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Preparing titanium oxide with various morphologies

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Abstract

Titanium oxide powder was prepared by hydrolyzing titanium tetraisopropoxide (TTIP) in aqueous solutions at pH 2, using TMC and NP-204 as surfactants. The anatase phase was formed when the precipitants were dried at 373 K. When the calcination temperature was below 773 K, all the powders were crystalline in the anatase phase. The powders changed to the rutile phase when the calcination temperature exceeded 1173 K. The powder calcined at 673 K has spherical primary particles with diameters of approximately 8 nm. When the powders calcined at 673 K were heated in NaOH solutions of various concentrations at 423 K for 20 h, titanium oxide powders with different morphologies were obtained. After the powders were refluxed in 5 M NaOH solutions, flower-like titanium oxide particles were formed. Nanotubes of titanium oxide about 8 nm in diameter and over 600 nm long were obtained when the powders were refluxed in 10 M NaOH solution.

Keywords: Titanium oxide; Nanomaterials; Nanotubes; Microstructure

1. Introduction

The preparation of nanoscale materials of various elements and compounds has attracted increasing interest because of the potential uses of such materials in both mesoscopic research and developing nanodevices. TiO_2 is such a material of interest for photocatalysts due to the positive oxidation potentials of its holes (h^+) induced under irradiation by UV lights below 400 nm [1]. The surface area of the materials, depending on the morphology, plays a significant role in governing the photocatalytic reaction. A larger surface area of the photocatalysts corresponds to more effective photocatalysis [2]. Additionally, the surface area becomes larger as the particles become smaller or more tubular.

Previous studies have presented many methods for preparing nanotubes, nanorods or nanowires, for example, electrochemical [3], redox [4,5], replication [6] and template methods [7–10]. However, the template method [8] is not inappropriate for preparing smaller nanotubes because of its high dependence on the template mold. In 1998, Kasuga et al. [11] were the first to prepare TiO_2 nanotubes in NaOH solutions using TiO_2–SiO_2 powders as precursors. After treating the powders in 10 M NaOH aqueous solution at 383 K for 20 h, they obtained 100 nm long TiO_2 nanotubes with diameters of about 8 nm. However, removing SiO_2, which reduces the activity of the powders, is difficult. In an experiment by Seo et al. [12] the TiO_2 powders in the anatase phase were digested in 5 M NaOH aqueous solution at 423 K for 12 h, yielding 150 nm long TiO_2 nanotubes with diameters of 15–20 nm.

In this work, titanium oxide powders with different morphologies are formed by calcination at various temperatures and treatment of titanium dioxide nanopowder in NaOH of various concentrations at 423 K. This paper also characterizes the microstructure of the powders, and closely examines the powder formation pathway.

2. Experimental

2.1. Preparing titanium oxide nanopowders

Titanium oxide powders were prepared by hydrolyzing titanium tetraisopropoxide (TTIP; supplied from the Aldrich Company). TTIP was used as received, without further purification. The general procedures of these reactions were as follows. The 0.1 M TTIP isopropanol solution was slowly dropped into an aqueous solution that contained TMC (from

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Taiwan Surfactant Company) and NP-204 (from En How Polymer Chemical Company) as surfactants, and was adjusted to pH 2 by adding HCl. The hydrolysis of TTIP occurred before a turbid solution was obtained. After the solution was centrifuged, the white precipitant was dried at 373 K for approximately 2 h in a vacuum system to remove water and IPA. Finally, the dried particles were calcined at temperatures of 523, 573, 673, 773, 873, 973 and 1173 K in an atmosphere of N_2.

2.2. Preparing titanium oxide with various morphologies

Titanium oxide with various morphologies was prepared by chemically treating titanium oxide powders. The powders were refluxed in various concentrated NaOH solutions at 423 K for 20 h. After washing in water to remove the alkali, the powders were collected and examined.

2.3. Characterizing the powder products

The structures of the powders were characterized by powder X-ray diffractometry (XRD) in a MAC-MO3S at 40 kV, 30 mA. The morphology of the powder was characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM measurement was made using a HITACHI S-4000 field emission gun equipped with an energy dispersive X-ray spectrometer (EDS); TEM was performed using a JEOL JEM-2000 FX II at 200 keV. The lattice image was obtained by high-resolution TEM in a JEOL JEM-4000EX at 400 kV. TEM samples were prepared by ultrasonically treating and dispersing the powders in acetone; they were dropped onto a carbon film supported on a copper grid, and dried in a vacuum system.

3. Results and discussion

TTIP was hydrolyzed in an aqueous solution using TMC and NP-204 as surfactants at pH 2 to yield a turbid solution. One day later, some gel precipitants were produced. After the precipitants were centrifuged and dried at 373 K in a vacuum system, yellow-white powders were collected. Then, the powders were further calcined for 2 h.

Fig. 1 displays the XRD patterns of the powders calcined for 2 h at various temperatures. The anatase phase was formed when the precipitants were only dried at 373 K. The peaks of anatase phase became sharper and their intensities increased with the calcination temperature. When the calcination temperature was 873 K, rutile phase peaks appeared; that is, a phase transition occurred from anatase to rutile at approximately 873 K. When the calcined temperature

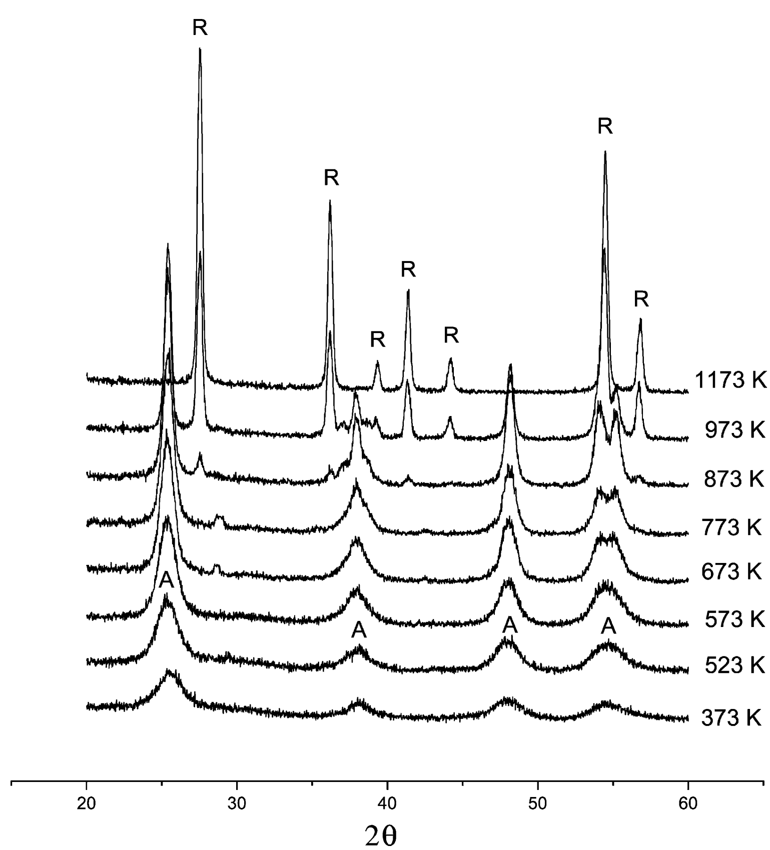


Fig. 1. XRD patterns of the powders calcined at various temperatures: A (anatase); R (rutile).

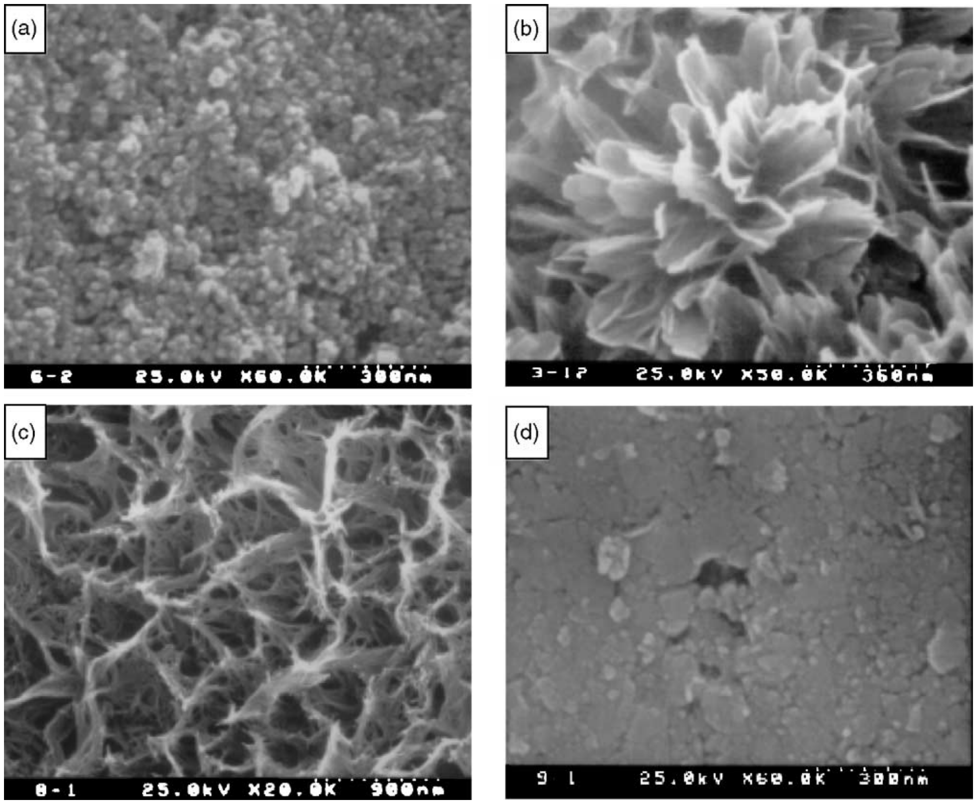


Fig. 2. SEM images for: (a) raw materials (calcined at 673 K), (b) treated by 5 M NaOH, (c) treated by 10 M NaOH, and (d) calcined at 1173 K followed by 10 M NaOH at 423 K for 20 h.

reached 1173 K, the particles were all rutile phase and the anatase peaks disappeared. These results suggest that the anatase phase is a metastable phase and that the rutile phase is thermodynamically stable. The results correspond to those in previous literature [13]. However, in this study, polycrystalline anatase titanium oxide is prepared at 373 K. The preparation temperature is much lower than reported [14].

Fig. 2 presents SEM micrographs of the chemically treated powders. Fig. 2(a) reveals that spherical particles were calcined at 673 K are uniform and aggregated. Fig. 2(b)–(d) illustrate the morphology of powders treated in concentrated NaOH solutions. A flower-shape image (Fig. 2(b)) was obtained from the powder treated in 5 M NaOH. When the spherical particles (Fig. 2(a)) were refluxed in 10 M NaOH, fibrous materials, shown in Fig. 2(c), were produced. Both flower-shape and fiber-like materials were observed when the powder was treated in 7.5 M NaOH. Fig. 2(d) shows the image of the powder calcined at 1173 K, and then refluxed in 10 M NaOH solution. This image reveals that the spherical particle is still the dominant morphology. Moreover, the EDS data show that titanium and oxygen are the main components of these powders.

Fig. 3 presents the TEM images of the powders obtained under various reaction conditions. Fig. 3(a) shows the TEM images and the select area electron diffraction (SAED) pattern of the powder, which was obtained by hydrolyzing TTIP and calcinating at 673 K. The spherical primary particles can be seen clearly, with diameter of approximately 8 nm. The SAED of the powder includes diffraction rings of the (1 0 1), (0 0 4), (2 0 0) and (1 0 5) planes of the anatase phase. Fig. 3(b) shows the TEM and SAED of the titanium oxide powders, treated in 5 M NaOH. According to this image the sample that consists of flower-shape structure, was composed of curled sheet-like material. The SAED of this sample includes a set of partial circles, indicating a preferred orientation. Fig. 3(c) shows the TEM and SAED of the titanium oxide powders, treated in 10 M NaOH: the powder consists of hollow nanotubes of uniform size. The outer diameter of these tubes is around 8 nm, and their length exceeds 600 nm. The wall of each tube is about 2 nm wide. The tubes are smaller in diameter and longer than those obtained by Kasuga et al. [11] and Seo et al. [12]. Kasuga et al. obtained nanotubes about 8 nm in diameter and 100 nm long, and Seo et al. obtained tubes 15–20 nm in diameter and 150 nm long.

Fig. 4 presents the HRTEM image of titanium oxide nanotubes. It indicates that the nanotubes are well ordered and have walls of a few layers, the distance between each of which around 0.71 nm.

The TEM results are thus consistent with the SEM observation. In the SEM image, the materials look like a flower; in TEM, they look like petals of a flower when treated with

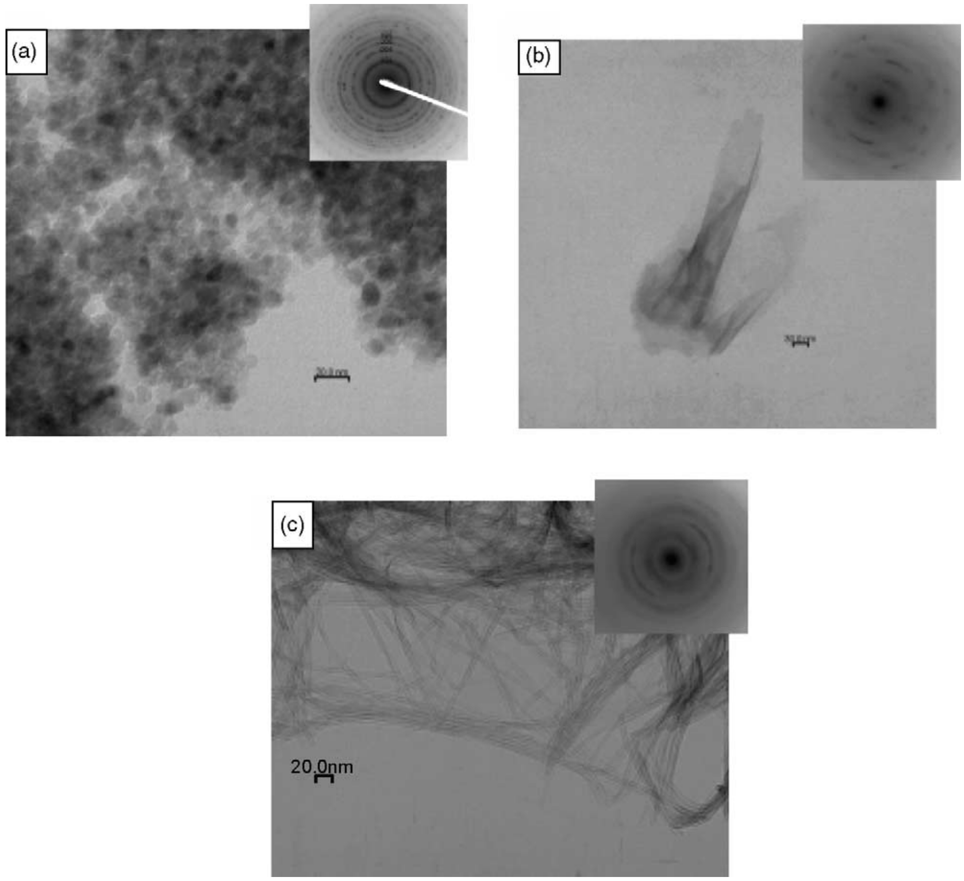


Fig. 3. TEM and SAED data of: (a) raw materials (calcined at 673 K), (b) treated by 5 M NaOH, and (c) treated by 10 M NaOH.

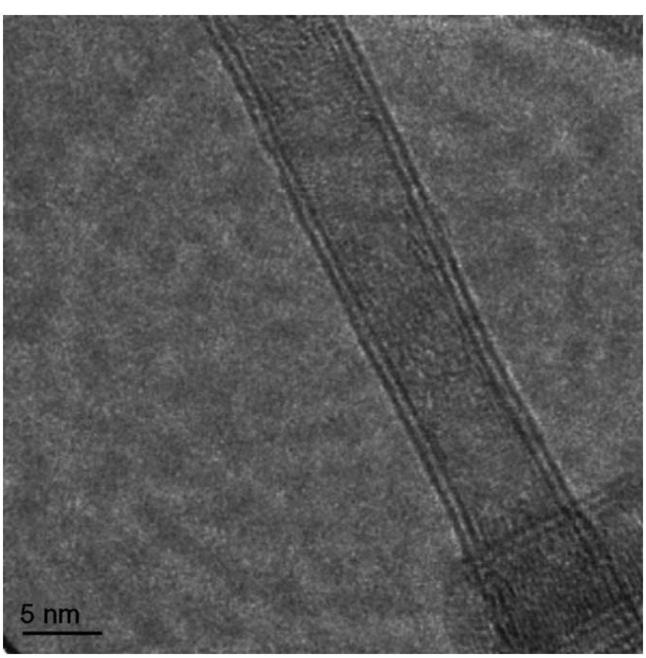
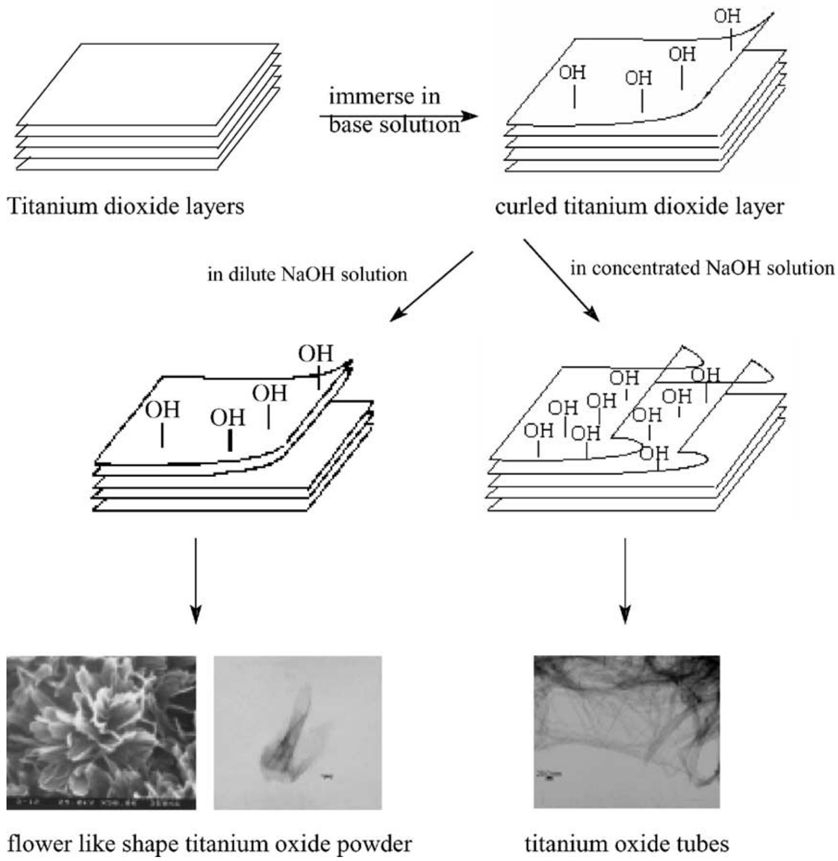


Fig. 4. HRTEM of nanotubes.

5 M NaOH. After treatment with 10 M NaOH, SEM shows a fibrous morphology and TEM shows nanotubes. The morphology of the hydrolyzed powder, calcined at 1173 K, does not change when treated with a base. These results suggest that the anatase titanium oxide, but not rutile phase material, can be morphologically altered by chemical treatment. Additionally, the concentration of NaOH strongly affects the morphological transformation of anatase titanium oxide. A particle is likely to adopt curled sheet morphology, when treated by 5 M NaOH. Increasing the concentration of NaOH to 10 M causes tubes to be formed.

The mechanism of formation of fibrous materials from the anatase titanium oxide by basic treatment is not well understood. Seo et al. [12] hypothesized that the anatase titanium oxide powders are expected to form nanotubes, because the anatase phase has a larger *c* than *a*. This work found a morphological transformation of the anatase phase under chemical treatment, but not of rutile. Dilute base treatment generates thin, curled sheet materials. According to these results, the following formation pathway is proposed (Scheme 1). At first, the anatase titanium oxide layer structure materials are assumed to be as a stack of paper. When immersed in a basic solution, the dangling bonds on the surface of the titanium oxide react with the hydroxide ions, making sheet of



Scheme 1. The formation pathway of nanotube.

titanium oxide curl. The curliness of the sheet of titanium oxide increases with the number of hydroxide ions. As the concentration of the base solution is low, the sheet of titanium oxide curled to thin curled flakes. The flakes did not complete separate, so it looks like a flower. As the concentration of the hydroxide increases, the layers separate and curl more. Titanium oxide nanotubes were thus obtained by refluxing titanium oxide powder in a 10 M NaOH solution. Details of a mechanism for formation of tubes will be elucidated in the near future. A parallel observation has been reported recently [15].

4. Conclusions

Titanium oxide powders were prepared by hydrolyzing TTIP in aqueous solutions at pH 2, using TMC and NP-204 as surfactants. The anatase phase was formed when the precipitants were dried at 373 K. When the calcination temperature was below 773 K, all the powders were crystalline in the anatase phase. The powders calcined at 673 K were spherical particles with a diameter of 8 nm. The powders transferred to the rutile phase when the calcination temperature exceeded 1173 K. Titanium oxide powders with various morphologies were obtained by chemical treatment in NaOH at various concentrations. After refluxing with 5 M NaOH, flower-like titanium oxide powders were formed. Nanotubes with a diameter of approximately 8 nm and over 600 nm long, were obtained when the concentration of NaOH was 10 M.

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