Hydrothermal synthesis of titanium dioxide nanotube with methylamine for photodegradation of Congo red

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Abstract. Titanium dioxide (TiO₂) nanotube photocatalyst is highly desired for the photodegradation of dye in wastewater treatment. A series of titanium dioxide nanotube photocatalysts were successfully synthesized using methylamine as N-ligand via hydrothermal treatment at different hydrothermal temperatures and durations. The effect of these two parameters on the photocatalytic activity of synthesized materials were investigated. TEM micrographs and XRD analysis depicted methylamine assisted the transformation of anatase TiO₂ nanoparticles to nanotube via the exfoliation of TiO₂ crystallite into layered sheet and promoted the curling of layered sheet. Hydrothermal temperature up to 180°C was able to fully transform the morphology of anatase TiO₂ nanoparticles into nanotube. The reaction duration was further modified. Fluorescence analysis showed that 24 h hydrothermal duration gave the slowest electron-hole recombination rate. DR-UV-Vis analysis indicated that the synthesized samples were active under UV region. The photocatalytic performance of the synthesized materials was tested in the photodegradation of Congo red under UV irradiation. The results suggested that among the materials synthesized, TiO₂ nanotube synthesized at 180°C, under 24 h hydrothermal duration appeared to be the most superior photocatalyst which gave the highest photocatalytic activity of 77%. Possible mechanism of the TiO₂ nanotube formation with methylamine as N-ligand is presented.

1. Introduction
Titanium dioxide (TiO₂) and TiO₂-based materials have been intensively investigated due to their excellent catalytic performance [1-5]. However, TiO₂ is suffering from its low surface area, hence leads to limited activity. Since last decade, TiO₂ nanotubes (NTs) have attracted much attraction as compared to the commonly used TiO₂ nanoparticles due to its excellent unique features, including high ion-exchangeability, large specific surface area and good photocatalytic activity [6]. The current developed fabrication methods of TiO₂ NT include the template-assisted method, sol-gel method, hydrothermal method, and electrochemical anodic oxidation [7-8]. Among these fabrication methods, hydrothermal fabrication is believed to be the most promising due to its environmentally friendly properties, simple setup and cheap apparatus is used. For the other methods, for instance, electrochemical anodic oxidation method, usage of extremely toxic aqueous hydrochloric acid solutions is needed for the anodization of titanium foil [9].

In this study, hydrothermal treatment method was used to synthesize TiO₂ nanotube (TNT). Although hydrothermal synthesis involves simple setup, every single step in the process from choice of
TiO₂ precursor to hydrothermal conditions and lastly the post-treatment process of TiO₂ NT is very important in determining the crystallography and morphology as well as the physical-chemical properties of the TiO₂ NT final products. The hydrothermal conditions include the temperature, hydrothermal time and concentration of reactant [3]. According to the study by Weng [10], increasing the hydrothermal time contributes to the lengthening of TNTs. When the hydrothermal duration exceeds 24 h, there is no further increase in the length of TNTs. From the other studies, however, it has been stated that the morphology of the synthesized products is dependent on the hydrothermal duration [11]. It seems that the hydrothermal duration plays an important role in affecting the morphology of TNTs formed which drives the author to further study on the effect of hydrothermal duration and temperature on the formation of TNTs in this study.

During the hydrothermal synthesis of TNTs, agglomeration of individual morphological form titanate into secondary particles occurs. Secondary particles include nanotubular bundles, nanofibers, nanofibers which are linked hierarchically and others [2]. Even though there were extensive studies on the effect of synthesizing condition on the geometry of single nanotube, there are few studies reported on the principles of controlling the agglomeration of nanotubes and treatment of the shape and geometry of secondary particles [12]. In addition, based on the study by Peng et al. [13], the -NH₂ functional group of DETA captured the Ti⁴⁺ in the solution hence facilitate crystal grow of TiO₂ to be formed uniformly on the carbon nanotube. Methylamine, which is also one of the N-atom bearing ligand, is expected to behave the same as DETA, holding the Ti⁴⁺ ion and could assist the titanate layer to curl up and thus promote the formation of TiO₂ NT in this research. Its effectiveness in helping the intermediate TiO₂ nanosheet to curl up, forming nanotubular structure is yet to be known. The mechanism for the formation of TiO₂ NT with methylamine as a N-bearing ligand was proposed in this research.

2. Experimental

2.1. Synthesis of titanium dioxide nanotube
TiO₂ NT was synthesized using hydrothermal method with the presence of methylamine. Commercial anatase titanium dioxide served as the Ti precursor while methylamine hydrochloride was used as N-ligand.

In a typical synthesis, methylamine hydrochloride was added to the 7 M NaOH aqueous solution, followed by the addition of TiO₂ into the reaction mixture based on the molar ratio TiO₂:CH₃NH₂ of 1:1. The reaction mixture was allowed to stir vigorously (1000 rpm) for one hour. Later, reaction mixture was transferred to a 100 mL Teflon-lined stainless-steel autoclave and kept in an electric oven at 130°C for 24 h. It should be noted that in order to ensure the desired structure to be formed successfully, any disturbance during the reaction, such as opening of the oven door, had to be prevented. After 24 h of hydrothermal duration, the autoclave was taken out and left to cool to room temperature. The white precipitate was obtained by centrifugation, washed thoroughly with sulphuric acid and double distilled water, then dried at 70°C overnight.

Experiment was repeated with different ratio titanium dioxide to methylamine of 1:1, 1:3, 1:5 and 1:8. The samples were notated as xM-TiO₂ NT-y-z, where x, y, and z represent the ratio of methylamine to TiO₂ and M represent methylamine, hydrothermal temperature and duration, respectively. The optimized ratio was then used to synthesize TiO₂ NT at different temperatures (130°C and 180°C) and different hydrothermal durations (6 h, 12 h and 24 h).

2.2. Characterization
The physical-chemical properties of synthesized TiO₂ NT were studied via characterization with Transmission Electron Spectrometer (TEM), X-ray diffractometer (XRD), Ultraviolet-Visible Diffuse Reflectance Spectrometer (DR-UV-Vis), and spectrofluorometer.

TEM (JEOL, JEM-2100F, 200 kV) was used to investigate the morphologic, crystallographic and compositional information on the TiO₂ samples. Meanwhile, the crystallinity and the crystal structure of the synthesized TiO₂ samples were examined via XRD (Bruker Advance D8 with Cu Kα radiation;
λ = 1.5406 Å; 40 kV, 40 mA). UV-Vis diffuse reflectance spectra of the prepared samples were evaluated using a UV-Vis spectrometer (Perkin-Elmer Lambda Lambda 35) equipped with a diffuse reflectance attachment with BaSO₄ coated 76 mm integration sphere as a reference material. The reflection in percentage was measured and presented by Kubalka-Munk function. Meanwhile, the electron-hole recombination rate was calculated using a spectrofluorometer (JASCO, FG-8500).

2.3. Photocatalytic testing

The synthesized TiO₂ anatase was tested for its photodegradation activity on Congo red under dark condition where the UV radiation is absent and normal condition where the UV radiation is present.

The photocatalytic activity of each of the synthesized TiO₂ NT was calculated by using the formula as follow:

\[
\text{Photodegradation activity} = \frac{C_0 - C_t}{C_0} \times 100\%
\]

where, \(C_0\) = Concentration of Congo red before reaction (ppm)
\(C_t\) = Concentration of Congo red after reaction (ppm)

3. Results and Discussion

3.1. Surface morphologies

Figure 1 shows the TEM micrographs of the synthesized samples. As shown, with the addition of methylamine, most of the structure of TiO₂ nanosheet had been fully transformed into nanotubes. Both the as-synthesized TiO₂ NT-130°C-24 h and 3M/TiO₂ NT-130°C-24 h had interplanar spacing of 0.35 nm, represented the (1 0 1) lattice plane of anatase TiO₂ [14]. Meanwhile, 3M/TiO₂ NT-130°C-24 h had one additional d-spacing of 0.64 nm, represented (001) lattice plane of nanotube [15].

Figure 1. (a) TEM images and (b) HRTEM image of as-synthesized TiO₂ NT-130°C-24 h; (c) and (d) HRTEM image of 3M/TiO₂ NT-130 ℃-24 h.
3.2. Surface morphologies

Figure 2(a) illustrates the XRD patterns of the methylamine modified titanium dioxide nanotube samples. As illustrated, the characteristic of anatase phase of titania could be observed clearly in all the samples at 2θ value of 25.35°, which attributed to the lattice plane (1 0 1) [16]. The intensity of the peak however, decreased as higher ratio of methylamine ligand was added to the titania. Peaks assigned to the tetragonal titania anatase phase were also observed at 37.90°, 53.90°, 54.05°, 55.10°, 62.85°, 68.85°, 70.25° and 75.20°, with lattice plane (0 0 4), (1 0 5), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0), and (2 1 5) respectively. As compared to the as-synthesized TiO$_2$ nanotube, samples modified with methylamine gave three feature peaks of Na$_2$Ti$_3$O$_7$ titanate at ~9.4°, 28.20°, and 48.15°, with lattice planes (0 0 2), (1 1 1), and (2 0 0), respectively. The calculated crystallite size of the synthesized samples decreased with the increasing molar ratio of methylamine and increased in crystallite size when the molar ratio reached 8. Possible explanation could be due to the promotion of crystal growth by eliminating the inter-crystallite pores.

Figure 2(b) shows the XRD patterns of materials synthesized at different hydrothermal temperatures, namely 130°C and 180°C. It can be seen that when the hydrothermal temperature was increased from 130°C to 180°C, the intensity of peaks corresponded to anatase phase of titania reduced and peaks corresponded to Na$_2$Ti$_3$O$_7$ type of titanate (JCPDS 31-1329) were observed with increasing intensity. Thus, it could be deduced that increase of hydrothermal temperature up to 180°C was able to fully transform the spherical morphology of anatase TiO$_2$ particle to nanotube shape. Meanwhile, the modification of reaction condition by varying the hydrothermal duration had insignificant changes within the samples. Increasing hydrothermal duration would not distort the nature of the synthesized materials.

3.3. Optical properties

Figure 3(a) illustrates the DR-UV-Vis spectra of the synthesized TiO$_2$ nanotubes. There were two absorption peaks located at 270 – 280 nm, which were contributed by amorphous Ti species in all the synthesized samples [17]. Also, an absorption peak at 320 nm was observed, which was associated to anatase TiO$_2$ [18]. The intensity of the absorption band at 270 nm decreased with increasing xM/TiO$_2$ ratio, while it was accompanied by an increased in the intensity of adsorption band at 320 nm. This proves that with an increasing amount of methylamine, amorphous TiO$_2$ could be reduced, transforming...
into crystalline anatase phase of TiO$_2$. Addition of methylamine increased the band gap energy of as-synthesized TiO$_2$ due to quantum size effect [19].

Figure 3(b) elucidates the DR UV-Vis spectra of the samples synthesized at different hydrothermal temperature, namely 130°C and 180°C. Increasing the hydrothermal temperature would increase the intensity of absorption band at 270 nm which assigned to amorphous Ti species and the absorption band at 320 nm which denoted the anatase TiO$_2$ was fully disappeared. It could be deduced that hydrothermal temperature of 180°C was able to fully transform the morphology of anatase TiO$_2$ particle into nanotube shape.

As for the modification of reaction condition based on hydrothermal duration (6 h, 12 h, 24 h), hydrothermal duration of 6 h and 12 h were too short for the complete formation of TiO$_2$ nanotube. As a result, mixture of unreacted nanoparticles, nanosheet and nanotube were present within the sample. The current findings strongly suggested that hydrothermal duration of 24 h was important for the complete transformation of spherical anatase TiO$_2$ nanoparticles into nanotube.

As for the fluorescence analysis, the fluorescence spectra of the as-synthesized TiO$_2$ and the best photocatalyst (3M/TiO$_2$ NT-130°C-24 h) were shown in Figure 3(c). With the addition of methylamine, the intensity of the peak decreased, denoting a decrease in the electron-hole recombination rate. A possible explanation to this is due to an increase in the separation effectiveness and longer lifetime of the photoinduced charge carriers [20]. It could be suggested that addition of methylamine as N-ligand suppressed the electron-hole recombination rate by increasing their lifetime.

As the hydrothermal temperature increased up to 180°C, the electron-hole recombination rate was greatly suppressed as evidence in Figure 3(d). Possible explanation could be the crystalline nature of the nanotube enable smooth, fast and efficient electron transfer to the surface hence retarded the electron-hole recombination rate [21]. Hydrothermal duration of 24 h was optimum for the complete transformation of nanoparticles to nanotube. The fluorescence intensity of 3M/TiO$_2$ NT-180°C-24 h was the lowest as compared to those synthesized at 6 h and 12 h, denoting the slowest recombination rate.
3.4. Photocatalytic activity

The photocatalytic performance of the synthesized samples was evaluated via photodegradation of Congo red dye under dark condition and with UV irradiation. The obtained absorbance at 498 nm was used to calculate the photodegradation efficiency of the synthesized samples. As illustrated in Table 1, the photocatalytic activities of the xM/TiO₂ (x = 1, 3, 5, 8) were higher than the as-synthesized TiO₂. The addition of methylamine increased the photocatalytic activity of TiO₂ by enhancing nanotubes formation. Methylamine might have assisted the scrolling of the intermediate nanosheet, forming nanotube. Sample 3M/TiO₂ had the best photocatalytic activity of 69.4% which could be attributed to the lowest electron-hole recombination rate.

Table 1. Photodegradation of Congo red over samples xM/TiO₂-130°C-24 h.

| x  | Photocatalytic activity (%) |
|----|-----------------------------|
| 1  | 68.2                        |
| 3  | 69.4                        |
| 5  | 60.5                        |
| 8  | 58.5                        |

Table 2 elucidates the photocatalytic activity of samples that were synthesized at different hydrothermal durations, namely 6 h and 24 h, under constant hydrothermal temperature at 180°C. It is demonstrated clearly in Table 2 that 3M/TiO₂ NT-180°C-24 h had a higher photocatalytic activity as compared to the sample synthesized at 6 h, which could be due to the reduction in electron-hole recombination rate of nanotube. The photocatalytic activity of the samples decreased drastically with hydrothermal duration, around 19%. The increase in photocatalytic activity of TiO₂ NT might be attributed to the higher amount of nanotube formation from mixture of unreacted particle, nanosheet and nanotube. Apparently, hydrothermal duration of 6 h was too short for the TiO₂ NT formation. Larger amount of nanotube could be formed at 24 h hydrothermal duration with the presence of methylamine that facilitated in scrolling up the edge of intermediate nanosheet.
The synthesis of titanium dioxide nanotube using methylamine as N-ligand via hydrothermal method was conducted successfully. Effect of different temperature and hydrothermal duration on the properties and photocatalytic activity were evaluated. At higher hydrothermal temperature, up to 180 °C, there was a reduction in the electron-hole recombination rate as all the anatase TiO\textsubscript{2} nanoparticles had transformed into nanotube. On the other hand, hydrothermal duration of 24 h was needed to allow complete transformation of spherical anatase TiO\textsubscript{2} nanoparticles to nanotube shape. Sample 3M/TiO\textsubscript{2} NT-180°C-24 h appeared to be the best photocatalyst due to its low electron-hole recombination rate, giving photocatalytic activity of 77.1% in photodegradation of Congo red organic dye. Evidently, methylamine was vital in assisting the complete TiO\textsubscript{2} nanotube formation and, hydrothermal temperature and hydrothermal duration were optimum at 180 °C and 24 h, respectively.

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