Triethanolamine – Solution for Rapid Hydrothermal Synthesis of Titanate Nanotubes

(Trietanolamina – Penyelesaian untuk Sintesis Tiub Nano Titanat melalui Hidroterma Pantas)

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ABSTRACT

Titanate nanotubes were prepared by a rapid hydrothermal method in the presence of triethanolamine (TEA) using TiO_2 nanoparticles as a precursor. The addition of TEA significantly reduced the formation time of the titanate nanotubes from 24 to 6 h. The crystalline structure of the titanate nanotubes was revealed to be $H_2Ti_2O_5$ through the X-ray diffraction (XRD) measurement. The morphology of the titanate nanotubes was confirmed using transmission electron microscopy (TEM) while the surface area was characterized using Brunauer-Emmett-Teller (BET) surface area analysis. The titanate nanotubes produced were several hundred nanometers in length and had an average outer diameter of ~ 11.5 nm, inner diameter of ~5.0 nm, interlayer spacing of 0.93 nm and surface area of >250 m^2/g. The photocatalytic activity of the titanate nanotubes was studied using methylene blue as a model dye; the titanate nanotubes showed better photocatalytic performance as compared to TiO_2 nanoparticles.

Keywords: Hydrothermal; photocatalyst; titanate nanotubes

ABSTRAK

Tiub nano titanat telah disediakan melalui kaedah hidroterma pantas dengan kehadiran trietanolamina (TEA) menggunakan partikel TiO_2 sebagai bahan pemula. Penambahan TEA telah mengurangkan masa pembentukan tiub nano titanat secara berkesan dari 24 jam ke 6 jam. Struktur hablur tiub nano titanat ialah $H_2Ti_2O_5$ berdasarkan pengukuran difraksi sinar-X (XRD). Morfologi tiub nano titanat telah dikenal pasti menggunakan mikroskop elektron transmisi (TEM) sementara luas permukaannya diperoleh daripada analisis luas permukaan Brunauer-Emmett-Teller (BET). Tiub nano titanat yang dihasilkan adalah beberapa ratus nanometer panjang serta mempunyai purata diameter luar ~ 11.5 nm, diameter dalam ~5.0 nm, ruang antara lapisan 0.93 nm dan luas permukaan >250 m^2/g. Aktiviti fotokatalitik tiub nano titanat telah dikaji menggunakan metilena biru sebagai pewarna modal; tiub nano titanat menunjukkan kuasa fotokalitik yang lebih baik berbanding dengan nanopartikel TiO_2.

Kata kunci: Fotokatalis; hidroterma; tiub nano titanat

INTRODUCTION

Amongst the one-dimensional structures, nanotubes are a novel and intensively studied class of structurally organized nanomaterial since the discovery of carbon nanotubes by Iijima in 1991. Recently, a number of nanotubes, made of materials other than carbon, have attracted the attention of many inorganic chemists. These reported nanotubes were boron nitride (BN_2) (Barnard et al. 2007), tungstic sulfide (WS_2) (Sun et al. 2009), molybdenum sulfide (MoS_2) (Lavayen et al. 2007), titanium oxide (TiO_2) (Kasuga et al. 1998), ferum oxide (Fe_2O_3) (Song et al. 2010) and vanadium oxide (V_2O_5) (Huang et al. 2006). Even though these inorganic nanotubes have many interesting properties, they have not been intensively studied compared with carbon nanotubes.

Titanate nanotubes with large specific surface area, typically in the range of 200 – 350 m^2/g, have been discovered by Kasuga et al. in 1998 based on the hydrothermal re-crystallization of TiO_2 particles in concentrated alkaline solution (~ 10M NaOH). Titanate nanotubes have gained promising prospects due to their fascinating microstructures and excellent properties. Titanate nanotubes have extensive potential applications in areas such as dye-sensitized solar cell (Gratzel 2003; Li et al. 2006; Mor et al. 2006), gas sensing (Hong et al. 2009; Mardare et al. 2007), photocatalyst (Peng et al. 2010; Song et al. 2005; Xiong et al. 2010), self-cleaning coating (Yamashita et al. 2003), electroluminescent hybrid device (Bai et al. 2002), water splitting catalysts for hydrogen generation (Jin et al. 2007) and energy storage technologies (Deb 2005). The formation mechanism and crystalline structures of the titanate nanotubes are extensively debated even after numerous researches. Kasuga, the first person who discovered TiO_2 nanotubes, concluded that the formation of nanotubes happened during the washing process using HCl and the resultant material was TiO_2 which retained the anatase phase. Several composition and structures have been proposed which include trititanate ($H_2Ti_3O_7$), tetratitanate ($H_2Ti_4O_9$), $H_2Ti_2O_5.H_2O$, $Na_xH_{2-x}Ti_3O_7$ and $H_{0.7}Ti_{1.825\ 0.175}O_{4.0}.H_2O$ (=vacancy) (Song et al. 2005).

Titanate nanotubes are usually synthesized by three methods, namely electrochemical approach (Chen et al. 2007), templated synthesis (Eswaramoorthi & Hwang 2007) and hydrothermal synthesis (Pavasupree et al. 2006; Seo et al. 2008). The hydrothermal method is the most commonly used method to produce titanate nanotubes. In this method, TiO_2 particles (anatase, rutile or mixtures) are used as starting materials to form nanotubes. One of the major advantages of the hydrothermal method is the high conversion/yield of titanate nanotubes, which is more than 99%. However, the disadvantage of this method is the long reaction time which usually ranged from a day to several days.

In this paper, we report a rapid formation of titanate nanotubes using TiO_2 nanopowder as a precursor in the presence of TEA using conventional hydrothermal method at reaction temperature of 180ºC. The presence of TEA was crucial to the formation of titanate nanotubes at this temperature and it was able to reduce the formation time of titanate nanotubes to only 6 h. The formation mechanism of the titanate nanotubes is postulated in this paper based on the typical characterizations. The photocatalytic activity of the titanate nanotubes has also been investigated.

EXPERIMENTAL DETAILS

TiO_2 nanopowder (99.9%), sodium hydroxide (NaOH), triethanolamine (TEA) and hydrocloric acid (HCl) were purchased from Sigma-Aldrich. Methylene blue was obtained from BDH. All the chemicals were used as received without further purification. Deionized water with resistivity of 18.2 MΩ was used throughout the sample preparation.

Titanate nanotubes were produced by a modified hydrothermal synthesis method using commercial TiO_2 nanoparticles powder as a starting material. The conversion of nanoparticles to nanotubes was achieved by treating the nanoparticles powder with 10 M of NaOH solution in a Teflon-lined stainless steel autoclave in addition of TEA. In a typical synthesis setting, 10 M of NaOH aqueous solution was mixed with 10 wt. % of TEA under a constant magnetic stirring. Exactly 2 g of TiO_2 nanopowder was added into the above mixture and stirred for 30 min before being transferred to a Teflon-lined stainless steel autoclave. The autoclave containing the mixture was then heated to 180°C in an oven for a specific period of reaction time. The reaction time for the hydrothermal synthesis varied from 1, 6, 12 and 24 h. The obtained white precipitates were filtered and washed three times with 0.1 M of HCl solution and deionized water. The samples were dried at 60°C in an oven for 3 h and later calcined at 350°C in a furnace for 3 h to remove the residual TEA.

A transmission electron microscope, TEM (Philips CM12 operated at 100 kV) was used to confirm the size and morphology of the titanate nanotubes. A drop of the titanate nanotubes solution was cast onto a 300 mesh carbon coated copper grid using a micropipette and was allowed to dry in an oven at 50ºC for 1 day. The measurement of the

average diameter of the nanoparticles was carried out using I-Solution-DT (version 6.5, IMT) image analysis software with at least 200 nanotubes being chosen as the sampling data. The nanotubes crystalline phase was determined by an X-ray diffraction (XRD) using a Philip diffractometer, employing a scanning rate of 0.02º s^{-1} in a 2θ range from 5 to 60º with CuK_{α} radiation ($\lambda = 1.5418$ Å). Qualitative analysis was performed with the PANanalytical Xpert HighScore using the JCPDS PDF-2 database (Brunauer et al. 1938). The ultraviolet-visible spectroscopy (UV-Vis) measurement was carried out at room temperature using a Perkin Elmer Lamda-35 spectrophotometer in the range of 350 to 800 nm. The samples' surface area was determined based on the N_2 adsorption/desorption isotherm pattern using a Micromeritics ASAP-2010. The Brunauer-Emmett-Teller (BET) method was used for surface area calculation. The photocatalytic activity of the titanate nanotubes was determined by the degradation of methylene blue (MB) under UV irradiation (365 nm, 8W). Methylene blue was used as a model dye with a concentration of 10 mg/L. Ten milligrams of titanate nanotubes sample synthesized at various reaction times of 1, 6, 12 and 24 h were added into 100 mL of methylene blue solution and exposed to UV irradiation in a photoreactor for a period of time ranging from 15 – 60 min. All the titanate nanotubes, mixed with MB, were magnetically stirred in the dark for 1 h to achieve adsorption-desorption equilibrium before they were irradiate under the UV light. The first sample was taken out at the end of the dark adsorption period, just before the light was turned on, in order to determine the MB concentration in the solution, which was considered as the initial concentration. Then, 3 mL of the solution was withdrawn, centrifuged at 5000 rpm for 2 min and the supernatant was immediately analyzed with a UV-Vis spectroscopy at an absorbance of 665 nm. Commercial titanium dioxide nanopowder was used as a comparison to the as-synthesized nanotubes. A methylene blue solution was irradiated without the addition of any photocatalyst, as a control.

RESULTS AND DISCUSSION

The original method for the preparation of titanate nanotubes using Kasuga's method involved a hydrothermal reaction at 110-150ºC for a long reaction time ranging from 24-72 h (Kasuga et al. 1998, 1999). In this work, TiO_2 nanoparticles were chemically treated using NaOH under a hydrothermal condition at a temperature of 180ºC with the addition of TEA. The elevated temperature increased the formation rate of titanate and the addition of TEA induced the formation of titanate nanotubes, which in turn resulted in reducing the reaction time for the formation of titanate nanotubes. At different hydrothermal treatment times (1, 6, 12 and 24 h), titanate samples were collected to monitor the crystal growth behavior. The titanate samples are hereafter denoted as TNT-1, TNT-6, TNT-12 and TNT-24 which refer to 1, 6, 12 and 24 h of hydrothermal reaction time, respectively.

Figure 1 shows the XRD patterns of the pure TiO$_2$ and titanate samples prepared using hydrothermal method in the presence of TEA at 180°C under the reaction times of 1 - 24 h. The XRD pattern for the sample treated with hydrothermal method without the presence of TEA is also provided for comparison. All the peaks for the pure TiO$_2$ nanopowder with 2θ = 25.3°, 36.9°, 37.8°, 36.6°, 48.0°, 53.8° and 55.0°, which are attributed to the (101), (103), (004), (112), (200), (105) and (211) planes, respectively, corresponding to the anatase phase of TiO$_2$ (JCPDS 84-1285).
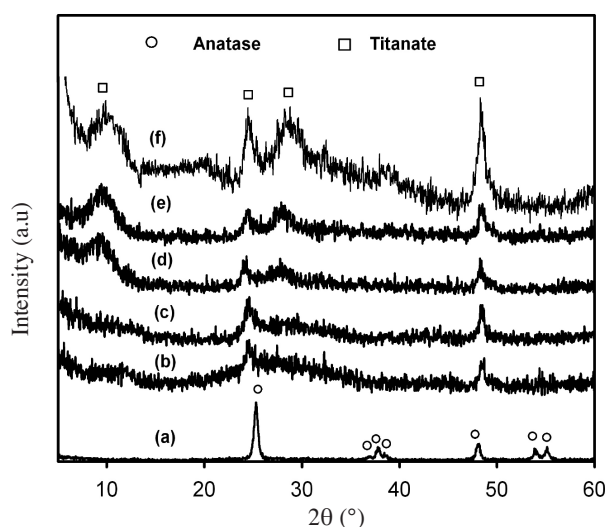

FIGURE 1. XRD spectra of (a) pure TiO$_2$ nanoparticles, (b) hydrothermally treated sample without the presence of TEA and hydrothermally treated sample with the addition of TEA after (c) 1 h, (d) 6 h, (e) 12 h and (f) 24 h

For the hydrothermally treated samples, the crystallinity of the titanate samples was influenced by the reaction time. All the hydrothermal treated samples, including the one prepared in the absence of TEA, show that the diffraction peaks at 2θ = 9.6°, 24.6°, 28.0° and 48.4° are attributed to the crystal planes of (200), (110), (310) and (020) for H$_2$Ti$_2$O$_5$ titanate with orthorhombic phase (JSCPDS 47-0124). In the scope of 1 – 24 h, the intensities of the diffraction peaks become stronger with the increase of hydrothermal time, suggesting enhanced crystallinity. The diffraction peak that exhibits the most obvious increase in intensity is at 2θ = 9.6° which corresponds to the (200) crystal facet. This peak with a d-spacing value of 0.93 nm also corresponds to the interlayer distance of multilayered-wall of titanate nanotubes. The very low diffraction peak intensity at 2θ = 9.6° for TNT-1 suggests that the formation of titanate nanotubes was partially completed. Moreover, there is no evidence of diffraction peaks exhibiting the anatase phase for all the titanate samples. The absence of TiO$_2$ anatase peaks suggests that the TiO$_2$ had transformed into H$_2$Ti$_2$O$_5$ titanate after 1 h of hydrothermal treatment.

The precursor used for the preparation of titanate nanotubes was TiO$_2$ nanoparticles of pure anatase phase, having a near spherical shape with an average size of ∼ 35 nm, as shown in Figure 2(a). We first carried out the hydrothermal treatment of the TiO$_2$ nanoparticles in the absence of TEA at 180°C for 24 h. Micron-sized titanate in sheets and rods forms were produced (Figure 2(b)). The formation of sheet-like and rod-like morphologies is consistent with the previous report on the hydrothermal treatment that exceeded 150°C (Lee et al. 2009). Recently, Song et al. (2005) reported the formation of titanate nanosheets by treating P25 at 180°C with concentrated NaOH. This observation is in line with our results without the presence of TEA. With the addition of 10 and 50% of TEA, the nanotubes were formed under the same hydrothermal condition as shown in Figure 2(c) and 2(d), respectively. The average outer and inner diameters of the nanotubes do not show any significant difference. This shows that the titanate nanotubes only formed in the presence of TEA at the hydrothermal temperature of 180°C. We also tried using different types of Ti sources such as TiO$_2$ micron-sized particles, P25 and TiO$_2$ pigment used for UV sunscreen as precursors for the same hydrothermal treatment. All of the TiO$_2$ sources resulted in the formation of titanate nanotubes.

In order to postulate the formation mechanism of the titanate nanotubes, the titanate samples TNT-1, TNT-6, TNT-12 and TNT-24 were viewed under TEM. For TNT-1, it was found that the sample consists of a mixture of nanosheets and nanotubes as shown in Figure 3(a). The nanosheets are titanate as evidence from the absence of anatase phase in the XRD result (Figure 1(c)). Only a small amount of titanate nanotubes were formed after 1 h of hydrothermal treatment, which is in accordance with the XRD pattern for TNT-1 where the diffraction peaks attributed to titanate are weak (Figure 1(c)). Extending the hydrothermal treatment time to 6 h shows a complete conversion of TiO$_2$ nanoparticles to titanate nanotubes (Figure 3(b)). The average outer and inner diameters of the nanotubes are 11 and 5 nm, respectively. Similar morphologies are found for the hydrothermal treatment carried out for 12 h (Figure 3(c)) and 24 h (Figure 3(d)). The length of the titanate nanotubes is around 100 - 200 nm, depending on the sonication duration and not on the hydrothermal treatment time. Although titanate nanotubes were also formed at a lower temperature of 130°C after 6 h of reaction, the yield was not satisfactory (figure not shown).

The growth mechanisms of titanate and TiO$_2$ nanotubes synthesized by the hydrothermal method from TiO nanoparticles had been reported previously (Guo et al. 2008; Pan et al. 2007; Wang et al. 2007; Wu et al. 2007). In this work, we discovered the importance of TEA in the rapid formation of titanate nanotubes, as depicted in Figure 4. Initially, the TiO$_2$ powder (Figure 4(a)) reacted with NaOH to form sheet-like titanate (Figure 4(b)). The formation of sheet-like titanate is estimated to be four times faster in the presence of TEA due to the higher temperature that increased the reaction rate. These thin sheets of titanates
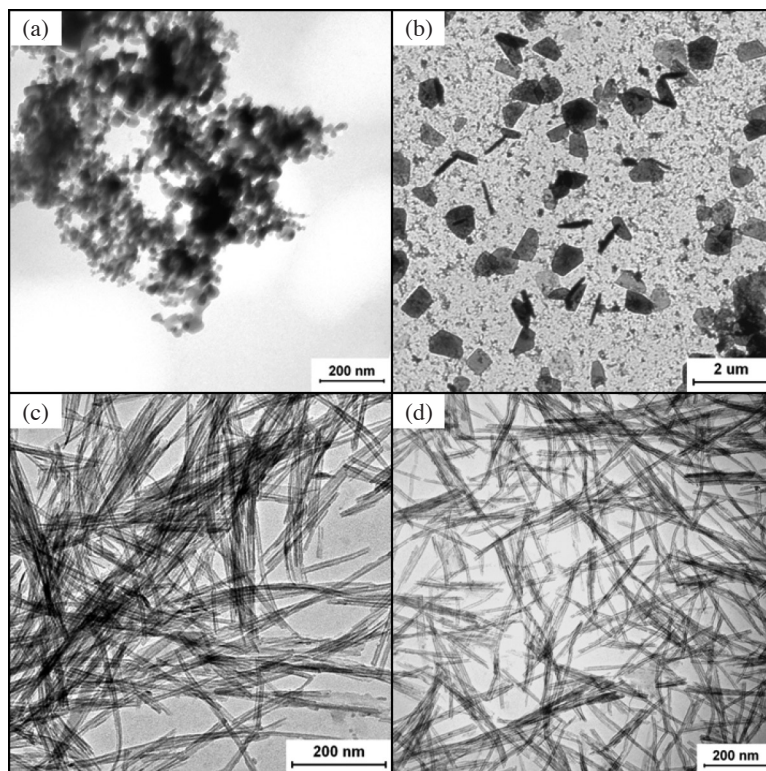
FIGURE 2. TEM micrographs of (a) TiO$_2$ nanopowder, (b) titanate nanosheets after hydrothermal treatment at 180ºC without TEA, titanate nanotubes with (c) 10 and 50% TEA and (d) under the same hydrothermal condition
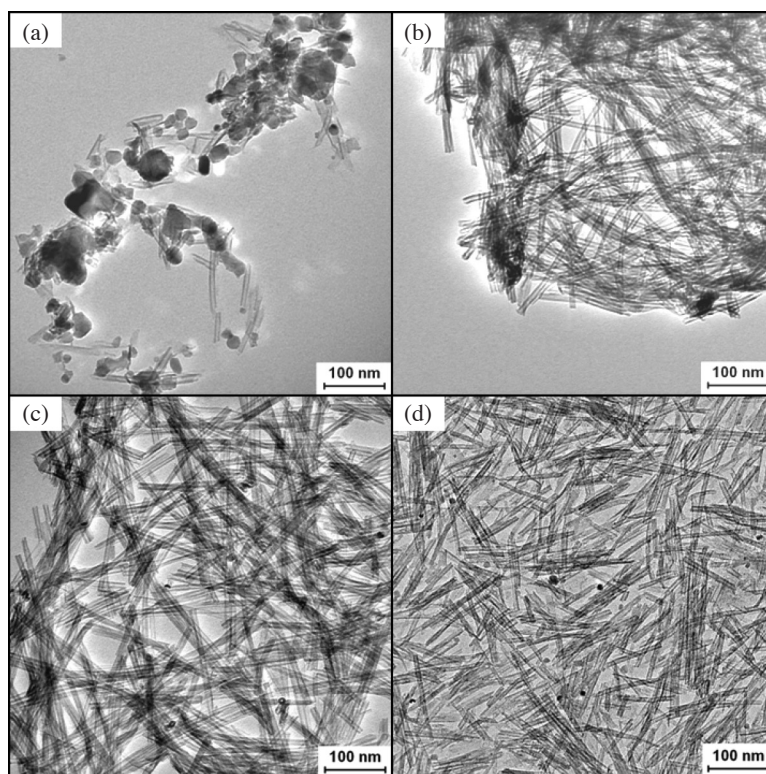

FIGURE 3. TEM micrographs of titanate samples after (a) 1 h, (b) 6 h, (c) 12 h and (d) 24 h of hydrothermal treatment at 180ºC

are not stable and have the tendency to transformed into other structures like rods or particles at temperature higher than 160°C (Das et al. 2008). However, with the presence of TEA, the nanosheets are stabilized, resulting in their lateral growth into larger nanosheets. The nanosheets are conditioned to curl due to surface tension caused by the charge on the surface of the layered titanate during the excessive intercalation of TEA at the primary stage of the hydrothermal treatment. This gives rise to the formation of nanotubes via layer-by-layer peeling of the layered titanate (Figure 4(c)). The formation of titanate nanotube is closely related to exfoliation and scrolling of nanosheets (Nakahira et al. 2010). In the absence of TEA, these titanate sheets did not roll up to form nanotubes at the temperature of 180°C, as shown in Figure 2(b).

Figure 5 exhibits the nitrogen adsorption isotherm of the titanate nanotubes for TNT-6 and TNT-24. The isotherm shows a typical IUPAC type IV pattern with a sharp inflection of nitrogen adsorbed volume at P/P_o of about 0.80 (type H_2 hysteresis loop) (Buchanan et al. 2000), indicating the existence of mesopores or tubular structures (Bavykin et al. 2004). The BET surface area of the titanate nanotubes is calculated to be ~ 250 m²/g for both TNT-6 and TNT-24, which is five times higher than the surface area of the untreated TiO_2 nanoparticles, ~ 50 m²/g (Qamar et al.

2008). By comparing TNT-6 and TNT-24, we concluded that the formation of titanate nanotubes was completed after 6 h of hydrothermal treatment.

The degradation of methylene blue was chosen as a representative model pollutant to evaluate the photocatalytic performance of the TNT samples. In Figure 6(a), the UV-vis absorption spectra of the MB solution after various irradiation periods in the presence of the TNT-6 samples show significant decrease at the absorption peak of 660 nm. The concentration of MB reduced to ~ 10% of the original concentration. Figure 6(b) shows the kinetic of the degradation of MB for TiO_2 nanopowder and various TNT samples. Without the presence of catalyst, the concentration of MB degraded by only about 5% after 60 min of irradiation time, showing very low degradation rate. With the addition of TiO_2 nanoparticles and TNT samples, the degradation of MB was significantly faster, confirming that the TNT samples were active photocatalysts for organic pollutants. The degree of MB degradation depended largely on the structure and morphology of the samples. For TiO_2 nanopowder, about 65% of MB degraded after 60 min of irradiation, which is almost comparable to the TNT-1 sample. For TNT-6, TNT-12 and TNT-24, the degradation rates were much higher and the amount of MB left after 60 min of irradiation is ~5%.
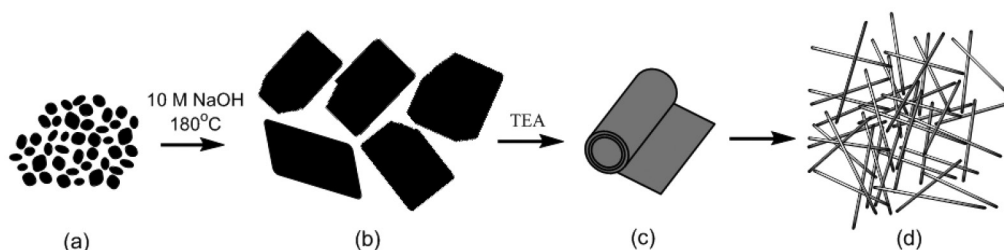

FIGURE 4. Postulated formation mechanism of $H_2Ti_2O_5$ titanate (a) TiO_2 nanoparticles, (b) titanate nanosheets, (c) rolling up of titanate nanosheets and (d) formation of titanate nanotubes
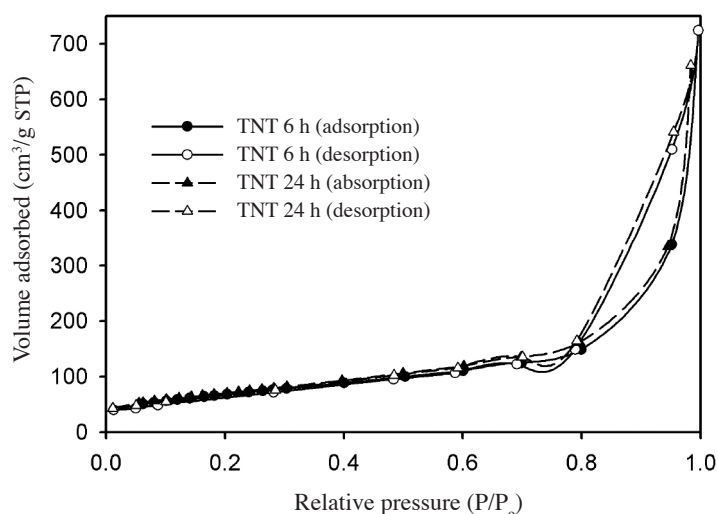

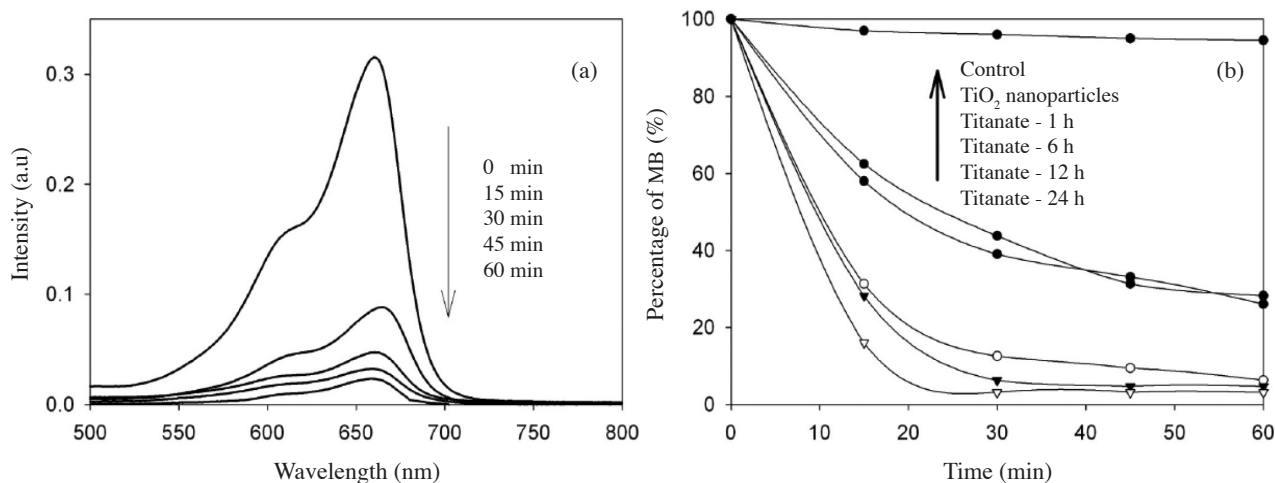FIGURE 5. BET surface area analyses of TNT-6 and TNT-24

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FIGURE 6. (a) Degradation of MB in the presence of TNT-6 with irradiation time of 15-60 min
and (b) degradation kinetic of MB for control, TiO$_2$ nanoparticles and TNT samples

The difference in the photocatalytic behavior for the TiO$_2$ and TNT samples could be explained by the accessibility of surface areas. It is well known that a higher surface area increases the actives sites and decreases the recombination rate of the electron-hole pairs in the photocatalytic reactions, resulting in higher photocatalytic activities. Hence, the lower photocatalytic activity in the TiO$_2$ nanopowder is accounted to its lower surface area which is ~ 50 m^2/g compared to that of the TNT samples which is ~ 250 m^2/g. Thus, all the TNT samples show higher photocatalytic activity. The degradation rate for TNT-12 and TNT-24 is slightly higher than TNT-6 due to the higher crystallinity of the sample as shown by the XRD profiles. This is because the defects found in the lower crystalline TNT-6 give rise to scattering centres that increase the recombination rate of electron-hole pairs, leading to reduce photocatalytic performance.

CONCLUSION

We had successfully synthesized titanate nanotubes using a rapid hydrothermal method where the reaction time was reduced from 24 to only 6 h. The crux of this rapid synthesis approach was by having TEA in the reaction system. The as-synthesized titanate nanotubes have similar structure and morphology as those produced by the conventional hydrothermal method. The synthesized titanate nanotubes exhibited good photocatalytic performance under the UV light exposure.

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