H$_2$ production of (CdS–ZnS)–TiO$_2$ supported photocatalytic system[1]

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Abstract

Mixed semiconductor (CdS–ZnS)–TiO$_2$(1 : 1 : 1) mixture system over different supports like MgO, CaO, γ-Al$_2$O$_3$, SiO$_2$ and modified MgO and CaO, have been prepared, characterized and tested for H$_2$ production in a S^{2-}/SO$_3^{2-}$ mixture solution. (CdS–ZnS)–TiO$_2$(D) over MgO support wherein the TiO$_2$ taken is from Degussa (D) sample gives 206.7 μmol/h of H$_2$ production and this catalyst sustain the H$_2$ production rate for longer durations. Dopants like Li$_2$O, Cs$_2$O or K$_2$O make MgO and CaO supports act like super basic oxide when they are doped and in turn increase the photocatalytic activity. The (CdS–ZnS)–TiO$_2$(I) system wherein the TiO$_2$ taken from Titanium Isopropoxide, supported on 20 wt% Li$_2$O doped CaO is found to give 209.8 μmol/h rate of H$_2$ production. Characterization studies like UV-Visible spectra, X-ray Diffraction spectra and Scanning Electron Microscope photographs were taken for all the catalysts and the data generated over these samples is evaluated. A scheme of H$_2$S photocatalytic decomposition of ZnCdS–TiO$_2$(D/I) over different supports in the presence of S^{2-}/SO$_3^{2-}$ substrate, is proposed indicating the formation of thiosulfate cycle at this heterojunction. © 1999 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

The photocleavage of H$_2$S to give H$_2$ and S has attained a lot of significance as this reaction requires less energy compared to photocleavage of H$_2$O. The cleavage of H$_2$S by two photons requires 9.4 kcal/mol. In the photocatalytic process, colloidal semiconductors are used as photocatalysts. Photoinduced charge separation occurs in the semiconductor particles which creates electron/hole pairs. The electron/hole pairs generated move towards the surface of the particle and bring about redox reaction on the adsorbed substrates [1, 2]. It is a proven fact that the coupling of two or more semiconductors decreases the extent of electron/hole recombination rendering the catalytic activity of the microheterojunction more efficient. When CdS is used in combination with TiO$_2$, charge transfer can be achieved through selective transfer of conduction band electrons from CdS to TiO$_2$ particles, the transfer of holes being inhibited for ener-getic reasons [3]. This can be achieved in a capped semiconductor system [4], which is said to have a core-shell geometry. Only one of the charge carrier is accessible at the surface in a capped semiconductor system, thus making selective charge transfer possible at the semiconductor-electrolyte interface. This selective transfer of electrons from CdS–TiO$_2$ brings about the thiosulfate cycle wherein there is no accumulation of sulfur and thiosulfate [3].

Recent work in our laboratory has established that the activity of CdS–ZnS system supported on MgO or CaO or γ-Al$_2$O$_3$ can be increased by doping promoters (basic nature) to the support material thus making it a super basic oxide support [5–8]. We report here the results obtained over (CdS–ZnS)–TiO$_2$ ternary mixed semiconductors over different supports as well as over super basic oxide supports.

2. Experimental

Commercial samples of MgO, γ-Al$_2$O$_3$ and CaO were used. MgO was kindly supplied by Martin Martia Magnesia, U.S.A., having a surface area of 170 m^2/g, CaO

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used was of laboratory grade and TiO$_2$(D) and was kindly supplied by Degussa, Germany. Powder catalytic supports of Li$_2$O–CaO and Li$_2$O–MgO containing 10, 20, 30, 40 and 50 wt% of Li were prepared from LiOH (laboratory grade) and activated at 450°C in air. K$_2$O and Cs$_2$O were prepared by their respective carbonate and chloride salts (laboratory grade). Ten wt% (CdS–ZnS)-TiO$_2$(I) (in each case semiconductor ratios are (1 : 1 : 1)) loadings were given on all the doped supports, and calcined at 350°C for 3 h. The precursor salt used for TiO$_2$(I) was Titanium isopropoxide. Ten wt% (CdS–ZnS)–TiO$_2$(D) loadings were also given on commercial samples of MgO, CaO, γ-Al$_2$O$_3$ and SiO$_2$; and were prepared by using TiO$_2$(D) as the source for TiO$_2$ and calcined at 350°C for 3 h.

The photocatalytic experiments were performed in a conventional batch reactor for 5 h. Irradiations were carried out in a pyrex 100 ml glass vial, equipped with a water jacket and in a closed vessel with a septum arrangement containing 50 ml solutions (invariable 1 M Na$_2$S, 0.1 M Na$_2$SO$_3$) with 500 mg catalyst. The suspensions were deairated with N$_2$ gas for 30 min to prevent uptake of photogenerated electrons by dissolved oxygen. The air space above the solution in the reactor was flushed with N$_2$ for 1 h in each experiment. A 250 W halogen lamp was used for illumination. Hydrogen gas was detected by

gas chromatography using a molecular sieve 5 A° column and N$_2$ as a carrier gas. The photogenerated dihydrogen was quantified by taking gas samples through the reactor septum (often tested for every repeated interval) and analyzed by a GC calibration curve. Results were reproducible in each case to within 10%. The UV-Visible spectra of the samples were derived from Shimadzu 240 Spectrophotometer. S.E.M. photographs of the samples were taken using an Hitachi S-520 and for XRD analysis, a Phillips (Holland) instrument was used with CuKα radiation. Thiosulfate estimations were done by iodometric titrations.

3. Results and discussion

UV-Visible spectra of the samples showed three peaks at 320, 350 and 520 nm respectively, indicating the presence of (CdS–ZnS)-TiO$_2$(D/I) supported on any support and no formation of homogeneous solid solutions. A comparative UV-Visible spectra is given in Fig. 1.

The diffraction studies reveal that CdS–ZnS exhibit hexagonal crystal structures and TiO$_2$ exhibits tetragonal crystal structure. MgO and CaO supported samples showed peaks corresponding to traces of Mg(OH)$_2$ and Ca(OH)$_2$ respectively. In the (CdS-ZnS)–TiO$_2$(D) sam-
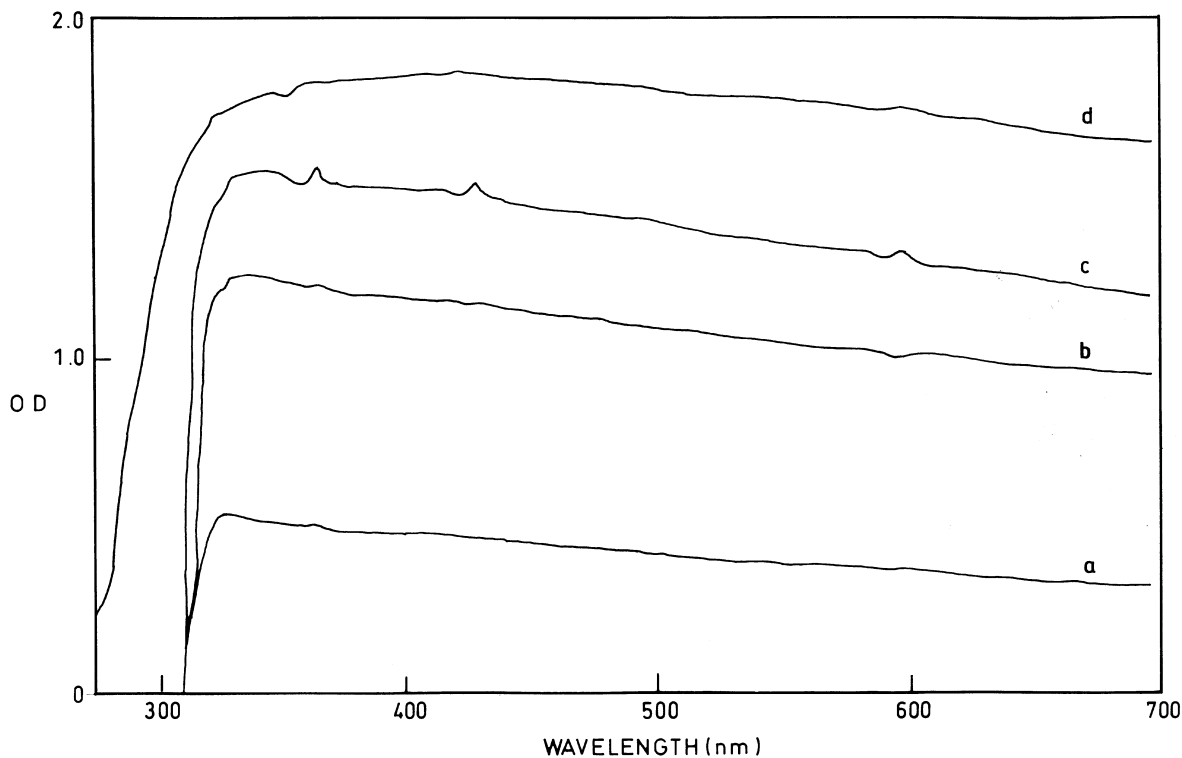
Fig. 1. UV-Visible spectra of (CdS–ZnS)–TiO$_2$(D)(1 : 1 : 1) supported on (a) γ-Al$_2$O$_3$ (b) SiO$_2$ (c) MgO (d) CaO.

ples there is good distribution of $TiO_2(D)$ on the supports especially on the MgO supported system. The crystal size of MgO decreases from 343 A° to 257 A° in (CdS–ZnS)–$TiO_2(D)$ system as compared to CdS–ZnS, MgO supported system [5] as it is calculated from the 'd' values. Average crystallite size of MgO was calculated from XRD patterns using Scherrer equation $L = k\lambda/\beta\cos\theta$, where $k = 0.9$, $\lambda = 0.15403$ nm for $CuK\alpha$ radiation and β = half width at full maximum. The comparative XRD analysis of MgO, 10 wt% CdS–ZnS(1:1)/MgO and 10 wt% (CdS–ZnS)–$TiO_2(D)$(1:1:1)/MgO are given in Figure 2. The decrease in crystal size is reflected in the activity data wherein the catalytic activity of 10 wt% (CdS–ZnS)–$TiO_2(D)$(1:1:1)/MgO is 206.7 μmol/h of H_2 production, whereas for 10 wt% CdS–ZnS(1:1)/MgO shows an activity of 71.4 μmol/h of H_2 production.

SEM photographs reveal that the distribution of $TiO_2(D)$ on the supports is even and crystallinity is observed at the surface. Addition of Li to CaO and MgO makes the catalyst surface porous having good phase distribution and crystallites being seen on the surface. This may be one of the reasons in enhancing the catalytic activity of the system. The SEM photographs of some (CdS–Zns)–$TiO_2(D/I)$ supported systems are given in Figure 3.

Catalytic activity data of all the samples are given in Table 1. 10 wt% (CdS–ZnS)–$TiO_2(D)$/MgO and 10 wt% (CdS–ZnS)–$TiO_2(I)$/CaO 10 wt% Li_2O doped supported sample exhibit the maximum activities of 206.7 and 209.8 μmol/h of H_2 production respectively. Table 2 gives the photocatalytic activity with respect to time on illumination for these two above mentioned catalysts. Comparison of the catalytic activities of CdS–ZnS systems reported earlier [5] and (Cds–ZnS)–$TiO_2(D)$ systems is given in Table 3. The increase in basicity of the support for (CdS–ZnS)–$TiO_2(D/I)$ systems is found to bring about an increase in the catalytic activity which is not as pronounced as is reported earlier for CdS–ZnS systems [6]. Doping of basic oxides as promoters to the supports makes it more porous thus attributing to the increase in catalytic activity of the system. Twenty wt% Li_2O–CaO support is found to give maximum catalytic activity as is seen from Table 1.

Borgarello et al. [3] have proved that CdS–TiO_2 systems give the thiosulfate cycle. Here, for the (CdS–ZnS)–TiO_2 supported systems, the thiosulfate estimations reveal that in comparison with the CdS–ZnS systems [5] there is a less thiosulfate present, which suggests that there is a thiosulfate cycle in this system which helps in sustaining the reaction for longer duration.
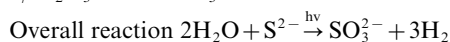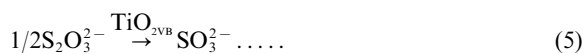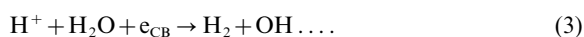
The reaction steps involved in the thiosulfate cycle are shown:

$$H_2S + OH \rightleftharpoons HS^- + H_2O \ldots \ldots \tag{1}$$

$$HS^- + h_{VB}^+ \rightarrow S^{2-} + H^+ \ldots \ldots \tag{2}$$

Table 1
Hydrogen production with 10 wt% (CdS–ZnS)–$TiO_2(I)$ (1:1:1) systems over different supports using (0.1 M) S^{2-} and (0.01 M) SO_3^{2-} solution. Amount of catalyst = 500 mg; lamp source = 250 W halogen lamp

S. No.	Support Used	Activity (Amount of H_2 produced in μmol/h)
I Different supports		
a	MgO	66.9
b	γ-Al_2O_3	13.3
c	CaO	7.1
II K_2O (wt%) doped CaO		
a	10	53.6
b	20	107.14
c	30	14.14
III Cs_2O (wt%) doped CaO		
a	10	79.0
b	20	102.7
c	30	52.2
IV Cs_2O (wt%) doped MgO		
a	10	60.3
V Li_2O (wt%) doped CaO		
a	10	47.9
b	20	209.8
c	30	71.8
VI Li_2O (wt%) doped MgO		
a	10	131.6
b	20	67.4
c	30	43.6
d	40	11.4
e	50	10.4
Different supports		
a	MgO	206.7
b	CaO	80.3
c	γ-Al_2O_3	77.0
d	SiO_2	80.9

$$H^+ + H_2O + e_{CB} \rightarrow H_2 + OH \ldots . \tag{3}$$

$$S^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} \ldots \ldots \tag{4}$$

$$1/2 S_2O_3^{2-} \xrightarrow{TiO_{2VB}} SO_3^{2-} \ldots \ldots \tag{5}$$

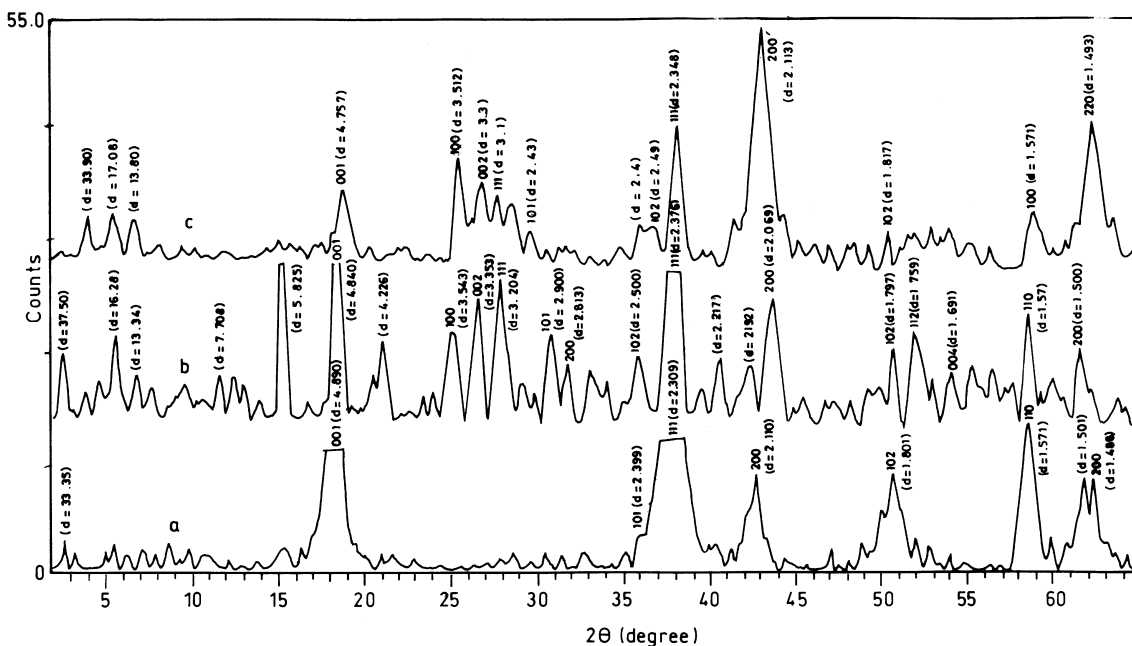Overall reaction $2H_2O + S^{2-} \xrightarrow{hv} SO_3^{2-} + 3H_2$

Fig. 2. X.R.D. spectra of (a) MgO (b) 10 wt% CdS–ZnS(1 : 1)/MgO (c) 10 wt% (CdS–ZnS)–TiO$_2$(D)(1 : 1 : 1)/MgO.

Step 4 is very important in the thiosulfate cycle for several reasons. This reaction helps in utilization of S^{2-} ions and prevents the formation of polysulphide ions which are photon absorbers (absorb $\geqslant$ 400 nm) and thus inhibit the catalytic activity of the system. Thiosulfate which is a product of this reaction is widely used in industrial processes such as photography. Presence of SO$_3^{2-}$ is useful for the photocleavage of H$_2$S and the rate of the reaction decreases in its absence. The H$_2$ production slows down with time due to the limited lifetimes of the semiconductors because of the energetic considerations.

Figure 4 gives the graphical representation of the data in Table 2, wherein the results tabulated are of some experiments performed to check the presence of thiosulfate cycle by taking the sacrificial agent 1 M Na$_2$S with and without 0.1 M Na$_2$SO$_3$ solutions. As is seen from the results, the mixture is giving more activity as SO$_3^{2-}$ is required for thiosulfate cycle (Step 4) which produces 3 moles of H$_2$.

Table 2
Variation H$_2$ evolution vs irradiation time for 10 wt% (CdS–ZnS)–TiO$_2$(1 : 1 : 1) for the best catalytic systems reported in Table 1

S. No.	Name of catalyst	Irradiation time (h)	Catalytic activity for 1M S^{2-} alone (μmol/h)	Catalytic activity for 1M S^{2-} +0.1M SO$_3^{2-}$ (μmol/h)
a	CdS–ZnS–TiO$_2$(D)/MgO			
1		5	18.6	206.7
2		10	4.7	84.7
3		15	3.2	28.12
4		20	2.3	2.14
b	CdS–ZnS–TiO$_2$(I)/20wt% Li$_2$O–CaO			
1		5	60.4	209.8
2		15	3.9	14.6
3		20	0.80	10.5

(a)

(b)

(c)

(d)

(e)
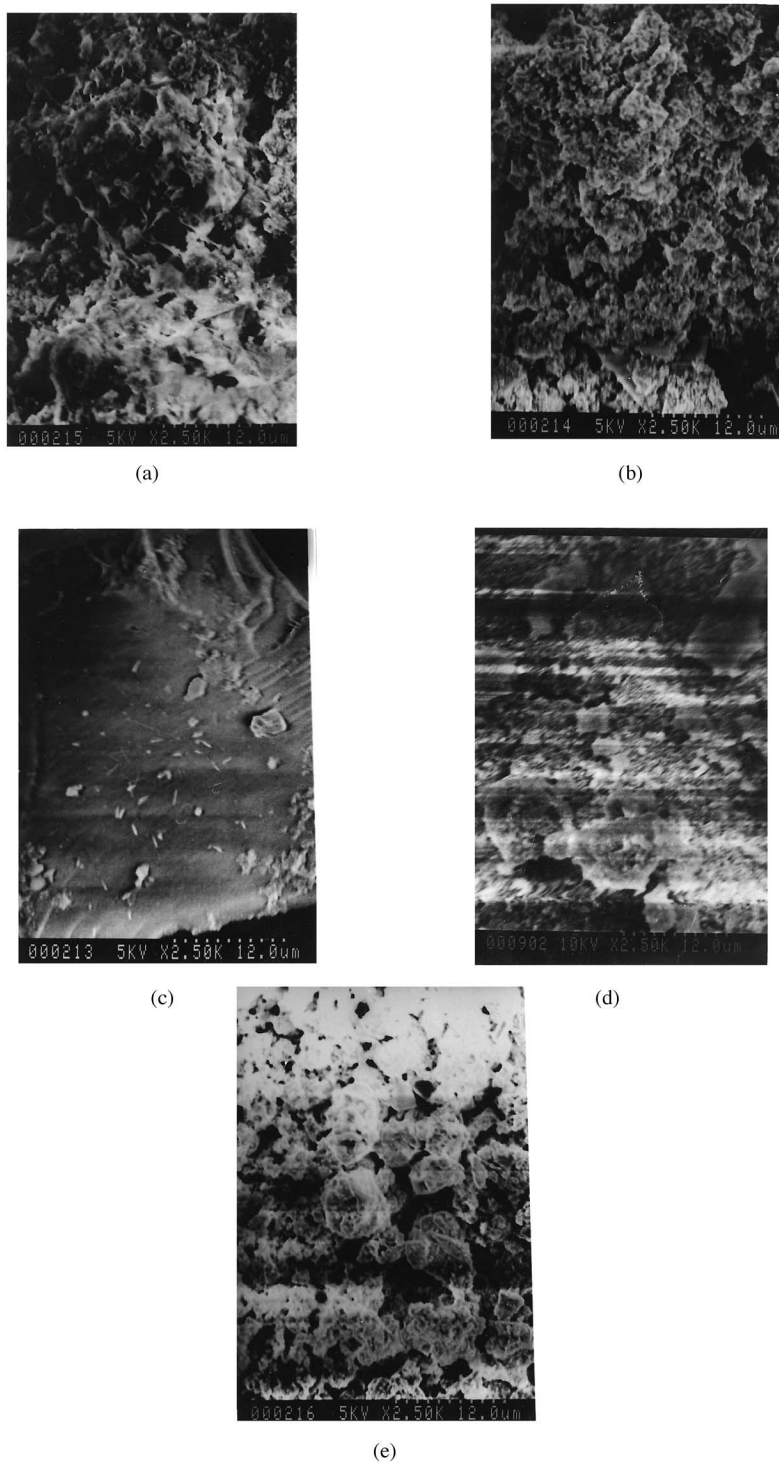
Fig. 3. S.E.M. photographs of 10 wt% (CdS–ZnS)–TiO_2(1 : 1 : 1) over (a) MgO (b) CaO (c) SiO_2 (d) γ-Al_2O_3 (e) 20 wt% Li_2O–CaO.
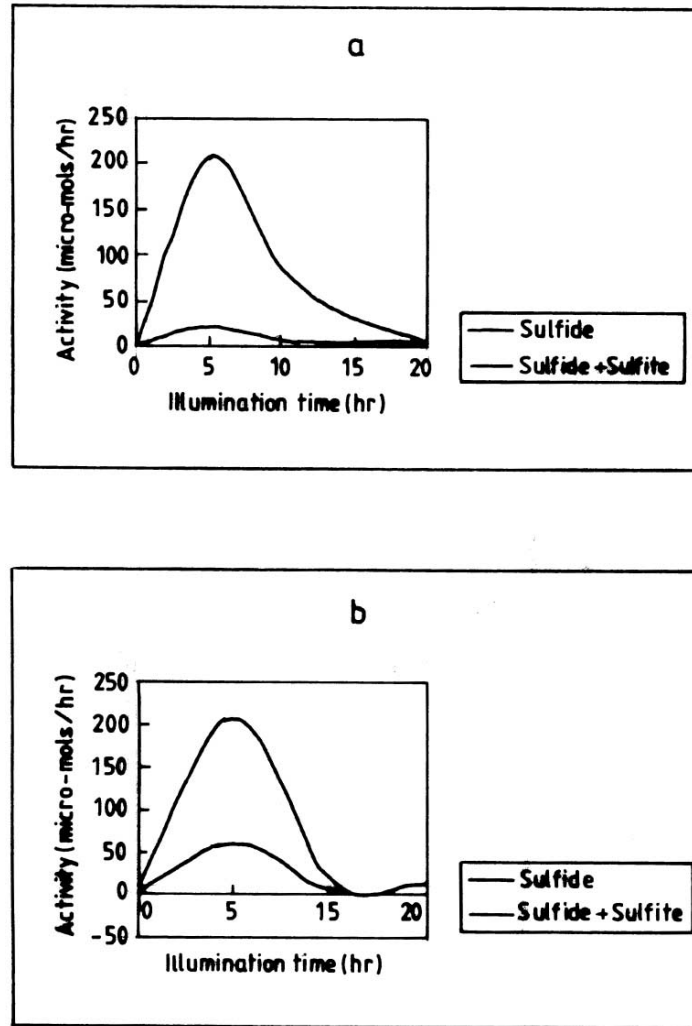
Fig. 4. Photocatalytic H_2 production activity with respect to time on illumination for (a) 10 wt% (CdS–ZnS)–TiO$_2$(D)[1 : 1 : 1]/ MgO and (b) 10 wt% (CdS–ZnS)–TiO$_2$(D)[1 : 1 : 1]/doped 20 wt% Li$_2$O–CaO supported sample.

Table 3
Comparison of H_2 production activity per hour for 10 wt% CdS–ZnS(1 : 1) system and 10 wt% (CdS–ZnS)–TiO$_2$(D)(1 : 1 : 1) supported systems for 5 h duration of a batch

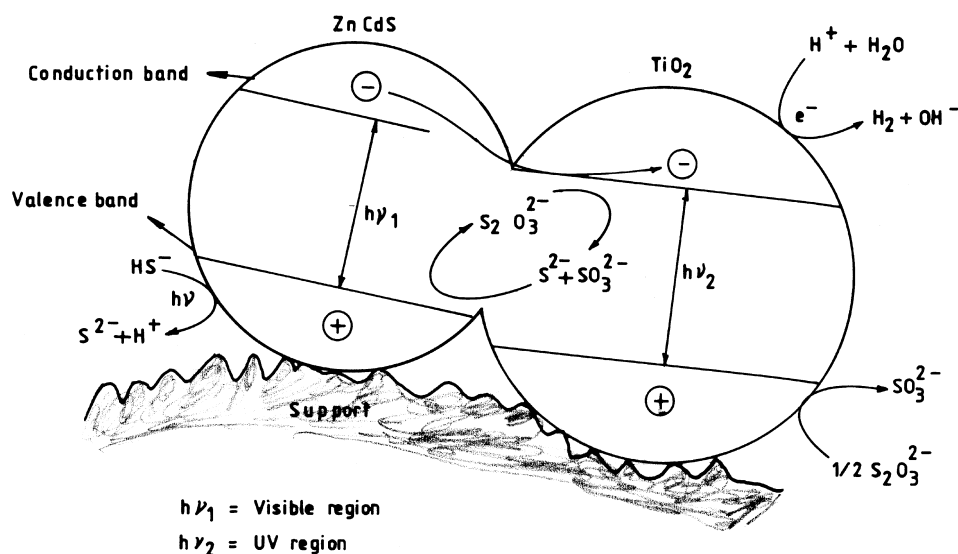| S. No.	Support	Activity of CdS–ZnS(1 : 1) system (μmol/h)	Activity of (CdS–ZnS)–TiO$_2$(I) system (μmol/h)	Activity of (CdS–ZnS)–TiO$_2$(D) system (μmol/h)
1	MgO	71.4	66.9	206.7
2	γ-Al$_2$O$_3$	18.4	13.3	77.4

Fig. 5. Schematic representation of H_2S photocatalytic decomposition at the formation of microheterojunction between ZnCdS–TiO_2(D/I) supported systems in a S^{2-}/SO_3^{2-} containing solution mixture.

Figure 5 gives the schematic representation of H_2S photocatalytic decomposition at the formation of microheterojunction between ZnCdS–TiO_2(D/I) system over different supports in the presence of S^{2-}/SO_3^{2-}, solution mixture. This scheme also indicates the formation of thiosulfate cycle at this heterojunction. The reactions involved in this scheme are steps 1–5, $h\nu_1$ indicates light absorbed by visible radiation and $h\nu_2$ indicates light absorbed by UV radiation.

4. Conclusion

(CdS–ZnS)-TiO_2 supported systems have been tried for photocatalytic activity to produce H_2 from H_2S. (CdS–ZnS)–TiO_2(D)/MgO system was giving the maximum hydrogen production. This catalyst can sustain the reaction for longer duration due to the formation of the thiosulfate cycle. UV-visible studies suggest that there are no formation of a homogeneous mixtures of (CdS–ZnS)–TiO_2(D/I) systems as revealed by their spectra. X.R.D. and S.E.M. data also reveal uniform distribution of the ternary mixed semiconductors on the supports. A scheme of photocatalytic H_2S decomposition by the formation of microheterojunction between ZnCdS–TiO_2(D/I) over supports in the presence of S^{2-}/SO_3^{2-} solution mixture, is suggested with an indication of thiosulfate cycle formation by this heterojunction. Further work is in progress to check the H_2 production from live H_2S containing samples available at Hyderabad city over the present reported photocatalytic systems.

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