Research Article

High-Efficiency CdS Quantum-Dots-Sensitized Solar Cells with Compressed Nanocrystalline TiO₂ Photoelectrodes

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Nanocrystalline TiO₂ films were fabricated on titanium substrates by compression method. The CdS quantum dots (QDs) were assembled onto the compressed TiO₂ layers, which serve as sensitizers. A maximum power conversion efficiency of 4.49% is achieved under 100 mW/cm² illumination. In this paper, we find that the compression can help increase the efficiency of the cell by increasing the absorption of the CdS QDs and improving the transportation of photogenerated electrons.

1. Introduction

Dye-sensitized solar cells (DSSCs) have established themselves as an alternative to conventional solar cells owing to their remarkably high power conversion efficiency, longtime stability, and low-cost production [1, 2]. The traditional DSSCs use organic dyes as sensitizers and the power conversion efficiency of 11% has been achieved using ruthenium dyes [3]. In addition to organic dyes, QDs [2, 4–7] can also serve as sensitizers of DSSCs. The use of semiconductor QDs as sensitizer has some advantages compared with the conventional systems. Firstly, the band gap of the nanocrystals can be adjusted by changing their size so that the absorption spectrum can be tuned to match the spectral distribution of sunlight [8]. Secondly, these QDs can use hot electrons or generate multiple charge carriers with a single photon [7].

In the past, QDs-sensitized solar cells usually use a sintered TiO₂ film as the photoelectrode. In such a device, a lot of energy and time is consumed in the fabrication of TiO₂ films; moreover, the power conversion efficiency (η) is mainly limited by the small amount of the QDs on the electrode surface and the electron recombination in the cell [2, 4]. In this study, the TiO₂ film was fabricated using the compression method developed by Anders Hagfeldt and coworkers [9–11]. This method can offer a simple and fast

way to fabricate TiO₂ films; moreover, it was proved that the resulting films are porous and mechanically stable [9, 11]. We expect that this method would help resolve the problems mentioned above.

2. Experiment

In this paper, the TiO₂ paste used was composed of a mixture of commercially available nanosized P25 and ethanol solvent at a concentration of 20 wt%. After ultrasonication, the suspension was applied onto the Ti sheet by hand using doctor blading. Then, pressure (1500 kg/cm²) treatment was applied. CdS QDs were deposited to the TiO₂ film by S-CBD method [5]. A TiO₂ film was dipped into a CdCl₂ water solution (0.05 M) for 30 s, rinsed with water, and dipped for another 30 s into a Na₂S water solution (0.05 M). The two-step dipping procedure is termed as one S-CBD cycle and the incorporated amount of CdS can be increased by repeating the assembly cycles.

The performances of the photoelectrochemical (PEC) solar cells were studied in a three-armed cell with a platinum filament counter electrode and a saturated calomel electrode (SCE) as a reference. 0.1 M Na₂S solution serves as the electrolyte. Measurements were carried out under AM 1.5 G at 100 mW/cm² illumination.

FIGURE 1: The schematic diagram of the process (a) and mechanism (b) of QDs-sensitized solar cell.

3. Results and Discussion

Figure 1 shows the process and mechanism of this QDs-sensitized solar cell. A suitable pressure can make a well packing TiO₂ film; after a series of S-CBD cycles some CdS QDs can formed on the surface of TiO₂ film and in the gaps between TiO₂ particles. When it illuminates under the light, the CdS QDs can absorb the light energy and an electron from the molecular ground state S^0 is excited to an excited state S^* . The excited electron of the CdS QDs is injected into the conduction band of the TiO₂ particles, leaving the QDs molecule to an oxidized state S^+ .

Figure 2 shows UV-vis absorption spectra of a bare TiO₂ film and TiO₂ films sensitized by CdS QDs with different S-CBD times. From Figure 2, we can see with the S-CBD cycles increasing, the UV-vis absorption shoulder and onset position become redshift, which indicating more visible light can be absorbed. By using the empirical equation proposed by Yu et al. [12], it is possible to estimate the sizes of CdS particles from the excitonic peaks of the absorption spectra. The mean diameter of CdS particles (10 S-CBD) was measured to be ca. 4.10 nm on the TiO₂ films, which indicating that the size of the CdS particles on the TiO₂ films is still within the scale of QDs.

To investigate the effect of compress and S-CBD cycles, different cells were made under the same condition. The most variation is the photoanode that we list in Table 1.

Figure 3 shows the photocurrent-voltage (J - V) characteristic curves of PEC solar cells as a function of S-CBD cycles. As seen in Figure 3, J - V measurements were performed under the conditions of illumination and darkness, respectively. A summary of J - V characteristics and the η of cells with different photoanodes are presented in Table 1. Under illumination, it is found that η can be markedly enhanced by the absorption of the CdS QDs. With the

FIGURE 2: UV-vis absorption spectra of a bare TiO₂ film and TiO₂ films sensitized by CdS QDs with different S-CBD times.

FIGURE 3: Photocurrent versus voltage in 0.1 M Na₂S (a) under AM 1.5 G at 100 mW/cm² illumination (b) in the dark. The TiO₂ film was made by compression method (cell 1 to cell 4), heat after pressure (cell 5), and heat (cell 6). The difference of cell 1 to cell 4 is the S-CBD cycles.

increase of S-CBD cycles to 10, generated photocurrent (J_{sc}) and open-circuit photovoltage (V_{oc}) are both enhanced, reaching their maximum of 5.91 mA/cm² and 1.17 V (versus SCE), respectively. An efficiency of 4.49% is achieved in such a cell. As the S-CBD cycles increases above 10, V_{oc} and J_{sc} both decrease. This trend can be explained as follows: when the amount of the CdS QDs due to the S-CBD cycles is too small, the absorbance of dye is insufficiently, which causes the low J_{sc} . When the amount of the CdS QDs is too large, the transmission process of the electrolyte inside the TiO₂ film's pore is restricted, which causes the serious electron recombination of the cell and also reduces cell performance.

TABLE 1: Parameters obtained from the photocurrent-voltage (J - V) measurements of the PEC solar cells constructed using various electrodes.

Cell	Photoanode	J_{sc} (mA/cm ²)	V_{oc} (V versus SCE)	ff	η (%)
Cell 1	Sample 1 (Ti/TiO ₂ (pressure)/S-CBD10)	5.91	1.17	0.65	4.49
Cell 2	Sample 2 (Ti/TiO ₂ (pressure)/S-CBD5)	3.63	1.19	0.68	2.94
Cell 3	Sample 3 (Ti/TiO ₂ (pressure)/S-CBD15)	4.99	1.14	0.60	3.41
Cell 4	Sample 4 (Ti/TiO ₂ (pressure)/S-CBD0)	0.16	0.87	0.61	0.08
Cell 5	Sample 5 (Ti/TiO ₂ (heat after pressure)/S-CBD10)	1.08	1.09	0.58	0.68
Cell 6	Sample 6 (Ti/TiO ₂ (heat)/S-CBD10)	0.55	1.16	0.70	0.44

FIGURE 4: SEM of (a) Ti/TiO₂ (compressed), (b) Ti/TiO₂ (heat treatment after compressed), and (c) Ti/TiO₂ (sintered).

FIGURE 5: EDS of (a) Ti/TiO₂ (compressed)/CdS(S-CBD10) and (b) Ti/TiO₂ (heat treatment after compressed)/CdS(S-CBD10). The inset lists their dates, respectively.

We also took J - V curves under the dark condition (Figure 3(b)). Figure 3(b) displays that the onset of the dark current of cell 1 occurs at higher bias than cell 4, which indicates the electron recombination in cell 1 is lower than cell 4.

Table 1 also lists the data of cell 5 and cell 6. The configuration of cell 5 and cell 6 is similar to cell 1; the only difference between them is the fabrication technique of TiO_2 films. The compressed TiO_2 film of cell 5 was posttreated by a heat treatment (450°C , 1.5 h) and the TiO_2 film of cell 6 was made by sintered (450°C , 1.5 h) directly. Surprisingly, both cell 5 and cell 6 show bad results compared with cell 1. Especially, the cell 5 (with J_{sc} of 1.08 mA/cm^2 , V_{oc} of 1.09 V versus SCE, ff of 0.58, and η of 0.68%) performs worse than the cell 1 with respect to all cell parameters, especially in J_{sc} response, the cell 1 is 5.5 times that of the cell 5. It seems the additional heat treatment makes no improvement in cell performance. As mentioned in the introduction, the power conversion efficiency is mainly limited by the small amount of the QDs on the electrode surface when using a sintered TiO_2 film as the photoelectrode. Here, on the basis of the results presented above, we assume that the compression method may help solve this problem. To verify it, we first conducted scanning electron microscopy (SEM) studies of their morphology.

Figure 4 shows plane-view SEM images of a blank TiO_2 film of cell 1 (Figure 4(a)), cell 5 (Figure 4(b)), and cell 6 (Figure 4(c)). All of films display porous structures, creating holes in the film. However, big holes and aggregation between particles can be seen more obviously in Figures 2(b) and 2(c), implying that the surface area per unit volume of the sintered TiO_2 film is smaller than that of unsintered TiO_2 film. This is consistent with Lindström's observation [11]. Kavan et al. [13] find the sintering can cause decrease in surface areas of coated TiO_2 films. They think this decrease is caused by the efficient filling of small pores in the aggregate by surface diffusion. At the same time, we assume that the heat treatment may induce some chemical changes, which may weaken the linkage between the TiO_2 particles and the CdS QDs (further researches are expected to certify it). And both of the phenomena we mentioned above limit the absorption of CdS QDs in cell 5 and cell 6, and thus decrease the J_{sc} . Support for this explanation is given by the EDS (Energy Dispersive X-ray Spectrometer) analysis. Figure 5 is the EDS spectrum of the cell 1 and cell 5, their values are listed inside the Figure 5. Although the EDS value cannot be considered very accurate, it offers us a simple and direct way to study the amount of the CdS QDs. The EDS results reveal the atomic ratio Cd/O of cell 1 and cell 5 is 7.4% and 2.3%, respectively. We can also change them into the volume ratio (CdS over TiO_2) of 22.8% and 7.1%, respectively; the details of the procedure can be found in the literature [5]. So we can find that the amount of CdS QDs of cell 1 is higher than that of cell 5. Noticeably, the above results verify our former explanation. In addition, as seen in Figure 4, the stacking of particles is enhanced by the pressure, which is conducive to the transportation of photogenerated electrons, and can also improve the cell performance.

At last, 4.49% is similar to that of the same structure solar cell (4.15%) [14]. In that literature, they use TiO_2 nanotubes as the photoanode. They think the crystalline nature of the nanotubes and the film geometry allows a fast and efficient transfer of the photogenerated electrons from CdS QDs to the Ti substrate. In our device, we have a large fine TiO_2 film which has a large surface area and the compression also can give a good cohesion between TiO_2 film and Ti sheet which can also improve the transportation of photogenerated electrons. There are also some important factors can affect our final result, as pressure, film's height, and so on. This time we just use a fixed value to assess our devices. And we will make further researches to study it.

In summary, high efficiency has been obtained for QDs-sensitized TiO_2 PEC solar cells prepared by pressing (up to 4.49%). Through the comparison, we conclude that the compression can increase the absorption of CdS QDs and improve the transportation of photogenerated electrons. Overall, the compression method shows promise as a fast, simple, and effective method for the preparation of photoelectrodes in QDs-sensitized solar cells.

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