H_2 Evolution from Aqueous Potassium Sulfite Solutions under Visible Light Irradiation over a Novel Sulfide Photocatalyst $NaInS_2$ with a Layered Structure

Akihiko Kudo,* Akira Nagane, Issei Tsuji, and Hideki Kato
Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

(Received May 15, 2002; CL-020416)

$NaInS_2$ which consisted of anion layers of $InS_2{}^-$ with a 2.3 eV band gap showed the photocatalytic activity for H_2 evolution from an aqueous K_2SO_3 solution under visible light irradiation ($\lambda > 420$ nm).

Development of photocatalysts with a visible light response has been urged for hydrogen production from water using a solar light energy. In general, oxide semiconductor photocatalysts which possess sufficient conduction band levels for H_2 evolution by the reduction of water have band gaps wider than ca. 3 eV.[1] Although these materials are stable toward photocatalytic reactions in aqueous media they respond to only UV light. On the other hand, although metal chalcogenide semiconductors such as CdS are generally not stable because of photocorrosion, many of them possess absorption bands in a visible light region.[2] Therefore, the metal chalcogenide semiconductor is a promising material group for surveying new visible light respondent photocatalysts for H_2 evolution from water. Well-known sulfide photocatalysts such as CdS and ZnS possess ordinary three-dimensional bulk structures. On the other hand, layered oxides such as $K_4Nb_6O_{17}$[3,4] and $K_2La_2Ti_3O_{10}$[3,5] show the high activities for water splitting into H_2 and O_2 in a stoichiometric amount under UV irradiation. The two dimensional structure contributes to separation of photogenerated electrons and holes, and active sites for H_2 and O_2 evolution resulting in showing the high activities. Therefore, studying photocatalytic properties of sulfides with such a layered structure will be interesting. The present paper reports the photocatalytic activity of $NaInS_2$ with a layered structure for H_2 evolution from an aqueous K_2SO_3 solution under visible light irradiation.

White precipitation of a Na–In sulfide precursor was prepared by adding an aqueous Na_2S solution (1.25 mol dm^{-3}, 120 ml) into an aqueous solution (0.25 mol dm^{-3} each, 80 ml) of $In(NO_3)_3$ (Kojunndo Chemical, 99.99%) and $NaNO_3$ (Kanto Chemical, 99.0%), and stirring the mixed solution for 20 h at 300 K. X-ray diffraction measurements (Rigaku; MiniFlex) were carried out for the product materials. In_2S_3 was not obtained in the present preparation process. The precursor precipitation was heated at 423 K for 0.5 h for drying and subsequently heated at 573 K for 2 h in an N_2 gas flow. The heat treatment gave crystalline $NaInS_2$ powder. The BET surface area of the crystalline $NaInS_2$ powder was 14 m^{2}g^{-1}. This crystalline $NaInS_2$ powder was further treated with water for 10 h at 300 K. 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 $NaInS_2$ powder was dispersed in an aqueous K_2SO_3 solution (0.5 mol dm^{-3}, 320 ml). The photocatalyst was 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 $NaInS_2$ 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 an on-line gas chromatography (Shimadzu; GC-8A, MS-5A column, TCD, Ar carrier). A quantum yield was measured at 440 nm using filers combined with a band-pass filter (Kenko; BP44, the half width: 8.9 nm) and a cut-off filter (HOYA; L42), and a thermopile (OPHIR; a 3A-P-SH head and a NOVA energy monitor).

Figure 1 shows the crystal structure of $NaInS_2$.[6] Anion layers consist of edge-shared InS_6 octahedra and Na^+ cations exist between the layers. Transition metal chalcogenides with layered structure such as MoS_2 have been studied as semiconductor photoelectrodes.[7] The layers of the photoactive transition metal chalcogenides are stacked with the van der Waals force while that of $NaInS_2$ is stacked with a Coulomb force. In this point, $NaInS_2$ is a new type of a photoactive layered sulfide.

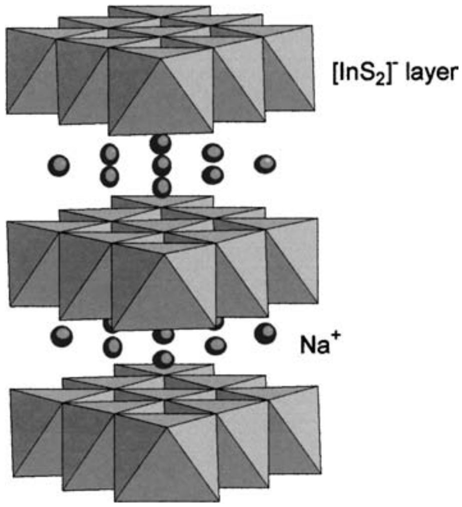

Figure 1. Crystal structure of $NaInS_2$.[6]

Figures 2 and 3 show diffuse reflection spectra and X-ray diffraction of $NaInS_2$ and the related compounds, respectively. The amorphous precursor as a precipitate was white. Heat-treated crystalline $NaInS_2$ was pale yellow. Water-treated $NaInS_2$ was orange-yellow and possessed intensive absorption band in the visible light region. The X-ray diffraction patterns did not change with the water treatment as shown in Figure 3. No difference in XRF measurement between nontreated and water-treated $NaInS_2$ was observed. The reason why the color changed by the water treatment is not clear at the present stage; it might be caused by the layered structure. The band gap of the water-treated $NaInS_2$ was

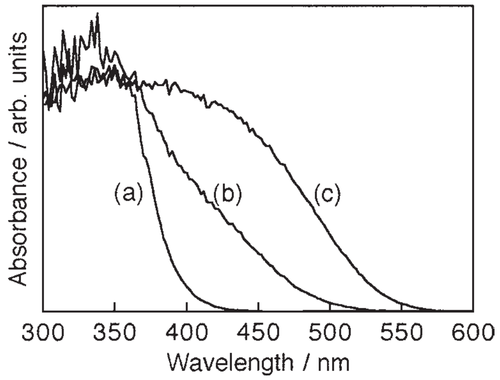

Figure 2. Diffuse reflection spectra of (a) precursor precipitation of $NaInS_2$, (b) heat-treated $NaInS_2$, and (c) heat-treated and water-treated $NaInS_2$.

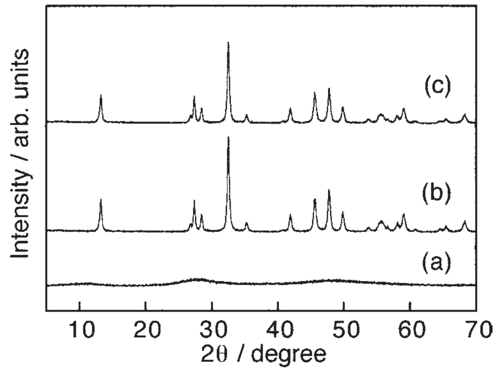

Figure 3. XRD patterns of (a) precursor precipitation of $NaInS_2$, (b) heat-treated $NaInS_2$, and (c) heat-treated and water-treated $NaInS_2$.

2.3 eV. The visible light absorption band is probably due to the band transition from the valence band of S3p to the conduction band of In5s in the anion layers of $InS_2{}^-$.

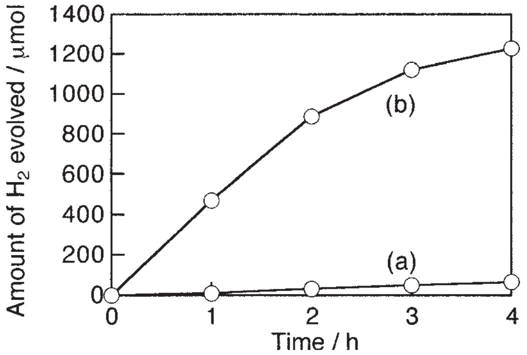

Figure 4. H_2 evolution from an aqueous K_2SO_3 solution ($0.5\,mol\,dm^{-3}$, 320 ml) under visible light irradiation ($\lambda > 420\,nm$) over (a) $NaInS_2$ and (b) Pt(0.7 wt%)/$NaInS_2$ (0.7 g). Light source; 300 W Xe lamp with a cut-off filter (L42).

Figure 4 shows H_2 evolution from an aqueous K_2SO_3 solution under visible light irradiation ($\lambda > 420\,nm$) over water-treated $NaInS_2$ with and without a Pt cocatalyst. $NaInS_2$ showed the photocatalytic activity ($28\,\mu mol\,h^{-1}$) even without the Pt cocatalyst. The activity was much improved by loading the Pt cocatalyst. The drastic enhancement by the Pt loading indicates that the conduction band level of $NaInS_2$ is slightly higher than the reduction potential of H_2O to H_2. The initial rate of the H_2 evolution was $470\,\mu mol\,h^{-1}$ and the quantum yield was ca. 6% at 440 nm. The photocatalyst was deactivated with the irradiation time. This may be due to the collapse of the layered structure and photocorrosion. However, the turnover number of reacted electrons to the number of a surface indium was about 20 at 4 h of the reaction time indicating that the photocatalytic reaction proceeded. The onset of the action spectrum was agreed with that of the absorption spectrum indicating that the photocatalytic reaction proceeded with the band gap excitation. Heat-treated $NaInS_2$ without water treatment also showed the activity ($330\,\mu mol\,h^{-1}$), while the amorphous precursor was not active even under UV irradiation. In_2S_3 with a three dimensional framework hardly showed the activity for the H_2 evolution although the conduction band should be formed with In5s similarly to $NaInS_2$. This result suggests that the high conduction band level of $NaInS_2$ compared with that of In_2S_3 would be due to the two dimensional structure and the complex sulfide with sodium. The difference in the photocatalytic property between $NaInS_2$ and In_2S_3 may also be due to the layered structure in which the interlayers can be reaction sites.

In conclusion, $NaInS_2$ was found to be an active photocatalyst for H_2 evolution from an aqueous solution under visible light irradiation. This is a new type sulfide photocatalyst material that possesses a two dimensional layered structure and its photoabsorption property changes with water treatment.

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

References

1 D. E. Scaife, *Sol. Energy*, **25**, 41 (1980).
2 T. Sakata, in "Photocatalysis: fundamentals and applications," ed. by N. Serpone and E. Pelizzetti, Wiley & Sons, New York (1989), Chap. 10, p 311.
3 K. Domen, J. N. Kondo, M. Hara, and T. Takata, *Bull. Chem. Soc. Jpn.*, **73**, 1307 (2000).
4 A. Kudo, K. Sayama, A. Tanaka, K. Asakura, K. Domen, K. Maruya, and T. Onishi, *J. Catal.*, **120**, 337 (1989).
5 T. Takata, Y. Furumi, K. Shinohara, A. Tanaka, M. Hara, J. N. Kondo, and K. Domen, *Chem. Mater.*, **9**, 1063 (1997).
6 V. R. Hoppe, W. Lidecke, and F.-C. Frorath, *Z. Anorg. Allg. Chem.*, **309**, 49 (1961).
7 H. Tributsch, in "Photocatalysis: fundamentals and applications," ed. by N. Serpone and E. Pelizzetti, Wiley & Sons, New York (1989), Chap. 11, p 339.