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Sodium titanate nanorods: Preparation, microstructure characterization and photocatalytic activity

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Abstract

A method for the preparation of sodium titanate nanorods with diameter around 50 nm and lengths up to 2–3 μm is described. The precursor prepared by the reaction of sodium titanate with ethylene glycol readily aggregated into 1D nanostructures. During heating of this precursor up to 900 °C the glycolate complex of sodium titanate decomposed and a crystalline product of the chemical composition $Na_2Ti_6O_{13}$ with the morphology of nanorods was formed. The initial sodium titanate sample as well as samples heat treated to 550–900 °C, respectively, were characterized by X-ray diffraction, infrared spectroscopy, electron microscopy (SEM, TEM, HRTEM) thermal analysis methods (DTA–TG-coupled with mass spectroscopy and emanation thermal analysis) as well as by surface area and porosity measurements. It was demonstrated that the nanorods formed by heating of the precursor at 900 °C/2 h exhibit a good photacatalytic activity for the decomposition of 4-chlorophenol in an aqueous slurry under UV radiation.

Keywords: Sodium titanate; Nanorods; Ethylene glycol; Photocatalytic activity; Surface area; Porosity; SEM; HRTEM; XRD; 4-Chlorophenol

1. Introduction

Alkaline metals and hydrogen titanates are of great interest for possible applications such as photocatalysts, as fuel-cell electrolytes or cation exchangers in the treatment of radioactive liquid waste [1–3]. The photocatalytic activity was evaluated [1] by measuring the total volume of hydrogen gas evolved during the irradiation of catalyst suspensions in water. Chemical and physical properties of sodium titanates depend on reactants and the method of preparation used. Sodium titanates can be obtained by treatment of TiO_2 in NaOH solution. For example, anatase or rutile was used as starting material in [4,5], whereas brookite was used in the preparation of sodium titanate nanowires by hydrothermal reaction [6,7]. A method for the preparation of potassium titanate nanowires by a hydrothermal reaction is described in [8]. The $Na_2Ti_6O_{13}$ whiskers were synthesized by the hydrothermal treatment of spherical TiO_2 anatase particles in NaOH solution at the temperature of 250 °C [9]. Sodium titanate whiskers were also prepared by the reaction of anatase with 10 M NaOH under ultrasound treatment [10], however, the sodium titanate precursor transformed to anatase during the subsequent reaction with HNO_3 and washing with deionized water. Moreover, a sol–gel method was used for the preparation of sodium titanates with the chemical composition $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ [11].

In this paper, we describe the preparation of sodium titanate nanorods using a precursor synthesized by the reaction of sodium titanate with ethylene glycol and subsequent heating of this precursor. It was shown, e.g. in [12], that polyethylene glycol has been used as a templating agent for the synthesis of mesoporous TiO_2. Recently Jiang et al. [13] used ethylene glycol in large-scale synthesis of metal oxide nanowires (including TiO_2) where tetra-alkyltitanium was added to ethylene glycol and the alkoxide transformed into a chain-like glycolate complex that subsequently crystallized into uniform nanowires.

In this study the ethylene glycol was used as an agent in the synthesis of a chemical complex with sodium titanate as a precursor to prepare sodium titanate nanowires and nanorods. The practical objective of this study is based on the fact that the used raw material in this study is a by-product in the pigment titania white production by using sulfate technology in

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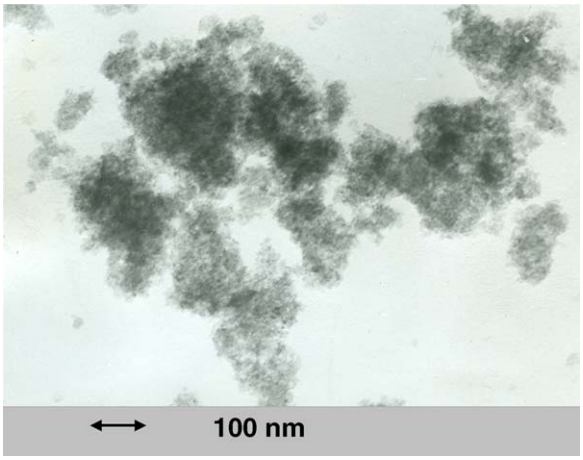

Fig. 1. TEM micrograph of the sodium titanate material supplied by Precheza Přerov Ltd.

Precheza Přerov Ltd. (Czech Republic) and therefore this raw material is significantly cheaper and more advantageous for the technological use in comparison with titanium alkoxide-based materials.

2. Experimental

2.1. Chemicals and raw materials

Ethylene glycol (molecular mass 92.0 p.a.) was supplied by Fluka, Munich, Germany. Sodium titanate from the production of Precheza Přerov Ltd. (Czech Republic) was used as raw material. It was a solid mixture of chemical composition $Na_{0.98}H_{1.02}Ti_4O_9{\cdot}3H_2O$ and $Na_2O{\cdot}3TiO_2$, as determined by XRD (Philips RW 1480). Chemical purity as determined by XRD method was 99.4%. The surface morphology of the raw material as characterized by TEM is presented in Fig. 1. Results of the EDAX analysis for the content of Na and Ti in the raw material are presented in Table 1.

2.2. Synthesis of sodium titanate glycolate complex as a precursor for nanorods

A suspension of sodium titanate raw material (100 g) in 100 mL of ethylene glycol (EG) was heated in an electrical heating nest in a round-bottom flask with a reflux cooler at the temperature of 198 °C/6 h. After cooling down to room temperature, excess of water was decanted and the white flocculate was washed with ethanol to remove excess EG from the sample. Finally, it was dried in a furnace at a temperature of 105 °C (this precursor was denoted as sample TIT252).

2.3. Heat treatment of titanium glycolate as the precursor for nanorods

The prepared sodium titanate glycolate complex precursor was placed in an oven and heated to a temperature of 550–900 °C, respectively, for 2 h. The temperature increase rate to achieve the respective temperature was 1 °C/min. (The products resulting after this heating were denoted as samples TIT252_550 and TIT252_900, respectively.) As it followed from the results of thermal analysis, XRD and SEM, the sodium titanate glycolate precursor decomposed during heating and crystallized as sodium titanate ($Na_2Ti_6O_{13}$) with uniform 1D morphology. Moreover, reference samples were prepared by using the similar heating schemes for the heat treatment of the raw material supplied by Precheza Přerov Ltd. (Czech Republic). The respective samples prepared by this way were denoted: rawmat_as received, rawmat_500 and rawmat_900.

2.4. Characterization methods

Surface area of the samples was determined from nitrogen adsorption–desorption isotherms at liquid nitrogen temperature using a Coulter SA 3100 instrument with 15 min lasting outgas at 120 °C. The surface area was calculated by BET method while the pore size distribution was determined by BJH method [14].

Transmission electron microscopy (TEM) instruments "Philips EM 201 (80 kV)" and "JEOL JEM 3010 (300 kV)" (LaB_6 cathode) were used. Copper grid coated with a holey carbon support film was used to prepare samples for HRTEM observation. The powdered sample was dispersed in ethanol and the suspension was treated in ultrasonic bath for 10 min. Then a copper grid was dipped into it.

SEM micrographs were obtained by using a Philips XL30 CP microscope equipped with EDX, Robinson, SE and BSE detectors. The sample was placed on an adhesive C slice and coated with a 10 nm thick layer of Au–Pd alloy.

X-ray powder diffraction patterns were obtained by Siemens D5005 and Philips RW 1480 instruments using Cu Kα radiation (40 kV, 30 mA) and a diffracted beam monochromator.

Table 1
Results of surface area, pore volume, EDX analysis and rate constant of 4-CP photodegradation that characterize the sodium titanate-based samples

Sample	Temperature of treatment (°C)	EDX_Na (wt.%)	EDX_Ti (wt.%)	Rate constant, K (min^{-1})	Surface area ($m^2\,g^{-1}$)	Total pore volume ($cm^3\,g^{-1}$)
TTIT252_900	900	8.85	51.09	1.0405	27.8	0.1655
TIT252_550	550	9.55	49.27	0.4803	190.5	1.2431
TIT252_precursor	105	15.01	33.13	n.d.	380.2	1.1693
Raw_titanate_900	900	n.d.	n.d.	0.7024	5.3	0.0232
Raw_titanate_550	550	n.d.	n.d.	0.6136	47.8	0.2597
Raw_titanate	105	18.60	31.14	0.7851	142.5	0.3328

n.d.: not determined.