



Preparation of high performance fibrous titania photocatalysts by the solvothermal reaction of protonated form of tetratitanate

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ABSTRACT

The phase transformation behaviors of fibrous protonated form of tetratitanate under solvothermal conditions in water, methanol and ethanol were focused on to form high performance titania photocatalyst. Regardless of the reaction solvents, the products showed similar fibrous morphology to the raw material. However, the crystalline phase of the product greatly changed depending on the properties of the solvent, i.e., the phase transformation was slowed down in low dielectric constant solvents. The obtained fibrous TiO₂ samples showed high photocatalytic activity for the oxidative photo-decomposition of NO gas.

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1. Introduction

The protonated form of tetratitanate, H₂Ti₄O₉·nH₂O, which is formed by the ion exchange reaction of K₂Ti₄O₉, is known to be applicable as an inorganic ion exchanger [1,2], a catalyst [3–7], and a precursor to forming other titanate and titania [8–13], etc. The dehydration of protonated form of tetratitanate, H₂Ti₄O₉·nH₂O, by heat treatment has attracted interest from many [14,15]. It has been reported [1,10,15,16] that by calcination in air, the layered structure condensed first to form H₂Ti₈O₁₇; further dehydration resulted in the formation of monoclinic TiO₂ which is a metastable phase possessing more open structures compared with other crystalline phases of TiO₂, and is expected to show excellent photocatalytic activity [17,18]. Higher calcination temperature will make monoclinic TiO₂ transform into the anatase phase, and a further rise in the calcination temperature will finally cause the formation of the most stable phase, rutile TiO₂.

The comparison of the phase transformation behaviors by the calcination in air and heat treatment under mild solvothermal conditions has been reported in our previous study [15]. The results revealed that the phase transformation to anatase TiO₂ was promoted in liquid media compared with calcination in air. However, due to the limit of the heat resistance of the reactor, the phase transformation behaviors under solvothermal treatment only below 250 °C were studied. In this study, a batch reactor made by a

heat-resistant alloy was employed to extend the reaction temperature up to 450 °C. Therefore, the phase transformation behaviors of H₂Ti₄O₉·nH₂O under solvothermal conditions at relatively high temperatures were studied, meanwhile the influence of solvents on the crystalline phase of the product was investigated. Moreover, the photocatalytic activities of the products formed by the solvothermal reactions were also evaluated, and the relationship between the phase transformations and the photocatalytic activity was discussed.

2. Experimental

2.1. Synthesis

K₂Ti₄O₉ was first reacted with a 5 M HCl aqueous solution to change K⁺ with H⁺ at 60 °C for 5 h, then the obtained H₂Ti₄O₉ was dispersed into water, methanol or ethanol. The mixture was moved into batch reactors made of a heat-resistant alloy, Hastelloy[®], with an internal volume of 20 ml (Akico Co. Ltd., Japan) to carry out the solvothermal reactions. The reaction temperature varied from 300 °C to 450 °C, and the reaction time was 1 h. After the reaction, the precipitates were separated by centrifugation, followed by a rinsing with distilled water and acetone. Finally, the products were dried in a vacuum at 60 °C overnight.

2.2. Characterization

The crystalline phases of the products were characterized by X-ray diffraction analysis (Shimadzu, XD-D1), and Raman spec-

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troscopy (Jasco NRS-3000FL). A transmission electron microscopy (JEOL, JEM-2010) and a scanning electron microscopy (Hitachi, Miniscope, TM-1000) were used to observe the morphologies. The UV–vis diffuse reflectance spectra were obtained using a UV–vis spectrophotometer (Shimadzu, UV-2450). The BET specific surface areas were determined by a multipoint BET method (Quantachrome Instruments, NOVA 4200e).

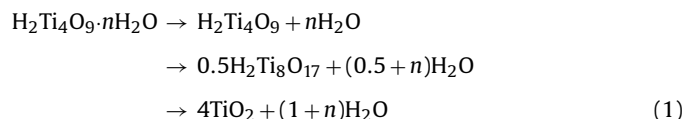
2.3. Photocatalytic reactions

To evaluate the photocatalytic activities of the prepared samples, the oxidative decomposition behavior of NO gas was investigated using a flow type reactor under irradiation of a 450 W high-pressure mercury arc. The experimental apparatus used for the photocatalytic reaction was reported in a previous paper [19]. For comparison, the photocatalytic reaction was also carried out using a standard commercial titania (AEROXIDE P 25) [20].

3. Results and discussion

3.1. Phase transformation behaviors

Fig. 1 shows the XRD patterns of the samples prepared in various solvents at different temperatures. As shown in Fig. 1(A), regardless of the reaction temperatures, all the samples prepared in H₂O showed the same diffraction profiles assigned to anatase phase TiO₂. The diffraction peaks were quite strong and sharp, suggesting that the samples were well crystallized. Fig. 1(B) shows the XRD patterns of the samples reacted in methanol. When the reaction temperature was 300 °C, diffraction peaks were relatively weak. Small peaks around 10° were attributed to the H₂Ti₄O₉·0.25H₂O precursor, and the peak around 12° is believed to have been attributed to the intermediate product, H₂Ti₈O₁₇ [14,15]. The reactions upon the solvothermal treatment were proposed as:



Besides the peaks assigned to layered titanates, the diffraction peaks attributable to the monoclinic TiO₂ were observed for the sample reacted in methanol at 300 °C. Due to the relatively high reaction temperature in this study, the diffraction peaks of H₂Ti₈O₁₇ could hardly be observed, except when the reaction temperature was 300 °C. When the reaction temperature was raised to 350 °C, the diffraction peaks corresponding to anatase TiO₂ appeared. Although the strongest peak of anatase TiO₂ around 25° overlapped with that of monoclinic TiO₂, the emerging of the peaks around 55° corresponding to the anatase phase could be observed easily. When the reaction temperature was further raised to 400 °C, the diffraction peaks corresponding to the anatase phase became stronger, especially the typical triple peaks around 38°. In contrast, the diffraction peaks assigned to the monoclinic phase became weaker. When the temperature reached 450 °C, the diffraction peaks of the monoclinic phase almost disappeared, and the peaks of anatase became stronger.

The phase transformations of H₂Ti₄O₉·nH₂O upon the reaction temperature in ethanol are shown in Fig. 1(C). The results were similar to those observed in methanol, but the appearance of the anatase phase was slow. When reacted in ethanol at 350 °C, only single monoclinic phase TiO₂ could be obtained. The diffraction peaks of the anatase phase appeared at 400 °C, but even at 450 °C the diffraction peaks corresponding to the monoclinic phase could still be observed easily, indicating that the phase transformation rate

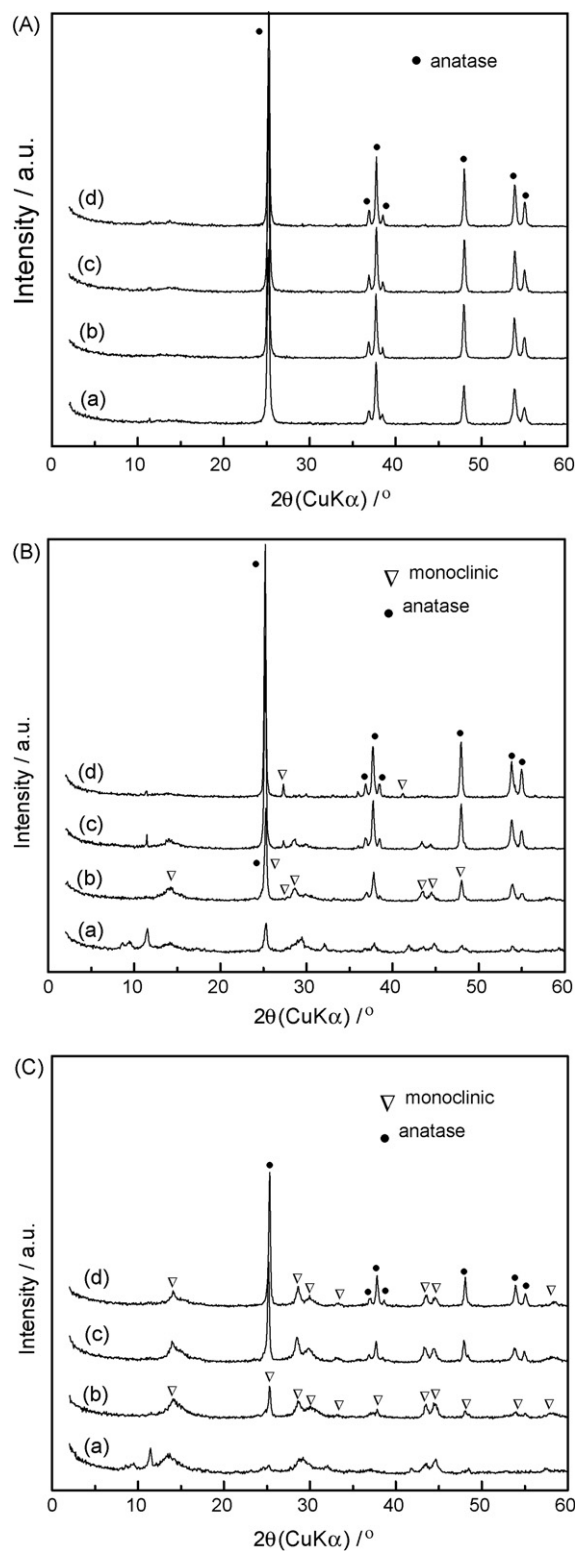


Fig. 1. XRD patterns of the samples prepared in (A) H₂O, (B) methanol, and (C) ethanol, at (a) 300 °C, (b) 350 °C, (c) 400 °C, and (d) 450 °C for 1 h.

of the monoclinic titania to anatase in ethanol was slower than in methanol.

Fig. 2(A) shows the Raman spectra of the samples prepared in H₂O at different reaction temperatures. It is obvious that all the prepared samples showed the same Raman shifts regardless of treatment time. All the observed shifts could be ascribed to the allowed vibrational frequencies of the anatase phase of titania [21].

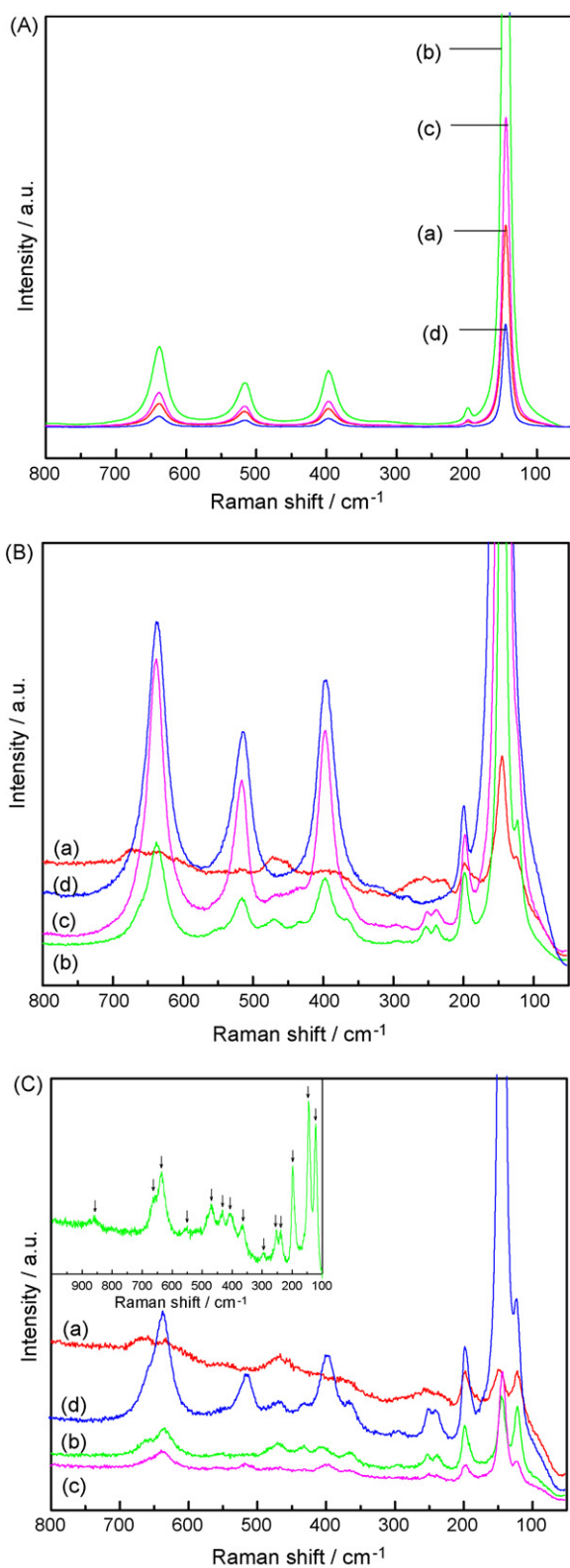


Fig. 2. Raman spectra of the samples prepared in (A) H_2O , (B) methanol, and (C) ethanol, at (a) 300°C , (b) 350°C , (c) 400°C , and (d) 450°C for 1 h (inset in (C) corresponding to the sample prepared in ethanol at 350°C).

Since the B_{1g} and E_g active modes at 144 cm^{-1} and 147 cm^{-1} were so close to each other, only a single sharp peak could be observed in the present study. These results are in good agreement with those obtained on the XRD patterns of the samples. Compared with the Raman spectra of the samples prepared in H_2O , those prepared in

methanol or ethanol showed much more complicated Raman shifts. At 300°C both samples showed wide and weak Raman shifts due to the poor crystallinity. When the reaction was conducted in ethanol at 350°C , as shown in the inset of Fig. 2(C), all the peaks could be assigned to those of monoclinic TiO_2 [14,22]. On the other hand, the sample treated in methanol at the same 350°C mainly showed shifts corresponding to anatase TiO_2 , and only a few weak peaks attributed to monoclinic phase of TiO_2 could be observed, which finally disappeared by raising the reaction temperature to 450°C . However, the sample prepared in ethanol still showed a Raman spectrum corresponding to the mixed phase of anatase and monoclinic TiO_2 even at 450°C . The results obtained here also are in good agreement with those from the XRD analysis.

Under heat treatment, dehydration occurs and $\text{H}_2\text{Ti}_4\text{O}_9$ first transforms into $\text{H}_2\text{Ti}_8\text{O}_{17}$. Further dehydration causes the formation of monoclinic TiO_2 from $\text{H}_2\text{Ti}_8\text{O}_{17}$. The transformation of TiO_2 from the monoclinic phase to the anatase phase results from crystallographic shear caused by the heat treatment [1,16]. Present experimental results actually suggested the different phase transformation behaviors in different solvents. These phenomena could be attributed to the different dielectric constant of the solvents. The dielectric constant of a solvent is a relative measure of its polarity. A popular aphorism used for predicting solubility is “Like dissolves like” [23]. This indicates that a solute will dissolve well in a solvent that has a similar polarity to itself. This is a rather simplistic view, since it ignores many solvent–solute interactions, but it is a useful rule-of-thumb. In the present reaction system, since the dielectric constant of water is much larger than those of methanol and ethanol, the $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$ precursor and products have larger solubility in water than in methanol and ethanol. It is known that hydrothermal/solvothermal reactions proceed via the dissolution/precipitation or dissolution/crystallization processes [24,25]. Larger solubility of the precursor in the solvent could accelerate the reaction rate; thus, the phase transformation rate would also become faster. Since water has a large dielectric constant, the phase transformation quickly proceeded in water and only anatase TiO_2 could be obtained even at 300°C . In our previous study [15], it has been revealed that when $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$ was treated in water, the product showed strong diffraction peaks attributed to anatase TiO_2 together with a very tiny proportion of peaks assigned to monoclinic TiO_2 even at such a low temperature as 225°C . In contrast, when methanol and ethanol possessing relatively low dielectric constants were used as solvents, the phase transformation slowly proceeded and metastable phase monoclinic TiO_2 could be obtained at the same temperature.

Fig. 3 shows the XRD patterns of the samples treated in ethanol and methanol at 300°C for 1 and 5 h. The samples treated in both methanol and ethanol for 1 h showed similar diffraction profiles consisting of $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ precursor, $\text{H}_2\text{Ti}_8\text{O}_{17}$ and monoclinic TiO_2 , but by prolonging the reaction time from 1 h to 5 h, the phase transformation further proceeded to show the diffraction peaks corresponding to the mixture of monoclinic TiO_2 and anatase TiO_2 and peaks at low 2θ angles assigned to layered titanate disappeared. The peak intensity of anatase TiO_2 in the sample treated in methanol was much stronger than in ethanol. It might be attributed to the higher dielectric constant of the methanol than of the ethanol.

Fig. 4 shows the specific surface areas of the samples prepared in various solvents at different reaction temperatures. The samples obtained at 300°C showed the specific surface area around $20\text{ m}^2/\text{g}$ and it decreased gradually by raising the reaction temperature due to the crystal growth at high reaction temperatures.

3.2. Optical properties

The diffuse reflectance spectra of the samples prepared in ethanol at different temperatures are shown in Fig. 5(A). To take

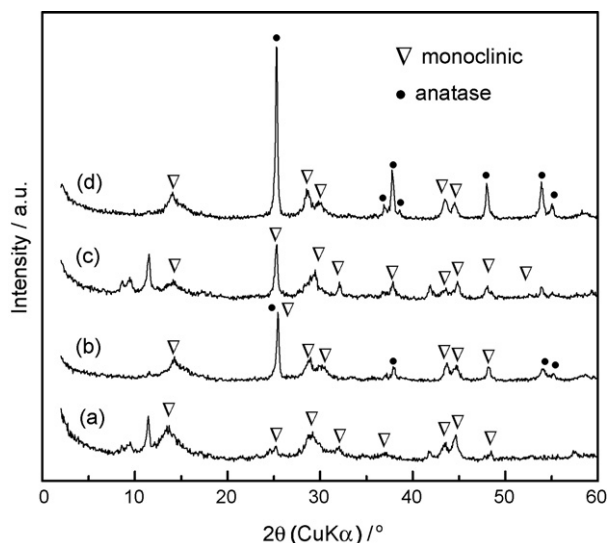


Fig. 3. XRD patterns of the samples prepared in ethanol ((a) and (b)) and methanol ((c) and (d)) at 300 °C for 1 h ((a) and (c)) and 5 h ((b) and (d)).

close observation, the DR spectra of the samples from 320 nm to 390 nm are shown in the inset of Fig. 5(A). It is observed that raising the reaction temperature would cause slight red shift of the absorption edge. This might be due to the transformation from layered titanate to TiO₂. Fig. 5(B) shows the diffuse reflectance spectra of the samples prepared at 350 °C in various solvents. The sample prepared in water, ethanol and methanol showed a single anatase phase, a single monoclinic phase, and a mixed phase of anatase and monoclinic, respectively. From the onset of absorption, the band gap energy of the monoclinic TiO₂ was determined as 3.4 eV, which was a little larger than that of anatase TiO₂, 3.2 eV.

3.3. Morphologies

Figs. 6 and 7 show the SEM and TEM images of the samples, respectively. As shown in Fig. 6, the raw material K₂Ti₄O₉ shows uniform fibrous morphology. After ion exchange and solvothermal reactions, the morphology was maintained, regardless of the difference in crystalline phase. Further analysis by TEM observation revealed that the TiO₂ fiber was composed of many small crystallites. From the high magnification TEM images, the difference in the microstructure of the TiO₂ fibers obtained in water and ethanol

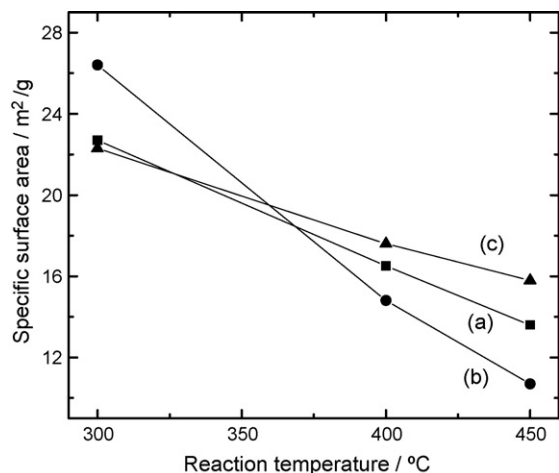


Fig. 4. Specific surface areas of the samples prepared in (a) H₂O, (b) methanol, and (c) ethanol at different temperatures.

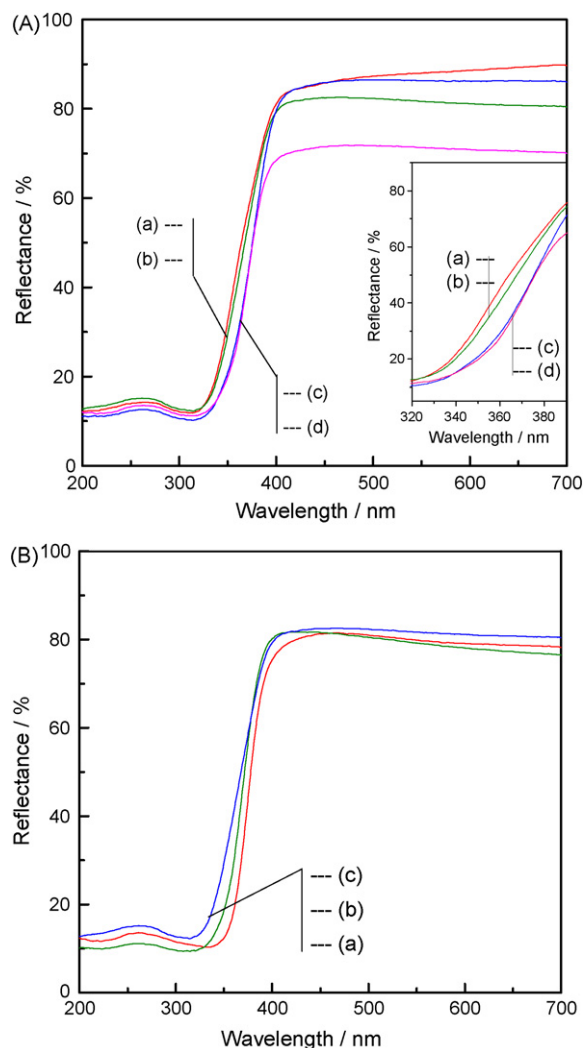


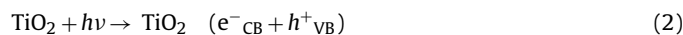
Fig. 5. (A) Diffuse reflectance spectra of the samples prepared in ethanol at (a) 300 °C, (b) 350 °C, (c) 400 °C, and (d) 450 °C. (B) Diffuse reflectance spectra of the samples prepared at 350 °C in (a) H₂O, (b) methanol, and (c) ethanol.

could also be observed. Comparing to the fibers prepared in water, those prepared in ethanol consisted of much smaller crystallite, indicating that the reaction in low dielectric constant solvent such as ethanol could not only slow down the phase transformation but also inhibit the crystal growth. This result is in good agreement with the XRD analysis, i.e., TiO₂ prepared in ethanol showed much weaker diffraction peak intensity than when prepared in water.

3.4. Photocatalytic activities

To investigate the photocatalytic activity of the prepared samples, the oxidative photo-decomposition of NO gas was performed.

It is accepted that by the photo-excitation, electron/hole pairs are formed on titania (Eq. (2)). In the presence of oxygen, the electrons in the conduction band are immediately trapped by the molecular oxygen to form $\bullet\text{O}^{2-}$ (Eq. (3)), from which active $\bullet\text{OOH}$ radicals can be generated (Eq. (4)) [26–28]. At the same time, the holes are trapped by water in air to produce $\bullet\text{OH}$ radicals (Eq. (5)) [26–28].



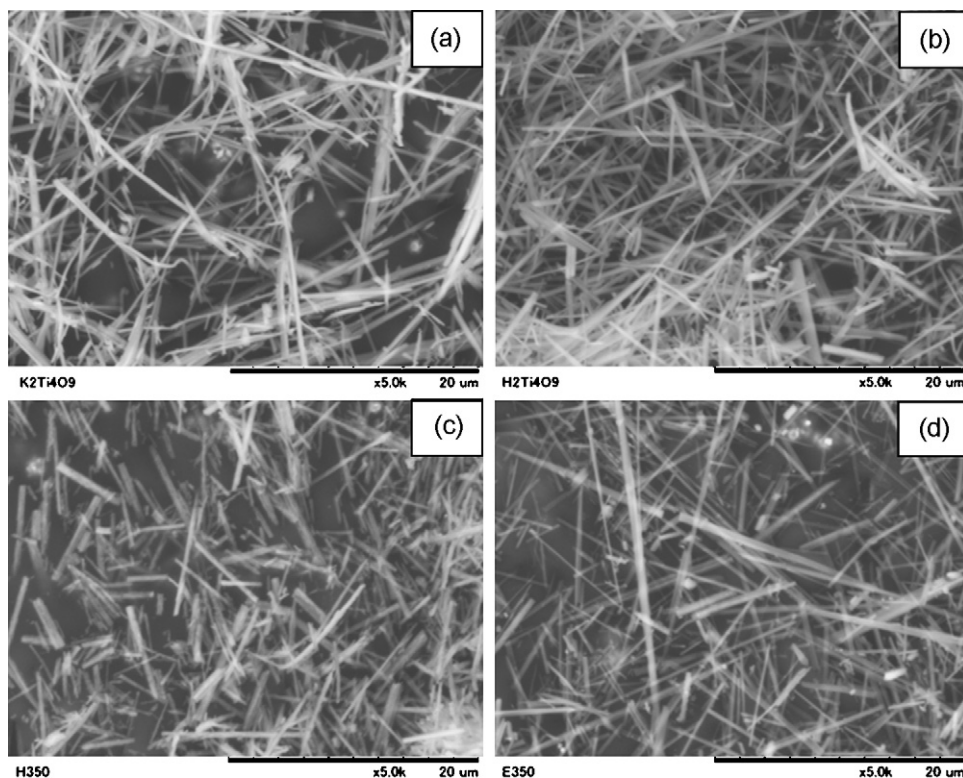


Fig. 6. SEM images of (a) $K_2Ti_4O_9$, (b) $H_2Ti_4O_9$, (c) sample prepared in water at $350^\circ C$, and (d) sample prepared in ethanol at $350^\circ C$ for 1 h.

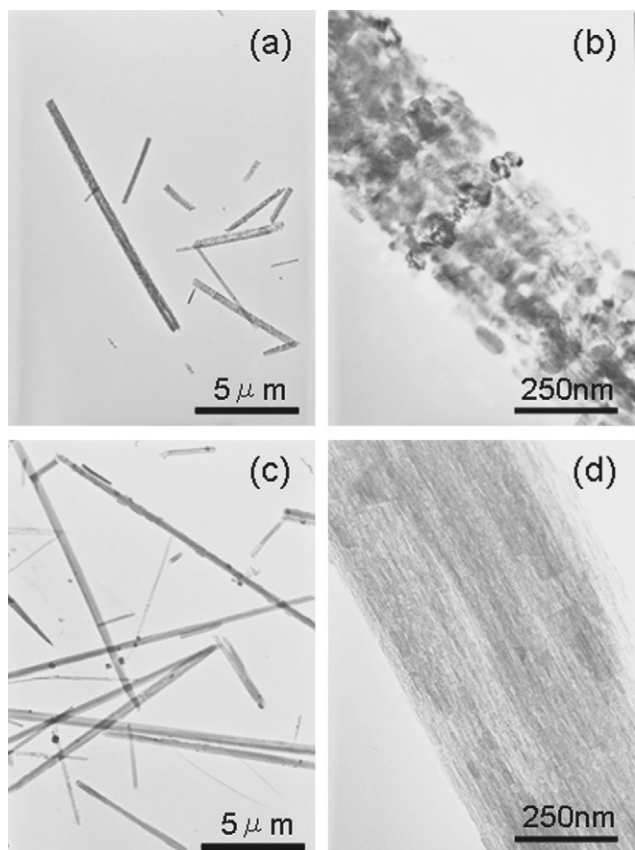
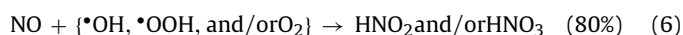


Fig. 7. TEM images of the samples prepared at $350^\circ C$ (a) and (b) in H_2O , and (c) and (d) in ethanol for 1 h.



The nitrogen monoxide reacts with these reactive radicals, molecular oxygen, and very small amount of water in air (humidity was about 25% in the present research) to produce HNO_2 or HNO_3 (Eq. (6)). It was reported that about 20% of nitrogen monoxide was decomposed to nitrogen and oxygen directly (Eq. (7)) [29,30].

Fig. 8 shows the rate of NO decomposition by the precursor $H_2Ti_4O_9$ and the samples prepared in ethanol at different reac-

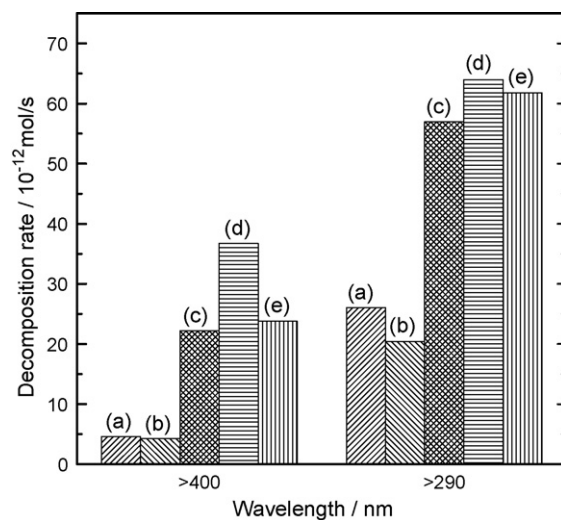


Fig. 8. Photocatalytic for the oxidative decomposition of NO gas by (a) $H_2Ti_4O_9$, and samples prepared in ethanol at (b) $300^\circ C$, (c) $350^\circ C$, (d) $400^\circ C$ and (e) $450^\circ C$ for 1 h.

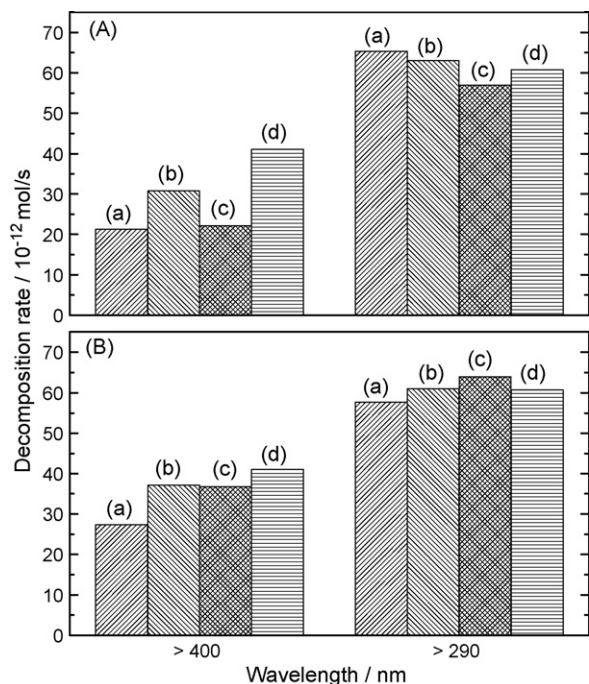


Fig. 9. Photocatalytic activities for the oxidative decomposition of NO gas by the samples prepared at (A) 350 °C and (B) 400 °C in (a) H₂O, (b) methanol, and (c) ethanol for 1 h, and that by (d) commercial TiO₂ (AEROXIDE P 25). Feeding rate of NO: 148×10^{-12} mol/s.

tion temperatures. It is observed that the layered titanate showed poor photocatalytic activity. The photocatalytic activity increased by increasing the solvothermal reaction temperature from 300 °C to 400 °C and then decreased at 450 °C. The low activity of the samples obtained at 300 °C might be due to the residual layered titanate

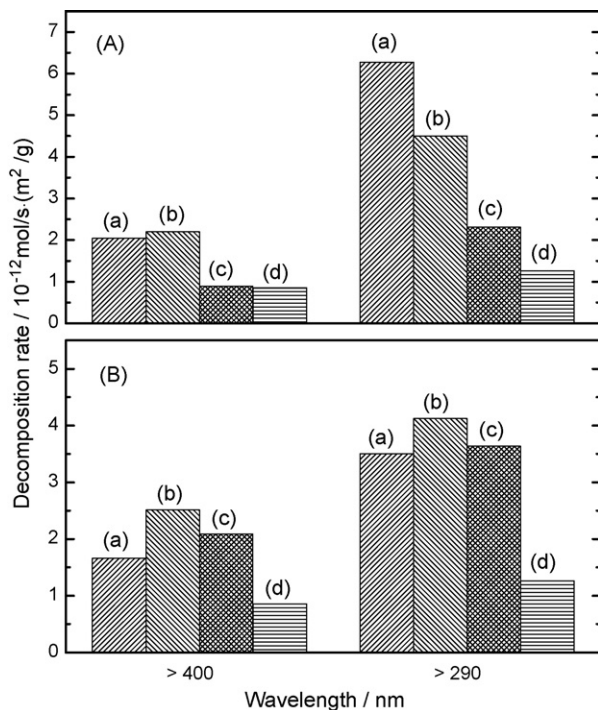


Fig. 10. Photocatalytic activities for the oxidative decomposition of NO gas by the samples prepared at (A) 350 °C and (B) 400 °C in (a) H₂O, (b) methanol, and (c) ethanol for 1 h, and that by (d) commercial TiO₂ (AEROXIDE P 25). Feeding rate of NO: 148×10^{-12} mol/s.

phase in the products and the poor crystallinity of titania. The sample prepared at 400 °C showed the highest decomposition rate, and the decrease in photocatalytic activity at 450 °C might be due to the decrease in specific surface area.

The rate of NO decomposition by the samples prepared in various solvents at 350 °C and 400 °C are shown in Fig. 9(A) and (B), respectively. In comparison, the activity of commercial TiO₂ (AEROXIDE P 25) was also plotted in the figure. The results suggested that TiO₂ prepared at 350 °C showed high photocatalytic activities under UV light (>290 nm) irradiation, but the activities under near UV light (>400 nm) irradiation were still low. By rising the reaction temperature to 400 °C, the fibrous TiO₂ prepared in methanol or ethanol showed relatively high activity similar to that of commercial TiO₂ under both UV (>290 nm) and near UV (>400 nm) light irradiations.

It is also worthy to mention that the specific surface area of the samples prepared in this study was much smaller (10–26 m²/g) than that of commercial P 25 TiO₂ (48 m²/g). Therefore, to eliminate the unfair advantage to P 25 catalyst, the decomposition rate was further divided by the BET surface area, and plotted in Fig. 10(A) and (B). It is observed that the prepared TiO₂ fibers showed obviously superior photocatalytic activity in decomposing NO to commercial P 25 TiO₂.

4. Conclusions

By the solvothermal reactions of fibrous protonated form of tetratitanate, H₂Ti₄O₉·nH₂O, in different solvents, fibrous TiO₂ with monoclinic, anatase, and mixed phases of monoclinic and anatase could be obtained. The fibrous morphology of the raw material was maintained even after the phase transformation, and the prepared fibrous TiO₂ showed high photocatalytic activities in destroying NO similar to commercial TiO₂ (AEROXIDE P 25). It was also found that the crystalline phases of the products greatly changed depending on the solvents. Solvents with low dielectric constant, such as ethanol, could slow down the phase transformation reaction and inhibit the crystal growth. These results suggest that by selecting a proper solvent, desired crystalline phase of products could be obtained without altering other reaction parameters.

Acknowledgments

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