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Study on Phase Transition of Hydrothermally Synthesized 1-D Titanate into Titania (TiO_2) as a Potential Nanobiomaterials

Mohd Hasmizam Razali*, Nur Arifah Ismail, Khairul Anuar Mat Amin

School of Fundamental Sciences, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.

Abstract

In this research, 1-D titanate was successfully synthesized using hydrothermal method at 150 and 200°C. They were calcined at different temperature (300, 400, 500 and 700 °C) to study the phase transition and thermal stability. Various characterization techniques was used such as field emission scanning electron microscopy (FESEM), thermogravimetry analysis (TGA) and x-ray diffraction (XRD). FESEM revealed that nanofibers and rod-like particles was obtained at 150 °C and 200 °C, respectively. They are belong to titanate crystal phase structure which are present as hydrogen titanate at 150 °C and sodium titanate at 200 °C as shown by XRD. The hydrogen titanate nanofibers transformed into titania (TiO_2) at 400 - 700 °C. Meanwhile the rod-like particles of sodium titanate only fully converted to TiO_2 at 700 °C. This can be concluded that, sodium titanate is higher thermally stable that hydrogen titanate as it's only decomposed into TiO_2 at highest temperature studied of 700 °C.

Keywords: Nanostructured, titanate, titania, biomaterials, calcination

INTRODUCTION

One-dimensional (1-D) nanomaterials have received high intention due to the promising in generating antibacterial capability and excellent in biocompatibility [1]. Verma et al. (2016), have proved TiO_2 nanoparticles inhibits the bacterial biofilm and has been proposed to be used in wound infection treatment [2]. Sivaranjani and

Philominathan (2016) shows that TiO_2 nanoparticles are effective for wound healing and skin infection treatments [3]. Thus, many studies has been conducted to synthesis TiO_2 nanomaterials using hydrothermal method. Hydrothermal method getting highest ranking for nanomaterial synthesis due to their simple and inexpensive technique with high percent of yields [4]. However, different crystal structure of yields has been reported. Instead of titania (TiO_2), many researchers claimed that the products are titanate. Therefore, in this study the hydrothermal method was used for TiO_2 synthesis and the hydrothermal treatment temperature was studied at 150 and 200 °C. The products obtained was calcined at different temperature (300, 400, 500, 700 °C) and was characterized in order to study the crystal phase structure and phase transition.

EXPERIMENTS

Preparation

2.0 gram of TiO_2 powder precursor (Merck) was dispersed in 10M NaOH (100 ml) with constant stirring for 30 minutes, then the mixture was sonicated in sonicator bath for 30 minutes after that continue with constant stirring for 30 minutes. Then, the mixture was transferred into Teflon vessel and subjected to hydrothermal treatment at different temperature (150 and 200 °C) for 24 hours in autoclave. When the reaction was completed, the white solid precipitate was collected and dispersed into 0.1 M HCL (200 ml) with continuous stirring for 30 minute for washing. Then, the washing was followed by distilled water until the pH of washing solution was 7 and subsequently dried at 80 °C for 24 hours in an oven. As-synthesized samples at 150 and 200 °C was calcined further at 300, 400, 500, and 700 °C.

Characterization

FESEM micrograph was captured using ZEISS SUPRATM 35VP FESEM coupled with EDX for morphological and elemental analysis, respectively. Thermogravimetric analysis was done using Pyris 6, Perkin-Elmer-TGA6 with heating rate at 10°C/min from room temperature to 1000 °C in an atmosphere of N_2 flow at 50 ml/min. XRD diffractogram were performed by Rigaku Miniflex (II) X-ray diffractometer operating at a scanning rate of 2.00° min^{-1}. The diffraction spectra were recorded at the diffraction angle, 2θ from 10° to 80° at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the FESEM micrographs of the as-synthesized samples at different hydrothermal treatment temperature. At 150 °C, nanofibers was observed with the diameter of 8-10 nm and several hundred nanometers in length (Figure 1a). The fibers was found to attach closely each other to form layer-like nanostructured materials. At 200 °C hydrothermal treatment, larger diameter of elongated nanostructures (rod-like particles) was produced. The diameter of rod-like particles was found to be 250 - 300 nm (Figure 1(b)). At higher hydrothermal treatment initial nucleation to be accelerated thus resulted in rapid growth of particles. Due to the rapid growth of particles, the particles tend to form the layered structures. The layered become thicker and finally rolling up into rods.

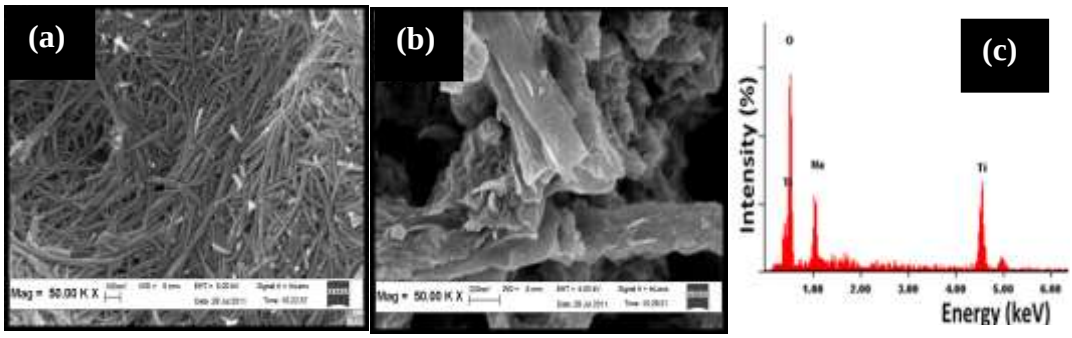

Figure 1: FESEM micrographs of as-synthesized samples at (a) 150 °C and (b) 200 °C (c) EDX of as-synthesized sample at 200 °C.

Figure 2(a) and 2(b) shows the thermogram of hydrothermally synthesis samples at 150 and 200°C, respectively. Similar TG curves was observed for both samples, which is showing decreased in mass starting at room temperature until 700 °C. Total mass loss is about 15% and 22%, respectively. Generally, the weight loss between room temperature till 100°C is due to the removal of adsorbed water from the surface.

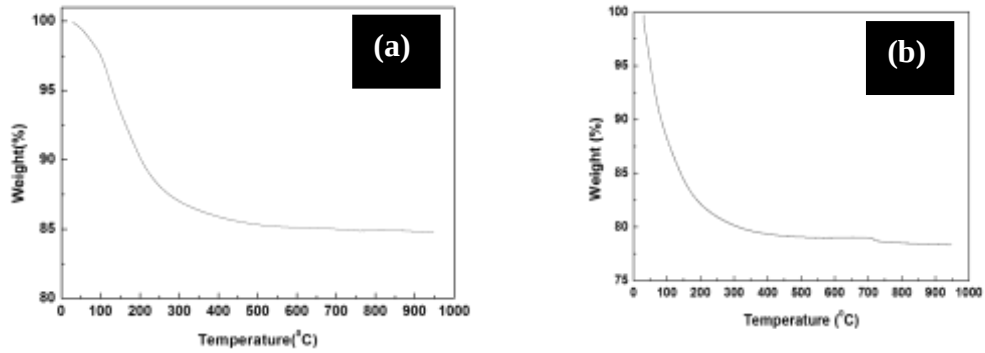

Figure 2: TGA themograms of as-synthesized samples at (a) 150 °C and (b) 200 °C.

When the temperature is further increased up to 300°C, the removal of the intercalated water molecules included dissociated molecular H_2O, physisorbed molecular H_2O and chemisorbed molecular H_2O are occurred. Subsequently, a small of weight loss in the region of 300-700°C, is probably due to the transformation of crystal structure of titanate into titania (TiO_2). In order to study the transition of titanate into titania, samples was calcined at 300, 400, 500, 700 ° C and was analyzed using XRD. The XRD patterns obtained is depicted in Figure 3 and Figure 4, respectively.

As can be seen in Figure 3(a), as-synthesized sample at 150 ^{o}C is belong to hydrogen titanate ($H_2Ti_3O_7$) nanofibers attributed to the existence of the peaks at $2\theta = 25.43°$ and 48.40° as reported previously by Razali et al. (2012). The hydrogen titanate was remained after calcination at 300 °C, somehow their peaks became broader due to the dimensionality changes [5]. The hydrogen titanate transformed into anatase TiO_2 after calcination at 400, 500 and 700 °C via simple chemical reaction as in equation 1.1;

$$H_2Ti_3O_7 \rightarrow {}_3TiO_2 + H_2O \qquad \text{Equation (1.1)}$$

This findings suggested that the hydrogen titanate has low thermal stability as it's decomposed to produce TiO_2 with anatase phase at low temperature, starting at 400 °C, 500 °C and 700 °C. Anatase TiO_2 can be recognized by the present of peaks at 25.4°, 37.9°, 48.2°, 54.1°, 55.15°, 62.74°, 70.37° and 75.07° with the highest peaks at ~25° (Figure 3(c)–(e)) [6]. As a calcination temperature increases, the XRD peaks became sharper and narrower indicated the crystallinity of sample enhanced. For as-synthesized sample at 200°C hydrothermal treatment, their XRD pattern shows the presence of peaks at 10.86°, 24.83°, and 48.59° which is identical to an orthorhombic phase of sodium titanate, $Na_xH_{2-x}Ti_3O_7$ (Figure 4(a)) [7]. The peaks at ~10° is corresponding to the interlayer spacing between the layered titanate [8]. This space was occupied by Na^{2+}, as the existence of Na was detected in EDX analysis (Figure 1(c). After calcination at 300, 400 and 500 °C, the peaks belonged to sodium titanate is remained, except at 10.86° was disappeared. The loss of the peak indicated there no space between the layered titanate thus confirmed the formation of rod-like structure [9]. At 500 °C, another three new peaks was emerged besides sodium titanate peaks. These peaks appeared at 14.1°, 29.0°, 44.07° with low intensity were assigned to metastable TiO_2(B). Like the other polymorphs of TiO_2, the crystal structure of TiO_2(B) consists of edge and corner sharing TiO_6 octahedra, but its framework is the same as that of Na_xTiO_2 [10]. The appearance of TiO_2(B) in sample occurred at some point between 300 to 500 ◦C. For example, Kuo et al. (2007), reported trititanate to TiO_2(B) transformation occurred at 300 °C [11]. In this study the formation of TiO_2(B) was found at 500 °C. After calcination at highest temperature studied (700 °C), only highly crystalline anatase TiO_2 was obtained showed that the sodium titanate and TiO_2(B) were transformed into anatase TiO_2. The appearance of the TiO_2(B) phase before the anatase formation is expected for the thermal decomposition of sodium titanates as reported by previous study [12].

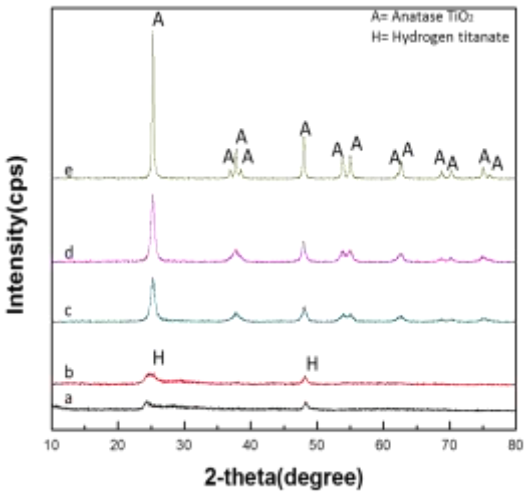

Figure 3: XRD patterns of (a) as-synthesized sample at 150 °C and calcined at (b) 300 °C (c) 400 °C (d) 500 °C and (e) 700 °C.

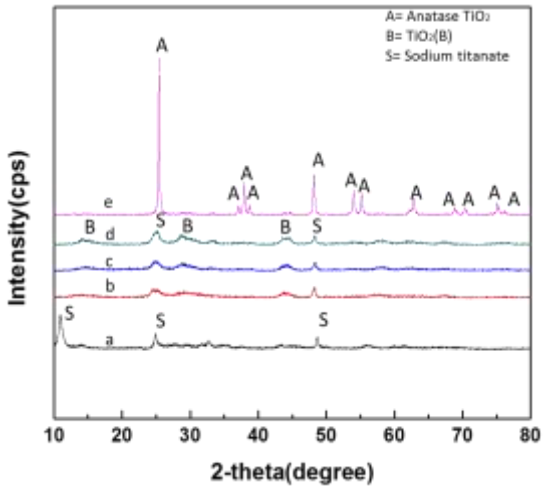

Figure 4: XRD patterns of (a) as-synthesized sample at 200 °C and calcined at (b) 300 °C (c) 400 °C (d) 500 °C and (e) 700 °C.

CONCLUSION

Hydrogen titanate nanofibers and sodium titanate rod-like particles were successfully synthesized using simple hydrothermal method at 150 and 200 °C, respectively. They are fully transformed into anatase TiO_2 at 400 and 700 °C proposed that sodium titanate possessed better thermal stability than hydrogen titanate. Thermally stable sodium titanate ascribed to the present of Na^{2+} in interlayer titanate.

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