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SYNTHESIS OF TITANIA NANOTUBES AND TITANIA NANOWIRES BY COMBINATION SONICATION-HYDROTHERMAL TREATMENT AND THEIR PHOTOCATALYTIC ACTIVITY FOR HYDROGEN PRODUCTION

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ABSTRACT
Titania nanotubes (TiO_2 NT) and Titania nanowires (TiO_2 NW) were fabricated using TiO_2 Degussa P25 (TiO_2 P25) nanoparticle as precursors via a sonication-hydrothermal combination approach. The prepared catalysts were characterized by means of an X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), ultraviolet-visible diffuse reflectance spectroscopy (DRS) and the Brunauer-Emmett-Teller technique (BET). The photocatalytic activity of prepared catalysts was evaluated for photocatalytic H_2 evolution from an aqueous methanol solution. The results showed that activity of the catalyst not only depends on the morphology of its catalysts, but also on the crystalinity and surface area. Hydrogen production of TiO_2 NT was about three times higher than TiO_2 P25 and TiO_2 NW was two times higher than TiO_2P25.

Keywords: Hydrogen production; Nanotubes; Nanowires; Photocatalytic; TiO_2

1. INTRODUCTION
Photocatalytic production of hydrogen from the dissociation of water represents a significant opportunity for the development of an alternative source of energy that is clean, abundant and storable. Since the first reported water splitting reaction over the TiO_2 photoelectrode (Fujishima & Honda, 1972), a variety of semiconductor materials have been developed for this purpose. Titanium oxide (TiO_2) is well known as a material with excellent photocatalytic activity and has been investigated for hydrogen production. Compared to other photocatalysts for H_2 production, TiO_2 has received more attention because it is stable, corrosion-resistant, non-toxic, abundant and cheap (Fujishima & Honda, 1972; Hoffmann et al., 1995).

In recent years one-dimensional TiO_2 materials such as nanotubes and nanowires have attracted considerable attention due to their unique microstructure and promising functions (Morales & Liber, 1998). Many different methods and techniques have been developed to prepare 1-D TiO_2-related materials, such as by the assisted-template method (Bavykin et al., 2006; Costa & Prado, 2009), by the sol-gel process (Kasuga et al., 1998), by electrochemical anodic oxidation (Gong et al., 2001, Sun et al., 2011, Zwilling et al., 1999), and by hydrothermal treatment (Chen & Mao, 2007; Dang et al., 2013; Kasuga et al., 1999; Wang et al., 2002; Wang et al., 2007; Zhang et al., 2003).

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Among those mentioned above, the hydrothermal method for synthesis TiO_2NT has been reported to be the most powerful technique, due to simplicity of synthesis, cost effectiveness and an environmentally innocuous route (Morgado et al., 2007). Furthermore, the hydrothermal method can also be applied to prepare TiO_2 NW (Jitputti et al., 2008; Ou & Lo, 2007; Asiah, et al., 2013). One of the disadvantages of the hydrothermal method is the long reaction duration needed, especially for TiO_2 NW (Ou & Lo, 2007). Jitputi et al. (2008) reported that producing TiO_2 NW by using hydrothermal method needed 75 hours. Therefore, the improvement of the hydrothermal synthesis process by shortening the reaction time is very important.

Many researchers have prepared TiO_2 NT by the hydrothermal technique with the assistance of sonication (Wang et al., 2008; Viriya-Empikul et al., 2009; Zhu et al., 2001). Unfortunately, this improvement is complicated because the sonication treatment has been used *in situ* with the hydrothermal process (Wang et al., 2008). Furthermore, to the best of our knowledge, there are few reports on producing TiO_2NW by using a combination of the sonication and hydrothermal process and also the effect that morphologies of TiO_2 nanostructures have on hydrogen production.

In this study a simple and fast method of combined sonication and hydrothermal treatment was proposed for the production of TiO_2NT and TiO_2NW. The physical properties of the TiO_2 NT and TiO_2NW were studied in relation to their photocatalytic activity for H_2 evolution.

2. EXPERIMENTAL

2.1. Catalyst preparation

TiO_2 Degussa P25 was used to synthesize TiO_2 NT through the following procedures: 3 grams of TiO_2 powders were dispersed in 150 mL of 10M NaOH and ultrasonicated for 15 minutes prior to hydrothermal treatment at 130°C for 12 hours using an autoclave, while for TiO_2 NW was KOH (Potassium Hydroxide) and the temperature of hydrothermal treatment was 150 °C for 15 hours. For comparison purposes, a second procedure was used to synthesize TiO_2 NT and TiO_2 NW. This was performed by the hydrothermal method without sonication. After the hydrothermal treatment, the precipitates were rinsed well with distilled water, then further rinsed with HCl (Hydrogen Chloride) and distilled 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 a programmable furnace at 150^{o} C then calcined or treated at a very high temperature of 500°C.

2.2. Catalyst 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 the results were used to determine the phases present and their crystallite size. The crystallite size was calculated using a diffraction peak from Scherrer's formula (Weller, 1993). The transmission electron microscopy (TEM) analyses were conducted with a JEOL JEM-1400 electron microscope using a 120kV accelerating voltage. Morphological observations were performed on a JEOL JSM-6390A scanning electron microscope (SEM) equipped with an energy dispersive X-ray detector. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was carried out using a Shimadzu 2450. The band gap energy of the samples was calculated using Kubelka-Munk equation (Yoong et al., 2009). The specific surface area of the samples was measured by BET of N_2 adsorption in a Quantachrome Autosorb-6.

2.3. Photocatalytic activity test

The photocatalytic activity test was carried using a pyrex reactor equipped with six black light lamps (10W) as the photon source. The powder photocatalyst was suspended in a 10% methanol/water mixture at a concentration of 1 gL^{-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 (Ar) gas for 15 minutes to remove undesired gases such as oxygen and hydrogen. Hydrogen was analyzed by gas chromatography (GC) using a Shimadzu GC-8A equipped with a thermal conductivity detector, i.e. a stainless steel column packed with molecular sieves and an Ar carrier.

3. RESULTS AND DISCUSSION

Figure 1 shows SEM and TEM images of the prepared TiO_2NT and TiO_2NW. The sonication-hydrothermal treatment with NaOH (Sodium Hydroxide) as a solvent produced tube morphology (Figure 1(a)) and KOH (Potassium Hydroxide) as a solvent produced wire-like morphology (Figure 1(b)). TEM images show the difference between these catalysts, TiO_2 NT has hollow morphology (Figure 1 (c)) and TiO_2 NW has solid morphology (Figure 1 (d)).

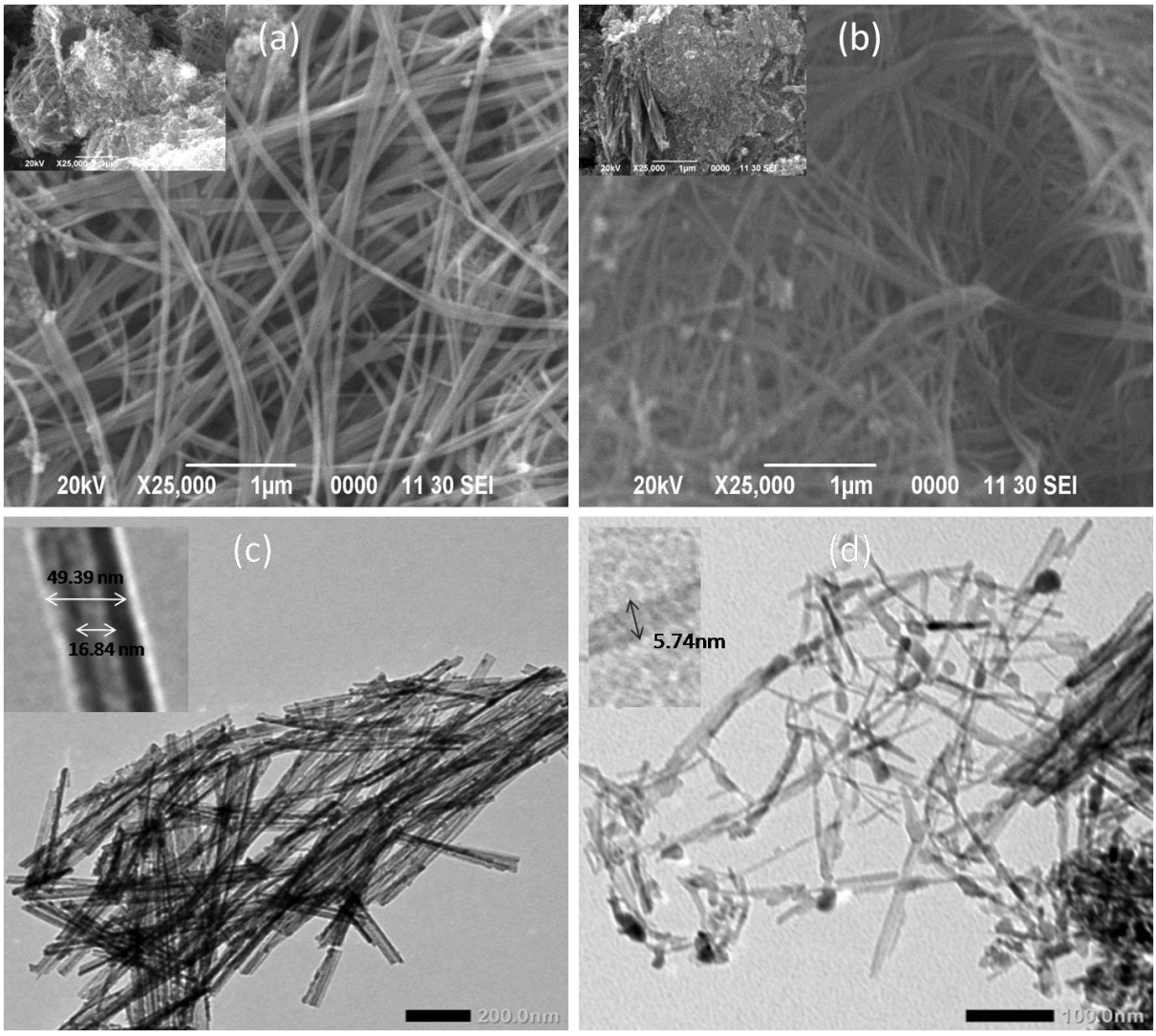

Figure 1 SEM images of: (a) TiO_2 NT; (b) TiO_2 NW; TEM images of: (c) TiO_2 NT; (d) TiO_2 NW. Inset in (a) and (b) shows prepared samples after hydrothermal treatment without sonication treatment. Inset in (c) and (d) shows diameter of TiO_2 NT and TiO_2 NW

The inner and outside diameter of TiO_2 NT was 16.84 nm and 49.39 nm respectively (the inset in Figure 1(c)), whereas the diameter of TiO_2 NW was 5.74 nm (the inset in Figure 1(d)). The difference in solvent that was used at hydrothermal treatment produced different morphology of catalysts. These results were confirmed by Yuan and Su who reported the difference morphology TiO_2 after hydrothermal process by using NaOH and KOH solvents (Yuan & Su, 2004). During the hydrothermal process, by using Ti-O-Ti, the bonds were broken to produce the sodium trititanates $Na_2Ti_3O_7$. The sodium trititanate sheets were then peeled off into nanosheets and subsequently folded into nanotubes. By using KOH as a solvent, some of Ti-O-Ti bonds of Titania crystals are broken and layered as octatitanates ($K_2Ti_8O_{17}$) that are formed on the titania surface along the (0 1 0) lattice plans of TiO_2. Their (2 0 0) plans may parallel to the (0 1 0) lattice plan of TiO_2. Further hydrothermal reactions cause the nanowires to grow out along the (0 1 0) direction (Yuan & Su, 2004).

The combination of sonication and hydrothermal processes can shorten the hydrothermal time to obtain nanotubes and nanowires. In this study by using this procedure could produce TiO_2 NT and TiO_2 NW in a short time. Without sonication treatment, the morphology of prepared samples after 12 hours of hydrothermal processes (NaOH as solvent) and 15 hours of hydrothermal (KOH as solvent) were not tube and wire shape, it can be seen as shown in the the inset in Figures 1(a) and 1(b). By using combination sonication hydrothermal treatment, nanotubes were obtained after 12-hour duration of hydrothermal processes, while otherwise nanowires were obtained after 15- hour duration. It is due to this sonication process that plays an important role in promoting intercalation or the insertion of the Na^+ (Sodium) or K^+ (Potassium) ions into lattices and breaking the Ti-O-Ti bonds without altering the morphology of TiO_2 Degussa P25. This result was much shorter than other researchers who obtained TiO_2 NT using the hydrothermal process without sonication. TiO_2 nanotubes usually obtained after 24-48 hours hydrothermal process at a temperature range of 110-150°C (Wang et al., 2008; Sreekantan & Wei, 2009). Other researchers reported TiO_2 NW was synthesized through a one-step hydrothermal process at 100-250°C for 24-72 hours (Yuan & Su, 2004). Viriya-empikul et al. (2009) synthesized TiO_2 NT and TiO_2 NW by using a combination of the sonication and hydrothermal process, but they still needed 3 days for the hydrothermal process at a temperature range between 90-180°C (Viriya-empikul et al., 2009).

Table 1 Summary of Crystallite size, BET surface and band gap energies of samples

Photocatalysts	BET Surface Area, m^2/g	Crystallite Size, nm	Band Gap Energy
TiO_2 P25	54	18	3.28
TiO_2 NT	123	13	3.29
TiO_2 NW	115	9	3.29

The results of this study indicated the largest specific surface area was obtained in the form of TiO_2 nanotubes. These can be observed from BET characterization results of these catalysts in Table 1. The specific areas of TiO_2 NT, TiO_2 NW and TiO_2 P25 were 123 m^2/g, 115 m^2/g and 54 m^2/g, respectively. The hollow shape on TiO_2 NT provided a high specific surface area that was greater than the wire shape on the TiO_2 NW and the nanoparticles on the TiO_2 P25. Although the TiO_2 NW did not have a hollow shape, its surface area was closer to that of the TiO_2 NT. This was due to the TiO_2 NW being formed in a porous condition. It can be shown in the TEM characterization, the tube wall of nanotubes (Figure 1(c)) were black, while the TiO_2 NW looked like a porous structure in diameter (Zhen, et al., 2013).

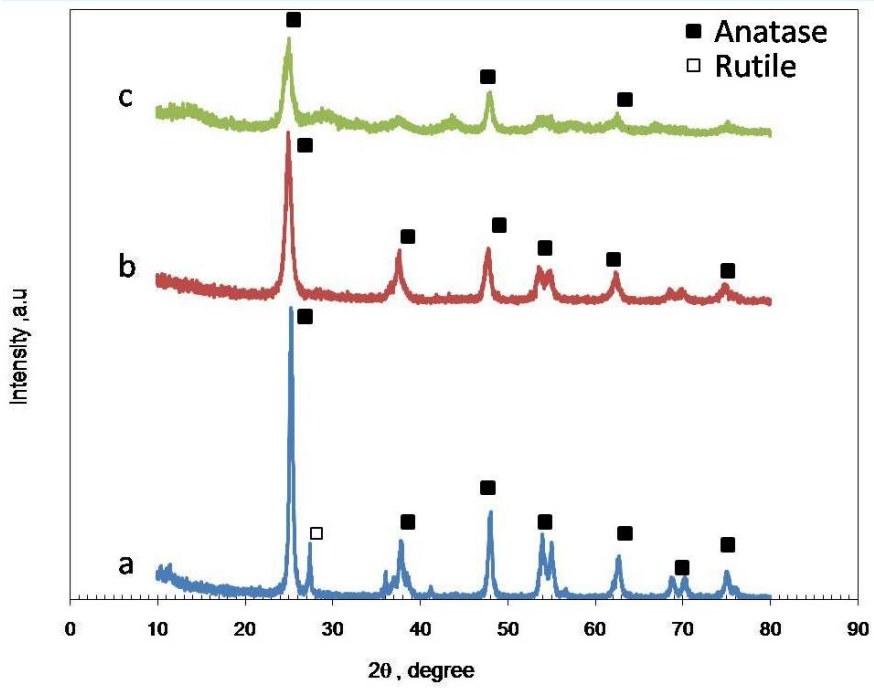

Figure 2 XRD patterns of: (a) TiO_2 P25; (b) TiO_2 NT; (c) TiO_2 NW

The phase composition, crystallite size and crystallinity of TiO_2 were reported to have a greater influence on the splitting of the water molecule. Therefore, XRD analyses of the samples were conducted. Figure 2 gives the XRD patterns of prepared sample (TiO_2 P25, TiO_2 NT and TiO_2 NW). The prepared catalysts annealed at temperatures in the region of 500°C in order to reveal the changes in phase structure and crystallite size caused by high temperature treatment. It was found that only the anatase phase was formed after calcination of the samples. A rutile peak at $2\theta = 28.8$ was shown only by TiO_2 Degussa P25. It indicates that both of TiO_2 NT and TiO_2 NW exhibited the completely crystalline structure of anatase TiO_2 but TiO_2 P25 consisted of mixed anatase and rutile.

The XRD pattern of the calcined TiO_2 NW is shown at Figure 2(c). It was found that the intensity of diffraction lines corresponded to the TiO_2 anatase. The diffraction peaks of anatase phase are not sharp as the TiO_2 NT anatase peaks, indicating the crystalinity of the anatase phase of TiO_2 NT is higher than TiO_2 NW. This is due to the tubular shape on the TiO_2 NT that afforded receiving heat more evenly during the calcination process rather than the wire shape on the TiO_2 NW. The crystalline sizes of all samples are summarized in Table 1. Table 1 shows that the highest crystallite size was TiO_2 P25. The decrease in crystallite size after treatment was due to the hydrothermal process during which the TiO_2 P25 was transformed into an amorphous sodium tritatane. The formation of the anatase phase from the amorphous sodium trititanate occurred during the calcination treatments. Furthermore, the morphology of the prepared catalyst might affect the growth rate of the crystal.

The UV-visible diffuse reflectance spectra for samples calcined at 500°C are shown in Figure 3. For comparison purposes, the spectrum of TiO_2 P25 is also displayed. Band gap energy of the samples has been calculated using Kubelka-Munk equation (Yoong et al., 2009). Energy band gap is obtained by extrapolating the plot of the absorption coefficient at the *y*-axis versus energy at the *x*-axis.

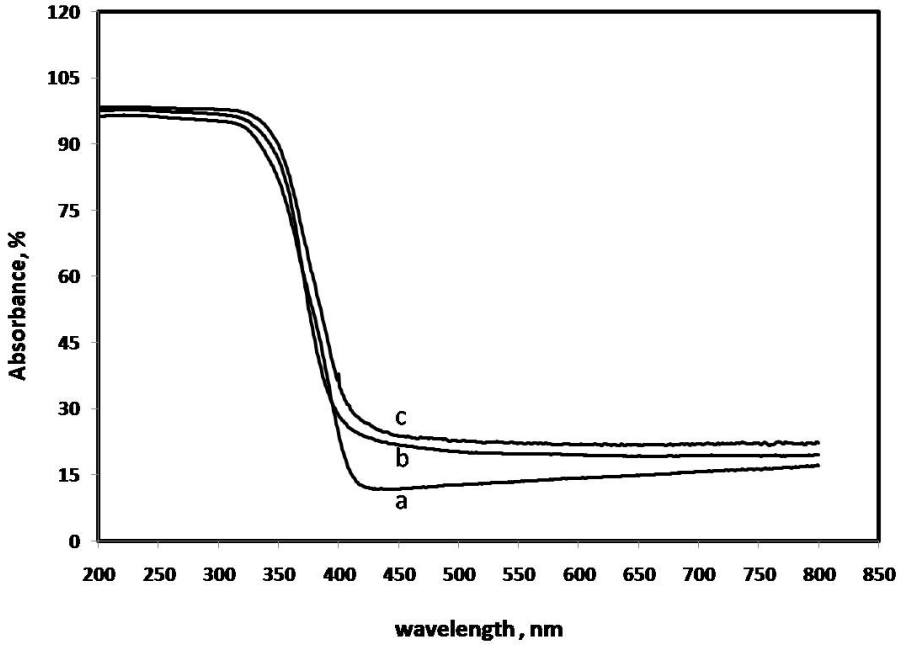

Figure 3 DRS characterization of: (a) TiO_2P25; (b) TiO_2NT; (c) TiO_2NW

The results are shown in Table 1. There was no significant effect of morphology differences on the energy band gap. This was due to the crystal size of TiO_2 NT and TiO_2 that were quite similar to those shown in Table 1. Moreover, the EDX results in Table 2 indicated there were no impurities which could influence the energy band gap level.

Table 2 The EDX analysis for TiO_2 nanotubes and TiO_2 nanowires

Samples	%Ti	%O	%Na	%K
TiO_2 nanotubes	45.32	47.87	3.7	-
TiO_2 nanowires	48.67	46.54	-	4.79

Figure 4 illustrates the comparison of photocatalytic activity between TiO_2 in the form of nanotubes, nanowires and nanoparticles. It was found that TiO_2 nanotubes exhibited the highest activity rates in comparison with other samples. The hydrogen production of TiO_2 NT was almost three times higher than the TiO_2 P25 nanoparticles and the TiO_2 NW were two times higher than the TiO_2 P25. Even though the crystalinity factors of TiO_2 NT and TiO_2 NW were lower than the TiO_2 P25, their respective activities were higher than TiO_2 P25. This was due to the specific surface area that also influenced the calibrated activity of the samples. The large specific area could accommodate more reactions and also could be attributed to reducing recombination (Su et al., 2006).

The difference of the specific surface area between TiO_2 NT and TiO_2 NW were not overly significant, but their activity in terms of hydrogen production was different. This is probably attributed to the tube shape on the TiO_2 NT that allows for more effective contact between active site, photons and water molecules, which then results in better photocatalytic activity. Sun *et al* (2006) reported that the tubular structure facilitated faster electron transfer due to reduced grain boundaries, which was expected to improve charge separation in photocatalytic reactions. This result indicated that morphology of TiO_2 plays an important role in generating hydrogen from water splitting.

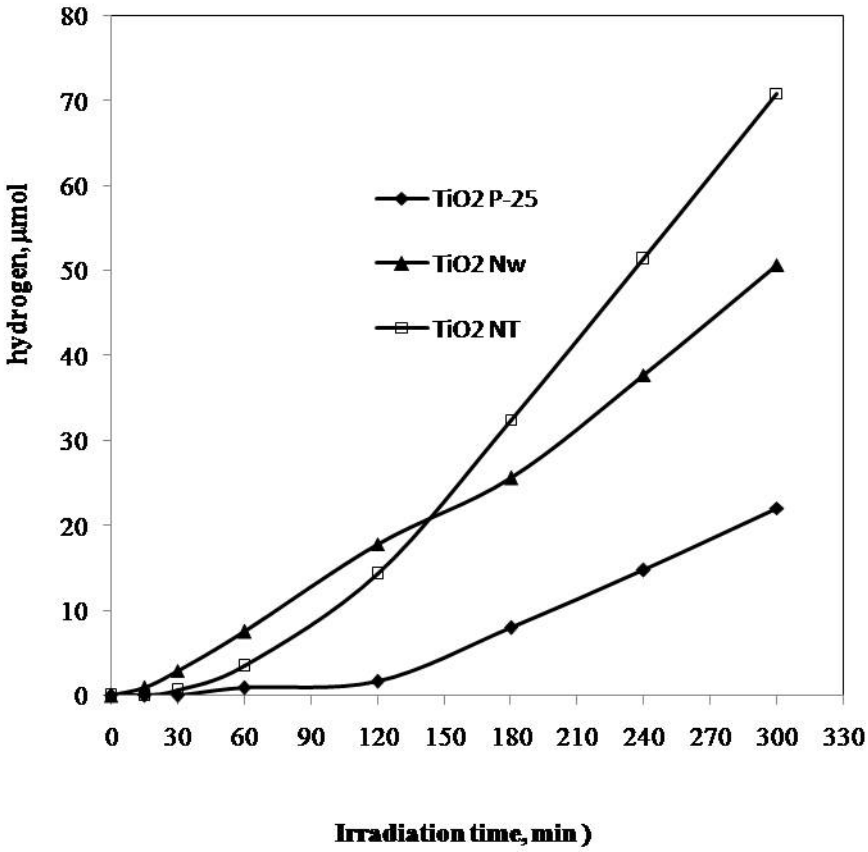

Figure 4 Hydrogen evolution over TiO_2 NT, TiO_2 NW and TiO_2 P25 nanoparticles (Vsolution = 500 ml, catalyst = 0.5 g, light source UV, Methanol concentration = 10%v)

This result was primarily attributed to the unique one-dimensional nanotubular structure. This one-dimensional tubular structure facilitated faster transfer of electrons due to reduced grain boundaries and this occurence was expected to improve charge separation in photocatalytic reactions.

4. CONCLUSION

TiO_2 Nanotubes and TiO_2 Nanowires with high crystallinity and large surface area were successfully produced by a simple combined sonication and hydrothermal method. A shorter duration of TiO_2 nanotubes and TiO_2 nanowires formations was achieved through this method with a 12-hour duration for TiO_2 NT and 15-hour duration for TiO_2 NW. The morphology of catalysts played a significant role in the specific surface area and their crystallinity. It also possibly affected the photon and charge transfer. Photocatalytic hydrogen production using TiO_2 nanotubes achieved a better performance level than TiO_2 nanowires.

5. ACKNOWLEDGEMENT

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