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PHOTOELECTROCHEMICAL CELLS USING n-TYPE ZnSe ELECTRODES IN AQUEOUS ELECTROLYTES

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Attempts have been made to enhance the conversion efficiency of photoelectrochemical cell using electrolytically deposited ZnSe semiconductor electrode in iodide–triiodide electrolytes. The performance parameters of the cell include measurements of photocurrent, photovoltage, fill factor, cell efficiency, flat band potential, band gap energy and stability. CdSe electrode material when mixed with ZnSe could enhance the performance of the photoelectrochemical cell.

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1. Introduction

Thin film semiconductor electrode can be employed to construct a photoelectrochemical cell based on liquid junction. The thin film electrodes are made on a substrate which can form an excellent ohmic contact and exhibit good adhesion to the semiconductor to the semiconductor thin film. The first work on ZnSe electrode was reported in the year 1967(1) by William who investigated the interface between n-type ZnSe and electrolyte solution. The ZnSe – HCl (1Molar) interface was assumed to be a Scotty barrier type where the barrier height was found to be 2.0 to 2.6 eV using single crystal. For getting n-type semiconductivity, ZnSe was doped with Aluminum at 1030^0C. He observed that due to photochemical decomposition of ZnSe, red elemental selenium layer was formed on the surface of the crystal according to following reaction.

$$ZnSe_{(s)} \rightarrow Zn^{+2} + Se^0 + 2e^- \quad (1)$$

Electrochemical reaction and electronic transport in ZnSe semiconductor electrode surface in the form of single crystal have been studied (2). ZnSe with low resistivity (1-10 ohm. cm) can be formed from single crystal by dipping with iodine followed by annealing under saturated vapor of Zinc for 13 hours at 600-1000^0C (3). ZnSe was found to undergo dissolution due to the following reactions when exposed to light.

$$ZnSe + 2H_2O + 2h^+ \xrightarrow{h\nu} Zn(OH)_2 + Se + 2H^+ \text{ anodic process}$$
$$2H^+ + 2e^- \rightarrow H_2 \text{ cathodic process}$$
$$ZnSe + 2H_2O \rightarrow Zn(OH)_2 + Se + 2H^+ \quad (2)$$

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Therefore it is found that ZnSe single crystal prepared in such an expensive and tedious manner is not stable due to photoanodic dissolution and thus not suitable for its use as photoanode in photoelectrochemical cell.

Polycrystalline ZnSe can be prepared by treating Zinc and Selenium powder in an evacuated quartz ampoule at 1380^0C (4). It has been shown that cathodic electrodeposition technique is superior to other process to prepare thin film semiconductor electrode in the polycrystalline form. Miller and Heller (5) prepared thin film of CdS by anodizing cadmium rod in an alkaline electrolyte solution containing sulphide ions. The same procedure was adopted again by miller et al (6) to produce polycrystalline CdSe using an electrolyte containing $1MK_2Se$ and 1MKOH. The efficiency of photoelectrochemical cell with anodically formed CdSe was low due to limited thickness of CdSe layer which is too thin to absorb maximum portion of the incident light. In contrast cathodic electrodeposition is not limited to thickness as electron transport through electrode-solution interface is required. The electrolyte contains Cd^{2+} ions and a selenium compound as seleneous acid (H_2SeO_3) which is reduced at the cathode forming a semiconductor thin film on the substrate.

$$Cd^{2+} + H_2SeO_3 + 4H^+ + 6e^- \xrightarrow{h\nu} CdSe + 3H_2O \quad (3)$$

It has been reported that (7) selenosulphite ion ($SeSO_3^{2-}$) may be used as the source of free selenide ions for subsequent reaction with Cd^{2+} ions.

$$SeSO_3^{2-} + 2e^- \rightarrow Se^{2-} + SO_3^{2-} \quad (4)$$

In our present investigation we have prepared ZnSe thin film by electrochemical method using selenosulphite as the source of free selenide ions. A simple two step method was followed to prepare ZnSe thin film on conducting glass substrate, the first method being cathodic deposition of zinc from electrolytic bath containing Zn(II) ions and the second being anodisation of the film anodically using selenosulphite ions. It is known that cadmium is soluble on zinc in solid state. The n-ZnSe is a wide band gap semiconductor with E_g value 2.6eV and CdSe has E_g value 1.7eV. Again the value of ionic radii of Cd (II) and Zn (II) are nearly the same and both are almost similar in all respect. Therefore, there is possibility of formation of solid solution when a small amount of CdSe is mixed with ZnSe. Mixing of CdSe to ZnSe may decrease the band gap energy of ZnSe and the ZnSe-CdSe with lower band gap energy would be more effective photoanode while used in photoelectrochemical cell.

Keeping in mind this idea, the study of photoelectrochemical cell using mixed ZnSe-CdSe semiconductor electrode has been under taken.

2. Experimental

The SnO_2 coated glass substrates were used for depositing semiconducting material. The glass substrates boiled in chromic acid were thoroughly washed with deionized water. They are then activated by dipping in $SnCl_2$ solution followed by drying in an oven at 250^0C for 30 minutes. An ultra thin layer of SnO_2 could be formed on the surface (8). Zinc was deposited on the cleaned substrates electrolytically from a cyanide bath containing $Na_2[Zn(CN)_4]$ complex in an alkaline medium. The current density of $2A/dm^2$ was allowed to pass for 8hrs at a temperature of 30^0C±1. The solution was slowly stirred by a magnetic stirrer. Due to low degree if dissociation of the complex Zinc cyanide ion, the metal ion concentration is very low and has a high throwing power. The uniform, coherent, and smooth thin film of zinc deposited on the substrate was cleaned slowly with deionized water. Now the deposited zinc metal was anodized from an aqueous solution of sodium selenosulphite (pH =10) having concentration about 0.4M. the anodizing current density was $0.6A/dm^2$ for a period of 40 minutes. A thin film of ZnSe was formed according to the following reactions.

$$Na_2[Zn(CN)_4] \rightarrow 2Na^+ + [Zn(CN)_4]^{2-} \quad (5)$$

$$\text{At the cathode} \quad [Zn(CN)_4]^{2-} \rightarrow Zn^{2+} + 4CN^- \quad (6)$$

$Zn^{+2} + 2e^- \rightarrow Zn$

At the anode $SeSO_3^{2-} + 2e^- \rightarrow Se^{2-} + SO_3^{2-}$

$Zn + Se^{2-} \rightarrow ZnSe$

$SeSO_3^{2-} + Zn \rightarrow ZnSe + SO_3^{2-}$

Thin film of mixed cyanide of Zn (Ii) and Cd (II) was prepared on the glass substrate in the same manner as above.

The thickness of the deposited film was found to be approximately 4m as measured from weight difference method.

3. Photovoltaic measurement

The electrochemical photovoltaic cells have been constructed with the above polycrystalline thin film electrodes using an aqueous solution of 1M KI and 0.01M I_2 which constitute the iodide-triiodide (I^-/I_3^-) redox couple. The potential of the redox system was -0.234 volt as measured against a SCE. The photovoltage is difference in potential in presence of light (V_L) and in dark (V_D) i.e. ($V_L - V_D$). The dimension of the cell was 4 x 4 x 6 cm^3. A platinum black electrode of 1cm^2 geometrical area was used as counter electrode (CE). While studying the current –voltage characteristics of the photoelectrochemical cell, the potential of the semiconductor electrode working electrode (WE) was measured against a saturated calomel electrode (SCE) with the help of a Yamuna digital multimeter (Model - 1010). The illumination intensity was 40mW/cm^2 as measured by Suryamapi solar intensity meter (obtained from central electronics Ltd, India).All the chemical employed in the study were of Anal R grade.

4. Results and discussion

The photovoltage (V_{ph}) of the photoelectrochemical cell based on n-ZnSe and mixed ZnSe-CdSe semiconductor electrodes was found to have a logarithmic relation with the intensity of light (fig-1). For the mixed ZnSe-CdSe electrode the slope ($dV_{ph}/d\ln I_L$) of the curve has been found to be greater than that for the value of slope for n-ZnSe indicating nonequilibrium distribution of electrons and holes which contributes to the open circuit voltage (9).

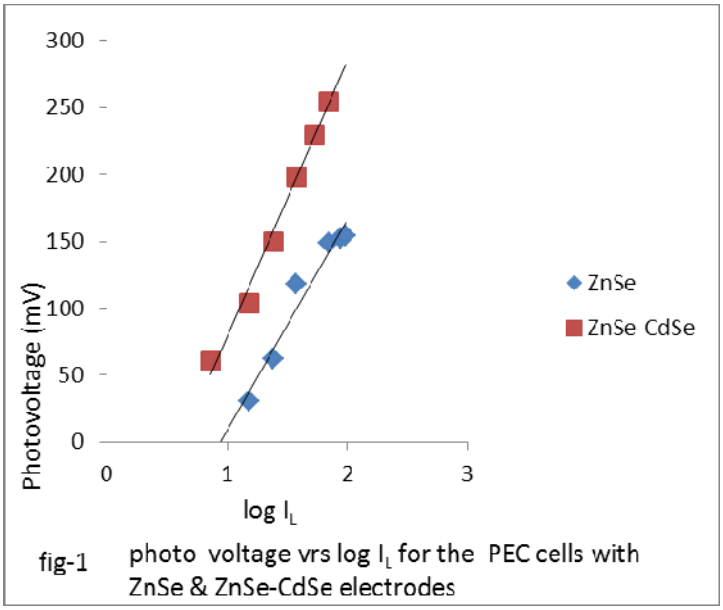
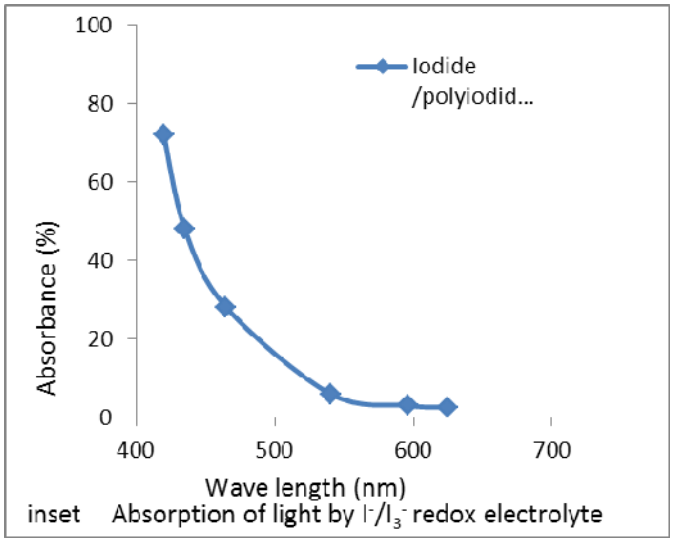


fig-1 photo voltage vrs log I_L for the PEC cells with ZnSe & ZnSe-CdSe electrodes

The spectral photoresponse of the photoelectrochemical cell was carried out by measuring photocurrent as a function of wavelength of light (λ) (fig2). The decrease of I_{ph} on shorter

wavelength side (400-450nm) is due to absorption of light in the iodide-polyiodide electrolyte (inset fig-2) and may also be probably due to high surface recombination of photogenerated carriers by surface state (10-11). The decrease of photoresponse on larger wavelength side of the peak (fig-2) may be attributed to transition between defect



inset Absorption of light by I^-/I_3^- redox electrolyte

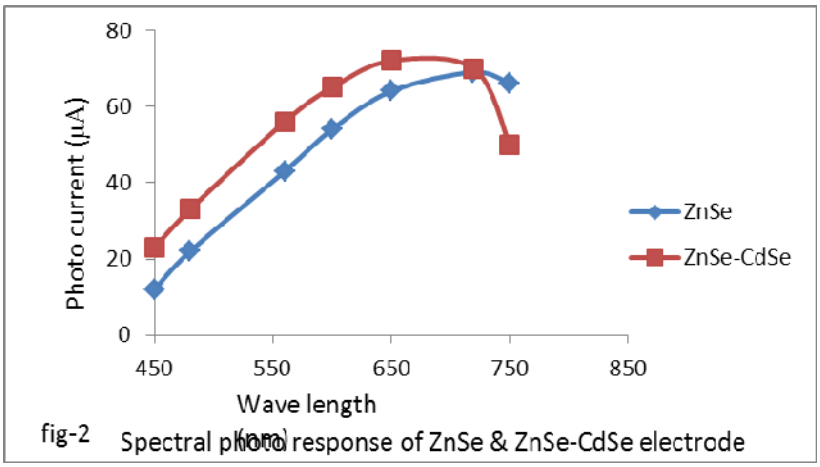


fig-2 Spectral photo response of ZnSe & ZnSe-CdSe electrode

levels so that no incident may be utilized (12). The peak current was more for mixed selenide semiconductor than ZnSe electrode. For the mixed ZnSe-CdSe electrode, shifting of peak in spectral response of photoelectrochemical cell towards the lower energy side was observed indicating a lowering of band gap energy value to some extent.

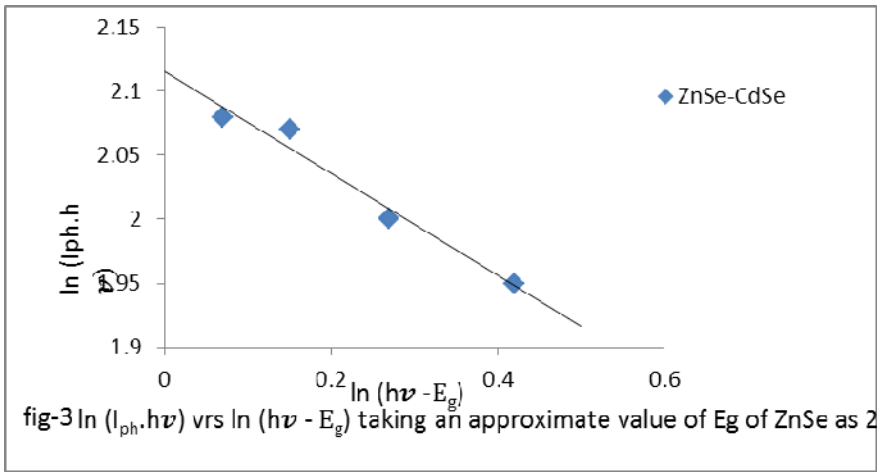


fig-3 ln (I_{ph}.hν) vrs ln (hν - E_g) taking an approximate value of Eg of ZnSe as 2

From ln(I_{ph}. hν) versus ln(hν-E_g) plot (fig-3) using E_g value of ZnSe as 2.6eV, the slope of the line was found to be approximately one and the electronic transition is direct. The band gap energy (Eg) of the electrodes was determined from the (I_{ph}.hν) ^{2} versus hν plot (fig-4). The E_g value for n-ZnSe and mixed ZnSe-CdSe electrodes have been found to be 2.7eV and 2.45eV respectively. The above value of E_g as found for n-ZnSe is similar to the value reported earlier (13). Therefore it is clear that by mixing CdSe material with ZnSe, the mixed semiconductor electrode was found to have lower E_g value than ZnSe.

From the current-voltage (I-V) behaviors under illumination intensity of 40mW/cm^2 (fig-5) the conversion efficiencies of photoelectrochemical cell using ZnSe and mixed ZnSe-CdSe electrodes have been found to be 0.20% and 0.60% respectively and fill factors 0.40 and 0.46. The low efficiency in the investigation might be due to high resistance of the cell and electrolyte absorption. However, it has been observed that fill factor (ff) and efficiency (η) increase with addition of CdSe into ZnSe semiconducting materials.

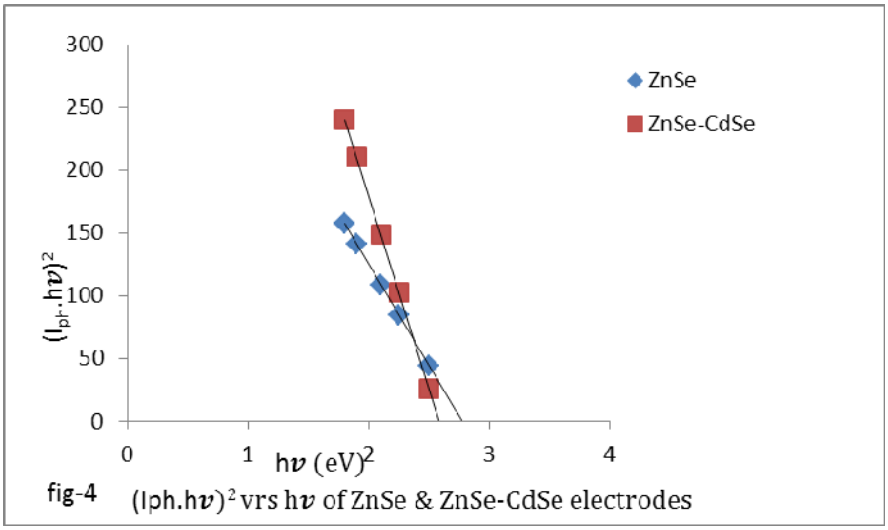


fig-4 (Iph.hν)^2 vrs hν of ZnSe & ZnSe-CdSe electrodes

The flat band potential (V_{fb}) of a semiconductor is an important factor in explaining the charge transfer process across the semiconductor-electrolyte junction of the photoelectrochemical cell. The V_{fb} values as obtained from (Iph)^2 versus V plot (fig-6) have been found to be 0.18 and 0.3 volts for ZnSe and mixed ZnSe-CdSe electrodes respectively. Higher negative value of V_{fb} for the mixed selenide semiconductor electrode of Zn (II) and Cd (II) indicate that more open circuit potential (V_{oc}) could be achieved by this doping method.

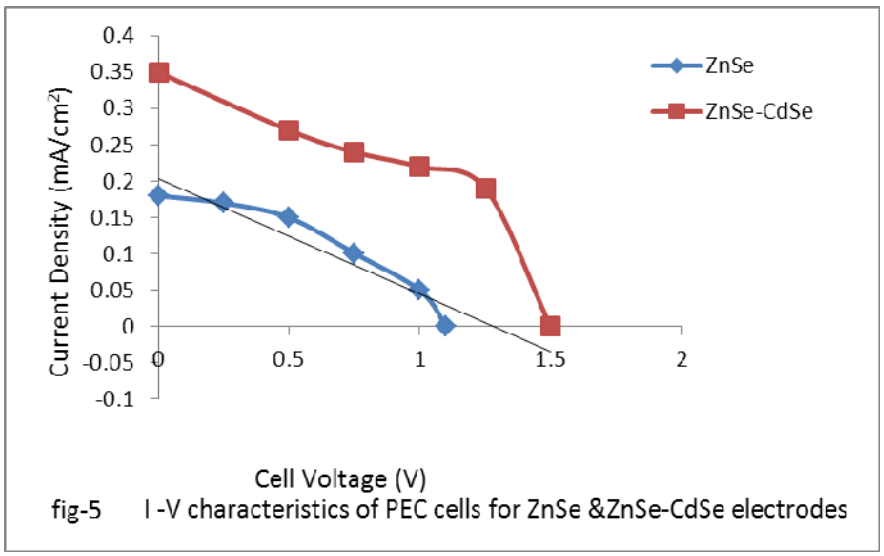


fig-5 I -V characteristics of PEC cells for ZnSe &ZnSe-CdSe electrodes

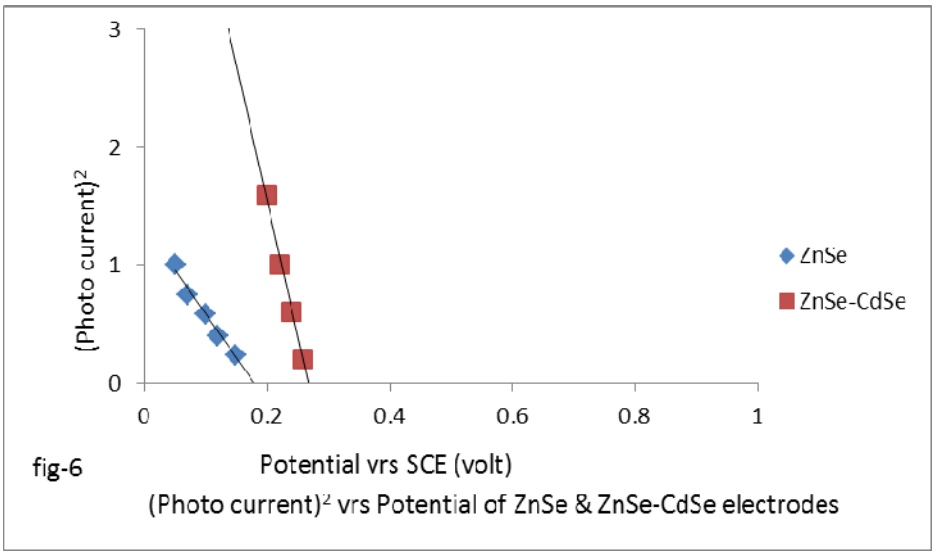


fig-6 (Photo current)² vrs Potential of ZnSe & ZnSe-CdSe electrodes

5. Conclusion

In our investigation, dark current observed was virtually negligible indicating no dissolution of the photoelectrode materials. The photocurrent was observed with illumination for 18 hours and found to be nearly constant indicating stability of the electrode. The photochemical decomposition of ZnSe could be suppressed by the use of higher concentration of iodide-triiodide redox electrolyte. Though we got reproducible result, the photocurrent obtained is not sufficient to be immediately useful for a practical application. However it is well known that conversion efficiency of such thin film can be enhanced considerably by proper thermal, photochemical and electrochemical surface treatments.

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