

# Solar photocatalytic generation of hydrogen under ultraviolet-visible light irradiation on (CdS/ZnS)/Ag<sub>2</sub>S + (RuO<sub>2</sub>/TiO<sub>2</sub>) photocatalysts

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**Abstract.** In order to efficiently use the UV-vis light in the photocatalytic reaction, a novel (CdS/ZnS)/Ag<sub>2</sub>S + RuO<sub>2</sub>/TiO<sub>2</sub> was synthesized by chemical coprecipitation and metal ion implantation. The composition and structure of this composite were characterized by BET, UV-vis spectroscopy, SEM, XRD and EDX. This composite exhibited much higher photocatalytic activity for the generation of hydrogen (H<sub>2</sub>).

**Keywords.** Hydrogen; hydrogen sulfide; solar photocatalysis; composite; photocatalysts.

## 1. Introduction

The photocatalytic generation of hydrogen (H<sub>2</sub>) using solar energy has been regarded as an attractive solution to resolve the global energy and environmental problems, but most of the photocatalysts only work in ultraviolet region due to their wide bandgap. In order to use the solar energy more effectively, visible-light-driven photocatalysts must be developed (Bao *et al* 2007). However, there are few of photocatalysts that can split water under visible light irradiation until now. It is necessary for photocatalysts with visible light response to have an appropriate bandgap. To control the band structure, both doping of foreign elements into active photocatalysts with wide bandgap and making solid solutions between photocatalysts with wide and narrow bandgaps are often used. Eventual realization of an hydrogen economy requires cheap and readily available hydrogen sources and a technology to convert them into pure hydrogen in an efficient and sustainable manner.

Water is an ideal hydrogen source, and thus photocatalysts that could produce hydrogen from water splitting under sunlight have been actively sought. Apart from water, H<sub>2</sub>S could become an alternative source of hydrogen. H<sub>2</sub>S is produced in large quantities as a byproduct in coal and petroleum industries, natural gas and oil wells, and geothermal plants. In most cases, this toxic H<sub>2</sub>S has to be converted into an environmentally less harmful form to comply with environmental regulations. Thus, simultaneous hydrogen production and H<sub>2</sub>S decomposition is a highly desirable process that could satisfy both energy and environment requirements. From a fundamental point of view, the cleavage of H<sub>2</sub>S is easier than H<sub>2</sub>O

requiring  $G$  of only 39.4 kJ/mol, which is much less than 284.7 kJ/mol required for water splitting. The most favoured photocatalyst is CdS by itself or as a mixture with other semiconductors such as TiO<sub>2</sub>, ZnS and SrTiO<sub>3</sub>. These semiconductor photocatalysts perform better when loaded with co-catalysts such as Pt or RuO<sub>2</sub>. The CdS-based photocatalysts are known to be the most active in hydrogen production. Unfortunately, they undergo severe photocorrosion under irradiation unless there exist hole scavengers in the solution (as sacrificial reagents) such as sulfides (S<sup>2-</sup>) and sulfites (SO<sub>3</sub><sup>2-</sup>) (Supriya and Subramanyam 1997). When H<sub>2</sub>S is dissolved into alkaline solution, the sulfide ions are formed *in situ* and can play the role of a sacrificial reagent. It maintains high activity and stability. For the hydrogen production from aqueous H<sub>2</sub>S solutions, the mechanisms have been proposed. In the presence of a strong base, a hydroxyl ion reacts with H<sub>2</sub>S molecules to form a sulfide ion (1), which is oxidized by the photogenerated holes on the surface of the photocatalyst (2). The photoelectrons now reduce H<sub>2</sub>O to H<sub>2</sub> (3):



In this study, photocatalyst (CdS/ZnS)/Ag<sub>2</sub>S + (RuO<sub>2</sub>/TiO<sub>2</sub>) was synthesized and it was characterized by BET, UV-vis spectroscopy, SEM, XRD and EDX.

## 2. Experimental

### 2.1 Materials

Cadmium carbonate, silver nitrate, sodium sulfide, sodium sulfite, and titanium dioxide (Degussa, P25) were

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procured from MERCK and zinc carbonate and ruthenium trichloride from CDH.

## 2.2 Synthesis of photocatalysts

The hot mixture of cadmium acetate and zinc acetate solutions were prepared by dissolving required amounts of  $\text{CdCO}_3$  and  $\text{ZnCO}_3$  in dilute acetic acid at 60–70°C. Mixing slowly the hot solution of  $\text{Na}_2\text{S}$  with the hot mixture of cadmium acetate and zinc acetate solutions precipitated  $\text{CdS/ZnS}$  (Koca and Sahin 2002). By using this procedure, 2 : 1 composition of photocatalyst systems were coprecipitated. The precipitate was washed with water, dried in oven at 70°C and powdered.  $\text{Ag}_2\text{S}$  was precipitated by slowly mixing  $\text{AgNO}_3$  and  $\text{Na}_2\text{S}$ . Appropriate amounts of  $\text{CdS/ZnS}$  were mixed with  $\text{Ag}_2\text{S}$  with the help of an agate mortar and pestle. This mixture was dried at 70°C.

$\text{RuO}_2/\text{TiO}_2$  was prepared by incipient wetness impregnation method (Serpone and Borgarello 1984).  $\text{TiO}_2$  powder was added to an aqueous solution of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  of sufficient concentration so as to obtain a  $\text{RuO}_2$  loading of 0.5 weight % in the product. The slurry was stirred at 80°C to evaporate water. The resulting paste was dried at 100°C for 24 h and was subsequently calcined at 400°C for 8 h to oxidize  $\text{Ru(III)}$  to  $\text{RuO}_2$ .  $\text{RuO}_2/\text{TiO}_2$  was then mixed with the  $(\text{CdS/ZnS})/\text{Ag}_2\text{S}$  with the help of an agate mortar.

## 2.3 Photoreactor

Batch reactors were used for the photocatalytic generation of  $\text{H}_2$  at 25°C. 50 mg of catalyst was added to 100 mL of 0.12 M  $\text{Na}_2\text{S}$  and 0.175 M  $\text{Na}_2\text{SO}_3$  solutions. Catalyst particles were kept suspended by magnetic stirrers. The whole apparatus was exposed to sunlight. The volume of  $\text{H}_2$  was measured for every 15 min intervals until evolution of  $\text{H}_2$  got ceased. The collected  $\text{H}_2$  was confirmed on a gas chromatograph (Chromatograph and Instruments Company) with TCD using Porapak Q column at 40°C and  $\text{N}_2$  as a carrier.

## 2.4 Characterization methods

The specific surface area of the photocatalyst was measured by BET method by Quantachrome Autosorb Automated Gas Sorption System. The optical property was analysed by UV-vis diffuse reflectance spectrometer (Shimadzu, UV 2401). Morphology of the photocatalyst was measured by scanning electron microscopy (SEM) (LEO StereoScan 440). It was used for studying the dispersion of all the catalytic material in the particulate mixture. The diffraction study revealed the particle size and structure of the photocatalyst (X-ray diffractometer). The

maximum rate depends upon the percentage composition of catalytic material in the particulate mixture. Energy dispersive X-ray spectroscopy (EDX) determined the composition of the photocatalyst.

## 3. Results and discussion

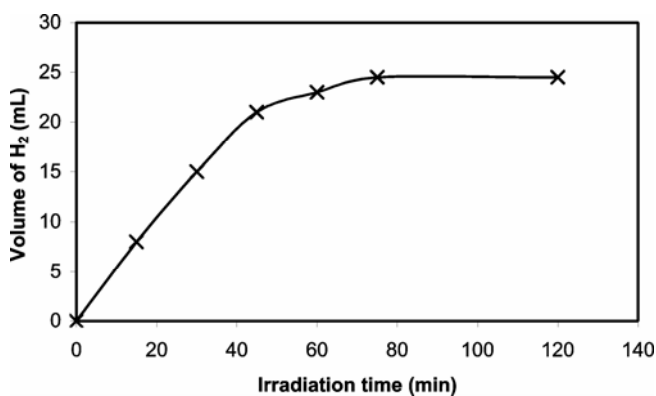
### 3.1 Photocatalytic evolution of hydrogen

The activity of the photocatalysts was studied under solar light irradiation, and the results are shown in figure 1.

$(\text{CdS/ZnS})/\text{Ag}_2\text{S} + (\text{RuO}_2/\text{TiO}_2)$  was generated at 392 mL/g/h, which is higher than the  $\text{H}_2$  generated by the  $\text{CdS/ZnS}$  catalytic system (Priya and Kanmani 2008). The improvement of  $\text{H}_2$  generation was attributed to a similar heterojunction mechanism. The broader bandgap semiconductor  $\text{TiO}_2$  had more positive conduction and valence band.  $\text{TiO}_2$  can absorb radiation only in the UV range, so there was no sensitization effect in adding it to  $\text{CdS}$ . Nevertheless,  $e^-$  excited by visible light in  $\text{CdS}$ , could be injected into  $\text{TiO}_2$ , where they could recombine or be transferred to  $\text{RuO}_x$ . The presence of  $\text{RuO}_x$  increased the  $\text{H}_2$  yield (Borrell *et al* 1992).

### 3.2 Characterization of photocatalyst $(\text{CdS/ZnS})/\text{Ag}_2\text{S} + (\text{RuO}_2/\text{TiO}_2)$

**3.2a Surface area:** The high BET surface area was found to be 196  $\text{m}^2/\text{g}$ , which indicates the finely divided nature of the particles. Consequently, more interfacial area and more surface active sites were available for the same amount of photocatalyst. The charge carriers generated by absorbed light can freely reach the interface and thus making them available at the interface without loss due to  $e^-/h^+$  recombination. These electrons were suitably transferred to photons to generate  $\text{H}_2$  and the hole to oxidize donor molecules freely. Because of high surface area, the diffusion length of charge carriers must be low. Similar



**Figure 1.** Effect of photocatalysts on  $\text{H}_2$  generation [ $(\text{CdS/ZnS})/\text{Ag}_2\text{S} + (\text{RuO}_2/\text{TiO}_2)$ ].

findings were reported by Borrell *et al* (1992), Ashok Kumar (1998) and Maruyama and Nishimoto (1991).

**3.2b Bandgap energy:** DRS UV-vis analysis of mixed semiconductor (CdS/ZnS)/Ag<sub>2</sub>S + RuO<sub>2</sub>/TiO<sub>2</sub> was carried out in the near UV and visible regions, covering the wavelength between 200 and 800 nm. The plot between % reflectance and wavelength is presented in figure 2. With decrease in wavelength from 800 to 600 nm, no change in % reflectance was observed. In the wavelength between 600 and 500 nm, there was a sharp fall in % reflectance. It was due to bandgap excitation of CdS particles. This closely matches the spectrum reported by Matsumara *et al* (1983). This excitation corresponds to the bandgap value = 2.48 (1240/500) eV. Similar drop in % reflectance was also observed between 400 and 450 nm. The decrease in absorbance started above 450 nm and

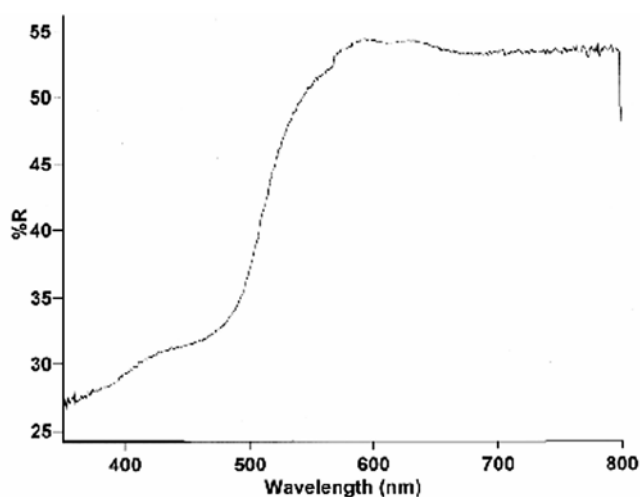


Figure 2. DRS-UV-vis of (CdS/ZnS)/Ag<sub>2</sub>S + (RuO<sub>2</sub>/TiO<sub>2</sub>).

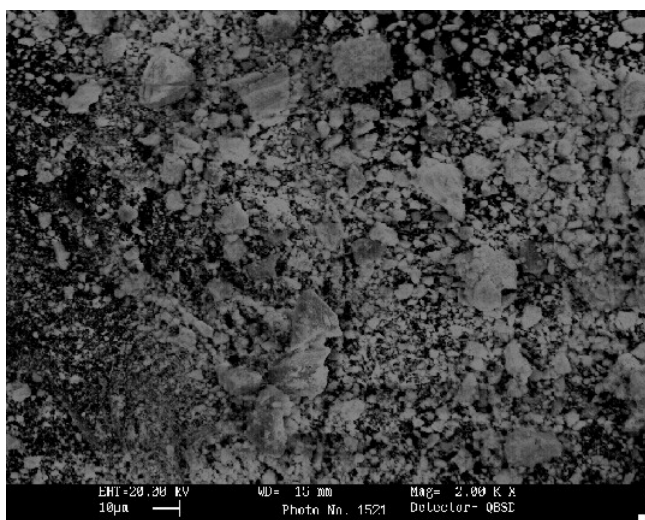


Figure 3. SEM of (CdS/ZnS)/Ag<sub>2</sub>S + (RuO<sub>2</sub>/TiO<sub>2</sub>).

ended at 400 nm. This excitation corresponds to bandgap value equal to 3.1 (1240/400) eV, not matching with any of the individual semiconductors, used for forming the mixture. It was due to formation of couple semiconductors. Even below 400 nm, the % reflectance did not show any steady value illustrating absence of TiO<sub>2</sub> and ZnS.

**3.2c Morphology:** The scanning electron microscope of the catalyst is shown in figure 3. Widely varying morphologies were observed. The catalyst was a mixture made of different components with different morphologies. The particles appeared as aggregates of tiny crystals. They were particles of both nano and bulk dimensions. The major constituents of particles were bulk dimensions. The average diameter of the particles was equal to  $18 \times 10^{-6}$  m.

**3.2d Crystal structure:** The XRD spectrum of the CdS/ZnS, TiO<sub>2</sub> and RuO<sub>2</sub> mixture is shown in figure 4.

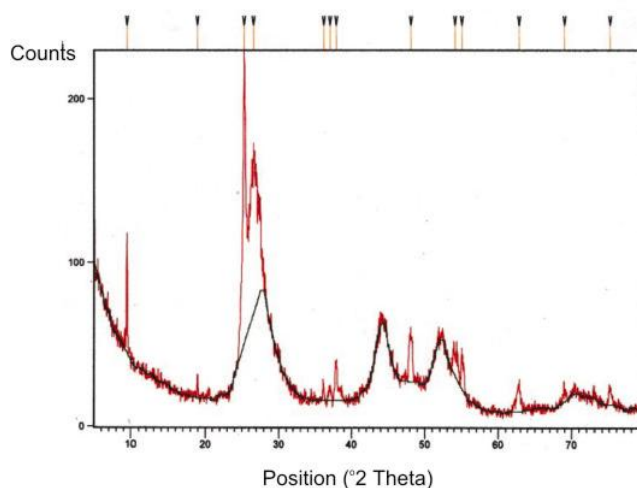


Figure 4. XRD of (CdS/ZnS)/Ag<sub>2</sub>S + (RuO<sub>2</sub>/TiO<sub>2</sub>).

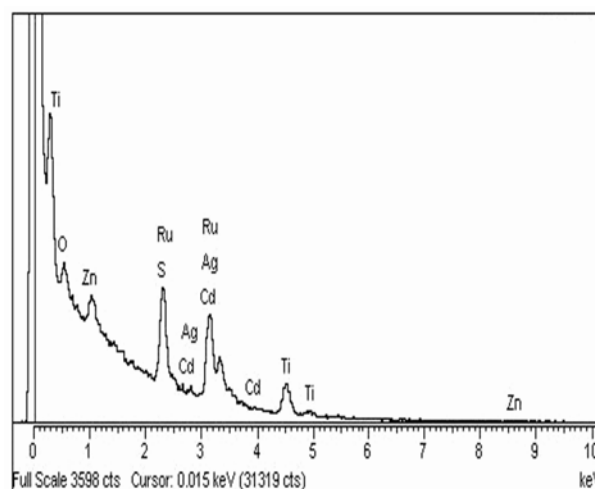
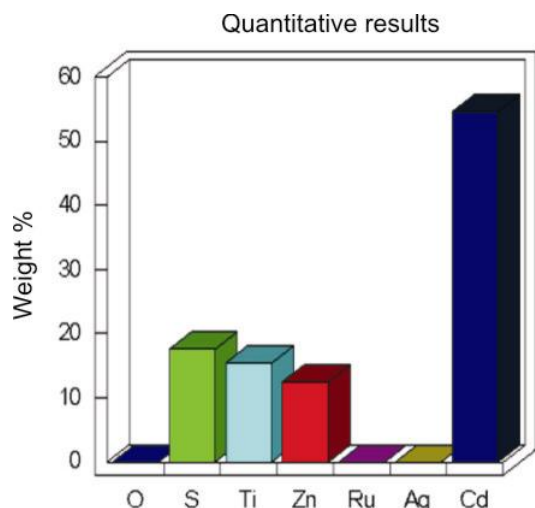


Figure 5. EDX of (CdS/ZnS)/Ag<sub>2</sub>S + (RuO<sub>2</sub>/TiO<sub>2</sub>).



**Figure 6.** Weight % of components (CdS/ZnS)/Ag<sub>2</sub>S + (RuO<sub>2</sub>/TiO<sub>2</sub>).

The spectrum carries patterns for the individual components which were reported by Enea and Bard (1986). The diffraction patterns at 8.97 ( $2\theta$ ), 25.292 ( $2\theta$ ), 36.087 ( $2\theta$ ), and 37.00 ( $2\theta$ ) were due to the TiO<sub>2</sub>. The pattern at 25.292 ( $2\theta$ ) was assigned to CdS and that at 26.591 ( $2\theta$ ) was due to ZnS. It was difficult to absorb the pattern due to RuO<sub>2</sub> and Ag<sub>2</sub>S as their content was very less.

**3.2e Composition:** The EDX spectra for the catalysts are shown in figure 5. The weight % of each element derived from the EDX spectra is illustrated in figure 6. From the weight % bar chart it was clearly evident that the major component of the catalyst mixture was CdS. The content varied in the order of CdS > TiO<sub>2</sub> > ZnS. It

was also the order by which the components were mixed experimentally.

#### 4. Conclusions

The composite photocatalyst (CdS/ZnS)/Ag<sub>2</sub>S + (RuO<sub>2</sub>/TiO<sub>2</sub>) was synthesized by simple chemical method. The composition and structure of this composite were characterized by BET, UV-vis spectroscopy, SEM, XRD and EDX. From the results, it was evident that the additions of wide bandgap semiconductors, promoters and metal dopants have significant effect on H<sub>2</sub> generation.

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