

Photocatalytic activity of platinum loaded fibrous titania prepared by solvothermal process

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Received 25 March 2004; accepted 31 May 2004

Available online 29 July 2004

Abstract

Fibrous titania (TiO_2/Pt) loaded with 1 wt.% Pt was prepared by the solvothermal reactions of $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ and $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$ precursors. The powders prepared by the solvothermal treatment of both precursors in methanol at 325°C possessed higher photocatalytic activity than those prepared by calcination and hydrothermal treatment. The powders prepared by the solvothermal reaction in methanol from $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursor showed higher photocatalytic activity than that from $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$. The phase transformation from protonic layered tetratitanate to titania and the reduction of platinum ion to Pt metal could proceed at the same time during the solvothermal reaction in methanol, resulting the uniform deposition of platinum fine particles on the surface of well-crystallized titania particles.

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Keywords: Platinum loaded fibrous TiO_2 ; Solvothermal reaction; Phase transformation; Hydrogen evolution; Photocatalytic activity

1. Introduction

Photoexcited semiconductor particles of titania have strong oxidation and reduction abilities and rivet researchers' much attention owing to their potential applications in photocatalysis and in environmental improvement, etc. [1–4]. It is well known that photocatalytic activity is greatly related to the crystallinity, phase composition, specific surface area, microstructure and morphology and preparation methods [5–10]. In previous papers [9,11], we reported that fibrous titania with different phase composition could be prepared by the solvothermal reactions of $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ in water, methanol and ethanol, etc. at $200\text{--}325^\circ\text{C}$ using fibrous $\text{K}_2\text{Ti}_4\text{O}_9$ precursor. One-dimensional titania is expected to possess many unique properties in preparation of thin film and composite materials. The powders prepared by the solvothermal reactions in methanol consisted of well-crystallized nanocrystals and showed excellent photocatalytic activity. In photocatalytic research, in order to elevate the charge separation on titania surface, usually a very small amount of noble metal such as platinum is required to be loaded on titania powders [12,13]. It is accepted that well-dispersed ultrafine noble particles can promote the charge separation efficiently. In the present research fibrous

TiO_2/Pt was prepared by calcination and by the solvothermal reactions of $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ and $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$ precursors in water and methanol. The photocatalytic activities of the prepared powders were characterized by the hydrogen evolution from 10% methanol solution and oxidative nitrogen monoxide destruction in gas atmosphere.

2. Experimental

Fibrous potassium tetratitanate ($\text{K}_2\text{Ti}_4\text{O}_9$, Otsuka Chemical Co. Ltd., Tokyo, Japan) was used as a starting material. After washing with hot water to remove flux, the sample was crushed to $\sim 355\ \mu\text{m}$. $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ was prepared by dispersing 12 g $\text{K}_2\text{Ti}_4\text{O}_9$ in $1200\ \text{cm}^3$ of vigorously stirred 1 M HCl at 30°C for 2 h. The solid product was separated by filtration and washed with distilled water three times followed by vacuum drying at 60°C overnight. $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursor was prepared by dispersing 10 g of $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ in 1000 ml of 0.5 mM $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ solution at room temperature followed by stirring at 600 rpm for 88 h. While $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$ precursor was obtained by UV irradiation of $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ at 25°C for 17 h.

One gram of $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ or $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$ was mixed with $75\ \text{cm}^3$ of reaction

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solution such as water and methanol. The obtained slurry was placed into a SUS 314 stainless steel autoclave of internal volume of 120 cm³ and heated at a desired temperature for 1 h to form platinum loaded fibrous titania. The product was filtered, washed with each special grade chemical solvent three times, and vacuum dried at 60 °C overnight. For comparison, the heat treatment of above precursors in air was also carried out.

The phase constitution of the products was determined by X-ray diffraction analysis (XRD, Shimadzu XD-D1) with continuous scanning mode at 2°/min using graphite-monochromatized Cu K α radiation. The amount of crystal water present in the precursor was determined by thermogravimetry and differential thermal analysis (TG, DTA, Rigaku TAS-200). The binding energy of the platinum in the sample was determined by X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA 750). The microstructure of TiO₂/Pt powders was observed by a transmission electron microscopy (TEM, JEOL, JEM-ARM1250) at 1250 kV. The photocatalytic reaction for hydrogen evolution was carried out in a Pyrex reactor of 500 cm³ capacity attached to an inner radiation type 100 W high-pressure mercury lamp. The inner cell had thermostatic water flowing through a jacket between the mercury lamp and the reaction chamber, and was constructed of Pyrex glass which served to filter out the UV emission of the mercury arc below 290 nm. The hydrogen evolution activity of the catalyst was determined by measuring the volume of H₂ evolved with a gas burette during the irradiation of the suspension of 0.25 g sample in 500 cm³ of 10:90 vol.% methanol/water mixed solution at 60 °C. Evolved H₂ gas was identified by a gas chromatography (Shimadzu, GC-8A). The photocatalytic activity for nitrogen monoxide oxidization was determined by measuring the concentration of NO gas at the outlet of the reactor [373 cm³] during the photo-irradiation of constant flowed 1 ppm NO–50 vol.% air mixed (balance N₂) gas [200 cm³ min⁻¹]. The photocatalyst sample was placed in a hollow place of 20 mm × 15 mm × 0.5 mm on a glass holder plate and set in the bottom 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, i.e., Pyrex glass for cutting off the light of wavelength <290 nm, Kenko L41 Super Pro (W) filter <400 nm [14]. The absorption edge and band gap energy of the products were determined from the onset of diffuse reflectance spectrum of the sample measured using an UV–vis spectrophotometer (Shimadzu, UV-2000). The specific surface area was determined by the amount of nitrogen adsorption at –196 °C (Quantachrome: NOVA 1000-TS).

3. Results and discussion

H₂Ti₄O₉·0.25H₂O and H_{2–2x}[Pt(NH₃)₄]_xTi₄O₉·0.25H₂O precursors were heat-treated in different media and temperatures. Fig. 1 shows the hydrogen evolution activity of

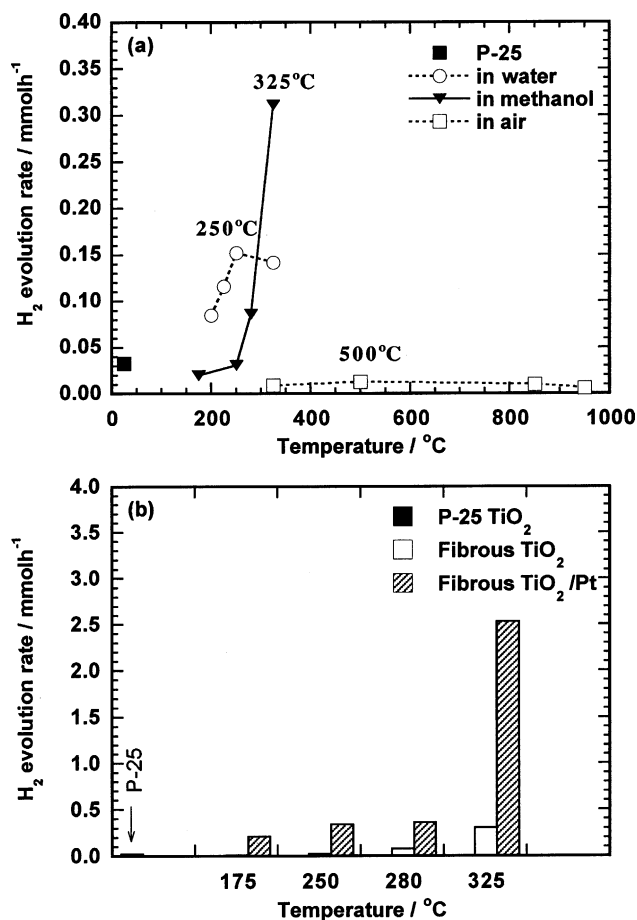


Fig. 1. Hydrogen evolution activity of (a) fibrous TiO₂ prepared by treatment of H₂Ti₄O₉·0.25H₂O in air, water and methanol at different temperatures; (b) fibrous TiO₂ and TiO₂/Pt powders prepared by treatment of H₂Ti₄O₉·0.25H₂O and H_{2–2x}[Pt(NH₃)₄]_xTi₄O₉·0.25H₂O precursor in methanol at 175–325 °C. Commercial titania powder, P-25, was also characterized.

fibrous TiO₂ prepared by treatment of H₂Ti₄O₉·0.25H₂O in different media at various temperatures, and fibrous TiO₂/Pt prepared by treatment of H_{2–2x}[Pt(NH₃)₄]_xTi₄O₉·0.25H₂O precursor in methanol. It is obvious that the photocatalytic activity of fibrous titania varied depending on the crystallisation temperature and reaction environment. The optimum treating temperatures for crystallization in air, water and methanol were 550, 250 and 325 °C, respectively. It is suggested that photocatalytic activity depended on the crystallinity, phase composition and specific surface area.

The hydrogen evolution activity of fibrous titania prepared in methanol at 325 °C increased from 0.31 to 2.54 mmol/h with loading 1 wt.% platinum, being about eight times higher than that of the powders before loading. Therefore, the charge separation on titania surface seemed to be effectively improved by loading with a small amount of platinum.

In our previous experiment [11], it was observed that powders transformed from H₂Ti₄O₉·0.25H₂O in methanol at 325 °C consisted of the mixture of monoclinic titania and anatase. Fig. 2 shows that the samples obtained by the heat

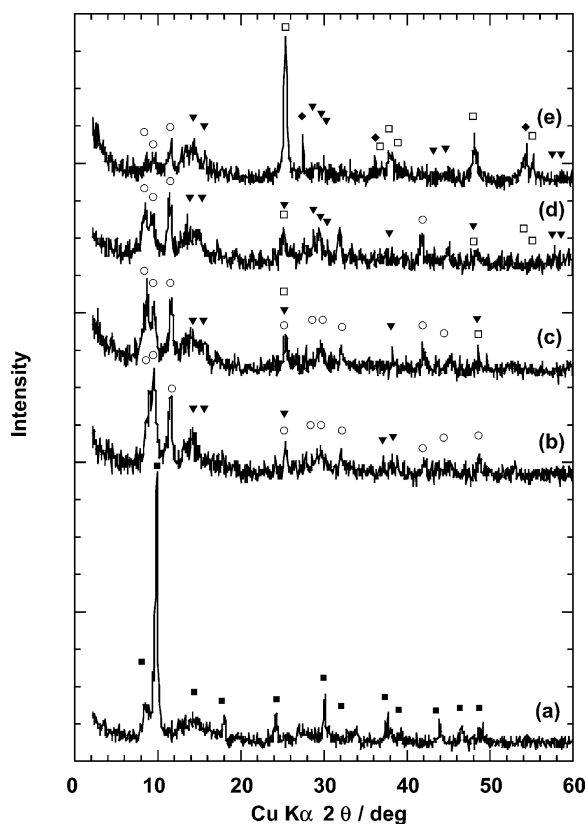


Fig. 2. XRD patterns of $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ (a) as-prepared and after heat treatment in methanol at (b) 175 °C; (c) 250 °C; (d) 280 °C; (e) 325 °C for 1 h. (◆) Rutile TiO_2 ; (□) anatase TiO_2 ; (▼) monoclinic TiO_2 ; (○) $\text{H}_2\text{Ti}_8\text{O}_{17}$; (■) $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$.

treatment of $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ in methanol consisted of the mixture of monoclinic titania and protonic octatitanate at 175–280 °C, and the peaks of anatase and rutile were also observed clearly at 325 °C. These results suggested that the phase transformation of tetratitanate was accelerated by the existence of platinum ion.

Fig. 3 shows an image of phase transformation from $\text{K}_2\text{Ti}_4\text{O}_9$ to titania. The protonic layered tetratitanate could be prepared by the ion exchange reaction of potassium tetratitanate in 1 M HCl at 30 °C for 2 h followed by vacuum drying at 60 °C for overnight. By the chemical analysis of the product it was confirmed that more than 99.9% of K^+ was exchanged with H^+ . The protonic layered tetratitanate showed similar layered structure to $\text{K}_2\text{Ti}_4\text{O}_9$. After heat treatment in air or liquid solvents, the interlayer distance of the layered structure decreased due to the dehydration. $\text{H}_2\text{Ti}_8\text{O}_{17}$ with a tunnel structure was formed at first, then it transformed to monoclinic $\text{TiO}_2(\text{B})$. At higher temperature, the monoclinic $\text{TiO}_2(\text{B})$ transformed to metastable tetragonal anatase, and finally thermodynamically stable rutile phase, which possessed a more compact texture of tetragonal. The total process could be described as

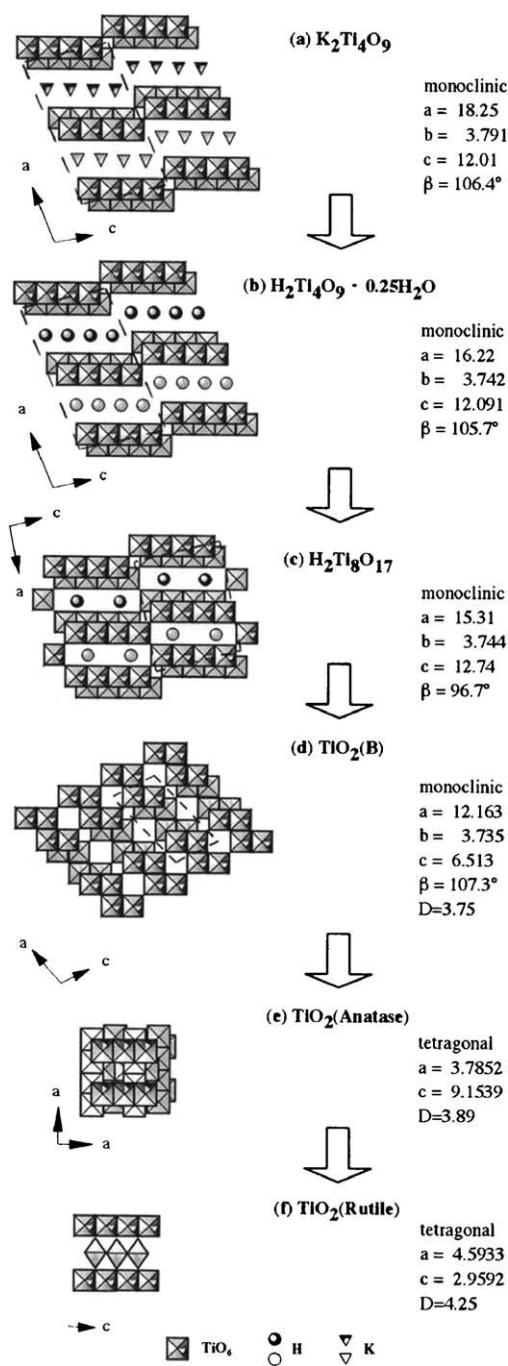
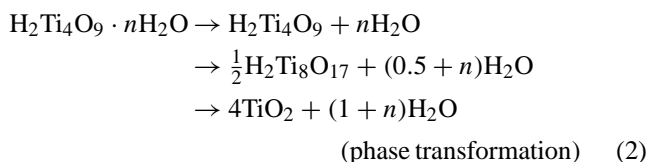


Fig. 3. An image of phase transformation from $\text{K}_2\text{Ti}_4\text{O}_9$ to TiO_2 .



Another reason why TiO_2/Pt prepared in methanol at 325 °C possesses higher photocatalytic activity is thought to be due to the valence state of platinum. Fig. 4 shows the X-ray photoelectron spectra of the powders treated in methanol

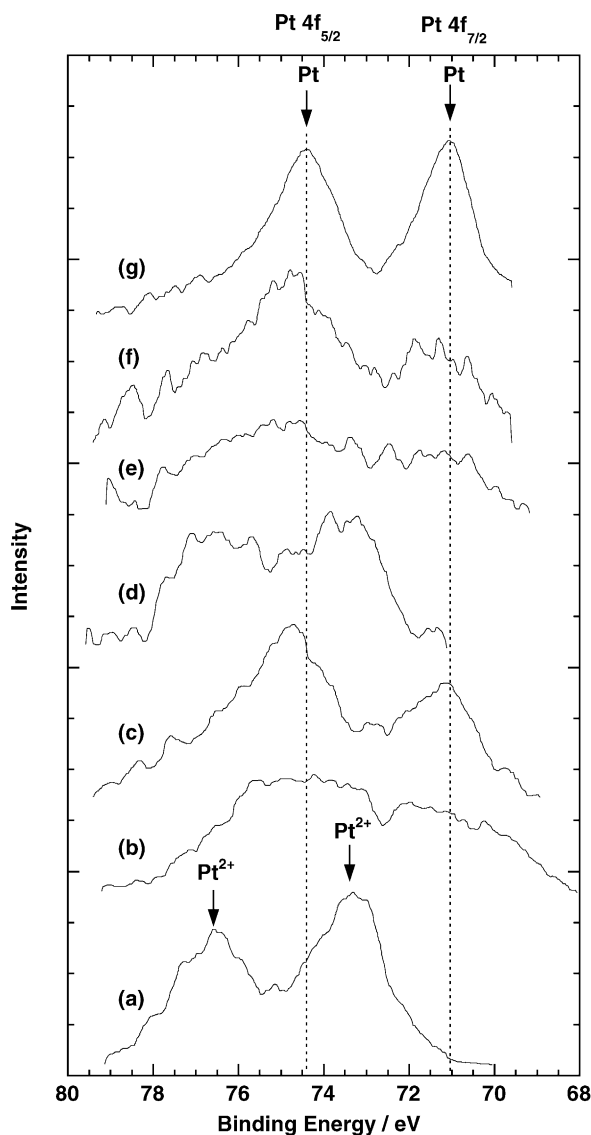


Fig. 4. X-ray photoelectron spectra of $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ (a) as-prepared and after heat treatment (b) in air at 550°C ; (c) in water at 250°C ; (d) in methanol at 175°C ; (e) 250°C ; (f) 280°C ; (g) 325°C for 1 h.

under different temperatures. The $4f_{5/2}$ and $4f_{7/2}$ binding energies of platinum in $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursor were observed at 76.5 and 73.3 eV, respectively, and shifted to 74.3 and 70.8 eV by heating in methanol due to the formation of Pt. It is seen that platinum ion contained in protonic tetratitanate was completely reduced to Pt at 325°C in methanol, but not completely below 280°C . Figs. 2 and 4 indicated that the reduction of Pt ion to Pt and the phase transformation from protonic tetratitanate to anatase titania proceeded at the same temperature.

From the result of Fig. 1, it is obvious that the optimum treating temperatures for crystallization in air, water and methanol were 550 , 250 and 325°C , respectively. Therefore, Pt loaded titania particles were prepared at these

temperatures. The hydrogen evolution activity of the powders prepared from $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ and $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$ precursors are shown in Fig. 5. The Pt loaded powders prepared by the solvothermal treatment of $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$ and $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursors in methanol at 325°C possessed higher photocatalytic activity than those by calcination and hydrothermal reaction. The powders prepared by calcination and hydrothermal reaction from $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursor showed lower photocatalytic activity than those from $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$ precursor. It was thought that platinum ion was not completely reduced to platinum metal by using $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursor under above conditions. On the other hand, the photocatalytic activity of TiO_2/Pt prepared by the solvothermal reaction in methanol from $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursor was higher than that from $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$ precursor. It was estimated to be due to the difference in the valence state of platinum.

Fig. 6 shows the TEM photographs of the powders prepared by the heat treatment of $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursor in different media. The matrix of the Pt loaded TiO_2 powders possessed similar microstructure to

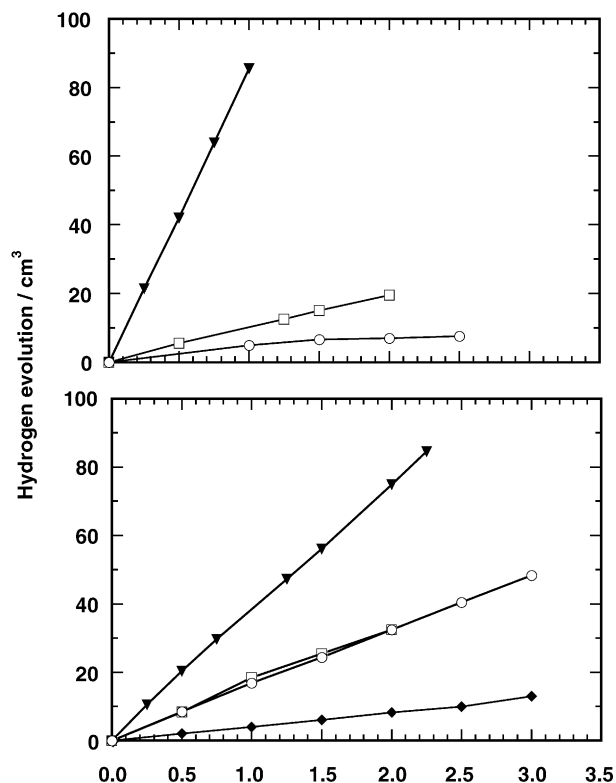


Fig. 5. Cumulative amounts of hydrogen evolution from 0.25 g of TiO_2/Pt powders dispersed in 500 cm^3 of 10 vol.% methanol solution at 60°C under 100 W high-pressure mercury-arc radiation. Powders are prepared by heat treatments in air at 500°C (\square), water at 250°C (\circ) and methanol at 325°C (\blacktriangledown) for 1 h using (a) $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ and (b) $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$ precursors; (\blacksquare) $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$ before heat treatment.

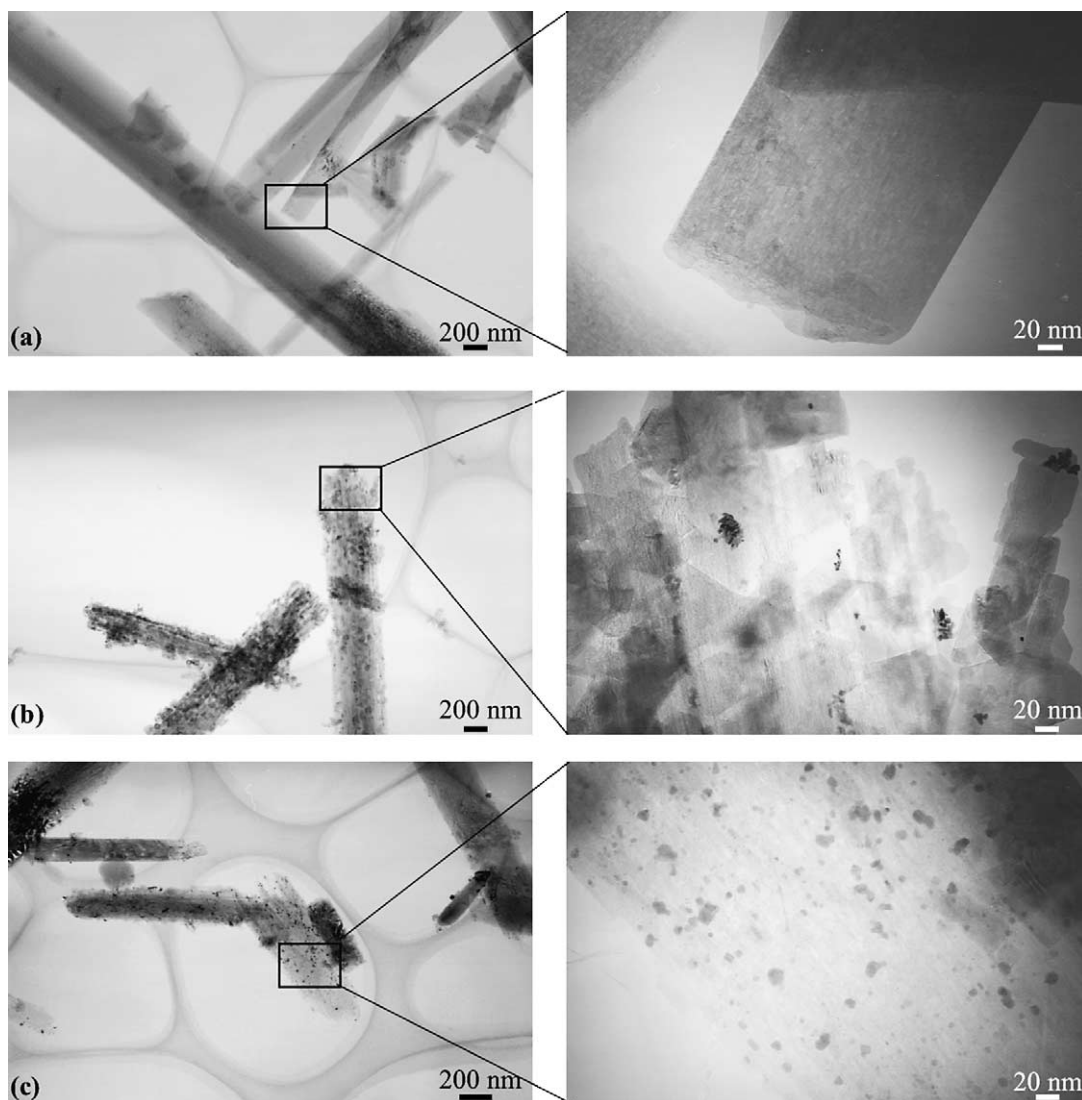


Fig. 6. TEM photographs of the powders prepared by heat treatment of $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursor in (a) air at 500°C ; (b) water at 250°C ; (c) methanol at 325°C .

unloaded ones [11]. The loading state of Pt was quite different depending on the heating environment. In Fig. 6(a), it was difficult to observe platinum particles on titania matrix when $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursor was heated in air at 550°C . Meanwhile, softly agglomerated Pt particles were observed on the surface of titania matrix after heat treatment in water at 250°C (Fig. 6(b)). In the case of heat treatment of precursor in methanol at 325°C , relatively well-dispersed nanoparticles of Pt (<5 nm in diameter) were observed on the surface of well-crystallized fine titania particles (Fig. 6(c)). Considering the result of Fig. 5, it might be suggested that the photocatalytic activity of titania powders increased greatly by loading with a small amount of well-dispersed ultrafine platinum.

The difference in the photocatalytic activity might be also explained by the difference in valence state of the platinum loaded on the surface of fibrous titania. Small XPS peaks

corresponded to platinum ion were observed in Fig. 4(b) and (c), indicating that the platinum ion contained in protonic tetratitanate could not be reduced to platinum metal effectively by heat treatment in air at 550°C and in water at 250°C . On the other hand, Fig. 4(g) showed that the Pt ion was completely reduced to Pt metal in methanol at 325°C , suggesting that ultrafine platinum particles were uniformly loaded on the surface of well-crystallized fine titania particles under the solvothermal conditions in methanol. The XPS peaks corresponded to Pt metal were also observed before and after heat treatment of $\text{H}_2\text{Ti}_4\text{O}_9/\text{Pt}$ precursor in methanol. This result indicated that the powder prepared from $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]_x\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursor resulted better dispersion state than that from $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}/\text{Pt}$ precursors.

Table 1 summarized the physico-chemical properties of fibrous TiO_2 and TiO_2/Pt prepared from $\text{H}_{2-2x}[\text{Pt}(\text{NH}_3)_4]$

Table 1

Physico-chemical properties and photocatalytic activities of fibrous TiO₂ and TiO₂/Pt powders prepared from H_{2-2x}[Pt(NH₃)₄]_xTi₄O₉·0.25H₂O precursor

Preparation conditions	Phase composition ^a	SSA (m ² g ⁻¹)	Band gap (eV)	H ₂ evolution ability (mmol h ⁻¹)	NO destruction ability (%)	
					>400 nm	>290 nm
As-received P-25 commercial sample	A + (R)	47.3	3.04	0.032	37.0	51.2
Fibrous TiO ₂ treated in methanol at 325 °C	M + (A)	22.1	3.31	0.311	5.2	30.1
Fibrous TiO ₂ /Pt treated in methanol at 325 °C	A + (M + H8 + R)	24.0	3.31	2.540	9.0	46.0

^a A: anatase TiO₂; M: monoclinic TiO₂; R: rutile TiO₂; H8: H₂Ti₈O₁₇; the phase described first is the major product and that in parenthesis is the minor product.

_xTi₄O₉·0.25H₂O precursor. The fibrous TiO₂ prepared by the solvothermal treatment in methanol at 325 °C possessed a mixture of monoclinic and anatase, while fibrous TiO₂/Pt prepared by the solvothermal treatment under the same conditions consisted of mainly anatase phase mixed with small amounts of monoclinic, H₂Ti₈O₁₇ and rutile. Although the fibrous TiO₂ and TiO₂/Pt possessed very high hydrogen evolution ability, they showed modest nitrogen monoxide destruction ability compared with that of commercial titania powder, P-25. This might be due to the low specific surface areas of the fibrous TiO₂ and TiO₂/Pt since P-25 had a much higher specific surface area of 47.3 m² g⁻¹. This result also agreed with that of our previous result [9], i.e., the photocatalytic reduction activity strongly related to the crystallinity, but the oxidation activity related to both crystallinity and specific surface area.

4. Conclusions

Based on the present results, the following conclusions may be drawn.

1. The hydrogen evolution activity of fibrous TiO₂ was greatly increased by loading with a small amount of platinum.
2. Fibrous TiO₂/Pt prepared by solvothermal reactions in methanol at 325 °C consisted of the mixture of protonic octatitanate, monoclinic titania, anatase and rutile.
3. The powders of TiO₂/Pt prepared by the solvothermal treatment of H_{2-2x}[Pt(NH₃)₄]_xTi₄O₉·0.25H₂O in methanol at 325 °C possessed higher hydrogen evolution photocatalytic activity than those prepared by calcination and hydrothermal treatment.
4. The reduction of platinum ion to Pt metal was not completely proceeded by calcination in air or by hydrothermal treatment.

5. The phase transformation from protonic layered tetratitanate to titania and the reduction of platinum ion to Pt metal could proceed at the same time by the solvothermal reaction in methanol to precipitate ultrafine platinum particles uniformly on the surface of well-crystallized fine titania particles.

Acknowledgements

This research was partially supported by the Ministry of Education, Culture, Sports, Science and Technology, a Grant-in-Aid for the COE project (Giant Molecules and Complex Systems), and a Grant-in-Aid for Science Research (No. 14750660).

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