

Solar photocatalytic generation of hydrogen from hydrogen sulphide using CdS-based photocatalysts

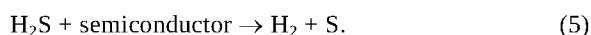
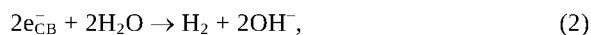
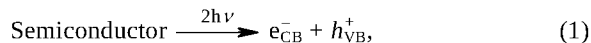
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Laboratory-scale feasibility studies on solar photocatalytic generation of hydrogen (H₂) from Na₂S/Na₂SO₃ solution by using CdS-based photocatalysts have been carried out in a batch solar photocatalytic reactor of 300 ml capacity. Three CdS-based photocatalytic mixtures [viz. CdS/ZnS, (CdS/ZnS)/Ag₂S and (CdS/ZnS)/Ag₂S + (RuO₂/TiO₂)] were synthesized by adding wide band-gap semiconductors (ZnS and TiO₂), promoters (Ag₂S) and metal dopants (RuO₂), and the activities of the three photocatalytic mixtures were evaluated. H₂ generation was found to be a maximum of 392 ml/g/h for the photocatalytic mixture of (CdS/ZnS)/Ag₂S + (RuO₂/TiO₂) whereas it was only 213 ml/g/h for the photocatalytic mixture of CdS/ZnS. Thus, the solar photocatalytic generation of H₂ from Na₂S/Na₂SO₃ solution using (CdS/ZnS)/Ag₂S + (RuO₂/TiO₂) was found to be feasible.

Keywords: Hydrogen, hydrogen sulphide, semiconductors, solar photocatalysis.

RECENTLY, various photocatalytic reactions with powdered semiconductors were actively studied for the generation of hydrogen (H₂) from natural feed stocks such as water and hydrogen sulphide (H₂S). Much interest has been given to H₂S, since it is abundant as a by-product of the oil or natural gas refinery and requires much lower energy for decomposition compared to water. Irradiation of semiconductor particles creates electron-hole (e⁻/h⁺) pairs. The e⁻/h⁺ pairs move towards the surface of the particles and bring about redox reactions on the adsorbed substrates under sunlight, as explained in eqs (1)–(5).



For efficient generation of H₂, a photocatalyst that has good absorption properties in the visible region is needed.

In this aspect, CdS is a promising material. Photoactivity of CdS can be improved by the addition of wide band-gap semiconductors like TiO₂ and ZnS. Photocatalytic activity can also be enhanced by promoters like Ag₂S, which motivate CdS and ZnS, and also act as hole scavengers. Recombination is the predominant route by which the excitation energy is dissipated. This can be prevented in semiconductor photocatalysts by incorporating suitable hole transfer agents like RuO₂.

In this study, an attempt has been made to improve the activity of CdS by the addition of wide band-gap semiconductors (ZnS and TiO₂), promoters (Ag₂S) and metal dopants (RuO₂). Three types of photocatalytic mixtures [viz. CdS/ZnS, (CdS/ZnS)/Ag₂S and (CdS/ZnS)/Ag₂S + (RuO₂/TiO₂)] have been prepared in the laboratory. A new solar photocatalytic reactor of 300 ml capacity was fabricated using Plexiglas material for conducting outdoor solar studies. The activities of the three photocatalytic mixtures were evaluated for generating H₂ from Na₂S/Na₂SO₃ solution.

All chemicals used in this study were analytical reagent grade and solutions were made up with triple-distilled water.

The photocatalysts were prepared as follows: Photocatalytic mixture 1 (CdS/ZnS): CdS is a visible light active photocatalyst and ZnS is a UV light photocatalyst. In order to get a wide band-gap semiconductor (UV-vis), a photocatalytic mixture of CdS/ZnS was prepared. The photocatalytic mixture of CdS/ZnS was synthesized by co-precipitation method. A hot mixture of cadmium acetate and zinc acetate solutions was prepared by dissolving the required amount of CdCO₃ and ZnCO₃ in dilute acetic acid at 60–70°C. Different compositions (1 : 0, 1 : 4, 1 : 2 and 2 : 1 by wt%) of CdS/ZnS were precipitated by mixing slowly the hot solution of Na₂S with the hot mixture of cadmium acetate and zinc acetate solutions. The precipitates were washed with water, dried in an oven at 70°C and powdered.

Photocatalytic mixture 2 [(CdS/ZnS)/Ag₂S]: In order to enhance the activity of CdS/ZnS, the promoter Ag₂S was added to CdS/ZnS. This photocatalytic mixture was prepared by physically mixing Ag₂S (1.5 wt%) with an appropriate composition of CdS/ZnS at which maximum H₂ generation was observed. This mixture was dried at 70°C.

Photocatalytic mixture 3 [(CdS/ZnS)/Ag₂S + (RuO₂/TiO₂)]: In order to enhance the photocatalytic activity of mixture 2, RuO₂ (metal dopant) and TiO₂ (wide band-gap semiconductor) were added to the mixture.

The photocatalytic experiments were performed in a batch solar photocatalytic reactor, made up of Plexiglas material (transmits 290–700 nm). It is a 300 ml capacity reaction vessel, provided with two tubes. One of the tubes was used for purging of nitrogen (N₂) gas and the other tube to collect gas in the water displacement arrangement. Next 50 mg of each photocatalyst was suspended by magnetic stirring in 100 ml of the solution (0.12 M

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Na_2S and $0.175 \text{ M Na}_2\text{SO}_3$). The suspensions were deaerated 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 during each experiment. The whole apparatus was placed on the terrace under sunlight. The evolved gas was collected in the water displacement arrangement and identified by a gas chromatograph (Chromatograph and Instruments Company) with TCD using Porapak Q column at 40°C and N_2 as a carrier. The photogenerated H_2 was quantified by taking samples through the reactor septum and analysed by a GC calibration curve. Blank tests showed that H_2 generation was not observed when samples were kept in

the dark. The average radiation intensity measured was 422 W/sq. m .

The effect of composition of CdS/ZnS on generation of H_2 was studied and the results are presented in Figure 1. H_2 generation was found to be 133, 147, 187 and 213 ml/g/h for the CdS/ZnS compositions of 1 : 0, 1 : 4, 1 : 2 and 2 : 1 (by wt%) respectively. It was found that CdS alone generated less volume of H_2 , which might be due to the presence of a large number of low-lying surface states and e^-/h^+ recombination. Maximum H_2 generation was observed for CdS/ZnS composition of 2 : 1, which might be due to the quick prevention of e^-/h^+ recombination and also repairing of low-lying surface states in CdS. Similar observations have been reported by Koca and Sahin¹.

The effect of Ag_2S on photocatalytic mixture 2 for the generation of H_2 was studied and the results are presented in Figure 2. H_2 generation was found to be a maximum of 267 ml/g/h for the photocatalytic mixture 2, whereas it was found to be 213 ml/g/h for photocatalytic mixture 1. This might be due to the fact that Ag_2S has the same lattice structure as CdS, and it facilitated the holes produced in the bulk of the semiconductor to move towards the semiconductor/electrolyte interface more easily as Ag_2S particles. Ag_2S acted as a hole-transfer catalyst for the oxidation of sulphide. Similar findings have been reported earlier²⁻⁴.

The effect of $\text{RuO}_2/\text{TiO}_2$ on photocatalytic mixture 2 for the generation H_2 was studied and the results are presented in Figure 3. H_2 generation was found to be a maximum of 392 ml/g/h for the photocatalytic mixture 3, whereas it was found to be only 320 ml/g/h for the photocatalytic mixture 2. Enhancement in H_2 generation might be due to the catalytic activity of $\text{RuO}_2/\text{TiO}_2$, and this was attributed to a heterojunction mechanism. Similar findings have been reported by Borrell *et al.*⁵. The surface area of photocatalytic mixture 3 was analysed using the BET method and it was found to be 196 sq. m/g . The enhancement in activity might be due to the higher surface area of the catalytic mixture. These results have been supported by the work of Reber and Rusek². The band-gap energy of the photocatalytic mixture 3 was analysed by DRS UV-vis analysis and it was found to be 2.48 and 3.1 eV. Enhancement in activity of the photocatalytic mixture 3 might be due to better absorption of UV as well as visible parts of the solar spectrum.

The solar photocatalytic generation of H_2 from $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ solution using CdS-based photocatalysts had been studied. The efficiency of the photocatalyst was found to increase in the order: (CdS/ZnS) (2 : 1) < (CdS/ZnS) (2 : 1)/ Ag_2S < (CdS/ZnS) (2 : 1)/(Ag_2S + $\text{RuO}_2/\text{TiO}_2$). Based on the study, it is evident that the composition, addition of wide band-gap semiconductors, promoters and metal dopants have a significant effect on H_2 generation.

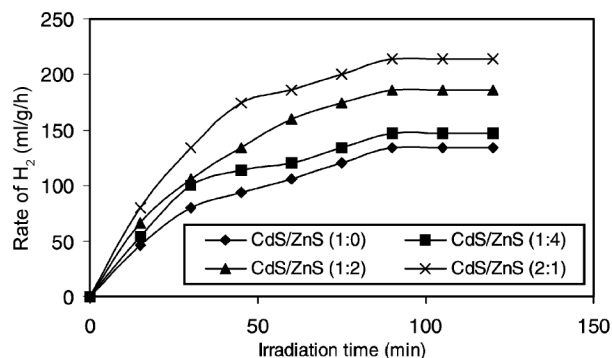


Figure 1. Effect of composition of CdS/ZnS on H_2 generation.

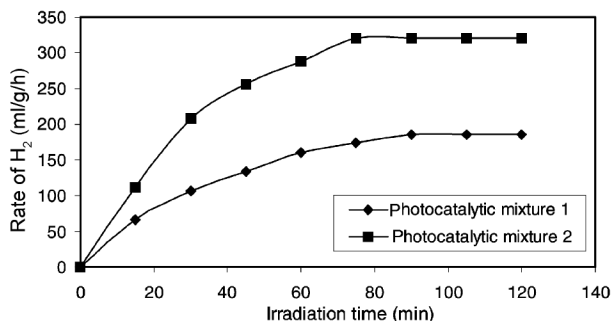


Figure 2. Effect of Ag_2S on photocatalytic mixture 1.

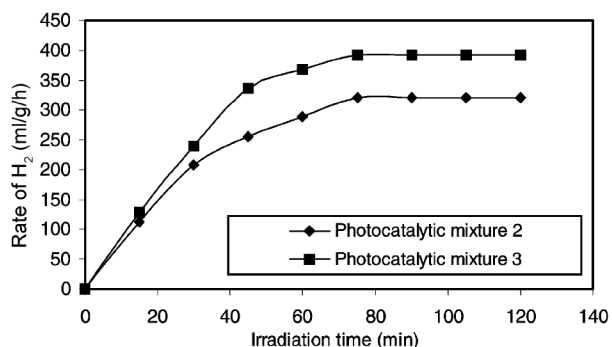


Figure 3. Effect of $\text{RuO}_2/\text{TiO}_2$ on photocatalytic mixture 2.

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A quantitative study on the chemical composition of renal stones and their fluoride content from Anantapur District, Andhra Pradesh, India

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The present study was designed to investigate and arrive at the quantitative chemical composition, inclusive of fluoride content, of 56 kidney stone (renal calculi) samples from 50 patients aged between 20 and 60 years, admitted to Sri Sathya Sai Institute of Higher Medical Sciences Hospital, Prasanthigram, Anantapur District, Andhra Pradesh. Analysis of the calculi was performed using Fourier Transform Infrared vibrational spectroscopic method along with Differential Scanning Calorimetry and the Fluoride Ion Selective Electrode. These are the preferred instrumental techniques with the inherent advantages of providing fast, sensitive, accurate and detailed data about the stone composition, enabling more reliable and efficient post-operative care of individual patients. The results indicate that calcium oxalate monohydrate (whewellite) and dihydrate (wedellite) stones are predominant in this region of Anantapur, with the binary combination of the two accounting for 90% of the stone composition in nearly 85% of the stones, with traces of carbonate-hydroxyapatite (dahllite) or uric acid being the ternary component. In the remaining 15% of the stones, uric acid was the major component. The mean fluoride content in renal calculi was determined to be 2.14 mg/g.

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A quantitative understanding of the exact chemical composition of the urinary calculi is of importance not only because of its relationship with dietary and other health factors, but also in prevention of nephrolithiasis.

Keywords: Chemical composition, fluoride, nephrolithiasis, renal calculi.

NEPHROLITHIASIS, the formation of stones in the urogenital system has afflicted humans since antiquity, with the earliest recorded example¹ being an urinary calculus found in the pelvic area of a young man in a tomb near El Amrah (Egypt) dating back to 4800 BC. Stone disease in man is as old as mankind. This common disorder of renal stone formation affects up to 15% of the population over a lifetime², and without proper treatment and preventive measures, approximately 75% of these patients will have at least one recurrence. An extrapolated incidence statistics of 3,915,700 kidney stones has been estimated from a population of 1,065,070,607 persons in India³, an indication of its high prevalence. The diagnostic usefulness in knowing the chemical composition of renal stones has been recognized since 1950s with significant improvement in therapeutic regimen since then, as exact determination of the compositional structure enables the classification of the disease and its subsequent treatment. In addition, the definite role of fluoride in renal stone formation has been arrived at⁴ after a lot of controversy⁵.

Anantapur District (lat. 13°14'–15°14'N and long. 76°47'–78°26'E), located in southwestern corner of the Andhra Pradesh (AP) in South India, is the most backward and drought-prone area of Rayalaseema. It is one of the poorest districts in the country, with a population of about 4 million, of which 3 million inhabitants depend on groundwater as a major source of water supply. To add to this plight, the district lies at a twin cross-section of the renal stone belt and fluoride belt of India. High levels of fluoride, beyond 3.0 mg/l, in groundwater as a source of drinking water is common in many of the 964 revenue villages included in 63 mandals of this district⁶. Fluoride-bearing minerals like apatite, micas and clay minerals present in the country rocks like shales and pyroclastic materials of the study area are the main source of fluoride ion (F⁻) in groundwater. This is concluded from the positive correlation between fluoride content in the bulk rock and F⁻ content in the nearby groundwater, and also between fluoride content in the soil leachates and F⁻ in the nearby surface water of the district. A good positive correlation between fluoride and lithogenic sodium is obtained, reflecting that weathering activity caused by a semi-arid climate and intensive irrigation practices are responsible for the leaching of F⁻ from mineralogical sources. Hence the fluoride-rich groundwater, used extensively as drinking water in the Anantapur region, causes permanent tooth and skeletal fluorosis due to high body fluoride in the population⁷. Scanty rainfall, a near-arid dehydrating envi-