Colloidal semiconductor nanocrystals, referred to as quantum dots (QDs), have unique and superb photophysical properties, promising a variety of applications ranging from optoelectronics and energy harvesting to agriculture. The last decade witnessed a tremendous advance in QDs and their successful debut in displays, and now, QDs are equipped with environmental benignity to expand their territory to everyday life. From this perspective, the current research status and future perspective of environmentally benign QDs as building blocks for light-generating and light-harvesting applications are provided. Also provided is an overview of the progress made in the chemistry (colloidal synthesis, surface chemistry, and heterostructuring) and in their photophysical and electrical properties from the viewpoint of their use in light-emitting or light-harvesting applications. Grounded on the current status of heavy-metal-free QDs compared with cutting-edge technologies, the perspective of environmentally benign QDs for practical use and future research directions is discussed.

1. Introduction

Colloidal quantum dots (QDs) refer to nanometer-size semiconductors in which the charge carriers are confined in three dimensions. Dictated by the quantum confinement effect, the electronic and optical properties of QDs are amenable to change depending on their size, shape, and composition [1,2]. In addition, engineering the QD surface consisting of a 10–70% atomic fraction of all the QDs allows for tailoring the electronic energy levels and the electrical properties of QDs [3,4]. The advances in the structural engineering of QDs aided by the surface chemistry have yielded a new class of materials that holds unprecedented photophysical properties, promising their use in a wide variety of applications, from optoelectronics to biology [2,5–8].

The first practicable application of QDs that the public encountered was the premium LCD TV, whose image quality was enhanced by QD color-converting films. After the successful debut of QDs, their role in displays was transformed from the passive light-converting pigment to the active light-generating source. Driven by the display industry, QDs have continued to evolve to be equipped with competitiveness both in performance and price compared with the commercialized phosphors or dyes, and now, QDs are expanding their application fields towards solar energy conversion and agriculture, beyond TV sets.

Nearly all commercial applications strictly forbid the use of toxic elements (e.g. Cd, Hg, or Pb) consisting of the main frame body of the majority of II–VI or IV–VI QDs [9]. Indeed, the success of QDs in the display industries was possible only with the advances in the material synthesis and surface chemistry of QDs made of non-toxic chemical compounds (i.e. InP), and so will mark the continuing success of QDs for other purposes. Despite the immediate and significant potential impact of the development of non-toxic QDs on wide-ranging applications, their chemistry and photophysical properties are...
still hardly understood, and the performance of their applications is thus lagging behind the state-of-the-art performance.

Presented herein are the recent progress made in heavy-metal-free QD materials and the potential for their use in real-life applications. Specifically, the present article covers the colloidal synthesis, surface chemistry, and heterostructuring of heavy-metal-free QDs, and their photophysical and electrical properties from the viewpoint of their use in light-emitting or light-harvesting applications. Based on the current status of heavy-metal-free QDs compared with cutting-edge technologies, the perspective of environmentally benign QDs for practical use and future research directions is discussed herein.

2. Light generation

The application field of light sources is mainly determined by the energy (wavelength) of light that governs the light–matter interactions, such as reflection, scattering, transmission, and other photophysical phenomena.

The photon energy corresponds to the energy discrepancy between the charge carriers (electrons and holes) that participate in the radiative recombination. In bulk, the photon energy generated from a semiconductor is fixed by its crystal structure and chemical composition. By contrast, the quantum confinement effect, which supplies additional energy to the charge carriers, allows for the expansion of the bandgap envelop towards higher energy than that of the bulk counterparts. The advances in chemistry enable the achievement of tunable emission covering the entire spectra, from ultraviolet (UV) to near-infrared (NIR) (Figure 1), with colloidal QDs [2].

Another important factor that determines the quality of light is the color purity, which is often evaluated with the linewidth (full width at half maximum [FWHM]) of the emission spectra: emission spectra with narrow FWHM imply purer colors. The narrow FWHM of emitters is of particular interest in the field of information display, where the purity of each primary color (blue, green, and red) accounts for the quality of images and the quantity of information. Compared to the conventional...

Figure 1. (a) Size-dependent bandgap tunability of QDs with various chemical compositions. The arrows start from the bandgap of the bulk counterparts (indicated as numbers, in eV) and reach the values achieved by the wet chemistry. (b) Schematics illustrating the application fields of the QDs covered in the present article.
organic dyes or inorganic phosphors, QDs display narrow emission spectra originating from the band edge transition of charge carriers with minimal electron–phonon coupling [2]. In principle, QDs with ideal size, shape, and composition uniformity permit visible emission with a spectral linewidth as narrow as 20 nm at room temperature [10].

The emission tunability and narrow spectra linewidth of QDs have attracted the display industry, which seeks to recruit primary color emitters with a narrow spectra linewidth to extend the color gamut so as to meet the requirements for the next-generation displays (e.g. Rec, 2020). Among the potential candidates, QDs made of ZnSe [11–13], ZnTe [14], or their alloys (ZnSe$_x$Te$_{1-x}$) [15,16], or InP [17], have been of particular interest. Research on two aspects has been conducted for display purposes: (1) the controllable synthesis of these QDs with a narrow size distribution to augment the color purity [18,19]; and (2) the surface passivation of QDs with wide-bandgap inorganic materials to enhance their luminescence efficiency and photochemical stability [20,21].

Visible InP QDs reside in the strong-confinement regime, where the bandgap alters rapidly upon the size variation, and the emission linewidth of InP QDs thus responds delicately to the size uniformity compared to that of Cd chalcogenide QDs with the same size distribution [22]. Unfortunately, the wet chemistry of the InP QDs that have been developed so far cannot fully address the size inhomogeneity; as a result, the typical InP QDs are approximately twice as large (ca. > 100 meV) as the high-quality CdSe QDs (ca. 60 meV) in the ensemble [23]. From the mechanistic view of the reaction chemistry of organometallic precursors, the broad size distribution of InP QDs is mainly attributed to the fast depletion of the highly reactive silylphosphine precursor (i.e. tris(trimethylsilyl)phosphine, P(TMS)$_3$) during the nucleation stage [24,25], promoting the Ostwald ripening processes of the InP nuclei rather than the size focusing of the QDs after the nucleation event (Figure 2(a)). As a chemical means to avoid the rapid depletion of the phosphine precursors, structural engineering of the phosphine precursor has been attempted to lower the chemical reactivity (e.g. substituting the methyl group in P(TMS)$_3$ with bulky tertiary butyl [26] or phenyl group [27], or the silyl group in P(TMS)$_3$ with germyl group [28]).

Figure 2. (a) La Mer plots depicting the concentration change of phosphine precursors as a function of the reaction time during the synthesis of InP. The rapid depletion of the reactive phosphine precursors promotes the Ostwald ripening of InP QDs, leading to the broadening of the size distribution (bottom line). By contrast, the stable phosphine precursors lead to the spontaneous growth of InP QDs with a regular size distribution (upper line). (b) Schematic illustration of the two-step nucleation process with the formation of stable intermediate MSCs. Reproduced with permission from ref. [18]. Copyright 2015 American Chemical Society. (c) Formation of monodisperse InP QDs using zinc-phosphorus complexes as the stable phosphine precursor. Reproduced with permission from ref. [19]. Copyright 2017, American Chemical Society. (d) UV-Vis absorption spectra of monodisperse InP QDs with varying radii. The inset indicates the energies of the first exciton peak of InP QDs with varying sizes.
example is dimethylaminophosphine (P(NMe₂)₃) with indium halide as an inexpensive, low-reactive alternative [21,29–31], yet the best outcome with respect to the size distribution of InP QDs results from the P(TMS)₃ complexes. The most widely used method is the addition of stable metal-phosphine intermediates and P(TMS)₃ as the phosphine precursor to sustain spontaneous growth (e.g. in the carboxylate-P(TMS)₃ complex [32], Zn carboxylate-P(TMS)₃ complex [19], and InP magic-size nuclei [18]) (Figure 2(b,c)). With these strategies, monodisperse InP QDs with various sizes can be synthesized (Figure 2(d)).

In addition to the emission center and the spectra linewidth, the luminescence efficiency and stability of QDs are of main importance for practicable use in light-emitting applications. The luminescence efficiency and stability of QDs are related with the surface properties of QDs [2]. From the spectroscopic viewpoint, the luminescence efficiency is defined as the ratio between the radiative recombination rate and the non-radiative recombination rate. In QDs, the broken bonds at the surface atoms indeed play the role of the non-radiative recombination centers, which are responsible for the reduction of the luminescence efficiency of QDs. In addition, the charge carriers localized at the surface atoms promote the chemical reactions of QDs with the environmental oxidative species (e.g. O₂), leading to irreversible degradation. As a means to improve the luminescence efficiency and stability, the epitaxial growth of a wide-bandgap inorganic semiconductor on the emissive core (the so-called core/shell heterostructure) [33] has been applied to InP QDs [20]. The first approach, based on the accumulated experience and knowledge obtained from Cd chalcogenides, was the growth of a ZnS shell on the exterior of the InP QD. Since after the success of such approach, the structural design of the core/shell heterostructure has evolved into a sophisticated one to attain high levels of luminescence efficiency and photochemical robustness. One representative example is the adoption of a buffer layer with an intermediate lattice constant and bandgap (ZnSe [34–36] or GaP [37]) between the InP emissive core and the ZnS exterior shell layer (Figure 3(a,b,c)). The ZnSe or GaP inner-shell buffer layers that mitigate the structural stress between the InP core and the ZnS exterior shell aid the uniform growth of the thick outermost shell layer, enabling the achievement of a narrow spectra linewidth as well as enhanced luminescence efficiency and stability. The authors recently devised a ZnSeₓS₁₋ₓ composition gradient shell layer in which the Se-rich region near

Figure 3. (a) Schematic illustration of the state-of-the-art visible QDs (core/multishells) and the compositions of each compartment. (b) Bulk bandgap and lattice constant of chemical compounds (InP, GaP, ZnTe, ZnSe, and ZnS) consisting of heavy-metal-free, visible QDs. (c) Photograph of environmentally benign red-(left, InP), green-(middle, InP), and blue-emitting (right, ZnSeₓTe₁₋ₓ) QD solutions under UV irradiation. (d) PL spectra envelop of heavy-metal-free, visible QDs (ZnSe for violet to blue emission, ZnSeₓTe₁₋ₓ for blue to green emission, and InP for green to red emission). (e) The CIE color space with a PL spectra of primary-colored QDs (ZnSeₓTe₁₋ₓ QDs for blue, InP QDs for green and red). For comparison, standard color spaces such as DCI-P3 and NTSC 1952 are also provided as dotted and dashed lines.
the InP core relaxes the structural stress and the S-rich region outside the shell effectively confines the charge carriers inside [38]. The resulting InP/ZnSe$_{x}$S$_{1-x}$ QDs successfully accomplish the emission spectrum from green to red (emission center: 500-650 nm), with a high photoluminescence quantum yield (PL QY > 90%), a narrow spectra linewidth (FWHM ~ 35 nm), and photochemical stability (Figure 3(c,d)), which goes beyond the color quality for high-quality cinema displays (DCI-P3) or for the standard full-HD television (NTSC 1953) (Figure 3(e)).

Together with InP QDs, QDs made of ZnSe, ZnTe, or their alloy (ZnSe$_{x}$Te$_{1-x}$), whose center emission covers violet to green, have been investigated to comprehend the entire visible spectra. Peng X. G. et al. reported the synthesis of ZnSe QDs with a narrow size distribution (emission center from 400 to 440 nm, FWHM as low as 14 nm) by adopting alkylamines as an activation agent for unreactive zinc carboxylates (Figure 3(d)) [13]. Unfortunately, it seems that the emission range of ZnSe QDs that will enable it to serve as a blue emitter in displays that should meet the emission center at 450–460 nm cannot be achieved. While the bulk bandgap of ZnSe corresponds to ca. 460 nm, an increase in size reaching the bulk regime accompanies the inevitable PL QY loss as a consequence of the lessened charge carrier confinement. As an alternative route, alloying ZnSe with ZnTe has been adopted to expand the spectral tunability. Omata et al. recently reported the synthesis of blue to green ZnSe$_{x}$Te$_{1-x}$ QDs with a narrow size distribution by introducing a Te precursor in the established ZnSe synthetic process (Figure 3(d)) [15,16]. As is the case with InP QDs, passivating ZnSe or ZnSe$_{x}$Te$_{1-x}$ QDs with ZnS has yielded PL QY enhancement (> 80%) and photochemical stability (unpublished results).

QD-based electroluminescence [5,39–41], converting electricity to light without intervening steps, has been studied for more than two decades to integrate the excellent optical properties of QDs to the form of energy-efficient and versatile light-emitting diodes (LEDs) for full-color displays [42], signages [43], and lightings [44]. The typical QD-LEDs are constructed with multiple functional layers that deliver electrons and holes directly into the QD emissive layer (Figure 4(a)). As an emitter for electroluminescence, QDs allow for the thermal exchange of singlet and triplet states and hence promise 100% device efficiency in the ideal case [45]. Unwanted factors, however, such as the structural defects in QDs [46,47], the imbalanced charge injection [48–51], or the exciton dissociation under the electric field [52,53], provoke non-radiative recombination processes of the charge carriers in QDs and deteriorate the performance of QD-LEDs. Multilateral efforts in the aspects of device physics (e.g. proper charge transport materials, structural design of devices, and fabrication process) and material science (e.g. improving the PL QY of QDs or developing elaborate core/shell heterostructures) have been made to address these daunting issues. As a result, the state-of-the-art QD-LEDs based on Cd-based QDs exhibit ca. 20% external quantum efficiency (EQE) for all the primary colors [54–56], which is close to the theoretical limit assuming a 20% outcoupling factor.

In contrast to the dazzling progress achieved in Cd-based QDs, QD-LEDs accommodating heavy-metal-free
alternatives are still pinned at a lower efficiency regime (Figure 4(b)). For instance, the peak EQEs of InP and CuInS2 QD-LEDs remain below 7% [57,58] as of this writing. QD-LEDs with ZnSe QDs reached this level of efficiency a bit earlier [12,59] but their efficiency is still far below that of the other II–VI families. Even worse is the fact that the operational stability of these devices has not been reported. Considering that QD-LEDs take the electrodes and charge transport layers with proven performance, the inferior device performance is primarily attributed to the immaturity of heavy-metal-free QDs. Despite the surprising progress in PL QYs, as discussed earlier, the limited choice for shell materials and the lack of an elaborate synthetic scheme hold back the realization of tailored core/shell heterostructures optimized for electroluminescence. In addition, the device engineering that has led to the enhancement of QD-LEDs adopting Cd-based QDs is not directly applicable to the Cd-free QDs owing to the discrepancy in the energy levels of the QDs [36] (Figure 4(c)), which further complicates the situation.

The non-radiative Auger recombination (AR) processes [2,60] within the QD active layer in working QD-LEDs are indeed responsible for the deterioration of the device performance [48–50]. Therefore, suppressing the AR processes [49,61] or circumventing the situation to encounter the AR processes [48,50] are the solutions that will enhance the device efficiency and operational stability of QD-LEDs. From the perspective of device physics, balancing the rates of electron and hole injection into the QD active layer is of crucial importance for improving the device performance [48,49,51]. In contrast to QD-LEDs with Cd-based QDs, whereby the hole injection into the QDs is largely restricted, the energy levels of ZnSe\(_{x}\)Te\(_{1-x}\) or InP QDs reside at positions (∼1 eV) higher than those of Cd-based QDs, and as such, the QD-LEDs employing these QDs suffer from electron injection deficiency (Figure 4(c)), which necessitates the modification of the electron transport layers or interfacial engineering between the QD active layer and the electron transport layer to facilitate electron injection into the QDs [36]. Simultaneously with the device optimization, the structural engineering of the core/shell heterostructures in QDs needs to be elaborated to suppress the AR processes in the QDs at working devices.

QDs consisting of I–II–VI\(_2\) (e.g. CuInS\(_2\) [62–64], CuInSe\(_2\) [65], and AgInS\(_2\) [66,67]) and doped QDs (e.g. Cu- or Mn-doped ZnSe [68,69]) have also been considered heavy-metal-free alternatives. The synthetic route and structural design of these emitters are quite similar to those of II–VI or III–V QDs. The pyrolysis of metal halides or metal carboxylates with chalcogentrialalkylphosphines or alkylthiols allows the control of the size [69,70], shape [71,72], and composition of QDs [63,68,69] with tunable emission from visible (ca. 520 nm) to NIR (up to ca. 1100 nm) (Figure 5(a,b)). Core/shell heterostructuring with wide-bandgap semiconductors can also improve the PL QY of these QDs to above 90%, as well as their photochemical stability [12,64,73], as demonstrated in the II–VI or III–V QDs’ similarities.

Regardless of the chemical intersection with II–VI or III–V QDs, the optical properties of I–II–VI\(_2\) or doped QDs contrast with respect to the extent of the Stokes shift and the emission linewidth. Whereas both light absorption and emission are associated with the band-to-band transition in the typical QDs, the charge carriers residing in the mid-gap intrinsic (e.g. Cu\(^+\) or Cu\(^{2+}\), depending on the stoichiometry of CuInS\(_2\) (Figure 5(c)) [74] or extrinsic defect states (Mn or Cu in ZnSe) [11,68,69] of those alternatives participate in the photon generation, and hence, the energy disparity between the absorption (through band-to-band transition) and emission (through band edge-to-defects or vice versa) bands increases with the extent of the trap energy. This large Stokes shift is beneficial for preventing the reabsorption of light by the emitter themselves in the form of dense films [75,76]. The uncontrollable chemical inhomogeneity around the emission center, however, imposes a large inhomogeneous broadening in the ensemble (≥300 meV, Figure 5(d,e)) [62]. Therefore, the application field of I–II–VI\(_2\) and doped QDs is suitable for lightings demanding a broadband continuous emission profile or reabsorption-less solar energy down-conversion [75,76] (see the next section) rather than displays.

3. Light harvesting

Colloidal QDs have been actively investigated as a light absorber in solar cells because of the ease of energy level engineering therein (i.e. bandgap, energy level position, polarity control) [2–4], the promise for overcoming the Shockley-Queisser limit by exploiting multiple carrier generation (MEG) [2,77], and the solution processability suitable to low-cost manufacturing. The advances in material science and device engineering have led to the continuing progress of the device performance, and QD solar cells with a power conversion efficiency (PCE) exceeding 16.6% appeared in the NREL efficiency chart of late. All these progresses have been made using Pb-based QDs [77–80], whose chemistry is well established, but there will be a demand particularly for heavy-metal-free QDs for the successful commercialization of this technology, as witnessed in the display case.
QDs composed of binary III–Vs (InAs [8, 81], InSb [82]) and ternary compounds (AgBiS₂ [83], AgBiSe₂ [84], AgSbS₂ [85]) have been identified as alternatives for the active materials in solar cells owing to their physical properties comparable with those of the Pb-based QDs (e.g. high dielectric constant and large extinction coefficient over the NIR range) promising efficient light absorption and charge separation. Up to now, the AgBiS₂-QD-based solar cell holds the record efficiency (6.31% PCE) [83] (Figure 6(a–c)), and further advancement is expected after the controlled synthesis of AgBiS₂ QD materials to preclude inhomogeneity in the crystal structure, size, and composition, and the surface chemistry for passivating high-density surface trap states is enabled.

InAs-QD-based solar cells were also recently demonstrated by Jeong et al. [8, 86] InAs has generated particular interest as a light absorber in the solar cell community owing to its intrinsic optoelectronic and electrical properties (i.e. high absorption coefficient, high electron mobility, and large exciton Bohr radius [\(\sim 34 \text{ nm}\)]) that are suited to high-efficiency, thin-film solar cells [87]. Moreover, the large disparity between the effective electron and the hole mass pushes the threshold of MEG down to 2\(E_g\), promising the full exploitation of solar energies to generate electricity [81]. Despite these benevolent physical properties of InAs, there have been few reports on InAs QD thin-film solar cells mainly due to the difficulties in the controlled synthesis of InAs QDs with a narrow size distribution. Reports on the surface chemistry for InAs QDs that governs the electrical conductivity of the QD active layers and thus the efficiency of devices have been few as well. A breakthrough has been made by Tamang et al., who developed schematics using InAs clusters as single-source precursors, enabling the scalable synthesis of InAs QDs with a narrow size distribution [86]. Song et al. [8] recently devised a chemical means to passivate the surface defects of InAs QD films using short surface ligands (e.g. 1,2-ethanedithiol, 3-mercaptopropionic acid, Br, Cl, and I), and reported a certified p-n junction solar cell with 7.92% PCE based on n-type InAs QDs and p-type PbS QDs (Figure 6(d,e)).

In addition to the active materials in solar cells, QDs are receiving a great deal of attention as the
light-converting pigments in luminescent solar concentrators (LSCs) [7,75,76]. LSCs are optically transparent devices that concentrate the external light coming from the front plane to their edges through the total internal reflection mode. The concentrated light is harvested in the form of electrical energy by the thin traditional photovoltaic cells terminated at the edges of the LSCs (Figure 7(a)) [75]. To fully exploit the light concentrated on the edges in the form of electricity, LSCs start to incorporate phosphors that convert the broadband solar spectrum to a certain narrow range (e.g. 800–900 nm for Si solar cells) where the photovoltaic devices hold the best photon conversion efficiency. LSCs were initially motivated to meet the grid parity of solar energy when solar cells were the most expensive component in the overall system. As the production cost of solar panels is currently declining, however, the role of LSCs has evolved from that of supplemental power generation devices to small power output devices integrated with various daily-life objects, such as transparent or colored windows, decorative walls, or roofs.

One of the major technical issues in LSCs is the unavoidable energy loss through the self-reabsorption originating from the small Stokes shift of the typical phosphors. The large spectral overlap between the absorption and emission spectra amplifies the reabsorption of the converted light by the phosphors themselves, leading to the reduction of the PL QYs of the media, and in turn, of the system efficiency. As a means to detour the self-reabsorption processes in LSCs, QDs with a large Stokes shift (e.g. I-III-VI2, doped QDs) have drawn keen attention (Figure 7). The different origins of the absorption and emission states in I–III–VI2 and doped QDs enlarge the Stokes shift by more than ~300 meV, which is able to fully eliminate the spectral overlap [75,76]. Moreover, achieving a tunable absorption range by controlling the size or chemical composition of LSCs allows the changing of their color appearance from visible-transparent (e.g. Mn2+ -doped ZnSe [76], Figure 7(c,d)) to tinted (CuInSe2-S2-x/ZnS [75], Figure 7(a)), which allows the ubiquitous use of LSCs for various purposes. LSCs are now expanding their territory to include other solar-energy-harvesting systems. Recently, UbiQD demonstrated that QD-LSCs can be adopted in greenhouses to convert the solar spectrum to a specific emission range optimized for the photosynthesis of plants (e.g. tomatoes, cucumbers, cannabis) (Figure 7(b)) [88].

4. Summary and perspective

The strict regulation of the use of toxic elements in real-life applications has motivated the research on a new class of quantum dots (QDs) made of...
Figure 7. (a) Schematic description of LSCs incorporating CuInSe$_2$$_{1-x}$ QDs and their band-edge electronic structures. Adopted with permission from ref. [75]. (b) Photograph of a spectrum-controlled greenhouse with CuInS$_2$ films to improve the plant production. Reproduced with permission from UbiQD, Inc. (c) Absorption and PL spectra of Mn$^{2+}$-doped ZnSe/ZnS QDs. (d) Photograph of LSCs containing Mn$^{2+}$-doped ZnSe/ZnS QDs under UV irradiation. Reproduced with permission from ref. [76]. Copyright 2014, American Chemical Society.

Among the potential candidates, group III–V (InP, InAs, and InSb), group II–VI (ZnS, ZnSe, ZnTe, and ZnSe$_x$Te$_{1-x}$), and group I–III–VI$_2$ or I–V–VI$_2$ (CuInS$_2$, CuInSe$_2$, AgInS$_2$, AgInSe$_2$, AgBiS$_2$, and AgSbS$_2$) semiconductors have been rigorously scrutinized as alternatives for Cd- or Pb-containing QDs. The advances in the synthesis and surface chemistry allow for the bandgap tunability covering the entire visible and NIR region, promising the practicable use of such QDs in a range of light-emitting or light-harvesting applications.

The recent achievements in visible QDs represent the success in controlling the single-exciton dynamics of QDs made of heavy-metal-free compounds. To expand their application fields, the photophysical properties and stability of these QDs still need improvement. Particularly, efforts to engineer the multicarrier dynamics of QDs that dictate the performance of QD-LEDs or high-power light sources are still largely lacking. It is believed, however, that the sophisticated design of the core/shell heterostructures with the aid of advances in chemistry and theoretical directives will facilitate the attainment of Auger-suppressed, high-efficiency, and environmentally benign QDs and will eventually permit their practicable use in displays, lightings, and lasers.

QD solar cells with Pb-free materials have been demonstrated, but their performance is currently inferior to that of the devices employing Pb-based QDs or other solution-processed competitors. The reason for the poor device performance is mainly attributed to the deficiency of the surface chemistry that enables the customization of the doping polarity, trap concentration, or conductivity of the QD active layer. Understanding and locating the surface state, followed by successful passivation without interfering carrier separation in Pb-free QDs, will increase the device efficiency and stability, and will thus accelerate the emergence of QD solar cells in the market.

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