Chapter IV

Photosensitization of mesoporous TiO$_2$ with Zinc Sulfide (ZnS) nanocrystals

4.1 Introduction

The requirement of inexpensive and renewable energies has pushed a amazing research in the area of photovoltaic’s, which includes the QDSSC, it stand for best capable inexpensive candidate and belong to third generation photovoltaic’s .The idea of QDSCs is taken from the dye sensitized solar cell, in which a mesoporous wide band semiconductor material like ZnO, TiO$_2$ etc. is used on which light harvesting material is deposited, permeate with a redox electrolyte, and sandwich by a counter electrode. Basic distinction between DSSCs and QDSCs is make utilize of quantum dots nanocrystals of semiconductor materials as light absorber as a substitute of dyes. QDs show a number of compensation with respect to organic dyes as light absorbers associated to large intrinsic dipole moments increasing separation of charge. Quantum dots are largely used in light emitting diodes and solar cells due to their size dependence properties, higher photostability, and flexible solution processing compared to conventional organic dyes. Today, instead of homostructures one-dimensional semiconductor-based heterostructures have been recognized to have enhanced performance in physical properties, these heterostructures alter properties of materials such as catalytic, optical, and electrical. Semiconductor sensitization is the method in which Photo generated electron transfer between a particulate narrow gap semiconductor and a broad gap semiconductor. The merits of semiconductor sensitization are it can soak up visible light in a broad wavelength range and is usually steadier as compared to organic dyes. Throughout photocatalysis experiment with large
bandgap semiconductor TiO$_2$ holes, electrons are produced on surface of TiO$_2$ and they transformed into in quantum states close to the surface later than energy relaxation. Through this course recombination of electron holes takes place very fast to generate the luminous excited ions states, therefore the charge carriers are not capably transfer to substrate for redox reaction. This can be achieve by creating a Heterojunction structure which can be created by loding by an additional semiconductor; generally QDs, at the surface of TiO$_2$ such as TiO$_2$/CdS, TiO$_2$/CdSe, TiO$_2$/PbS Heterojunction and thus improve the catalytic performance of photo-catalysts. The most of QDSSCs the sensitzers QDs used are poisonous elements such as cadmium, lead, and arsenic, etc. and there is a reasonable need to develop low toxic QD sensitizers. Toxicity, antireflective and optical coatings like properties of Zinc Sulfide create this material an outstanding applicant for solar cells third generation. In case of heterostructures solar cell thin films of ZnS are generally used as components, performance of solar cell made from PbS can be improved be using ZnS as a passivation layer. Band gap energy of ZnS is about 3.7 eV; it appears to be a very hopeful material for photocatalysis application due to its fast creation of electron–hole pairs by photo excitation and highly negative reduction potentials of excited electrons. Due to some restrictions of zinc sulfide nanoparticles such as big band gap of 3.6 eV photocatalytic activity has not been studied in detail; it works only under UV light irradiation, which accounts as a small part of the solar energy.

In this chapter ZnS has been successfully deposited onto a mesoporous 0.1M TiCl$_4$ concentration TiO$_2$ surface prepared by chemical bath deposition (CBD) using SILAR with different cycles (adsorption times). In this method immersion of TiO$_2$ nanostructured electrodes in solutions of Zn$^+$ and S$^-$ to deposit ZnS nanocrystallites on the TiO$_2$ surface successively. The combination was then assembled to typical QD-sensitized solar cells to
investigate its photovoltaic application. The effect of different deposition time on the cell performance was studied as well.

4.2 About zinc sulfide

ZnS is a significant II–VI semiconductor, its optical transparency lies in region from ultraviolet to the infrared. As this optical transparency is shared with thermal, chemical stabilities ZnS acts as a extensively used materials for optical windows. Due to the large exciton binding energy in contrast with the room temperature thermal energy it is also capable for room temperature exciton devices. Sphalerite, cubic and hexagonal are the three forms ZnS. At room temperature cubic form is stable, while the wurtzite is stable above 1020 °C at atmospheric pressure. Various methods are developed to create one dimensional (1D) ZnS nanostructures like CVD, thermal evaporation of ZnS powder, electrochemical deposition.

4.2.1 Application of ZnS

* It is used in DNA detectors. Electroluminescence devices and photonic crystal devices.
* Photocatalyst property of ZnS is applicable for degradation of water pollutants and decrease of toxic heavy metals
* Due to its large refractive index it is used in making an antireflective coating
* It used in optoelectronics detectors, modulators and emitters.

4.3 Experimental details

All chemicals used in this research were of investigative grade obtained from Merck and used with no further purifications. FTO substrates were used because of their transparency and fine stability at high temperature. Using acetone FTO base were cleaned in ultrasonic bath at normal temperature for 30min and dried with nitrogen (N₂) air stream. The concentration of TiCl₄ was
changed by adding a suitable amount of deionized water in stock TiCl$_4$ solution. Preparation of thin films of TiO$_2$ for different concentrations of TiCl$_4$ is explained in previous chapter i.e. 3, for further work we have used 0.1M concentration TiCl$_4$ for making thin films TiO$_2$. ZnS quantum dots were adsorbed onto the mesoporous film of TiO$_2$ by using SILAR method. Aqueous solution of 0.1M zinc nitrate (Zn(NO$_3$)$_2$) in ethanol for zinc precursor and 0.1M sodium sulfide (Na$_2$S) in water for sulfur precursor were prepared for cationic (Zn$^{2+}$) and anionic (S$^{2-}$) precursors, respectively, so as to form ZnS QDs.

### 4.3.1 Experimental setup for deposition of ZnS on TiO$_2$ films by SILAR method

Schematic of SILAR method for deposition semiconductor QDs on TiO$_2$ films is explained in chapter 3 (Fig. 3.2). The deposition of ZnS on TiO$_2$ (0.1M concentration of TiCl$_4$) thin film is carried out using four beakers system at room temperature. The beaker one was containing the aqueous solution of 0.1M zinc nitrate (Zn(NO$_3$)$_2$) in ethanol and in beaker two and four were filled with water deionized water. The beaker three was having 0.1M sodium sulfide (Na$_2$S) with water as solvent. One SILAR cycle was design as follows; (1) deposition of zinc species for 10 s, (2) rinsing with DI water for 5 s to purge loosely bounded zinc species, (3) to form stable ZnS reaction with Na$_2$S precursor solution for 10 s (4) rinsing with DI water for 5s to remove excess species ZnS. The quality of the film was poor due to a powdery deposit due to the higher concentration of precursor solutions resulted in to a higher growth rate. Initially bare TiO$_2$ sample were deep in zinc nitrate (Zn (NO$_3$)$_2$) solution. Zinc nitrate dissociates as and Zn$^{2+}$ ions were adsorbed onto the surface. After that, S$^{2-}$ anions created in the solution of sodium sulfide reacted with Zn$^{2+}$ ions on the surface to produce ZnS. the ionic reaction of ZnS as follows
\[ \text{Zn}^{+2} + \text{S}^{2-} \rightarrow \text{ZnS} \]

After the washing process ZnS loaded TiO\(_2\) electrode was dried with a N\(_2\) air stream. The TiO\(_2\) films loaded with ZnS QDs by 10 cycles, 20 cycles and 30 cycles were presented as Z\(_1\), Z\(_2\) and Z\(_3\), respectively. Annealing of TiO\(_2\)/ZnS film was carried for 60 min in air at 523 k and this film is used for further characterizations.

4.3.2 Measurements

X-ray diffractometer was used to find out Crystal structure of ZnS adsorbed TiO\(_2\) electrodes. The surface morphologies of ZnS adsorbed TiO\(_2\) electrode was observed by field-emission scanning electron microscopy. UV-Vis spectrophotometry was used for the measurement of absorbance spectra of ZnS loaded TiO\(_2\) electrode. Under air mass 1.5 and by using a Keithley 2400 source meter with the help of provided software. The current-voltage (IV) characteristics of the ZnS QDSSCs were measured. EIS spectra were recorded with an Impedance Analyzer in a frequency range of 0.01 Hz–1.5 MHz with 50 mV amplitude. EIS measurement were carried out at open circuit potentials under 1 sun AM 1.5 G light illumination. Impedance parameters were determined by fitting impedance spectra using Z-view software. All the cells were covered with a black mask except for the active area during the measurements. IPCE of TiO\(_2\)/ZnS photoanodes were measured by incorporating individual cell with an active area of 0.5 X 0.5 cm\(^2\) which was sealed using a spacer film with polysulfide electrolyte.

4.4 Characterization details

4.4.1 Structure analysis measurements
The information obtained by this family of characterisation offered a robust image of crystallographic structure. Figure 4.1 shows the XRD of the photoelectrode TiO$_2$ after ZnS deposition by SILAR method for 10, 20 and 30 cycles named as Z$_1$, Z$_2$ and Z$_3$ electrodes. The intensity of the peaks was increased with the amount of deposited material due to increase of number deposition cycle. The comparatively low intensities and broadness of X-ray diffraction peaks were supposed to come up from the fact that the particles were nano-sized and the ZnS was thinly covered on TiO$_2$. The spectra obtained had the characteristic diffraction peaks at $2\Theta = 33.11^\circ$, $37.17^\circ$, $50.90^\circ$, $53.89^\circ$, $61.0^\circ$ and $64.90^\circ$ corresponding to the (310), (401), (203), (601), (422) and (604) peaks which are in a good agreement with those given in JCPD data card [46-1238] corresponds to rutile TiO$_2$. The diffraction peaks at $2\Theta = 25.76^\circ$ and $26.8^\circ$ were for (201) and (100) peaks of ZnS; in good agreement with those given JCPDS data card [02-1330] corresponds to ZnS.
4.4.2 Morphological change

**Figure:** 4.2. FESEM images of bare and ZnS deposited TiO$_2$ electrodes (10, 20 and 30 SILAR cycles).

A FESEM image was taken to understand effect SILAR ZnO layers on the morphological growth of TiO$_2$. Diagram 4.2 shows SEM images of the pristine and TiO$_2$ deposited with ZnS film electrodes obtained for 10, 20 and 30 SILAR cycles. The entire film surface has compact, dense and uniform morphology due to the homogeneous nucleation process. After deposition of ZnS NPs on TiO$_2$ by SILAR method with different cycles same TiO$_2$ FESEM image was turned to different forms, the significant morphological change was confirmed. The porous structure of TiO$_2$ film was unchanged even after the ZnS deposition and a flake form of ZnS was also demonstrated. Morphology of the sample $Z_1$ showed irregular microspheres. While with increasing the SILAR cycle number, the morphology of $Z_2$ was spherical but bit aggregate-type and with air cracks. Smooth surface, good substrate coverage without cracks and compact morphology were confirmed for sample $Z_3$. 
4.4.3 EDAX analysis

![EDAX spectrum of ZnS deposited TiO₂](image)

Figure 4.3 EDAX spectrum of ZnS deposited TiO₂

In addition to XRD measurement the EDAX analysis were carried out with the aim to conform the atomic percent of Zn and S on Z₂ sample i.e. obtained after 20 cycles. EDX mapping proved the presence of Zn and S. Only Zn and S mapping was carried out so to avoid interference of Ti and O from TiO₂ sample and atomic % ration was almost 1:1, supporting for the formation of ZnS over TiO₂.

4.4.4 Optical studies
The photoabsorption property of semiconductors is a main task in the photocatalytic activity, optical absorption properties of samples were carried out by UV–vis absorption spectra. Fig. 4.4 gives the UV-Vis absorbance spectra of ZnS decorated TiO$_2$ film electrode obtained for 10, 20 and 30 SILAR cycles. The optical absorbance was measured in wavelength of range 375 - 850 nm. The absorption edge was obtained at a shorter wavelength side. From fig. of spectra it was found that ZnS shows strong photo-absorption property in the UV light region at 410 nm. As compared to absorption spectra of bare TiO$_2$ electrode (from chapter 3 figure 3.12) absorption for ZnS decorated TiO$_2$ was much higher supporting for the capping of ZnO over TiO$_2$.

4.4.5 Incident photo-to-electron conversion efficiency
Figure 4.5 IPCE spectra of ZnS deposited TiO$_2$ electrode $Z_1$, $Z_2$, and $Z_3$.

External quantum efficiency of the TiO$_2$ surface treated with ZnS with electrodes $Z_1$, $Z_2$, and $Z_3$ were measured and is shown figure 4.5. The IPCE spectra of $Z_1$-$Z_3$ electrodes showed maximum conversion efficiency in the wave length range i.e. 320 to 500 nm. As number of SILAR cycles increases followed by an increase in IPCE over entire visible light region, The obtained IPCE values for 10, 20, and 30 cycles were ~7%, ~13% and ~24% respectively.
4.4.6 Photoelectrochemical measurements

![J-V curves of ZnS deposited TiO₂ electrode Z₁, Z₂, and Z₃.](image)

**Figure**: 4.6 J-V curves of ZnS deposited TiO₂ electrode Z₁, Z₂, and Z₃.

**Table 4.1.** J-V performance of ZnS-TiO₂ electrodes for different cycle numbers.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Efficiency(η)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z₁</td>
<td>0.62</td>
<td>0.50</td>
<td>0.48</td>
<td>0.14</td>
</tr>
<tr>
<td>Z₂</td>
<td>1.41</td>
<td>0.63</td>
<td>0.45</td>
<td>0.43</td>
</tr>
<tr>
<td>Z₃</td>
<td>2.47</td>
<td>0.67</td>
<td>0.42</td>
<td>0.71</td>
</tr>
</tbody>
</table>

After successfully deposition of ZnS NPs on TiO₂ electrode by SILAR method for different cycles, these modified nanostructured electrodes were envisaged in photoelectrochemical cells application. **Fig 4.6** gives the comparison of photocurrent-voltage (J-V) characteristics of three electrodes namely $Z₁$, $Z₂$ and $Z₃$ with Air Mass 1.5G illumination at 100mWcm$^{-2}$ from xenon lamp. When ZnS layer deposited on TiO₂ electrode, ZnS acted as passivation layer. From literature survey, Zinc sulfide proven a good passivation layer for minimizing recombination
process at the TiO$_2$/QD/electrolyte interface. In the present case, presence of ZnS in addition to TiO$_2$ increased the UV part of visible light and thereby the photoconversion efficiency was increased from 0.14 to 0.71% from Z$_1$ to Z$_3$ electrodes. Device parameters such as J$_{sc}$, the V$_{oc}$, FF, and conversion efficiency of these cells measured in 0.1 M polysulfide electrolyte were deduced from J-V curves is summarized in Table 4.1 The bare TiO$_2$ (0.1M conc. of TiCl$_4$) photoanode showed J$_{sc}$ as 2.18 mA/cm$^2$ and V$_{oc}$ as 0.55V with overall photoconversion efficiency of 0.55%. When these TiO$_2$ electrodes surface treated by ZnS layer for different SILAR cycles, initially for 10 and 20 SILAR cycles the J$_{sc}$ drops from 2.18 to 1.41 mA/cm$^2$ also PCE decreases to 0.55% -0.14%. But for larger thickness i.e. For 30 SILAR cycles PCE increases to 0.71%, at this thickness ZnS acts as passivation layer. The J$_{sc}$, V$_{oc}$ and η for electrode Z$_3$ are 2.47mA cm$^{-2}$, 0.67V and 0.71%.

4.4.7 Electrochemical impedance spectroscopy

![Nyquist spectra of ZnS/TiO$_2$ electrodes Z1, Z2 and Z3.](image.png)
The EIS spectrum was employed to analyze the electron transport behavior, which distinguishes the charge transport resistance and chemical capacitance of the device. The high and low frequency arcs were because transport of charge behavior at Pt/electrolyte boundary and second representing contribution of electron transfer through the photoanode consisting of nanocrystallites semiconductor. The EIS measurement was carried out by Nyquest plot which is shown in Fig. 4.7 and the values of $R_s$, $R_1$ and $R_2$ were calculated by using Z-view software and are tabulated in Table 4.2. Thickness of ZnS on surface of TiO$_2$ electrode was increased with 10, 20, 30 cycles. As number SILAR cycles of ZnS increased value of $R_s$ get increases from 2.40 $\Omega$ cm$^2$ to 3.55 $\Omega$ cm$^2$ for Z$_1$ to Z$_3$ electrodes. Also $R_1$ value get decreased from 6.81 to 4.30 $\Omega$ cm$^2$, but as compared to this $R_2$ show significant variation in charge transfer resistance, it directly effect on photoconversion efficiency. $R_2$ is get decreased from 148.82 to 94.39 $\Omega$ cm$^2$ for Z$_1$ to Z$_3$ electrode.

**Table 4.2.** Parameters obtained by EIS spectra.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$R_s$</th>
<th>$R_1$</th>
<th>$R_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z$_1$</td>
<td>2.40</td>
<td>6.81</td>
<td>148.82</td>
</tr>
<tr>
<td>Z$_2$</td>
<td>3.03</td>
<td>4.94</td>
<td>130.97</td>
</tr>
<tr>
<td>Z$_3$</td>
<td>3.55</td>
<td>4.30</td>
<td>94.39</td>
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