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Boosting the Performance of ZnO/CdS Core-Shell Nanorod Array-based Solar Cells by ZnS Surface Treatment

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1. Introduction

Semiconductor sensitized solar cells (SSSCs) have recently attracted significant attention as a promising alternative to dye sensitized solar cell (DSSCs) owing to their unique properties. Some of these are higher light absorption coefficients, wide-range band gap tunability, and greater stability, as well as multiple exciton generation in semiconductor quantum dots. The working principle of the SSSC is very similar to the DSSC, only the light-absorbing dye is replaced by inorganic semiconductor quantum dots. The highest efficiency achieved with SSSCs is less than with DSSCs, as many efficiency reducing factors in SSSCs have yet to be resolved. One major concern is recombination losses of photogenerated charge carriers. Usually, in SSSCs, recombination losses are attributed to surface states of the semiconductor, which arise due to dangling bonds at the surface of the semiconductor.

Various recombination pathways in SSSCs are shown in Figure 1. Consider the SSSC made up of ZnO as an electron-transporting, wide band gap semiconductor, and CdS as a sensitizer semiconductor. The charge transport routes shown by solid red lines lead to a photoconversion process, whereas those indicated by dotted red lines lead to charge recombination. The recombination losses that take place between electrons in the conduction band of ZnO and the electrolyte species can be reduced by avoiding direct contact between ZnO and the electrolyte. It can be done by the synthesis of a uniform shell of CdS.
over the ZnO. Among all the recombination losses shown in Figure 1, the injection of electrons from the absorber semiconductor (CdS) to the electrolyte is a serious pathway of recombination. Particularly if the electrons are trapped in the surface states of the absorbing semiconductor (CdS), their lifetime in that absorbing semiconductor increases, which enhances the probability of recombination with the electrolyte species.

Thus, to prevent injection of electrons from the absorbing semiconductor (CdS) to the electrolyte, the most logical treatment is the passivation of surface states, or to coat the absorbing semiconductor with a semiconductor shell having a conduction band edge higher than that of the absorbing semiconductor. As per the above rudiments, ZnS seems to be an appropriate material to coat a ZnO/CdS core-shell structure. The higher conduction band edge of ZnS can create a potential barrier for electron injection from the absorbing semiconductor towards the electrolyte without affecting the injection of electrons from the absorbing semiconductor to the oxide, as shown in Figure 1. Also, a ZnS coating with an appropriate thickness does not prevent hole transport to the electrolyte, i.e., the ZnS thin layer facilitates easy hole tunneling. Thus, the ZnS layer passivates the surface states of the absorbing semiconductor (CdS) and blocks the back electron flow from the semiconductor to the electrolyte, leading to a reduction in most of the recombination losses, thereby enhancing solar cell performance.

Considering the above factors, we have applied a ZnS layer to a 1D ZnO/CdS core-shell nanorod array-based photoelectrode, with a view to enhancing the solar cell performance of SSSCs. The preferred use of the core-shell structure lays in the fact that 1D ZnO can provide a maximum surface area for the adsorption of the absorbing semiconductor (CdS) and fast charge transport through a 1D structure, while the CdS shell affirms the maximum loading of sensitizer semiconductor. The synthesis of ZnO/CdS core-shell film (ZCS) is carried out by a simple two-step chemical technique. The application of the ZnS layer is done by a facile SILAR technique. To get the optimum thickness of the ZnS layer, and thereby, improved solar cell performance, we have varied the number of SILAR cycles.

2. Experimental Procedure

The growth of high aspect ratio ZnO nanorods, and their sensitization with CdS to form CdS nanoshells, has been carried out as mentioned in our earlier reports. For the application of the ZnS thin layer over the ZnO/CdS core-shell structure, we have adopted the SILAR technique shown in Figure 2. For the deposition of the ZnS layer, a 0.1 M zinc acetate dihydrate solution prepared in double distilled water was used as a cationic precursor, while aqueous 0.1 M sodium sulfide solution was used as an anionic precursor. In the actual deposition process, ZnO/CdS core-shell nanorod thin film (ZCS) was first immersed into the zinc acetate solution for 1 min. In this process, zinc ions were adsorbed onto the film surface. The film was then rinsed in double distilled water for 1 min to remove loosely bound excess zinc ions. Then this
film was immersed in the anionic precursor for 1 min, where sulfur ions were reacted with pre-adsorbed zinc ions on the film to form ZnS film. Again the film was rinsed in double distilled water to remove loosely bound molecules. This procedure completes one SILAR cycle. The deposition of ZnS was carried out at room temperature. The thickness of the ZnS layer can be varied by changing number of SILAR cycles. Here, we varied the number of SILAR cycles from 1 to 3. The corresponding films were denoted as ZCSZ-1, ZCSZ-2, and ZCSZ-3.

2.1 Characterization

The optical absorption studies of the samples were done by means of UV-Vis absorbance spectra of samples, obtained from a UV-Vis spectrophotometer (UV1800 Shimadzu, Japan). The crystallinity and phase formation of the film was studied by X-ray diffraction (XRD) using a Bruker AXS D8 Advance Model with copper radiation ($K_{\alpha}$ of $\lambda = 1.54 \text{ Å}$). The morphological study of the film was carried out by FESEM using a HITACHI S-4700 instrument with an accelerating voltage of 30 kV. The detailed study of nanostructures and crystal phases was done using HRTEM images collected from a Jeol JEM 2100F. The $J$-$V$ characteristics of the fabricated devices were recorded using a semiconductor characterization system (SCS-4200 Keithley, Germany) with a two-electrode configuration, under the illumination of a halogen lamp (27 mWcm$^{-2}$). PEC measurements were performed using the cell configuration of glass/FTO/ZnO-CdS-ZnS/Na$_2$S-NaOH-S/graphite. The average area of the film was 1 cm$^2$.

3. Results and Discussion

3.1 Optical Absorption Study

Figure 3 shows the optical absorption spectra of ZnO, ZCS, and all the ZnS treated ZCS films. The inset figure shows the absorption spectra magnified at absorption edge. The optical absorption spectrums of films were recorded in the wavelength range 350 to 750 nm at room temperature. Here, we observe that the ZnO/CdS/ZnS films show an absorption edge in the visible region at $\sim$520 nm, which is a synergistic effect of UV absorption of ZnO and visible light absorption of CdS, while it seems that ZnS is not contributing more to the absorption spectra in terms of optical density enhancement and absorption edge shifting. It is may be due to the deposition of a very thin ZnS layer from a lower number of SILAR cycles.

3.2 Photoelectrochemical Study (PEC)

The schematic of an SSSC formed with a ZnS treated ZnO/CdS core-shell photoelectrode is shown in Figure 4 (a). Figure 4 (b) shows the current density-voltage ($J$-$V$) properties of ZnS treated and untreated ZCS films. The output parameters obtained from the $J$-$V$ curve are given in Table 1. A significant increment in solar cell performance was observed after ZnS surface treatment. The
efficiency of the ZCS film was enhanced from 1.23% to 1.31% on the application of a single ZnS layer, which was further increased to 1.54% after the application of a second ZnS layer. Thereafter, it was found to decrease to 1.29% on the application of a third ZnS layer. These results reveal that the efficiency of solar cells is significantly improved with ZnS surface treatment, and the improvement in solar cell performance depends on the thickness of the ZnS layer.

The enhancement in solar cell performance of ZnS treated ZnO/CdS thin films can be attributed to the generation of a barrier potential for the backflow of electrons from the CdS shell to the electrolyte. This barrier potential is created due to the higher conduction band energy of the ZnS layer. Also, the application of the ZnS layer passivates the surface states on the CdS shell, which improves the photoconversion by reducing the trapping of electrons in surface states on the CdS shell surface. Thus, cumulatively, the blocking of the recombination paths and passivation of the surface states boosts the solar conversion efficiency of ZnS treated samples.

Also, the enhancement in efficiency depends on the thickness of the ZnS layer. From the PEC plots, we observe that ZCSZ-1 film possesses lower performance than ZCSZ-2, which may be due to incomplete coverage of the CdS surface with ZnS in single SILAR cycles. Further, on application of ZnS using three SILAR cycles, i.e., in ZCSZ-3 film, PEC performance is found to be decreased; which may be due to the enhanced thickness of ZnS preventing the tunneling of holes towards the electrolyte. Thus, the optimized film is ZCSZ-2, i.e., the film prepared with two SILAR cycles of ZnS deposition.

The role of ZnS treatment in the reduction of recombination losses, and thereby enhancement in PEC performance, is again confirmed by incident photon to current conversion efficiency (IPCE) measurements. Figure 5 shows the IPCE performance of the ZCS and ZCSZ-2 photoelectrodes. The IPCE performance is found to be enhanced from 20.8% to 34% on application of ZnS surface treatment. The optimized film is further characterized by XRD, SEM, TEM, and HRTEM to confirm the presence of the ZnS layer.

3.3 X-ray Diffraction Studies

The XRD patterns of the ZCS and ZCSZ-2 films are given in Figure 6. The XRD pattern of the ZCS film is included for comparative analysis. The XRD patterns of both films possess peaks corresponding to the (100), (002), (101), (110), and (112) planes of CdS at 24.8°, 26.5°, 28.1°, 43.7°, and 51.8°, respectively (JCPDS data card No. 41-1049). It reveals the formation of a hexagonal CdS phase. Also, both XRD spectra possess the peaks at 31.7°, 34.4°, 36.2°, 47.5°, 62.8°, and 72.5°, which belong to the (100), (002), (101), (102), (103), and (004) planes of hexagonal wurtzite ZnO nanorods (JCPDS data card No. 36-1451). The peaks marked with an asterisk belong to the FTO substrate (JCPDS data card No. 46-1088). There is no any peak belonging to ZnS in the ZCSZ-2 film; it may be due to the very thin layer of ZnS.[12] Therefore, the XRD patterns of the ZCS and ZCSZ-2 films are well matched with each other.

### Table 1. Solar cell output parameters of the ZCS, ZCSZ-1, ZCSZ-2 and ZCSZ-3 films.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Short circuit current density $J$ (mA cm$^{-2}$)</th>
<th>Open circuit voltage $V$ (mV)</th>
<th>Series resistance $R_s$ ($\Omega$ cm$^{-2}$)</th>
<th>Shunt resistance $R_{sh}$ ($\Omega$ cm$^{-2}$)</th>
<th>Fill factor $FF$ (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZCS</td>
<td>1.44</td>
<td>589</td>
<td>139</td>
<td>1.24</td>
<td>0.39</td>
<td>1.23</td>
</tr>
<tr>
<td>ZCSZ-1</td>
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<td>620</td>
<td>149</td>
<td>1.17</td>
<td>0.38</td>
<td>1.31</td>
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<tr>
<td>ZCSZ-2</td>
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<td>648</td>
<td>144</td>
<td>1.16</td>
<td>0.39</td>
<td>1.54</td>
</tr>
<tr>
<td>ZCSZ-3</td>
<td>1.56</td>
<td>602</td>
<td>157</td>
<td>1.1</td>
<td>0.37</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Figure 5. Incident photon to current conversion efficiency (IPCE) performance of ZCS and ZCSZ-2 film-based SSSCs.

Figure 6. XRD patterns of ZCS and ZCSZ-2 films.
3.4 Scanning Electron Microscopy (SEM)

The surface morphological characterization of the optimized film was carried out by FESEM. Figure 7 shows the top surface and the cross-sectional view of the ZCSZ-2 film. Figure 7 reveals the formation of roughly textured vertically aligned rods. These nanorods seem to be more or less uniformly spaced under the limitations of the hydrothermal growth technique. It is clear from the SEM images that the array of vertically aligned nanorods are free from inclined intersections or unexpected cross linkage due to excessive deposition of either CdS or ZnS, which implies a proper and controlled growth of both the layers achieved over the ZnO nanorods. As compared with the SEM images of the ZnO/CdS film from our earlier report, there is no significant visible change in the morphology on the application of the ZnS layer. This is due to the ultrathin coating of ZnS achieved over the CdS layer.

3.5 Transmission Electron Microscopy (TEM)

Though the application of the ZnS layer has shown a significant rise in the PEC performance of films, the actual presence and morphological features of the ZnS layer were not detected from XRD, optical, and FESEM studies; it may be due to the ultrathin layer of ZnS. Thus, further, we characterized the films using HRTEM. Figure 8 (a–d) shows the TEM and HRTEM images of the ZCSZ-2 film. Figure 8 depicts the formation of the thin ZnS layer over the CdS shell on the ZnO nanorod. The low resolution TEM image displayed in Figure 8 (a–c) shows two distinct ZnO nanorods, which consist of a uniform coating of CdS over the entire ZnO nanorod. The distinctness of the ZnS layer on the ZnO/CdS core-shell structure is clearly viewed in Figure 8 (d). A more detailed structural analysis of the ZnS layer over ZnO/CdS core-shell structure is provided in the HRTEM image, as depicted in Figure (9). The HRTEM analysis shows the shell structure comprised of a CdS layer bearing a uniform coating of ZnS. The CdS layer has a uniform thickness of ca. 7–10 nm, while that for the ZnS layer is at most ca. 2–3 nm. (The scale bar in the image is 5 nm). The CdS layer shows a well formed crystal structure along the ZnO nanorod. The FFT image of the CdS coating at two distinct places shows lattice spacing of about 0.34 nm, which belongs to the (002) plane of wurtzite CdS structure. The HR image shows the presence of a distinct layer over the CdS coating. This layer has the presence of a crystalline phase throughout the coating. The FFT image of this layer can be seen in the inset with a lattice spacing of 0.33 nm, which belongs to the interplanar distance of (100) plane in the hexagonal crystal structure of ZnS. Thus, it is quite evident that the ZnO nanorods are uniformly and successively coated by CdS and ZnS nano layers, forming ZnO/CdS/ZnS core-shell structures.
4. Conclusion

An ultrathin layer of ZnS has been successfully applied over ZnO/CdS core-shell nanorods using a simple SILAR technique. The presence of the ZnS layer is confirmed by HRTEM analysis. The ZnS surface treatment significantly enhances the solar cell performance of ZnO/CdS core-shell photoelectrodes from 1.23% to 1.54%. This enhancement in solar cell performance is attributed to the ZnS surface treatment, as it passivates the surface states on the absorbing semiconductor (CdS) and blocks the backflow of electrons from CdS to the electrolyte, resulting in a reduction in recombination losses.

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