Lanthanum–Indium Oxysulfide as a Visible Light Driven Photocatalyst for Water Splitting

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La–In-based oxysulfide is demonstrated to act as a photocatalyst for the reduction of H^+ to H_2 and the oxidation of H_2O to O_2 in the presence of sacrificial reagents under visible light ($420 \leq \lambda \leq 480$ nm). Loading with IrO_2 is effective for promoting O_2 evolution, while Pt is effective as a cocatalyst for H_2 evolution.

Certain sulfides, such as CdS[1,2] and $(AgIn)_xZn_{2(1-x)}S_2$,[3] exhibit good absorption in the visible-light region[4–6] and display activity for the photoreduction of H^+ to H_2 in the presence of an electron donor such as S^{2-} and $SO_3{}^{2-}$. However, sulfides are generally unstable in water oxidation to form O_2 because the S^{2-} anions are sensitive to oxidation by photogenerated holes.[7,8] Recently, $Ln_2Ti_2S_2O_5$ (Ln = Pr–Er) oxysulfides have been demonstrated to act as stable photocatalysts for both H^+ reduction and the oxidation of H_2O to O_2.[9,10] In the present study, La–In oxysulfide with d^{10} electric configuration is investigated as another potential photocatalytic material for water splitting under visible light.

Following the example of Kabbour et al.,[11] the preparation of $LaInS_2O$ was attempted in this study by heating a mixture of La_2S_3, La_2O_3, and In_2S_3 at a stoichiometric molar ratio (La_2S_3:La_2O_3:In_2S_3 = 1:2:3) in a sealed quartz tube under vacuum at temperatures of 873–1273 K for 6–24 h.[11] In this study, we henceforth report the sample obtained at 1073 K for 12 h, which showed the highest photocatalytic activities among all prepared samples. The sintered samples were then ground and heated at 573 K for 1 h in air to remove absorbed sulfur[9] to yield a yellow powder. The crystal structure of the resulting material was examined by powder X-ray diffraction (XRD) using a Rigaku Geigerflex RAD-B instrument with Cu Kα radiation. Ultraviolet–visible diffuse reflectance (UV–vis DR) spectra were obtained using a Jasco V-560 spectrometer. Photoreduction of H^+ to H_2 and photooxidation of H_2O to O_2 in the presence of sacrificial reagents were carried out in a Pyrex reaction vessel connected to a gas-circulation system. H_2 evolution was examined using an aqueous solution (200 mL) containing 0.1 g of the oxysulfide loaded with Pt metals by in situ photodeposition, and 0.01 M Na_2S and 0.01 M Na_2SO_3 as sacrificial electron donors. O_2 evolution was examined using an aqueous 0.01 M $AgNO_3$ solution containing 0.1 g of the oxysulfide loaded with IrO_2 by the impregnation method with Na_2IrCl_6 solution and then the treatment in air at 573 K for 1 h. La_2O_3 was used as a buffer material to maintain the pH of the solution at 7–8.

The reaction solution was evacuated several times to remove air and then irradiated under visible light using a 300-W Xe lamp with a cutoff filter ($\lambda > 420$ nm) to eliminate UV light and water filter to remove infrared light.

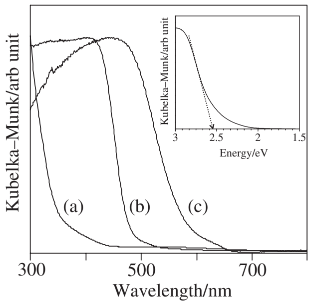

Figure 1. UV–vis diffuse reflectance spectra for (a) $LaInO_3$, (b) La–In oxysulfide, and (c) $Sm_2Ti_2S_2O_5$.[9]

Most of the crystalline peaks produced by the present samples matched those for $LaInS_2O$ reported by Kabbour et al.[11] Yet, the structural detail of the $LaInS_2O$ phase is unknown. Given the presence of In_2O_3 in the XRD pattern, the oxysulfide obtained by the present preparation procedure is considered to be a mixture of In-poor $La_5In_3S_9O_3$ and minor impurity phases, most likely $La_{1.33}In_{1.33}S_4$[12] and $LaIn_2S_4$.[13] As a single-phase $La_5In_3S_9O_3$ powder sample could not be obtained from starting materials with a nominal composition of La:In = 5:3, $La_5In_3S_9O_3$ may exist in the present samples as a metastable phase in an overall In-rich (La:In = 1:1) system. Therefore, the prepared samples containing those phases henceforth are denoted as La–In oxysulfide.

Figure 1 shows the UV–vis DR spectra for the present La–In oxysulfide and $LaInO_3$. For comparison, UV–vis DR spectrum of $Sm_2Ti_2S_2O_5$ is also shown. Plane–wave–based density function theory (DFT) calculations have suggested that the valence band (E_{VB}) of $Sm_2Ti_2S_2O_5$ is made up of the O2p and S3p hybridized orbitals and the conduction band (E_{CB}) consists of Ti3d; as a result, $Sm_2Ti_2S_2O_5$ has a smaller band-gap energy ($\approx$2.1 eV) compared with that of $Sm_2Ti_2O_7$ ($\approx$3.5 eV).[9] Similarly, the E_{VB} of the La–In oxysulfide appears to consist of the O2p and S3p orbitals. On the other hand, the E_{CB} of La–In oxysulfide and $LaInO_3$ in both cases would be composed of hybridized In5s5p orbitals.[14] Accordingly, the La–In oxysulfide has a smaller band-gap energy ($\approx$2.6 eV) than $LaInO_3$ ($\approx$4.1 eV).

Figure 2 shows the time course of repeated H_2 evolution over La–In oxysulfide loaded with 1.0 wt % Pt under visible-light irradiation ($\lambda > 420$ nm) in the presence of Na_2S–Na_2SO_3. The reaction system was evacuated every 5 h. In the early stage of the reaction (2 h), H_2PtCl_6 was reduced to Pt as an H_2 evolution promoter on the catalyst surface. The rate of H_2 evolution, however, remained essentially stable after this induction period. The XRD pattern of the catalyst after the H_2 evolution reaction was the same as before the reaction. The Pt-loaded La–In oxysulfide therefore functions as a stable photocatalyst for the reduction of H^+ to H_2 under visible-light irradiation.

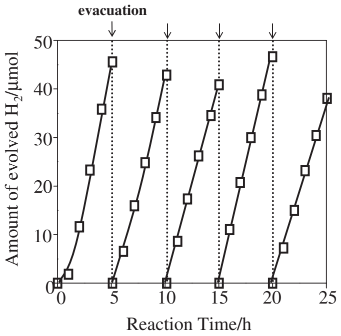

Figure 2. Time course of repeated H_2 evolution over La–In oxysulfide (Pt-loaded catalyst, 0.1 g; 0.01 M Na_2S–0.01 M Na_2SO_3 solution, 200 mL).

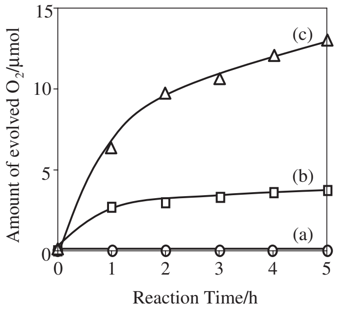

Figure 3. Time course of O_2 evolution over (a) CdS, (b) La–In oxysulfide, and (c) 2 wt % IrO_2/La–In oxysulfide under visible-light irradiation ($\lambda > 420$ nm) (catal., 0.1 g; 0.01 M $AgNO_3$ solution, 200 mL; La_2O_3, 0.2 g).

Figure 3 shows the time courses of O_2 evolution over bare and IrO_2-loaded La–In oxysulfide, and over CdS for comparison. O_2 evolution was not observed over CdS owing to the photodecomposition of CdS by photogenerated holes. In contrast, over the bare La–In oxysulfide, O_2 evolution was observed immediately with the onset of irradiation. Loading with 2 wt % IrO_2 increased the evolution rate by approximately three-fold, indicating that IrO_2 is an effective O_2 evolution promoter for the La–In oxysulfide. After an initial period (1 h), the rate of O_2 evolution decreased over time owing to the deposition of metallic silver on the surface of the catalyst.

Figure 4 shows the relationship between the H_2 and O_2 evolution rates and the cutoff wavelength of incident light. The steady rate of H_2 evolution and the initial rate of O_2 evolution decreased with increasing cutoff wavelength, confirming the position of the absorption edge of the La–In oxysulfide and the procession of these photocatalytic reactions via band-gap transitions. No O_2 evolution was observed under visible-light irradiation with longer wavelength than 500 nm because of our detection limit to be ≈ 0.1 μmol h^{-1}.

The apparent quantum efficiencies (QE)[15] of H_2 and O_2 for La–In oxysulfide (Fig. 2 and Fig. 3b) were estimated to be ≈ 0.2 and ≈ 0.1%, respectively, indicating that La–In oxysulfide exhibited superior QE for H_2 evolution and lower QE for O_2 evolution compared to those of $Sm_2Ti_2S_2O_5$ [QE: 0.1% (H_2), 0.2% (O_2)].[9] Although many factors should affect photocatalytic activity, it seems that E_{CB} of In5s5p orbitals with large dispersion[14] mainly led to the higher QE of H_2 evolution and the purity of La–In oxysulfide containing sulfide phases influenced the QE for O_2 evolution.

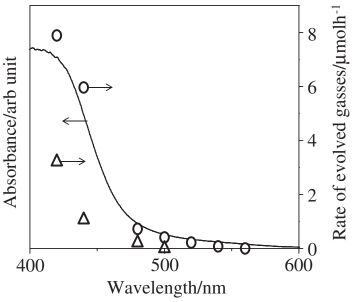

Figure 4. Dependence of rate of H_2 and O_2 evolution on cutoff wavelength of incident light, and UV–vis DR spectrum of La–In oxysulfide. Circles denote H_2 evolution (1 wt % Pt-loaded catal., 0.1 g; 0.01 M Na_2S–0.01 M Na_2SO_3 solution), and triangles denote O_2 evolution (2 wt % IrO_2-loaded catal., 0.1 g; 0.01 M $AgNO_3$ solution, La_2O_3, 0.2 g).

La–In oxysulfide was demonstrated to catalyze the reduction of H^+ to H_2 and the oxidation of H_2O to O_2 under visible-light irradiation in the presence of a sacrificial electron donor (Na_2S–Na_2SO_3) or acceptor (Ag^+), respectively. This oxysulfide, with a band gap of 2.6 eV, was thus confirmed to be a photocatalyst with reduction and oxidation abilities, having conduction and valence bands at suitable potentials for the reduction of H^+ and oxidation of H_2O. O_2 evolution was effectively enhanced by loading with IrO_2, while Pt proved to be suitable as a cocatalyst for H_2 evolution.

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15 Quantum efficiency values were calculated with using the coefficients (H_2: 2, O_2: 4), steady H_2 or initial O_2 evolution rate, the rate of absorption of incident photons [$Sm_2Ti_2S_2O_5$: 8.6×10^{21} photons h^{-1} at $440 \le \lambda \le 650$ nm, La–In oxysulfide: 7.4×10^{21} photons h^{-1} at $420 \le \lambda \le 600$ nm].

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