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A study of thermal properties of sodium titanate nanotubes synthesized by microwave-assisted hydrothermal method

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ABSTRACT

Sodium titanate nanotubes (NaTiNTs) were synthesized by microwave-assisted hydrothermal treatment of commercial TiO_2, at constant temperature (135 °C) and different irradiation times (15 min, 1, 4, 8 and 16 h). The products were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, differential scanning calorimetry and specific surface area measurements. The irradiation time turned out to be the key parameter for morphological control of the material. Nanotubes were observed already after 15 min of microwave irradiation. The analyses of the products irradiated for 8 and 16 h confirm the complete transformation of the starting TiO_2 powder to NaTiNTs. The nanotubes are open ended with multi-wall structures, with the average outer diameter of 8 nm and specific surface area up to 210 m^2/g. The morphology, surface area and crystal structure of the sodium titanate nanotubes synthesized by microwave-assisted hydrothermal method were similar to those obtained by conventional hydrothermal method.

1. Introduction

Sodium titanate nanotubes (NaTiNTs) are thoroughly studied because of their large specific surface area, ion-exchange ability and proton conductivity which render them attractive for applications as catalysts [1,2] and catalyst support [3,4], in the area of pollutants removal [5,6], electrodes for energy storage [7,8], and proton exchange membrane fuel cells [9]. Recent applications of this material are spreading in the bio-area, as nanobiocatalyst (enzyme immobilization) mainly due to its biocompatibility and hydrophobicity [10]. The electron–hole pair rapid recombination and the wide bandgap limit the application of these materials as photocatalysts [11,12]. Intensive work was done to improve the photocatalytic activity, like doping [13,14], surface modification [15,16], and composite synthesis [17,18], but also chemical modifications of the hydrothermal method [19].

The mechanism of the nanotubes was subject of intense research. All the proposed mechanisms follow a 3d-2D-1D model [20]. Kasuga et al. [21] and other groups [22] suggested that lamellar sheets are formed during alkaline hydrothermal treatment, than removal of sodium ions by acid washing process leads to the scrolling of sheets to nanotubes (acid washing mechanism). Other groups [20,23–25] suggested that the nanotubes are formed during the hydrothermal treatment, following a four stages mechanism (peeling–scrolling mechanism). Kukovecz et al. [26] presented evidence against the rolling-up mechanism. Under alkaline attack, small amount of precursor is dismantled from the surface, than recrystallizes into trititanate sheets that curves to nanoloops. These nanoloops become seeds for an oriented crystal growths process, leading to nanotubes.

A microwave irradiated 10 M NaOH solution will provide an uniform heated reaction environment, accelerating the particle to high velocities and high density of interparticle collisions [27]. The microwave radiation will accelerate drastically the kinetics of dissolution/recrystallization mechanism (Ostwald-ripening) [28]. Therefore, the nanotube morphology can be rapidly achieved by the use of the microwave-assisted hydrothermal treatment. According to Zhang et al. [29], microwave radiation is capable of changing the polarization of hydroxyl species on the surface of the solid, facilitating reaction between solid and liquid. Also, the high density of OH^- will provide enhanced reaction rate acceleration by dipolar polarization conduction mechanism and the sodium cations in the solution will contribute to ionic conduction [30].

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Different synthesis methods have been used for nanotube preparation. Extended reviews dedicated to titania/titanate nanostructures summarized different preparation methods and compared them in terms of process complexity, cost effectiveness, and processing time [31,32]. Nanotubes of uniform size and controlled dimensions are synthesized by a template-assisted method. Template removal, impurifications, time consumption and limited choice of the substrates are the main drawbacks of this method [33]. Nanotubes arrays with controlled dimensions and a high aspect ratio are prepared by anodic oxidation of Ti foil. Amorphous nature and morphology collapse during annealing are the disadvantages [34]. Hydrothermal method is the most used procedure since it provides open-ended nanotubes with good crystalline structure, pure-phase composition, and synthesis of NaTiNTs in gram quantities. The drawbacks of the method are random orientation of nanotubes, long reaction times (from 12 h to several days) [35] and high energy consumption (electric power over a thousand Watts) [36].

Microwave-assisted hydrothermal (MW-H) method was classified as a modification of the classical hydrothermal method for the synthesis nanostructured titanates [37]. Microwave-assisted method requires significantly shorter times (from minutes to several hours) and lower energy consumption (hundred of Watts) [36], rendering it as a cost effective method in comparison with the conventional hydrothermal method.

Furthermore, the additional advantage of this method is an efficient internal "in core", directly and uniformly volumetric heating [30]. In the case of NaTiNTs, the energy delivered to the system through molecular interactions with electromagnetic field, accelerates the reaction rates and, at the same time by high-energy density of the microwave irradiation the crystallinity of formed NaTiNTs is improved [38,39]. This method was used by few groups for synthesis of NaTiNTs, using different reaction parameters. For instance, reactions were performed at the constant microwave power [40], constant temperature [38,41,42], or on/off irradiation mode [43]. A characteristic feature of the nanotubes obtained by MW-H method was the nanotubes' smaller outer diameter; values of 7.36 nm [38], 7.6–8 nm [44], 11 nm [45] or 8–12 nm [40] were reported. The nanotubes were considered ultrathin [44] but with thicker walls [45] when compared to those obtained by conventional hydrothermal method.

The aim of this work is to determine the optimal reaction time for the synthesis of NaTiNTs by microwave assisted hydrothermal (MW-H) method and the impact of microwave irradiation on the dimensions of NaTiNTs and their thermal properties.

2. Experimental

2.1. Synthesis

0.7 g of TiO_2 (Aldrich, 325-mesh) was dispersed in 7 ml of 10 M NaOH, stirred at room temperature for 1 h, followed by ultrasonication for about 15 min and stirred again for 10 min. Then a SiC vial was filled with 6 ml of the reaction mixture and placed into a microwave reactor (Anton Paar, Monowave 300). Reactions took place at the constant temperature of 135 °C for 15 min, and 1, 4, 8 and 16 h. Microwave (MW) power reached the maximum of about 200 W in the beginning of the reaction. After the ramp temperature of 135 °C was reached (in 2.5 min), the MW power decreased and stayed constant in the range of 5–10 W. For the reaction times 8 and 16 h the reactions lasted 2×4 h and 4×4 h due to the time limitations of the microwave reactor operating at 135 °C. When the reaction mixture was cooled down to room temperature the products were dispersed in 100 ml of distilled water, filtered and dried over night at 100 °C. The isolated products were labeled according to the reaction time: **MW-1/4 h** (15 min), **MW-1 h** (1 h), **MW-4 h** (4 h), **MW-8 h** (8 h) and **MW-16 h** (16 h). In addition, for the reactions that lasted for 8 and 16 h, when the first heating block at 135 °C was finished, the reaction mixture was cooled down to 60 °C as fast as possible and then heated as fast as possible to 135 °C. The time interval between two heating blocks at 135 °C was around 7 min.

2.2. Characterization

Field-emission scanning electron (FE-SEM; Jeol 7600F, operating at 1.5 keV) and transmission electron microscopes (TEM; Jeol 2100, operating at 200 keV) were used for the morphology characterization. The elemental compositions of the samples were investigated with the FE-SEM equipped with an EDS (energy dispersive X-ray spectrometer). Nitrogen sorption isotherms at −196 °C were recorded on a Micromeritics ASAP 2020 automated gas sorption system. The samples were outgassed at 200 °C for 4 h under vacuum prior to N_2 adsorption. Specific surface areas (S_{BET}) were calculated according to the Brunauer–Emmett–Teller (BET) equation using adsorption data in the relative pressure range between 0.05 and 0.30. The total pore volume (V_{total}) was estimated from the adsorbed amount of N_2 at the relative pressure of 0.99. The pore size distribution curves were obtained using Barrett–Joyner–Halenda (BJH) method from the desorption branch. The phase composition was determined by powder X-ray diffraction (XRD), using a Rigaku Ultima IV diffractometer in θ–θ mode, using Cu-Kα radiation (1.5406 Å), at a fixed power source (40 kV and 30 mA). Data were collected in the 2θ range of 3–90°, at a step size of 0.02° and a scan rate of 1°/min. Phase identification was performed using Rigaku's PDXL software, connected to ICDD PDF-2 database. Qualitative *in-situ* powder XRD was measured in the temperature range from 100 to 600 °C, using the same equipment. Qualitative analysis of the physico-chemical transformations was investigated by differential scanning calorimetry (DSC), using a Mettler-Toledo DSC 823^e apparatus and by thermogravimetric analysis (TG), using a Mettler-Toledo TGA/SDTA 851^e. Both measurements proceeded under nitrogen atmosphere during the heating from 30 to 600 °C, with a heating rate of 20 °C/min.

3. Results and discussion

All the products were characterized by XRD in order to determine an optimum reaction time for a complete transformation of the starting anatase powder to sodium titanate nanotubes (Fig. 1). Analyzing the diffractograms of the samples reacted between 15 min and 16 h, one can notice that the **MW-8 h** sample contains single-phase NaTiNTs, with no traces of anatase precursor.

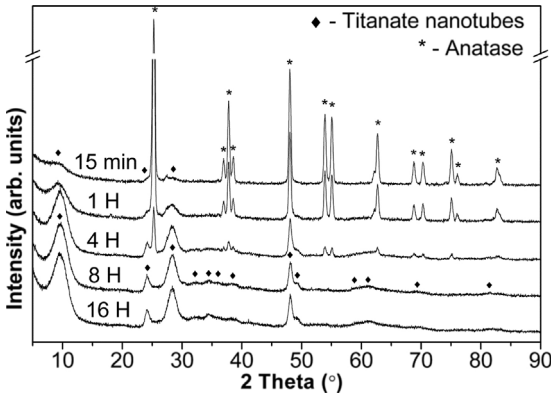

Fig. 1. X-ray diffraction patterns of the samples isolated after 15 min and 1, 4, 8, and 16 h or microwave treatment.