CdS quantum dots sensitized one-dimensional ZnO solar cells with improved efficiency using ZnS shell coating

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Abstract—CdS quantum dots (QDs) were adsorbed onto ZnO nanowire arrays by using a chemical bath deposition method in order to produce QD-sensitized solar cells (QDSSCs). Surface modification was done by coating ZnS layers onto the CdS QDs. The optical absorption and current-voltage characteristics of these devices were studied. The photovoltaic properties of short-circuit current density, open-circuit voltage, and photovoltaic conversion efficiency were improved after modifying the surface with ZnS coating.

Keyword: Quantum Dots; Zinc Oxide; Solar Cells; Efficiency.

I. INTRODUCTION

Increasing energy demand and depletion of fossil fuels dictate the development of green, efficient solar energy conversion technology. Dye-sensitized solar cells (DSSCs) have a significant potential as low-cost solar cells [1-3] and are able to reach sunlight-to-electric power conversion efficiencies of 8–11%. [4-5] However in order to replace conventional Si-based solar cells in practical application, further efforts is needed to improve the efficiency of DSSCs. A great amount of work has been done on the design of optimal sensitizer which will absorb across the entire visible light absorption for favorable electron-transfer dynamics. [6-7] Compared to the complicated synthesis process of organic dye molecules, narrow-gap semiconductors quantum dots (QDs), such as CdS, CdSe, InP and PbS QDs, have drawn significant attention in recent years because of their ability to modulate the photoresponse in the visible light spectrum by means of size control. [8-11]

ZnO is being intensely investigated as a photoanode material in solar cell because of its similarities with the traditional one, TiO2, i.e. it is a wide band gap semiconductor oxide (3.37 eV) with a conduction band edge located at approximately the same level as TiO2. Besides, for their application in solar cell, ZnO is more attractive because the electron mobility of ZnO has been proven to be higher than TiO2, which means lower charge recombination. [12]

So in this work, to take both the advantages of QDs and ZnO in light harvest and electron transport, CdS QDs are used as sensitzers for the ZnO nanowire arrays. Furthermore, to passivate the QDs surface states, ZnS thin layer which has higher band gap is deposited on the CdS surface. The sequentially assembled CdS QDs and ZnS barrier on the ZnO nanowire arrays form a cascade co-sensitized structure. This structure has proved to have a superior stability and higher energy conversion efficiency.

II. EXPERIMENTAL

The preparation process of ZnO nanowire arrays includes substrate pre-treatment and hydrothermal deposition, similarly to that described in the literature report. [13] To prepare ZnO nanowires, ZnO nanoparticles were deposited as a seed layer on FTO by dip-coating method. The precursor aqueous solution of 0.05 M zinc nitrate hexahydrate and 0.05 M hexamethylenetetramine at 90°C for 2h was used to grow ZnO nanowire arrays. Then, the resulting products were annealed at 450 °C for 2h.

CdS quantum dots were deposition by chemical bath deposition (CBD) method. The ZnO nanowires prepared by the above described procedure were immersed in a solution of Cd(NO3)2 (0.1 M) for five minutes. They were then rinsed with distilled water and immersed in a Na2S (0.1 M) solution for another five minutes followed by another rinsing with distilled water. This CBD process was repeated until the desired deposition of CdS nanocrystallites was achieved.

ZnS coating was realized by a similar method. Typically, the samples were successively immersed in two different solutions at 60 °C for a period of time in each beaker. One beaker contained 5 mM Zn (NO3)2, another contained 5 mM Na2S. After the process, the samples were rinsed with distilled water, dried for further characterization.

The solar cell was constructed by using FTO substrate with ZnO/CdS nanostructure as photoanode, Pt-coated FTO glass as a counter electrode, and an iodide-based solution as the liquid electrolyte. Current-voltage (I-V) characteristics were recorded using a Keithley 2611 digital multimeter. The light source was a 150 W Xenon lamp (Sciencetech, SS150) calibrated to 100 mW/cm2 with a radiometer. The morphology of samples was observed using a Hitachi S-4800 scanning electron microscope (SEM) and a FEI Tecnai G2 F20 transmission electron microscope (TEM) with a field-emission gun operating at 200 kV. The X-ray diffractometry (XRD) for the crystal structure of the products was carried out in a Rigaku D/Max 2500v/pc diffractometer. Uv-vis absorption spectra were recorded on a
RESULTS AND DISCUSSION

X-ray diffraction was used to confirm the crystal structure of the as-synthesized nanostructure. As shown in Figure 1, in addition to hexagonal structure ZnO (JCPDS 79-2205) and SnO2 from the FTO glass, new peaks appear, which can be indexed to the cubic CdS and ZnS (JCPDS 79-0043). So it is definitely demonstrated the successful coverage of ZnO nanowire arrays with CdS quantum dots and ZnS layer.

A typical SEM image of the ZnO nanowire arrays is shown in Figure 2a. The top view shows that ZnO nanowires distribute uniformly on the FTO substrate. The morphology changes of the ZnO nanowire arrays are observed by SEM and HRTEM after the CdS QDs and ZnS coating were deposited. As shown in Figure 2b, the surface morphology of ZnO nanowires becomes coarse after the deposition. And the contrast between the edge and center in the HRTEM image (Figure 2c) is indicative of the multilayer structure, with the ZnS shell thickness about 5 nm after 0.5 h deposition. The HRTEM image further demonstrates the highly crystalline (001) direction-oriented ZnO core and the composition of CdS and ZnS nanocrystals in the shell, which is in agreement with Figure 3 shows UV–vis absorption spectra of ZnO, ZnO/CdS and ZnO/CdS/ZnS on ITO. It can be seen that the absorption edge shifts to red with CdS deposition. That is to say the formation of CdS quantum dots sensitizers on ZnO nanorods can be desirable for light harvesting of solar energy.
Furthermore, the coating of ZnS layer does not decrease the absorbency.

The photocurrent density-voltage (J-V) curves of the sandwich-type CdS QDSSCs with different ZnS deposition time were measured under illumination of one sun (AM 1.5, 100mW/cm²). Figure 4 shows the J-V characteristics of the QDSSCs with the ZnS coating 0min, 30min and 1h, respectively. The values of the short-circuit-current density (Jsc), the open-circuit voltage (Voc), the fill factor (FF), and the photovoltaic conversion efficiency (η) are given in Table 1. It can be seen that that both Jsc and Voc increases with adsorption time and reaches a maximum value, after which it decreases. As a result, the photovoltaic conversion efficiency first increases with increasing ZnS adsorption time and have a maximum value of 0.9% at 0.5 h.

Table 1. Photocurrent-Voltage Characteristics of ZnO-Based QDSSCs

<table>
<thead>
<tr>
<th>Samples</th>
<th>Voc (mV)</th>
<th>Jsc (mA/cm²)</th>
<th>FF</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/CdS</td>
<td>480</td>
<td>2.44</td>
<td>0.36</td>
<td>0.42%</td>
</tr>
<tr>
<td>ZnO/CdS/ZnS 0.5h</td>
<td>626</td>
<td>5.53</td>
<td>0.28</td>
<td>0.9%</td>
</tr>
<tr>
<td>ZnO/CdS/ZnS 1h</td>
<td>500</td>
<td>2.43</td>
<td>0.39</td>
<td>0.47%</td>
</tr>
</tbody>
</table>

Compared to the CdS QDSSCs without the ZnS coating, the values of Jsc for the electrodes with the ZnS coating dramatically increase, as shown in Table 1. Voc also greatly increases as a result of the ZnS coating (e.g., from 480 to 626 mV). The above results can be explained as follows: on the one hand the effects of ZnS coating is to passivate the surface states of CdS, which results in the suppression of the surface trapping of photoexcited electrons and holes in the CdS QDs. Thus, the photoexcited electrons can efficiently transfer into the ZnO conduction band. On the other hand, the ZnS coating can also be considered to be a potential barrier at the CdS-electrolyte interface, since the ZnS band gap of 3.8 eV is much larger than that of CdS. Consequently, the leakage of electrons from the CdS into the electrolyte can be suppressed. Both of above factors might help to enhance the Voc.

IV. CONCLUSION

ZnO/CdS quantum dots sensitized solar cells were assembled and to increase the efficiency and stability of the system, ZnS coating was deposited on the surface of CdS quantum dots. We found that there was an optimum ZnS adsorption time for achieving the highest energy conversion efficiency. Further optimization of the conditions for the CdS adsorption and the ZnS coating are in progress and it is expected that better solar cell performance will be achieved in the near future.

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REFERENCES
