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Enhanced performance of a solar cell based on a layer-by-layer self-assembled luminescence down-shifting layer of core–shell quantum dots*

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In this paper, core–shell quantum dots (QDs) with two polar surface functional groups (ZnSe/ZnS–COOH QDs and ZnSe/ZnS–NH_2 QDs) are synthesized in an aqueous phase. Photoluminescence (PL) and absorption spectra clearly indicate luminescence down-shifting (LDS) properties. On the basis of QDs, surface functional group multilayer LDS films (M-LDSs) are fabricated through an electrostatic layer-by-layer (LBL) self-assembly method. The PL intensity increases linearly with the number of bilayers, showing a regular and uniform film growth. When the M-LDS is placed on the surface of a Si-based solar cell as an optical conversion layer for the first time, the external quantum efficiency (EQE) and short-circuit current density (J_{sc}) notably increases for the LDS process. The EQE response improves in a wavelength region extending from the UV region to the blue region, and its maximum increase reaches more than 15% between 350 nm and 460 nm.

Keywords: two-surface functional group, LBL self-assembly, LDS

PACS: 73.61.Ga, 73.21.La, 85.30.–z **DOI:** 10.1088/1674-1056/27/12/127303

1. Introduction

With the rapid development of the photovoltaic industry, the high efficiency and the low cost of photovoltaics becomes a main research target. One of the most main constraints of solar cell efficiency is the energy loss caused by spectral mismatch.[1–3] The latter refers to the fact that the photon energy on the surface of the solar cell is lower than the forbidden bandwidth of the material, so this part of the energy cannot be effectively utilized. For example, the response (short-wave spectral response) is low for Si-based cells and CdTe thin film solar cells, but the spectral response is relatively high in the visible wavelength region.[4] There are two effective approaches to solving this spectral mismatch. One is to adjust the battery structure in order to utilize the sunlight to a maximum extent; the other is to adopt spectrum conversion to increase the spectral response of the solar cell.[5–7] Luminescent down-shifting (LDS) is one of the most effective methods for spectral conversion. The LDS process is a simple and pure spectral conversion procedure, in which the material absorbs a high-energy photon and emits low-energy photons.[8,9] This spectral transfer property results in the weakness of response in short wave region of Si-based solar cells and CdTe thin film solar cells. In this regard, core–shell quantum dots (QDs) with unique photoelectric properties become an excellent candidate material for LDS.[10–12]

In order to effectively utilize the fluorescence transfer characteristics of QDs, direct spin-coating on the surface of solar cells was used initially.[13] This specific approach has the advantage that the structure of the cell is not changed and the absorption of the converted spectrum reaches a maximum value.[14,15] However, if the QDs are placed directly on the surface of the solar cell, then they will be easy to cluster and show poor light stability. For the LDS application, the difficulty of controlling film quality is a major drawback. In order to further improve the film-forming quality of the QDs, many kinds of amphiphilic surfactants mixed with QDs have been employed.[16,17] The quality of the film is better than that of simple QDs, and the thickness can be accurately controlled by changing the coating time. Although this method modifies the surface of QDs to make them photobleaching-resistant, the method has limited applications because a polymer layer with opposite polarity is required; the luminescence efficiency of QD layer is affected; the QDs can be easily caused to cluster by the direct mixing with polymer; the polymer flexible polymer chains intertwine; and other problems.[18] These disadvantages will affect the structure, uniformity, thermal stability and luminescence efficiency of LDS films.

In this paper, we prepare ZnSe/ZnS core–shell QDs with –NH_2 and –COOH groups. The composition, morphology and

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luminescence characteristics of ZnSe/ZnS core–shell QDs are studied. The M-LDSs are fabricated for the first time by alternate adsorption of the ZnSe/ZnS–NH_2 QDs endowed with positive groups (NH_2^+) and ZnSe/ZnS–COOH QDs endowed with negative groups (COO^-) using electrostatic interactions between each layer. The LDS film is deposited with these two kinds of ZnSe/ZnS QDs by an electrostatic layer-by-layer self-assembly process on the surface of Si-based solar cell, as shown in Fig. 1. We also systematically analyze the external quantum efficiency (EQE) values and short-circuit current density (J–V) values of LDS films with different thicknesses.

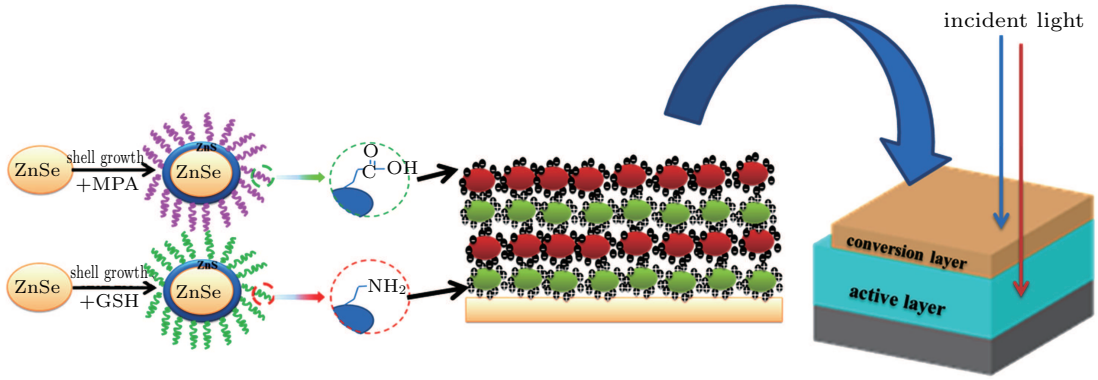


Fig. 1. (color online) Scheme of the LBL self-assembly process based on two surface functional groups of QDs (ZnSe/ZnS–COOH QDs and ZnSe/ZnS–NH_2 QDs) and the M-LDSs as spectra conversion layer.

2. Experiment

2.1. Preparation of ZnSe/ZnS–COOH QDs

ZnSe/ZnS–NH_2 QDs were prepared in water phase.[19] Se powder was initially added to the $NaBH_4$ solution ($NaBH_4$:Se = 2:1) in N_2 atmosphere. When the solution becomes transparent it is added to deionized water to form 0.5-M NaHSe solution. The solution was rapidly injected into $ZnNO_3{\cdot}6H_2O$ and 3-Mercaptopropionic acid (MPA) mixed solution and heated at 100 °C. The ratio of Zn^{2+}/Se^{2-}/MPA was 1:0.9:20. The reaction solution was centrifuged at 1.8×10^4 r/min$\sim 2.0\times10^4$ r/min speed to remove the supernatant and the remaining precipitate was washed several times with anhydrous ethanol to obtain pure ZnSe nanoparticles. After purification, the ZnSe nanoparticles were dispersed in deionized water. The 20-ml $ZnNO_3{\cdot}6H_2O$ as the precursor, and 2-ml MPA were added into the purification solution of ZnSe. The mixture was heated at 90 °C until the reaction was completed. The pure ZnSe/ZnS–COOH QDs were obtained by centrifuging and cleaning in the same way.

2.2. Preparation of ZnSe/ZnS–NH_2 QDs

The preparation procedure of ZnSe/ZnS–NH_2 QDs was the same as that of ZnSe/ZnS–COOH QDs, except that the functional group precursors were changed from MPA to cysteamine.

2.3. Fabrication of an LDS layer on surface of a Si solar cell by the layer-by-layer (LBL) self-assembly method

Ultrasonic dispersion of 0.6-mo/L ZnSe/ZnS–COOH QDs solution and ZnSe/ZnS–NH_2 QDs solution were spin-coated on Si-based solar cells LBL at a rotational speed of 300 rpm/s. Finally, one bilayer film (BL) is formed uniformly by electrostatic interaction for 20 s.

3. Results and discussion

The two functional groups (–COOH and –NH_2) of the ZnSe/ZnS core–shell QDs can be confirmed by x-ray photoelectric spectroscopy (XPS) measurements, as shown in Figs. 2(a) and 2(c). Figure 2(a) shows the identical peaks of the ZnSe/ZnS–COOH QDs at 284.8 eV and 533.14 eV, which are assigned to the C 1s and O 1s level, respectively.[20] In comparison with the ZnSe/ZnS–COOH QDs, the peak at 400 eV is due to the N 1s in the ZnSe/ZnS–NH_2 QDs, as shown in Fig. 2(c). In addition, the XPS spectra confirm the core–shell structure of ZnSe/ZnS QDs. Figures 2(a) and 2(c) show identical peaks between the two functional group QD samples at 1045.2 eV and 1021.9 eV, which are assigned to the Zn 2p1/2 and Zn 2p3/2 core levels of ZnSe QDs, respectively. The S2p (161.8 eV) binding energy of the ZnSe/ZnS core–shell QD is clearly assigned to the ZnS on the core surface.[21]

The transmission electron microscopy (TEM) images and selective area electron diffraction (SAED) patterns of ZnSe/ZnS–COOH QDs and ZnSe/ZnS–NH_2 QDs are depicted in Figs. 2(b) and 2(d). The average diameters of these two kinds of QDs are about 9.2 nm and 10 nm, respectively. In addition, the homogeneous distribution of the QDs can be observed (see the inset in Figs. 2(b) and 2(d)).

The optical properties of ZnSe/ZnS–COOH QDs and ZnSe/ZnS–NH_2 QDs are presented in Figs. 3(a) and 3(b). The absorption and emission spectra of the two QDs are very similar. It can be seen that the first exciton absorption peaks of two QDs are both at 370 nm (3.35 eV). Accordingly, their luminescence peak excited by a light source with a wavelength of 370 nm is at 425 nm, with a narrow peak width due to

the monodisperse size distribution. The characteristic luminescence of the two samples indicates that the ZnSe/ZnS–COOH and ZnSe/ZnS–NH_2 QDs have LDS properties. For Si-based solar cells, the optimal spectral response is in a range of 400 nm–1000 nm, implying that these two QDs can effectively enhance the absorption in the ultraviolet band region for Si-based solar cells.

The multilayer LDS films (M-LDSs) based on two surface functional groups of QDs (ZnSe/ZnS–COOH QDs and ZnSe/ZnS–NH_2 QDs) are fabricated through the LBL self-assembly method as described above. The bilayer (BL) indicates that the film is prepared once by LBL assembly of opposite charged QDs. The PL and absorption spectra of different M-LDSs are also obtained as shown in Figs. 3(c) and 3(d). The PL intensity of the fluorescence peak at about 430 nm increases gradually with the number of bilayers (5, 10, 15, 20, and 30), which indicates the successful deposition of each layer. The absorption spectrum also exhibits a stable absorption peak at 375 nm. In addition, it is noticeable that neither significant shift nor broadening of the emission nor absorption band is observed for different bilayers, indicating no obvious changes in intermolecular interactions nor in the nature of QDs in assembly process (Section 2). The latter is very advantageous in terms of the effective utilization of the LDS characteristics of the two QDs.

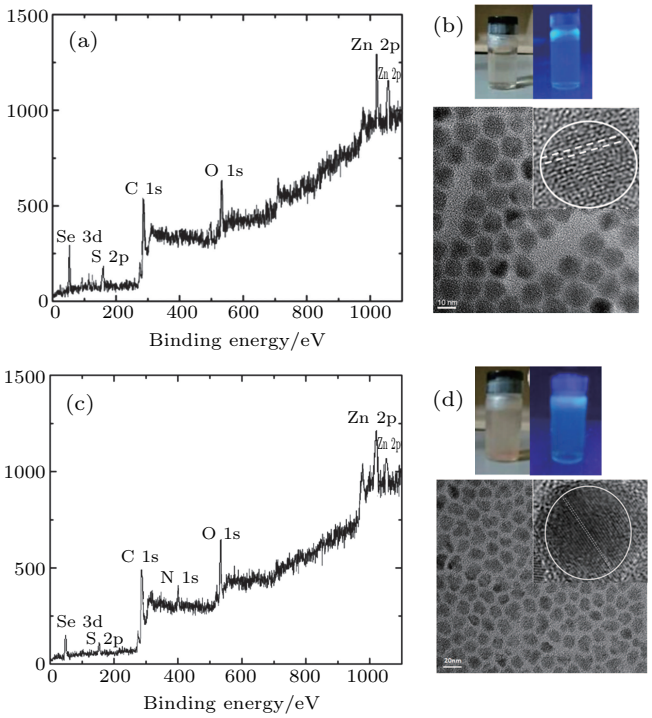


Fig. 2. (color online) XPS survey spectrum of (a) ZnSe/ZnS–COOH QDs and (c) ZnSe/ZnS–NH_2 QDs; TEM images of (b) ZnSe/ZnS–COOH QDs and (d) ZnSe/ZnS–NH_2 QDs. Inset: corresponding selective area electron diffraction (SAED) pattern of two QDs; ((b) and (d)) (upper) images of ZnSe/ZnS–COOH and ZnSe/ZnS–NH_2 QDs in solution under visible (left) and UV light (right).

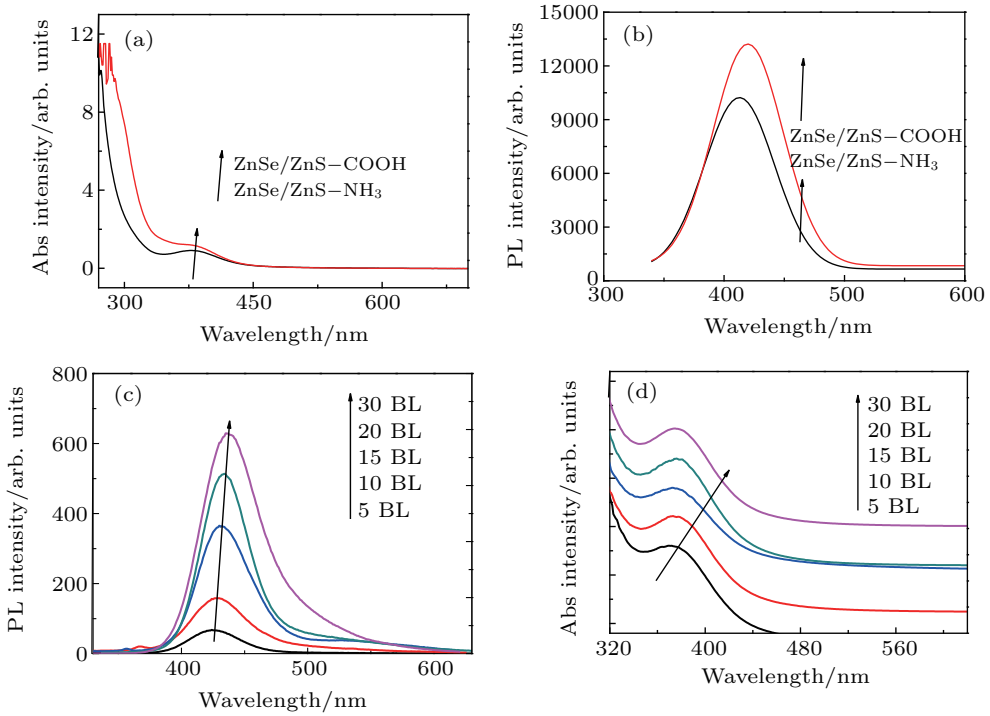


Fig. 3. (color online) (a) Absorption and (b) PL spectra of ZnSe/ZnS–COOH and ZnSe/ZnS–NH_2 QDs; (c) PL and (d) absorption spectra of different bilayers (5 BL, 10 BL, 15 BL, 20 BL, and 30 BL), respectively.

The ZnSe/ZnS–COOH and ZnSe/ZnS–NH_2 QDs with two functional groups are self-assembled by the electrostatic LBL process on the surface of the Si solar cell as an optical conversion layer. The EQE and J_{sc} are measured to evaluate the spectrum response of the fabricated Si solar cells with different numbers of bilayers as shown in Fig. 4. Figure 4(a) shows that the spectrum response is relatively weak below 400 nm for the bare Si solar cell, and the EQE is only 34%.

However, for M-LDSs of ZnSe/ZnS–COOH and ZnSe/ZnS–NH_2 QDs coated on the surface of a bare Si solar cell, the EQE increases significantly due to the luminescent down-shifting process. The EQE response improves in a wavelength region extending from the UV to the blue region, with the maximum increasing more than 15% between 350 nm and 460 nm, which is consistent with the absorption wavelength range of ZnSe/ZnS QDs as shown in Fig. 3(d). The enhancement of spectral response is indeed due to the down-transfer effect of ZnSe/ZnS QDs.

Figure 4(b) illustrates the *J*–*V* characteristics of a Si-based solar cell with different M-LDSs (0, 5, 10, 15, 20, and 30 BL). The J_{sc} of Si solar cell increases from 22 mA/cm^2 (0 BL) to 31 mA/cm^2 (30 BL). Compared with the J_{sc} of pure ZnSe–MPA QD-Si solar cell, the J_{sc} increases obviously.[22] The open circuit voltage (V_{OC}) is about 0.62 V, and no variation is observed upon increasing the number of bilayers. The latter is consistent with the general trend in solar cells, *i.e.*, the sunlight adsorption increases with J_{sc} increasing, in contrast to V_{OC} which remains practically unchanged.

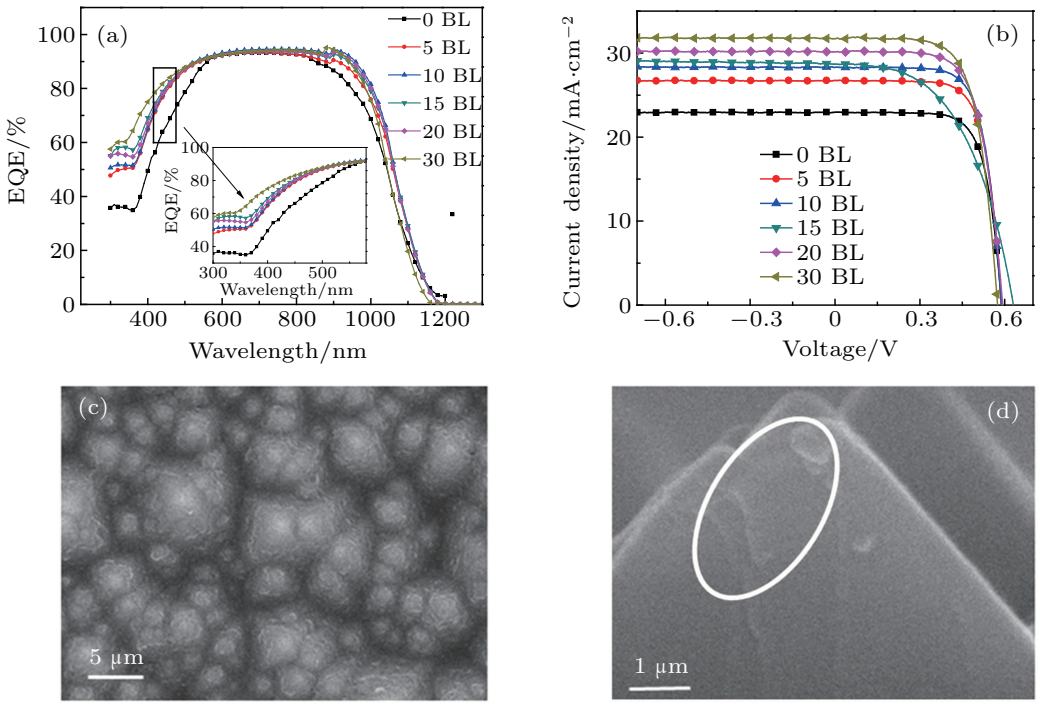


Fig. 4. (color online) (a) EQE and (b) *J*–*V* curves of the Si-based solar cell coated with different numbers of bilayers. (c) and (d) Plane views of Si solar cell surfaces coated with ZnSe and ZnS QDs thin films of 20 BL, respectively.

The surface profiles of the Si solar cells with 20-BL LDSs were confirmed by SEM (Figs. 4(c) and 4(d)), and the ZnSe/ZnS QDs were uniformly coated on the surface of the Si solar cell and the average thickness was about 200 nm.

4. Conclusions

In this work, we have synthesized ZnSe/ZnS core–shell QDs with positive (–NH_2) and negative (–COOH) functional group on the surface. On the basis of these QDs, novel multilayer LDS films are fabricated via an electrostatic LBL self-assembly process. The two functional groups are confirmed by XPS results. The PL intensity of the fluorescence peak increases linearly with the number of bilayers. For M-LDSs of ZnSe/ZnS–COOH and ZnSe/ZnS–NH_2 QDs coated on the surface of bare Si-based solar cells, the EQE notably increases due to the luminescent down-shifting process. The EQE response is improved by more than 15% between 350 nm and 460 nm, whereas the J_{sc} of Si solar cell is increased from 22 mA/cm^2 (0 BL) to 31 mA/cm^2 (30 BL). Such small but distinct improvements are expected to provide the fundamental and practical basis for developing Si-based solar cells with mass-compatible techniques that could promote their widespread utilization.

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