Rhodium and Rhodium Sulfide Coated Cadmium Sulfide as a Photocatalyst for Photochemical Decomposition of Aqueous Sulfide

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Among CdS, Rh/CdS, Rh_2S_3/CdS, and Rh_2S_3/Rh/CdS, the ternary material, viz., Rh_2S_3/Rh/CdS, is found to be the most active photocatalyst for the decomposition of aqueous sulfide. X-ray photoelectron spectroscopic studies show that Rh as it is photodeposited on CdS is in the zero oxidation state but is prone to aerial oxidation.

Introduction

Photocatalytic decomposition of sulfides serves to destroy the pollutant and can also generate hydrogen—a clean fuel. Over the years, CdS has been used as a photocatalyst for this reaction.[1-11] Several modifications of the photocatalysts, such as metallization,[2,10,11] deposition of metal oxides,[1,7] and mixing with large band gap semiconductors like TiO_2,[3,8] have been tried to improve the efficiency of decomposition of hydrogen sulfide

$$H_2S \xrightarrow[CdS]{h\nu} H_2 + S$$
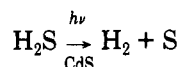
Recently, Borgarello and co-workers[10] reported that a dispersion of CdS and 0.2% Rh^{3+} is quite efficient for the generation of hydrogen from aqueous solutions of sulfide and sulfite. The present work deals with the effect of the deposition of Rh and Rh_2S_3 on CdS on the photocatalytic activity of CdS.

Experimental Section

Rh was deposited on CdS (99.999%, Fluka) by the photoreduction of $RhCl_3$ (Johnson Mathey Co., London) in acetic acid medium at pH 4.5.[2,7,10,11] The photocatalytic activity was measured in an all-glass apparatus by monitoring the pressure changes as a function of time with a 1000-W tungsten–halogen lamp. Other details of the measurement are given elsewhere.[11]

A Hitachi 150-20 spectrophotometer was used to record the diffuse reflectance spectra (DRS). X-ray photoelectron spec-

troscopic (XPS) studies were made with an ESCA-Lab MK.II (VG Scientific Co., U.K.). Photoelectrochemical studies were made with a Wenking POS 73 potentioscan coupled with an Ominigraphic X-Y-t recorder. Addition of $RhCl_3$ to the sulfide solution results in the formation of a brown precipitate. The X-ray diffraction pattern of the above precipitate was obtained by using a Cu Kα source. Triply distilled water was used in all the experiments.

Results and Discussion

Diffuse reflectance spectra (DRS) of several modified CdS samples (Figure 1) reveal that the photodeposition of Rh on CdS extends the light absorption of CdS to wavelengths longer than the characteristic absorption edge (517 nm), retaining, however, the normal absorption. This indicates that the valence band (VB) electrons are excited to the energy levels which lie between the conduction and valence bands of CdS, probably energy states formed by the addition of Rh. Interestingly, when an aqueous solution of Na_2S is added to the CdS powder, the DRS (Figure 1) showed similar tail end absorption. This effect is more pronounced when Rh is also added, clearly indicating that Rh produces deep-seated change in the absorption of CdS.

X-ray photoelectron spectroscopic investigation of Rh/CdS (Table I) shows that the Rh $3d_{5/2}$ XPS peak appears at a binding energy (309.1 eV) higher than that reported for Rh metal (307 eV).[12] With argon ion sputtering, the binding energy of the Rh $3d_{5/2}$ peak shifts toward lower binding energy, and after 15 min of sputtering the observed binding energy of the Rh $3d_{5/2}$ XPS peak (307 eV) approaches the value reported for Rh(0), viz., 307 eV.[12] These observations imply that Rh as it is photodeposited on CdS is in the zero oxidation state but is susceptible to aerial oxidation. Argon ion sputtering could reduce the metal oxides to metal or to lower metal oxides.[13] Kim et al.[13] reported that this reduction process occurs easily for oxides with $-\Delta G_f°$ below 60 kcal/mol. The $-\Delta G_f°$ for Rh_2O_3 formation is 50.0 kcal/mol,[14] indicating that the reduction of Rh_2O_3 is relatively difficult. In the case of Rh/CdS, the possibility of the formation of Rh_2O_3 is

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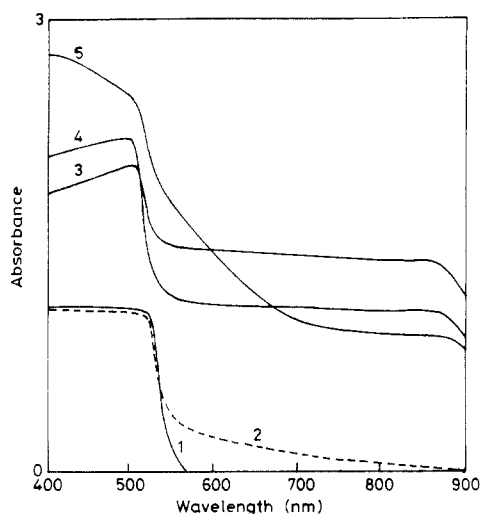(15) Brinen, J. S.; Mehera, A. *J. Phys. Chem.* 1972, *76*, 2525.

Figure 1. Diffuse reflectance spectra of (1) CdS, (2) Rh/CdS, (3) Rh/CdS + S^{2-}, (4) CdS + S^{2-}, and (5) CdS + RhCl$_3$ + S^{2-}.

Table I. X-ray Photoelectron Spectroscopic Data on Rh/CdS

argon ion sputtering time at 50 μA, min	Rh 3d$_{5/2}$ XPS peak binding energy,[a] eV
0	309.1
4.8	308.4
8	308.1
11	307.4
15	307.0

[a] Rh 3d$_{5/2}$ XPS peak binding energy reported for Rh metal is 307 eV[12] and that reported for Rh$_2$O$_3$ is 308.4 eV.[15]

Table II. *d* Values from X-ray Diffraction Data on Rh$_2$S$_3$

observed	reported
2.680	2.687
3.979	3.820

by the aerial oxidation of Rh. The oxidation could occur to a certain depth of Rh only, and the oxide layer could act as a protective coating preventing further oxidation of Rh. Hence the appearance of the Rh metal peak could be due to the presence of Rh° on the surface of CdS, which remained unoxidized due to the covering of Rh$_2$O$_3$.

X-ray diffraction data (Table II) show that the observed *d* values agree with those reported for Rh$_2$S$_3$, indicating the formation of Rh$_2$S$_3$ when RhCl$_3$ is added to an aqueous solution of sulfide.

Photocatalytic studies (Figure 2 and Table III) reveal that Rh/CdS and Rh$_2$S$_3$/CdS are better photocatalysts than CdS. Addition of Rh^{3+} to the reaction mixture to deposit Rh in situ reduces the possibility of aerial oxidation of Rh. Under these conditions, we have a system consisting of Rh$_2$S$_3$, Rh/CdS, and S^{2-}. The light absorption by this system is greater than that by the Rh/CdS + S^{2-} system (Figure 1). This ternary system shows the maximum activity.

Several authors have reported that the metal in the metallized (noble metal) CdS acts as a proton reduction center,[2-5,7] owing to its low overvoltage for hydrogen evolution and its ability to function as the sink for the electrons. Thus, Rh in Rh/CdS can also serve as a proton reduction center. Hence, the deposition of Rh on CdS increases the photocatalytic activity of CdS (Table III). XPS studies indicate the presence of Rh$_2$O$_3$ on the surface of Rh/CdS. Just like RuO$_2$, the Rh$_2$O$_3$ present on
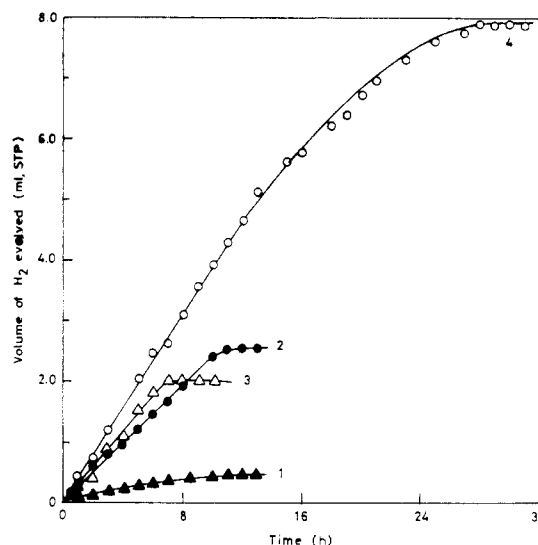

Figure 2. Volume of H$_2$ evolved vs time of irradiation curves for (1) CdS, (2) Rh/CdS, (3) Rh$_2$S$_3$/CdS, and (4) CdS + RhCl$_3$ + S^{2-}.

Table III. Photocatalytic Hydrogen Evolution from Aqueous Sulfide Solution[a]

photocatalyst	initial H$_2$ evolution rate, mL/h per g
CdS	0.31
Rh/CdS (Rh 1.37 wt %)	2.53
Rh$_2$S$_3$/CdS (Rh 1.37 wt %)	2.83
CdS + Rh^{3+} (Rh 1.37 wt % as RhCl$_3$)	4.15
Rh^{3+} (Rh 1.37 wt % as RhCl$_3$)	

[a] Reactant: 0.25 M Na$_2$S solution (20 mL).

Rh/CdS can act as a hole-transferring agent,[16,17] promoting the oxidation of sulfide ions. Hence, Rh/CdS which contains Rh$_2$O$_3$ serves as an effective bifunctional photocatalyst, facilitating both the reduction of proton and the oxidation of SH$^-$ ions. RuS$_2$ is a good catalyst for hydrodesulfurization.[18,19] RuS$_2$/CdS serves as a better photocatalyst than RuO$_2$/CdS for the photocatalytic decomposition of aqueous sulfide.[6] Rh$_2$S$_3$ is also known to be a good catalyst for hydrodesulfurization.[18-20] Rh$_2$S$_3$ could serve as a site for the oxidation of the SH$^-$ ions. Just like RuS$_2$/CdS, Rh$_2$S$_3$/CdS also serves as a better photocatalyst than Rh/CdS (Table III). The in situ deposition of Rh on CdS in the presence of sulfide yields an effective bifunctional photocatalyst, viz., Rh$_2$S$_3$/Rh/CdS. In this case, the conduction band (CB) electrons (e$^-$) can move to the Rh sites and the valence band holes (h$^+$) can move toward Rh$_2$S$_3$ and can react with the protons and SH$^-$ ions, respectively. Thus, the effective charge separation is facilitated, and a large number of electrons and holes are available (the probability of recombination of the charge carriers is reduced) for the photocatalytic decomposition of aqueous sulfide. Thus, Rh$_2$S$_3$/Rh/CdS serves as the most effective photocatalyst among the catalysts examined. On the basis of these observations, the following scheme can be given for the

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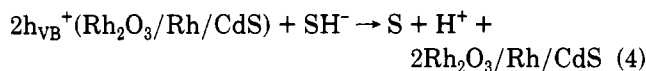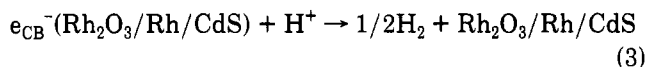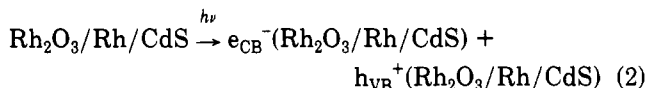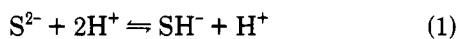
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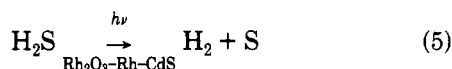
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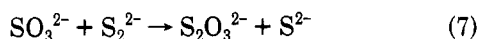photocatalytic decomposition of aqueous sulfide:

Scheme I

$$S^{2-} + 2H^+ \rightleftharpoons SH^- + H^+ \qquad (1)$$

$$Rh_2O_3/Rh/CdS \xrightarrow{h\nu} e_{CB}^-(Rh_2O_3/Rh/CdS) + \\ h_{VB}^+(Rh_2O_3/Rh/CdS) \quad (2)$$

$$e_{CB}^-(Rh_2O_3/Rh/CdS) + H^+ \rightarrow 1/2H_2 + Rh_2O_3/Rh/CdS \\ (3)$$

$$2h_{VB}^+(Rh_2O_3/Rh/CdS) + SH^- \rightarrow S + H^+ + \\ 2Rh_2O_3/Rh/CdS \quad (4)$$

overall reaction:

$$H_2S \xrightarrow[Rh_2O_3-Rh-CdS]{h\nu} H_2 + S \qquad (5)$$

in alkaline medium:

$$S + S^{2-} \rightarrow S_2^{2-} \qquad (6)$$

in the presence of sulfite ions:

$$SO_3^{2-} + S_2^{2-} \rightarrow S_2O_3^{2-} + S^{2-} \qquad (7)$$

In alkaline medium (pH 13), the sulfur formed reacts with the sulfide ions (reactant) to give yellow disulfide ions which hinder the light absorption by CdS. This could be avoided by the addition of sulfite ions (SO_3^{2-}) to the reaction mixture, which react with the disulfide ions to give colorless thiosulfate ions (eq 7).[2] Scheme I holds good in the case of $Rh_2S_3/Rh/CdS$ also, the only difference being the replacement of Rh_2O_3 by Rh_2S_3.

Photoelectrochemical studies show that the photocurrent at a bias of +1 V vs SCE, which is mainly due to the photocorrosion of CdS ($CdS + 2h_{VB}^+ \rightarrow Cd^{2+} + S$)[21,22] with Rh/CdS as the photoanode (170 μA) is less than that observed in the case of CdS (245 μA), indicating that the photodeposition of Rh on CdS decreases the photocorrosion of CdS.

In conclusion, it can be stated that Rh/CdS is more stable toward photocorrosion and absorbs most of the visible light. Rh, which acts as a sink for the electrons, serves as a good proton reduction center. Hence, Rh/CdS is a better photocatalyst than CdS. Rh_2S_3/CdS also functions as a better photocatalyst than CdS. Among the photocatalysts investigated, Rh_2S_3/Rh/CdS is found to be the most active photocatalyst for the decomposition of aqueous sulfide. The order of activity of the photocatalysts can be given as follows: Rh_2S_3/Rh/CdS (Rh 1.37 wt %) > Rh_2S_3/CdS (Rh 1.37 wt %) > Rh/CdS (Rh 1.37 wt %) > CdS.

Registry No. Rh, 7440-16-6; Rh_2S_3, 12067-06-0; CdS, 1306-23-6; Na$_2$S, 1313-82-2; H, 12385-13-6.

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Electron Transfer in Aqueous Colloidal SnO$_2$ Solutions

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Electron-transfer reactions on transparent colloidal SnO$_2$ have been examined by use of radiolytically generated reducing radicals, direct band-gap excitation, and photosensitization using Ru(bpy)$_3$$^{2+}$. Colloidal SnO$_2$ was found to be cathodically stable under the reducing conditions examined. Quantitative amounts of H$_2$ formed in solution following electron transfer from radiolytically generated isopropyl alcohol radicals. No hydrogen, however, was produced if the sol was illuminated at 300 nm, even in the presence of a hole scavenger. Yet, if the electron acceptor methylviologen was present, the characteristic blue color of the viologen radical formed readily with time of illumination. Charge transfer from excited, adsorbed Ru(bpy)$_3$$^{2+}$ was found to be strongly dependent on pH and electrolyte concentration. This has been scribed to the effect that pH and added electrolyte both control the electrostatic potential on the colloidal SnO$_2$, which in turn influences the adsorption of the ruthenium complex and therefore the extent of quenching.

Introduction

Tin dioxide is a wide-band-gap (3.5 eV) oxide[1] which is relatively inert under both cathodic and anodic bias.

The flat band potential is placed very close to the redox level of water.[2] Photoelectrochemical investigations have suggested that reduction of the oxide competes only weakly with hydrogen evolution under a cathodic bias.[3] In order

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