

Optimization of TiO₂ nanowires synthesis using hydrothermal method for hydrogen production

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ABSTRACT

Effects of sonication and hydrothermal treatment time on TiO₂ nanowires (TNWs) formation have been investigated. Sonication of TiO₂ P25 sol was performed using sonicator water bath Cole for 0.5, 1 and 2 hours followed by hydrothermal treatment. The hydrothermal treatment was carried out in a teflon lined stainless steel autoclave for 12, 15 and 24 hours. The samples were characterized by means of Scanning Electron Microscope (SEM), X-ray powder diffractometer (XRD), UV-vis diffuse and reflectance spectroscopy (UV-vis DRS). The specific surface area of each sample was determined by the BET nitrogen gas adsorption/desorption method. The photocatalytic activity of TNWs was evaluated with photocatalytic H₂ evolution from aqueous methanol solution. The result showed that the best TNWs was obtained at 1 hr sonication followed by hydrothermal process for 12 hours. By using this catalyst hydrogen production reached 82 μmol after 5h while using TiO₂ P25 could only reach 23 μmol.

Keywords: TiO₂; nanowires; photocatalytic; hydrogen; Sonication; Hydrothermal

INTRODUCTION

Hydrogen is well known as one of the alternative clean energy. However, on the earth hydrogen molecules do not form naturally but must be produced from other materials containing hydrogen [1,2]. Hydrogen production from photocatalytic water splitting provides a potential opportunity to obtain clean, renewable and storable energy from abundant water using solar energy. Titanium dioxide (TiO₂) is regarded as a material with excellent photocatalytic activity and has been investigated for water splitting [3-5], photocatalytic activity [6,7] and photovoltaics [8,9]. TiO₂ also has high stability, biological and chemical inertness, strong oxidizing power, non-toxicity and long term stability against photo and chemical corrosion [10-14].

In the last years, novel nanostructures such as nanowires [15], nanotubes [4,16-18], and nanorods [19-21] derived from TiO₂ have been employed in water splitting [22]. These structures have high specific surface area, ion-exchange and photocatalytic abilities [23,24]. In the last year, new routes to synthesize TiO₂ with 1D structure have been continuously proposed, such as thermal treatment [25], the assisted-template method [26,27], the sol-gel process [28], electrochemical anodic oxidation [4,29-32] and hydrothermal treatment [14-16,24,33,34]. Among these approaches, the hydrothermal treatment is regarded as one of the most efficient methods to synthesize 1d TiO₂ because it can dramatically decrease the required processing temperature from 850°C to 180°C

under a more alkali environment [6]. Beside that this method has high reactivity, low energy requirement, relatively non-polluting set-up and simple control of the aqueous solution [22]. Previous researchers demonstrated that the hydrothermal method can also be applied to prepare TiO₂ nanowires but this method required a long reaction time [15,23]. Jitputi et al reported for producing TiO₂ NW by using hydrothermal method needed 75 h [23]. Therefore, the improvement of the hydrothermal synthesis process by shortening the reaction time is very important. In this study a simple and fast method of combined sonication and hydrothermal treatment is proposed for the production of TiO₂ nanowires. The objective of this study is to investigate the effect of sonication process on hydrothermal treatment for the production of TiO₂ nanowires, such as morphological structures, photoelectrochemical properties and photocatalytic activity as evidenced by hydrogen production.

METHODS AND MATERIAL

Synthesis of TiO₂ nanowires

In a typical synthesis, 3 grams of TiO₂ Degussa P25 were dispersed in 150 mL of 10M KOH and ultra-sonicated for 0.5 h, 1 h and 2 h followed hydrothermal process. The hydrothermal process was carried out at temperature of 150°C with variation of reaction time for 12 h, 15 h and 24 h. After the hydrothermal treatment, the prepared samples were rinsed well with distilled water then further rinsed with Hydrogen Chloride and distilled water repeatedly until the pH value of the washing solution was lower than 7. The TiO₂ nanowires were obtained through centrifugation and further dried in a programmable furnace at 150°C then calcined at 500°C.

Characterization of TiO₂ nanowires

The crystal structures of as-synthesized TiO₂ nanowires were determined using a Philips PW 1710 XRD diffractometer with Cu K α radiation ($\lambda = 1.5406\text{\AA}$ at a scan rate of 0.025°s⁻¹). The crystallite size was calculated using a diffraction peak from Scherrer's formula [35]. Morphological observations were performed on a JEOL JSM-6390A scanning electron microscope (SEM) equipped with an energy dispersive X-ray detector. The transmission electron microscopy (TEM) analyses were conducted with a JEOL JEM-1400 electron microscope using a 120kV accelerating voltage. The band gap energy of the prepared samples was calculated using Kubelka-Munk equation [34]. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was carried out using a Shimadzu 2450. The specific surface area of the catalysts was measured by BET of N₂ adsorption in a Quantachrome Autosorb-6.

Photocatalytic activity evaluation of TiO₂ nanowires

The photocatalytic activity test was performed using a pyrex reactor equipped with six black light lamps (10W, 352 nm) as the photon source. The powder TiO₂ nanowires was suspended in a 10% methanol/water mixture at a concentration of 1g/L. 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 gas for 15 minutes to remove undesired gases. Hydrogen was analyzed by gas chromatography (GC) using a Shimadzu steel column packed with molecular sieves and an Argon carrier.

RESULTS AND DISCUSSION

The effect of sonication time on the synthesis of TiO₂ nanowires

In order to investigate the effect of sonication on the formation of TiO₂ nanowires, samples were prepared using different treatments: 1 h sonication process followed 15 h hydrothermal treatment (TiO₂Nw-1s-15h) and 15 h hydrothermal treatment without sonication (TiO₂Nw-0s-15h).

Figure 1(b₁) and (b₂) shows hydrothermal process for 15 hours without sonication has produced nanowires morphology but not uniform. With the addition of sonication process for 1 hour before hydrothermal treatment for 15 hours produced TiO₂ nanowires uniformly, it can be seen in Figure 1 (c₁ and c₂). The results indicated that the time of formation TiO₂ nanowires could be shortened by using combination of sonication and the hydrothermal process. It due to with sonication treatment the reaction of KOH on the surface of de-agglomerated TiO₂ particles was much faster and uniform [36]. The Sonication process was promoting the intercalation of K⁺ into titania lattices and breaking the Ti-O-Ti bonds without altering the morphology of TiO₂ Degussa P25. As a result, formation trititanate sheets in hydrothermal treatment become faster than hydrothermal without sonication.

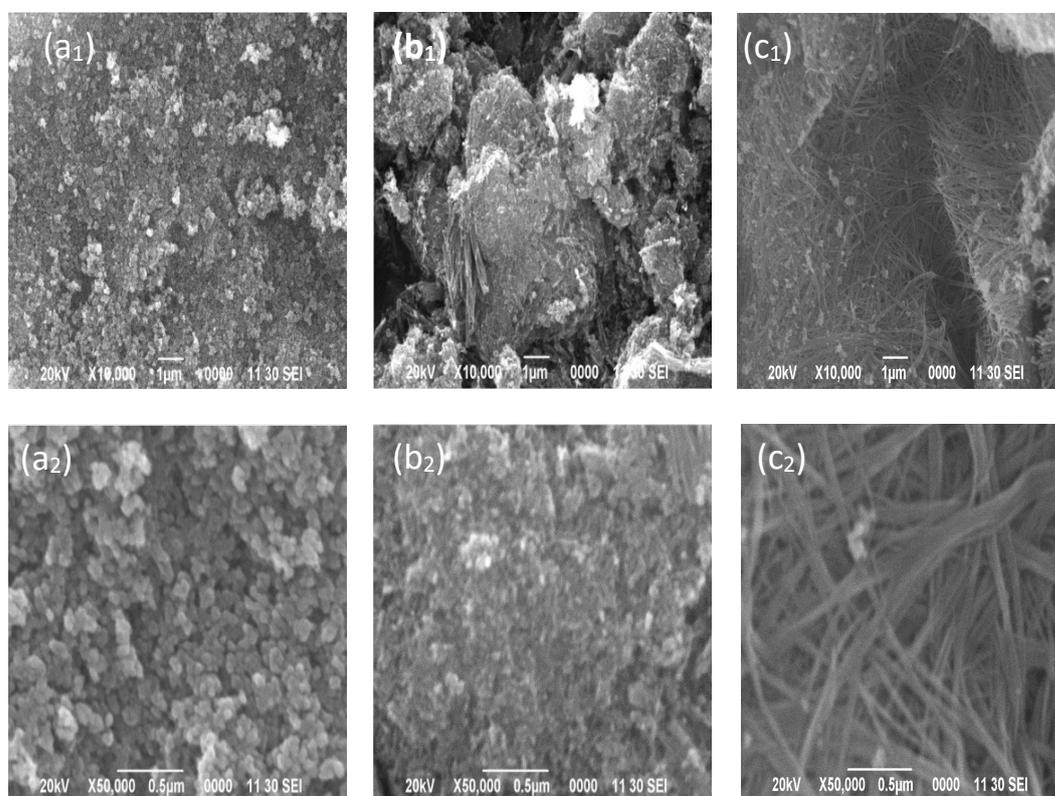


Figure 1. Scanning electron micrographs of (a) TiO₂ P25 and (b) TiO₂NWs-0s-15h (c) TiO₂NWs-1s-15h. a₁, b₁, c₁ are images at magnification 10,000; a₂, b₂, c₂ are at 50,000.

The SEM images of the samples obtained using sonication times of 0.5 (TiO₂ NWs 0.5s-15h), 1h (TiO₂ NWs 1s-15h) and 2 h (TiO₂ NWs 2s-15h) followed hydrothermal treatment for 15 h are shown at Figure 2. It shows the time of sonication greatly influenced on change in shape and morphology samples. Figure 2(a) shows the SEM image of sample subjected to sonication time of 0.5 h. It indicated that morphology of nanowires was formed but not yet uniform. It can be seen clearly on image which higher magnification at Figure 2(a₂). Figure 2(b) shows the samples were found to be completely transformed into nanowires shapes after sonication 1 h followed by hydrothermal. However, the longer sonication time before hydrothermal treatment was undesirable for the formation of TiO₂ nanowires. The samples obtained sonication for 2h were wider and had morphology similar to nanoribbons.

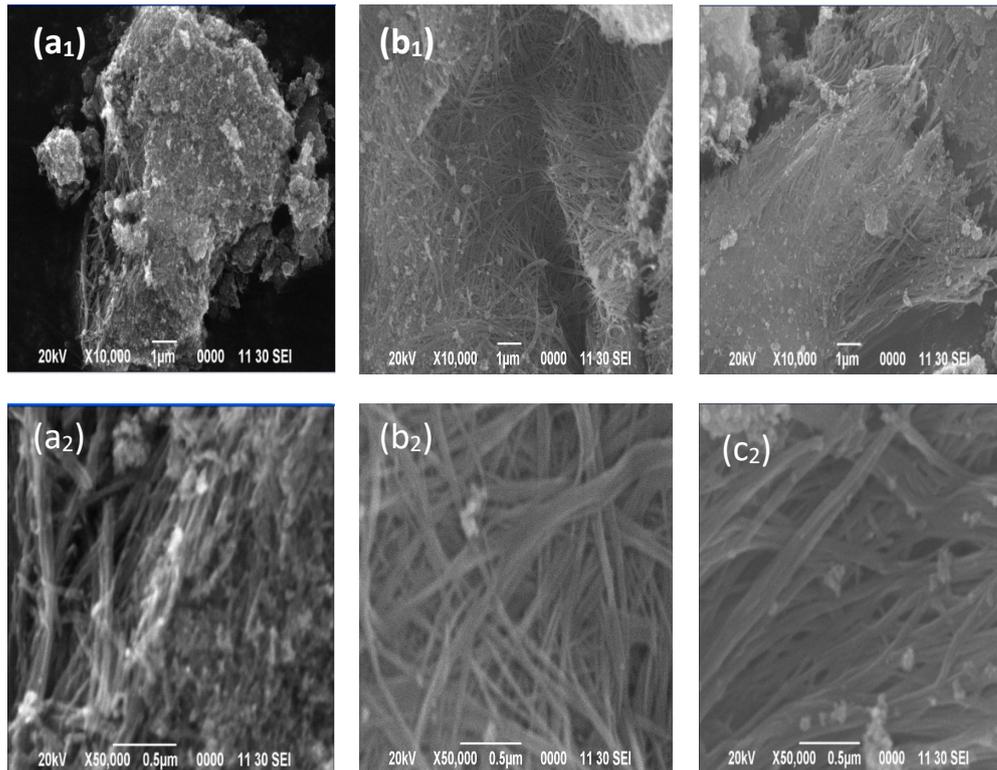


Figure 2. SEM of samples prepared using sonication and hydrothermal treatment, sonication for: (a) TiO₂ NWs 0.5s-15h; (b) 1 h; (c) 2h. a₁, b₁, c₁ are images at magnification 10,000; a₂, b₂, c₂ are at 50,000.

Effect of hydrothermal treatment on TiO₂ Nanowires formation

The reaction time of hydrothermal treatment plays an important role in the formation of TiO₂ nanowires. In order to investigate this, the TiO₂ nanowires were prepared with a sonication process for 1 h and continued with hydrothermal treatment for 12 hours, 15 hours and 24 hours. The SEM images of the samples are shown in Figure 3.

Figure 3(a) shows that TiO₂ nanowires had formed in small amounts after hydrothermal treatment for 12 hours. It was very different with the samples that were produced through hydrothermal treatment for 15 hours, as shown in Figure 3(b). In this product, the morphology of TiO₂ nanowires was evenly formed and had a good shape. However, the longer duration of hydrothermal treatment with sonication for 1 hour did not provide a better form of TiO₂ nanowires. It can be seen clearly in Figure 3(c) that hydrothermal treatment for 24 hours generated TiO₂ nanowires which were wider and had a morphology similar to nanoribbons.

The formation of TiO₂ nanowires occurred during the hydrothermal process. Due to the reaction between TiO₂-P25 with KOH as solvent, some of the Ti-O-Ti bonds of titania crystals are broken to produce Ti-O-K and Ti-OH and layered as octatitanates (K₂Ti₈O₁₇) that are formed on the titania surface along the (0 1 0) lattice planes of TiO₂. Their (2 0 0) planes may be parallel to the (0 1 0) lattice plane of TiO₂. Further hydrothermal reactions cause the nanowires to grow out along the (0 1 0) direction [36]. The growth of TiO₂ nanowires caused by high operating temperature and pressure in the autoclave during the hydrothermal process ($T > 130^{\circ}\text{C}$), it caused no tendency to form a coil-like nanotube morphology. Further growth of nanowires increased during the hydrothermal time and it caused TiO₂ nanowires to grow along the direction of growing photocatalyst [38].

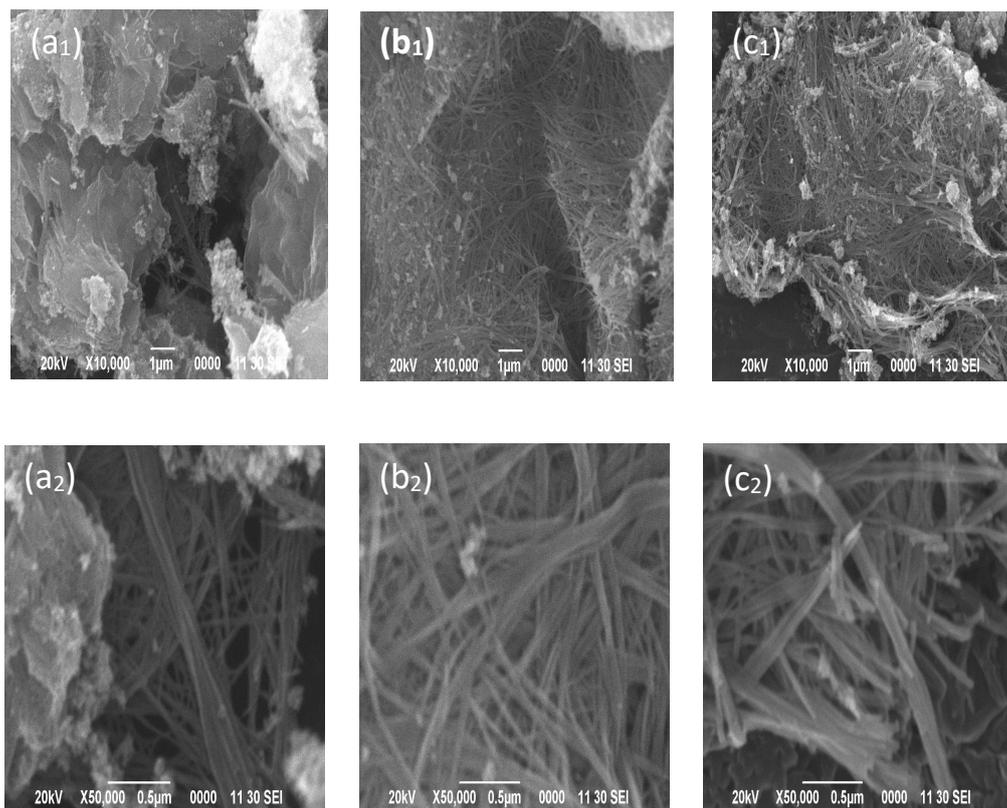


Figure 3. Scanning electron micrographs of sonication 1h followed hydrothermal treatment; (a) 12 h; (b) 15 h; (c) 24 h. a₁, b₁, c₁ are images at magnification 10,000; a₂, b₂, c₂ are at 50,000.

Figure 4 shows the Transmission electron Microscope of TiO₂ nanowires from 1 h sonication followed 15 hydrothermal. It shows hydrothermal with KOH as a solvent produced wire-like morphology with a porous structure. The diameter of TiO₂ nanowires was 5,7 nm. Yuan & Su (2004) reported that the morphology of nanowires usually has a diameter in the range of 5-10 nm [38].

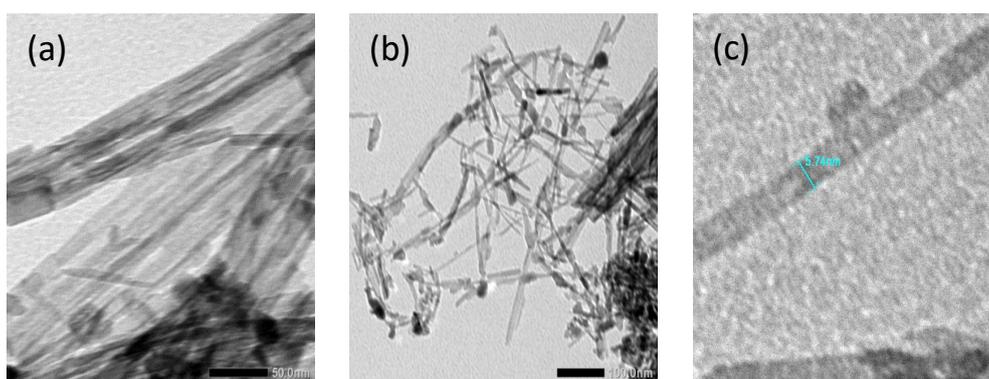


Figure 4. The transmission electron microscope of TiO₂ nanowires (a) image at magnification 50nm, (b) image at magnification 100 nm dan (c) diameter of TiO₂ NWs

The morphology of the catalyst caused the significant difference of surface area. The surface area of TiO₂ nanowires and nanopartikel were 115,74 m²/g and 32.77 m²/g respectively. The large surface area of TiO₂ nanowires indicates this product had a porous structure. The surface area of TiO₂ NWs was higher than TiO₂ NW which obtained by other researcher. Jitputi et al (2008)

obtained the surface area of TiO₂ NW was 58,20 m²/g after hydrothermal treatment for 72 hours [15].

The X-Ray Diffraction of TiO₂ nanowires

The phase composition, crystallite size and crystallinity of TiO₂ were reported to have a great influence on photocatalytic activity such as water splitting.

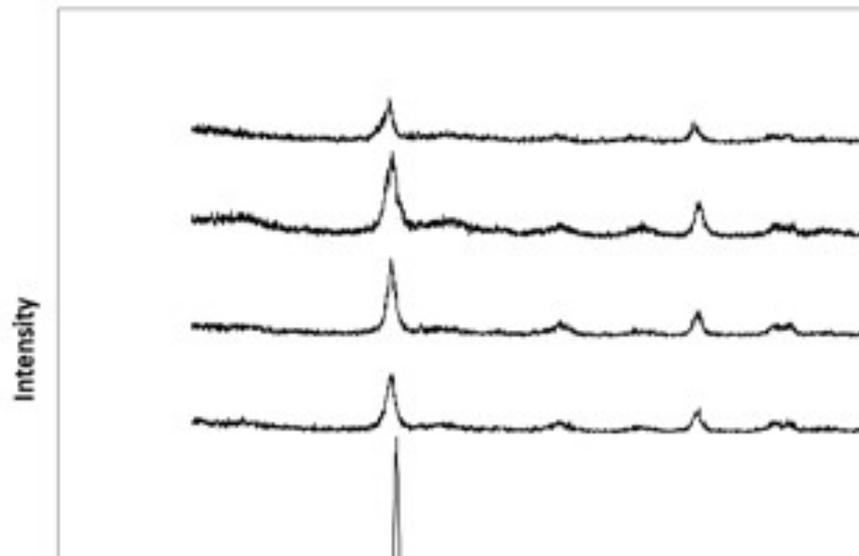


Figure 5. XRD patterns of (a) TiO₂ P25; (b) TiO₂ NWS-0s-12h; (c) TiO₂ NWS-0.5s-12h; (d)TiO₂ NWS-1s-12h; (e) TiO₂ NWS-2s-12h

Therefore, the XRD analysis of TiO₂ NWs was conducted in this research. Figure 5 shows the XRD patterns of TiO₂ P25 and TiO₂ NWs prepared with different sonication times followed hydrothermal treatment 12 h. The XRD patterns for TiO₂ NWs was obtained from combination 1 h sonication followed by hydrothermal for various time can be seen at Figure 6.



Figure 6. XRD patterns of (a) TiO₂ P25; TiO₂ NWs 1h sonication followed hydrothermal for (b) TiO₂ NWS-1s-12h; (c) TiO₂ NWS-1s-15 h; (d) TiO₂ NWS-1s-24h

All products of TiO₂ nanowires, both Figure 5 and Figure 6 had completely crystalline structure of anatase TiO₂ but the TiO₂ Degussa P25 nanoparticles consisted of mixed anatase and rutile. This was because of at hydrothermal process, TiO₂ P25, which had anatase and rutile phase, transformed into sodium trititanate as amorphous, only anatase phase was formed after calcination at 500°C [24]. The rutile phase was formed at calcination temperature above 700°C. Similar results have been reported by many researchers, that only anatase phase was formed after calcination of hydrogen titanate nanotubes at 500°C [16,24,40,43].

Table 1. The crystalline size of TiO₂ P25 and TiO₂ nanowires at various time of sonication followed by hydrothermal treatment for 12 h

Samples	Crystalline size (nm)
TiO ₂ P-25	18
TiO ₂ NWs-0s-12h	10.16
TiO ₂ NWs-0.5s-12h	11.11
TiO ₂ NWs-1s-12h	15.09
TiO ₂ NWs-2s-12h	13.92

The Crystalline sizes of TiO₂ NWs at various time sonication and hydrothermal are summarized in Table 1 and Table 3 respectively. Both of Tables show that all crystalline sizes of product were smaller than TiO₂ P25. It due to during hydrothermal process TiO₂ P25 transformed into amorphous sodium trititanate.

Table 2. The crystalline size of TiO₂ nanowires prepared using combination 1 h sonication followed hydrothermal treatment at various times

Samples	Crystalline size (nm)
TiO ₂ P-25	18
TiO ₂ NWs-1s-12h	15.09
TiO ₂ NWs-1s-15h	8.92
TiO ₂ NWs-1s-24h	12.72

The formation of anatase phase from amorphous sodium trititanate was occurred during calcinations treatment. Table 1 and Table 2 show that both of sonication time and hydrothermal time did not affect significantly at crystallite size. It also could be seen both Figure 5 and Figure 6. It indicates the formation of crystalline was strongly affected by temperature. The higher temperature of calcinations obtained higher crystallite size, but the temperature above 500°C could destroy the nanotubes shape and beside that the phase of crystal changed to be rutile [42].

The Diffuse Reflectance Spectroscopy of TiO₂ nanowires.

The Uv-visible diffuse reflectance spectra for TiO₂ P25 and TiO₂NWs-1s-1h are displayed in Figure 7. Band gap energy of the samples have been calculated using Kubelka-Munk equation [36]. Band gap energy is obtained by extrapolating the plot of the absorption coefficient at the y-axis versus energy at the x-axis.

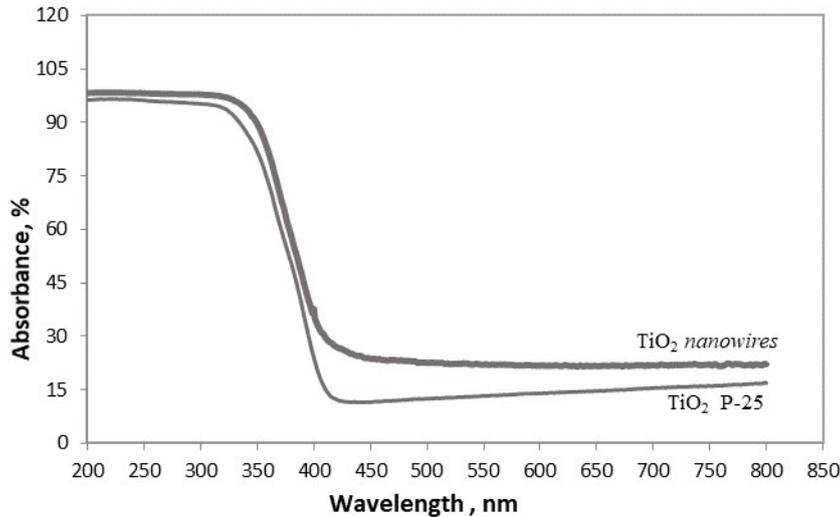


Figure 7. The Diffuse Reflectance Spectroscopy of TiO₂ nanowires and TiO₂ P25

Figure 7 shows that spectra TiO₂ P25 and TiO₂ Nanowires are almost same. It showed that both of TiO₂ nanowires and TiO₂ P25 had strong UV absorption in the range 300 nm and 430 nm. The band gap energy of these samples can be seen at Table 3.

Table 3. Band gap energy of TiO₂ P25 and TiO₂ NWS-1s-12h

Samples	Band Gap Energy, eV
TiO ₂ P25	3.05
TiO ₂ NWS-1s-12h	2.90

As shown at Table 3, the bandgap for TiO₂ P25 was approximately 3.05 e, it was corresponded to the absorption of wavelength < 400 nm. The bandgap of the TiO₂ nanowires was almost same with bandgap of TiO₂ P25. It due to all prepared samples were crystalline TiO₂ and the crystallite sizes were almost same.

Effect of hydrothermal time on the TiO₂ Nanowires activity

The activity of TiO₂ nanowires was evaluated by photocatalytic water splitting from aqueous methanol solution. Methanol was used as the sacrificial agent because of its ability to remove the photogenerated holes, thereby it reduces the mutual electron-hole recombination [42]. Photocatalytic water splitting by using TiO₂ nanowires were obtained by combination 1h sonication and hydrothermal at various time are shown at Figure. 8. For comparison we also observed the activity of TiO₂ P25 for hydrogen production. Figure 8 shows all prepared samples had higher activity than TiO₂ P25, however the production of hydrogen by TiO₂ NWS 24 h was almost same as TiO₂ P25. It indicated that morphology influenced the activity of sample for producing hydrogen. It was probably due to nanowires morphology had a higher surface area than the TiO₂ P25 nanoparticles. This was due to the specific surface area that also influenced the activity of the samples. The large specific area could accommodate more reactions and also could be attributed to reducing recombination. Furthermore, it might have attributed to the wires shape on the TiO₂ NT that allows for more effective contact between active site, photons and water molecules, which then results in better photocatalytic activity.

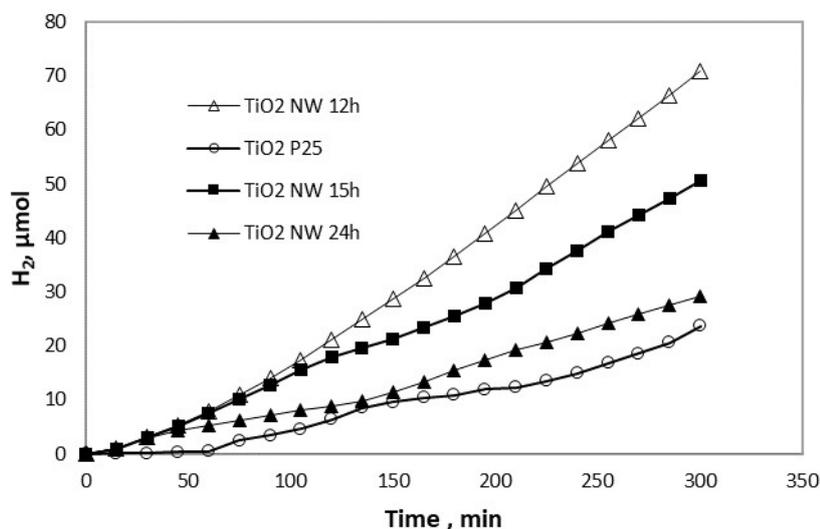


Figure 8. Hydrogen evolution over TiO₂ P25 and TiO₂ NWs at various hydrothermal treatment (V_{solution} = 500 ml, catalyst = 0.5 g, light source UV, Methanol concentration = 10%v).

Figure 8 shows TiO₂ NWs was prepared using 1 h sonication followed 12 h hydrothermal exhibited higher than other TiO₂ nanowires. Hydrogen was obtained using this catalyst after 5 h was 82 μmol. It was about two times higher than TiO₂ NWs from hydrothermal for 24h. Even though TiO₂ NWs-1s-15h has the best morphology of nanowires, the crystallinity of TiO₂NWs-1s-15h is lower than that of TiO₂ NWs-1s-12h. It can be seen at Table 1 and Table 2. It can be seen clearly that hydrogen production was affected to morphology and also crystallinity of catalyst.

CONCLUSIONS

TiO₂ Nanowires with high crystallinity and large surface area has been successfully synthesized with faster reaction time by combination sonication and hydrothermal treatment. The morphology and crystallinity of catalysts played significant role in the specific surface area and their activity for producing hydrogen. The TiO₂ NWs was synthesized by 1h sonication followed hydrothermal treatment for 12 h produced hydrogen two fold than that of TiO₂ nanoparticles.

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