Vacuum xxx (2016) 1–5

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Structure and stability of boron doped titanate nanotubes and nanowires

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ARTICLE INFO

Article history:
Received 6 July 2016
Received in revised form
23 November 2016
Accepted 28 November 2016
Available online xxx

Keywords:
Titanate nanotube
Titanate nanowire
Boron doping
Ion exchange

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 (trititanate to anatase) changes. These effects were not so pronounced on titanate nanowires.

1. Introduction

Among various semiconductors, titanium dioxide (TiO_2) 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 TiO_2, 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 TiO_2-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 TiO_2 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 TiO_2 are well documented in the previous excellent review [1]. There has been a turning point in the literature on anion-doping of TiO_2 since Asahi and coworkers' 2001 Science report on visible light activity in nitrogen doped TiO_2 [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 TiO_2 nanoparticles calcined at 773 K showed higher photocatalytic activity than pure

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http://dx.doi.org/10.1016/j.vacuum.2016.11.038

TiO_2 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 TiO_2 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 $Na_{2-x}H_xTi_3O_7$ 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 TiO_2 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, TiONW and commercial TiO_2 (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, TiO_2 and the boron modified counterparts underwent thermal annealing process in the temperature range between 473 K and 873 K for 1 h in N_2 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 ($h\nu = 1486.6$ 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 G^2 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 Kα 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 B_2O_3 (or in H_3BO_3) 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 B^{3+} state. This drastic change indicates that the boron (B_2O_3) interact with the titanate nanostructures. The observed

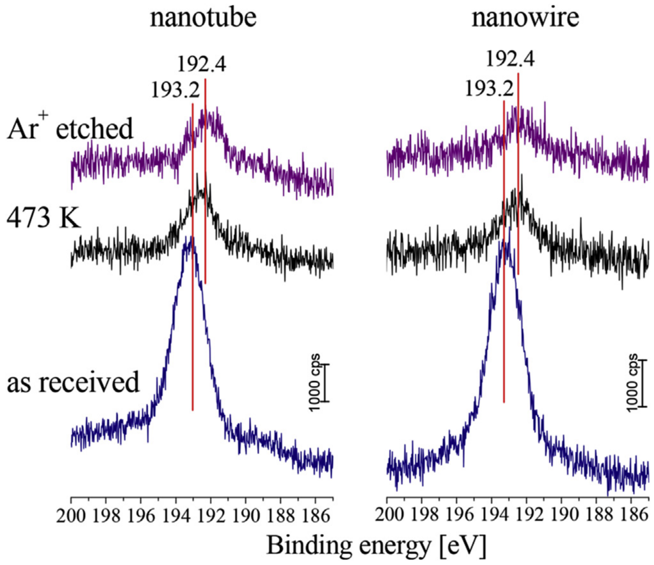

Fig. 1. B 1s photoelectron spectra of boron-doped titanate nanotubes and nanowires.

Please cite this article in press as: B. Buchholcz, et al., Structure and stability of boron doped titanate nanotubes and nanowires, Vacuum (2016), http://dx.doi.org/10.1016/j.vacuum.2016.11.038