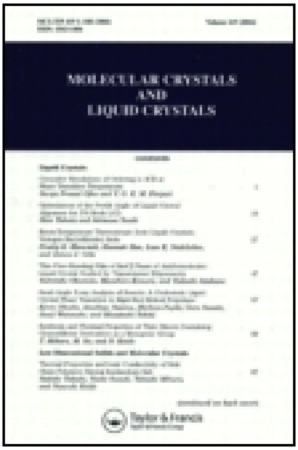

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Synthesis and Photocatalytic Properties of TiO_2 Intercalated $H_4Nb_6O_{17}$

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Synthesis and Photocatalytic Properties of TiO_2 Intercalated $H_4Nb_6O_{17}$

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TiO_2 intercalated $H_4Nb_6O_{17}$ has been synthesized by the reactions of $H_4Nb_6O_{17}$ with a titanyl acylate complex followed by UV irradiation. The gallery height, specific surface area and Ti content of the sample synthesized by using titanyl acylate complex were larger than that using TiO_2 sol solution. Furthermore, the photocatalytic activity of the TiO_2 pillared $H_4Nb_6O_{17}$ prepared using a titanyl acylate precursor was twice larger than that fabricated using a TiO_2 sol solution.

Keywords: TiO_2 pillar; $H_4Nb_6O_{17}$; titanyl acylate complex; photocatalytic activity

INTRODUCTION

The intercalation of layered compounds is a unique method for fabricating new functional materials. Numerous attempts have been made to take other element such as semiconductor pillars into layered materials because of their excellent photocatalytic activity[1-6]. In the previous studies, we found that the photocatalytic activities of semiconductor pillars were dependent on the physicochemical properties of the host layer due to charge transfer from the guest semiconductor to the host semiconductor layer[7].

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 cations[8]. 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 titanium complex, (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[9-10]. In this paper, the preparation and photocatalytic activity of TiO_2 pillared $H_4Nb_6O_{17}$ using the titanyl acylate precursor were investigated.

EXPERIMENTAL

Synthesis of TiO_2 pillared $H_4Nb_6O_{17}$

$H_4Nb_6O_{17}$ was prepared as reported previously[6]. $H_4Nb_6O_{17}/TiO_2$ 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, glacial acetic acid and water in a 1:16:20 volume ratio. $H_4Nb_6O_{17}$ was converted to $(C_3H_7NH_3)_4Nb_6O_{17}$ by stirring in a 50 vol. % $C_3H_7NH_2$ aqueous solution at 323 K. After separation by filtration, $(C_3H_7NH_3)_4Nb_6O_{17}$ was added to a clear solution of $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$ and stirred at room temperature for 120 h 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 as $H_4Nb_6O_{17}/TiO_2(c)$.

A TiO_2 pillar was also constructed in the interlayer of $H_4Nb_6O_{17}$ using TiO_2 sol for 6 h at room temperature, as reported previously[6]. 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(Shimadzu KD-D1). The chemical compositions of the products were determined by inductively coupled plasma-atomic emission spectroscopy (SEIKO SPS-1200A). The band gap energies of the products were measured using a Shimadzu Model UV-2000 UV-Vis spectrophotometer. The specific surface area was determined by the BET method.

Photocatalytic activity

Photocatalytic reactions were performed in a Pyrex reactor with a capacity of 1250 ml 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 reaction chamber. The photocatalytic activity of the samples was determined by measuring the gas volume of H_2 and O_2 evolved during the irradiation of the photocatalyst suspensions in water with a gas burette after confirming the production of H_2 and O_2 by gas chromatography(Yanagimoto G2800) using a Molecular Sieve 13X(30-60mesh) column.

RESULTS AND DISCUSSION

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 Figure 1. A sharp peak at 291 ℃ (which corresponds to the combustion of the $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$) observed for $[Ti(OH)_x(CH_3CO_2)_y]_{z/4}Nb_6O_{17}$, disappeared in $H_4Nb_6O_{17}/TiO_2$(c), indicating that it was photochemically decomposed by UV light irradiation.

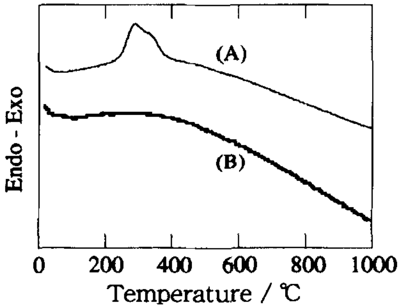

FIGURE 1 DTA curves of (A) $[Ti(OH)_x(CH_3CO_2)_y]_{z/4}Nb_6O_{17}$ and (B) $H_4Nb_6O_{17}/TiO_2$(c).

Figure 2 depicts the XRD patterns of (A) $H_4Nb_6O_{17}$, (B) $(C_3H_7NH_3)_4Nb_6O_{17}$ and (C) $H_4Nb_6O_{17}/TiO_2$(c). The main peaks which correspond to (040) peak of the samples shifted to lower angles as compared to $H_4Nb_6O_{17}$, 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 maintained after the intercalation of $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$ and after UV light irradiation.

Time dependence of the amount of TiO_2 incorporated using both (A) $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$ and (B) TiO_2 sol solution is shown in Figure 3. The amount of TiO_2 increased rapidly with time up to 50 h, then increased more

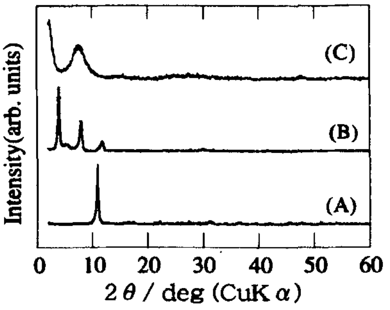

FIGURE 2 XRD patterns of (A) $H_4Nb_6O_{17}$, (B) $(C_3H_7NH_3)_4Nb_6O_{17}$ and (C) $H_4Nb_6O_{17}/TiO_2$(c).

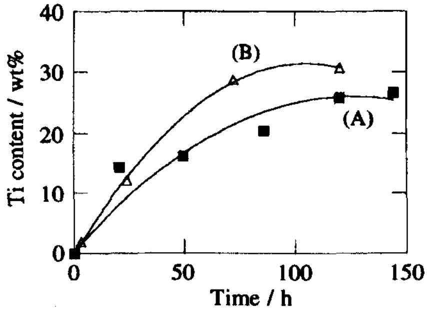

FIGURE 3 Time courses of TiO_2 content using by (A) $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$ and (B) TiO_2 sol solution.

gradually and was almost constant after 120 h. The amount of TiO_2 incorporated using the TiO_2 sol is larger than that using $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$.

As seen in Figure 4, the diffraction of TiO_2 was not observed until 6 h, but became noticeable after 24 h and increased with time. Therefore, it is suspected that when a TiO_2 sol is used, TiO_2 is incorporated in the interlayer until 6 h, but thereafter significant amount of TiO_2 is precipitated on the outerlayer.

The gallery heights, BET surface areas and band gap energies of the samples are listed in Table 1. The gallery height and BET surface area of the $H_4Nb_6O_{17}/TiO_2$(c) were greater than those of $H_4Nb_6O_{17}$ and $H_4Nb_6O_{17}/TiO_2$(s). Consequently, TiO_2 pillars are selectively constructed in the interlayer using $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$. Although the spectrum showed the shift upon the incorporation of TiO_2, the band gap energy of the TiO_2 pillar could not be determined by UV-Vis diffuse reflectance spectra since $H_4Nb_6O_{17}/TiO_2$ did not

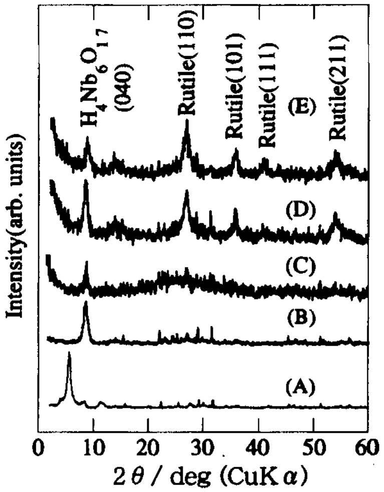

FIGURE 4 XRD patterns of $H_4Nb_6O_{17}/TiO_2$(s) prepared by reacting with $(C_3H_7NH_3)_4Nb_6O_{17}$ and TiO_2 sol solution for (A) 0, (B) 6, (C) 24, (D) 71 and (E) 120 h.

TABLE 1 Gallery heights, specific surface areas and band gap energies of the samples.

Product	Gallery height (nm)	Specific surface area ($m^2\ g^{-1}$)	Band gap energy (eV)
$H_4Nb_6O_{17}$	0.51	3.4	3.4
$H_4Nb_6O_{17}/TiO_2$(s)	0.58	19.4	3.1
$H_4Nb_6O_{17}/TiO_2$(c)	0.61	126.1	3.2

show separate onsets corresponding to $H_4Nb_6O_{17}$ and incorporated TiO_2.

The total gas evolution rates from 1250 cm^3 of water containing 0.5 g of dispersed $H_4Nb_6O_{17}/TiO_2$(c), $H_4Nb_6O_{17}/TiO_2$(s), $H_4Nb_6O_{17}/TiO_2$(s)* and a mixture of 75 wt% $H_4Nb_6O_{17}$ and 25 wt% TiO_2 at 333 K exposed to irradiation from a 450 W high pressure mercury lamp are shown in Figure 5, where $H_4Nb_6O_{17}/TiO_2$(s)* was prepared with TiO_2 sol solution for 120 h. Significant gas evolution was observed in the presence of $H_4Nb_6O_{17}/TiO_2$(c), $H_4Nb_6O_{17}/TiO_2$(s) and $H_4Nb_6O_{17}/TiO_2$(s)*, but no gas evolution was observed in the presence of 75 wt% $H_4Nb_6O_{17}$ and 25 wt% TiO_2 mixture, indicating that TiO_2 at the outerlayer does not possess photocatalytic activity for water cleavage. Previously, we found the charge injection from excited TiO_2 pillars to the conduction band of $H_4Nb_6O_{17}$ occurs quickly at a rate of subnano second order while hole remain in the TiO_2 pillar[7]. Consequently, the recombination between the photoinduced charge carriers was effectively depressed and the photocatalytic water cleavage was enhanced. From Figure 5, the photocatalytic activity of $H_4Nb_6O_{17}/TiO_2(c)$ is about twice larger than those of $H_4Nb_6O_{17}/TiO_2(s)$ and $H_4Nb_6O_{17}/TiO_2(s)^*$. The decrease in photocatalytic activity in $H_4Nb_6O_{17}/TiO_2(s)$ and $H_4Nb_6O_{17}/TiO_2(s)^*$ 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.

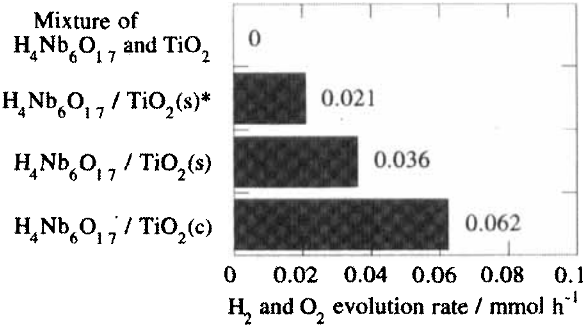

FIGURE 5 Comparison of H_2 and O_2 evolution rate from 1250 cm^3 of water containing 0.5 g of dispersed photocatalyst at 333 K exposed to irradiation from a 450 W high pressure mercury lamp. $H_4Nb_6O_{17}/TiO_2(s)^*$ was prepared with TiO_2 sol solution for 120 h.

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