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Photocatalytic water reduction under visible light on a novel $ZnIn_2S_4$ catalyst synthesized by hydrothermal method

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A novel $ZnIn_2S_4$ catalyst synthesized by hydrothermal method shows high and stable photocatalytic activity for water reduction under visible light illumination.

In recent years photocatalytic water splitting using solar energy has received a great deal of attention because of the global energy and environmental problems. During the past decades many mixed oxide photocatalysts such as $SrTiO_3$,[1] KNb_6O_{17}[2] and $NaTaO_3$[3] have been reported to show high activity for overall water splitting. These photocatalysts, however, are effective only in the ultraviolet region due to their wide band gap. In order to improve the efficiency of utilizing the solar energy, the development of visible-light-driven photocatalysts for water splitting is indispensable. Unfortunately, the number of photocatalysts working under visible light irradiation is still limited.[4–6]

In contrast to the metal oxide photocatalysts, many metal sulfides have the narrower band gaps that correspond to the visible light absorption.[7] The ternary sulfides with strong absorption in the visible region may be good candidates for photocatalytic water splitting to produce hydrogen. But, it is commonly believed that metal sulfides are unstable during the photocatalytic reaction. Improving the stability of metal sulfide catalyst such as CdS for water splitting is challenging. A few efforts have been made, for example, by incorporating the nanoparticles of metal sulfide into the interlayer[8] or mesoporous silica[9] to stabilize the metal sulfides. The preparation procedure is complicated and the photocatalytic efficiency is still very low. It has recently been reported that multicomponent metal sulfide[7] and oxysulfide[4] show stable photocatalytic activity for water reduction and oxidation. These results imply that the multicomponent metal sulfide could be a new class of stable photocatalyst for water reduction.

Zinc indium sulfide, $ZnIn_2S_4$, is a ternary chalcogenide which belongs to the family of ternary compound AB_2X_4. $ZnIn_2S_4$ is a potential photoconducting material[10] and has been extensively applied to the electrochemical recording and photovariable capacitor. But, there is no report on the photocatalytic water reduction over the ternary compound of AB_2X_4. These compounds are conventionally prepared by the chemical transport method.[11] This method usually requires high temperature and high vacuum, as well as a transporting agent such as iodine. In this communication, we report a chemically stable $ZnIn_2S_4$ photocatalyst prepared by a direct hydrothermal synthesis method. UV-visible diffuse reflectance spectra shows that the absorption edge of $ZnIn_2S_4$ is in the visible region, corresponding to the band gap of 2.3 eV. It is found that the $ZnIn_2S_4$ shows high activity for photocatalytic water reduction under visible light ($\lambda > 420$ nm) irradiation. More interestingly, the H_2 evolution rate gradually increases with prolonged photocatalytic reaction time. No deactivation is observed even after photocatalytic reaction for 150 h.

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The ZnS powder was obtained from Wako Pure Chemical Inc. of Japan. UV-vis diffuse reflectance spectra were recorded on a JASCO V-550 UV-vis spectrophotometer. The photocatalytic reaction was performed in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. 0.3 g powder of $ZnIn_2S_4$ catalyst was suspended in 200 ml aqueous solution containing 0.43 M Na_2S–0.5M Na_2SO_3. About 40 torr of Ar gas was then introduced into this reaction cell. 2.0 wt% Pt was loaded on the $ZnIn_2S_4$ catalyst by photoreduction method using H_2PtCl_6 solution. The catalyst was irradiated by 300 W Xe lamp equipped with an optical cut-off filter ($\lambda > 420$ nm). The amount of H_2 produced was analyzed using an on-line gas chromatograph.

The $ZnIn_2S_4$ photocatalyst was prepared through the following procedure. Typically, the stoichiometric amount of $Zn(NO_3)_2\cdot 6H_2O$, $In(NO_3)_3\cdot 4.5H_2O$ and double excess thiourea were added to a Teflon-lined stainless steel autoclave of 20 ml capacity. The autoclave was filled with double-distilled water up to 80% of its volume and then maintained at 160 °C for 60 h. A yellow precipitate was obtained and then washed with water and ethanol and dried at 70 °C. During the hydrothermal synthesis of the $ZnIn_2S_4$ photocatalyst, thiourea was used as sulfur source and it can coordinate with Zn^{2+} and In^{3+} to form complexes.[12] When the reaction temperature is raised, the complexes undergo thermal decomposition to release S^{2-} ions, which react with Zn^{2+} and In^{3+} in the solution to produce yellow $ZnIn_2S_4$ precipitate. Compared with the conventional solid-state reaction, the present synthesis method is mild, convenient and easy to handle.

The surface nature of the $ZnIn_2S_4$ catalyst was characterized by X-ray photoelectron spectra (XPS) analysis. The S2p peak at 161.8 eV is indicative of the presence of sulfur ion. Both Zn2p and In3d show two peaks (1021.2 and 1044.2 eV for Zn2p level, 444.7 and 452.3 eV for In3d level), corresponding to the spin–orbit split components. The XPS peak of O1s is at 531.3 eV, suggesting partial oxidation on the surface of the $ZnIn_2S_4$ sample. The shape and size of the as-synthesized $ZnIn_2S_4$ photocatalyst was examined by transmission electron microscopy (TEM). The $ZnIn_2S_4$ sample is mainly in the form of sphere-like particles with diameter of 20 ~ 25 nm. Broad peaks of X-ray diffraction at $2\theta = 27°$ and 47.5° are characteristic of the cubic spinel phase of $ZnIn_2S_4$.[13] Based on the Scherrer formula, the average particle size of $ZnIn_2S_4$ is estimated to be 20 nm, which is in agreement with the TEM results. The BET surface area of the $ZnIn_2S_4$ catalyst is 103 $m^2\cdot g^{-1}$, based on the N_2 adsorption–desorption isotherm.

Fig. 1 shows the UV-visible diffuse reflectance spectra of bulk ZnS and $ZnIn_2S_4$ prepared by the hydrothermal method. The absorption edge of $ZnIn_2S_4$ is at 570 nm, with a red shift of about 210 nm compared to that of ZnS. The band gap, which is estimated from the onset of the absorption edge, correspondingly decreases from 3.4 eV for ZnS to 2.3 eV for $ZnIn_2S_4$. The

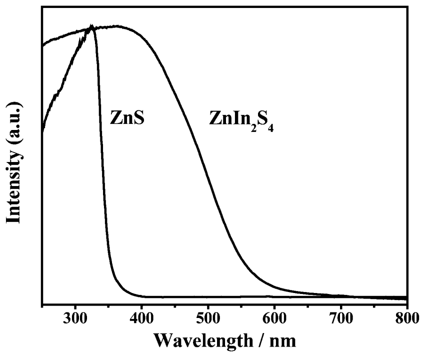

Fig. 1 UV-visible diffuse reflectance spectra of bulk ZnS and ZnIn$_2$S$_4$ prepared by the hydrothermal synthesis method.

narrowing of the band gap is due to the contribution of the In5s orbital to the conduction band of ZnIn$_2$S$_4$. The steep shape in the visible edge and strong absorption in the visible region also indicate that the absorption band of ZnIn$_2$S$_4$ is ascribed to the transition between the valence band to the conduction band but not to the transition between the impurity level to the conduction band.[14]

Fig. 2 displays the short-term photocatalytic H_2 evolution from 0.43 M Na_2S–0.5 M Na_2SO_3 aqueous solution. The H_2 produced was evacuated every 24 hours. H_2 can be produced with an average rate of 57 μmol·h^{-1}·g^{-1}over the naked ZnIn$_2$S$_4$ catalyst, suggesting that ZnIn$_2$S$_4$ itself is an active catalyst for water reduction under visible light irradiation. The rate of the H_2 evolution was dramatically enhanced by loading 2.0 wt% of Pt on ZnIn$_2$S$_4$ catalyst. In the initial stage of the first cycle, the H_2PtCl_6 is reduced to Pt, which serves as promoter for H_2 evolution. Although the rate of H_2 evolution in the induction period is relatively low, approximately 800 μmol H_2 is still produced in the first 24 hours. The turnover number (TON), which is defined as the ratio of the number of reacted electrons to the amount of photocatalyst,[7] exceeds 2 in the first cycle, indicating that the reaction proceeds photocatalytically.

In the second and third cycles, the average rate of hydrogen evolution is increased from the low rate of 107 μmol·h^{-1}·g^{-1} in the induction period to 130 and 213 μmol·h^{-1}·g^{-1} respectively. The higher rate in the third cycle indicates that the activity of ZnIn$_2$S$_4$ photocatalyst has the tendency to increase with the prolonged photocatalytic reaction time. After the photocatalytic reaction in the fourth cycle, the activity of the photocatalyst was recovered in the fifth cycle and H_2 evolution rate further increased and eventually reached the maximum of 257 μmol·h^{-1}·g^{-1} in the sixth cycle. The phenomenon that the activity is increased with prolonged reaction time is quite different from the usual metal sulfides, which generally show a decline in activity during the photocatalytic reaction. After the photocatalytic reaction for 150 h, more than 8.7 mmol H_2 is produced over 0.3 g 2 wt% Pt–ZnIn$_2$S$_4$ catalyst, corresponding to TON of 24. There was no difference in XRD patterns of the catalyst before and after the photoreaction for 150 h, confirming the photocatalyst is essentially stable.

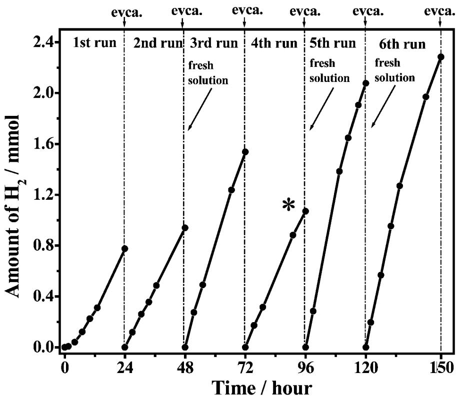

Fig. 2 Photocatalytic H_2 evolution from 0.43 M Na_2S–0.5 M Na_2SO_3 aqueous solution over 0.3 g 2%Pt–ZnIn$_2$S$_4$ catalyst. Light source, 300 W Xe Lamp, $\lambda > 420$ nm. *Due to the consumption of Na_2S and Na_2SO_3 in the third cycle, the H_2 evolution rate decreases in the fourth cycle. After displacing the Na_2S and Na_2SO_3 aqueous solution with a fresh one, the activity is recovered; see the fifth and sixth cycles.

The stability of ZnIn$_2$S$_4$ photocatalyst is related to the condition of hydrothermal synthesis. The hydrothermal method allows the crystallization of catalyst under mild conditions over a long period of time. The catalyst crystallizing in the water medium of hydrothermal condition indicates that it could show stable activity for photocatalytic water reduction.

In conclusion, we have demonstrated the feasibility of preparing ZnIn$_2$S$_4$ by hydrothermal synthesis. The ZnIn$_2$S$_4$ synthesized by hydrothermal method was found to be very active for water reduction to produce H_2 under visible light irradiation. It represents a new class of AB$_2$X$_4$ type photocatalyst working under visible light. No deactivation is observed during the photocatalytic reaction for at least 150 h, and the activity is slightly enhanced with the reaction time. This result indicates that it is possible to synthesize stable photocatalysts of ternary metal sulfides by the hydrothermal synthesis method.

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