Reconstruction of Lepidocrocite Nanosheets into Anatase TiO_2 by Rolling in Low Temperature

Fumin Wang,[†,††] Jinting Jiu,[††] Lihua Pei,[††] Keizo Nakagawa,[††] Seiji Isoda,[†††] and Motonari Adachi*[††]
[†]*School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China*
[††]*Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011*
[†††]*Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011*

(Received June 2, 2005; CL-050717)

Highly crystallized anatase nanotubes and nanorods were prepared by rolling of molecular nanosheets, i.e., lepidocrocite, by surfactant-assisted hydrothermal method in low temperature (413 K). Alcohol played an important role for deintercalation of the surfactant between lepidocrocite nanosheets. Morphology of nanoscale anatase TiO_2 materials was controlled by choosing pH and composition.

Among the oxide nanotubes, single-crystalline TiO_2 nanotube is one of the most investigated oxide materials because of its facile electron-transfer properties and potential in electronic applications.[1] Although polycrystalline titania tubules have been successfully synthesized by anodic aluminum oxide method[2–4] and also soft template method,[5] the synthesis of single-crystalline TiO_2 nanotube is still a big challenge.[6] There are some previous reports on the synthesis of titanium oxide or trititanate ($H_2Ti_3O_7$) nanotubes in hydrothermal or sonochemical treatments of TiO_2 nanoparticles in concentrated NaOH solution, but crystal structure and composites of titanium oxide made in these methods are still disputable and could not be indexed to anatase phase.[7–10] In our previous work,[11] by using triethanolamine (TEOA) as a stabilizer of Ti(IV) ion against hydrolysis and dodecanediamine (DDA) as the surfactant to form lamella phase, we have successfully synthesized molecular lepidocrocite nanosheet of titanium oxide by hydrolyzing titanium isopropoxide (TIPT) in hydrothermal solution. If the interlayer interaction of this kind of lamellar could be diminished from the edges under certain conditions, rolling of the layers into tubules should be expected. Sasaki et al. reported the rolling process from 2D lepidocrocite titanium oxide nanosheet into 1D nanotube in 2004,[12,13] but the yield is very low, and the process is complicated and time-consuming. Moreover, according to Fukuda et al.,[14] a very high temperature is usually needed for reconstruction of lepidocrocite nanosheets into anatase. In this paper, we report a simple route for anatase nanotube and nanorod formation in very high yield. The anatase was reconstructed from lepidocrocite nanosheets in relatively lower temperature (413 K).

The process for lepidocrocite nanosheet formation has been illustrated very well in our previous work and the nanosheet structure of the sample has been testified by transmission electron microscopy (TEM), selected-area electron diffraction (SAED), X-ray diffraction (XRD), and UV–vis spectra analysis.[11] The typical TEM images of the sample were shown in Figure 1A. The SAED patterns of the samples (inset in Figure 1A) were composed of a series of diffraction rings. The spacings for rings are 0.38, 0.24, 0.19, 0.15, and 0.12 nm, respectively, which corresponds to the indices of 10, 11, 20, 02, and 22 for the two-dimensional unit cell ($0.38 \times 0.30\,nm^2$) of nanosheet structure very well.

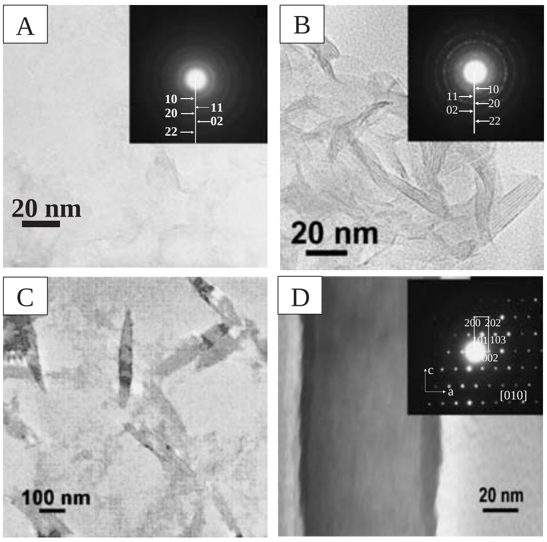

Figure 1. TEM images of the samples, (A) nanosheets structure, inset: SAED patterns; (B) sample A post-treated in water for another 24 h, inset: SAED patterns; (C) sample A post-treated in alcohol for another 24 h; (D) HRTEM image for the needle-like structure in Figure C, inset: SAED patterns.

We divided the nanosheets sample into two parts, subjecting one part to hydrothermal treatment in water for more 24 h at 413 K and another part to solvothermal treatment in ethyl alcohol for the same period at the same temperature. The sample post-treated in hydrothermal solution kept the multisheet structure, and the crystallinity of the molecular nanosheet was improved (Figure 1B), indicating that the post-treatment in water increased the crystallinity of the molecular nanosheet. From the TEM image it can be seen very clearly that the nanosheets prepared in our method prefers to present as multisheet structure.

On the other hand, the sample post-treated in ethanol solution showed a completely different result, most of the multisheets have rolled into needle-like structure (Figure 1C). It can be clearly seen that the needle-like structure results from the rolled sheet. The contrast of the light-colored center and the black edges of the formed needle-like structure shown in the HRTEM image (Figure 1D) suggests that the nanoneedle is hollow. The SAED patterns inset in Figure 1D indicated its single crystalline nature and can be indexed to anatase phase. The molecular nanosheet structure has reconstructed into anatase nanotube in alcohol solution. The reconstruction process occurred simultaneously with the rolling. In the case of without rolling, the multisheet structure was preserved without reconstruction. Another conclusion we can get is that alcohol plays an important role in the rolling of nanosheets.

The formation of 1D nanotubes from the 2D nanosheets may be explained as follows. Under high pH values of 12.8, the DDA shows high hydrophobicity, which makes the rigid lamellar structure by strong hydrophobic interaction between DDA molecules and also by interaction between Ti–OH group and DDA. The condensation reaction of Ti–OH forming Ti–O–Ti bonding in the layered two-dimensional space makes the molecular nanosheet structure under suitable conditions (suitable ratio of TIPT to DDA and pH values). The DDA molecules sandwiched by two TiO_2 nanosheets played a role in pinning the adjacent sheets. The alcohol has higher solubility to DDA than water and acts the role of deintercalation agent for DDA. After the DDA was removed from the gap between adjacent nanosheets, the electrostatic interaction between neighboring sheets was thus significantly reduced. Under hydrothermal or solvothermal condition, the free nanosheet prefers to be folded owing to the high surface area of the nanosheet. If some particular optimum geometrical requirement is fulfilled, nanotube formation takes place. During the rolling, the condensation reaction between the liberated Ti–OH groups may occur, and the nanosheets reconstruct into anatase.

The alcohol generated from the hydrolysis of TIPT can also play the role of deintercalation agent for DDA. In this case, the fact that the sample kept the multisheet structure without rolling is due to the low ratio of TIPT to DDA (refered as $R = [\mathrm{TIPT}]/[\mathrm{DDA}]$ in this paper), which means that the concentration of alcohol is not high enough for deintercalation of DDA. The experiments were done again in the same condition with the nanosheet preparation only the ratio of TIPT to DDA was rejusted into 5 instead of 2.5. The SEM images of the sample prepared in this case were shown in Figure 2A. Under this condition, the sample shows nanotubes and nanorods structure clearly and are orderly aligned as a flower-like aggregates. Figure 2A also shows a single tube and a half-closed nanotube indicating that the TiO_2 nanotubes were also formed from the rolled sheet structure. In order to elucidate the formation mechanism of titania nanotube, the time-dependant experiment was done. The SEM images of the sample at different hydrothermal time (which were provided in Supporting Information) showed the formation process of the nanotubes and nanorods, in which we can clearly see that the sheets formed first and then rolled into the nanotubes or nanorods in very high yield (more than 90%) at the end. The XRD patterns of the sample (as shown in Figure 3) show the high purity of anatase of this sample. Typical TEM images of the sample in the process for nanotube formation in this case are shown in Figure 2B. Figure 2B showed the rolling sheets were forming into the nanotube. From this image it was concluded that the anatase TiO_2 nanotubes and nanorods were formed from the rolled sheets.

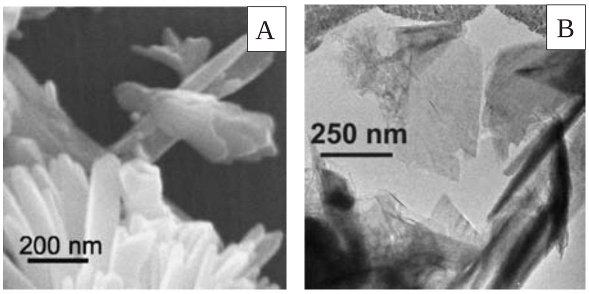

Figure 2. A: SEM image of the prepared sample under $R = 5$; B: TEM images of the samples during the process for nanotube formation under $R = 5$.

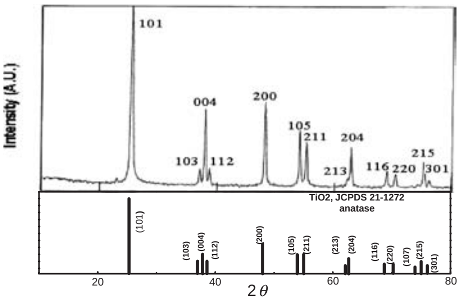

Figure 3. XRD patterns of TiO_2 nanotube at $R = 5$.

The above experimental results show that the interaction between DDA and Ti–OH is necessary for the formation and existence of the lepidocrocite nanosheet. Without DDA and after the DDA was removed from the gap between adjacent sheet, the multisheet structure can not exist steadily and form anatase in hydrothermal or solvothermal solution, which may be a more stable structure under this condition. The lower reconstruction temperature is due to the rolling process. By rolling, the liberated Ti–OH groups in one sheet owing deintercalation of DDA reacted with each other and formed Ti–O–Ti. The lepidocrocite nanosheet structure was reconstructed into anatase. The condensation reaction between the adjacent liberated Ti–OH groups in one sheet is much easier than that between those in two adjacent sheets. Through the rolling process, the anatase nanotubes or nanorods are very easily formed from the reconstruction of nanosheets in high yield and in low temperature.

References

1 T. Cassagneau, J. H. Fendler, S. A. Johnson, and T. E. Mallouk, *Adv. Mater.*, **12**, 1363 (2000).
2 P. Hoyer, *Langmuir*, **12**, 1411 (1996).
3 A. Michailowski, D. AlMawlawi, G. Cheng, and M. Moskovits, *Chem. Phys. Lett.*, **349**, 1 (2001).
4 H. Imai, Y. Takei, K. Shimizu, M. Matsuda, and H. Hirashima, *J. Mater. Chem.*, **9**, 2971 (1999).
5 T. Peng, A. Hasagawa, J. Qiu, and K. Hirao, *Chem. Mater.*, **15**, 2011 (2003).
6 S. M. Liu, L. M. Gan, L. H. Liu, W. D. Zhang, and H. C. Zeng, *Chem. Mater.*, **14**, 1391 (2002).
7 T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, *Adv. Mater.*, **116**, 137 (1999).
8 Y. C. Zhu, H. L. Li, Y. R. Koltypin, Y. R. Hacohen, and A. Gedanken, *Chem. Commun.*, **2001**, 2616.
9 Q. Chen, G. H. Du, S. Zhang, and L. M. Peng, *Acta Crystallogr.*, **B58**, 587 (2002).
10 R. Ma, Y. Bando, and T. Sasaki, *Chem. Phys. Lett.*, **380**, 577 (2003).
11 F. Wang, J. Jiu, L. Pei, K. Nakagawa, S. Isoda, and M. Adachi, *Chem. Lett.*, **34**, 418 (2005).
12 T. Sasaki, M. Watanabe, H. Hashizume, and H. Yamada, *J. Am. Chem. Soc.*, **118**, 8329 (1996).
13 R. Ma, Y. Bando, and T. Sasaki, *J. Phys. Chem. B*, **108**, 2115 (2004).
14 K. Fukuda, T. Sasaki, M. Watanabe, I. Nakai, K. Inaba, and K. Omote, *Cryst. Growth Des.*, **3**, 281 (2003).