Performance enhancement evaluation dye-sensitized solar cells Based on Sensitization different cycles of PbS on TiO$_2$ surface through SILAR method

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**ABSTRACT:** In this investigation, TiO$_2$ NPs were deposited on FTO glasses substrate by electrophoretic deposition method (EPD) in applied voltage of 10 V and electrophoretic deposition time of 5-25 second. Lead sulfide (PbS) quantum dots QDs with various thickness have been synthesized through successive ionic layer adsorption and reaction (SILAR) on a TiO$_2$ film for the fabrication of quantum dot-sensitized solar cells QDSCs. We optimum amount of TiO$_2$ and PbS thickness is essential for arriving the highest efficiency. Then for dye-sensitized solar cells DSSC made, fabricated working electrode and investigated by current density-voltage(J-V) curve. The surfaces was characterized by scanning electron microscopy (SEM), cross-section SEM, , atomic force microscopy (AFM), UV-Vis diffuse reflectance spectroscopy (DRS), energy dispersive X-ray analysis spectroscopy (EDX) and X-ray diffraction (XRD). Highest power conversion efficiency of 3.065, with a $V_{OC}$ of 0.64 V, $J_{SC}$ of 13.26 mA, and FF of 0.361 has been observed in an optimized DSSC.

**Keywords:** TiO$_2$; PbS; SILAR; thickness; DSSC

**INTRODUCTION**

Dye sensitized solar cell (DSCs) is one of the noteworthy scopes in recent decade because of high energy conversion efficiency, low-cost and simple fabrication (1-4). The photoelectrode of the DSSC fabricate from Titanium dioxide (TiO$_2$) nanostructures commonly. Titanium dioxide is a semiconductor with band-gap (3.0–3.2 eV) is one of the eminent oxide materials for performing various kinds of industrial applications such as water and air purification(5), photocatalytic(6-8) and photochromic(9). The electron mobility and prompt recombination rate of electron( e$^{-}$)/ hole( h$^{+}$) on the TiO$_2$ nanoparticles limit to obtain high efficiency TiO$_2$ nanoparticle based solar cells low(10). It also does not absorb light in the visible region also reduces the efficiency of solar cells(11). In recent years, various methods such as drop-casting(12), chemical vapour Deposition(CVD) (13), chemical bath deposition(CBD) (14), doctor blade method(15) and electrophoretic deposition (EPD) use for deposition of TiO$_2$ on ITO or FTO glass. Although screen printing and doctor blade was used for the TiO$_2$ nanostructure deposition in recent years, the EPD method has attracted particular attention because of its facile and low cost deposition perspective. Semiconductors such as CdS(16), PbS(17), Bi$_2$S$_3$(18), CdSe, CdTe,and CuInS$_2$ Can help to absorb light in the visible region and transfer electrons to large bandgap semiconductors such as TiO$_2$, ZnO or SnO$_2$(19).

As an alternative to dye molecules, quantum dots (QDs) such as, PbS, Bi$_2$S$_3$, CdSe, CdTe, CdS and others as well as very thin inorganic absorber layers have been used(20). Quantum dot due to the band gap by changing their size changes are highly regarded and possibility to design multilayer absorber structures. The use of quantum dot and dye together, enhances the absorption of light in the visible region and increase the production of electrons, which increases the efficiency of solar cells (21, 22). Various techniques such as hydrothermal (HT), chemical bath deposition (CBD), microwave (MW), doctor blade (DB) and successive ionic layer adsorption and reaction SILAR were can be used for deposition quantum dots (QDs) on the TiO$_2$. 
In this work, TiO₂ NPs were dispersed in ethanol and then the cyclic electrophoretic deposition (EPD) that used at different cycles for deposition of TiO₂ layer on the FTO glass. Then use a successive ionic layer adsorption and reaction SILAR method at different cycles and the efficiency of obtained cells was evaluated. And finally, dye-sensitized solar cells (DSSC) made by the fabricated electrodes. The morphology and physicochemical characteristic of the prepared compounds were analyzed by scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Atomic force microscopy (AFM) and UV-Vis DRS spectroscopy.

MATERIAL AND METHODS

2.1. Materials and characterization

Commercially available TiO₂ powder of P25 (av. 30 nm by Brunauer-Emmett-Teller (BET), 80% anatase (d = 21 nm) and 20% rutile (d = 50 nm)) was prepared from Degussa, Germany. Lead (II) nitrate Pb(NO₃)₂, 4H₂O, Sodium sulfide nonahydrate (Na₂S.9H₂O), ethanol, Iodine (I₂), Potassium chloride (KCl), Sulfur (S), acetonitrile and acetyl acetone (acac) from Merck Company were used as received without further purification. Pt solution, surlyn and N719, form Dyesol. H₂O was purified by distillation and filtration. All the materials used as received without further purification.

For characterization of the products XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Ka radiation. SEM micrographs were taken by using a field-emission scanning electron microscope (HITACHI S4160, Japan). Cross-section SEM image s were obtained by scanning electron microscope (SEM) (Philips XL-30ESM). The energy dispersive spectrometry (EDS) analysis was studied by XL30, Philips microscope. Atomic force microscopy (AFM) model NT-MDT Solver P47 was used in tapping mode for morphological characterization using ultra sharp Si cantilevers. 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 a simulated sun light source, and its light intensity (or radiant power) was adjusted to simulated AM 1.5 radiation at 100 mW/cm² with a filter for this purpose.

2.2. Electrophoretic deposition (EPD)

Electrophoretic deposition (EPD) was used to preparation of TiO₂-based electrodes. During EPD, the scavenged 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 2.5 cm. Power was provide by a Motech Programmable Dc source meter. The applied voltage was 10 V. The deposition cycle was 4 times with each time of 5 (sample A1), 10 (sample A2), 15 (sample A3), 20 (sample A4) and 25 s (sample A5), and the temperature of the electrolyte solution was 25 °C. The coated substrates were air dried. Apparent area of the film was 1x1.5 cm². The resulting layer was annealed at 450 °C in air for 1 h. To obtain a high-quality surface, it is very important to correct the electrolyte solution. Based on previous experiments (23, 24), we used optimal concentrations of additives in the electrolyte solution as follows: I₂ 120 mg/l, acetone 48 ml/l, acetylacetone 4 ml/l, TiO₂ (P25) 8 g/l and water 20 ml/l. scheme 1 shows EPD process.

2.3. Fabrication of FTO/TiO₂/PbS

For deposition PbS use a SILAR method was beginning by preparation of three solutions, separately. 40 ml of 0.01 M Pb(NO₃)₂, 4H₂O ethanol solution (solution 1), 40 ml of ethanol solution (solution 2) and 40 ml of 0.01 M Na₂S.9H₂O ethanol solution (solution 3). Therefore, the TiO₂ electrodes were dipped into 0.01 M Pb(NO₃)₂, 4H₂O for 1 min, washed with ethanol for 1 min, immersed into 0.01 M Na₂S aqueous solution for 1 min, and washed again and dried in air atmosphere for 3 min. This deposition cycle was repeated for 4 (sample B1), 6 (sample B2), 8 (sample B3), and 10 (sample B4) times to get suitable PbS loading. Scheme 2 shows SILAR method. A
Pt solution coated FTO glass electrode was prepared as a counter electrode. The Pt electrode was put over the TiO$_2$/PbS electrode and the edges of the cell were sealed with thick sealing sheet (Surlyn 50, Dyesol). Sealing was done by pressing the two electrodes together on a double hot-plate at a temperature of about 110 °C. The S$^2$/S$^2$ electrolyte was injection into the cell through one of two small holes 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.

2.4 Fabrication of FTO/TiO$_2$/N719 and FTO/TiO$_2$/PbS/N719

The FTO/TiO$_2$/PbS electrodes were one by one immersed into a (N-719) dye solution in ethanol (0.5 mM) and kept at room temperature for 40 h to complete the sensitizer uptake. The fabricated FTO/TiO$_2$ (sample A3) was separately immersed into (N-719) dye solution in ethanol (0.5 mM) and kept at room temperature for 40 h to complete the sensitizer uptake (sample C1). Then PbS was deposited 1 time (sample C2), 2 times (sample C3), 4 times (sample C4) and 6 times (sample C5) by SILAR method at different cycles on the as-prepared FTO/TiO$_2$. After a 40 h, the glass bringing out form dye solution and dried under a nitrogen stream.

For prepared of counter electrode, we coated Pt on the FTO glass and dried for 3 min in air atmosphere. The Pt electrode was placed over the FTO/TiO$_2$/PbS/dye electrode and the edge of the cell was sealed with thick sealing sheet (Surlyn). To seal the electrodes, two electrodes put on a hot plate at 110°C. The I$_3$/I$_1$ electrolyte was injection into the cell through two small holes drilled in the counter electrode scheme 3. Finally, these two holes were sealed by a small square of sealing sheet.

RESULTS AND DISCUSSION

Fig. 1a shows XRD patterns of FTO/TiO$_2$ sample A3. It Show that the TiO$_2$ nanoparticles are deposited upon the FTO surface. The TiO$_2$ consisted of anatase and rutile phase and appears to have Peaks at 2θ= 25.6, 28, 31, 37.9, 48.1, 54.15, 55.13, 62, 69, 70.25 and the SnO$_2$ structure of FTO glass shows peaks at 50.5 and 62. Fig. 1b shows XRD patterns of FTO/TiO$_2$/PbS sample B3. This pattern certified that the PbS were successfully deposit on the surface of the porous TiO$_2$ film by SILAR method.

Fig. 2 shows EDS spectrum of sample B3. Presence of Ti, O, F and Sn shows that TiO$_2$ was successfully deposited on glass substrate. Also, presence of Pb and S indicates the deposition of PbS precipitate on TiO$_2$ by SILAR method. The morphology of fabricated films was characterized by SEM. Fig. 3a show SEM image of samples A3, that show TiO$_2$ film was deposited uniformly on glass substrate. Fig. 3b show SEM image of samples B3, that nanoparticles of PbS were deposited well on TiO$_2$ film. Fig. 3c show the SEM micrograph of cross-section of the P25 NPs electrode which reveals the thickness of the fabricated P25 electrode with 4 cycles for 15 s electrophoresis (sample A3) has 4.1 µm. Fig. 3d shows SEM cross-section of TiO$_2$/PbS nanocomposite that deposited on the substrate by SILAR method (sample B3) that indicate increased thickness to 9.3 µm. Fig. 4 shows 2D and 3D atomic force microscopy (AFM) images of A3 and B3, respectively. In Fig. 4a shows the uniform surface of TiO$_2$ electrode. Pores on the TiO$_2$ electrode increases the of PbS and dye absorption on the surface
and accordingly increase the solar cell efficiency. Fig. 4b shows AFM image of TiO$_2$/PbS electrode. Fig. 5a and b shows The UV-Vis Diffuse reflectance spectroscopy of bare TiO$_2$ (sample A3) and TiO$_2$/PbS (sample B3), respectively. We see that, when deposition of PbS on TiO$_2$, band-gap was decreased from 3.4 to 3.08. This shift enhancement visible light absorption and therefore 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. First we investigation of TiO$_2$ thickness effect were performed by different cycles of TiO$_2$ deposition on glass substrate. Fig. 6 shows the J-V curves of samples A1-A5 obtained in 5, 10, 15, 20 and 25 s, respectively. Fig. 6 and Table 1 it shows that Results of the optimum time and thickness. According to the results sample A3 achieving the highest efficiency. According to Table 1 by increasing the thickness TiO$_2$ film reduced efficiency and sample A3 with thickness 7.3 µm has the highest efficiency. According to these results, we can conclude that the limited electron transport for the thick films due to increase of charger combination centers. The cell efficiency is increased as the TiO$_2$ thickness increases to 7.3 µm because electron transporting TiO$_2$/PbS/electrolyte increased and internal resistance decreased. So electron lifetime and cell efficiency are increased. Therefore DSSC performance with the higher film thickness is decreased, since increasing the thickness causing the recombination is increased. Fig. 7 shows the J-V curves of samples B1-B4 obtained from PbS at the number of cycles 4, 6, 8 and 10, respectively. Table 2 are shows that the photovoltaic parameters samples (B1-B4). Accordingly, sample B3 is an optimum thickness for PbS QDs. Fig. 8 shows the J-V curves of samples C1-C5 ready from different thicknesses of PbS in presence of dye N719. The photovoltaic parameters are shown in fig. Sample C1 is related to FTO/TiO$_2$/N719. Sample C2 related to FTO/TiO$_2$/PbS/ N719 with 1 cycle of PbS, which highest efficiency was achieved. With the increasing number cycles of PbS, increasing the PbS thickness and the efficiency will be decreased. Since increasing thickness barricade attain enough light to N719 and moreover, recombination will be increased.

![Fig 1. XRD patterns of a) FTO/TiO$_2$ sample A3, b) FTO/TiO$_2$/PbS sample B3](image1)

![Fig 2. EDX spectrum of sample B3](image2)
Fig 3. SEM images of a) samples A3 and b) sample B3

Fig 3. SEM cross section of sample c) A3 and d) B3

Fig 4. 2D and 3D atomic force microscopy (AFM) images of sample a) A3 and b) B3
Fig 5. UV-Vis Diffuse Reflectance spectroscopy of a) TiO\textsubscript{2} (sample A3) and b) TiO\textsubscript{2}/PbS (sample B3)

Fig 6. J-V curves of samples A1-A5

Fig 7. J-V curves of samples B1-B4

Fig 8. J-V curves of samples C1-C5

Table 1. The samples A1-A5 DSSC performance

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$</th>
<th>FF</th>
<th>$\eta$ (%)</th>
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<tbody>
<tr>
<td>A1</td>
<td>1.79</td>
<td>0.42</td>
<td>0.347</td>
<td>0.262</td>
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<tr>
<td>A2</td>
<td>1.58</td>
<td>0.38</td>
<td>0.364</td>
<td>0.219</td>
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<tr>
<td>A3</td>
<td>2.84</td>
<td>0.4</td>
<td>0.346</td>
<td>0.394</td>
</tr>
<tr>
<td>A4</td>
<td>2.37</td>
<td>0.36</td>
<td>0.385</td>
<td>0.328</td>
</tr>
<tr>
<td>A5</td>
<td>1.33</td>
<td>0.7</td>
<td>0.371</td>
<td>0.323</td>
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Table 2. The samples B1-B4 DSSC performance

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$</th>
<th>FF</th>
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<tbody>
<tr>
<td>B1</td>
<td>1.63</td>
<td>0.69</td>
<td>0.347</td>
<td>0.395</td>
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<tr>
<td>B2</td>
<td>3.32</td>
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<td>0.385</td>
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<tr>
<td>B3</td>
<td>1.63</td>
<td>1.06</td>
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<td>B4</td>
<td>1.5</td>
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Table 3. The samples C1-C5 DSSC performance

<table>
<thead>
<tr>
<th>Sample</th>
<th>SILAR Cycle</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$</th>
<th>FF</th>
<th>$\eta$ (%)</th>
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<tbody>
<tr>
<td>C1</td>
<td>0</td>
<td>11.02</td>
<td>0.66</td>
<td>0.351</td>
<td>2.55</td>
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<tr>
<td>C2</td>
<td>1</td>
<td>13.26</td>
<td>0.64</td>
<td>0.361</td>
<td>3.065</td>
</tr>
<tr>
<td>C3</td>
<td>2</td>
<td>6.135</td>
<td>0.6</td>
<td>0.371</td>
<td>1.36</td>
</tr>
<tr>
<td>C4</td>
<td>4</td>
<td>6.68</td>
<td>0.32</td>
<td>0.338</td>
<td>0.724</td>
</tr>
<tr>
<td>C5</td>
<td>6</td>
<td>2.2</td>
<td>0.3</td>
<td>0.33</td>
<td>0.21</td>
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CONCLUSIONS

In this paper, we first TiO$_2$ nanoparticles were deposited on FTO glass substrate by electrophoresis deposition method and effect of TiO$_2$ thicknesses on efficiency was investigated. Then we optimum PbS thickness because amount of PbS thickness is important for achieving the highest efficiency and performance. Lead sulfide with various thicknesses was deposited on TiO$_2$ by SILAR method and also effect of PbS thicknesses on efficiency was investigated. The highest efficiency has been observed for sample B2. The surfaces were characterized by SEM, DRS, cross-section SEM, EDS, XRD and AFM. Dye-sensitized solar cells constructed by the fabricated electrodes as working electrode and then check by current density-voltage (J-V) curve. The best conversion efficiency was related to sample C2.

REFERENCES

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