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Synthesis and photocatalytic properties of titania pillared $H_4Nb_6O_{17}$ using titanyl acylate precursor

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Titania pillared $H_4Nb_6O_{17}$ has been synthesised by the intercalation of $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$ followed by photodecomposition with UV light irradiation. The incorporation of TiO_2 in the interlayer of $H_4Nb_6O_{17}$ has been confirmed by powder X-ray diffraction, DTA, UV-VIS reflectance and BET measurements. The incorporation of TiO_2 in the interlayer of $H_4Nb_6O_{17}$ results in enhanced water cleavage by band gap irradiation. The photocatalytic activity of TiO_2 pillared $H_4Nb_6O_{17}$ prepared using $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$ was higher than that of a sample prepared using a TiO_2 sol solution.

Introduction

The pillaring of layered compounds by inorganic compounds is a promising method for fabricating unique porous materials that possess some of the properties of zeolites. Semiconductor pillars have attracted special attention from researchers because of their excellent photocatalytic activity. The photocatalytic activity of semiconductor pillars such as CdS–ZnS, Fe_2O_3 and TiO_2 was much higher than those of unsupported catalysts.[1–7] In the previous studies,[5,7] we found that the photoactivities of semiconductor pillars were dependent on the physico-chemical properties of the host layer (*e.g.* CdS–ZnS pillars which are constructed in the interlayer of semiconductors, such as $H_4Nb_6O_{17}$ and $H_2Ti_4O_9$) showed much higher photoactivities than those of insulators (such as montmorillonite and layered double hydroxide), since electron and hole recombination was effectively depressed due to charge transfer from the guest semiconductor to the host semiconductor layer.

In general, semiconductor pillars are constructed by the intercalation of soluble inorganic ion precursors, followed by the precipitation of the intercalated ions by chemical, thermal, and/or photochemical reactions. TiO_2 pillars, however, have been made using TiO_2 sol solutions because of the lack of water soluble titanium complex ions.[8] By using TiO_2 sols, TiO_2 pillars were successfully constructed in clay minerals which swell in water[8] such as smectite. However, it is not easy to construct TiO_2 pillars in semiconductor layer compounds such as $H_4Nb_6O_{17}$ and $H_2Ti_4O_9$, since they do not easily swell in water. A recent study found that a water soluble ionic molecular precursor [the titanyl acylate complex, $Ti(OH)_x(CH_3CO_2)_y{}^{z+}$] can be obtained by the reaction of titanium isopropoxide, glacial acetic acid and water,[9] and was used as a source of TiO_2 in the preparation of a strontium titanate ceramic.[10] In the continuation of our studies on the photocleavage of water, a series of tests were performed to evaluate the synthesis of titania pillared $H_4Nb_6O_{17}$ by using titanyl acylate precursors.

Experimental

Synthesis of titania pillared $H_4Nb_6O_{17}$ using a titanyl acylate complex

$H_4Nb_6O_{17}$ was prepared by the ion-exchange reaction of $K_4Nb_6O_{17}$ in 5 M HCl at 60 °C for 5 h, $K_4Nb_6O_{17}$ being prepared by the calcination of K_2CO_3 and Nb_2O_3 in 2:3 molar ratio at 1200 °C for 20 min. $H_4Nb_6O_{17}/TiO_2$ was prepared by stepwise incorporation of TiO_2 as follows. $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$ was prepared by modifying Kao and Yang's method[10] starting with titanium isopropoxide, acetic acid and water in a 1:16:20 volume ratio. In a typical experiment, acetic acid (400 cm^3) was mixed first with titanium isopropoxide (25 cm^3) for 30 min, followed by the addition of water (500 cm^3), resulting in the formation of a white precipitate, which was dissolved to give a clear solution upon continuous stirring for 5 h at room temperature. $H_4Nb_6O_{17}$ (5 g) was converted to $(C_3H_7NH_3)_4Nb_6O_{17}$ by stirring in a 50 vol.% $C_3H_7NH_2$ aqueous solution (1 dm^3) at 60 °C for 3 days. After separation by filtration, $(C_3H_7NH_3)_4Nb_6O_{17}$ (1 g) was added to a clear aqueous solution of $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$ and allowed to stand for 120 h at room temperature to allow intercalation of $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$. The obtained sample, $[Ti(OH)_x(CH_3CO_2)_y]_{z/4}Nb_6O_{17}$ after being filtered off and washed with water, was dispersed in water, and irradiated with UV light from a 450 W high pressure mercury lamp at room temperature for 12 h in order to decompose $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$ in the interlayer. The resulting material is designated $H_4Nb_6O_{17}/TiO_2$(c).

Synthesis of titania pillared $H_4Nb_6O_{17}$ using a titania sol solution

A titania pillar was constructed in the interlayer of $H_4Nb_6O_{17}$ using titania sol, as reported previously.[7] Titanium tetraisopropoxide (25 cm^3) was added dropwise to vigorously stirred 1 M HCl (250 cm^3) so as to give a final molar ratio of alkoxide to HCl of 0.25. The resulting slurry was peptized by further stirring for 3 h so as to give a clear TiO_2 sol solution. Then $(C_3H_7NH_3)_4Nb_6O_{17}$ (1 g) was added to the TiO_2 sol solution, and the suspension was continuously stirred for the desired time at room temperature in order to incorporate TiO_2. After being filtered off and washed with water, the specimen was dispersed in water and irradiated with UV light from a 450 W high pressure mercury lamp at 60 °C for 12 h in order to decompose the $C_3H_7NH_3{}^+$ remaining in the interlayer. The sample thus obtained is designated as $H_4Nb_6O_{17}/TiO_2$(s).

Analysis

The crystalline phases of the products were identified by X-ray diffraction analysis (Rigaku Denki Geiger-flex 2013) using graphite-monochromatized Cu-Kα radiation. The chemical compositions of the products were determined by inductively coupled plasma–atomic emission spectroscopy (Seiko SPS-1200A) after alkali fusion with Na_2CO_3 followed by dissolving the samples in 6 M HCl-15 wt.% H_2O_2. The band gap energies of the products were determined from the onset of the diffuse reflectance spectra of the powders measured using a Shimadzu Model UV-2000 UV–VIS spectrophotometer. The specific surface area was determined by the nitrogen gas adsorption method (Shibata SA-1000).

Photocatalytic reactions

Photocatalytic reactions were performed in a Pyrex reactor with a capacity of 1250 cm^3 which was attached to an inner radiation type 450 W high-pressure mercury lamp. The inner cell had thermostated water flowing through a jacket between the mercury lamp and the reaction chamber, and was constructed of quartz glass. The photoactivity of the catalyst was determined by measuring the total gas volume of hydrogen and oxygen evolved during the irradiation of the catalyst suspensions in water with a gas burette after confirming the production of both hydrogen and oxygen by gas chromatography (Yanagimoto G2800) using a Molecular Sieve 13X (30–60 mesh) column.

Results and discussion

Synthesis of $H_4Nb_6O_{17}/TiO_2$

DTA curves of (A) $[Ti(OH)_x(CH_3CO_2)_y]_{z/4}Nb_6O_{17}$ and (B) $H_4Nb_6O_{17}/TiO_2(c)$ (measured in air) are shown in Fig. 1. A sharp exothermic peak at 291 °C (which corresponds to the combustion of the titanyl acylate complex) was observed for $[Ti(OH)_x(CH_3CO_2)_y]_{z/4}Nb_6O_{17}$, but was absent in $H_4Nb_6O_{17}/TiO_2(c)$, indicating that it was photochemically decomposed by UV-light irradiation.

Fig. 2 depicts the powder X-ray diffraction patterns of (A) $H_4Nb_6O_{17}$, (B) $[Ti(OH)_x(CH_3CO_2)_y]_{z/4}Nb_6O_{17}$ and (C) $H_4Nb_6O_{17}/TiO_2$. The main peaks (which correspond to (040) of $H_4Nb_6O_{17}$ of samples (B) and (C)) shifted significantly to lower 2θ angles as compared to sample (A), indicating the expansion of the interlayer by the incorporation of $Ti(OH)_x(CH_3CO_2)_y{}^{z+}$ and TiO_2. These results indicate that the layer structure was still retained after the intercalation of $Ti(OH)_x(CH_3CO_2)_y{}^{z+}$ and after photochemical decomposition of $Ti(OH)_x(CH_3CO_2)_y{}^{z+}$ to TiO_2 in the interlayer. The gallery heights of $H_4Nb_6O_{17}$, $[Ti(OH)_x(CH_3CO_2)_y]_{z/4}Nb_6O_{17}$ and $H_4Nb_6O_{17}/TiO_2(c)$ (determined by XRD by subtracting the $Nb_6O_{17}{}^{4-}$ layer thicknesses of 0.56 nm) were 0.40, 0.62 and 0.52 nm, respectively.

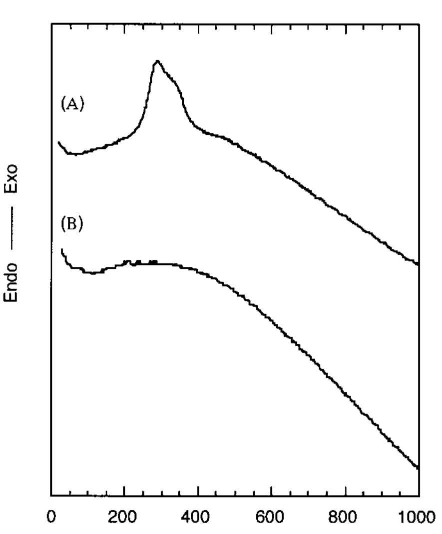

Fig. 1 DTA patterns of $[Ti(OH)_x(CH_3CO_2)_y]_{z/4}Nb_6O_{17}$ before (A) and after (B) UV irradiation, where $[Ti(OH)_x(CH_3CO_2)_y]_{z/4}Nb_6O_{17}$ was prepared by the reaction of $(C_3H_7NH_3)_4Nb_6O_{17}$ and the titanyl acylate complex for 120 h at room temperature.

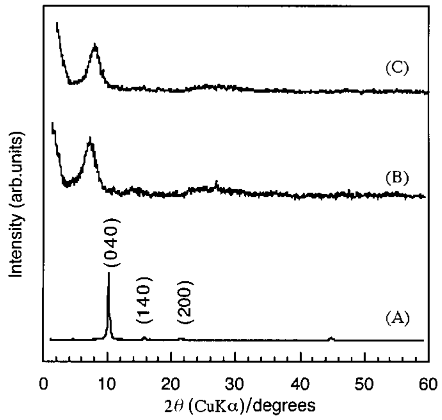

Fig. 2 XRD patterns of (A) $H_4Nb_6O_{17}$, (B) $[Ti(OH)_x(CH_3CO_2)_y]_{z/4}Nb_6O_{17}$ prepared by the reaction of $(C_3H_7NH_3)_4Nb_6O_{17}$ and the titanyl acylate complex for 120 h at room temperature and (C) $H_4Nb_6O_{17}/TiO_2(c)$ prepared by photodecomposition of (B).

UV–VIS reflection spectra of (A) $H_4Nb_6O_{17}$, (B) $H_4Nb_6O_{17}/TiO_2(c)$ and (C) unsupported TiO_2 are shown in Fig. 3. From the onset of the spectra, the band gap energies of TiO_2 gel, $H_4Nb_6O_{17}/TiO_2(c)$ and $H_4Nb_6O_{17}$ were determined as 3.0, 3.26 and 3.34 eV, respectively. Although the spectrum showed a red shift upon the incorporation of TiO_2, the band gap energy of the TiO_2 pillar could not be determined by UV–VIS reflection spectra since $H_4Nb_6O_{17}/TiO_2(c)$ did not show separate onsets corresponding to $H_4Nb_6O_{17}$ and incorporated TiO_2.

The time dependence of the amount of TiO_2 incorporated using both (A) titanyl acylate complex and (B) TiO_2 sol solution is shown in Fig. 4. The amount of TiO_2 pillar increased rapidly with time up to 50 h, then increased more gradually and was almost constant after 120 h. The amount of TiO_2 incorporated using the TiO_2 sol was slightly larger than that using the titanyl acylate complex after 120 h.

As seen in Fig. 2, $H_4Nb_6O_{17}/TiO_2(c)$ (prepared using the titanyl acylate precursor for 120 h) showed XRD diffraction peaks corresponding only to $H_4Nb_6O_{17}$, indicating that TiO_2 was incorporated in the interlayer. On the other hand, diffraction peaks corresponding not only to $H_4Nb_6O_{17}$ but also to rutile were observed for $H_4Nb_6O_{17}/TiO_2$ (s) as shown in Fig. 5: the diffraction peaks corresponding to rutile were not observed up to 6 h, but became noticeable after 24 h and increased with time. In general, TiO_2 sols transform into rutile *via* anatase above 500 °C. The unusual formation of rutile at such a low temperature as 60 °C indicates that the $H_4Nb_6O_{17}$ acts as nuclei to form rutile. Therefore, it appears that, when a TiO_2 sol is used as a precursor, TiO_2 is incorporated mainly in the

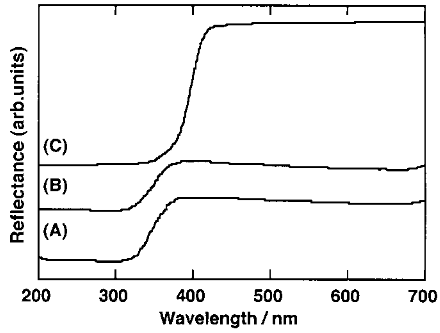

Fig. 3 Diffuse reflectance spectra of (A) $H_4Nb_6O_{17}$, (B) $H_4Nb_6O_{17}/TiO_2(c)$ and (C) unsupported TiO_2 sol.

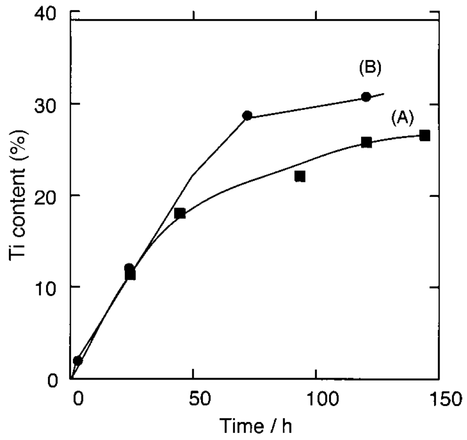

Fig. 4 Time dependence of the amounts of TiO_2 incorporated using (A) the titanyl acylate complex (■) and (B) a TiO_2 sol (●).

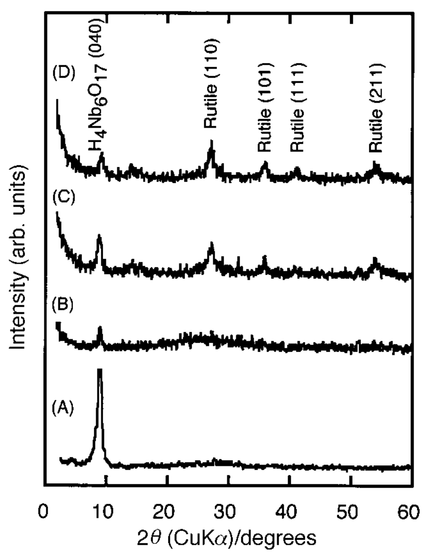

Fig. 5 XRD diffraction patterns of $H_4Nb_6O_{17}/TiO_2(s)$ prepared by reacting $(C_3H_7NH_3)_4Nb_6O_{17}$ and TiO_2 sol solutions for (A) 6, (B) 24, (C) 71 and (D) 120 h.

interlayer of $H_4Nb_6O_{17}$ in the initial stage, but a significant amount of TiO_2 is precipitated on the outerlayer after 24 h. Consequently, the amount of TiO_2 pillars constructed in the interlayer can be increased using the titanyl acylate complex as precursor.

The gallery height, the amounts of TiO_2 incorporated, and the specific surface area of $H_4Nb_6O_{17}$, $H_4Nb_6O_{17}/TiO_2(c)$ and $H_4Nb_6O_{17}/TiO_2(s)$ are listed in Table 1, where $H_4Nb_6O_{17}/TiO_2(c)$ and $H_4Nb_6O_{17}/TiO_2(s)$ were prepared using the titanyl acylate complex and TiO_2 sol solution for 120 and 6 h, respectively. The amounts of TiO_2 incorporated in $H_4Nb_6O_{17}/TiO_2(c)$ and $H_4Nb_6O_{17}/TiO_2(s)$ were 26.7 and 7.3 wt.%, respectively. The specific surface area increased greatly with increase in the amount of TiO_2, indicating the construction of titania pillars. $H_4Nb_6O_{17}/TiO_2(c)$ and $H_4Nb_6O_{17}/TiO_2(s)$ possessed gallery heights of 0.52 and 0.48 nm, indicating that the gallery height of the titania pillared $H_4Nb_6O_{17}$ increased slightly when the titania pillar was prepared using the titanyl acylate precursor.

Table 1 Amounts of TiO_2 incorporated, gallery heights and specific surface areas of the samples

Sample	Gallery height/ nm	TiO_2 content (wt.%)	Specific surface area/m^2 g^{-1}
$H_4Nb_6O_{17}$	0.40	0	16.1
$H_4Nb_6O_{17}/TiO_2$ (c)	0.52	26.7	125.6
$H_4Nb_6O_{17}/TiO_2(s)$	0.48	7.3	38.6

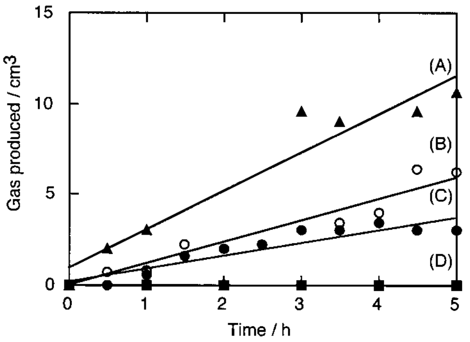

Fig. 6 Cumulative amounts of hydrogen and oxygen gas produced from 1250 cm^3 of water containing 1 g of dispersed catalysts at 60 °C exposed to irradiation from a 450 W mercury arc. (A) $H_4Nb_6O_{17}/TiO_2(c)$, (B) $H_4Nb_6O_{17}/TiO_2(s)$ intercalated for 6 h, (C) $H_4Nb_6O_{17}/TiO_2(s)$ intercalated for 144 h and (D) mixture of $H_4Nb_6O_{17}$ and TiO_2 sol.

Photocatalytic water cleavage

The amounts of gas produced from 1250 cm^3 of water containing 1 g of dispersed $H_4Nb_6O_{17}/TiO_2(c)$, $H_4Nb_6O_{17}/TiO_2(6s)$, $H_4Nb_6O_{17}/TiO_2(144s)$ and a mixture of 75 wt.% $H_4Nb_6O_{17}$ and 25 wt.% TiO_2 sol at 60 °C exposed to irradiation from a 450 W mercury arc were measured, where $H_4Nb_6O_{17}/TiO_2(6s)$ and $H_4Nb_6O_{17}/TiO_2(144s)$ were prepared using TiO_2 sol for 6 and 144 h, respectively. Significant gas evolution was observed in the presence of $H_4Nb_6O_{17}/TiO_2(c)$, $H_4Nb_6O_{17}/TiO_2(6s)$ and $H_4Nb_6O_{17}/TiO_2(144s)$, but no noticeable gas was evolved for a mixture of $H_4Nb_6O_{17}$ and TiO_2 sol. Therefore, the titanium oxide pillar which was incorporated in the interlayer plays an important part in photocatalytic water cleavage, whereas TiO_2 at the outerlayer does not possess photocatalytic activity for water cleavage. Previously[7] we found that the charge injection from an excited TiO_2 pillar into the conduction band of $H_4Nb_6O_{17}$ occurs at a rate of 0.12×10^9 s^{-1}; therefore, photogenerated electrons can quickly be transferred from a TiO_2 pillar into a $H_4Nb_6O_{17}$ layer while the holes remain in the TiO_2 pillar. Consequently, the recombination between the photoinduced charge carriers was effectively depressed and the photocatalytic water cleavage was enhanced. Taking into acount a saturated water vapour pressure of 20.0 kPa at 60 °C and the molar ratio of hydrogen : oxygen evolved as 2 : 1, from the slope of the straight lines in Fig. 6 the rates of hydrogen evolution in the presence of $H_4Nb_6O_{17}/TiO_2(c)$, $H_4Nb_6O_{17}/TiO_2(6s)$ and $H_4Nb_6O_{17}/TiO_2(144s)$ were determined as 0.0417, 0.0241 and 0.0142 mmol h^{-1}, *i.e.*, the photocatalytic activity of $H_4Nb_6O_{17}/TiO_2(c)$ was 1.7 times larger than that of $H_4Nb_6O_{17}/TiO_2(6s)$. This may be due to an increase in the amount of TiO_2 pillars. On the other hand, the photoactivity of $H_4Nb_6O_{17}/TiO_2(144s)$ was about half that of $H_4Nb_6O_{17}/TiO_2(6s)$, although the TiO_2 content was 3.7 times larger. This may be attributed to the precipitation of TiO_2 on the outerlayer, because such TiO_2 does not possess photocatalytic activity for water cleavage and may cut off the light required to excite TiO_2 pillars in the interlayer.

Conclusion

The conclusions from this study are: (i) titania pillared $H_4Nb_6O_{17}$ is first fabricated by the reactions of $H_4Nb_6O_{17}$ with a titanyl acylate complex followed by UV light irradiation. (ii) The amount of the titania pillar and the photocatalytic activity of $H_4Nb_6O_{17}/TiO_2$ prepared using the titanyl acylate precursor were larger than those fabricated using a TiO_2 sol solution.

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