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Structure and stability of boron doped titanate nanotubes and nanowires

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ABSTRACT

Boron doped titanate nanoparticles were prepared from protonated (H-form) titanate nanotubes (TiONT) and nanowires (TiONW). The chemical nature and morphology of boron were monitored by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and transmission electron microscopy (TEM). XPS proved that significant part of the boron incorporated into interstitial position (Ti–O–B) of titanate nanotubes and nanowires, while a smaller part of the boron formed boron titanates via ion-exchange process. In the case of titanate nanotubes the presence of boron induced morphological (tubular to rod-like) and structural (tritanate to anatase) changes. These effects were not so pronounced on titanate nanowires.

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1. Introduction

Among various semiconductors, titanium dioxide (TiO₂) as a photocatalyst has been researched excessively due to its advantages such as relative cheapness, availability in excess, chemically and biologically stable character and possession of higher oxidative potentials. UV-irradiation is able to generate electrons and holes in TiO₂, which are good reductants and powerful oxidants for redox reactions [1–4]. Due to its favorable electronic and optoelectronic properties, it has been widely applied to solar cells and photocatalysts. However, improved properties are necessary to meet high demand and complex requirements. The prosperous development of titanium dioxide nanomaterials has thrived the investigation of a class of TiO₂-based nanostructures; layered titanate materials. Layered titanate materials have attractive features of their own, including extremely large ion-exchange capacity, fast ion diffusion and intercalation [5–7].

One-dimensional TiO₂ related nanomaterials with high morphological specificity, such as nanotubes and nanowires have attracted considerable attention due to their interesting chemical and physicochemical properties. On the basis of the pioneering work of Kasuga et al. [8], research efforts on titanates were at first concentrated on the hydrothermal synthesis and structure elucidation of titanate nanotubes. Recently, hydrothermal conversion of self-assembled titanate nanotubes (TiONT) into nanowires (TiONW) in a revolving autoclave was achieved in our laboratory [9], [10]. Titanate nanostructures are of great interest for catalytic applications, since their high surface area and cation exchange capacity provides the possibility of achieving a high metal (e.g. Co, Cu, Ni, Ag, Rh and Au) dispersion [11–16].

In the light of modified nanostructures it is worth dealing for comparison the structure of non-metal doped titanate nanowires and nanotubes. The results obtained on non-metal and anion doped TiO₂ are well documented in the previous excellent review [1]. There has been a turning point in the literature on anion-doping of TiO₂ since Asahi and coworkers' 2001 Science report on visible light activity in nitrogen doped TiO₂ [17]. By far, the most extensively studied anion dopant has been N, but other anion dopant anion e.g. C, halides, P and B have also been examined both experimentally and theoretically [1]. B-doped TiO₂ nanoparticles calcined at 773 K showed higher photocatalytic activity than pure

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TiO₂ sample [18]. The general idea is that anion which are less electronegative than O, when substitutionally doped the lattice will have some their valence p-states pushed up out of the TiO₂ valence band (VB) into the bandgap. The issue of how non-substitutional anion dopant also remains an important issue.

In the field of titanate nanostructures the most non-metal dopant was also the nitrogen. H-form titanate nanotubes were prepared by alkaline hydrothermal method and subsequently doped with nitrogen obtained from the thermal decomposition of urea. The developed method offers the lowest temperature (500 K) route to N-doped trititanate-derived nanostructures to date [19]. The amount of incorporated nitrogen could be controlled by the duration of the reaction. Nitrogen in high concentration induced both structural and morphological changes even without any additional heat treatment. However, by calcining the doped samples it was possible to facilitate nitrogen-related transitions in the oxide morphology and crystalline phase, resulting in materials with higher crystallinity and a more regular shape. Interstitial linkage to titanate via Ti–O–N and Ti–N–O is also confirmed by X-ray photoelectron spectroscopy (XPS) [20].

In the present work the structure and thermal stability of boron doped titanate nanowires and nanotubes were investigated. The samples were characterized by x-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM) and X-ray diffraction (XRD).

2. Experimental

Elongated titanate nanotubes and nanowires have been synthesized via alkaline hydrothermal method as previously reported elsewhere [8], [9]. 50 g of titanium(IV)-oxide powder (anatase, 99.8%, Sigma-Aldrich) have been mixed in 1 L of 10 M NaOH (99.93%, Molar) solution during continuous stirring. The as prepared milk-like white suspension has been kept in a polytetrafluorethylene (PTFE)-lined stainless steel autoclave (diameter: 120 mm, height: 250 mm) for 24 h. In all cases the autoclave were permanently rotated perpendicularly to its longer axis. In order to prepare tubular titanates the reaction temperature was set to 428 K with a rev of 3 rpm. Since the titanate nanowires in situ forms by associated trititanate nanotubes the temperature has been set to a higher value (458 K) and relatively vigorous rotation (28 rpm), respectively [9]. The as-prepared nanostructures have been treated by deionized water to neutralize the basic system. Sodium cations in the Na_{2-x}H_xTi₃O₇ structure were changed to protons by an ion exchanging process in the presence of 0.01 M HCl (Molar) solution then the remained chlorine ions were washed out by deionized water. Protonated titanates are able to form anatase and/or rutile TiO₂ by a calcination step [21]. H-form samples were dried at 60 °C in air for 72 h.

In order to prepare boron modified titania materials boric anhydride (≥98%, Sigma-Aldrich) was dissolved in 100 ml deionized water and stirred for 24 h in the presence of 0.5 g TiONT, TiONV and commercial TiO₂ (Thomasker, ≥99%) as well. The B/Ti atomic ratio was set to 0.1%. The as-prepared samples were washed out by deionized water several times to remove the remained boron species then dried it 60 °C in air for 48 h.

The pristine titanates, TiO₂ and the boron modified counterparts underwent thermal annealing process in the temperature range between 473 K and 873 K for 1 h in N₂ atmosphere. Samples were characterized after each calcination steps.

XP spectra were taken with a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical analyzer. The analyzer was operated in the FAT mode with 20 eV pass energy. The Al K_α radiation (hν = 1486.6 eV) of a dual anode X-ray gun was used as an excitation source. The gun was operated at a power of 150 W

(12.5 kV, 12 mA). The energy step was 25 meV, electrons were collected for 100 ms in one channel. Typically five scans were summed to get a single high-resolution spectrum. The Ti 2p_{3/2} maximum (458.9 eV) was used as the energy reference. The sample preparation chamber was directly connected to the measuring chamber to avoid the contamination of samples between the steps. For spectrum acquisition and evaluation both manufacturer's (SpecsLab2) and commercial (CasaXPS, Origin) software packages were used.

Morphology of the as-received and boron modified titanates before and after the heat treatments was characterized by transmission electron microscopy (HRTEM) using an FEI Tecnai G² 20 X-Twin instrument (200 kV operation voltage). The samples were drop-casted from ethanol suspension onto holey carbon coated grids. The crystal structures were identified by a Rigaku Miniflex II powder X-ray diffractometer using Cu K_α irradiation source (0.15418 nm) operating at 30 kV and 15 mA at ambient atmosphere and temperature.

3. Results and discussion

X-ray photoelectron spectroscopic (XPS) survey spectrum of as received B-doped titanates showed Ti, O, B and C elements and the binding energies of Ti 2p, O 1s, B 1s and C 1s can be found at 458.9, 531.0, 193.0 and 284.0 eV, respectively. The presence of carbon can be ascribed to the residual carbon from precursor solution and the adventitious hydrocarbon from XPS instrument itself. Fig. 1 shows the high-resolution XPS of the B 1s region on the surface of boron-doped titanate nanotubes and nanowires after different heat treatments. After doping, only one symmetric B 1s peak appeared at 193.2 eV at 300 K. Taking into account that the standard binding energy of B 1s in B₂O₃ (or in H₃BO₃) is 193.0 eV (B–O bond) it can be stated that during the impregnation process (done at 300 K) no strong interaction was evolved between the boron and the titanate structures.

When the boron containing samples were heated to 573 K the intensity of B 1s markedly dropped. The position of the main component in XPS shifted to 192.4 eV due to initial state effect. A shoulder at 193.2 eV indicates that certain amount of boron remained in B³⁺ state. This drastic change indicates that the boron (B₂O₃) interact with the titanate nanostructures. The observed

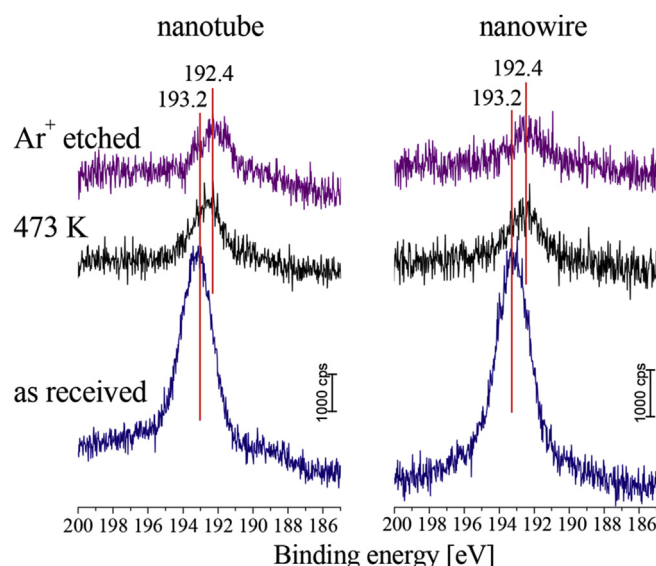


Fig. 1. B 1s photoelectron spectra of boron-doped titanate nanotubes and nanowires.

binding energy is less than in B_2O_3 and higher than in TiB_2 (187.5 eV). The observed B 1s spectrum at 192.4 eV at this elevated temperature can be ascribed to Ti–O–B bond [18], [20]. No spectral change in B 1s was detected at higher temperature.

In the O 1s region three peaks were detected at 535.3 eV, 532.5 and 530.2 eV which are attributed to adsorbed water, B–O [22] and Ti–O bond, respectively. The peak at 532.5 eV may contain OH group contribution as well (Fig. 2). O 1s due to adsorbed water at 535.3 eV disappeared upon heating, the O 1s intensity at 532.5 eV decreased indicating the significant loss of OH group (Fig. 2). When the sample was heated to 673 K, this photoemission remained. Interestingly an XPS signal developed at 528.0 eV in the O 1s region. This low binding energy peak can be attributed to the formation of Ti–O–B bond.

The formed Ti–O–B structure suggests that B could be localized at the interstitial position. The other possible scenario is that B act as substitute for the H in the lattice of $H_2Ti_3O_7$ similar to other metal containing titanate nanowires and nanotubes [11–16]. We assume that both reactions happen on boron-doped titanates upon heat treatment. The B 1s at 193.2 eV and O 1s at 532.5 eV can be identified to the formation of boron titanate due to ion exchange. Similar O 1s peak at higher binding energy developed during Au–H exchange on titanate nanotubes (Fig. 2). In this case XP signal at 528.0 eV was not observed; interstitial Au position was not assumed [16]. When the surface was ion etched by Ar ions (2 keV) the Ti–O–B structure remained, indicating that interstitial incorporation is escalated to the subsurface region.

During thermal annealing process crystal structure of titanate nanotubes and nanowires can be transformed into other phases, like anatase or rutile [5,23]. However, this phase transformation can be easily influenced by using different metal nanoparticles,

intercalated, ion-exchanged species or doping agents. For example, various nanoparticles (rhodium [13], bismuth [24]), or nitrogen doping [19] can catalyze the trititanate-to-anatase phase transition, and contrarily, in the presence of gold [16] or antimony [24] nanoparticles the titanate nanostructure can be stabilized. In this case we investigated the role of the boron in the above mentioned phase transitions. The XRD pattern of the as-received TiONT depicted in Fig. 3a. Reflections at $2\theta = 9.3^\circ, 24.4^\circ, 25.5^\circ, 27.8^\circ$ and 48.5° are characteristic for the layered trititanate nanotubes [5], where the first reflection corresponds to the interlayer distance in the tubular structure. In comparison the boron modified nanotubes (Fig. 3c) have the same reflections. When the temperature was elevated to 573 K there was no significant change in the structure of the pristine and the modified nanotubes. At 673 K both in the pristine and the B-modified samples the asymmetric trititanate reflections disappeared and a new symmetric reflection shown up which characteristic to the anatase (101) as it can be seen from the anatase TiO_2 reference XRD pattern. This result is typical to the formation of the trititanate to anatase nanotube [5,23,25]. Elevated the temperature to 773 K anatase reflections appeared in the B-modified titania with Miller indices of (101), (004), (200), (105), (211) and (204) at $2\theta = 25.3, 37.8, 48.1, 53.91, 55.1$ and 62.4 , respectively (JCPDS: 21-1276). However, the as-received titanate also shows anatase TiO_2 reflections but with lower crystallinity degree. Thus, the boron content enhanced the trititanate-anatase phase transition. At 873 K the former effect increased.

Trititanate nanowires shows literary reflections (Fig. 3b) as reported by Horváth et al. [9]. We identified four phases: bulk $\beta-TiO_2$ (JCPDS: 35-0088), $H_2Ti_3O_7$ (JCPDS: 36-0654), $Na_2Ti_3O_7$ (JCPDS: 31-1329), $Na_xH_{2-x}Ti_3O_7$ (JCPDS: 48-0693), respectively. The intensive reflection at $2\theta \sim 11.3$ is belongs to the (101) reflection of layered $H_2Ti_3O_7$. It is clearly seen the boron content does not affect structural change neither in the as-received TiONW nor in the heat treated counterparts (Fig. 3b–d). At 473–773 K the $H_2Ti_3O_7$ totally formed to $\beta-TiO_2$ [26]. Moreover, the $Na_xH_{2-x}Ti_3O_7$ phase with low intensity reflections totally disappeared from the system. Having elevated the temperature to 873 K anatase TiO_2 phase also exists beside the $\beta-TiO_2$.

It is well known that elevated temperature causes collapse of the protonated trititanate nanotubes and nanowires [5,13–15,23]. Fig. 4a shows the HRTEM image of the as-received open-ended titanate nanotubes. The average length is between 100 and 120 nm with ca. 10 nm outer and 5 nm inner diameter. The pristine nanowires (Fig. 4b) have length more than one μm and width of 70–80 nm. At 473 K neither B-TiONT (Fig. 4c) nor B-TiONW (Fig. 4d) showed any change. There are some nanotube fragments with 20–30 nm length besides the elongated ones in the samples calcined at 673 K (Fig. 4e). This temperature does not induce significant morphological change in the case of nanowires (Fig. 4f). The nanotubes turned into nanorods and quasi isomorph nanoparticles by the thermal annealing at 873 K (Fig. 4g). Collapse of the nanowires was not observed at this temperature but it is clearly seen in Fig. 4h that the end of the nanowires are round in shape and small anisotropic nanoparticles formed at on the nanowires surface.

4. Conclusion

Anisotropic titanates nanostructures (nanotubes and nanowires) were successfully synthesized and modified by boron using aqueous solution of B_2O_3 as doping source. The chemical nature, structure and morphology of the pristine and the doped samples were investigated by XPS, XRD and TEM before and after thermal annealing processes in the temperatures range between 473 K and 873 K.

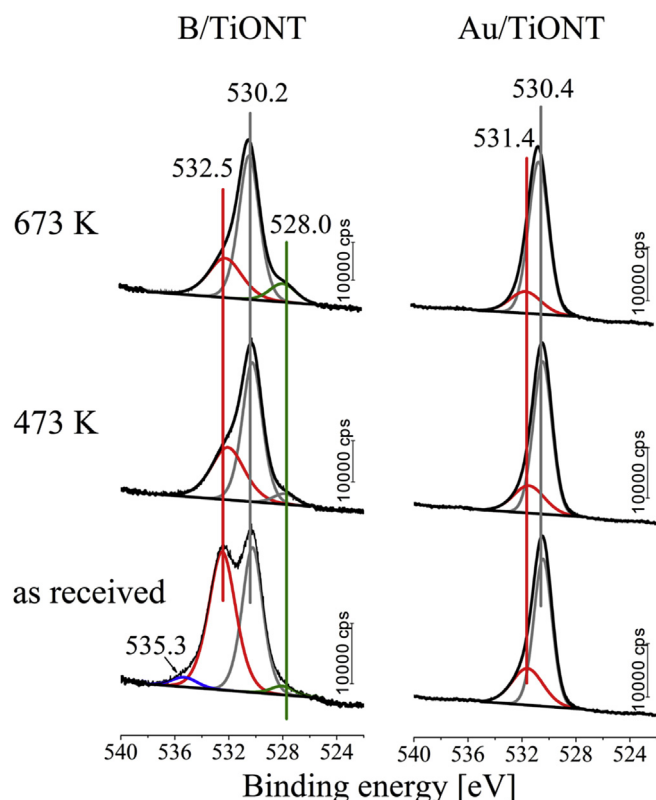


Fig. 2. O 1s photoelectron spectra of boron- and gold-doped titanate nanotubes.

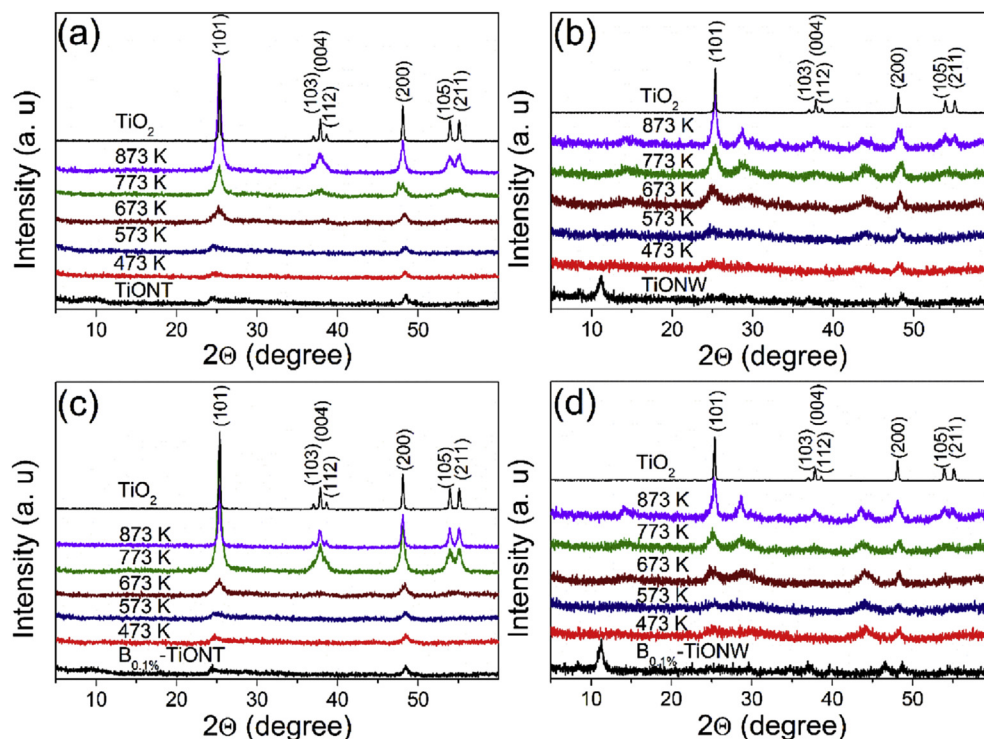


Fig. 3. XRD patterns of the as-received titanate nanotubes (a), titanate nanowires (b), boron modified nanotubes (c) and boron modified nanowires (d). Each panel shows the XRD patterns before and after the thermal annealing processes. As reference each panel shows the XRD pattern of anatase TiO_2 with its Miller indices.

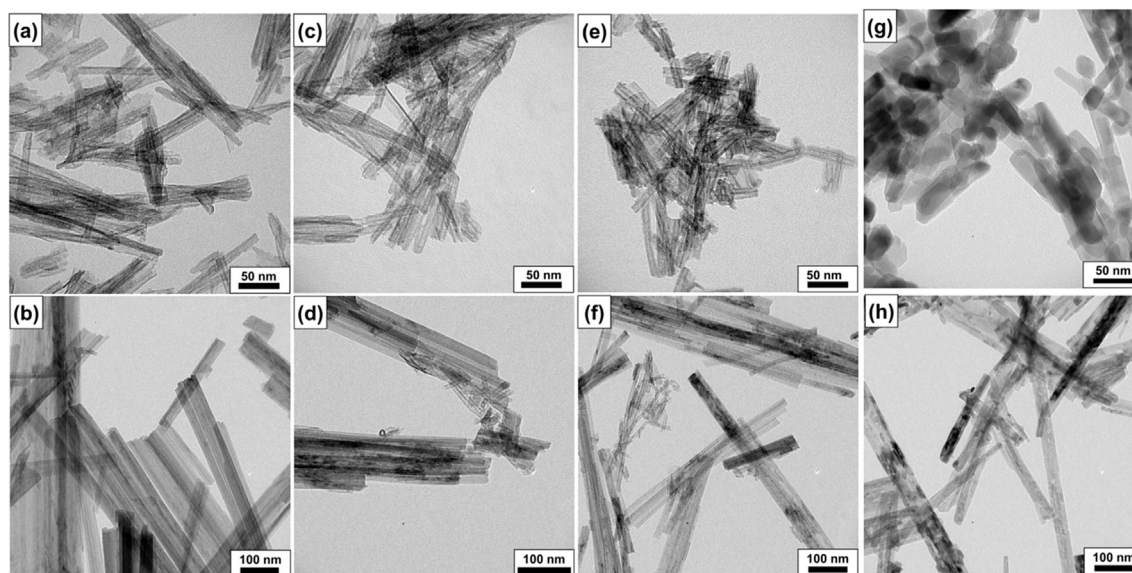


Fig. 4. TEM images of as-received titanate nanotube (a) and nanowire (b) and the B-modified counterparts calcined at 473 K (c, d), 673 K (e, f) and 873 K (g, h). Upper row belongs to the nanotubes and the other one to the nanowires, respectively.

XPS results reveals that a small part of boron may undergo ion-exchange process forming boron titanates. XP spectra also proved that significant part of boron incorporates into interstitial position (Ti–O–B) of the titanate nanotubes and nanowires.

XRD and HRTEM experiments showed that the presence of boron accelerates the phase transformation of tubular structured trititanate to anatase nanostructures (the product were nanorods and isomorphous nanoparticles). On the other hand, no significant catalytic effect was observed in phase transformation (wire structure to anatase) in the case of titanate nanowires.

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