

Effect of calcination temperatures on structures of TiO₂ powders prepared by hydrothermal method using Thai leucoxene mineral

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Abstract—TiO₂ powders were synthesized by hydrothermal method with 10M NaOH solution at 115 °C for 24 h using natural Thai leucoxene mineral as the starting materials. The effects of calcination temperatures on structures of the prepared materials were investigated. The structures of the prepared samples were characterized by X-ray diffraction (XRD) technique and scanning electron microscopy (SEM). The as-synthesized sample showed the nanotubes-nanofibers structures with ~10-20 nm in diameter of nanotubes and ~20-50 nm in diameter of nanofibers. The XRD results showed that the as-prepared sample before being calcined were mixed phase of titanate and rutile. The titanate phase could transformed to anatase phase at the calcination temperature higher than 300 °C. As the calcination temperature increased, crystallization of the anatase phase enhanced. With further increase in the calcination temperature from 700 to 900 °C, the intensity of rutile phase increased. When the calcinations temperature reached 1000 °C, only rutile phase was found in the XRD pattern.

Keywords— Hydrothermal, Leucoxene, TiO₂

1. INTRODUCTION

Titanium dioxide (TiO₂) nanostructured materials have attracted a great deal of attention due to their unique properties and novel application [1-4]. Much effort has focused on the important metal oxides such as TiO₂, SnO₂, VO₂, and ZnO [1-8]. Among them, TiO₂ and TiO₂-derived materials are importance for utilizing solar energy and environmental purification. TiO₂ 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 [9-14]. In addition, many studies indicated that TiO₂ nanotubes has excellent properties in photocatalysis [15,16]. Following the researching works, the obtained nanotubes were actually not TiO₂, but may be hydrogen titanate [17,18]. The obtained nanotubes will offer another possibility to design various TiO₂-related materials by post-treatment methods. Moreover, it is an important point to study the structure of the nanotubes and their corresponding crystalline phase at various calcination temperatures from the issue of view of practical use of titanate nanotubes.

In this study, the TiO₂ powders were synthesized by hydrothermal method with 10M NaOH solution at 115 °C for 24 h using natural Thai leucoxene mineral as the starting materials. The prepared product was washed and then calcined at various temperatures. The effects of calcination temperature on the phase and structure of the prepared sample were investigated.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of TiO₂ Powders

TiO₂ powders were synthesized by hydrothermal method using natural leucoxene mineral from Prachuapkhirikhan province in the south of Thailand (92.3% TiO₂, Sakorn Minerals Co., Ltd., Prachuapkhirikhan, Thailand) as starting material. The primary particle size of natural leucoxene mineral is about 20-50 μm. In a typical preparation, the natural leucoxene mineral (16 g) was mixed with 1000 ml of 10M NaOH solution followed by hydrothermal treatment of the mixture at 115 °C in a Teflon-lined stainless steel autoclave (Thai made) for 24 h with stirring condition. After hydrothermal reaction, the precipitate was separated by filtration and washed with a 0.1M HCl solution and distilled water until the pH value of the rinsing solution reached ca. 6.5, approaching the pH value of the distilled water. The washed samples were dried in the oven at 60 °C for 12 h and then calcined at 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1,000 °C in air for 2 h, respectively.

2.2 Characterization

X-ray diffraction (XRD) patterns were obtained on the X'Pert PRO MRD X-ray diffractometer (PANalytical, Netherlands) using Cu Kα irradiation at a scan rate (θ) of 0.01 °s⁻¹ and were used to determine the identity of any phase present and their crystalline structure. The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. Transmission electron microscopy (TEM) analyses were conducted with a JEM-2010 electron microscope (JEOL, Japan). Morphology

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observation was performed on a JSM-6510 scanning electron microscope (SEM, JEOL, Japan).

3. RESULTS AND DISCUSSION

3.1 As-synthesized sample

Fig.1 shows SEM image of the prepared powder obtained by a hydrothermal reaction using natural Thai leucoxene mineral and 10M NaOH aqueous solution as precursors at 115 °C for 24 h. The as-synthesized sample showed fiber-like morphology. The length of the fiber-like structure ranges from several μm to more than 10 μm. The X-ray diffraction pattern (XRD) of the prepared samples observed at 2θ~10°, 24° correlated to the hydrogen titanate (H₂Ti₃O₇) [19-21] (Fig.2).

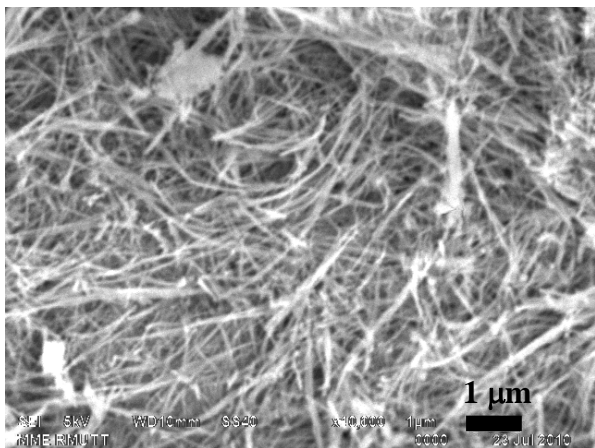


Fig.1. SEM image of the as-synthesized sample at 115 °C for 24 h.

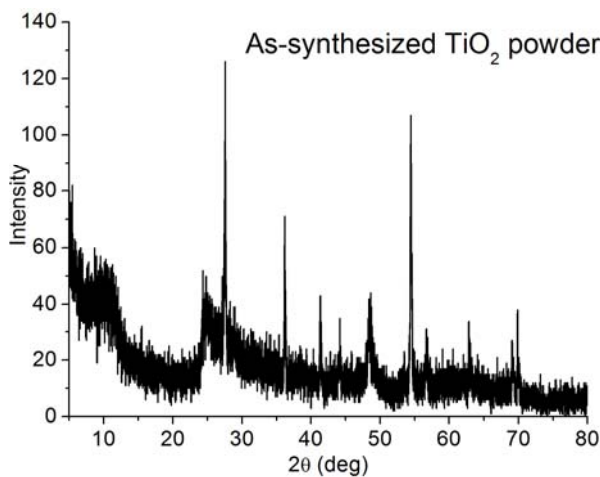


Fig.2. X-ray diffraction pattern of the as-synthesized sample at 115 °C for 24 h.

In order to determine tubular structure of TiO₂ powder, TEM experiment was investigated. Fig.3 shows the TEM photograph of the as-synthesized sample with ~10-20 nm in diameter of nanotubes and ~20-50 nm in diameter of nanofibers. The lengths of the nanofibers structure were longer than the nanotubes structure.

Fig.3. TEM image of the as-synthesized sample at 115 °C for 24 h.

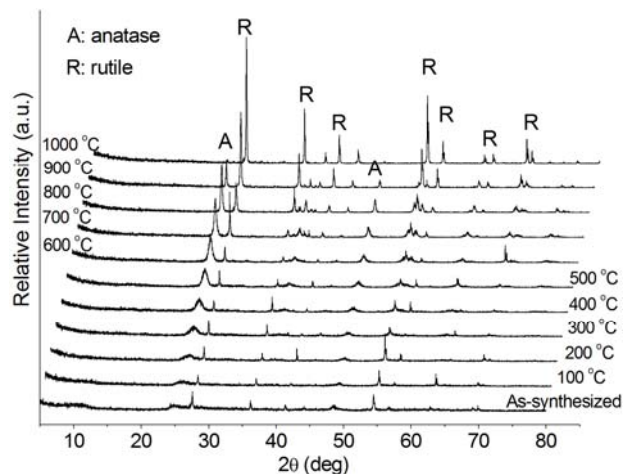
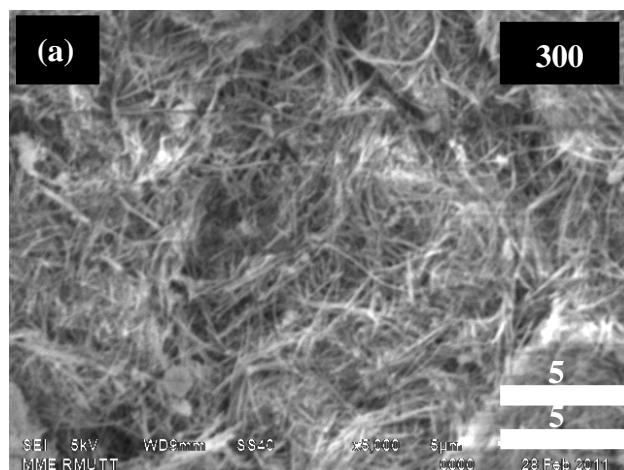


Fig.4. XRD patterns of the prepared sample calcined at various temperatures.

3.2 Effects of calcination temperatures on the structures of the TiO₂ powders

The XRD technique was used to investigate the phase transformation of the prepared samples. Fig. 4 shows the XRD patterns of the prepared samples without and with calcination at 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 °C in air for 2 h. Titanate phase could transform to anatase phase at the calcination temperature higher than 300 °C. With increasing calcination temperature from 300 to 800 °C, the peak intensities of anatase increased, indicating the improvement of crystallization of anatase phase. With further increase in the calcination temperature from 700 to 900 °C, the intensity of rutile phase increased. When the calcinations temperature reached 1000 °C, only rutile phase was found in the XRD pattern.



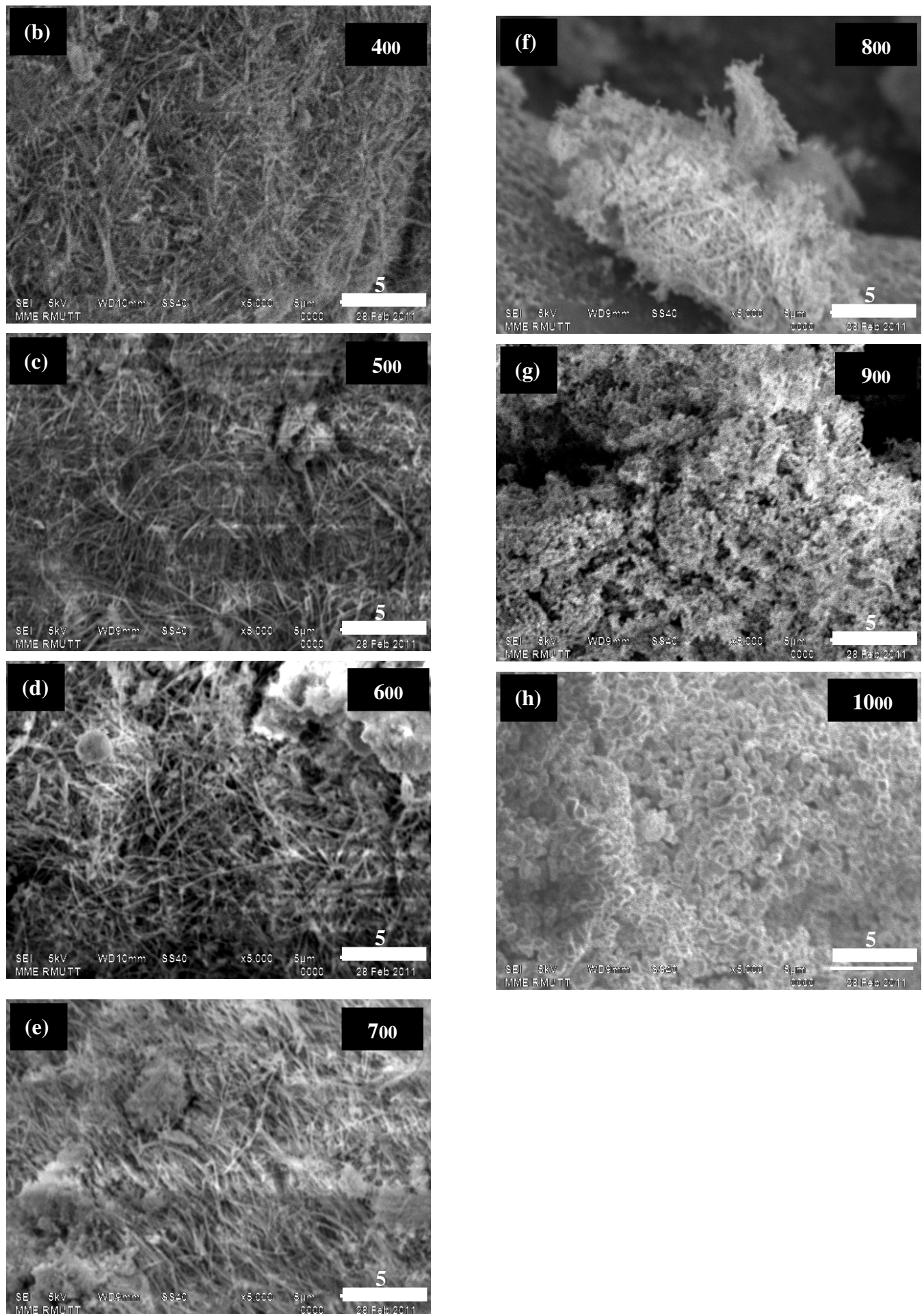


Fig.5. SEM images of the prepared TiO₂ powders before and after calcined in air at various temperatures for 2 h: 300 °C (a), 400 °C (b), 500 °C (c), 600 °C (d), 700 °C (e), 800 °C (f), 900 °C (g), and 1000 °C (h)

Fig. 5 shows SEM images of the calcined sample at 300-1000 °C. At calcination temperature of 300-500 °C, the length of the nanotubes-nanofibers structure of the calcined samples were shorter than the sample before calcination (Fig.5a-5c). Further observation indicated that the nanotubes-nanofibers structures were aggregated. When the calcinations temperature was increased to 600 °C, the surface morphology of the calcined sample consisted of TiO₂ particles with a wide particle size distribution from several hundreds of nanometers to several micrometers as shown in Fig. 5d. When increased calcinations temperature to 700 °C, the surface morphology of the calcined sample retained a consisted of TiO₂ particles similar to that of the sample calcined at 600 °C (Fig.5e). At 800 °C, the surface morphology of the calcined sample had been changed. The nanotubes-nanofibers structure was difficult to be seen and the nanotubes-nanofibers structures were aggregate to TiO₂ particles (Fig.5f). With further increase in the calcination temperature from 800 to 900 °C, the whole surface was covered by TiO₂ particles and the surface morphology showed pore in the structure (Fig.5g). When the calcinations temperature reached 1000 °C, only dense TiO₂ particles with diameters of 200–500 nm was found in calcined sample (Fig.5h). This can be attributed to the phase transformation of anatase to rutile.

4. CONCLUSION

In summary, TiO₂ powders were synthesized by hydrothermal method using natural leucoxene mineral as the starting material. After the hydrothermal treatment at 115 °C. The as-synthesized sample showed morphology of nanotubes-nanofibers with the diameters of ~20-50 nm and ~10-20 nm for nanofibers and nanotubes, respectively. The crystalline phase and morphology of the nanotubes-nanofibers structure are depending on the calcination temperature. The titanate phase transformed to anatase phase at the calcination temperature higher than 500 °C. When the calcinations temperature reached 1000 °C, only rutile phase was found in the XRD pattern. This preparation method provided a simple route to fabrication nanostructures TiO₂ powders from Thai leucoxene mineral.

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