Highly Efficient dye-sensitized solar cells Based on Sensitization of CdS on TiO₂ surface via SILAR method: Evaluation of the CdS and TiO₂ thickness effect

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ABSTRACT: In this study, TiO₂ nanoparticles solution were prepared for electrophoresis deposition (EPD) that used for fabrication of TiO₂ layer on the FTO glass substrate. Moreover, for promoting efficiency of energy conversion, calcium sulfide (CdS) nanoparticle with various thickness was deposited on TiO₂ by successive ion layer adsorption and reaction (SILAR) method. Effect of TiO₂ and CdS thickness on efficiency was evaluated. The surfaces was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), cross-section SEM, UV-Vis diffuse reflectance spectroscopy (DRS), energy dispersive X-ray analysis spectroscopy (EDX), atomic force microscopy (AFM). In addition, dye-sensitized solar cells (DSSC) made by the fabricated electrodes as working electrode and then investigated by current density-voltage(J-V) curve. It was found that CdS and TiO₂ thickness has significant role in solar cell performance and efficiency and an optimum amount of CdS and TiO₂ thickness is required for achieving the highest efficiency and performance. Highest power conversion efficiency of 7.831, with a Vₚₑₚ of 0.7 V, Jₚₑₚ of 18.4 mA, and FF of 0.608 has been observed in an optimized DSSC.

Keywords: TiO₂; CdS; SILAR; Solar cell; Deposition

INTRODUCTION

Dye-sensitized solar cells (DSSCs) have received a great deal of scientific attraction and technical interest because of their easy-fabrication and low cost production [1-3]. Titanium dioxide (TiO₂), a wide band-gap (3.0–3.2 eV) semiconductor, is one of the most prominent oxide materials for performing various kinds of industrial applications such as photovoltaic [2], photocatalytic [4, 5], photonic crystals [6], photochromic [7, 8]. The band gap of TiO₂ (3.2 eV) limits its absorption to the ultraviolet region of the solar spectrum [9]. Also, the electron mobility of TiO₂ is too low, thus inferior conversion efficiency of solar cells [10, 11]. To enhance light harvest in the visible light region, many efforts have been made by focusing on the development of high performance sensitzers [12-15]. It is still a challenge to obtain an ideal organic dye as sensitizer to absorb photons in the full sunlight spectra. For this reason, semiconductors such as CdS, CdSe, CdTe, PbS, Bi₂S₃, CuInS₂, and so on, which absorb light in the visible, can serve asssistizers because they are able to transfer electrons to large bandgap semiconductors such as TiO₂ or ZnO [9]. Among this materials CdS with suitable band gaps and band positions compared with TiO₂ create a long distance charge separated state with electron and holes at sites far from each other and hence is useful for using in DSSC. Up to now, different methods have been used for deposition of CdS on TiO₂ surface. For example, in a comprehensive study, Sabet et al. [16] deposited CdS on TiO₂ by Different chemical methods such as microwave, hydrothermal, chemical bath deposition (CBD), successive ion layer adsorption and reaction (SILAR) and doctor blade (DB). Their results showed that deposition via different methods leads to fabrication of cells with different optical properties and therefore different energy conversion efficiencies. However, to the best of our knowledge, no studies have been done to investigate of CdS thickness effect on energy conversion efficiency. So in this study, the effect of CdS thickness on efficiency was evaluated and among the different methods for deposition, SILAR was chosen because the thickness of CdS is controllable easily by this method. SILAR has a number of advantages for using in deposition process: (i) it offers...
extremely easy way to dope film with virtually any element in any proportion by merely adding it in some form of the cationic solution. (ii) unlike closed vapor deposition method, SILAR does not require high quality target and/or substrates nor does it require vacuum at any stage, which is a great advantage if the method will be used for industrial application, (iii) the deposition rate and the thickness of the film can be easily controlled over a wide range by changing the deposition cycles, (iv) operating at room temperature can produce films on less robust materials, (v) unlike high power methods such as radio frequency magnetron sputtering (RFMS), it does not cause local over heating that can be detrimental for materials to be deposited and (vi) there are virtually no restrictions on substrate material, dimensions or its surface profile. Moreover, it is relatively inexpensive, simple and convenient for large area deposition [17]. In this present study, first, TiO$_2$ nanoparticles solution were prepared for electrophoresis deposition (EPD) that used at different cycles for deposition of TiO$_2$ layer on the FTO glass. Then, CdS was deposited on TiO$_2$ by SILAR method at different cycles and the efficiency of obtained cells was evaluated. In addition, dye-sensitized solar cells (DSSC) made by the fabricated electrodes and then investigated.

**MATERIAL AND METHODS**

The chemical reagents including Cadmium Nitrate (Cd(NO$_3$)$_3$.4H$_2$O), thioacetamide (TAA), Sodium sulfide nonahydrate (Na$_2$S.9H$_2$O), Potassium chloride (KCl), Sulfur (S), ethanol and methanol used in our experiments were purchased from Merck. N719, Pt solution and surlyn were purchased from Dyesol. TiO$_2$ powder of P25 (av. 30 nm, 80% anatase (d = 21 nm) and 20% rutile (d = 50 nm)) was prepared from Degussa, Germany. All the mentioned chemicals were used as received without further purification.

**Preparation of TiO$_2$ nanoparticles solution for electrophoresis**

8 g of TiO$_2$ was added to 1 L flask and 4 ml acetyl acetone, 48 ml of acetone, 20 ml of water and 120 mg iodine were added to mentioned flask. Afterwards, 99.99% ethanol was added enough to bring the final volume of solution up to 1 L. Then, the obtained solution was put into ultrasonic bath for 30 min. Finally, the solution was left on the magnetic stirrer for 24 h.

**Deposition method (FTO/TiO$_2$)**

EPD was utilized to the preparation of P25 NPs-based films used in DSSCs. During EPD, the cleaned FTO glass remained at a positive potential (anode) while a pure steel mesh was used as the counter (cathode) electrode. The linear distance between the two electrodes was about 1 cm. Power was supplied by a Megatek Programmable DC Power Supply (MP-3005D). The applied voltage was 10 V. The deposition cycle was 4 times with each time of 5 (sample B1), 10 (sample B2), 15 (sample B3), 20 (sample B4) and 25 s (sample B5), and the temperature of the electrolyte solution was 25°C. The coated substrates were air dried. The apparent area of the film was 1 x 1 cm$^2$. The resulting layer was annealed under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and at 500 °C for 15 min. Electrolyte solution and the amount of additives are important for creation a surface with high quality. Scheme 1a shows EPD process.

**Fabrication of FTO/TiO$_2$/CdS**

Deposition of CdS via SILAR method was initiated by preparation of three solutions, separately. 60 ml of 0.01 M Cd(NO$_3$)$_3$.4H$_2$O ethanol solution (solution 1), 60 ml of ethanol solution (solution 2) and 60 ml of 0.01 M Na$_2$S.9H$_2$O ethanol solution (solution 3). The TiO$_2$ electrode was immersed in the solution 1 for 1 min, to allow Cd$^{2+}$ to adsorb onto the TiO$_2$ surface and rinsed with ethanol (solution 2) for 1 min to remove the excess Cd$^{2+}$ and then electrode was dipped in to the solution 3 for 1 min. The electrode was then rinsed in ethanol (solution 2) for 1 min and dried in air atmosphere for 1 min. This deposition cycle was repeated for 4 (sample C1), 6 (sample C2), 8 (sample C3), and 10 (sample C4) times to get desired CdS loading (Scheme 1b). The TiO$_2$/CdS electrodes were then rinsed with ethanol and dried under a nitrogen stream. A Pt solution coated FTO glass electrode was prepared as a counter electrode. The Pt electrode was placed over the TiO$_2$/CdS electrode and the edges of the cell were sealed with 50 lm thick sealing sheet (Surlyn 50, Dyesol). Sealing was accomplished by pressing the two electrodes together on a double hot-plate at a temperature of about 110 °C. The S$^2$/$S_2^2$ electrolyte was introduced into the cell through one of two small holes drilled in the counter electrode. Finally, these two holes were sealed by a small square of sealing sheet. After that these samples were characterized by J-V.
Fabrication of FTO/TiO$_2$/N719 and FTO/TiO$_2$/CdS/N719

The fabricated FTO/TiO$_2$ (sample B3) was separately immersed into a cis-di(thiocyanato)-N,N'-bis(2,2'-bipyridyl-4-carboxylic acid-40-tetraethylammonium) ruthenium (II) (N-719) dye solution in ethanol (0.5 mM) and kept at room temperature for 48 h to complete the sensitizer uptake (sample D1). Then CdS was deposited 1 time (sample D2), 2 times (sample D3), 4 times (sample D4) and 6 times (sample D5) by SILAR method at different cycles on the as-prepared FTO/TiO$_2$. The dye-adsorbed TiO$_2$ electrodes were then rinsed with ethanol and dried under a nitrogen stream. A Pt coated FTO glass electrode was prepared as a counter electrode. The Pt electrode was placed over the dye-adsorbed TiO$_2$ electrode and the edges of the cell were sealed with 50 lm thick sealing sheet (Surlyn 50). Sealing was accomplished by pressing the two electrodes together on a double hot-plate at a temperature of about 110 °C. The I$_3$-/I$^-$ electrolyte was introduced into the cell through one of two small holes drilled in the counter electrode (Scheme 2). Finally, these two holes were sealed by a small square of sealing sheet. Moreover, for fabrication of FTO/TiO$_2$/CdS/N719, CdS at different cycles 1 (sample D2), 2 (sample D3), 4 (sample D4) and 6 (sample D5) was deposited on the FTO/TiO$_2$. After that DSSCs were characterized by J-V.

Characterization

X-ray diffraction (XRD) patterns were recorded by a Philips-X'PertPro, X-ray diffractometer using Ni-filtered Cu Kα radiation at scan range of 10<2θ<80. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. The energy dispersive spectrometry (EDS) analysis was studied by XL30, Philips microscope. The diffused reflectance UV-visible spectrum (DRS) of the sample was recorded by an Ava Spec-2048TEC spectrometer. Photocurrent density-voltage (J-V) curve was measured by using computerized digital multimeters (Ivium-n-Stat Multichannel potentiostat) and a variable load. A 300 W metal xenon lamp (Luzchem) served as assimilated sun light source, and its light intensity (or radiant power) was adjusted to simulated AM 1.5 radiation at 100 mW/cm$^2$ with a filter for this purpose.
RESULTS AND DISCUSSION

Spectral and morphological analysis

Fig. 1 shows XRD patterns of FTO glass substrate, samples B3 and C3, respectively. XRD pattern of bare FTO glass (Fig. 1a) shows the diffraction peaks around 2θ= 26.5°, 33.7°, 37.8°, 51.6°, 54.6° and 61.7°. The characteristic diffraction peaks of sample B3 are present in Fig. 1b. It is well known that the diffraction peaks of TiO\(_2\) nanoparticles are consistent with that of anatase and rutile, and anatase is the main phase. Fig. 1c shows XRD pattern of sample C3. This pattern confirmed that the CdS were successfully formed on the surface of the porous TiO\(_2\) film by SILAR method. EDX analysis was used to identify the elemental composition of products. Figs. 2a and b show EDX spectrum of samples B3 and C3, respectively. Presence of Ti, O and Sn in Fig. 2a shows that TiO\(_2\) was successfully deposited on glass substrate. Moreover, presence of Cd and S in Fig. 2b indicates the deposition of CdS precipitation on TiO\(_2\). The morphology of products was characterized by SEM. Figs. 3a and b show SEM images of samples B3 and C3, respectively. As shown in Fig. 3a, TiO\(_2\) film consists spherical nanoparticles that was deposited uniformly on glass substrate. In Fig. 3b, the fine nanoparticles of CdS were deposited well on TiO\(_2\) film. Fig. 3c shows the SEM micrographs of cross-section of the TiO\(_2\) nanoparticles electrode which reveals the thickness of the fabricated TiO\(_2\) electrodes with 4 cycles for 15 s electrophoresis (sample B3) has 6.4 µm. Fig. 3d shows SEM cross-section of TiO\(_2\)/CdS nanocomposite that deposited on the FTO substrate (sample C3) and indicates that by deposition of CdS precipitation on TiO\(_2\) film, the thickness was increased to 8.87 µm. Figs. 4a and b shows 2D and 3D atomic force microscopy (AFM) images of B3 and C3, respectively. It can be seen that bare TiO\(_2\) electrode shows the uniform surface (Fig. 4a). Also its porosity is high that can improve the dye and CdS absorption on the surface and subsequently increase the solar cell efficiency. Fig. 4b shows AFM image of TiO\(_2\)/CdS electrode. As shown in Fig. 4b, the uniformity was improved and there are fine CdS nanoparticles in pores of TiO\(_2\). The UV-Vis Diffuse reflectance spectroscopy of bare TiO\(_2\) (sample B3) and TiO\(_2\)/CdS (sample C3) are shown in Fig. 5a and b, respectively. As can be seen, by deposition of CdS on TiO\(_2\), band-gap was decreased from 3.44 to 3.26. This shift increases visible light absorption and hence is useful for solar cell application. For having a comparison between performances of DSSCs fabricated from different samples, current density–voltage (J–V) curves were obtained. For investigation of TiO\(_2\) thickness effect several experiments were performed by different cycles of TiO\(_2\) deposition on glass substrate. Fig. 6 shows the J-V curves of samples D1-D5 prepared from different thicknesses of CdS in presence of N719 (The photovoltaic parameters are shown in Table 2). As can be seen, an optimum thickness is also required for CdS (sample C3). Fig. 8 shows the J-V curves of samples D1-D5 prepared from different thicknesses of CdS in presence of N719 (The photovoltaic parameters are shown in Table 3). Fig. 8a is related to FTO/TiO\(_2\)/N719 (sample D1). As can be seen, by CdS deposition on TiO\(_2\) at different cycles and in more precise words, at different thicknesses, the efficiency was enhanced remarkably (Fig. 8b) and the highest efficiency was achieved by 1 cycle of CdS (sample D2). Generally, by deposition of CdS between TiO\(_2\) and N719 (FTO/TiO\(_2\)/CdS/N719) the efficiency compared to electrode without using CdS (FTO/TiO\(_2\)/N719) can be increased or decreased that is related to thickness of CdS. As the results show, by using CdS, the efficiency was increased that can be related to formation of middle levels by CdS and in more precise words, can be related to extending life of electron but by increasing the CdS thickness, the efficiency will be decreased. Because much thickness prevent reaching enough light to N719 and moreover, recombination will be increased.

Table 1. The samples B1-B5 DSSC performance

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Jsc (mA/cm(^2))</th>
<th>Voc</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>2.156</td>
<td>0.36</td>
<td>0.23</td>
<td>0.288</td>
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<tr>
<td>B2</td>
<td>2.54</td>
<td>0.52</td>
<td>0.191</td>
<td>0.251</td>
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<tr>
<td>B3</td>
<td>3.648</td>
<td>0.465</td>
<td>0.222</td>
<td>0.376</td>
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<tr>
<td>B4</td>
<td>2.125</td>
<td>0.39</td>
<td>0.225</td>
<td>0.323</td>
</tr>
<tr>
<td>B5</td>
<td>3.331</td>
<td>0.575</td>
<td>0.18</td>
<td>0.344</td>
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Table 2. The samples C1-C4 DSSC performance

<table>
<thead>
<tr>
<th>Sample No</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>3.648</td>
<td>0.465</td>
<td>0.222</td>
<td>0.376</td>
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<tr>
<td>C2</td>
<td>3.93</td>
<td>0.485</td>
<td>0.21</td>
<td>0.399</td>
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<tr>
<td>C3</td>
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<td>0.656</td>
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<tr>
<td>C4</td>
<td>3.797</td>
<td>0.425</td>
<td>0.204</td>
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Table 3. The samples D1-D5 DSSC performance

<table>
<thead>
<tr>
<th>Sample No</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
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<tbody>
<tr>
<td>D1</td>
<td>15.66</td>
<td>0.74</td>
<td>0.610</td>
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<tr>
<td>D2</td>
<td>18.4</td>
<td>0.7</td>
<td>0.608</td>
<td>7.831</td>
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<tr>
<td>D3</td>
<td>10.938</td>
<td>0.66</td>
<td>0.314</td>
<td>2.333</td>
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<tr>
<td>D4</td>
<td>4.972</td>
<td>0.67</td>
<td>0.278</td>
<td>0.938</td>
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<tr>
<td>D5</td>
<td>1.96</td>
<td>0.59</td>
<td>0.21</td>
<td>0.242</td>
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Fig 1. XRD patterns of a) FTO glass substrate, b) sample B3 and c) sample C3

Fig 2. EDX spectrum of a) sample B3 and b) sample C3
Fig 3. SEM images of a) samples B3 and b) sample C3; SEM cross section of sample c) B3 and d) C3

Fig 4. 2D and 3D atomic force microscopy (AFM) images of sample a) B3 and b) C3

Fig 5. UV-Vis Diffuse Reflectance spectroscopy of a) TiO₂ (sample B3) and b) TiO₂/CdS (sample C3)

Fig 6. J-V curves of samples B1-B5
CONCLUSIONS

In this work, TiO$_2$ nanoparticles were successfully deposited on FTO glass substrate by electrophoresis deposition method. Cadmium sulfide with various thickness was deposited on TiO$_2$ by SILAR method for improving efficiency of energy conversion. Effect of TiO$_2$ and CdS thickness on efficiency was investigated. The surfaces was characterized by XRD, SEM, cross-section SEM, DRS, EDX, AFM and dye-sensitized solar cells made by the fabricated electrodes as working electrode and then investigated by current density-voltage (J-V) curve. The highest efficiency has been observed for sample D2. It was found that CdS and TiO$_2$ thickness has significant role in solar cell performance and efficiency and an optimum amount of CdS and TiO$_2$ thickness is required for achieving the highest efficiency and performance.

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