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Morphology, structure and adsorption of titanate nanotubes prepared using a solvothermal method

Chau Thanh Nam [a], John L. Falconer [b], Le Minh Duc [c], Wein-Duo Yang [a,b,*]

[a] Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 415 Chien-Kung Road, Kaohsiung 807, Taiwan, ROC
[b] Department of Chemical and Biological Engineering, University of Colorado at Boulder, Boulder, CO 80309, USA
[c] Department of Chemical Engineering, Danang University of Technology, Danang, Viet Nam

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ABSTRACT

Titanate nanotubes were synthesized with a low temperature solvothermal process in a highly alkaline solution with a 30:70 organic solvent/water (by volume) ratio using TiO_2-P25 as a precursor. The organic solvents had boiling points below 100 °C and included methanol (M), ethanol (E), acetone (A), methyl ethyl ketone (MEK), *n*-propanol (NP) or isopropanol (IP). The solvents helped control the morphology of the product; the samples prepared using M, E, and MEK exhibited nanotube structures. The titanate samples were tested via the adsorption of methylene blue (MB) dye. The samples produced using M, E, and MEK had higher surface areas than the other samples (using the solvents A, NP and IP) and therefore exhibited high MB adsorption loadings.

1. Introduction

Kasuga et al. [1,2] synthesized TiO_2 nanotubes using a simple hydrothermal treatment of TiO_2-P25 powder in an aqueous 10 M NaOH solution; titanates were obtained as the intermediate phase. Recent studies have prepared titanate nanotubes (TNTs) with a wet method beginning with TiO_2-P25 in a concentrated alkaline solution [3,4]. TNTs exhibit a large specific surface area and good adsorption properties. Nanotubular TiO_2 has a high surface area, providing a high adsorption capability. In addition, TiO_2 has been prepared as nanowires/nanofibers, nanorods, nanotubes and nanobelts/nanoribbons. Liquid-phase processing is one of the most convenient and commonly used methods in chemical synthesis. In particular, the hydrothermal/solvothermal processing used to synthesize TiO_2 nanotubes is a soft-chemical technique; the reactions occur at relatively low temperatures [5].

Liquid-phase processing at low temperatures produces TiO_2 nanostructures under hydrothermal conditions [6–11], and hydrothermal/solvothermal techniques are commonly used to synthesize TiO_2 nanostructures [12–16]. Hydrothermal/solvothermal syntheses facilitate the synthesis of nanometer-sized crystalline TiO_2 powder at relatively low temperatures [11,14,16]. Solvothermal reactions use a solvent under conditions of high pressure and mild temperature and show promise for developing nanotechnologies [17]. Using organic solvents during solvothermal synthesis helps to control the structure and morphology of the products due to the shape- and size-dependent properties of the products [16,18]. Numerous different solvents have been used during solvothermal synthesis to investigate the growth mechanisms and characteristics of titania [16,18]. Researchers have investigated the effect of co-solvents (water-ethanol), temperature and NaOH concentrations on the morphology of titanate nanostructures (nanoflakes, nanotubes, and nanofibers) [19]. The effects of reaction temperature, stirring conditions and co-solvent (water-ethanol, water-ethylene glycol) on the morphologies of the as-prepared nanostructures (nanotubes, nanorods, nanowires, and nanoribbons), as well as their growth mechanism, have been investigated [20]. The solvent helps to determine the crystal morphology. Solvents with different physical and chemical properties can influence the solubility, reactivity, and diffusion behavior of the reactants; in particular, the polarity and coordinating ability of the solvent can influence the morphology and the crystallization behavior of the final products [21].

The hydrothermal method is superior for the synthesis of TNTs. Under solvothermal conditions, adding an organic solvent to water generates an excellent reaction medium for the hydrothermal processing of nanoparticles because the reaction rate and the equilibrium can be modulated by adjusting the dielectric constant,

* Corresponding author at: Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 415 Chien-Kung Road, Kaohsiung 807, Taiwan, ROC. Tel.: +886 73814526x5116; fax: +886 7 3830674.
E-mail address: ywd@cc.kuas.edu.tw (W.-D. Yang).

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leading to higher reaction rates and smaller particles [22]. In this work, TNTs are synthesized using a solvothermal route in a 130 °C aqueous solution containing solvents and NaOH and TiO_2-P25 nanoparticles as precursors. This study focuses on the influence of different alcohol and ketone solvents with low boiling points (methanol (M), ethanol (E), acetone (A), methyl ethyl ketone (MEK), *n*-propanol (NP) and isopropanol (IP)) on the morphology of titanate nanocrystals under solvothermal conditions; the solvent to water (W) ratios were all 30:70. The adsorption efficiency of methylene blue dye was measured for these TNTs. This study also includes the use of a co-solvent (methanol–ethanol (M-E) and acetone–MEK (A-MEK)) in a 1:1 ratio and a 30% by volume solution to evaluate the effect.

2. Materials and methods

2.1. Reagents

All of the chemicals used in this study were of analytical grade and were used as received without any further purification. NaOH, TiO_2 (P25) powder, and methylene blue (MB) were purchased from Acros Organics (New Jersey, USA). Two hundred milliliters of MB solution (300 ppm) was prepared in double-distilled water and diluted as needed.

2.2. Instrumentation

All of the glass apparatuses were thoroughly washed in tap water and then in distilled water. The apparatuses were dried overnight in a hot-air oven at 50 °C. The crystal structures of the products were characterized by X-ray diffraction (BRUKER, D8 Advance X-ray diffractometer, CuK_α radiation) and micro-Raman spectroscopy (Dimension-P2 Raman). A Micromeritics ASAP 2020 Analyzer was used for the BET analysis. TEM measurements were performed using a Philips M-200 transmission electron microscope operating at 200 kV. Before the TEM analysis, the samples were sonicated in ethanol for 15 min, and 2–3 drops of the sample were deposited onto a thin carbon film supported by a perforated copper grid. The samples were dried overnight at 60 °C. Fourier transform infrared spectroscopy (FTIR) was conducted using a spectrometer from Perkin Elmer instruments. UV–vis diffuse reflectance spectra from 300–800 nm were obtained using a Jasco V-600 UV–vis spectrophotometer; this instrument was used to measure the red shifts in the samples. Photoluminescence (PL) spectra were recorded at room temperature with a fluorescence spectrophotometer (F-4500, HITACHI) at 285 nm (excitation). Additionally, all of the absorbance measurements were conducted using a UV–vis spectrophotometer (HITACHI, U-2800) equipped with a 1 cm quartz cell.

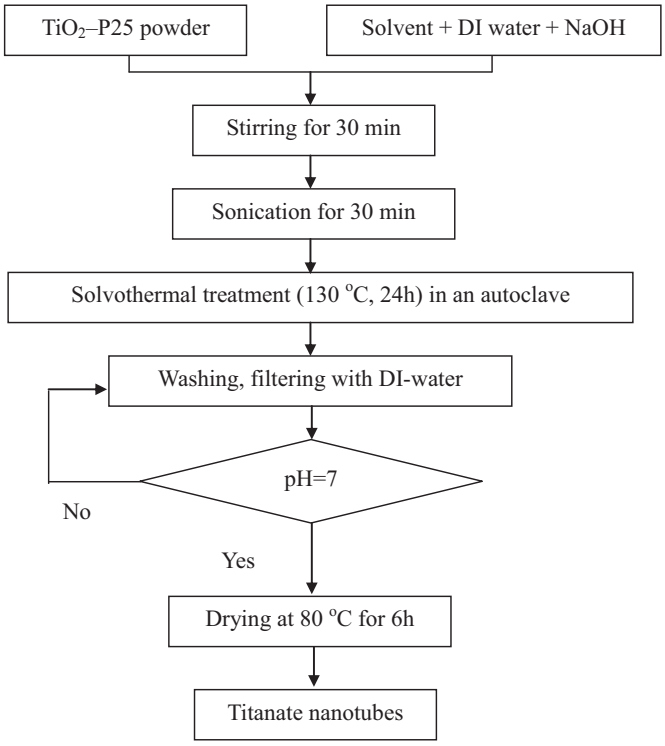

Fig. 1. Flow chart describing the solvothermal synthesis of the titanate nanotubes.

2.3. Preparation of the TNT nanotubes

During this study, the solvothermal method was used to synthesize titanate nanotubes, and the synthetic process is illustrated in Fig. 1. First, 10 M NaOH solutions were prepared by adding 28 g of NaOH to 70 mL of a mixed solvent that consisted of distilled water and an organic solvent (70:30, by volume). All of the solvents were either alcohols or ketones that had boiling points below that of water (100 °C). The samples were labeled as listed in Table 1. In a typical procedure, 2.1 g of TiO_2-P25 powder was added to 70 mL of the 10 M NaOH water-organic solution. This mixture of the solution and the TiO_2 powder was magnetically stirred for 30 min. Afterward, the mixture was sonicated for 30 min. This homogeneous suspension was hydrothermally treated in a stainless steel Teflon-lined autoclave at 130 °C for 24 h. After the reaction, the reactor was cooled to room temperature in air. The final reaction products were thoroughly washed with large volumes of double-distilled water until a neutral pH (~7) was achieved. The resulting solid was filtered and separated for drying at 80 °C for 6 h. Additionally, to study the effect of a co-solvent with the same alcohol or ketone on the morphologies and properties of

Table 1
The effects of different solvents on the morphology, size and band gap of the titanate nanostructure.

Solvent	Sample	Morphology	Diameter (nm) from TEM	Band gap (eV)
Water	W	Nanotube	7–8	3.14
Methanol	M	Nanotube	7–8	3.23
Ethanol	E	Nanotube	7–8	3.22
Methanol:ethanol (1:1)	M-E	Nanotube	7–8	3.18
Methyl ethyl ketone	MEK	Nanotube	7–8	3.14
Acetone:methyl ethyl ketone (1:1)	A-MEK	Nanotube Nanoparticle	6–7 68	3.56
Acetone	A	Nanoparticle	53	3.45
n-Propanol	NP	Nanoparticle	73	3.60
Isopropanol	IP	Nanoparticle	35	3.52
TiO_2 precursor	TiO_2-P25	Nanoparticle	25	3.25