Organic-inorganic hybrid nanostructured materials for photovoltaics and solar fuels
Lai, Lai-Hung

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Sensitized Solar Cells with Colloidal PbS/CdS Core/Shell Quantum Dots

In this chapter, we report the fabrication of PbS/CdS (core/shell) quantum dot (QD)-sensitized solar cells by direct adsorption of core/shell QDs on mesoporous TiO$_2$ followed by 3-mercaptopropionic acid ligands exchange. PbS/CdS QD-sensitized solar cells show 4 times higher efficiency with respect to solar cells sensitized with PbS QDs. The significantly enhanced mean electron lifetime and electron diffusion length provide crucial evidences for the higher efficiency of the cell.*

2.1 Introduction

Quantum dot-based solar cells have attracted considerable attention due to their unique optical properties, their tunable bandgap, their high extinction coefficient and stability. The quantum confinement allows the fine-tuning of their optical properties and it is also expected to favor efficient multiple exciton generation (MEG),\textsuperscript{[1]} making the theoretical efficiency (Shockley–Queisser limit)\textsuperscript{[21]} of quantum dots solar cells break. In 2011, Nozik successfully demonstrated heterojunction solar cells based on lead selenide (PbSe) QDs with internal quantum efficiency of \(\sim 130\%\),\textsuperscript{[3]} Earlier, PbS quantum dot-sensitized solar cells have been reported by Parkinson to display multiple exciton generation,\textsuperscript{[4]}

QDs solar cells have shown in the last few years remarkable efficiencies and high photocurrent not only in depleted heterojunction\textsuperscript{[5]} but also in Schottky configuration,\textsuperscript{[6]} reaching 7.3\% and 5.2\%, respectively. QD-sensitized solar cells still show limited efficiency, which is ascribed to serious charge recombination at the interface of the quantum dots.\textsuperscript{[7, 8]} In-situ and ex-situ growth methods have been widely used to make PbS,\textsuperscript{[9-11]} CdS,\textsuperscript{[12, 13]} and CdSe\textsuperscript{[14, 15]} QDs-decorated TiO\textsubscript{2} photoanodes. In-situ growth includes chemical bath deposition (CBD),\textsuperscript{[16, 17, 18]} successive ionic layer adsorption, and reaction (SILAR),\textsuperscript{[11, 19, 20]} ex-situ growth includes direct adsorption (DA),\textsuperscript{[16]} linker-assisted adsorption (LA),\textsuperscript{[10, 16, 19, 21]} and electrophoresis (EP).\textsuperscript{[14, 22]}

Since QDs have large surface to volume ratio, defect states at the surface are one of the causes of charge trapping.\textsuperscript{[23]} This largely affects the performances of the devices, confining the power conversion efficiency of PbS QD-sensitized solar cell made by SILAR below 2\%.\textsuperscript{[11, 20]} Only recently the incorporation of Hg\textsuperscript{2+} into the interstitial site of PbS by SILAR and the use of organic ligands as passivating agents resulted in device efficiencies above 5\%.\textsuperscript{[24]}

Owing to the partial passivation provided by the organic ligands, the dangling bonds remaining on the QDs surface can act as carrier trapping sites, which degrade the solar cell performance.\textsuperscript{[25]} Inorganic materials such as CdS and ZnS are known to provide more complete passivation for the QD surface.\textsuperscript{[26]} ZnS SILAR coating technique has been used to protect QDs from photo-corrosion and to suppress electron recombination with the electrolyte.\textsuperscript{[12, 18, 27]}

The size of quantum dots, to which the optical properties are sensitive, is difficult to be precisely controlled by in-situ growth methods.\textsuperscript{[12]} Thus, ex-
situ techniques have great advantages in terms of control of the particle size distribution.

Herein, we report for the first time the use of ex-situ growth PbS/CdS core/shell QDs in QD-sensitized solar cells. The effects of the CdS shell on the efficiency, charge transfer dynamics, and the solar cell stability is studied. The electron lifetime shows a clear dependence on the shell thickness; namely, the thicker the shell the higher is the mean electron lifetime. The considerable improvement of the electron lifetime (from 39 ms to 174 ms) and electron transit time (from 594 ms to 21 ms) have positive effects on the electron diffusion length and on the charge collection efficiency. However, the cell efficiency is not only determined by the charge collection efficiency, but also by the light absorption efficiency of the QDs and by the charge injection efficiency from the QDs to TiO₂. Because of the energy barrier provided by the CdS shell, the charge injection efficiency decreases with increasing of the shell thickness. Therefore, a trade-off between charge injection efficiency and the charge collection efficiency is necessary. Power conversion efficiency of 1.28% is obtained with PbS QDs with CdS shell of about 0.5 nm thickness. Importantly, the photostability is significantly improved in the solar cell sensitized by PbS/CdS (1.1 nm) QDs.

2.2 Sensitized solar cell with core/shell PbS/CdS QDs

The general structure of the quantum dot-sensitized solar cells (QDSSCs) is shown in Figure 2.1(a). The cells are composed of the QD-sensitized electrode, the polysulfide electrolyte, and a Cu₃S counter electrode. Because

Figure 2.1. (a) Schematic of the QDSSC. (b) STEM micrograph of PbS/CdS (core/shell) QDs. The red circle indicates the boundary between core and shell.
of the easy corrosion of the metal chalcogenides QDs in the I\(^{-}/I\(^{+}\) electrolyte, 
S\(^2-/S\(^{2-}\) shuttles are the best choice for QDSSCs. Moreover, in the polysulfide electrolyte 
CuS and CoS counter electrodes give lower over-potential.\(^{[28]}\)
Mono-dispersed oleic acid capped-PbS-QDs are used to sensitize 
mesoporous TiO\(_2\). In Figure 2.1(b), the STEM micrograph shows the uniform 
PbS/CdS QDs with average core size of 3.8 nm and shell thickness of about 
1.1 nm.

Figure 2.2(a) shows the J-V characteristics of the QDSSCs sensitized by 
QDs having different CdS shells. The J-V curves were measured in the 
electrochemical configuration; namely, the photoanode (TiO\(_2/QDs\)) was 
connected with a working electrode and the CuS with a counter electrode 
of the potentiostat. As a result, the current and potential are reversed respect 
to conventional photovoltaic devices. All the device parameters are reported 
in Table 2.1. The PbS/CdS QDSSCs show much higher photocurrent (5.7 mA 
cm\(^{-2}\)) and photovoltage (-0.47 V) compared with PbS QDSSCs. The open 
circuit voltage increases with the growing thickness of the CdS shell because 
of the lower carrier recombination induced by surface trap states.

Solar cells fabricated with core/shell QD with 0.5 nm CdS show the 
highest photocurrent and 4 times higher efficiency (1.28\%) than what is 
obtained with simple PbS QD coated with ZnS after deposition. The ZnS 
coating is believed by most scientists to have the effect of either blocking 
electrons,\(^{[16]}\) which could otherwise recombine with electrolyte, or 
passivating defect states that may trap carriers.\(^{[7]}\) A detail discussion of the 
working mechanism of ZnS layer is out of the scope of this work. All devices 
reported in this work are coated with 5 SILAR layers of ZnS, which have 
been found to have the same stabilizing effect in all the devices investigated.

Figure 2.2(b) shows the external quantum efficiency (EQE) of the QD- 
sensitized solar cells obtained with different QDs. The samples fabricated 
with core-shell particles having a 0.5 nm shell show significantly enhanced 
E QE, reaching 40\% at 440 nm. The E QE spectra of solar cells fabricated with 
different QDs show dissimilar onset at low energy, which is caused by the 
slightly difference in size of the PbS core. The theoretical short circuit current 
obtained by AM 1.5G-weighted integration of the E QE spectrum are 
1.1 mA cm\(^{-2}\), 5.7 mA cm\(^{-2}\) and 3.5 mA cm\(^{-2}\), respectively, for PbS, PbS/CdS 
(0.5 nm), and PbS/CdS (1.1 nm). The ratio of theoretical short circuit current 
for 0.5 nm shell thickness to 1.1 nm shell thickness is 1.6, which is smaller 
than the short circuit current ratio obtained from J-V curves shown in
Figure 2.2. (a) J-V characteristics of QDSSCs fabricated with PbS and PbS/CdS QDs-decorated TiO$_2$ (all devices are coated with ZnS) under AM 1.5, 100 mW cm$^{-2}$ (symbol) and in dark (line); (b) EQE spectra of QD-sensitized solar cells.

Table 2.1. Summary of device parameters

<table>
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<tr>
<th>Sample</th>
<th>$I_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
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<tr>
<td>PbS</td>
<td>1.64</td>
<td>-0.32</td>
<td>0.55</td>
<td>0.29</td>
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<td>PbS/CdS(0.5nm)</td>
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<td>-0.47</td>
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<td>PbS/CdS(1.1nm)</td>
<td>2.85</td>
<td>-0.50</td>
<td>0.51</td>
<td>0.73</td>
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</table>

Figure 2.2 (a), where the 0.5 nm shell thickness cell has 2 times higher short circuit current compared to 1.1 nm shell thickness cell. We believe this is caused by the fast degradation of thin CdS shell as shown in Figure 2.8, resulting in the difference in short circuit current ratio got from EQE spectra and J-V curves. It is important to underline that the core-shell particles having thicker shell shows a slightly lower band-gap (from the EQE spectra), while the J-V characteristics of the solar cells of the same sample reported in Figure 2.2(a) show a higher open circuit voltage. This confirms
that the increased open circuit voltage is due to the lower recombination losses in the QDSSCs and not to a band gap dissimilarity which would have cause a decrease on open circuit voltage.

The $EQE$ depends on a series of device parameters:

$$EQE = LHE \cdot \phi_{inj} \cdot \eta_c \quad \text{(Eq. 2.1)}$$

where $LHE$ is the light harvesting efficiency, $\phi_{inj}$ is the electron injection efficiency, and $\eta_c$ is charge collection efficiency. The PbS/CdS QD-sensitized solar cells show better performances, with the $EQE$ spectra extending from the near ultraviolet to the near-infrared spectral (NIR) range. This resemble closely the absorption spectra of the colloidal solution (Figure 2.3). The similarity between the $EQE$ of the solar cell and the absorption of the QDs provides a proof of carrier transfer from the PbS core to TiO$_2$.

### 2.3 Carrier dynamics measurement

To understand the carrier transport dynamics in these devices, the first step is to find out the electron transport resistance ($r_{ct}$) and the interfacial charge recombination resistance ($r_r$). Both parameters can be fitted from impedance spectra using a transmission line model.$^{[29]}$ The transmission line model is a commonly used model to fit the charge transport parameters in mesoporous electrodes, where the equivalent circuit of the transmission line model is shown in Figure 2.4(a). The impedance spectra of QDSSCs comprise two arcs (shown in Figure 2.4(b)): one at high frequency is associated with the charge transfer at the counter electrode (Cu$_x$S) interface;

![Figure 2.3. Absorbance of oleic-acid passivated colloidal QDs in chloroform.](image-url)
and, the second one at low frequency is associated with the charge transfer at the TiO$_2$/QDs/electrolyte interface. In the measured frequency range, the third arc corresponding to the diffusion of the redox species is not observed in Figure 2.4(b), thus the diffusion impedance is not considered in the equivalent circuit model shown in Figure 2.4(a). The low frequency arc of the sample with PbS QD-sensitized electrodes is extremely asymmetric compared to the one of the photoelectrode sensitized with PbS/CdS QDs, resulting in a high $r_{ct}$ and a low $r_r$.[30] The equivalent circuit parameters obtained by fitting the measurements with the proposed model are listed in Table 2.2.

![Equivalent circuit](image)

![Nyquist plot](image)

Figure 2.4. (a) Equivalent circuit for the transmission line model, where $R_s$ is the series resistance, $r_{ct}$ is the electron transport resistance, $r_r$ is the interfacial charge recombination resistance, $Q_μ$ is the chemical capacitance between photoanode and electrolyte, $R_c$ is the charge transfer resistance between the CuS counter electrodes and the electrolyte, $Q_c$ is the chemical capacitance between the CuS counter electrodes and the electrolyte. (b) Nyquist impedance plots of QDSSCs measured under AM 1.5 solar illumination at 100 mW cm$^2$ at open circuit voltage (symbols) and fitting curves (line).
Sensitized solar cells with colloidal PbS/CdS core/shell quantum dots

The electron mobility, electron lifetime, electron transit time and electron diffusion length are the most direct parameters to monitor the carrier transport dynamics in QDSSC. All these parameters are analyzed as follows. The electron transport in TiO$_2$ is diffusion-like because the electrolyte shields the space charge.$^{[31]}$ The electron diffusion coefficient can be derived from:

$$D_e = \frac{\mu_e}{r_{act}} L^2 f_p \quad \text{(Eq. 2.2)}$$

where $L$ is the thickness of TiO$_2$, $f_p$ is the peak frequency of the low frequency arc in the Nyquist impedance plot (Figure 2.5(b)). The electron mobility can be derived from the Einstein relation, $\mu_e = D_e/k_BT_e$ from which it is found that the PbS/CdS QD-sensitized cells have higher electron mobility ($3\times10^4$ cm$^2$/V-s) than the PbS QDs in TiO$_2$ ($10^5$ cm$^2$/V-s$^2$) (Table 2.2).

Table 2.2. Equivalent circuit fitting results and other parameters of cells$^a$

<table>
<thead>
<tr>
<th>Light Intensity (mWcm$^{-2}$)</th>
<th>$c_p$ ($\mu$cm$^3$)</th>
<th>$r_{eq}$ ($\Omega$ cm$^{-1}$)</th>
<th>$r_0$ ($\Omega$ cm$^{-1}$)</th>
<th>$\tau_{act}$ (ms)</th>
<th>$\tau_0$ (ms)</th>
<th>$D_e$ ($\mu$m)</th>
<th>$\mu_e$ ($\Omega$ cm)</th>
<th>$L^2$</th>
<th>$\eta_e$ (%)</th>
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<td></td>
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$^a$ Values are determined based on the data measured at open-circuit condition under different light intensity by transmission line model fitting as the equivalent circuit shown in Figure 2.4(a).
The chemical capacitance per cm² produced by the accumulation of electrons in the TiO₂ and interface, \( C'_e = (\epsilon_e / L) \), where \( L \) is the thickness of the TiO₂. \( C'_e = Q(2\pi f_p)^{-1} \), where \( Q \) is constant phase element (CPE), \( \alpha \) is a constant, and \( f_p \) is the peak frequency of Nyquist impedance plots.

Electron transport resistance, \( R_{ct}' = \tau_{ct}' / L \)

Interfacial charge recombination resistance, \( R'_i = \tau'_i / L \)

The average electron lifetime in TiO₂, \( \tau_n = C'_i \tau'_{ct} \)

The average electron transit time, \( \tau_d = L^2 / D_e \)

Electron diffusion coefficient, \( D_e = \left( \frac{r_c}{v_{ct}} \right) L^2 / (2\pi \tau_n) \)

Electron mobility, \( \mu_e = D_e / k_B T \)

Electron diffusion length, \( L_d = (\tau_n D_e)^{0.5} \)

Charge collection efficiency, \( \eta_c = \frac{-L_e \alpha \cosh\left(\frac{L_e}{\tau_n}\right) \sinh\left(\frac{L_e}{\tau_n}\right) + L_e \alpha e^{-\alpha L_e}}{1 - e^{-\alpha L_e}} \), where \( \alpha \) is the extinction coefficient of quantum dot-sensitized TiO₂ film.

Here we assume the \( \alpha L \) equals to 1 for the calculation. Another well-adopted formula for the charge collection efficiency is \( \eta_c = 1 - \left( \frac{L_e}{\tau_n} \right)^2 \). However, it is only valid when the cell active layer is thin enough so that the photo-generated electrons either immediately transport to the electrodes or recombine. In the case \( L = L_d \) results in \( \eta_c = 0 \), indicating this formula obviously deviates the real situation of the quantum dot-sensitized solar cells.

The electron lifetime (\( \tau_n \)) is one of the key parameters to estimate the interfacial charge recombination dynamics. It can be determined by either small perturbation techniques, such as impedance spectroscopy and intensity modulated photovoltage spectroscopy (IMVS)\(^{22, 32} \) or by transient techniques such as open-circuit voltage decay (OCVD).\(^{14} \) Herein, the average electron lifetime is obtained by two different methods, the first method derives it from the product of the interfacial charge recombination resistance (\( r_c \)) and the chemical capacitance (\( C_i \)) obtained from electrochemical impedance spectroscopy (EIS) fitting using the transmission line model. The second method is derived from IMVS. Here the electron lifetime can be evaluated from the expression \( \tau_e = 1 / (2\pi f_{\text{mix}}) \), where \( f_{\text{mix}} \) is the frequency of the peak of imaginary component of the IMVS spectra (Figure 2.5(a)). The values obtained in these two ways are plotted in Figure 2.6(a) and Figure 2.5(b), respectively, from which it is evident that samples prepared with QDs with thicker CdS shell have longer average electron lifetimes.

The carrier transport dynamics in the different samples can be monitored by comparing the electron transit time and the electron lifetime. The electron transit time (\( \tau_o \)) is the average diffusion time of the electrons to travel from
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Figure 2.5. (a) Nyquist plot of IMVS spectra of PbS/CdS (1.1 nm) QD sensitized solar cells, measured by employing a 528 nm LED, scanned from 10 mA (corresponding to 0.22 mW cm\(^{-2}\) light intensity) to 500 mA (corresponding to 5.57 mW cm\(^{-2}\) light intensity). (b) Light intensity dependent mean electron lifetime determined by IMVS measured under 528 nm LED illumination.

QDs to the electrode, which can be defined as: \(\tau_d = L^2/D_e\). Table 2.2 shows that for PbS QD-sensitized solar cell, the electron transit time (594 ms) is one order of magnitude higher than electron lifetime (39 ms) under 1 sun illumination; on the other hand, as for the one with PbS/CdS (0.5 nm) QD sensitization, the electron transit time has the same magnitude (~50 ms) as the electron lifetime. However, for the one with PbS/CdS (1.1 nm) QD sensitization, the electron transit time (21 ms) is one order of magnitude lower than the electron lifetime (174 ms). These results support the idea that the CdS shell passivates the traps on the surface of the PbS QDs and strongly improves the electron transport properties.
The electron diffusion length is derived from $L_d = (\tau_e D_e)^{0.5}$, where $\tau_e$ is the mean electron lifetime and $D_e$ is the electron diffusion coefficient. Figure 2.6(b) shows that the electron diffusion lengths are 1 µm, 3.7 µm, and 11.4 µm for PbS, PbS/CdS (0.5 nm), and PbS/CdS (1.1 nm), respectively. The enhanced electron diffusion length of core/shell QD-sensitized solar cells, resulting from the longer electron lifetime and higher electron mobility, is the main reason for the higher performance of the solar cells.

In Figure 2.6(a), the light intensity dependent characteristics of the carrier transport dynamics, in which the electron lifetime decreases with the increasing light intensity, is reported. The recombination of electrons at open circuit voltage under illumination is affected by the Fermi-level difference between the photoanodes and the redox potential of electrolyte, as well as by the Schottky barrier between the photoanodes and the electrolyte interface. Higher light intensity results in lower Schottky barrier and larger Fermi-level difference, which accelerate carrier recombination.

![Figure 2.6](image.png)

Figure 2.6. (a) Light intensity dependent mean electron lifetime determined by EIS measurement. (b) Light intensity dependent electron diffusion coefficient ($D_e$) and mean electron diffusion length ($L_d$).
The increasing diffusion coefficient with stronger light intensity is caused by a larger number of free carriers under stronger illumination, which have first filled the available traps.\textsuperscript{[33]} Since the diffusion length is related to diffusion coefficient and electron lifetime, the electron lifetime strongly depends on light intensity while diffusion coefficient is only slightly affected by light intensity, resulting in a light intensity dependent diffusion length with a similar trend as the electron lifetime (Figure 2.6(a)).

Based on the carrier dynamics studies, the working mechanism of our devices and the carrier transport model is reconstructed as shown in Figure 2.7. The photoexcited electrons (route 1) are quickly injected from the PbS QDs into TiO\textsubscript{2} in sub-picosecond timescale (route 3), while the remaining holes react with the holes scavengers S\textsuperscript{2–} (route 6). After electron injection into TiO\textsubscript{2}, these electrons can recombine by several routes as shown by the dashed lines in Figure 2.7; for instance, they can recombine with holes via surface trap-assisted recombination processes (route 4). The trapping states in the band gap of PbS QDs cannot be ignored because of the large amount of surface defects in the nanocrystals.\textsuperscript{[23], [33]} The trap-assisted recombination leads to decreasing of charge collection efficiency (Table 2.2) and to the degradation of the solar cell performance. In Figure 2.7(b), CdS shell effectively passivates the defect states of PbS, resulting in a longer electron lifetime, which indicates that route 4 is inhibited in the PbS/CdS QDSSCs.

Figure 2.7. Carrier transport routes of (a) the PbS QD sensitized solar cell and (b) PbS/CdS QD sensitized solar cell: 1. Electrons excitation in the QDs: PbS+hv → PbS(e+). 2. Recombination of electrons in the QDs: PbS(e+∙) → PbS+hv. 3. Electrons injection into TiO\textsubscript{2} conduction band: TiO\textsubscript{2}+PbS(e+∙) → TiO\textsubscript{2}(e−)+PbS(h+). 4. Back electron injection from TiO\textsubscript{2} to QDs: TiO\textsubscript{2}(e−)+PbS → TiO\textsubscript{2}+PbS(e−). 5. Back electron injection from TiO\textsubscript{2} to electrolyte: TiO\textsubscript{2}(e−)+S\textsuperscript{2–} → (S\textsubscript{x}−)\textsubscript{2}+S\textsuperscript{−}. (dotted lines are the recombination processes) 6. Hole scavenging from PbS: PbS(h+)S\textsuperscript{2–} → PbS+S\textsuperscript{−}.
2.4 Sensitized solar cell stability

Further evidence of the proposed mechanism is provided by the solar cell stability reported in Figure 2.8. Here, the increasing photocurrent in the first 1000 s results from the infiltration of polysulfide electrolyte into the mesoporous structure in PbS/CdS (1.1 nm) QD-sensitized solar cells. For the PbS QD-sensitized solar cell, the photocurrent degrades more than 50% after 1 h light illumination under AM 1.5, 1 sun. Here, the PbS/CdS (1.1 nm) core/shell QD-sensitized solar cells show minimum degradation during 1 h measurement, demonstrating the importance of CdS shell in preventing PbS core from photocorrosion.

Figure 2.8. Stability test of QDSSCs fabricated with PbS and PbS/CdS QDs-decorated TiO₂ in 1 h (normalized photocurrent) in short circuit condition under AM 1.5, 1 sun chopped light (1 sec on and 1 sec off).

2.5 Conclusions

We studied the influence of the CdS-shell thickness and the light intensity dependent carrier dynamics of PbS/CdS QD-sensitized solar cells. The bad performance of PbS QD-sensitized solar cells is ascribed to the low electron diffusion length caused by the low electron lifetime as well as the low electron mobility of the PbS-sensitized electrodes. To enhance the electron diffusion length, the trapping states on the surface of the PbS QDs need to be passivated as is done by the CdS shell. The CdS shell is proved to efficiently passivate PbS QDs, which allows increasing the electron lifetime, electron mobility, and electron diffusion length. The significant improvement of the device parameters allows reaching EQE of 40% at 440
nm with 0.5 nm CdS shell QDs and overall power conversion efficiency of 1.28%, which is 4 times higher than what is measured with PbS QD-sensitized solar cells. Further evidence of the role of the CdS shell is provided by the noticeable photostability of the core-shell QD-sensitized solar cells.

2.6 Methods

Nanocrystal synthesis.

PbS and PbS/CdS core/shell QDs were synthesized by hot injection method. In a three-neck reaction flask, PbAc₂•3H₂O (2 mmol, 0.758 g), ODE (10 mL) and OA (10 mL) were dried at 100 °C under vacuum for 2 h to dissolve lead salt and to dry the solution. The temperature was raised to 145 °C. In a glovebox, a sulfur precursor solution was prepared by mixing TMS₃S (0.21 mL, 1 mmol) with ODE (10 mL). Sulfur solution was quickly injected into the reaction flask at 145 °C followed by the removal of the heating mantle for 3 minutes and cooling to room temperature with a water bath. The washing procedure was carried out in air. Hexane (20 mL) and ethanol (40 mL) were added to the crude solution followed by centrifugation to separate the QDs. The obtained PbS QDs were re-dispersed in hexane (20 mL), and again precipitated with ethanol (15 mL). After one more washing step with ethanol/hexane the particles were re-dispersed in chloroform (6 mL).

In a second flask, CdO (1 g, ~7.8 mmol), OA (6 mL, ~18.9 mmol) and 20 mL ODE were heated to 200-250 °C until the solution turned colorless. The solution was cooled to 100 °C and dried under vacuum for 30 minutes. The temperature was further decreased to 100 °C and, 12 mL of PbS QDs were added via a syringe. The solution was maintained at 100 °C for 45 minutes and then cooled to room temperature. To wash PbS/CdS QDs ethanol was added to precipitate the QDs. The precipitate was re-dispersed in toluene and again precipitated with ethanol. The re-dispersion/precipitation procedure was repeated two times.

Preparation of the photoanode.

The FTO substrates (Sigma-Aldrich, sheet resistivity ~7 Ω sq⁻¹) were cleaned with soap water and sonicated in DI water, aceton and isopropyl alcohol in ultrasonic bath for 10 minutes for each cleaning step. A thin and compact TiO₂ layer was coated on FTO by immersing the substrates into 40 mM TiCl₄ at 70 °C for 30 minutes. Mesoporous TiO₂ films were prepared with TiO₂ paste (Solaronix D/SP, 15-20 nm Anatase TiO₂ mixed with > 100
nm diffusion particle) by doctor blading. Samples were annealed at 450 °C for 30 minutes to remove organics and make the film porous. Another thin TiO$_2$ layer was formed using TiCl$_4$ as the procedure before. Further annealing was done at 450 °C for 30 minutes. The TiO$_2$ thickness obtained is ~4 μm measured by a step profiler (Veeco DEKTAK 150). The QDs colloidal solution (5 mg ml$^{-1}$) was drop-casted on the TiO$_2$ photoelectrodes and left without drying for 30 minutes. After deposition samples were washed with chloroform to remove residual QDs, which are not absorbed on the TiO$_2$ surface. Ligand exchange was performed by immersing the QD-sensitized TiO$_2$ into 10% (v/v) 3-mercaptopropionic acid (3-MPA)(99%, Sigma-Aldrich) in methanol solution for 10 min. Samples were again washed with methanol followed by annealing at 90 °C for 10 minutes to remove extra solvent. ZnS was deposited by a two-step dipping procedure. First, samples were dipped into 0.1 M aqueous Zn(NO$_3$)$_2$ (Zn(NO$_3$)$_2$·6H$_2$O, 98%, Sigma-Aldrich) for 1 minute, followed by rinsing with DI water, and drying with N$_2$ gun. For another half cycle, samples were dipped into 0.1 M aqueous Na$_2$S (Na$_2$S·9H$_2$O, 98%, Sigma-Aldrich) for 1 minute, followed by rinsing with DI water, and drying with N$_2$ gun. The two-step dipping procedure is termed as one SILAR cycle. The SILAR cycle was done five times for each sample.

**Preparation of Cu$_2$S counter electrode.**

Brass was cleaned with acetone in an ultrasonic bath for 10 minutes. The porous copper surface was formed by immersing brass into 0.5 M HCl at 70 °C for 30 minutes. The porous copper substrate was further dipped into a 1 M Na$_2$S/1 M S (polysulfide solution) for 30 minutes and finally washed with water and dried with a N$_2$ gun.

**Assembly of PbS/CdS QDSSCs.**

The photoanode (active area is 1 cm$^2$) and the Cu$_2$S counter electrode were sandwiched together with a Teflon spacer (~2 mm thickness), the 2 M Na$_2$S/2 M S in H$_2$O-MeOH (3:7, v/v) (polysulfide electrolyte) was injected into the cell. Normally, thinner spacer may help the diffusion of redox species, thus the higher efficiency is expected after replacing by thinner spacer.

**Characterization.**

The size of core/shell QD is measured by scanning transmission electron microscopy (STEM), an aberration-corrected HD-2700CS (Hitachi; cold-field emitter), operated at an acceleration potential of 200 kV. A probe corrector (CEOS) is incorporated in the microscope column between the condenser lens and the probe-forming objective lens providing excellent high-
resolution capability (beam diameter ca. 0.1 nm in ultra-high resolution mode). Different detectors were chosen for imaging in bright field (BF) and high-angle annular dark field (HAADF) modes. Absorbance, reflection and transmission are measured by UV-3600 UV-Vis-NIR spectrophotometer (Shimadzu Scientific Instruments) equipped with 3 detectors (PMT, InGaAs and PbS) and integrating sphere.

I-V curves were measured by a SP-200, Bio-Logic potentiostat equipped with electrochemical impedance spectroscopy analyzer. Solar cells measurements were performed under 100 mW cm\(^{-2}\) AM 1.5G conditions obtained with a solar simulator (SF150 class A, Scientech) calibrated by a Si reference cell (SRC-1000-RTD-QZ, VLSI Standards Incorporated).

External quantum efficiencies (EQE) measurements were performed at short circuit voltage by using 250 W quartz tungsten halogen lamp (6334NS, Newport) with lamp housing (67009, Newport). Wavelength selection was done by a set of band pass filters (Thorlabs) with full width half maximum (FWHM) of 10 ± 2 nm from 400 nm to 1300 nm and FWHM of 12 ± 2.4 nm from 1300 nm to 1400 nm. PD300 and PD300IR (Ophir Optics) are used as calibrated photodiodes. Impedance spectroscopy was performed by applying a 15 mV ac signal over the frequency range 1 MHz-50 mHz at open circuit voltage under different light intensities (from AM1.5, 1 sun to 0.1sun). Intensity modulated photo-voltage spectroscopy (IMVS) measurements were performed by employing a 528 nm LED (ILH-GD01-TRGR-SC201, OSRAM) scanned from 10 mA to 500 mA. The distance between LED and solar cell was 3 cm.

2.7 References

Chapter 2

Sensitized solar cells with colloidal PbS/CdS core/shell quantum dots