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Study of titanate nanotubes by X-ray and electron diffraction and electron microscopy

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ABSTRACT

The structure of titanate nanotubes (Ti-NTs) was studied by a combination of powder X-ray diffraction (PXRD), electron diffraction and high resolution transmission electron microscopy (HRTEM). Ti-NTs are prepared by hydrothermal treatment of TiO_2 powder. The structure is identified by powder X-ray diffraction as the one based on the structure of $H_2Ti_2O_5{\cdot}H_2O$ phase. The same structure is obtained by projected potential from HRTEM through-focus image series. The structure is verified by simulated PXRD pattern with the aid of the Debye formula. The validity of the model is tested by computing Fourier transformation of a single nanotube which is proportional to measured electron diffraction intensities. A good agreement of this calculation with measured precession electron diffraction data is achieved.

1. Introduction

Recently, high interest has been given to titanate (titania) nanotubes (Ti-TNs) in particular, due to their potential use in different applications. Ti-NTs can be used in many applications where TiO_2 powders are utilized nowadays. However, the advantage of utilizing Ti-NTs is mainly due to their elongated structure assisting the electron transport. Bavykin and Walsh [1] discussed their possible uses in dye sensitive solar cells, lithium batteries, photocatalysis, magnetic materials, hydrogen storage or covering orthopedic or dental implants.

Unfortunately, the structure of Ti-NTs has not been clearly understood yet. An inexpensive method of preparation of Ti-NTs was described by Kasuga [2]. The preparation is based on a hydrothermal treatment of TiO_2 powder with NaOH. That publication initiated quite a huge interest on Ti-NTs and also the discussion about their structure. Kasuga [2] reported the structure of Ti-NTs as the one of anatase. Other structures based on TiO_2 phases were reported by Deng [3] as brookite structure and by Armstrong [4] as beta TiO_2 phase. On the other hand, Chen [5] showed that the structure of Ti-NTs could possibly be assigned as $H_2Ti_3O_7$. The tubular structure could not be obtained by just replacing NaOH by LiOH or KOH in the synthesis. The authors [5] removed Na ions from the structure by washing it in H_2O. Another reported structure of Ti-NTs was $H_2Ti_2O_5{\cdot}H_2O$, by Chen [6]. The authors studied the necessary time for obtaining Ti-NTs. The final tubular structure was obtained after 20 h of reaction time and the resulting Ti-NTs had a multiwall structure with four walls. The structure of Ti-NTs was related to the one of $Na_2Ti_2O_5{\cdot}H_2O$ and it

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was possible to remove Na ions [7]. Nakahira [8] suggested that the possible structure of Ti-NTs was $H_2Ti_4O_9{\cdot}H_2O$. The authors studied the influence of the structure of TiO_2 initial powder on the structure of Ti-NTs. They used different initial powders: anatase TiO_2 powder, a mixture of anatase and rutile TiO_2 powder (3:1) and rutile TiO_2 powder. Surprisingly, they found that all powders gave the same final structure of Ti-NTs. By replacing NaOH by KOH the $H_2Ti_4O_9{\cdot}H_2O$ structure of Ti-NTs was formed. The nanotube had a diameter of about 10 nm. The sodium salt (for example $Na_2Ti_2O_5{\cdot}H_2O$) of these structures could be found as well if the sample was not well washed and some sodium ions are still presented.

Our aim was to find the structure of Ti-NTs prepared by the hydrothermal method. In order to accomplish this task, a combination of three complementary methods: powder X-ray diffraction (PXRD), high resolution transmission electron microscopy (HRTEM) and electron diffraction (ED) was used. A computer simulation of PXRD pattern utilizing the Debye formula was used for the structure verification. The intensity distribution in the calculated Fourier transformation of the single nanotube based on model is comparable to that of precession electron diffraction.

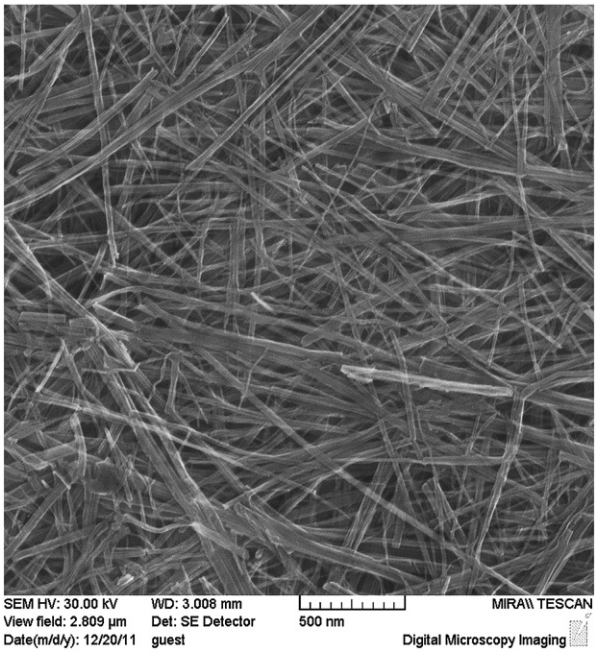

Fig. 1 – SEM image of nanotubes.

2. Methods

The investigated Ti-NT samples were prepared by hydrothermal treatment of nanocrystalline TiO_2 anatase powder. The powder was dispersed in 10 M NaOH aqueous solution. This suspension was put into a closed vessel and heated at 120 °C for 48 h. After the synthesis, the sample was washed and neutralized by HCl. In order to obtain powder samples of Ti-NTs, the sample was freeze-dried.

The structure investigations were performed by three complementary methods: X-ray diffraction (XRD), HRTEM and ED.

The XRD is a widely used method for structure determination. The X-ray measurements on the Ti-NT samples were performed on a PANanalytical MPD diffractometer with the CuKα radiation. The sample was mixed with a solvent and spread on a glass or the so-called non-diffracting Si substrate holder. The sample was measured in the Bragg–Brentano geometry with variable slits and the PIXcel detector, in the 2θ range from 5° to 80°. Powder diffraction patterns were measured with the step size of 0.0263° 2θ; total integrating time for one step was 180 s. Incident beam was conditioned by Soller slit (divergence 0.04 rad) and a beam mask of width 5 mm was used. Automatic divergence slits were used both in primary and diffracted beam in order to achieve constant irradiated area during measurement (5×8 mm^2.) In front of the PiXCel detector (in scanning mode), Soller slits (0.04 rad divergence) and a beta-filter (Ni) were placed.

PXRD gives information on the crystalline structure averaged over irradiated volume. On the other hand, HRTEM can be used to visualize the structure of a single nanotube. One of the challenges of this study was to find the required single nanotube because nanotubes prefer to stick together as shown in Fig. 1.

Ti-NTs were ultrasonically dispersed in ethanol and then a drop of the sample was spread on a holey carbon-coated microscope copper grid. Individual nanotubes were studied by HRTEM imaging, performed on JEOL JEM 2100 F FEG (field emission gun) operated at 200 kV accelerating voltage.

A through-focus series of HRTEM images consisting 20 images at different defocus values were taken. These images were corrected for distortions by contrast transfer function (CTF) and the individual CTF-corrected images were combined into a reconstructed image of structure using the structure projection reconstruction method [9].

ED patterns were collected on the single nanotube as well. As the interaction of electrons with matter is ~104 times stronger than that for X-rays, dynamical effects should be taken into account and the interpretation of ED patterns is more complicated than that of XRD patterns. In order to overcome this problem, digital precession electron diffraction (PED) [10] was used to collect ED data. In this method the electron microscope is controlled by dedicated software only. The electron beam is rotated along a circle at a certain angle (so-called precession angle; 2° in this work) around the optical axis of the microscope. The beam rotation along the circle is sampled with a fixed azimuthal step (3° in this work) which results in 120 individually beam-tilted ED patterns. These patterns are combined into the final PED pattern by (1) aligning all patterns against each other using cross-correlation and (2) summing up the aligned patterns. The set of structure factors extracted from the final PED pattern is closer to kinematical intensities.

PED patterns were recorded on JEOL JEM 2100 LaB_6 operated at 200 kV accelerating voltage. The sample preparation was the same as in for HRTEM imaging.

EDS was used for investigation of chemical compositions of the sample. EDS studies were performed on a Tescan Mira1 microscope. This microscope had auto emission electron gun operated at 15 keV. Scanning electron microscopy (SEM) studies were performed also on this microscope at 30 keV in