

Photocatalytic H₂ evolution under visible light irradiation on Ni-doped ZnS photocatalyst

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Zn_{0.999}Ni_{0.001}S photocatalysts (energy gap = 2.3 eV) heat-treated at 773 K in an N₂ flow showed activity for hydrogen evolution from aqueous solutions containing K₂SO₃ and Na₂S as reducing reagents under visible light irradiation without co-catalysts such as Pt.

Water splitting using photocatalysts is an important reaction from the viewpoint of global energy and environmental concerns. Although some photocatalysts have been reported to show high activities for the water splitting, they are active only under UV-light irradiation.^{1,2} However, photocatalysts which are active for the water splitting under visible light irradiation have not been developed. Even in the presence of sacrificial reagents, the only well-known photocatalysts that can produce hydrogen or oxygen from aqueous solutions under visible light irradiation are Pt/CdS and WO₃.^{3–5} Therefore, development of new visible-light-driven photocatalysts is a priority. One of us has recently found that BiVO₄ prepared in an aqueous process showed high activity for oxygen evolution from aqueous solutions containing Ag⁺ as an electron scavenger.^{6,7} On the other hand, it is important to develop new and less harmful visible-light-driven photocatalysts than Pt/CdS for hydrogen evolution from aqueous solutions. We have studied the development of new visible-light-driven photocatalysts based on ZnS and have previously reported a CuS–ZnS solid solution photocatalyst.⁸ However, this CuS–ZnS photocatalyst has poor thermal and chemical stability. The present work reports thermally and chemically stable Ni-doped ZnS photocatalysts for hydrogen evolution from aqueous K₂SO₃ and Na₂S solutions under visible light irradiation.

Ni-doped ZnS photocatalysts were prepared by mixing an aqueous Zn(NO₃)₂ and Ni(NO₃)₂ solution with an aqueous Na₂S solution. The obtained precipitates were washed with distilled water using a centrifuge and then were heat-treated at 773 K in an N₂ flow. Photocatalytic reactions were carried out in a closed gas circulation system by using a 300 W Xe illuminator (CERMAX, LX300) and optical cut-off filters. The Ni-doped ZnS photocatalyst (1 g) was dispersed in aqueous K₂SO₃ and Na₂S solutions in a Pyrex reaction cell. The amounts of H₂ evolved were determined by using a gas chromatograph (Ohkura, Model 802, TCD, Ar carrier). Quantum yields were measured using an interference filter (λ_{max}: 420 nm, half width; 11 nm) and chemical actinometry measured using ammonium ferrioxalate.

Fig. 1 shows photocatalytic H₂ evolution from an aqueous solution containing K₂SO₃ and Na₂S as reducing reagents on Zn_{0.999}Ni_{0.001}S powder heat-treated at 773 K in an N₂ flow under visible light irradiation. H₂ efficiently evolved even without co-catalysts such as Pt. The rate of H₂ evolution was 280 μmol h⁻¹, a relatively large value under the present experimental conditions (300W Xe lamp, λ > 420 nm). The turnover number of reacted electrons to the amount of Ni doped reached 170 at 8 h of the reaction time and the quantum yield at 420 nm was 1.3%. More than 7500 μmol of H₂ was formed in a prolonged experiment (>50 h). The number of electrons reacted exceeded the amount of the catalyst (10 mmol),

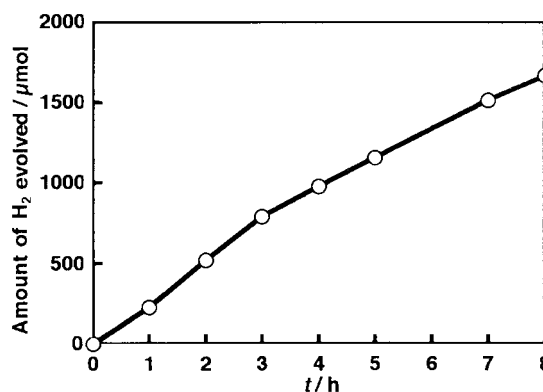


Fig. 1 Photocatalytic H₂ evolution from an aqueous K₂SO₃ (0.5 mol l⁻¹)–Na₂S (0.005 mol l⁻¹) solution (300 ml) on Zn_{0.999}Ni_{0.001}S powder (1 g) heat-treated at 773 K in an N₂ flow under visible light irradiation (λ > 420 nm). Light source: 300 W Xe lamp.

indicating the reaction proceeded photocatalytically with negligible photocorrosion.

Fig. 2 shows diffuse reflectance spectra of non-doped ZnS and Zn_{0.999}Ni_{0.001}S heat-treated powders. The spectrum of Zn_{0.999}Ni_{0.001}S showed a visible light absorption band with the onset around 540 nm in addition to the UV light absorption band derived from ZnS. The energy gap estimated from the onset of the visible light absorption band was 2.3 eV. The color of the photocatalyst was pale yellow and did not change after photocatalytic reactions. The shape of the diffuse reflectance spectrum of Zn_{0.999}Ni_{0.001}S indicates that the doped nickel forms a new energy level in the band structure of ZnS. The visible light absorption band is assigned as due to the transition from the Ni 3d level to the conduction band level of ZnS, since the Zn_{0.999}Ni_{0.001}S photocatalyst possesses highly active H₂ evolution sites as well as ZnS. Unless the conduction band was not derived from that of ZnS, such a high activity for the H₂ evolution without co-catalysts as evidenced in Fig. 1 would not be obtained. The photoexcitation of electrons from the Ni 3d level to the conduction band suggests that the photocorrosion

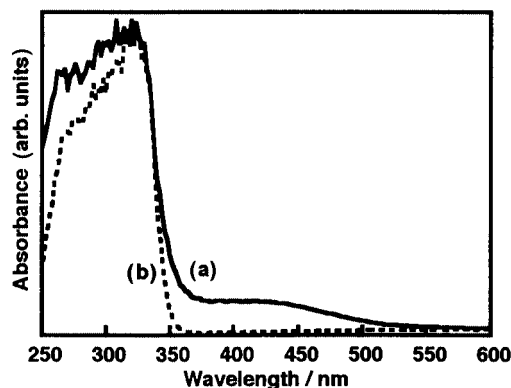


Fig. 2 Diffuse reflectance spectra of Zn_{0.999}Ni_{0.001}S (a) and ZnS (b) powder heat-treated at 773 K in an N₂ flow.

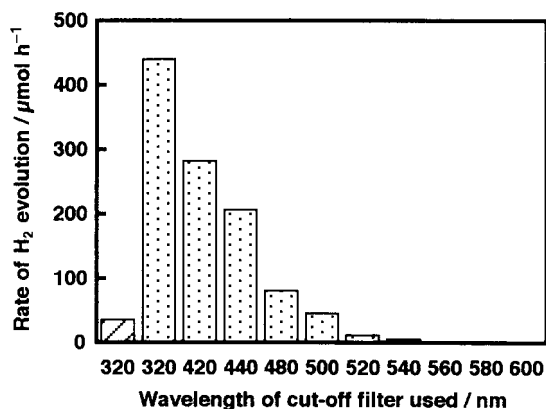


Fig. 3 The dependence of photocatalytic activities for H₂ evolution from an aqueous K₂SO₃ (0.5 mol l⁻¹)-Na₂S (0.005 mol l⁻¹) solution (300 ml) over Zn_{0.999}Ni_{0.001}S (dotted bar) and ZnS (hatched bar) powder heat-treated at 773 K in an N₂ flow upon wavelength (controlled *via* cut-off filters). Light source: 300 W Xe lamp.

observed for ZnS photocatalysts under band gap irradiation should be suppressed in the present system.

The wavelength dependence of the photocatalytic H₂ evolution on the Zn_{0.999}Ni_{0.001}S photocatalysts was investigated as shown in Fig. 3. The number of incident photons was increased as the wavelength of cut-off filters was shortened. Although Fig. 3 is different from an ordinary action spectrum, it indicates the following points. When a cut-off filter of 540 nm was used, H₂ evolution was clearly observed. This wavelength corresponds to the onset of the diffuse reflectance spectrum as shown in Fig. 2. The Zn_{0.999}Ni_{0.001}S photocatalyst showed considerably higher activity than non-doped ZnS even under full-arc irradiation ($\lambda > 320$ nm). It is often observed that doping transition metals with partly-filled d orbitals into photocatalysts such as TiO₂ strongly decreases the photocatalytic activities. However, such an suppression effect by the doping was not predominant in the present metal ion-doped ZnS photocatalyst system.

There were some problems concerning the thermal and chemical stability for the previously reported Cu-doped ZnS

photocatalyst.⁸ When the Cu-doped ZnS photocatalyst was dried or heat-treated to obtain good crystallinity, the photocatalytic activity for H₂ evolution was drastically decreased and the color of the photocatalyst changed after the photocatalytic reaction. In contrast to the Cu-doped ZnS photocatalyst, although the activity of the Ni-doped ZnS photocatalyst was lower, it was thermally and chemically stable. Moreover, the energy gap of Ni-doped ZnS (2.3 eV) was smaller than that of Cu-doped ZnS (2.5 eV) indicating that Ni-doped ZnS can utilize a wider spectral region of visible light than Cu-doped ZnS. The Ni-doped ZnS photocatalyst can produce H₂ using reducing reagents of sulfur compounds which are formed as by-products in petrochemical industries. Therefore, the Ni-doped photocatalyst is expected to be a practically useful photocatalyst.

In conclusion, Ni-doped ZnS has been developed as a new visible-light-driven photocatalyst for H₂ evolution from aqueous solutions. The development seems to suggest a way in making UV respondant photocatalysts respondant also to visible light.

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