Transformation of TiO2 Film to Titanate Nanotube Thin Film Using Hydrothermal Method

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Abstract : In this study, the technology to grow oriented nanotube thin film from dip-coated TiO_2 using hydrothermal method has been successfully developed. The effects of preparation parameters, such as reaction temperature, duration and post treatment conditions on the film morphologies and the adherence to the substrate, have been examined. A general formation mechanism of oriented titanate nanotube thin film is proposed in terms of the detailed observation of the products via two dimensional surface FESEM studies and HRTEM images. The overall formation of TiO_2-based nanotube thin film can be summarized with three successive steps: (1) TiO_2 dissolving and amorphous Na_2TiO_3 deposition process; (2) layered $Na_2Ti_3O_7$ formation via spontaneous crystallization and rapid growth process; (3) formation of nanotube thin film via $Na_2Ti_3O_7$ splitting and multilayer scrolling process of (100) planes around the c axis of $Na_2Ti_3O_7$.

1. Introduction

There have been significant efforts to develop TiO_2-based nanotube(TNT), including anodic oxidation,[1] template-based approaches[2] and the wet chemical method[3] including hydrothermal technique. The hydrothermal technique is widely employed to prepare titanate nanotubes by treating the TiO_2 powder precursors inconcentrated NaOH. Most of the titanate nanotube is powder type. However, thin films and coatings of oriented nanostructures are often more desirable for applications. Tian et al. reported that hydrothermal and seeded growth method to prepare continuous films[4]. However, the thin film seems not always to be stable and will be exfoliated.

The aim of the present study is to find the effect of hydrothermal conditions. The formation mechanism of titanate nanotubes is also to be discussed in terms of the detailed observation of the products by electron microscopy.

2. Experimental Procedure

A dilute TiO_2 suspension was prepared by dispersing 1.0 g of Degussa P25 TiO_2 powder in 50 g of deionized (DI) H_2O. Titanium (99.7% pure) flake as a substrate was degreased by sonicating in acetone and ethanol, followed by rinsing with DI water. TiO_2 nanoparticles were deposited on a titanium flake through dip coating from this TiO_2 suspension at room temperature and then dried at 60℃ for 20min. All the TiO_2 films were prepared by 20 consecutive drain-coating processes, resulting approximately in 8×10^{-2} mg/cm^2 of TiO_2. The Ti flake containing TiO_2 thin films was then reacted with 10 M NaOH solution in an autoclave reactor. The reaction temperature ranged was 110-150 ℃. After the reaction, the Ti flake, covered with the newly formed film, were soaked and washed with DI H_2O by a pH-decreasing treatment process, and then dried in air.

Characterization of these thin films was carried out using scanning electron microscopy (SEM, Hitachi S-4700) with energy dispersive x-ray spectroscopy and powder x-ray diffraction (Simens-D50050D).

3. Results and Discussion

In the present work, the morphology evolution of hydrothermal treatment of Ti flake with P25 coated at 110 ℃-150 ℃ is displayed in Figure 1.

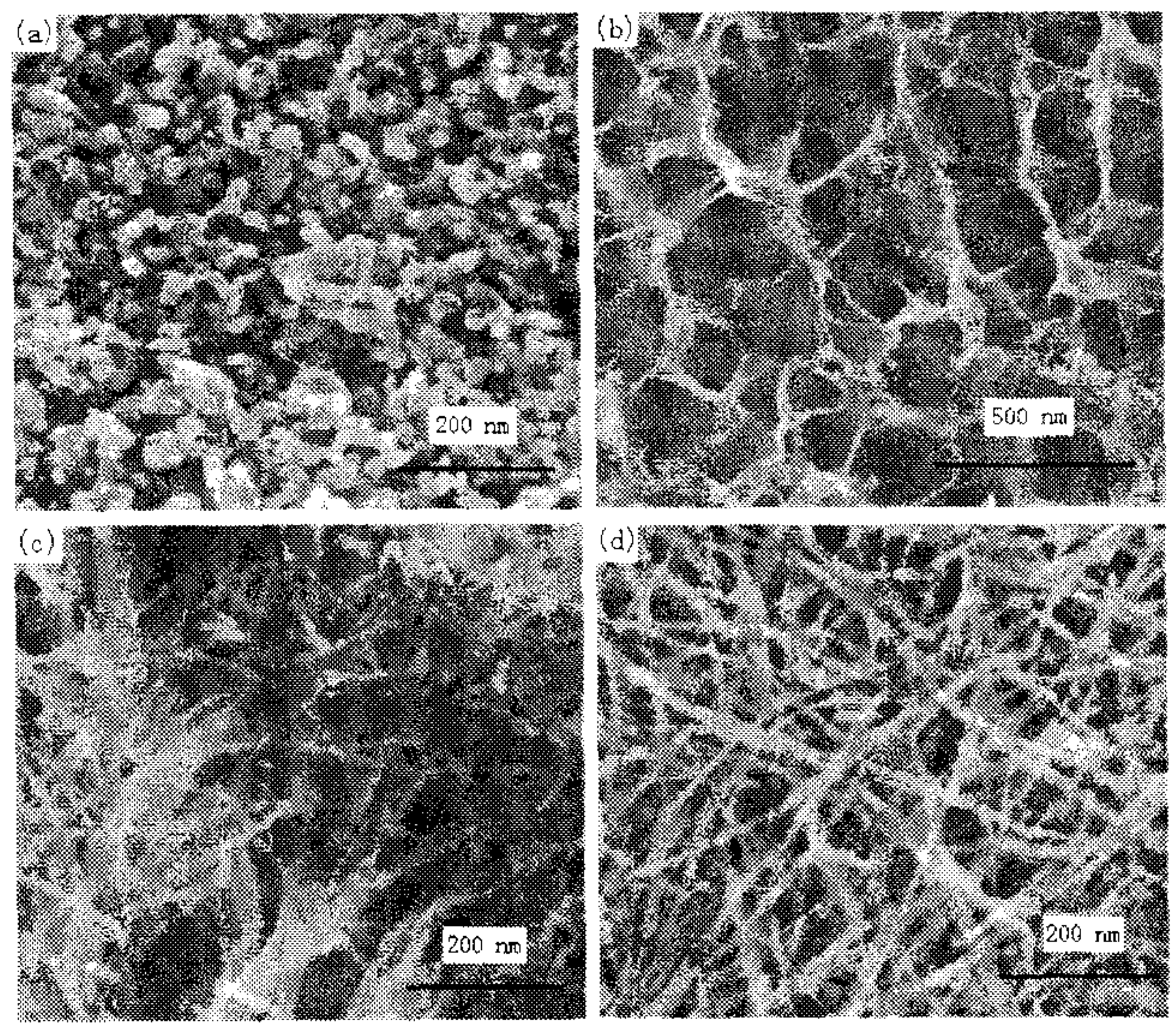

Figure 1. FESEM micrographs of (a) Ti flake with P25 deposited, (b) 110 ℃ for 3 h, (c) 130℃ for 9 h, and (d) 150 ℃ for 6 h.

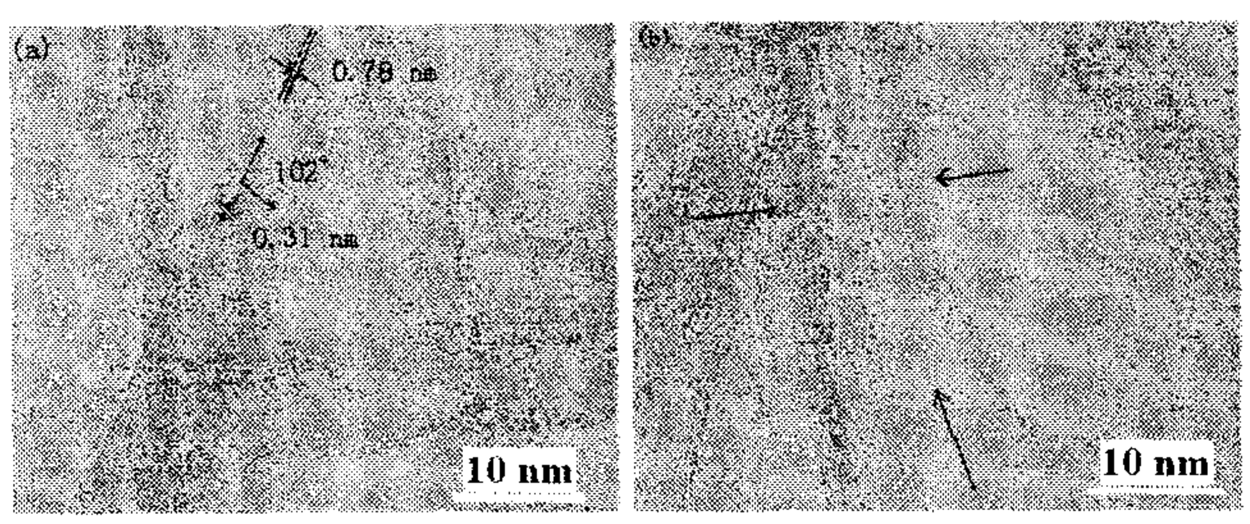

Figure 2. HRTEM images of the nanotubes obtained from hydrothermal treatment at 140 ℃ for 12 h, (a) the asymmetric number of layers at the two sides, and (b) splitting nanotube crystalline sheets.

Typical HRTEM images of the nanotube are shown in Figure 2. All the multi-walled nanotubes are open at both ends and multilayered. The wall thickness of the tube is asymmetric (Figure 2(b)), indicating that the tubes may probably be formed by scrolling a multilayer nanosheet. The interlayer spacing is about 0.78 nm, and these HRTEM results were similar to those reported by Chen and Wu et al.,[5] who suggested a $H_2Ti_3O_7$ structure (monoclinic, C2/m, a = 1.603, b = 0.375, c = 0.919 nm, = 101.47°). It was observed that split nanotube were formed by splitting $H_2Ti_3O_7$ crystalline sheets between (010) planes, as evidenced in Figure 2(b) as indicated by the arrow that point to the split. The proposed sequence of events for the formation processes is depicted in Figure 3.

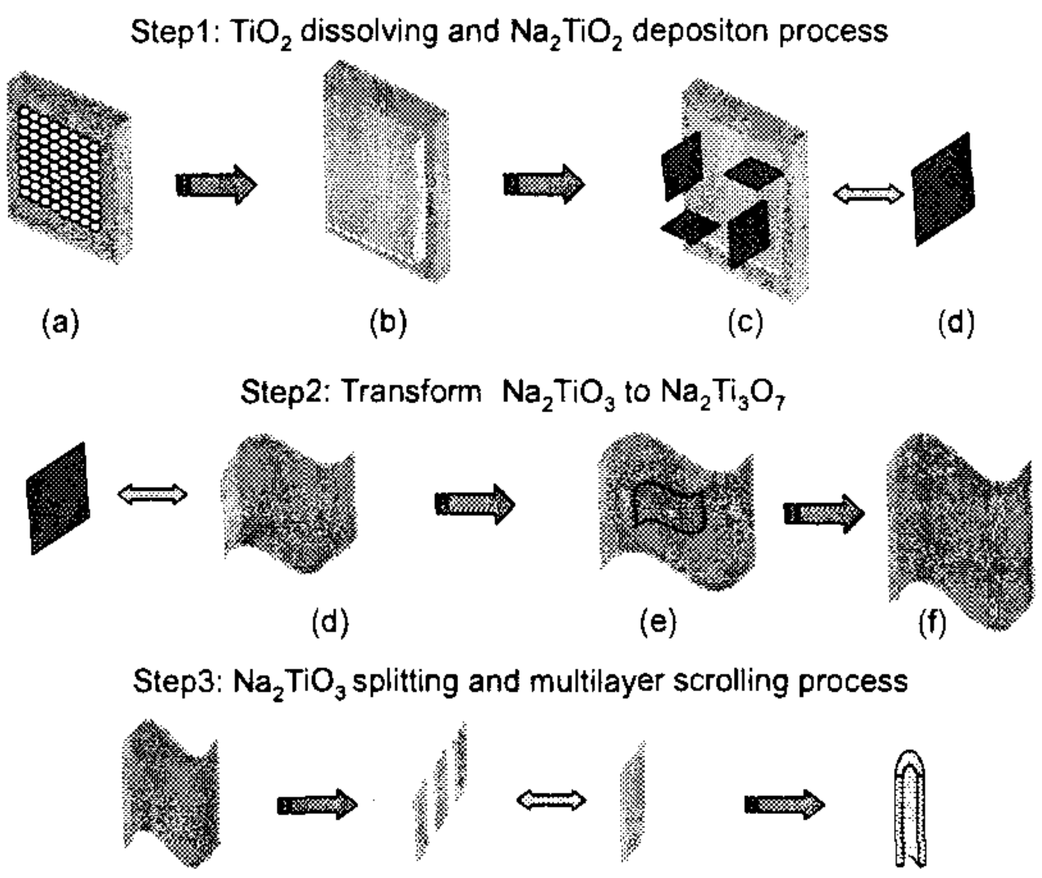

Figure 3. Schematic drawing depicting the trititante nanotube thin films formation process.

Energy dispersive X-ray spectroscopy (EDX) studies show that Ti, Na and O are present in the nanotubes films. In the sample after treatment with 0.1 M HCl for 24 h, only Ti and O are present. $H_2Ti_3O_7$ is generally proposed to appear in the washing process due to proton exchange of sodium trititanate ($Na_2Ti_3O_7$) formed during autoclaving. So this novel structure of H-titanate nanotubes may provide a very promising channel for lithium ion intercalation and release reversibly. In addition, it is expected that a new type of titanate nanotube films having new properties will be formed by controlling the amount of residual Na^+ ions and by replacing residual Na^+ ions with other ions.

3. Conclusions

The fixed titanate nanotubes films were successfully obtained directly from titania using dip-coating and hydrothermal method. A pH-decreasing post-treatments can prevent exfoliation of the thin film. A universal formation mechanism is proposed: (1) TiO_2 dissolving and amorphous Na_2TiO_3 deposition; (2) layered $Na_2Ti_3O_7$ crystallization and rapid growth; (3) $Na_2Ti_3O_7$ splitting, scrolling and titanate nanotubes formation. The $Na_2Ti_3O_7$ lamella structures split between (010) planes into nanosheets. The nanotubes were confirmed as a result of mutilayer nanosheets of (100) planes scrolling around the c axis of $Na_2Ti_3O_7$.

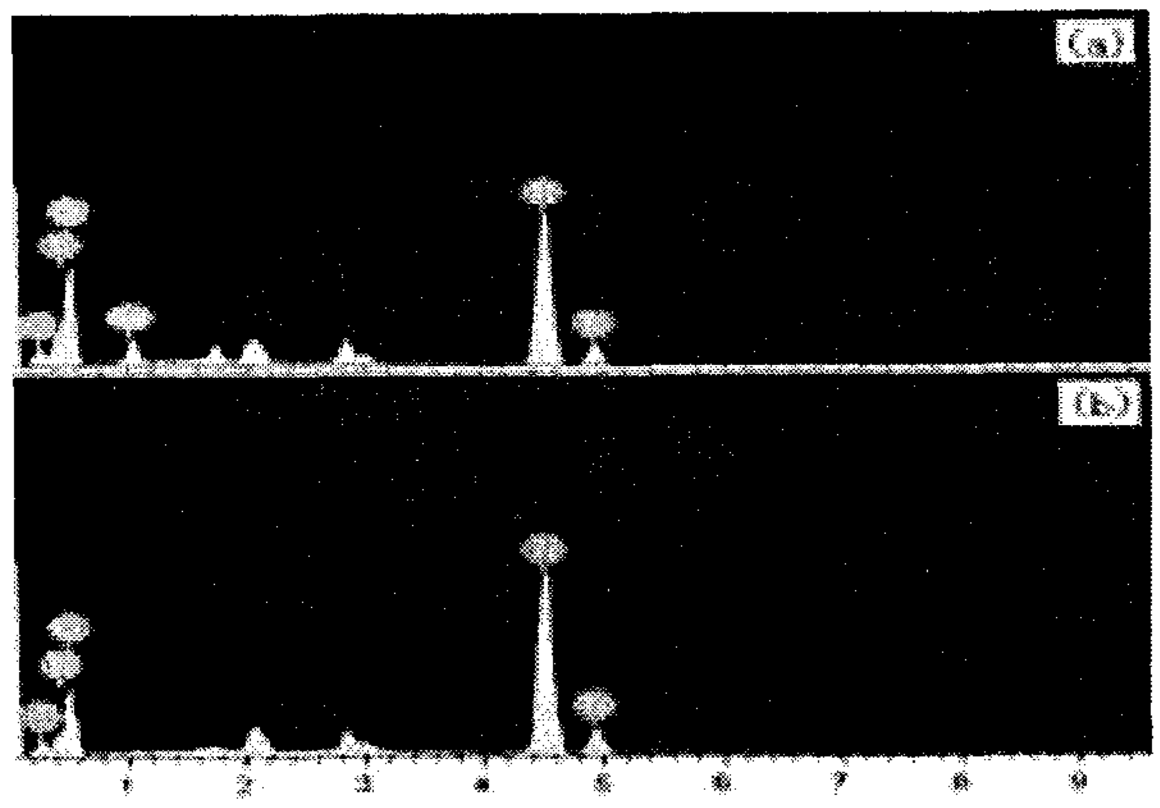

Figure 4. EDX spectra obtained from film (140℃,12 h)washed with (a) only DI water, and (b) HCl for 24 h at 25℃.

Acknowledgements

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