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Photoassisted fabrication of zinc indium oxide/oxysulfide composite for enhanced photocatalytic H₂ evolution under visible-light irradiation

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Abstract

A photoassisted approach has been developed to synthesize a zinc indium oxide (Zn₅In₂O₈)/oxysulfide composite through in situ sulfuration of vacancy-rich Zn₅In₂O₈. It was found that vacancies have a considerable impact on the formation of the composite. The composite exhibited an increased photocatalytic H₂ evolution activity under visible-light irradiation, which probably resulted from the enhanced ability to separate photoinduced electrons and holes. The H₂ evolution rate over the composite was about 17 times higher when using vacancy-rich rather than conventional Zn₅In₂O₈. This study provides a new method of improving the activity of photocatalysts.

Keywords: zinc indium oxide, zinc indium oxysulfide, photocatalyst composite, hydrogen evolution, water splitting

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1. Introduction

Intensive research interest has been devoted to semiconductor photocatalysts that can produce H₂ from water using solar energy because of the increasing energy requirements and environmental concerns. Many types of photocatalyst have been reported to produce H₂ or/and O₂ from water under illumination, such as metal oxides [1–7] and metal oxysulfides [8, 9]. To efficiently utilize solar energy, bandgap modification is necessary to obtain wide-bandgap photocatalysts responsive to visible light. Doping is an effective way of designing visible-light-responsive photocatalysts [10–13]. However, dopants also act as recombination centers for the photogenerated electrons and holes, which reduce the photocatalytic activity. Therefore, nondoped visible-light-responsive photocatalysts
are drawing increasing attention. Photocatalysts that contain a p-block metal ion with a d$^{10}$ configuration, such as In$^{3+}$, exhibit good photocatalytic activity for water splitting [14]. Zinc indium oxides (In$_2$O$_3$($\text{ZnO}$)$_k$, $k$ = integer) show excellent electron transport properties [15] and are promising visible-light-responsive photocatalysts for water splitting [16]. 

Appropriate composites can promote the separation of photoinduced electrons and holes and accordingly enhance the photocatalytic activity of H$_2$ evolution, because rapid recombination of photogenerated electron–hole pairs is one of the most disadvantageous factors for photocatalytic water splitting [17]. Many reports reveal that semiconductor composites can effectively suppress the recombination of photogenerated electron–hole pairs [17–20]. The valence bands (VBs) and conduction bands (CBs) of the semiconductors in a composite have different energies, and the resulting potential difference assists the separation of photoinduced electrons and holes [18].

Generally, the VB top in metal oxides consists of the O 2p orbital. Whereas in oxysulfides, it involves both the S 3p and O 2p orbitals, which narrow the band gap [21]. A similar phenomenon is observed in oxyfluorides and oxynitrides [22, 23]. Therefore, we considered that a zinc indium oxide/oxysulfide composite could have an enhanced photocatalytic H$_2$ evolution efficiency compared with that of zinc indium oxide. Oxysulfides can be synthesized by many techniques, including hydrothermal synthesis, thermal decomposition of precursors, solid-state reaction, and polymerized complex method [24–28]. However, it is difficult to fabricate an oxysulfide on the surface of the oxide precursor (oxide/oxysulfide) by these methods. A recent report on ZnS synthesis using ZnO as the template [29] provided us a clue that partial in situ sulfuration of an oxide can be used to synthesize an oxide/oxysulfide composite.

Surface vacancies significantly affect the crystal growth, especially in the weak driving force regime, and provide nucleation sites for phase transformations [30]. Here, we developed a facile photoassisted method of fabricating zinc indium oxide/oxysulfide composites using vacancy-rich Zn$_5$In$_2$O$_8$ as the precursor. Zinc indium oxysulfide was in situ generated on the surfaces of precursors in a Na$_2$S/K$_2$SO$_3$ aqueous solution. This composite showed high stability and photocatalytic evolution activity of H$_2$ from water under visible-light irradiation.

**Figure 1.** Schematic of the formation process of ZIO/V-ZIOS composite.

2. **Experimental section**

2.1. **Synthesis of Zn$_5$In$_2$O$_8$ (ZIO) and vacancy-rich ZIO**

All chemicals were purchased from Wako Company, including zinc oxide (ZnO, 99.9%), indium oxide (In$_2$O$_3$, 99.9%), sodium chloride (NaCl, >99.5%), potassium chloride (KCl, >99.5%), and copper metal powder (Cu, >98.8%). They were used without further treatment. Powders of ZIO and vacancy-rich ZIO were synthesized by the molten-salt method. The typical fabrication steps were as follows. NaCl (7.3050 g)/KCl (9.3188 g) and ZnO (1.0174 g)/In$_2$O$_3$ (0.6941 g) were mixed evenly and then milled with an appropriate amount of ethanol in a mortar for 30 min. The mixture was dried in an oven at 60°C for 2–3 h and then heated at 1200°C for 3 h. The products were cleaned with distilled water until Cl$^-$ ions could not be detected using silver nitrate (AgNO$_3$), and then dried in an oven at 60°C for one day.

ZIO was further treated to generate artificial vacancies. In this study, we adopted the high-temperature molten-salt process to prepare vacancy-rich Zn$_5$In$_2$O$_8$ under Ar atmosphere because vacancies can be generated at high temperatures [31]. Cu metal powder was added as a getter of the trace O$_2$ resulting from leaks. In a typical procedure, ZIO (0.95 g), NaCl (5.844 g)/KCl (7.455 g), and 9.5 mg of Cu powder were mixed together and milled with an appropriate amount of ethanol. Then, the mixture was dried in an oven at 60°C for 2–3 h and heated in a horizontal tube furnace at 850°C for 18 h under Ar atmosphere. The red-colored Cu layer and the concretionary molten salt were washed away using distilled water until Cl$^-$ ions could not be detected. This vacancy-rich ZIO powder was dried in an oven at 60°C for 24 h. It is worth noting that the color of the vacancy-rich ZIO was blue, but it turned yellow during the milling. Hence, vacancies were only introduced on the ZIO surface.

2.2. **Synthesis of zinc indium oxide/oxysulfide composite**

In a typical procedure, 0.30 g of vacancy-rich ZIO was suspended in 270 ml of Na$_2$S (0.35 M)/K$_2$SO$_3$ (0.25 M) aqueous solution containing H$_2$PtCl$_6$·6H$_2$O under continuous magnetic stirring. Then, this mixture was irradiated by a 300 W Xe lamp for 48 h to sulfurize the surface layer and form a vacancy-rich zinc indium oxide/oxysulfide (ZIO/V-ZIOS) composite. Figure 1 shows the formation mechanism of ZIO/V-ZIOS. First, ZIO was treated to produce In and O vacancies; then, it was irradiated by UV and visible light in a
Na$_2$S/K$_2$SO$_3$ aqueous solution. As a result, the vacancy-rich surface part reacted with Na$_2$S to form a ZIOS layer on the ZIO surface. At the same time, a Pt cocatalyst (0.5 wt%) was loaded on the surface of the composite during the sulfuration process under this combined irradiation with UV and visible light. Then, the ZIO/V-ZIOS composite was continuously irradiated by the Xe lamp with a UV-cut-off filter (L42, Hoya Co., Japan) for 5 cycles (24 h per cycle). For comparison, the pristine ZIO was treated by the same procedure to prepare a zinc indium oxide/oxysulfide (ZIO/ZIOS) composite. This procedure was performed in a closed gas-circulation system.

2.3. Characterization

The surface morphology of the synthesized samples was characterized with a field-emission scanning electron microscope (SEM, JSM-6701F, JEOL Co., Japan) equipped with an energy-dispersive x-ray spectrometer (EDX). Powder x-ray diffraction (XRD) characterization was performed using a Rint-2000 diffractometer (Rigaku Co., Japan, Cu K$_\alpha$ radiation, $\lambda = 1.5406$ Å) operated at 40 kV and 20 mA. The XRD patterns were refined with PowderX software, where the zero shift, K$_\alpha$2 elimination, and other factors were taken into account. Inductively coupled plasma optical emission spectroscopy (ICP-OES) characterization for Zn and In elements was carried out with an IRIS Advantage setup (Nippon Jarrell-Ash Co., Japan), whereas sulfur was detected with a carbon/sulfur analyzer (CS-444LS, LECO Co., USA). The Brunauer–Emmett–Teller (BET) surface area was measured by nitrogen adsorption at 77 K with a BELSORP mini II surface area analyzer (Bel Japan Co., Japan). X-ray photoelectron spectroscopy (XPS) studies were carried out with a Theta Probe using monochromatized Al K$_\alpha$ radiation (1486.6 eV). UV-visible diffuse reflection spectra were recorded on a UV-2500PC spectrophotometer (Shimadzu Co., Japan) equipped with a radiant power energy meter (Ushio Spectroradiometer, USR-40). The AQE was calculated using the following equation:

$$\text{AQE} \% = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\%$$

$$= \frac{\text{Number of evolved H}_2\text{molecules} \times 2}{\text{Number of incident photons}} \times 100\%.$$

3. Results and discussion

3.1. Crystal structure, morphology, and optical properties of ZIO and vacancy-rich ZIO

The XRD patterns of ZIO and vacancy-rich ZIO are given in figure S1 (supplementary information available at stacks.iop.org/STAM/13/055001/mmedia). The XRD patterns show similar peaks among the products and can be indexed to the pure hexagonal Zn$_x$In$_{2-2x}$O$_3$ phase (JCPDS card: 020–1440). Therefore, it can be concluded that the crystal structure of ZIO was unchanged by the vacancy generation. However, the peak intensities decreased after the treatment, implying loss of crystallinity. Figure S2 (supplementary information) shows the typical SEM images of ZIO and vacancy-rich ZIO. Frequency analysis indicates that ZIO consists of particles with average diameters of 2.45 and 3.28 μm for untreated and vacancy-rich ZIO, respectively (figure S3).

ICP-OES data indicated a slightly larger Zn/In molar ratio in the vacancy-rich (Zn/In = 2.43) than in the untreated ZIO (Zn/In = 2.40), which can be explained by a higher concentration of In vacancies in the former material. Those indium vacancies could be produced at high temperatures via indium sublimation, as reported for indium tin oxide \cite{et al}. Indium evaporates from the ZIO bulk as In$_2$O gas and, simultaneously, O$_2$ gas forms at high temperatures in inert atmosphere. A possible formation mechanism of vacancies in ZIO can be expressed as:

$$\text{Zn}_x\text{In}_2\text{O}_3 \rightarrow \text{Zn}_x\text{In}_{2-2x}\text{O}_{3-2x} + 0.5 \times \text{In}_2\text{O.(gas)} + 0.5 \times \text{O}_2\text{(gas)}.$$

Figure S4 (supplementary information) shows the optical absorption spectra of ZIO and vacancy-rich ZIO. ZIO absorbs wavelengths shorter than 500 nm via transitions between the VB and CB. The spectrum of vacancy-rich ZIO is blue-shifted compared with that of ZIO. A similar phenomenon was reported for the Sr(TiO$_3$)$_{1-x}$(LaTiO$_2$N)$_x$ solid solution by Luo \etal \cite{33}.

The blue-shift in the vacancy-rich ZIO is consistent with the formation of indium vacancies. For In$_2$O$_3$ (ZnO)$_k$ ($k$ = integer), the CB bottom mainly consists of the In 5s level with a minor contribution from the Zn 4s level \cite{15}, and the In 5s level is located below the Zn 4s level \cite{34}. Therefore, the loss of indium widens the bandgap of vacancy-rich ZIO. Furthermore, since Cu doping narrows the bandgap by introducing Cu 3d levels above the VB of ZIO \cite{35}, it can be concluded that the Cu concentration was low in the vacancy-rich ZIO.
3.2. Photocatalytic H₂ evolution

As mentioned above, the samples were pretreated in a Na₂S/K₂SO₃ aqueous solution for 48 h under UV and visible-light irradiation using a Xe lamp (300 W) before the evaluation of photocatalytic activity. Figure 2 shows the H₂ evolution rates of ZIO/V-ZIOS and ZIO/ZIOS composites under visible-light irradiation (λ > 400 nm). The H₂ evolution rates are summarized in Table 1, revealing much higher values for ZIO/V-ZIOS than for ZIO/ZIOS at every 24-h cycle. The maximum rate of ZIO/V-ZIOS was 94.7 μmol h⁻¹, about 18 times as high as that of ZIO/ZIOS in the same cycle. The AQE for ZIO/V-ZIOS was about 5.2% at 420 nm.

3.3. Characterization of oxide/oxysulfide composites

The samples after photocatalytic H₂ evolution were cleaned several times with distilled water, dried, and collected for further characterization. Figures 3(a) and (b) show SEM images of ZIO/ZIOS and ZIO/V-ZIOS composites. The edges and corners of particles are more diffuse compared with those in figure S2 and fine particles appear on the surface, revealing that the surface was perturbed by the sulfuration. According to BET analysis, the surface area was increased from 0.20 to 44 and 26 m²g⁻¹ for ZIO/V-ZIOS and ZIO/ZIOS, respectively. Figures 3(c) and (d) show the EDX spectra of ZIO/ZIOS and ZIO/V-ZIOS composites, revealing Zn, In, O, and S elements.

Figure 4(a) shows XRD patterns of ZIO, vacancy-rich ZIO, ZIO/ZIOS, and ZIO/V-ZIOS composites. PowderX analysis indicated a hexagonal structure for all the samples as in the previous report [36]. A minor ZnS impurity was detected in the ZIO/ZIOS and ZIO/V-ZIOS composites, which was a by-product of the sulfuration process. The estimated lattice parameters of ZIO/ZIOS (a = 3.3308(1), c = 58.2089(16)) and ZIO/V-ZIOS (a = 3.3299(1), c = 58.1992(4)) were slightly larger than those of ZIO (a = 3.3296(7), c = 58.1201(5)). Such lattice expansion can be attributed to the substitution of S²⁻ ions (1.84 Å radius) for O²⁻ ions (1.4 Å radius). This substitution is also revealed by the shift in the (0 0 21) peak for the ZIO/ZIOS and ZIO/V-ZIOS composites in figure 4(b). From the lattice expansion, we can estimate the degree of S/O substitution in V-ZIOS as ZnₓInₓO₋ₓSₓ (x ≈ 0.03).

Figure 5 shows the UV-vis absorption spectra of ZIO/ZIOS and ZIO/V-ZIOS. They are redshifted compared with those of ZIO and vacancy-rich ZIO, which can be explained by the bandgap narrowing due to a VB shift by the S 2p orbitals. XPS was employed for the surface analysis of ZIO/ZIOS and ZIO/V-ZIOS composites as shown in figure 6. Peak positions were internally referenced to the C1s signal at 284.6 eV. The spectra exhibit the similar peaks of Zn, In, O, and S elements for the two composites. All the Zn 2p, O 1s, and S 2p peaks consist of two peaks. The core lines are located at 1045.0 and 1022.0 eV for the Zn 2p level, 452.4 and 444.9 eV for the In 3d level, 533.3 and 532.0 eV for the O 1s level, and 168.7 and 161.8 eV for the S 2p level. The positions of Zn 2p and In 3d peaks are consistent with the spin orbit separations (23.0 eV for Zn 2p and 7.5 eV for In 3d). For O 1s, the 533.3 eV signal should belong to water adsorbed on the sample surface [37], whereas the 532.0 eV peak is related to the sample. The S 2p peak at 168.7 eV is due to the trace sulfate adsorbed on the sample surface [38–41], which is the oxidation product of SO₃²⁻ by photogenerated holes [42], whereas the 161.8 eV signal is attributed to S²⁻ [43].

The structures of vacancy-rich ZIO and ZIO/V-ZIOS composite were characterized by HRTEM as shown in figure 7. The interplanar spacing of 2.88 Å in figure 7(a) is consistent with the spacing between the (101) planes of hexagonal ZnIn₂O₄. We could not probe the inner part of ZIO/V-ZIOS (figure 7(b)) owing to the large sample thickness in that area. ZIO has a polycrystalline structure, and the spacing of 3.2 Å in figure 7(b) corresponds to the (0 0 18) planes of V-ZIOS. Figure 8 shows STEM maps revealing a homogeneous distribution of Zn, In, O, and S elements in ZIO/V-ZIOS.

3.4. Mechanism of the enhanced photocatalytic activity

As mentioned above, indium vacancies were produced by the high-temperature treatment in Ar atmosphere, as confirmed by the increased Zn/In molar ratio in vacancy-rich ZIO compared with ZIO. The vacancies were introduced near the surface because the color changed from blue to yellow after milling the vacancy-rich ZIO. The In deficiency on the surface resulted in the blue-shift of the UV-vis absorption spectrum due to the bandgap widening in vacancy-rich ZIO. Oxide/oxysulfide composites were successfully synthesized, although ZnS was detected in both
ZnS did not affect the photoactivity of ZIO/ZIOS and ZIO/V-ZIOS composites because it has a wide bandgap and is therefore insensitive to visible light \[44\]. The formation of ZIOS on ZIO and vacancy-rich ZIO samples was confirmed by UV-vis absorption spectra, EDX, XPS, HRTEM, STEM elemental mapping, and the crystal structure refinement using PowderX software. The photocatalytic H\(_2\) evolution rate of ZIO/V-ZIOS composite was 17 times higher than that of ZIO/ZIOS.

The mechanism of this enhanced photoactivity is unclear, and a possible explanation based on the band diagrams of ZIO/V-ZIOS and ZIO/ZIOS composites is shown in figure 9.
Figure 7. HRTEM images of (a) vacancy-rich ZIO and (b) ZIO/V-ZIOS composite.

Figure 8. (a) STEM image and elemental maps of (b) Zn, (c) In, (d) O and (e) S in the ZIO/V-ZIOS composite.

The CB bottom of V-ZIOS synthesized from vacancy-rich ZIO is shifted up compared with that of ZIO as shown in figure 9(a), whereas the CBs have the same energies in ZIOS and ZIO as shown in figure 9(b). However, the UV-vis absorption spectra are redshifted (figure 5) both for ZIO/ZIOS and ZIO/V-ZIOS because the VB top was lifted up by the S 2p orbitals. For the ZIO/V-ZIOS composite, ZIO and V-ZIOS have different potentials both for CB and VB. These different potentials result in a more efficient separation of electron-hole pairs and thus in a higher photocatalytic activity.

Figure 9. Schematic mechanism of electron-hole pair separation in (a) ZIO/V-ZIOS and (b) ZIO/ZIOS composites.

4. Conclusions

We have developed a photoassisted method of fabricating zinc indium oxide/oxy sulfide composites using vacancy-rich ZIO as the precursor. These composites exhibited much higher photocatalytic activity for H₂ evolution in a Na₂S/K₂SO₃ aqueous solution under visible-light irradiation than the material prepared using conventional ZIO. Na₂S can act as not only a sacrificial reagent, but also a chemical reagent to form an oxy sulfide. We found that indium vacancies play an important role in enhancing the photocatalytic activity, which is related to the more efficient separation of photogenerated electrons and holes and the utilization of incident light. Our results provide useful information for improving the activity of photocatalysts.

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References


[34] Zhou X H, Hu Q H and Fu Y 2008 *J. Appl. Phys.* **104** 063703


