Effect of photosensitizers and inorganic ions on hydrogen generation from hydrogen sulfide

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This study presents hydrogen (H\textsubscript{2}) generation from hydrogen sulfide (H\textsubscript{2}S) using photocatalyst [(CdS/ZnS)/Ag\textsubscript{2}S+(RuO\textsubscript{2}/TiO\textsubscript{2})] with photosensitizers (Rhodamine B, Eosin Y, Methylene Blue and Methyl Violet). In presence of Rhodamine B, photocatalyst yields 1.3 times more H\textsubscript{2} than control. In presence of anions (I\textsuperscript{-}, Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-} and SO\textsubscript{4}\textsuperscript{2-}) and cations (Fe\textsuperscript{3+}, Cu\textsuperscript{2+}), photocatalyst yields less H\textsubscript{2}.

Keywords: Dye sensitization, Hydrogen, Hydrogen sulfide, Solar photocatalysis

Introduction

Hydrogen generation from cheap raw materials like hydrogen sulfide (H\textsubscript{2}S) is a challenging process for future energy needs. Methods for H\textsubscript{2}S removal are claus and wet absorption methods and thermochemical, electrochemical and photochemical processes. In photocatalysis, using colloidal semiconductors (TiO\textsubscript{2}, CdS, ZnS, CdSe, ZnO etc.) as photocatalysts, solar energy photodecomposes H\textsubscript{2}S. Being a promising photocatalyst, photoactivity of CdS can be improved by adding ZnS wide band gap energy semiconductor. Promoters like Ag\textsubscript{2}S can also enhance activity in catalysts\textsuperscript{1}. In photocatalytic H\textsubscript{2} generation, synthetic dyes were used as photosensitizers to sensitize wide band gap semiconductors\textsuperscript{2}.

This study presents effect of organic dyes as photosensitizers in presence of photocatalyst [(CdS/ZnS)/Ag\textsubscript{2}S+(RuO\textsubscript{2}/TiO\textsubscript{2})] and inorganic ions on H\textsubscript{2} generation from H\textsubscript{2}S.

Materials and Methods

Cadmium carbonate, silver nitrate, sodium sulfide, sodium sulfite, and titanium dioxide (Degussa, P25), zinc carbonate and ruthenium trichloride (Merek) were used. Cadmium acetate and zinc acetate were prepared by dissolving purified cadmium carbonate and zinc carbonate in acetic acid. Other chemicals used were of analytical reagent grade. Mixed semiconductor photocatalyst [(CdS/ZnS)/Ag\textsubscript{2}S+(RuO\textsubscript{2}/TiO\textsubscript{2})] was prepared by mixing of CdS/ZnS/Ag\textsubscript{2}S and RuO\textsubscript{2}/TiO\textsubscript{2}. CdS/ZnS/Ag\textsubscript{2}S was prepared by mixing of coprecipitated CdS/ZnS and Ag\textsubscript{2}S. RuO\textsubscript{2}/TiO\textsubscript{2} was prepared by incipient wetness impregnation method. Dye solutions were prepared by dissolving required quantity of dye powders of Rhodamine B (RB), Eosin Y (EY), Methylene blue (MB) and Methyl violet (MV).

Experiments were carried out in a batch (300 ml) three phase (s-l-g) photocatalytic reactor for H\textsubscript{2} generation. Suspensions were deaerated with N\textsubscript{2} for 30 min to prevent uptake of photogenerated electrons by dissolved O\textsubscript{2}. Catalyst particles were kept suspended by magnetic stirrers. Reactor temperature was maintained by external circulation of water. Whole apparatus was placed on terrace under sunlight. Volume of H\textsubscript{2} was measured at 15 min interval till H\textsubscript{2} generation ceases. H\textsubscript{2} gas, collected by water displacement arrangement, was confirmed on a gas chromatograph (chromatograph and Instruments Company) with TCD using Porapak Q column at 40°C and N\textsubscript{2} as a carrier. Average radiation intensity measured was 422 W/m\textsuperscript{2}.

Results and Discussion

Effect of Photosensitizers

To study effect of photosensitizers on H\textsubscript{2} generation, experiments were conducted using organic dyes. Photocatalyst powders (75 mg) were dispersed in 0.5 M sulfide/0.25 M sulfite solution (50 ml). H\textsubscript{2} (38 ml) was
generated without photosensitizers or control. Concentration of organic dyes was varied (0.25-3 µm) (Fig. 1). RB dye (conc. 0.5 µm) generated maximum H₂ (54 ml), whereas RB (conc. 0.25 µm) generated only 40 ml of H₂. With increase in RB (conc. 1-2 µm), generation of H₂ decreased from 45.5 to 45 ml. Rozenkevich & Sakharovsky³ supported increase in H₂ generation with RB.

In order to justify unadsorbed RB (conc.0.25-3 µm), a mixture of photocatalyst (75 mg) with sulfide/sulfite solution (50 ml) was shaken and allowed to stand still for 1 h. It was filtered through Whatman filter paper no. 42. Filtrate contained RB, indicating presence of unadsorbed dye in the medium. For photosensitizing action, dye is required to be adsorbed on photocatalyst. This condition was well achieved with RB, as it poses carboxyl function. With increase in dye concentration, there might be increase in RB amount adsorbed on catalyst surface. Such a linear dependence was favourable up to 0.5 µm. With further increase in RB concentration, concentration of RB in solution in bulk also increased. Hence, light absorption also increased.

Almost similar results were obtained with EY, which (conc.0.5 µm) generated maximum H₂ ion (50.5 ml). With further increase of EY (conc.1-3 µm), H₂ generation increased from 18 ml to 44 ml. Such a non-linear behavior in H₂ generation was due to different adsorption amount of EY in different catalysts³⁴. Similarly, MB dye (conc.1 µm) generated maximum H₂ (38 ml), due to presence of free unadsorbed MB particles on adsorbed catalyst surface. MB adsorption on catalyst particles had given positive effect and free unadsorbed MB on catalyst particles had given negative effect on H₂ generation. Hence, net effect became equalizing to H₂ volume in comparison with control sample. In case of MB, structure did not pose an adsorbing sight similar to RB. Hence, there might be decrease in absorption of light on catalyst surface as compared to RB. With increase in dye concentration, there might be increase in dye adsorption. MB ions aggregated at 1 µm and left less dye ions for adsorption on catalyst surface. Hence, H₂ generation decreased. With increase in MB concentration (>1 µm), H₂ generation increased. Hence, there must be supply of some dye ions towards adsorption on catalyst surface. It accounted for increase in H₂ generation. Similar behavior was also observed for EY.

At lower concentrations (0.25-1 µm), effect of MV on H₂ generation had shown non-linear behaviour. H₂ volume generated was less (50%) than control samples, due to presence of enough free unadsorbed MV particles. At higher MV (conc.3 µm), H₂ volume generated was nearly equal to control sample, due to enough adsorption of MV on catalyst surface.

**Effect of Inorganic Ions**

Effect of inorganic anions [iodide (I⁻), chloride (Cl⁻), nitrate (NO₃⁻), carbonate (CO₃²⁻) and sulphate (SO₄²⁻)] at different concentration (0.5, 1, and 2 g/l) on H₂ generation was studied (Fig. 2) by dispersing photocatalyst powders (150 mg) in 0.5 M sulfide/0.25 M sulfite solution (100 ml). H₂ generation was found to decrease as follows: potassium iodide, 76-88; sodium nitrate, 78-56; sodium carbonate, 46; and sodium sulphate, 46%. Sodium chloride increased H₂ generation from 2.4% to
6.8%, whereas absence of \( \text{H}_2 \) anions (41 ml) was generated. Presence of Cl\(^-\) ion had shown little enhancement in \( \text{H}_2 \) generation. Except Cl\(^-\) ions, other ions decreased \( \text{H}_2 \) generation\(^5\). Presence of various cations is common in industrial effluents. A reduction in photocatalytic generation of \( \text{H}_2 \) was observed in presence of \( \text{FeSO}_4 \) (0.5 g/l) and \( \text{CuSO}_4 \) (0.5 g/l) (Fig. 3), which can be attributed to negative effect on adsorption of \( \text{SO}_4^{2-} \). Reduction in \( \text{H}_2 \) volume generated was found to be 7.3-14.6% in presence of \( \text{CuSO}_4 \).

**Conclusions**

Effect of photosensitizers and inorganic ions on solar photocatalytic generation of \( \text{H}_2 \) from \( \text{H}_2\text{S} \) was investigated. RB yielded maximum \( \text{H}_2 \) (1.3 times higher than control). Except Cl\(^-\), other anions (I\(^-\), NO\(_3\), CO\(_3^{2-}\), SO\(_4^{2-}\)) and cations (Fe\(^{3+}\) and Cu\(^{2+}\)) retarded \( \text{H}_2 \) generation rates.

**References**