



Original Research Paper

Dissolution/recrystallization growth of titanate nanostructures by amorphous precursor



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ARTICLE INFO

Article history:

Received 17 July 2013

Received in revised form 23 October 2013

Accepted 12 November 2013

Available online 27 November 2013

Keywords:

Amorphous materials

Nanostructure

Titanate

Crystal growth

Catalytic properties

ABSTRACT

Understanding of growth mechanism is of technical importance for tailoring the size and morphology of titanate nanostructures. However, the growth mechanism of titanate nanostructures in alkali solution systems by using crystalline TiO_2 remains debating currently. In the present work, the amorphous precursor of titanium hydroxide precipitates, a highly disordered raw material, was used as the precursor to prepare the titanate nanostructures under hydrothermal conditions. SEM and TEM results show that the morphology of the titanate nanostructures developed from nanoparticles to nanosheets and then the titanate nanowires with an interlayer spacing of 0.786 nm as the reaction time prolonged. XRD and Raman spectra results display that layered titanate nanostructure were formed. These phenomena are similar to that of the titanate nanostructures prepared by the TiO_2 crystal in alkali solution systems. The findings provide direct evidence to strongly support that titanate nanostructures grow from dissolution/recrystallization process under hydrothermal process, allowing mediating the size and morphology of titanate nanostructures. Moreover, SEM and photocatalytic results implied that the washing process improved the photocatalytic activities, which had no effect on the overall morphology.

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1. Introduction

Titanate nanostructures, such as nanotubes or nanowires, which were synthesized by hydrothermal treatment for TiO_2 in alkali solution systems [1,2], have attracted much attention because of their potential applications, including electrochromism [3], photocatalysts [4–6], dye-sensitizing solar batteries [7,8] and photoelectronic devices [9]. Furthermore, these titanate nanostructures were used to prepare thin film and bulk vigorously [10–11]. In particular, in order to achieve the optimal properties by tailoring the titanate nanostructures, many efforts have been devoted to understanding the crystal growth process of TiO_2 -derived nanostructures. Two different mechanisms have been proposed to describe how the titanate nanostructures are formed for the TiO_2 as the titanium source. For the exfoliation model, it is assumed that the alkali solution initially disturbs the crystalline structure, allowing single-layer 2D sheets to exfoliate completely from the crystalline TiO_2 raw materials [12]. Subsequently, these sheets roll up to form titanate nanostructures through $\text{M}^+(\text{Na}^+, \text{K}^+) \rightarrow \text{H}^+$ substitution [13,14] or driven by a decrease of surface energy [2] or the formation of undercoordinated surface sites [15]. For the

dissolution/recrystallization model, crystalline TiO_2 reacts with the alkali solution, forming a highly disordered phase and then precipitate as layered alkali titanates [16,17]. From these layered precipitates, titanate nanostructures can be formed because of the asymmetric environment caused by hydrogen deficiency [16] or mechanical stress [18]. Recent work tends to agree with that nanostructures are commonly formed through the dissolution and subsequently recrystallization of crystalline TiO_2 in alkali solution [19–21]. However, the alkaline hydrothermal kinetics in titanate nanostructure formation remains unclear. In addition, the effect of washing process on the formation of the nanotubes is also under controversy. It is argued that the final pH value of the washing water after the washing process has much effect on the structure of the nanostructures [13,22–24]. In contrast, other studies reported that the washing procedure has no significant influence on the overall morphology of the products, but affect other properties, such as the specific surface area and annealing behavior [17].

This work aims to provide experimental evidence to shine some light on these contradictory findings through a systematic investigation. TiO_2 -derived nanostructures were mostly synthesized by the hydrothermal treatment of crystalline TiO_2 in alkali solution systems. The focus of debate on the formation mechanism is whether the crystalline structure of TiO_2 is broken during the crystal growth process of titanate nanostructures. Recently, amorphous

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precursor material has been used to synthesize titanate nanostructure [25]. Inspired by the previous work, the amorphous precursor of titanium hydroxide precipitation synthesized by sol–gel process was used to hydrothermally prepare the titanate nanostructures. The results reveal that the formation mechanism for titanate nanostructures is dissolution/recrystallization model, where the precursor is disorder. Furthermore, the effect of different experimental parameters on the formation of the titanate nanostructures, such as alkali solution concentration and hydrothermal temperature, has also been investigated. Moreover, the morphology and the photocatalytic activities of the titanate nanostructures were studied after the washing process.

2. Experimental details

Synthesis: 5 mM analytical grade tetrabutyl titanate ($(C_4H_9O)_4Ti$) was dissolved with analytical grade ethylene glycol monomethyl ether ($HOCH_2CH_2OCH_3$). In order to obtain amorphous precursor powder of titanium hydroxide precipitates, 2 mL 25% $NH_3 \cdot H_2O$ was used to induce hydrolysis and condensation. After filtering and washing the precipitation with deionized water for five times, the amorphous precipitation was added to KOH aqueous solution under stirring for 30 min. Subsequently, the specimens were treated under hydrothermal reaction at different temperatures for different times. Obtained products after hydrothermal treatments were sufficiently washed with deionized water and 2% dilute HCl aqueous solution, respectively. The final pH value for these two washing systems was 6–7 and 2–3, respectively. After washing treatment, the products were dried at 60 °C for more than 24 h in the oven.

Characterization: The prepared samples were characterized by scanning electron microscope (field emission SEM, S-4800, Hitachi, Tokyo, Japan), high-resolution TEM (HRTEM, F20 using an accelerating voltage of 200 kV, FEI, America), X-ray diffraction (XRD, ARLXTRA, Thermo, Switzerland, Cu $K\alpha$) and Raman spectrometer ($\lambda = 532$ nm, Renishaw InVia, Serial 40C504, the United Kingdom). The photocatalytic activity of titanate nanotubes was evaluated by the degradation of rhodamine-B (RhB) in aqueous solution. The initial concentration of the RhB solution is 1×10^{-5} mol/L. Sixty milligrams of titanate nanotubes were dispersed in 60 mL RhB solution. The resulting suspension was equilibrated by stirring in

the dark for 2 h to stabilize the adsorption of the RhB dye over the surface of the titanate nanotubes. The ultraviolet (UV) source contains two 15 W tubes, which emitted the UV radiation with the wavelength within the range of 200–400 nm. The stable aqueous suspensions were irradiated with UV light under the continuous magnetic stirring. Six milliliters of the aqueous suspension was taken out at different interval time for obtaining the absorption spectra using a Hitachi U-4100 spectrophotometer (Tokyo, Japan). The BET surface area was determined from the linear part of the BET isotherm (Brunauer curve in 0.05–0.35 partial pressure range, AsAp-2020, Micromeritics, Norcross, GA).

3. Results and discussion

Figs. 1 and 2 present time-dependent experiments of products prepared by hydrothermal treatment of the amorphous precipitation precursor at 200 °C in 6 M KOH solution. The as-prepared products have been characterized by using SEM (Fig. 1) and TEM (Fig. 2). The morphology of the as-prepared products changed significantly upon the time increased. When the product was prepared at 0.5 h, the amorphous particle-like morphology was observed. With the time prolonged to 1–2 h, some nanosheet-like products were formed. The nanorod-like products with the length of ~ 130 nm were obtained with the reaction time of 4 h. And there were still some amorphous particles on the surface of the products. It is clearly shown that large amounts of long nanowires with a length of ~ 400 nm were synthesized after a reaction of 24 h, where no obvious amorphous particles can be observed. When the reaction was prolonged to 96 h, longer nanowires with the length of ~ 700 nm were synthesized. In addition, TEM results matched well with the observation of SEM (see images of Fig. 2). Without the hydrothermal treatment, a large number of amorphous particles with the diameter of 3–5 nm were observed (as shown in Fig. 2(a)). When the prepared time was 0.5 h, the products were almost amorphous particles and some nanocrystalline phase was obtained. Nanosheet-like products, as shown in Fig. 2(c), were observed after hydrothermal treatment for 1 h. Some nanosheet-like products began to curl and scroll into titanate nanostructures. After hydrothermal treatment for 4 h and 96 h, the nanowires were observed. The average diameter of the titanate nanowires, which was ~ 6.30 nm, has no obvious change with the time prolonged.

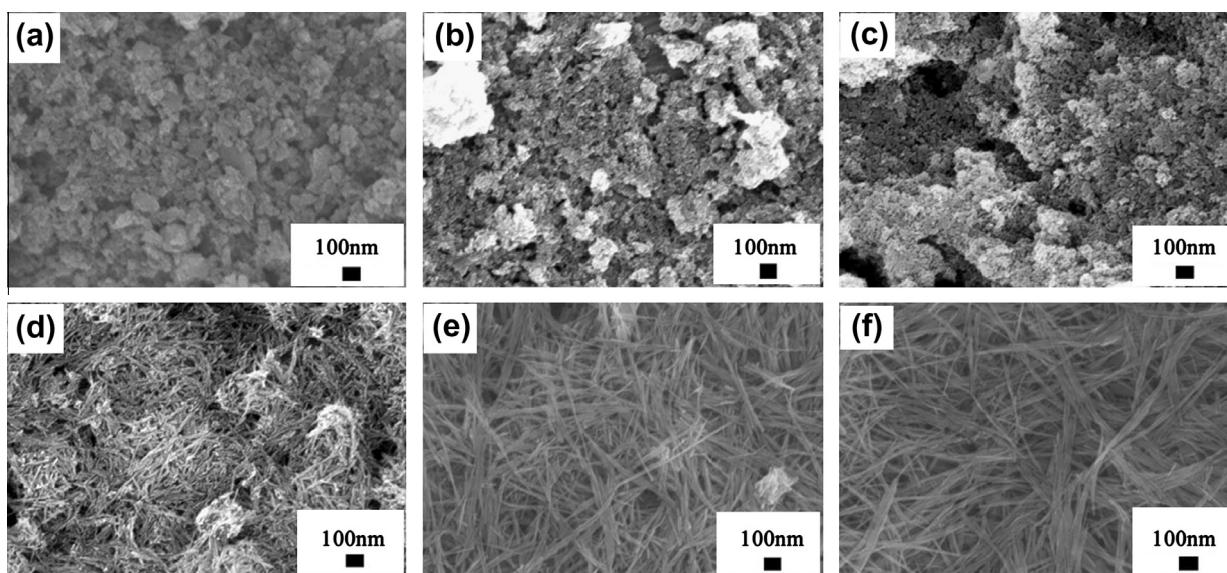


Fig. 1. SEM images of the products prepared by hydrothermal treatment of the amorphous precipitation precursor at 200 °C for different times in 6 M KOH solution. (a) 0.5 h, (b) 1.0 h, (c) 2.0 h, (d) 4.0 h, (e) 24 h, and (f) 96 h.

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