Effect of post-treatments on the photocatalytic activity of Sm$_2$Ti$_2$S$_2$O$_5$ for the hydrogen evolution reaction

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The oxysulphide photocatalyst Sm$_2$Ti$_2$S$_2$O$_5$ was synthesized by sulphurizing an amorphous Sm$_2$Ti$_2$O$_7$ prepared using a polymerized complex method under a H$_2$S flow and was used as a H$_2$ evolution photocatalyst in the sacrificial H$_2$ evolution and Z-scheme water splitting reactions. The H$_2$ evolution activity of Rh-loaded Sm$_2$Ti$_2$S$_2$O$_5$ was improved by annealing with sulphur powder and etching with nitric acid. Characterization using XRD, SEM, DRS and XPS suggested that annealing with sulphur decreased the density of the reduced Ti species in Sm$_2$Ti$_2$S$_2$O$_5$ and etching with nitric acid removed the amorphous phases and excessive sulphur species on the surface. After the two post-treatments, platinized Sm$_2$Ti$_2$S$_2$O$_5$ combined with rutile-type TiO$_2$ and NaI showed activity for Z-scheme water splitting under UV irradiation. Although UV irradiation was necessary owing to the use of TiO$_2$, this work provided the first evidence that an oxysulphide photocatalyst was applicable to Z-scheme water splitting.

Introduction

Photocatalytic water splitting has attracted worldwide interest as a promising method for conversion of solar energy into chemical fuels.$^{1-4}$ In order to utilize solar energy effectively, a photocatalyst must harvest visible light of up to 600 nm or even longer.$^2$ Z-scheme water splitting systems based on two-step photoexcitation are typically composed of a H$_2$ evolution photocatalyst, an O$_2$ evolution photocatalyst, and electron mediators.$^{3,4}$ During photoexcitation, electrons reduce H$^+$ to H$_2$ and holes oxidize the reduced form of redox mediators on the H$_2$ evolution photocatalyst, while on the O$_2$ evolution photocatalyst, electrons reduce the oxidized form of redox mediators and holes oxidize H$_2$O to O$_2$. It has also been found that Z-scheme water splitting can complete even in the absence of redox couples owing to the interparticle electron transfer, where holes in a H$_2$ evolution photocatalyst and electrons in an O$_2$ evolution photocatalyst recombine via physical contact.$^{4,5}$ Compared to the one-step excitation mechanism that uses a single visible-light-responsive photocatalyst, the two-step excitation mechanism has several advantages: it enables the use of a semiconductor that is active for either water reduction or oxidation alone as long as it is active for the oxidation or reduction of the redox mediators, respectively. Because the energy required to drive either photocatalyst can be lower, a wider range of visible-light-active photocatalysts are applicable. For example, WO$_3$, BiVO$_4$, and Rh-doped SrTiO$_3$ have been employed in Z-scheme water splitting although they are active only for H$_2$ or O$_2$ evolution in the presence of appropriate sacrificial reagents.$^{6-8}$ Photocatalysts that are capable of both the H$_2$ and O$_2$ evolution reactions with sacrificial reagents are also applicable to Z-scheme water splitting, as has been demonstrated with TaON$^{6,9}$ and Ta$_3$N$_5$. Moreover, H$_2$ and O$_2$ are generated on different photocatalysts, which could in principle offer a simple means of separating the gaseous products using an appropriate membrane filter.$^9$ Much effort has been devoted to construction of efficient Z-scheme systems by developing new materials and efficient electron relays.

Sm$_2$Ti$_2$S$_2$O$_5$, an oxysulphide semiconductor photocatalyst, has a crystal structure similar to that of a Ruddlesden–Popper-type layered perovskite oxide.$^{11}$ Under visible light irradiation (λ < 650 nm), Sm$_2$Ti$_2$S$_2$O$_5$ can evolve H$_2$ or O$_2$ from aqueous solutions containing sacrificial electron donors (Na$_2$S–Na$_2$SO$_3$ or methanol) or acceptors (Ag$^+$), respectively.$^{11}$ This indicates
that Sm₂Ti₂S₂O₅ has band positions suitable for water splitting under visible light irradiation. However, Sm₂Ti₂S₂O₅ and other oxysulphides have not been applied to Z-scheme water splitting successfully. Earlier studies on the photocatalyst Sm₂Ti₂S₂O₅ involved the H₂S gas sulphurization method for the preparation of fine Sm₂Ti₂S₂O₅ particles, and the loading and addition of various metal species to Sm₂Ti₂S₂O₅. It was found that promoting both the photocatalytic reduction of water and the oxidation of sacrificial electron donors as well as reducing the photocatalytic H₂ evolution rate on Sm₂Ti₂S₂O₅ from an aqueous solution of Na₂S and Na₂SO₃. In this study, methods of modifying Sm₂Ti₂S₂O₅ were investigated to improve the H₂ evolution activity. After appropriate post-treatments such as annealing with sulphur and etching with nitric acid, Sm₂Ti₂S₂O₅ loaded with TiO₂ (rutile) exhibited a higher activity for the sacrificial H₂ evolution reaction. The modified Sm₂Ti₂S₂O₅ was used as a H₂ photocatalyst in Z-scheme water splitting. It was found that Pt-loaded Sm₂Ti₂S₂O₅ suspended with TiO₂ (rutile) in an aqueous NaI solution was capable of splitting water into H₂ and O₂ under UV irradiation (λ > 300 nm).

Experimental

Amorphous Sm₂Ti₂O₅ was synthesized as an oxide precursor by a polymerized complex method. Titanium tetraisopropoxide (0.02 mol, Kanto Chemical Co., 97%) and anhydrous citric acid (0.3 mol, Wako Pure Chemicals, 98%) were dissolved in ethylene glycol (0.2 mol, Kanto Chemical Co., 99.5%) at room temperature, and the mixture was heated at 333 K until the reagents were completely dissolved. Subsequently, Sm(NO₃)₃·6H₂O (0.02 mol, Wako Pure Chemicals Co., 99.5%) and 20 mL methanol were added to the solution. The mixture was stirred at 403 K until a transparent gel was formed. It was polymerized and carbonized at 523, 573, and 623 K for 1 h each and finally calcined at 773 K for 12 h to remove the carbon completely. The resulting amorphous oxide was sulphurized at 1223 K for 1 h under a flow of H₂S (10 mL min⁻¹) and calcined for 2 h in 573 K.

As-synthesized Sm₂Ti₂S₂O₅ was sealed in evacuated quartz tubes with 5 wt% sulphur powder (High Purity Chemicals Co., 99.99%) with respect to Sm₂Ti₂S₂O₅ and annealed at 1223 K for 20 h. Nitric acid treatment was conducted by dispersing Sm₂Ti₂S₂O₅ powder (ca. 0.5 g) in HNO₃ (Wako Pure Chemicals Co., 69.8 wt%) for 10 min at room temperature, followed by rinsing with distilled water, filtration, drying at 343 K, and heat treatment at 573 K for 1 h in air. The mass loss during the whole nitric acid etching procedure was approximately 40%, while the mass loss during the rinsing and filtration procedures was approximately 8%. When both treatments were carried out, the nitric acid etching was performed after the sulphur annealing. Sm₂Ti₂S₂O₅ samples subjected to the sulphur annealing alone, to the nitric acid etching alone, and to both procedures will hereafter be denoted as Sm₂Ti₂S₂O₅ (S), Sm₂Ti₂S₂O₅ (HNO₃), and Sm₂Ti₂S₂O₅ (S + HNO₃), respectively.

The samples were characterized using X-ray powder diffraction (XRD; RINT-Ultima III, Rigaku; Cu Kα), ultraviolet-visible diffuse-reflectance spectroscopy (DRS; V-670, JASCO), field-emission scanning electron microscopy (FE-SEM; S-4700, Hitachi) and X-ray photoelectron spectroscopy (XPS; JPS-9000, JEOL). The binding energy for each sample was corrected by the reference C 1s peak (285.0 eV). The peak areas of Sm 3dₓ/₂, Ti 2p, S 2pₓ/₂, and O 1s were acquired by integrating the signals over 1090.0–1077.0, 468.0–455.8, 171.8–157.4, and 535.7–526.5 eV, respectively.

The photocatalytic H₂ evolution reactions were carried out in an inner irradiation-type Pyrex reaction vessel connected to an air-tight closed gas circulation system made of Pyrex glass. An aqueous solution (400 mL) containing the photocatalyst sample (0.2 g), Na₂S–Na₂SO₃ (0.2 M each) was irradiated with a 450 W high-pressure Hg lamp through a NaNO₂ solution (2 M) as an optical filter, the cutoff wavelength of which was 400 nm. For the H₂ evolution reaction, Rh (1.5 wt%) was loaded as a H₂ evolution cocatalyst by photodeposition from the Na₂S–Na₂SO₃ aqueous solutions. A calculated amount of RhCl₃·H₂O (Aldrich, 38–40% as Rh) precursor added to the solution was reduced to metallic Rh by photoexcited electrons from the photocatalyst in the initial stage of the reaction. The reactant solution was maintained at room temperature by flowing cooling water during the reaction. The evolved gas was analyzed by gas chromatography (GC, TCD, Shimadzu).

For Z-scheme water splitting, Pt-loaded Sm₂Ti₂S₂O₅ (0.2 g), rutile TiO₂ (0.2 g), and NaI (50 mM) were used as a H₂ evolution photocatalyst, O₂ evolution photocatalyst, and redox mediator, respectively. Pt is employed as an effective H₂ evolution cocatalyst in Z-scheme water splitting involving the redox couple IO₃⁻/I⁻. Pt (2 wt%) was photodeposited on Sm₂Ti₂S₂O₅ from a calculated amount of H₂PtCl₆·6H₂O (Aldrich, 38–40% Pt) in an aqueous NaI solution (pH = 6). The platinized sample was collected and used for Z-scheme water splitting. The pH of the solution containing the H₂ evolution photocatalyst, O₂ evolution photocatalyst, and redox mediator was adjusted using an aqueous NaOH solution. The solution was evacuated and irradiated with a 450 W high-pressure Hg lamp (λ > 300 nm). Note that conventional TiO₂ (rutile) was employed to assess the applicability of Sm₂Ti₂S₂O₅ as a H₂ evolution photocatalyst in Z-scheme water splitting, since rutile-type TiO₂ worked effectively as an O₂ evolution photocatalyst in Z-scheme systems involving IO₃⁻/I⁻ owing to preferential adsorption of IO₃⁻ ions onto rutile-type TiO₂ and its sufficient activity of for IO₃⁻ reduction even without elaborate modifications while necessitating UV illumination.

Results and discussion

Effects of post-treatments

Fig. 1 shows XRD patterns of the Sm₂Ti₂S₂O₅ samples before and after the post-treatments. The diffraction profile of the Sm₂Ti₂S₂O₅ phase was unchanged and no impurity phase was generated by the post-treatments. The peak intensities of Sm₂Ti₂S₂O₅ and Sm₂Ti₂S₂O₅ (HNO₃) were identical, while those of Sm₂Ti₂S₂O₅ (S) and Sm₂Ti₂S₂O₅ (S + HNO₃) became somewhat stronger. This suggests that the sulphur annealing at 1223 K improved the crystallinity of Sm₂Ti₂S₂O₅ and that the
nitric acid etching did not change the bulk crystallinity of Sm$_2$Ti$_2$S$_2$O$_5$.

Fig. 2 shows SEM images of the corresponding Sm$_2$Ti$_2$S$_2$O$_5$ samples. Sm$_2$Ti$_2$S$_2$O$_5$ consisted of plate-like submicron particles, which formed massive secondary particles several micrometers in size. During the sulphur annealing, these aggregates were sintered into 0.5–1 μm particles with smoother surfaces. When the samples were etched with HNO$_3$, dramatic changes were observed in the surface morphologies of Sm$_2$Ti$_2$S$_2$O$_5$ and Sm$_2$Ti$_2$S$_2$O$_5$ (S). It appeared that the outer surface of the samples had dissolved, exposing the interior consisting of submicron Sm$_2$Ti$_2$S$_2$O$_5$ grains. This verified the speculation of our previous study that the large Sm$_2$Ti$_2$S$_2$O$_5$ (S) particles were polycrystalline. The Sm$_2$Ti$_2$S$_2$O$_5$ (S + HNO$_3$) grains were, on average, larger than the Sm$_2$Ti$_2$S$_2$O$_5$ (HNO$_3$) grains.

The surface compositions of the Sm$_2$Ti$_2$S$_2$O$_5$ samples before and after the post-treatments are tabulated in Table 1. Pristine Sm$_2$Ti$_2$S$_2$O$_5$ nearly exhibited the stoichiometric Sm/Ti ratio, while the S/Ti and O/Ti ratios were larger than the corresponding stoichiometric ratios. We obtained similar results in our previous study. This is because the Sm$_2$Ti$_2$S$_2$O$_5$ surface was enriched with elemental and oxidized sulphur species when Sm$_2$Ti$_2$S$_2$O$_5$ was sulphurized under a H$_2$S flow and annealed in air. Sm$_2$Ti$_2$S$_2$O$_5$ (HNO$_3$) after the nitric acid etching exhibited a smaller Sm/Ti ratio than pristine Sm$_2$Ti$_2$S$_2$O$_5$. This indicates that the Sm$_2$Ti$_2$S$_2$O$_5$ surface was indeed dissolved by nitric acid, particularly the Sm component with weak basicity. The sulphur annealing did not change the surface Sm/Ti ratio significantly, while generating excessive sulphur on the surface of Sm$_2$Ti$_2$S$_2$O$_5$ (S). Sm$_2$Ti$_2$S$_2$O$_5$ (S + HNO$_3$) maintained the Sm/Ti ratio of Sm$_2$Ti$_2$S$_2$O$_5$ (S), unlike the case of Sm$_2$Ti$_2$S$_2$O$_5$ (HNO$_3$) after the nitric acid treatment. It is thought that a part of the pristine Sm$_2$Ti$_2$S$_2$O$_5$ sample was rather amorphous and thus the nitric acid etching resulted in preferential dissolution of Sm species. However, annealing in the presence of sulphur improved the crystallinity of Sm$_2$Ti$_2$S$_2$O$_5$, incorporating amorphous Sm species into the crystal structure, thereby suppressing the leaching of Sm species during the nitric acid treatment. Note that the surface of Sm$_2$Ti$_2$S$_2$O$_5$ (S) was still etched, as was evident from the SEM images. This resulted in the partial removal of the excess sulphur species on the surface.

The DRS shown in Fig. 3 confirms that the pristine sample exhibited a light absorption onset at approximately 650 nm, which corresponded to the band gap transition of Sm$_2$Ti$_2$S$_2$O$_5$. The background absorption was also observed, presumably because of reduced Ti species. The reduced Ti species may have been generated by the exposure to heated H$_2$S. Sm$_2$Ti$_2$S$_2$O$_5$ (HNO$_3$) had a similar absorption onset and background absorption. The fact that etching of the surface did not weaken the background absorption indicates that the reduced Ti species were present in the bulk of the sample. Sm$_2$Ti$_2$S$_2$O$_5$ (S) and Sm$_2$Ti$_2$S$_2$O$_5$ (S + HNO$_3$), which were subjected to the sulphur annealing treatment, had similar absorption onsets but lower background absorption. Considering the dramatic changes in morphology that occurred during the sulphur annealing, it is reasonable to assume that the reduced Ti species in the bulk were oxidized by elemental sulphur upon annealing at 1223 K.

Fig. 4 shows the reaction time courses of photocatalytic H$_2$ evolution using pristine and post-treated Sm$_2$Ti$_2$S$_2$O$_5$ samples. The photocatalytic activity of Sm$_2$Ti$_2$S$_2$O$_5$ was improved by the sulphur annealing and the nitric acid etching, and combining these post-treatments resulted in the highest activity. During the sulphurization of amorphous Sm$_2$Ti$_2$O$_7$ to Sm$_2$Ti$_2$S$_2$O$_5$, a certain amount of Ti$^{3+}$ species was generated because of the

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**Table 1** Surface atomic ratios of Sm$_2$Ti$_2$S$_2$O$_5$ before and after the post-treatments, as estimated by XPS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sm/Ti</th>
<th>S/Ti</th>
<th>O/Ti</th>
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<tr>
<td>Sm$_2$Ti$_2$S$_2$O$_5$</td>
<td>1.1</td>
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<td>Sm$_2$Ti$_2$S$_2$O$_5$ (HNO$_3$)</td>
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<tr>
<td>Sm$_2$Ti$_2$S$_2$O$_5$ (S)</td>
<td>0.9</td>
<td>2.6</td>
<td>7.5</td>
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<td>Sm$_2$Ti$_2$S$_2$O$_5$ (S + HNO$_3$)</td>
<td>0.9</td>
<td>2.0</td>
<td>6.5</td>
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of Rh as H2 evolution sites.12 The sintering of Sm2Ti3S4O5 may also have led to the lower-than-expected photocatalytic activity.12

The nitric acid etching improved the H2 evolution activity by a factor of three although the Sm component was deficient on the sample surface. The SEM and XPS results suggest that the enhanced activity of Sm2Ti3S4O5 (HNO3) is attributable to the elimination of the defective amorphous layers on the surface that would otherwise have prevented charge transfer. Sm2Ti3S4O5 (S + HNO3) benefited from both post-treatments. Moreover, the excess sulphur species on Sm2Ti3S4O5 (S) were eliminated in part by the nitric acid etching, and the Sm deficiency on the surface observed in the case of Sm2Ti3S4O5 (HNO3) was avoided owing to the improved crystallinity. As a result, Sm2Ti3S4O5 (S + HNO3) showed a H2 evolution rate that was 4.5 times higher than that of pristine Sm2Ti3S4O5.

Application of Sm2Ti3S4O5 to Z-scheme water splitting

Table 2 shows the amounts of H2 and O2 evolved in Z-scheme water splitting reactions over 5 h using Pt-loaded Sm2Ti3S4O5 samples as a H2 evolution photocatalyst. Simultaneous evolution of H2 and O2 was observed only when Sm2Ti3S4O5 (S + HNO3) was used as a H2 evolution photocatalyst together with TiO2 (rutile) as an O2 evolution photocatalyst and NaI as a redox mediator. The ratio of H2 to O2 produced was higher than the stoichiometry of overall water splitting because of the presence of excess electron donors (NaI) in the beginning of the reaction. When one of the components, i.e., the H2 evolution photocatalyst, O2 evolution photocatalyst, or redox mediator, was missing, the gas evolution was negligible. This confirms that the water splitting reaction occurred via the Z-scheme mechanism.

The use of pristine Sm2Ti3S4O5, Sm2Ti3S4O5 (S), and Sm2Ti3S4O5 (HNO3) did not lead to successful O2 evolution, while producing a certain amount of H2. In addition, the H2 evolution ceased during the initial stage of the reaction. In Z-scheme water splitting in the presence of reversible redox couples, simultaneous evolution of H2 and O2 is often difficult because of backward reactions on the respective photocatalysts. IO3− produced by the oxidation of I− on Sm2Ti3S4O5 could largely be reduced back to I− unless the H2 evolution activity was high enough to outweigh the thermodynamically favorable reduction of Ti4+ under the heated H2S atmosphere. The generation of reduced Ti species is accompanied by the formation of anion vacancies. These vacancies tend to act as recombination centres for photoexcited electrons and holes and suppress the photocatalytic activity.12,13 The sulphur annealing can potentially produce a higher activity owing to the lower density of reduced Ti species in Sm2Ti3S4O5. In reality, however, hardly any activity enhancement was observed upon sulphur annealing. This is likely due to the presence of excess sulphur species on the surface, which blocked the surface active sites and thus prevented the deposition of sulphur on the sample surface.

<table>
<thead>
<tr>
<th>Photocatalytic activity for Z-scheme water splitting using Sm2Ti3S4O5</th>
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<tr>
<td>H2 evolution</td>
<td>O2 evolution</td>
<td>Redox mediator</td>
<td>Activity/mmol</td>
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<tr>
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<td>photocatalyst</td>
<td></td>
<td>H2</td>
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<tr>
<td>Sm2Ti3S4O5</td>
<td>TiO2 (rutile)</td>
<td>NaI</td>
<td>10</td>
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<td>TiO2 (rutile)</td>
<td>NaI</td>
<td>13</td>
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<tr>
<td>Sm2Ti3S4O5 (HNO3)</td>
<td>TiO2 (rutile)</td>
<td>NaI</td>
<td>11</td>
</tr>
<tr>
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<td>NaI</td>
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</tr>
<tr>
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<td>TiO2 (rutile)</td>
<td>NaI</td>
<td>0</td>
</tr>
<tr>
<td>Sm2Ti3S4O5 (S + HNO3)</td>
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<td>NaI</td>
<td>0.6</td>
</tr>
<tr>
<td>Sm2Ti3S4O5 (S + HNO3)</td>
<td>TiO2 (rutile)</td>
<td>None</td>
<td>0</td>
</tr>
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</table>

* Reaction conditions: photocatalysts, 0.2 g each; reaction solution, aqueous NaI solution (430 mL, 50 mM, pH = 12); light source, 450 W high-pressure Hg lamp. * Loaded with 2 wt% of Pt by photodeposition. * Estimated from the amount of gases evolved in 5 h.

Fig. 4 Time courses of H2 evolution over Sm2Ti3S4O5 after various post-treatments: (a) Sm2Ti3S4O5, (b) Sm2Ti3S4O5 (S), (c) Sm2Ti3S4O5 (HNO3), and (d) Sm2Ti3S4O5 (S + HNO3). Reaction conditions: catalyst, 0.2 g; cocatalyst, 1.5 wt% Rh (in situ photodeposition); sacrificial electron donor, Na2S + Na2SO3 (0.2 M each in 400 mL of water); light source, 450 W high-pressure Hg lamp (> 400 nm, 2 M NaNO2 (aq.) as a filter solution).

Fig. 3 UV-vis DRS of (a) Sm2Ti3S4O5, (b) Sm2Ti3S4O5 (S), (c) Sm2Ti3S4O5 (HNO3), and (d) Sm2Ti3S4O5 (S + HNO3).
backward reaction. In addition, the oxygen evolution on rutile-type TiO$_2$ could be suppressed by the oxidation of I$^-$ when the concentration of I$^-$ was high.\textsuperscript{17} The absence of O$_2$ evolution thus suggests that the activities of the above three Sm$_2$Ti$_2$S$_2$O$_5$ samples for H$_2$ evolution and I$^-$ oxidation were too low to provide a sufficient amount of IO$_3^-$ in the reaction solution. Further characterization is necessary to determine why, among the Sm$_2$Ti$_2$S$_2$O$_5$ samples subjected to different post-treatments, only Sm$_2$Ti$_2$S$_2$O$_5$ ($S + HNO_3$) was active for Z-scheme water splitting. However, the present results suffice to show that the appropriate post-treatments enabled the oxysulphide photocatalyst to be used as a H$_2$ evolution photocatalyst for Z-scheme water splitting and that lowering the densities of both reduced Ti species and surface impurities was necessary.

Fig. 5 shows the dependence of the photocatalytic activity of the Z-scheme system for water splitting on the pH of the reaction solution. Z-scheme water splitting was enhanced significantly as the pH increased from 6 to 12 and was suppressed at pH > 12. O$_2$ evolution was almost negligible at pH < 9. This is because the main oxidative product on Pt-loaded Sm$_2$Ti$_2$S$_2$O$_5$ ($S + HNO_3$) was I$_3^-$, which failed to serve as an efficient electron acceptor for O$_2$ evolution over rutile TiO$_2$. The photocatalytic activity decreased at pH > 12. This is probably because of the decreasing driving force of Sm$_2$Ti$_2$S$_2$O$_5$ for H$_2$ evolution with increasing pH. It has been found previously that the potential of the band gap of Sm$_2$Ti$_2$S$_2$O$_5$ was independent of the pH of the solution,\textsuperscript{11} while the H$_2$ evolution potential shifted negatively with increasing pH. Thus, a basic solution at a pH of around 11–12 was the most favourable for Z-scheme water splitting using Sm$_2$Ti$_2$S$_2$O$_5$, TiO$_2$, and I$^-$/IO$_3^-$. Fig. 6 shows the results of Z-scheme water splitting with intermittent evacuations. The ratio of H$_2$ and O$_2$ approached 2 : 1 after the first five-hour reaction and subsequent evacuation as the excess I$^-$ was converted into IO$_3^-$ during the reaction. The rate of gas evolution gradually decreased as the gas product accumulated in the closed system because the backward reaction from H$_2$ and O$_2$ to H$_2$O occurred on the Pt used as a cocatalyst. The rate of water splitting recovered to some extent upon evacuation. However, the photocatalytic activity of the system gradually decreased. XRD patterns presented in Fig. 7 show that the sample after the reaction was a mixture of Sm$_2$Ti$_2$S$_2$O$_5$,
(S + HNO₃) and rutile-type TiO₂. This result suggests that the bulk of Sm₂Ti₂S₂O₅ (S + HNO₃) was mostly stable during the water splitting reaction. The deactivation may be due to the photo-oxidation of the surface of Sm₂Ti₂S₂O₅ by photoexcited holes under the intense UV illumination. Although UV illumination and stabilization of Sm₂Ti₂S₂O₅ were still necessary, this represents the first instance of Z-scheme water splitting achieved using an oxysulphide photocatalyst as a H₂ evolution photocatalyst. It is expected that dual cocatalyst loading on Sm₂Ti₂S₂O₅ could be used as a H₂ evolution photocatalyst in multiple phases and excess sulphur species, respectively.

Conclusions

The processes of annealing with sulphur and etching with nitric acid were studied to improve the photocatalytic activity of Sm₂Ti₂S₂O₅ for H₂ evolution in sacrificial water reduction and Z-scheme water splitting. The photocatalytic activity improved by a factor of 4.5 when the sulphur annealing and nitric acid etching were applied in combination. The effects of these post-treatments were attributed to the oxidation of reduced Ti³⁺ species and the removal of amorphous surface phases and excess sulphur species, respectively.

Following the sulphur annealing and the nitric acid etching, Sm₂Ti₂S₂O₅ could be used as a H₂ evolution photocatalyst in Z-scheme water splitting in combination with TiO₂ as an O₂ evolution photocatalyst and NaI as a redox mediator. All three of the components were necessary to drive Z-scheme water splitting. Employing both post-treatments was essential for successful Z-scheme water splitting, which indicated the importance of removing reduced Ti³⁺ species and surface impurities from Sm₂Ti₂S₂O₅. Although UV irradiation was necessary because of the use of TiO₂, the present study revealed that appropriate modifications allowed an oxysulphide photocatalyst to serve as a H₂ evolution photocatalyst in Z-scheme water splitting.

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Notes and references