Research Article

Effect of Mn Doping on Properties of CdS Quantum Dot-Sensitized Solar Cells

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Quantum dot-sensitized solar cells (QDSSCs) have received extensive attention in recent years due to their characteristics of quantum dots (QDs), such as high absorption coefficient, tunable band gap, and multiple exciton generation (MEG) effect [1–4]. However, its photoelectric conversion efficiency is still low compared to the theoretical value. The main factors limiting the efficiency of QDSSCs include the carriers recombination with redox couple on the semiconductor interface, a slower rate of hole transport, and the properties of the electrode. Recently, many efforts on the improvement of quantum dots (QDs), electrolyte, and electrode have made quite a lot of progress [5–7]. Among those researches doping optically active transition metal ions, such as Mn, Mg, Co, Cu, and In, has achieved obvious improvement in the photoelectric conversion efficiency of QDSSCs [8–12]. The doped system modifies the electronic and photophysical properties of QDs [13]. In addition, it is also possible to tune the optical and electronic properties of semiconductor nanocrystals by controlling the type of dopant [14]. Very recently, Santra and Kamat fabricated Mn-doped-CdS/CdSe quantum dot solar cells and yielded the efficiency (5.42%) for the QDSSCs [8]. And, the next year, Lee et al. reported on a PbS:Hg QD-sensitized solar cells with an extremely high photocurrent density (38 mA/cm²) [15].

CdS, as an important II-VI semiconductor compound, with the band gap of 2.42 eV at room temperature [16], has good optical absorption properties in the visible region. Simultaneously, it has a large extinction coefficient and photochemical stability. Moreover, CdS quantum dots of different sizes can be synthesized to achieve broad spectral absorption through the relationship between the particle size and energy level of QDs. Therefore, the CdS quantum dots became a favorite QDs material for many researchers [17].

In this paper, we introduced impurity element Mn²⁺ into the precursor solution of cadmium sulfide (CdS). And Mn-doped-CdS QDs have been in situ deposited onto TiO₂...
mesoporous substrates by the successive ionic layer adsorption and reaction (SILAR). Then, we assembled Mn-doped-CdS quantum dot-sensitized solar cells with the structure of photoanode/polysulfide electrolyte/Pt counter and incidentally discussed the impact of doping. We emphatically analyzed the effect of doped ratio and SILAR cycles on the properties of QDSSCs. At last, the power conversion efficiency of Mn-doped-CdS QDSSCs showed 1.51% under air mass (AM) 1.5 condition (100 mW/cm²) with the optimized parameters (the doped ratio of Mn:CdS fixed on 1:10 and the six cycles of SILAR) obtained by experiment. Although the conversion efficiency is still low, it is much higher than the undoped CdS QDSSCs. And, with increased doping ratio, the efficiency had no further improvement but beginning to reduce.

2. Experimental

The TiO₂ nanoparticles are uniformly coated on the surface of the FTO (fluorine-doped tin oxide) by screen printing method and then annealed at 450°C for 30 min. And the counter electrode is prepared with Pt which is obtained from the thermal decomposition of chloroplatinic acid. Like the preparation of TiO₂ photoanode, the counter electrode has also been annealed at 450°C for 30 min. A mixed methanol and deionized water solution (1:1) of Na₂S (0.5 M), S (2 M), and KCl (0.2 M) is used as the polysulfide electrolyte.

Here, in this work, we used C₄H₆MnO₄ which contains impurity elements incorporated into the precursor solution by doping Mn in situ for the fabrication of Mn-doped-CdS QDs on the TiO₂ photoanode. In brief, specific concentration of the C₄H₆MnO₄ was mixed with Cd(NO₃)₂ (0.1 M) in the ethanol solution as cation source. Na₂S (0.1 M) in methanol was used as anion source. The prepared TiO₂ photoanode was immersed in the mixed ethanol solution of C₄H₆MnO₄ and Cd(NO₃)₂ for 5 min, followed by rinsing with ethanol and drying with nitrogen. Subsequently, the TiO₂ photoanode was dipped into Na₂S (0.1 M) methanol solution for 5 min at 30°C. And, then, one cycle of SILAR has been completed. During the experiment, to meet the research needs, we changed the ratio of molar concentration of C₄H₆MnO₄ in the cation source solution (i.e., doping ratio of Mn-doped-CdS).

3. Result and Discussion

Figure 1(a) shows scanning electron micrograph (SEM) of the TiO₂ film deposited by Mn-doped-CdS (1:10) with a thickness of 7.87 μm. Figure 1(d) suggests that the vertical...
morphology of TiO$_2$ photoanode is deposited by Mn-doped-CdS. There is no obvious change of the vertical morphology of the film between (b) and (c) images. It is proved that the QDs are small enough for the interspace of TiO$_2$ mesoporous film. And the existence of those interspaces makes sure of the full penetration of electrolyte. For the existence of quantum dots is unknown, the EDS spectrum is shown in inset of Figures 1(c) and 1(d). And the comparison between two spectrums demonstrated that the Mn is existent in the film.

Figure 2(a) shows the UV-Vis absorption spectra of different working electrodes based on Mn concentration. Compared to the undoped one; the Mn-doped-CdS show the obvious red shift in the UV-Vis absorption spectra. The initial response in the wavelength of undoped one, like the Mn-doped-CdS QDs, is approximated to be 500 nm. But the spectral response range has been extended after deposition. This phenomenon is due to the introduction of midgap states between the conduction band and the valence band of TiO$_2$ QDs by Mn doping, which could provide electron in the long wavelength region of the spectrum. And the complementary in the spectral responses can enhance photoelectric conversion efficiency of QDSSCs. The absorption spectra of Mn-CdS (1:1) is very similar to Mn-CdS (1:10), which is red shift compared to the sample of Mn-CdS (1:100).

Table 1: Different photovoltaic parameters for different samples.

| Sample          | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (mV) | FF  | $\eta$ (%) |
|-----------------|----------------------|---------------|-----|------------|
| TiO$_2$/CdS(4)  | 4.29                 | 474           | 0.35| 0.71       |
| TiO$_2$/Mn-CdS(4) (1:1) | 4.13                 | 482           | 0.44| 0.88       |
| TiO$_2$/Mn-CdS(4) (1:10) | 5.88                 | 514           | 0.41| 1.24       |
| TiO$_2$/Mn-CdS(4) (1:100) | 4.82                 | 438           | 0.33| 0.70       |

Table 2: ICP-OES test data of Mn-doped-CdS.

| Sample | Cd  | Mn  | Cd ($\times 10^{-6}$ mol) | Mn ($\times 10^{-6}$ mol) | Molar ratio of Mn |
|--------|-----|-----|---------------------------|---------------------------|------------------|
| Mn-CdS | 1045| 5.373| 9.297                     | 0.098                     | 1.054%           |

As can be seen from the chart, Mn-doped-CdS QDSSCs exhibited considerable increment close to 58% (from 0.71% to 1.24%) in the power conversion efficiency, compared to the corresponding undoped sample. The highest overall power conversion efficiency (1.24%) was achieved with the most optimized Mn doped amount. And the actual Mn concentration, applied on an inductively coupled plasma optical emission spectroscopy (ICP-OES), shown in Table 2, was found to be 1.054% in the CdS film. Higher Mn concentration might damage the performance. Therefore, as the proportion of Mn doping gradually reduced, the $J_{sc}$ increased from 4.13 mA/cm$^2$ (1:1) to 5.88 mA/cm$^2$ (1:10). But when the
concentration continues to decrease, the performance of cells is declined. Meanwhile, the fill factor (FF) remained stable.

The higher $J_{sc}$ of the Mn-doped-CdS films is mainly attributed to the midgap states created by Mn doping, which not only enhances the capture for electrons and slows the speed of electrons transport but also screens partly the charge recombination with the hole and polysulfide electrolyte after oxidation. Indeed, the improved photovoltage in the QDSSCs with doped semiconductor films indicates that Mn-doping assists in electron accumulation within the QDs layers, thus shifting the Fermi level to more negative potentials and increasing the conduction band of CdS. As shown in Figure 4, the Fermi energy is adjusted to an even lower electric potential, due to the promotion of electron collection by doping.

In addition, the $J_{sc}$ of the CdS QDSSCs will be improved by the Mn doping with the relatively high doped ratio. However, a large number of recombination centers, which have been introduced along with the Mn ions doped on the CdS QDs, are an unfavorable factor for the performance of solar cells. The enhancement for the $J_{sc}$ by Mn doping increased firstly when the doping ratio is decreased. In contrast, as the doped ratio decreased, the enhancement is weakened. And the crystal defects caused by Mn doping still exist, so that the short-circuit current density and photoelectric conversion efficiency began to decline. In this experiment, we just changed the ratio of molar concentration of $C_4H_6MnO_4$ and Cd(NO$_3$)$_2$. It has little effect on the fill factor, so there is no significant change about it.

Based on the above discussion, the doped ratio is fixed on 1:10 as the most optimized Mn-doped concentration. Figure 5(a) gives the UV-Vis absorption spectra of four samples based on different SILAR cycles. It shows that the exciton absorption peak of those samples moved in a direction toward the long wavelength. And there is a sample exciton absorption peak at about 680nm, which means manganese sulfur compounds may be formed during the deposition.

The IPCE recorded at different SILAR cycles for QDSC that employ three different photoactive semiconductor electrodes is shown in Figure 5(b). The overlap photocurrent response matching the absorption features also increases along with the repetition of SILAR cycles.

The $J-V$ characteristics and the corresponding performance parameters of those Mn-doped-CdS QDSSCs are presented in Figure 6 and Table 3. Obviously, as the times of SILAR cycles increased, there was a clearly different performance from the $J_{sc}$, FF, and $V_{oc}$. The best performance is obtained with the sample of 6 cycles of SILAR. When we
repeat the process of deposition by Mn-doped-Cds QDs, more QDs will be generated on the mesoscopic TiO$_2$ film, leading to the accumulation of photo-generated electron. Therefore, the quasi-Fermi level of Mn-doped-Cds QDs is shifted to more negative potentials like the effect of Mn doping. But excessive deposition of QDs caused stoppage of interspace of the mesoscopic TiO$_2$ film and severe recombination of electrons. So the $J_{sc}$ is enhanced at first but got down finally. In contrast, because the conduction band of QDs increased with the repetition of SILAR cycles, the $V_{oc}$ keep increasing.

4. Conclusions

In summary, the doping of Cds films with Mn has enabled us to achieve a significant improvement as compared to undoped films. After the optimization of experimental parameters, the photoelectric conversion efficiency of Mn-doped-Cds QDSSCs shows the maximum value (1.51%). Although the performance is still lower than the expected value, it gives us another optional approach for making QDSSCs competitive.

Conflict of Interests

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

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