Hydrothermal synthesis of one-dimensional (1D) Na_xTiO_2 nanostructures

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Nanorods of sodium titanium dioxide bronze Na_xTiO_2 were synthesized by the hydrothermal treatment of the amorphous $TiO_2 \cdot nH_2O$ gel with 10 *M* NaOH followed by ultrasonication in 0.1 *M* HCl and thermal treatment (500°C, 10 h). The thermal treatment of the nanorods does not change the morphology of the particles. According to the electron diffraction data, the Na_xTiO_2 nanorods grow along the *c* axis.

Key words: hydrothermal synthesis, one-dimensional nanostructures, nanorods, sodium titanium dioxide bronze, Na_xTiO_2.

In the recent decade, researchers are greatly interested in the creation of functional nanodimensional materials based on one-dimensional (1D) nanostructures. Since the dimensionality is a critical factor that determines the properties of a material,[1] these nanostructures are characterized by the unique physical properties and seem to be promising in opto- and nanoelectronics.[2]

Highly dispersed powders based on various TiO_2 modifications and layered titanates find wide use as photocatalysts, gas sensors, dyes, dielectric ceramics, *etc*.[3] An important advantage is their nontoxicity.

In this work, we synthesized 1D nanorods of sodium titanium dioxide bronze Na_xTiO_2 by the hydrothermal method.

Results and Discussion

One-dimensional nanostructures of the sodium titanium dioxide bronze were prepared by the hydrothermal treatment of the amorphous $TiO_2 \cdot nH_2O$ gel with 10 *M* NaOH followed by ultrasonication in 0.1 *M* HCl. The conditions of synthesis and the phase composition of the products are presented in Table 1.

According to the scanning electron microscopy (SEM) data, the nanorods are formed when the hydrothermal synthesis is carried out at 200 °C (sample **1**, Fig. 1, *a*) and 250 °C (samples **2** and **3**). The microstructures of the samples after 10-h annealing at 500 °C are retained (see Fig. 1, *b*, sample **1´**), *i.e.*, no considerable change in the morphology (*e.g.*, growing together of the nanorods) is observed.

Table 1. Conditions of synthesis and physicochemical characteristics of the samples* synthesized by the hydrothermal treatment of the amorphous $TiO_2 \cdot nH_2O$ gel in 10 *M* NaOH

Sample	Conditions of synthesis		Size of nanostructures** (±10%)	
	T/°C	τ/h	*l*/nm	*L*/μm
1	200	20	80—1300	1—12
2	250	20	60—700	0.8—6
3	250	24	50—500	0.3—10

* Phase composition: $Na_xTiO_2 + Na_xH_{2-x}Ti_3O_7$.
** *L* is length, and *l* is width.

Transmission electron microscopic study (TEM) showed a tendency for decreasing the average size of the nanorods with the temperature increase and elongation of the hydrothermal synthesis (see Table 1). However, the particle size distribution is strongly nonuniform for each particular sample. To achieve a uniform nanoparticle distribution, one has to study additionally factors affecting the mechanism of nanorod crystallization under hydrothermal conditions of synthesis.

According to the X-ray diffraction data, samples **1**, **2**, and **3** have similar X-ray diffraction patterns, which do not coincide with those of the most popular TiO_2 modifications (anatase, rutile, and brookite). The resulting X-ray

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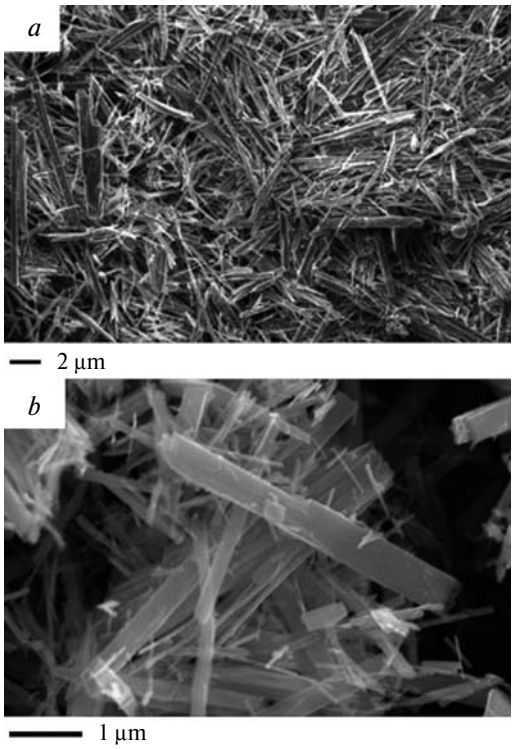

Fig. 1. Electron microphotographs (SEM) of samples **1** (*a*) and **1´** (*b*).

diffraction patterns were analyzed using the JCPDS PDF-2 database, indicating that all the samples were a mixture of the sodium titanium dioxide bronze Na_xTiO_2 (card no. [22-1404]) and sodium salt of titanic acid $H_2Ti_3O_7$ of the composition $Na_xH_{2-x}Ti_3O_7$ (card no. [48-963]).

Table 2. Physicochemical characteristics of the samples* annealed at 500 °C for 10 h

Annealed sample	Size of nanostructures** (±10%)	
	l/nm	*L*/μm
1´	80—600	0.1—8
2´	50—500	0.2—6
3´	70—1200	0.1—16

* Phase composition: Na_xTiO_2.
** *L* is length, and *l* is width.

The structure of the sodium-containing compound Na_xTiO_2 [4] is similar to the reported layered modification of titanium dioxide TiO_2(B).[5] These two structures contain the same framework of TiO_6 octahedra linked through the common vertices and edges (Fig. 2). The sodium-containing compound differs from the above structures in that some holes of its framework are filled with sodium atoms (Fig. 2, *b*). For the compound Na_xTiO_2, $x = 0.2$. This compound is nonstochiometric, and the compound with other x values ($0 \leq x \leq 0.25$) can also be obtained.[4]

The thermal treatment of samples **1—3** at 500 °C for 10 h increases their crystallinity. According to the X-ray diffraction data, all samples after annealing are monophase with the composition Na_xTiO_2 (Table 2). To prove that the synthesized nanorods contain so-

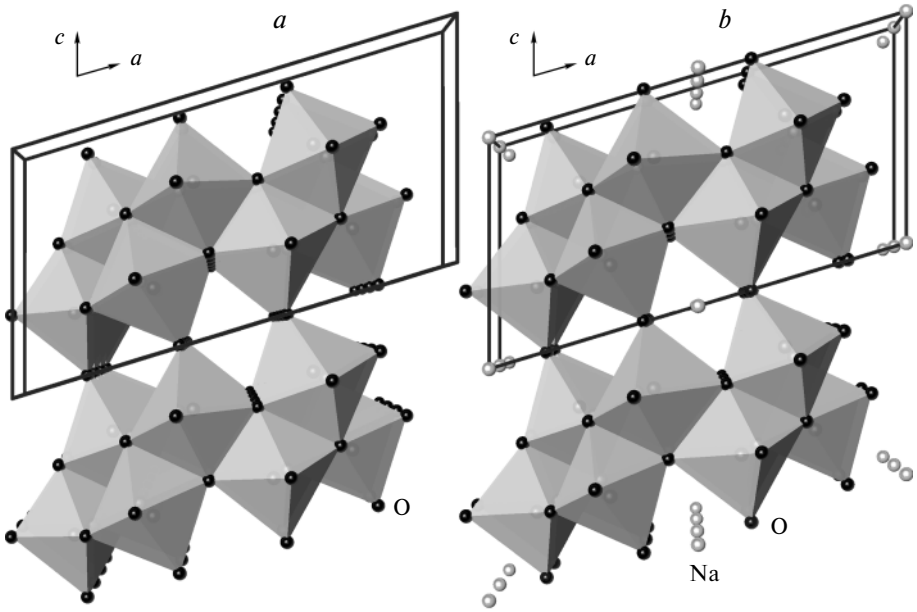

Fig. 2. *a*. General view of the crystal structure of the TiO_2(B) phase. *b*. General view of the perfect crystal structure of sodium titanium dioxide bronze $Na_{0.25}TiO_2$ (positions of the sodium atoms in the real structure are populated by 80%).

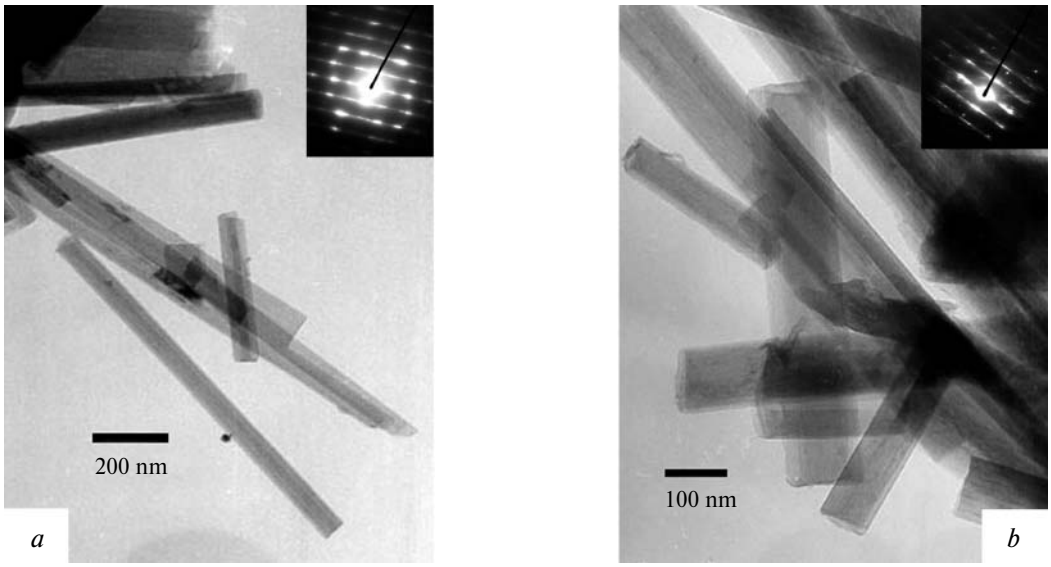

Fig. 3. Electron microphotographs (TEM) of samples **1** (*a*) and **2** (*b*).

dium, we calculated the unit cell (monoclinic) parameters of annealed sample **3**′: a = 12.17(1), b = 6.519(6), c = 6.519(6) Å, β = 106.74(6)°, and V = 286.4(8) Å^3. According to the published data, the volume of the monoclinic unit cell of the TiO_2(B) phase is 284.25(5) Å^3, and that of the Na_xTiO_2 phase (x = 0.2) is 289.6(4) Å^3. Based on these data, we can suggest that the prepared phase contains sodium, *i.e.*, it has the composition Na_xTiO_2; however, x is less than 0.2 (6 at.%). To confirm this assumption, we carried out an additional energy dispersive X-ray spectroscopy (EDX). According to the EDX data, all the samples synthesized contain Na both before and after annealing. Therefore, the EDX data agree with the X-ray diffraction data, *i.e.*, the prepared structures contain small amounts of sodium. It should be noted that the accuracy of determination of light elements by the EDX method is rather low and, hence, we cannot estimate quantitatively the sodium content in Na_xTiO_2.

The samples synthesized are pale blue with the metallic luster characteristic of bronzes,[6] which is an additional evidence that the nanorods synthesized contain sodium, because all known TiO_2 modifications are white.

The prepared nanorods exhibit the electron diffraction pattern typical of this particle shape (see inserts in Fig. 3, *a*, *b*). So-called strands are seen in the electron diffraction patterns. The electron diffraction data processing showed that the nanorods grow in the {001} direction, *i.e.*, along the *c* axis.

Thus, nanorods of the sodium titanium bronze Na_xTiO_2 were synthesized by the hydrothermal treatment (200 and 250 °C, 20 and 24 h) of the amorphous $TiO_2 \cdot nH_2O$ gel in 10 *M* NaOH. The bronze nanorods were established to grow along the *c* axis.

Experimental

Preparation of the amorphous $TiO_2 \cdot nH_2O$ gel. The following reagents were used to synthesize the initial substances: $TiCl_4$ (>99%, Merck), HCl (analytically pure grade), NH_3 (25%, analytically pure grade), NaOH (analytically pure grade), and distilled water.

Titanium tetrachloride was added dropwise to concentrated hydrochloric acid until a ratio of 2 : 1 (HCl : $TiCl_4$, mol/mol) was achieved. This procedure produced a complex H_2TiCl_6. Then the resulting H_2TiCl_6 complex was added to excess ammonia solution, which was accompanied by hydrolysis with the formation of a white amorphous gel $TiO_2 \cdot nH_2O$. The resulting precipitate was washed with distilled water to the neutral reaction to Cl^-.

Hydrothermal synthesis of one-dimensional (1D) nanostructures. The amorphous $TiO_2 \cdot nH_2O$ gel was hydrothermally treated in a 10 *M* solution of NaOH at 200 and 250 °C for 20 and 24 h. The product of the synthesis was isolated by centrifugation and washed several times with distilled water. Then the product was doubly ultrasonicated in 0.1 *M* HCl for 8 min on an UZG-100 Ultrasonic Generator setup (Impul´s Co., Russia), separated by centrifugation, washed, and dried in air at 90 °C.

The samples synthesized were annealed at 500 °C for 10 h in hydrogen.

Methods of investigation. X-ray diffraction studies were carried out on a DRON-3M diffractometer using Cu-K_α radiation (average wavelength λ = 1.54183 Å, nickel β-filter). The resulting powder X-ray patterns were examined using the JCPDS PDF-2 database.

The microstructures of the samples were studied by transmission electron microscopy on a JEM-2000FXII electron

microscope (Jeol, Japan) and using scanning electron microscopy. Scanning electron microscopy and EDX analysis (INCA Energy spectrometer, England) of the synthesized TiO_2-based 1D structures were carried out on a Leo Supra 50 VP electron microscope (Germany). The composition was determined for both large surface regions and in five local points.

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