Nanostructured materials based on Nb-doped titanium dioxide

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Abstract. Oxide materials based on TiO₂ (anatase) and doped with Nb⁵⁺ cations have been fabricated by the template sol–gel method. Two types of templates were used: activated carbon fiber and siloxane-acrylate emulsion. The morphology and structure of the samples have been studied and the conditions of their surface have been characterized. It has been demonstrated that the material morphology and structure are primarily determined by the type of the used template. Formation of microtubes consisting of nanoparticles (NP) on the carbon template was established. It has been shown that at the Nb-dopant content of up to 5 % (wt.) nanoparticles have the structure of anatase, in which the dopant cation occupies the position of the Ti⁴⁺ cation. Studies of the sample doped with 5 % Nb by the method of electrochemical impedance spectroscopy (EIS) demonstrated that introduction of Nb⁵⁺ ions into the TiO₂ structure resulted in the increase of the material electroconductivity from 7.6 10⁻¹³ S/cm (nondoped sample) up to 2.3 10⁻¹ S/cm. The increase of electroconductivity extends the potential fields of application of the above samples as anode materials for high-power Li-ion batteries. At using the siloxane-acrylate emulsion as a template, highly dispersed powders with a mesoporous structure consisting of heterogeneous in composition nanoparticles with a “core-shell” structure are formed.

1. Introduction

Up to present, numerous versatile TiO₂-based materials have been fabricated, and good prospects of their application have been demonstrated. TiO₂ doping by various metal ions (Mo⁶⁺, Y³⁺, Fe³⁺, Zr⁴⁺, Nb⁵⁺ etc.) results in changes in its properties and extends substantially the fields of its application. Use of a template enables one to obtain three-dimensional nanosized structures (such as nanotubes or nanorods) and provides extra possibilities to control the material architecture.

For example, the Nb-doped TiO₂ has attracted a great research interest as a potential candidate for application in photocatalysis, photoelectric p-n-transition devices, and energy storage [1,2,3]. Also, Nb-doped composites of variable compositions were tested as anode materials for Li-ion batteries [4,5,6]. It has been demonstrated that the electron conductivity of Nb/TiO₂ can be adjusted by changing the dopant concentration.

Thus, the present task for researchers consists in the development of a simplified procedure of synthesis of nanomaterials with the possibility of providing a simple control of their composition and obtaining required physical-chemical parameters.

In the present work, two series of samples of the composition TiO₂/Nb₂O₅/SiO₂ (table 1) with variable contents of the Nb-dopant were synthesized by the template sol-gel method. Activated carbon

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fiber or siloxane-acrylate emulsion were used as templates. Their morphology and structure were studied by the methods of scanning electron microscopy (SEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The specific surface area (BET) and pore size distribution (BJH) were obtained by the method of low-temperature nitrogen adsorption.

Table 1. Sample markings and compositions.

| OT Marking | TiO$_2$/Nb$_2$O$_5$/SiO$_2$ wt. % | D$_{NP}$ nm | TE Marking | TiO$_2$/Nb$_2$O$_5$/SiO$_2$ wt. % | D$_{NP}$ nm |
|------------|----------------------------------|-------------|------------|----------------------------------|-------------|
| OT-0       | 0                                | 17          | TE-0       | 0                                | 13          |
| OT-1       | 97.3/1.4/1.3                     | 16          | TE-2       | 95.5/2.0/2.5                     | 8           |
| OT-4       | 94.5/3.7/1.8                     | 15          | TE-4       | 93.5/3.8/2.7                     | 9           |
| OT-5       | 93.0/5.0/2.0                     | 13          | TE-6       | 91.8/5.6/2.6                     | 10          |
| OT-6       | 93.2/5.8/2.0                     | 16          | TE-7       | 90.3/7.1/2.6                     | 12          |
| OT-9       | 88.4/8.9/2.7                     | 18          |            |                                   |             |
| OT-11      | 86.7/11.3/2.0                    | 20          |            |                                   |             |
| OT-23      | 74.8/22.9/2.3                    | 25          |            |                                   |             |

2. Synthesis of materials and methods of study

2.1. Synthesis

Nanostructured oxide materials of variable compositions (TiO$_2$/Nb$_2$O$_5$/SiO$_2$) were prepared by the template sol-gel method. Activated carbon fiber (OT samples) or siloxane-acrylate emulsion (TE) were used as templates. The used synthesis method is based on a slow hydrolysis of inorganic precursors of titanium (TiCl$_4$) and dopant metal salt (NbCl$_5$) in aqueous solutions by thermal decomposition of carbamide (N$_2$H$_4$CO) with oxides deposition on the template surface.

Samples of the TE group were obtained through a slow hydrolysis of inorganic precursors of titanium and NbCl$_5$ salt in aqueous solution by addition of NH$_4$OH solution with subsequent deposition of oxides on a template. Template annealing was performed at 500°C for 2 hours in air. Template annealing results in dehydrolysis and partial crystallization of the synthesized material. Annealing was controlled using Raman spectra.

The synthesized samples contain small amounts of SiO$_2$, as both used templates contain silicon, and their complete annealing is impossible under the above conditions. The decrease of the SiO$_2$ concentration was realized using an autoclave pretreatment of the initial template by ammonium difluoride and changes in the template/oxide ratio during synthesis.

The selected synthesis method enables one to change the oxides ratio in a broad range through variation of solution components at deposition. Selection of annealing conditions and temperature provides the possibility to obtain TiO$_2$/Nb$_2$O$_5$/SiO$_2$ oxide samples of different structural properties.

2.2. Methods of study

The oxides ratio in the samples under study was determined by the method of X-ray energy-dispersive analysis using an EDX 700 spectrometer (Shimadzu, Japan). The compositions and markings of the synthesized according to the data of X-ray fluorescence analysis of TiO$_2$/Nb$_2$O$_5$/SiO$_2$ are shown in Table 1. The morphology was studied by the method of scanning electron microscopy (SEM) using an S5500 high-resolution device (Hitachi, Japan). The samples surface characteristics were studied on the basis of low-temperature nitrogen adsorption isotherms using an Autosorb-IQ specific surface area analyzer (Quantachrome, USA) and calculated by the methods of Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH). The X-ray photoelectron spectra (XPS) were measured using a SPECS spectrometer with a 150-mm hemispheric electrostatic analyzer. MgK$_\alpha$-radiation was used for spectra excitation. Pressure in the analyzer chamber was equal to about 5x10$^{-7}$ Pa, the analyzer transmission energy – to 50 eV. Registration of Raman spectra was carried out using an RFS-100/S IR Fourier
spectrometer (Bruker, Germany) equipped with a high-sensitivity germanium detector. Electrophysical characteristics of the materials under study were determined by the method of electrochemical impedance spectroscopy (EIS) using a complex of devices including an Impedance/Gain-Phase Analyzer SI 1260 frequency response analyzer and a Solartron Dielectric Interface 1296 device. To study the conducting properties, the material under study was compacted into pellets of a diameter of 4 mm and a thickness of 0.05–0.1 mm. Taking into account the sample geometry, specific electroconductivity values were calculated using the formula $\sigma = l/(R \cdot S)$, where $l$ and $S$ – the pellet thickness and area of its contact with an electrode, respectively, while $R$ – the specific volume resistance calculated from impedance spectra by the method of equivalent electric circuits. Impedance spectra were recorded in the frequency range $10^6 – 1 \text{ Hz}$.

3. Discussion of results

3.1. Morphology

OT materials obtained by deposition on a carbon template were formed as microtubes of a length of 10–100 µm (figure 1a). Microtubes are characterized with a developed surface and consist of nanoparticles (NP) of a size of 15÷25 nm. The nanotubes length and external and internal size and NP size change in dependence on the Nb-dopant content. It was found that at the dopant content above 5 % one observed particles agglomeration and microtubes destruction, and elevated contents of Nb-doping components were determined on the surface of nanotubes from the EDS data.

As was shown at studies by the method of low-temperature nitrogen adsorption, OT microtubes were characterized with a developed surface with a specific surface area of up to 80 m$^2$/g. Nb-doping up to 5% is accompanied with the decrease of the specific surface area due to the increase of a number of macropores and the decrease of that of mesopores. The increase of the doping level above 5 % results in a noticeable decrease of the specific surface area down to 50 m$^2$/g and the average pore volume, which is caused, according to the shape of the adsorption-desorption curve (figure 2a), by a capillary filling of meso- and macropores in the TiO$_2$ matrix by an amorphous component with an increased Nb content (from the XPS data for Nb$_2$O$_5$).

![Figure 1](image1.png)

Figure 1. SEM-images of Nb-doped samples. OT-4 (a), TE-2 (b).

Use of siloxane-acrylate emulsion as a template results in formation of highly dispersed powders consisting of heterogeneous in composition (from the EDS data) nanoparticles of a size of 8÷13 nm (figure 1b). Nanoparticles form a developed surface.
Nitrogen adsorption-desorption isotherms for TE comprise typical isotherms of the IV type with a separate hysteresis loop indicating to mesoporous properties. The nondoped TE sample has a specific surface area of 155 m$^2$/g with the maximal contribution of intermediate-size pores (8–13 nm). Doped samples manifest the decrease of the specific surface area down to 145 m$^2$/g accompanied with the increase of the pore volume up to 0.7–1.0 cm$^3$/g. Changes in the dopant content affects insignificantly the specific surface area. The pore size distribution confirms that doping is accompanied with the decrease of the number of mesopores and formation of macropores (figure 2b). Similar process was observed [7] for the TiO$_2$–YO$_x$ substrate upon high-temperature treatment and was associated with NP agglomeration. Thus, one can assume, analyzing the pore size distribution obtained by the BJH method, that the increase of the doping level results in destruction of the structure of open mesopores, which become sealed in the course of doping. According to the EDS data, TE samples are inhomogeneous independently of the content, whereas the surface of the formed NP is coated by an amorphous shell with the increased Nb$^{5+}$ content.

![Figure 2. Pore size distribution of the samples: OT (a), TE (b).](image)

3.2. XPS analysis

To obtain more comprehensive information on the (surface) element composition of the materials under study and the state of chemical oxidation of the forming NPs, XPS measurements were performed (figure 3).

OT and TE samples (figure 3a) are characterized with the presence of Ti, Nb, O, and C elements on the material surface. According to the XPS data, the Nb/Ti atomic ratio in samples is in agreement with the synthesis procedure. A homogeneous distribution of Ti and Nb atoms was corroborated for OT samples with the dopant content of up to 5 %, which is in agreement with the results of [6]. More significant relative Nb content in TE samples indicates to heterogeneity of its distribution over the depth and its concentrating in surface layers.

As follows from the $E_b$ Ti 2p$_{3/2}$ values, titanium is present in the oxidation state Ti$^{4+}$, which is in quantitative and qualitative agreement with the oxygen data indicating to the presence of a respective metal-oxide form ($E_b$ O 1s = 530 eV). The two-component spectrum with maxima at 209.5 and 207.2 eV indicates the presence of five-valence Nb$^{5+}$ (3d$_{3/2}$ and 3d$_{5/2}$) and corroborates that of Nb$_2$O$_5$ in composition of the samples under study. Also, for the TE series, one observes the increase of the relative intensity of Nb$^{5+}$ peaks along with the increase of the doping level.
**Figure 3.** XPS spectra of OT-2(1) and TE-3(2) samples (a), Nb3d, Ti2p, and O1s lines in the spectrum of TE-3 (b).
3.3. Raman spectroscopy

According to the XRD and Raman spectroscopy data, OT samples at a dopant content of up to 5 % have the structure of TiO$_2$ crystallized in the anatase structure (space group $I4_1/amd$, JCPDS No. 01-071-1169) (Fig. 4). According to the irreducible representation $\Gamma_{D4h} = A1g(\nu_1) + 2B1g(\nu_2, \nu_3) + 3Eg(\nu_4, \nu_5, \nu_6)$, six vibrations are active in the anatase Raman spectrum. A detailed examination of positions of the most intensive bands ($\nu_3(B1g)$, $\nu_4(Eg)$, and $\nu_6(Eg)$) enables one to trace thoroughly changes in the NP crystal structure in the course of Nb-doping.

In OT Raman spectra, doping up to 5 % is accompanied with a frequency shift of $\nu_3(B1g)$, $\nu_4(Eg)$, and $\nu_6(Eg)$ bands (figure 4) related to the dimension effect and the emergence of a heterogeneous stress in the NP crystal structure due to the impact of Nb$^{5+}$ cations [8]. Along with doping up to 5 %, the half-widths of the bands in the spectra increase as well. And starting from the OT-6 sample, the anatase bands narrow and the positions $\nu_3$, $\nu_6$ do not virtually change. The latter is related to the achievement of the isomorphic capacity of the NP crystal lattice at 5 % dopant content. Thus, changes in OT Raman spectra at doping up to 5 % corroborate the increase of parameters of the NP unit cell due to substitution of Ti$^{4+}$ cations (0.064 nm) by Nb$^{5+}$ cations with an increased ionic radius Nb$^{5+}$ (0.069 nm) and formation of solid solutions of the Ti$_{1-x}$Nb$_x$O$_2$ ($x\approx0.03$) composition with the structure of anatase. The $\nu_4$ mode in the spectra of doped samples associated with the bonds valence stretching is shifted to the low-frequency range until 637 cm$^{-1}$, which indicates to general weakening of Ti-O bonds upon heterovalence substitution of Ti$^{4+}$ cations by those of Nb$^{5+}$.

Figure 4. Band positions in Raman spectra of the samples: OT (1), TE(2).

The $\nu_3$ and $\nu_6$ vibrations related to bending of O–Ti–O bonds are contributed by Ti$^{4+}$ ions: their substitution by Nb$^{5+}$ ions affects the most pronouncedly the positions of respective bands in Raman spectra. As was show earlier, the shift of $\nu_3$ and $\nu_6$ in spectra upon variation of the dopant content has a good correlation with changes in NP sizes [9, 10].

In the OT spectra, one observes shifts of $\nu_3$ (396.4 → 391.9 cm$^{-1}$) and $\nu_6$ (144.0 → 148.0 cm$^{-1}$) modes in the course of 0–5 % doping, which is in agreement with changes in particle sizes (Table 1), i.e., the NP size decreases during the OT-0 → OT-5 transition, thus corroborating the dopant restraining role in the NP crystal lattice [11]. Also, the XRD analysis demonstrates the increase of the level of crystallinity at the transition to OT-5 with preservation of the anatase structure, whereas, starting from the OT-9 sample, the presence of a dopant is manifested in Raman spectra on the background of anatase bands as low-resolution low-intensity bands with maxima at 124, 246, and 360 cm$^{-1}$. The content increase up to 23 % results in the increase of these bands intensities. Also, one
observes reflections corresponding to the orthorhombic phase of Nb$_2$O$_5$ in X-ray diffraction images of the samples with the Nb-dopant content higher than 8\% [12, 13, 14].

To sum up, the above facts demonstrate that at the dopant content in OT samples above 5\% NPs consist of a mixture of phases due to the increase of the defects number and the stress in the NP lattice. Consequently, a phase enriched with the Nb-dopant covers the surface of both microtubes and NPs, as seen from the EDS analysis results. Such an enrichment of the NP surface by the dopant amorphous phase was mentioned in [15] at studies of TiO$_2$ nanorods doped with Zr, which was explained by differences in kinetics and temperatures of crystallization of their oxides.

Unlike OT samples, in Raman spectra of TE samples just an insignificant shift of anatase bands was observed, which indicated to preservation of parameters of the NP crystal lattice unit cell. Trace quantities of the dopant phase are seen almost immediately on X-ray images of TE annealed at 850°C. Thus, the maximal isomorphic capacity of samples obtained from the emulsion toward the dopant is reduced in comparison with that for OT samples, so that, assumingly, as early as at the dopant content higher than 2\%, NPs with a core-shell structure are formed. The TiO$_2$ phase is concentrated in the core, while an amorphous phase enriched by Nb$^{5+}$ – in the shell. The X-ray diffraction images of products that had undergone annealing at 850°C contained an insignificant contribution of the tetragonal NbO$_2$ phase, aside from the monoclinic Nb$_2$O$_5$ phase.

3.4. EIS studies

According to the EIS data (figure 5), Nb-doping of titanium dioxide results in the increase of electroconductivity of TiO$_2$. In particular, the electroconductivity of the OT-1, OT-5, and OT-11 samples attained 8.2·10$^{-9}$, 2.3·10$^{-7}$, and 1.3·10$^{-7}$ S/cm, respectively, whereas that of the nondoped TiO$_2$ was just 7.6·10$^{-13}$ S/cm [16]. As follows from the obtained data, the highest electroconductivity value was for OT-5 sample that allows concluding on its good prospects as an anode material for Li-ion batteries functioning under accelerated charging conditions.
4. Conclusions
Oxide materials based on TiO\(_2\) (anatase) and doped with Nb\(^{5+}\) cations have been fabricated by the template sol-gel method. Two types of template were used: activated carbon fiber and siloxane-acrylate emulsion. At using siloxane-acrylate emulsion as a template, highly dispersed powders with the mesoporous structure consisting of inhomogeneous in composition nanoparticles (NP) of a “core-shell” structure of a size of (7÷13 nm) are formed. The NP core has the structure of anatase, while the shell is characterized with an increased dopant content. Along with the increase of the doping level, the phase enriched by the Nb-dopant is squeezed out on the NP surface and into the intercrystallite space. Mesoporous samples are characterized with a developed surface of a specific surface area of up to 145 m\(^2\)/g. Samples deposited on the carbon template are formed from microtubes consisting of NPs (15÷25 nm). The isomorphic capacity of the TiO\(_2\) (anatase) phase toward Nb\(^{5+}\) ions attains 5 wt. %. At the dopant content of 0–5 %, NPs are homogeneous in composition and have the structure of anatase, in which the Nb-dopant cations occupy the positions of the Ti\(^{4+}\) cation. Nb-doping of microtubes affects essentially the titanium dioxide electroconductivity. In particular, the electroconductivity of TiO\(_2\) (anatase) with Nb-dopant content of 5 % (2.3·10\(^{-7}\) S/cm) increases by 6 orders of magnitude in comparison with that of the nondoped sample (7.6·10\(^{-13}\) S/cm). Thus, TiO\(_2\) doping by Nb\(^{5+}\) ions enables one to obtain a material applicable as an anode for Li-ion batteries operated under enforced charging conditions.

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