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TiO_2 nanoparticles prepared using an aqueous peroxotitanate solution

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Abstract

A novel preparation method for nanocrystalline titanium dioxide (TiO_2) was introduced in this paper. We prepared a new aqueous peroxotitanate solution using H_2TiO_3, ammonia and H_2O_2 as starting materials. Amorphous precursor powder with different morphology was formed at near room temperature, which was transformed to anatase after annealing at 300 °C followed by rutile at 850 °C. This method is simple, environmental friendly and promising to be used for TiO_2 synthesis.

Keywords: D. TiO_2; Nanocrystalline; Aqueous peroxotitanate solution

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1. Introduction

Titanium dioxide (TiO_2) is widely applied as a white pigment for paints or cosmetics, a support in catalysis, and a photocatalyst. The uses and performance are strongly influenced by the crystalline structure, the morphology and the particle size. Nanocrystalline TiO_2 particles are of particular interest because of their specifically size-related properties, and therefore many works have focused on the synthesis of nanocrystalline titanium dioxide.

As for anatase TiO_2 nanocrystallites, much attention has been paid to hydrothermal methods using amorphous TiO_2 [1], $TiCl_4$ [2–4] or $TiOCl_2$ aqueous solution [5], and sol–gel methods using titanium alkoxides [6,7]. TiO_2 can be also obtained by hydrolysis of titanium compounds, such as titanium tetrachloride ($TiCl_4$) [8,9] or titanium alkoxides ($Ti(OR)_4$) [10,11], in solution. However, the use of starting materials containing of chlorine or organic ligand usually resulted in the residue of chlorine or carbon in the as-prepared powder, which should increase the environmental impact. Therefore, chlorine- or organic-free route for preparation of high-purity TiO_2 nanoparticle is preferable for practical application.

Recently, Kumar [12] reported that several complex titanate such as $BaTiO_3$ was prepared by the peroxide-based route. We applied the peroxide-based route for preparation of nanocrystalline TiO_2 particle by annealing of an amorphous precursor. As a result, we successfully obtained chlorine- and organics-free TiO_2 nanoparticles. Here, we report the preparation and characterization of TiO_2 nanoparticles by low-temperature annealing of the amorphous powder which was precipitated in an aqueous peroxotitanate solution.

2. Experimental

H_2TiO_3 can be dissolved only in the presence of H_2O_2 and $NH_3 \cdot H_2O$ in appropriate quantities. Specifically, 3 g of H_2TiO_3 (80%, Mitsuwa) was added to an ice-cooled solvent consisting of 25 cm^3 of H_2O_2 (30%, Mitsubishi) and 5 cm^3 of ammonia (25%, Kishida). After stirring for 90 min, a homogeneous pale yellow–green solution was obtained, which can be stable for several weeks at temperatures of less than 5 °C.

Fresh aqueous peroxotitanium solution was diluted by deionized water (>18 MΩcm) to 5 mM Ti^{4+} under pH 2.4 (by HNO_3). After retaining in air at room temperature or 10 °C for 12 h, the precipitate was obtained and collected. The powder was then carefully rinsed by deionized water and dried.

The phase for the as-prepared powder and those after annealing was characterized by X-ray diffraction (XRD;

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Rint 2100; $\lambda = 1.5418$ nm, Rigaku Co.) operated at 40 kV and 30 mA with Cu Kα radiation; scan rate was 1°/min. Fourier-transform infrared spectroscopy (FT-IR-610, JASCO) was measured at a resolution of 4 cm^{-1} with KBr as a reference. The particle size was measured by transmission electron microscope (TEM; JEM 4010, 400 kV, point-to-point resolution 0.15 nm, JEOL Co., Ltd.).

3. Results and discussion

The XRD result (Fig. 1) showed that the as-prepared powder was amorphous. Crystalline anatase was formed after annealing at a temperature of as low as 300 °C and the anatase phase remained until 800 °C, which was much higher than that for the sol–gel-derived TiO_2 [13]. This indicates that it might be easy to prepare a thin film of well-crystallized pure anatase phase by using the present technique. Obvious transformation to the rutile phase was found at about 850 °C, while some small diffraction peaks of anatase were also observed. After annealing at 900 °C, about 39% rutile formed as evaluated by the relative intensity of the XRD peaks that belong to anatase (1 0 1) and rutile (1 1 0). The full-width at half-maximum (FWHM) of the anatase (1 0 1) diffraction peak decreased with increasing annealing temperature, suggesting that the average crystallite size was increased by thermal annealing. In fact, the crystallite size estimated using Scherrer's equation ($0.89\lambda/(\beta\cos\theta)$) for the powder annealed at 600 and 900 °C were 30 and 50 nm, respectively.

In the FT-IR spectrum (Fig. 2) of the collected precipitate, a broad peak appearing at 3100–3600 cm^{-1} was assigned to fundamental stretching vibration of O–H hydroxyl groups (free or bonded) [14], which was further confirmed by a weak band at about 1620 cm^{-1}. The absorption band at 1620 cm^{-1} was caused by bending vibration of coordinated H_2O as well as from the Ti–OH. The bending vibrational mode of water may appear as shoulders on the spectrum such as 3240 cm^{-1}. Peaks located at 500 and 430 cm^{-1} were likely due to the vibration of the Ti–O bond in the TiO_2 lattice [15]. The peak centered at 900 cm^{-1} may be assigned to characteristic O–O stretching vibration of peroxo groups [15a], thus the shoulder observed at 690 cm^{-1} may have been due to the vibration of the Ti–O–O bond. Although the peak detected at 1409 cm^{-1} could not be assigned, the FT-IR measurement firmly suggested the presence of Ti–O bonds, peroxo groups, and OH groups in the as-prepared precipitate.

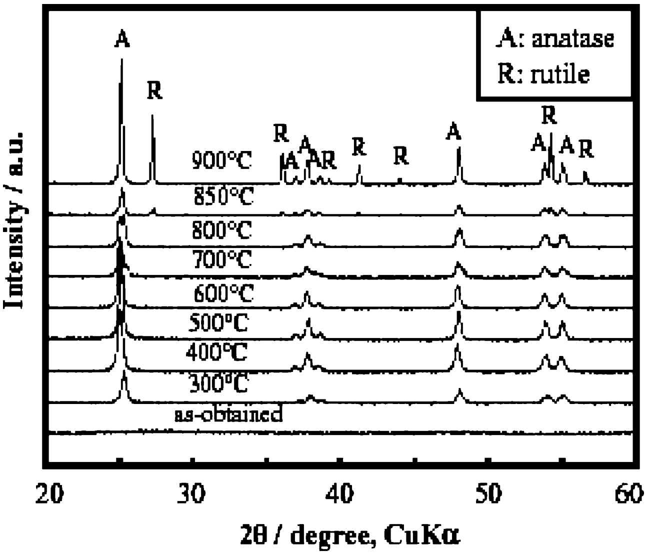


Fig. 1. XRD patterns of the as-prepared powder and those after annealing at different temperatures. (A: anatase, R: rutile).

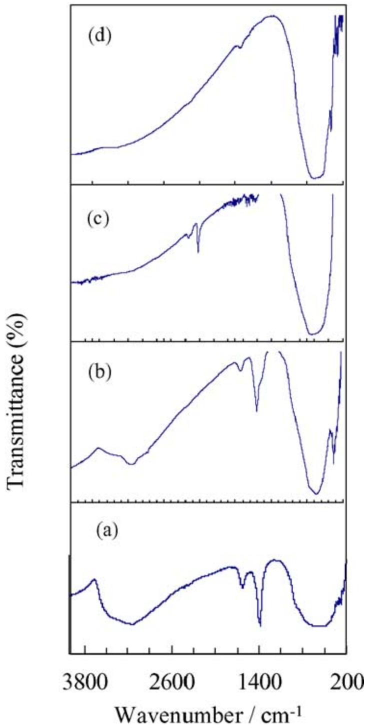
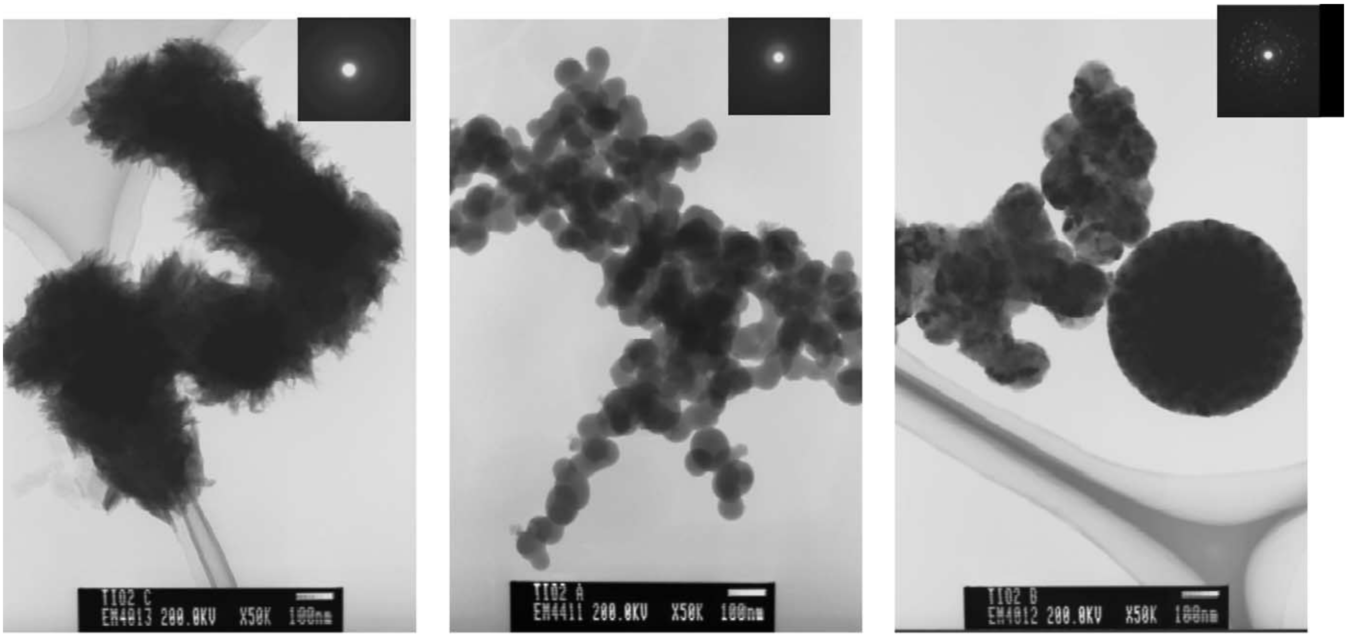


Fig. 2. (a) FT-IR spectra of the as-prepared powder and those after annealing at different temperatures (b) 200 °C (c) 300 °C, and (d) 400 °C.

After annealing at 200 °C, the shoulder assigned to peroxo groups became weak, suggesting the decomposition. Peaks attributed to adsorbed water almost disappeared, while vibration of hydroxyl groups still could be observed at about 3140 cm^{-1}, which was not detected after annealing at 300 °C. After annealing at 400 °C, the residual were only peaks for Ti–O vibration located at 400–700 cm^{-1}.

We have characterized the TiO_2 film prepared by the peroxotitanate complex deposition method, and found that the O_{1s} binding energy can be fitted to Ti–OH bond (531–532 eV), Ti–O bond (530–531 eV) and peroxo groups (532–533 eV) [16,17]. These findings along with the thermal-gravity analysis suggested the possible chemical formula of the as-prepared powder ($TiO_{1.4}(O_2)_{0.5}(OH)_{0.2}$).

Fig. 3 shows the TEM images for the as-prepared powder and those after annealing at several temperatures. The powder obtained at 10 °C shows whisker-shaped morphology,



(a) (b) (c)

Fig. 3. TEM images of the as-prepared powder obtained by soaking at (a) 10 °C, at (b) room temperature and (c) that after annealing of sample b at 600 °C for 2 h in air .

while that obtained at room temperature exhibits particulate characteristic. The diameter for the whisker-shaped powder was much smaller than that for the sphere-shaped particle. The latter gave a particle size of about 50 nm in diameter. The morphology changes should be correlated to the solution conditions. When retaining at lower temperatures, the supersaturation of the solution was low, the initial formed particles proffered to grow. The growth along a specific direction resulted in heterogeneous whisker-shaped particles. While at higher temperatures, the supersaturation was high, implying that large quantities of nuclei were preferred to generate rather than the growth of the old ones. The electron-diffraction patterns in the inset of the corresponding image suggest that the as-prepared powder were amorphous. After annealing of the sphere-shaped particle (Fig. 3b) at 600 °C, particles of about 30–40 nm in diameter was obtained (Fig. 3c), which is consistent with the value estimated from XRD result (∼30 nm). The formation of the random-oriented anatase TiO_2 was also confirmed by the electron-diffraction pattern. The diffraction spots of 101, 004, 105, 200 and 301 for anatase TiO_2 were observed (Fig. 3c).

4. Conclusion

We described a novel method for preparation of nanocrystalline TiO_2. The precursor with residual peroxo and hydroxyl groups was obtained by directly precipitation in an aqueous peroxotitanate solution. Anatase TiO_2 was formed after annealing at 300 °C in air. The particle morphology and size were characterized by TEM. Our process enables to produce nanocrystalline TiO_2 of organics and chlorine-free. It is promising route to prepare TiO_2 nanoparticles of high-purity for commercial application.

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