ZnS:Mn$^{2+}$ nanoparticles as compact layer to enhance the conversion efficiency of CdS QD-sensitized solar cells

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ABSTRACT

The CdS quantum dots sensitized ZnO nanorods solar cells with ZnS:Mn$^{2+}$ nanoparticles as compact layer were fabricated. The effects of Mn$^{2+}$ doping concentration on the photovoltaic performance of ZnO/ZnS:Mn$^{2+}$ photoanode were investigated. Besides the suppression of the back transfer of photoelectrons by ZnS:Mn$^{2+}$ compact layer, with the increase of Mn$^{2+}$ doping concentration, the energy level of conduction band of ZnS:Mn$^{2+}$ nanoparticles turned lower, which is beneficial for the charge transfer from the conduction band of CdS. Thus, the photoelectric conversion efficiency of the cell with ZnS:Mn$^{2+}$ (5%) exhibited 3.6 folds increments of as-synthesized bare ZnO solar cell.

1. Introduction

Recently, the power conversion efficiency of 12.3% under simulated air mass 1.5 global sunlight for TiO$_2$ DSSCs was obtained by cosensitizing YD2-o-C8 with another organic dye [1]. Although the conversion efficiencies of 0.4–5.8% obtained for ZnO solar cells are much lower than that of 12.3% for TiO$_2$, ZnO is still considered as a distinguished alternative to TiO$_2$ due to its easy crystallization and anisotropic growth [2–4]. Compared with the conventional dyes, the quantum dot (QD) sensitizer exhibits fantastic advantages of quantum confinement effect including the impact ionization and miniband effect, which is known to increase the exciton concentration, quantum yield and lifetime of hot electron, therefore, the performance of QD-sensitized solar cells (QDSSCs) [5–7].

So far, the obtained photocurrent of QDSSCs is rather low due to the existence of a competitive process of charge recombination [8,9]. Recently, for DSSCs, Yu et al. proposed that ZnS layer could retard the back transfer of electrons to the dye and electrolyte. However, using the ZnS compact layer, the electron transfer from the CdS to ZnO photoanode will be blocked due to the existence of potential barrier. Since the energy level of conduction band (CB) of ZnS is higher than that of ZnO [10]. Doping is a useful method to adjust the band gap of nanoparticles. ZnS nanocrystals doped with transition-metal ions such as Mn$^{2+}$ have been regarded as a promising photoelectric material, owing to their tunable band gap [11,12]. According to the work of Jindal et al. [12], the band gap energy (Eg) of Mn$^{2+}$ doped ZnS nanoparticles is reduced with increasing the Mn$^{2+}$ concentration.

2. Experimental methods

ZnO nanorods were grown on ITO substrates by a two-step CBD method [13]. A typical procedure of producing ZnS:Mn$^{2+}$ nanoparticles is similar to the report of Wang et al. [14]. ZnS:Mn$^{2+}$ nanoparticles were spin coated onto ZnO nanorods as compact layer. The substrates with ZnO/ZnS:Mn$^{2+}$ composite structures were annealed at 150°C for 30 min. Then the CdS quantum dots were deposited on them by successive ionic layer adsorption and reaction (SILAR) method. ZnO/ZnS:Mn$^{2+}$ photoanode grown on ITO glass substrates was sandwiched and bonded with platinum-coated indium tin oxide (ITO) (20 nm thick) counter electrode to construct QDSSCs. The photoanode and the counter electrode were separated by a 60 μm thick polypropylene spacer. A mixture of 0.5 M LiI and 0.05 M I$_2$ aqueous solution was used as electrolyte.

3. Results and discussion

It can be seen from Fig. 1a that the size of ZnS:Mn$^{2+}$ (5%) nanoparticles is uniform with an average diameter around 15 nm. Fig. 2b shows the HRTEM image of ZnS:Mn$^{2+}$ (5%) nanoparticles, in which the crystalline planes of the ZnS:Mn$^{2+}$ nanoparticles...
clearly represent the (1 1 1) d spacing of 0.31 nm. From the tilted-view SEM image of ZnO nanorods (Fig. 1c), we can see that the large-scale, vertically aligned ZnO nanorods were uniformly grown over the entire surface of the ITO substrate. As shown in Fig. 1d, the ZnS:Mn\(^{2+}\) nanoparticles were partly penetrated and dispersed between the ZnO nanorods but with the certain fraction remained and coated on the surface of ZnO nanorods arrays.

Fig. 2 shows the XRD pattern of ZnO nanorods with spin-coating ZnS:Mn\(^{2+}\) (5%) nanoparticles. The diffraction peaks of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), (2 0 1) and (0 0 4) can be indexed to a wurtzite hexagonal-phase of pure ZnO (JCPDS card, No. 80-0074). In addition to the diffraction peaks from ZnO, a broad peak appears at 28°, which can be indexed to (1 1 1) plane of wurtzite ZnS structure. Moreover, no extra diffraction peak from manganese or its oxide can be detected in XRD pattern, which indicates that the Mn\(^{2+}\) ions were incorporated into the ZnS nanoparticles [15]. The inset shows the EDAX pattern of ZnO/ZnS:Mn\(^{2+}\) composite structures, Zn, S, Mn, Au and O as the elementary components are presented.

Fig. 3a shows the UV–vis absorption spectra of ZnO/ZnS nanocomposites with different Mn\(^{2+}\) concentrations. Optical band gaps can be estimated by the Urbach model with fitting the absorption coefficient \(\alpha\) according to the Eq. [16]

\[
\alpha = \frac{A(h\nu - E_g)^\nu}{h\nu}
\]

where \(A\) is a constant related to the refractive index and the electron/hole mass, which is equal to 1/2 for direct band gap semiconductor. The plot of \((ah\nu)^2\) versus \(h\nu\) (photon energy) (Fig. 3b) was used to calculate the optical band gap of ZnS nanoparticles with different Mn\(^{2+}\) doping concentrations. The \(E_g\) is determined by extrapolating the linear portion of the \((ah\nu)^2\) versus \(h\nu\) curve to the energy axis at a value of \(\alpha = 0\). It is found to be 3.66, 3.61, 3.51 eV for ZnS nanoparticles with Mn\(^{2+}\) concentrations of 0%; 1.5%; 5% respectively. We can see that the \(E_g\) value decreases with the increase of Mn\(^{2+}\) doping concentration. As we know that \(E_g\) generally refers to the energy difference between the valence band and the conduction band in insulators and semiconductors. We guess that the decreased \(E_g\) is simultaneously determined by the decreased conduction band and...
increased valence band of ZnS:Mn$^{2+}$ nanoparticles. So the Mn$^{2+}$ doping reduces the conduction band of ZnS and thus increases the light-to-electricity conversion efficiency.

The photocurrent–voltage curves are shown in Fig. 4a. For bare ZnO nanorod arrays, the short-circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor ($FF$) and light-to-electricity conversion efficiency ($\eta$) value is 1.23 mA/cm$^2$, 0.52 V, 0.30 and 0.19% respectively. The low $J_{sc}$ and $\eta$ may be attributed to the strong recombination between photoexcited carriers in the nanorods and tri-iodide ions in the electrolyte. Whereas for the ZnO/ZnS nanocomposite, the $V_{oc}$ can be improved from 0.52 V to 0.56 V, which can be attributed to the larger energy difference between the valence band (VB) of CdS and conduction band (CB) of ZnS than that between the VB of CdS and the CB of ZnO. The $J_{sc}$ and $\eta$ were 1.29 mA/cm$^2$ and 0.25% respectively. The efficiency enhancement mechanism of ZnO/ZnS nanocomposite QDSSCs can be explained by Fig. 4b and c. Fig. 4b shows that after spin-coating ZnS nanoparticles, the surface of the ZnO nanorods becomes rougher. In principle, the rougher surface can increase series resistance and decrease current density. Plus, the rougher surface can enhance the loading amount of CdS QDs as well as diminish the reflection of incident light so as to increase the volume of the optically active component, which can lead to the increase of current density. The increase of short-circuit indicates that photoabsorption plays a more important role on the final conversion efficiency than series resistance [9]. In addition, the CB of ZnS is higher than that of ZnO and CdS. Thus, the compact ZnS shell is very efficient on retarding the back transfer of electrons.
and minimizing electron-hole recombination, which significantly decreases the dark current. However, the potential barrier will be formed due to the higher conduction band (CB) of ZnS, which is not beneficial for electrons transferring from CdS to ZnS.

From Fig. 4a, we can notice that the photocurrent and efficiency are clearly enhanced with increasing the Mn\(^{2+}\) doping concentration. When Mn\(^{2+}\) doping concentration increases up to 5\%, the solar cell with ZnO/ZnS:Mn\(^{2+}\) (5\%) nanocomposite exhibits the highest \(J_{sc}\) and \(\eta\) of 1.85 mA/cm\(^2\) and 0.37\% respectively. The results suggest that the ZnS:Mn\(^{2+}\) layer effectively passivates the defect sites on ZnO nanorods so as to inhibit the recombination of electrons at the anode/CdS/electrolyte interfaces. As shown in Fig. 4c, with the increase of Mn\(^{2+}\) doping concentration, the conduction band of ZnS:Mn\(^{2+}\) nanoparticles decreased, which is beneficial for the charge transfer from the CB of CdS to that of ZnO. Therefore, the ZnS:Mn\(^{2+}\) nanoparticles spin-coated on ZnO can significantly increase the current density. Moreover, ZnS:Mn\(^{2+}\) nanoparticles spin-coated on ZnO nanorods can protect them from etching by electrolyte due to the higher chemical stability of ZnS:Mn\(^{2+}\) [17], which is beneficial for the steadiness of the QD sensitized ZnO/ZnS:Mn\(^{2+}\) solar cells.

We also investigated the spin-coating times of ZnS:Mn\(^{2+}\) nanoparticles on the performance of ZnO/ZnS:Mn\(^{2+}\) (5\%) nanocomposite solar cells. As shown in Fig. 4d, we can see that after twice spin-coating of ZnO/ZnS:Mn\(^{2+}\) (5\%) nanoparticles, the \(J_{SC}\) and \(\eta\) values of solar cell can reach a maximum of 3 mA/cm\(^2\) and 0.68\%, corresponded to ~2.4 and ~3.6 folds increments of as-synthesized ZnO solar cell. This result may due to the homogeneous ZnS:Mn\(^{2+}\) nanoparticles and smaller resistance of ZnS:Mn\(^{2+}\) nanoparticles.

4. Conclusions

In summary, the solar cell made of ZnO/ZnS:Mn\(^{2+}\) (5\%) nanocomposite exhibited the best performance, which was mainly due to the rough surface of the ZnO nanorods and lower conduction band edge of ZnS:Mn\(^{2+}\) nanoparticles. Our results provide an effective way to adjust the energy level of the compact layer of ZnS to enhance the photovoltaic performance of solar cell.

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References