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Employing ZnS as a capping material for PbS quantum dots and bulk heterojunction solar cells

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ABSTRACT Formation of bulk heterojunctions by incorporating colloidal quantum dots into a mesoporous substrate is anticipated to yield efficient charge collection and complete light absorption. However, it is still challenging in view of the bulky nature of the colloidal quantum dots and the *ex situ* deposition route. In this study, the feasibility of employing ZnS as a capping material for PbS quantum dots is dissected by carefully designed control experiments, with reference to the formation of bulk heterojunctions by successive ionic layer adsorption and reaction (SILAR) at ambient conditions. The results reveal that the underlying ZnS layer facilitates the PbS deposition by an ion exchange process, while the overlaying ZnS layer tends to cover the PbS in a manner similar to a physical stacking process. Therefore, PbS quantum dots capped with amorphous ZnS are developed with the SILAR technique, which could be used to fill up the mesoporous substrates and thus construct bulk heterojunctions. The hole collection is the limiting factor of such bulk heterojunction solar cells, as demonstrated by inserting a conductive polymer layer in the control devices. Further development of the quantum dot system is discussed in consideration of the fundamental issues presented in this study.

Keywords: quantum dots, solar cells, SILAR, bulk heterojunction, PbS

INTRODUCTION

Semiconductor quantum dots (QDs) exhibit unique size-dependent properties as compared to their bulks, because of the quantum confinement effect [1]. It has been extensively applied in a wide spectrum of applications, including photodetectors [2], photovoltaics [3], light-emitting diodes [4], and so on [5]. The QDs of high quality are usually synthesized with a hot injection method, where organic molecules of long chains are used as capping materials to produce monodisperse colloids [6]. However, thin

films of such colloidal QDs display insulating feature, in light of the large spacing between neighboring QDs, which impedes efficient charge transport in the films. As such, ligand exchange with small molecules is developed to reduce the spacing [7], such as amines [8], thiols [9], etc. The conductivity of the films is highly promoted after ligand exchange, suitable for various optoelectronic and photovoltaic devices. QD solar cells display impressive performances based on the monodisperse colloids capped with small molecules. Nevertheless, surface states existing in such QDs substantially hamper their further development [10]. Accordingly, surface passivation by inorganic halides boosts the efficiency of the solar cells from 6% to recently over 10% [11–14]. In this regard, replacing the organic molecules with inorganic chalcogenides even gives rise to band-like transport [15], rendering a promising way for further efficiency enhancement of the solar cells. This indicates that an appropriate capping material is significant for the QDs and corresponding functional films.

In parallel, successive ionic layer adsorption and reaction (SILAR) is another approach to synthesize semiconductor QDs [16,17]. Development of photovoltaic devices based on the SILAR method lags relatively far behind, in view of uncontrollable QD growth and also unfavorable liquid-containing components [18]. However, the SILAR technique offers an *in situ* deposition route, resulting in high surface coverage and hence large loading quantity of the QDs inside a mesoporous substrate [19]. In contrast, it is difficult for colloidal QDs to incorporate into the mesoporous substrate to form a bulk heterojunction [20,21], because of the bulky nature and *ex situ* deposition way. The mesoporous substrate has been widely applied in dye-/QD-sensitized solar cells and recent perovskite

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solar cells [22,23], which provides high surface area for accommodating light-absorbing species and rapid charge separation at the interfaces. It is anticipated that efficient charge collection and complete light absorption could be achieved by forming a bulk heterojunction between the mesoporous substrate and colloidal QDs. A number of studies were thus devoted to constructing such bulk heterojunctions, but only succeeded using macroporous counterparts with considerably enhanced charge collection [24–26]. To this end, it is essential to explore alternative approach to fabricate the QD bulk heterojunctions. Back to the SILAR method, it implements based on reaction between ionic species at atomic scale, thus possible to fill up the mesoporous substrates. The key point is the choice of appropriate capping materials to imitate the organic molecules used in colloidal QDs.

Our previous studies reported the first trial to fabricate bulk heterojunctions with the SILAR technique [27,28], and therefore demonstrated its feasibility with impressive photovoltaic performances. Nonetheless, a few fundamental concerns were still ambiguous. In this study, the role of ZnS as the capping material is dissected with carefully designed control experiments, meanwhile its influence on the charge collection process is unveiled by inserting a conducting polymer layer in the control devices. Future development is thus highlighted based on present fundamental studies.

EXPERIMENTAL SECTION

Mesoporous TiO_2 substrates were prepared by a modified standard procedure, as described in our previous report [29]. Briefly, fluorine-doped tin oxide (FTO, Pilkington TEC-15) glasses were cleaned ultrasonically in 5% Decon 90 solution, deionized water, and ethanol for 10 min each. A compact TiO_2 layer was then synthesized onto the FTO glasses by spray pyrolysis of 0.2 mol L^{-1} ethanolic solution of titanium diisopropoxy bis(acetylacetonate) at 500°C [30]. Subsequently, mesoporous TiO_2 films were fabricated by screen printing dilute paste (Dyesol, DSL 90-T) onto the above electrodes. The resulting substrates were heated gradually and held at 450°C and 500°C for 15 min each, as detailed elsewhere [31]. After cooling to room temperature, the substrates were treated with 40 mmol L^{-1} TiCl_4 solution at 70°C for 30 min, followed by annealing at 500°C for 30 min. In this study, substrates of approximately 2 μm and 500 nm were used for absorption measurement and device fabrication, respectively.

Both PbS and ZnS were deposited by SILAR at ambient conditions. Deposition of PbS was carried out as follows:

1) dipping in 0.02 mol L^{-1} $\text{Pb}(\text{NO}_3)_2$ methanolic solution for 30 s; 2) rinsing with methanol for 1 min vigorously and drying with N_2 stream; 3) dipping in 0.02 mol L^{-1} Na_2S dissolved in a mixture of methanol and water ($v:v=1:1$) for 30 s; 4) rinsing with methanol for 1 min vigorously and drying with N_2 stream. These procedures were repeated consecutively for different cycles to produce PbS QDs of different sizes. It was denoted as $\text{PbS}(m)$, where m is the deposition cycle for PbS. Deposition of ZnS was conducted as follows: 1) dipping in 0.1 mol L^{-1} $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution for 1 min; 2) rinsing with deionized water for 1 min vigorously; 3) dipping in 0.1 mol L^{-1} Na_2S aqueous solution for 1 min; 4) rinsing with deionized water for 1 min vigorously. These procedures were repeated successively for different cycles to yield ZnS underlying or overlaying films of different thicknesses. It was presented as $\text{ZnS}(n)$, where n is the deposition cycle for ZnS. Alternating deposition of $\text{PbS}(m)$ and $\text{ZnS}(n)$ was exploited to tailor the configuration of PbS QDs capped with amorphous ZnS.

For photovoltaic devices, alternating deposition of $\text{PbS}(5)$ and $\text{ZnS}(5)$ was performed for different rounds to fill up the mesoporous substrates as well as to develop compact overlayers, i.e., $[\text{PbS}(5)/\text{ZnS}(5)]_x$, where x is the deposition round. Two kinds of devices were assembled in this study: 1) directly using graphite powders (<20 μm , Sigma-Aldrich) as the counter electrodes, and 2) spin coating poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) layer onto the heterojunction at 2000 rpm for 45 s and then annealing at 120°C for 10 min, thereafter employing graphite powders as the counter electrodes. The active area was fixed at 0.20 cm^2 . The photocurrent-voltage curves were measured with an AM1.5G solar simulator (Newport, 2612A, calibrated with a silicon reference cell) at 100 mW cm^{-2} . The external quantum efficiency was recorded using a 300 W Xenon lamp and a grating monochromator equipped with order sorting filters (E0201b, Chinese Academy of Sciences).

Absorption spectra were examined using a UV-vis-NIR spectrophotometer (Shimadzu, Solidspec-3700) equipped with an integrating sphere. Cross-sectional morphologies were characterized with field-emission scanning electron microscopy (FESEM, Zeiss Auriga). Morphology of the PbS QDs was acquired with a transmission electron microscope (TEM, JEOL-JEM 2010F). Crystallographic information was collected by powder X-ray diffraction (XRD, D/max 1200, Cu K α).

RESULTS AND DISCUSSION

Fig. 1a shows the absorption spectra of PbS QDs after de-

Figure 1 Absorption spectra of PbS(*m*) (a) and PbS(5)/ZnS(*n*)/PbS(5) (b) on TiO₂ mesoporous substrates (about 2 μm), where *m* and *n* represent the deposition cycle for PbS and ZnS, respectively.

positing on mesoporous TiO₂ substrates (about 2 μm) for different cycles. The spectra exhibit red shift with the deposition cycle, indicating gradually increased size as well as amount of the QDs. Considering the band alignment with reference to TiO₂ substrates [20,21,32,33], five deposition cycles for PbS QDs were adopted in this study for efficient electron injection (smaller than 5.5 nm) [27,28]. In conventional colloidal QDs, organic molecules are used as the capping ligands to control the QD size. In this case, while stacking one layer of QDs on top of another to fabricate thin films, no bonding or strong interaction arises between adjacent ligands. As such, the two layers are physically separated in the presence of ligands. In this study, ZnS was exploited as the capping material, in view of 1) the formation of Type I heterojunction with PbS, 2) inability to form any solid solution with PbS at room temperature, and 3) accessibility with solution-based process [27]. The nature of continuous crystal structure enables the ZnS perform as a bridging layer between two ensembles of PbS QDs by chemical bonding. To examine such a possibility, a series of films with configuration of PbS(5)/ZnS(*n*)/PbS(5) were prepared first, where *n* is the deposition cycle of ZnS between two PbS(5) layers. Fig. 1b reveals that intensity of the spectrum increases substantially by inserting just a single cycle of ZnS (i.e., *n*=1), in obvious contrast to PbS(10) alone. The spectrum also displays red shift with the increasing deposition cycle for the intermediate ZnS. It is interesting that no apparent change in spectrum is observed with the ZnS deposition being over 3 cycles, as evidenced by the well-matched absorption profile between PbS(5)/ZnS(3)/PbS(5) and PbS(5)/ZnS(10)/PbS(5). In general, a red shift of absorption spectrum can be attributed to enlarged QD size [16], strengthened electronic

coupling between QDs [7,34], enhanced light scattering [35,36], and the polarization effect [37]. Considering the ZnS intercalation and unchanged spectrum beyond 3 deposition cycles, it suggests that the intermediate deposition of ZnS substantially affects the growth of PbS QDs.

To figure out the role of ZnS deposition, a series of control experiments were carried out. Fig. 2a exhibits that deposition of ZnS(3) atop of PbS(5), i.e., PbS(5)/ZnS(3), results in a slight increment of the absorption spectrum compared with PbS(5) alone. A simple calculation by adding the individual absorption of ZnS(3) to PbS(5) makes a good agreement with the measurement (see the triangle symbol line in Fig. 2a). This demonstrates that the deposition of ZnS onto PbS influences little to each individual, analogous to a physical stacking process. In contrast, while depositing ZnS(3) first and then PbS(5), the absorption of ZnS(3)/PbS(5) drastically increases, showing much higher intensity than PbS(5) alone and also PbS(5)/ZnS(3). This is attributed to the cation exchange process, where the solubility product of PbS is much smaller than ZnS (K_{sp} , 3.4×10^{-28} vs. 1.2×10^{-23} for PbS vs. ZnS) [38]. The SILAR deposition consists of four important steps: 1) dipping in cation precursor, 2) rinsing and drying, 3) dipping in anion precursor, 4) rinsing and drying. The cation exchange of Zn²⁺ with Pb²⁺ ions takes place only in Step 1, producing the nuclei of PbS QDs; meanwhile the exchanged Zn²⁺ ions are inclined to reside at the outer surface of PbS nuclei. In the subsequent deposition steps, the nuclei grow up gradually. Consequently, partial of the ZnS bottom layer is exchanged into PbS, leading to enlarged PbS QD size. To verify this point, the absorption of PbS(5) alone is subtracted from the multiple film of ZnS(3)/PbS(5), as shown in Fig. 2b. The resulting spectrum is expected to attribute to the

Figure 2 Influence of deposition sequence on the absorption spectra (a), where the calculated spectra are shown with symbol lines in (a) and (b).

absorption of ZnS(3) alone for a physical stacking mode, which however displays much higher intensity than that obtained from the measurement in Fig. 2a. This confirms the cation exchange process and thus increased size of PbS QDs. A sandwiched structure of ZnS(3)/PbS(5)/ZnS(3) was also fabricated by alternating deposition of ZnS and PbS in the control experiments. The relevant calculations well echoes the above discussion, as shown in Fig. 2, further consolidating the statement that ZnS deposition onto PbS is similar to a physical stacking process, while PbS deposition onto ZnS is accompanied by a cation exchange process. On the other hand, it is noteworthy that the enlarged QD size itself is difficult to account for such a large increment in absorption (cf. Figs 1a and 2b), therefore it is believed that the ZnS deposition also facilitates the nucleation of subsequent PbS QDs (bearing higher extinction coefficient than ZnS). In other words, both the size and amount of the QDs are promoted with the assistance of ZnS deposition.

Fig. 2a also reveals that the growth of PbS QDs on TiO₂ and ZnS is distinctly different. As such, to produce identical ensemble of PbS QDs and also to test the isolation behavior of ZnS as a capping agent, multiple sandwiched structure was designed and fabricated, as shown in Fig. 3. In this design, each ZnS(3)/PbS(5)/ZnS(3) is considered as the building block for a cascade architecture. Accordingly, the absorption of ZnS(3)/PbS(5)/ZnS(3)/PbS(5)/ZnS(3) is expected to be doubled with respect to that of the building block. Fig. 3 discloses a good agreement on peak intensity between the measurement and the simulation (circle symbol line vs. solid line). Nevertheless, the measured spectrum renders red shift and broadening relative to the simulated one. Taking into account the control experiments in Fig. 2, quasi-identical ensemble of PbS QDs is anticipated for each building unit, thus the peak shift and broadening

Figure 3 Absorption spectra of ZnS(3)/PbS(5)/ZnS(3) and ZnS(3)/PbS(5)/ZnS(3)/PbS(5)/ZnS(3) for isolation test, where the calculated spectrum for the latter is given as solid line.

are plausibly due to the electronic coupling between the neighboring building blocks. Such a coupling is important for electronic, optoelectronic and photovoltaic devices for efficient charge transport in the films.

The above results demonstrate that it is feasible to employ ZnS as a capping material for PbS QDs, which can be achieved by alternating deposition of ZnS and PbS with SILAR approach. The underlying ZnS layer facilitates the deposition of PbS with a cation exchange process, while the overlaying ZnS layer tends to fully cover the PbS QDs in light of much smaller surface energy (i.e., 0.65 vs. 2.45 J m⁻² for ZnS film [39,40] and PbS nanocrystals [41], respectively). Meanwhile, in such manners the ZnS performs as a bridging layer between two adjacent ensembles of PbS QDs, and dominates the electronic coupling by controlling the deposition cycle and hence the distance between QDs.

In the above control experiments and isolation test, a configuration of ZnS(3) was adopted to fit the PbS(5), based on the critical cycle in Fig. 1b. In view of a continuous deposition process where the later deposition may affect the existing deposits, the cycle is increased to ZnS(5) while filling up the mesoporous substrates for device fabrication. Fig. 4a is an FESEM image showing the cross section of a pristine mesoporous substrate of about 500 nm, in which the porous nature of the substrate is clearly visible. Alternating deposition of PbS(5) and ZnS(5) was used to fill up the mesopores with PbS QDs capped with ZnS, i.e., [PbS(5)/ZnS(5)] x , where x is the deposition round. After 5 rounds, the substrate is completely filled up, thereby rendering a dense feature, as presented in Figs 4b and d. Further deposition develops a compact overlayer consisting of PbS QDs embedded in ZnS matrix, which also acts as an electron blocking layer in the device. The compact overlayer is about 370 nm after 15 deposition rounds, as exemplified in Fig. 4c. Fig. 4e shows a typical TEM image of the bulk heterojunction, where the large particle is ascribed to TiO₂ substrate while the small particles are assigned to PbS QDs either embedded in ZnS matrix or attached to TiO₂ substrate. Corresponding XRD patterns (see Fig. 5a) manifest the presence of FTO, TiO₂ and PbS in the resulting films, whereas ZnS is undetectable

because of the amorphous state, as elucidated in our previous studies [27,28].

A bulk heterojunction suitable for photovoltaic devices is thus constructed between *n*-TiO₂ and *p*-PbS QDs capped with amorphous ZnS. By simply employing graphite as the counter electrode, a photovoltaic device is obtained, as illustrated in Fig. 5b (left illustration). Once soaking under light, photon energy is absorbed by the PbS QDs, thus yielding electron-hole pairs. The electrons and holes subsequently transport via tunneling through localized states of the QDs [42], and separate at the TiO₂/QDs interfaces by electron injection into TiO₂ substrate, leaving the holes percolate through the QD network. As such, the hole transport process is a limiting factor in such devices. This is further confirmed by the photovoltaic performances of the devices. The best performance originates from devices bearing a configuration of [PbS(5)/ZnS(5)]5, as shown in Fig. 6a, in which a very thin compact overlayer (see Fig. 4d) is present and offers a short hole transport distance.

To improve the hole transport in the bulk heterojunction solar cells, the conducting polymer of PEDOT:PSS was prepared on top of the compact overlayer, as illustrated in Fig. 5b (right illustration). In this scenario, the best device furnishes a feature of [PbS(5)/ZnS(5)]15 with a compact overlayer up to 370 nm (see Fig. 4c), in obvious contrast to the

Figure 4 Cross-sectional FESEM images of bare TiO₂ substrate (a) and that filled with [PbS(5)/ZnS(5)]5 (b) and [PbS(5)/ZnS(5)]15 (c). A local magnification of (b) is given in (d), showing more details of the junction. A corresponding TEM image of the bulk heterojunction is shown in (e), where the large particle belongs to TiO₂ substrate while the small particles are assigned to PbS QDs.

Figure 5 (a) XRD patterns of bulk heterojunctions filled with [PbS(5)/ZnS(5)]5 and [PbS(5)/ZnS(5)]15. (b) Schematic illustrations of two device structures used in this study: without (left) and with (right) PEDOT:PSS hole transport layer, where a red dot highlights a QD absorbing one photon and then producing an electron-hole pair. NP: nanoparticles; BLK: blocking layer.

Figure 6 Comparative performances of the best devices from [PbS(5)/ZnS(5)] x series without ($x=5$) and with ($x=15$) PEDOT:PSS as the hole scavenger: I - V measurements (a) and corresponding EQE spectra (b). The inset is the dark current measurement of two devices of the same configuration [PbS(5)/ZnS(5)]5, showing the junction quality without and with PEDOT:PSS layer.

very thin compact layer in devices without the conducting polymer (see Fig. 4d). Fig. 6a compares the performances from the best devices without ($x=5$) and with ($x=15$) PEDOT:PSS as the hole transport layer. It unveils that the short-circuit photocurrent density is increased by about 1 mA cm^{-2} . This benefits from the highly promoted hole extraction in the presence of conducting polymer, consistent with the dark current measurement where much higher current is produced under forward bias, as displayed in the inset of Fig. 6a. Corresponding external quantum efficiency (EQE) spectra also exhibit higher photoresponse nearly over the whole measurement range, as shown in Fig. 6b. In particular, appreciable enhancement in visible region is achieved, most of which is in principle absorbed in the heterojunction close to FTO substrate because of high extinction coefficient at short wavelength. This indicates

much improved hole diffusion length with the assistance of conducting polymer. On the other hand, the photocurrent increment proceeds at the expense of photovoltage. It could be induced by a number of factors, such as band alignment, interface quality, and so on, which is still under investigation in our group.

CONCLUSIONS

In conclusion, ZnS is capable of performing as a capping material for PbS QDs. This is achievable with an alternating deposition of ZnS and PbS by SILAR at ambient conditions. The underlying ZnS contributes to PbS growth by cation exchange process in the light of difference in solubility product, while the overlaying ZnS is analogous to a physical stacking process atop of PbS to reduce the surface energy of the system, thus forming the structure of PbS

QDs capped with amorphous ZnS. Photovoltaic devices are constructed by filling up mesoporous TiO₂ substrates with these QDs. Device performances are limited with the hole transport in the bulk heterojunction, as indicated by photocurrent improvement with the addition of a hole extraction layer, such as conducting polymer of PEDOT:PSS used in this study. Further development of the photovoltaic devices is envisaged by means of 1) employing highly oriented TiO₂ nanotube arrays as the substrates for vectorial and efficient charge transport [43–45], 2) selecting suitable conducting polymers for efficient hole collection, 3) optimizing the configuration of PbS QDs with reference to ZnS deposition, 4) narrowing size distribution of the QDs, etc.

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Author contributions Sun L completed the whole work.

Conflict of interest The author declares that he has no conflict of interest.

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采用ZnS作为PbS量子点包覆材料及其体相太阳能电池研究

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摘要 将胶体量子点引入到介孔基体中形成体相异质结预期能够产生高效的电荷收集和完全的光吸收。然而, 鉴于胶体量子点个体积较大和薄膜异位生长的特性, 形成这样的异质结结构仍然存在巨大挑战。本论文针对此问题, 通过严谨的实验设计, 分析了采用连续离子层吸附反应法(SILAR)以ZnS作为PbS量子点包覆材料的可行性。实验结果表明底层ZnS通过离子交换的方式促进PbS的沉积, 而顶层ZnS趋于通过物理堆垛的方式覆盖PbS, 进而形成非晶态ZnS包覆的PbS量子点结构。该方法可用以填充介孔基体而形成体相异质结结构。在该体相异质结器件中加入导电有机物的研究表明该体系太阳能电池受限于空穴收集。在此基础上, 讨论了该体系量子点太阳能电池进一步提升的途径。