Fabrication and Characterization of ZnS based Photoelectrochemical Solar Cell

Priyanka M. Mana, Pankaj K. Bhujbal and Habib M. Pathan*

Abstract

Zinc sulphide photoanode was prepared by a cost-effective and simple successive ionic layer adsorption and reaction (SILAR) process on to a fluorine doped tin oxide (FTO) substrate for photoelectrochemical solar cell application. From the optical absorption spectrum, a bandgap of synthesized ZnS photoanode was obtained around 3.47-3.62 eV. The surface morphology of the deposited photoanode was characterized using field emission scanning electron microscopy (FESEM). The average thickness of the deposited film was found to be 2.25 µm. We have fabricated photoelectrochemical solar cells using low crystalline ZnS as photoanode material and Coumarin-343 (C-343) dye as a sensitizer. photoelectrochemical solar cells have been built and their photocurrent, open-circuit voltage, fill factor and efficiency has been measured under one sun. Nyquist plot and Bode plot were plotted using electron impedance spectroscopy (EIS). The effective parameters were found. The photovoltaic properties of the ZnS based photoelectrochemical solar cell were studied. The maximum efficiency of 0.1% was observed for ZnS based photoelectrochemical solar cells.

Keywords: Zinc sulphide (ZnS); SILAR; Photoelectrochemical solar cell; Electrochemical characterizations.
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1. Introduction

The era of innovations and discoveries in the field of Solar cells began in the early 19th century when scientists observed that the solar energy was directly converted to usable electric energy. The necessity of large-scale solar electricity production has become progressively crucial for the reasons of energy security and climate change mitigation. Utilizing solar energy for various needs has become easy by the innovations in the field of solar technologies.[1] To date, solar energy technologies can be classified into three stages of its development such as the first generation based on single crystalline semiconductors,[2] a second-generation based on inorganic thin films,[3] and a third-generation being photovoltaic solar cells.[4] Semiconducting organic macromolecules, inorganic nanoparticles, or hybrids play a key role in third-generation solar cells which are indeed a solution in the semiconductor industry for tackling the energy crisis.[5] Compared to conventional silicon solar cells, photovoltaic solar cells[5] are considered with low fabrication cost and simple structures. Therefore, in the past two decades, a lot of researches has been reported in improving photoelectrochemical solar cell efficiency, new photo-anode materials, study of new electrolytes, and various dyes for sensitization of the photo-anodes.[6-9]

Surface morphology,[10] band structure, photochemical stability, and surface area[11] are some of the important factors to be considered while selecting a photoanode for the photoelectrochemical solar cell. Nano-sized TiO2 has been extensively studied as a photoanode for photoelectrochemical solar cell because of its porous nature, appropriate band structure for excitation of dye molecules, and excellent photochemical stability.[12] Light-harvesting efficiency of dye molecules[13] plays a vital role in the photo conversion efficiency of photoelectrochemical solar cells. High surface area of photoelectrode enables it for large uptake of dye molecules and to make it for an effective harvest of incoming light. Higher the light scattering better will be the light harvesting of the dye molecules for a typical nano-porous photo-anode.

In this study, we have introduced a metal chalcogenide family[14] as a photoanode for photoelectrochemical solar cells. ZnS is the material we have selected as a metal chalcogenide photoanode for photoelectrochemical solar cell application. A novel approach of replacing conventional metal oxide nano-
porous photoanode with metal chalcogenide was done effectively. For this demonstration, zinc sulfide (ZnS) is selected as the photo-electrode as it is an important II-VI semiconductor material, nontoxic, low-cost chemical and better chemical stability. The important physical properties of ZnS film are summarised in Table 1. The ZnS facilitates the incident photons of high energy to arrive at the window-absorber junction, improving the blue response of the photovoltaic cells, which provides better performance of the PEC cell. The position of the conduction and valance band of ZnS is at -4.25 and -7.45 eV respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the Coumarin-343 (C-343) dye are -5.7 and -3.11 eV respectively. The LUMO level position and the ZnS conductive band are compatible. Since it is suitable as a photoanode in PECs. Fig. 1 shows the band diagram and electron transport mechanism of C343 sensitized ZnS photoanode based DSSC.

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Band gap (eV)</td>
<td>3.68 at 300K</td>
<td>[23]</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>4.090</td>
<td></td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.356</td>
<td></td>
</tr>
<tr>
<td>Electron mobility (cm²/V-s)</td>
<td>250</td>
<td>[22]</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (µm/K)</td>
<td>6.36</td>
<td></td>
</tr>
<tr>
<td>Relative dielectric constant</td>
<td>8.9</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Physical properties of ZnS film.

Various researchers have reported that ZnS thin films have been deposited using different physical and chemical methods, as pulsed laser deposition,[15] thermal evaporation,[16] sputtering,[17] electrodeposition,[18] metal organic chemical vapor deposition,[19] chemical bath deposition,[20] SILAR (Successive Ionic Layer Adsorption and Reaction)[21] etc. Among these techniques, the SILAR technique is simple and economical. It is a unique method by which thin films of compound semiconductors can be deposited by alternate immersion of a substrate into solutions containing ions of each precursor. We can easily control the growth of the film by simply varying the deposition parameters.

In this report, optical studies were done for various SILAR cycles and the Tauc plot was plotted. It was observed that as the number of SILAR cycles increases the bandgap of ZnS photoelectrode was found to be decreasing. FESEM morphology of ZnS photoelectrode was showing a nanoporous nature which seems good for a photoelectrochemical solar cell photoanode. XRD pattern was showingallow crystalline nature of ZnS thin films. Later-on increasing the number of SILAR cycles the crystalline nature of thin films may be observed. M. Ragam et al.[22] reported a ZnS based photoelectrochemical solar cell with maximum solar conversion efficiency (η) of the photoelectrochemical solar cell with iodide electrolyte up to 0.016% with Methyl Blue sensitizer and 0.099% with Eosin-Y dye.

2. Experimental section
2.1 Materials
Zinc nitrate hexahydrate and sodium sulfide were purchased from Sigma Aldrich respectively. H₂O was purified by distillation and filtration. Pure double distilled water is used for SILAR cycles. Liquid electrolyte (EL141) containing I⁻/I³⁻ redox couple were supplied by Dyesol Co. Fluorine-doped tin oxide (FTO) glass (14 ohm/square) was from Pilkington.

2.2 Experimental methods
2.2.1 Pre-cleaning of FTO and glass substrates
The pre-cleaning of FTO and Glass substrates was achieved by sonicating it in soap solution, ethanol and distilled water. The zinc sulphide thin film was prepared at room temperature on thus pre-cleaned FTO and glass substrates.

2.2.2 Preparation of cationic and anionic precursors
Zinc Sulphide thin films were deposited on FTO using Zn(NO₃)₂ as cationic precursor and Na₂S as anionic precursor. 0.1M equivalent Zn(NO₃)₂ and Na₂S were taken and dissolved in 25 ml of DDW water respectively. Parameters used for the deposition of ZnS thin film are summarized in Table 2.

We have selected simple and cost-effective chemical route successive ionic layer adsorption and reaction (SILAR) for the synthesis of ZnS thin film photo-anodes. One SILAR cycle contains four steps: (a) the immersion of the substrate into the first beaker containing the aqueous cationic precursor, (b) rinsed with water, (c) immersion into the anionic precursor solution, and (d) rinsing with water. Numbers of SILAR cycles were repeated for uniform deposition of ZnS films on the pre-cleaned FTO substrate.[24-29]
2.2.3 Sensitization using coumarin-343

Before solar cell testing, the prepared films were immersed in standard metal-free organic Coumarin-343 dye (Sigma Aldrich, USA) with a concentration of 0.3 mM solution in ethanol for 180 minutes for sensitization. Table 3 shows the detailed description of the dye used for the sensitization of the ZnS photoanode.

Table 3. Detail description of dye used for sensitization of ZnS photoanode.

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>IUPAC Name</th>
<th>Chemical formulae</th>
<th>Molecular Weight (g/mol)</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin</td>
<td>C343</td>
<td>C_{26}H_{14}N_2O_7</td>
<td>486.565</td>
<td>3 \times 10^{-3}</td>
</tr>
</tbody>
</table>

3. Experimental characterizations

The microstructural properties of amorphous and crystalline nature of SILAR deposited ZnS thin films were carried out using X-ray diffractometer model Bruker D8 with CuKα radiation of wavelength 1.5405 Å in the range of 20°-80° using Rigaku D/Max-IIIc diffractometer. The surface morphology has been studied using Field emission scanning electron microscopy (FESEM: FEI Nova NanoSEM450) with an attached energy dispersive X-ray spectrometer (EDS: Bruker XFlash 6130) to qualitatively measure the sample stoichiometry. The sintered films were found porous signifying its suitability for photoelectrochemical solar cell applications. The absorption spectra of ZnS thin films with different SILAR cycles were measured with an optical JASCO V-770 UV-Vis spectrophotometer. The Absorption spectra were plotted in the wavelength range of 300-800 nm. Photovoltaic parameters of the fabricated cell were measured using a solar simulator (Oriel Sol-2A, Newport, USA). AM1.5 sunlight filters with illumination intensities 50 mW/cm² and 33 mW/cm² LED (Nvis Clean Tech, India). Keithley source meter 2420 (Keithley Instruments Ltd., USA) was used to measure J-V characteristics. The incident intensity of illuminating light sources was measured using sun meter (Solartron DSM 01, India) and digital lux meter (Lutron LX-101A, Lutron Electronic Enterprise CO., LTD., Taiwan). Optical luminescence of illuminated light source was measured using an optical spectrometer (Ocean Optics HR 4000, USA). The J-V curve of the solar cell was obtained in the dark condition. The J-V characteristics used to obtain open circuit voltage (Voc), short circuit current density (Isc), fill factor (FF), efficiency (Eff). Electrochemical impedance measurements were carried out using potentiostat/galvanostat (Vertex IVIUM Technologies, Netherlands).

4. Results and discussion

4.1 Optical study

The Absorption Spectra of as-deposited ZnS films with varied numbers of SILAR cycles were plotted as shown in Fig. 3. The absorption peaks were in the visible range of the spectrum.
Fig. 3 The absorption spectrum of ZnS thin films for various SILAR cycles.

Fig. 4 shows the tauc plot for various cycles of as-deposited ZnS films. The band-gap was found to be 3.62 eV - 3.47 eV for various deposition cycles. The calculated values are given in Table 4.

Table 4. The calculated bandgap Energy for the varied thickness of ZnS photoanodes.

<table>
<thead>
<tr>
<th>Varied SILAR Cycles</th>
<th>Energy Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS (40)</td>
<td>3.62</td>
</tr>
<tr>
<td>ZnS (50)</td>
<td>3.54</td>
</tr>
<tr>
<td>ZnS (60)</td>
<td>3.52</td>
</tr>
<tr>
<td>ZnS (70)</td>
<td>3.50</td>
</tr>
</tbody>
</table>

Fig. 4 The tauc plot of ZnS thin films for various SILAR cycles.

It was observed that as the number of SILAR cycles increases the optical bandgap was found to be decreasing. The energy gaps of the films of various temperatures have been determined by extrapolating the linear portion of the plots of \((\alpha h)\) against \(h\) to the energy axis. Sensitization of ZnS photoanode using Coumarin-343 in ethanol medium was carried out and the absorption spectrum was plotted in the wavelength range 200-800 nm.

Fig. 5 The UV-Visible spectra for the C-343 sensitized ZnS photoanode.

The UV-Visible spectra for the C-343 sensitized ZnS photoanode is as shown in Fig. 5. The spectrum shows two distinct peaks at 316 nm and 426 nm. The spectrum is attributed to organic dye C-343 and the absorption results are in reasonable agreement with the literature. It can be noted that the C-343 absorption spectrum consists of one sole peak at 460 nm.

Fig. 6 Low crystalline nature of deposited ZnS thin films deposited on an FTO substrate.
4.2 Structural studies
The SILAR Deposited ZnS films deposited on the glass substrate has been characterized by X-ray diffraction (XRD). Fig. 6 shows the Low Crystalline nature of deposited ZnS films on an FTO substrate were studied. From the XRD Graph, it was observed that peak at 28.7° (111) which confirmed the presence of ZnS in a low crystalline form which was matched with JCPDS Card No: 05-0566. Here in this article, the low crystalline nature of ZnS is exploited as an advantage in the sense that it provides a more uniform coverage of the FTO substrate by ZnS without gaps between the grains. The bilayer form of solar cell assembly plays an added advantageous since a second new layer will not come into direct contact with the FTO front through any possible gaps between ZnS grains.

4.3 Morphological studies
A field emission scanning electron microscope has been used to study the morphology of ZnS surface films. Fig. 7 shows the FESEM images of deposited films in the magnification range of 30000 and 100000. The FESEM image establishes the mesoporous nature of ZnS films which is a suitable morphology for the application of a photoelectrochemical solar cell. The average thickness of the ZnS film was found to be 1.43 µm using cross-section measurement in FESEM.

4.4 Compositional analysis
Energy Dispersive X-ray Spectrometer (EDS) was used to study the compositional analysis of SILAR deposited ZnS films. Fig. 8 shows the EDS spectrum of the surface film. The elemental analysis shows the presence of Zinc (Zn) and sulphur (S) along with some other elements. In the spectra, a carbon peak is observed due to the substrate holder and an oxygen peak might be due to the partial oxidation of the film. Presence of Si and Sn results from the substrate. The relative average atomic percentage ratio of Zn:S is nearly 1:1 for the films, indicating the formation of a film with stoichiometric composition.
The EDS spectra shows two peaks for the Zn atom attributable to the Kα and Lα. EDS characteristic peaks (keV) for Zn are 8.630 (Kα) and 1.012 (Lα) respectively. Although Zn atom has a peak (keV) characteristic at 2.307 (Kα).

4.5 Solar cell characteristics

Fig. 9 shows J-V Characteristics the C-343 sensitized ZnS photoanode photoelectrochemical solar cell with Platinum as counter and polyiodide as electrolyte. The J-V characteristics of the thus fabricated solar cell was carried out using a solar simulator (Oriel Sol-2A, Newport, USA). AM1.5 sunlight filters with illumination intensities 50 mW/cm² and 33 mW/cm² LED (Nvis Clean Tech, India). Keithleysource meter 2420 (Keithley Instruments Ltd., USA) was used to measure J-V Characteristics. The incident intensity of illuminating light source was measured using sun meter (Solatron DSM 01, India) and digital lux meter (Lutron LX-101A, Lutron Electronic Enterprise CO., LTD., Taiwan). The characteristics such as open circuit voltage (Voc), short circuit current density (Jsc), fill factor (FF), efficiency (η) were found as 0.52 V, 0.35 mA/cm², 0.59 and 0.1%, respectively. The calculated values are given in Table 5. Since ZnS is usually attempted as a collecting layer; here we try to study ZnS separately for solar cell applications. Further refinement will be done to enhance the efficiency with some efficiently.
Table 5. The Solar Cell parameters from J-V Characteristics under one Sun condition.

<table>
<thead>
<tr>
<th>Sample (No. Of Cycles)</th>
<th>J_sc (mA/cm²)</th>
<th>V_oc (V)</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS (40)</td>
<td>0.118</td>
<td>0.108</td>
<td>0.24</td>
<td>0.0031</td>
</tr>
<tr>
<td>ZnS (50)</td>
<td>0.004</td>
<td>0.040</td>
<td>0.25</td>
<td>0.0004</td>
</tr>
<tr>
<td>ZnS (60)</td>
<td>0.023</td>
<td>0.353</td>
<td>0.27</td>
<td>0.0022</td>
</tr>
<tr>
<td>ZnS (70)</td>
<td>0.350</td>
<td>0.520</td>
<td>0.59</td>
<td>0.1000</td>
</tr>
</tbody>
</table>

Table 6. Detailed report of EIS study of SILAR prepared ZnS photoanode (40-70 cycles) for photoelectrochemical solar cell application.

<table>
<thead>
<tr>
<th>Sample in Dark Room (No. of cycles)</th>
<th>R_TR (ohms)</th>
<th>R_CT (ohms)</th>
<th>R_CT/R_TR</th>
<th>L_n (μm)</th>
<th>η_conv (%)</th>
<th>τ_eff (ms)</th>
<th>τ_d (ms)</th>
<th>D_eff (cm²/s)</th>
<th>L_eff (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1: ZnS (70)</td>
<td>24.29</td>
<td>254</td>
<td>10.45</td>
<td>3.233</td>
<td>0.904</td>
<td>1.59</td>
<td>0.15</td>
<td>1.343</td>
<td>4.62</td>
</tr>
<tr>
<td>Sample 2: ZnS (60)</td>
<td>310.8</td>
<td>2170</td>
<td>6.981</td>
<td>2.64</td>
<td>0.856</td>
<td>0.014</td>
<td>2.03</td>
<td>0.031</td>
<td>6.60</td>
</tr>
<tr>
<td>Sample 3: ZnS (50)</td>
<td>428.9</td>
<td>1026</td>
<td>23.92</td>
<td>4.89</td>
<td>0.958</td>
<td>0.012</td>
<td>0.50</td>
<td>0.079</td>
<td>9.73</td>
</tr>
<tr>
<td>Sample 4: ZnS (40)</td>
<td>11050</td>
<td>11490</td>
<td>10.39</td>
<td>3.22</td>
<td>0.903</td>
<td>0.010</td>
<td>0.96</td>
<td>0.021</td>
<td>4.58</td>
</tr>
</tbody>
</table>

Fig. 10 shows the Bode plot of a) 40, b) 50, c) 60 and d) 70 SILAR cycles respectively sensitized with C343 Dye using EIS characterisation for photoelectrochemical solar cell applications.

4.6 Electrochemical impedance spectroscopy

Electrochemical Impedance spectroscopy was carried out in MHz to Hz frequency range with -0.8 V constant applied potential. Fig. 10 shows the Bode plot with characteristic frequency peak in the middle frequency range. The mean electron lifetime calculated from the relation:

\[ \tau_{\text{max}} = \frac{1}{2\pi f_{\text{max}}} \]  

Where, \( f_{\text{max}} \) is the maximum frequency. The electron lifetime was observed under dark conditions. When light is incident on the cell, the electrons are generated and current flows through the external circuit, which reduces the charge recombination resistance and this reduces the electron lifetime. The EIS study is carried out to determine electron transport and recombination resistance. Fig. 11 shows the Nyquist plot for the ZnS based photoelectrochemical solar cell.

The series resistance of solar cell was calculated from the Nyquist plot as ~16.6 ohms. The EIS equivalent circuit fitted parameters \( R_{\text{TR}} \) and \( R_{\text{CT}} \) can be used to calculate the parameters such as diffusion length \( (L_n) \), charge collection efficiency \( (\eta_{\text{cc}}) \), effective electron diffusion coefficient \( (D_{\text{eff}}) \), effective electron diffusion length \( (L_{\text{eff}}) \), which is useful to study the electron transport properties of the solar cell. With the help of the EIS Nyquist plot, the diffusion length is calculated using formula \( L_n = \sqrt{R_{\text{CT}}/R_{\text{TR}}} \) \[34\] Further effective electron diffusion co-efficient in the photoanode is given by \( D_{\text{eff}} = (R_{\text{CT}}/R_{\text{TR}}) \times (l^2/\tau_{\text{eff}}) \) \[35\] Where \( l \) is the thickness of ZnS thin film. Charge collection efficiency is calculated using \( \eta_{\text{cc}} = 1 - (R_{\text{TR}}/R_{\text{CT}}) \) \[36\]. Effective electron diffusion length calculated using \( L_{\text{eff}} = \sqrt{D_{\text{eff}} \times \tau_{\text{eff}}} \) \[37\] Effective electron diffusion length calculated using \( \tau_{D} = \tau_{\text{eff}} \times (R_{\text{TR}}/R_{\text{CT}}) \) \[38\] The calculated values are given in Table 6. \[39\]
Fig. 11 shows the Nyquist plot of a) 40, b) 50, c) 60 and d) 70 SILAR cycles respectively sensitized with C343 Dye using EIS characterisation for photoelectrochemical solar cell application.

5. Conclusions
We reported a low crystalline or amorphous nature of zinc sulfide (ZnS) as a photoanode for photoelectrochemical solar cell applications. For the synthesis of ZnS thin film photoanodes, we used simple and cost-effective chemical route successive ionic layer adsorption and reaction (SILAR) method. The dye sensitized ZnS nanoparticles show a strong visible absorption at 460 nm in UV-Vis analysis. The fill factor and efficiency of the device was found to be 0.59 and 0.1% respectively. Electrochemical studies of thus prepared ZnS photoanode were carried out. The mean electron lifetime and effective electron diffusion length were calculated as 1.59 ms and 4.62 μm respectively under dark condition. Structural Analysis shows that the nanoporous and crystalline nature of the ZnS thin films which implies that it is a suitable and considerable candidate for photoanode in the Photoelectrochemical solar cell.

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Conflict of interest
There are no conflicts to declare.

Supporting information
Not applicable

References

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