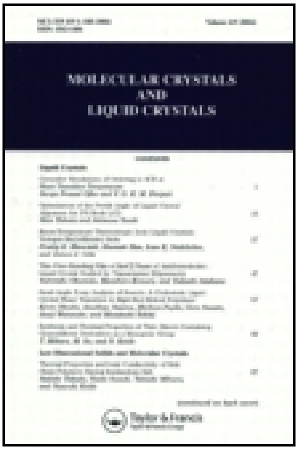

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Nanodiffraction and Characterization of Titanate Nanotube Prepared by Hydrothermal Method

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Nanodiffraction and Characterization of Titanate Nanotube Prepared by Hydrothermal Method

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Titanate nanotubes were synthesized by simple hydrothermal treatment of TiO_2 anatase powders. Their crystal structure was conclusively determined by TEM observation, especially by nanodiffraction mode. As a result, the nanotube has lepidocrocite-type titanate based structure.

Keywords: nanodiffraction; nanotube; TEM; TiO_2; titanate

INTRODUCTION

Titanate nanotubes have been of great interest recently due to their potential application to dye sensitized solar cells, gas sensors and photocatalysts. Though the nanotubes are widely believed to be formed by rolling up sheet-like precursors, their detailed formation mechanism and crystal structure have been still under discussion.

Kasuga *et al*. and some other researchers considered that the nanotubes had the anatase structure of titania [1–3], but Chen *et al*. pointed out that they were based on the trititanate $H_2Ti_3O_7$ structure rather than anatase [4–7]. On the other hand, Ma *et al*. proposed the lepidocrocite layered structure $H_xTi_{2-x/4}(\text{vacancy})_{x/4}O_4$ $(x \sim 0.7)$ [8,11]. And most recently, Yang *et al*. proposed the $Na_{2-x}H_xTi_2O_4(OH)_2$ structure model [9,10].

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The problem is that none of these reports has a conclusive answer to the crystal structure of the nanotubes. Most of their discussions are based on macro/micro-scopic analyses such as XRD or SAED, but the measured samples usually contain considerable numbers of co-products or impurities. For that reason, it is necessary to examine the samples from much smaller area. We carefully investigate the local structure of a single nanotube as well as its co-product by using electron nanodiffraction technique.

EXPERIMENTAL CONDITIONS

Our synthesis procedure of nanotubes was the same as previous works [1–10]. The acid treatment was not always necessary for the formation of nanotubes as indicated by Du *et al*. [4].

All experiments were performed by using a transmission electron microscope, JEOL JEM-2200FS (200 kV) equipped with a field-emission gun and Gatan 2k × 2k CCD camera (UltraScan 1000). Especially in nanodiffraction mode, we used the smallest condenser aperture of 10 μm in diameter and focused the electron beam at the front of the focal plane of the objective pre-field. Even under such a condition, we could get a nearly parallel beam of 1∼40 nm in diameter and the diffraction pattern could be interpreted straightforwardly, like selected-area diffraction patterns [13,14]. Though this technique has not been widely used, it offers intuitive ease of use in the study of nanostructures.

RESULTS AND DISCUSSIONS

Figure 1 is a typical TEM image of the nanotubes observed at low (a) and high (b) magnification. There are many sheet-like co-products

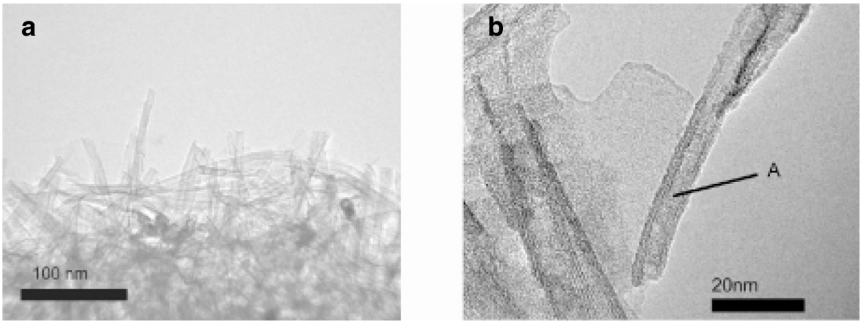

FIGURE 1 Typical TEM images of titanate nanotubes and their sheet-like co-products observed at low (a) and high (b) magnification.

together with nanotubes. These images have the same features as described in the previous papers [1–10].

Figure 2a and 2b are the nanodiffraction patterns from the center of a nanotube and from a sheet-like co-product, respectively. The probe size of the incident beam was about 2∼4 nm in diameter. Obviously the same face-centered rectangular patterns are observed in both patterns, which ensures that the sheet-like co-product is the intermediate of the nanotube.

But the most important point is that these patterns are inconsistent with the anatase model [1–3] or the trititanate model [4–7] ($H_2Ti_3O_7$; a = 1.603, b = 0.375, c = 0.919 nm, monoclinic). Either of these structures dose not show any face-centered rectangular diffraction patterns.

On the other hand, the lepidocrocite-type titanate model [8] (Fig. 3a; a = 0.372, b = 1.602, c = 0.303 nm) and the $Na_{2-x}H_xTi_2O_4(OH)_2$ model [9,10] (in case of x = 0, a = 1.926, b = 0.378, c = 0.300 nm) are acceptable because they have the orthorhombic crystal structure that can show face-centered rectangular patterns. In addition, their lattice plane distances, assumed in both models, are almost closed to those determined from the diffraction patterns.

However, in terms of the diffraction geometry, the $Na_{2-x}H_x Ti_2O_4(OH)_2$ model dose not agree well to the experimental results in Figure 2. In the model, if the incident beam enters along the b-axis of the unit cell, which is perpendicular to the sheet-like structure, the a* and c*-axes will appear in the diffraction plane. But this does not agree with the experimental results in Figure 2. On the other

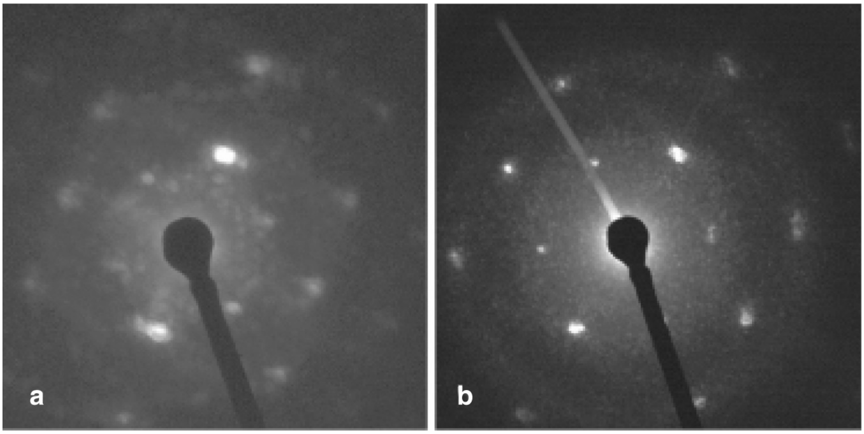

FIGURE 2 Nanodiffraction patterns from the center (the point indicated as A in Fig. 1b) of a nanotube (a) and from a sheet-like co-product (b).

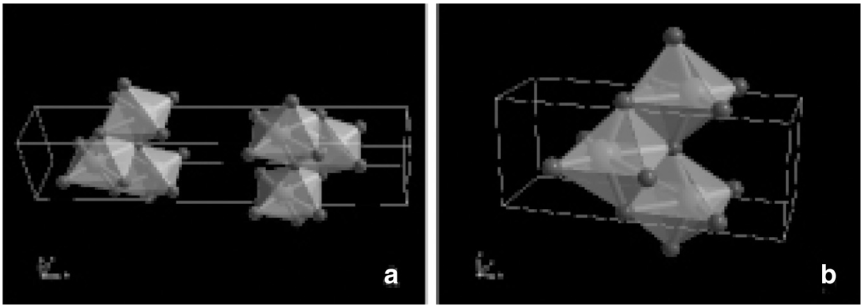

FIGURE 3 The unit cell of lepidocrocite-type titanate unit cell [11] (a) and our modified structure (b) Each sheet plane of lepidocrocite titanate is exfoliated independently and formed a half-length unit cell.

hand, Figure 2a and 2b is quite explainable as the a^*-c^* plane of the lepidocrocite-type titanate, which corresponds to the normal incidence to the sheet-like structure. This is most acceptable among the four reported models. Although the lepidocrocite-type structure consists of the double layers stacked along b-axis as shown in Figure 3a, we propose a modified structure with single layer in a-c plane (Fig. 3b, $b = 0.801\,\text{nm}$) because of the extinction rule explained later. We assumed that the nanotubes are formed by exfoliating and rolling up each sheet plane of lepidocrocite-type titanate without any correlation between adjacent layers.

As mentioned by Ma *et al.*, it still remains uncertain why the lepidocrocite sheets and nanotubes are formed in a Na-rich environment. Generally, $Na_2Ti_3O_7$ [12] is supposed to be stabilized in such conditions. It may occur that some Na ions substitute for H ions composing the nanotubes in alkali conditions. But we believe that the basic crystal structure is already retained before the acid treatment because almost the same diffraction patterns were found before and after the treatment.

To observe the change of the diffraction pattern in the different small area, we focused an electron probe as small as 1 nm in diameter and moved it across the nanotube (Fig. 4a). Figure 4b and 4d were taken from the center and the side of a single nanotube, respectively. Figure 4c was taken from between them. As mentioned above, the face-centered rectangular patterns can be clearly identified from the center of a nanotube (Fig. 4b) but the diffraction patterns deviated from the center of the nanotube show different features.

By assuming our model described previously, the diffraction patterns are simulated along three different incident electron directions. The

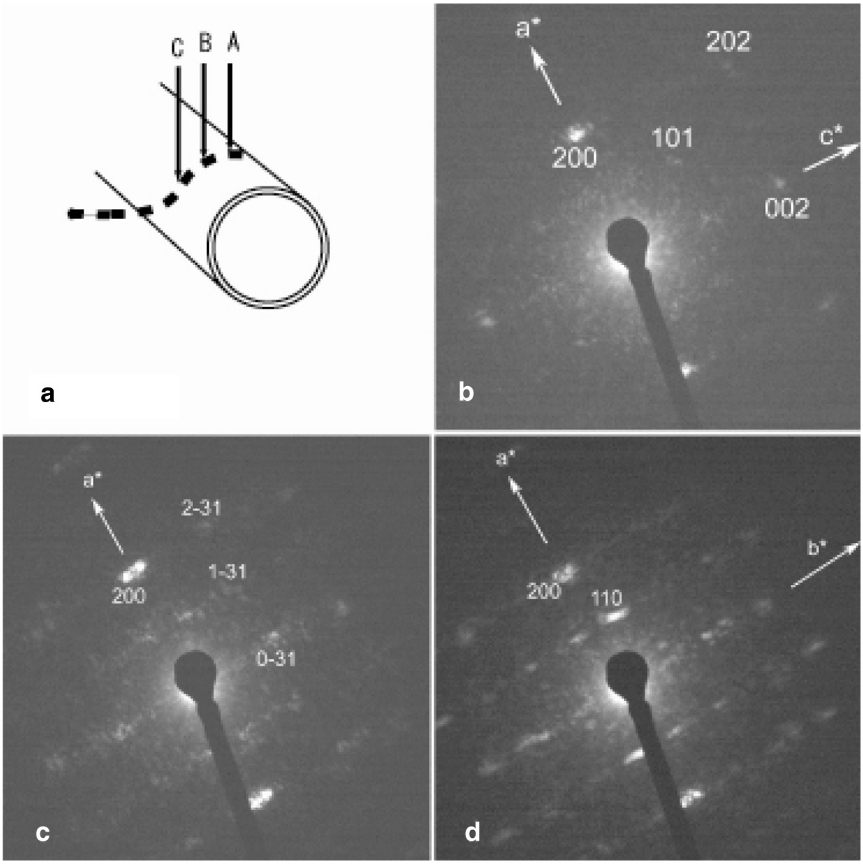

FIGURE 4 (a) The incident electron beam was moved across the nanotubes from the center (indicated as A) to the side (indicated as C) of one nanotube. The point indicated as B is between the center and the side of the nanotube. The change of the nanodiffraction pattern obtained as shown in (b) from the center, (c) from the middle and (d) from the left side of a single nanotube.

simulated pattern along [010] zone axis reproduces the observed pattern at the center of the nanotube (Fig. 4b). It should be noted that the 101 spot was observed in Figure 4b, which should be forbidden if the the lepidocrocite-type structure with double layers (Fig. 3a) was assumed. This is a reason why we proposed the single layer model (Fig. 3b) as mentioned above. In the same way, the simulated pattern along [001] zone axis is well consistent with the observed pattern at the side of the nanotube (Fig. 4d). Furthermore, several spots observed in Figure 4c can be indexed as the simulated patterns along [013] incident direction.

Hence, it is concluded that nanotubes are formed by rolling up the titanate nanosheet based on lepidocrocite-type structure along [100] zone axis.

In addition, Figures 2a and 4b indicate that titanate nanotubes do not have any helicity. If the nanotube had the helicity like many carbon nanotubes, diffraction patterns from the center of the nanotube would be the superposition of patterns rotating around the (000) spot [15,16].

Finally, we show a diffraction pattern from the whole nanotube with an electron probe of about 40 nm in diameter (Fig. 5). This pattern can be understood to be the superposition of a series of diffraction patterns obtained by tilting the incident electron beam from normal to parallel to the lepidocrocite sheet plane of Figure 3b.

The intensities of each spot were also calculated via simple kinematical method, where atomic scattering factors were derived from a relativistic Hartree-Fock atomic wave function calculation [17]. Qualitatively, relative intensities, such as 200, 002, 202, 110 and 120 are in good agreement with the experimental results in Figure 5. The streak-like features appearing especially around 110 or 120 spots in Figure 5

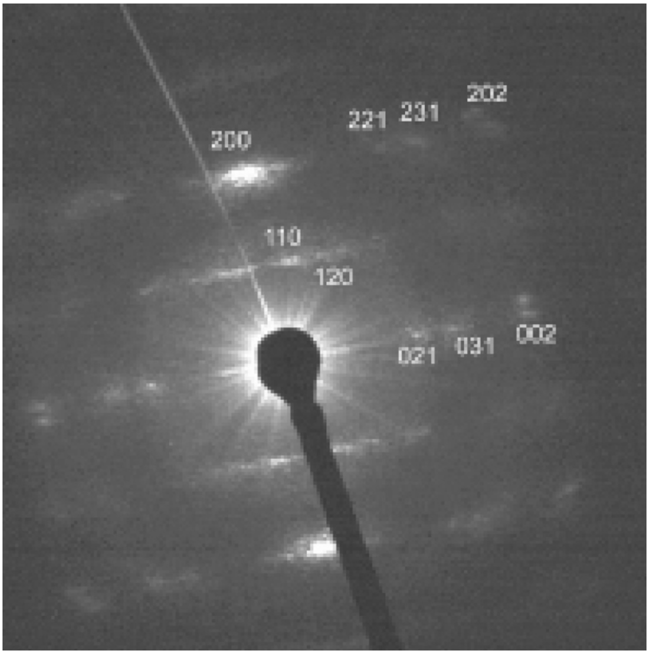

FIGURE 5 A diffraction pattern from the whole nanotube.

is arguably caused by the curvature effect of the nanotubes. This is commonly seen in the observation of carbon nanotubes.

CONCLUSION

Our detailed local observations via electron nanodiffraction strongly suggest that the nanotubes are formed by rolling up the exfoliated lepidocrocite-type titanate sheet along the [100] direction without helicity.

There still exists some ambiguity about the presence of Na ions related to the pH condition. To confirm it, we are planning to perform precise EELS analysis of nanoarea before and after the acid treatment.

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