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Journal of Photochemistry and Photobiology A: Chemistry 156 (2003) 249–252

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

H_2 evolution from aqueous sulfite solutions under visible-light irradiation over Pb and halogen-codoped ZnS photocatalysts

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Received 25 July 2002; received in revised form 30 October 2002; accepted 4 December 2002

Abstract

Pb-doped ZnS showed a photocatalytic activity for H_2 evolution from an aqueous K_2SO_3 solution under visible-light irradiation ($\lambda > 420$ nm) even without a Pt cocatalyst. Codoping of a halogen ion with Pb improved the photocatalytic activity. The visible-light response was due to the transition from a 6s orbital of Pb^{2+} to the conduction band of ZnS of the host material.

Keywords: Photocatalyst; H_2 evolution; Visible-light response; Zinc sulfide; Lead

1. Introduction

Cu or Ni-doped ZnS photocatalysts show high activities for H_2 evolution from aqueous solutions in the presence of a sacrificial reagent such as sulfite ions under visible-light irradiation ($\lambda > 420$ nm) even without a platinum cocatalyst [1–3]. The visible-light response is obtained by the formation of donor levels by the doped Cu^{2+} and Ni^{2+} of transition metal cations in the wide band gap of the ZnS host material [3–5]. The conduction band level of ZnS is so high that H_2 evolution from water efficiently proceeds even without a cocatalyst such as Pt in the presence of a hole scavenger [6]. On the other hand, ZnS is a well-known luminescent material [7,8]. Doping of halogen contributes to the formation of luminescence centers [9,10]. Therefore, halogen doping is expected to affect the photocatalytic properties of ZnS.

It is important to develop photocatalyst materials with visible-light response from a viewpoint of a solar light energy conversion. For oxide semiconductor photocatalysts, making a valence band with orbitals of some elements except for O2p is indispensable for the development of visible-light-driven photocatalysts. The present authors have paid attention to Bi^{3+} with $6s^2$ configuration [11,12] and Ag^+ with d^{10} configuration [13]. Band gaps of $AgTaO_3$ and $AgNbO_3$ are narrower than those of $NaTaO_3$ and $NaNbO_3$ with the similar perovskite structure. It is due to that the Ag3d orbital contributes to the valence band formation by hybridization with the O2p orbital. $BiVO_4$ shows the high activity for O_2 evolution from aqueous solution under visible-light irradiation in the presence of an electron scavenger such as Ag^+. The valence band of $BiVO_4$ consists of Bi6s and O2p orbitals and its level is more negative than that consisting of only O2p. It results in the decrease in the band gap. Pb6s orbitals can also form such a valence band similarly to Bi6s. $RbPb_2Nb_3O_{10}$ has been reported to be an active photocatalyst working under visible-light irradiation [14]. Therefore, Pb^{2+} is expected to form a valence band or an electron donor level also in a band gap of sulfide semiconductor photocatalysts.

In the present paper, photocatalytic H_2 evolution under visible-light irradiation ($\lambda > 420$ nm) on ZnS doped with Pb^{2+} with $6s^2$ configuration was studied. The role of doped Pb for the visible-light response was discussed. Effects of codoping of halogen anions with Pb^{2+} on the photocatalytic activity were also examined.

2. Experimental

$Zn_{1-x}Pb_xS$ powder was prepared by adding an aqueous Na_2S solution (1 mol/l, 50 ml) into a mixed aqueous solution of $Zn(NO_3)_2$ (0.2 mol/l, 100 ml, Wako Chemicals, 99%) and $Pb(NO_3)_2$ (Wako Chemicals, 99.5%) and by stirring the mixed solution for 15 h at 300 K. Halogen anions were added in the starting Na_2S solution when they were doped. Obtained precipitation was heat-treated in a N_2 gas flow. The structure of the obtained powders was confirmed by X-ray diffraction (Rigaku; RINT-1400). Surface areas were determined by BET measurement (Coulter; SA3100). Diffuse

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doi:10.1016/S1010-6030(02)00433-1

reflection spectra were obtained using a UV-Vis-NIR spectrometer (Jasco; Ubest V-570) and were converted from reflection to absorbance by the Kubelka–Munk method.

Photocatalytic reactions were conducted in a gas-closed circulation system. The photocatalyst powder was dispersed in an aqueous solution containing SO_3^{2-} as an electron donor. Photocatalysts were irradiated with visible-light ($\lambda >$ 420 nm) through a cut-off filter (HOYA, L42) from a 300 W Xe lamp (ILC technology; CERMAX LX-300). The amount of H_2 evolved was determined using an on-line gas chromatography (Shimadzu; GC-8A, MS-5A column, TCD, Ar carrier).

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of ZnS doped with different amounts of Pb^{2+}. The crystal structure of these powders heat-treated at 773 K in a N_2 gas flow was a mixture of zinc blende and wurtzite phases. An ionic radius of Pb^{2+} (1.12 Å) is larger than that of Zn^{2+} (0.74 Å). As the amount of doped Pb^{2+} was increased the diffraction peaks shifted to low angles and broadened. The broadening indicated the decrease in the crystallinity. These observations concluded that Pb^{2+} ions were doped in the ZnS lattice by replacing at Zn sites. An X-ray diffraction pattern of PbS was observed at 2 at.% of the doping level. This was due to the limitation of a doping amount in the ZnS lattice.

Fig. 2 shows diffuse reflectance spectra of ZnS doped with different amounts of Pb^{2+}. A new absorption band in a visible-light region was observed by the doping of Pb^{2+} in addition to the fundamental UV absorption band of ZnS. The visible-light absorption band shifted to a long wavelength as the doping amount was increased. The energy gaps were estimated to be from 2.2 eV for 1.6 at.%-doping to 2.9 eV for 0.1 at.%-doping from the onset wavelengths. These powders were yellow. The visible-light absorption band was assigned to be the transition from a Pb6s level to the conduction band of ZnS. In contrast, an additional broad band ($\lambda >$ 550 nm) was observed for Pb (2.0 at.%)-doped ZnS. This was due to the impurity PbS phase as indicated by X-ray diffraction.

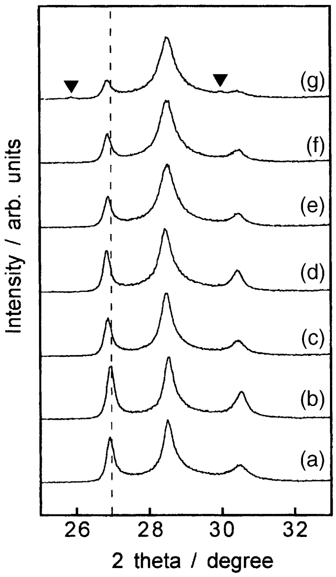

Fig. 1. XRD patterns of ZnS doped with Pb: (a) non-doped, (b) 0.1%, (c) 0.6%, (d) 1.0%, (e) 1.4%, (f) 1.6%, and (g) 2.0%. Heat-treatment: 773 K for 2 h. Marked peaks indicate the PbS.

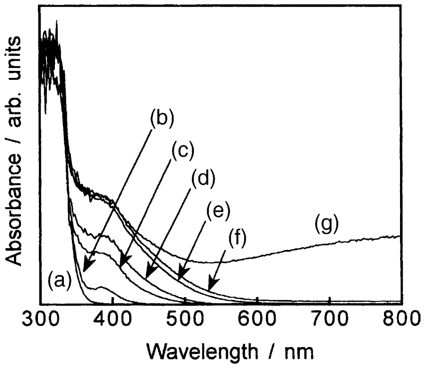

Fig. 2. Diffuse reflectance spectra of ZnS doped with Pb: (a) non-doped, (b) 0.1%, (c) 0.6%, (d) 1.0%, (e) 1.4%, (f) 1.6%, and (g) 2.0%. Heat-treatment: 773 K for 2 h.

Fig. 3 shows the dependence of photocatalytic H_2 evolution from an aqueous K_2SO_3 solution on Pb–ZnS under visible-light irradiation upon the amount of Pb^{2+} doping. As the amount of doped Pb was increased the photocatalytic activity for H_2 evolution under visible-light irradiation was increased, because the visible-light absorption band of Pb–ZnS grew. However, 2 at.% of Pb doping lowered the activity due to the impurity phase of PbS. The PbS impurity may shield the incident light and work as recombination sites between photogenerated electrons and holes. The maximum activity was obtained at 1.4 at.% of Pb doping.

Table 1 shows photocatalytic activities for H_2 evolution under visible-light irradiation and BET surface areas of Pb (1.4 at.%)–ZnS heat-treated at different temperatures. The heat-treatment improved the photocatalytic activity. The

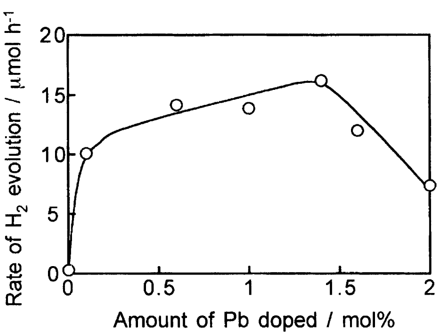

Fig. 3. Dependence of photocatalytic activities for H_2 evolution from an aqueous K_2SO_3 solution (0.5 mol/l 300 ml) over ZnS:Pb (1 g) upon the amount of doped Pb. Light source: Xe lamp with a cut-off filter ($\lambda >$ 420 nm). Heat-treatment: 773 K for 2 h.

Table 1
Effects of heat-treatment on BET surface areas and photocatalytic activities of ZnS doped with Pb (1.4 at.%)

Heat-treatment		Surface area (m^2/g)	Rate of H_2 evolution (μmol/h)
Temperature (K)	Time (h)		
Non-treated	–	192	0.4
573	2	63	3
623	2	44	21
673	2	36	18
773	2	18	16
873	2	9	9
573	9	56	19
623	14	36	31

Catalyst: 1 g, heat-treated in N_2 flow. Reactant: 0.5 mol/l K_2SO_3 and 0.005 mol/l Na_2S solution. Light source: 300 W Xe lamp ($\lambda > 420$ nm).

maximum activities were obtained by the heat-treatment around 623–673 K. However, the photocatalytic activity was decreased by the high temperature treatment at 873 K. Diffuse reflectance spectra and X-ray diffraction were measured to investigate the effect of the heat-treatment on the photocatalytic activity.

Non-treatment as just dried and heat-treatment at 573 K gave absorption bands tailing to the near infrared region as shown in Fig. 4. These Pb–ZnS photocatalysts showed low activities and were gray. In contrast, Pb–ZnS heat-treated at 623–673 K which showed the highest activity possessed the absorption edge at 530 nm and was yellow. It suggested that Pb was doped into the ZnS lattice by the heat-treatment. Pb–ZnS heat-treated at 873 K possessed an additional broad band ($\lambda > 550$ nm) as also observed in Fig. 2 (g). This absorption band was due to PbS liberated by the high temperature treatment. Fig. 5 shows X-ray diffraction patterns of Pb–ZnS heat-treated at different temperature. As the temperature was increased the crystal structure was changed from zinc blende to wurtzite and the peaks sharpened. The increase in the crystallinity by the heat-treatment improved the photocatalytic activity as shown in Table 1. PbS was liberated at 873 K as suggested by a diffuse reflectance spectrum and X-ray diffraction. As the crystal structure was changed from zinc blende to wurtzite by the heat-treatment, large Pb^{2+} cations were turned out from the ZnS lattice. The reasons why the photocatalytic activity was decreased by the high temperature treatment were a decrease in surface areas and a shielding effect by a liberated PbS. Long time heat-treatment at 573 and 623 K was carried out to obtain Pb–ZnS photocatalysts with zinc blende structure and a good crystallinity. The treatment improved the photocatalytic activity as shown in Table 1 even though the surface areas were decreased. This result indicated that the crystallinity was a more important factor than the surface area for this photocatalyst system.

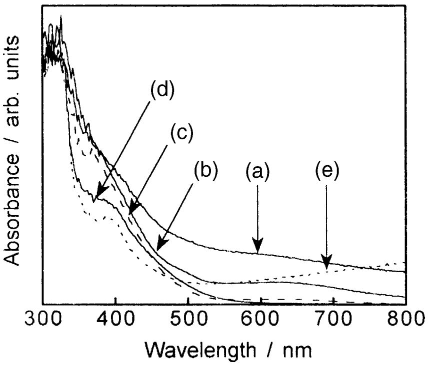

Fig. 4. Diffuse reflectance spectra of ZnS doped with Pb (1.4 at.%): (a) untreated, and heat-treated at (b) 573 K, (c) 673 K, (d) 773 K, and (e) 873 K in N_2 flow.

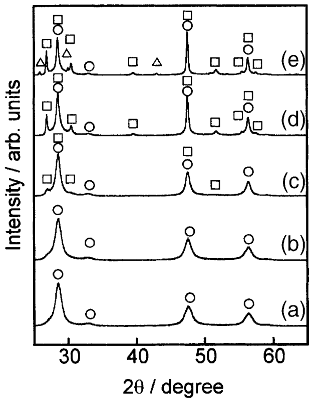

Fig. 5. XRD patterns of ZnS doped with Pb (1.4 at.%) heat-treated at (a) 573 K, (b) 623 K, (c) 673 K, (d) 773 K, and (e) 873 K in N_2 flow. Circles and squares indicate zinc blende and wurtzite structure of ZnS, respectively, and triangles indicate PbS.

Codoping of halogen anions was also effective as shown in Fig. 6. The doped halogen ions may be useful for the relaxation of the distortion by the doping of large Pb cations and suppress the formation of non-radiative transition site in which recombination between photogenerated electrons and holes occurs. The photocatalytic activity of Ni- or Cu-doped ZnS was increased by about 20% by codoping of a halogen ion. On the other hand, the activity of halogen-codoped with Pb was about three times higher than that of Pb-doped ZnS

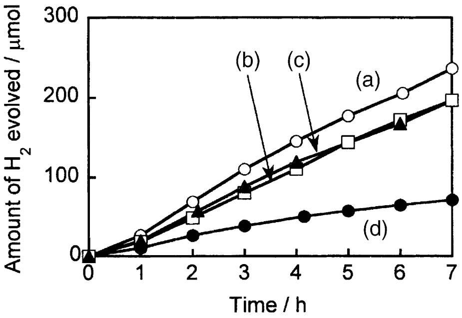

Fig. 6. Photocatalytic H_2 evolution from an aqueous K_2SO_3 solution (0.5 mol/l, 300 ml) under visible-light irradiation on ZnS:Pb (1.0 at.%) codoped with halogen (2.0–2.5 at.%): (a) Cl, (b) Br, (c) I, and (d) none.

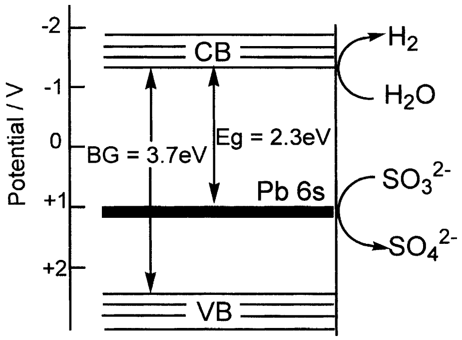

Fig. 7. Band structure of ZnS doped with Pb.

photocatalysts. Thus, the effect of the halogen codoping was drastic in the Pb–ZnS photocatalyst.

We have previously reported that Ni,Cu-doped ZnS photocatalysts which showed the high activity for H_2 evolution [1–3]. The visible-light response of the photocatalysts was due to the transition from metal ions donor levels formed in the band gap of ZnS to the conduction band of ZnS of the host material. In the present study, Pb-doped ZnS was found to be an active photocatalyst for H_2 evolution under visible-light irradiation without co-catalysts such as Pt as well as Ni, Cu-doped ZnS photocatalysts. It indicated that the high conduction band level due to the host ZnS semiconductor material should be maintained. The visible-light response was appeared when Pb was doped. These results led to the scheme as shown in Fig. 7. The filled Pb6s orbitals form electron donor levels in the band gap of ZnS, being different from Cu,Ni-doped ZnS photocatalysts in which the donor levels were partially filled 3d orbitals of Cu^{2+} and Ni^{2+}. Visible-light absorption occurs by the transition from the Pb6s levels to the conduction band level of ZnS, and H_2 evolution proceeds by the reduction of water by the photogenerated electrons in the conduction band accompanied with the oxidation of sulfite ions by holes formed in the Pb sites. Although the activity of Pb-doped ZnS was lower than these of Cu,Ni-doped ZnS photocatalysts, it was interesting that the formation of donor level formed by the fully filled 6s orbital resulted in the visible-light response.

Acknowledgements

This work was supported by Core Research for Evolutional Science and Technology (CREST), a Grant-in-Aid (no. 14050090) from the Ministry of Education, Culture, Science, and Technology, and Tokyo Ohka Foundation for the Promotion of Science and Technology.

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