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SYNTHESIS OF TIO_2 NANOTUBES BY USING COMBINATION OF SONICATION AND HYDROTHERMAL TREATMENT AND THEIR PHOTOCATALYTIC ACTIVITY FOR HYDROGEN EVOLUTION

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Abstract

Effect of sonication and hydrothermal treatments on the synthesized of Titania nanotubes (TiO_2 NT)has been investigated. Sonication of TiO_2 P25 sol was performed using ultrasonic probe for certain time followed by hydrothermal treatment in a teflon lined stainless steel autoclave. The samples were characterized by means of X-ray powder diffractometer (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), UV-vis diffuse reflectance spectroscopy (UV-vis DRS) and Brunauer-Emmett-Teller (BET).The photocatalytic activity of prepared samples was evaluated with photocatalytic H_2 evolution from aqueous methanol solution. The result showed that TiO_2 NT was formed rapidly along with the duration of sonication treatment but the longer processing time of it would destroy the morphology of TiO_2 NT. The optimal sonication time for the TiO_2 NT formation was 10 min. It was obtained TiO_2 NT with high crystallinity, high surface area and a perfect nanotubes structure. Hydrogen production by using this sample was about two times higher than TiO_2 P25 nanoparticle.

Keywords: *hydrogen; hydrothermal; sonication; TiO_2 nanotubes*

Abstrak

SINTESIS TiO_2 NANOTUBES MENGGUNAKAN KOMBINASI PROSES SONIKASI DAN HIDROTERMAL DAN AKTIFITAS FOTOKATALITIK UNTUK PRODUKSI HIDROGEN
Efek kombinasi proses sonikasi dan hidrotermal pada pembentukan TiO_2 nanotubes telah dilakukan. TiO_2 P25 disonikasi menggunakan ultrasonik probe dengan waktu tertentu kemudian dilanjutkan dengan proses hidrotermal di autoklaf berbahan teflon dan stainless steel. Sampel yang diperoleh di karakteriksasi menggunakan X-ray powder diffractometer (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), UV-vis diffuse reflectance spectroscopy (UV-vis DRS) and Brunauer-Emmett-Teller (BET). Aktifitas fotokatalis dari sampel diuji untuk produksi hidrogen dari larutan metanol. Dari hasil yang diperoleh TiO_2 nanotubes lebih cepat terbentuk dengan adanya proses sonikasi, akan tetapi semakin lama waktu sonikasi bentuk nanotubes yang diperoleh menjadi rusak. Waktu optimal untuk proses sonikasi adalah 10 menit. Pada kondisi ini TiO_2 yang terbentuk memiliki kristalinitas dan luas permukaan tinggi serta bentuk nanotubes yang sempurna. Produksi hidrogen pada kondisi inipun dua kali lebih besar dibandingkan dengan TiO_2 P25 nano partikel.

Kata kunci : *hidrogen; hidrotermal; sonikasi; nanotube TiO_2*

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INTRODUCTION

The growth of environmental concerns related to the extensive use of non-sustainable fossil fuels (oil, natural gas and coal) and a constantly increasing energy demand will force mankind, sooner or later, to tap into clean and sustainable source of energy (Zhu

and Zach, 2009). Hydrogen production from photocatalytic water splitting provides a potential opportunity to obtain clean, renewable and storable energy from abundant water using solar energy. Titanium oxide is well known as a material with an excellent photocatalytic activity and has been investigated for producing hydrogen by photocatalytic water splitting (Fujishima and Honda, 1972). Furthermore it has been applied in photocatalysis such as NOx removal, water purification and decomposition of pollutants and also catalytic reactions for hydrogen generation (Fujishima *et al.*, 1972; Hoffmann *et al.*, 1995; Zhao *et al.*, 1998; Barka *et al.*, 2011; Nazir *et al.*, 2003). Titanium oxide also has high stability, biological and chemical inertness, strong oxidizing power, non toxicity and long term stability against photo and chemical corrosion (Fujishima *et al.*, 1972; Hoffmann *et al.*, 1995; Zhao *et al.*, 1998).

In recent years, many one dimensional TiO_2 materials such as nanowires, nanotubes and nanorods have been successively synthesized (Ou and Lo, 2007). TiO_2NT therefore, attracted extensive and engrossing interest.It has high specific surface area, ion exchange ability and photocatalytic ability (Ou and Lo, 2007). Much effort has been directed at obtaining TiO_2NT with a large surface area such as the assisted-template method (Bavykin *et al.*, 2006; Costa and Prado, 2009), the sol gel process (Kasuga *et al.*, 1998), electrochemical anodic oxidation (Zwilling *et al.*, 1999; Gong *et al.*, 2001; Sun *et al.*, 2011) and hydrothermal treatment (Zhang *et al.*, 2003; Kasuga *et al.*, 1999; Chen and Mao 2007; Wang *et al.*, 2007; Wang 2002). Among them the hydrothermal method has been reported to be the most powerful technique due to the simplicity of the synthesis and to the fact that the nanotubes can be obtained by simple, cost effective and environmentally innocuous route (Bavykin *et al.*, 2006; Costa *et al.*, 2009; Kasuga *et al.*, 1998; Zwilling *et al.*, 1999; Gong *et al.*, 2001; Sun *et al.*, 2011; Zhang *et al.*, 2003; Kasuga *et al.*, 1999; Chen *et al.*, 2007; Wang *et al.*, 2007; Wang 2002). One of the disadvantages of hydrothermal method is long reaction duration is needed (Ou and Lo, 2007). Therefore, improvement of the hydrothermal synthesis process for shortening of the reaction time is very important. Many researchers have prepared TiO_2NTby hydrothermal technique with the assistance of sonication (Meskin *et al.*, 2006; Zhu *et al.*, 2001). Unfortunately this improvement is complicated because sonication treatment was used in situ with hydrothermal process (Meskin *et al.*, 2006). Ma *et al.* (2006) used sonicationbefore hydrothermal treatment with simplemethod than previous research, but the sonication time stillrequired1 hour.Furthermore, to our best knowledge, there are few reports on the effect of combination sonication and hydrothermal process on the hydrogen production of TiO_2 NT.

In this study we proposed the simple and fast method of combination sonication and hydrothermal treatment for the production of TiO_2NT. The influence of sonication time on the morphology structures, photoelectrochemical properties and photocatalytic activity evaluated by hydrogen production was systematically investigated.

EXPERIMENTAL

Preparation of TiO_2 Nanotubes

The preparation of TiO_2 NT has been conducted by using hydrothermal treatment and simple combination sonication and hydrothermal treatment. The hydrothermal treatment was performed in a Teflon lined stainless steel autoclave at 130°C for 12 and 24 h. The simple combination sonication and hydrothermal method was basically same as in previous work (Kustiningsih *et al.*,, 2009). First 2 g of TiO_2 DegussaP25 was dispersed in 100 ml NaOH 10M followed by sonication process in a ultrasonic processorCT ChromTech (800 watt) for different times, 5, 10 and 15 min.After sonication treatment, the sonicated solution was moved into a teflonlined stainless steel autoclave for carrying out the hydrothermal treatment at 130^{o}C for 12 h. After the hydrothermal treatment, the precipitates were rinsed well with distilled water, and further rinsed with HCl anddistilled water repeatedly until the pH value of the washing solution was lower than 7. The final products were obtained through centrifugation and further dried in atmospheric furnace at 150^{o}C then calcined at 500°C.

Characterization

The structure and morphology of products were characterized by several techniques. Powder X-ray diffraction (XRD) data were collected using a Philips PW 1710 Diffractometer with Cu Kα *radiation* (λ = 1.5406Å) at a scan rate of 0.025°s^{-1} and were used to determine of any phase present and their crystallite size. The Transmission electron microscopy (TEM) analyses were conducted with a JEOL JEM-1400 electron microscope using120kV accelerating voltage. Morphology observation was performed on a JEOL JSM-6390A scanning electron microscope (SEM) equipped electron dispersive X-Ray (EDX). The UV-vis diffuse reflectance spectroscopy (UV-vis DRS) were determined by a SHIMADZU 2450. The surface area of the powders was measured using Brunauer-Emmet-Teller (BET) (Autosorb 6, Quantacrome) technique.

Photocatalytic Hydrogen Production

The photocatalytic hydrogen production was carried out in a photoreactor made of pyrex glass equipped with 6 black light lamps (10W). The powder photocatalyst was suspended in 10% methanol water mixture at a concentration of 1 g L^{-1}. A magnetic stirrer was placed at the bottom of the reactor to ensure homogeneity of the suspension during reaction. The suspensions were then flushed with argon for 15 min to remove undesired gases. Hydrogen was

analyzed by gas chromatography (GC) using a Shimadzu GC-8A equipped with a thermal conductivity detector (TCD) and a stainless steel column packed with molecular sieves.

RESULTS AND DISCUSSION

The Effect of Hydrothermal Treatment on Formation TiO_2 NT

The hydrothermal duration plays on important role on the formation of TiO_2 nanotubes. The time of hydrothermal was conducted at 12 h and 24 h. In order to investigate the influence of HCl treatment after hydrothermal on the TiO_2 nanotubes formation sample at 24 h prepared at different treatment, some of them after hydrothermal followed by HCl treatment and some of sample without HCl treatment. SEM image of the samples is shown in Figure 1.

Figure 1(a) shows the image of the sample after 12 h hydrothermal and HCl aqueous solution treatment. It shows the change of the morphology from spherical to the scroll conFigureuration. Without sonication process, after 12 hours hydrothermal treatment, nanotubes morphology has not been formed yet. Figure 1(b) shows nanotubes morphology has been formed uniformlyafter 24 h hydrothermal. The longer hydrothermal treatment can produce TiO_2 NT in good shapes. It indicated that the formation TiO_2 NT was strongly influenced by duration of hydrothermal.

The SEM image of the sample after 24 h hydrothermal treatment without washing treatment is shown in Figure 1(c). Itindicates TiO_2 NT has been formed after 24 h hydrothermal treatment even though without washing treatment. As shown in Figure 1(b) after washing treatment the morphology of nanotubes was increasingly evident. It indicated that hydrothermal treatment is significantly the more important step than washing process in the mechanism of nanotubes formation. During the hydrothermal the Ti-O-Ti bonds were broken due to reaction with NaOH. The free octahedral shapes shared edges between the Ti ions to form hydroxyl bridges, then a zigzag structure were formed. Thus, the crystalline sheets rolled up in order to saturate these dangling bonds from the surface. This lowered total energy and hence TiO_2 NT was formed (Chen and Mao, 2007). Similar results have been reported by Bavykin *et al.*, (2004), Zhao *et al.,* (2009), and Poudel *et al.,* (2005), but essentially contradicting with the assumptions of Kasuga *et al.,* (1999). They revealed an acid washing treatment step following the hydrothermal process to form tri-titanate nanotubes.

The Effect of Sonication Treatment on Formation TiO_2 NT

The effect of sonication on the growth mechanism of TiO_2 nanotubes is still under discussion but there were few reports about the growth mechanism of TiO_2 nanotubes by using combination sonication-hydrothermal treatment. In order to investigate the effect of sonication on formation of TiO_2 nanotubes, samples were prepared with different treatments: 10 min sonicationwithout hydrothermal and varied sonication time followed 12 h hydrothermal. Figure 2 shows the SEM images of of the TiO_2 Degussa P25 and TiO_2after 10 min sonication without hydrothermal treatment.

Figure 2(a) shows TiO_2 P25 has spherical nanoparticles with an average 30 nm. The sample 10 min sonication without hydrothermal has morphology like TiO_2 P25 with smaller diameter is shown in Figure 2(b). It indicated tubular shape was not formed after sonication without hydrothermal treatment. The images of the product obtained at the sonication times of 5, 10, 15 min followed by hydrothermal and HCl aqueous solution treatments is shown in Figure 3. The change in shape and morphology of the samples occurred with respect to the sonication time. The SEM image of sample with sonication time at 5 min indicated that nanotubes morphology was not much formed. The samples were found completely transformed into likely tubular shape after 10 sonication min followed by hydrothermal and HCl aqueous solution treatment. It can be seen at Figure 3(b) that TiO_2 nanotubes has been formed uniformly. This result indicated that time of formation TiO_2 nanotubes can be shortened by using combination of sonication and hydrothermal process. By adding 10 min sonication before hydrothermal process, TiO_2 nanotubes have been completely formed after 12 h.

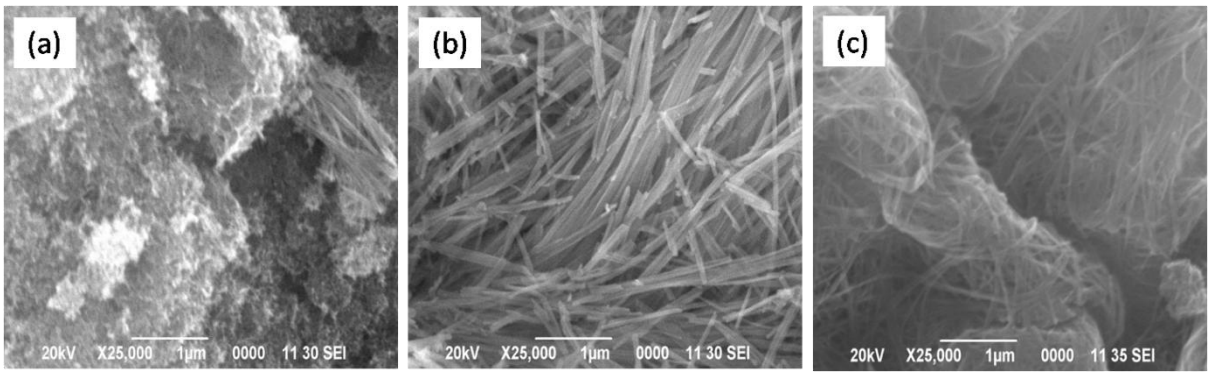

Figure 1. SEM image of samples: (a) after 12 h hydrothermal followed by HCl treatment, (b) 24 h hydrothermal followed by HCl treatment, (c) 24 h hydrothermal without HCl treatment

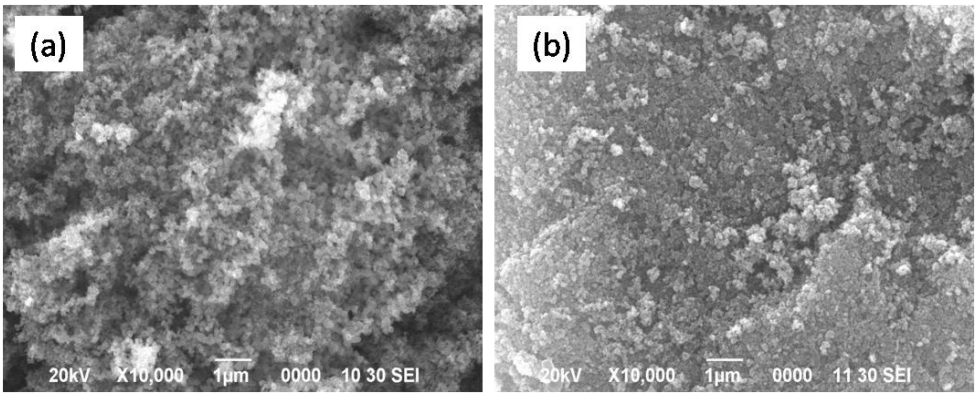

Figure 2. SEM images of the samples: (a)TiO_2 Degussa P25, (b) TiO_2 after 10 min sonication without hydrothermal treatment

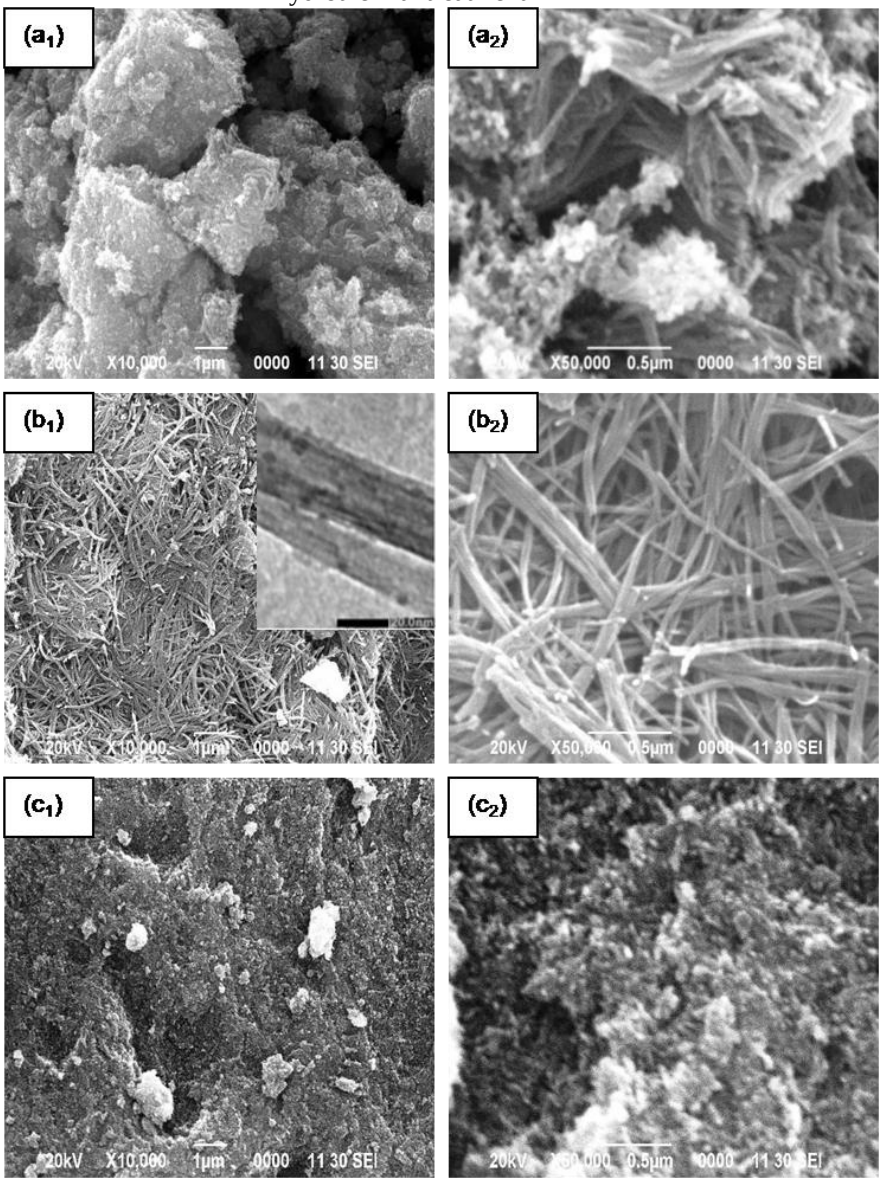

Figure 3. SEM images of the samples (subscript1) sample which zoom 10,000, (subscript 2) sample which zoom 50,000 all samples are followed by 12 h hydrothermal and HCl treatment: (a) sonication at 5 min (b) sonication at 10 min (c)sonication at 15 min TEM images of TiO_2 NT after 10 min sonication followed by hydrothermal treatment inset at (b_1)

Table 1. Summary of XRD, adsorption-desorption analyses and Band Gap enery of prepared TiO_2 Degussa P25 and TiO_2 nanotubes

Samples	Crystallite size, (nm)	BET surface area	Band gap energy, (eV)
TiO_2 Degussa P25	18	54	3,02
TiO_2 NT 5 min sonication	10	124	3,12
TiO_2 NT 10 min sonication	11	134	3,05
TiO_2NT 15 min sonication	11	119	3,09

As can be seen at Figure 2(a) after 12 h hydrothermal treatment without sonication, TiO_2 nanotubes had notbeen formed yet. SEM image of sample obtained at sonication time 15 min is shown in Figure 2(C). It shows the spherical shapes which diameter smaller than TiO_2 Degussa P25. It indicated the longer sonication time before hydrothermal treatment was undesirable for the nanotubes formation.

Ma *et al.* (2006) reported the power of sonication play an important role in the formation of the titanate nanotubes (Ma *et al.*, 2006). They reported that tubular conFigureuration was obtained under sonication treatment of 380 W for 60 min followed by hydrothermal. Sheet and fibrous morphologies are presented for the products under sonication treatments of 100 and 280 W. They suggested that sonication with the sufficient power plays an important role to promote intercalating Na^+ into titania lattices and breaking the Ti-O-Ti bonds. As the result, the TiO_2 nanoparticles are swollen and transformed from the spherical into the rod conFigureuration as increasing as sonication time.The growth the nanorods is carried out during hyrothermal treatment.

In this study by using high power sonication (800W) tubular morphologies was obtained under sonication treatment for 10 min and hydrothermal 12 h. More than 10 min of sonication treatment, the morphologies of product was spherical shape, but have high surface area (see Table 1). It shown using high power sonication can shortened the sonication time for producing nanotubes. The influence of sonication treatment at high power is different with low power. Ma *et al.* (2006) reported the product after sonication treatment without hydrothermal, at low power has rod conFigureuration, but at this study by using high power the product has spherical morphology (Figure 2b).

The TEM image (inset in Figure $3B_1$) shows TiO_2 nanotubes obtained at the 10 min sonication followed by hydrothermal and HCl solution treatment. It was observed that tubular morphology was clearly observed in the sample with diameter 20 nm. Sonication process plays an important role to promote intercalating Na^+ into lattices and breaking the Ti-O-Ti bonds without giving the alteration to the morphology of TiO_2 Degussa P25. The forming of layered alkali titanate is carried out during the hydrothermal process. These layered are very thin and easily exfoliate into individual nanosheets that are highly anisotropic in two dimensions. At a high temperature (130°C), the layered structure would roll up into nanotubes due to surface tension. So the tubular structure is formed in the hydrothermal process.

The phase composition, crystallite size and crystallinity of TiO_2were reported to have a great influence on the water splitting. Therefore, XRD analyzed of the samples has been conducted. Figure4. gives the XRD patterns of TiO_2 samples prepared with different time of sonication and TiO_2 Degussa P25 nanoparticles. It indicates the TiO_2 Degussa P25 nanoparticles consist of mixed anatase and rutile, but for all products exhibited the complete crystallite structure of anatase TiO_2. The samples annealed at temperatures 500°C to reveal the changes of phase structure and crystallite size after the high temperature treatment.

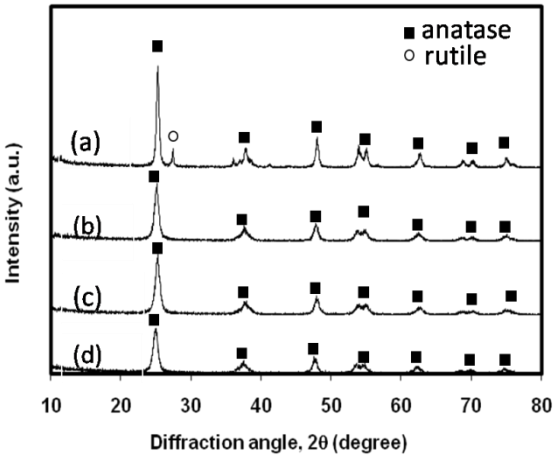

Figure 4. XRD patterns of (a) TiO_2 Degussa P25, (b) TiO_2 NT 15min, (c) TiO_2NT 10 min, (d) TiO_2 NT 5 min

As shown in Figure 4, XRD pattern of the samplesrepresentthe peaks at 2θ = 25.3, 38.0, 48.18, 54.8, 55.8, 62.58, 67.21, 68.79, 75.18 corresponding to (101), (004), (200), (105), (211), (204), (116), (220), (215) phases, respectively. It has been found that only anatase phase was formed after calcination of the samples.A rutile peak at the 2θ of 28.8, it was shown only at TiO_2 Degussa P25. Similar results have been reported many researchers that only anatase phase was formed after calcinations of hydrogen titanate nanotubes at 500°C. This profile is similar to that TiO_2 nanotubes prepared by anodic oxidation (Quan *et al.*, 1998), sol gel method (Imai *et al.*, 1999).

Different results have been reported by Suzuki and Yoshikawa, (2004). They reported that formation of TiO_2 phase (a metastable polymorph of titanium dioxide) after calcinations and no anatase phase was

found. Bruce and co-workers, (2004) reported after calcinations 400-600°C layered hydrogen titanates nanowires were converted to the titanium dioxide polymorph TiO_2, while layered hydrogen titanates nanotubes were transformed to anatase with the loss of the tubular morphology. Mohapatra *et al.*, (2007) reported TiO_2 nanotubular arrays prepared by sonochemical method and annealed under N_2 at 500°C had predominantly anatase TiO_2 but rutile phase was found at their result. The crystalline size was calculating using a diffraction peak from Scherer's formula (Weller, 1993). The crystalline sizes of all samples are summarized in Table 1. It shows the crystallite size samples lower than TiO_2 Degussa P25.

The surface area of TiO_2 NT determined on a basis of N_2 adsorption-desorption measurements are presented in Table 1. These surface areas were measured after calcined at 500°C.It can be observed that the BET specific surface area increased along with sonication time. The highest BET surface area (125 m^2g^{-1}) was observed for sample at 10 min sonication time.

The shape and size of particle have a significant impact on the optical and electronic properties of nanoparticles. The UV-vis reflectance band edge is a strong function of TiO_2 particle size, which can be attributed to quantum size effect of semiconductors. Extrapolating the spherical curves to the long wavelength side provides a measure of the band gap energy of the nanoparticles.

The UV-visible diffuse reflectance spectra for samples calcined at 500°C and are shown in Figure 5. For comparison, the spectra of TiO_2 Degussa P25 are also displayed. The spectra of samples showed low absorbance from 400 nm to entire visible region. The highest of absorbance visible region was TiO_2 nanotubes 10 min sonication. The absorption edge of TiO_2 nanotubes at 5 min sonication was similar to that of TiO_2 nanotubes at 15 min sonication. Table 1 shows the band gap energies of the samples. The band gap energy of TiO_2 nanotubes at 10 min sonication was 3.05 eV. It was the lowest band gap energy among the samples but still higher than TiO_2 Degussa P25. Some researchers found that band gap energy of TiO_2 nanotubes was higher than that of TiO_2 anatase, while others reported inverse relation. Yu and Yu, (2006) reported that band gap energy of TiO_2 nanotubes prepared from rutile ranged from 3.02 to 3.15 depending on hydrothermal treatment time. Khan *et al.*, (2009) found the band gap 3.1 eV, while Wang *et al.*, (2006) determined the band gap 3.6 eV. Bavykin *et al.*, (2005) reported band gap value of TiO_2 nanotubes was 3.87 eV.

Photocatalytic Activity of TiO_2 NT

Photocatalytic activity of the TiO_2 nanotubes was evaluated by photocatalytic H_2 evolution from aqueous methanol solution. Methanol was used as sacrificial agent because of its ability for removing the photogenerated holes thereby preventing the mutual electron-hole recombination (Zalas and Laniecki, 2005; Sun *et al.*, 2006).

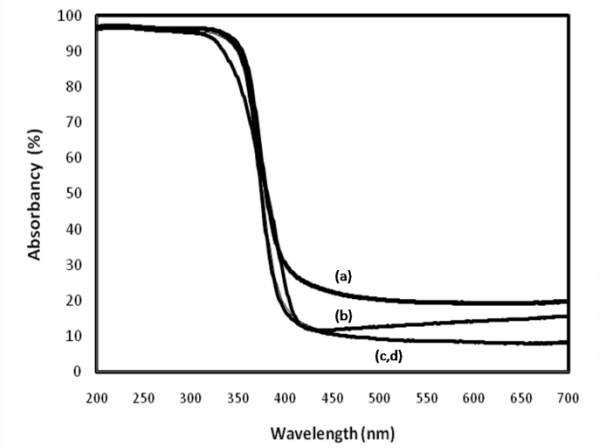

Figure 5. UV-vis DRS spectra of (a)TiO_2 Nanotubes sonication 10 min (b) TiO_2 Degussa P25 (c) TiO_2 Nanotubes 15 min (d) TiO_2 nanotubes 5 min

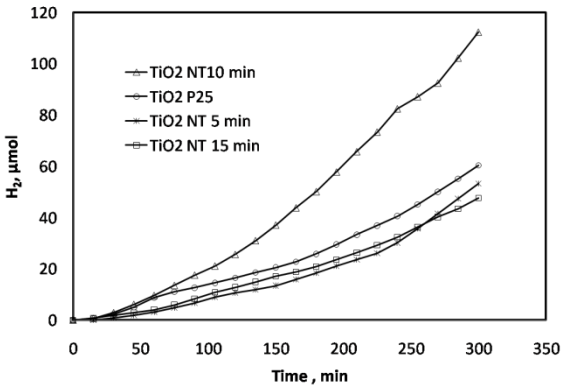

Figure 6. Hydrogen evolution over TiO_2 nanotubes and TiO_2 Degussa P25 nanoparticle.

Figure 6 illustrates the results of photocatalytic hydrogen production using TiO_2 nanotubes and TiO_2 P25. It was found that TiO_2 nanotubes at 10 min sonication exhibited higher activities than that of other samples. After 5 h, the hydrogen evolution was 112 µmol, about two times than TiO_2 P25 nanoparticle.Even though the crystallinity of TiO_2 nanotubes at 10 min sonication was lower than TiO_2 P25. The result indicated that surface area also plays important role for generating hydrogen from water splitting. It was primarily attributed to the unique 1-D nanotubular structure. 1-Dtubular structure facilitated fast electrons transfer due to reduced grain boundary and was expected to improve charge separation in photocatalytic reactions (Khan and Yang, 2009). However, an interesting phenomenon is detected that even though other samples have larger surface area than TiO_2 P25 nanoparticle, TiO_2 NT 5 min and TiO_2 NT 15 min exhibited lower photocatalytic activity than TiO_2 P25. The crystalinity sizes of both samples are smaller than TiO_2 P25 as shown in Table 1. It indicatedthat the surface area is not the only factor

effecting photocatalytic activity, but structure of TiO_2, microstructure and surface morphology together influence the efficiency of the photocatalyst.

CONCLUSION

TiO_2NT with high crystallinity and high surface area was successfully produced by simple combination sonication and hydrothermal method. The duration of hydrothermal treatment for TiO_2 nanotubes formation can be shortened by using sonication process before hydrothermal. The time of sonication process influenced the formation TiO_2 NT and the structure and crystalinity of TiO_2 NT. The optimum of time sonication for producing TiO_2 NT obtained at 10 min. Hydrogen evolution over this sample during 5 h reaction was two times higher than that of TiO_2 P25 nanoparticles. The factors that effecting hydrogen production is not only surface area, but alsostructure, microstructure and surface morphology of the TiO_2.

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