Synthesis of HTaWO$_6$/\(\text{Pt, TiO}_2\) nanocomposite with high photocatalytic activities for hydrogen evolution and nitrogen monoxide destruction

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Abstract

HTaWO$_6$/\(\text{Pt, TiO}_2\) nanocomposite was synthesized by successive intercalation reactions of HTaWO$_6$ with \(\text{Pt(NH}_3)_4\text{Cl}_2\)\(^{2+}\), \(\text{C}_2\text{H}_5\text{NH}_2\)-heptane mixed solution and TiO$_2$ acidic sol, followed by UV irradiation. The height of TiO$_2$ and Pt pillar is less than 0.51 nm. The host HTaWO$_6$ was white and possessed band gap energy of 3.11 eV, whereas the HTaWO$_6$/\(\text{Pt, TiO}_2\) nanocomposite was yellow and showed broad reflection over 400–600 nm together with that corresponding to the host layer, and possessed both excellent hydrogen evolution and nitrogen monoxide destruction photocatalytic activities even under visible light irradiation (\(\lambda\geq510\) nm). The HTaWO$_6$/\(\text{Pt, TiO}_2\) possessed higher photocatalytic activity than those of undoped HTaWO$_6$, commercial titania powder (Degussa P-25), fibrous titania and Pt-doped fibrous titania.

Keywords: Layered compounds; Semiconductors; Intercalation reactions; Hydrogen evolution; Nitrogen monoxide destruction

1. Introduction

Photoelectrochemical processes at semiconductor interface have aroused special attention because of their possible application for the conversion of solar energy into chemical energy [1–5]. It is well known that nanocrystalline semiconductors possess quite different optical, electrical and chemical properties compared with those of bulk ones. It is expected that the photocatalytic activity of the semiconductor might be improved by being incorporated in the interlayer of layered compound [6,7]. Some researchers have reported the incorporation of extremely small particles of TiO$_2$, Fe$_2$O$_3$, CdS and ZnS–CdS into the interlayer of layered compounds such as montmorillonite, layered double hydroxides, layered niobate and layered titanate [8–10]. As expected, the photocatalytic activities of the incorporated semiconductors were much higher than those of the unsupported semiconductors. In the present study, HTaWO$_6$/\(\text{Pt, TiO}_2\) nanocomposite was synthesized and its photocatalytic activities, including hydrogen evolution and nitrogen monoxide oxidation, were characterized. The reaction mechanisms for photocatalytic reduction of water and photocatalytic oxidation of nitrogen monoxide were discussed.

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2. Experimental

2.1. Synthesis of photocatalyst

HTaWO₆ was prepared by ion exchange of LiTaWO₆ with 3 M HNO₃ at room temperature for 72 h. LiTaWO₆ was synthesized by calcining a stoichiometric mixture of Li₂CO₃, WO₃ and Ta₂O₅ at 900 °C in air for 24 h. HTaWO₆/(Pt, TiO₂) was synthesized by successive intercalation reactions of HTaWO₆ with 0.6 mM [Pt(NH₃)₄]Cl₂ aqueous solution for 72 h at room temperature, 20 vol.% n-C₃H₇NH₂/n-heptane solution for 72 h at 50 °C and acidic TiO₂ colloid solution for 6 h at room temperature, respectively, followed by UV light irradiation. The acidic TiO₂ colloid solution was made by adding titanium tetrachloride to 1 M HCl solution with TiO₂/HCl molar ratio of 0.25. In order to remove most of the Pt ion and TiO₂ colloid solution on the outer surface, the specimen was filtered and washed with distilled water, then dispersed in 1250 cm³ of water before UV light irradiation. Fibrous TiO₂ and fibrous TiO₂/Pt were prepared by heat treatment of H₂Ti₄O₉·0.25H₂O and H₂–2x[Pt(NH₃)₄]xTi₄O₉ in methanol at 325 °C for 1 h, respectively [11].

2.2. Analysis

The crystalline phases of the products were identified by X-ray diffraction (Shimadzu XD DI) using graphite monochromized CuKα radiation. The chemical compositions of the products were determined by TG-DTA analysis (Rigaku Denki TAS 200 TG-DTA) and by inductively coupled plasma atomic emission
spectroscopy (Seiko SPS-1200A) by dissolving the samples in water after mixing 0.1-g samples with 4 g Na₂CO₃ and calcining at 800 °C for 4 h. The band gap energies of the products were determined from the onset of diffuse reflectance spectra of the powders measured by using a UV–VIS spectrophotometer (Shimadzu UV-2000). The specific surface areas of samples were determined by nitrogen gas adsorption method (Quantachrome: NOV A 1000-TS). The spectra of the light sources were measured by a multi-channel spectrophotometer (JASCO, MD-100).

2.3. Photocatalytic reaction

The photocatalytic activity for hydrogen evolution was determined by measuring the volume of the hydrogen gas evolved with a gas burette during the irradiation of 10 vol.% methanol solution of 1250 cm³ containing 1.0 g dispersed catalyst at 60 °C. The apparatus used was reported in a previous paper [12]. The experiment under sunlight was carried out from 13:00 to 16:00 on October 18, 1999 on the roof of IMRAM, Tohoku University (N38°1' E140°54').

The photocatalytic activity for nitrogen monoxide destruction was determined by measuring the concentration of NO gas at the outlet of the reactor (373 cm³) during the photoirradiation of constant flowed 1 ppm NO 50 vol.% air-mixed (balance N₂) gas (200 cm³/min). Fig. 1 shows the experimental apparatus used for photocatalytic destruction of nitrogen monoxide. The humidity of the gas was kept at about 50% by bubbling the air into a water-filled trap before mixed with NO gas.

As illustrated in this figure, the photocatalyst was placed in a hollow place of 20 × 15 × 0.5 mm on a glass holder/plate and set in the center of the reactor. A 450-W high-pressure mercury lamp was used as the light source, where the light wavelength was controlled by selecting various filters.

3. Results and discussion

3.1. Intercalation of TiO₂ and Pt into the interlayer of HTaWO₆

HTaWO₆ prepared in the present study showed the same XRD pattern as that reported by Kumada et al. [13]. Strong (002) and (110) peaks were observed, indicating the existence of layer structure. By the X-ray diffraction analysis, it was confirmed that the layer structure of HTaWO₆ was still retained after intercalation of C₃H₇NH₂, TiO₂ and Pt, although the interlayer distance changed depending on the species intercalated. The main peak corresponding to (002) of HTaWO₆ shifted to lower angle after intercalation of Pt, TiO₂ or TiO₂/Pt, indicating the expansion of layer distance of HTaWO₆. The UV–visible diffuse reflection spectra of (a) HTaWO₆, (b) HTaWO₆/TiO₂, (c) HTaWO₆/Pt and (d) HTaWO₆/(Pt, TiO₂) are shown in Fig. 2.

HTaWO₆ and HTaWO₆/TiO₂ were white and showed an absorption onset around 400 nm (3.11 eV). Commercial titania (Degussa P-25) and fibrous
titania possessed similar band gap energies (3.16–3.31 eV). However, HTaWO₆/Pt and HTaWO₆/(Pt, TiO₂) were yellow and showed two absorption onsets around 400 and 550 nm, indicating a possibility of visible light-induced photocatalytic activity. It was reported that HTaWO₆ decomposed to TaWO₅.₅, then to Ta₂O₅ and WO₃ by laser irradiation [13–15]. Therefore, the yellow coloring may be due to the formation of TaWO₅.₅ and/or WO₃ by the similar photoinduced phase transformation of HTaWO₆ since HTaWO₆/Pt and HTaWO₆/(Pt, TiO₂) were irradiated with UV light for 5 and 12 h for the photodeposition of Pt and photodecomposition of C₃H₇NH₃⁺ in the interlayer. Although HTaWO₆/TiO₂ was also irradiated with UV light for 12 h, no color change was observed. Therefore, it is suspected that platinum promoted the photoinduced decomposition of HTaWO₆. No peaks due to WO₃ in XRD patterns was observed in the Pt-doped composite after UV light irradiation. This might be caused by the very small amount in the composite. It was reported that small amount of decomposition products from HTaWO₆ could be identified by Raman analysis [13], although it was not carried out in the present study.

The interlayer distances, contents of Ti and Pt elements, band gap energies and specific surface areas of prepared composites are summarized in Table 1. For comparison, the data of commercial titania (Degussa P-25) and platinum undoped/doped fibrous titania which showed high photocatalytic activity were also listed. The P-25 TiO₂ powder consists of about 30% rutile–70% anatase phase and possesses a high specific surface area of 47.0 m²/g. The fibrous TiO₂ and fibrous TiO₂/Pt were prepared by the heat treatment of H₂Ti₄O₉·0.25H₂O and H₂–₂x[Pt(NH₃)₄]₂Ti₆O₉ precursors, respectively, in methanol at 325 °C for 1 h [11,12]. These fibrous titania powders consist of a mixture of monoclinic and anatase phases and possess the specific surface areas of 22.1–25.0 m²/g [16].

The interlayer distance of HTaWO₆ was expanded from 0.28 to 0.51 nm, and specific surface area increased several times by intercalating TiO₂ and Pt. Especially, the specific surface area increased from 4.2 to 27.1 m²/g with incorporating TiO₂ and Pt simultaneously. These results also imply the formation of the pillars in the interlayer.

### 3.2. Photocatalytic hydrogen evolution and nitrogen monoxide destruction

The photocatalytic activities of the prepared samples were investigated under irradiating lights of various wavelengths. Fig. 3 shows the spectra of the light source filtered by different filters. It is seen that the light of the wavelength less than 290, 400 and 510 nm could be filtered out using a Pyrex glass jacket, 400-nm cut-off filter or 1 M NaNO₂ solution, and 510-nm cut-off filter, respectively. The photocatalytic hydrogen evolution activities of HTaWO₆ composites were determined at 60 °C under irradiating light λ>290 and 400 nm. At this time, the intensity of light reaching the catalysts was about 8970 and 6880 µmol/m² s, respectively. The results are shown in Fig. 4 together with those of fibrous TiO₂, fibrous TiO₂/Pt and commercial TiO₂ powder (Degussa P-25). The hydrogen evolution rate was in the sequence of: HTaWO₆/(Pt, TiO₂) > fibrous TiO₂/Pt > fibrous TiO₂ > HTaWO₆/Pt > HTaWO₆/TiO₂ > Degussa P-25 TiO₂. The high photocatalytic activity of HTaWO₆/(Pt, TiO₂) also implies the incorporation of Pt and TiO₂ in the interlayer of HTaWO₆. Since the light receiving area was 237 cm², the quantum efficiency from photon to hydrogen gas by HTaWO₆/(Pt, TiO₂) was calculated for about 1.60% and 0.14% under irradiating lights λ>290 and 400 nm. It is notable that the HTaWO₆/(Pt, TiO₂)

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gallery height (nm)</th>
<th>Ti content (wt.%)</th>
<th>Pt content (wt.%)</th>
<th>Band gap (eV)</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ (P-25)</td>
<td>–</td>
<td>59.8</td>
<td>0</td>
<td>3.26</td>
<td>47.0</td>
</tr>
<tr>
<td>Fibrous TiO₂</td>
<td>–</td>
<td>59.3</td>
<td>0</td>
<td>3.31</td>
<td>22.1</td>
</tr>
<tr>
<td>Fibrous</td>
<td>–</td>
<td>59.1</td>
<td>0.35</td>
<td>3.16</td>
<td>25.0</td>
</tr>
<tr>
<td>TiO₂/Pt</td>
<td>–</td>
<td>59.8</td>
<td>0</td>
<td>3.26</td>
<td>47.0</td>
</tr>
<tr>
<td>HTaWO₆</td>
<td>0.28</td>
<td>0</td>
<td>0</td>
<td>3.06</td>
<td>4.2</td>
</tr>
<tr>
<td>HTaWO₆/TiO₂</td>
<td>0.44</td>
<td>6.8</td>
<td>0</td>
<td>3.11</td>
<td>18.5</td>
</tr>
<tr>
<td>HTaWO₆/Pt</td>
<td>0.30</td>
<td>0</td>
<td>0.63</td>
<td>3.35, 2.22</td>
<td>5.0</td>
</tr>
<tr>
<td>HTaWO₆/(Pt, TiO₂)</td>
<td>0.51</td>
<td>10.1</td>
<td>0.51</td>
<td>3.12, 2.28</td>
<td>27.1</td>
</tr>
</tbody>
</table>
showed photocatalytic hydrogen evolution activity under visible light irradiation although the reason has not been clarified yet.

The photocatalytic hydrogen evolution from 1.0 g of HTaWO$_6$/(Pt, TiO$_2$) powders dispersed in 1250 cm$^3$ of 10 vol.% methanol solution at ca. 20 °C under sunlight irradiation (October 18, 1999, 13:00–16:00) is showed in Fig. 5. The sunlight intensity during the experiment was 1260–1530 μmol/m$^2$ s. No noticeable gas evolution was observed without catalyst. However, more than 10 cm$^3$/h of gas evolution was conformed in the presence of HTaWO$_6$/(Pt, TiO$_2$) catalyst. Since the light receiving area of the outer side of apparatus was 200 cm$^2$, the quantum efficiency from photon to hydrogen gas was calculated as about 0.41—0.50%. This result suggests that the photocatalyst could be utilized under sunlight irradiation. The quantum efficiency is different to that under irradiating 450-W mercury lamp, this is thought to be due to the different wavelength distribution of light sources.

Photocatalytic oxidation of nitrogen monoxide with various catalysts were conducted at room temperature under irradiating lights $\lambda>290$, 400 and 510 nm. The light receiving area of catalysts was 3.0 cm$^2$, and the intensity of light reaching the catalysts was about 500, 430 and 285 μmol/m$^2$ s, respectively. The duration time of nitrogen monoxide gas in the reactor

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**Fig. 3.** Wavelength distribution of the light irradiated from a 450-W high-pressure mercury lamp (a) without filter, (b) light (a) filtered by Pyrex glass jacket, (c) light (b) filtered by a 400-nm cut-off filter, (d) light (b) filtered by 1 M NaNO$_2$ solution, and (e) light (c) filtered by a 510-nm cut-off filter.

**Fig. 4.** Photocatalytic hydrogen evolution from 1250 ml of 10 vol.% methanol solution containing 1 g of catalyst under irradiation of a 450-W high-pressure mercury arc at 60 °C (■: HTaWO$_6$/(Pt, TiO$_2$); □: HTaWO$_6$/P: TaWO$_6$/P; □: HTaWO$_6$/TiO$_2$; □: Degussa P-25 TiO$_2$; ■: fibrous TiO$_2$; □: fibrous TiO$_2$/Pt).
was 112 s. As shown in Fig. 6, the nitrogen monoxide oxidation degree was in the sequence, HTaWO₆/(Pt, TiO₂) > Degussa P-25 TiO₂ > fibrous TiO₂/Pt > fibrous TiO₂ > HTaWO₆. HTaWO₆, fibrous TiO₂ and fibrous TiO₂/Pt did not show NO oxidation ability under visible light irradiation. However, significant amounts of NO were oxidized in the presence of HTaWO₆/(Pt, TiO₂) and P-25 TiO₂ under irradiating visible light. It is noticeable that about 37% and 17% of 1 ppm nitrogen monoxide could be oxidized by HTaWO₆/(Pt, TiO₂) at room temperature under the irradiation of light λ>400 and 510 nm, respectively. Assume that NO was transformed to nitric acid, the quantum efficiency for the reaction by HTaWO₆/(Pt, TiO₂) was calculated as about 0.25%, 0.19% and 0.14%, respectively, under irradiating lights λ>290, 400 and 510 nm.

3.3. Photocatalytic reaction mechanism

It is accepted that photocatalyst particles (denoted as M) absorb light of energy greater than the band gap to generate electron/hole pairs (Eq. (1)). The electrons are photoinduced to conduction band (e⁻CB/C₀CB), and the holes in valence band (h⁺VB).

\[ \text{M} \xrightarrow{hv} \text{M}(e_{\text{CB}}^- + h_{\text{VB}}^+) \] (1)

In the absence of oxygen and presence of sacrificial species such as methanol, the holes generated by the light were trapped by H₂O to yield H⁺ and ·OH radicals (Eq. (2)), and subsequently the ·OH radicals would oxidize methanol to HCHO, etc., while electrons in the conduction band of the particle would simultaneously reduce water and/or protons in the solution to form gaseous H₂ as shown by Eqs. (2)–(5) [17,18]. These reactions proceed competitively with the recombination of the photoinduced electrons and holes.

\[
h_{\text{VB}}^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ \tag{2}
\]

\[
\text{CH}_3\text{OH} + \cdot\text{OH} \rightarrow \cdot\text{CH}_2\text{OH} + \text{H}_2\text{O} \tag{3}
\]

\[
\cdot\text{CH}_2\text{OH} \rightarrow \text{HCHO} + \text{H}^+ + e_{\text{CB}}^- \tag{4}
\]

\[
2\text{H}_2\text{O} + 2e_{\text{CB}}^- \rightarrow \text{H}_2 \uparrow + 2\text{OH}^- \tag{5}
\]

On the other hand, in the presence of oxygen and a little amount of water vapor, the electrons in conduction band can be rapidly trapped by the molecular oxygen, adsorbed on catalyst particle, to form ·O₂• that can then generate highly active ·OOH radicals [17] (Eqs. (6)–(7)). The nitrogen monoxide reacts with these reactive oxygen radicals, and/or molecular oxygen, to produce the mixture of

\[
\text{CH}_3\text{OH} + \cdot\text{OH} \rightarrow \text{HCHO} + \cdot\text{OH} + \text{H}^+ 
\]

\[
2\cdot\text{OH}^- + \text{O}_2 \rightarrow \cdot\text{OOH}^- + \cdot\text{OH}^- + \text{H}^+ 
\]

On the other hand, in the presence of oxygen and a little amount of water vapor, the electrons in conduction band can be rapidly trapped by the molecular oxygen, adsorbed on catalyst particle, to form ·O₂• that can then generate highly active ·OOH radicals [17] (Eqs. (6)–(7)). The nitrogen monoxide reacts with these reactive oxygen radicals, and/or molecular oxygen, to produce the mixture of...
nitrous acid and nitric acid and, finally, nitric acid (Eq. (8)).

$$h_{VB}^+ + H_2 O \rightarrow \cdot OH + H^+$$  \hspace{1cm} (2)

$$e_{CB}^- + O_2 \rightarrow \cdot O_2^-$$  \hspace{1cm} (6)

$$\cdot O_2^- + H^+ \rightarrow \cdot OOH$$  \hspace{1cm} (7)

$$\text{NO}^+ (\cdot OH, \cdot OOH, \text{ and/or } O_2) \rightarrow HNO_2$$

$$+ HNO_3 \rightarrow HNO_3$$  \hspace{1cm} (8)

In this case, the recombination between electrons and holes is difficult comparatively because the oxygen molecules quickly consume the photoinduced electrons. The reaction between holes and nitrogen monoxide molecules becomes to be a controlling factor of the nitrogen monoxide destruction. The holes in the valence band could be used effectively for the oxidation reaction with increasing the specific surface area. This is one of the reason why HTaWO$_6$(Pt, TiO$_2$) nanocomposite (27.1 m$^2$/g) possessed higher photocatalytic oxidation activity than that of undoped HTaWO$_6$ (4.22 m$^2$/g). The platinum could promote the charge separation on titania particle surface and lead to a great increasing on the photocatalytic activity. Besides, this photoinduced electrons and holes in the interlayer space could be effectively separated by the heterogeneous electron transfer between host layer to guest semiconductor and/or metal, therefore, the recombination of the electrons and holes was suppressed [7]. This is why the HTaWO$_6$(Pt, TiO$_2$) nanocomposite possessed both higher photocatalytic oxidation and reduction activities than those of platinum doped and/or undoped titania. In addition, as mentioned above, it is thought that the visible light photocatalytic activity of HTaWO$_6$(Pt, TiO$_2$) is caused by the formation of little amount of TaWO$_5.5$. Although the precise band gap positions of HTaWO$_6$ and TaWO$_5.5$ were not understood yet. It is supposed that HTaWO$_6$ possesses similar band positions and band gap value with those of TiO$_2$, while TaWO$_5.5$ might possess more negative conduction band position and smaller band gap value compare with that of TiO$_2$. The high photocatalytic NO oxidation activity of P-25 titania powders is thought to be due to its high specific surface area and the existence of ca. 30% of rutile phase, which possesses a smaller band gap value than that of anatase phase.

4. Conclusions

In this study, the HTaWO$_6$(Pt, TiO$_2$) nanocomposite was fabricated by successive reaction of HTaWO$_6$ with Pt(NH$_3$)$_4^{2+}$, C$_3$H$_7$NH$_2$/heptane solution, TiO$_2$ acidic sol, followed by UV irradiation. The HTaWO$_6$(Pt, TiO$_2$) possessed higher photocatalytic activity than those of undoped HTaWO$_6$, commercial titania P-25, Pt-doped and undoped fibrous titania. The nanocomposite showed both excellent hydrogen evolution and nitrogen monoxide destruction activities even under visible light irradiation.

References