Fabrication and Characterization of Porous CdS/Dye Sensitized Solar Cells

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1. Introduction

The world urgently needs alternative sources of environmentally sustainable energy supply for industrial development and electricity supply. Solar power is one of the important clean sources of power. Thus, conversion methods of this power to useful energy have attracted a great deal of attention from scientific researchers and dye-sensitized solar cells (DSSCs) are one of the types of solar cells that show promising properties such as high conversion efficiency, use of environmentally friendly materials, ease of preparation, and low cost of production [1–3]. Nanomaterials are widely used to fabricate solar cells, especially DSSC types, due to their unique physical properties.

Cadmium sulfide (CdS) is an n-type semiconductor with a wide band gap of 2.42 eV (in bulk) that makes it a very suitable semiconductor material for use in preparing optoelectronic devices, especially as a window layer in solar cells [4, 5]. CdS in nanocrystalline thin films can be prepared by a variety of physical and chemical methods like vacuum evaporation [6], pulsed-laser deposition [7], sol–gel [8], successive ionic layer adsorption and reaction (SILAR) [9], and chemical bath deposition (CBD) [10]. The CBD method produces nanocrystalline, uniform, large area, as well as inexpensive thin films [4, 11]. CdS nanocrystalline thin films, which are grown by CBD, show important interesting properties. Thus, it is used for electrooptical applications [12]. CdS nanoparticles are used to fabricate DSSCs with different nanomaterials such as TiO2 and ZnO.

Hossain et al. [13] deposited CdS nanoparticles by the CBD method onto nanoporous TiO2 to fabricate DSSCs and they obtained a conversion efficiency of about 1.13%. Mali and coworkers [14] found that the efficiency for TiO2 microspheres covered by CdS nanoparticles reached 2.34%, while Choi et al. [15] obtained 3.14% from the device that they synthesized, based on TiO2/CdS quantum dots. Moreover, Meng et al. [16] prepared devices with ZnO spheres/CdS quantum dots and obtained an efficiency of about 1.39%.

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Dye sensitized solar cells (DSSCs) are fabricated from porous cadmium sulfide (CdS) nanocrystalline thin films. The porous CdS nanostructured thin films are deposited onto FTO/glass substrates by the chemical bath deposition (CBD) method. The surface morphology, crystalline structure, and optical properties of the prepared nanocrystalline thin films are investigated. Rhodamine B, Malachite green, Eosin methylene blue, and Cresyl violet dyes are used to fabricate the DSSC devices. Comparing the absorption spectra of porous CdS nanocrystalline films, all dyes show an absorption peak in the transparent range of CdS thin films indicating that they are suitable for the preparation of DSSCs with CdS. Current-voltage (I–V) characteristics show that the solar cell that is fabricated using Malachite green dye shows the highest conversion efficiency of 0.83% while using Rhodamine B dye produces a solar cell with lowest efficiency of 0.38%. However, heat treatment of the fabricated solar cells causes significant enhancement in the output of all devices.
The use of porous electrodes in DSSCs is much different to thin films because the inherent conductivity of the film is very low and the small size of the nanocrystalline particles does not support a built-in electrical field. Additionally, porous thin films can help in bringing about ionic conduction when it is in contact with an electrolyte and that led to efficient electrical conductivity in the device [17]. Therefore, using porous electrodes in DSSCs led to efficient transport of photogenerated electrons and this enhances the conversion efficiency. Moreover, the electrolyte penetrates the porous film all the way to the back-contact making the semiconductor/electrolyte interface essentially three-dimensional [18].

In the present work, for the first time, we used porous CdS nanocrystalline thin film as a photoelectrode, instead of ZnO or TiO₂, to fabricate DSSCs using Rhodamine B, Malachite green, Eosin methylene blue, and Cresyl violet perchlorate or TiO nanocrystalline thin film as a photoelectrode, instead of ZnO film all the way to the back-contact making the semiconductor/electrolyte interface essentially three-dimensional [18].

In the present work, for the first time, we used porous CdS nanocrystalline thin film as a photoelectrode, instead of ZnO or TiO₂, to fabricate DSSCs using Rhodamine B, Malachite green, Eosin methylene blue, and Cresyl violet perchlorate dyes. The morphology, crystalline structure, and optical and electrical characteristics of the fabricated solar cells were investigated.

2. Experimental Details

2.1. Synthesis of CdS Nanocrystalline Thin Films. Fluorine-doped tin oxide (FTO) coated glass substrates with a resistivity of 10 Ω-cm⁻² were washed in hot distilled water and then cleaned ultrasonically for 2 minutes using diluted HCl, acetone, ethanol, and isopropanol solutions, respectively. Finally, the substrates were cleaned ultrasonically with distilled water for 5 min and left to dry naturally.

Porous CdS nanocrystalline thin films were deposited on the FTO/glass substrates using the chemical bath deposition (CBD) method in an alkaline aqueous solution containing 0.05 M of cadmium nitrate [Cd(NO₃)₂] and 0.1 M thiourea [CS(NH₂)₂]. These were used as Cd²⁺ and S²⁻ ion sources, respectively. Ammonium acetate (NH₄CH₂COO) with a concentration of 1 M was added to the solution as a buffer to control the reaction rate. Some drops of ammonia solution (28%) were added to adjust the pH of the reaction to 10 and the total volume was 100 mL. After stirring the solution for 5 min, the FTO/glass substrates were immersed vertically in the beaker and then placed on the hot plate under the preparation temperature of 75°C for 45 min. Finally, the samples were taken out of the solution and washed by distilled water to remove any contaminants. The preparation process was repeated to increase the thickness of the CdS nanocrystalline thin film. The thickness of the prepared CdS nanocrystalline thin film was 725 nm and this was calculated using the Swanepoel method [19]. The surface morphology of the obtained CdS nanocrystalline thin films was analyzed by scanning electron microscopy (Zeiss Supra 55VP), X-ray diffraction (XRD; PANalytical X’Pert PRO-MRD with CuKa (L5406 A) radiation) was employed to determine the crystalline structure of the CdS nanocrystalline thin films. To fabricate a CdS/dyes solar cell, the dye is spread onto the deposited CdS nanocrystalline thin film on FTO/glass. Then the back contact was black carbon spread electrolyte (polysulfide) that is injected between the dye and carbon electrode from a small hole made for this purpose. The current-voltage (I-V) measurement for the devices was investigated before and after heat treatment of the device under various temperatures for 30 min, depending on the type of the dye used. The current-voltage (I-V) measurements were performed using a Keithley2400 source meter in the dark and under the illumination of one sun (AM 1.5, 1000 W/m²).

2.2. Preparation of Electrolyte. A suitable polysulfide liquid electrolyte was developed for the application based on CdS thin film dye-sensitized solar cells (DSSCs). A solvent consisting of methanol and water in the volume ratio of 7:3 has been found to be the optimum solvent for preparing the liquid electrolytes [20]. This solvent ratio appears to give a higher conversion efficiency of the solar cell compared with pure methanol or water as a solvent. Furthermore, Na₂S and S give rise to a good redox couple in the electrolyte for DSSCs operation, and the optimum concentrations required are 0.5 M and 0.1 M, respectively. Addition of potassium chloride (KCl) to the electrolyte further enhances the performance. Then, the solution was stirred for 2 hours. Finally, the solution obtained was kept in the dark to use in DSSC device fabrication.

3. Principle of DSSC Operation

Porous n-CdS nanostructured thin film is used as the photoelectrode to fabricate DSSC devices while conductive carbon was used as a counter electrode. Polysulfide electrolyte is injected to fill the space between the porous CdS photovoltaic electrode and that covered by dye and the counter electrode. When the solar cell is illuminated by light, charge carriers will be generated. Figure 1 shows a scheme of the charge separation process at the Donor:Acceptor interface of a DSSC. At first, light induces the dye to produce photoexcitation into excitons (D⁺) as described by the following equation:

\[
\text{D} + \text{hv} \rightarrow \text{D}^* \rightarrow \text{D}^+ \rightarrow \text{D}^+ + e^- \tag{1}
\]

Then, the excitons will migrate and separate at the CdS/dye interface and inject electrons into the conduction band of the CdS semiconductor, leaving holes (D⁺) in the dye as shown by

\[
\frac{\text{D}^+}{\text{CdS}} \rightarrow \frac{\text{D}^+ + e^-}{\text{CdS}} \tag{2}
\]

The injection process of electrons from the excited dye molecules to the conduction band of the CdS should be very fast to obtain an efficient DSSC device.

The dye will regenerate by accepting electrons from the reduced state of the redox couple (RE), producing the oxidized state of the redox couple (OX) in the electrolyte:

\[
\frac{\text{D}^+}{\text{CdS}} + \text{RE} \rightarrow \frac{\text{D} + \text{OX}}{\text{CdS}} \tag{3}
\]

After that, electrolyte regeneration occurs via OX accepting electrons from the counter electrode and producing RE:

\[
\text{OX} + e^- \rightarrow \text{RE} \tag{4}
\]
The injecting electrons will recombine by donating electrons to D⁺:

\[
\text{e}^- + \frac{D^+}{\text{CdS}} \xrightarrow{\text{Recombination-by-D^+, Dark-reaction}} \frac{D}{\text{CdS}} \quad (5)
\]

Finally, the injected electrons recombine by donating electrons to OX:

\[
\text{e}^- + \frac{\text{OX}}{\text{CdS}} \xrightarrow{\text{Recombination-by-\text{OX}, Dark-reaction}} \text{RE} \quad (6)
\]

Fast photogeneration of electrons and translation from the conduction band of CdS to the FTO electrode is very important to obtain an efficient DSSC device. It is worth mentioning that CdS is toxic, especially when inhaled as dust, but we can avoid this danger by following laboratory safety instructions.

4. Results and Discussion

4.1. Surface Morphology. Figure 2 shows the FE-SEM images of a prepared CdS nanocrystalline thin film. The CdS is grown on the surface of FTO-glass substrate as a porous structure. The pores with different diameters are distributed over the surface of the CdS thin film that covers the entire area of the substrate. The type of nanostructure prepared by the CBD method can be controlled by adjusting the synthesis parameters such as molar concentration, temperature, rate of deposition, and the type of substrate [11]. Two ideas have been proposed for describing the mechanism of synthesis of thin films by the CBD method: they are ion-by-ion and cluster. However, according to the ion-by-ion mechanism, the Cd²⁺ and S²⁻ ions are absorbed on the surface of the substrate and then combine to form CdS nanoparticles that act as seeds to grow the nanostructure. Gosavi et al. [17] suggested that the CdS nanoparticles will aggregate together to form a uniform layer which in turn led to the formation of
Table 1: Output of as-prepared porous CdS nanocrystalline thin films/dyes DSSCs.

<table>
<thead>
<tr>
<th>Dye</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>(V_{oc}) (mV)</th>
<th>(R_{sh}) ((\Omega))</th>
<th>(R_{s}) ((\Omega))</th>
<th>FF%</th>
<th>(\eta)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine B</td>
<td>4.7</td>
<td>245.5</td>
<td>1257</td>
<td>507</td>
<td>33</td>
<td>0.38</td>
</tr>
<tr>
<td>Malachite green</td>
<td>5.7</td>
<td>405</td>
<td>1950</td>
<td>594</td>
<td>35</td>
<td>0.82</td>
</tr>
<tr>
<td>Eosin methylene blue</td>
<td>4.2</td>
<td>385.9</td>
<td>1561</td>
<td>1017</td>
<td>33</td>
<td>0.53</td>
</tr>
<tr>
<td>Cresyl Violet</td>
<td>3.1</td>
<td>500.3</td>
<td>3495</td>
<td>1235</td>
<td>38</td>
<td>0.57</td>
</tr>
</tbody>
</table>

4.2. Crystalline Structure. The crystalline structure of the prepared porous CdS nanocrystalline thin film was investigated by the XRD method as shown in Figure 3. The XRD pattern contains diffraction peaks corresponding to (101), (200), and (110) planes of the FTO-glass substrate and other peaks are related to the CdS structure. However, the diffraction peaks located at 26.64° could be related to the (111) plane of CdS cubic (zinc blende) structure or to the hexagonal (wurtzite) phase of CdS according to the standard data base PDF-4 (00-001-0647 and 00-001-0780). In addition, the diffraction peak at 44.08° could correspond to the c(220) or h(110) plane. The close location of the diffraction peaks of the cubic and hexagonal phases of CdS makes it difficult to determine the structure type, but the absence of (101) and (100) hexagonal planes may indicate that the crystalline structure of the CdS porous thin film is zincblende [4].

4.3. Optical Properties. Figure 4(a) shows the UV-Vis absorbance and reflectance spectra of the prepared porous CdS nanocrystalline thin films on the FTO/glass substrate. The absorption edge was observed around the wavelength of 495 nm (2.5 eV), and the prepared thin films appeared to have a low reflection value (~0.5%) for the wavelength range of 500–700 nm. The optical absorption of the dyes is shown in Figure 4(b). Comparing with the absorption spectrum of CdS nanocrystalline films, all dyes show absorption peaks in the transparent range of CdS. The absorption peaks of 548, 580, 620, and 650 nm can be absorbed by the dyes, Rhodamine B, Cresyl violet, Malachite green, and Eosin, respectively. The optical band gap (E\(_g\)) of porous CdS nanocrystalline thin film is calculated from the reflection spectrum using the relationship [21]:

\[
2\alpha d = \ln \left( \frac{R_{max} - R_{min}}{R - R_{min}} \right),
\]

where \(\alpha\) is absorption coefficient, \(d\) is the thickness of thin film, \(R\) is the reflectance at any wavelength, and \(R_{max}\) and \(R_{min}\) are the maximum and minimum values of the reflectance. Thus, the optical band gap can be estimated from Figure 5 in which the square of \(hv[ln((R_{max} - R_{min})/(R - R_{min}))]\) is plotted against \(hv\). The absorption coefficient (\(\alpha\)) increases sharply with photon energy beyond the absorption edge. The calculated optical band gap of the prepared CdS nanocrystalline thin film is 2.51 eV and is higher than that for bulk CdS of 2.42 eV [22]. The increase in the optical band gap of the prepared porous CdS thin film can be related to the quantum size effect that appears in nanocrystalline structures [23]. The optical properties of the CdS nanocrystalline thin films indicate that they are suitable for use in fabricating DSSCs.

4.4. J-V Characteristics. Figure 6 shows the current density-voltage characteristics of as-fabricated solar cells under illumination. The porous CdS/Cresyl violet device showed the highest open circuit voltage (\(V_{oc}\)) of 500.3 mV while the CdS/Rhodamine B was the lowest \(V_{oc}\) of 245.5 mV. In addition, the DSSC prepared on porous CdS/Malachite green gave the highest value of \(J_{sc}\) of 5.7 mA/cm\(^2\) in contrast to the CdS/Cresyl violet solar cell that showed the lowest value of \(J_{sc}\) of 3.1 mA/cm\(^2\) (Table 1). We observed strong enhancement of the output of the fabricated DSSCs after heat treatment (see Figure 7). The short circuit photocurrent density \(J_{sc}\) increased for all prepared solar cells and that could be attributed to enhancement of the contact between the porous CdS thin films and the dyes. In addition the heat treatment could have caused an increase in the crystallinity of dyes that in turn led to an increase in the \(J_{sc}\) of DSSCs. The power
conversion efficiencies of the solar cells were calculated using the relationship [24]:

$$\eta = \left( \frac{J_m V_m}{P_{in}} \right) \times 100\%,$$

where $P_{in}$ is the power of the incident light, $J_m$ is the current density at the maximum power point, and $V_m$ is the voltage at the maximum power point. The fill factor (FF) is calculated using the relationship [24]:

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}}$$

The solar cell that was fabricated using Malachite green dye shows the highest conversion efficiency before annealing of 0.83% while that using Rhodamine B dye had the lowest conversion efficiency of 0.38%. All fabricated solar cells show a low value of the fill factor in Table 1. The main reason for the low conversion efficiencies could be the poor fill factors of the as-prepared DSSC devices. However, the electrolyte type is another important parameter that could affect the value of the FF and $\eta$ of the DSSC. The low value of fill factor may be ascribed to the lower hole recovery rate of the polysulfide electrolyte, which leads to a higher probability for charge recombination [25].

Furthermore, heat treatment of the fabricated solar cells caused significant enhancement in the output of all devices.
as shown in Table 2. The $\eta$ of the solar cells fabricated using Rhodamine B, Malachite green, Eosin methylene blue, and Cresyl violet dyes is increased by the ratio of 231%, 140%, 230%, and 219% respectively, after the heating treatment process.

The series resistance ($R_s$) is another parameter that can affect cell performance and high $R_s$ value reduces the output voltage under load, thereby decreasing the FF. Thus $R_s$ should be low because increasing the $R_s$ of a solar cell increases the voltage drop within the solar cell [24]. The value of $R_s$ for all prepared solar cells decreased after heat treatment as shown in Table 1. At the same time, the shunt resistance ($R_{sh}$) of DSSCs increased after heat treatment for two devices (except for the Cresyl and Eosin solar cells) and that contributed to the increase in the $J_{sc}$ value.

Decreasing the $R_s$ and increasing $R_{sh}$ could be a main factor that could lead to increases in the FF and efficiency of the solar cells. In addition, surface recombination is another parameter that has a significant effect on the $J_{sc}$ and $V_{oc}$ values of DSSC devices. The $V_{oc}$ of all prepared DSSCs (except for the Cresyl violet device) increased after heat treatment indicating the enhancement of the CdS/dye coupling that led to fast charge injection (electrons) from the dye molecules to the porous CdS nanostructure thin films and then transfer to the FTO substrate with simultaneous transfer of the holes from the dye to the electrolyte.

Figure 7: J-V characteristics of prepared DSSCs after annealing process (A) porous CdS/Rhodamine B dye, (B) porous CdS/Malachite green dye, (C) porous CdS/Eosin-methylene blue dye, and (D) porous CdS/Cresyl violet dye.

Sankapal et al. [26] fabricated DSSCs based on the structure FTO/CdS-flat/CdS nanowires/dye using Rhodamine B and Rose Bengal dyes. They obtained $\eta$ of the solar cell prepared using Rhodamine B of 0.12% while the other one showed $\eta$ of 0.125%. Sun et al. [27] noted that the efficiency of the solar cell based on CdS QD with a TiO$_2$ photoanode using polysulfide as electrolyte increased from 0.054% to 0.22% when the $R_s$ decreased from 218 $\Omega$ to 53.8 $\Omega$. CdS quantum dots are used to prepare DSSCs with other nanomaterials, especially TiO$_2$. Sun et al. [27] noted that the efficiency of a CdS QD/TiO$_2$ nanotube array increased about 35 times to reach 4.15% when the CdS QDs are used with TiO$_2$ [27].

5. Conclusions

Porous CdS nanocrystalline thin films can be prepared by CBD onto a FTO/glass substrate. The porous CdS thin films could be structured with cubic phase as concluded from the XRD pattern. Porous CdS/dye solar cells were fabricated using Rhodamine B, Malachite green, Eosin methylene blue, and Cresyl violet dyes. The DSSCs that were prepared using Malachite green dye showed a high conversion efficiency of 0.88% compared with other dyes while the CdS/Rhodamine B solar cell shows the lowest efficiency of 0.38%. Heat treatment of the fabricated DSSCs led to enhancement of the performance of the output of all devices. The conversion efficiency was increased for CdS/Rhodamine B from 0.38% to 0.88% when the device was annealed at 185 °C for 30 min. However, the maximum efficiency of 1.25% was obtained from a Cresyl violet solar cell after heat treatment at 130 °C. The enhancement in the output of fabricated DSSCs after heat treatment could be attributed to decreasing the $R_s$ and increasing $R_{sh}$ compared with as-fabricated solar cells.

Competing Interests

The authors declare that they have no competing interests.

References


