Preparation of Nanofibers from Natural Ilmenite Mineral by Simple Hydrothermal Method

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Abstract

Titanate nanofibers were synthesized via hydrothermal method (120 °C for 72 h) using natural ilmenite mineral as the starting material. The prepared samples were characterized by XRD, XRF and SEM. The prepared nanofibers showed the diameters of 6-100 nm and the lengths of 2-7 μm. This synthesis method provides a simple route to fabricate one-dimensional nanostructured TiO_2 from low-cost material.

Keywords: Nanofibers, ilmenite, Hydrothermal, Titanium dioxide

1. Introduction

The synthesis and characterization of TiO_2 one-dimensional (1-D) nanostructured (nanotubes, nanorods, and nanowires) have received considerable attention due to their unique properties and novel applications such as light weight, high surface area and high chemical, mechanical, electrical and magnetic properties [1–6]. TiO_2 and TiO_2-derived materials are of importance for utilizing solar energy and environmental purification. TiO_2 has been widely used for various applications such as a semiconductor in dye-sensitized solar cell, water treatment materials, catalysts, gas sensors, and so on [7–11]. Recent studies indicated that the nanofibers were conveniently prepared via the hydrothermal method. Thus, the hydrothermal preparation is the simple synthesis, low-cost and environmental friendly process [12-16]. In this study, nanofibers were prepared by simple hydrothermal method from low-cost Thai ilmenite minerals due to the high cost of commercial TiO_2 nanoparticles (starting material) [17-19]. The characterization of the prepared nanofibers will be reported.

2. Experimental

2.1 Synthesis

Titanate nanofibers were synthesized by hydrothermal method using natural ilmenite mineral (Sakorn Minerals Co.,Ltd., Thailand) as the starting material. The 5 g of ilmenite mineral (without further purification) black granules were put into a Teflon-lined stainless steel autoclave (Thai made) (Fig. 1). Then, the autoclave was added with 200 ml of 10M NaOH aqueous solution and heated at 120 °C (setting temperature) for 72 h with stirring condition. The hydrothermal method at 120 °C for 72 h result in the formation of solid nanowires and/or long nanofibers [16]. After the autoclave was naturally cooled to room temperature, the obtained product was washed with HCl aqueous solution, distilled water for several times, followed by hot air drying.

Fig. 1. Teflon-lined stainless steel autoclave.

2.2 Characterization

Chemical composition of the as-synthesized sample was analyzed by X-ray fluorescence (XRF, Philips, PW-2404, 4 kW). The crystalline structure of the samples was evaluated by X-ray diffraction (XRD, X'Pert PRO MPD model pw 3040/60, PANalytical) using Cu Kα irradiation at a scan rate of 0.02° 2θ s^{-1}. The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. The microstructure of the prepared materials was analyzed by scanning electron microscopy (SEM, JEM-6510, JEOL) with

acceleration voltage of 5-20 kV. The distribution of nanofiber's diameter size was measured by SEM image.

3. Results and Discussion

The as-synthesized sample was brown-colored while as the starting ilmenite mineral was black-colored (Fig. 2). This phenomenon indicates that a large portion of Fe impurities can be removed by the NaOH (aq.) hydrothermal treatment and following neutralization/ washing processes [13]. The results of chemical composition of ilmenite mineral and the as-synthesized sample using X-ray fluorescence were shown in Table 1. After hydrothermal method, quantity of impurities such as Fe_2O_3, Al_2O_3, SiO_2, MnO and so on was reduced while TiO_2 was increased from 66.99 to 76.21 %wt. Results revealed that TiO_2 increased with decreasing impurities content [20, 21].

The XRD patterns of the starting ilmenite mineral and the as-synthesized sample were shown in Fig. 3. The crystalline structure of starting ilmenite mineral appeared rutile phase while as the crystalline structure of the as-synthesized nanofibers demonstrated layered titanate $H_2Ti_xO_{2x+1}$, probably trititanate ($H_2Ti_3O_7$), indicating the hydrogen (from water) in the prepared nanofibers [13-16]. No diffraction peaks of other impurities (such as starting rutile and NaCl) were observed. The Na content in the nanofibers can be reduced by repeated HCl leaching and water washing. The reduced Na in the nanofibers occurred in the post-treatment washing as a result of the replacement of Na^+ in $Na_2Ti_2O_5{\cdot}H_2O$ by H^+ [22, 23]. The replacement would result in the decrease of intensity of diffraction peak at $2\theta = 24.5^o$ [22]. However, when compared with the titanate nanotubes [17, 24], the nanofibers tended to contain more residual Na ions under the same ion-exchanging conditions. The primary reason of this difference is attributable to the geometry of nanofibers, i.e., solid and thicker structure. Alkali metal ions in these tunnels usually are stable and do not leach out so easily via aqueous HCl treatment at room temperature. [13, 25-27].

SEM image of the starting Ilmenite mineral showed the granules size about 150-200 μm (Fig. 4). After hydrothermal treatment, the as-synthesized sample showed fiber-like morphology (Fig. 5). The prepared nanofibers ranges showed the length of 2-7 μm with the diameter about 6-100 nm (Fig. 6). The diameter size of the prepared nanofibers was smaller than the diameter size of nanostructured TiO_2 prepared by electrospinning [28-35], anodic oxidation [36] and template assisted methods [37].

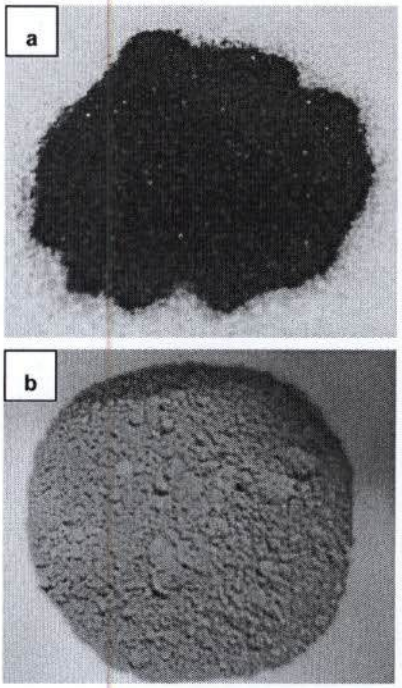

Fig. 2. The powders of (a) the starting Ilmenite mineral and (b) the as-synthesized sample.

Table 1 Chemical analysis of the Ilmenite mineral and the as-synthesized sample.

Oxide	Ilmenite mineral (%wt)	As-synthesized sample (%wt)
TiO_2	66.99	76.21
Fe_2O_3	24.01	21.80
Al_2O_3	3.38	0.12
SiO_2	2.11	0.30
MnO	0.82	0.68
ThO_2	0.64	0.01
ZrO_2	0.62	0.12
MgO	0.27	0.09
Cr_2O_3	0.26	<0.01
P_2O_5	0.25	<0.01
SO_3	0.15	0.05
Y_2O_3	0.09	-
ZnO	0.21	<0.01
NaO_2	<0.01	0.16
Nb_2O_5	0.24	0.15
CaO	0.16	0.08

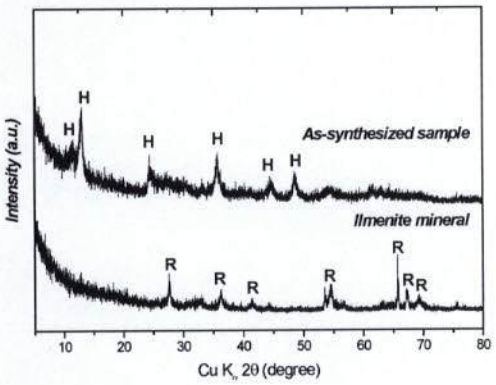

Fig. 3. XRD patterns of the starting ilmenite mineral and the as-synthesized sample, H = hydrogen titanate and R = rutile TiO_2.

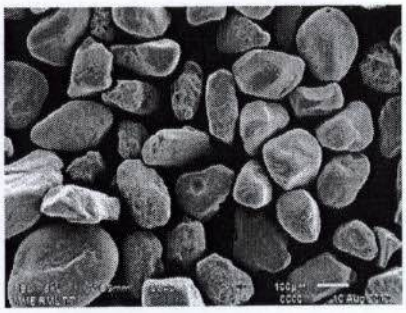

Fig. 4. SEM image of the starting ilmenite mineral.

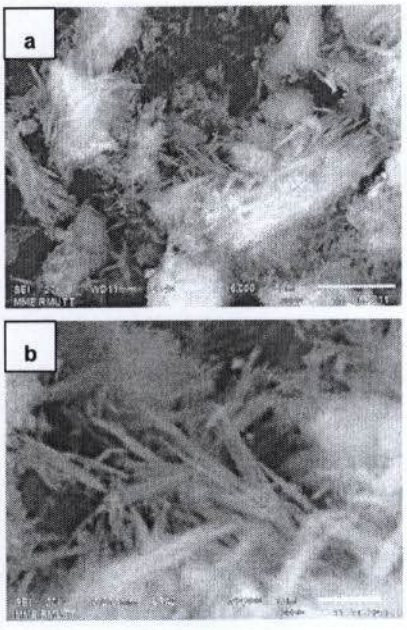

Fig. 5. SEM images of the as-synthesized nanofibers at (a) x 5,000 and (b) x 20,000 magnified.

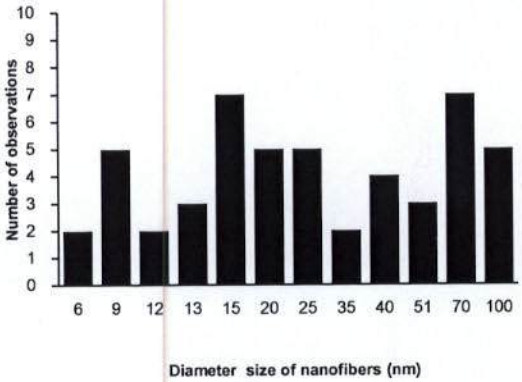

Fig. 6. Distribution of the prepared nanofiber's diameter size.

4. Conclusions

Titanate nanofibers were synthesized by hydrothermal method (120 °C for 72 h) using low-cost ilmenite mineral as the starting material. After hydrothermal method, quantity of TiO_2 increased due to decreasing of impurities content. The prepared nanofibers showed the length of 2-7 μm and formed some bundles of 6-100 nm in diameter. The operation of this synthesis method is a simple hydrothermal method using Thai autoclave unit.

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