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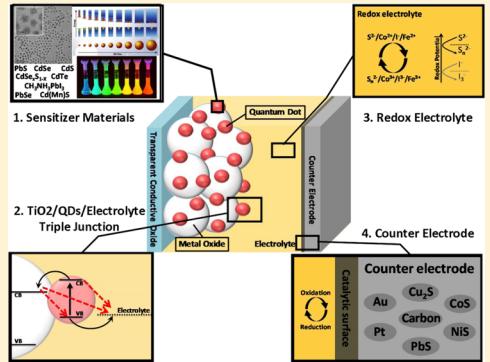
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Materials and Interfaces in Quantum Dot Sensitized Solar Cells: Challenges, Advances and Prospects

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ABSTRACT: In recent years, quantum dot-sensitized solar cells (QDSSCs) have emerged as attractive candidates for constructing efficient third-generation photoelectrochemical solar cells. Despite a starting point of relatively low performing solar cells, we have been witnessing a boost in scientific research conducted both from the material and the physical points of view, leading to a huge leap in our understanding of the operational mechanisms of QDSSCs followed by a significant improvement of their conversion efficiencies to about 7%. In this feature article, we give an overview of the four main materials and interfaces constructing the QDSSC: (1) sensitizer materials, (2) TiO_2/QDs /electrolyte interface, (3) redox electrolyte, and (4) counter electrode. We focus on the scientific challenges associated with each one of the materials/interfaces while highlighting the recent advances achieved in overcoming those obstacles. Finally, we discuss possible future directions for this field of research with an aim toward highly efficient QD-sensitized solar cells.



1. INTRODUCTION

One of the promising technologies for future alternative energy sources is the direct conversion of sunlight into electricity by using photovoltaic (PV) cells.¹ The greatest challenge in the photovoltaic field is to develop new types of advanced materials with the desired electrical and optical properties that will allow the fabrication of robust, highly efficiency, inexpensive PVs. The field of photovoltaic devices has been dominated by solid-state junction devices, typically made of silicon and profiting from the experience and material availability resulting from the semiconductor industry. Currently, crystalline silicon-based PVs offer the best possibilities in terms of large-scale manufacturing of efficient, robust, and relatively low cost devices.

The thermodynamic limit for light conversion efficiency, also known as the Shockley–Queisser limit, is 32.9% for a single junction cell under 1 sun illumination. Recently, attempts to overcome this limitation have been carried out through the emergence of third-generation systems such as the photoelectrochemical solar cell (PESC) family, which includes dye-sensitized solar cells (DSSCs)^{2,3} and quantum dot (QD)-sensitized solar cells (QDSSCs),^{4–6} which hold promise for both high conversion efficiency and low-cost cell fabrication. In particular, QDSSCs are attracting attention because of the fact that the use of QDs as sensitizers opens new possibilities owing to their large absorption coefficient, the tunability of their absorption spectrum by quantum size confinement, and the possibility of hot electron injection⁷ and multiexciton generation (MEG).⁸ It was recently shown that a PbSe-based solar cell exhibits over 100% quantum efficiency using the MEG mechanism,⁹ thus providing great promise for the design of QD-based solar cells with efficiencies beyond the Shockley–Queisser limit.

A QDSSC is composed of a mesoporous wide-band-gap semiconductor (usually TiO_2), which is sensitized with narrow-band-gap semiconductor nanocrystals, a redox electrolyte solution, and a counter electrode. Upon excitation, electrons are injected from the semiconductor nanocrystals into the conduction band of the TiO_2 followed by diffusion to the front contact while holes are transferred to the electrolyte for regeneration at the counter electrode (Figure 1).

The synthesis of QDs and their incorporation into the QDSSC photoactive electrode as sensitizers is carried out by several techniques:

A. Chemical Bath Deposition (CBD).¹⁰ This is a simple, reproducible, cost-effective technique of fabricating high-quality compound semiconductor metal halides and chalcogenide thin films on both metallic and nonmetallic substrates. The method is well studied and produces films that have comparable structural, optical, and electrical properties to those produced when using other sophisticated thin-film deposition techniques. The technology is based on the slow controlled precipitation of the desired compound from its ions in a reaction bath solution.

B. Successive Ionic Layer Adsorption Reaction (SILAR).¹¹ This method is inexpensive, simple, and convenient for large-area thin film deposition. The SILAR method is mainly based on the adsorption and reaction of the ions from the solutions and rinsing between every immersion with deionized water to avoid homogeneous precipitation in the solution. The growth mechanism involves three important steps: (i) specific adsorption of the most strongly adsorbed ions of the compound to be grown by the substrate immersed in a

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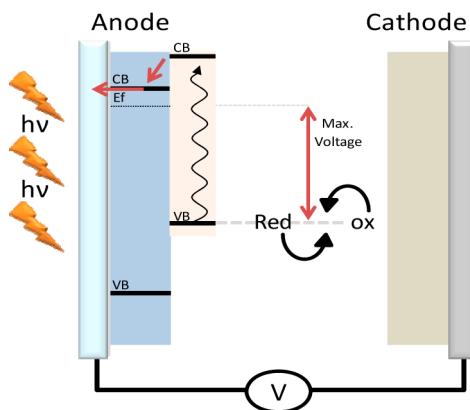


Figure 1. Principle of operation and energy-level scheme of the QD-sensitized solar cell. Photoexcitation of the sensitizer is followed by electron injection into the conduction band of the wide-band-gap semiconductor. The sensitizer is regenerated by the redox system, which itself is regenerated at the counter electrode (cathode) by electrons passing through the load.

solution of one of its cationic precursors, (ii) water rinsing of the excess solution still adhering to the substrate, and (iii) chemical reaction between the most strongly specific adsorbed cations and the less strongly adsorbed anions by subsequent substrate immersion in the solution. The prime requirements for obtaining high-quality thin films are the optimization of the precursor's concentrations, the nature of the complexing agent, the pH of the precursor solutions, and adsorption, reaction, and rinsing time durations.

C. Deposition of Ex-Situ-Grown QDs.^{12,13} First, monodisperse QDs are synthesized using organic capping ligands to control the QDs' shape and size. After synthesis, the QDs are separated from the excess organic ligands and dissolved in an organic solvent; they are then ready to be attached to the TiO₂ electrodes. Because the mesoporous TiO₂ layer and the QDs do not readily adhere, a bifunctional molecular linker such as mercapto-carboxylic acid is used. First, the surface of TiO₂ is modified by dip coating the electrode in mercapto-carboxylic acid ligands, which enables the carboxylic acid groups to attach to the surface of TiO₂, and the mercapto groups faces the solution, ready to be attached to the surface of the QDs. In the following step, the modified mesoporous TiO₂ electrode is immersed in the solution of the QDs, enabling the QDs to diffuse into the pores, and by partial ligand exchange, the mercapto groups attach the QDs to the surface of the TiO₂. An electrophoretic QD deposition technique could also be used to deposit the particles on the surface of TiO₂. We were able to demonstrate that the adsorption of charged QDs under an applied electric field leads to uniform QD coverage with stable attachment to the electrode.¹²

Over the past few years, there has been great progress in the development of high-performance QDSSCs, and recent reports presented light to electric power conversion efficiencies of 5–7%,^{14–17} providing a huge step forward in competing with the performance of dye-sensitized solar cells (DSSCs). However, further development is still required in order to commercialize this technology. Below we identify four topics that hold the key to significant progress in QDSSCs, all involving materials and interfaces (Figure 2): (A) Sensitizer materials: The insufficient spectral response window of the solar cell is limited by both the

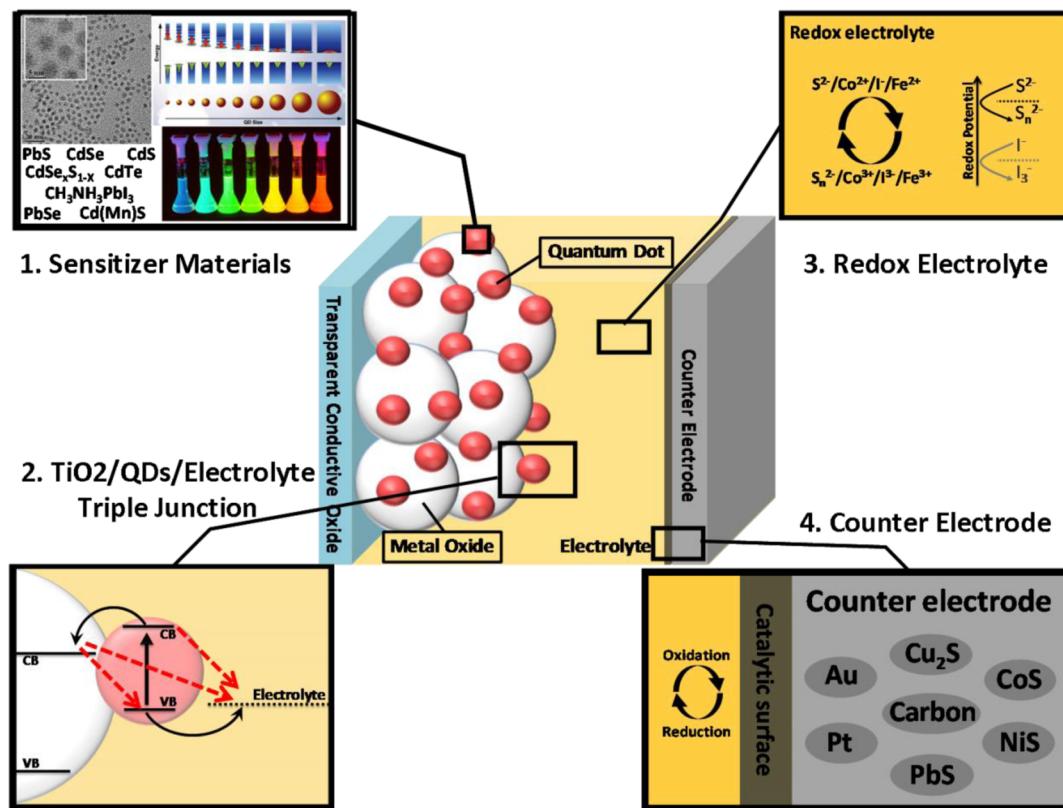


Figure 2. Schematic representation of the main interfaces/materials constituting the QDSSC: (1) sensitizer materials, (2) TiO₂/QDs/electrolyte triple junction, (3) redox electrolyte, and (4) counter electrode.

relative energetics at the QD–TiO₂ interface and the lack of efficient IR-sensitizing QD materials. (B) The inherent triple junction of TiO₂/QDs/electrolyte, which is formed at the photoactive electrode, affects the energy-level alignments among the three components while creating several routes for charge recombination, thus lowering the cell efficiency. (C) Redox electrolyte: The relatively low cell open circuit photovoltage (V_{oc}) results from the negative potential of the commonly used polysulfide electrochemical mediator. (D) Counter electrode: The lack of a highly efficient counter electrode (CE), which is able to catalyze the regeneration of the oxidized charge carrier ions, increases the photocurrent and reduces recombination losses.

In this feature article, we shall focus on each of the mentioned limiting factors while pointing out the recent achievements made in the quest to overcome these restrictions. Furthermore, using the knowledge attained regarding the basic operation principles of QDSSCs and on the basis of recent important results, we discuss optional future research directions for the development of QDSSCs toward a highly efficient solar cell.

2. SENSITIZER MATERIALS

The conventional choice of semiconducting sensitizer materials to be used in a QDSSC is CdS and CdSe.^{18,19} Numerous studies over the past few years have shown the possibility of using these materials as QD sensitizers because of (a) their ability to harvest a portion of the visible region of the sun's spectrum and (b) their good charge-separation properties (electron injection into a wide-band-gap oxide coupled with hole removal by the redox electrolyte), resulting in the rapid growth of QDSSC conversion efficiencies. Several modifications have been employed in the standard CdS/CdSe configuration in order to improve the performance of QDSSCs further. One approach involves the design of ternary alloy materials such as CdSe_xS_{1-x}²⁰ CdSe_xTe_{1-x}¹⁴ and CuInSe_xS_{2-x}²¹. By varying the compositional ratio between Se and S, one can engineer the semiconductor's physical characteristics, such as the band gap, energy band position, and photoelectrical properties. Kamat et al. have introduced a new QDSSC configuration consisting of a tandem architecture composed of layered stacks of alternating-band-gap CdSe_xS_{1-x} monodisperse QDs.²⁰ This solar cell configuration generates an energy band edge cascade for better charge transport within the QD film while optimizing the light-harvesting ability of the cell (Figure 3).

An additional path for manipulating the optoelectronic properties of the QDs is based on the introduction of optically active transition metal ion dopants. For example, the doping of CdS QDs with Mn²⁺ creates new sub-band-gap electronic states that alter their charge transfer and recombination kinetics. These newly formed states belong to the Mn d-d transition that possesses a long emission lifetime of a few hundred microseconds. Excited electrons in the CdS conduction band quickly transfer to the long-lived Mn d trap state, which in turn slows down recombination processes to the redox electrolyte or to trapped holes in the QD. A QDSSC composed of Mn-doped CdS/CdSe sensitizers fabricated using a simple SILAR method exhibited an impressive conversion efficiency of 5.42% (Figure 4).¹⁶

However, because of their relatively large band gaps, CdS (2.3 eV) and CdSe (1.8 eV) absorb only a fraction of the sun's spectrum. As a consequence, to improve the performance of

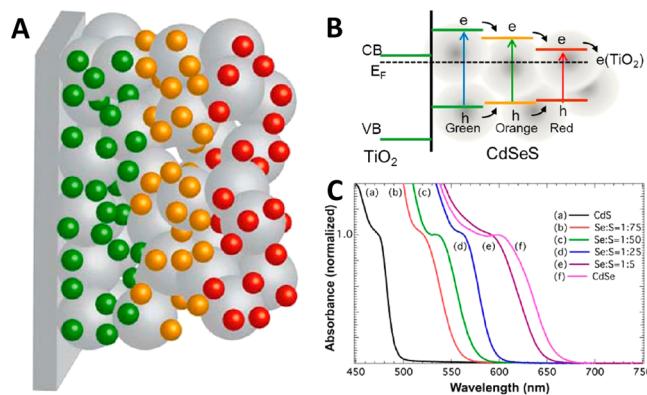


Figure 3. (A) Illustration of the tandem CdSe_xS_{1-x} structure. (B) Energy band diagram showing the band edge cascade for improved charge transfer. (C) Absorption spectra of different composition ratios (Se/S) and their effect on the QD band gaps. Reprinted with permission from ref 20, copyright (2013) American Chemical Society.

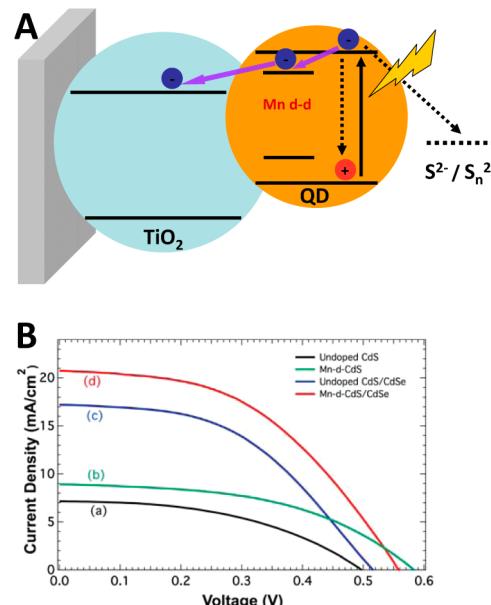


Figure 4. (A) Energy diagram of Mn-doped QDs. Electrons in the QD's conduction band are rapidly transferred to the Mn sub-band-gap state while inhibiting recombination with either the electrolyte or holes in the QD (dashed arrows). (B) i - V curve comparing (a) undoped CdS, (b) Mn-doped CdS, (c) undoped CdS/CdSe, and (d) Mn-doped CdS/CdSe. Adapted with permission from ref 16, copyright (2012) American Chemical Society.

QDSSC further, an expansion of its spectral response window further into the IR region is required. This obstacle has led to the emergence of new kinds of alternative narrow-band-gap semiconductors, such as PbS,^{15,22,23} PbSe,²⁴ and Ag₂S.²⁵

Although PbS has a high potential to be used as a sensitizer material in QDSSCs because of its broad absorption spectrum, it suffers from high recombination rates in polysulfide electrolyte coupled with relatively poor stability. Mora-Sero et al. have shown that the application of a CdS cover layer on top of the PbS QDs can act both as a recombination inhibitor and as a protective coating, stabilizing the solar cell while reaching impressively high photocurrents and a conversion efficiency of 4.2%.^{22,23} In addition, Park and co-workers recently published a SILAR procedure to fabricate Hg²⁺-doped PbS-sensitized solar

cells with a record high photocurrent of 30 mA/cm^2 and a conversion efficiency of 5.6% (Figure 5).¹⁵ The Hg^{2+} ion

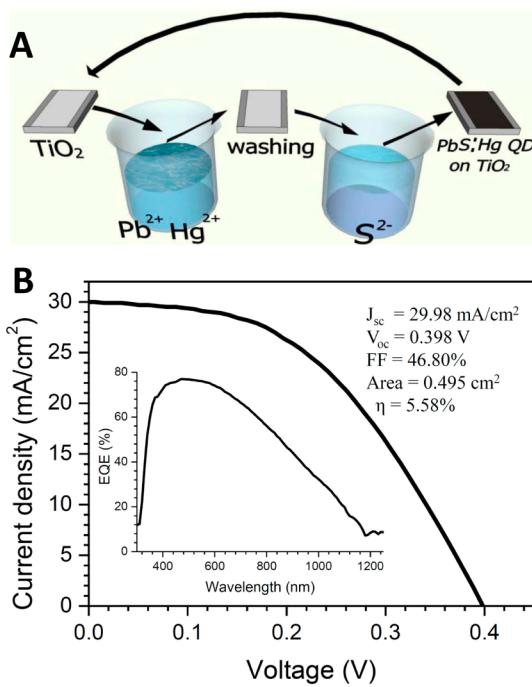


Figure 5. (A) Drawing demonstrating the SILAR fabrication process of an Hg-doped PbS photoanode. (B) i - V curve of an Hg-doped PbS-sensitized solar cell. The inset shows the external quantum efficiency of the solar cell. Reprinted by permission from Macmillan Publishers Ltd.: Scientific Reports, ref 15, copyright 2013.

dopant is incorporated into the PbS lattice, improving the ordering around each lead atom and shortening the Pb–S bond length. As a result, charge injection rates from the QDs to TiO_2 are accelerated while recombination processes are suppressed.

A different type of approach implemented to expand the spectral response of the system is the co-sensitization of TiO_2 photoanodes with both QD semiconductors and molecular dyes, which have complementary absorption profiles. The charge-transfer mechanisms in such configurations are mainly divided into two paths: first, a system in which both sensitizers can inject electrons in parallel into TiO_2 . We introduced a system incorporating a CdS QD/N3 dye bilayer configuration.²⁶ It was shown that by the utilization of two sensitizing layers we were able to increase the optical density of our photoanodes. Furthermore, because of the fact that both sensitizers can inject electrons into TiO_2 , we obtained a 250% increase in cell efficiency compared to that in a CdS QD monolayer cell (Figure 6a,b). The second possible charge-transfer path in the bilayer configuration is the energy-transfer mechanism. By replacing the charge-injecting CdS QDs with noninjecting highly fluorescent CdSe/CdS/ZnS core–shell–shell QDs, we have shown that the energy of photons absorbed by the QDs can be transferred to a squaraine dye using Förster resonance energy transfer (FRET).²⁷ In this manner, one can separate the actions of light harvesting and charge separation. As a consequence, improved solar cell performance can be achieved using a combination of a high-extinction-coefficient light-absorbing QD donor with an efficient electron-injecting acceptor dye molecule (Figure 6c,d).

A promising new breed of semiconducting sensitizing materials has recently emerged as a strong candidate for use in high-efficiency solid-state nanostructured solar cells. These materials are based on organic–inorganic perovskite crystal structures such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$, which can absorb light throughout the entire visible region while maintaining extremely good quantum efficiencies. Recent reports show perovskite-based solar cells with conversion efficiencies of more than 15%.^{28–33}

3. $\text{TiO}_2/\text{QDS}/\text{ELECTROLYTE TRIPLE JUNCTION}$

The overall performance of QDSSCs is highly dependent on the mechanisms of charge-transfer processes occurring at the

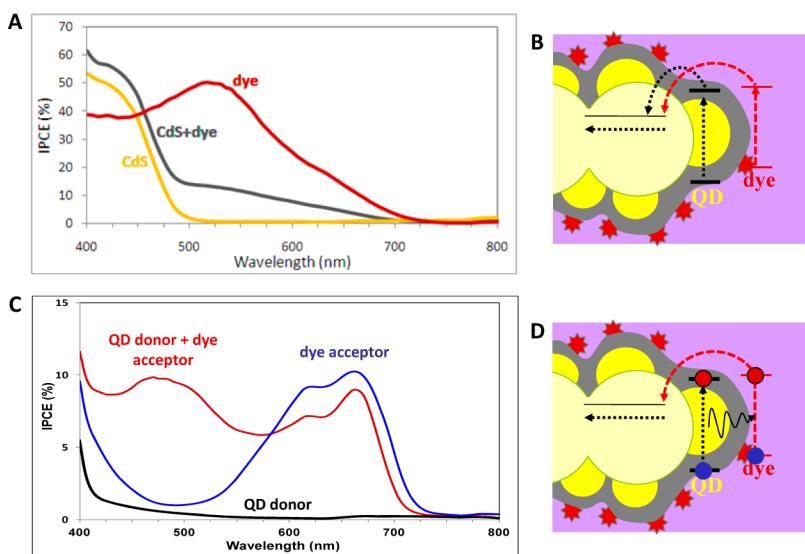


Figure 6. (A) Incident photon to current efficiency (IPCE) of a QD-N3 bilayer configuration showing parallel electron injection paths. (B) Schematic representation of electron injection from both the QDs and the dye molecule. (C) IPCE of a QD-SQ1 dye bilayer configuration showing the energy transfer (FRET) from the QD donor to the dye acceptor. (D) Schematic representation of the FRET mechanism in which photon energy absorbed by the QD is transferred to the dye, which in turn injects electrons into the TiO_2 .

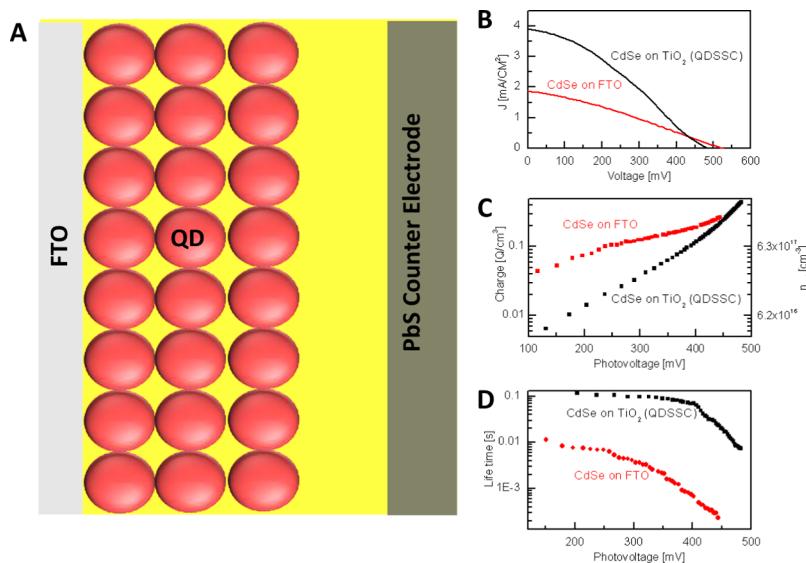


Figure 7. (A) Illustration of a photoelectrochemical solar cell composed solely of QDs. (B) *i*-V measurement comparing the photovoltaic performance of a standard QDSSC with a QD-based photoelectrochemical solar cell. (C) Charge extraction measurement showing that QDs can accumulate charge and build chemical potential. (D) Transient photovoltage measurement showing the lifetime of electrons within the QD film as a function of the cell photovoltage. Adopted with permission from ref 34, copyright (2011) American Chemical Society.

complex interfaces formed among the nanostructured TiO_2 , the sensitizing QDs, and the aqueous polysulfide electrolyte.^{34–36} One of the most important parameters affecting charge injection and recombination processes and altering the photocurrent and photovoltage of the solar cell is the energy-level alignment among the materials constructing the triple junction. In QDSSCs, as in the case of conventional DSSCs, it is possible to tune the band edges of TiO_2 with respect to the redox electrolyte by several routes. These routes include the manipulation of the chemical environment at the surface of the TiO_2 by altering the solution pH,³⁷ the insertion of additives into the electrolyte,³⁸ and the direct attachment of molecular dipoles.³⁹ TiO_2 band edge shifting can affect the solar cell's V_{oc} by altering the charge recombination rates and by changing the energy difference between the electrons' Fermi level of the TiO_2 and the redox potential of the electrolyte. Whereas in DSSCs there is no option of tuning the energy levels of the dye with respect to the redox electrolyte, in the case of QDSSCs the energetic properties of QD sensitizers are extremely sensitive to chemical surface treatments. We have succeeded in systematically manipulating the energy-level alignment of the QDs in QDSSCs by utilizing different derivatives of benzenethiol molecular dipoles.⁴⁰ The use of benzenethiols with a dipole moment pointing toward the surface of the QDs resulted in a negative shift of the QD's energy bands. Consequently, the driving force for electron injection from the QDs to TiO_2 has increased while dramatically improving the photocurrents of the cells.

Moreover, the energy-level alignment of QDs is also influenced by the identity of the electron-conducting metal oxide. For example, ZrO_2 has a far more negative conduction band energy compared to the conduction band energies of TiO_2 , CdS , and CdSe . However, QDs exhibit an unexpected ability to inject electrons into ZrO_2 , implying that the energy positions of ZrO_2 and QDs are significantly altered upon the creation of the ZrO_2/QD interface.⁴¹

One of the most significant conceptual differences between the operational principles of DSSCs and QDSSCs is the fact

that unlike molecular dyes, QDs have the ability to accumulate charge and build chemical potential. A breakthrough in our understanding of the basic physical concepts controlling QDSSC operation was made after we were able to fabricate a working photoelectrochemical solar cell composed solely of CdS/CdSe QDs deposited on an FTO conductive substrate.³⁴ The cell exhibited photovoltaic activity with a photocurrent of $\sim 2 \text{ mA/cm}^2$ and a photovoltage of above 500 mV (Figure 7a,b). Further photoelectrochemical characterization of the QD-based device was carried out using the charge extraction and transient photovoltage (TPV) techniques, as shown in Figure 7c,d. The obtained charge extraction results proved that QDs can accumulate electrons under illumination. In addition, the TPV measurement revealed the lifetime of electrons trapped in the QD's electronic states before they recombine with the polysulfide redox electrolyte.

The coupling of an FTO/CdSe photoanode to an FTO/CdS photocathode has led to the development of a tandem photoelectrochemical solar cell based solely on QDs. Because the total V_{oc} of the tandem cell is equal to the sum of the V_{oc} 's of both photoactive electrodes, we were able to measure an impressive total V_{oc} of 810 mV in polysulfide electrolyte.⁴²

Knowing that charges can be transported through a film composed of a QD multilayer, we confronted the question regarding the optimal anode structure for constructing a high-performance QDSSC. By measuring a series of cells made of flat TiO_2 with varying thicknesses of CdSe QDs, we were able to show an increase in photocurrents at a QD thickness of up to 100 nm whereas at thicknesses above 100 nm we observed a decline in photocurrents. Moreover, the optical density and the internal quantum efficiency measurements revealed that the desired surface area of the TiO_2 electrode should be increased only by a factor of 17 compared to that of a compact electrode. We show that the sensitization of a low-surface-area TiO_2 electrode with QD layers increases the performance of the solar cell, resulting in an efficiency of 3.86%.⁴³

Following the knowledge gained in our previous work, we were interested to discover the role played by the QDs in a

complete QDSSC (QDs deposited on TiO_2) in terms of recombination processes. Furthermore, we wanted to know if it is possible to detect the QD's contribution to the total chemical capacitance of the QDSSC. Using electrochemical impedance spectroscopy, we were able to point out the significant contribution of the QDs to the charge-transfer processes in the solar cell by exploring the electrical properties of the TiO_2 /QDs/electrolyte triple junction formed at the sensitized electrode.³⁵ We showed, for the first time, that a fingerprint of QDs is present in the QDSSC device capacitance, indicating that QD surface states participate in the electrode's density of states, alongside the well-known contribution of TiO_2 . This discovery provided an important proof of the major role played by QDs in the recombination processes in the cell (Figure 8).

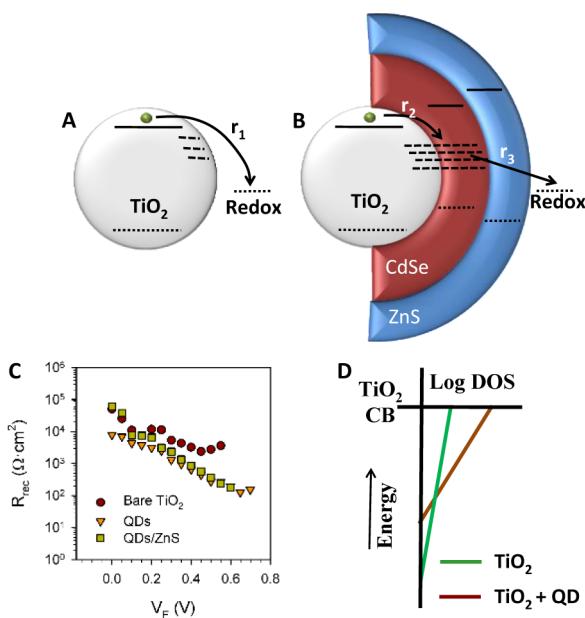


Figure 8. (A) Recombination of electrons from a bare TiO_2 to the electrolyte (r_1). Electrons are accumulated at electronic states of TiO_2 . (B) Recombination of electrons from TiO_2 through the QD's trap states to the electrolyte. Electrons are accumulated at electronic states of both TiO_2 and QDs. (C) Recombination resistance vs applied potential plot extracted from impedance measurements, showing that electrodes containing QDs exhibit higher recombination rates than bare TiO_2 electrodes. This result provides proof for the major role played by QDs in QDSSC recombination processes. (D) Energy diagram showing the contribution of QDs to the total density of states (DOS) of a QDSSC. Adopted with permission from ref 35, copyright (2011) American Chemical Society.

As a consequence, these insights provide a new understanding of QDSSCs. As a result, our attempts to improve and optimize the performance of QDSSCs accounted for the results of this research by treating QDs from a perspective different from that of a regular dye.

A significant improvement in the QDSSC performance was obtained by using an MgO thin layer coating, which served as a recombination barrier reducing losses at the TiO_2 /QDs, QDs/electrolyte and TiO_2 /electrolyte interfaces.⁴⁴ We showed that the recombination of electrons at the TiO_2 /QDs interface is as important as the recombination from TiO_2 and QDs to the electrolyte. By the application of a conformal MgO coating both above and below the QD surface, recombination rates were significantly reduced, and an improvement of more than

20% in cell efficiency was recorded (Figure 9). In addition, we have found that the recombination of electrons from the bare FTO substrate to the polysulfide electrolyte cannot be neglected. By placing a compact TiO_2 layer between the exposed FTO and the nanostructured TiO_2 film, we demonstrated a 4% efficiency QDSSC.⁴⁵

An additional strategy to reduce recombination losses at the TiO_2 /QDs/electrolyte triple junction is the utilization of semiconducting quantum rods (QRs) to replace the traditional spherical QD particles.⁴⁶ The high-aspect-ratio rodlike particles exhibit the ability to separate the photogenerated charges efficiently, meaning that holes diffuse to one end of the particle while electrons diffuse to the other end. By doing so, much higher electron lifetimes and injection efficiencies are obtained, resulting in a major improvement in the overall cell performance compared to the usual QDSSC.

4. REDOX ELECTROLYTE

To date, the development of an efficient electrolyte solution, able to transfer electrons rapidly to regenerate the oxidized QD sensitizers while having good long-term stability under working conditions, constitutes one of the major challenges in the field of QDSSCs.

Although the well-known I^-/I_3^- redox couple shows excellent performance in standard DSSCs, in the case of QDSSCs, the iodine causes severe corrosion of the inorganic semiconducting QDs, leading to fast function degradation of the photoactive electrode. As a consequence, the most popular choice of electrolyte for this kind of cell is the polysulfide redox couple in aqueous solution. Even though the use of a polysulfide electrolyte⁴⁷ demonstrates high regeneration rates of oxidized QDs, it still suffers from relatively low cell V_{oc} compared to the common DSSC. The V_{oc} of a QDSSC is determined by the energy difference between the TiO_2 Fermi level and the electrolyte redox potential. Consequently, the intrinsic polysulfide property of the highly negative redox potential dramatically limits the maximum theoretical solar cell V_{oc} that can be obtained.

To overcome this limitation, a great deal of effort has been invested in the design of new types of liquid electrolytes that, on one hand, maintain the stability of the QDs but, on the other hand, possesses significantly more positive redox potentials to increase V_{oc} .

Hagfeldt and Sun et al. have reported a new type of modified polysulfide electrolyte composed of tetramethylammonium sulfide/polysulfide, $[(\text{CH}_3)_4\text{N}]_2\text{S}/[(\text{CH}_3)_4\text{N}]_2\text{S}_n$, in an organic medium of 3-methoxypropionitrile (MPN). Using this redox couple, they succeeded in fabricating a CdS-based QDSSC with a V_{oc} of 1.2 V, resulting in a 3.2% conversion efficiency cell. The extremely high V_{oc} value is explained by the highly positive redox potential of the electrolyte (1.045 V vs NHE).⁴⁸

Another recent work by Sun and Agren et al. introduced a CdS-based QDSSC that employs an organic electrolyte based on the McMT^-/BMT redox couple.⁴⁹ The new electrolyte exhibited superior performance in terms of both the fill factor and V_{oc} as a result of slower charge recombination kinetics.

Bisquert et al. have introduced the possibility of using a pyrrolidinium ionic liquid electrolyte that contains $\text{S}^{2-}/\text{S}_n^{2-}$. The resulting QDSSC exhibited high photocurrents while improving the long-term stability of the solar cell.⁵⁰

Gratzel and co-workers have shown the possibility of using a $\text{Co}(\text{o-phen})_{3}^{2+/3+}$ complex-based electrolyte¹⁸ for several types of semiconductor sensitizers such as CdS, PbS, and CdSe while

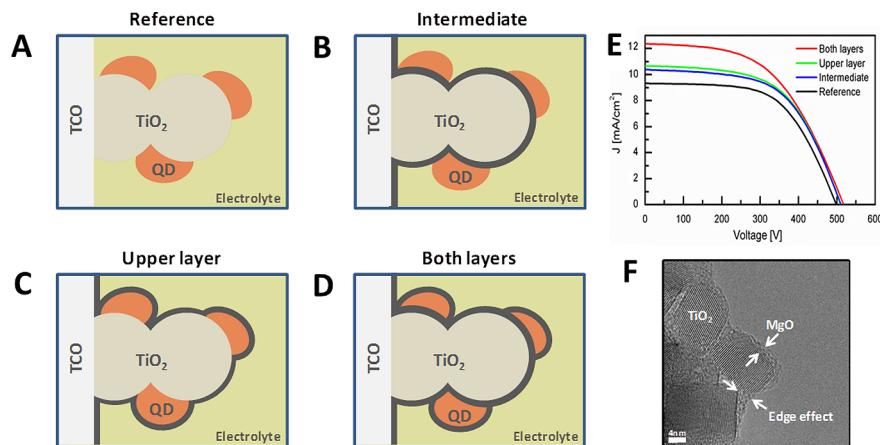


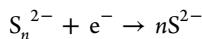
Figure 9. (A) Reference QDSSC without an MgO coating. (B) QDSSC containing an MgO coating at the TiO_2/QD interface. (Intermediate C) QDSSC containing an MgO coating above the QDs. (Upper layer D) QDSSC containing both types of MgO coatings. (Both layers E) i - V curve showing the effect of each type of MgO coating on the performance of the QDSSC. (F) High-resolution TEM image showing the conformal nature of the MgO coating on top of TiO_2 nanoparticles. Adopted with permission from ref 44, copyright (2013) American Chemical Society.

obtaining up to 4.2% efficiency for the CdSe device under 0.1 sun illumination. Moreover, several other alternative redox couples have been tested for suitability in QDSSCs, among them $\text{Fe}(\text{CN})_6^{4-}/\text{I}^-$ ⁵¹ and nickel ($\text{Ni}^{3+}/\text{Ni}^{4+}$);⁵² however, their overall performances were lower compared to that of the conventional polysulfide electrolyte.

Because the use of a sulfur-based liquid electrolyte is known to suffer from insufficient long-term stability, commercializing QDSSCs requires finding alternative solutions. Therefore, alongside liquid-based electrolytes, a new brand of redox mediators based on solid-state hole conducting materials is emerging. Materials such as spiro-OMeTAD,⁵³ PEDOT,⁵⁴ and CuSCN⁵⁵ are deposited on the surface of the sensitizing semiconductor, after which a layer of metal contact is evaporated on top of the hole-transporting material. Among the advantages of using solid-state electrolytes are possible long-term stability through easier and better device sealing and higher photovoltages compared to those of the aqueous polysulfide electrolyte.

5. COUNTER ELECTRODE

To maximize the performance of QDSSCs, one needs to discharge the electrons quickly at the counter electrode. Although polysulfide electrolyte is beneficial to the stability of the photoanode in liquid junction QDSSCs, power conversion efficiencies have remained lower than those of DSSCs. A general polysulfide reduction is represented below:



Even though platinum counter electrodes are highly catalytic for a wide variety of electrochemical reactions, including the reduction of the I_3^-/I^- redox couple used in DSSCs, their performance under the polysulfide electrolyte is poor.⁵⁶ Sulfur compounds are known to chemisorb on platinum surfaces and induce poisoning effects toward electrode performance. A poor charge-transfer rate at the counter electrode results in a high overpotential for the reduction reaction, which creates a bottleneck for the electron flow, thereby promoting back electron transfer at the photoanode. These effects are realized from the low current density and fill factor of such QDSSCs.^{57,58}

Significant efforts have been made in recent years to develop an alternative counter electrode material that will both efficiently catalyze the polysulfide reduction reaction and that will possess good stability in the electrolyte solution under working conditions. As of now, a few counter electrodes have been found to have better catalytic properties than platinum, such as CoS ⁵⁹ and Cu_2S .^{60,61} We have developed a new kind of counter electrode made of nanostructured PbS ,⁶² which exhibits high catalytic activity. Compared to the use of Pt, a PbS counter electrode introduced great improvement in all cell performance parameters while boosting the conversion efficiencies by a factor of 4. In addition, improved counter electrode configurations have been presented with the application of high-surface-area carbon serving as the conductive substrate. However, there is still a need for better-performing counter electrodes that will have no stability limitations in order to boost the efficiencies of existing QDSSCs.

To gain deeper insight into the factors limiting the performance of QDSSCs, we have developed a unique electrochemical characterization method that offers the possibility to separate the contribution of each cell component to the overall cell operation. This method utilizes the novel concept of a photoreference electrode for electrochemical measurements in a three-electrode mode, performed under the working conditions of a thin electrolyte sandwich-type photoelectrochemical solar cell.⁵⁸ Using this technique, we were able to provide quantitative information regarding the potential losses associated with the counter electrode as well as direct mapping of the effective potentials of the two-cell electrodes throughout a voltage scan from open to short circuit. Moreover, the photoreference electrode method revealed a major effect of the counter electrode quality on the recombination losses at the sensitized electrode. Figure 10 presents an illustration of the photoreference utilization in a working QDSSC and i - V plots measured with both two- and three-electrode setups when comparing Pt and PbS counter electrodes.

6. SUMMARY AND FUTURE OUTLOOK

Over the past few years, quantum dot-sensitized solar cells (QDSSCs) have been the subject of extensive research effort in

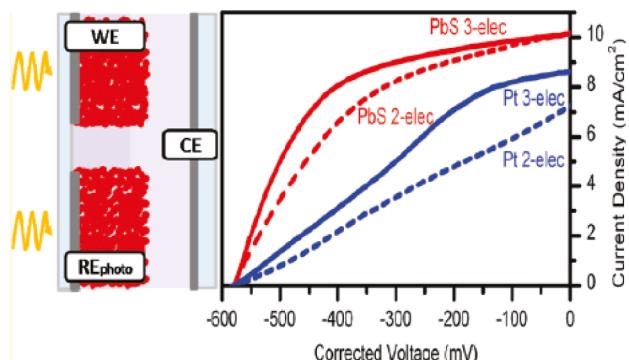


Figure 10. (Left) Sandwich-type photoelectrochemical solar cell consisting of an internal photoreference (RE_{photo}). (Right) i – V curves of a QDSSC measured in two- and three-electrode modes when comparing Pt and PbS counter electrodes. Reprinted with permission from ref 58, copyright (2011) American Chemical Society.

the fields of materials science and physical chemistry. During this period, the conversion efficiency of QDSSCs has greatly improved from less than 1% up to almost 6%. Our understanding concerning the fundamental physical mechanisms governing the cell's operation has grown tremendously, leading to the development and design of sophisticated solutions to overcome the intrinsic drawbacks of this system, as surveyed in this feature article. As of today, it seems that achieving high-enough photocurrents is a fairly feasible task, following the recent report of a doped PbS-sensitized solar cell with current densities of 30 mA/cm^2 . As a consequence, the next big leap in the performance of QDSSCs will involve a strategy to increase the V_{oc} of the cells significantly, either by utilizing a new type of liquid redox electrolyte replacing the conventional polysulfide or by the use of appropriate solid hole conductors, as has been successfully demonstrated in perovskite-based solar cells.

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Notes

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Idan Hod completed his B.Sc and M.Sc (cum laude) studies in the department of chemistry at Bar Ilan University, Israel, in 2008. During his Ph.D., his research focused on understanding the fundamental physical mechanisms of charge-transfer processes in quantum dot

sensitized solar cells (QDSSCs) using photoelectrochemical characterization methods.



Arie Zaban earned his B.Sc. in chemistry (summa cum laude) and Ph.D. in electrochemistry (with highest distinction) at Bar Ilan University (1987–1995). After a 2 year postdoctoral stint at the U.S. National Renewable Energy Laboratory (Denver, CO), he was appointed to the senior faculty at Bar Ilan, where he is currently a full professor of chemistry and Director of the Bar Ilan Institute for Nanotechnology and Advanced Materials. His research focuses on the development of new materials and concepts for photovoltaics.

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