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Titanate nanotubes produced from microwave-assisted hydrothermal synthesis: Photocatalytic and structural properties

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Abstract

Titanate nanotubes were successfully synthesized using the microwave-assisted hydrothermal method from commercial TiO_2-anatase powder. Several samples were obtained at varying temperatures and time. Powder samples containing titanate nanotube ($Na_2Ti_6O_{13}$) single phase were obtained at 130 °C for 4 h and 150 °C for 2 h, demonstrating the kinetics dependence of reaction temperature. Through XRD analysis and electron diffraction pattern, the nanotube structures were found to be composed of a short range ordering, thus giving rise to a broad XRD peak profile. The higher time and temperature (150 °C for 4 h) led to the formation of more organized structures. The nanotubes UV–vis spectra showed a band gap of 3.90 eV and a shoulder on the curve which led to another band gap value 3.25 eV. The photoluminescence spectrum emission peak presented a significant decrease, indicating the reduction of surface or structural defects of titanate nanotubes due to longer hydrothermal treatment duration. All structural, electronics and morphologics transformation led to an improvement on photocatalytic activities for nanotubes, especially the sample obtained at 150 °C for 1 h that rate of decolorization is 0.01879 min^{-1}, 2.25 times faster than TiO_2-anatase (starting phase).

Keywords: Microwave hydrotermal synthesis; Titanate nanotubes; Photoluminescence; Photocatalysis

1. Introduction

The increasing demand in materials exhibiting high surface areas for technological purposes such as adsorbents [1], sensors [2–4], photocatalysts [5,6], agriculture [7] and drug delivery [8,9] has led to innovative approaches for dioxide titanium (TiO_2) based materials. To this end and for attaining success in the above-mentioned applications, the need for more efficient materials with higher surface area cannot be over-emphasized. Chemical synthesis methods can also be used for this purpose, such as microemulsion technique [10], sol–gel [11], Polymeric Precursor [12], and Hydrothermal [13], as well as changes in synthesis parameters like temperature, time and pH, or the use of modifiers as carbon [14], nitrogen [15] and basic cations (Mg^{2+}, K^{+}, Ba^{2+}, Zn^{2+}) [16] wich led to improvement on materials properties. These approaches can enhance the morphological, mechanical, electric, optical and thermal properties of nanoparticles surfaces, including the development of 1D nanostructures, such as tubes, wires or needles [17]. Several synthesis routes have been studied since titanium nanotube synthesis was described for hydrothermal conventional method from the titanium oxide [18,19]. Other studies have also been conducted using similar methodology [20–22]. The effects of the concentration of NaOH on the structures and formation mechanisms of various titanate was presented in a detailed in a study and was found that the morphologies of the titanate products were determined by the concentration of NaOH [23]. Starting from titanium dioxide at low temperature, an effective 1D structure only occurs after about 20 h using the conventional hydrothermal method. Microwave as the heat source was found to reduce the reaction time to around 2 or 3 h, but a further reduction can be attained with an increase in temperature [24,25]. The parameters of the

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microwave-assisted hydrothermal synthesis, such as reaction time and temperature, TiO_2 amount and power source of the equipment were studied in order to understand their influence on the process of obtaining nanowires. Results have shown that the temperature affects most notably the product morphology, while the treatment time affects the final length as well as the amount of nanowires[24]. Indeed, the structure–property correlation for these materials requires yet further investigations and the primary goal of this work is to investigate some of these aspects for the sodium titanate nanotube synthesis by the microwave-assisted hydrothermal method. This paper shows the influence of time and temperature on the sodium titanate nanotube synthesis as well as the variations in photoluminescence, electronic properties and photocatalysis activities as a consequence of the structure and morphology obtained.

2. Material and methods

2.1. Synthesis

The microwave-assisted hydrothermal method (MAH) was used to synthesize sodium titanate nanotubes. By using a digester CEM Corp. brand. (Matthews, NC), model-5 MARS set to 450 W in operating power, reagents which have not been previously purified were inserted into a closed Teflon® (XP-1500) vessel. A sodium hydroxide solution at concentration of 10 mol L^{-1} was prepared using NaOH pellets (Synth). Then 0.4286 g of TiO_2-anatase powder (VETEC) with particles size of about 100 nm was added to the previous solution in order to obtain a suspension volume of 50 mL. A number of synthesis conditions were investigated, varying the temperature from 130 to 200 °C and the time reaction from 30 min to 4 h. The powder samples obtained were washed with deionized water until the pH was stabilized to about 6.0 and were then dried at room temperature.

2.2. Samples characterization

All of the samples were morphologically and structurally characterized by X-ray diffractometry (XRD), Raman spectroscopy and scanning and transmission electron microscopy. For the XRD technique, a Rigaku 2000 diffractometer with monochromatic Cu Kα radiation at 2θ range of 10–80° with step of 0.01° was used. The particles morphology was investigated by scanning electron microscopy (SEM) on a JEOL FEG-SEM, JSM-7500F and Transmission Electron Microscopy (TEM) Philips CM 200. For the Raman spectroscopy characterization, a Bruker equipment RFS100/S with a Nd:YAG laser providing an excitation light at 1.064 with a spectral resolution of 2 cm^{-1}, in the range 1100–20 cm^{-1} and 64 scans was used. The photonic characteristics were analyzed by UV–vis diffuse reflectance using a Cary spectrophotometer UV–vis NIR and 500 by MgO as a reflectance standard in order to calculate the band gap values. Besides that, the photoluminescence spectra were collected through a Thermal Jarrel-Ash monochromator Monospec 27 and a Hamamatsu R446 photomultiplier, with wavelength of 350 nm for excitation of krypton laser ions (Coherent Innova) with power maintained at 550 mW.

Photocatalytic studies were carried out using 100 mg L^{-1} of TiO_2-anatase and nanotubes sample dispersed in 500 mL of 0.01 mmol L^{-1} aqueous solution of rhodamine-B. The suspended solution was stirred a few minutes in the dark and then it was put under a Phillips germicide lamp (254 nm). Degradation was monitored by taking aliquots at increasing time intervals. These aliquots were filtered with Millipore® (0,45 μm) membranes and then tested using a UV–vis Femto Cirrus 80PR spectrometer to get the absorption spectra. The concentration curve was obtained by max rhodamine-B absorbance peak (554 nm). The rate of degradation was obtained according to Eq. (1):

$$\ln\left(\frac{A_0}{A}\right) = kt \quad (1)$$

where A_0 is the initial absorbance, namely, after stirred a few minutes in the dark, and A is the characteristic absorbance peak at degradation for a time, t.

3. Results and discussion

The XRD patterns for the powder samples obtained by MAH at 130 °C, 150 °C, 180 °C and 200 °C for varying reaction times (0.5–4 h) are shown in Fig. 1. For a temperature of 130 °C (Fig. 1a), the anatase phase (A), which is the single one in the starting powder remains highly crystalline with the time of reaction in spite of its rapid consumption toward the formation of the nanotube phase (✻). The anatase TiO_2 phase was identified following its comparison with JCPDS card no. 21-1272, which possesses space group I41/amd and lattice volume of 136.26 $Å^3$. Through the Rietveld refinement mechanism using structural model found in ICSD database (card no. 200392), the anatase phase in the starting powder was found to have a and c lattice parameters of 3.7848 and 9.5119 Å, respectively.

The sodium titanate nanotube formed in the reaction presents to a large extent very broad peaks both to the excessive peak overlapping and to the small nanometer size dimensions of the tubes. The main peaks are localized at $2\theta = 24$, 28 and 48° and the most intense one at $2\theta = 10°$, which can be related to these nanostructures, that have originated from titanate interlayers. In Fig. 1 it is possible to see that the difractograms start at $2\theta = 10°$, except for sample obtained at 180 °C (Fig. 1c) which starts at $2\theta = 5°$ and shows these peaks profile clearly. From these peaks profiles there are several possible structures, such as $Na_2Ti_2O_5 \cdot H_2O$, $H_2Ti_4O_9 \cdot H_2O$ or the lepidocrocite titanate $Na_xH_{2-x}Ti_3O_7$, and $H_2Ti_2O_4(OH)_2$, the non-washed hydrated titanic acid $H_2Ti_2O_5 . H_2O$ and the sodium trititanate nanotube ($Na_2Ti_3O_7$) as reported in the literature [26–29]. However, following a series of attempts to refine them all including the other ones, it was noted that the structure that exhibited the best adjustment corresponded to the composition $Na_2Ti_6O_{13}$ and C2/m