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$AgInZn_7S_9$ solid solution photocatalyst for H_2 evolution from aqueous solutions under visible light irradiation

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Received (in Cambridge, UK) 3rd May 2002, Accepted 18th July 2002
First published as an Advance Article on the web 1st August 2002

$AgInZn_7S_9$ with a 2.3 eV band gap, which was a solid solution of $AgInS_2$ and ZnS semiconductors, showed photocatalytic activity for H_2 evolution from an aqueous solution containing sacrificial reagents SO_3^{2-} and S^{2-} under visible light irradiation ($\lambda > 420$ nm) even without a Pt cocatalyst, and loading of the Pt cocatalyst improved the photocatalytic activity.

Development of photocatalysts with visible light response has been urged for hydrogen production from water using solar light energy. $NiO_x/In_{1-x}Ni_xTaO_4$ has recently been reported to be an active photocatalyst for water splitting into H_2 and O_2 in a stoichiometric amount under visible light irradiation.[1] However, highly efficient water splitting utilizing wide range visible light has not been accomplished. The number of photocatalyst materials with visible light response for H_2 or O_2 evolution from aqueous solutions is still limited. The platinized CdS photocatalyst with a 2.4 eV band gap has extensively been studied for H_2 evolution under visible light irradiation in the presence of sacrificial reagents such as SO_3^{2-} and S^{2-}.[2,3] One of the present authors has reported that Cu or Ni-doped ZnS showed photocatalytic activities for H_2 evolution from aqueous solutions even without a Pt cocatalyst.[4,5] The high ability for H_2 evolution is due to the high conduction band level consisting of the Zn 4s orbital of the ZnS host material.[6] On the other hand, valence bands of $AgMO_3$ (M = Nb and Ta) photocatalysts which are active for H_2 or O_2 evolution consist of Ag 4d and O 2p orbitals.[7] This result indicates that Ag is expected to be an element forming a stable valence band. These facts have led the present authors to survey sulfide photocatalyst materials consisting of Zn and Ag. In the present paper, it is reported that $AgInZn_7S_9$ powder shows high photocatalytic activity for H_2 evolution from an aqueous solution containing sacrificial reagents SO_3^{2-} and S^{2-} under visible light irradiation.

A grayish precipitate of a Ag–In–Zn sulfide precursor was prepared by bubbling H_2S gas into an aqueous solution of $AgNO_3$ (Tanaka Kikinzoku, 99.8%), $In(NO_3)_3$ (Kojundo-kagaku, 99.99%), and $Zn(NO_3)_2$ (Wako Chemicals, 99.0%) in the molar ratio of 1 : 1 : 7. The precipitate was heat-treated at 1123 K for 5 h in an evacuated quartz ampule tube. The obtained yellow powder was confirmed to be a single phase of $AgInZn_7S_9$ with wurtzite structure by X-ray diffraction (Rigaku; MiniFlex). The BET surface area of the $AgInZn_7S_9$ powder was 0.6 m^2 g^{-1}. Diffuse 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 $AgInZn_7S_9$ powder was dispersed in an aqueous solution containing SO_3^{2-} and S^{2-} of electron donors. 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). A Pt cocatalyst was photodeposited on the $AgInZn_7S_9$ powder *in situ* using $H_2PtCl_6{\cdot}6H_2O$ (Tanaka Kikinzoku, 37.55% as Pt). The amount of H_2 evolved was determined using on-line gas chromatography (Shimadzu; GC-8A, MS-5A column, TCD, Ar carrier). The quantum yield was measured at 420 nm using filters combined with a band-pass filter (Kenko; BP42, half width: 10.6 nm), a cut-off filter (HOYA; L42), and a thermopile (OPHIR; a 3A-P-SH head and a NOVA energy monitor).

DOI: 10.1039/b204259b

Fig. 1 shows diffuse reflection spectra of $AgInZn_7S_9$ powder and the related materials. $AgInZn_7S_9$ had an intense absorption band with a steep edge in the visible light region. This shape indicated that the visible light absorption band was not due to the transition from impurity levels as observed for Cu and Ni-doped ZnS photocatalysts but the band gap transition. The band gap was estimated to be 2.3 eV from the onset of the absorption edge. $AgInZn_7S_9$ with wurtzite structure is the solid solution between $AgInS_2$ and ZnS. The absorption edge of $AgInZn_7S_9$ was in the position between $AgInS_2$ and ZnS. The band gap of $AgInZn_xS_{x+2}$ became narrow monotonously as the value of x was small. When x was equal to seven ($AgInZn_7S_9$), the highest photocatalytic activity for the H_2 evolution was obtained. The valence band of $AgInS_2$ consists of S 3p and Ag 4d orbitals.[8] The formation of a valence band by Ag 4d orbitals was also observed for $AgMO_3$ (M = Na and Ta) photocatalysts.[7] In 5s orbitals are able to form hybrid orbitals with other orbitals consisting of conduction bands.[9] Therefore, it is considered that the conduction and valence bands of $AgInZn_7S_9$ consist of orbitals of Zn 4s + In 5s and S 3p + Ag 5d, respectively. The band levels continuously shift with the ratio of the solid solution.

Fig. 2 shows H_2 evolution from an aqueous solution containing sacrificial reagents SO_3^{2-} and S^{2-} over $AgInZn_7S_9$ powder under visible light irradiation. H_2 evolves with the reduction of water molecules by photogenerated electrons. SO_3^{2-} is oxidized by photogenerated holes to form SO_4^{2-} and/or $S_2O_3^{2-}$.[3]

$$\text{Photocatalyst} + h\nu \rightarrow e^-(CB) + h^+(VB) \tag{1}$$

$$2H^+ + 2e^-(CB) \rightarrow H_2 \tag{2}$$

$$SO_3^{2-} + H_2O + 2h^+(VB) \rightarrow SO_4^{2-} + 2H^+ \tag{3}$$

$$SO_3^{2-} + S^{2-} + 2h^+(VB) \rightarrow S_2O_3^{2-} \tag{4}$$

H_2 evolution was observed using $AgInZn_7S_9$ powder. It should be noted that the $AgInZn_7S_9$ photocatalyst showed high activity even without a Pt cocatalyst, differing from the CdS photocatalyst. This indicated that the conduction band level of $AgInZn_7S_9$ was relatively high compared with a reduction potential of H_2O to form H_2 as well as that of ZnS.[6] The

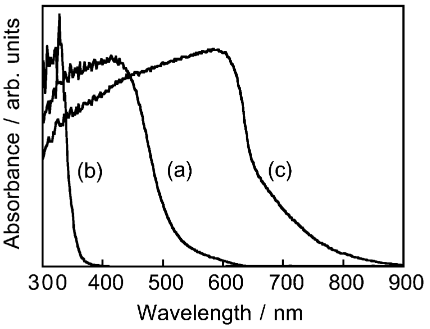

Fig. 1 Diffuse reflection spectra of $AgInZn_7S_9$ (a), ZnS (b) and $AgInS_2$ (c).

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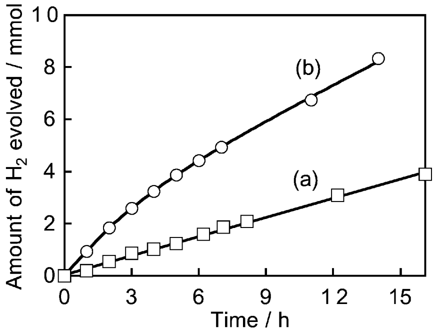

Fig. 2 Photocatalytic H_2 evolution from an aqueous K_2SO_3 (0.25 mol l^{-1})–Na_2S (0.35 mol l^{-1}) solution (300 ml) over $AgInZn_7S_9$ (a) and Pt(3 wt%)/$AgInZn_7S_9$ (b) powder (0.3 g) heat-treated at 1123 K under visible light irradiation ($\lambda > 420$ nm). Light source: 300 W Xe lamp with a cut-off filter (L42).

photocatalytic activity was increased when the Pt cocatalyst, which worked as active sites for H_2 evolution, was loaded on the $AgInZn_7S_9$ photocatalyst. The rate of H_2 evolution over the Pt/$AgInZn_7S_9$ photocatalyst was 940 μmol h^{-1} at the initial stage. The H_2 evolution was not observed under dark conditions. The quantum yield of the Pt/$AgInZn_7S_9$ photocatalyst was 15% at 420 nm; it was considerably high even in the presence of sacrificial reagents, except for the well-known Pt/CdS photocatalyst (QY: ≈35%) which includes harmful cadmium and always require the Pt cocatalyst. The turnover number, defined as eqn. (5), for the Pt/$AgInZn_7S_9$ photocatalyst was 54 at 14 h of reaction time, at which the activity was still steady.

$$\text{Turnover number} = \frac{\text{Number of reacted electrons}}{\text{Amount of AgInZn}_7\text{S}_9\text{ photocatalyst}} = \frac{\text{Molar quantity of evolved H}_2 \times 2}{\text{Molar quantity of used AgInZn}_7\text{S}_9} \quad (5)$$

The turnover number indicated that the reaction proceeded photocatalytically and that the remarkable deactivation due to photocorrosion was not observed because of the presence of a sacrificial reagent. The turnover number is usually defined as the number of a product per the number of active sites in catalysts. It is usually difficult to determine the number of active sites for heterogeneous photocatalysts. The turnover number, defined as eqn. (5), gives the minimum value. The turnover number we indicated is enough to prove that the reaction proceeded photocatalytically, not a quantitative reaction or photocorrosion. This stable activity also seems to be due to the valence band consisting of Ag 4d orbitals. This photocatalyst may be used for H_2 production from water using junk sulfur compounds as electron donors. In contrast, $AgInS_2$, of which the conduction band would consist of In 5s orbitals, showed negligible photocatalytic activity for the H_2 evolution even if it absorbed visible light in a wide range. Although the ZnS photocatalyst possesses high activity for H_2 evolution under ultraviolet light,[10] it did not show activity under visible light irradiation.

H_2 evolved over the $AgInZn_7S_9$ photocatalyst even in pure water in the absence of a sacrificial reagent. The rates of H_2 evolution over naked and platinized $AgInZn_7S_9$ photocatalysts were 2.5 and 35 μmol h^{-1}, respectively. However, O_2 evolution, which had to proceed for water splitting, was not observed. Therefore, the authors can not guarantee these reactions in pure water to have proceeded photocatalytically. They may be accompanied by photocorrosion.

In conclusion, it was found that $AgInZn_7S_9$ was an active photocatalyst for H_2 evolution under visible light irradiation even though it was the solid solution between $AgInS_2$ and ZnS which hardly possessed activity under visible light irradiation. The control of the band structure is important for development of visible light-driven photocatalysts. The present result indicates that band structure control by making solid solutions is a promising strategy to develop photocatalysts with visible light response.

This work was supported by Core Research for Evolutional Science and Technology (CREST) and Technology, and Tokyo Ohka Foundation for the Promotion of Science and Technology.

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