This is a promising approach, which simultaneously combines renewable energy conversion and storage, because H₂ is a solar fuel with multiple advantages, such as high mass energy storage density, ease of transportation, cost-effectiveness, and generation of water as the only byproduct. PEC solar-driven H₂ production is considered to be a promising clean route in comparison with other approaches. PEC cells perform redox reactions driven by electron-hole pairs created by incident photons, namely, the holes oxidize water and hole scavengers at the surface of the photoanode, and the electrons migrate to the counter electrode to reduce water and produce hydrogen. The ideal PEC cell is composed of inexpensive semiconducting materials with proper electronic band structure, leading to strong sunlight absorption, effective charge separation, and high photochemical stability. Metal oxide semiconductors such as TiO₂ and ZnO were demonstrated as promising photocatalysts for H₂ evolution as a result of their efficient solar to H₂ conversion and stability. However, their activation requires UV light (5% of incident solar spectrum) because of their large bandgap (3.2 eV). QDs have been recently developed to sensitize TiO₂ to extend light absorption, providing a convenient heterostructured platform for PEC H₂.

### Table 1. Photovoltaic Parameters of QDSCs

<table>
<thead>
<tr>
<th>Cell</th>
<th>Type</th>
<th>J_{sc} (mA/cm²)</th>
<th>V_{oc} (V)</th>
<th>Fill Factor (FF)</th>
<th>PCE (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCuInSe₃</td>
<td>liquid</td>
<td>25.25</td>
<td>0.739</td>
<td>0.622</td>
<td>11.6</td>
<td>Du et al. 30</td>
</tr>
<tr>
<td>ZnCuInSe₅</td>
<td>liquid</td>
<td>25.21</td>
<td>0.626</td>
<td>0.765</td>
<td>12.07</td>
<td>Jiao et al. 81</td>
</tr>
<tr>
<td>CuInGaSe₂</td>
<td>liquid</td>
<td>25.01</td>
<td>0.74</td>
<td>0.621</td>
<td>11.49</td>
<td>Peng et al. 82</td>
</tr>
<tr>
<td>PbS</td>
<td>solid</td>
<td>24.3</td>
<td>0.61</td>
<td>0.71</td>
<td>10.6</td>
<td>Lan et al. 31</td>
</tr>
<tr>
<td>PbS/CdS</td>
<td>solid</td>
<td>27.23</td>
<td>0.61</td>
<td>0.68</td>
<td>11.28</td>
<td>Liu et al. 83</td>
</tr>
<tr>
<td>PbS/CdS</td>
<td>solid</td>
<td>21.9</td>
<td>0.63</td>
<td>0.38</td>
<td>5.6</td>
<td>Neo et al. 59</td>
</tr>
</tbody>
</table>

*Counter electrode based on Cu₂S.

bCounter electrode based on nitrogen-doped mesoporous carbons.

QDs were surface treated by MAI.

QDs were surface treated by hybrid organic-inorganic ligands (lead halide and ammonium acetate).
production. Various types of metal chalcogenide QDs, including bare QDs or core-thin-shell QDs have been used for H₂ production, such as CdS/TiO₂, CdSe/TiO₂, PbS/CdS/TiO₂, CdS/CdSe/ZnO, CdSe/CdS/TiO₂. For example, Jin et al. used a heterostructured photoanode containing core-shell structured QDs and CdS layer for H₂ generation. They further demonstrated the possibility of integrating the PEC cell in a stand-alone device by coupling it with properly sized dye-sensitized solar cells to supply an external bias. The architecture of the PEC cell is shown in Figure 13A. Photogenerated exciton dissociation occurs at the QD-oxide interface, and electrons are injected into TiO₂. Electron transport occurs in the TiO₂ mesoporous film, and electrons are collected at the front electrode and then transferred to the Pt counter electrode, where hydrogen generation takes place. Na₂S and Na₂SO₃ hole scavengers in the electrolyte provide shuttle transport for the photogenerated holes. A ZnS capping layer was applied to protect the photoabsorber from light-induced corrosion. The photoresponse was measured by a Scientech SLB-300A solar simulator (AM 1.5 G). The sample was placed 15 cm away from the window of the light source, and the light intensity measured by thermopile was 100 mW cm⁻². The hybrid heterostructured photoanode can produce a photocurrent density as high as 11 mA/cm² (equal to 110 L cm⁻² day⁻¹) under 1 sun illumination (Figure 13B). In addition, irradiation under both standard (1 sun) and...
high-intensity illumination (8 sun) demonstrated better stability of the system than bare PbS QDs (Figures 13C and 13D). Because of the presence of hole scavengers in their electrolyte, only H₂ was produced in the PEC cell, without O₂.

QD-sensitized TiO₂ is considered a highly promising photoanode material for PEC solar hydrogen production. However, because of its limited stability, the photoanode suffers from degradation of its long-term PEC performance. Adhikari et al. designed a high-efficiency and long-term stable PEC cell on the basis of “giant” core-shell QDs. Figure 14A reports the overall integrated PEC cell architecture. An unprecedented photocurrent density (∼10 mA/cm²) was obtained for “giant” QD-based PEC devices with promising stability after ZnS coating (Figures 14B and 14C), indicating that the proposed cell architecture is a good
candidate for long-term stable QD-based PEC solar hydrogen generation. The thick shell enhances light absorption in the visible range, increasing the stability of the QDs.32

Table 2 summarizes the most recent advances in PEC hydrogen production using photoanodes made of various types of QDs. Future research directions for H₂ production should focus on identifying more efficient stable systems by using cost-effective and environmental friendly QDs.

The photocurrent density is low, indicating limited hydrogen generation efficiency, which is not favorable for commercial production. Current research efforts still focus on increasing the hydrogen generation rate by improving the charge separation and transport in the PEC cell through controlling both the structure and composition of QDs and the structure of the PEC layers. Another major difficulty lies in maintaining the colloidal stability of QDs during post-synthesis storage, device fabrication, and PEC cell operation over long periods of time (at least 1 year). A promising solution is to use carbon QDs, which present the best stability of PEC cells. Within 2 hr illumination under 1 sun, there is no significant decrease in the hydrogen generation rate, benefiting both the superior stability of carbon dots and efficient separation and transfer in the NiOOH/FeOOH/CQD/BiVO₄ hybrid photoanode.90 Other solutions to improve the stability of QD-based PEC devices could use “giant” core-alloyed-shell CdSe/PbₓCd₁₋ₓS/CdS QDs or SnO₂ metal oxide, which is not sensitive to UV light. UV-induced hole accumulation is in general the reason for self-oxidation of QDs, which leads to a gradual decrease of photocurrent density during cell operation.32

Another limitation is that currently used QDs contain heavy metals (such as Pb, Cd, etc.), hindering their prospective commercial development because of health and environmental concerns.32,86,89 This challenge could be addressed with the use of green QDs, such as CuInSe/ZnS or carbon QDs.28,90

QD-Based LSCs

LSCs are yet another emerging technology of current interest as a platform for solar energy harvesting. LSCs can serve as large-area sunlight collectors for photovoltaic cells to reduce the cost of electricity by decreasing the use of expensive photovoltaic materials (e.g., single-crystal silicon).12,26,33 LSCs can also provide adaptability to the needs of architects for building-integrated photovoltaics (BIPVs), such as a variety of colors, shapes, transparencies, light weight, and flexibility, which make them an attractive option for structural buildings or turning common objects into transparent or non-transparent electricity generators.12,26,33

In LSCs, chromophores embedded in a planar waveguide absorb direct and diffused sunlight and re-emit concentrated light at a longer wavelength. The latter is
collected in a photovoltaic cell placed at the edge of the waveguide, where it is converted into electrical power (Figure 15). In general, several factors can limit the PCE of LSCs.91–95 As shown in Figure 15, light is lost in different ways (processes 1–5 in the scheme). (1) Only a fraction of incident light can be absorbed because of the limited overlap between the QD absorption and solar spectra, and unabsorbed radiation is transmitted and lost. (2) Part of the radiation is reflected at the front surface of the LSC. (3) Light is lost during re-emission because the PLQY of the photoluminescence emission is below 100%. (4) The fraction of radiation that is re-emitted with an emission angle falling into the so-called escape cone cannot undergo total reflectance inside the waveguide and is lost. Typically, at most about 75% of the incident radiation can be captured by an LSC waveguide, in which the typical refractive index of the polymer is \( \frac{1}{24} \). (5) Part of the light is lost as a result of re-absorption (caused by the overlap between the absorption and emission spectra of the QDs). Other minor light losses could be caused by the absorption of emitted light by the polymer matrix.

Among all the aforementioned processes of light loss, re-absorption from the QDs is one of the most critical issues in fabricating high-efficiency large-scale LSCs, because of the small energy separation between the emission line and the band-edge absorption peak.29 This re-absorption reduces the overall PCE of the device. Colloidal QDs are attractive for use in LSCs because of their high PLQY, broad absorption spectrum, large absorption cross-sections, and enhanced chemical and photostability with respect to organic chromophores. More importantly, their Stokes shift can be engineered to reduce the re-absorption losses in large-area LSC devices.29,96

Recent studies demonstrated that the formation of a quasi type II band “giant” core-shell structure or ternary I-III-VI₂ semiconductors can largely increase the Stokes shift (the difference in wavelength between the positions of the band maxima of the first excitonic absorption and emission spectra), thus reducing re-absorption losses.29,91–93 For example, Meinardi et al.93 fabricated a large-scale LSC on the basis of a quasi type II “giant” CdSe/CdS QD embedded in poly(methyl methacrylate) (PMMA) polymer (Figure 16A). In this configuration, the electrons can typically

---

**Figure 15. Schematic Representation of a QD-Based LSC**

The numbers indicate the typical processes of energy loss in an LSC. (1) Unabsorbed light; (2) light reflects from the top surface; (3) the light was absorbed by the QDs, but there is partial loss because of the non-unity of fluorescence quantum yield; (4) re-emitted incident light escapes from the surface because of the escape cone (the angle larger than the critical angle); and (5) light is re-absorbed by another QD.

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leak into the shell region, whereas the holes are confined in the structure’s core, leading to spectral separation between emission and absorption (Figure 16B). In such heterostructured QDs, the volume ratio of shell to core is high, and the shell material dominates the absorption properties. Red-shifted luminescence occurs either from the core or from the spatially indirect transitions across the heterointerface. The as-fabricated LSC is as long as 21.5 cm with an effective light concentration of 4.4 at the edge in comparison with the absorbed light. A PCE of \( \frac{1}{C24} \)% was achieved, enabling high light intensity at the edge of the LSC. This value is low as a result of re-absorption loss and the limited absorption spectrum (300–500 nm).

Figure 16. Large-Area LSC Based on Stokes-Shift-Engineered QDs
(A) Left: photograph of a QD-PMMA-based LSC (dimensions: 21.5 \( \times \) 1.35 \( \times \) 0.5 cm) comprising CdSe/CdS QDs (R/H, 1.5/4.2 nm) illuminated by a UV lamp emitting at 365 nm (top) and under ambient illumination (bottom). Scale bar, 5 cm. Right: the same LSC during measurement of the concentration factor with illumination from a solar simulator (1.5 AM).
(B) Optical absorption spectra of the QD solution (dotted line) and the QD-PMMA composite (same as in A) (solid line) showing a minimal contribution from scattering and normalized photoluminescence spectra (excitation at 473 nm) collected at the edge of the LSC when the excitation spot is located at distances \( d = 0 \) cm (black line) or \( d = 20 \) cm (purple line) from the edge. The lack of a \( d \)-dependent change in the shape of the photoluminescence spectrum suggests that losses to re-absorption by the QD material are negligibly small. Non-normalized photoluminescence spectra as a function of \( d (0–20 \text{ cm}) \) are shown in the inset (logarithmic scale is used on the intensity axis), they indicate that the overall photoluminescence intensity drops with increasing \( d \) as a result of scattering at optical imperfections within the PMMA matrix and photon escape from the waveguide.

Adapted with permission from Meinardi et al.\(^93\) Copyright 2014 Nature Publishing Group.
Further improvement of the PCE for the LSC is still required with a target PCE of 6%.

The absorption spectrum of “giant” core-shell QDs is dominated by the shell, which strongly absorbs radiation below 500 nm (bandgap $E_g$ of 2.49 eV) covering the UV and part of the visible range, strongly limiting the application of LSCs. Further research is underway to use NIR-emitting QDs for LSCs, such as core-shell CISSe/ZnS or PbS/CdS QDs.

It is challenging to fabricate large-area LSCs on the basis of QDs with good efficiency because of the energy loss caused by re-absorption. Table 3 summarizes the most recent achievements in QD-based LSCs. Among various types of QDs with direct bandgap, indirect bandgap silicon QDs have been used as emitters for high-efficiency LSCs. Because of the absence of re-absorption energy loss, LSCs based on silicon QDs show an optical efficiency of $\eta = 2.85\%$. Further research directions still need to focus on improving the optical efficiency of LSCs by designing and synthesizing QDs with high PLQY, broad absorption spectrum, large Stokes shift, and excellent photo-, colloidal-, and thermal stability through careful selection of materials and accurate control of core size, shell thickness, and chemical composition.

### CONCLUSIONS AND OUTLOOK

In summary, in this review we have highlighted recent research on the design and synthesis of various types of QDs, their optical and electronic properties, and their use in emerging solar technologies. We have provided an overview of various strategies developed for the synthesis of QDs, including bare QDs and core-shell QDs with controlled structure for applications such as photovoltaic devices, solar-driven hydrogen production, and LSCs. Controlling the synthesis and optoelectronic properties of colloidal QDs has emerged as a promising approach to improve the efficiency and stability of next-generation solar devices. Although recent QD research has led to significant advances in synthetic approaches and device efficiency, there are still several key challenges.

The first is to synthesize QDs with well-controlled structure. Depending on the intended application, QDs need to exhibit specific optoelectronic properties. A low-cost and environmentally friendly approach is still urgent for the development of trap-free QDs. For example, current methodologies rely on relatively toxic organometallic precursors in organic solvent at a relatively high temperature (typically $>100^\circ C$) because of the high decomposition temperature of the precursors. In addition, typically the ligands are long-chain surfactant molecules, which serve

<table>
<thead>
<tr>
<th>Device</th>
<th>Band Structure</th>
<th>Stokes Shift (meV)</th>
<th>PLQY (%)</th>
<th>Area (cm$^2$)</th>
<th>Quantum Efficiency (%)</th>
<th>Optical Efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$ doped ZnSe/ZnS</td>
<td>type I</td>
<td>~1000</td>
<td>~50</td>
<td>2.5 \times 7.5</td>
<td>37</td>
<td>–</td>
<td>Erickson et al.95</td>
</tr>
<tr>
<td>CISeS/ZnS</td>
<td>type I</td>
<td>~530</td>
<td>~40</td>
<td>12 \times 12</td>
<td>17</td>
<td>3.2</td>
<td>Meinardi et al.29</td>
</tr>
<tr>
<td>“Giant” CdSe/CdZnS</td>
<td>type I</td>
<td>~720</td>
<td>~70</td>
<td>20 \times 20</td>
<td>15</td>
<td>–</td>
<td>Li et al.94</td>
</tr>
<tr>
<td>PbS/CdS</td>
<td>quasi type II</td>
<td>~250</td>
<td>~50</td>
<td>1.5 \times 7</td>
<td>4.5</td>
<td>1</td>
<td>Zhou et al.33</td>
</tr>
<tr>
<td>“Giant” CdSe/CdS</td>
<td>quasi-type II</td>
<td>~400</td>
<td>~40</td>
<td>1.3 \times 21.5</td>
<td>10</td>
<td>1</td>
<td>Meinardi et al.93</td>
</tr>
<tr>
<td>Silicon</td>
<td>–</td>
<td>~400</td>
<td>~50</td>
<td>12 \times 12</td>
<td>30</td>
<td>2.85</td>
<td>Meinardi et al.97</td>
</tr>
</tbody>
</table>
as electrical insulator in solar energy devices. Thus, identifying new precursors for the low-temperature synthesis of QDs with short-chain ligands or electroactive ligands is an emerging direction. For instance, atomic layer deposition can be used to produce structurally controllable core-shell QDs at room temperature with active precursors. For core-shell QDs, future directions should focus on developing a simple, lower-temperature synthesis procedure to realize core-shell QDs with a gradient interfacial structure to tune the electronic properties of QDs to facilitate charge separation and transfer. Other approaches to improve optoelectronic properties should focus on treatment after QD synthesis. Novel post-surface passivation strategies, including inorganic ligands and hybrid organic-inorganic ligands, can reduce trap states created during QD synthesis and device fabrication.

The second is to improve the efficiency and stability of solar devices based on QDs. To date, the reported PCEs for solar energy devices based on colloidal QDs still do not meet the requirements for commercial applications. It is still challenging to produce high-efficiency, low-cost, large-scale, and long-term stable solar energy devices.

In solid-state QDSCs, even though the certified PCE is over 10%, the active area is still very small (<1 cm²), and the stability is not competitive with existing commercial technologies. New strategies to improve PCE and stability are still urgently needed. For example, efficiency could be improved by optimization of the QD film thickness, film uniformity, and engineering of the band structure of the QD film, etc. The stability can be addressed with the use of trap-free QDs or post-treatment of the QD film for the removal of traps. Addressing these challenges could lead to a more profound understanding of the structure-property relationships in these materials and to exciting technological opportunities for solar energy.

In relation to solar-driven PEC devices for hydrogen generation, the focus should be on improving the efficiency of solar-gas conversion efficiency because the current value is far from commercialization; this requires a target conversion efficiency of 10%. Possible strategies could involve quasi type II “giant” core-alloyed-shell QDs with an interfacial layer combination with SnO₂ nanostructures as electron acceptor. Another direction could use carbon nanotubes or graphene to improve the conductivity of the QD-metal-oxide anode and hinder charge recombination. Another important open question is how to improve the stability of PEC devices. Hybrid photoanode materials such as NiOOH/FeOOH/CQD/BiVO₄ could present interesting opportunities because this type of composite exhibits long-term stability.

In QD-based LSCs, the synthesis of QDs with large Stokes shift and wide absorption spectrum is still a major challenge. In this context, carbon QDs are considered promising because they can be synthesized in large quantities via a simple solvothermal technique in ambient conditions with abundant, low-cost precursors. They exhibit a relatively high PLQY with tunable absorption up to the NIR range. Compared with organic dyes and polymers and inorganic QDs, carbon dots are thermal and photostable. Other possible approaches to improving the efficiency of QD-based LSCs could use indirect-bandgap QDs (such as silicon QDs), tandem architecture, and plasmonic nanostructure to enhance absorption and emission.

**AUTHOR CONTRIBUTIONS**

F.R. proposed the topic of the review. H.Z. investigated the literature and wrote the first draft of the manuscript. F.R. and H.Z. jointly discussed and revised the manuscript.
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REFERENCES AND NOTES


