Research Article

Performance Study of CdS/Co-Doped-CdSe Quantum Dot Sensitized Solar Cells

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In order to optimize the charge transfer path in quantum dot sensitized solar cells (QDSCs), we employed successive ionic layer adsorption and reaction method to dope CdSe with Co for fabricating CdS/Co-doped-CdSe QDSCs constructed with CdS/Co-doped-CdSe deposited on mesoscopic TiO$_2$ film as photoanode, Pt counter electrode, and sulfide/polysulfide electrolyte. After Co doping, the bandgap of CdSe quantum dot decreases, and the conduction band and valence band all improve, forming a cascade energy level which is more conducive to charge transport inside the solar cell and reducing the recombination of electron-hole thus improving the photocurrent and ultimately improving the power conversion efficiency. This work has not been found in the literature.

1. Introduction

Quantum dot sensitized solar cells (QDSCs) have received wide attention recently. Quantum dots (QDs) have significant advantages over conventional organic dyes, such as tunability of the bandgap [1, 2], extremely high absorption coefficient [3], generation of multiple electron carriers under high energy excitation [4], and delivery of hot electrons [5, 6]. Especially, the theoretical efficiency of QDSCs is estimated up to 44% due to the multiple exciton generation effect. However, the best record power conversion efficiency of QDSCs remains quite low.

Controlling conductivity via doping in semiconductor quantum dots is an important part of nanoparticle research. Recent effort to improve the power conversion efficiency is to modify the intrinsic property of semiconductor nanocrystals by introducing dopants [7, 8]. By doping optically active transition metal ions, it is possible to modify the electronic and photophysical properties of QDs [9–13]. The dopant significantly changes the electronic structure of the quantum dot. Santana et al. explored CdSe quantum dots doping with indium and tin. In agreement with the expected n-type behavior, the photoluminescence (PL) of both indium and tin doped samples exhibits significantly steeper temperature dependence, compared to undoped CdSe quantum dots [14]. Pralay and Prashant employed Mn$^{2+}$ doping of CdS; they had succeeded in significantly improving the performance of QDSCs. QDSCs constructed with Mn-doped-CdS/CdSe deposited on mesoscopic TiO$_2$ film as photoanode deliver power conversion efficiency of 5.4% [15]. Huang et al. employed successive ionic layer adsorption and reaction method to dope PbS with Cu$^{2+}$. The power conversion efficiency (~2.01%) coupled with a remarkably superior short circuit current density (21 mA/cm$^2$) was achieved in the resulting Cu-doped-PbS/CdS quantum dot sensitized solar cells [16]. Lee et al. reported on a PbS:Hg QD-sensitized solar cell with an unprecedentedly high $I_{SC}$ of 30 mA/cm$^2$; the power conversion efficiency of 5.6% is demonstrated at one sun illumination [17]. Wang et al. used electrochemical deposition method to deposit Co doped CdSe quantum dots on TiO$_2$ single-crystal nanorods array [18]. On the one hand, CdSe doping with Co can tune its bandgap, so that the absorption in the visible light range is enhanced, the absorption range gets broadened, and then improves the light utilization efficiency. On the other hand, Co doping can increase the carrier concentration and the rate of electron
transfer and increase the efficiency of electron collection; thus the photocurrent density is increased.

Inspired by the previous doping on CdSe and that Co doping has excellent effect on quantum dot sensitized solar cells, we used successive ionic layer adsorption and reaction (SILAR) method to assemble into CdS/Co-doped-CdSe quantum dot sensitized solar cells. Doping CdSe with Co significantly improves the short circuit current density ($J_{SC}$) and open circuit voltage ($V_{OC}$) and eventually increases the power conversion efficiency. Using SILAR method, doping CdS with Co, and preparing CdS/Co-doped-CdSe quantum dot sensitized solar cells have not been reported in the literature.

2. Experimental

2.1. Preparation of CdS/Co-Doped-CdSe Co-Sensitized Mesoporous TiO$_2$ Photoanode. The mesoporous TiO$_2$ photoanodes were in situ sensitized by CdS and CdS QDs grown by successive ionic layer adsorption and reaction (SILAR) method [19]. Specifically, CdS was prepared by cadmium nitrate (Cd(NO$_3$)$_2$) and sodium sulfide (Na$_2$S). 0.1 M Cd(NO$_3$)$_2$ in ethanol and 0.1 M Na$_2$S in methanol were used as cation source and anion source, respectively. Each SILAR cycle consists of successive immersion of the FTO glass photoanode, which was precoated with a transparent TiO$_2$ layer, in metal cation and sulfide anion solutions for 5 min. Following each immersion, the TiO$_2$ photoanodes were rinsed with ethanol and methanol, respectively, and then dried with a N$_2$ gun, respectively. To incorporate doping of Co$^{2+}$, cobalt acetate (C$_6$H$_5$CO$_2$) was mixed with cadmium nitrate. Co-doped-CdS was prepared by Cd(NO$_3$)$_2$ and sodium selenosulphate (Na$_2$SeSO$_3$) mixing with C$_6$H$_5$CO$_2$. The Na$_2$SeSO$_3$ aqueous solution was prepared by refluxing 0.06 M Se in an aqueous solution of 0.12 M Na$_2$SO$_3$ at 70°C for 7 h [20]. The SILAR processes of Co-doped-CdS were similar to those of CdS QDs. The TiO$_2$/CdS photoanodes were successively immersed in ethanol solution containing Cd(NO$_3$)$_2$ and C$_6$H$_5$CO$_2$ for 5 min at room temperature, and then in Na$_2$SeSO$_3$ aqueous solution for 0.5 h at 50°C. Following each immersion, rinsing and drying were undertaken using pure solvent and a N$_2$ gun, respectively. All these processes are termed as one SILAR cycle of CdSe.

2.2. Fabrication of QDSCs. The polysulfide electrolyte used in this work was prepared freshly by dissolving 1 M sodium sulfide and 1 M sulfur in ultrapure water. The CdS/Co-doped-CdSe cosensitized TiO$_2$ photoanode and Pt-counter electrode were assembled into a sandwich cell using a parafilm spacer. The active area of QDSCs was 0.25 cm$^2$. Solar cell performance was evaluated under simulated AM 1.5 irradiation conditions.

3. Results and Discussion

We firstly studied the influence of different Co doping concentration on CdS/Co-doped-CdSe quantum dots sensitized solar cells’ performance. Here, we doped Co in CdSe with different doping concentration. M-10 represents the ratio of Co molarity versus Cd molarity as 1:10, and the total SILAR cycles include 4 cycles CdS and 4 cycles Co-doped-CdSe. The same is true to others. M-0 represents the undoped CdSe.

Figure 1 shows the $J$-$V$ curves of different working electrodes based on Co doped CdSe. The corresponding parameters are shown in the upper right corner.

![Figure 1: The $J$-$V$ curves of different working electrodes based on Co doped CdSe.](image)

In Figure 1, we find that due to the difference in Co doping concentration, the performance of some Co doped solar cells is better than the undoped; however, some Co doped solar cells have worse performance. From the solar cells’ performance parameters in the upper right corner, it is easy to find the laws: with the decrease in Co doping concentration (decreasing from 1:10 to 1:500), the short circuit current concentration, the performance of some Co doped solar cells has not been reported in the literature.

On the basis of the optimal doping ratio in the front, we discussed CdS SILAR cycles on the performance of CdS/Co-doped-CdSe. S-2 represents the SILAR cycles of CdS as 2 and the total SILAR cycles as including 2 cycles CdS and 4 cycles
Co-doped-CdSe. The Co doping concentration is all 1:200, and the SILAR cycles of CdSe are all 4. The same is true to others.

Figure 2 shows the J-V curves of different working electrodes based on different CdS SILAR cycles. The corresponding parameters are shown in the upper right corner. It is easy to find that with the increase in CdS SILAR cycles, \( J_{SC} \) and \( V_{OC} \) consistently increase. When CdS SILAR cycles are 10, they all reach the maximum; they are 8.51 mA/cm\(^2\), and 0.41 V, respectively. But taking the impact of the fill factor into account, the power conversion efficiency gets the maximum when CdS SILAR cycle is 8; it is 0.89%.

Through the above experiments, we found that CdSe doping with Co has a great promotion effect on the performance of CdS/CdSe quantum dots sensitized solar cells. So a series of comparative experiments among CdS/Co-doped-CdSe and undoped CdS/CdSe quantum dots sensitized solar cells was conducted to systematically analyze the mechanism of CdSe doping with Co having influence on the performance of CdS/CdSe quantum dots sensitized solar cells.

Figure 3 shows the top view SEM images of (a) bare TiO\(_2\) and (b) TiO\(_2\) mesoporous film deposited by CdS/Co-doped-CdSe. From (a) we can find the morphology of TiO\(_2\) particles in 20 nm sizes. The morphology of semiconductor films deposited on mesoscopic TiO\(_2\) films is shown in (b). It is easy to find that after depositing quantum dots, the surface of mesoscopic TiO\(_2\) film becomes much rougher. And due to the adsorption of quantum dots on the surface, the size of TiO\(_2\) particle becomes bigger, too.

Figure 4 shows the low-magnification and high-magnification TEM images of CdS/Co-doped-CdSe films. A clear morphology with a grain size of QDs nanoparticles ranges from 4 to 6 nm remained on the surface of TiO\(_2\) nanoparticles after the doped precursor solution immersion, indicating that CdS/Co-doped-CdSe QDs are markedly adsorbed on the surface of TiO\(_2\) nanoparticles.

Figure 5 shows the XRD patterns of CdS/Co-doped-CdSe films. It is found that after Co doping, the diffraction peak of CdSe slightly shifted from 41.96° to 42.40°. It is suggested that the Co doping leads to the lattice distortion of CdSe, which exhibits the formation of Co in the as-prepared samples. Although only the most intense peak of the Co doped CdSe was observed, this is due to the relatively low quantity of Co dopant.

The UV-visible absorption spectra of CdS(4)/Co-CdSe(4) and CdS(4)/CdSe(4) photoanodes are shown in Figure 6. It is found that in the same wavelength range, the photoanode of CdS(4)/Co-CdSe(4) has stronger light absorption intensity than the undoped photoanode; this is corresponding to an increase in current density of Co-doped solar cell. And the addition of Co atoms results in a red shift of the first exciton absorption peaks. An alternative source of the spectral shifts can be associated with electronic doping by the impurities [21].

The incident-photon-to-carrier conversion efficiency (IPCE) recorded at different incident light wavelength for QDSCs that employ CdS(8)/CdSe(4) and CdS(8)/Co-CdSe(4) photoanodes is shown in Figure 7. It is found that in the wavelength range of 350–475 nm, the maximum IPCE value increases from 42% of the undoped to 45% of the Co-doped solar cell. In the wavelength range of 475–675 nm, the Co-doped solar cell has higher IPCE than the undoped solar cell. This is consistent with the change rule of previous absorption spectra and current density.

The diagram of Co doping to the adjustment of CdSe energy level is shown in Figure 8. It is finding that after Co doping, the bandgap of CdSe quantum dot decreases, the conduction band and valence band all improve, forming a cascade energy level which is more conducive to charge transport inside the solar cell [22, 23]. That is advantageous to the electron injection and hole-recovery, reducing the recombination of electron-hole, and improving the ability of photoanode to capture light thus improving the photocurrent and ultimately improving the power conversion efficiency. This is consistent with the experimental results.

4. Conclusions

In summary, SILAR method was used to dope CdSe with Co for fabricating CdS/Co-doped-CdSe quantum dots sensitized solar cells. CdSe doping with Co has a great promotion effect on the performance of CdS/CdSe quantum dots sensitized solar cells, mainly reflected in the improvement of current density and fill factor. After Co doping, the bandgap of CdSe quantum dot decreases, the conduction band and valence band all improve, forming a cascade energy level which is more conducive to charge transport inside the solar cell and reducing the recombination of electron-hole thus improving the photocurrent and ultimately improving...
Figure 3: SEM images of (a) bare TiO\(_2\) and (b) TiO\(_2\) mesoporous film deposited by CdS/Co-doped-CdSe.

Figure 4: The TEM images of CdS/Co-doped-CdSe films: (a) low-magnification, (b) high-magnification.

Figure 5: The XRD patterns of CdS/Co-doped-CdSe films.

Figure 6: The UV-visible absorption spectra of CdS(4)/Co-CdSe(4) and CdS(4)/CdSe(4) photoanodes.
the power conversion efficiency. This work provides a new approach of improving the power conversion efficiency of QDSCs.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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