

# Study on photocatalysis of TiO<sub>2</sub> nanotubes prepared by methanol-thermal synthesis at low temperature

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MS received 13 February 2012; revised 5 June 2012

**Abstract.** TiO<sub>2</sub> nanotubes were synthesized by the solvothermal process at low temperature in a highly alkaline water–methanol mixed solution. Their characteristics were identified by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), specific surface area (BET), Fourier transform infrared spectroscopy (FTIR) and UV–Vis absorption spectroscopy. The as-prepared samples were tested by the photodegradation reaction of methylene blue (MB) dye under visible-light irradiation. The ratios of methanol and water, as well as calcination temperature, affected the morphology, nanostructure and photocatalytic performance. The methanol solvent plays an important role in improving crystallization of the anatase phase, which affects the photocatalytic reaction. Titanate nanotubes were synthesized in methanol–water volume ratios of 10:90, 20:80 and 30:70 which still had high absorbability. Titania nanotubes formed at a calcination temperature of 300 °C using methanol–water volume ratio of 30:70 showed highest photocatalytic performance, much higher than that using water solvent and TiO<sub>2</sub>–P25 powder.

**Keywords.** Solvothermal; nanostructured TiO<sub>2</sub>; photocatalyst; dye degradation.

## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) is a common metal–oxide semiconductor. This material has many applications in key industries such as photocatalysis, solar cells, microelectronics and electrochemistry. Many researchers have focused on applied research in the field of TiO<sub>2</sub> photocatalytic materials, especially in dye wastewater treatment. TiO<sub>2</sub> semiconductor materials are often used in photocatalysis because TiO<sub>2</sub> has a low bandgap (3.2 eV); thus, they are extensively tested to combat environmental pollution. In addition, it is important that various forms of nano-TiO<sub>2</sub> are used as photocatalysts because their oxidative power is very strong. Furthermore, they are biologically and chemically inert and have long-term stability against optical and chemical corrosion.

Titania nanotubes have attracted much interest in scientific research because of their wide range of functional properties. Titania exists in three major crystalline phases: anatase, rutile and brookite. Each structure has different physical and chemical properties (Aruna *et al* 2000). The rutile phase can be formed from high-temperature processing of the anatase form. However, efforts to transform anatase into rutile nanotubes by heat treatment often leads to collapse of the structure with a loss in structural control (Varghese *et al* 2003). It is well known that both TiO<sub>2</sub> anatase and rutile phases are composed of TiO<sub>6</sub> octahedra and the transition phase

is achieved by rearranging the octahedra. The arrangement of TiO<sub>6</sub> octahedra through face-sharing initiates the anatase phase, while edge-sharing leads to the rutile phase (Yin *et al* 2001; Masuda and Kazumi 2009).

There are many methods for synthesizing TiO<sub>2</sub> nanotubes, but those with well-shaped anatase crystals may exhibit highest photocatalytic activity. Currently, method of liquid-phase processing at low temperatures is an effective synthesis route for producing nanocrystalline tubes of sodium titanate and TiO<sub>2</sub> anatase under hydrothermal conditions (Kasuga *et al* 1998; Du *et al* 2001; Yao *et al* 2003; Poudel *et al* 2005; Khan *et al* 2006; Menzel *et al* 2006; Bavykin and Walsh 2009; Huang *et al* 2009). The hydrothermal method has been proved superior for the synthesis of TiO<sub>2</sub> nanotubes. The use of solvents other than water under solvothermal conditions alters the structure, shape, size and transformation of titania phases (Yan *et al* 2010). When using these solvents, alcohol is often utilized and is believed to play an important role in the formation of titania phases (Yan *et al* 2010).

In recent years, some authors have used the solvothermal method to synthesize TiO<sub>2</sub> nanotubes, mainly using ethanol as the solvent. However, researchers have stopped investigating the structure, morphology and states of phase transformation, as well as identifying the characteristics and growth mechanism of the nanostructure of the products (Das *et al* 2008; Yan *et al* 2010). They have also predicted that these products will certainly have potential applications in the field of photocatalysis.

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In this paper, we synthesized TiO<sub>2</sub> anatase phase nanotubes using a solvothermal route at low temperature in aqueous methanol and NaOH using TiO<sub>2</sub>-P25 nanoparticles as precursors. We researched the influence of different solvent ratios of methanol–water on the morphology of TiO<sub>2</sub> nanocrystals under solvothermal conditions, as well as the efficiency of photocatalytic reactions associated with the degradation of dye (methylene blue). The different methanol–water ratios have an important influence on shape and structure of the product phase. In particular, methanol solvent affects the crystalline anatase phase of the final product (after calcination), which affects the photocatalytic performance in the degradation of MB dye.

In addition, we researched the synthesis of TiO<sub>2</sub> nanotubes prepared by the solvothermal method and calcined at different temperatures. The as-prepared samples were compared simultaneously with other forms of nano-TiO<sub>2</sub> such as titanate nanotubes and even TiO<sub>2</sub>-P25 with respect to their behaviour in photocatalytic applications of the methylene blue treatment under visible-light irradiation. The synthesis of TiO<sub>2</sub> nanotubes by the solvothermal method using methanol–water mixed solvent promises to provide efficiency in energy-saving applications because the nanotubes are synthesized and calcined at low temperatures; moreover, the nanotubes still allow for the highly efficient generation of products during photocatalysis, as evidenced by the decolouration of organic dye contaminants under visible-light irradiation.

## 2. Materials and methods

### 2.1 Reagents

All the chemicals used were of analytical grade and were used as received without any further purification. HNO<sub>3</sub>, NaOH, TiO<sub>2</sub> (P25) powder and methylene blue (MB) were purchased from Across Organics (New Jersey, USA). A volume of 200 ml of MB solution (300 ppm) was prepared in double-distilled water and diluted as required. The chemical structure of MB is shown in figure 1. Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula, C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl. At room temperature, it appears as a solid, odourless, dark-green powder that yields a blue solution when dissolved in water.

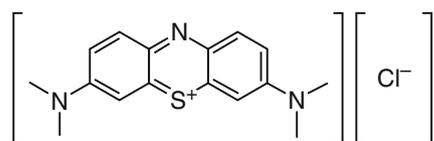


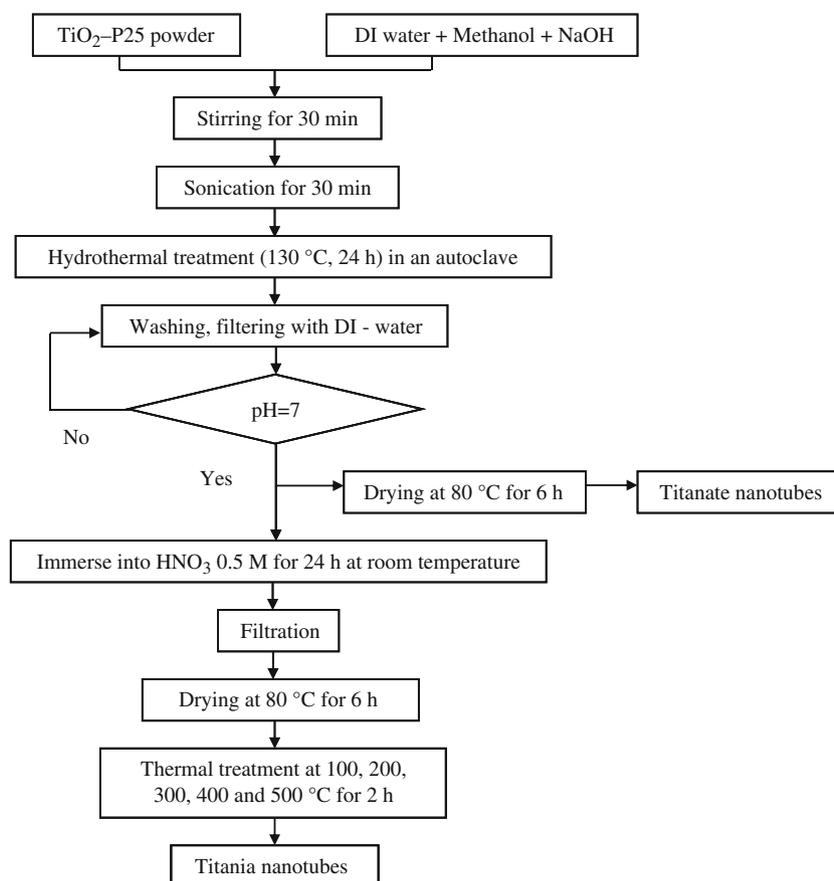
Figure 1. Chemical structure of methylene blue.

### 2.2 Instrumentation

All the glass apparatus used were soaked in concentrated HNO<sub>3</sub> for 12 h, thoroughly washed in tap water and then with double-distilled water. The apparatus were then dried in a hot-air oven for 2 h at 90 °C. To achieve high-accuracy weighing, a highly precise digital electronic pH meter was used to measure pH of the medium. Powder X-ray diffraction patterns (XRD) were recorded using PANalytical, X Pert PRO X-ray diffractometer and CuK<sub>α</sub> (1.5406 Å) radiation. A Micromeritics, ASAP 2020 Analyser was used for BET analysis. TEM measurement was performed using a Philips M-200 transmission electron microscope operated at 200 kV. Before being analysed by TEM, the samples were sonicated in ethanol for 15 min and then deposited in 2–3 drops on thin carbon film supported on a holey copper grid; the samples were then dried at 60 °C overnight. Fourier transform infrared spectroscopy (FTIR) study was conducted with a spectrometer of Perkin–Elmer instruments. UV–Vis diffuse reflectance spectra were obtained using a Jasco V-600 UV–Vis spectrophotometer between 300 and 800 nm; the instrument was used to measure red shift in the samples. In addition, all absorbance measurements were carried out using UV–Vis spectrophotometer (Hitachi, U-2800) equipped with 1 cm quartz cell. Gilson micropipette and microtips were used to handle samples.

### 2.3 Preparation of TiO<sub>2</sub> nanotube

In this study, the solvothermal method was used to synthesize TiO<sub>2</sub> nanotube; the synthesis process is illustrated in figure 2. Solutions of 10 M NaOH were prepared by introducing 28 g NaOH into 70 ml of a mixed solvent of methanol and distilled water. The volume ratios of methanol (MeOH) and distilled water (DIW) were 10:90, 20:80, 30:70, 40:60, 50:50 and 70:30. The use of TiO<sub>2</sub> nanoparticles in the solution was divided into two parts: in the first, only 1.2 g powder was added to 70 ml of 10 M NaOH aqueous methanol at different ratios. In this experiment, titanate nanotubes were synthesized to determine the ratio between methanol and water that exhibited a high adsorption efficiency for methylene blue. In the second step, selected ratios were used for the next experiments, followed by the addition of 3 g of TiO<sub>2</sub> powder to a mixed solution of methanol and water at the selected ratio to synthesize titania nanotubes. The experimental conditions of the two cases were as follows: the mixture solution included water, methanol, NaOH and TiO<sub>2</sub> powder stirred continuously for 30 min with a magnetic stirrer. Then the mixture was transferred and sonicated for 30 min. Next, this homogeneous suspension was hydrothermally treated in a stainless teflon-lined autoclave at 130 °C for 24 h. After the reaction time was reached, the reactor cooled naturally in air to room temperature. Then the final reaction products were thoroughly washed with large volumes of double-distilled water to achieve a neutral pH (~7). The obtained white cotton batting-like solid was filtrated and separated for drying



**Figure 2.** Flow chart of synthesis of TiO<sub>2</sub> nanotube types by solvothermal process.

at 80 °C for 6 h in the form of obtained titanate. The other part was then immersed in a solution of 0.5 M HNO<sub>3</sub> for 24 h at room temperature to ensure that the protonation of the surface and final filtration were achieved. The filtrate was washed several times with double-distilled water to achieve a pH of 7 for the product and then dried at 80 °C for 6 h. The dried product was calcined at different temperatures for 2 h to obtain TiO<sub>2</sub> nanotubes with the desired characteristics. Finally, various forms of TiO<sub>2</sub> nanotubes were synthesized as described above to remove MB by photocatalytic degradation methods under visible-light irradiation.

#### 2.4 Photocatalytic degradation of aqueous methylene blue (MB)

In the experiments, 0.01 g of as-prepared TiO<sub>2</sub> nanotubes was dispersed in 100 ml of MB solution with an initial dye concentration (*C*) of 12 mg L<sup>-1</sup> (dose 0.1 g L<sup>-1</sup>) by stirring for 1 h in the dark. Suspensions of dyes and catalysts were added to a photocatalytic reaction vessel under visible-light irradiation. A 300 W halogen lamp with a 410 nm cut-off glass filter was used as the source of light. The experiment was conducted at room temperature ( $\sim 25 \pm 2$  °C) and atmospheric pressure. The reaction temperature was con-

trolled by continuously adding cool water outside the vessel during the irradiation process. The total time of visible-light irradiation was 2 h. After every 15 min,  $\sim 8$  ml of solution was removed and immediately centrifuged at 4000 rpm for 10 min to separate the solid and liquid phases from the solution experiments. The supernatant fluid was collected after centrifugation and the dye concentration remaining in the solution was measured by UV-Vis spectroscopy at 664 nm. Blue colour of the solution gradually faded over time due to the adsorption and degradation of MB. The concentration of MB solution was determined as a function of irradiation time from the change in absorbance at 664 nm.

### 3. Results and discussion

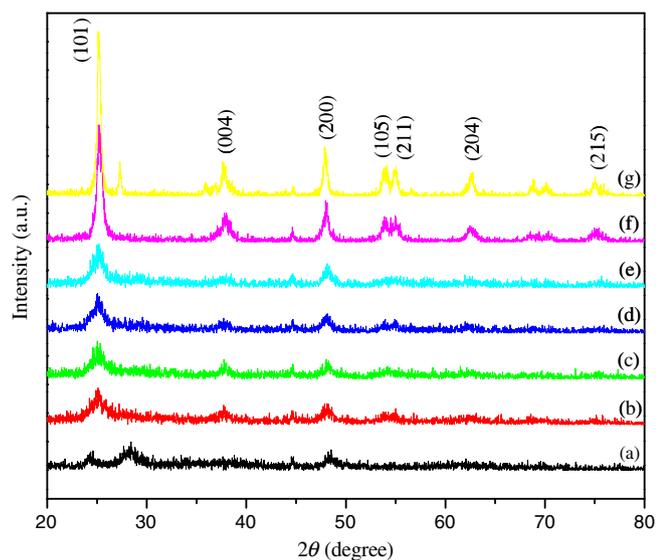
#### 3.1 Synthesis and characterization of TiO<sub>2</sub> nanotubes

The crystal structure, morphology and size of the synthesized products were determined by XRD, SEM and TEM. The purpose of this study was to determine the methanol-water ratio providing highest photocatalytic performance. Therefore, XRD analysis results for the sample possessing methanol-water ratio of 30:70 by volume are mainly presented and compared with the samples synthesized at 100%

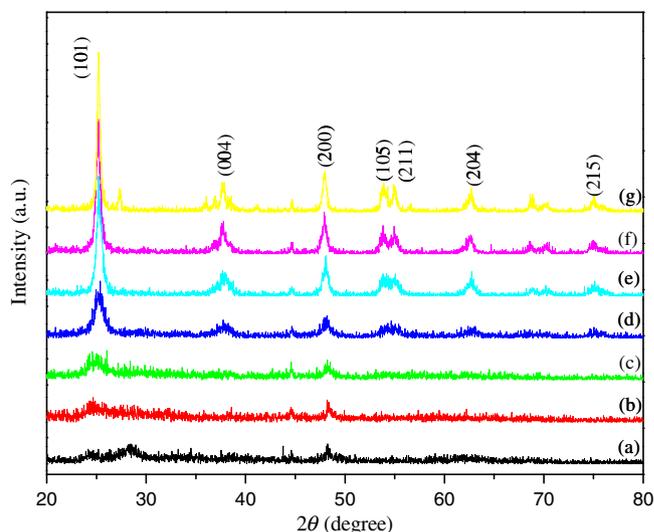
water. The explanation for this choice is provided in the photocatalyst section.

Titanate is formed by the dissolution and recrystallization of  $\text{TiO}_2$  in a highly concentrated  $\text{NaOH}$  aqueous solution (Du *et al* 2001; Huang *et al* 2009). Figures 3 and 4 show XRD patterns of titanate products that were solvothermally and hydrothermally prepared at  $130^\circ\text{C}$  and calcined at different temperatures to produce  $\text{TiO}_2$  nanotubes. As a result, the obtained product presents the most anatase phase nanoparticles after calcining at different temperatures. However, compared with the case using methanol solvent (methanol–water ratio of 30:70), XRD pattern of the first case shows a clearer and sharper anatase phase, even when the sample was calcined at a low temperature of  $100^\circ\text{C}$ . This result is entirely consistent with the photocatalytic efficiency presented in the last section, especially when using methanol–water ratio of 30:70, which exhibited the highest photocatalytic efficiency. This suggests that the role of methanol solvent is very important in promoting the formation of anatase phase during liquid-phase synthesis of  $\text{TiO}_2$  nanocrystals. Because, the methanol solvent has a lower boiling temperature ( $65^\circ\text{C}$ ) than water, it evaporates more quickly when heated to  $130^\circ\text{C}$ , which affects the accelerated formation of anatase phase compared to the case in which only water is used as the solvent. The ratio of anatase phase increased with calcination temperature. At a calcination temperature of  $500^\circ\text{C}$ , in particular, the content of anatase phase is quite high and close to that of  $\text{TiO}_2\text{-P25}$  nanoparticles.

Figure 3 shows XRD patterns of all of the samples, showing all the peaks corresponding to the reflections from (101), (004), (200), (105), (211) and (204) planes of anatase for



**Figure 3.** XRD patterns of products synthesized at  $130^\circ\text{C}$  for 24 h using volume ratio of methanol and water at 30:70 with 70 ml total volume and calcined at different temperatures: (a) titanate form; (b)  $100^\circ\text{C}$ ; (c)  $200^\circ\text{C}$ ; (d)  $300^\circ\text{C}$ ; (e)  $400^\circ\text{C}$ ; (f)  $500^\circ\text{C}$  and (g)  $\text{TiO}_2\text{-P25}$ .



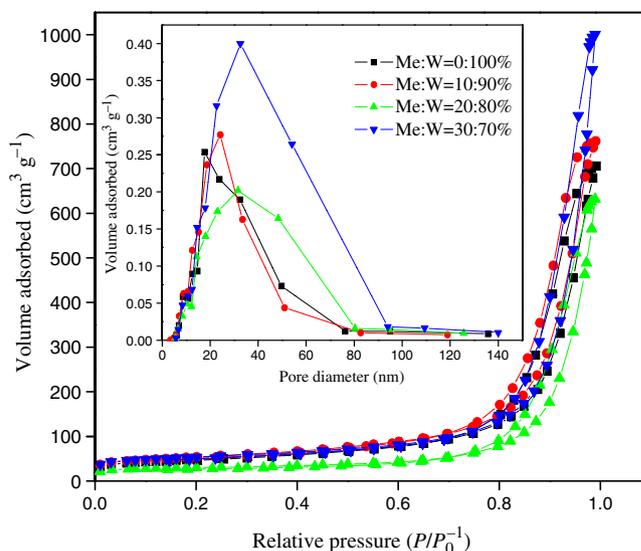
**Figure 4.** XRD patterns of products synthesized at  $130^\circ\text{C}$  for 24 h using 70 ml volume of water and calcined at different temperatures: (a) titanate form; (b)  $100^\circ\text{C}$ ; (c)  $200^\circ\text{C}$ ; (d)  $300^\circ\text{C}$ ; (e)  $400^\circ\text{C}$ ; (f)  $500^\circ\text{C}$  and (g)  $\text{TiO}_2\text{-P25}$ .

samples featuring methanol–water ratio of 30:70 and calcined at different temperatures. These closely match the standard reported values (JCPDS file no. 21-1272). From (101) peaks of all the samples, we can see that width of the peak becomes increasingly narrow with increasing calcination temperature. In addition, the samples featuring methanol solvent show clearer peaks than those featuring water solvent. This may be attributed to the improved crystallinity of the samples with increasing calcination temperature. The titanate phase from XRD pattern also indicates the presence of  $\text{H}_2\text{Ti}_3\text{O}_7$  in the products washed with water by substitution of  $\text{Na}^+$  by  $\text{H}^+$ . Similarly, the proportion of  $\text{H}_2\text{Ti}_3\text{O}_7$  in the samples synthesized using methanol solvent appeared stronger compared to those synthesized using water solvent.

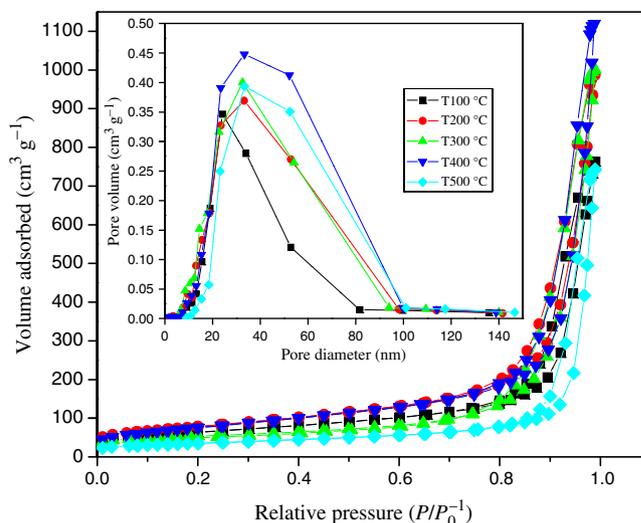
Figures 3 and 4 show that all the diffraction peaks of the samples calcined at  $100\text{--}500^\circ\text{C}$  could be indexed as belonging to the anatase phase of  $\text{TiO}_2$ , particularly for samples featuring the methanol solvent. With an increase in the calcination temperature from  $300$  to  $500^\circ\text{C}$ , the peak intensities of anatase increased significantly, indicating improved crystallization of the anatase phase. Simultaneously, the width of (101) peak became narrower, suggesting the growth of anatase crystallites. When using the methanol solvent, three small peaks appeared at  $2\theta \sim 25.3, 37.8$  and  $48.0^\circ$  for the samples calcined at  $100\text{--}300^\circ\text{C}$ , indicating the existence of small amounts of anatase. As shown, the peaks at  $25.3, 37.8, 48.0, 53.8, 54.9$  and  $62.5^\circ$  were attributed to the diffractions of 101, 004, 200, 105, 211, and 204 planes of anatase, respectively (Huang *et al* 2007). In addition, the synthesis of  $\text{TiO}_2$  nanotube powder at low temperatures tends to result in the formation of finer crystallites with larger specific surface areas. The gradual narrowing of XRD lines with increasing calcination temperature reflects a corresponding increase in the average grain size (Klug and Alexander 1974).

Here, we compare our results with those from experiments in which TiO<sub>2</sub> nanotubes were synthesized by the hydrothermal method using water as the solvent. Most previous studies have confirmed that the hydrothermal temperature is one factor affecting the morphological characteristics of titania nanotubes (Wang *et al* 2008). The yield of the tubes (up to 80–90%) increases with hydrothermal temperatures between 100 and 150 °C (Yuan and Su 2004). The surface area and pore volume of the largest titania nanotubes were observed at a synthesis temperature of 130 °C (Ou and Lo 2007). The hydrothermal temperature plays an important role in promoting the nucleation and crystal growth of titanate nanotubes (Lan *et al* 2005). The combination of hydrothermal temperature between 130 and 150 °C applied over 24–72 h generates titanate nanotubes of the highest yield and purity (Lan *et al* 2005; Ma *et al* 2005). However, at hydrothermal temperatures up to 160 °C, the pore volume and specific surface area of titanate nanotubes are reduced. The pore volume and surface area of samples become smaller at temperatures above 170 °C (Lee *et al* 2009). Many researchers have studied phase transition of titanate nanotubes during the heating process. Moreover, the calcination process is believed to affect phase structure and microstructure of titanate nanotubes (Wang *et al* 2008). Indeed, crystallinity of the titanate nanotubes increases with calcination temperature (Weng *et al* 2006). Above 600 °C, titanate nanotubes begin to collapse as titania nanocrystals start to grow. The crystallinity of the anatase phase begins to increase at 300 °C (Sreekantan and Lai 2010). Titanate nanotubes are easily destroyed at high temperatures, causing tubular structures to transform into nanoparticles after heat treatment (Vuong *et al* 2009). Thus, for TiO<sub>2</sub> nanotubes synthesized using a conventional water solvent, the anatase phase is usually observed at an annealing temperature between 300 and 400 °C or above; at ~600–700 °C, the samples are shown to transform from tubes into particles (Yu *et al* 2006; Lee *et al* 2007, 2009). Moreover, the increase in peak intensity and the decrease in width of the peaks at 400–700 °C indicates improvement of crystallization of anatase phase and growth of anatase crystallites, respectively. At 700 °C, the rutile phase appears (Lee *et al* 2009). Many researchers have observed that the anatase phase is retained after the heat treatment process and crystallization, morphology, pore structure and specific surface area of titania nanotubes are strongly dependent on calcination temperature. TiO<sub>2</sub> nanotubes synthesized by the solvothermal method using a mixed solvent composed of methanol and water also follow these rules. However, the difference here is that at a low calcination temperature of 100 °C, the anatase phase appears in relatively low amounts and if calcined at 500 °C, the tubular structures can be observed to transform into particles. This demonstrates how the role of methanol solvent is very important in increasing the anatase crystalline phase content.

The nitrogen adsorption–desorption isotherms of titania nanotubes at various ratios of methanol and water and at various calcination temperatures are presented in figures 5 and 6. The specific surface areas ( $S_{\text{BET}}$ ), average pore



**Figure 5.** Nitrogen adsorption–desorption isotherms of titania nanotubes at various ratios of methanol and water (calcined at temperature of 300 °C). Inset shows pore distribution.



**Figure 6.** Nitrogen adsorption–desorption isotherms of titania nanotubes calcined at different temperatures (volume ratio of methanol and water at 30:70). Inset shows pore distribution.

volumes and pore sizes of the samples are summarized in tables 1 and 2. BDDT classification shows that all the samples are of type IV with type-H3 hysteresis loops, indicating a mesoporous structure (2–50 nm). In general, the sample synthesized using methanol–water ratio of 30:70 by volume exhibits a specific surface area greater than that of the remaining samples, including the sample synthesized using only water as a solvent. The hysteresis loops shift to higher relative pressures, indicating that the pore size grows gradually because TiO<sub>2</sub> crystal growth leads to the formation of

**Table 1.** Effects of various ratios of methanol and water on specific surface area ( $S_{\text{BET}}$ ) and pore parameters.

Samples	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size (nm)
Me:W = 0:100	219.36	1.109	20.2
Me:W = 10:90	190.72	0.792	16.6
Me:W = 20:80	182.37	1.018	22.3
Me:W = 30:70	279.49	1.545	22.1

All those samples are in the form of titania nanotubes calcined at a temperature of 300 °C.

**Table 2.** Effects of different calcination temperatures on specific surface area ( $S_{\text{BET}}$ ) and pore parameters of titania nanotube.

Samples	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size (nm)
100 °C	224.04	1.180	21.1
200 °C	279.44	1.527	21.8
300 °C	279.49	1.545	22.1
400 °C	276.65	1.731	25.0
500 °C	123.35	1.149	37.3

All those samples are synthesized at 130 °C for 24 h using volume ratio of methanol and water at 30:70 with 70 ml total volume.

larger pores. The hysteresis loops of the sample calcined at a temperature of 500 °C move more towards higher relative pressures. This sample exhibits smallest specific surface area due to the collapse of the nanotube structures to nanoparticles; this result is consistent with TEM observations. Tables 1 and 2 show that the samples synthesized using methanol solvent and those that were calcined at different temperatures exhibited  $S_{\text{BET}}$  and pore volume higher than that of the precursor P25, which greatly benefits efficiency of the associated absorbability. Similar to the case in which  $\text{TiO}_2$  nanotubes were synthesized with the conventional water solvent, titanate nanotubes calcined at different temperatures exhibited an average pore size of 18.1–31.5 nm when the calcination temperature increased to 400–600 °C (Yu *et al* 2006). Beyond this temperature range, pore size of the nanotubes increases steadily with a decrease in surface area (from 219.2 to 64.3  $\text{m}^2/\text{g}$ ) and pore volume (from 0.992 to 0.347  $\text{cm}^3/\text{g}$ ) (Das *et al* 2008). The aggregation of the nanotubes is attributed to the increase in average pore size. It is remarkable that the specific surface area of titanate nanotubes after calcination is higher than that of Degussa P25 titanium dioxide precursor.

Figure 7 shows TEM images of  $\text{TiO}_2$  nanotube products prepared from the solvothermal method at a temperature of 130 °C for 24 h using methanol–water ratio of 30:70 by volume and calcined at different temperatures ranging from 100 to 500 °C. The insets show the corresponding selected area electron diffraction (SAED) patterns and the dimensions of

$\text{TiO}_2$  nanotubes. SAED patterns show that the crystallites in the as-prepared samples exist as polycrystalline phases in the anatase phase. In addition, TEM pictures show that almost all of the samples exhibit predominantly tube-like structures, except for the sample calcined at a temperature of 500 °C. This sample collapsed into nanoparticles resembling the structure of the initial  $\text{TiO}_2$ -P25 precursor. The samples prepared at a calcination temperature of 400 °C were found to be gradually broken into shorter tubes. A large number of nanotubes exhibited an outside diameter of  $\sim 10$  nm, and nanotube lengths of several hundreds of nanometers were obtained. Furthermore, the ends were observed to be open, which is extremely beneficial for adsorption and photocatalysis.

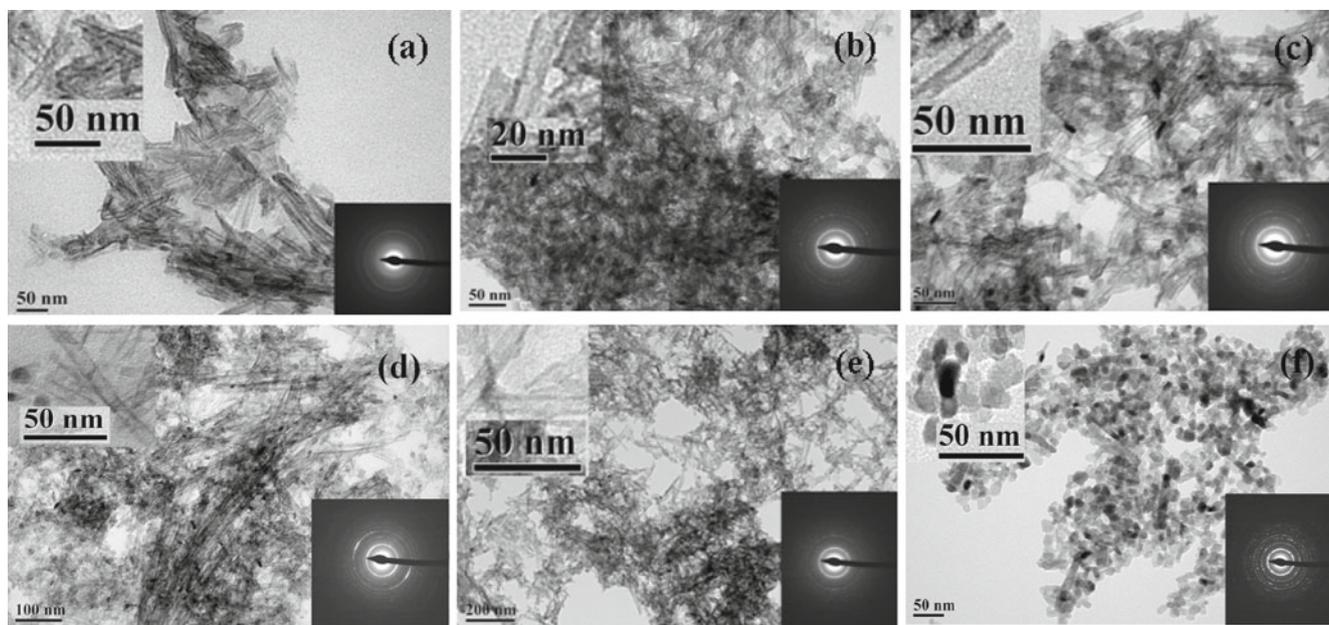
Left inset in figure 7 is an enlarged picture of a tube wall. For the sample calcined at a temperature of 500 °C, TEM image (figure 7(f)) shows nanoparticles measuring 15 nm in average diameter. The TEM images revealed that all the samples synthesized using mixed methanol–water solvent and calcined at different temperatures showed a nearly 1-D nanostructure with the same diameter as the nanotubes, except for the sample calcined at a temperature of 500 °C, which was formed of nanoparticles. The above examples are very beneficial for interpreting the effectiveness of the photocatalytic reactions that are presented in detail in a later section. Moreover, introduction of methanol into an aqueous NaOH solution still promotes the formation of nanotubes. This reveals the positive effect of alcohols in the hydrothermal method used to synthesize titania nanotubes (Yan *et al* 2010).

Figure 8 shows FTIR spectra of different samples. As seen from this figure, the range of 3000–3650  $\text{cm}^{-1}$  bands due to adsorbed water and hydroxyl groups can be observed in all the samples, which can be attributed to the stretching vibration of  $-\text{OH}$  from water. In particular, the content of water adsorbed in titania nanotubes was significantly higher than  $\text{TiO}_2$ -P25 due to the increase of specific surface areas and pore volumes. The band observed in all the samples at 1630  $\text{cm}^{-1}$  can be assigned to molecular water bending mode (Maira *et al* 2001). Distinct broad bands in 400–800  $\text{cm}^{-1}$  region were assigned to Ti–O and Ti–O–Ti skeletal frequency regions (Guo *et al* 2007). A difference here is that when compared to  $\text{TiO}_2$  precursor sample i.e the samples of titania nanotubes began to appear as a new peak (figures 8(b–g)) at 1384  $\text{cm}^{-1}$ , even with the sample using 100% solvent of water which also appeared in this peak. It is probable that during protonation of the surface,  $\text{TiO}_2$  under acidic solution to form  $\text{Ti}-\text{OH}_2^+$  groups. Compared with the previous studies, titania nanotube products were synthesized by the hydrothermal method without the protonation stage not occurring in this absorption peak. For the samples using the mixed solvent of methanol and water in volume ratio at 30:70, intensity of absorption bands at 1384  $\text{cm}^{-1}$  decreased gradually after increasing the calcination temperature. When the calcination temperature is higher than 400 °C (figures 8(h–i)), this peak also disappeared at high temperatures to remove water molecules.

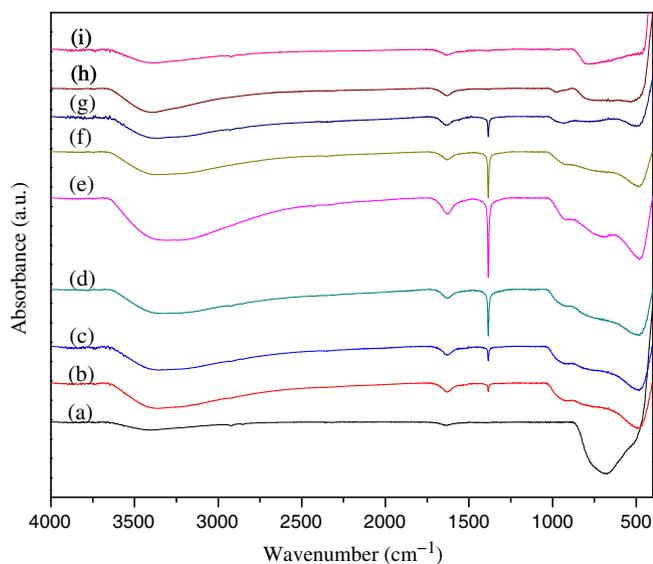
UV–Vis diffuse reflection spectra of  $\text{TiO}_2$ -P25 powder and the products obtained at different calcination temperatures

ranging from 100 to 500 °C are shown in figure 9. The products using mixed solvent of methanol and water in various volume ratios are shown in figure 10, which shows that compared with pure TiO<sub>2</sub>-P25, all the samples generally exhibit high

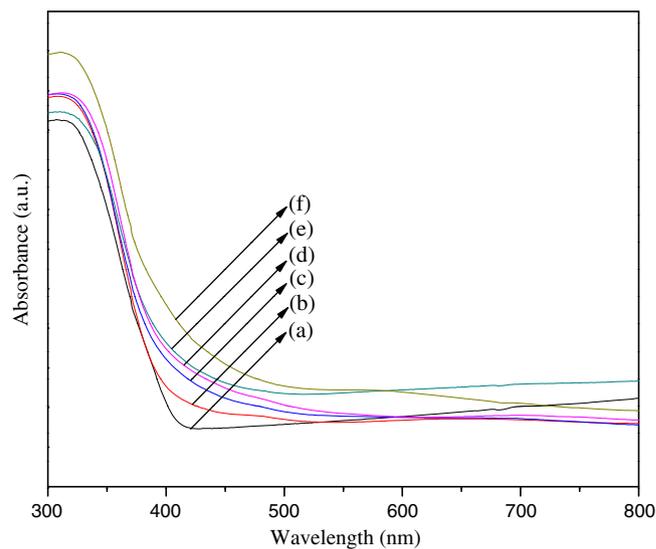
absorption in the visible region. The bandgaps of the samples can be calculated from the intercepts of UV-Vis spectra using the following equation:  $E_g = 1240/\lambda$ . Optical absorption edge of the above samples show an appreciable red shift



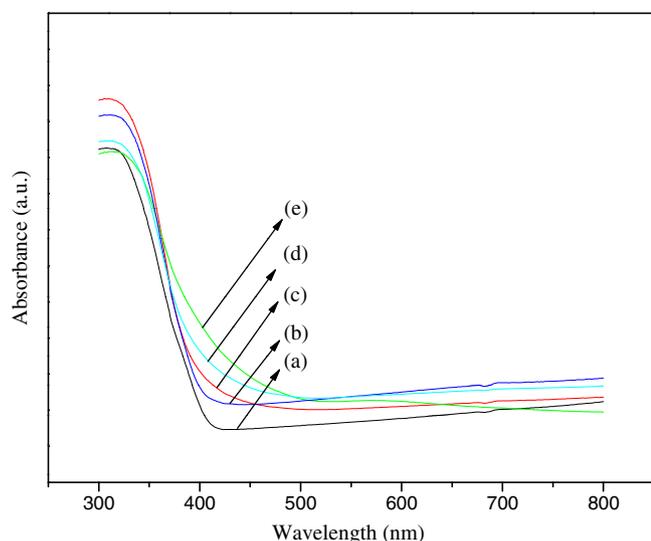
**Figure 7.** TEM images of (a) sample of titanate nanotube and products obtained at different calcination temperatures: (b) 100 °C; (c) 200 °C; (d) 300 °C; (e) 400 °C and (f) 500 °C. All samples are carried out in solvothermal reaction at 130 °C for 24 h in a mixed solvent of methanol–water with volume ratio, 30:70. Insets: magnifications of TiO<sub>2</sub> nanotubes (left upper) and SEAD patterns (lower right).



**Figure 8.** FTIR spectra of various samples. (a) TiO<sub>2</sub>-P25 powder. Products use mixed solvent of methanol and water in volume ratios: (b) 0:100, (c) 10:90, (d) 20:80 and all those samples are calcined at temperature of 300 °C. Products use mixed solvent of methanol and water in volume ratio of 30:70 and calcined at different temperatures: (e) 100 °C, (f) 200 °C, (g) 300 °C, (h) 400 °C and (i) 500 °C.



**Figure 9.** UV-Vis absorbance spectra of (a) TiO<sub>2</sub>-P25 powder and products obtained at different calcination temperatures: (b) 100 °C; (c) 200 °C; (d) 400 °C; (e) 300 °C and (f) 500 °C. All products are carried out in solvothermal reaction at 130 °C for 24 h in a mixed solvent of methanol and water in volume ratio, 30:70.



**Figure 10.** UV-Vis absorbance spectra of (a)  $\text{TiO}_2$ -P25 powder and products synthesized at  $130\text{ }^\circ\text{C}$  for 24 h using mixed solvent of methanol and water in volume ratios are (b) 20:80; (c) 0:100; (d) 30:70 and (e) 10:90. All those samples are in the form of titania nanotubes that are calcined at a temperature of  $300\text{ }^\circ\text{C}$ .

towards longer wavelengths compared with that of raw  $\text{TiO}_2$ , indicating a decrease in the energy bandgap. These results are fully consistent with high photocatalytic efficiency exhibited by the samples in comparison with  $\text{TiO}_2$ -P25 sample, which will be discussed later. For the samples synthesized at  $130\text{ }^\circ\text{C}$  for 24 h using the mixed solvent of methanol and water in various volume ratios, the optical absorption edges show red shift towards the visible light region. These samples exhibited greater red shift than that observed for the pure  $\text{TiO}_2$ -P25 sample. This is entirely consistent with the photocatalysis results presented in a later section, in which higher photocatalytic efficiency is exhibited.

In general, the above discussions suggest that, we can determine the role of methanol in the system. The solvothermal method normally exerts better control than the hydrothermal method over the size and shape distributions and the crystallinity of  $\text{TiO}_2$  nanoparticles. The polarity and coordinating ability of the solvent can influence morphology and crystallization behaviour of the final products (Chen and Mao 2007). The fact that methanol solvent has a lower critical temperature and pressure compared to water is a boon to the processing of materials at much lower temperature and pressure conditions. The addition of methanol solvent to water provides an excellent reaction medium for the hydrothermal processing of nanoparticles because, it allows modulation of the reaction rate and equilibrium by adjusting the dielectric constant and density of the solvent with respect to pressure and temperature, thus generating higher reaction rates and smaller particles (Byrappa and Adschiri 2007). In the hydrothermal treatment of titania powders in basic solution, parameters such as the autoclave pressure influence the morphology and crystal phase of the final products (Poudel *et al* 2005; Menzel *et al* 2006). Therefore, at the same

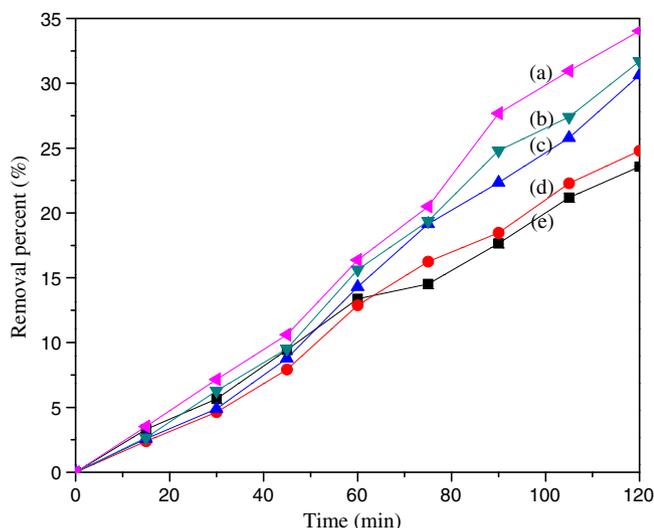
temperature used during heat treatment ( $130\text{ }^\circ\text{C}$ ), methanol has a low boiling point and might influence the crystal phase. It is likely that the presence of methanol solvent in a system exhibits a synergistic effect to facilitate the face-sharing of adjoining octahedra to form the anatase phase during recrystallization of  $\text{TiO}_6$  octahedra. Moreover, according to the growth process, sheets rolled into nanotubes are speculated also to be composed of anatase phase. Additionally, since methanol has a small molecular size and solubility in water, drying and calcination at low temperatures ( $100\text{ }^\circ\text{C}$ ) will facilitate dehydration to generate anatase phase (shown as XRD pattern).

Water molecules also act as bridges between the surface OH groups of different octahedra and connect the octahedra closely during recrystallization (Yanagisawa and Ovenstone 1999). Under hydrothermal conditions,  $\text{Na}^+$  is gradually released with intercalated  $\text{H}_2\text{O}$  molecules into the interlayer spaces of  $\text{TiO}_6$  sheets. The inclusion of methanol up to 30% in the mixed solvent may not affect transformation efficiency of sheets into nanotubes due to the replacement of  $\text{H}_2\text{O}$  molecule into the interlayer spaces of  $\text{TiO}_6$  sheets. BET analysis showed that these sample groups remain at a relatively high specific surface area. XRD diagram also showed the samples using methanol up to 30% which resulted in the appearance of anatase phase in the calcined products. Finally, these products are experimentally shown to affect photocatalytic efficiency with positive effects (presented in later section).

### 3.2 Photocatalytic degradation of MB

Samples of titanate nanotubes were synthesized using the solvothermal method and methanol-water volume ratios of 10:90, 20:80, 30:70, 40:60, 50:50 and 70:30. The purpose of the first experiment was to choose the titanate nanotube samples that were highly effective at adsorbing methylene blue dye. After 60 min stirring in the dark, two groups of samples were observed to be relatively distinct: groups of samples with high adsorption efficiency featuring methanol-water volume ratios of 30:70, 20:80 and 10:90 (the adsorption yield of MB solution is from 63.1 to 65.9%) and sample groups with lower adsorption efficiency featuring methanol-water volume ratios of 40:60, 50:50 and 70:30. The experimental results regarding titanate nanotube samples are not shown here. Previous studies using a conventional water solvent to synthesize nanotube samples have confirmed that such samples exhibit very high adsorption capacities due to their high specific surface areas (Yu *et al* 2006; Lee *et al* 2009; Xiong *et al* 2010). Inclusion of 10–30% methanol in the mixed solvent may not be sufficiently high to affect the reaction; however, these titanate samples retain high specific surface areas, much like those featuring the conventional water solvent, although the relevant data are not presented here.

Figure 11 shows photodegradation ratio of MB under visible-light irradiation at various volume ratios of methanol and water for samples of titania nanotubes calcined at a temperature of  $300\text{ }^\circ\text{C}$ . The results show that the samples using



**Figure 11.** Photodegradation ratio of MB under visible light irradiation: in case of using mixed solvent of methanol and water in volume ratios: (a) 30:70, (b) 20:80, (c) 10:90, (d) 0:100 and (e) TiO<sub>2</sub>-P25 powder. All those samples are in the form of titania nanotubes calcined at a temperature of 300 °C.

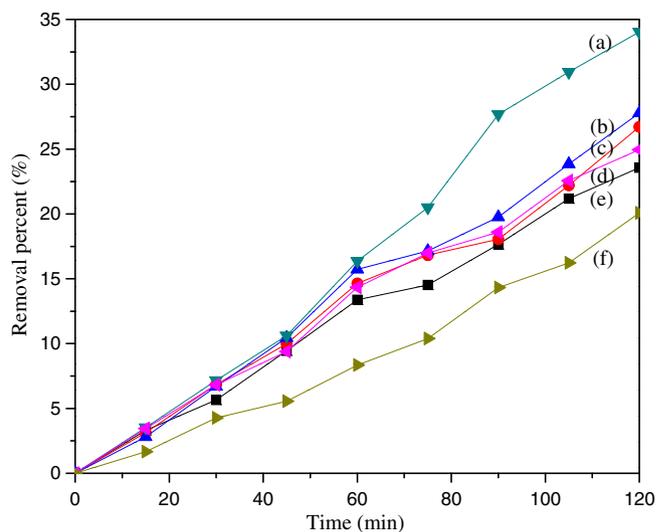
methanol–water volume ratio of 30:70 were the most efficient photocatalysts, even when adsorbing MB dye in the dark and being irradiated by visible light. The adsorption yield of MB solution is from 48.5 to 53.2% for the titania nanotube products using methanol–water volume ratios of 10:90, 20:80 and 30:70. Consider that  $C_0$  is the initial concentration of the dye solution (MB) after stirring in the dark. In this case, MB removal percentage was equal to 34% after an irradiation time of 120 min. It was found that the photocatalytic performance using methanol–water volume ratio of 30:70 (a) is much higher than that of using 100% water solvent (d) and TiO<sub>2</sub>-P25 powder (e). For the samples shown in figure 11(d and e), MB removal percentages were equal to 24.7 and 23.5%, respectively, following 120 min of irradiation. This is consistent with the results shown in XRD and UV-Vis spectra presented in the previous section, which showed that the sample featuring methanol–water volume ratio of 30:70 exhibited better intense diffraction peaks for the crystalline anatase phase and that these peaks were red shifted toward the visible-light region to a greater extent than the peaks of the other samples using 100% water and TiO<sub>2</sub>-P25 powder. Moreover, results shown in table 1, for  $S_{BET}$  analysis also show that the sample featuring methanol–water ratio of 30:70 by volume exhibited the highest  $S_{BET}$ .

The results clearly demonstrate the important role played by the mixed solvent composed of methanol and water in the formation of crystalline anatase. The boiling point of methanol at 65 °C is lower than water, which helps to increase the vapour pressure in an autoclave below 130 °C and thereby accelerates the formation of the crystalline anatase phase. It can be clearly observed in XRD patterns that the titania samples using a mixed solvent composed of methanol and water exhibit clearer and sharper anatase

peaks. This helps to effectively enhance the photocatalysis of such samples to a greater extent than the samples using water solvent and TiO<sub>2</sub>-P25 powder.

To evaluate the photocatalytic activity of titania nanotubes after calcination at various temperatures, the samples were treated at different temperatures when using various methanol–water ratios. The samples using methanol–water volume ratio of 30:70 were then selected and reviewed (figure 12). Photocatalytic activity of the calcined nanotube samples was observed to increase with increasing calcination temperature. When the calcination temperature was 300 °C, the photocatalytic activity reached a maximum (34%) which was higher than that of the samples composed of TiO<sub>2</sub>-P25 powder (23.5%) after an irradiation time of 120 min. However, groups of samples calcined at temperatures ranging from 100 to 400 °C, generally retained a high adsorption efficiency (adsorption yield of MB solution is from 36.4–47.2%); this can be ascribed to their higher  $S_{BET}$  and pore volumes (table 2). Moreover, as indicated by XRD analysis above, it has been shown that at a low calcination temperature, the anatase phase also appeared in relatively low amounts; this is beneficial to photocatalytic reactions. Compared with other samples, the sample calcined at 500 °C showed better crystallization of the anatase phase (see XRD pattern, figures 3 and 4). However, TEM images clearly show that the sample's structure collapsed into nanoparticles. This could be attributed to the sintering and growth of TiO<sub>2</sub> crystallites and the decrease in specific surface area and pore volume. Therefore, photocatalytic activity of the calcined samples decreased significantly.

The results indicate that the role of methanol solvent is very important in increasing the crystalline anatase content in the resulting particles. The results also show that using



**Figure 12.** Photodegradation ratio of MB under visible light irradiation: in case of using mixed solvent of methanol and water in volume ratio of 30:70 and calcined at different temperatures: (a) 300 °C; (b) 200 °C; (c) 100 °C; (d) 400 °C; (e) 500 °C and (f) TiO<sub>2</sub>-P25 powder.

methanol solvent allows for highly effective energy savings due to reduction in the synthesis and calcination temperature and an increase in photocatalytic efficiency.

#### 4. Conclusions

Titanate and titania nanotubes were synthesized by a simple solvothermal method at low temperature using a mixed solvent composed of methanol and water in various ratios at different calcination temperatures. The nanotubes were produced in methanol–water mixed solvent and their morphology was observed via SEM and TEM. XRD observations revealed that the methanol solvent played an important role in improving crystallization of the titania anatase phase. Various ratios of methanol to water affected the morphology and structure of the final product, as well as the photocatalytic performance in the degradation of MB dye.

The samples featuring methanol–water volume ratios of 10:90, 20:80 and 30:70 were observed to remain highly effective in adsorbing MB dye when the initial concentration was  $12 \text{ mg L}^{-1}$ . It was observed that the adsorption yield of MB solution is from 48.5 to 53.2% after 60 min stirring in the dark. When titania nanotubes formed by calcination at different temperatures were used, it was found that the crystalline phase, morphology, structure and photocatalytic activity are strongly dependent on the calcination temperature. The sample featuring methanol–water volume ratio of 30:70 achieved the highest photocatalytic efficiency, even when adsorbing MB in the dark and being irradiated by visible light. In this case, MB removal percentage equaled 34% after an irradiation time of 120 min. The photocatalytic performance of this sample was much higher than that of using 100% water solvent (24.7%) and  $\text{TiO}_2\text{-P25}$  powder (23.5%). This clearly demonstrates the important role of the mixed methanol solvent in the formation of the crystalline anatase phase, which contributed to increased photocatalytic efficiency.

For samples featuring methanol–water volume ratio of 30:70, the photocatalytic activity of the calcined nanotube samples increased with increasing calcination temperature. When the calcination temperature was  $300^\circ\text{C}$ , photocatalytic activity reached a maximum (34%) that was higher than that of  $\text{TiO}_2\text{-P25}$  powder. At  $500^\circ\text{C}$ , the sample showed better crystallization of the anatase phase. However, the sample was transformed into a particulate form, which decreased the photocatalytic activity of the calcined samples.

#### Acknowledgement

The authors wish to thank the National Science Council, NSC 99-2221-E-151-062 for their financial support of this work.

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