Quantum Dot Sensitized Solar Cells

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ABSTRACT

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In response to rapidly increasing global energy demand, the development of alternative energy sources to fossil fuels has emerged as one of the most urgent technological challenges. Solar energy, which represents a nearly unlimited source of clean power, has been considered as one of the most promising new energy sources. In addition to the current success of silicon based solar cells, quantum dot sensitized solar cells have shown great potential as next generation, high performance, and low-cost photovoltaics due to the outstanding optoelectronic properties of quantum dots and their multiple exciton generation (MEG) capability. This review focuses on recent advances in quantum dot sensitized solar cells, including the synthesis of quantum dots via colloidal chemistry and chemical bath deposition (CBD), novel quantum dot nanostructures for solar energy conversion, high performance electrolyte, and the electronic interaction between quantum dots and electron acceptors. In addition, the current technical difficulties facing quantum dot sensitized solar cells are summarized, and a perspective on the future of the field is offered.

KEYWORDS: Quantum Dots, Solar Cells, Nanostructures, Surface Functionalization.

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1. INTRODUCTION

As one of the major renewable energy sources, solar energy has the potential to become an essential component of future global energy production. Commercially available single- crystalline silicon solar cells exhibit a power conversion efficiency (*PCE*) of ~15%; however, these first generation devices suffer from the high cost of silicon fabrication.¹ Although polycrystalline silicon solar cells offer dramatically reduced fabrication costs than their single-crystalline counterparts, their *PCE* is markedly lower.¹ Despite having high solar-to-electric

energy conversion efficiency, the use of silicon-based solar cells is restricted by their lack of flexibility, high manufacturing and installation cost, and heavy weight. As a result, many research efforts have been made to utilize tailored, nanostructured semiconductors, including conjugated polymers, carbon nanotubes, and quantum dots (ODs) for the development of next generation, light weight, low cost, high efficiency solar cells. For example, these efforts have produced dye sensitized solar cells with a PCE higher than 10%;²⁻¹³ organic/inorganic bulk heterojunction (BHJ) solar cells;¹⁴⁻²⁴ hybrid solar cells from a mixture of quantum dots and conjugated polymer;²⁵⁻³⁰ and thin film solar cells from quantum dot-conjugated polymer nanocomposites.³¹⁻³³ However, to date, the PCE of these solar cells is still low due to inefficient charge transport to the electrode and significant charge recombination of excitons prior to reaching the electrodes. In this context, improving the photon-to-electricity conversion efficiency has been one of the biggest issues in solar energy research. Dye sensitized solar cells (DSSCs), one of the most promising of several alternative cost-effective concepts for solar energy conversion, have received considerable attention over the past decade. To further improve the *PCE* of DSSCs, much research has been performed to optimize three constituents: the photo-sensitizer, electron collecting semiconductor, and hole conducting electrolyte. Because of their outstanding optoelectronic properties, QDs have been utilized in solar cells with the possibility of obtaining a PCE exceeding the traditional Shockley-Queisser limit of efficiency of 32%.^{34, 35} Among several

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schemes of OD solar cells, OD sensitized solar cells (ODSSCs), which are the focus of this review, have the most potential for next generation, high performance and low-cost solar cells. There are a number of advantages to utilizing ODs as sensitizers, not least being their capacity for multiple exciton generation (MEG).36-47 When incident energy is higher than the bandgap of QDs, instead of dissipation in terms of heat loss, as in p-n junction solar cells, QDs (e.g., PbSe⁴⁷) have been shown to generate more than one exciton per photon absorbed. This is considered as an efficient way to increase photocurrent, and thus, enhance power conversion efficiency. Theoretical calculation and experimental results show that as many as seven excitons can be generated upon absorption of one photon by QDs at a certain energy level,⁴⁵ thus an ideal PCE higher than 40% can be expected.^{34,48} Furthermore, QDs have tunable optoelectronic properties as a function of particle size and chemical composition, which facilitates the absorption of sunlight ranging from UV to near IR.⁴⁹ Finally, QDs exhibit better heterojunction formation with solid hole conductors.⁵⁰ To date, various QDs (e.g., CdSe, CdS, CdTe, InAs, InP, PbSe) have been demonstrated as a substitute for dyes in conventional DSSCs.^{34, 48, 51–62}

QDs used in solar cells are usually synthesized via colloidal chemistry and chemical bath deposition. Colloidal chemistry yields QDs with well-defined size, shape, and chemical composition as well as good solvent solubility due to the fact that the surface is passivated with surfactant, which also prevents particle aggregation. Surface functionalization of QDs is necessary to enhance their filling into hydrophilic nanoporous films and to promote the interaction between QDs and electron acceptor surfaces in



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nanoscopic structures, hierarchical structure formation and assembly, ferroelectric nanocrystals, multiferroic nanocrystals, negative giant magnetocaloric effect nanoparticles, TiO_2 nanoparticles and nanotubes, porous alumina membranes, phase equilibrium and phase separation kinetics, surface and interfacial properties, electrohydrodynamic instabilities. He is a recipient of an NSF Career Award and a 3 M Non-Tenured Faculty Award, and an invited participant at the National Academy of Engineering's (NAE) 2010 U.S. Frontiers of Engineering Symposium (US FOE).

order to increase photocurrent in QDSSCs. A commonly adopted approach for surface functionalization of QDs is ligand exchange, i.e., replacing the original hydrophobic ligand with bifunctional molecules. Due to the fact that air is easily trapped in nanoporous photoanodes, sufficient filling of colloidal QDs into nanopores is rarely achieved, resulting in less efficient absorption of incident light. Thus, chemical bath deposition of QDs has been investigated to increase the loading of QDs in nanoporous photoanodes; however, control over the QD size and shape and the interaction between QDs and the surface of photoanodes needs to be further investigated and optimized.

To date, in most QDSSCs, mesoporous TiO₂ films are used as electron acceptors (i.e., photoanodes). ODSSCs have been assembled by infiltrating colloidal QDs or by chemical bath deposition of ODs into these mesoporous electron acceptor films. Hole transport electrolytes are injected between the QD-doped photoanodes and counter electrode (e.g., Pt coated conductive substrate). It is worth noting that structural disorder at the contact between adjacent TiO₂ nanoparticles leads to increased scattering of electrons (i.e., trapping/de-trapping for charge hopping) and reduced electron collection at the bottom electrodes. Recent advances in nanotechnology have led to the successful fabrication of highly ordered semiconductor nanowire and nanotube arrays, in which the precise orientation of the crystalline nanowires and nanotubes makes them excellent electron percolation pathways for vectorial charge transport to electrodes,⁶³ thereby reducing the chance for charge recombination.^{7,64–71} Other novel nanostructures have also been developed for efficient charge collection in sensitized solar cells, such as hierarchical TiO₂ photoanodes⁷² and hollow TiO₂ fibers.⁷³

The power conversion efficiency of QDSSCs is determined by the following factors: the QD light absorption efficiency, the degree of QD loading, the interaction between QDs and the electron acceptors, and the hole transport efficiency of the electrolyte.

In this review, recent progress in QD sensitized nanostructures for use in photovoltaic applications is discussed, including the synthesis and surface functionalization of colloidal QDs, chemical bath deposition of QDs, novel QD sensitized nanostructures (including semiconductor nanoparticles, nanowires, and nanotubes), and attempts at optimization of the electronic interaction between QDs and electron acceptors. Finally, current technical difficulties in QDSSCs are summarized and possible solutions are discussed.

2. SYNTHESIS OF QUANTUM DOTS

2.1. Synthesis of Colloidal QDs and Surface Functionalization

QDs are highly emissive, spherical nanoparticles that are a few nanometers in diameter.^{74, 75} They provide a

functional platform for a new class of materials for use in solar cells,^{25, 27, 30} LEDs,^{76, 77} tunable lasers,⁷⁸ optical storage media,⁷⁹ nonradiative energy transfer,^{79–81} biosensors,^{49, 82–85} and bioimaging.^{86, 87} For QDs such as CdSe,^{88, 89} variation of particle size provides continuous and predictable changes in light absorption and fluorescence emission due to their quantum-confined nature. Appropriate surface passivation with a monolayer of coordinating ligands is crucial to ensuring the solubility and miscibility of QDs with the host environment and to retaining the spectroscopic properties of the materials by preventing QDs from aggregating. Subsequent ligand exchange permits derivatization with a broad range of functional terminal groups on the surface of QDs.

Among all the synthetic approaches, colloidal synthesis is the most widely used technique for the preparation of high quality QDs. These colloidal semiconductor nanocrystals are usually synthesized from organometallic precursor compounds dissolved in solution. The synthesis is based on a three-component system composed of precursors, organic surfactants, and solvents.⁸⁰ By tuning the reaction conditions, QDs with controlled size, shape, and chemical composition can be readily obtained.⁹⁰⁻⁹³ Figure 1 shows examples of CdSe/CdS core/shell ODs of different shapes.93 QDs synthesized through conventional organometallic high temperature growth procedures are functionalized with hydrophobic ligands (e.g., trioctylphosphine oxide; TOPO).90,92 However, on many occasions it is desirable to prepare water soluble QDs for use in bioimaging, biosensors, and QDSSCs. In the latter context, due to the size-dependent optoelectronic properties and MEG capability,^{36–39,43} QDs can be exploited as the sensitizer in QD sensitized TiO₂ solar cells. Placing the water soluble QDs in intimate contact with the hydrophilic TiO2 nanocrystals is expected to facilitate efficient charge transfer from QDs to TiO₂. This can be realized by utilizing both QDs (e.g., dithiocarbamate functionalized QDs with the carboxyl group on the surface⁹⁴) and TiO_2 (e.g., the hydroxyl group on the TiO_2 surface^{7, 95, 96}) with complementary functional groups, which allows them to react with each other under mild conditions to form strong chemical linking.

Bifunctional molecules with thiol and carboxyl groups at each end (e.g., mercaptopropionic acid; MPA^{61, 66, 96}) have been used as effective ligands to prepare water dispersible QDs. The thiol group provides chemical affinity to QDs, while the carboxyl group imparts water solubility. Notably, thiol functionalized QDs suffer from instability against photooxidation.^{97–99} This drawback was recently overcome by using dithiocarbamate moieties as ligands due to their strong chelate-type binding to metal atoms.^{100, 101} The resulting dithiocarbamate functionalized QDs exhibited improved resistance against photooxidation. Figure 2 shows the successful transformation of TOPO functionalized CdSe in chloroform from water-insoluble



Fig. 1. TEM images of CdSe/CdS core/shell QDs of different shapes: (a) nanodots, (b) nanorods, and (c) tetrapods; scale bars = 20 nm. Reprinted with permission from Ref. [93], C. L. Choi et al., *Nano Lett.* 9, 3544 (2009). © 2009, American Chemical Society.

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to water-soluble by replacing TOPO with dithiocarbamate moieties; owing to the good solubility of amine in water, this biphasic ligand exchange method can be potentially used for large scale preparation of dithiocarbamate functionalized QDs.⁹⁴ Other approaches, including the use of polyelectrolytes as surface capping ligands, were also developed to impart water solubility on hydrophobic QDs.¹⁰² It is worth noting that the terminal functional groups (i.e., carboxyl group) offer the possibility to further control the surface properties of QDs or to link them to functional molecules.

Most recently, a series of inorganic ligands, molecular metal chalcogenide ligands (e.g., SnS_4^{4-} , $\text{Sn}_2\text{S}_6^{4-}$, AsS_3^{3-} , etc.), have been developed for the surface functionalization of quantum dots, yielding all inorganic QDs.¹⁰³⁻¹⁰⁵ Upon gentle heat treatment, the inorganic ligands could be transformed into a semiconductor solid, which is expected to provide much better electronic interaction between nanoparticles compared to organic molecules. The use

of these new molecular metal chalcogenide ligands for surface functionalization of QDs could potentially provide more efficient electron injection from QDs to electron acceptors compared to those with organic linking molecules.

2.2. Chemical Bath Deposition of QDs

Chemical bath deposition (CBD) is another way to deposit QDs onto semiconducting metal oxide electron collectors that dispenses with need for the use of colloidal QDs with surface passivation.^{48, 61, 62, 66, 106} A much better interface between QDs and an electron accepting semiconductor and more efficient filling of QDs into mesoporous films can be achieved using CBD. In a CBD process, anionic and cationic precursors react slowly under a given condition. Traditional CBD adds two ionic precursors together and controls the reaction rate, usually by controlling the pH of solution to adjust the ionic concentration.^{107–110} A new



Fig. 2. (a) Transformation of hydrophobic CdSe QDs in chloroform into hydrophilic QDs in water, and (b) schematic illustration of the ligand exchange with dithiocarbamate. Reprinted with permission from Ref. [94], J. Wang et al., *J. Mater. Chem.* 18, 3270 (2008). © 2008, The Royal Society of Chemistry.

means for rate control involves separating the cationic and anionic precursors into separate containers and mixing them by alternately immersing the metal oxide into the two precursor solutions.^{60, 111} This method is also called successive ionic layer adsorption and reaction (SILAR). Compared to the traditional CBD method, the SILAR process is more efficient (less than 1 hour as opposed to several hours to overnight), well-controlled in terms of the density and size of the QDs, and selective with respect to only acting on the metal oxides (in comparison to on all surrounding parts, including the container surface), making it the best process to deposit QDs into nanostructured photoanodes.^{60, 106, 112, 113}

SILAR has been successfully employed for the preparation of various QDs (e.g., PbS, CdSe, and CdTe) of II to VI elementals on semiconductor electron collectors (usually TiO₂) with photocurrent yields up to 70%.⁶⁰ Two solutions, one containing anions and the other containing cations, are prepared and the metal oxide electron collector (e.g., TiO₂) is immersed into one of the ionic solutions. Trace amount of ion adsorbs to the surface of the metal oxide. After rinsing with water or ethanol, the metal oxide is soaked into the other oppositely charged ion solution. The residual ion on the metal oxide surface reacts with the oppositely charged ion in the solution to form a thin layer of semiconductor QDs. QDs of a desired thickness can be achieved by repeating the deposition cycles several times.

One obstacle for the SILAR process is the preparation of ionic solution, especially metal anionic solution, as it is very easily oxidized in air. To date, most of the SILAR experiments are based on metal sulfide QDs, for example PbS and CdS,^{70,113–115} due to the high stability of sulfide ions. A recent breakthrough in preparing stable selenide and telluride anion solutions extended the type of QDs that can be deposited using SILAR, in which unstable selenide and telluride anion solutions were stabilized by adding a reducing agent, NaBH₄, into an ethanol solution containing selenium oxide or tellurium oxide.¹¹²

3. QUANTUM DOT SENSITIZED SOLAR CELLS

3.1. Quantum Dot Sensitized Nanoparticle Films

Mesoporous TiO₂ films consisting of nanocrystalline TiO₂ particles have been extensively used as photoanodes in conventional dye sensitized solar cells (DSSCs) and QDSSCs. The film is usually prepared from a presynthesized TiO₂ colloidal solution via the 'doctor blade' technique, followed by annealing at high temperature to yield a crystalline anatase phase. The nanoparticles can be synthesized by a variety of methods, including hydrolysis of a Ti organic complex (e.g., Ti tetraisopropoxide^{8, 10, 61}), templated synthesis,^{116, 117} microemulsion processes,¹¹⁸ etc. Typically, two approaches have been employed to deposit

QDs into mesoporous TiO_2 films: the solution deposition of pre-synthesized colloidal QDs and chemical bath deposition of QDs. As previously discussed, QDs produced from colloidal chemistry possess well-controlled size, shape, chemical composition, and surface properties; however, efficient infiltration of QDs into the mesopores and effective electronic interaction between QDs and TiO₂ remain a challenge. By contrast, chemical bath deposition of QDs provides efficient filling of the mesopores through the atomic scale addition process, but the size and shape of deposited QDs cannot be well-controlled.

In early studies, pre-synthesized colloidal QDs were deposited on mesoporous TiO_2 films to yield QDSSCs. Although the *PCE* of these solar cells was low, considerable knowledge has been gained regarding the optimization of device performance.^{119–121} Low bandgap QDs, such as InP and InAs, have been investigated as photosensitizers due to their high absorption coefficient and optimized bandgap for the full spectral absorption of sunlight.^{48, 62} The photovoltaic performance of InP and InAs QDSSCs is shown in Figure 3.

The low *PCE* can be attributed to the following:

(1) insufficient filling of hydrophobic QDs into hydrophilic mesoporous TiO₂ films;

(2) less effective electronic interaction between QDs and TiO_2 surfaces; and

(3) rapid corrosion of QDs by iodide-based electrolyte. Thereafter, efforts have been made to optimize QDSSCs.

For example, Cobalt redox electrolyte^{48, 106, 112, 113} and polysulfide electrolyte⁶¹ have been used to provide long term stability for QDs in the devices; in addition, QDs and TiO₂ surfaces have been engineered to promote electronic interaction (i.e., charge injection from QDs to TiO₂).^{7, 61, 65, 119, 121} Chemical bath deposition has also been used for high-efficiency deposition of QDs into mesopores.^{107, 109, 111, 112, 114, 122–124}

Since pre-synthesized QDs are usually capped with hydrophobic ligand, for example TOPO, surface functionalization of QDs is a commonly used approach to control surface properties.¹⁰² Surface functionalization not only provides desired surface properties, but also influences the intrinsic physical properties of QDs. For example, enhanced quantum yield of CdSe QDs was observed upon ligand exchange with dithiocarbamate ligand.⁹⁴ In order to increase the loading of QDs and improve electronic interaction between QDs and TiO₂, one widely used method is to use bifunctional molecules (e.g., mercaptopropionic acid; MPA) as the linker to obtain molecular linking between QDs and TiO₂.⁶¹ As shown in Figure 4, CdSe QDs are chemically linked to mesoporous TiO₂ films. The TiO₂ surface was first functionalized with molecules that have carboxyl and thiol groups at each end. The carboxyl groups preferentially attached to the TiO₂ surface while the terminal thiol groups anchored to the CdSe QD surface via ligand exchange with TOPO.⁶¹



Fig. 3. (a) Current–voltage characteristic of InP sensitized TiO₂ solar cells. Inset shows the photocurrent performance. 6.5 nm InP QDs were used. Reprinted with permission for Ref. [62], A. Zaban et al., *Lang-muir* 14, 3153 (**1998**). © 1998, American Chemical Society; (b) Current–voltage characteristic of InAs QD sensitized TiO₂ solar cells, exhibiting a *PCE* of 1.74% under 5 mW/cm² illumination and 0.3% under 100 mW/cm² illumination; 3.4 nm InAs QDs were used. Reprinted with permission from Ref. [48], P. Yu et al., *J. Phys. Chem. B* 110, 25451 (**2006**). © 2006, American Chemical Society.

A scheme illustrating charge injection, charge transport, and charge recombination upon the visible light excitation of CdSe QDs that are linked to TiO_2 is given in Figure 5. By using bifunctional molecules as the linker, CdSe QDs can be effectively assembled on the TiO_2 surface, thereby facilitating efficient electron injection from the conduction band of QDs to TiO_2 , which was confirmed by femtosecond transient absorption and emission quenching characterizations.⁶¹ It is worth noting that higher incident light intensities can lead to increased scattering as well as charge recombination due to accumulated carriers in the TiO₂ domains, which results in low overall *PCE*; this is probably due to inefficient charge transfer from QDs to TiO₂ and inefficient charge collection at bottom electrodes.^{48,61}

Oleic acid capped CdSe QDs have been used as a substitute for TOPO capped CdSe QDs in QDSSCs. It was found that surface capping with oleic acid increased the loading of QDs in mesoporous TiO₂ films, extended the absorption range, and possibly suppressed surface charge recombination events;¹¹⁹ the TiO₂ film was functionalized with the bifunctional molecule MPA prior to loading the QDs. The difference between two capping ligands is their bonding strength to the CdSe surface. The weak bonding between the carboxyl group and CdSe allowed for the formation of strong bonding between MPA and CdSe upon the ligand exchange, leading to a high rate of ligand exchange between oleic acid and MPA. On the other hand, TOPO molecules interact strongly with CdSe, preventing MPA from approaching the CdSe surface, which results in a low rate of ligand exchange between TOPO and MPA. As a result, improved loading of CdSe QDs and extended absorption were achieved, and the overall PCE of QDSSCs with oleic acid capped CdSe showed 64% improvement over those with TOPO capped CdSe.119

According to a recent investigation on the charge injection rate from QDs to TiO₂ using a transient absorption technique, the size dependent optical properties of QDs makes it possible to engineer the semiconductor bandgap.⁹⁶ It was found that as the size of QDs decreases (i.e., larger bandgap), the electron transfer rate from QDs to TiO₂ increases, which is due to the increased energy difference between the conduction band of CdSe and that of TiO_2 (Fig. 6). As a result, the fastest electron transfer rate was observed from 2.4-nm CdSe QDs. A recent study on the modulation of electron injection in CdSe-TiO₂ system revealed that medium alkalinity affects the energetic band position of TiO₂, and thus, influences the charge injection process between CdSe QDs and TiO2.125 Figure 7 shows the pH dependent emission spectra, emission response of CdSe on the TiO₂ film, and emission lifetime response of CdSe on the TiO₂ and SiO₂ films. SiO₂ is an inert substrate and does not directly influence the radiative recombination process in CdSe; therefore it was used as the control experiment. It was clearly shown that a mild acidic medium is favorable for the electron injection from CdSe QDs to TiO_2 , and a nearly 5-fold increase in the apparent electron transfer rate constant was observed upon decreasing the pH from 12 to 5.5 based on the emission lifetime measurement.¹²⁵ This result is of great importance for promoting charge injection from QDs by controlling the pH of the medium. It is also worth noting that the change in the emission response is reversible, making it possible to use CdSe-TiO₂ systems for sensing the pH of a medium.¹²⁵

One challenge in QDSSCs is to capture photogenerated electrons as quickly as they are generated, and



Fig. 4. Schematic illustration of chemical linking of CdSe QDs to a Ti Q_2 surface using bifunctional molecules, for example, mercaptopropionic acid (MPA). Reprinted with permission from Ref. [61], I. Robel et al., J. Am. Chem. Soc., 128, 2385 (2006). © 2006, American Chemical Society.

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subsequently transport them to the electrode in an efficient manner.¹²⁶ Recently, a QDs-C₆₀ composite film was deposited on mesoporous TiO₂ films for the efficient capture of a photogenerated electron.^{126, 127} C₆₀ and its derivatives have been widely used in organic thin film solar cells because of their outstanding electron accepting property.¹²⁸ Electrophoretic deposition of CdSe-C₆₀ composites provide better interaction between CdSe and C_{60} by encapsulating CdSe QDs with C₆₀ clusters. Emission quenching and emission lifetime measurements showed that C₆₀ can efficiently capture the electrons from photoexcited CdSe QDs, which was further confirmed by the photoelectrochemical experiment, i.e., the observed photocurrent generation efficiency within CdSe-C₆₀ films is two orders of magnitude greater than the CdSe films alone (Fig. 8). Other carbon nanostructures can also be used for efficiently capturing photogenerated electrons in QDs, for example, stacked-cup carbon nanotubes (SCCNT).¹²⁷ Electrophoretic deposition can efficiently deposit SCCNT-CdSe on the TiO₂ electrode; ultrafast electron transfer from photoexcited CdSe QDs to SCCNT was achieved and



Fig. 5. Schematic illustration of the charge injection, charge transport, and charge recombination in CdSe QD sensitized mesoporous TiO₂ films at (A) low and (B) high excitation intensities. Reprinted with permission from Ref. [61], I. Robel et al., *J. Am. Chem. Soc.* 128, 2385 (**2006**). © 2006, American Chemical Society.

20 confirmed by emission quenching and transient absorption measurements. Moreover, it was found that decreasing the size of QDs further increased the charge transfer rate.¹²⁷ These observations suggest that integrating CdSe QDs with carbon nanostructures may be a promising direction toward the development of high performance QDSSCs.

Infiltrating QDs into mesoporous TiO₂ films remains a challenge in QDSSCs, mainly because the size of QDs is much larger than ruthenium dye molecules used in traditional DSSCs and because non-polar solvents (i.e., toluene) used to disperse QDs cannot wet the hydrophilic surface of TiO₂. Chemical bath deposition (CBD), unlike the pre-synthesized colloidal QDs capped with ligand, involves the atomic scale build-up of elements on the TiO₂ surface. Anionic and cationic precursors are usually prepared in aqueous or polar solvent, which can wet the hydrophilic TiO₂ surface, thereby achieving a higher degree of filling. In addition, CBD of QDs provides intimate contact between QDs and the TiO₂ surface, resulting in much better electronic interaction. In the conventional CBD process, anionic and cationic precursors react slowly under a given condition. Two ionic precursors are usually put together and the reaction speed can be controlled by the pH value of the solution and the ionic concentration.¹⁰⁷⁻¹¹⁰ Recently, a new way to control the reaction rate has been developed by simply immersing the electrode alternately into two precursor solutions.^{60, 111} This method, as discussed above, is also called successive ionic layer adsorption and reaction (SILAR). Various QDs have been successfully prepared by CBD technique.^{60, 106, 111–113} The most recent advances in the preparation of stable Se^{2-} and $Te^{2-}\ensuremath{\text{ precursors}}$ make it possible to deposit CdSe and CdTe QDs onto mesoporous TiO₂ films.¹¹² The absorption spectra, digital image of mesoporous TiO₂ films after SILAR deposition



Fig. 6. (A) The transient recovery recorded at the bleaching maximum following 387 nm laser pulse excitation of CdSe QDs in 1:1 ethanol/THF containing mercaptopropionic acid (a) without and (b) with linked TiO_2 particles. (B) Schematic illustration of the principle of electron transfer from quantized CdSe into TiO_2 , and (C) the dependence of the electron transfer rate constant on the energy difference between conduction bands; the top axis represents assumed CdSe conduction band energy positions. Reprinted with permission from Ref. [96], I. Robel et al., *J. Am. Chem. Soc.* 129, 4136 (2007). © 2007, American Chemical Society.



Fig. 7. (A) Emission spectra and (B) emission response of CdSe on TiO_2 films at three different pH values. Distilled water was flowed through the cell before changing the pH. (C and D) Emission lifetime responses of CdSe on TiO_2 and SiO_2 films at varying pH, respectively. Reprinted with permission from Ref. [125], V. Chakrapani, et al., *J. Am. Chem. Soc.*, 132, 1228 (2010). © 2010, American Chemical Society.



Fig. 8. (A) Dependence of the incident photon to current generation efficiency (*IPCE*) on the incident wavelength, and (B) the photocurrent response of electrodes to ON-OFF cycles of illumination: (a) C60, (b) CdSe QDs, and (c) CdSe- C_{60} clusters on SnO₂ film electrodes. The electrolyte was 0.1 M Na₂S in water. Reprinted with permission from Ref. [126], P. Brown and P. V. Kamat, *J. Am. Chem. Soc.* 130, 8890 (**2008**). © 2008, American Chemical Society.

of CdSe QDs, and TEM images of the CdSe-TiO₂ particles are shown in Figure 9. As the deposition cycles increased, the color of the TiO₂ film became deeper, indicating the increased amount and size of CdSe QDs. The UV-vis absorption spectra also confirmed the successive deposition of QDs onto mesoporous TiO₂. From TEM and HRTEM characterizations, it is clear that SILAR-deposited CdSe QDs had intimate contact with TiO₂ nanoparticles, thereby providing effective electronic interaction between CdSe and TiO₂ without the use of any molecular linkers (e.g., MPA).

It was also observed that a thin terminating layer of CdTe could dramatically increase charge collection



Fig. 9. Absorption spectra of a $2-\mu$ m thick film made of 20 nm TiO₂ after the SILAR deposition of CdSe QDs (one-six cycles) and photographs of the corresponding films (inset; left). TEM images of CdSe QDs/TiO₂ particles after six cycles of the SILAR process are also shown. Reprinted with permission from Ref. [112], H. Lee et al., *Nano Lett.* 9, 4221 (**2009**). © 2009, American Chemical Society.

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efficiency. Transient photovoltage and photocurrent decay measurements suggested a lower charge recombination with the presence of a thin CdTe terminating layer, which served as a barrier layer and retarded the recombination between photogenerated electrons and the oxidized cobalt electrolyte.¹¹² As a result, a longer electron diffusion length could be achieved, and an overall PCE over 4% under 100 W/m² illumination was observed. Upon optimizing the structure of QDSSCs, a cascade electrode of TiO₂/CdS/CdSe has recently been developed for solar cell applications, in which the reorganization of energy levels between CdS and CdSe formed stepwise band-edge levels to facilitate the electron injection and hole-recovery of CdS and CdSe QDs; in addition, CdS and CdSe QDs have a complementary effect in light harvesting. In the end, an overall PCE of 4.22% was obtained under AM 1.5G illumination, which is the highest reported value for QD sensitized solar cells.111

3.2. Quantum Dot Sensitized Nanowire Arrays

As discussed above, the most commonly used semiconductor electrode for sensitized solar cells are mesoporous TiO_2 films composed of crystalline TiO_2 nanoparticles. However, the random dispersion of TiO_2 nanoparticles in thin films leads to increased scattering of free electrons and electron trapping at the interfaces between nanoparticles, thereby reducing electron mobility.¹²⁹ In this context, the use of aligned, single-crystalline wide bandgap semiconductor nanorods and nanowires in DSSCs allows for direct electron transport along the long axis of nanorods and nanowires that are normal to the electrode.^{64, 67, 129–132} Recently, ZnO single- crystalline nanowires have been extensively studied in terms of synthesis and application in DSSCs;^{2, 132, 133} the vectorial electron transport along the nanowire axis resulted in improved charge collection efficiency. However, due to its poor chemical stability, limited *PCE* has been achieved in ZnO nanowire-based sensitized solar cells.

QD sensitized ZnO nanowire arrays have been reported and oxygen plasma treatment was found to activate the ZnO surface, resulting in increased anchoring of CdSe quantum dots.⁶⁶ An array of ZnO nanowires was grown vertically from a fluorine-doped tin oxide (FTO) conducting substrate. Subsequently, MPA functionalized CdSe ODs were chemically anchored to the ZnO nanowires surface via the interaction of a terminal carboxyl group on functionalized CdSe and the hydroxyl group on the ZnO surface. Upon photoexcitation, excitons were generated in CdSe QDs and subsequently injected from CdSe QDs to ZnO nanowires. On the initial attempt, the grafting density of MPA capped CdSe ODs onto ZnO nanowires was low. This was increased by modifying the ZnO surface with oxygen plasma prior to the QDs adsorption (Fig. 10). Oxygen plasma treatment may charge the nanowire surface, create dangling bonds through ion bombardment, remove surface contaminants, and saturate the surface with hydroxyl groups,^{66,71} which in turn contributed to the increased grafting of QDs onto ZnO nanowires. Photoelectrochemical results showed that both the PCE (0.4%) under AM1.5G illumination) and short-circuit current density of the quantum dot sensitized solar cells assembled using the oxygen plasma-treated ZnO nanowires was more than an order of magnitude higher than those assembled using non-treated nanowires.⁶⁶

> Quantum dots (*e.g.*, CdSe) attached to nanowires (*e.g.*, ZnO)



Fig. 10. Schematic of the quantum dot sensitized solar cell. An array of ZnO nanowires, grown vertically from an F-doped SnO₂/ glass substrate and decorated with CdSe QDs serves as the photoanode. A second F-doped SnO₂/glass substrate, coated with a 100 Å layer of Pt, is the photocathode. The space between the two electrodes is filled with a liquid electrolyte. Reprinted with permission from Ref. [66], K. S. Leschkies et al., *Nano Lett.* 7, 1793 (**2007**). © 2007, American Chemical Society.

Single-crystalline TiO₂ nanowires can be directly grown on a transparent conductive substrate via a solvent thermal technique, and their application in DSSCs has recently been demonstrated.^{64,67} These single crystalline TiO₂ nanowire arrays are also promising photoanodes for QDSSCs. Moreover, TiO₂ has much better chemical stability than ZnO, making it suitable for stable, highperformance solar cells.

Although the performance of quantum dot sensitized nanowire solar cells is low, further optimization, including the size and chemical composition of QDs, selection of surface capping ligand, chemical bath deposition (CBD) of QDs, high-performance hole transport electrolyte, etc., is expected to enhance the *PCE* of this type of solar cell.

3.3. Quantum Dot Sensitized Nanotube Arrays

Highly ordered, vertically oriented TiO_2 nanotube arrays of different aspect ratios and surface qualities have recently been fabricated and utilized as alternative nanoscale architectures to substitute for sintered TiO_2 nanoparticle films in DSSCs.^{68,71,134} They also exhibited promising performance for use in gas sensors,^{135–137} water splitting,^{134,138–140} photocatalysts,^{141,142} and cell separation.^{143,144} In highly ordered TiO_2 nanotube arrays, each nanotube is oriented perpendicular to the film surface and extends through the entire thickness of the film, thus providing a separated channel for electron transport.

Highly ordered TiO₂ nanotube arrays can be fabricated via electrochemical anodization of Ti (i.e., Ti foil or Ti thin film deposited on substrates) in a fluorine containing electrolyte, which has been extensively investigated in the past several years.^{145–154} In an electrochemical anodization process, TiO₂ nanotube arrays were formed via selforganization of TiO₂ as a result of a delicate balance of electrochemical oxidation of Ti into TiO₂, electrical field induced dissolution of TiO2, and the chemical dissolution of TiO_2 by fluorine ions as the fluorine ions quickly reacted with TiO₂.^{134, 155-160} By tuning the electrochemical anodization conditions (i.e., electrolyte, temperature, anodization potential, etc.), highly ordered TiO₂ nanotube arrays with pore diameters ranging from 20 to 100 nm, tunable wall thicknesses, and variable film thicknesses can be obtained.63, 161, 162

It is noteworthy that due to the weak connection between the TiO₂ nanotubes and the Ti substrate through the TiO₂ "barrier layer", a thick freestanding TiO₂ nanotube film can be readily obtained by mechanically detaching it from the Ti substrate via a mild ultrasonication.^{163,164} Alternatively, selective chemical etching of the metallic Ti substrate using a bromine-containing methanol solution also yielded freestanding TiO₂ nanotube arrays; however, the employed etching solution was highly corrosive.¹⁴¹ After a long anodization time(e.g., 60 hr) in organic electrolyte, the top surface of the TiO₂ nanotube arrays was usually covered by a thin layer of TiO_2 nanowires, which formed due to the electric field induced chemical etching of nanotubes in a 'bamboo-splitting' mode.¹⁶⁵ This thin layer of nanowires can be readily removed by ultrasonication, exposing the nanotubes buried underneath.¹⁶³

The ability to produce a freestanding TiO_2 nanotube film makes it possible to transfer the film to a variety of substrates (e.g., Si or transparent conductive FTO-coated glass). On the other hand, the poor mechanical strength of the freestanding film makes it difficult to handle, especially in the case of a very thin TiO₂ film. Therefore, it is crucial to grow the TiO₂ nanotubes directly from a desired substrate (e.g., transparent FTO-coated glass). For example, for the use of TiO₂ nanotube arrays in DSSCs, it is more advantageous to exploit TiO₂ nanotubes obtained by anodization on a transparent conductive substrate than those formed on a metallic Ti substrate. In the so-called "front-side-illuminated" DSSC, the incident light directly illuminates the dye sensitized TiO₂ nanotubes through the FTO-coated glass. However, in the "back-side-illuminated" mode, the incident photons have to pass through the semitransparent top electrode and the redox electrolyte (e.g. I_3^-/I^-) before reaching the dye sensitized TiO₂ nanotube, leading to a significantly less efficient absorption of the incident light.

In comparison to transferring a freestanding TiO₂ nanotube film onto the transparent conductive substrate for use in DSSCs, an intimate contact between TiO₂ nanotube arrays and the transparent conductive substrate is readily present when anodizing Ti thin film that is predeposited on the substrate by sputtering (e.g., radio frequency (RF)-sputter deposition).^{166, 167} Interestingly, the as-prepared black TiO₂ nanotube film obtained after annodization transforms into a transparent film after high temperature annealing to induce crystallinity.^{162, 167} The optically transparent TiO₂ nanotube arrays have also been used as sensing elements for hydrogen sensing, exhibiting very promising performance compared to the nanotube arrays formed on Ti substrates.¹⁶⁸ It is worth noting that the attainable thickness of TiO₂ nanotube arrays is restricted to only a few hundred nanometers because of limitations on the ability to deposit thicker, high-quality Ti on the substrate with current deposition techniques (e.g., 360 nm thick TiO₂ nanotubes obtained from anodization of 500 nm thick pure Ti film deposited on the substrate).^{68, 167} Very recently, an elegant study has demonstrated that a 1000 nm thick TiO₂ nanotube film can be fabricated by anodizing the deposited Ti film in an ethylene glycol electrolyte.169

 TiO_2 nanotube arrays are amorphous directly after anodization. Many potential applications require the use of crystallized TiO_2 because of its unique electrical and optical properties. Furthermore, specific crystalline phases are ideal for different applications; the anatase phase of TiO_2 is preferred in DSSC and photocatalysis, whereas the rutile form is mostly used in the area of dielectrics and high-temperature oxygen gas sensors.¹⁷⁰ To transform the amorphous TiO₂ into the crystalline phases (anatase, rutile, etc.), thermal annealing is often carried out. Notably, the TiO₂ nanotube structures are retained after annealing at high temperature, and the phase conversion has been confirmed by X-ray diffraction. Additionally, Raman scattering can be performed to determine the crystalline phases of TiO₂ nanotubes due to different crystalline phases having specific Raman signatures. For example, the anatase phase has Raman peaks at 145, 198, 399, 516, and 640 cm^{-1} ; while the rutile phase possesses Raman peaks at 143, 240, 447, and 612 cm^{-1} . Amorphous TiO₂ nanotube arrays exhibit a broad spectrum; by contrast, TiO₂ nanotubes annealed at 500 °C in air display characteristic peaks of the anatase phase.^{163, 171} Thermal stability studies on the TiO₂ nanotube arrays showed that the nanotube structure was stable with annealing temperature up to 600 °C; with thermal treatment at higher temperatures, the nanotube structure collapsed due the expansion of crystalline domains in the nanotube walls.¹⁷¹ When the annealing temperature was higher than 700 °C, the crystalline phase transformed from anatase to rutile, as confirmed by Raman scattering.¹⁷¹ According to systematic studies of crystalline formation in TiO₂ nanotube arrays, an optimal annealing temperature falls between 400 °C and 600 °C. This heat treatment allowed the formation of highly crystalline anatase TiO₂ while maintaining the nanotube structures.¹⁷¹ Figure 11 shows the SEM characterization of highly ordered TiO₂ nanotube arrays and the formation of anatase phase as revealed by Raman scattering.71

As noted above, highly ordered TiO₂ nanotube arrays have been used as a substitute for conventional TiO₂ nanoparticle films in DSSCs and have shown promising performance.^{7, 65, 95, 134, 161, 172, 173} A 2.9% PCE was achieved using 360 nm thick transparent TiO₂ nanotube arrays to assemble DSSCs in a front side illumination mode.95 A PCE as high as 6.89% has recently been achieved in a back side illumination mode using TiO₂ nanotube arrays that were grown on Ti foil with film thicknesses of 20 μ m.¹³⁴ Very recently, the efficiency of dye sensitized TiO₂ nanotube solar cells has been further improved to 7.37% upon TiO₂surface treatment with TiCl₄ and oxygen plasma.⁷¹ Compared to the TiO₂ nanoparticle film-based DSSCs, enhanced charge collection efficiency and enhanced light scattering in TiO₂ nanotube array-based DSSCs were observed.⁷ From the dye loading measurement, it was found that the dye loading in both TiO₂ nanotube arrays and TiO₂ nanoparticle films were similar for identical film thicknesses.⁷

When CdSe QDs were used to sensitize TiO_2 ,^{61,96} higher *PCE* was obtained by using highly ordered TiO_2 nanotube arrays to replace the TiO_2 nanoparticle films.⁶⁵ Pre-synthesized CdSe QDs were molecularly linked to TiO_2 nanotube surfaces using the bifunctional molecule,



Fig. 11. Structural characterization of highly ordered TiO₂ nanotube arrays: (a) SEM topology, scale bar = 1 μ m; (b) SEM cross-sectional view, scale bar = 1 μ m; (c) SEM cross-sectional view, scale bar = 1 μ m; and (d) Raman spectra of amorphous (black curve) and crystalline (red curve) TiO₂ nanotube arrays, where the Raman peaks at 145, 196, 399, 516, and 640 cm⁻¹ suggest the formation of anatase TiO₂. Reprinted with permission from Ref. [71], J. Wang and Z. Q. Lin, *Chem. Mater.* 22, 579 (**2010**). © 2010, American Chemical Society.

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MPA. Compared to mesoporous TiO_2 films, the difference in TiO_2 morphology had little effect on the charge injection rate but influenced electron transport within the film. The maximum *IPCE* obtained with CdSe/TiO₂(NT) (45%) is greater than that of CdSe/TiO₂(NP) (35%). The nanotubular TiO₂ architecture provides a better scaffold for the construction of QDs solar cells, and the photovoltaic performance can be further improved by fabricating rainbow QDSSCs, in which QDs of different sizes are successively deposited into highly ordered TiO₂ nanotubes to render full spectrum absorption of sunlight (Fig. 12).⁶⁵

Chemical bath deposition (CBD) of CdS QDs was also carried out on highly ordered anodic TiO_2 nanotube arrays.⁷⁰ The CBD approach possesses several advantages, including sufficient filling of QDs in the nanotubes and intimate contact between QDs and the TiO₂ surface, as revealed by TEM imaging of the TiO₂ nanotube after CBD deposition of CdS QDs. A cell efficiency of 4.15% was obtained from the CdS modified TiO₂ nanotube arrays.⁷⁰

By taking advantage of recent advances in the preparation of stable Se^{2-} and Te^{2-} precursors, CdSe, PbSe, and CdTe QDs can be deposited into TiO_2 nanotube arrays through the SILAR process. Due to the flexibility of tuning the structural parameters of TiO_2 nanotube arrays, it is possible to obtain optimized filling of QDs as well as a balance between light absorption and charge transport. Thus enhanced solar energy conversion efficiency can be expected from using QDs to sensitize highly ordered TiO_2 nanotube arrays.

3.4. High Performance Electrolyte

In early studies of QDSSCs, iodine-iodide based electrolyte was used. Although it has been proven to be quite



Fig. 12. A rainbow solar cell assembled with different-sized CdSe QDs on a TiO_2 nanotube array. Reprinted with permission from Ref. [65], A. Kongkanand et al., *J. Am. Chem. Soc.* 130, 4007 (**2008**). © 2008, American Chemical Society.

efficient for hole transport in conventional dye sensitized solar cells, iodine based electrolyte was found to be corrosive to QDs, resulting in degradation of QDs and short lifetime of QDSSCs. As an alternative, polysulfide based aqueous electrolytes have been used in QDSSCs.^{1, 61, 65, 126} More recently, cobalt redox electrolyte has been developed as a high performance, non-corrosive electrolyte for QDSSCs that provides long term stability.^{48, 106, 112, 113} Solid state electrolytes have also be investigated for QDSSCs,^{3, 172} with the purpose of eventually fabricating all solid-state high performance QDSSCs.

4. ELECTRONIC INTERACTION BETWEEN QUANTUM DOTS AND PHOTOANODES

When QDs absorb incident photons of sufficient energy (equal or higher than bandgap of QDs), an electron is excited from the valence band to the conduction band, by leaving a positively charged hole in the valence band, The positively charged hole strongly attracts an excited elect tron, forcing the electron to recombine with it. In this case, the electron stays inside the QDs, rather than transferring to the electron acceptor. The very high incident photon to current coversion efficiency (IPCE) of QDs (up to 80%) and relatively low external quantum efficiency (EOE) (less than 4%) indicates that only a very small amount of electrons generated in QDs can actually be transferred to the electron acceptor, and the rest recombine with holes inside the QDs. Since the recombination process involves both electrons and holes, efficient separation of excited electrons and holes is desired to decrease the recombination rate;^{88, 174–176} this can be achieved by rapid injection of electron from QDs to electron acceptors, and efficient hole tranpsort to counter electrodes through hole conducting electrolytes.

Spontaneous charge separation at the donor-acceptor interface involves the electron injection from QDs into the electron acceptor. The transfer rate of electrons from QDs to the acceptor is determined by several parameters, among which the difference of conduction band energy between QDs and electron acceptor is the most important. The charge transfer rate can be estimated by comparing the lifetime of exited electrons inside QDs with and without the electron acceptor.⁹⁶

The kinetics of the electron transfer can be described using Marcus theory in a nonadiabatic reaction in the classical activation limit,^{177, 178} which implies that the electron transfer rate is exponential to a quadratic function of the driving force, i.e., the difference of the Gibbs free energy between QDs and electron acceptor. The charge injection rate from QDs to the electron acceptor exhibits a strong size-dependent characteristic according to transient absorption measurements.⁹⁶ The energy difference between QDs and the acceptor is determined by the difference of their conduction band energies. The larger the difference, the stronger the driving force, and, in turn, the faster the electron transfer rate. 96

Since the mass of an electron is much less than that of a hole, the shift in the conduction band is more significant than the shift in the valence band when the size of QDs changes.¹⁷⁹ Therefore the conduction band energy can be expected to become more negative with a decrease in the ODs size.¹ The electron transfer rate increases as the energy difference increases. The change in size of CdSe QDs from 7.5 nm to 2.4 nm resulted in a change in the energy difference from 0.3 eV to 0.8 eV; as a consequence, as high as a three orders of magnitude increase in the electron transfer rate, from 10^7 s^{-1} to 10^{10} s^{-1} , was observed.¹ The average electron lifetime in the 2.4-nm CdSe QDs is 83 ps as compared to 2-50 ps in the CdS/TiO₂ systems,^{180, 181} in which the derease in electron lifetime indicates efficient electron injection from QDs to TiO_2 .

In In addition to the efficient electron injection from QDs to the acceptor, the removal of holes in QDs can also promote charge separation. While the electrons transfer from the higher to lower conduction band, the holes transfer from the lower to higher valance band under the same driving force of Gibbs free energy. Although the size variation cannot influence the valance band level as much as the conduction band level, the design toward using different materials with different energy levels to yield a core/shell or multilayer structure has been introduced, which could facilitate charge separation by the efficient extraction of holes in the valence band of QDs.^{111,112} Figure 13 shows an example of utilizing a thin layer of CdTe QDs to effectively extract holes in CdSe QDs, thereby allowing longer time for the electron injection from CdSe QDs to TiO2.112 The level of conduction bands for CdTe, CdSe and TiO₂ are -3.7, -4.1 and -4.2 eV, respectively; thus the electrons generated in CdSe transfer to TiO₂. On the other hand, the level of valence bands for CdTe, CdSe and TiO₂ are -5.0, -5.2, -6.0 eV, respectively; therefore the holes generated in CdSe can transfer to CdTe. Compared to the CdSe/TiO₂ system, the extraction of holes by CdTe in



Fig. 13. Energy diagram of the bulk band offsets in the $TiO_2/CdSe/CdTe$ system. Reprinted with permission from Ref. [112], H. Lee et al., *Nano Lett.* 9, 4221 (**2009**). © 2009, American Chemical Society.

the CdTe/CdSe/TiO₂ system lowered the concentration of holes in CdSe, resulting in a decreased charge recombination rate.

Core/shell QDs have also been introduced for efficient charge separation.¹⁸² In the case of CdSe/ZnS core/shell QDs, the conduction band of ZnS is higher than that of CdSe while the valance band is lower, suggesting that both the electrons and holes generated from CdSe would have less chance to transfer outside the QDs through the ZnS barrier (Fig. 14). Therefore, they are effectively trapped inside the CdSe core. This trapping effect is not advantageous for charge separation and photocurrent generation. However, the ZnS shell works as a protection layer, increasing the half-life of the CdSe core from 2.4 min to 84.1 min; a total of 21.2% initial efficiency is retained even after 20 h of continuous illumination, as compared to 90% loss during 2 h illumination of the CdSe core.¹⁸²

In order to take advantage of the protective ability of ZnS and increase the photocurrent, a novel design of QDSSCs based on nonradiative Forster resonance energy transfer (FRET) has recently been proposed (Fig. 15),¹⁸³ in which the excited electron and hole within QDs are considered as an oscillating dipole donor, and the energy can be transferred to a nearby dipole acceptor (organic dye in this design) through resonance effects without direct contact of the two dipoles.¹⁸⁴ This transfer requires a short distance between the donor and acceptor, typically 1 to 10 nm, to sustain the interaction. The excited donor is treated as an oscillating dipole, which transfers its energy to another dipole with the same resonance frequency. Namely, the fluorescence emission spectrum of the donor overlaps the absorption spectrum of the acceptor. CdSe was used as the donor QD, and unsymmetrical squaraine dye was used as the acceptor. The ZnS barrier prevented direct electron injection from the CdSe core to nanocrystallized TiO₂; thus all excited electrons in the CdSe donor were trapped, recombined, and transferred energy to the acceptor dye molecules. As a result, the dye was excited and excited electrons were transferred to nanocrystalline TiO₂ through a thin layer of amorphous TiO2.183 FRET may also take place at a QD films with a single composition but different size.¹⁸⁵ When QDs of different sizes are closely packed together, which may happen due to uncontrollable size



Fig. 14. Energy band position of CdSe/ZnS core/shell QDs. Reprinted with permission from Ref. [182], J. B. Sambur and B. A. Parkinson, J. Am. Chem. Soc. 132, 2130 (2010). © 2010, American Chemical Society.



Fig. 15. Schematic representation of QD sensitized solar cells based on nonradiative energy transfer. Reprinted with permission from Ref. [183], S. Buhbut et al., *ACS Nano* 4, 1293 (2010). © 2010, American Chemical Society.

under chemical bath deposition, the smaller QDs that have a larger bandgap and therefore higher emission energy would serve as donors to transfer energy to the acceptors (i.e., larger QDs) that have smaller bandgaps and lower absorption energy.

In A recent work suggested that the design of injection and recombination in QDSSCs could be achieved by the appropriate use of molecular dipoles (i.e., benzylthiol) and conformal coatings (i.e., ZnS), resulting in increased electron injection from QDs to TiO_2 and reduced charge recombination. With optimized surface treatment by molecular dipoles and conformal coatings, a dramatic 600 % increase of photovoltaic performance in CdSe QD sensitized TiO_2 solar cells was obtained under full 1 sun illumination.¹⁸⁶

5. SUMMARY AND OUTLOOK

QDSSCs possess the transformative potential to increase the maximum attainable conversion efficiency of solar energy because of the outstanding optical properties and multiple exciton generation (MEG) capability of QDs. However, so far the achievable power conversion efficiency remains low, mainly due to the following:

(1) limited success in the synthesis of QDs with broad spectrum absorption and high absorption coefficient;

(2) insufficient filling of QDs in nanoporous photoanodes;(3) inefficient separation of excitons (i.e., electron-hole pairs) in QDs upon absorption of incident light; and

(4) low performance electrolytes. Revolutionary breakthroughs in QD synthesis and deposition techniques are required for QDSSCs to reach their full potential.

These include the synthesis of QDs with broad absorption and high absorption coefficient; the use of QD/carbon nanostructures to promote the electron injection from QDs to TiO_2 ; the deposition of multiple QDs with novel energy alignment on the TiO_2 surface to not only increase light absorption, but also facilitate charge separation by the efficient extraction of excited electrons and holes; the development and optimization of new and efficient deposition techniques, such as SILAR, to better control the deposition process and QD quality; the use of highly ordered nanostructures for better charge transport to enhance charge collection efficiency while reducing the chance of charge recombination; the surface modification and activation of TiO_2 surfaces to further enhance the electronic interaction between QDs and electron acceptors; and the development of novel device designs (e.g., QDSSCs based on FRET). Therefore, future efforts should focus on high-efficiency light absorption by QDs, efficient deposition/impregnation of ODs on photoanodes, improved electronic interaction between QDs and electron acceptors, high-performance non-corrosive hole transporting electrolytes, etc. All these are the key to realizing high-efficiency QDSSCs. The increasing interest in solar-to-electric energy conversion coupled with recent advances in the synthesis of QDs and fabrication of novel 3D semiconductor nanostructures fosters an environment for continued breakthroughs in QDSSCs, and devices with high performance, low fabrication cost, and long term stability can be expected in the future.

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