Anchoring Cadmium Chalcogenide Quantum Dots (QDs) onto Stable Oxide Semiconductors for QD Sensitized Solar Cells

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Anchoring quantum dots (QDs) onto thermodynamically stable, large band gap oxide semiconductors is a very important strategy to enhance their quantum yields for solar energy conversion in both visible and near-IR regions. We describe a general procedure for anchoring a few chalcogenide QDs onto the titanium oxide layer. To anchor the colloidal QDs onto a mesoporous TiO_2 layer, linker molecules containing both carboxylate and thiol functional groups were initially attached to TiO_2 layers and subsequently used to capture dispersed QDs with the thiol group. Employing the procedure, we exploited cadmium selenide (CdSe) and cadmium telluride (CdTe) quantum dots (QDs) as inorganic sensitizers for a large band gap TiO_2 layer of dye-sensitized solar cells (DSSCs). Their attachment was confirmed by naked eyes, absorption spectra, and photovoltaic effects. A few QD-TiO_2 systems thus obtained have been characterized for photoelectrochemical solar energy conversion.

Key Words : Quantum dot, Dye-sensitized solar cell, Quantum dot sensitization

Introduction

Since O'Regan and Grätzel first reported an efficient dye-sensitized solar cell (DSSC) system in 1991,[1] similar cells have been studied by many investigators from both academic and practical viewpoints and considered as one of the most promising unconventional photovoltaic systems.[2] In these new solar cells, organic dye molecules are anchored to a mesoporous TiO_2 layer with high surface areas, absorbing incident solar radiation. Engineering the dye molecules is one of the key processes to improve the overall conversion efficiency of the DSSC, and many different dye molecules have been studied extensively.[3] However, molecular engineering of organic dyes for light-harvesting has its limitations such as difficulties in utilizing the infra-red regime of the solar spectrum and instability for long-term uses. Recently, sensitization of mesoporous TiO_2 layers with various semiconducting QDs or nanoparticles including CdS,[4] PbS,[5] InP,[6] and Bi_2S_3[7] has been proposed and their photovoltaic properties tested.[8] QDs can be well suited for solar cell sensitization because they are robust, tunable for their effective band gaps, and easy to process, hence ideal to optimize a solar cell for a maximum efficiency. Moreover, QDs can offer an advantage of the simple spin-casting process, which makes it cost effective by avoiding high temperature or vacuum microfabrication processes. Thus far, however, quantum dot-sensitized solar cells have not been fully explored and evaluated, although a study of mesoscopic TiO_2 films modified with CdSe and InAs QDs has recently been reported.[9] There are many variables to be studied and improved such as synthetic routes for the QDs and preparation methods of sensitizing-QD layers including chemical bath deposition, electrodeposition, spray deposition, molecular linking between QDs and the large band gap metal oxides, and other methods. Recent popularity of preparation of well-defined colloidal QDs by wet chemical synthesis and studies of their physical properties[10] have opened a variety of applications in diverse areas such as biological tagging,[11] light-emitting diodes,[12] lasers,[13] and solar cells.[14] Further, recent experiments demonstrated that multiple excitons can be efficiently generated from single photon absorption in colloidal PbSe and PbS QDs through impact ionization (inverse Auger process),[15] leading to QD-solar cells of over 100% incident photon-to-current conversion efficiency (IPCE) by providing a judicious way to collect the photogenerated excitons before they recombine. Despite the great potential of QDs for inorganic dyes in DSSCs, systematic investigations of the QD applications in DSSCs are still at an early stage. For instance, advantages of colloidal QDs have not been fully exploited for their narrow size distribution, good crystallinity, and flexible band-gap tuning. We report here a general procedure to attach colloidal QDs onto a mesoporous large band gap oxide layer, replacing organic dyes in DSSC systems, and the roles of different linker molecules between QDs and TiO_2 layers have also been studied by measuring solar conversion efficiencies of thus assembled QDs-TiO_2 cells. We then compare the performances of various linker molecules as well as CdSe and CdTe QDs by assembling regenerative solar cells to demonstrate the proof of concept.

Experimental Method

Chemicals. Technical grade trioctylphosphine oxide (TOPO, 90%), technical grade trioctylphosphine (TOP, 90%), selenium powder (−100 mesh, 99.999%), tellurium powder (−200 mesh, 99.8%), 4-mercaptobenzoic acid (MBA, 97%), 3-mercaptopropionic acid (MPA, 99+%), 11-mercaptoundecanoic acid (MUA, 95%), anhydrous toluene (99.8 %), chloroform, pyridine, and hexane were obtained from Aldrich. Cadmium acetate hydrate (99.999%) was purchased from Alfa Aesar. Ethanol and methanol were of HPLC grade. Iodine, LiI, titanium diisopropoxide bis(acetylacetonate), and anhydrous acetonitrile were purchased from Aldrich. *cis*-Bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) (N3 dye), TiO_2 paste (Ti-Nanoxide T), Pt catalyst paste, SX-1170 thermoplastic hot-melt sealing sheets, and fluorine doped tin oxide (SnO_2:F, FTO) (15 ohm/sq) glass were purchased from Solaronix.

Synthesis of CdSe and CdTe QDs. CdSe nanocrystal QDs were prepared according to the procedure developed by Peng *et al.*[16] with a few modifications. A selenium (Se) solution was prepared by mixing 0.80 g of Se powder, 24 mL of trioctylphosphine (TOP), and 0.40 mL of toluene. 50 g of technical grade trioctylphosphineoxide (TOPO) and 0.80 g of cadmium acetate hydrate were placed in a three-necked round-bottom flask and heated to ~150 °C. After the solution was degassed and purged with nitrogen a few times at this temperature, it was heated to 330 °C. At this temperature, the Se solution was quickly injected into the reaction vessel through the rubber septum. The instant color change indicated formation of CdSe nanocrystals. The heat was immediately removed from the reaction vessel and small aliquots of the reaction solution were taken to monitor the reaction progress with a UV-Vis spectrometer. When larger QDs are desired, the heat was restored until the first exciton peak at a desired wavelength was observed in the absorption spectrum. Then, the resulting solution was cooled to ~50 °C. After addition of 10 mL of $CHCl_3$, the CdSe QDs were precipitated with a copious amount of methanol and collected by centrifugation and decantation. CdTe QDs were prepared as described previously.[10a]

Ligand exchange of QDs. About 0.50 g of TOPO/TOP-coated CdSe was put into 150 mL of pyridine, and refluxed at 60 °C overnight under the dark condition. Pyridine-coated CdSe was precipitated with hexane and collected by centrifugation and decantation. The precipitate was dissolved in pyridine/methanol (1:5 v/v), which was used for the sensitization of TiO_2 with CdSe and CdTe QDs. MPA-coated CdSe QDs were prepared as described in the literature.[16]

Assembling solar cells and efficiency measurements. After FTO glasses had been cleaned, the TiO_2 precursor, titanium diisopropoxide bis(acetylacetonate) (20 mM in ethanol), was cast onto them by a spray-pyrolysis method and then sintered at 450 °C for 30 min to form a blocking layer. A commercial TiO_2 paste (Ti-Nanoxide T) was spread onto the blocking layer by a blading method using a slide glass, then sintered at 450 °C for 1 h. This TiO_2-coated FTO (TiO_2 thickness: ~8 μm and active area: 0.21 cm^2) was immersed in an ethanol solution containing linker molecules overnight, then washed, and dipped in the pyridine-capped QD solution for a day. The platinum-coated counter electrode was prepared by spreading the Pt paste onto the FTO substrate and then sintering at 400 °C for 30 min. The two electrodes were separated by a piece of 60 μm hot-melt sealing sheet and sealed up by heating. The internal space was filled with an electrolyte of 0.50 M LiI/0.050 M I_2 in acetonitrile. The holes made on the counter electrode glass for injecting electrolytes were sealed by heating hot-melt sealing sheets and thin glass covers. The 400 W xenon arc lamp and a set of Oriel air mass (A.M.) filters, 0, 1, and 1.5, were used to give a simulated irradiance of 80 mW/cm^2 at the surface of the solar cells. The intensity of illumination was measured by a power meter. The current-voltage curves of the cell were measured under these conditions using an EG&G model 263 potentiostat. For the measurement of the incident photon-to-current conversion efficiency (IPCE), the incident monochromatic light was chopped at a frequency of 0.10 Hz and the resulting photocurrent was measured using a Stanford Research SR830 digital lock-in amplifier system.

Results and Discussion

To prepare and test QD-sensitized TiO_2 electrodes, CdSe and CdTe QDs have been prepared according to the procedures described in the Experimental section. QDs were initially prepared with their surface surrounded by hydrophobic ligands such as TOPO or TOP. The typical absorption spectra of CdSe and CdTe QDs in $CHCl_3$ show characteristic sharp peaks at their band edges, and their sizes were estimated to be about 2.8 nm (CdSe) and 3.9 nm (CdTe), respectively, from reported calibration data.[17] After replacing the ligands with pyridine, CdSe and CdTe QDs were successfully attached onto the TiO_2 mesoporous layer by following the procedure described below.

The main objective of this work is to develop a simple and yet general methodology for using colloidal QDs as an inorganic dye sensitizer in DSSCs and also to provide quantitative data for such cells. Thus, we had to devise a general linking method to anchor colloidal QDs onto a mesoporous TiO_2 layer as for the case of organic dyes. The simplest idea adopted from the organic dye systems was to use a molecular linker having a carboxylate or phosphonate group to attach QDs to the TiO_2 surface.[18] Direct attachment of QDs having a ligand with a carboxylate group on one terminal and a thiol group on the other was examined first. Thus, 3-mercaptopropionic acid (MPA) was chosen for the first example as it has two end groups, a carboxylate group on one side of the molecule for anchoring onto the TiO_2 surface and a thiol group on the other side to attach the molecules to the CdSe QDs. This ligand has been very popular due to its capability to solubilize MPA-QDs in aqueous media.[11] To separate the MPA-covered CdSe QDs from the ligand exchange medium, the pH had to be adjusted to greater than 10.[16] Thus, the surfaces of the CdSe QDs are surrounded by negatively charged carboxylate ($-COO^-$) groups, whose excess charges are compensated by cations in the surrounding medium. When the mesoporous TiO_2 layer on the FTO glass was exposed to the negatively charged MPA-CdSe dissolved in methanol solution and left overnight, no color change was detected. If CdSe QDs were anchored onto the TiO_2 layer using MPA-surface ligands, the

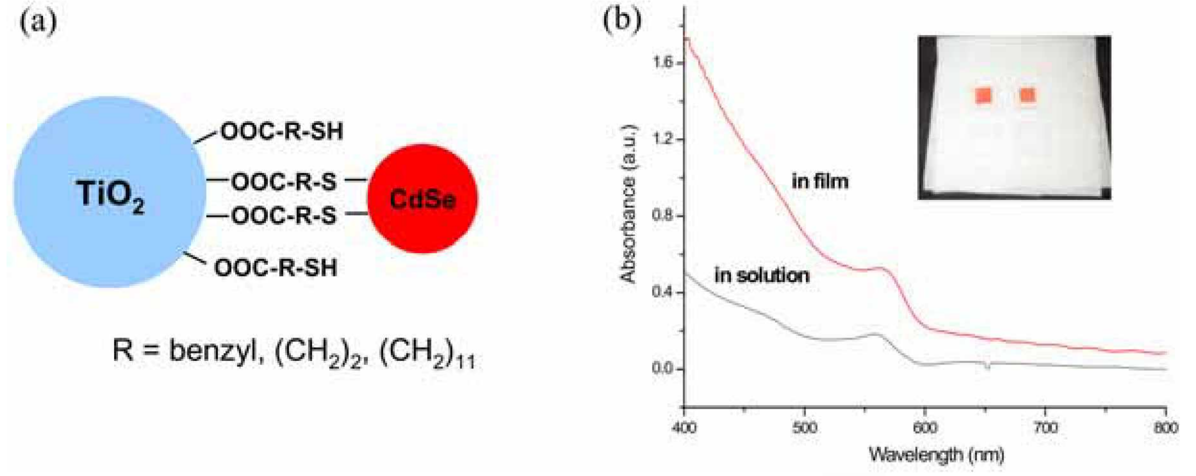

Figure 1. (a) A simplified diagram depicting a connection between TiO_2 and CdSe QD through linking molecules. (b) Absorption spectra of CdSe QDs in $CHCl_3$ (lower curve) and CdSe QDs attached into a mesoporous TiO_2 layer (upper curve). Inset: a picture of CdSe-TiO_2 and TiO_2 film on glass.

layer would be turned red due to the color of CdSe QDs, which was not the case. The excess charges on the surface of QDs might have hindered efficient penetration and adsorption onto the TiO_2 surface. A similar effect, in which the charges on QD ligands play an important role, has been reported[19] and an anionic organic dye was shown to have a lower surface coverage on TiO_2 than the neutral dye due to Coulombic repulsion in DSSCs.[20]

To avoid the charge effect, a two-step procedure was evaluated using a mercapto-R-acid molecule, where R is an alkyl or aryl group (Figure 1a). *Neutral* MPA molecules were first attached to a mesoporous TiO_2 layer in ethanol by anchoring them onto the TiO_2 layer *via* the carboxylate groups with their thiol groups facing outside. The thiol groups were then used to capture CdSe QDs, whose TOPO ligands had been exchanged with pyridine, so that the pyridine-capped CdSe QDs can be captured by the thiol groups. After the FTO electrode with an MPA-modified TiO_2 layer was dipped into a pyridine/methanol solution of the pyridine-capped CdSe QDs for a day, it was washed by pyridine and methanol and the red-colored TiO_2 layer was readily visible with naked eyes (Figure 1b inset). The absorption spectrum of this CdSe-TiO_2 layer is shown in Figure 1b, which is practically identical to the one obtained in solution except for the scattering effects from TiO_2 layers. These observations manifest that the two step procedure is effective in anchoring the dispersed CdSe QDs in solution onto the TiO_2 layer. The colors of QDs dissolved in solution and the dried film of the QD-linker molecule-TiO_2 layer thus prepared matched well as can be seen in Figure 2. A similar procedure was used to link CdSe QDs with TiO_2 using MPA independently by the Kamat group recently without the QD-ligand exchange preceded.[9a] and electron transfer rates between the excited state of CdSe QDs and the TiO_2 conduction band were shown to be comparable with the values from conventional molecular dyes.[9a,b] We also found that the TOPO/TOP-capped CdSe QDs could be attached to the linker molecule-modified TiO_2 layer; however, they were not anchored efficiently onto the *bare* TiO_2 layer contrary to the case of InP-TiO_2 system,[6,21] in which authors also mentioned that QDs are effectively captured by linker molecules. The photovoltaic conversion efficiency was also very low when the TOPO/TOP-capped QDs were anchored onto the TiO_2 layer through the linker molecules.

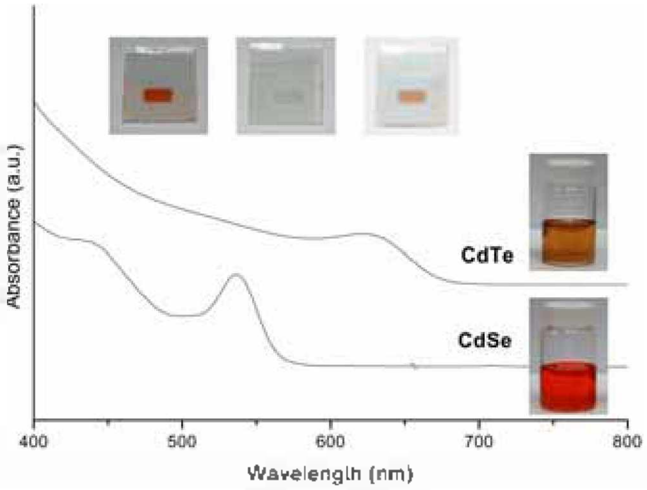

Figure 2. Absorption spectra of CdSe and CdTe QDs in $CHCl_3$ with their pictures showing QDs dissolved in $CHCl_3$. Inset: a picture clearly showing the sensitized active area of CdSe-TiO_2 (left) and CdTe-TiO_2 (right) films, and bare TiO_2 (middle) on FTO glass.

We then assembled a regenerative solar cell like a DSSC employing a mesoporous TiO_2 layer sensitized by QDs on the FTO electrode (working electrode), a platinum-catalyst coated FTO electrode (counter electrode), and an I^-/I_3^- redox couple in acetonitrile and evaluated its performance. Working and counter electrodes were assembled into a sandwich-type and photocurrent-voltage traces were measured. Figure 3a shows the current-voltage characteristics obtained under illumination of simulated AM 1.5 radiation with a 400 nm cut-off filter while data in Figure 3b were obtained without the filter. The overall conversion efficiency

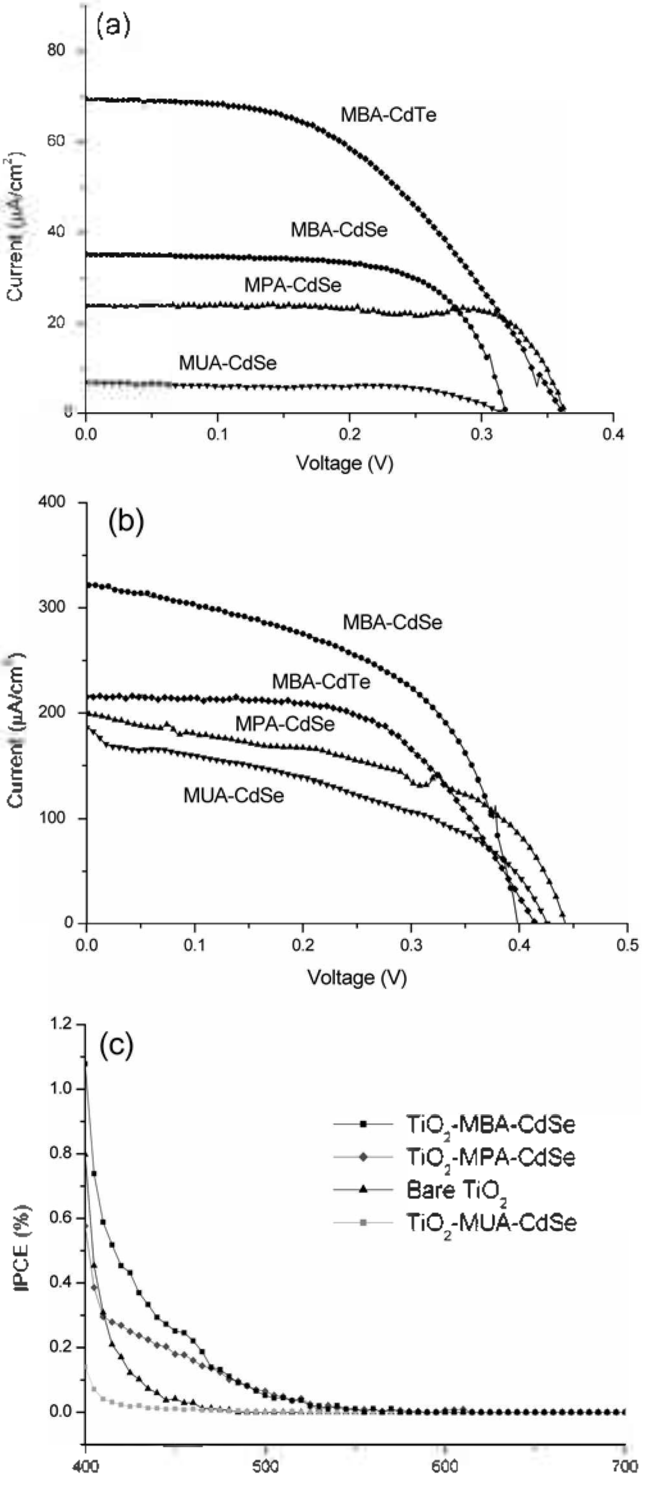

Figure 3. Current-voltage curves of FTO/TiO_2-QDs/I^-, I_3^-/Pt counter electrode cell using three linking molecules indicated under an intensity of simulated 80 mW/cm^2 with a 400 nm cut-off filter (a) and without the filter (b). IPCE data of CdSe-linker molecule-TiO_2 systems (c).

Table 1. Characteristics of the DSSCs Constructed from QD-Sensitized TiO_2^{a}

Type of Sensitization	Open Circuit Voltage, V	Short Circuit Current Density, μA/cm^2	Fill Factor	Overall Efficiency, %
MBA-CdSe	0.32	35.1	0.67	0.0094
	(0.40)	(322)	(0.52)	(0.084)
MPA-CdSe	0.36	24.0	0.80	0.0086
	(0.44)	(200)	(0.55)	(0.060)
MUA-CdSe	0.32	6.9	0.69	0.0019
	(0.43)	(193)	(0.40)	(0.041)
MBA-CdTe	0.36	69.5	0.48	0.015
	(0.41)	(216)	(0.58)	(0.065)

^{a}Numbers in parentheses represent those when no cutoff filters are used.

was always higher with the light source with the UV region included (Figure 3b) when compared to the case without it (Figure 3a), although the incident power was adjusted to have the same power at 80 mW/cm^2. These are due to an enhanced absorption of both TiO_2 and QDs in the UV region as well. The open circuit voltages and short circuit currents as well as fill factors and overall conversion efficiencies calculated thereof are summarized in Table 1.

The roles of linker molecules between QDs and TiO_2 layers have been studied. Linker molecules containing a long alkyl chain as in 11-mercaptoundecanoic acid (MUA) showed the lowest efficiency among all the CdSe-TiO_2 systems examined. The rate of charge transfer was shown to decrease exponentially as the number of alkyl chains increased.[22] In fact, the MUA-linked CdSe-TiO_2 cell was less efficient than the bare TiO_2 system. After all, MUA is acting as a blocking layer to the charge transfer from QDs to TiO_2. In the case of a short chain molecules such as 3-MPA and 4-MBA, the short circuit current was about 3.5 and 5.1 times of that for MUA, respectively, when the visible light source (> 400 nm) was used for illumination (Figure 3a). The most efficient result was obtained from the 4-MBA linked CdSe-TiO_2 system; a short circuit current of 322 μA/cm^2, an open circuit voltage of 0.40 mV, and a fill factor of 0.52 were obtained, giving an overall conversion efficiency of 0.084%. We may be able to improve the efficiency further by optimizing experimental conditions such as the thickness of the TiO_2 layer, TiO_2 surface treatment, composition of the solvent and redox couple, etc. The CdTe QDs also showed a similar trend as CdSe, and the CdTe-MBA-TiO_2 cell gave the highest efficiency in the spectral region longer than 400 nm due perhaps to the favorable location of the CdTe conduction band with respect to that of TiO_2 compared to that of CdSe/TiO_2. The reason why 4-MBA-linked QDs give the best results should be because the electron transfer through the π-conjugated ring structure in the 4-MBA molecule is more facile, although the distance between QDs and TiO_2 through 4-MBA and 3-MPA is almost identical.

To check the photo-response as a function of the incident photon energy, the IPCE measurements have been made for the QD-sensitized CdSe systems (Figure 3c). Photocurrents start to flow below about 550 nm in the case of MPA and MBA-linked cells albeit their signals are relatively low. Our IPCE spectra are similar to that reported from a regenerative InP-TiO_2 system,[5] but the CdS-TiO_2 system showed a relatively high (20-40%) IPCE values with a similar spectral shape to the absorption spectrum of the sensitizer when hole scavengers were used.[4a] The relatively low IPCE values in the visible region resulted in the low short circuit current and the low overall conversion efficiency as shown in Figure 3a. From the low IPCE values in the visible region and the higher overall efficiency in the UV-included spectral region, it seems that some extra energy is necessary to make an efficient charge transfer between TiO_2 and QDs as well as QDs and the redox couple. The small offset of the conduction band of CdSe with respect to that of TiO_2 may render the electron transfer rather difficult and the linker molecules used might have given some barrier as well. This aspect was pointed out in the case of PbS QDs deposited by the chemical bath method onto the TiO_2 layer.[5b] It was proposed that a difference of ~0.35 eV between the conduction band of the PbS QD and that of TiO_2 is needed for an efficient electron transfer; smaller offsets would probably lead to localization or recombination of the photogenerated electron-hole pair. It was also pointed out in a previous report that the optimization of hole transfer and its transport from the InP QDs through the liquid electrolyte to the counter electrode is also required.[6] Moreover, the liquid electrolyte is known to cause photocorrosion due to its aggressive nature[5a] and ingenious engineering of band energies is also required to prevent photocorrosion.[23] Our liquid electrolyte cell was no exception to this, undergoing a gradual decrease in photocurrent. It is thus necessary to make an effort to find a non-corrosive redox couple in liquid cell[9c] or a proper solid-state hole conductor for this kind of QD-sensitized cell.[24]

Thus far, we have demonstrated how organic dye molecules can be replaced by colloidal QDs in regenerative DSSCs. The methodology reported herein can serve as a general strategy for chalcogenide QDs of any band gaps. Besides, it is expected that this method should also be applicable to many other II-VI or III-V semiconductor QDs because those QD surfaces are typically known to have high affinity to the thiol functional group,[16] a common moiety in the linker molecule used, as well. To fully exploit the advantages of the colloidal QDs and achieve high conversion efficiencies, it is important to find an appropriate linking method and optimize the interface energetics of QDs. The importance of the interface engineering has been shown in this work by displaying the dramatic changes due to the different linker molecules examined; further investigations on charge transfer between QDs and interfacing materials would help find optimum conditions and materials.[21,25] Although overall conversion efficiencies of QD-sensitized solar cells are not as satisfactory as initially expected,[8] we hope that our report would serve as a stepping-stone on the path to making more efficient and stable QD-sensitized cells.

Conclusion

In this study, we have prepared CdSe and CdTe QDs by a well-known colloidal method and developed a two-step linking procedure to anchor QDs onto the mesoporous TiO_2 layer. To the best of our knowledge, this is the first result of quantitative cell tests using colloidal CdSe and CdTe QDs as an inorganic dye in a regenerative form of DSSC. Although the short circuit current measured from the QD-sensitized solar cell was smaller than those of the organic dye-cell, it was shown that the photocurrent can be increased by choosing a proper linking molecule such as MBA. These results are encouraging, and the cells can be improved by optimizing conditions for the linking method and preferential interfaces between TiO_2/CdSe and CdSe/hole conductors.

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