Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 11 (7): 1267-1272, 2011
ISSN 1812-5654 / DOI: 10.3923/jas.2011.1267.1272

The Effects of Hydrothermal Growth Parameters on Titanium Dioxide Nanomaterial

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Abstract: Titanium dioxide (titania) nanomaterials have been extensively studied for various applications. It is mainly applied as white pigment to provide whiteness and opacity to different kinds of products such as coatings, paints, foods and etc. Titania nanomaterials can be produced using various methods, as such the optimization of methods used is the key to produce nanomaterials with desired properties. The objective of the work is to study the hydrothermal growth parameters, such as the effect of treatment time and sodium hydroxide concentration (NaOH) on the nanomaterials produced. Titania P25 (Degussa, Germany) and concentrated NaOH were treated hydrothermally under various conditions. Hydrothermal treatment for 12 and 24 h at 150°C produced nanoparticles, while treatment for 48 h at 150°C produced nanotubes. Analysis of nanomaterials formed shows nanoparticles are in the range of 80 to 120 nm. The results further indicate the formation of hydrous titanate molecule. This work allows for better understanding of the parameters that control the growth of the titania nanomaterials. This is very important as it can be used to produce titania nanomaterials with various surface morphology for all kinds of applications.

Key words: Titanium dioxide nanomaterial, hydrothermal synthesis, titania

INTRODUCTION

Titanium dioxide (titania) nanomaterials have attracted a lot of interests by the industries and the scientific community. This is due to the very nature of titanium dioxide nanomaterials which have a lot of different properties, such as high oxidative power, non-toxicity, photo-stability, water insolubility, wide band gap, high refractive index and the ability to function as a photocatalyst under UV radiation. These properties have made titania to be widely used in many industries and various applications.

There are many fabrication methods available to synthesize TiO_2 nanomaterials. These methods can be generally classified as sol-gel (Li *et al*., 2008; Ferreira da Silva *et al*., 2006), hydrothermal syntheses (Zhijie *et al*., 2005), chemical vapour deposition (Zhang *et al*., 2007), flame combustion (Kitamura *et al*., 2007) and electrochemical anodization (Gong *et al*., 2001; Mor *et al*., 2005). Each of these techniques has their own advantages and disadvantages. Specific application requires nanomaterials with specific morphology for optimum performance. Certain techniques are more suitable to produce nanomaterials for specific application such as gas sensor and solar application. These techniques can be used to produce Titania with specific properties such as hydrophobic materials.

Titania has been extensively studied as a photo-electrode material for third generation solar cell also known as Dye sensitized Solar Cell (DSC). The objective of the research is to study the effect of hydrothermal growth; mainly the effects of treatment time and NaOH concentration. As such it will allow the establishment of the relationship between growth parameters and surface morphology of the titania nanomaterial produced.

MATERIALS AND METHODS

Titania P25 particles (anatase:rutile = 7:3) supplied by Degussa (Germany) with an average particle diameter of 30 nm was used as received. The P25 nanomaterial was mixed with highly concentrated Sodium hydroxide (NaOH) aqueous solution (initial experiments uses 5 M concentration). The mixture was sonicated and stirred using a magnetic stirrer for a few hours. The solution is then poured into a Teflon-lined stainless steel autoclave and heated at 150°C for 12 h (this parameter can be varied). The resulting slurry is washed and filtered using 0.1 M aqueous Hydrochloric acid (HCl) and de-ionized water until the pH is neutral. The filtered slurry is then dried at room temperature for 2 days and calcined at 600°C. The produced sample is then characterized using Zeiss Supra 55VP Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectros copy (EDX) for

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elemental composition analysis and Transmission Electron Microscopy (TEM) to view the internal structure/morphology of nanomaterials formed.

Effects of treatment time: In order to understand the growth parameters, the first set of experiment is designed to investigate the effect of reaction time. The autoclave containing 5 M NaOH and P25 titania is treated in the oven at 150°C at various time interval of 12, 24 and 48 h. Hydrothermal treatment for 48 h is expected to yield bulk and randomly grown nanotubes.

Effect of sodium hydroxide concentration: Another parameter that was considered to have an effect on the surface morphology produced is the concentration of sodium hydroxide aqueous solution. This specific experimental work was designed by varying the concentration of sodium hydroxide typically 5, 10 and 20 M.

RESULTS AND DISCUSSION

Analysis of the results obtained from SEM, XRD and TEM characterization indicates the formation of several different surface morphologies such as nanoparticles, nanotubes and nanowires. The discussing is focused on the effects of treatment time and sodium concentration on the surface morphology. In addition, several other effects of growth parameters are also included in synthesizing nanotubes and nanowires.

Effects of treatment time: Figure 1-3 show the SEM images of nanomaterials obtained from autoclaving P25 titania. It is found that particles and nanowires have been produced. By varying the growth parameters, different types of nanomaterials can be obtained. It is observed from Fig. 1 that the nanomaterials formed shows a very similar surface morphology to the starting material, however these particles average size are larger than average size of P25 titania. Figure 2 shows the surface morphology for titania powder that was obtained from autoclaving for 24 h. Autoclave treatment for 12 and 24 h did not show any significant change to the surface morphology. However, these particles have formed aggregates and are clumping together forming bulky chunks of titania. Figure 3 shows the results of autoclaving for 48 h at 150°C, clearly from this figure we can see that the surface morphology has been significantly altered. What is observed here are bulk nanotubes that have random growth. The exact measurements for the nanotubes formed is very difficult to determine as the material is in bulk form and formed a

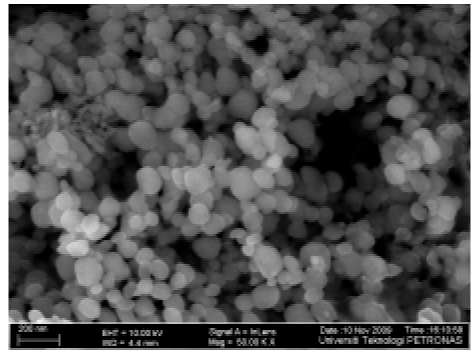

Fig. 1: SEM image of synthesized TiO_2 hydrothermally for 12 h

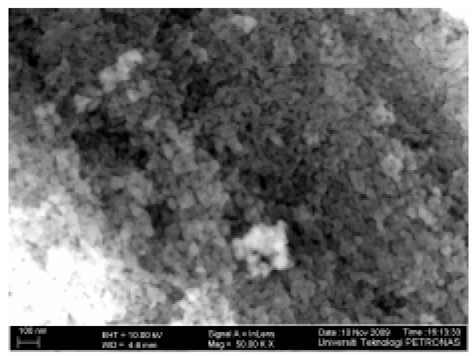

Fig. 2: SEM image of synthesized TiO_2 hydrothermally for 24 h

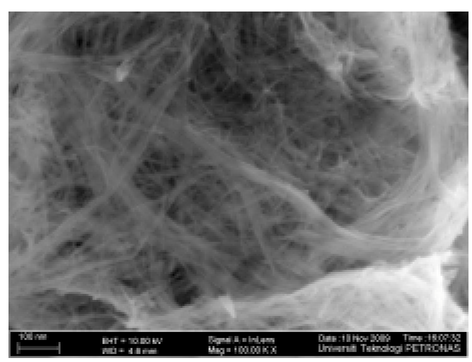

Fig. 3: SEM image of synthesized TiO_2 hydrothermally for 48 h

tangled mesh leaving it impossible to identify a single strand. The TEM result for TiO_2 sample that was hydrothermally treated for 48 h is shown in Fig. 4. The TEM image clearly indicates that the wire like morphology observed from SEM image is nanotubes. The inner walls

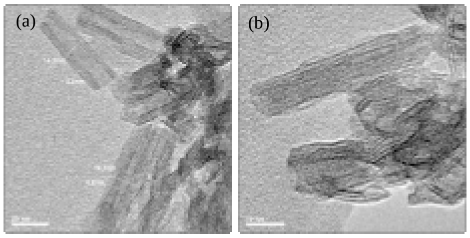

Fig. 4: TEM images of TiO_2 sample produced after 48 h hydrothermal treatment indicating the formation of nanotubes

showing a thickness of 4.2 and 6.8 nm are clearly visible from the TEM image. These measurements were taken from strands that a visible, even after sample preparation a lot of the nanotubes are overlapping. The porous part of the nanotube (pore diameter) is roughly estimated to be 4.9 nm (Fig. 4a, b). In summary the nanotubes shows a very needle like morphology with small pore diameter. This is also reflected in the SEM image (Fig. 3), where the surface morphology observed shows a needle/wire like formation, however, the TEM indicates that these are nanotubes with hollow centre.

Table 1 summarizes SEM and EDX analysis conducted on all samples produced. However, due the nature of the nanotubes and nanowires formed it is not possible to estimate the length and the diameter of nanotubes formed, as a lot of strands overlap each other. The TEM analysis allowed for some rough estimates the dimensions of the nanotubes formed. Figure 5 shows EDX result.

The hydrothermal treatment time bears a significant impact of the morphology of nanomaterials formed. A short treatment time will cause the formation of nanoparticles with a variety of size, tends to be larger than the starting material (P25). Although the results indicate that nanotubes are formed at 48 h treatment time, this is not always the case. The treatment time correlates directly with the treatment temperature and volume of mixture used. The particles are larger because it is possible that a more complex molecule is formed due to reaction with the highly concentrated sodium hydroxide. The EDX results as shown in Table 2 indicates that titania is formed, however, there are some impurities such as sodium and calcium. About 9% of sodium is observed in the sample, this is just simply an unwanted result from the hydrothermal processing. Further purification and cleaning is needed using diluted hydrochloric acid (HCl) to remove the remaining sodium. However, it is possible that upon treatment with diluted acid, a hydrous sodium-titanium complex is formed. The EDX and XRD results

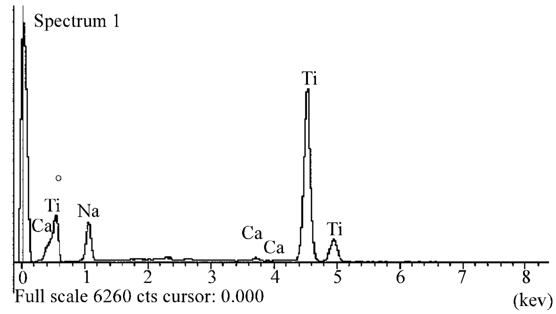

Fig. 5: EDX result showing the composition of hydrothermally synthesized TiO_2

Table 1: Summary of TiO_2 samples produced hydrothermally

Samples	SEM Analysis	Estimated size
Treatment for 12 h/150°C	Nanoparticles	80 -120 nm
Treatment for 24 h/150°C	Nanoparticles (aggregates)	80 -100 nm
Treatment for 48 h/150°C	Nanotubes	W: 15 -20 nm
5 M NaOH/150°C	Nanotubes	W: 25 nm
10 M NaOH/150°C	Nanoparticles (aggregates)	200 −500 nm
20 M NaOH/150°C	Nanowires	W: 200 nm +

Table 2: EDX result of hydrothermally synthesized TiO_2

Element	Weight (%)	Atomic (%)
O	47.45	69.40
Na	9.24	9.40
Ca	0.42	0.24
Ti	42.89	20.95
Total	100.00	

indicate the formation of hydrous and mesoporous molecule. This outcome is similar to what have been reported by Armstrong *et al.* (2005) and others (Asagoe *et al.*, 2007) where this molecule is sodium hydrogen titanate $Na_yH_{2-y}Ti_nO_{2n+1}xH_2O$. This accounts for the high amount of sodium found in the sample. Armstrong *et al.* (2005) further discussed that sodium hydrogen titanate could be heated at 400°C to turn into TiO_2 B nanoparticle. TiO_2 B form can occur naturally and it is usually found on Tektite materials (glass rock) which have been thought to be fragments of meteorite.

The SEM images in Fig. 1 and 2 indicate particles formation and both of these samples contain very high amount of sodium as indicated by the EDX result in Table 2. The EDX result suggests that the particles formed are in fact sodium hydrogen titanate because the amount of sodium remaining in the sample is very high to simply regard it as impurities. The high percentage of sodium present in the sample suggests that the powder obtained can be sodium hydrogen titanate. This can be confirmed by analyzing and comparing the XRD results (Fig. 6) with other published result (Armstrong *et al.*, 2005). The spectrum does support the theory that the materials formed are sodium hydrogen titanate or TiO_2-B, as this material has a specific spectrum

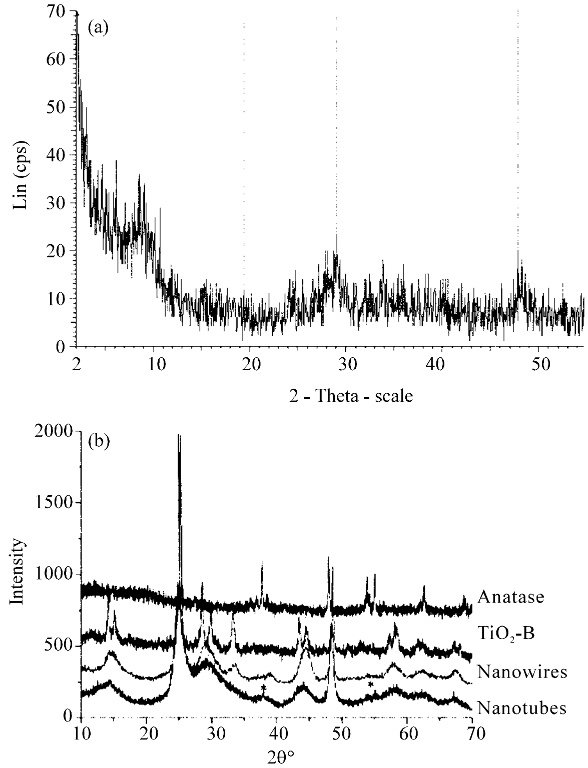

Fig. 6: (a) XRD pattern for TiO_2 produced after 48 h hydrothermal treatment. (B) XRD patterns of TiO_2-B nanotubes, TiO_2-B nanowires, bulk TiO_2-B and anatase. *indicates anatase impurity. Reproduced from Armstrong *et al*. (2005)

(Fig. 7). Figure 6 shows the XRD spectrum obtained by Armstrong *et al*. (2005). The TiO_2 nanotube spectrum produced by Graham has similar peaks to the spectrum obtained for treatment for 48 h (sample 3), which suggest that the surface morphology obtained is nanotube as opposed to nanowires.

Effects of sodium concentration: Three different samples were synthesized hydrothermally with variations in the sodium concentrations namely 5 M, 10 M and 20 M NaOH were used. Figure 7 describes the SEM images for all the samples produced. Observation from Fig. 7 indicates the formation of bulk nanowires when treated with 5 M, however, according to literature (Armstrong *et al*., 2005; Chen and Mao 2006), growth using the hydrothermal parameters should yield nanotubes. The sample has formed aggregates which makes it very difficult to estimate the dimensions. However, the EDX result (Fig. 5) indicates the same high contents of sodium. This is another indication of the formation of sodium hydrogen titanate. Currently all three samples

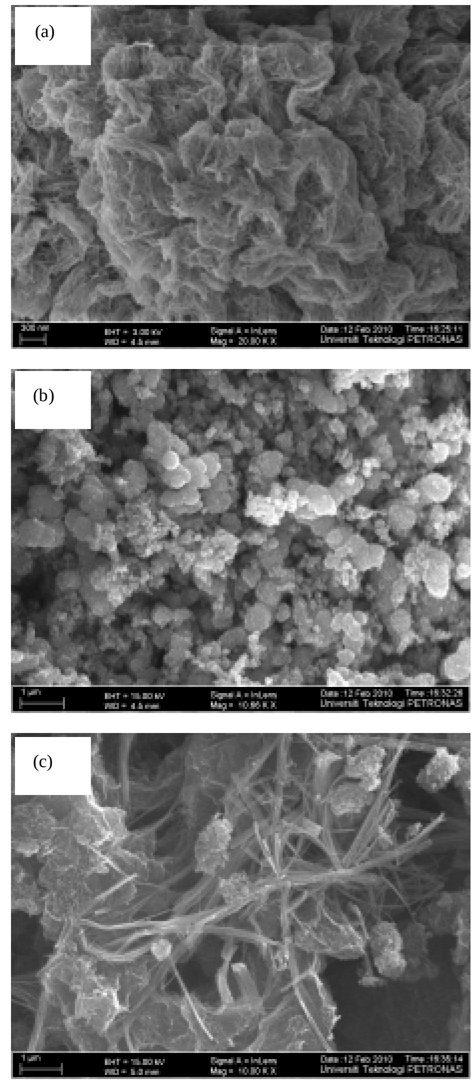

Fig. 7: (a) SEM image of TiO_2 treated with 5 M NaOH, (b) SEM image of TiO_2 treated with 10 M NaOH and (c) SEM image of TiO_2 treated with 20 M NaOH

(4, 5 and 6) contain high amount of sodium. There are different morphologies observed from the SEM results.

There are different morphology observed such as nanowires, nanotubes and naoparticles. The concentration of sodium hydroxide does not affect the surface morphology as indicated by the SEM results (Fig. 7). Result obtained from treatment using 10M NaOH (Fig. 7b) is an anomaly as during the cleaning process with diluted HCl, heat is given off (exothermic reaction) which indicates an occurrence of a chemical reaction.

During this cleaning process the aggregated particle formation is observed. The particles observed (Fig. 7) indicates the formation of sodium hydrogen titanate.

Nanowire vs nanotubes: It is observed that the surface morphology of the output from hydrothermal treatment for 48 h is nanotubes. The XRD result shown in Fig. 6 can be used to determine whether it is nanotube or nanowires. The TEM image which is shown as Fig. 4 shows that the TiO_2 nanomaterial formed is indeed nanotubes. This is also reflected by the XRD result, the distortion observed (in the range of 2-10 2θ scale) suggest that material is mesoporous. The formation of these morphologies is controlled by the hydrothermal treatment time and temperature, however, this is not always the case. The treatment time correlates directly with temperature, time and volume of mixture used.

Autoclaving the titania mixture at temperature above 170°C has been reported to yield nanowires, where autoclaving at temperatures less than 170°C will produce nanotubes (Armstrong *et al*., 2005; Asagoe *et al*., 2007). However, there is dispute regarding the effect of the volume of the mixture used. Other research groups (Armstrong *et al*., 2005) have reported that a small volume with high temperature is known to yield nanowires, whereas higher temperatures will yield larger nanotubes and nanowires. Asagoe *et al*. (2007) reported the formation of TiO_2 nanowire formed using commercial anatase powder with hydrothermal treatment of 10M NaOH for 120 h at 150°C. The obtained nanowires were calcined at 700°C to remove any TiO_2-B formation. The finding reported by Asagoe *et al*. (2007) contradicts with the findings of Armstrong *et al*. (2005), and will be a good area for further experimental work. This experimental work is needed to confirm the finding when autoclaving the titania mixture at temperature above 170°C would yield nanowires, whereas temperatures less than 170°C would yield nanotubes.

CONCLUSIONS

The synthesis of titania nanomaterials using commercial product (P25) as the starting material is reproduced here. It is established that certain autoclaving parameters can produce nanoparticles, nanowires and nanotubes. TEM images indicated the formation of nanotubes as opposed to nanowires. The surface morphologies are directly controlled by the hydrothermal treatment time, temperature and volume of mixture. The treatment time control the type of nanomaterials formed. Nanotubes formation is observed from 48 h hydrothermal treatment. Treatment time less than 48 h yield nanoparticles as opposed to nanotubes. Nanotubes that are formed by hydrothermal treatment are usually obtained at temperature of 150°C with various treatment times.

The effect of sodium hydroxide concentration does not effect the surface morphology of titania formed. The treatment time has a significant impact on the types of nanomaterials produced compared to the effect of sodium hydroxide concentration. The results indicate that sodium hydroxide concentration could alter the dimensions of the materials formed where higher concentration produces wider nanotubes.

There is evidence that the materials synthesized could be sodium hydrogen titanate as reported by others. As such heat treatment of 400°C can be applied to materials formed to force a phase change to TiO_2-B which has a monoclinic crystal system. The crystal structure is a polymorph which composes of edge and corner sharing TiO_6 but it has lower density compared to rutile, anatase and brookite titania. Furthermore, calcination at temperature range of 600 to 700°C could be use to remove TiO_2-B and form anatase titania.

The experimental findings concluded in this work allows for better understanding of the parameters that control the growth of the titania nanomaterials. It is significant as it can be used to produce titania nanomaterials with various surface morphology for all kinds of applications.

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