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Immobilisation of CdS, ZnS and mixed ZnS–CdS on filter paper Effect of hydrogen production from alkaline $Na_2S/Na_2S_2O_3$ solution

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Abstract

The rate of production of molecular hydrogen upon illumination with solar radiation/visible light of immobilised CdS, ZnS and mixed CdS–ZnS on Whatman filter paper in Na_2S/Na_2SO_3 solution have been studied. Enhancement of rate of hydrogen evolution has been observed by codeposited CdS with ZnS on Whatman filter paper. Mark enhancement in the rate of hydrogen liberation has been achieved by the catalyst at about 80 mol% Zn for a solid solution of Cadmium–Zinc sulphide embedded in Whatman filter paper.

Keywords: Cadmium–zinc sulphide embedded in Whatman filter paper; Electron hole separation; Hydrogen production

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1. Introduction

CdS [1–18] in spite of so many favourable characteristic properties is not efficient generator of hydrogen using sunlight. But improved result has been obtained if other chalcogenides like ZnS having conduction band much more negative than that of CdS, is mixed with the latter [2,8,18–23] to see if it enhanced hydrogen generation from solution containing 0.24 M Na_2S, 0.35 M Na_2SO_3.

It has been observed that efficiency of hydrogen production depends on exposed surface area of photocatalyst. The more the exposed surface area of the photocatalyst, the more will be the efficiency. It is very difficult to measure the exposed surface area of suspended photocatalyst powder. Moreover, powdered sample cannot remain suspended in strong electrolyte for long time. For this reason, the photocatalyst in mixed sodium sulphide–sodium sulphite solution was stirred magnetically with magnetic stirrer to keep it in suspension. Such a system can be used in batch process. Changing the deplenished solution/putting in fresh solution is cumbersome. To avoid these difficulties we have attempted to embed a photocatalyst in different matrices. It is a great advantage to use immobilised photocatalyst matrices for efficient production of hydrogen employing minimum volume of sodium sulphide solution, and minimum amount of photocatalyst with large surface area. We have tried different materials like filter paper, glass plate, perchment paper, perspex sheet, etc. as matrices for immobilisation of the photocatalyst. Out of these, the photocatalyst immobilised on filter paper was found to be most efficient for production of hydrogen from Na_2S–Na_2SO_3 solution in presence of sunlight.

2. Experimental details

2.1. Deposition of photocatalysts on filter paper

CdS or ZnS immobilised filter paper (Whatman no. 1) was prepared by using $Cd(CH_3COO)_2$ or $Zn(CH_3COO)_2$ solution and H_2S. Acetate or mixed acetate solutions with different molar concentrations were used (Table 1) for deposition of sulphide or mixed sulphide with different molar ratio on filter paper. The efficiency of production of hydrogen was found to be maximum when solutions containing $Cd(CH_3COO)_2$ and $Zn(CH_3COO)_2$ in 1:4 molar ratio was used for soaking the paper and subsequent conversion to sulphide. The semiconductor photocatalyst immobilised on filter paper was prepared by different methods.

(i) The mixed semiconductor catalysts (CdS–ZnS) immobilised on filter paper was prepared by dipping a piece of Whatman filter paper no. 1 (area and weight of the filter paper was known) in a solution of zinc and cadmium acetate for 2 min and dried in hot air. It was

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Table 1
Rate of evolution of hydrogen with different modes of preparation of photocatalyst on filter paper (Whatman no. 1)

Sample	Mode of preparation of photocatalyst (deposited)	Amount of catalyst deposited (g)	Volume of hydrogen produced[a] (ml)	Rate (ml/h/g)
1	Cadmium sulphide codeposited with zinc sulphide on Whatman filter paper no. 1 using a solution containing 0.02 M $Cd(CH_3COO)_2$ and 0.08 M $Zn(CH_3COO)_2$ and H_2S	0.0413	11.0	51.16
2	Cadmium sulphide codeposited with zinc sulphide on Whatman filter paper no. 1 using a solution containing 0.2 M $Cd(CH_3COO)_2$ and 0.8 M $Zn(CH_3COO)_2$ and H_2S	0.1375	10.4	15.13
3	Cadmium sulphide codeposited with zinc sulphide on Whatman filter paper no. 1 using a solution containing 0.002 M $Cd(CH_3COO)_2$ and 0.008 M $Zn(CH_3COO)_2$ and H_2S	0.0387	6.0	31.04
4	Zinc sulphide codeposited with cadmium sulphide on Whatman filter paper no. 1 four times successively using 0.08 M zinc acetate H_2S onto which CdS deposited once using 0.02 M cadmium acetate and H_2S	0.0395	1.0	5.06
5	Cadmium sulphide codeposited with zinc sulphide on Whatman filter paper no.1 once using 0.02 M $Cd(CH_3COO)_2$ and H_2S onto which ZnS deposited four times using 0.08 M $Zn(CH_3COO)_2$ and H_2S	0.0412	0.0	0.00
6	Cadmium sulphide was deposited on Whatman filter paper no. 1 from a solution of 0.02 M $Cd(CH_3COO)_2$ and H_2S	0.0430	2.0	9.30
7	Zinc sulphide was deposited on Whatman filter paper no. 1 from a solution of 0.08 M $Zn(CH_3COO)_2$ and H_2S	0.0416	0.0	0.00

[a] Illumination time: 5 h.

then introduced into H_2S chamber and kept in it for 15 min for conversion of acetate into sulphide. Finally the mixed zinc–cadmium sulphide coated filter paper was dried in hot air and final weight was taken. From a knowledge of the initial weight of the paper, the weight of catalyst immobilised could be found.

(ii) Deposition of mixed zinc–cadmium sulphide on filter paper was done by soaking a piece of Whatman filter paper no. 1 (area and weight was known) in $Zn(CH_3COO)_2$ and drying it in hot air. This process was repeated four times followed by soaking in $Cd(CH_3COO)_2$ solution once. Finally the moist paper was introduced into H_2S chamber and kept for 15 min for conversion of acetate into sulphide.

(iii) In another method mixed sulphide was deposited on Whatman filter paper by soaking in $Cd(CH_3COOO)_2$ followed by four successive times in $Zn(CH_3COO)_2$ and finally treated in H_2S chamber.

2.2. Determination of photocatalytic activity of the immobilised semiconductor particulates

For testing the efficiency of the photocatalysts towards liberation of hydrogen the following set up was used.

Volumetric flasks (100 ml) were used for the experiment. These flasks were well stoppered with rubber stoppers. A fine glass tube (inner diameter is 3 mm) was inserted through each stopper. Each flask contained an immobilised semiconductor bed and was filled with 0.24 M Na_2S and 0.35 M Na_2SO_3 solution. Before illumination in sunlight every flask was made airtight using the rubber stopper. The liberated gas was collected in the neck of volumetric flask by downward displacement of stock solution. In order to make correct comparison between experiments, each of the sets of the experiment was done simultaneously to avoid any difference of incident radiation of sunlight. Average radiation intensity measured was 25 mW/cm^2.

2.3. Solar hydrogen production and energy conversion efficiency

The solar production of hydrogen with concomitant oxidation of sulphide and sulphite has been carried out in a 500 ml conical flask that was placed on the terrace of our building in Kolkata (India). The area of the immobilised bed was 252 cm^2 and weight of the photocatalyst deposited on the filter paper bed was 0.210 g. The immobilised filter paper bed containing mixed CdS–ZnS on its surface deposited from a mixture of 0.02 M $Cd(CH_3COOO)_2$ and 0.08 M $Zn(CH_3COO)_2$ solution. In 145 h 1250 ml of hydrogen was produced from solution 0.2418 M Na_2S and 0.35 M Na_2SO_3. The average rate of production was 8.62 ml/h (in sunny day and temperature 34 °C) and in a cloudy day, the average rate was 3.6 ml/h. The decrease in concentration of Na_2S was 41% after 30 days and the catalytic activity persist for more than 1 month. In a cloudy day, the activity was reduced to almost 50%. Considering the energy of combustion of hydrogen (68.3 kcal/mol), energy conversion efficiency was 0.43% when the average irradiation intensity of sunlight 25 mW/cm^2.

3. Results and discussions

For the CdS–ZnS photocatalyst embedded in Whatman no. 1 filter paper, we prepared CdS–ZnS catalyst with varying mole percentage of ZnS embedded in filter paper starting with solution containing different composition of $Cd(CH_3COO)_2$ and $Zn(CH_3COO)_2$.

Fig. 1 shows the rate of hydrogen production with the variation in the mole ratio of ZnS–CdS in the mixed semiconductor catalyst. It may be seen starting with CdS (0 mol% ZnS) as the mole percentage of ZnS increases the catalytic activity increases up to 50 mol%, then decreases and again it reaches a maximum around 80 mol% ZnS. The CdS–ZnS catalyst with 80 mol% of ZnS shows better catalytic activity than the one of about 50 mol% of ZnS. The same type of variation in catalytic activity has been found with particulate system.

It is interesting to note that Reber and Rusek [2] reported about the maximum activity of the catalyst at about 80 mol% of ZnS for solid solution of cadmium–zinc sulphide. They referred to the difference of their finding from that reported by Kakuta and others [19,20]. White et al. found maximum activity for concentration of about 50 mol% ZnS. This difference, Reber and Rusek [2] attributed to the presence of two phases. Kakuta et al. [19] studied the mixed semiconductor up to a mole ratio of 1:2 for Cd:Zn. Reber and Rusek do not mention anything about the range of composition. Our studies, in which we scanned the whole range of composition of CdS–ZnS, from 0 to 100 mol% of ZnS show two maxima in the photocatalytic activity with variation in composition of the semiconductor catalyst. The first one is around 50 mol% of ZnS and the second one around 80 mol% of ZnS.

In order to be definite that the mixed CdS–ZnS catalyst embedded in the filter paper had the correct composition of 80 mol% of ZnS we have checked it by analysis. From a small piece of filter paper containing the embedded catalyst, the sulphides are dissolved in strong hydrochloric acid. The concentration of Cd and Zn have been estimated by atomic absorption spectroscopy. The mole ratio has been found to be CdS:ZnS = 1:4.

We have also analysed the sodium sulphide–sodium sulphite solution containing CdS–ZnS catalysts after irradiating in sunlight, to see if any Cd^{2+} and/or Zn^{2+} ions have been found formed by photocorrosion. Atomic absorption spectroscopic analysis has shown presence of no Cd^{2+} or Zn^{2+} ions. This confirms our presumption that in presence of high concentration of S^{2-} ions CdS–ZnS catalyst undergoes no photocorrosion.

We have seen that CdS–ZnS photoctalyst containing 80 mol% of ZnS shows maximum activity. We have embedded this catalyst in Whatman no. 1 filter paper yielding best photocatalytic activity. We have also studied the different modes of preparation to have the most effective catalyst embedded in filter paper. Table 1 also presents some typical results.

The photocatalyst, CdS–ZnS deposited on filter paper (Whatman no. 1) soaked in a solution containing 0.02 M $Cd(CH_3COO)_2$ and 0.08 M $Zn(CH_3COO)_2$ subsequent exposure to H_2S shows the highest activity. The photocatalysts deposited on filter paper successively from 0.08 M

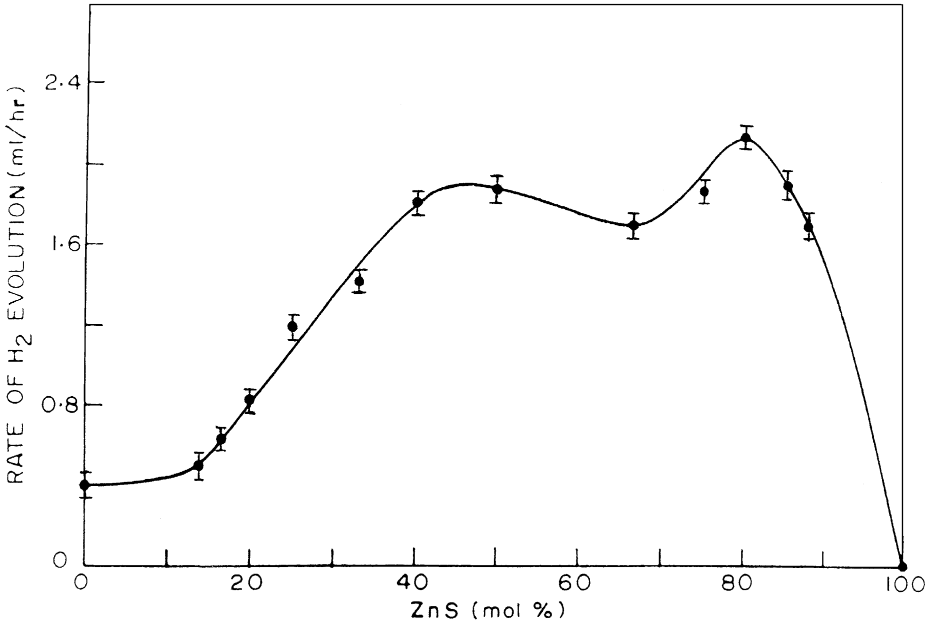

Fig. 1. Rate of production of hydrogen with variation of composition of CdS and ZnS in mixed CdS–ZnS.

$Zn(CH_3COO)_2$ and 0.02 M $Cd(CH_3COO)_2$ (successive layers) and vice versa (Table 1, samples 4 and 5) do not exhibit satisfactory activities. This is probably due to the fact that ZnS layer is deposited on CdS layer on filter paper, the thickness of the ZnS layer is high enough to prevent light absorption by the inner CdS layer leading to very low photocatalytic activity. When CdS layer is deposited on ZnS layer (sequential precipitation) the mixed ZnS–CdS is as good as bare CdS surface. In case of codeposition on paper the mechanism of formation of sulphides is different from that in case of formation of powders. In the former case since metal ions (Cd^{2+} and Zn^{2+}) are absorbed simultaneously on the paper, formation of mixed sulphide, $Zn_xCd_{1-x}S$, is more likely (rather than ZnS coated CdS) while it is treated in H_2S chamber. The effect of concentration of the solutions used is seen from samples 1–3. The photocatalytic activity of the mixed sulphide has been found to be maximum when the concentration of cadmium and zinc ions are also low as 0.02 and 0.08 M, respectively, in the mixed solution. This may be attributed to the fact that the photocatalyst, when deposited from high concentration of metal ions, undergoes agglomeration and peels off from the bed during illumination in presence of alkaline sodium sulphide solution (Table 1).

The rate of hydrogen evolution with bare CdS is very low but when the same CdS is coprecipitated with ZnS (in 1:4 molar ratio), the evolution rate increases enormously. The enhancement in photocatalytic activity towards hydrogen evolution with CdS in presence of ZnS have been observed by several other workers [2,8,19–25]. Bare CdS upon absorption of photons, produces electrons in the conduction band and holes in the valence band which are uniformly distributed throughout the CdS particles. Youn et al. [23] have pointed out that these free delocalised carriers migrate to the particle surface and get trapped at the various surface sites or undergo site-mediated recombination among themselves subsequently reduction of protons to hydrogen takes place by these trapped electrons in the surface states. The very low efficiency of bare CdS towards photocatalytic hydrogen generation results from the presence of a large number of low-lying surface states (acceptor levels) that are ineffective towards hydrogen ion reduction. Since CdS is well known to precipitate with a sulphur-deficient stoichiometry, positively charged sulphite (S^{2-}) vacancies are assumed by Youn et al. to be electron traps [23]. They have suggested that ZnS coated CdS, removes or repairs these surface states in CdS. Now, since these low-lying surface states are blocked, there is an increased fraction of conduction band electrons available at more negative potential for hydrogen production resulting in an improved hydrogen production efficiency. Alternatively, Kakuta et al. [21] have shown that during the formation of ZnS coated CdS some Zn^{2+} get absorbed on CdS layer and have proposed that Zn^{2+} is intimate contact with CdS is crucial for higher photocatalytic activity towards hydrogen generation. From a more negative value of CdS flatband potential and enhanced photocurrent in presence of Zn^{2+} they have suggested that Zn^{2+} ion blocks CdS surface states, thereby resulting an improvement in the photocatalytic activity of the semiconductor systems.

The delocalised conduction band electrons produced immediately after light absorption by the CdS are, as Youn et al. [23] suggest selectively trapped on the ZnS surface. This would led to small metallic zinc nuclei which due to low overpotential of H_2 evolution could act as efficient hydrogen production centre. They have justified the necessary induction period of zinc nuclei on the particle surface by photoreduction of zinc ions. On the other hand, Kakuta et al. [21] have detected Cd^0 after illumination of CdS in presence of ZnS supported on Nafion film by XPS measurements. Cd^0 is not formed in absence of ZnS. Henglein and Gutierrez [24] reported that Cd metal catalysed hydrogen formation of CdS colloids. Since it is known that overpotential for H_2 production of Cd metal is less than that of Zn metal, the higher photocatalytic efficiency in presence of cadmium metal is more reasonable compared to Zn metal.

Reber and Rusek [2] explained the enhancement in photocatalytic efficiency of CdS coprecipitated with ZnS toward hydrogen production by assuming a shift of the flatband potential towards more negative value. From photovoltage measurement [26] we found that flatband potential (E_{fb}) of CdS, CdS–ZnS (1:1 molar ratio) and CdS–ZnS (1:4 molar ratio) are −0.724, −0.941 and −1.003 V, respectively, against SCE at pH 14. By increasing the ZnS fraction, the energy level of the conduction band of the mixed CdS–ZnS is shifted towards more negative potential values compared to that of pure CdS. The higher reduction potential of the conduction band electrons of such semiconductor would allow a more efficient hydrogen generation. The conclusion is supported by photoelectrochemical measurement [22] showing an enhanced photocurrent in the presence of Zn^{2+} and a more negative value for the CdS flatband potential in presence Zn^{2+} suggest that Zn^{2+} blocks CdS surface states.

To have an idea about the extent of the shift in the flatband potential we determined the bandgap of the immobilised mixed semiconductor photocatalysts by reflectance method. Fig. 2 presents the second derivative of the reflectance spectra of the ternary CdS–ZnS photocatalysts deposited on Whatman no. 1 filter paper. The bandgaps, E_g’s, are plotted against mole ratio of CdS–ZnS (Fig. 3). The curve is similar to that obtained by Gordillo [27] indicating the formation of possibly the same type of ternary compound ($Zn_xCd_{1-x}S$). The bandgap of the CdS simultaneously deposited with ZnS (1:4 molar ratio) has been found to be 2.7 eV. Formation of homogeneous solid solution has also been found to be 2.7 eV. Formation of homogeneous solid solution has also been confirmed in the case where CdS was coprecipitated with ZnS in AOT-heptane-water reverse micelles from the absorption spectral data [10]. Roy et al. [28] have also reported the formation of homogeneous solid solution incorporated in DHP vesicles.

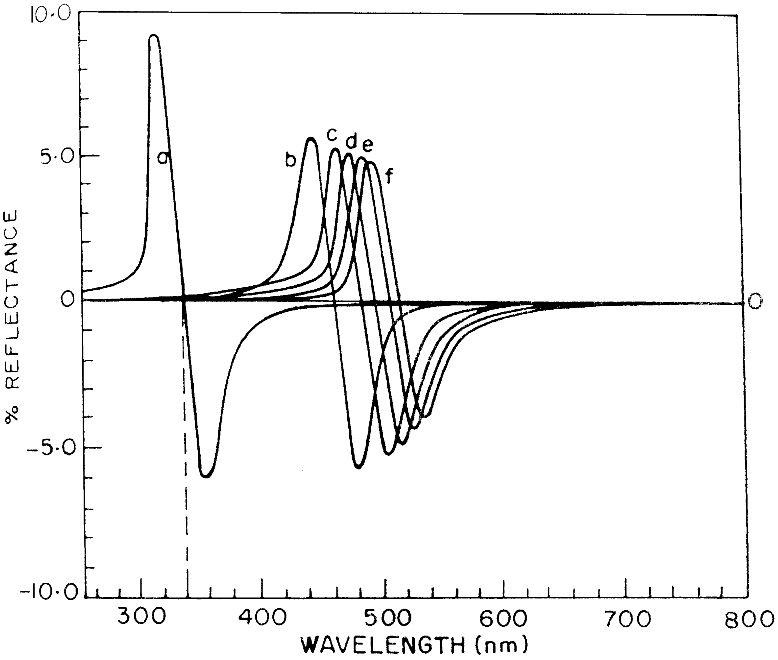

Fig. 2. Second derivation of reflectance spectra of semiconductor deposited on Whatman no. 1 filter paper (excitation wavelength is 363.30 nm): (a) ZnS; (b) mixed CdS–ZnS (1:4 molar ratio); (c) mixed CdS–ZnS (2:3 molar ratio); (d) mixed CdS–ZnS (3:2 molar ratio); (e) mixed CdS–ZnS (4:1 molar ratio); (f) CdS.

From reflectance spectra (Fig. 2) as already mentioned it has been found that the bandgap of mixed sulphide (i.e. CdS coprecipitated with ZnS in 1:4 molar ratio) is 2.7 eV (which is greater than that of CdS but lower than the bandgap of ZnS). As the valence band of CdS and ZnS lie almost at the same energy level (i.e. +1.8 V (NHE) for ZnS and +1.7 V (NHE) for CdS at pH 7). So presuming the valence band of mixed sulphide be almost equal to that of CdS, the conduction band is located at −1.0 V (NHE) at pH 7 (Fig. 4).

It has been seen from fluorescence spectra [28] (photocatalyst synthesised in AOT-heptane-water reverse miceller medium) that emission maximum for CdS–ZnS (1:4 molar ratio) was blue shifted than that from bare CdS. The emission spectra indicates that there is a donor state at 528 nm (2.35 eV) which is close to conduction band of CdS. This is probably due to fact that Zn^{2+} ions repaired or removed low-lying surface state of CdS (low-lying surface states lying just above valence band of semiconductor and created by positively charged sulphide (S^{2+}) vacancies and act as electron trap centres), therefore increased in electron-fraction

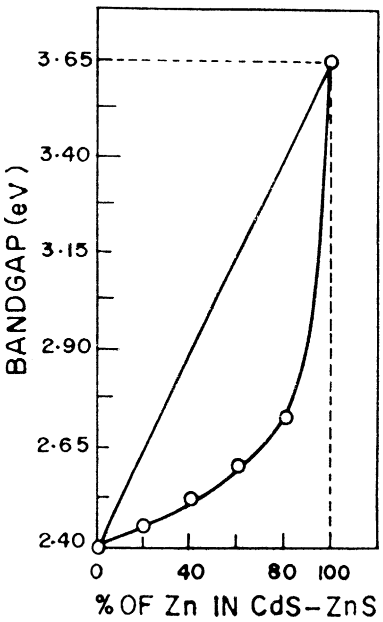

Fig. 3. Bandgap of mixed sulphide (coprecipitated CdS–ZnS) vs. composition of mixed CdS–ZnS.

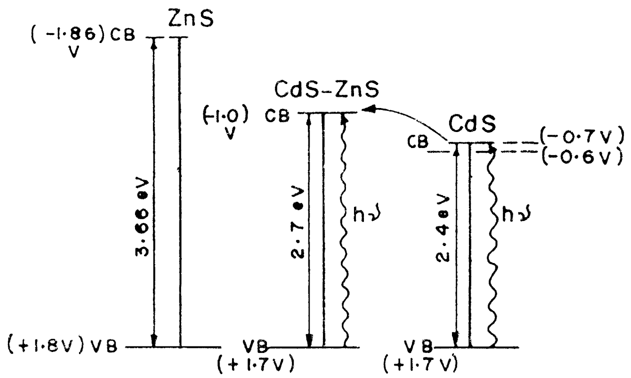

Fig. 4. Energy level diagram.

in conduction band. When mixed sulphide is illuminated electron–hole (e^-–h^+) is regenerated and due to presence of donor state at −0.65 V, transition of electrons to the conduction band may be routed through this donor level. The electrons in this conduction band are more energetic. So they will reduce protons more easily.

Apart from blocking of acceptor levels, the homogeneous solid solution begets a new conduction band energy level of 2.7 eV (corresponding to 460 nm) which is higher than E^0 of H^+/H_2 levels. Since conduction band of this mixed semiconductor is more negative than E^0 of H^+/H_2 levels compared to that of bare CdS, proton (H^+) reduction should be more facile thermodynamically.

Gordillo [27] in connection with studies on the sensitivity of suitably prepared CdS–ZnS photoconductors reports that the increment of the Zn concentration of $Zn_xCd_{1-x}S$ leads to an increment of both the optical gap and the resistivity of the films. The resistivity is largely influenced by the Zn concentration because an increase in Zn content leads to a decrease in carrier density and mobility. The band at 528 nm-transition between shallow donor states created by sulphur vacancies and valence band or transition between electrons and acceptor states created by metal vacancies. Cd and Zn vacancies behave as acceptors.

The high sensitivity of these mixed semiconductors is associated with the presence of a particular type of sensitised centres caused by Zn and Cd vacancies with energy levels of 1.6 and 1.1 eV above the valence band [27]. The proper choice of the concentration of Zn in the CdS–ZnS system can shift the photosensitivity from UV to near IR.

The mixed semiconductors seem to utilise wider range of solar insolation.

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