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Cadmium sulfide with iridium sulfide and platinum sulfide deposits as a photocatalyst for the decomposition of aqueous sulfide

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Abstract

The in situ deposition of Pt and Ir on CdS during the photocatalytic decomposition of aqueous sulfide results in the formation of an effective bifunctional photocatalyst (MS/CdS/M, where MS is Pt or Ir sulfide and M is Pt or Ir) which is more active than CdS and metallized CdS. In situ metallization provides a convenient method for the preparation of metal- and metal-sulfide-deposited CdS. The order of reactivity for the in situ metallization of CdS in the case of the photocatalytic decomposition of aqueous sulfide is Rh > Pt > Pd > Ru = Ir > Co ≈ Ni = Fe. Based on the observed results a mechanism for the photocatalytic decomposition of aqueous sulfide is proposed.

Keywords: Photocatalysis; Photoelectrochemistry; Iridium sulfides; Platinum sulfides; CdS

1. Introduction

CdS-based photocatalysts have been widely used for the photocatalytic decomposition of aqueous sulfides [1–7]. The deposition of some of the group VIII metals, noble metal oxides such as RuO_2 and Rh_2O_3 and noble metal sulfides such as RuS_2 and Rh_2S_3 enhance the photocatalytic activity of CdS [7–10]. Although the preparation of metallized CdS by the photodeposition of metals is simple and easy, it is energy and time consuming. Furthermore, the exposure of metallized CdS to air leads to the oxidation of the deposited metals [6,7]. To save time and energy and to avoid the oxidation of metals by air, in situ metallization has been used and found to be advantageous [5–7]. Depending on the various reactants used in the photocatalytic reactions, a variety of metal compounds will also be formed during the in situ photodeposition of metals. Some of the noble metal sulfides, which are good catalysts for hydrodesulfurization [11–13], when deposited on CdS enhance the photocatalytic activity [7,10]. Metal sulfides formed during the in situ deposition of Rh and Ru on CdS enhance the photocatalytic activity of CdS [7,10]. However, the effect of the in situ deposition of Ir and Pt on the photocatalytic activity of CdS for the decomposition of aqueous sulfide has not been studied. Therefore we have investigated the effect of the in situ photodeposition of Pt and Ir on the photocatalytic activity of CdS. Furthermore, the photocatalytic decomposition of aqueous sulfide using CdS-based photocatalysts provides a method for the conversion and storage of solar energy and the removal of the pollutant sulfide and leads to the production of hydrogen, which is a clean fuel and a starting material for many industries.

2. Experimental section

The in situ deposition of Pt and Ir sulfides on CdS (Fluka, 99.999%) was achieved by the addition of hexachloroplatinic acid (Arora Mathey Ltd.) and iridium(III) chloride (Alfa Inorganic) to a mixture of CdS and aqueous sulfide. The details of the photocatalytic measurements are reported elsewhere [6,7]. A 1000 W tungsten–halogen lamp was used as the light source. The details of the photoelectrochemical measurements are reported elsewhere [14].

3. Results and discussion

From Fig. 1 and Table 1, it can be seen that the deposition of Pt on CdS increases the rate of hydrogen evolution from an aqueous sulfide solution, indicating that Pt serves as a good proton reduction center or sink for electrons. For metals to act as efficient reduction centers, the contact with an n-type semiconductor, such as n-CdS, should be ohmic as a Schottky barrier would drive the electrons away from the

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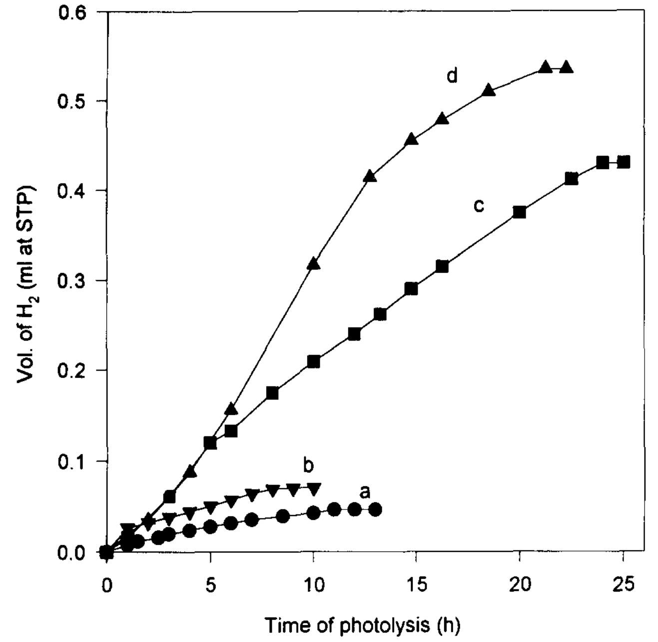

Fig. 1. Volume of H_2 evolved as a function of irradiation time: (a) CdS; (b) CdS + 1.37 wt.% Ir^{3+} as $IrCl_3$; (c) Pt/CdS (1.37 wt.%); (d) CdS + 1.37 wt.% Pt^{4+} as H_2PtCl_6.

Table 1

Effect of the in situ deposition of group VIII metals on the photocatalytic activity of CdS (reactant, 0.25 M aqueous Na_2S solution; weight of photocatalyst, 100 mg; temperature, 303 K; pH 13)

Sample	Photocatalyst	Initial H_2 evolution rate ($\mu l\ h^{-1}$)
1	CdS	31
2	Pt/CdS (1.37 wt.%)	208
3	CdS + 1.37 wt.% Pt^{4+} as H_2PtCl_6	289
4	CdS + 1.37 wt.% Ir^{3+} as $IrCl_3$	96
5	CdS + 1.37 wt.% Ru^{3+} as $RuCl_3$	97
6	CdS + 1.37 wt.% Rh^{3+} as $RhCl_3$ [7]	415
7	CdS + 1.37 wt.% Pd^{2+} as $PdCl_2$ [6]	255
8	CdS + 1.37 wt.% Ni^{2+} as $NiCl_2$ [15]	53
9	CdS + 1.37 wt.% Co^{2+} as $CoCl_2$ [15]	58
10	CdS + 1.37 wt.% Fe^{3+} as $FeCl_3$ [15]	52
11	1.37 wt.% Pt^{4+} as H_2PtCl_6	0

metal [16]. Thus the photocatalytic studies on Pt/CdS and CdS indicate that photodeposited Pt forms an ohmic contact with CdS.

To probe further the nature of the contact between Pt and CdS, photoelectrochemical measurements were also carried out. From Table 2, it can be seen that the photodeposition of Pt on CdS decreases $R_{\mathrm{cell(dark)}}$ of the photoelectrochemical (PEC) cell as the highly conductive metal Pt is deposited on a relatively less conducting semiconductor n-CdS. Certainly, the decrease in $R_{\mathrm{cell(dark)}}$ is due to the photodeposition of Pt on the CdS photoanode as the other elements of the PEC cell are unaltered. Normally, with a decrease in $R_{\mathrm{cell(dark)}}$, an increase in the photocurrent is expected. However, in the present case, the photocurrent decreases, indicating that only part of the conduction band electrons flow through the external circuit, and the other part is transferred to Pt on the surface of CdS. This also leads to an apparent increase in $R_{\mathrm{cell(photo)}}$ of the PEC cell [14,17–19]. $R_{\mathrm{cell(photo)}}$ of a PEC cell increases only when the metal deposited on the photoanode forms an ohmic contact with the n-type semiconductor [14,15,20]. $R_{\mathrm{cell(photo)}}$ in both cases (CdS and Pt/CdS) is much lower than $R_{\mathrm{cell(dark)}}$ as the charge carriers (electrons and holes) produced during the illumination of the photoanodes aid the effective transport of the current. The conduction band electrons of CdS can be transferred to Pt only if the contact between CdS and Pt is ohmic. Thus the decrease in the photocurrent and the increase in $R_{\mathrm{cell(photo)}}$ on photodeposition of Pt on the CdS photoanode imply that the contact between Pt and n-CdS is ohmic. As explained earlier, the photocatalytic studies also show that Pt forms an ohmic contact with CdS.

X-Ray photoelectron spectroscopy of Pt/CdS showed that the photodeposited Pt is in the zero oxidation state, forms an ohmic contact with CdS and hence does not affect the binding energy of the Cd 4d electrons of CdS [21]. Detailed surface studies on Pt/CdS will be published separately.

During the in situ metallization of CdS in the presence of aqueous sulfide (reactant), some of the metal ions are deposited as metal sulfides and some are photoreduced by the conduction band electrons of CdS to form metal deposits. As explained earlier and reported in Refs. [2,3,22–24], the photodeposited noble metals act as good proton reduction centers owing to their low overvoltage for hydrogen evolution and their ability to function as sinks for the photoelectrons. Thus the photodeposited Pt and Ir on CdS, during the in situ photodeposition, also serve as good proton reduction centers, increasing the rate of hydrogen evolution from aqueous sulfide solution.

Table 2

Photoelectrochemical characteristics of CdS and Pt/CdS (counterelectrode, Pt foil; reference electrode, saturated calomel electrode (SCE); electrolyte, 0.1 M KCl; temperature, 303 K)

Photoanode	Dark			Photo		
	V_{oc} (mV)	I_{sc} (mA)	$R_{\mathrm{cell(dark)}}$ (kΩ)	V_{oc} (mV)	I_{sc} (mA)	$R_{\mathrm{cell(photo)}}$ (kΩ)
CdS	350	0.001	350	130	0.048	2.7
Pt/CdS ($\theta_{Pt}=0.29$)	24	0.001	24	256	0.034	7.5

V_{oc}, open circuit voltage; I_{sc}, short circuit current; θ_{Pt}, fraction of the surface of CdS photoanode covered by Pt; $R_{\mathrm{cell(dark)}}$, internal resistance of the PEC cell in the dark; $R_{\mathrm{cell(photo)}}$, internal resistance of the PEC cell under illumination.

Most of the group VIII metals are good catalysts for hydrodesulfurization [11–13]. It is reported that CdS with Ru or Rh sulfide deposits functions as a better photocatalyst than naked CdS [7,10]; similarly the deposition of Pt and Ir sulfides also increases the photocatalytic activity of CdS (Fig. 1 and Table 1). The Pt and Ir sulfides formed on the surface of CdS during the in situ deposition of Pt and Ir could serve as hole transferring agents or as sites for oxidation. Thus in situ deposition of Pt and Ir on CdS in the presence of sulfide ions yields effective bifunctional photocatalysts, i.e. MS/CdS/M (MS ≡ Pt or Ir sulfide; M ≡ Pt or Ir). During the illumination of MS/CdS/M with visible light in the presence of aqueous sulfide ions, the conduction band (CB) electrons (e^-) of CdS can be transferred to M (Pt or Ir) sites and the valence band (VB) holes (h^+) can move towards MS (Pt or Ir sulfide) and can react with the protons and SH^- ions respectively. Thus effective charge separation is facilitated, and as the probability of recombination of the charge carriers is reduced, a large number of electrons and holes are available for the photocatalytic decomposition of aqueous sulfide. Hence the bifunctional photocatalysts (MS/CdS/M) produced during the in situ deposition of Pt and Ir serve as better photocatalysts than naked and metallized CdS (Fig. 1 and Table 1). For comparison, the effect of the in situ deposition of other group VIII metals is also given in Table 1. The order of reactivity in the case of in situ metallization is Rh > Pt > Pd > Ru = Ir > Co ≈ Ni = Fe.

On the basis of these observations, the following scheme can be given for the photocatalytic decomposition of aqueous sulfide by the bifunctional photocatalyst MS/CdS/M

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

$$\mathrm{MS/CdS/M} \xrightarrow{h\nu} e_{CB}^-(\mathrm{MS/CdS/M}) + h_{VB}^+(\mathrm{MS/CdS/M}) \qquad (2)$$

$$e_{CB}^-(\mathrm{MS/CdS/M}) \longrightarrow e^-(\mathrm{M/CdS/MS}) \qquad (3)$$

$$h_{VB}^+(\mathrm{MS/CdS/M}) \longrightarrow h^+(\mathrm{MS/CdS/M}) \qquad (4)$$

$$2e^-(\mathrm{M/CdS/MS}) + 2H^+ \longrightarrow H_2 + 2\mathrm{MS/CdS/M} \qquad (5)$$

$$2h^+(\mathrm{MS/CdS/M}) + SH^- \longrightarrow S + H^+ + 2\mathrm{MS/CdS/M} \qquad (6)$$

where VB is the valence band, CB is the conduction band, e^-(M/CdS/MS) is the electron on Pt or Ir and h^+(MS/CdS/M) is the hole on Pt or Ir sulfide. The overall reaction is

$$H_2S \xrightarrow[2\mathrm{MS/CdS/M}]{h\nu} H_2 + S \qquad (7)$$

It is known that, in alkaline medium, the photocatalytic decomposition of aqueous sulfide leads to the formation of disulfide ions (Eq. (8)) and no sulfur precipitation is observed [1–5]

$$2S^{2-} + 2h^+ \longrightarrow S_2^{2-} \qquad (8)$$

However, hydrogen and sulfur are produced in acidic solutions with a small quantum yield. In the present study, the colorless aqueous sulfide solution turns yellow after prolonged photocatalytic decomposition, indicating the formation of disulfide and polysulfide ions which can be electrochemically and spectrophotometrically detected. Thus in this investigation, as the photocatalytic reaction is carried out in alkaline medium (pH 13), only the formation of disulfides and polysulfides is observed. No sulfur precipitation is detected. The yellow disulfides and polysulfides thus formed compete with the light absorption by CdS acting as internal filters. Hence the formation of disulfides and polysulfides decreases the efficiency of the reaction. This can be overcome by the addition of sulfite ions (SO_3^{2-}) to the reaction mixture, which react with yellow disulfide ions to give colorless thiosulfate ions (Eq. (9)) [3]

$$S_2^{2-} + SO_3^{2-} \longrightarrow S_2O_3^{2-} + S^{2-} \qquad (9)$$

4. Conclusions

The results of this study show that the in situ deposition of Pt and Ir on CdS during the photocatalytic decomposition of aqueous sulfide yields an effective bifunctional photocatalyst, i.e. MS/CdS/M (MS ≡ Pt or Ir sulfide; M ≡ Pt or Ir), which is more active than CdS and metallized (Pt) CdS. The in situ deposition of group VIII metals during the photocatalytic decomposition of aqueous sulfide yields a simple and easy preparation of bifunctional photocatalysts and avoids the oxidation of the metals by air. The following order of reactivity is observed for the in situ metallization of CdS with group VIII metals in the case of the photocatalytic decomposition of aqueous sulfide: Rh > Pt > Pd > Ru = Ir > Co ≈ Ni = Fe. A mechanism for the photocatalytic decomposition of aqueous sulfide is proposed.

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