Synthesis of N-doped TiO₂ Nanoparticle by Solvothermal Method for Dye Treatment

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Abstract. Nitrogen-doped titanium dioxide (NT) was synthesized by solvothermal method. Titanium (IV) butoxide (TBOT) was used as a titanium source and diethyleneamine (DEA) was used as a nitrogen source. The DEA concentration was fixed at 5% mol. The effect of the synthesized temperatures was studied (150 º C to 200 º C). The characterization results showed that the XRD patterns of NT synthesized by solvothermal method exhibited only anatase structure of TiO₂ at 25.56º (101), 37.76º (004), 48.04º (200), 48.18º (105), 54.06º (211), 55.24º (204), 62.76º (116), 69.04º (220), 70.32º (215) and 75.30º (303). The crystallite sizes of NT (13-14 nm) were smaller than that of TiO₂ (22.39 nm) while the surface area of NT (31- 47 m²g⁻¹) was larger than that of TiO₂ (6.42 m²g⁻¹). This indicated that doping N on TiO₂ had a significant effect on crystallite size and surface area of TiO₂. The photocatalytic activities of NT were evaluated by decolorization of 10⁻⁵ M methylene blue (MB) under LED visible light irradiation. The result showed that the photocatalytic performance of TiO₂ was significantly improved by N dopant with the efficiency of 90%. However, the synthesized temperatures had no significant effect on the physical properties and the photocatalytic reactivity of NT.

1. Introduction
TiO₂ is commonly used as a catalyst for the photocatalytic degradation of organic pollutants. It has interesting physical and chemical properties such as good stability, low cost and non-toxicity [1]. Therefore, the TiO₂ is mostly used for environmental treatment such as air purification [2], water treatment [3], self-cleaning [4] and degradation of organic pollutants [5,6]. However, TiO₂ must be activated only under ultraviolet light for photocatalytic activities because it has wide band gap energy about 3.2 eV. Several researchers studied the enhancement of TiO₂ efficiency under visible light by doping non-metal and metal, which are carbon (C), phosphorus (P), bromine (B) and nitrogen (N) for non-metal dopants and silver (Ag), iron (Fe) and copper (Cu) for metal dopants.

Lee, et al. (2005) studied the photocatalytic reactivity of Ag doped TiO₂ by sol-gel method. The photocatalytic efficiency of the doped photocatalyst was examined by p-nitrophenol treatment under UV light irradiation. It was reported that 1 mmol of AgNO₃ provided the highest photocatalytic efficiency compared to the bare TiO₂ [7]. Tongon, et al. (2014) prepared Ag doped TiO₂ and
incorporated into as-synthesized MCM-41 by microwave assisted sol-gel technique. Then, the nanocomposite was coated on the glass substrate by dip coating. The performance of the thin film was tested by MB dye reduction under UV and visible light irradiation. The optimal Ag/Ti/Si molar ratio was 0.1/1/2, which gave the highest photocatalytic efficiency about 81% under UV and 30% under visible light irradiation [8].

Although metal doping can reduce the band gap of TiO₂, metal dopant can act as a recombination site which reduces the photocatalytic reactivity [9-13]. Non-metal doping is another attractive method. He, et al. (2016) prepared N-doped TiO₂ by solvothermal method using tetrabutyl titanate and titanium sulphate as silica sources and trimethyamine and diethylene-triamine as nitrogen sources. The photocatalysis efficiency was evaluated by methyl orange (MO) reduction under visible light irradiation. The result indicated that N-doped TiO₂ prepared from titanium sulphate and diethylenetriamine gave high photocatalytic degradation efficiency of MO about 90% [14].

Yang, et al. (2010) prepared N-doped anatase TiO₂ by solvothermal method and used titanium butoxide and ethylenediamine as a titanium source and a nitrogen source, respectively. The photocatalysis efficiency of N-doped TiO₂ was tested by methylene blue (MB) and methyl orange (MO) decolorization under visible light irradiation. It was found that N-doped TiO₂ (N:Ti molar ratio of 1:1) gave the highest decolorization rate about 92% [15].

Tee, et al. (2018) modified mesoporous TiO₂ by N-doping. The studied parameters were molar ratio of nitrogen and titanium (N:Ti), synthesized temperatures and calcined temperatures. The optimal condition of N-doped TiO₂ synthesis was N:Ti molar ratio of 1:1, synthesized temperatures at 175 °C to 200 °C and calcined temperatures at 550 °C. The performance of N-doped TiO₂ was tested by MB and MO decolorization under visible light irradiation. N-doped TiO₂ gave the highest decolorization rate of MB and MO about 98% and 90%, respectively. According to the previous studies, nitrogen doping was widely used to enhance the photocatalytic properties of TiO₂ [16].

In the recent years, solvothermal method become more attractive for the synthesis of N-doped TiO₂. Because this method uses a solvent (aqueous and non-aqueous solution) and a temperature higher than that of the boiling point of a solvent in a closed system to synthesise highly reactive TiO₂ [17]. The advantages of this method are controllable crystallite size and tailor-made morphology by varying synthesis parameters such as temperature, pressure, process duration and the pH value of the solution [18].

Therefore, this study focused on the improvement of the photocatalytic reactivity of TiO₂ by doping nitrogen via solvothermal method. The effect of synthesis temperatures on the photocatalytic reactivity was studies. Additionally, the photocatalytic decolorization of methylene blue by N-doped TiO₂ under LED visible light irradiation was examined.

2. Experimental

2.1. Material

All chemicals used in this research were analytical grade. Titanium (IV) butoxide (TBOT, 97%, Sigma-Aldrich), and diethylenamine (DEA, Merck) were used as sources of titanium and nitrogen, respectively. Ethanol (Merck) was used as a solvent.

2.2. Synthesis of N-doped TiO₂ and TiO₂

N doped TiO₂ were prepared by solvothermal method. N-doped TiO₂ was prepared by mixing TBOT and ethanol, then the solution was stirred for 30 min. Deionize water and nitric acid were added into the TBOT solution with the molar ratio of 1Ti(OC₄H₉)₄:18C₂H₄OH:2H₂O:0.2HNO₃. After that, the mixture was added with 5% mol of DEA. Then, the solution was stirred for 30 min at room temperature. After that, the mixture was poured into a Teflon-lined stainless-steel autoclave and heated at 150 °C (NT-150), 170 °C (NT-170), 190 °C (NT-190) and 200 °C (NT-200) °C for 3 h. The suspended solid was centrifuged and washed by ethanol and deionized water. The powder of N-doped TiO₂ was dried by oven at 110 °C overnight. Finally, the powder was calcined at 450 °C for 3 h.
TiO$_2$ was prepared by solvothermal method (TiO$_2$-150). TBOT was used for titanium source. TBOT and ethanol were mixed and then added deionize water and nitric acid. Then, the solution was stirred for 2 h at room temperature. After that, the mixture was poured into a Teflon-lined stainless-steel autoclave and heated at 150ºC for 3 h. The suspended solid was centrifuged and washed by ethanol and deionized water. The TiO$_2$ powder was dried by oven at 110 ºC overnight. Finally, the powder was calcined at 450 ºC for 3 h.

2.3. Characterization of N-doped TiO$_2$

The crystalline structure of the synthesized N-doped TiO$_2$ was analyzed by X-ray diffractometer (XRD: Rigaku TTRAX III). The porosity was analysed by Brunauer-Emmet-Teller surface analyzer (BET:Belsorp mini II, Osaka) and the morphology was examined by scanning electron microscope (SEM:JSM-5420LV, JOEL). Finally, the absorption edge and band gap energy were analyzed by UV-vis NIR spectrophotometer (Perkin Elmer, Lambda 950).

2.4. Photocatalytic decolorization of methylene blue (MB)

The photocatalytic reactivity of N-doped TiO$_2$ was evaluated by the decolorization of MB under visible light irradiation (>400 nm). A LED lamp of 15 W was used as a light source for testing. 1g of the N-doped TiO$_2$ powder was added into 100 ml of $10^{-5}$ MB solution. Before open LED light, the suspension was put in the reactor and stirred until dye adsorption was completed. After that, the LED light was turned on. The dye solution was evaluated by UV-vis spectrophotometry at wavelength of 664 nm (λ$_{max}$) every 30 min until the concentration of MB was stable.

3. Results and discussion

3.1. Crystalline structure

Figure 1 shows the XRD patterns of N-doped TiO$_2$ prepared by different temperatures. The results show that all N-doped TiO$_2$ samples exhibit similar diffraction peaks appeared at 25.56º, 37.76º, 48.04º, 48.18º, 54.06º, 55.24º, 62.76º, 69.04º, 70.32º and 75.30º. These peaks represent to (101), (004), (200), (105), (211), (204), (116), (220), (215) and (303) planes, respectively, which is anatase structure of TiO$_2$ as followed Joint Committee on Powder Diffraction Standard (JCPDS no. 84-1286). All peaks of N-doped TiO$_2$ are slightly border than the peaks of bare TiO$_2$ (undoped) due to incorporating N atom into the anatase TiO$_2$ structure. The average crystallite size of the samples was calculated by Debye-Scherrer equation based on the strong peak (101). It was found that the crystallite sizes of N-doped TiO$_2$ were smaller than that of undoped TiO$_2$ (see Table 1). This indicated that N doping into TiO$_2$ anatase structure had significant effect on crystallites size [16]. However, these results can be concluded that the synthesized temperatures had no effect on crystallites size.

3.2. Morphology

SEM images illustrate the morphology of N-doped TiO$_2$ prepared by different temperatures compared with the undoped TiO$_2$ as shown in Figure 2. All samples exhibit the agglomerated spherical particles. The particle size of N-doped TiO$_2$ is approximately 0.02 μm while that of undoped TiO$_2$ is approximately 0.06 μm. The particle size of N-doped TiO$_2$ is smaller than that of undoped TiO$_2$. Among all doped samples, NT-200 had very small and well-dispersed particles, compared with the others.
Figure 1. The XRD patterns of N-doped TiO$_2$ and undoped TiO$_2$ prepared by solvothermal with different synthesized temperatures.

Table 1. The crystallite sizes of N-doped TiO$_2$ and undoped TiO$_2$ prepared by solvothermal with different synthesized temperatures.

| Sample   | Crystallite size (nm) |
|----------|-----------------------|
| TiO$_2$-150 | 22.39                |
| NT-150    | 14.67                 |
| NT-170    | 13.72                 |
| NT-190    | 13.72                 |
| NT-200    | 14.18                 |

a) TiO$_2$-150
Figure 2. SEM images N-doped TiO$_2$ and undoped TiO$_2$ prepared by solvothermal with different synthesized temperatures.

3.3. Porosity

The specific surface area, total pore volume and average pore diameter of N-doped TiO$_2$ prepared by different temperatures were analyzed by BET technique as shown in Table 2. The specific surface area and total pore volume of the N-doped TiO$_2$ samples were significantly increased when compared with the undoped TiO$_2$. This is caused by the incorporation of nitrogen in anatase TiO$_2$ structure. Nitrogen atoms could interfere the growth of anatase TiO$_2$ crystals leading to the decrease of crystallite size. The NT-190 and NT-200 had larger specific surface area than the NT-150 and NT-170. Figure 3 presents the N$_2$ adsorption-desorption isotherms of N-doped TiO$_2$ which are identified as type IV isotherms according to the IUPAC classification [16]. It was indicated that N-doped TiO$_2$ was classified as a mesoporous material (diameter in the range of 2-50 nm) with uniform pore size. This result is agreement with the calculated crystallite sizes as discussed previously.

Table 2. Porosity N-doped TiO$_2$ and undoped TiO$_2$ prepared by solvothermal with different synthesized temperatures.

| Sample   | Specific surface area (m$^2$ g$^{-1}$) | Total pore volume (cm$^3$ g$^{-1}$) | Average pore diameter (nm) |
|----------|----------------------------------------|-----------------------------------|---------------------------|
| TiO$_2$-150 | 6.42                                   | 0.02                              | 12.94                     |
| NT-150   | 38.16                                  | 0.15                              | 15.29                     |
| NT-170   | 31.96                                  | 0.14                              | 16.94                     |
| NT-190   | 47.08                                  | 0.15                              | 12.65                     |
| NT-200   | 45.06                                  | 0.14                              | 12.49                     |
Figure 3. $N_2$ adsorption-desorption isotherm of N-doped TiO$_2$ prepared by solvothermal with different synthesized temperatures.

3.4. Absorption edge and band gap energy

Figure 4 shows the UV-visible adsorption spectra of N-doped TiO$_2$ and the undoped TiO$_2$ prepared by different temperatures. The adsorption edges of the doped samples were not shifted to higher wavelength, resulting to not decrease of band gap energy. The band gap energy of N-doped TiO$_2$ and the undoped TiO$_2$ were 3.07 eV. However, the change of synthesis temperatures did not have the significant effect on the band gap energy.

Figure 4. UV-vis absorption spectra N-doped TiO$_2$ and undoped TiO$_2$ prepared by solvothermal with different synthesized temperatures.
3.5. Photocatalytic activity

The photocatalytic reactivity of doped and undoped TiO$_2$ was tested by decolorization of methylene blue (MB) under LED visible light irradiation. The results were shown in Figure 5 and 6. The decolorization efficiency of undoped TiO$_2$ was 23% within 300 min. While that of NT-150, NT-170, NT-190 and NT-200 were 89, 85, 84 and 92%, respectively within 500 min. It was found that N dopant could enhance the photocatalytic reactivity of TiO$_2$. Even though the NT-200 had the highest MB decolorization efficiency, its efficiency was not significantly different from the other doped samples. Thus, this paper recommended NT-150 as the promising photocatalyst.

The photocatalytic mechanism of N-doped TiO$_2$ was shown in Figure 7. The role of N atom was creating mid energy band gap above valence band of TiO$_2$. As a result, the band gap energy was reduced, and the electrons could excited under visible light irradiation. The excited electrons in valence band move to conduction band. This moving creates electron-hole and leaves a hole in valence band. When electron-hole and hole react with oxygen and water (H$_2$O) in atmosphere to produce super dioxide (O$_2^-$) and hydroxyl radical (·OH). The super dioxide and hydroxyl radical can oxidize the molecules of MB. Finally, carbon dioxide (CO$_2$), water and intermediate product are formed.

![Figure 5. MB decolorization under visible light irradiation by N-doped TiO$_2$ and undoped TiO$_2$ prepared by solvothermal with different synthesized temperatures.](image-url)
Figure 6. MB decolorization efficiency of N-doped TiO$_2$ and undoped TiO$_2$ prepared by solvothermal with different synthesized temperatures under visible light.

Figure 7. The mechanism of photocatalytic reaction of N-doped TiO$_2$. 
4. Conclusion
The photocatalytic reactivity of TiO\textsubscript{2} was successfully enhanced by N dopant via solvothermal method. The synthesized temperature at 150°C was recommended as the optimal condition to prepare N-doped TiO\textsubscript{2}. N dopant could reduce the band gap energy, decrease crystallite size and increase surface area of TiO\textsubscript{2}.

5. References
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