

REVIEW

A perspective of mesoscopic solar cells based on metal chalcogenide quantum dots and organometal-halide perovskites

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We review two types of inorganic nanomaterials—metal chalcogenide quantum dots (QDs) and lead halide perovskites—that serve as prospective light harvesters in hybrid mesoscopic solar cells. Metal chalcogenide QDs are introduced in three parts: chalcogenides of cadmium (CdS, CdSe and CdTe), chalcogenides of lead (PbS and PbSe) and chalcogenides of antimony (Sb₂S₃ and Sb₂Se₃). The devices made using these chalcogenide QDs in a liquid-type electrolyte showed the best cell efficiencies, ranging from 3 to 6%. For solid-state QD-sensitized solar cells (QDSCs), the device performances were generally poor; only devices made of Sb₂S₃ and PbS QDs attained cell efficiencies approaching ~7%. In contrast, nanocrystalline lead halide perovskites have emerged since 2009 as potential photosensitizers in liquid-type sensitized TiO₂ solar cells. In 2012, the efficiencies of the all-solid-state perovskite solar cells were enhanced to 9.7 and 10.9% using anodes of TiO₂ and Al₂O₃ films, respectively, with 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD) as a hole-transporting material. In 2013, the performance of a TiO₂ solar cell sensitized with lead iodide perovskite (CH₃NH₃PbI₃) was optimized further to attain an overall power conversion efficiency $\eta = 15\%$, which is a new milestone for solar cells of this type having a device structure similar to that of a dye-sensitized solar cell.

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INTRODUCTION

Generating cost-effective and environmentally benign renewable energy remains a major challenge for scientific development. Solar energy, which is abundant and sustainable, has attracted enormous interest in terms of research and development for many years. The developments in emerging photovoltaic techniques are taking place at a rapid pace. Most such devices involve inexpensive solution processing with high device performance.^{1–3} Solar cells (SCs) of these new types differ from traditional SCs in their unique mesoscopic structural features, with large surface areas that dominate their photovoltaic performance.^{4–6} For example, a dye-sensitized SC (DSSC) uses a monolayer of light-absorbing sensitizer anchored on nanocrystalline TiO₂ to enhance light harvesting in a mesoporous environment in which charge separation also occurs at this interface. The design of a DSSC involves an important feature: the light harvesting and charge transport are spatially decoupled.⁷ Since the early success of using nanocrystalline TiO₂ as a charge collector, DSSCs have been considered a low-cost alternative to semiconductor-based photovoltaic devices.⁸ In 2011, Yeh, Diau and Grätzel developed an efficient DSSC based on an *ortho*-substituted porphyrin sensitizer, YD2-oC8, co-sensitized with an organic dye (Y123) with a cobalt

electrolyte to attain remarkable power conversion efficiency (PCE = 12.3%),⁹ which opened a new research area on porphyrin-sensitized SCs (PSSCs).¹⁰ However, the absorption spectrum of the YD2-oC8 system covers only the visible spectral region, 400–700 nm, and the lack of light-harvesting ability beyond 700 nm (near infrared) limits the PSSC from further enhancement of the device performance. Moreover, the enduring stability of PSSCs might be an issue for future commercialization. Various inorganic light absorbers with a light-harvesting capability that extends into the near-infrared region were hence sought to replace the delicate organic dyes.

Inorganic semiconductor quantum dots (QDs) have been extensively investigated as new photosensitizers or light absorbers to replace conventional organic-type sensitizers in DSSCs because of their excellent properties—tunable energy band gaps via varied and controlled size and shape of the nanocrystals, large optical absorption coefficients, large dipole moments for enhanced charge separation, and multiple exciton generation (MEG).^{11–18} For example, the performance of QD-sensitized SCs (QDSCs) has been significantly enhanced for Sb₂S₃-sensitized TiO₂ solar cells using a blended layer of poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT)

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and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) as a hole-transporting material (HTM) to attain $\eta = 6.3\%$.¹⁵ Hybrid passivated QDSCs using PbS colloidal QDs (CQDs) as a photosensitizer attained an efficiency of more than 7.0%,¹³ and a large short-circuit photocurrent density ($J_{SC} \sim 30 \text{ mA cm}^{-2}$) was reported for a PbS:Hg QDSC.¹⁸ In general, using an inorganic light-harvesting material to replace a conventional organic or organometallic sensitizer has the advantage of obtaining superior device durability.

Typical semiconductor QDs have an average diameter of 1–10 nm, which indicates that surface states or midgap trap states can be produced on the surfaces of the nanocrystals during the synthesis of the QDs via layer deposition on the photoanode of the solar cells. For mesoporous TiO_2 /QD solar cells, nanocrystalline QDs can be adsorbed and deposited on the surface of the TiO_2 nanoparticles, but the QD coverage on the surface of the TiO_2 nanoparticles may be a problem. As a result, these QDSC devices typically show a small open-circuit voltage (V_{OC}) and a poor fill factor (FF) because of the charge loss at the interface of the TiO_2 /QD/HTM layers. To increase V_{OC} and FF, we must decrease the charge loss in the QD layer and suppress the charge recombination in the TiO_2 /QD and TiO_2 /HTM interfaces. For this purpose, an insulating Al_2O_3 scaffold, surface passivation of QD films and interfacial engineering of buffer layers with organic and inorganic modifications have been employed to enhance the charge separation and charge transport in solar cells.^{2,13,17}

A major advance in the development of novel inorganic sensitizers occurred in 2012: Park and Grätzel reported submicrometer thin-film solid-state solar cells attaining a PCE of 9.7% with a methyl ammonium lead-iodide perovskite sensitizer, $\text{CH}_3\text{NH}_3\text{PbI}_3$, in a mesoporous TiO_2 film (thickness 0.6 μm).¹² This perovskite sensitizer has a band gap of 1.5 eV with the energy levels of the conduction band (CB) and the valence band (VB) matching well the CB of TiO_2 and the highest occupied molecular orbital of HTM, respectively. At nearly the same time, Snaith and co-workers¹¹ reported a similar perovskite, $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$, that served as a light absorber for mesoscopic thin-film solid-state solar cells to attain a PCE of 10.9%, for which the mesoporous Al_2O_3 film served as a scaffold to replace the *n*-type TiO_2 electron-transporting layer. In 2013, Snaith and co-workers reported a significantly enhanced PCE of 12.3% for perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ solar cells with the same device structure based on Al_2O_3 .² Concurrently, Seok and co-workers³ reported the same superior PCE of 12.3% for another perovskite solar cell, $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$, with the mesoporous TiO_2 -based device structure. Also in 2013, Grätzel and co-workers¹ reported perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) TiO_2 solar cells with a PCE approaching 15%, which set a new record for all-solid-state hybrid mesoscopic solar cells (HMSCs). The significant discovery of perovskites as novel photovoltaic materials has hence opened a new channel for the development of third-generation solar cells with the advantages of very high efficiency, low cost, ease of processing and considerable durability.

In this review, we summarize the recent investigations into novel inorganic materials, including both metal chalcogenide QDs and halide perovskite nanocrystals, applied as light-harvesting layers for HMSCs. Figures 1a and b are diagrams of the potential levels of various metal chalcogenide QDs and halide perovskites, respectively. Metal chalcogenide sensitizers of three types were introduced for QDSCs: they are classified as cadmium (Cd) chalcogenides, lead (Pb) chalcogenides and antimony (Sb) chalcogenides. The band gap energies (E_g /eV) of the metal chalcogenides decreased systematically as the chalcogenides varied from sulfur (S) through

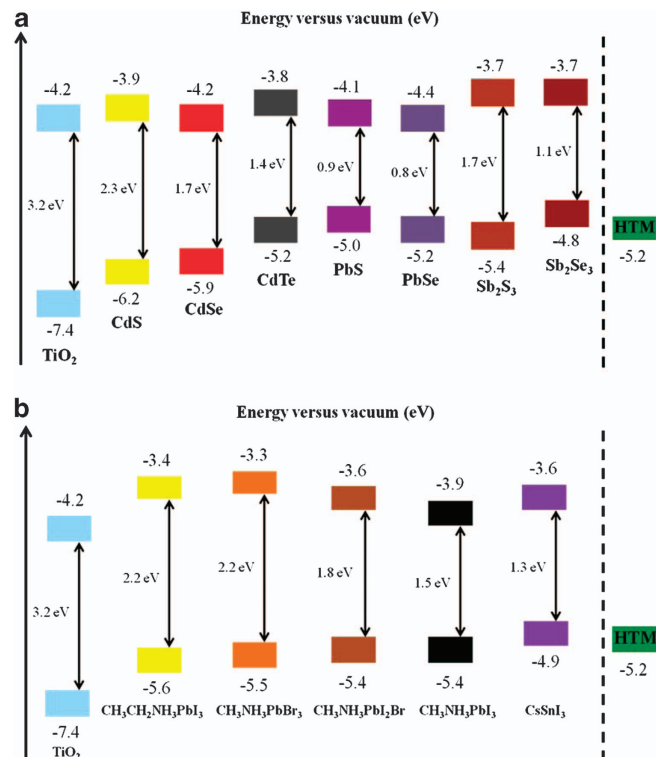


Figure 1 Energy levels vs vacuum of various (a) metal-chalcogenide quantum dots (QDs) and (b) organometal-halide perovskites as prospective light absorbers for hybrid mesoscopic solar cells. The particle sizes are shown in parentheses with the related references shown as superscripts for TiO_2 (bulk),¹⁸ CdS (5 nm),⁸⁸ CdSe (3 nm),³³ CdTe (3.8 nm),³³ PbS (2.4 nm),¹⁸ PbSe (4.5 nm),⁴⁸ Sb_2S_3 (5 nm),⁸⁶ Sb_2Se_3 (5 nm),⁹⁹ $\text{CH}_3\text{CH}_2\text{NH}_3\text{PbI}_3$ (1.8 nm),¹⁰² $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (7 nm),¹⁰⁶ $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Br}$ (10 nm),¹⁰⁷ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (2.5 nm)¹² and CsSnI_3 (bulk)¹¹²; HTM represents spiro-OMeTAD.¹²

selenium (Se) to tellurium (Te). For the halide perovskite materials, tuning the band gap of $\text{CH}_3\text{NH}_3\text{PbX}_3$ was achieved by varying the halide constituents ($X = \text{Cl}, \text{Br}$ or I); the E_g of the system decreased along this direction. This review provides detailed descriptions of the synthesis, characterization, photovoltaic performance and challenges for two inorganic materials, Sb_2S_3 QDs and perovskite nanocrystals, because of their efficient performance as light-harvesting materials for HMSCs. We also introduce strategies for the improvement of the performances of these QD devices and perovskite materials via surface passivation and interfacial modification with varied device structures.

CADMIUM CHALCOGENIDE QDSCS

Cadmium-chalcogenide QD-based solar cells have been intensively studied over the past two decades to improve device performance and stability in ambient conditions. The photoactive sensitizers of these solar cells are composed of cadmium sulfide (CdS),^{19–25} cadmium selenide (CdSe),^{26–33} cadmium telluride (CdTe)^{34–38} and their alloy nanocrystals.^{39–46} CdS has an optical band gap of 2.25 eV, and thus it can only absorb light up to $\sim 550 \text{ nm}$; CdSe, with a band gap of 1.7 eV, can absorb light below $\sim 720 \text{ nm}$; CdTe has an energy gap of 1.45 eV and an optical absorption edge at $\sim 860 \text{ nm}$. The CB edges of CdSe and some CdTe nanocrystals were located below that of the TiO_2 film (Figure 2), which resulted in poor and limited electron

injection from the QD to the TiO₂, and substantial charge recombination occurred at the TiO₂/QD/HTM interfaces.^{34,39} Moreover, the use of iodide and polysulfide electrolytes led to the degradation of these QD nanocrystals and a gradual deterioration of the photovoltaic performances.^{20,27,28,34}

To find a solution for the above problem, co-sensitization of CdS/CdSe QDs on a TiO₂ film was reported.³⁹ The co-sensitized CdS/CdSe system showed improved light absorption, incident photon-to-current conversion efficiency (IPCE), and PCE over individual CdS or CdSe systems because more CdSe QDs were loaded onto the TiO₂ film. The rate of electron injection from CdSe to TiO₂ was significantly improved via the CdS layer and adjustment of the Fermi level, as shown in Figure 2.³⁹ ZnS passivation served to protect the QD sensitizers from the polysulfide electrolyte and to inhibit the charge recombination at the TiO₂/electrolyte interface. For devices made of CdSe_xTe_{1-x} alloy nanocrystals, the range of optical

absorption could be extended to ~900 nm, which reflects the band gap tuning effect of the CdSe–CdTe alloys, especially to enhance light harvesting in the range of 750–900 nm. Figure 3 shows the procedure used to synthesize the CdSe–CdTe QD nanocrystals by means of the layer-by-layer deposition approach, for which the optical band gaps of the alloy were systematically varied from 1.38 to 1.73 eV.⁴⁰ Using core–shell nanocrystals, recombination losses at the TiO₂/CdTe/CdSe interface can be effectively diminished through a cascade potential approach that yields a superior charge separation, as shown in Figure 4. The most striking feature of this CdTe/CdSe core–shell system, with a particle size ~10 nm, is its smaller band gap for light absorption toward the near-infrared region (~1000 nm).⁴¹ Instead of polysulfide electrolytes, quasi-solid-state polysulfide gel electrolytes, polymer electrolytes and solid-state HTM have been developed and examined for this type of QDSC, but the device efficiencies were reported to be less than 5%.^{20,27,28,42,43}

The solid-state solar cells based on CdS, CdSe and CdTe QDs have shown PCEs less than 6% because of their large band gaps, slow electron injection rates and substantial charge recombination at the TiO₂/QD/HTM interfaces. Thin-film solar cells made of CdSe_xTe_{1-x} alloys ($x = 0.9$ or 0.8) exhibited a PCE (~7.1%) smaller than that of a CdTe-only device (PCE = 7.3% at $x = 0$) because J_{SC} of the former is smaller than that of the latter, indicating that the electron transport and charge collection through the alloy layers encountered some difficulties in the devices. In summary, the ideal cadmium chalcogenide QDSC devices should have a large recombination resistance, a small chemical capacitance and a small series resistance due to a decreased rate of recombination and fewer trap sites at the TiO₂/QD interface. Furthermore, the device performance of the CdTe/CdSe QDSCs can be further improved by increasing the QD loading on the TiO₂ film to enhance the efficiency of light harvesting.

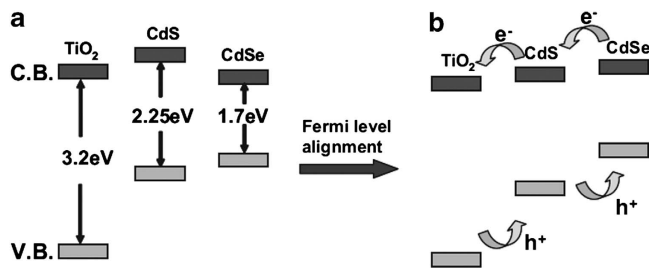


Figure 2 (a) Relative band edges of TiO₂, CdS and CdSe in bulk and (b) the proposed band edge structure for a TiO₂/CdS/CdSe electrode after redistribution of the electrons between the CdS and CdSe interface (described as alignment of the Fermi level of bulk materials) (adapted from Lee and Lo,³⁹ copyright 2009, Wiley-VCH Verlag GmbH & Co.).

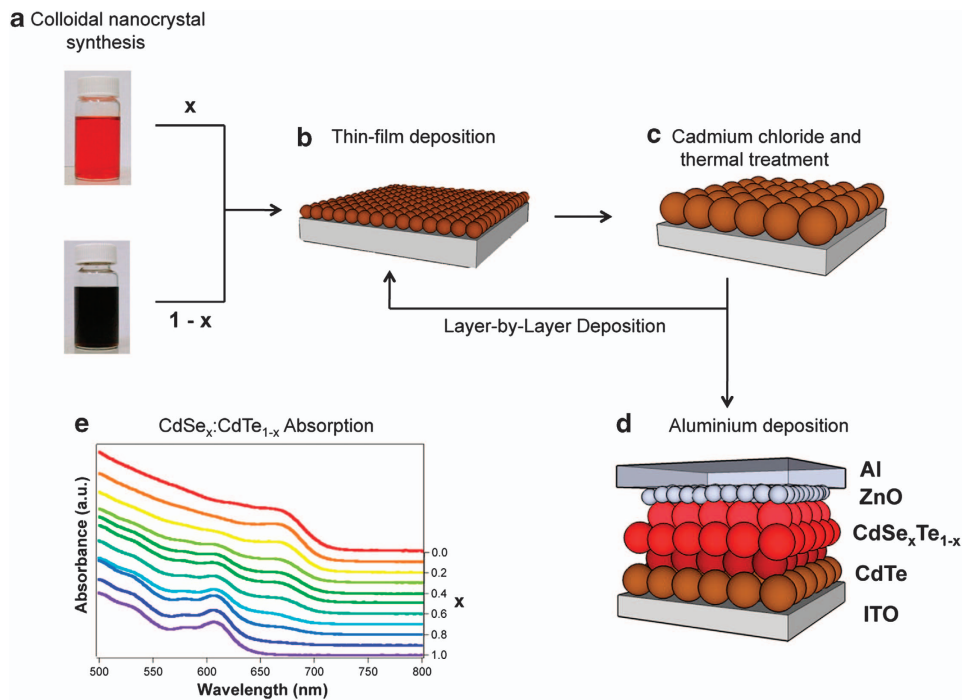


Figure 3 Schematic outline of the layer-by-layer fabrication process for CdSe_xTe_{1-x} nanocrystal solar cells. (a) CdSe and CdTe nanocrystals dispersed in pyridine/1-propanol are mixed at the desired ratio. (b) A thin film of CdSe_xCdTe_{1-x} is deposited by spin coating onto the ITO substrate. (c) The thin film is subjected to treatment with CdCl₂ followed by thermal annealing to promote crystal growth. This process is repeated as necessary to yield the desired device composition and active layer thickness. (d) Schematic image of a completed device, which includes a layer of nanocrystalline ZnO and an evaporated aluminum top contact. (e) Absorption spectra of CdSe_xCdTe_{1-x} solutions (adapted from MacDonald *et al.*,⁴⁰ copyright 2012, American Chemical Society).

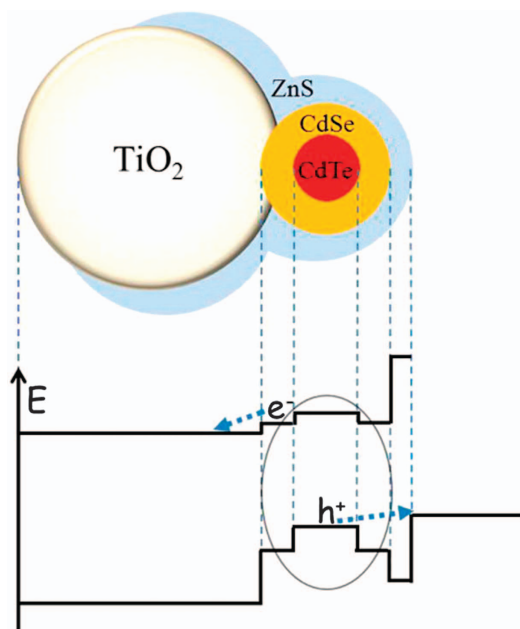


Figure 4 Schematic representation of a system consisting of a CdTe/CdSe type-II core/shell QD adsorbed on nanocrystalline TiO₂ and coated with a ZnS shell. An assumed band diagram of the system is also shown. Arrows show the charge directions after exciton generation (adapted from Itzhakov *et al.*,⁴¹ copyright 2013, American Chemical Society).

LEAD CHALCOGENIDE QDSCS

Lead-chalcogenide QD-based solar cells have been intensively examined in recent years because of the small band gaps of the QDs, which allow solar energy harvesting in the near-infrared region. For example, PbS QDs have an energy band gap in the range of 0.9–1.1 eV, and the optical absorption edge can be extended to ~ 1300 nm;^{13,18} the band gap energies of PbSe QDs were tuned from 0.7 to 1.7 eV by varying the sizes of the QDs, and the optical absorption edge was further extended to ~ 1500 nm.^{17,47,48} Under light illumination, the shunt resistance of the QDSCs was smaller than in the dark; the rates of charge recombination increased at the interfaces of QD–QD and TiO₂–QD because of the increased surface states and trap states. For the PbS CQD films, a high density of midgap trap states ($\sim 10^{17}$ cm⁻³ eV⁻¹) may deteriorate the device performance (Figure 5), which could be a crucial limiting factor in improving the device efficiency.¹³ PbSe QD solar cells suffered from significant current leakage and interfacial charge recombination; the film thickness of the photoactive layer was expected to be an important parameter in optimizing the PbSe device performance.⁴⁸

For PbS devices treated with CdCl₂, the trap states near the middle of the PbS band gap were determined to be $\sim 10^{16}$ cm⁻³ eV⁻¹, which is one-fifth of that in organic cross-linked and inorganic-treated PbS films.¹³ The PbS film treated with CdCl₂ showed the greatest hole mobility, $\mu_p = 4.2 \times 10^{-3}$ cm² V⁻¹ s⁻¹, and CdCl₂ plays a major role in the passivation of the midgap trap states and charge transport in the valence band. Greater photocurrent and voltage are achieved through decreased recombination and improved charge transport in the PbS device. Using PbS:Hg nanocrystals, the short-circuit photocurrent density of the device attained 30 mA cm⁻².¹⁸ The CB of the PbS QDs shifted upward with Hg²⁺ doping, and more rapid electron injection became feasible in the PbS:Hg QDSCs, as shown in Figure 6. The structural reinforcement of the Pb–S bonds and the

stability provided by the addition of Hg²⁺ were two major factors for the decreased charge recombination and enhanced charge transport in the PbS:Hg device. For the hydrazine-treated PbSe QDs, the external quantum efficiency (EQE) and internal quantum efficiency (IQE) were 114% and 130%, respectively, proving the MEG effect in the PbSe device shown in Figure 7.¹⁷ PbSe QDs were treated with ethane dithiol and hydrazine to increase the electronic coupling of the QD nanocrystals and decrease the surface states and trap states in the PbSe film. Approximately 1 mA cm⁻², or $\sim 4\%$ of the total photocurrent, was estimated to derive from the MEG effect in the PbSe device.¹⁷

In the core–shell structure, the PbSe core was covered with a PbS layer (thickness 0.5 nm). PbSe/PbS core–shell QDs have an absorption edge at 960 nm ($E_g \sim 1.29$ eV).⁴⁹ The PbS shell covering the PbSe core acted as surface passivation to protect the PbSe core, thus improving the chemical stability of the QD film. The IPCE reached $\sim 100\%$ at ~ 420 nm, indicating that the core–shell QDs on the TiO₂ surface had efficient light harvesting, enhanced electron injection from the QD to the TiO₂ CB, superior charge transport in the TiO₂ layer and retarded charge recombination in the QD film. For PbS_{0.9}Se_{0.1} alloy QDSCs, an EQE above 100% at a photon energy of 2.76 eV (~ 440 nm) was obtained.⁵⁰ PbS_{0.9}Se_{0.1} alloy QDs showed a sharp absorption peak at 1076 nm due to strong quantum confinement. PbS_{0.9}Se_{0.1} alloy QD films were treated with ethane dithiol to increase electronic coupling in the PbS_{0.9}Se_{0.1} QDs. Greater EQE and J_{SC} values were obtained upon increasing the film thickness to 360 nm because of the increased optical absorption and higher charge generation in the device. Other PbS(Se) QD solar cells have been reported with efforts to improve the charge transport and retard the charge recombination in the devices.^{51–83}

ANTIMONY CHALCOGENIDE QDSCS

Synthesis of Sb₂S₃ QDs on a mesoporous TiO₂ film

Antimony sulfide Sb₂S₃ QDs have been synthesized on a mesoporous TiO₂ film by means of the chemical bath deposition (CBD) method.^{14,15,84} Messina *et al.* reported a CBD procedure to form an Sb₂S₃ thin film coating on microscope glass slides.⁸⁴ SbCl₃ (1.3 g) was dissolved in acetone (5 ml); this SbCl₃ solution was kept at a temperature below 4 °C for several hours. A Na₂S₂O₃ solution (50 ml, 1 M) and deionized water (145 ml) were also kept at a temperature below 4 °C for several hours before the solutions were mixed. The cold SbCl₃ and Na₂S₂O₃ solutions were mixed with continuous stirring, and the cold deionized water was added to the mixed solution. This final mixing initially gave a nearly clear solution. The substrates containing the TiO₂ films were placed vertically in the CBD bath for 2–3 h in a refrigerator (4–7 °C). The color of the Sb₂S₃-coated TiO₂ film changed from yellow to orange-yellow and finally to brown during the CBD. Thereafter, the TiO₂ films coated with Sb₂S₃ were carefully washed with deionized water and dried at around 23 °C for several hours in air.

As the CBD-processed Sb₂S₃ exhibited an amorphous phase, the Sb₂S₃-coated TiO₂ films were annealed at 300–330 °C for 30 min under Ar (or N₂) inert conditions to form a crystalline stibnite structure. Itzhak *et al.*⁸⁵ reported that this annealing method, which forms an Sb₂O₃ surface passivation layer on the surface of the Sb₂S₃ sensitizer, improved the device performance, resulting in a PCE of 3.4%. This passivation layer on the Sb₂S₃ surface can inhibit the electron-hole recombination through its insulating nature ($E_g \sim 3.7$ eV), but an Sb₂O₃ layer that was thick enough to act as an energy barrier, disturbing the electron injection from the Sb₂S₃ sensitizer to the TiO₂ film, thus degrading the device performance significantly.

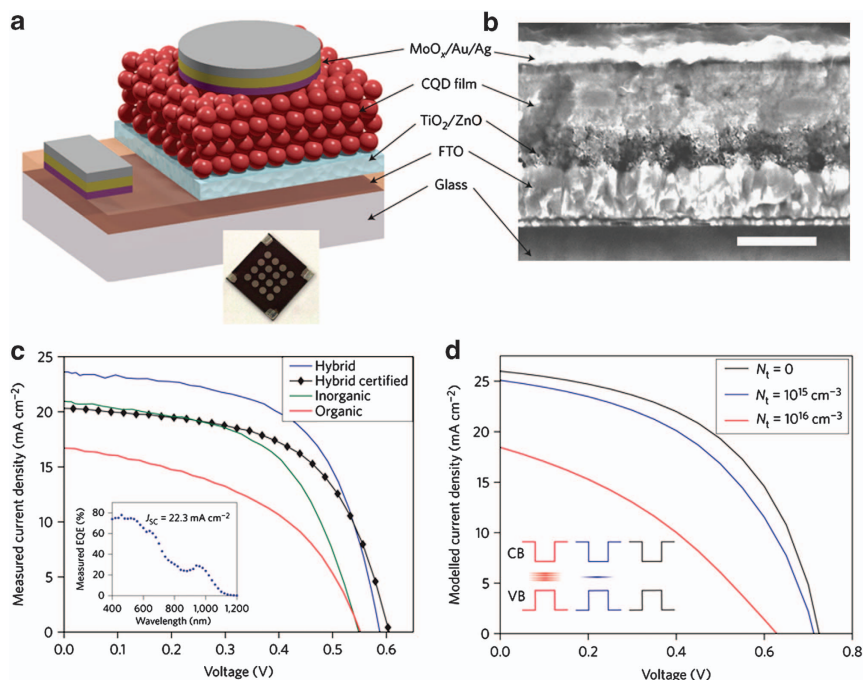


Figure 5 Performance of CQD photovoltaics as a function of passivation. (a) Schematic of the depleted heterojunction CQD device used in this work. Inset: photograph of a typical device (substrate dimensions, 25 mm × 25 mm). (b) Cross-sectional s.e.m. image of the same device. Scale bar, 500 nm. (c) Measured current–voltage characteristics under AM1.5-simulated solar illumination for representative devices employing organic (red), inorganic (green) and hybrid (blue) passivation schemes. Black diamonds denote the J – V curve for a hybrid passivated device as measured in an accredited photovoltaic calibration laboratory (Newport Technology and Application Center-PV Lab). Inset: EQE curve of a hybrid passivated device. The integrated current value is also shown. (d) Simulated J – V curves of devices with varying midgap trap densities, demonstrating the detrimental effect of traps (adapted from Ip *et al.*¹³ copyright 2012, Macmillan Publishers Limited).

Electronic properties of Sb₂S₃ sensitized on TiO₂ films

Patrick and Giustino⁸⁶ reported on the structural and electronic properties of Sb₂S₃-sensitized QDSCs and found an almost perfect interface between the TiO₂ film and the QD sensitizer because of the lattice match of the TiO₂ substrate with the Sb₂S₃ layer. As Figure 8 shows, no significant structural defects in the TiO₂/Sb₂S₃ interface were found; the electronic distributions corresponding to the CB of Sb₂S₃ show a direct interfacial Ti–S coupling between Sb₂S₃ and TiO₂. The CB edge (E_{CB}) of the Sb₂S₃ sensitizer is located ~ 0.5 eV above the E_{CB} of the TiO₂ film (Figure 1a); superior electron injection from the CB of Sb₂S₃ to the CB of TiO₂ would hence be expected. For the TiO₂/Sb₂S₃ solar cells, the theoretical value of V_{OC} can be predicted to be as high as 1.6 V, based on the calculated energy-level diagram; this value indicates that V_{OC} might be increased experimentally by optimizing the other parameters related to hole-transporting materials.

Optical absorption and IPCE of the Sb₂S₃-based solar cells

Crystalline Sb₂S₃ has an optical absorption coefficient $\alpha \sim 10^5$ cm⁻¹ in the visible region. Stibnite Sb₂S₃ nanocrystals deposited on a mesoporous TiO₂ film have a particle size of ~ 5 – 10 nm.^{14,15} The TiO₂/Sb₂S₃ system shows an excellent match of energy levels for electron injection and transport after light harvesting by the Sb₂S₃ sensitizer. The corresponding TiO₂/Sb₂S₃ solar cell (SC) showed IPCE values between 70 and 90% in the visible region with various hole-transporting materials, such as CuSCN, spiro-OMeTAD and poly(3-hexylthiophene-2,5-diyl) (P3HT).^{14,15,87–94} The IPCE curves feature an optical absorption onset at ~ 750 nm, which is consistent with the crystalline Sb₂S₃ band gap of ~ 1.65 eV. Seok and co-workers reported

an IPCE loss¹⁵ in the wavelength range of 450–650 nm, as P3HT can absorb light in this wavelength region, but the charges generated by P3HT were incompletely transferred to the Au counter electrode (CE) in the TiO₂/Sb₂S₃/P3HT device. This IPCE loss was fully recovered by adding PCBM for additional conducting channels, as shown in Figure 9.

Photovoltaic properties of the Sb₂S₃-based solar cells

Etgar and co-workers fabricated Sb₂S₃/P3HT solar cells with a 1-decyl phosphonic acid (DPA) surface treatment to improve the device performance.⁹⁴ Such a device attained a PCE of 3.9%, which was significantly superior to that of a device without this surface treatment ($\eta = 3.1\%$). The enhanced performance was due to the smaller dark current and greater electron lifetime after the DPA surface treatment. For Sb₂S₃/CuSCN solar cells, oxygen plays an important role during the fabrication of solar cells: oxygen can decrease the series resistance of the device to enhance the overall device performance.⁸⁷ It was also reported that the formation of the Sb₂O₃ surface passivation layer helps to promote the device performance.⁸⁵ For the Sb₂S₃/spiro-OMeTAD solar cells, J_{SC} increased nonlinearly with increasing light intensity.⁹² This condition might indicate that the hole diffusion from spiro-OMeTAD to the Au electrode is a bottleneck responsible for the nonlinear behavior of the photocurrents with increasing light intensity. The charge losses at higher light intensities can be decreased by improving the Sb₂S₃/Spiro-OMeTAD interface and using new HTM with a greater hole mobility. The highest efficiency of Sb₂S₃-based solar cells was reported to be 6.3% using PCPDTBT as an HTM layer, giving the device a remarkable photovoltaic

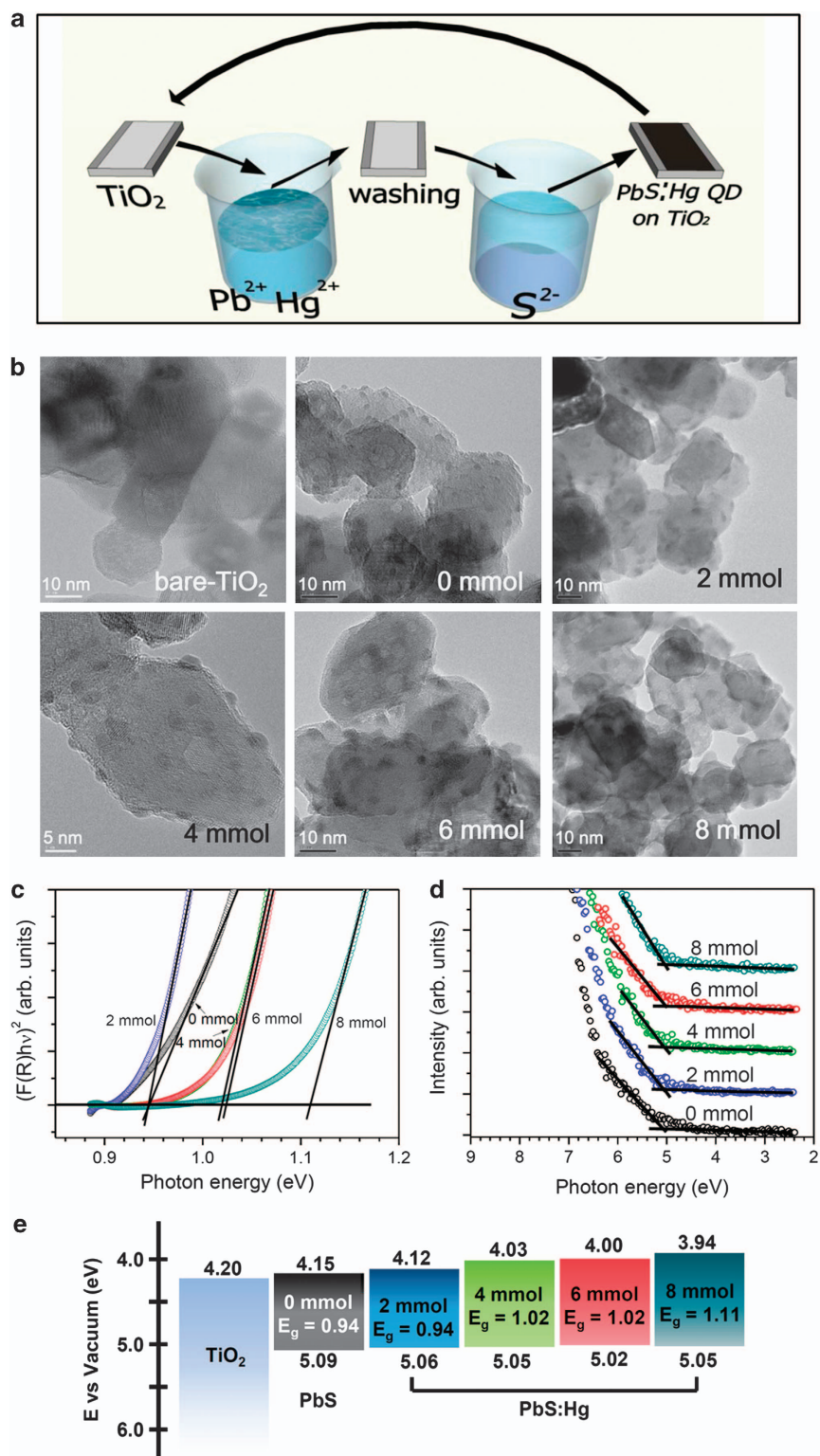


Figure 6 Morphology and energetic properties of PbS and PbS:Hg QDs. **(a)** Deposition of a PbS:Hg QD on a mesoporous TiO₂ nanostructure using successive ionic layer adsorption and reaction (SILAR). **(b)** TEM micrograph of bare TiO₂ and QD-coated TiO₂ nanoparticles using a cationic solution containing 0, 2, 4, 6 and 8 mmol of HgCl₂. **(c)** Tauc plot calculated using the Kubelka-Munk equation from the reflectance spectra. **(d)** UPS spectra of PbS:Hg QD-adsorbed TiO₂ and extrapolation of the region of small binding energy. **(e)** Band edge alignment diagram of PbS and PbS:Hg QD (adapted from Lee *et al.*,¹⁸ copyright 2013, Scientific Reports).

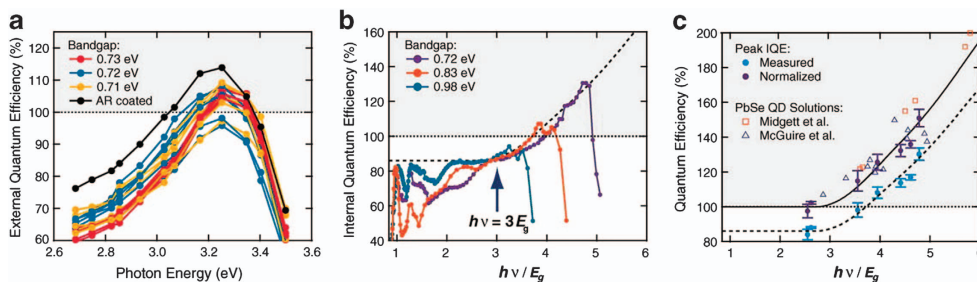


Figure 7 (a) EQE signals for 18 independent devices made with QD band gaps of 0.71 eV (yellow), 0.72 eV (blue) and 0.73 eV (red) and for a device with an antireflective coating (black). (b) Collected IQE curves vs the ratio of photon energy to band gap, $h\nu/E_g$, for the three QD sizes. The dashed curve is a published fit for colloidal QD, whereas here it has been normalized for intrinsic loss in the cell due to recombination. (c) Maximum IQE values for seven QD sizes. The peak IQE values have been corrected for the intrinsic loss in the solar cell (estimated at $\sim 15\%$). Error bars indicate the propagated uncertainty of 5 to 30 measurements at the given wavelength of both the reference detector and the test solar cell. The solid black curve is the original fit to colloidal QD; the dashed curve is the same as in (b). Hollow triangles and squares represent ultrarapid transient absorption measurements of PbSe QD solutions (adapted from Semonin *et al.*,¹⁷ copyright 2011, American Association for the Advancement of Science).

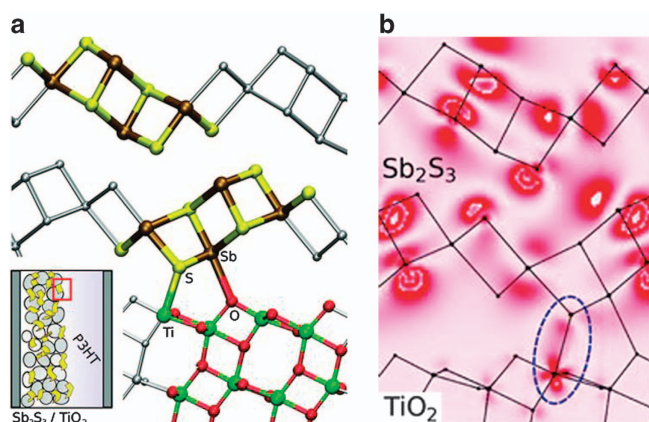


Figure 8 (a) Atomistic model of the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface derived in this work. The colored atoms represent the periodic repeat unit; the view is along the TiO_2 [010] direction. The lengths of the Ti-S and O-Sb bonds are 2.67 and 2.81 Å, respectively. Inset: Schematic representation of the stibnite-sensitized solar cell of Chang *et al.*, with the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface highlighted. (b) Isodensity plot of the Kohn-Sham LUMO state of Sb_2S_3 at the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface. The charge density is plotted in a plane through the Ti-S bond. The coupling between the S-3p states of the sensitizer and the Ti-3d states of the substrate, which provides a path for electron injection, is highlighted (adapted from Patrick and Giustino,⁸⁶ copyright 2011, WILEY-VCH Verlag GmbH & Co., Weinheim Germany).

performance, with $J_{\text{SC}} = 16.0 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.595 \text{ V}$ and $\text{FF} = 0.655$.¹⁵ Ito and co-workers⁸⁹ reported $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{CuSCN}$ solar cells with a TiO_2 surface treatment ($\eta = 4.1\%$). The TiO_2 devices in which the surface was treated with $\text{BaTiO}_3/\text{MgO}$ showed much greater efficiency compared with untreated $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{CuSCN}$ devices (4.1% vs 2.8%). The $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface has been improved by a $\text{BaTiO}_3/\text{MgO}$ surface treatment; passivation of the TiO_2 surface was also performed at the $\text{TiO}_2/\text{CuSCN}$ interface.

Challenges in Sb_2S_3 -based solar cells

For Sb_2S_3 -based solar cells, theoretical simulations by Bisquert and co-workers⁸⁸ have shown an optimized efficiency of $\sim 8.5\%$ upon decreasing the series and hole-transport resistances and increasing the charge-collection efficiency. Because the electron-hole

recombination occurs mostly between the electrons of the CB in the TiO_2 layer and the holes in the HTM layer, the hole-transport properties of the HTM become important to improve the device efficiency of solar cells of this type.^{88,93} The challenge is hence to find new HTMs with great hole mobility and stability.

Haque and co-workers recorded nanosecond transient absorption spectra (TAS) of thin film samples with a $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{spiro-OMeTAD}$ configuration.⁹³ As Figure 10 shows, the rate of charge recombination at the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface decreased when more successive ionic layer adsorption and reaction (SILAR) cycles were involved, making the optical onsets of the Sb_2S_3 nanocrystals systematically red-shifted. This effect might decrease the rate of electron injection from the Sb_2S_3 sensitizer to the TiO_2 film and thus decrease the device efficiency, particularly in the wavelength region beyond 750 nm. Hole transfer from the Sb_2S_3 sensitizer to spiro-OMeTAD was much less sensitive to the spectral shift of the Sb_2S_3 absorption onset, indicating that the hole transport to spiro-OMeTAD might initiate charge separation at the $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{spiro-OMeTAD}$ interface and thus improve the device performance. The same group investigated $\text{Sb}_2\text{S}_3/\text{P3HT}$ films using the TAS technique.⁹⁵ After excitation at 567 nm, the P3HT^+ polaron band at 950 nm was monitored to investigate the kinetics of hole transport and charge recombination in $\text{Sb}_2\text{S}_3/\text{P3HT}$ films. According to the TAS results, the P3HT^+ polaron band was strongly dependent on the hole transfer from Sb_2S_3 to P3HT, indicating that this interfacial hole transport is a key parameter for improving the device performance.

Another approach for improving the device efficiency of QDSCs is to extend the optical absorption range of the QD to $\sim 1000 \text{ nm}$ to improve the light-harvesting performance of the device. The Sb_2S_3 nanocrystals can absorb light up to 750 nm with an optical band gap of $\sim 1.65 \text{ eV}$. To further extend the optical absorption into the near-infrared region, we must consider semiconductors with smaller band gaps, $E_g < 1.3 \text{ eV}$, such as Sb_2Se_3 .

Sb_2Se_3 -sensitized solar cells

Antimony chalcogenide semiconductor Sb_2Se_3 has an optical band gap of 1.0–1.2 eV and shows a strong optical absorption, with a coefficient α of $\sim 10^5 \text{ cm}^{-1}$ in the visible region.^{84,96–98} Theoretical predictions for J_{SC} as a function of the band gap E_g give the upper limits as 22 and 43 mA cm^{-2} for Sb_2S_3 ($E_g = 1.7 \text{ eV}$) and Sb_2Se_3 ($E_g = 1.13 \text{ eV}$) sensitizers, respectively.⁹⁶ For the Sb_2Se_3 -based

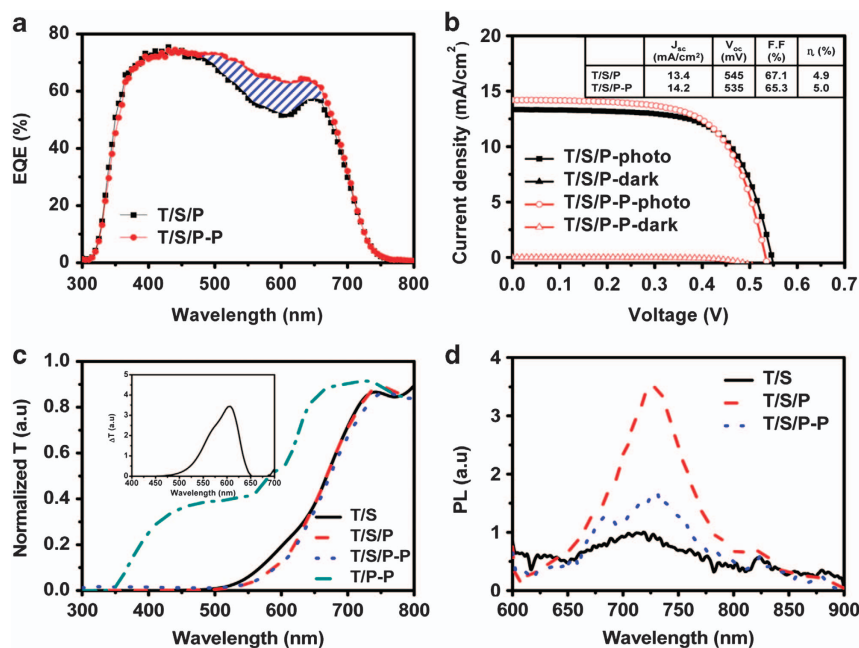


Figure 9 (a) EQE spectra: the region marked with blue lines is the EQE difference between the T/S/P-P and T/S/P samples. (b) J - V curves at $100\text{ mW}\cdot\text{cm}^{-2}$ light illumination (photo) and no illumination (dark). (c) Transmission spectra: the inset shows the transmission difference between the T/S/P-P and T/S/P samples. (d) PL spectra. The following abbreviations appear in the figure: T = mp-TiO₂, S = Sb₂Se₃, P = P3HT and P - P = P3HT/PCBM (adapted from Chang *et al.*,¹⁵ copyright 2012, American Chemical Society).

devices, the challenges involve finding an effective synthetic method for the Sb₂Se₃ nanocrystals deposited on the mesoporous film and finding a suitable HTM to match the energy levels.

Haque and co-workers reported TAS results for TiO₂/Sb₂Se₃/spiro-OMeTAD devices.⁹⁹ Sb₂Se₃ nanocrystals were deposited on the surface of TiO₂ (or ZrO₂ as a control experiment) with the SILAR method using SbCl₃ dissolved in acetone and selenide dissolved in ethanol under a N₂ atmosphere. The optical absorption of the Sb₂Se₃ nanocrystals increased and red-shifted with increasing SILAR cycles because of the increased surface coverage (QD loading) and size of the nanoparticles. Figure 11 shows the TA profiles and the energy level diagrams for the Sb₂Se₃ system with TiO₂ and ZrO₂ films; the yield of long-lived charge-separated states in the TiO₂ films was triple that in the ZrO₂ films because of the more rapid charge recombination of the latter. With increasing annealing temperature, the yield of charge separation was decreased, and the recombination lifetime also decreased because of the increased aggregation of the Sb₂Se₃ nanoparticles and the oxidation of the Sb₂Se₃ surface. A passivation layer of In_x(OH)_yS_z between TiO₂ and Sb₂Se₃ can diminish the interfacial charge recombination and thus increase the decay coefficients of the transient signals by ~ 10 times. For the TiO₂/Sb₂Se₃/spiro-OMeTAD devices, the spiro-OMeTAD⁺ charge yield was increased from 45 to 80%, and the lifetime of the separated charges was ~ 50 ms because of an effective match of the energy levels, a greater Sb₂Se₃ coverage on the TiO₂ film and the decreased interfacial charge recombination. For the ZrO₂/Sb₂Se₃/spiro-OMeTAD devices, small transient signals were observed due to an electron transfer from Sb₂Se₃ to the spiro-OMeTAD. In this device, the transient signals in the ZrO₂ films decayed much more rapidly than those in the TiO₂ film. The rapid decays observed in the ZrO₂ films are related to the recombination of the localized electrons inside the Sb₂Se₃ layer and the holes in the spiro-OMeTAD. The TAS results thus indicate that

Sb₂Se₃ might be an effective material for light harvesting in a highly efficient solid-state solar cell.

PEROVSKITE-BASED MESOSCOPIC SOLAR CELLS

Perovskite originally referred to a mineral containing CaTiO₃, named after Russian mineralogist Lev Perovski, and the term was later extended to encompass a class of compounds with a crystal structure of the same type as CaTiO₃. Figure 12 shows the unit cell of a three-dimensional crystal structure for perovskite compounds with the general chemical formula ABX₃. Instead of oxide perovskite species (X = O), halide perovskite compounds (X = Cl, Br or I) were found to feature excellent light-harvesting and electron-conducting properties and are perfectly suitable for use as prospective photovoltaic materials.¹⁻³

Perovskite-sensitized solar cells with liquid electrolytes

In 2009, Miyasaka and co-workers¹⁰⁰ reported the first perovskite-sensitized TiO₂ solar cell using liquid electrolytes based on iodide and bromide. According to their approach, lead bromide perovskite (CH₃NH₃PbBr₃) was deposited on the TiO₂ film with a spin-coating procedure with the precursor solution containing CH₃NH₃Br and PbBr₂. The coated TiO₂ film showed nanocrystalline particles approximately 2–3 nm in size on the surface of the TiO₂ nanoparticles. For these TiO₂/CH₃NH₃PbBr₃ solar cells, the IPCE action spectrum showed a maximum value of 65% at ~ 400 nm, but it fell to zero beyond 550 nm. The corresponding device with $J_{SC} = 5.57\text{ mA cm}^{-2}$, $V_{OC} = 0.96\text{ V}$ and $FF = 0.59$ gave a PCE of 3.1% under one-sun illumination.¹⁰⁰ For these TiO₂/CH₃NH₃PbI₃ solar cells, the IPCE spectrum showed effective optical absorption up to 800 nm with a maximum value of 45% at ~ 500 nm. As a result, the PCE (3.8%) was larger for the iodide perovskite device than for the bromide perovskite device because J_{SC} (11.0 mA cm^{-2})

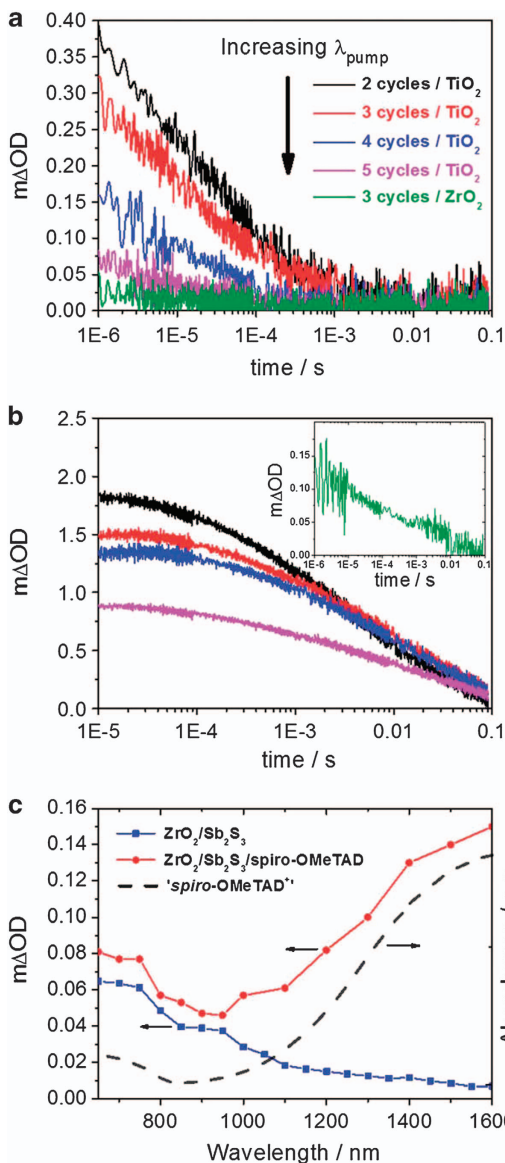


Figure 10 (a) Decay kinetics of the transient absorption of Sb₂S₃-localized holes in metal-oxide/Sb₂S₃/films probed at 800 nm. (b) Transient decay kinetics of spiro-OMeTAD⁺ absorption in TiO₂/Sb₂S₃/spiro-OMeTAD (main figure) and ZrO₂/Sb₂S₃/spiro-OMeTAD (inset) films probed at 1600 nm. In both (a) and (b), λ_{pump} is varied to probe increasingly red-absorbing nanocrystals while ensuring similar ground state absorbance (2 SILAR cycles (black trace)—450 nm excitation, 3 cycles (red)—510 nm, 4 cycles (blue)—570 nm, 5 cycles (pink)—650 nm). Values of ΔOD are scaled to the number of photons absorbed at λ_{pump}. Laser excitation energy density = 26 μJ cm⁻² at 450 nm. (c) Transient absorption spectra of ZrO₂/Sb₂S₃ (blue trace) and ZrO₂/Sb₂S₃/spiro-OMeTAD (red trace) recorded 1 μs after photoexcitation at 510 nm (laser excitation energy density = 40 μJ cm⁻²). Absorption spectrum of spiro-OMeTAD in chlorobenzene chemically oxidized with N(PhBr)₃SbCl₆ (black dashed trace) (adapted from OMahony *et al.*,⁹³ copyright 2012, Royal Society of Chemistry).

was much greater for the former than for the latter, even though the V_{OC} of the former device was only 0.61 V.

Later in 2011, Park and co-workers¹⁰¹ reported on the improved efficiency of TiO₂ solar cells sensitized with lead iodide perovskite (CH₃NH₃PbI₃) and an electrolyte based on iodide. In their approach,

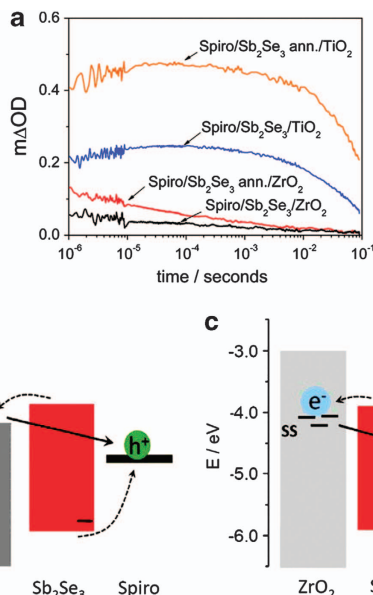


Figure 11 (a) Transient kinetics of spiro-OMeTAD/Sb₂Se₃/TiO₂ and spiro-OMeTAD/Sb₂Se₃/ZrO₂ films recorded at 1600 nm. (b, c) The energy diagrams of the systems include the recombination paths monitored with transient optical measurements (solid arrows) and previous processes (dashed arrows). All measurements were taken under N₂, exciting all samples at 450 nm (fluency 6.9 μJ cm⁻²). The energy level for spiro-OMeTAD was reported elsewhere (adapted from Guijjaro *et al.*,⁹⁹ copyright 2012, American Chemical Society).

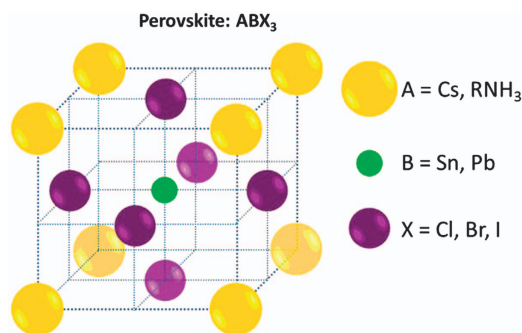


Figure 12 Schematic representation of the organometal-halide perovskite structures ABX₃ with possible species A, B and X as indicated.

Pb(NO₃)₂ was used for modification of the surface of a mesoporous TiO₂ film before coating the perovskite QD, such that Pb(NO₃)₂ acted as a blocking layer in the solar cells. After the TiO₂ surface modification, the device showed an improved PCE of 6.5% with J_{SC} = 15.8 mA cm⁻², V_{OC} = 0.70 V and FF = 0.58; the improved V_{OC} was due to the retarded charge recombination effected by the surface treatment. The authors also mentioned the stability of the perovskite nanocrystals in the iodide electrolyte, whereby the perovskite QD gradually dissolved into the iodide electrolyte after being irradiated for 10 min.

The organic part of the perovskite species is modifiable through a similar synthetic approach. For example, a CH₃CH₂NH₃PbI₃ sensitizer can be deposited on a mesoporous TiO₂ film via spin coating with an equimolar mixture of CH₃CH₂NH₃I and PbI₂ in a γ-butyrolactone solution.¹⁰² The average diameter of the

$\text{CH}_3\text{CH}_2\text{NH}_3\text{PbI}_3$ nanocrystals was approximately 1.8 nm; the optical band gap of this species increased to ~ 2.2 eV, as estimated from the diffuse reflectance spectra. For the $\text{TiO}_2/\text{CH}_3\text{CH}_2\text{NH}_3\text{PbI}_3$ solar cells, the IPCE spectrum attained a maximum value of $\sim 60\%$ at ~ 600 nm, giving a PCE of 2.4% in the iodide-based electrolyte. The poor performance of the device was due to the large optical band gap of the perovskite sensitizer of this type, which limited light harvesting in the visible region.

Synthesis of lead-iodide perovskites on metal-oxide films

Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanocrystals were formed on mesoporous TiO_2 films via spin coating with a solution containing $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 in an equimolar ratio.^{12,101} The concentrations of the spin-coating solution were varied from 10 to 40% by mass in γ -butyrolactone. The nanocrystalline $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ layer formed on the surface of the TiO_2 film after drying at temperatures from 40 to 160 °C for 30 min, typically at 100 °C for 30 min. With an increasing concentration of the coating solution, the color of the perovskite $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ on the TiO_2 film varied from yellow (10% by mass) to black (40% by mass). These perovskite nanocrystalline materials have an average diameter of approximately 2.5 nm, showing QD behavior on the surface of the TiO_2 nanoparticles, according to the TEM images shown in Figure 13.¹⁰¹

Instead of the mesoporous TiO_2 film, an insulating Al_2O_3 layer served as a scaffold for coating the perovskite halide ($\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$) as a light harvester on the surface of the Al_2O_3 film. The perovskite nanocrystalline film was prepared from a precursor solution containing $\text{CH}_3\text{NH}_3\text{I}$ and PbCl_2 in a molar ratio of 3:1 in anhydrous N,N -dimethylformamide.¹¹ After spin-coating and drying, the halide perovskite absorber on the Al_2O_3 film had an I:Cl ratio of approximately 2:1, according to the energy-dispersive X-ray analysis.

Electronic properties of lead iodide perovskites on metal-oxide films

Park and co-workers reported an alignment of the energy levels in a lead iodide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) QDSC. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanocrystals served as the light absorber, and spiro-OMeTAD was used as the hole-transporting layer. This perovskite nanomaterial adsorbed on a TiO_2 film had a direct optical transition with an energy gap E_g of ~ 1.5 eV.¹² From the energy-level alignment shown in Figure 1, we expect excellent properties of the device for electron injection and charge separation; that is, electrons can feasibly inject from the perovskite species into the CB of a TiO_2 film, and holes can transfer from the sensitizer perovskite to the spiro-OMeTAD HTM.

Snaith and co-workers¹¹ reported on a perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$) absorber on the surface of an insulating Al_2O_3 film. This insulating Al_2O_3 has a wide band gap E_g of 7–9 eV and acts purely as a mesoporous scaffold for the perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$) to be deposited. In this case, the photo-induced electrons could not inject into the Al_2O_3 film because of the insulating nature of the metal-oxide film, but the holes generated in the perovskite could propagate into the HTM layer, as shown in Figure 14. After charge separation between the $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$ absorber and the spiro-OMeTAD HTM, the photo-induced electrons were transported directly from the perovskite on the surface of the Al_2O_3 to the FTO electrode. The perovskite species thus acts as a bi-functional material to perform both light-absorbing and electron-transport functions. The authors also found that the rates of electron transport (diffusion) in the Al_2O_3 -based devices were 10 times those in TiO_2 -based devices, according to the data for the transient photocurrent decay shown in Figure 14. These data demonstrate the superior photovoltaic performance of the perovskite SCs using a mesoporous insulating metal-oxide layer rather than a conventional mesoporous TiO_2 film.

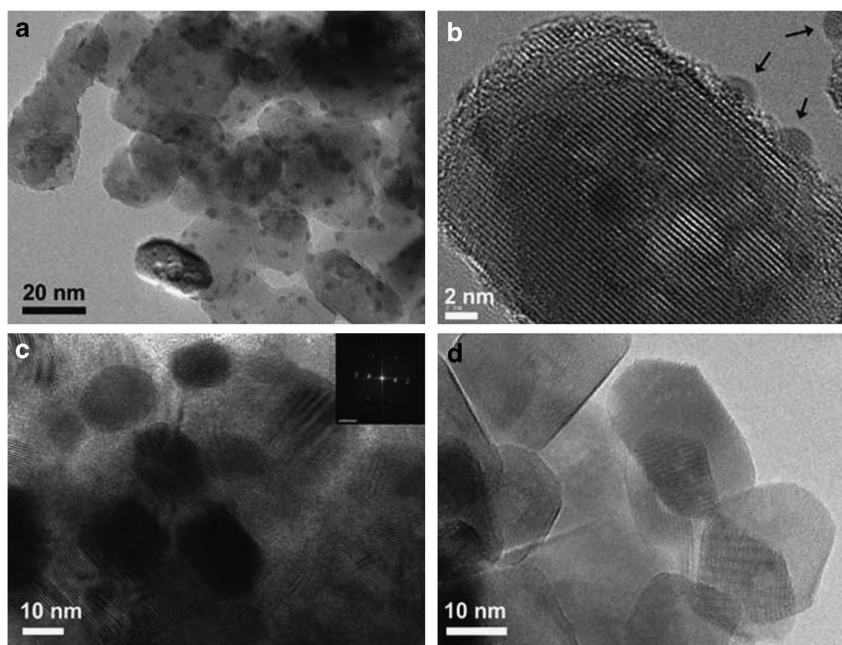


Figure 13 TEM micrographs of (a) a wide view of $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ deposited on TiO_2 , (b) a magnified image of $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ deposited on TiO_2 , (c) pure $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ and (d) bare TiO_2 . Arrows in (b) indicate quantum dot perovskite $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ with a hemispherical shape. Inset in (c) shows a selected-area electron-diffraction pattern of pure $(\text{CH}_3\text{NH}_3)\text{PbI}_3$. For the (a) and (b) TEM images, 30.18 and 40.26% (by mass) perovskite precursor solutions were used, respectively (adapted from Im *et al.*,¹⁰¹ copyright 2011, Royal Society of Chemistry).

Photovoltaic characteristics of perovskite solar cells

Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanocrystals have large coefficients of optical absorption in the visible region, ranging from 10^4 to 10^5 cm^{-1} .¹² These nanocrystals also have excellent matching of energy levels with those of TiO_2 . Interfacial bonding of perovskites with TiO_2 and spiro-OMeTAD was effective in ensuring uniform penetration and complete filling of the pores. Figure 15 shows the photovoltaic performance of the corresponding device; the IPCE values attained a maximum higher than 60% at 450 nm and were maintained greater than 50% up to 750 nm. The IPCE characteristics indicate that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanocrystals deposited on the mesoporous TiO_2 film feature excellent light-harvesting properties, bestowing an excellent quantum efficiency to the device in the visible region. The perovskite device of 0.6- μm film thickness showed a high photocurrent density ($J_{\text{SC}} = 17.6 \text{ mA cm}^{-2}$) and $V_{\text{OC}} (=0.88 \text{ V})$, a satisfactory FF ($=0.62$) and excellent overall device performance ($\eta = 9.7\%$) under one-sun irradiation.¹² With increased thickness of the TiO_2 film, both V_{OC} and FF of the device decreased because of the increased dark current and resistance to electron transport. The results obtained from the TAS measurements indicate that the holes were completely transferred from the perovskite sensitizer to the spiro-OMeTAD HTM after

charge separation in the sensitizer; the normalized photocurrent density was linearly proportional to the light intensity (Figure 15), without charge loss.¹²

Mixed-halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$) nanocrystals have an optical absorption onset ($\lambda \sim 800 \text{ nm}$) similar to that of the iodide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) mentioned previously. Figure 16 presents a comparison of the photovoltaic performance of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ SCs using either the TiO_2 or the Al_2O_3 film as the metal-oxide layer.¹¹ For the Al_2O_3 -based device, the IPCE curve attains a maximum value greater than 80% at 400 nm, and the values are maintained at greater than 60% up to 700 nm; for the TiO_2 -based device, the IPCE values are slightly smaller than those of the Al_2O_3 -based device, with similar J_{SC} for both devices.¹¹ The V_{OC} of the Al_2O_3 device was, however, much greater than that of the TiO_2 device because the loss of injection potential was much less for the former than for the latter. As a result, V_{OC} significantly increased ($\sim 200 \text{ mV}$) for the devices from the TiO_2 film to the insulating Al_2O_3 film, and the best device efficiency of 10.9% was found for the Al_2O_3 device under one-sun conditions.¹¹

In 2013, Snaith and co-workers² reported highly efficient perovskite $\text{CH}_3\text{NH}_3\text{Pb}(\text{I},\text{Cl})_3$ solar cells, with the efficiency of the best device approaching 12.3% based on a mesoporous Al_2O_3 film that was

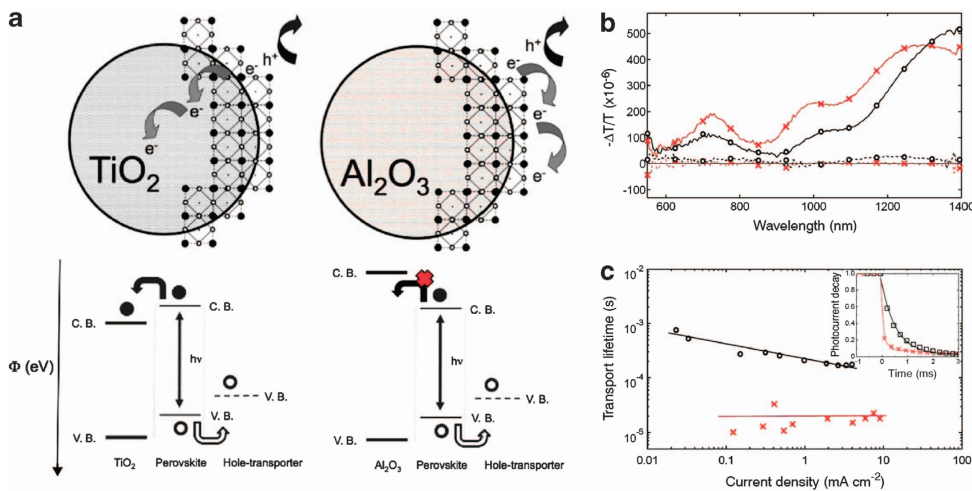


Figure 14 (a) Illustration of charge transfer and transport in a perovskite-sensitized TiO_2 solar cell (left) and a non-injecting Al_2O_3 -based perovskite solar cell (right). (b) Photo-induced absorbance (PIA) spectra of mesoporous TiO_2 (black open circles) and Al_2O_3 (red crosses) films coated with perovskite with (solid lines) and without (dashed lines) spiro-OMeTAD hole transporter. $\lambda_{\text{ex}} = 496.5 \text{ nm}$, repetition rate 23 Hz. (c) Charge transport lifetime determined with a small-perturbation transient photocurrent decay of perovskite-sensitized TiO_2 (circles with a black line) and Al_2O_3 cells (red crosses with a line). Inset shows normalized photocurrent transients for Al_2O_3 (red trace with crosses every seventh point) and TiO_2 (black trace with circles every seventh point) cells, set to generate 5 mA cm^{-2} photocurrent from a background light bias (adapted from Lee *et al.*,¹¹ copyright 2012, American Association for the Advancement of Science).

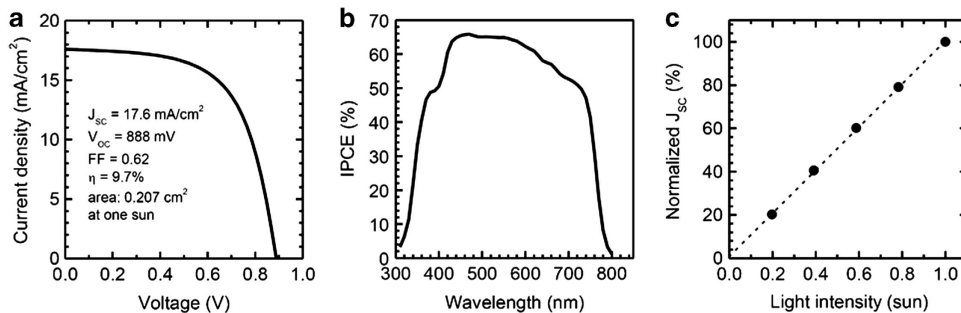


Figure 15 Photovoltaic characteristics of a $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ perovskite-sensitized solar cell. (a) Photocurrent density as a function of forward bias voltage. (b) IPCE as a function of incident wavelength. (c) Short-circuit photocurrent density as a function of light intensity (adapted from Kim *et al.*,¹² copyright 2012, Scientific Reports).

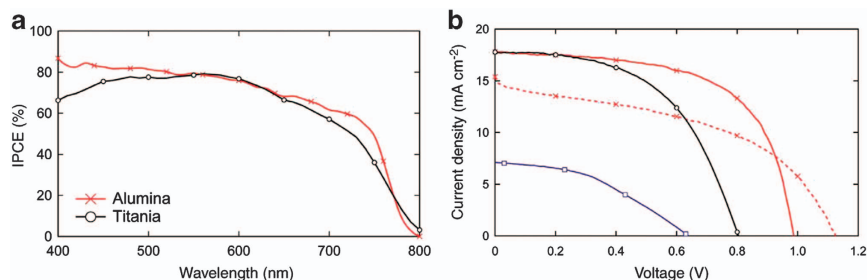


Figure 16 (a) IPCE action spectrum of an Al_2O_3 -based and perovskite-sensitized TiO_2 solar cell, with a device structure of FTO/compact TiO_2 /mesoporous Al_2O_3 (red trace with crosses) or mesoporous TiO_2 (black trace with circles)/ $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}/\text{Spiro-OMeTAD}/\text{Ag}$. (b) Current-voltage characteristics under illumination (simulated AM1.5G 100mWcm^{-2}) for Al_2O_3 -based cells, with one cell exhibiting great efficiency (red solid trace with crosses) and one exhibiting greater than $V_{\text{OC}} 1.1\text{V}$ (red dashed line with crosses); a perovskite TiO_2 -sensitized solar cell (black trace with circles); and a planar-junction diode with a structure FTO/compact $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}/\text{Spiro-OMeTAD}/\text{Ag}$ (purple trace with squares) (adapted from Lee *et al.*,¹¹ copyright 2012, American Association for the Advancement of Science).

$\sim 0.4\ \mu\text{m}$ thick. For the Al_2O_3 films with a thickness less than $0.4\ \mu\text{m}$, the perovskite solar cell had an efficiency of $\sim 9.1\%$ with a capping layer of thickness of $0.3\text{--}0.4\ \mu\text{m}$. For the Al_2O_3 films with a thickness greater than $0.4\ \mu\text{m}$, the perovskite solar cells had, in contrast, an efficiency near 12% without a perovskite capping layer. Seok and co-workers reported on perovskite $\text{CH}_3\text{NH}_3\text{Pb}(\text{I},\text{Br})_3$ solar cells with a maximum efficiency of 12.3% .³ In contrast with the approach of Snaith, using the Al_2O_3 film as a scaffold for perovskites, the best device performance of Seok's method was achieved using TiO_2 films of thickness $\sim 0.6\ \mu\text{m}$. For the mesoporous TiO_2 -based devices, the efficiency was optimized by using an alloy comprising both $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ crystals, resulting in increased device efficiency and superior device stability. The mixing ratios of the solutions containing perovskites $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ were reported for x varying in the range of $0.06\text{--}0.20$. Figure 17 presents the stability data of the devices, indicating that the devices containing less Br ($x=0.06$ or zero) had a higher efficiency than the others in the initial stage of the test, whereas those containing more Br ($x=0.20$ or 0.29) exhibited superior durability under ambient conditions because of their compact nanocrystalline structure.

Seok and co-workers also fabricated perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{poly-triarylamine (PTAA)}$ solar cells with an efficiency of 12% .¹⁰³ The device using PTAA as an HTM layer showed much better performance than those using other polymeric hole conductors such as P3HT ($\eta \sim 6.7\%$), PCPDVTBT ($\eta \sim 5.3\%$) and PCDTBT ($\eta \sim 4.2\%$). Park and co-workers¹⁰⁴ demonstrated perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells based on rutile TiO_2 nanorods with an efficiency of 9.4% . Park's results indicate that the photovoltaic performance was strongly dependent on the length of the TiO_2 nanorods because of the efficiency of charge generation rather than because of the kinetics of charge recombination. Hagfeldt and co-workers¹⁰⁵ reported perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{spiro-OMeTAD}$ solar cells with an efficiency of 8.5% . The spiro-OMeTAD device showed a much improved performance compared with devices using P3HT ($\eta \sim 4.5\%$) and 4-(diethylamino)-benzaldehyde diphenylhydrazone (DEH) ($\eta \sim 1.6\%$) because of the greater electron lifetime of the former. Other perovskite-based HMSCs have been studied, with various TiO_2 nanostructures and HTMs.^{106–109} Hagfeldt and co-workers¹¹⁰ reported $\text{ZrO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{spiro-OMeTAD}$ solar cells with an efficiency of 10.8% . Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{fullerene}$ heterojunction hybrid solar cells have also been fabricated.¹¹¹

Chung *et al.*¹¹² reported the use of perovskite CsSnI_3 as an HTM in solid-state DSSCs. Perovskite CsSnI_3 is a direct band gap p -type

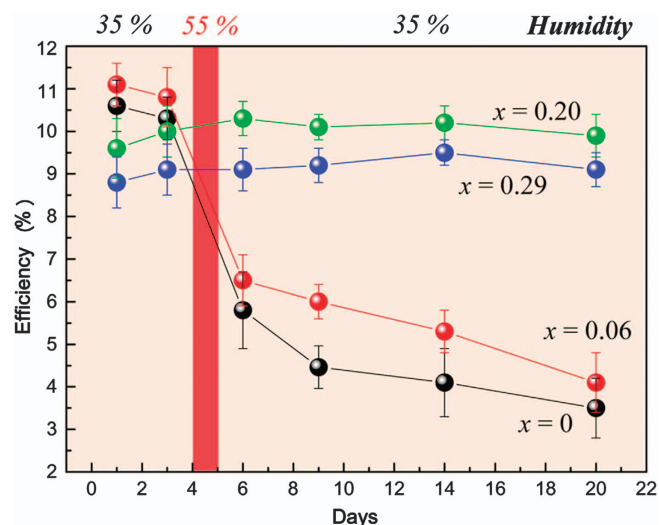


Figure 17 Variation of the power conversion efficiency of heterojunction solar cells based on $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ ($x=0, 0.06, 0.20, 0.29$) with time, stored in air at around $23\ ^\circ\text{C}$ without encapsulation. The humidity was maintained at 35% ; the cells were exposed to 55% humidity on the fourth day to investigate the variation in performance under high humidity (adapted from Noh *et al.*,³ copyright 2013, American Chemical Society).

semiconductor with an optical absorption onset at $1.3\ \text{eV}$ (Figure 1b), and it has a large hole mobility ($\mu_{\text{h}} = 585\ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$) near $23\ ^\circ\text{C}$; the latter value is $100\text{--}1000$ times that of a polymer-type HTM. As a result, the device consisting of $\text{CsSnI}_{2.95}\text{F}_{0.05}/\text{N719 dye}/\text{TiO}_2$ attained a PCE of 8.5% with an enhanced IPCE in the red visible region.¹¹² Chen *et al.*¹¹³ reported Schottky solar cells based on perovskite CsSnI_3 thin films; these films were prepared by coating multiple layers of SnCl_2 and CsI on a glass substrate followed by annealing at $175\ ^\circ\text{C}$ on a hotplate for $1\ \text{min}$ under ambient conditions. The CsSnI_3 film was formed during annealing from the SnCl_2/CsI stack. The JV characteristic curve showed a small PCE (0.88%) for an SC of this type. The perovskite mesoscopic solar cell without an HTM layer was reported to possess a PCE of 5.5% .¹¹⁴

Challenges in perovskite-based solar cells

The synthesis of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanocrystals is sensitive to ambient humidity. According to results reported elsewhere,¹⁰¹ the

perovskites gradually dissolved into a liquid-type electrolyte after irradiation for 10 min. As a result, anhydrous starting materials should be used in a dry box during synthesis. Another issue is the thickness and porosity of the HTM layer (such as spiro-OMeTAD) coated on the surface of the perovskite. For example, the contact resistance and series resistance at the interface of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ /spiro-OMeTAD/cathode must be decreased by optimizing the thickness of the spiro-OMeTAD layer. A thinner spiro-OMeTAD layer is required to decrease the series resistance and hole-transport

resistance through the spiro-OMeTAD to the cathode. As the conductivity of a typical halide perovskite is on the order of $10^{-3} \text{ S cm}^{-1}$, the spiro-OMeTAD layer should be thick enough to prevent an electrical short circuit between the perovskite layer and the counter electrode. Greater FF and PCE of the devices can be achieved by employing new types of HTMs with greater mobility and by introducing a thin capping layer on the perovskite sensitizer. Nevertheless, the best-performing perovskite solar cell was reported in 2013 with a structure of TiO_2 /perovskite/spiro-OMeTAD/Au, which exhibited a remarkable PCE of 15.0% ($J_{\text{SC}} = 20.0 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.993 \text{ V}$, $\text{FF} = 0.73$) under an illumination of 96.4 mW cm^{-2} .¹ It is worth noting that when the device was encapsulated under argon, it could maintain greater than 80% of its initial PCE after 500 h.¹

Table 1 Summary of the device performances for liquid-type QDSCs and perovskite solar cells

Anode	Active layer	Electrolyte/CE	PCE (%)	References
TiO_2	$\text{CuInS}_2/\text{CdS}$	Polysulfide/PbS	4.7	71
TiO_2	CdSe	Polysulfide/Pt	2.7	26
TiO_2	CdSe	Polysulfide/PbS	3.3	30
TiO_2	CdS/CdSe	Polysulfide/PbS	3.9	72
TiO_2	CdS/CdSe	QS polysulfide ⁹ / Cu_2S	4.0	42
TiO_2	CdS/CdSe	Polysulfide/Au	4.2	39
TiO_2	CdS/CdSe	Polysulfide/ Cu_2S	5.4	44
TiO_2	CdSeS	Polysulfide/ Cu_2S	3.2	45
TiO_2	CdTe/CdSe	Polysulfide/PbS	2.4	41
TiO_2	PbS	Polysulfide/ Cu_2S	2.1	80
TiO_2	PbS/CdS	Polysulfide/ Cu_2S	3.8	68
TiO_2	PbS:Hg	Polysulfide/ Cu_2S	5.6	18
TiO_2	PbS	Polysulfide/Au/ CuS	5.7	73
TiO_2	PbSeS	Polysulfide/ Cu_2S	1.5	80
TiO_2	Sb_2S_3	Cobalt-phen/Pt	3.3	115
TiO_2	$\text{CH}_3\text{CH}_2\text{NH}_3\text{PbI}_3$	Iodide/Pt	2.4	102
TiO_2	$\text{CH}_3\text{NH}_3\text{PbBr}_3$	Bromide/Pt	3.1	100
TiO_2	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Iodide/Pt	3.8	100
TiO_2	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Iodide/Pt	6.5	101

Abbreviations: CE, counter electrode; QD, quantum dot; QS polysulfide, quasi-solid-state polysulfide; PCE, power conversion efficiency. ⁹QS poly sulfide represents quasi-solid-state polysulfide.

CONCLUSIONS

Highly efficient dye-sensitized nanocrystalline TiO_2 solar cells have been developed since 1991⁸; the most promising devices are based on

Table 2 Summary of the device performances for solid-state QDSCs and perovskite solar cells

Anode	Active layer	HTM/CE	PCE (%)	References
TiO_2	CdS	Spiro-OMeTAD/Ag	0.2	22
TiO_2	CdS	Spiro-OMeTAD/Au	0.8	21
TiO_2	CdS	P3HT/Ag	0.8	25
TiO_2	CdS	P3HT/Au	1.4,2.1	23,24
TiO_2	CdSe	QT12,pTPA/FTO	0.3	31
TiO_2	CdSe	P3HT/Au	1.6	28
TiO_2	CdS/CdSe	Spiro-OMeTAD/Au	0.8	46
TiO_2	CdTe	PCBM,P3HT/Pt,C60	3.4	35
TiO_2	CdTe	PNV, MoO_x /Au	3.6	34
TiO_2	PbS	Spiro-OMeTAD/Au	1.4	21
TiO_2	PbS	P3HT/Au	3.3,2.9	57,58
TiO_2 NS	PbS	Au	4.7	62
TiO_2 NP	PbS	MoO_x /Au	5.6	56
TiO_2	PbS	Au	5.5,6.0	52,53
TiO_2/ZnO	PbS	MoO_x /Au	7.4	13
TiO_2 NW	PbS	Au	5.4	59
TiO_2 NS	PbSe/PbS	Au	3.9	49
TiO_2	$\text{PbS}_{0.9}\text{Se}_{0.1}$	Au	4.2	50
TiO_2	Sb_2S_3	spiro-OMeTAD/Au	3.1	92
TiO_2	Sb_2S_3	CuSCN/Au	4.1,3.3,3.7	85,87,89
TiO_2	Sb_2S_3	P3HT/Au	3.9,4.9,5.1	14,90,94
TiO_2	Sb_2S_3	PCPDTBT/Au	6.3	15
TiO_2	$\text{CH}_3\text{NH}_3\text{PbBr}_3$	PCBDTPP/Au	3.0	106
Al_2O_3	$\text{CH}_3\text{NH}_3\text{PbBr}_3$	PCBM/Au	0.7	108
TiO_2 NW	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Spiro-OMeTAD/Au	4.2	107
TiO_2 NW	$\text{CH}_3\text{NH}_3\text{PbI}_2\text{Br}$	Spiro-OMeTAD/Au	4.8	107
TiO_2	$\text{CH}_3\text{NH}_3\text{PbI}_3$	PCPDTBT/Au	5.3	103
TiO_2 NS	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Au	5.5	114
TiO_2	$\text{CH}_3\text{NH}_3\text{PbI}_3$	PCBDTPP/Au	5.5	106
TiO_2	$\text{CH}_3\text{NH}_3\text{PbI}_3$	P3HT/Au	6.7	103
TiO_2 NR	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Spiro-OMeTAD/Au	9.4	104
TiO_2	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Spiro-OMeTAD/Ag	8.5	105
TiO_2	$\text{CH}_3\text{NH}_3\text{PbI}_3$	PTAA/Au	12.0	103
TiO_2	$\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$	PTAA/Au	12.3	3
TiO_2	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Spiro-OMeTAD/Au	9.7,15.0	1.12
Al_2O_3	$\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$	Spiro-OMeTAD/Ag	10.9	11
Al_2O_3	$\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$	Spiro-OMeTAD/Ag	12.3	2
ZrO_2	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Spiro-OMeTAD	10.8	110

Abbreviations: NP, nanopillars; NR, nanorods; NS, nanosheets; NW, nanowires.

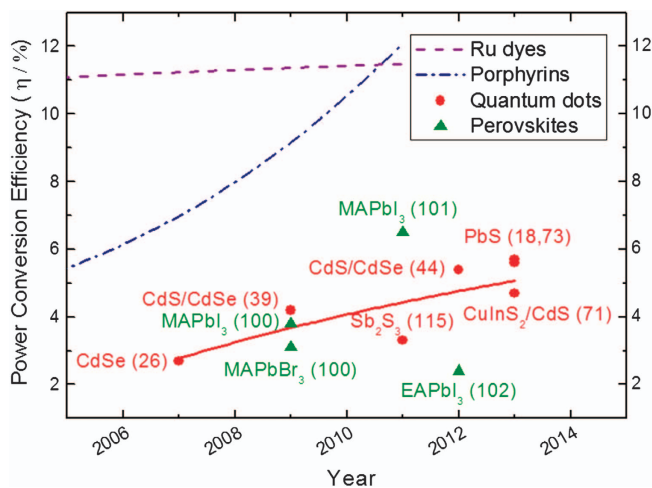


Figure 18 Charts of the efficiency progress of liquid-type QDSCs and perovskite-based SCs developed during the period 2007–2013. The solid curve represents the average progress trend with the corresponding references cited in parentheses. The dashed and dashed-dotted curves represent those of DSSCs with sensitizers of ruthenium complexes and porphyrin dyes, respectively. The symbols MA and EA represent perovskites with organic components of CH_3NH_3 and $\text{CH}_3\text{CH}_2\text{NH}_3$, respectively.

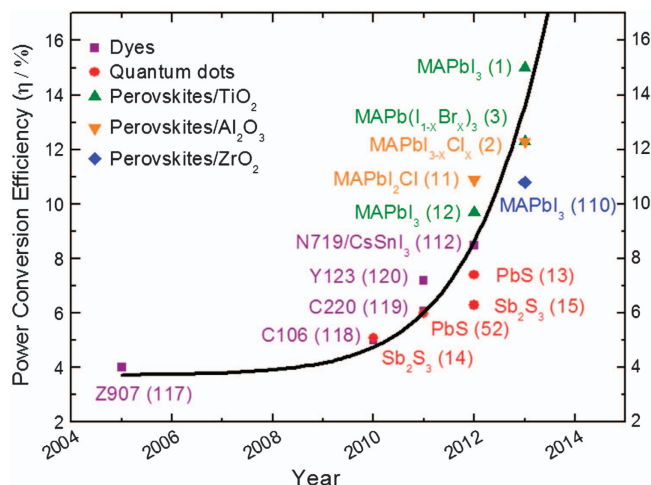


Figure 19 Efficiency progress charts of all-solid-state DSSCs, QDSCs and perovskite-based SCs developed during 2005–2013. The solid curve represents the average progress trend with the corresponding references quoted in parentheses. The symbol MA represents perovskites with an organic component of CH_3NH_3 .

ruthenium or porphyrin dyes with efficiencies of power conversion exceeding 12%,^{9,10} but these traditional DSSCs have durability problems due to (i) instability of the organic sensitizers and (ii) leakage of the devices containing typical liquid-type electrolytes. To solve these critical problems for DSSCs, various inorganic light harvesters have been intensively developed, in combination with hole-conducting materials of organic or polymer type. Therefore, herein we have reviewed inorganic nanomaterials of two types—metal chalcogenides and halide perovskites—as prospective photosensitizers or light absorbers for hybrid mesoscopic solar cells. A summary of the photovoltaic performances of these inorganic photosensitizers in liquid-type electrolytes appears in Table 1. The power conversion efficiencies of these devices are randomly distributed from 2 to 6%, and their performances are much poorer than those of the liquid-type DSSCs, according to the comparison shown in Figure 18. Although a large photocurrent was reported for a mercury-doped PbS-sensitized SC ($J_{\text{SC}} = 30 \text{ mA cm}^{-2}$),¹⁸ its poor photovoltage is a typical problem for QD-based solar cells. All-solid-state mesoscopic solar cells have been rapidly developing and have shown astonishing progress in their device performance during the period 2012–2013. A summary of the photovoltaic performances of all-solid-state quantum-dot-sensitized solar cells and lead halide perovskite-based solar cells appears in Table 2; their progress trends are demonstrated in Figure 19. The first all-solid-state DSSC was reported in 1998 with a small PCE (0.74%); it had a ruthenium complex dye and an organic HTM (spiro-OMeTAD) as a solid-state electrolyte.¹¹⁶ The device efficiency of an all-solid-state DSSC quickly rose to 4.0% in 2005 (Z907)¹¹⁷ and to 5.0% in 2010 (C106).¹¹⁸ In 2011, two metal-free organic dyes, C220¹¹⁹ and Y123,¹²⁰ showed promising performances for all-solid-state devices, attaining efficiencies of 6.1 and 7.2%, respectively. Since 2010, metal chalcogenide QDs have played an important role as suitable sensitizers for solid-state mesoscopic TiO_2 solar cells. The two most promising QD sensitizers are PbS and Sb_2S_3 ; the PCEs of these QDSCs reached $\sim 7\%$ in 2012. The most remarkable advancement in the development of all-solid-state mesoscopic solar cells was the discovery of light harvesters of the perovskite

type. As Figure 19 shows, the development of perovskite-based solar cells has progressed expeditiously, with achieved PCEs of 10%^{11,12} in 2012, followed by 12%^{2,3,103} and then 15%¹ in 2013. Such striking and rapid progress in the development of organic-inorganic hybrid photovoltaic devices indicates the threshold of a new era for the commercialization of all-solid-state mesoscopic solar cells in the near future.

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