FORMATION OF SINGLE CRYSTALLINE ANATASE TITANIA NANOTUBES

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We succeeded in the formation of silica nanotubes in laurylamine hydrochloricde (LAHC) / tetraethoxysilane (TEOS) system [1,2], and extended the method to synthesize titania nanotubes (TiNTs) using LAHC/ tetraisopropylorthotitanate (TIPT) modified with acetylicetone (ACA) system [3]. In this paper, we present the effect of operating parameters for synthesis of TiNTs in detail and show how to make long TiNTs with single crystalline anatase structure.

The experimental procedure has been descryibed in the previous paper [3]. The reactions in the mixture of LAHC aqueous solution and TIPT modified with ACA proceeded as follows. When these two solution were mixed, precipitates were formed immediately. This precipitates had an amorphous atructure which was confirmed by X-ray diffraction (XRD). After stirring at 313 K for three days, the solution became transparent. Turning to the transparent solution means that the precipitates were divided into small materials, which were smaller than the wavelength of light. Small angle X-ray scattering (SAXS) showed that short cylindrical micelles were formed already in this stage and became longer after the reaction temperature was changed to 353 K.

TEM image of titania nanotubes in the gel sample is shown in Figure 1. We can see a nanotubes with diameter 10 nm and length 200 nm. Also we can see a lot of short nanotubes with about 30 nm length. SAXS results indicates that these short nanotubes are predominant. The electron diffraction image of these TiNTs showed clear Debye-Scherrer rings of anatase rystalline structure.

XRD pattern was measured for the samples taken out at 2 h, 8 h, and 3 days after temperature change. These samples were dried at room temperature in order to prevent the proceeding of condensation reactions. The sample taken out at 2 h showed an almost amorphous structure. 8 h sample showed weak anatase peaks, which became shape for the sample taken out at 3 days. These results indicated that crystallization to anatase structure proceeded gradually in the solution of 353 K.

The effect of calcinations temperature and period was examined by observation of TEM images. Figure 2 shows a TEM image for the sample calcined at 773 K for 24 h. Many long nanotubes with length 200-600 nm were observed. High resoluteion TEM image of the nanotubes is shown in Figure 3. The lattice image was observed along the tubular axis. The spacing of this lattice image was calculated as 0.35 nm, which agreed with 101-spacing of anatase crystal. These TEM observation results showed that we can made a lot of long nanotubes with single crystalline anatase structure by calcinations at 773 K for 24 h.

Reference

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[2]M.Adachi, T.Harada, M.Harada, *Langmuir*, **16**, 2376-2384 (2000)
[3]M.Adachi, Y.Murata, M.Harada, S.Yoshikawa, *Chem.Lett.*, 942-943 (2000)

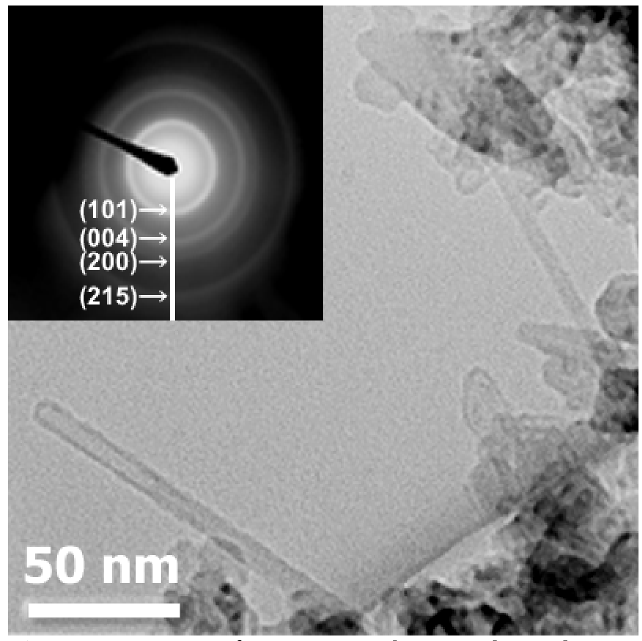

Fig 1. TEM image of titania nanotubes in gel sample. Inset: Electron diffraction of titania nanotubes.

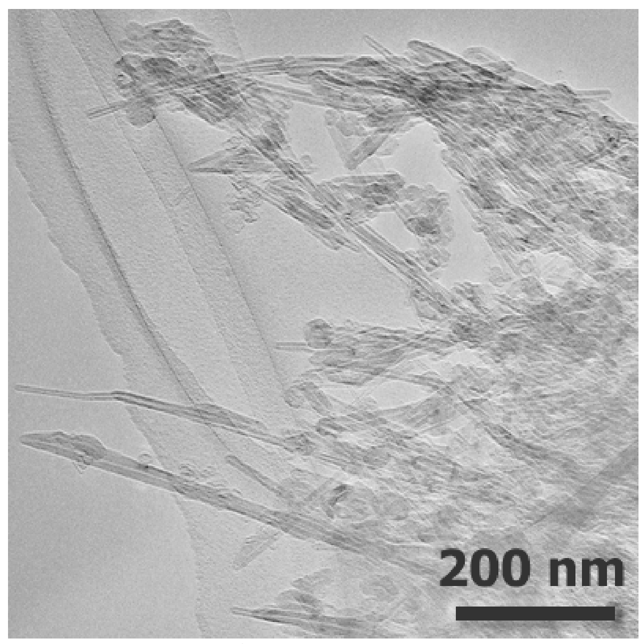

Fig 2. TEM image of titanium oxide nanotubes calcined at 773 K for 24 h.

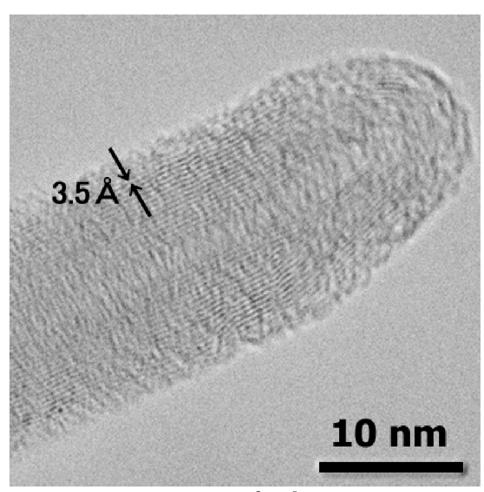

Fig 3. HRTEM image of the structure with the mono-crystalline nanotube wall. The tube tip is closed. The spacing of lattice image was determined as about 3.5 Å, and corresponds to 101-spacing of anatase crystalline structure.