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RESEARCH ARTICLE

Significant effect of concentration ratio in synthesizing titania nanoflowers (TNF) powder via facile hydrothermal method

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Abstract

The significant effect of titanium butoxide and hydrochloric acid (TBut/HCl) concentration ratio in synthesizing titania nanoflowers (TNF) towards powder morphologies, crystallographic phases, surface area and band gap were investigated. Various synthesized titania nanostructure were prepared via facile hydrothermal method using titanium butoxide and hydrochloric acid as a mixing composition. The morphologies of synthesizing titania powder were analyzed by using FE-SEM to observe the shape and geometry of the synthesized powder. XRD was used to determine the crystallographic phases of synthesized powder at 2θ angles of 25° to 75°. Each sample was then investigated under BET analyzer to observe the particle surface area and UV-Vis analyzer to determine the band gap. The results demonstrated that the concentration of TBut/HCl ratio gave a very significant effect in transforming the mixing solution into geometrical shape of microspheres, nanoflowers and nanorods of titania as increasing the ratio. At TN0.5, the synthesized powder was clearly showing a circle geometrical shape of particles. The shape was suddenly changed into a round nanoflowers form consist of tiny nanorods at TN1. At TN1.5, the powder morphology shows the nanoflowers started to form in an irregular pattern. As the concentration ratio increased, the nanoflowers form disappeared and nanorods begin to clump. In addition, all synthesized powder was in rutile phases guided by XRD peaks and the band gap value reported from previous works. The particle surface area was also different for each sample since the geometrical shape of powder was changed by increasing the concentration (TBut/HCl) ratio. Thus, concentration ratio of the mixing composition plays a major role in transforming the overall morphologies and structures of hydrothermal synthesis titania particles.

Keywords: Titania nanoflower (TNF), titanium dioxide, nanostructure, titanium butoxide, hydrothermal method

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INTRODUCTION

Nanoparticles Titanium dioxde (TiO_2) is well known inorganic material which is commonly used for oxide semiconductor materials due to their unique properties of strong oxidizing power, non-toxic in nature, biological and structure stability, easy handling and low cost material (Byranvand *et al.*, 2013; Karkare, 2014; Di Paola *et al.*, 2013). Until recently, the nanostructured of TiO_2 such as nanorods, nanotubes and nanoflowers was widely investigated due to its excellent improvement in various applications such as photocatalytic, solar energy conversion, paint, cosmetics, textiles and photovoltaics (Ahmad & Murakami, 2012; Mcnulty, 2008; Theivasanthi & Alagar, 2013). Many method has been introduced and proposed to prepare and modify the nanostructure of TiO_2 powder, such as solvothermal method (Yang & Gao, 2006), direct oxidation method (Sun *et al.*, 2013), chemical vapor deposition (Qu *et al.*, 2013), electrodeposition (Mali *et al.*, 2012), sonochemical method (Prabhu & Poulose, 2012), microwave method (Roy, 2013), and hydrothermal method (Sekino, 2010; Safarpour *et al.*, 2015; Xu *et al.*, 2012)

The hydrothermal method is known as the most cost effective methods to synthesize the TiO_2 nanostructured powders. Generally, synthesis using hydrothermal can be described as a process of growing a single crystal from an aqueous solution in an autoclave at high temperature followed by applying pressure parameter (Abdullahi *et al.*, 2017; Byrappa & Yoshimura, 2008). By using this simple approach, the morphologies or the structure of the semiconductor materials can be controlled by several variables such as precursor (Seok *et al.*, 2010), pH (Houas *et al.*, 2001), acid concentration (Song *et al.*, 2016), hydrothermal time (Huang *et al.*, 2012), and concentration ratio of the synthesize solution (Karkare, 2014; Miao et al., 2015). Unfortunately, this approach involved high chemical reaction which can easily disturb and influences the preparation and synthesis steps and sometimes affects the overall synthesis time.

Basically, TiO_2 has three different crystalline phases which are rutile phase (tetragonal), anatase phase (tetragonal) and brookite phase (orthorhombic) (Kaplan *et al*., 2016; Paulauskas *et al*., 2013; Xu *et al*, 2015). As known, the rutile phase is the most stable phase at high temperature condition, while anatase and brookite are metastable phases that could be transformed into rutile phases with annealing or calcination at very high temperature (Ahmad & Murakami, 2012; Reyes-Coronado *et al*., 2008; Wang *et al*, 2014)

In this study, we investigated the effect of concentration (TBut/HCl) ratio in synthesizing titania nanoflowers (TNF) powder, with the intention to further enhance the unique and special properties of TNF by providing more effective and reactive surface area that can be suitable for many applications.

EXPERIMENTAL

Materials

All chemicals were purchased from BG Oil Chem SDN, BHD. Titanium butoxide (TBut, reagent grade, 97%, Sigma-Aldrich) and hydrochloric acid (HCl, AR, 37%, QReC), were used as only synthesized materials. Absolute ethanol (EtOH, HmbG® Chemicals) was used in cleaning and naturalized titania nanoflower (TNF). Iso-propanol (C_3H_8O, AR, QReC) was used as solvent for band gap characterization.

Synthesis of titania nanoflowers (TNF) by using facile hydrothermal method

Titania Nanoflowers (TNF) were synthesized by using titanium butoxide (TBut) and concentrated Hydrochloric Acid (HCl) as the only raw materials. Both solutions were mixed together by applying different concentration (TBut/HCl) ratio as shown in Table 1. The total weight of synthesized nanoflowers powder from each sample were also being included as further reference.

Table 1 Synthesizing Titania nanoflowers (TNF) parameter.

Samples	TBut (ml)	HCl (ml)	Concentration ratio	Mass (g)
TN2.5	20	8	2.5	3.6
TN2	20	10	2	3.3
TN1.5	20	13	1.5	3
TN1	20	20	1	3.8
TN0.5	10	20	0.5	1.8

In sequence, the stated volume of HCl was added onto 20 ml of TBut, the mixture is then transferred into a Teflon-lined autoclave which has the maximum capacity of 50 ml. Then, the hydrothermal treatment was conducted at a temperature of 150 °C for 24 hours in an oven. At the end of the hydrothermal process, the Teflon-lined autoclave was removed from the oven and allowed to cool down naturally at room temperature. After that, the white precipitate was collected and went through a cleaning process using distilled water and ethanol for several times to naturalize the pH value before centrifuging at 7500 rpm. The white samples were dried in an oven for 24 hours at 80 °C. After drying process, the samples were ground using agate mortar to get the desired size of a fine powder. The synthesis process was illustrated in Fig. 1.

Characterization of titania nanoflowers (TNF)

The structure and morphologies of the synthesized titania nanoflowers (TNF) was characterized by Field-Emission Scanning Electron Microscopy (FE-SEM, JOEL, JSM-7600F, 10kV). The samples for testing were prepared by sealed on top of carbon tape and purged using nitrogen gas. The phases of crystallographic TNF were carried out by X-ray diffraction (XRD) patterns using D8 Advanced Bruker System which operated at 40 mA and 45 kV with a 2θ range of 25°-75°. For surface area analysis, Brunauer Emmett Teller (BET) model V-Sorp 4800P was used by weighing 1g of each sample and through the process of degassing. After the degassing process, the sample's weight was measured again to get the actual sample weight for the analysis. The weighted sample was then fed in to the BET machine for the conduct of the analysis under a continuous full immersion in liquid nitrogen throughout the process. Band gap characterization was carried out using UV-Vis Spectrophotometer model 'GENESYS 10S'. 0.05g TNF powder was diluted in Iso-propanol (IPA) solvent and sonicated for 15 minutes before filling into quartz cuvette. The used wavelength range was 300 nm to 800 nm

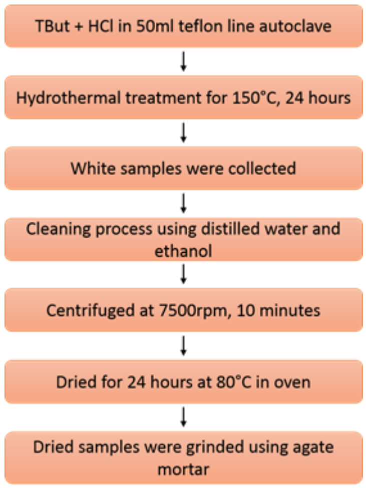

Fig. 1 Titania Nanoflowers (TNF) synthesized process

RESULTS AND DISCUSSION

Morphologies and structure analysis

Fig. 2 shows the FESEM image of different morphologies obtained by synthesizing titania nanoflower (TNF) using a different concentration ratio of TBut/HCl. The obtained structures are microspheres, nanorods, and nanoflowers. Fig. 1(a) shows the image of Titania microsphere with the lowest concentration (TBut/HCl) ratio of TN0.5 after hydrothermal treatment for 24 hours at a temperature of 150 °C. As observed, the surface of Titania microsphere at x50 000 magnification shows an attachment of tiny nanorods that has not been disassembled with the diameter particle size of 1.70 µm – 5.49 µm. At TN1 ratio, the TNF was disassembled and produced nanorods segment containing numerous flower-like structure formation with the diameter size ranging from 240 nm – 1,500 nm. Meanwhile, for Fig. 1(c), the micrograph for TN1.5 ratio shows that the structure of the nanoflowers started to split up whereby the segment of nanorod begins to separate and detach from the nanoflower. The distribution of the nanorods particles was nonhomogenous and irregular in shape, and the irregular pattern of the nanorods particles was continued to be formed until the highest concentration (TBut/HCl) ratio of TN2.5. Based on FESEM images, it clearly showed that, at high concentration of (TBut/HCl), varying the HCl volume content ratio does affect the formation of nanoparticles morphologies of titania particles. The results also has tallied with (Phan *et al*., 2009) where they stated that the HCl itself act as an inhibiter or accelerator for further self-assembly, nucleation, and the crystal growth inside titania during hydrothermal treatment. The HCl solvent play significant role on the titania particle growth by promoting its growth on the TiO_2 microsphere to form titania nanoflowers and titania nanorods shapes (Shinde *et al*., 2011). Therefore, by decreasing the HCl volume the structure of nanorods begin to change from microspheres to titania nanoflower (TNF) structures with reduced diameter ranging from 240nm – 1500nm.

Phase characterization

Fig. 3 shows the XRD pattern of synthesized Titania Nanoflowers (TNF) using varying concentration (TBut/HCl) ratio results. All diffraction peaks are referred to titanium dioxide (TiO_2) rutile phase (JCPDS card no. 00-021-1276). The rutile diffraction peaks were showed at 2θ = 27.5°, 36.1°, 41.2°, 54.3° and 56.6°. All these peaks can be attributed to (110), (101), (111), (211), (220) plane for rutile phases and was in-line with previous synthesis reports (Hamed *et al*., 2016; Li *et al*., 2013; Min *et al*., 2010)

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Through XRD observation and analysis, the obtained result of XRD pattern was confirmed TiO_2 by matching the peaks and plane with JCPDS data. However, the intensity level of each sample were slightly different. As observed, the intensity for TN0.5 was quite low compared to other samples. Nonetheless, as the volume of HCl is increased at TN1, the XRD peak intensity of the sample also increased. This finding was also proved by FE-SEM results where the nanoflowers formation begins to form from microsphere structure. However, the intensity peaks were decreased as the concentration ratio achieved at TN2.5. The phenomena might have occurred due to the surface morphologies of the titanium nanoflowers (TNF) particles that started to break and separated from the main structure of nanoflower with scattered distributed which affected the intensity of crystallization. These results was also tally with (Ahmad & Murakami, 2015; Khalid *et al.*, 2015) where the clear form of nanoflowers generated with a good crystal structure compared to other samples thus give highest intensity peak.In addition, these varying rutile peaks intensity might be also caused by the different volume of acid that interrupt the hydrolysis rate of Titanium butoxide (TBut) and eventually reacted to the growth of TiO_2 (Hamed *et al*., 2016)

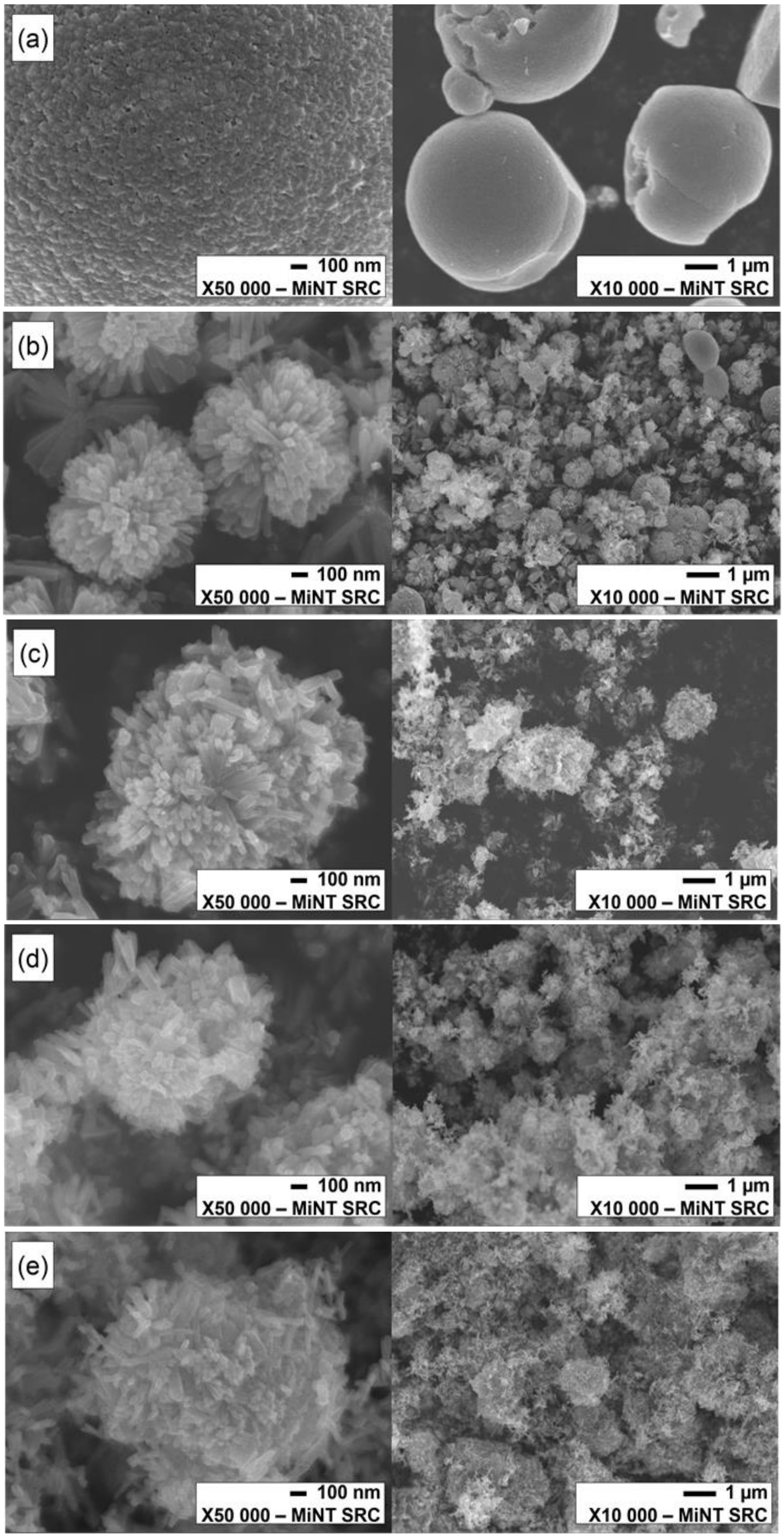

Fig. 2 FESEM images of different concentration (TBut/HCl) ratio (a) TN0.5, (b) TN1, (c) TN 1.5, (d) TN2, (e) TN2.5.

Surface area and band gap analysis

Fig.4(a) shows the BET plot of synthesized titania nanoflowers (TNF) at different concentration (TBut/HCl) ratio. The specific surface area of TN0.5, TN1, TN1.5, TN2 and TN2.5 are 21.09 m^2/g, 21.10 m^2/g, 27.25 m^2/g, 28.64 m^2/g and 35.39 m^2/g respectively. From the results, the surface area for each sample were increased gradually as the HCl volume decreased. As comparison, the results for TN0.5 and TN1 produced less significant different eventhough the particle size from FESEM result shows very much different. Whereas, TN2.5 samples produced the largest surface area compared to other samples due to its irregular shape of particles as detached from the nanoflowers structure. As reported in other works (Ma *et al.*, 2016; Wu *et al.*, 2006) by providing more effective surface area ultimately will produced less specific surface energy that able to increase reaction mechanism. Similar result also was reported by (He *et al*., 2013) that revealed the agglomeration of the nanorods particles for TN1.5, TN2 and TN2.5 as proved in FESEM observation able to increase the total surface area of the particles and provide less specific surface. As being observed in the above section, the concentration (TBut/HCl) ratio was able to produce titania nanopowder with different surface area and morphologies of particles, thus definitely this will influences the total surface area that can be of benefit towards improving the particle reactivity in certain applications.

The band gap (Eg) of a semiconductor material can be identified from the Tauc plot of $(\alpha h\nu)^2$ againt photon energy (hv). The band gap value energy can be determined by extrapolating the curve across the x-axis shown in Fig. 4(b). From the results in Table 2, TN0.5 indicates the lowest band gap value compared to other samples. Smaller values of band gap can be described that the sample can absorb more photon and generates additional photo-generated electron-hole pairs to enhance the photocatalytic activity (Song et al., 2014; Tang *et al*., 2013; Yin *et al*., 2013). TN2.5 shows the highest result value by 3.05 eV. However, the value of band gap was still in the range of rutile phases as reported by previous studied which is lower than 3.2 eV anatase phase (Ahmad *et al*., 2017; Pal *et al*., 2007; Reyes-Coronado *et al*., 2008). These varying band gap values indicate that titania is strongly influenced by its morphology (Dhandayuthapani *et al.*, 2016).

Table 2 BET surface area and band gap results.

Samples	BET surface area (m^2/g)	Band gap (eV)
TN2.5	35.39	3.05
TN2	28.64	2.99
TN1.5	27.25	2.95
TN1	21.10	2.79
TN0.5	21.09	2.76

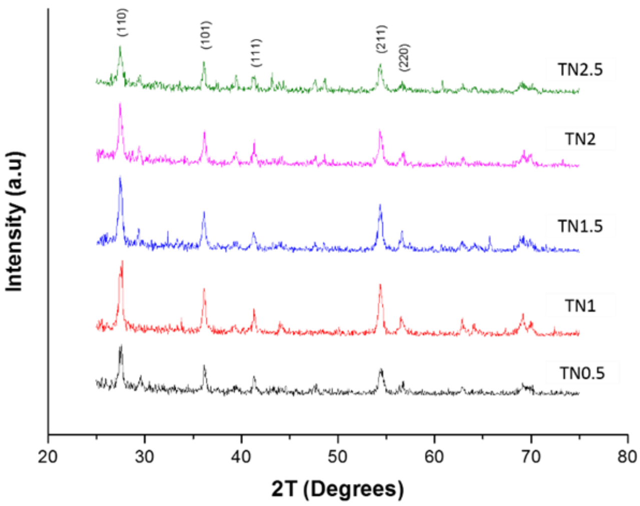

Fig. 3 X-ray diffraction (XRD) patterns analysis for different concentration (TBut/HCl) ratio

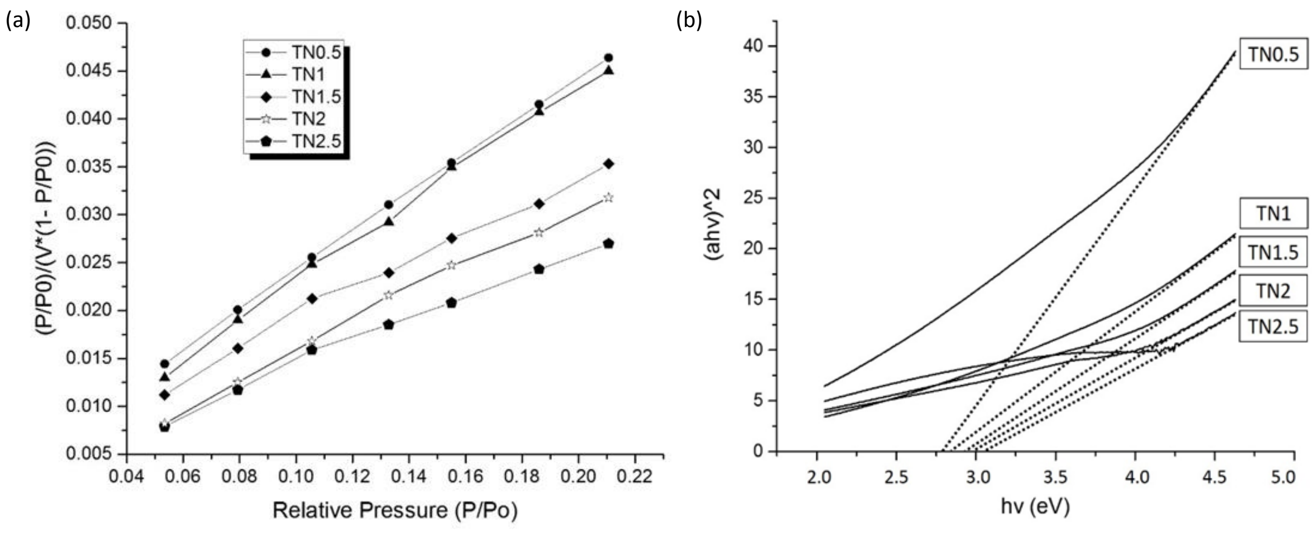

Fig. 4 (a) BET plot of synthesized titania nanoflower (TNF) for all concentration (TBut/HCl) ratio and (b) Tauc plot of $(\alpha h\nu)^2$ againts photon energy (hv).

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CONCLUSION

Titania nanoflowers (TNF) was synthesized using facile hydrothermal method by varying the volume of hydrochloric acid (HCl) to control (TBut/HCl) ratio concentration. The volume of hydrochloric acid was able to change the morphologies and the structure of the synthesized titania as observed under FE-SEM images. Clear formation of nanoflowers was notice at ratio TN1. There were also different type of structure obtained which are microsphere and nanorods. The patterns of XRD for all sampele were also slightly different in term of intensity indicates that the affected crystallynity after varying the (TBut/HCl) ratio concentration. BET surface area and band gap results analysis for each titania sample showed that each mixing concentration ratio controlled by HCl volume able to change all morphologies, XRD pattern, BET surface area and band gap value characteristics as well.

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