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Characterization of Nanostructured Titania and Titanate Materials Synthesized by Simple Hydrothermal Method

Nur Arifah Ismail[a], Mohd Hasmizam Razali[b], Khairul Anuar and Mat Amin[c]

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

[a]nurarifahismail@ymail.com, [b]mdhasmizam@umt.edu.my, [c]kerol@umt.edu.my

Corresponding Author: Mohd Hasmizam Razali, mdhasmizam@umt.edu.my

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Abstract. In this research, the effect of different hydrothermal treatment temperature (100, 150, and 200 °C) on the products obtained by hydrothermal method was studied. Various characterization techniques was carried out such as X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), energy dispersive of x-ray spectroscopy (EDX) and fourier transform infrared spectroscopy (FTIR). XRD analysis shows that titanate phase was formed at 150 and 200 °C hydrothermal treatment. On the other hand, at 100 °C anatase TiO_2 phase structured was gained which is similar with the TiO_2 precursor. Morphological study using FESEM revealed that nanofibers and nanorods samples obtained at 150 °C and 200 °C, respectively. At 100°C, irregular shaped particle was attained similar with TiO_2 precursors. FTIR spectra for the all studied sample displayed three main broad peaks at the range of 3700-2800, and 1800-1400 assigned to –OH stretching and deformation mode due to H_2O molecules and M-O stretching mode at 900-400 cm^{-1} assigned to Ti-O bond.

Introduction

The discovery of titanium dioxide (titania) TiO_2 nanotubes by Kasuga et al. (1998) using hydrothermal method has attracted a widely interest among the researchers since this method was inception, simple and fast [1]. The hydrothermal method does not require the use of organic solvents or additional processing of the product; grinding and calcination, which makes it a simple and environmentally friendly technique. The synthesis takes place in an autoclave, where the mixture of substrates is heated gradually to a temperature above 100°C and left for several days. Hydrothermal method had offerred a simple path and effectiveness to prepare uniform, enaggregated, well-crytalline nanostructured titania materials [2]. Titania nanomaterials such as nanopowders, nanotubes, nanowires and nanorods getting the highest target materials among the researchers since it is favourable in diversity of application fields [3]. Among them were photovoltaics, self-cleaning coatings, photocatalysis, and electrochronic display devices [4]. In particular, titania nanotubes have been used as nonlinear optics, photocatalyst, gas sensor, photovoltaics and high effect solar cell [5-7]. Kasuga et al. reported that the hydrothermal treatment of TiO_2 particles in NaOH resulted in the formation of titania nanotubes with large surface areas [1]. Apart from that, some titanate structures, such as tetratitanate $H_2Ti_4O_9.H_2O$ [8], trititanate $H_2Ti_3O_7$ [9], $Na_xH_{2-x}Ti_3O_7$ [10], and lepidocrocite titanates [11] have been testified. Titanate nanostructures also have received a great deal of attention, because of their large surface area that leads to a wide variety of applications, including secondary lithium batteries, dye sensitized solar cells, photocatalysts, and sensors [12,13]. Thus researchers have been extensively study regarding to the formation of titania and titanate nanostructures. The formation of titania and titanate nanostructure can be obtained through further reaction of titania particles. For instance, the titanate nanowires can be fabricated by the reaction of titania particles in a highly concentrated of KOH solutions at 150 °C for 24 hours [14]. On the other hand, Kasuga et al., reported titania nanotubes was produced at 150 °C hydrothermal treatment overnight [1]. In this study the hydrothermal temperature was studied at various hydrothermal treatment temperature (100, 150 and 200 °C) and the products obtained was charaterised using various techniques in order to classify either titania or titanate compunds.

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 100, 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. The products obtained at 100, 150 and 200 °C hydrothermal treatments named as T100, T150, and T200, repectively and were characterized using XRD, FTIR, FESEM and EDX.

Characterization

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. FTIR spectra were collected using a Perkin Elmer Spectrum 100 FT-IR spectrophotometer (single-bounce beam path, 45° incident angle, 16 scans, 4 cm^{-1} resolution). An advanced FTIR correction was applied to all spectra in the region from 4000 to 400 cm^{-1}. FESEM micrograph was captured using ZEISS SUPRATM 35VP FESEM coupled with EDX for morphological and elemental analysis.

Results and discussion

XRD analysis was carried out to study the crystal phase structure of hydrothermally synthesized samples at different reaction temperature. For comparison the XRD pattern of TiO_2 precursors (commercial TiO_2 merck) was also included. As can be seen in Fig. 1(a) and (b), the TiO_2 precursor and synthesised sample at 100 °C (T100) shows a series of sharp and narrow peaks assigned to anatase TiO_2 attributed to the existence of highest peaks at ~25° [15]. Similar XRD pattern of TiO_2 precursor and T100 suggested the hydrothermal reaction of TiO_2 precursor at low temperature (100 °C) was not happen. This probably because of the TiO_2 is stable compounds especially at low temperature. Meanwhile, for synthesised samples at 150 °C (T150) and 200 °C (T200) hydrothermal treatment, their XRD pattern shows the presence of the peaks at 25.43° and 48.40° (Figure 1(c)) which is identical as hydrogen titanate and at 10.86°, 24.83°, and 48.59° belongs to sodium titanate (Figure 1(d)) [10]. Both synthesised samples were the titanate compounds proposed that the hydrothermal reaction of TiO_2 precursor and NaOH occurs to produce titanate compounds. In general, the reaction between TiO_2 and NaOH produced sodium titanate and transformed into hydrogen titanate after washing with HCl. Thus, hydrogen titanate was obtained at 150 °C. Somehow at 200 °C, sodium titanate was produced indicated that sodium titanate was remained even after washing with HCl. This is probably due to the formation of stable sodium (Na) compound at 200°C, whereby Na has intercalated in TiO_2 in form of $Na_2Ti_3O_7$. Thus the sodium titanate was remained even after washing with HCl. The occurrence of sodium in the sample was proved by EDX analysis (Fig. 2(b)). Otherwise, at 150 °C, Na^+ cations and the $[TiO_6]$ octahedral layers are held by static interaction in sodium trititanate ($Na_2Ti_3O_7$) [16]. When the larger cations was introduced, it can replace the Na^+ cations in the interlayer space of $[TiO_6]$ sheets because the interlayer distance is enlarged and reduces the static interaction. Subsequentlly, the Na^+ was totally exchanged with larger cation of H^+ during HCl washing, to form hydrogen trititanate ($H_2Ti_3O_7$). The absence of sodium element in the T150 sample can be noticed in the EDX results (Fig. 2(a)).

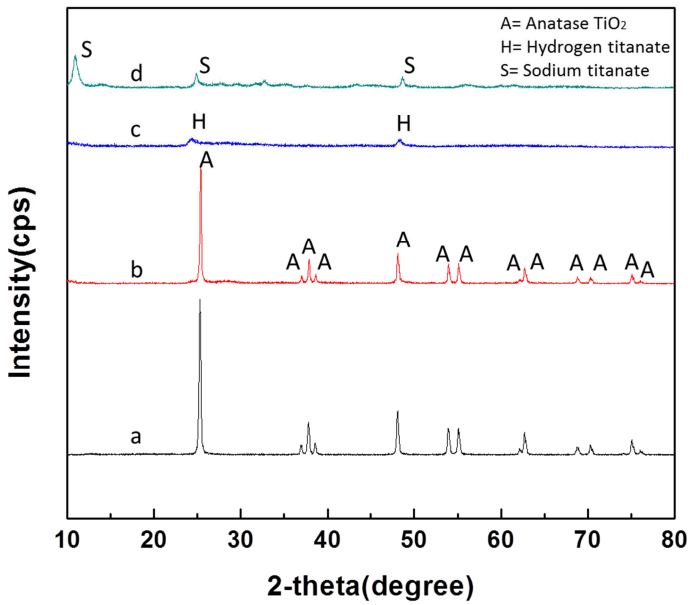

Fig. 1: XRD diffractogram of (a) TiO_2 precursor, (b) T100, (c) T150, and (d) T200.

The morpholgy of the synthesised samples and TiO_2 precursors have been studied using FESEM (Fig. 2). From the micrograph in Fig. 3(a), the TiO_2 precursor possesed irregular shape particles with the diameter within 200 – 300 nm. Similar morpholgy was observed for T100 sample (Fig. 3(b)). This finding recommended that no reaction between TiO_2 and NaOH at 100 °C hydrothermal treatment. Interestingly, at 150 °C (T150) nanofibers was viewed as in Fig. 3(c). It could be expected that TiO_2 particles reacted with OH^- (from NaOH) to form nanosheet at the initial stage of hydrothermal treatment, and then turned to nanofibers at 150 °C. The diameters of nanofibers are within 25 – 30 nm with several hundreds nanometer in length and attached to each other to form layered like structures. Meanwhile, rods like particles are formed when the hydrothermal treatment is done at 200 °C (Fig. 3(d). At a high hydrothermal treatment initial nucleation to be accelerated thus resulted in rapid growth of particles. Due to the rapid growth of particles, the layered structures of nanofibers are very thick and resulting in rolling up into rods with the diameter of 250 – 300 nm.

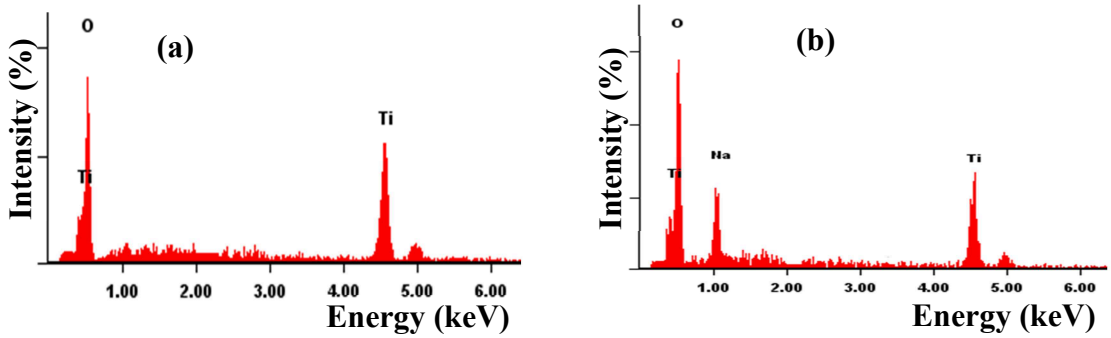

Fig. 2: EDX spectra of (a) T150 and (b) T200.

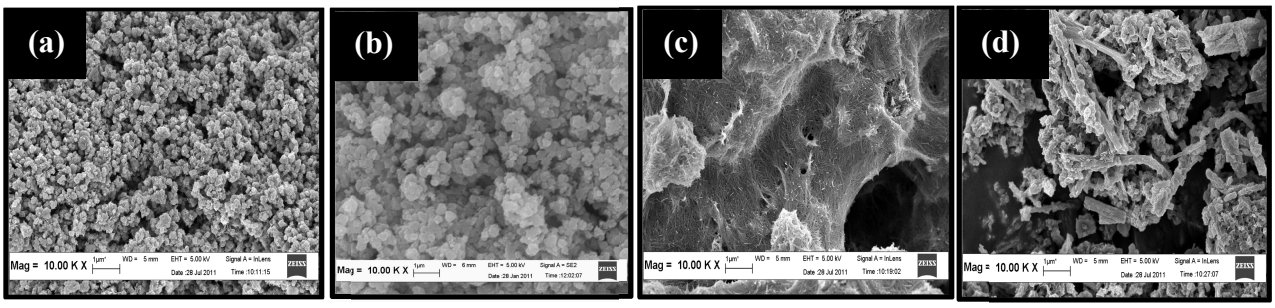

Fig. 3: FESEM micrographs of (a) TiO_2 precursors (b) T100 (c) T150 and (d) T200.

Fig. 4 shows the FTIR spectra of TiO_2 precursor, T100, T150, and T200 samples. For TiO_2 precursor, T100 and T200, a broad band has been observed in the range of 3700-2800 cm^{-1} which is referred to the OH stretching mode (Table 1). However, for the T150, a high transmittance and sharp peak has been observed on the OH stretching mode range. Apart from that, the OH deformation mode at the range 1800-1400 cm^{-1} also has been observed which is corresponding to the presence of the water molecule on the surface of the material [17]. Subsequently, the metal-oxygen stretching mode has been detected below the 650 cm^{-1} of wavelength in the T150 and T200. A sharp and narrow peak have been observed due to the Ti-O stretching vibrations mode of surface bridging oxide formed by condensation of adjacent surface hydroxyl group.

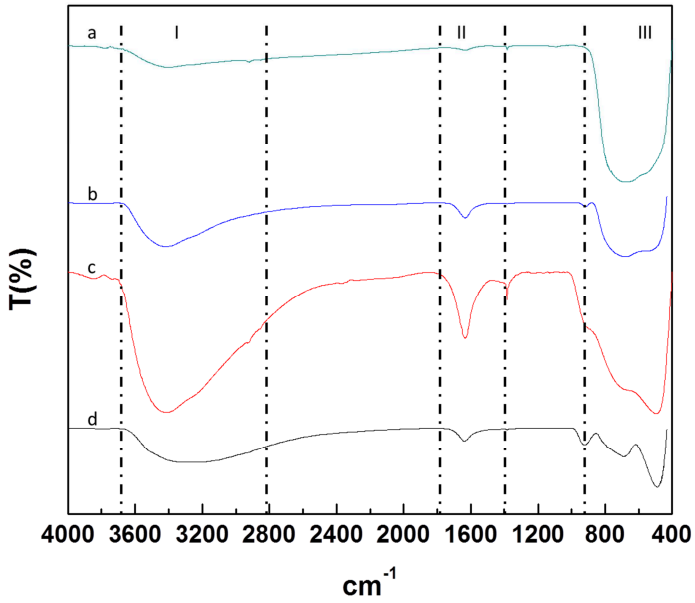

Fig. 4: FTIR spectra of (a) TiO_2 precursor, (b) T100, (c) T150 and (d) T200.

Table 1: Assignment of FTIR bands for TiO_2 precursor, T100, T150, and T200.

Region	Wavelength (cm^{-1})	Assignment
I	3700 – 2800	OH stretching mode from water molecule
II	1800 – 1400	OH deformation mode from water molecule
III	<1000	Metal-oxygen stretching mode

Conclusion

Titania and titanate nanostructured materials was successfully synthesized using simple hydrothermal method at different temperature. At low hydrothermal treatment temperature (100 °C) no reaction was materialized, thus similar properties of the synthesised material with TiO_2 precursors was found. At 150 and 200 °C, titanate compounds was produce belong to hydrogen titanate nanofibers and rods like sodium titanate, respectively. Different type of titania and titanate nanostructured materials can be controlled by the appropriate hydrothermal synthesis temperature.

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