Room-temperature Formation of Alkoxide-derived Anatase Nanoparticles by Peroxotitanic Acid Approach

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A controlled procedure leads to formation of pure anatase nanoparticles from titanium alkoxide near room temperature, without using any organic solvent by the peroxotitanic acid approach. The nanoparticles are highly mesoporous, with the surface covered by peroxo groups, and have excellent photodecomposition activity as compared to those prepared from ordinary procedures.

As one of n-type semiconductors, titania has been attracting a great deal of concerns since the finding of its high functionality in photon-electron charge transfer.[1] The photocatalytic activity of titania is dependent not only on its crystalline phases and sizes but also on its morphology, surface properties, porosities, etc.[2] Anatase having a larger band gap is often more active in many photocatalytic reactions as compared to its structural counterparts rutile and brookite.[2b]

Pure anatase materials can be prepared either by the ordinary sol–gel method[3] or recently by the peroxotitanic acid (PTA) approach[4] in which pure anatase is obtained by oxidizing amorphous titanium oxide/hydroxide precipitates using peroxide, followed by a subsequent hydrothermal treatment. PTA approach is of great importance because it makes formation of pure anatase at relative low temperature and under neutral pH condition. In a large part of previous researches, inorganic Ti salts such as $TiCl_4$, $TiOSO_4$, etc. are usually applied as precursors of the PTA method, which left impurities such as NH_4^+ in anatase product.[4a] Some researches using organic precursor reported only the mixed phase product of anatase and rutile.[5] Further researches pointed that alcohol addition is very effective to control titania phase.[6] However, no research up to now successfully synthesized pure anatase without using organic solvents in PTA method using organic precursor. Here, we reported that, by a simple procedure appropriately controlling the synthetic condition, nanoparticles with single anatase phase can be formed from alkoxide precursor even near room temperature by an organic solvent-free PTA method.

The synthetic procedure is the same as that reported by Ichinose et al.[4a] except some modifications due to using of titanium tetraisopropoxide ($Ti(i\text{-}OC_3H_7)_4$) precursor. Briefly, $TiO(OH)_2$ precipitates were first obtained by dripping $Ti(i\text{-}OC_3H_7)_4$ into deionized water (d.w.) without adding any solvent or acid/base catalysts. The precipitates were washed several times with d.w. and finally filtered to remove organic by-products and d.w. Next, PTA solution was obtained by adding 30% H_2O_2 solution into the wet $TiO(OH)_2$ powders under vigorous agitation. A clear solution with a deep orange color was formed immediately after H_2O_2 addition, and the exothermic reaction leads to radical bubbling. Once bubbling occurs, the solution was soon moved into an ice bath so as to make the solution cooling down to room temperature (rt). Then, the ice bath was moved out again, allowing reaction continuing at rt. This cooling process was repeated until no bubbles released from the solution at rt. The anatase nanoparticles (PTA–A-*T* where *T* is temperature) were obtained by evaporating water from the PTA solution at 333 K and further calcined at 523 K in air for 2 h. For comparison, the sample (PTA–A-333-wc) using the above procedure, however, without the cooling process,[5] and that (PTA–B-333) using $TiCl_4$ precursor and the reported procedure[4a] were also prepared. Samples were characterized by XRD, Raman, N_2 adsorption, UV–vis methods. Their photodecomposing activities toward Methyl Orange (MO) were examined.

XRD patterns of the obtained samples are shown in Figure 1A. A large halo peak broadening around $2\theta = 25°$ is present for PTA–B-333 owing to scattering of disordered particles, indicating almost amorphous property. A slight peak at $2\theta = 24.48°$ overloaded on the broad background can be observed for PTA–A-333-wc, implying that its crystalline growth degree is very limited. By contrast, PTA–A-333 presents a sharp peak at $2\theta = 25.34°$. This peak, which can be indexed to the (101) plane of anatase, further grows with increasing calcination temperature. Calculation using Scherrer's equation indicates the crystalline sizes increasing from 7.4 to 9.7 nm when *T* increases from 333 to 523 K. Besides the anatase peaks, only a disregardful peak at $2\theta = 30.80°$ due to brookite, which is known often coexisting with the low-temperature anatase or rutile phase, is detective, demonstrating that PTA–A-333 is almost of single anatase phase. As shown in Figure 1B, single anatase structures of PTA–A-*T* samples can also be confirmed from the evident peaks typical of anatase at 146, 397, 516, and 638 cm^{-1} in their Raman spectra.[7] The absence of these peaks for the PTA–B-333 sample further evidences almost no crystalline structure. It is known that peroxide oxidation leads to formation of peroxo groups (–O–O–) on the surface of titanium oxide, producing yellowish particles.[4a] The representative Raman shifts of organic –O–O– groups are reported around 875 cm^{-1}, and those of the inorganic ones were observed lower than 500 cm^{-1}.[8] Thereby, the common peaks at 282, 522, 676, and 905 cm^{-1} on the three 333-K samples can be assigned to the surface –O–O– groups, in accordance with their common yellow color. The absence of these peaks on PTA–A-523 indicates the disappearance of the bond by calcination at 523 K, which is confirmed by another FT-IR result and also supported by the previous research.[4a] Thus,

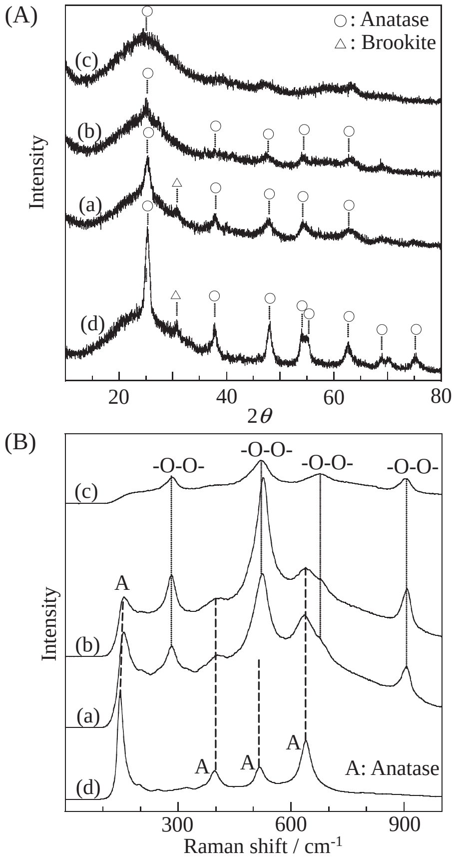

Figure 1. (A) XRD patterns and (B) Raman spectra of (a) PTA–A-333, (b) PTA–A-333-wc, (c) PTA–B-333, and (d) PTA–A-523.

the above synthetic procedure readily gives anatase nanoparticles (PTA–A-333) at rt with the –O–O– groups bonded to the surface.

N_2 adsorption isotherm at 77 K on PTA–A-333 shows an evident adsorption hysteresis at the medium relative pressure range, indicating the presence of mesopores. On the contrary, adsorption hysteresis is either absent for PTA–A-333-wc or unobvious for PTA–B-333, indicating absence or less amounts of mesopores in the two samples. Barrett–Joyner–Halenda (BJH) analysis indicates that PTA–A-T samples are highly mesoporous with a large distribution around a pore width (D_P) of 4.0 nm (Table 1). Similar values of BET specific surface area (S_{BET}) of the three 333-K samples indicate that PTA–A-333-wc and PTA–B-333 are also porous, but mainly microporous by further analysis. The reason for the results can be inferred from the structural differences of the three samples because larger interstitial spaces are easily formed between the grown larger anatase nanocrystals in PTA–A-333 with respect to the smaller disordered particles in the other two samples. The UV–vis spectra of the three samples show an absorption peak at 325 nm due to titania structure and another one at 380 nm due to –O–O– bond. The intensity of the latter peak, relative to the former one, decreases with a sequence of PTA–B-333 > PTA–A-333-wc > PTA–A-333, and the latter peak completely disappears for PTA–A-523 which has no –O–O– bonds. Figure 2 shows the time courses of MO degradation at 303 K on the samples. A greater decrease of C/C_0 on PTA–A-333 under dark state indicates the better MO adsorptivity due to the mesoporosity or a better surface property. MO degradation rates on PTA–A-T are much faster than those on the other samples. The first-order initial rate constants of PTA–A-T are enhanced by more than 50 folds as compared to that of PTA–B-333 (Table 1). The notable MO decomposition rate can be attributed to the perfect nanocrystal structure of anatase, the mesoporosity, and less deficiencies on PTA–A-333.

Table 1. Pore parameters and MO degradation rate constants

Sample	S_{BET} /$m^2 g^{-1}$	V_{meso} /$mL g^{-1}$	D_p /nm	k_{app} /$10^{-2} h^{-1}$
PTA–A-333	235	0.13	3.8	11.4
PTA–A-523	125	0.19	4.0	14.5
PTA–A-333-wc	240	—	—	0.97
PTA–B-333	220	—	—	0.23

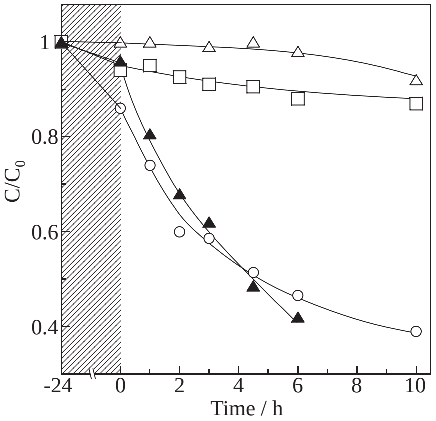

Figure 2. Time courses of MO degradation at 303 K on PTA–A-333 (○), PTA–A-333-wc (□), PTA–B-333 (△), and PTA–A-523 (▲) where 10 mg of titania was added to 3 ml of solution of $C_0 = 50$ mg/L. Areas with and without slanting lines show the dark and irradiation (with 6 × 15 W black light) states, respectively.

In conclusion, by appropriately controlling synthetic conditions, nanoparticles with single anatase phase can be obtained from alkoxide precursor even near rt and without adding any organic solvent in the PTA approach. The highly mesoporous nanoparticles with the –O–O– bond-ended surface demonstrate a superior photodegradation activity and are prospective for application as a new kind of photocatalyst.

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