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Structure and stability of pristine and Bi and/or Sb decorated titanate nanotubes

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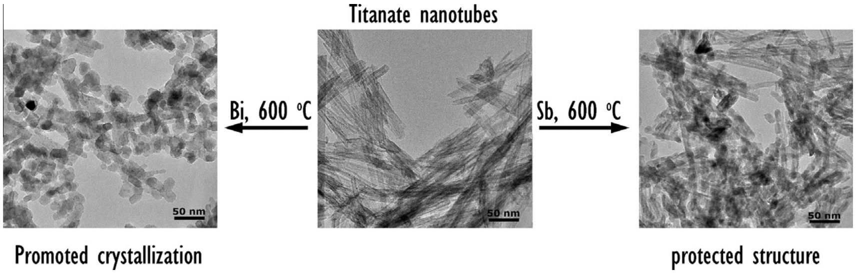
GRAPHICAL ABSTRACT



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ABSTRACT

90–100 nm long protonated titanate nanotubes were synthesized by hydrothermal method from anatase at 155 °C. The bismuth and antimony affected crystallization of the tubular titanate structures during calcination was studied by transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy. It was shown that bismuth and antimony have different effects on the transformation; while in the presence of antimony oxide the trititanate–anatase–rutile phase transformation is hindered, the bismuth oxide promotes the crystallization process to rutile.

1. Introduction

The discovery of carbon nanotubes encouraged researchers to widen their knowledge in the synthesis and characterization of the nanotubular materials. In the last decades several studies have been published about the synthesis and characterization of different inorganic nanotubes [1–3]. Titanium oxide based nanotubes have become a particular research subject because of their applications to photocatalytic [4–7], biomedical [8], energy storing [9] and semiconductor devices [10], to name a few.

The first sodium–trititanate nanotube synthesis was showed by Kasuga et al. [11]. The procedure was the hydrothermal treatment of TiO_2 powders in 10 M NaOH solution and needle-shaped nanotubes were obtained after the reaction.

Titanate nanotubes have been used for heterogeneous catalytic studies as support. The Au decorated titanate nanotubes could be promising catalysts in the low-temperature water–gas shift reaction [12]. Platinum nanoparticles can improve this behavior [13] as well. Pd(II)/titanate nanotubes have high activity and selectivity to the double-bond migration for example in the isomerization of allylbenzene [14]. The photocatalytic activity of trititanate nanotubes is weaker than that of anatase or other titanium-oxide nanocrystals [20] because of the distorted structure and wider band gap. Thus, several studies were published about the photosensitization of the titanate nanotubes. One possible sensitizer is cadmium sulfide, a versatile semiconductor with tunable 2.4–4.2 eV band gap [15] which can be obtained as layered assembly or as core/shell heterostructure [16]. The photocatalytic activity could be improved by framework doping using iron [17] or nitrogen [18] dopants as well.

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Metal ion incorporation into titanate nanotubes will definitely change their properties, however, as a result of the metal ion insertion the structure of the nanotubes can be strongly influenced as well. In the present study, we show the affect of bismuth and antimony on the heat treatment induced structural changes of the titanate nanotubes.

2. Experimental

All the chemicals were of analytical grade. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Molar Chemicals, while titanium dioxide (TiO_2, Degussa P-25) bismuth(III) acetate and antimony(III) acetate were purchased from Sigma–Aldrich®. The reagents were used without further purification. Deionized water was used in all aqueous solution for both preparations and washings.

2.1. Titanate nanotubes synthesis

The titanate nanotubes (TiONTs) were prepared by an alkaline hydrothermal method detailed elsewhere [19–24]. In a typical synthesis 50 g of TiO_2 powder and 1 L of 10 M NaOH aqueous solution were mixed. When a white suspension appeared, it was transferred into a Teflon-lined stainless steel autoclave (diameter 4 cm, height 14 cm) and kept at 155 °C for 24 h under continuous rotation (around the short axis of the autoclave, with a speed of 3 rpm). The as-prepared nanotubes were washed thoroughly with deionized water to neutral pH then subsequently with 0.1 M HCl solution to pH 2 and finally with water again to obtain a neutral salt-free product. The nanotubes were dried in air at 60 °C for 24 h.

2.2. Ion exchange and heat treatment

Bismuth-, antimony- and bismuth–antimony/titanate nanocomposites were prepared by ion exchange technique. The titanate nanotubes were dispersed in deionized water by ultrasonication and then bismuth acetate, antimony acetate and bismuth- and antimony acetate was added to the solution (the overall metal content was 10 wt.% for all samples). After stirring for 24 h the suspension was filtered and washed with deionized water to remove the remaining acetate ions and finally all the samples were dried at 60 °C for 24 h. All of the as-prepared samples (including the non-ion exchanged titanate nanotubes) underwent a thermal annealing process in air atmosphere at elevated temperature (100–900 °C) for 1 h. Samples were removed after each thermal operation for further characterization.

2.3. Characterization

The morphology of the pristine and modified titanate nanotubes was characterized by transmission electron microscopy (TEM). The TEM observations were performed on a FEI Tecnai G^2 20 X-Twin instrument (200 kV accelerating voltage) using copper mounted holey carbon grids.

The crystal structure was characterized by X-ray powder diffraction (XRD). The scans were performed with a Rigaku MiniFlex II powder diffractometer using Cu Kα radiation.

Energy dispersive X-ray spectroscopy (EDX) was used to estimate the elemental analysis of the heat treated pristine and ion exchanged samples. The EDX measurements were carried out on a Hitachi S-4700 scanning electron microscope equipped with a Röntec energy dispersive X-ray spectrometer.

Raman spectra of samples were measured at 532 nm laser excitation using a Thermo Scientific DXR Raman microscope. Scans were integrated at 4 cm^{-1} resolution until the desired signal-to-noise ratio of 1000 or better was achieved (max. 2 min).

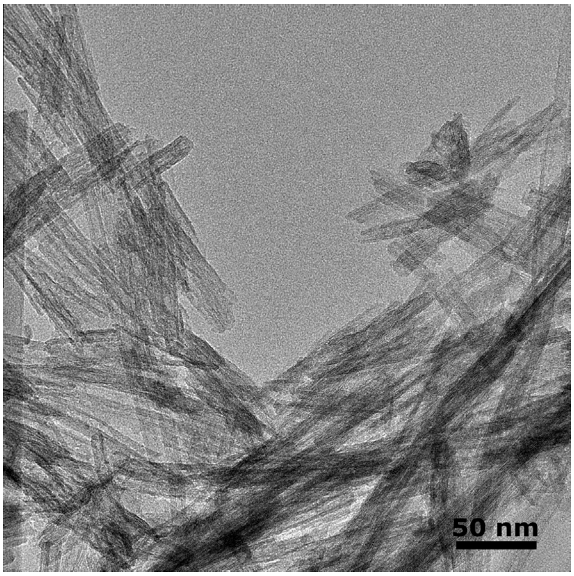

Fig. 1. TEM image of the as-synthesized titanate nanotubes.

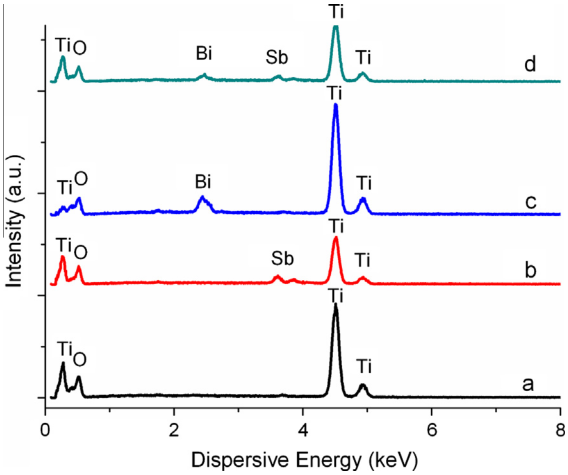

Fig. 2. EDX spectra of the pristine (a), antimony (b), bismuth (c), and antimony/bismuth (d) modified titanate nanotubes.

Heat treatment was carried out at 100–900 °C but structural changes appeared only at 600 °C and higher temperatures, therefore, only those results (as-synthesized and at 600, 750 and 900 °C calcined samples) will be shown here.

3. Results and discussion

The hydrothermally synthesized titanate nanotubes are open-ended tubular structures with 90–100 nm length and 8–10 nm width (Fig. 1).

Energy dispersive X-ray spectroscopy (EDX) was carried out for the elemental analysis of the different titanate nanotubes (Fig. 2). It is obvious that the samples contain Ti, O, Sb, Bi and are free from other elements.

Fig. 3 shows TEM images of pristine, antimony, bismuth, and antimony–bismuth modified titanate nanotubes calcined at