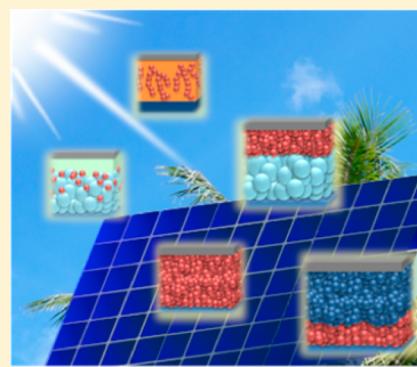


Quantum-Dot-Based Solar Cells: Recent Advances, Strategies, and Challenges

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ABSTRACT: Among next-generation photovoltaic systems requiring low cost and high efficiency, quantum dot (QD)-based solar cells stand out as a very promising candidate because of the unique and versatile characteristics of QDs. The past decade has already seen rapid conceptual and technological advances on various aspects of QD solar cells, and diverse opportunities, which QDs can offer, predict that there is still ample room for further development and breakthroughs. In this Perspective, we first review the attractive advantages of QDs, such as size-tunable band gaps and multiple exciton generation (MEG), beneficial to solar cell applications. We then analyze major strategies, which have been extensively explored and have largely contributed to the most recent and significant achievements in QD solar cells. Finally, their high potential and challenges are discussed. In particular, QD solar cells are considered to hold immense potential to overcome the theoretical efficiency limit of 31% for single-junction cells.



Extensive research has been carried out by a significant number of researchers in the field of solar cells, which convert the sunlight, the most interesting renewable energy resource, to electricity. Diverse solar cells have been developed in research laboratories, and great efforts have also been made toward commercial manufacturing.¹ However, except for Si solar cells, most solar cell devices are still far from real-world applications due to their relatively low power conversion efficiency (PCE), the lack of long-term stability, and/or toxic substances involved in materials or during processing.

The next generation of photovoltaics targets high-efficiency and low-cost solar cells made of inexpensive, abundant, and environment-friendly materials as well as those fabricated by using cheap manufacturing processes.

Solar cells can be classified, according to photoactive materials, as single- and poly-crystalline silicon solar cells, CdTe solar cells, Cu(In,Ga)Se₂ (CIGS) solar cells, dye-sensitized solar cells, organic solar cells, perovskite solar cells, quantum dot (QD) solar cells, and so forth (Figure 1). They can also be classified according to the generation of solar cells. Single-crystalline silicon solar cells, the so-called first-generation solar cells, are already commercialized,^{2,3} delivering typical and sufficiently high efficiencies of 15–20% (with a certified high efficiency reaching 25%) because they have great charge transport properties and excellent stability and are environmentally benign as well. Nonetheless, the complicated manufacturing

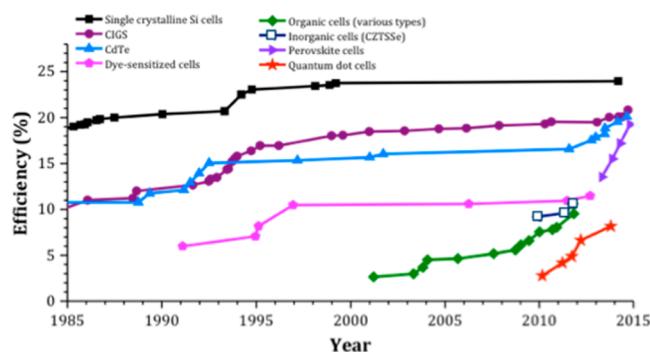


Figure 1. Timeline of the highest certified research cell efficiencies. (The source is the National Renewable Energy Laboratory from ref 17.)

processes, high producing cost, and long energy payback time have slowed down their implementation worldwide. Mainly motivated by cost reduction, the second-generation solar cells, known as amorphous or polycrystalline thin-film solar cells, were developed, which allow the large decrease of the use of semiconductor materials.^{4,5} CdTe and CIGS thin-film cells are typical examples of this kind, the efficiencies of which need to be further improved. On the basis of the second-generation technologies, the third generation of photovoltaics targets high-efficiency and low-cost solar cells made of inexpensive, abundant, and environment-friendly materials as well as those fabricated by using cheap manufacturing processes. Large-area fabrication, flexibility, and lightweight are also among the goals

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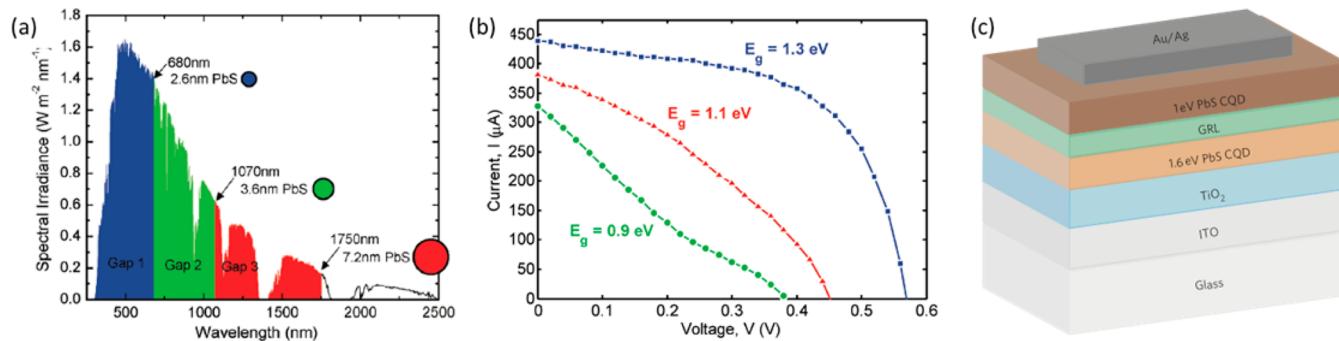


Figure 2. (a) Size-tunable absorption (band gaps) of PbS QDs. Reprinted from ref 33 with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. (b) Current–voltage (*I*–*V*) response of fluorine-doped tin oxide (FTO)/porous TiO₂/PbS QD/Au photovoltaic devices from three different CQD sizes (device area, 0.03 cm²). Reprinted from ref 8. (c) Device architecture for colloidal QD (CQD) tandem solar cells having quantum-confined band gaps of 1.6 and 1.0 eV. Reprinted from ref 31 with permission from Macmillan Publishers Limited.

of future solar cells. Dye-sensitized solar cells and organic solar cells are two typical examples of cost-effective promising solar cells. Dye-sensitized solar cells, made of simple materials and produced with inexpensive equipment, have been studied since 1988 and have achieved 12.3% efficiency to date.⁶ Regarding organic solar cells, enabling low-cost fabrication on flexible substrates, diverse organic semiconductors have been synthesized and investigated to improve the PCE, and the best value of 10.3% was reported recently.⁷ Both types of solar cells, however, are not satisfactorily stable for long-term use, in addition to having other shortcomings, such as possible electrolyte leakage in dye-sensitized solar cells. Due to unique and versatile advantages of QDs, such as wide tunability of band gaps, easy solution processability, and impressive capability of generating multiple excitons and slowing down the cooling of hot electrons, QD-based solar cells have attracted tremendous research interest and have been considered as the most promising candidate for the next generation of photovoltaic devices.^{8–10} First reported in 1998, their efficiency has considerably increased from far below 1% to over 8%, thanks to great efforts from numerous researchers.^{11,12} Very recently, a new type of solar cells, involving the use of metal halide perovskite materials, emerged and has shown impressively rapid development in their efficiency at the speed far beyond that ever shown in the history of other types of solar cells.^{13–16} Since its birth in 2009, in short, several years, their efficiency has been sharply increased from 3.8 to 20.1% (most recently reported certified value).^{14,17} In addition, they also share some benefits with QD solar cells, such as low-cost solution processability. As such, they have quickly become a new star in the field of solar cells and are considered now also as a very promising candidate for low-cost and high-efficiency solar cells. Such remarkable rising-up of perovskite solar cells introduces questions. What is the future of QD solar cells? Do they have potential to compete with perovskite cells in future photovoltaic technology? In this Perspective, we analyze the development of QD solar cells and their potential to be realized, with the hope to provide some hints to the above questions. Specifically, we first briefly summarize the attractive features of QDs. Then, we describe the most significant achievements made recently in QD solar cells. Major strategies, that is, rational device architecture design and QD surface engineering, will be highlighted and analyzed. We will conclude with potentials and challenges.

Advantages of QDs Relevant to Solar Cell Applications. High-quality QDs can be synthesized routinely in solution at present. The earliest, most important milestone in the QD synthesis

history was the application of the high-temperature organometallic approach for the synthesis of highly crystalline QDs, which are free of major defects, by Murray et al. in 1993.¹⁸ In their work, high-quality cadmium chalcogenide QDs were prepared through the pyrolysis of organometallic reagents in hot coordinating solvents. Nonetheless, in this initial stage of the QD development in the early 1990s, QDs needed to go through size selection steps due to their broad size distributions in as-synthesized samples.^{19–21} Soon following this first success, another important advance was made in 1994, where the hot injection synthesis method that relies on the rapid injection of a precursor into a reaction solution containing other precursors was invented to produce nearly monodisperse QDs.²² This method allows the rapid homogeneous nucleation process and distinct separation of nanocrystal (NC) nucleation and growth stages, and therefore, QDs are synthesized with a narrow size distribution. Since then, separate size selection steps can be generally skipped.^{9,23} As a result of the monodispersity and high quality, these as-prepared QDs can show well-defined absorption and photoluminescence features, which are highly desired in solar cell applications. Otherwise, the charge transfer between randomly mixed small and large QDs in a disordered film can lead to the eventual trapping and recombination of charge carriers in the largest QDs. The low-cost synthesis in solution is very attractive for future solar cells.

Perhaps the most attractive characteristic of QDs to the field of solar cells is their tunable band gaps, easily achievable by adjusting QD sizes, thanks to the quantum confinement effect.

Perhaps the most attractive characteristic of QDs to the field of solar cells is their tunable band gaps, easily achievable by adjusting QD sizes (Figure 2a), thanks to the quantum confinement effect. When the size of NCs is close to or below the Bohr radius of the bound state of an electron and a hole (also called an exciton), the motions of electrons and holes are spatially confined, and electron and hole energy levels become discrete.²⁴ The smaller the QD size, the larger the band gap. As a result, both their optical and electronic properties can be conveniently tuned. One of the most straightforward benefits

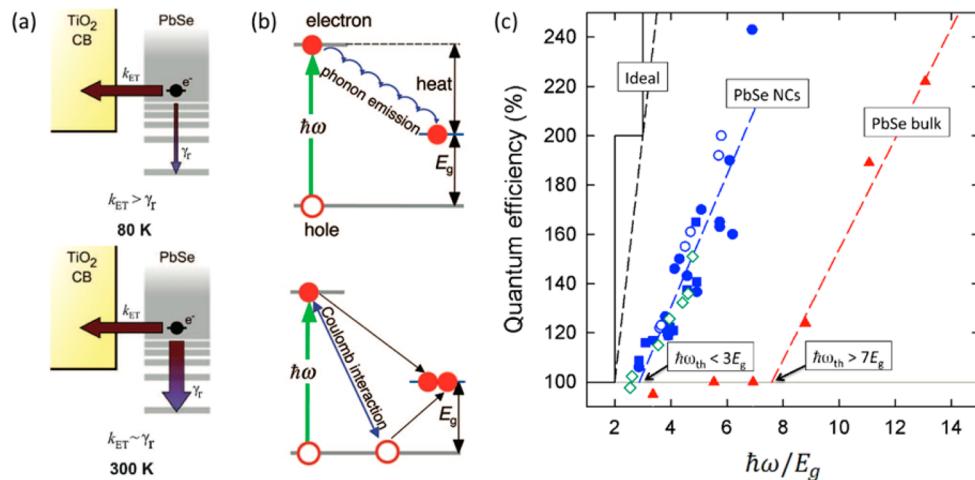


Figure 3. (a) Illustration of the competing pathways of interfacial hot electron transfer and intra-QD relaxation. At higher temperatures, hot electron relaxation (γ_r) becomes competitive with interfacial hot electron transfer (k_{ET}). Reprinted from ref 39 with permission from The American Association for the Advancement of Science. (b) (Top) Conventional photoexcitation. Absorption of a single photon (green arrow) with energy $\hbar\omega \geq E_g$ processes a single electron–hole pair independent of $\hbar\omega$. In this case, the photon energy in excess of the energy gap is dissipated as heat by exciting phonons (blue arrows). (Bottom) MEG. A high-energy conduction band electron excited by a photon loses its energy by transferring it via the Coulomb interaction to a valence band electron, which is excited across the energy gap to produce a secondary electron–hole pair. Reprinted from ref 10. (c) MEG efficiencies of PbSe NCs (blue and green symbols) and bulk PbSe films (red solid triangles) as a function of $\hbar\omega/E_g$. The MEG threshold ($\hbar\omega_{th}$) in NCs is greatly reduced compared to that in bulk. Note the excellent agreement between transient absorption (blue open circles, blue solid circles), photoluminescence (blue solid squares), and photocurrent (green open diamonds) measurements. Ideal cases set by energy conservation are shown by a solid black line (ideal “staircase”) and a dashed black line (more realistic dependence with $E_{eh} = E_g$). Reprinted from ref 41.

from this phenomenon is the extended absorption range to the near-infrared (NIR) by using NIR-absorbing QDs. The sunlight in the NIR range contains about half of the sun irradiation, being largely untouched by most dye molecules and organic semiconductors. Harvesting NIR photons represents a great opportunity to sharply increase the solar cell efficiency. Among narrow band gap (e.g., ~ 1.4 – 0.8 eV or even lower) QDs,²³ particularly, PbS and PbSe have attracted great attention and have been extensively employed for thin-film photovoltaic applications.^{26–28}

For typical single-junction solar cells, the band gap tunability of QDs allows the optimization of solar cells by optimizing the size of the QDs and therefore their band gaps. According to theoretical calculations of Shockley and Queisser, the highest PCE of $\sim 31\%$ can be achieved in single-junction, unconcentrated solar cells with a semiconductor absorber having an optimal band gap of 1.1 eV.²⁹ Although this imposes a strong limit on the selection of ideal and bulk semiconductors, it is readily realized in low-band-gap QDs, such as PbS and PbSe QDs, simply by varying the QD size in a controlled fashion. The size-tunable band gaps therefore offer great latitude in achieving optimal solar cells. In reality, in addition to absorption, the solar cell performance is affected by multiple factors, depending on the specific architecture of solar cell devices. Among this, for instance, charge separation at the QD/semiconductor junction area is one of the key parameters for p–n heterojunction solar cells. In this case, the charge separation will be influenced by the electronic structure of QDs, which, once again, is dominated by the size of QDs. The optimal size and thereby the optimal band gap will be determined by the interplay of multiple relevant factors. Sargent's group studied the photovoltaic performance of p–n heterojunction solar cells based on the PbS QDs/ TiO_2 junction involving QDs of three different diameters and band gaps (3.7 nm: 1.3 eV; 4.3 nm: 1.1 eV; 5.5 nm: 0.9 eV) and found that 1.3 eV was the optimal band gap (Figure 2b), yielding the largest open-circuit voltage (V_{OC}), short-circuit current density (I_{SC}),

fill factor (FF), and PCE.⁸ Beard's group reported its detailed investigation on the complicated effect of the QD size on various parameters of their PbS/ZnO solar cells.³⁰ The optimal band gap was not specified though. The highest certified efficiency to date for all colloidal QD (CQD) solar cells was achieved by Bawendi's group on PbS QDs with the band gap of 1.33 eV,¹² quite consistent with the optimal band gap value reported by Sargent's group.⁸

Another key benefit of the size-tunable band gap is that it enables the facile construction of tandem (two junctions) or multijunction solar cells, potentially absorbing the most part of the solar spectrum.^{31,32} The idea is to stack multiple layers of QDs, each made of differently sized QDs, together to efficiently harvest solar photons at different wavelengths over a broader range to sharply improve the efficiency.³³ The maximum theoretical efficiency is expected to increase from the Shockley limit of 31 to 42% and further to 49% for tandem (i.e., double-junction) and triple-junction cells, respectively.³⁴ Although the concept of this type of solar cells has been demonstrated for epitaxial compound semiconductor thin films, the manufacturing complexity and cost, partially stemming from stringent requirements on the close lattice matching among semiconductor materials in different layers, have prohibited their widespread application. The use of size-tunable QDs may alleviate the complexity in preparing photoactive materials and in fabrication of such multijunction cells. Recently, a readily processable graded recombination layer (GRL) between junctions, which is also compatible with QD processing, has been designed and realized.³¹ The tandem QD solar cell, reported in this work, employed a 1.6 eV QD layer in the front cell and a 1.0 eV QD layer in the seriously connected back cell and showed the V_{OC} very close to the sum of the V_{OC} 's of the constituent cells (Figure 2c).³¹ The work provides the foundation for the future implementation of multijunction solar cells.

From the carrier dynamics perspective, QDs possess very unique and attractive characters of extended hot carrier

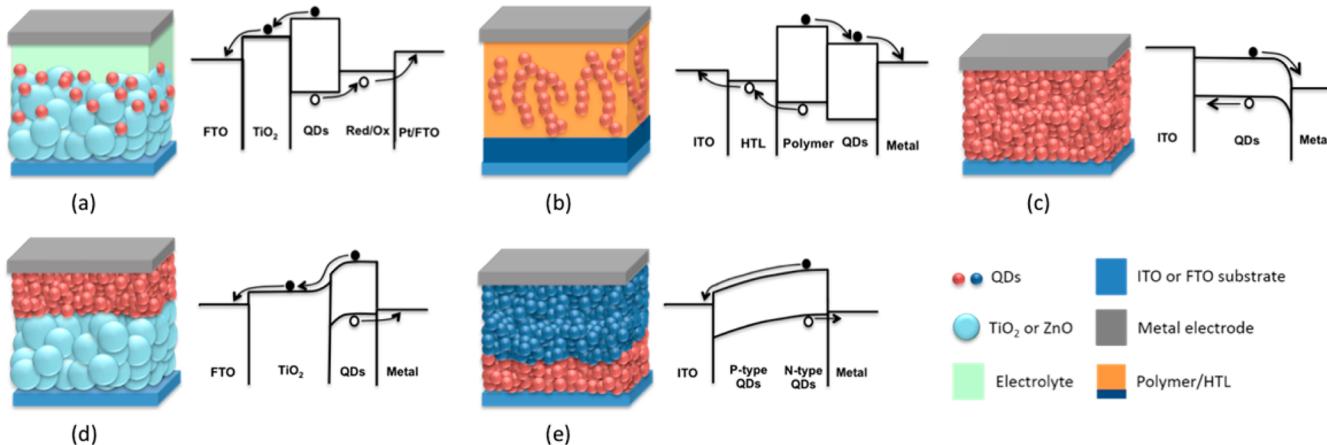


Figure 4. Schematic illustration of device configurations and energy band diagram of QD-based solar cells: (a) QD-sensitized solar cell, (b) hybrid QD–polymer solar cell, (c) Schottky junction solar cell, (d) p–n heterojunction solar cell, and (e) p–n homojunction solar cell.

lifetimes and multiple exciton generation (MEG) from single absorbed photons (in other words, carrier multiplication) when photons with higher energy than the semiconductor band gap (E_g) are absorbed (Figure 3).¹⁰ Although almost impossible to harvest hot carriers and multiple excitons from dye and organic materials, it is possible to do it with QDs.³⁵ The exploitation of both features in the field of solar cells holds high promise to overcome the constraint of the ultimate theoretical limit of 31% predicted by Shockley and Queisser by reducing or minimizing one dominant energy loss process, that is, thermalization loss, encountered typically in solar cells. The excess energy of hot carriers relative to the band gap, generally wasted as heat through phonon emission, can in principle be “saved” by directly extracting hot carriers from QDs before they thermally relax into the band gap edge and become cooled, thanks to the phonon bottleneck and thus the slower rate of relaxation in quantum-confined QDs (the lifetime can be as long as 1 ns) as compared with bulk semiconductors (the typically lifetime is within 1 ps).^{36–38} Hot electron transfer from PbSe QDs to TiO₂ has been experimentally observed by means of time-resolved optical second harmonic generation, suggesting that hot carrier extraction can be a feasible strategy to improve the efficiency of QD solar cells (Figure 3a).³⁹ Alternatively, single photons with high energy at least twice the band gap energy may be wisely used to create more than one electron–hole pair to avoid energy loss.⁴⁰ This process becomes favored once again in quantum-confined semiconductor NCs, as compared with bulk semiconductors, owing to the slowing down of the relaxation of excitons from higher energy levels to the band edge due to the increased Coulomb interactions between electrons and holes and the relaxation of the momentum conservation rules (Figure 3b). It is to say that QDs enter the phonon bottleneck regime, thereby allowing the observation of MEG. Experimentally, up to three excitons for PbSe QDs were observed using the ultrafast transient absorption technique (Figure 3c).⁴¹ For solar cells, this physical phenomenon bears actual significance if multiple excitons can be efficiently captured prior to their recombination. The efficient collection of multiple charge carriers has a potential to remarkably increase the performance of photovoltaic cells, leading to a quantum efficiency greater than 100% at certain wavelengths and eventually much higher PCE.^{35,42} The further combination of MEG with solar concentration is expected to largely increase the efficiency to 75% at 500× based on theoretical calculations,

much more significant than the expected theoretical increase for conventional single-junction solar cells (absolute value of 38% at 500× versus 33% at 1×).⁴³ Different experimental approaches have been employed in order to enhance the MEG efficiency. A promising approach is to use quasi-type-II QDs. Nearly a 4-fold increase in the MEG yield was observed for thick-shell PbSe/CdSe QDs with respect to conventional PbSe QDs, thanks to the efficient separation of electrons and holes through the effective capture of holes into long-lived shell-localized states.⁴⁴ In another scenario, it was shown that the MEG in a PbSe QD solid was activated by infiltrating it with Al₂O₃ or Al₂O₃/ZnO.⁴⁵ The effect of the aspect ratio on MEG was also studied. PbSe nanorods were found to show higher MEG yields than PbSe QDs.⁴⁶ Although QDs bring hope to considerably increased photovoltage by capturing hot carriers or photocurrent by extracting multiple excitons, technically, the efficient realization of either process represents a great challenge due to the still fast relaxation rate of charge carriers.

Recent Major Advances of QD Solar Cells. Since QD-based solar cells were first reported in 1998, their PCE has been increased from below 1 to 8.6%.^{11,12} Although they have attracted extensive research interest since the very beginning, the improvement of the device performance was relatively steady and slow in the first 10 years or so. The past several years have seen a rapid progress of this field. Not only was the efficiency largely improved, with the highest ever certificated efficiency of 8.6% reported this year,¹² other device properties have also been greatly enhanced. The impressive improvements have mainly been achieved via designing and improving device architectures and QD surface engineering.

Recent Major Advances—Architecture of Devices. Diverse device architectures of QD-based solar cells have been developed to improve the photon-to-electron conversion efficiency. We herein focus on five classes of QD-based solar cell devices (Figure 4). They are a QD-sensitized solar cell, hybrid QD–polymer solar cell, Schottky junction solar cell, p–n heterojunction solar cell, and p–n homojunction solar cell. Almost all of these solar cells favor the use of presynthesized monodisperse, high-quality QDs to avoid possible charge carrier trapping and recombination in relatively larger QDs. Thanks to the remarkable advances of the wet chemical synthesis of monodisperse and high-quality QDs, they provide the important and solid basis toward achieving high device performance.

QD-sensitized solar cells represent one of the earliest configurations of QD solar cells. They were inspired by the so-called dye-sensitized solar cells. The operative mechanism is the same as that of dye-sensitized solar cells, except for the dye sensitizer being replaced by QDs. CQDs play a role of primary absorbers in these solar cells, harvesting solar photons, generating excitons, and then injecting electrons to other semiconductor materials.⁴⁷ The cells are typically made up by coupling presynthesized semiconductor QDs to other wider-band-gap semiconductor materials, mainly TiO₂ (or ZnO) with favorable band offset, referred as a type-II structure, to enable the charge separation at their interface. One way to achieve it is using bifunctional linker molecules. For example, Kamat's group successfully linked CdSe QDs with TiO₂ by employing mercaptopropionic acid (MPA) and observed a photon-to-charge carrier conversion efficiency of 12%.⁴⁸ By reducing the surface-related trap state with mild Cd²⁺ or Zn²⁺ cation exchange and using a methanol-based polysulfide electrolyte, Klimov's group was able to achieve a champion efficiency of 5.5% in 2013.⁴⁹ In 2014, the highest efficiency for CQD-sensitized solar cells was further increased to 7.0% (with certified efficiency of 6.7%) by utilizing CuInS₂/ZnS type-I core-shell QDs as a sensitizer.⁵⁰ It is noteworthy that these high-efficiency solar cells do not contain toxic heavy metals, and this high efficiency has not been previously achieved by any Cd- and Pb-containing QD-sensitized solar cells. In general, to overcome the lower light absorption of a QD monolayer as compared to a dye layer due to the higher surface coverage of the latter, thicker porous TiO₂ (or ZnO) films are required for sensitization with more QDs in order to absorb more incident light. Paradoxically, it becomes more difficult to fully infiltrate presynthesized QDs into the thick porous film through a conventional soaking procedure. An alternative approach is to synthesize QDs in the presence of TiO₂ (or ZnO) at the same time of depositing QDs onto it. An efficiency of 5.4%, the highest of this kind, has been recently achieved with the QDs prepared by a successive ionic layer adsorption and reaction method.⁵¹ A common down side of this type of solar cells containing liquid electrolytes is that they usually suffer from problematic corrosion of QDs.⁵² Further considering possible electrolyte leakage, efforts have been made in using solid-state hole-transporting material instead, following the same concept in developing solid-state dye-sensitized solar cells.⁵³

The earliest work on hybrid QD-polymer solar cells was reported at almost the same time as QD-sensitized solar cells.⁵⁴ In this type of cells, the single photoactive layer is prepared via blending QDs with conjugated polymers, or alternatively QDs and polymers are arranged into separate layers to build a bilayer or planar configuration cell.^{55,56} The charge separation takes place at the QD/polymer interface and is dictated by their energy levels. Due to the low charge carrier mobility of organic semiconducting polymers, the thickness of the photoactive layer is restricted to about 100 nm, limiting the efficiency of the solar cells because of the low light absorption capacity. To date, the best efficiency of 4.1% was achieved by Ren et al. in 2011 using CdS QDs.⁵⁶ QD-polymer solar cells have not been developed very well with respect to other low-cost photovoltaic cells but possess a possibility to attain better photoconversion performance by improving the QD/polymer interface and phase structure (or morphology) in the photoactive layer. Because presynthesized CQDs are commonly covered by long alkyl chain ligands, potentially acting as an insulator, appropriate interface engineering is required for the efficient charge

transfer between CQDs and semiconducting polymers. Ligand exchange on QDs in solution prior to their mixing with polymers or processing into a QD layer in the case of bilayer cells could be a solution. However, such ligand exchange on a few-nm QDs with much shorter ligand molecules in solution, with the strict requirement of not leading to any QD agglomeration, remains a tough task. As for the morphology, the interpenetrating network of QDs and polymers is ideal from the standpoints of enhanced exciton dissociation and reduced charge carrier recombination. Making efforts toward these challenging, ultimate goals, in one case, PbS QDs (before their blending with polymers) were attached to highly conductive one-dimensional carbon nanotubes, which served as a highway for transporting electrons photogenerated inside of the QDs.⁵⁷ Meanwhile, this strategy helped to avoid undesired random QD agglomeration and thus maximize the QD/polymer interface. With this strategy, ~20% increase in efficiency was observed as compared to control devices made with hole-transporting poly(3-hexylthiophene) (P3HT) and electron-transporting fullerene derivative of [6,6]-phenyl C-61-butyric acid methyl ester (PCBM) fabricated and tested under identical conditions. Thinking of exceeding the efficiency of 9% reported recently for purely organic solar cells,⁵⁸ it is still a long way to go before this type of QD cells can become competitive in terms of efficiency. Perhaps, they do not really need to compete with other types of solar cells. Instead, they can be used as an add-up, in combination with visible-responsive organic solar cells in a tandem configuration, to bring NIR photon-to-electron conversion capability via using NIR-absorbing QDs. Such NIR responsiveness is almost impossible for purely organic solar cells.

The first Schottky QD solar cell involving a thin and compact QD film was reported by Nozik's group in 2008.⁵⁹ This type of solar cells was once leading in the efficiency in all types of QD solar cells, with the highest reported efficiency reaching 4.5% in 2011.⁶⁰ The structure is quite simple and is constructed by sandwiching the QD layer in between an Ohmic-contact transparent electrode (such as indium-doped tin oxide (ITO)) and a low-work-function metal electrode.^{60–62} In general, electron-hole pairs are photogenerated in the active QD film and separated at the Schottky junction imposed in between the back metallic contact and the semiconducting QD film. Although the Schottky junction architecture demonstrates functional simplicity and ease of fabrication, it suffers from some inherent problems of limited QD film thickness and low V_{OC} . The former constraint arises from the dilemma of poor diffusion of minority carriers generated on the illumination side and the location of the Schottky contact at the back, while the latter limitation is set by Fermi level pinning, with the upper limit only being approximately half of the band gap of QDs.^{61,62}

The p-n heterojunction solar cells based on QDs have only been developed recently since 2009,⁶³ with the purpose of overcoming certain inherent limitations encountered in Schottky solar cells. They have shown remarkably rapid development in achieving significant efficiencies in a short-term, considerably higher than those of Schottky solar cells, and soon have become a star in this field. The solar cells typically use the depleted heterojunction region between a p-type colloidal semiconductor QD film and an n-type TiO₂ (or ZnO) layer to separate charge carriers mainly photogenerated in the QD layer.⁸ Following initial efforts in refining device components and studying relevant mechanisms, many efforts have also been devoted into other aspects.^{64,65} In particular, one important piece of work marking a milestone in this field applied the

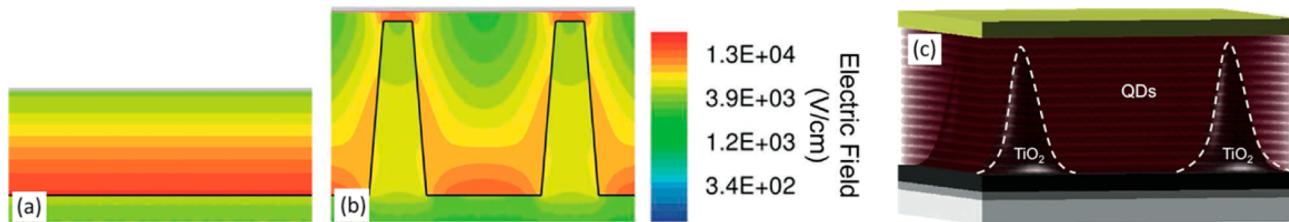


Figure 5. Electric field distributions in (a) planar and (b) nanopillar devices indicating that carriers generated deeper in the device will still encounter the charge-extracting field. (c) Cartoon depiction of fabricated heterojunction solar cells based on PbS QDs and TiO₂ nanopillars. Adopted from ref 67 with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

concept of the interpenetrating network, initially proposed for organic solar cells, into the inorganic p–n heterojunction cells.⁶⁶ In this design, QDs and TiO₂ nanostructures are assembled in such a way to create a certain level of interpenetration. As such, the interfacial area is maximized, and the depletion region is allowed to spread in all three dimensions in the photoactive layer. Therefore, in principle, the photoactive layer can be made thicker so as to absorb more solar photons yet still enable efficient charge carrier collection. As a consequence, the authors achieved the impressive efficiency of 5.5%, a record high at that time.⁶⁶ Soon after this success, perhaps the most delicate realization of this concept was demonstrated on ordered TiO₂ nanopillar arrays fabricated by the lithography technique (Figure 5).⁶⁷ The nanopillar spacing was rationalized based on the dimension of the depletion region. The optoelectronic modeling clearly shows that the distribution of the strong electric field is broader in the QD volume in the case of nanopillars, with respect to the planar configuration, thereby permitting carriers generated deeper in the device still to encounter the charge-extracting field and thus enhancing charge extraction. Besides, with the same strategy, ZnO nanowires were also employed into the p–n heterojunction solar cells as an n-type semiconductor to improve the carrier collection.^{68,69} For the vertically oriented ZnO nanowires grown by a simple hydrothermal process, Bulovic's group observed a 35% efficiency enhancement over corresponding planar devices with a maximum efficiency of 4.9%.⁶⁸ Segawa's group used a spray pyrolysis deposition method to synthesize ZnO nanowires and, by controlling ZnO morphology, achieved the efficiency of 6.1%.⁶⁹ Very recently, by manipulating the QD's surface in such heterojunction cells, Bawendi's group was able to break the world record of QD solar cells, with the highest certified efficiency of 8.6%.¹² The high efficiency was achieved in ZnO/PbS QD solar cells by engineering the band alignment of two QD layers undergoing different ligand treatments, one passivated by inorganic ligands and serving as the major light-absorbing layer while the other was passivated by organic ligands and acted as a hole extraction layer. The large conduction band offset between these two layers provides an energy barrier to prevent photo-generated electrons from flowing toward the anode, and the large valence band offset offers an additional driving force for the flow of photogenerated holes toward the anode. In addition to high efficiency, these room-temperature-processed solar cells exhibited excellent stability for over 150 days in air.

The p–n homojunction QD solar cells represent the most recent development.^{70–73} They were developed to further address some limitations of previous architectures, mainly low V_{OC} and stability. Their development was largely enabled by the most recent advent on solid-state ligand exchange and on understanding ligand effects on QD properties. By replacing the

thick electron-acceptor layer of TiO₂ (or ZnO) with an n-type QD layer, obtained via engineering the QD surface chemistry, the heterojunction can be solely comprised of QDs, p-type on one side and n-type on the other (Figure 4e). Because solar photons are now absorbed by both sides of the rectifying junction, charge carriers can be efficiently generated and separated. Another benefit of this design is the removal of band offset challenges between QDs and electron acceptors. The concern of the low carrier mobility of the QD film is also somewhat relieved following the investigation of the carrier mobility in the n-type QD film. With this architecture, an efficiency of 6.6% has been achieved.⁷³ Although it is still lower than that of the bulk heterojunction solar cells, further increase is expected. Along with other advantages, such as dramatically enhanced stability, this type of QD solar cells is believed to hold high promise for future-generation solar cells. In addition, p–n homojunction realization opens the avenue to prospective inverted p–n homojunction and multijunction solar cells.

Recent Major Advances—QD Surface Engineering: Ligand Chemistry. Other achievements have mainly been made on QD surface engineering. The use of the surface engineering concept in the field of solar cells has been proven to be very helpful in the advancement of QD solar cells. As-prepared CQDs can be introduced to solar cell devices via soaking, dip-coating and spin-coating deposition, as well as blending with polymers and so forth, depending on the type of QD solar cells.^{8,52,55,56} Among them, the layer-by-layer spin-coating deposition method is most widely employed to make QD films for solid-state QD solar cells.⁷⁴ In this process, each layer of QDs is deposited by spin-coating, and solid-state ligand exchange by treating the QD layer with a solution containing short-chain ligands is sequentially carried out. This procedure is repeated until the desired film thickness is obtained. The method is particularly favorable to make thick QD solid films, avoiding small cracks that can arise from significant volume contraction while bulky organic ligands are removed. The performance of solar cells is in large part determined by the quality of the QD film, which further depends on inter-QD coupling and QD surface passivation.

Less important for QD-sensitized solar cells, interdot coupling and efficient charge transport are of critical importance for the solar cells relying on a densely packed QD layer for the transport of at least one type of charge carriers. The charge transport in the QD film takes place through band-like transport or hopping mechanisms.⁷⁵ Despite the debate on actual transport mechanisms, it is a common understanding that both mechanisms favor a short interdot distance. In general, wet chemically synthesized QDs are surrounded by long alkyl chain organic ligands.⁷⁶ These long-chain organic ligands help QDs to stably disperse in solution and reduce their defect states, but on the other hand, in the solid film, they increase the interdot

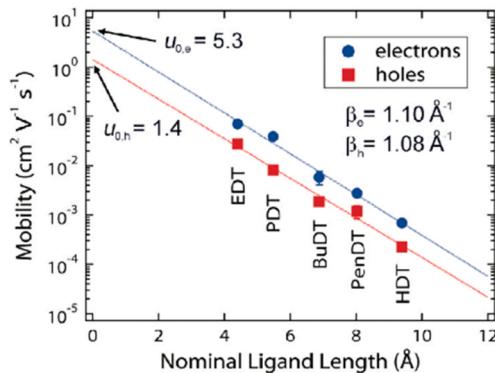


Figure 6. Carrier mobility as a function of ligand length in ambipolar PbSe NC field effect transistors (6.1 nm NCs). Each data point is the average of 6–12 devices prepared on different days. Error bars are mostly smaller than the symbols. Molecular lengths were calculated using MM2 energy minimization in the ChemBio 3D software package considering only the projected sulfur-to-sulfur distance ($\sim 1.5 \text{ \AA}$ per C–S bond and $\sim 1.25 \text{ \AA}$ per C–C bond) and neglecting S–Pb bonding. The plot assumes that the inter-NC spacing is proportional to the extended length of each ligand. Channel dimensions: length = $10 \mu\text{m}$; width = $1000 \mu\text{m}$; film thickness = 20–35 nm. Reprinted from ref 80.

spacing and act as an insulating barrier, thereby being detrimental to charge transport in the QD film.⁷⁶ Exchanging long-chain organic ligands with shorter ones improves electronic coupling between QDs, thereby increasing the charge-transport rate.^{77,78} Ligand exchange has been carried out using various short-chain ligands, such as short alkylthiols, aromatic thiols, alkylamines, and mercapto carboxylic acids.⁷⁹ The effect of ligand length on mobility has also been studied for common short ligands. As shown in Figure 6,⁸⁰ electron and hole mobilities measured in PbSe QD field effect transistors decreased exponentially with increasing chain length of alkanethiol on the QD surface, with a decay length characteristic of hopping transport. Although these mobilities measured in field effect transistors cannot be taken as actual mobilities in

solar cells, the trend can be clearly seen. For PbS QD solar cells, short thiol ligands have been found most helpful. For instance, the use of simple MPA for ligand exchange without any further annealing process has led to efficiency of 5.1% for a PbS/TiO₂ heterojunction solar cell, the highest at the time that it was reported.⁸

Although ligand exchange in solution before spin-coating has also been attempted, most commonly, it is performed during the spin-coating process. It is to say that the solid-state ligand exchange is still most popular and dominant for QD solar cell fabrication at the current stage. To have successful ligand exchange in a short spin-coating period, shorter ligands should bind more strongly to the QD surface than original long-chain ligands from QD synthesis. A potential problem arising from this process is the generation of trap states, which can trap charge carriers and result in unacceptable carrier recombination due to incomplete coverage and degraded passivation. This concern has initiated the use of smaller inorganic ligands to better passivate air-sensitive surfaces. First proposed by Talapin et al. to use metal chalcogenide complexes to treat QDs to get dramatically increased carrier mobilities,^{81,82} Sargent's group was the first to apply inorganic halide-treated PbS QDs into solar cells with the goal of achieving improved QD passivation (Figure 7a).⁷⁴ After capping exposed S²⁻ anions on the surface of PbS QDs with Cd²⁺ ions, halide ions were used to bind Pb²⁺ ions, including hard-to-access sites. In addition to having the size as small as 0.1 nm, beneficial to avoid the steric hindrance effect during the passivation, halide anions such as Cl⁻, Br⁻, and I⁻ also exhibited a strong affinity to cations on the QD surface, thus promoting better surface passivation, considerably decreasing the number of traps, and increasing QD stability. As shown in Figure 7b, in comparison to organic ligands of ethanedithiol (EDT) and MPA, Br⁻-treated QD films exhibited a considerable lower density of trapped carriers, as experimentally proved by time-resolved infrared spectroscopy (TRIR) results. The level of passivation was found to increase in the order of Cl⁻ < Br⁻ < I⁻.⁷⁴ The importance of this atomic inorganic ligand passivation strategy has been clearly demonstrated by leading to $\sim 6\%$ efficiency for QD solar cells.

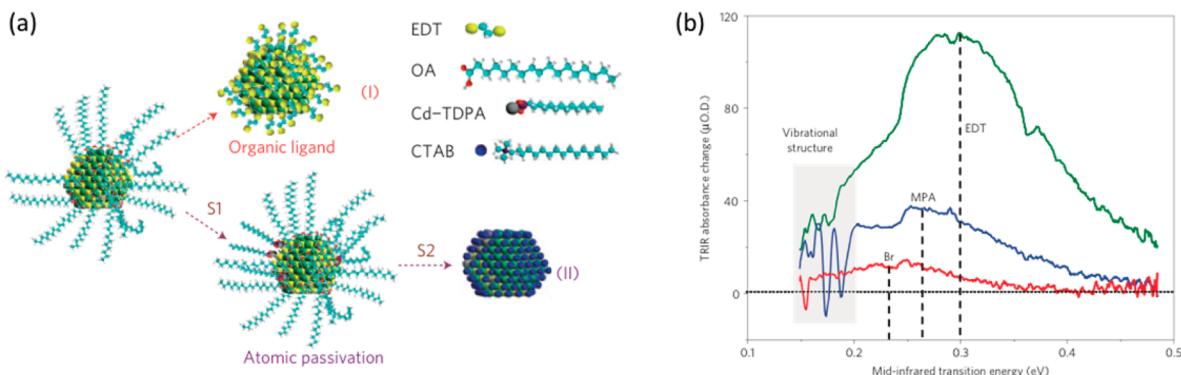


Figure 7. (a) Organic and atomic passivation strategies. Colloidal PbS QDs having a Pb²⁺-rich surface are initially capped with deprotonated oleic acid (OA). In the organic route, EDT substitutes the long OA ligands and binds to Pb²⁺ on the surface. In the atomic ligand route, a cadmium–tetradecylphosphonic acid (Cd–TDPA) complex was first introduced to the colloidal PbS QD surface to passivate the exposed S²⁻ anions (S1). A solid-state halide anion treatment, such as that employing cetyltrimethylammonium bromide (CTAB), introduced Br⁻ to cap the surface cations (S2), forming all-inorganic, halide anion-passivated PbS QDs. The molecular structures of EDT, OA, Cd–TDPA, and CTAB are shown as insets. Colors are green (lead), yellow (sulfur), cyan (carbon), white (hydrogen), red (oxygen), gray (cadmium), blue (bromine), and purple (nitrogen). (b) The broad features in the TRIR spectra result from trap-to-band transitions observed in PbS QDs treated with various ligands. The amplitude and shape of the spectra reflect the number and depth of trapped carriers. The narrow features appearing between 0.15 and 0.2 eV correspond to vibrational spectra of ligands that are perturbed by localization of charges at surface trap sites. Reprinted from ref 74 with permission from Macmillan Publishers Limited.

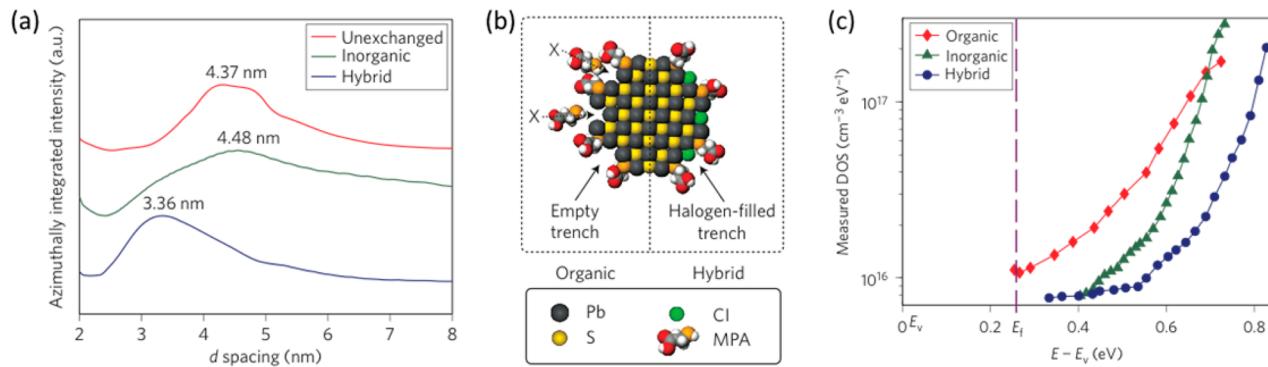


Figure 8. (a) Average interparticle spacing before and after ligand exchange. Inorganic passivation (green curve), despite minimally sized atomic ligands, does not increase the film density compared with initially cast dot films (red curve). An exchange using short bidentate organic thiols (blue curve) results in a significant reduction in average interparticle spacing. (b) Schematic cross section of a PbS QD with organic passivation (left) based on MPA and the hybrid passivation scheme (right), in which both MPA and halides are present after solution-phase treatment and solid-state exchange. In the organic case, the MPA molecules are unable to fill all of the interatom trenches on the lead-rich surface because of steric considerations (top) or lack of proper coordination number (bottom). In the hybrid case, halogen atoms are small enough to fill the trenches easily and can be multiply coordinated. (c) Density of states (DOS) in the band gap calculated from transient photovoltaic measurements for organic (red), inorganic (green), and hybrid (blue) passivation of PbS QD films. Reprinted from ref 83 with permission from Macmillan Publishers Limited.

Very soon, the same group further combined a previous organic bidentate cross-linking approach with this halide treatment. The idea was to maximize QD film packing, meanwhile achieving the best possible QD surface passivation. On the basis of synchrotron grazing incidence small-angle X-ray scattering (GISAXS) measurements, the average center-to-center distance of QDs in films remained unchanged at 4.4 nm with the halide treatment, while it was largely reduced to 3.4 nm after the short bidentate cross-linker MPA was used during the ligand exchange, suggesting the important role of the bidentate organic cross-linkers in achieving densification during solid-state treatment (Figure 8a).⁸³ At the same time, such a hybrid approach also promoted better surface passivation (Figure 8b and c), likely due to the fact that the surface complexity of QDs prefers multiple types of ligands to a single type to achieve ideal passivation. The use of this hybrid approach led to high hole mobility of $4.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and further pushed up the efficiency to 7.0%.⁸³

Important understanding has also been acquired on the more complicated impact of QD surface engineering on QD solar cells, in addition to manipulating trap states. It was found that the electronic nature of a QD film and the band energy levels of QDs can all be changed by the ligand exchange.^{79,84} The actual role of the ligand exchange goes beyond surface passivation and QD bridging. For instance, QD films treated with a short organic ligand of MPA in air possess the p-type semiconductor property like as-synthesized QDs, whereas QDs treated with halide in an inert atmosphere show the n-type semiconductor character.^{74,85} As shown in Figure 9a, both the nature of doping and doping density of PbS QDs were varied with the type of surface ligands and atmosphere.⁸⁴ In addition, the Fermi level and band gap energy can be modified (Figure 9b),¹² allowing the band alignment of QD layers through the use of different ligand treatments. Successfully using this feature, Bawden's group achieved the highest certified efficiency of 8.6% for PbS/ZnO heterojunction solar cells.¹² The success essentially relies on the rational tuning of energy level alignments between different components via different ligand treatments in such a way that they direct charge carrier transport in a correct direction and promote charge extraction (Figure 10). To be more specific, in their PbS-QD/ZnO cells, the QD layer was

made of two sublayers. The thin QD sublayer in contact with the metal anode was treated with EDT, while the thicker sublayer in contact with the ZnO layer, which served as the major light absorber, was treated with tetrabutylammonium iodide (TBAI). More importantly, without any encapsulation, these solar cells showed unchanged performance, after being stored in air for over 150 days. The use of the ligand doping concept in solar cells also opens up the facile avenue to the development of p–n homojunction QD solar cells composed of differently passivated QDs on each side of the junction.

Recent Major Advances—QD Surface Engineering: Core–Shell Strategy. Another promising approach to improve QD surface passivation and eliminate surface defect states is to form the so-called type-I core–shell QDs, where the QDs are ideally coated epitaxially with a semiconducting material having a larger band gap in such a way that both the conduction and valence band edges of the core are located in the band gap of the shell. Essentially by designing such a type-I core–shell nanostructure, it is understood that the surface of the core QDs can be better passivated by removing both anionic and cationic dangling bonds, and consequently, the defect states on the QD surface can be largely eliminated.⁸⁶ This core–shell strategy has also been shown to be effective in largely enhancing the chemical, thermal, and photochemical stability because the inorganic shell can provide a more robust protection to core QDs with respect to typical organic ligands. Another potential benefit of the core–shell strategy consists in MEG. For instance, quasi-type-II thick-shell PbSe/CdS QDs showed an almost 4-fold increase in the MEG yield with respect to PbSe QDs owing to a significant slowing down of intraband relaxation.⁴⁴

Since the first seminal report of the wet chemical synthesis of core–shell QDs reported by Hines and Guyot-Sionnest in 1996,⁸⁷ core–shell semiconductor QDs have attracted great attention.^{21,88,89} Diverse synthesis methods, such as one- or two-step precursor coprecipitation and a successive ionic layer adsorption and reaction, have been developed to form uniform core–shell QDs. Very rapidly, these high-quality UV–visible-emitting QDs or, in particular, those involving II–IV cadmium chalcogenide became most popular among diverse semiconductor nanomaterials, and now, they can be routinely synthesized in many laboratories. The synthesis of high-quality NIR-emitting

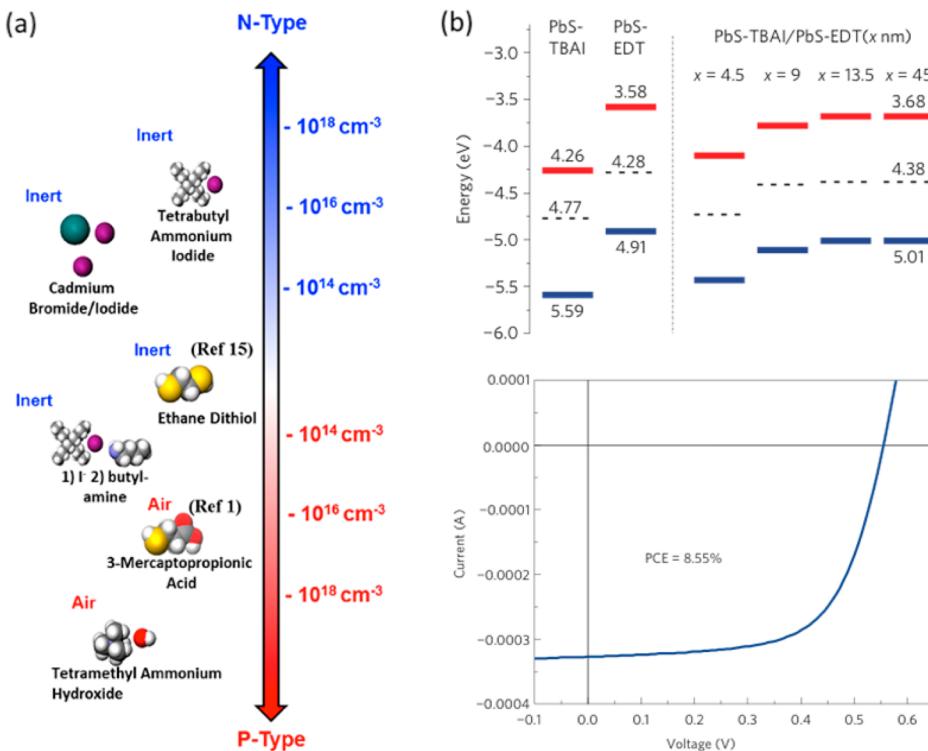


Figure 9. (a) Illustration of the effect of various treatments of colloidal PbS QD films conducted under various atmospheres (shown on the left) on the doping density (shown on the right). Reprinted from ref 84. (b) (Top) Energy levels with respect to vacuum for pure PbS-TBAI, pure PbS-EDT, and PbS-TBAI films covered with different thicknesses of PbS-EDT layers. The Fermi levels (E_F , dashed line) and valence band edges (E_V , blue lines) were determined by ultraviolet photoelectron spectroscopy. The conduction band edges (E_C , red lines) were calculated by adding the optical band gap energy of 1.33 eV, as determined from the first exciton absorption peak in the QD thin films, to E_V . (Bottom) Device performance of a PbS-TBAI/PbS-EDT device certified by an accredited laboratory (Newport) after 37 days of air storage. Reprinted from ref 12 with permission from Macmillan Publishers Limited.

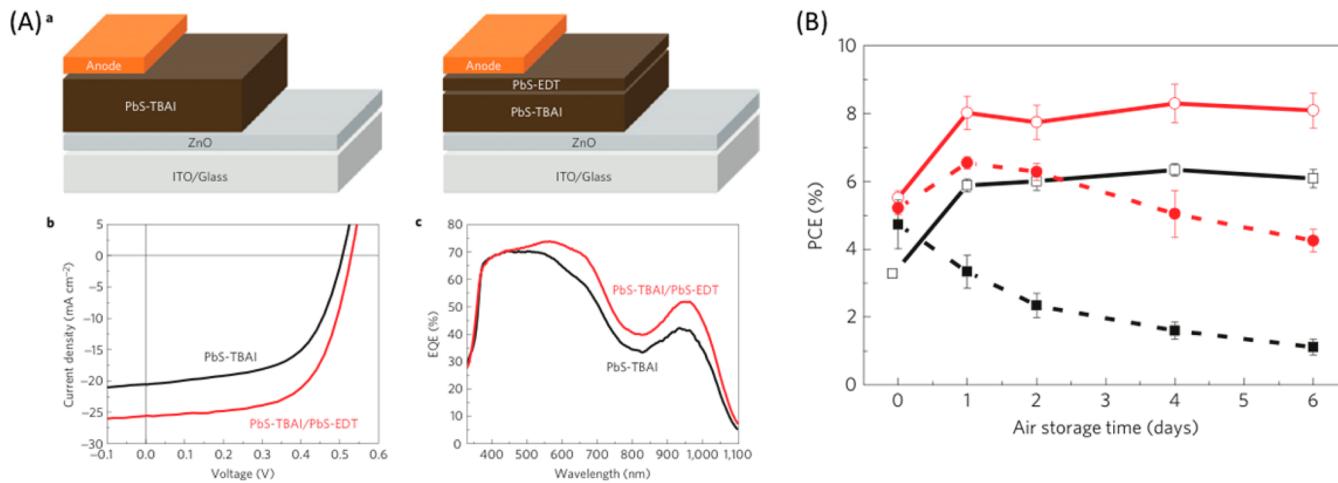


Figure 10. (A) Photovoltaic device architectures and performance. (a) Device architectures. (b) Representative $J-V$ characteristics of devices with Au anodes under simulated AM1.5G irradiation (100 mW cm^{-2}). The PbS-TBAI device consists of 12 layers of PbS-TBAI, and the PbS-TBAI/PbS-EDT device consists of 10 layers of PbS-TBAI and 2 layers of PbS-EDT. (c) External quantum efficiency (EQE) spectra for the same devices. (B) Evolution of the PCE. Measurements were performed in a nitrogen-filled glovebox. Day 0 denotes measurements performed after anode evaporation in vacuum. Between each measurement, the unencapsulated devices were stored in air without any humidity control. The average (symbols) and standard deviation (error bars) were calculated from a sample of six to nine devices on the same substrate. Reprinted from ref 12 with permission from Macmillan Publishers Limited.

core-shell QDs, nonetheless, is less mature and was only developed lately.^{38,90} For PbS QDs, which has led to the highest efficiency in all QD solar cells, their high-quality core–shell versions, PbS/CdS QDs, were reported only recently.^{38,91–93} These PbS/CdS QDs were synthesized by a cation approach,

quite different from the most commonly adopted approaches for UV-visible-emitting core–shell QDs. In this approach, only the precursor of cationic constituents of a shell material was introduced, and the shell growth proceeded through the gradual replacement of core cations by newly introduced cations in

solution, and the anion sublattice remained basically undisturbed. Very recently, we succeeded in further improving the quality of PbS/CdS core–shell QDs by using microwave irradiation as a heating source for the cation exchange process.⁹⁴ The more uniform core–shell QDs and significantly enhanced quantum yields, as compared with those achieved by using conventional heating in a silicone oil bath, are attributed to the uniform heating nature, inherent in the microwave-assisted synthesis method.

Although the core–shell QDs, in particular, visible-emitting QDs of CdSe/ZnS, have been extensively exploited in the past decade for improving optical properties of QDs for various applications including imaging, the type-I QDs in general are scarcely explored in QD-based solar cells.⁹⁵ In part, it is because type-I QDs are believed to be not preferred in solar cells because the shell may serve as a barrier for charge transfer and carrier extraction. A delicate balance needs to be pursued between sufficiently good surface passivation and yet still efficient carrier transport. Taking this concern into consideration, we recently studied the charge-transfer behavior of high-quality PbS/CdS core–shell QDs of various core sizes and shell thicknesses using electron and hole scavengers that do not allow energy transfer with QDs.⁹⁶ It was found that both electrons and holes could be efficiently transferred when the shell was not very thick, and the core size was appropriate to offer suitable energy level alignment between the QDs and charge carrier scavengers. Similar results were obtained when these core–shell QDs were hybridized with carbon nanotubes. As the first demonstration, colloidal PbS/CdS core–shell QDs were deposited under an ambient atmosphere on vertically grown TiO₂ nanorod arrays to make bulk heterojunction solar cells.⁹⁷ The devices showed about 40% higher PCE than similar devices involving PbS QDs processed in an inert atmosphere. Clearly, the PbS/CdS core–shell QDs offered dual advantages of easy processing in air and better performance as compared with PbS QD solar cells. Very recently, the core–shell strategy was combined with the halide treatment for building a QD/ZnO heterojunction solar cell.⁹⁸ The shell thickness of PbS/CdS core–shell QDs was first optimized and then followed by ligand treatment with a combination of halide and bifunctional organic molecules.⁹⁸ With these strategies, an efficiency of 5.6% was achieved. Although overall the efficiency of core–shell QD solar cells is still not very high, considering their better surface passivation, improved stability, and easier fabrication in ambient atmosphere, obviously they have high potential, and substantial improvement can be expected in the near future through further device optimization. It is noteworthy that type-II QDs (and nanorods) have also been used for solar cells.⁹⁹ Type-II QDs are defined as the QDs, in which either the conduction band edge or the valence band edge of the core is located in the band gap of the shell. The primary purposes of using type-II QDs in solar cells are different from type-I QDs though. They are mainly used to extend the solar cell absorption to longer wavelengths and/or the spatial separation of electrons and holes, both in favor of enhancing charge carrier extraction.¹⁰⁰

Despite rapid and great progress, more work needs to be done to understand the exact surface chemistry of QDs and how it can be manipulated to positively contribute to solar cell performance. Recently, a novel method of pulsed-laser deposition has been reported as a novel, top-down approach to prepare PbS QD-based solar cells.¹⁰¹ In this case, the synthesis and deposition of QDs on a semiconductor film of TiO₂ nanorod arrays were done in a single step, and no ligand exchange step was involved. Without any ligands and without any

intentionally deposited shell on the QD surface, surprisingly, these solar cells showed good stability in air without any encapsulation. Although this fabrication method is difficult to scale up and also the size distribution of the QDs prepared from this method is not as narrow as that of wet chemically prepared QDs, it initiates research interest to further study the surface of such prepared QDs and compare it with that of chemically prepared QDs toward further improving the QD solar cell performance by surface engineering.

Challenges and Outlook. The prime challenge for QD solar cells is to further improve their efficiency in order for them to be competitive with other existing solar technologies.

On one hand, the device architecture and QD surface can be further optimized as the continuation of the mainstream development path taken in the past several years. Recent advances in these two aspects have provided a solid foundation as well as shed light for the future development of more efficient solar cells. Better structuring electrodes and semiconductors in a low-cost version that allows for efficient charge separation, transportation, and extraction of both holes and electrons by, for instance, forming a well-ordered interpenetrating network, is one direction worthwhile for future efforts. Meanwhile, despite largely accumulated knowledge on QDs through decades of research efforts, surface chemistry knowledge, including the exact nature of surface geometry, facets, and ligand passivation is still lacking yet highly desired. Investigations combining a high spatial resolution microscope with theoretical modeling and calculations are urgently needed. The goal is to develop QD films with as few as possible charge carrier recombination centers and with as high as possible mobilities (10^{-2} – 10^{-1} cm² V⁻¹ s⁻¹ or higher) of electrons and holes. Substantial improvement in charge carrier transport is crucial to further tangible improvement in QD solar cells.

On the other hand, QDs also hold high promise for low-cost and facile room-temperature construction of multijunction solar cells. The report on QD multijunction solar cells is still rather limited, but interesting concepts have been proposed and attempted. The prime advance is the realization of a GRL, which addresses the nontrivial, important issue in all multijunction cells, that is, the connection layer among junctions. It is also compatible with QD processing. The invention of such a GRL represents an important step toward achieving ultimate

Quite distinct pathways can also be taken by largely taking advantages of MEG and hot electron extraction enabled by the use of QDs and motivated by the idea of avoiding substantial amounts of energy loss related to the part of the photon energy exceeding the band gap. The exploitation of both effects in solar cells can potentially allow for the booming of solar cell efficiencies, far beyond the theoretical Shockley–Queisser limit of 31% imposed on single-junction solar cells.

multiplication cells. Although the highest efficiency of 4.2% is still much lower than that has been achieved by traditional epitaxial compound multiplication cells, future improvements are expected by further optimizing the efficiency of each single-junction cell and their combination.

Quite distinct pathways can also be taken by largely taking advantages of MEG and hot electron extraction enabled by the use of QDs and motivated by the idea of avoiding substantial amounts of energy loss related to the part of the photon energy exceeding the band gap. The exploitation of both effects in solar cells can potentially allow for the booming of solar cell efficiencies, far beyond the theoretical Shockley–Queisser limit of 31% imposed on single-junction solar cells. On the basis of thermodynamic calculations at 1 sun, when two excitons can be generated by a single absorbed photon, the maximum efficiency can reach 42%, which represents ~35% improvement.¹⁰² Likewise, the theoretical upper efficiency limit can be more than doubled to 66% by harvesting hot electrons.¹⁰³ Although the relaxation rates are slower with respect to those in bulk semiconductors, capturing hot electrons and extracting multiple excitons from QDs still remain great challenges due to the fast relaxation rate of charge carriers. Extensive exploration is required on both fundamental understanding and technological aspects to significantly increase the hot carrier lifetime and the extraction of multiple excitons. They are the key to realizing these unprecedented potentials of QDs and may be realized through suitably structuring QDs or better engineering the heterointerface between QDs and other materials. Along these thought lines, one possible strategy is to design core–shell QDs to spatially separate hot electrons and holes, thus elongating their lifetime.³⁶ Regarding MEG, after going through some early stage controversies and then a dim time period, it has been experimentally proven recently to be a viable approach to push up even the external quantum efficiency (EQE) appreciably above 100%.³⁵ This is expected to encourage much more exciting research in this field. Clearly, once successfully realized in solar cells, these two features will endow QD-based solar cells' unprecedented capability of surpassing the Shockley–Queisser limit. Such a huge potential motivates further QD solar cell research, although recently, low-cost perovskite solar cells have shown impressively rapid progress and achieved a much higher efficiency.

Using plasmonic nanostructures to enhance solar cell efficiency is a recently emerging area, termed as plasmon-enhanced photovoltaics, yet it has attracted considerable research interest.^{104,105} Plasmonic nanostructures can in principle enhance the solar cell efficiency via significantly increasing light trapping and exciton generation rates through the excitation of localized surface plasmons or surface plasmon polaritons at the plasmonic metal/photoactive semiconductor interface. They have been mainly studied in thin-film solar cell devices but only attempted in a very limited scope for QD solar cells.¹⁰⁴ The challenges, such as poor reproducibility in the preparation of photoactive QD films containing plasmonic nanoparticles and negative effects related to the introduction of charge carrier recombination centers, need to be overcome in order to maximize the beneficial contribution from plasmonic nanostructures.

For the successful realization of QDs in commercial solar cells, other factors also need to be considered in addition to efficiency. For instance, breakthroughs are vastly demanded in the scale-up of synthesis and film fabrication of QDs. For the most successful QD solar cells, high-quality PbS QDs are often involved. They are typically synthesized from a hot injection

method, which nonetheless is expected to be only able to work well in a quite limited volume. The scale-up of this synthesis allowing the transfer of QD production from laboratories to industry is not trivial at this moment. As for the QD film fabrication, most often, spin coating and solid-state ligand exchange are applied, which are once again not suitable for large-scale manufacture. Although efficiency remains to be improved, some new film deposition methods, such as CQD inks, have been attempted for QD solar cells.^{106,107} A key requirement to such potentially large-scale solution processing is to use QDs already undergoing ligand exchange with short ligands in solution. The task still requires more work, but definitely, it is not nonviable. Stability is another important concern for QD-based solar cells. In addition to ideal QD surface passivation (desirable for easy QD processing in air and also good for long-term stability), robust device encapsulation is regarded as critical in order to meet the commercial requirement of stability on a time scale of ~100 000 h.

Another important issue of QD-based solar cells is toxicity. Although II–VI and IV–VI QDs are most commonly used and lead to relatively high energy conversion efficiencies among all QD solar cells, they have brought increasing health and environmental concerns because they contain cadmium or lead. Nontoxic or less toxic QDs, made of Sb₂S₃, Ag₂S, Ag₂Se, AgI, CuInS₂, CuInSe₂, CuInSe_xS_{2-x}, or Cu₂ZnSnS₄, are thus highly desired for solar cell applications.^{25,108–110} Although most of these alternatives have not been able to yield satisfactory results, considerable progress has been made recently. In particular, very encouraging results have been obtained in CuInS₂ QD-sensitized solar cells, showing a certified efficiency of 6.7%.⁵⁰ Although it is still lower than the highest certified efficiency of 8.6% reported for solid-phase QD solar cells, room for further improvement by materials and device optimization clearly exists. Carbon and graphene QDs are also attractive for solar cell applications.^{111–113} They have already received great attention due to their easy synthesis and nontoxicity.

Although the current Perspective is focused on QD-based solar cells, it is worthwhile to mention that QDs can also be potentially used as luminescent solar concentrators to enhance the performance of other types of solar cells. Some breakthroughs have been made in this regard recently.^{114–116} Therefore, in terms of a wider scope of solar-cell-related applications, the significance of QDs can go far beyond what is highlighted in this Perspective.

Attracted by their vast potential and, meanwhile, realizing various challenges, researchers are continuously making great efforts to address all kinds of important issues and pave a way toward the ultimate successful realization of low-cost and high-efficiency QD solar cells. In this path, the active communication between engineers, chemists, physicists, and materials scientists and their concerted efforts are highly desired to make breakthroughs in the near future.

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Notes

The authors declare no competing financial interest.

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