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Sensitized solar cells with colloidal PbS–CdS core–shell quantum dots†

Lai-Hung Lai, Loredana Protesescu, Maksym V. Kovalenko and Maria A. Loi*

We report on the fabrication of PbS–CdS (core–shell) quantum dot (QD)-sensitized solar cells by direct adsorption of core–shell QDs on mesoporous TiO2 followed by 3-mercaptopropionic acid ligand 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 evidence for the higher efficiency of the cell. The average electron lifetime increases with the thickness of the CdS shell, demonstrating that the CdS shell plays an important role in preventing carrier recombination. However, owing to the barrier provided by the offset between the conduction bands of CdS and the PbS core, the CdS shell also hinders carrier injection from PbS to TiO2. Herein, we studied the effect of the shell thickness on cell’s performance, showing a power conversion efficiency of 1.28% for PbS QDs with a 0.5 nm CdS shell. In addition, we demonstrate that the CdS shell effectively prevents photo-corrosion of PbS, resulting in devices with highly stable photocurrent.

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 the optical properties but it is also expected to favour efficient multiple exciton generation (MEG).1–3 breaking the theoretical efficiency (Shockley–Queisser4 limit) of quantum dot solar cells. In 2011, Nozik5 successfully demonstrated heterojunctions based on lead selenide (PbSe) QD solar cells with an internal quantum efficiency of ~130%. Earlier, PbS quantum dot-sensitized solar cells have been reported by Parkinson6 to display multiple exciton generation.

PQD solar cells have shown in the last few years remarkable efficiencies and high photocurrent in depleted heterojunctions,7 but also in the Schottky configuration8 reaching values of 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.9,10 In situ and ex situ growth methods have been widely used to make PbS11–13 CdS14,15 and CdSe16,17 QD-decorated TiO2 photoanodes. In situ growth includes chemical bath deposition (CBD),18–21 and successive ionic layer adsorption and reaction (SILAR);13,22,23 ex situ growth includes direct adsorption (DA),18 linker-assisted adsorption (LA)12,16,22,24–26 and electrophoresis (EP).16,27

Since QDs have a large surface to volume ratio, defect states at the surface are one of the causes of charge trapping.28 This largely affects the performance of the devices confining the power conversion efficiency of PbS QD-sensitized solar cells made by SILAR to below 2%.13,23 Only recently the incorporation of Hg2+ into the interstitial site of PbS by SILAR and the use of ZnS; as passivating agent resulted in device efficiencies of above 5%.29

Owing to the partial passivation provided by the organic ligands, the dangling bonds remaining on the QD surface can act as carrier trapping sites, which degrade the solar cell performance.30,31 Inorganic materials such as CdS and ZnS are known to provide more complete passivation for the QD surface.32 The ZnS SILAR coating technique has been used to protect QDs from photocorrosion and to suppress electron recombination with the electrolyte.14,20,31

The size of quantum dots, to which the optical properties are sensitive, is difficult to be precisely controlled by in situ growth methods.14 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 effect 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) has 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 TiO$_2$. Because of the energy barrier provided by the CdS shell, the charge injection efficiency decreases with increase of the shell thickness. A trade-off between charge injection efficiency and the charge collection efficiency is necessary. A power conversion efficiency of 1.28% is obtained with PbS QDs with a CdS shell of about 0.5 nm thickness. Importantly, the photo-stability is significantly improved for the solar cell sensitized with PbS-CdS (1.1 nm) QDs.

**Experimental details**

**Nanocrystal synthesis**

PbS and PbS–CdS core–shell QDs were synthesized using the hot injection method. In a three-neck reaction flask, PbAc$_2$•3H$_2$O (2 mmol, 0.758 g), ODE (10 mL) and OA (10 mL) were dried at 100 °C under vacuum for 2 hours to dissolve the lead salt and to dry the solution. The temperature was raised to 145 °C. In a glovebox, a sulphur precursor solution was prepared by mixing TMS3S (0.21 mL, 1 mmol) with ODE (10 mL). Sulphur 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 using 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 NCs. The obtained PbS NCs 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 for 2 hours to dissolve the lead salt and to dry the solution. 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 NCs 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 NCs ethanol was added to precipitate the NCs. The precipitate was re-dispersed in toluene and again precipitated with ethanol. The re-dispersion–precipitation procedure was repeated two times.

**Preparation of the Cu$_x$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 of 1 cm$^2$) and the Cu$_x$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, a thinner spacer may help the diffusion of redox species, thus higher efficiencies are expected after replacing the spacer with a thinner one.

**Characterization**

The size of core–shell QD is measured by scanning transmission electron microscopy (STEM), using 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 using a UV-3600 UV-vis-NIR spectrophotometer (Shimadzu Scientific Instruments) equipped with 3 detectors (PMT, InGaAs and PbS) and an integrating sphere.

$I$–$V$ curves were obtained using a SP-200, Bio-Logic potentiostat equipped with an electrochemical impedance spectroscopy (EIS) module.
Results and discussion

The general structure of the quantum dot-sensitized solar cells (QDSSCs) is shown in Fig. 1(a). The cells are composed of the QD-sensitized electrode, the polysulfide electrolyte and a Cu$_x$S counter electrode. Because of the easy corrosion of the metal chalcogenides QDs in the $I_2$/I$^-$ electrolyte, $S^{2-}$/S$_2^{2-}$ shuttles are the best choice for QDSSCs. Moreover, in the polysulfide electrolyte Cu$_x$S and Co$_x$S counter electrodes give lower overpotential. Mono-dispersed oleic acid capped-PbS-QDs are used to sensitize mesoporous TiO$_2$. In Fig. 1(b), the STEM micrograph shows the uniform PbS–CdS QDs with an average core size of 3.8 nm and a shell thickness of about 1.1 nm. Fig. 1(c) shows the details of the core–shell QD sensitized solar cells.

Fig. 2(a) shows the $J$–$V$ characteristics of the QDSSCs sensitized with 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 Cu$_x$S with a counter electrode of the potentiostat. As a result, the current and potential are reversed with respect to conventional photovoltaic devices. All the device parameters are reported in Table 1. The PbS–CdS QDSSCs show a much higher photocurrent (5.7 mA cm$^{-2}$) and photovoltage ($–0.47$ V) compared with PbS QDSSCs. The open circuit voltage increases with the thickness of the CdS shell, because of the lower carrier recombination induced by surface trap states.

Solar cells fabricated using core–shell QDs with 0.5 nm CdS show the highest photocurrent and 4 times higher efficiency (1.28%) than what is obtained with simple PbS QDs coated with ZnS after deposition. The ZnS coating is believed by most scientists to have the effect of either blocking electrons, which could otherwise recombine with the electrolyte, or passivating defect states that may trap carriers. A detailed discussion of the working mechanism of ZnS 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. Moreover, the effect of methanol in the polysulfide electrolyte is reported in Fig. S1 (ESI†), showing that the photocurrent and FF are higher when methanol is added as a hole scavenger.

Fig. 2(b) shows the external quantum efficiency (EQE) of the QD-sensitized solar cells obtained using different QDs. The samples fabricated with core–shell particles having a 0.5 nm shell show significantly enhanced EQE, reaching 40% at 440 nm. The theoretical short circuit currents obtained by AM 1.5G-weighted integration of the EQE spectrum are 1.1 mA cm$^{-2}$, 5.7 mA cm$^{-2}$ and 3.5 mA cm$^{-2}$, for PbS, PbS–CdS (0.5 nm) and PbS–CdS (1.1 nm). The ratio of the theoretical short circuit current for 0.5 nm and 1.1 nm thick shell QDs is 1.6, which is smaller than the short circuit current ratio (2) obtained from the $J$–$V$ curves reported in Fig. 2(a). We believe this is caused by the degradation of the thin CdS shell solar cells as shown in Fig. 6.

The EQE spectra of solar cells fabricated using different QDs show dissimilar onset at low energy, which is caused by the slight difference in the size of the PbS core. It is important to underline that the core–shell particles having thicker shells showed a slightly lower band-gap (from the EQE and internal quantum efficiency (IQE) spectra), while for the same sample the $J$–$V$ characteristics of the solar cells reported in Fig. 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 caused a decrease of open circuit voltage.
The EQE depends on a series of device parameters:

\[ \text{EQE} = \frac{\text{LHE}}{\phi_{\text{inj}}} \eta_c \]  

(1)

where LHE is the light harvesting efficiency, \( \phi_{\text{inj}} \) 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, which resemble closely the absorption spectra of the colloidal solution (Fig. S2, ESI†). It is generally supposed that the light harvesting efficiency is the light absorbed by the solar cells (for the spectra see Fig. S2 and S3, ESI†). The similarity of the EQE of the solar cell with the absorption of the QDs provides a proof of carrier transfer from the PbS core to TiO₂. Fig. 2(c) shows the IQE of the QD-sensitized solar cells. According to the definition:

\[ \text{IQE} = \frac{\text{EQE}}{\text{LHE}} \]  

(2)

The sample fabricated using 0.5 nm core–shell QDs shows significantly enhanced IQE, reaching 60% at 440 nm. The sample with the 0.5 nm CdS shell shows a higher IQE value in the visible range compared to that with the 1.1 nm CdS shell, indicating that the CdS does not play an important role in the increase of the photocurrent. The charge injection efficiency derived according to eqn (1) is shown in Fig. S5 (ESI†). Here the sample with the 1.1 nm shell shows lower charge injection efficiency, which could be ascribed to the stronger confinement caused by the thick CdS shell.

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.\(^{35-42}\) The transmission line model is commonly used to simulate the charge transport parameters in mesoporous electrodes, and the equivalent circuit of the transmission line model is shown in Fig. 3(a). The impedance spectra of QDSSCs comprise two arcs (shown in Fig. 3(b)): one at high frequency is associated with the charge transfer at the counter electrode (Cu₂S) interface; and, the second one at low frequency is associated with the charge transfer at the TiO₂/QDs/electrolyte interface. In the measured frequency range, the third arc corresponding to the diffusion of the redox species is not observed in Fig. 3(b), thus the diffusion impedance is not considered in the equivalent circuit model shown in Fig. 3(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, the consequence of a high \( r_{ct} \) and a low \( r_r \).\(^{43}\) The equivalent circuit parameters obtained by fitting the measurements with the proposed model are listed in Table S1 of the ESI.

The electron mobility, electron lifetime, electron transit time and electron diffusion length are the most direct parameters to monitor the carrier transport dynamics in QDSSCs. All these parameters are obtained as follows. The electron transport in TiO₂ is diffusion-like because the electrolyte shields the space charge.\(^{44}\) The electron diffusion coefficient can be derived from:

\[ D_e = \frac{r_r}{r_{ct}} L^2 f_0 \]  

(3)

where \( L \) is the thickness of TiO₂, and \( f_0 \) is the peak frequency of the low frequency arc in the Nyquist impedance plot (Fig. S4(b), ESI†). The electron mobility can be derived from the Einstein relation, \( \mu_e = D_e/k_B T \), from which it is found that the PbS–CdS QD-sensitized solar cells...
cells have higher electron mobility (3 × 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) than the PbS QDs in TiO_2 (10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) (Table S1, ESI†).

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)\textsuperscript{27,45–47} or by transient techniques such as open-circuit voltage decay (OCVD).\textsuperscript{16} 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 (\(r_r\)) and the chemical capacitance between the photoanode and the electrolyte, \(Q_m\), obtained from electrochemical impedance spectroscopy (EIS) fitted using the transmission line model. The second method is derived from IMVS, here the electron lifetime can be evaluated from the expression \(\tau_n = 1 / (2\pi f_{\text{max}})\), where \(f_{\text{max}}\) is the frequency of the peak imaginary component of the IMVS spectra (Fig. S4(a), ESI†). The values obtained in these two ways are plotted in Fig. 4(a) and Fig. S4(b) (ESI†), respectively, from which it is evident that samples prepared using 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 (\(\tau_d\)) is the average diffusion time of the electrons to travel from QDs to the electrode, which can be defined as: \(\tau_d = L^2 / D_e\). Table S1 (ESI†) shows that for the PbS QD-sensitized solar cell, the electron transit time (594 ms) is one order higher than electron lifetime (39 ms) under 1 sun illumination; on the other hand, for the samples with PbS–CdS (0.5 nm) QD sensitization, the electron transit time has the same magnitude (~50 ms) as the electron lifetime. However, for samples 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 \(L_d = (\tau_n D_e)^{0.5}\), where \(\tau_n\) is the mean electron lifetime and \(D_e\) is the electron diffusion coefficient. Fig. 4(b) shows that the electron diffusion lengths are 1 \text{ \mu m}, 3.7 \text{ \mu m}, and 11.4 \text{ \mu m} for PbS, PbS–CdS (0.5 nm), and PbS–CdS (1.1 nm). 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 Fig. 4(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 accelerates carrier recombination. 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{48} 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 for the electron lifetime (Fig. 4(a)).

Based on the carrier dynamics studies, the working mechanism of our devices and the carrier transport model is reconstructed as shown in Fig. 5. The photoexcited electrons (route 1) are quickly injected from the PbS QDs into TiO\textsubscript{2} in sub-picoseconds (route 3),\textsuperscript{49} and the remaining holes react with the hole scavengers S\textsubscript{2}/C\textsubscript{0} (route 6). After electron injection into TiO\textsubscript{2}, these electrons can recombine by several routes as shown by the dashed lines in Fig. 5; 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{38,48} The trap-assisted recombination leads to a decrease of charge collection efficiency (Table S1, ESI\textsuperscript{†}) and to the degradation of the solar cell performance. In Fig. 5(b), the 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.

Further evidence of the proposed mechanism is provided by the solar cell stability reported in Fig. 6. Here the increasing photocurrent in the first 1000 seconds results from the infiltration of the 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 to more than 50% after 1 h illumination with 1 sun at AM 1.5. The PbS–CdS (1.1 nm) core–shell QD-sensitized solar cells show minimum degradation during 1 h measurement demonstrating the importance of the CdS shell in preventing the PbS core from photocorrosion.

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 poor 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. The CdS shell passivating the PbS surface allows increasing the electron lifetime, electron mobility and electron diffusion length. The device parameters significantly improved, with EQE reaching 40% and IQE reaching 60% at 440 nm using 0.5 nm CdS shell QDs and the overall power conversion efficiency is 1.28%, which is 4 times higher than 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.

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Notes and references
