Photocatalytic H_2 evolution under visible light irradiation on $Zn_{1-x}Cu_xS$ solid solution

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The H_2 evolution reaction from an aqueous Na_2SO_3 solution proceeded with 3.7% quantum yield under visible light irradiation ($\lambda > 420$ nm) on a $Zn_{0.957}Cu_{0.043}S$ solid solution photocatalyst without co-catalysts such as Pt.

Keywords: photocatalyst, solid solution, CuS–ZnS, visible light response, H_2 evolution

1. Introduction

Development of visible-light-driven photocatalysts has been urged from the viewpoint of artificial photosynthesis. Although photocatalysts for splitting water into H_2 and O_2 in stoichiometric amounts under visible light irradiation have not been found, CdS [1] and WO_3 [2–4] are well-known to produce H_2 and O_2 from aqueous solutions including sacrificial reagents. The authors have recently reported that $BiVO_4$ with a 2.3 eV band gap is also an active photocatalyst under visible light irradiation for O_2 evolution from an aqueous $AgNO_3$ solution [5]. However, the number of visible light driven photocatalysts is limited. On the other hand, ZnS is a highly active photocatalyst for H_2 evolution from aqueous solutions containing sacrificial reagents such as organic compounds, SO_3^{2-} and S^{2-} without Pt [1,6–9], indicating that the surface of ZnS possesses active sites for H_2 evolution. However, the band gap is 3.7 eV (α phase: 3.8 eV, β phase: 3.6 eV), showing that only UV light can be used [10]. It is interesting if ZnS becomes visible light responsive maintaining the high H_2 evolution ability by some modification. Photophysical and photocatalytic properties of ZnS combined with well-known small band gap semiconductors such as CdS have been studied [11–13]. However, photocatalytic activities of solid solutions of ZnS with other elements except for Cd have hardly been reported. This paper reports efficient H_2 evolution under visible light irradiation on a $Zn_{1-x}Cu_xS$ solid solution photocatalyst without co-catalysts such as Pt.

2. Experimental

$Zn_{1-x}Cu_xS$ solid solutions (1 g) were prepared by mixing an aqueous $Zn(NO_3)_2$ and $Cu(NO_3)_2$ solution (Zn^{2+}: 0.2 mol/l, 50 ml) with an aqueous Na_2S solution (1 mol/l, 50 ml). The precipitates were washed with distilled water using a centrifuge and transferred into an aqueous Na_2SO_3 solution (0.5 mol/l, 300 ml) without drying them.

Photocatalytic reactions were carried out in a closed gas circulation system by using a 300 W Xe illuminator (CERMAX, LX300) and optical filters for visible light irradiation. The amounts of H_2 evolved were determined by using a gas chromatograph (Ohkura, model 802, TCD, Ar carrier). The photocatalytic activity of the well-known CdS photocatalyst (Kojyundo Chemicals, purity 99.99%, mainly cubic sphalerite phase) with photodeposited Pt was also measured in order to compare with that of the $Zn_{1-x}Cu_xS$ solid solution. A quantum yield was measured by using an interference filter (λ: 420 nm, half width: 11 nm) and chemical actinometry using potassium ferrioxalate.

3. Results and discussion

Only the broad pattern of cubic sphalerite (zinc blende), but not CuS, was observed by the XRD measurement of $Zn_{0.957}Cu_{0.043}S$ powder indicating that Cu was incorporated in the ZnS lattice. It is reasonable because the ionic radii of Zn^{2+} and Cu^{2+} in four-coordination states are 0.60 and 0.63 Å, respectively.

Figure 1 shows diffuse reflection spectra of the $Zn_{0.957}Cu_{0.043}S$ solid solution, and of ZnS and CuS prepared by the same procedure. ZnS has an absorption band only in the UV region whereas the absorption edge of the $Zn_{0.957}Cu_{0.043}S$ solid solution reaches a visible light region around 500 nm. The energy gap of the $Zn_{0.957}Cu_{0.043}S$ solid solution was estimated to be 2.5 eV and the color was pale yellow. In contrast, CuS absorbs the whole region of UV and visible light, and has no distinguishable absorption edge. This observation also indicates that $Zn_{0.957}Cu_{0.043}S$ forms the solid solution, but not mixture of ZnS and CuS.

$Zn_{0.957}Cu_{0.043}S$ efficiently produces H_2 with the rate of 450 μmol/h under visible light irradiation from an aqueous

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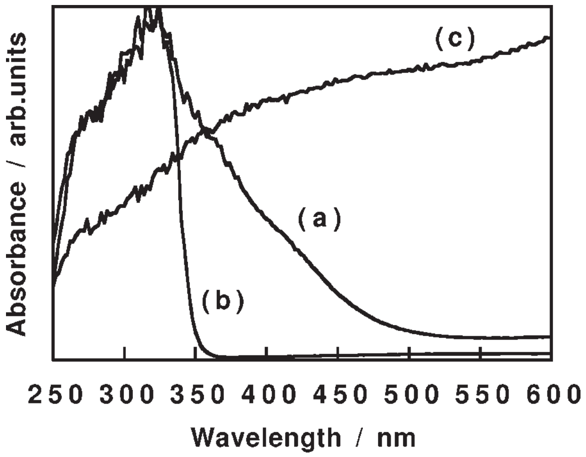

Figure 1. Diffuse reflectance spectra of (a) $Zn_{0.957}Cu_{0.043}S$, (b) ZnS, and (c) CuS.

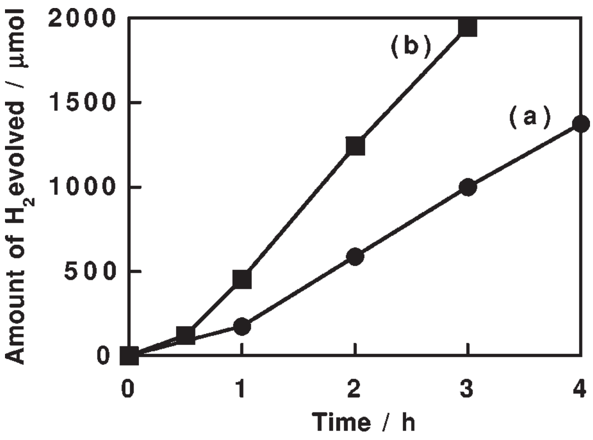

Figure 2. Photocatalytic H_2 evolution from an aqueous Na_2SO_3 solution (0.5 mol/l) under visible light irradiation ($\lambda > 420$ nm) over (a) $Zn_{0.957}Cu_{0.043}S$ and (b) Pt(1 wt%)/CdS. Catalyst: 1 g; light source: 300 W Xe illuminator.

Na_2SO_3 solution, as shown in figure 2. The activity was comparable to that of Pt/CdS so much. It is noteworthy that $Zn_{0.957}Cu_{0.043}S$ showed such a high activity without a Pt co-catalyst. The addition of Pt did not enhance the reaction, suggesting that the surface of $Zn_{0.957}Cu_{0.043}S$ possesses the high catalytic ability for the H_2 formation. The maximum activity was obtained when x in $Zn_{1-x}Cu_xS$ ($0 \leqslant x \leqslant 1$) was 0.043. The quantum yield at 420 nm was 3.7%. The ZnS photocatalyst is photochemically stable in the presence of sacrificial reagents. However, one might suspect that the doped Cu^{2+}, which is a center of visible light absorption, is photoreduced. The turnover number of the amount of reacted electrons to that of Cu in 1 g of the catalyst was 6 at 4 h, showing photochemical processes on the doped Cu^{2+} are cycled.

Figure 3 shows the dependence of the photocatalytic activity on the wavelength irradiated. Cutoff filters were employed for this experiment. This response agrees well to the diffuse reflection spectrum shown in figure 1 indicating that the reaction proceeds photocatalytically.

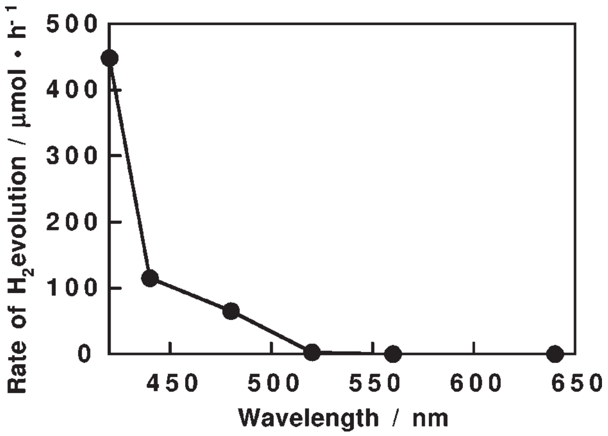

Figure 3. Visible light response of $Zn_{0.957}Cu_{0.043}S$ on the photocatalytic H_2 evolution from an aqueous Na_2SO_3 solution (0.5 mol/l).

Effects of a Cu impurity on the luminescence and photoconductivity of IIB–VIB semiconductors have been studied. The excitation band around 350–450 nm has been observed in addition to the band of pure ZnS in the excitation spectrum of ZnS with a Cu impurity [14]. The excitation band agrees well with the absorption band shown in figure 1. Cu doped in ZnSe and ZnS forms energy levels around valence bands of ZnSe and ZnS [15,16]. In the $Zn_{1-x}Cu_xS$ solid solution system, similar energy levels may be formed resulting in the visible light response of the $Zn_{1-x}Cu_xS$ photocatalyst.

$Cd_{1-x}Zn_xS$ has extensively been studied as sulfide solid solution photocatalysts [12,13]. The band gaps of the solid solution are between those of CdS and ZnS. The quantum yield for H_2 evolution on $Cd_{0.5}Zn_{0.5}S$ using benzyl alcohol as a sacrificial reagent is 0.62% [13]. Some photocatalyst systems combining CdS and $Cd_{1-x}Zn_xS$ with other sulfides have also been reported. The photocatalytic activity for H_2 evolution is much enhanced by an addition of Ag_2S [17]. In this system, the support of Pt is necessary for showing the high activity. The H_2 evolution reaction from an aqueous ethanol solution on a CdS photocatalyst is enhanced by treating the CdS catalyst with Cu^{2+} to form CuS on the surface [18]. In these systems, sulfides added form not solid solutions but microheterojunctions with CdS. On the other hand, studies to make ZnS photocatalysts possess response to visible light by adding some elements except for Cd have hardly been done. From these facts, the following characteristics have arisen for the $Zn_{1-x}Cu_xS$ system: (i) ZnS photocatalysts became visible light responsive with maintaining the H_2 evolution ability without Pt by making solid solutions with Cu. (ii) The quantum yield for H_2 evolution from an aqueous Na_2SO_3 solution reached 3.7% at 420 nm. (iii) $Zn_{1-x}Cu_xS$ is the visible-light-driven photocatalyst containing no harmful Cd.

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