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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 °C to 200 °C). The characterization results showed that the XRD patterns of NT synthesized by solvothermal method exhibited only anatase structure of TiO₂ at 25.56 °(101), 37.76 °(004), 48.04 °(200), 48.18 °(105), 54.06 °(211), 55.24 °(204), 62.76 °(116), 69.04 °(220), 70.32 °(215) and 75.30 °(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 TiO_2 , 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 TiO_2 by solvothermal method using tetrabutyl titanate and titanium sulphate as silica sources and trimethylamine, triethanolamine 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 TiO_2 prepared from titanium sulphate and diethylenetriamine gave high photocatalytic degradation efficiency of MO about 90% [14].

Yang, et al. (2010) prepared N-doped anatase TiO_2 by solvothermal method and used titanium butoxide and ethylenediamine as a titanium source and a nitrogen source, respectively. The photocatalysis efficiency of N-doped TiO_2 was tested by methylene blue (MB) and methyl orange (MO) decolorization under visible light irradiation. It was found that N-doped TiO_2 (N:Ti molar ratio of 1:1) gave the highest decolorization rate about 92% [15].

Toe, et al. (2018) modified mesoporous TiO_2 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 TiO_2 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 TiO_2 was tested by MB and MO decolorization under visible light irradiation. N-doped TiO_2 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 TiO_2 [16].

In the recent years, solvothermal method become more attractive for the synthesis of N-doped TiO_2 . 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 synthesize highly reactive TiO_2 [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 TiO_2 by doping nitrogen via solvothermal method. The effect of synthesis temperatures on the photocatalytic reactivity was studied. Additionally, the photocatalytic decolorization of methylene blue by N-doped TiO_2 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 diethyleneamine (DEA, Merck) were used as sources of titanium and nitrogen, respectively. Ethanol (Merck) was used as a solvent.

2.2. Synthesis of N-doped TiO_2 and TiO_2

N doped TiO_2 were prepared by solvothermal method. N-doped TiO_2 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 $1\text{Ti}(\text{OC}_4\text{H}_9)_4:18\text{C}_2\text{H}_5\text{OH}:2\text{H}_2\text{O}:0.2\text{HNO}_3$. 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) for 3 h. The suspended solid was centrifuged and washed by ethanol and deionized water. The powder of N-doped TiO_2 was dried by oven at 110 °C overnight. Finally, the powder was calcined at 450 °C for 3 h.

TiO₂ was prepared by solvothermal method (TiO₂-150). TBOT was used for titanium source. TBOT and ethanol were mixed and then added deionized 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 150 °C for 3 h. The suspended solid was centrifuged and washed by ethanol and deionized water. The TiO₂ powder was dried by oven at 110 °C overnight. Finally, the powder was calcined at 450 °C for 3 h.

2.3. Characterization of N-doped TiO₂

The crystalline structure of the synthesized N-doped TiO₂ was analyzed by X-ray diffractometer (XRD: Rigaku TTRAX III). The porosity was analysed by Brunauer-Emmett-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 TiO₂ 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. 1 g of the N-doped TiO₂ powder was added into 100 ml of 10⁻⁵ M 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 TiO₂ prepared by different temperatures. The results show that all N-doped TiO₂ samples exhibit similar diffraction peaks appeared at 25.56°, 37.76°, 48.04°, 48.18°, 54.06°, 55.24°, 62.76°, 69.04°, 70.32° and 75.30°. These peaks represent to (101), (004), (200), (105), (211), (204), (116), (220), (215) and (303) planes, respectively, which is anatase structure of TiO₂ as followed Joint Committee on Powder Diffraction Standard (JCPDS no. 84-1286). All peaks of N-doped TiO₂ are slightly broader than the peaks of bare TiO₂ (undoped) due to incorporating N atom into the anatase TiO₂ 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 TiO₂ were smaller than that of undoped TiO₂ (see Table 1). This indicated that N doping into TiO₂ anatase structure had significant effect on crystallite size [16]. However, these results can be concluded that the synthesized temperatures had no effect on crystallite size.

3.2. Morphology

SEM images illustrate the morphology of N-doped TiO₂ prepared by different temperatures compared with the undoped TiO₂ as shown in Figure 2. All samples exhibit the agglomerated spherical particles. The particle size of N-doped TiO₂ is approximately 0.02 µm while that of undoped TiO₂ is approximately 0.06 µm. The particle size of N-doped TiO₂ is smaller than that of undoped TiO₂. Among all doped samples, NT-200 had very small and well-dispersed particles, compared with the others.

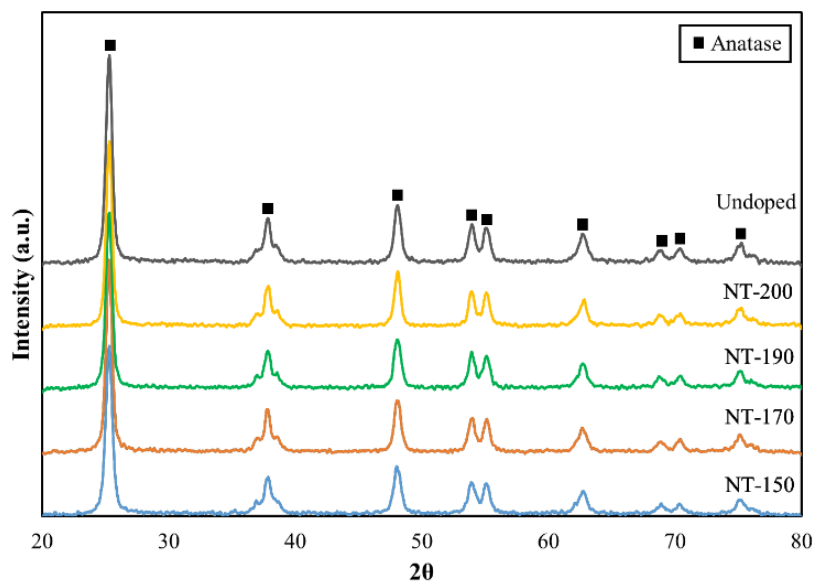
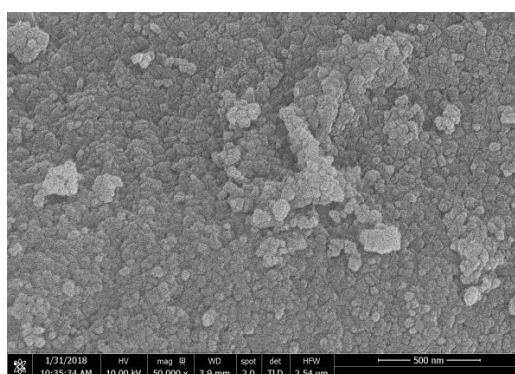


Figure 1. The XRD patterns of N-doped TiO_2 and undoped TiO_2 prepared by solvothermal with different synthesized temperatures

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

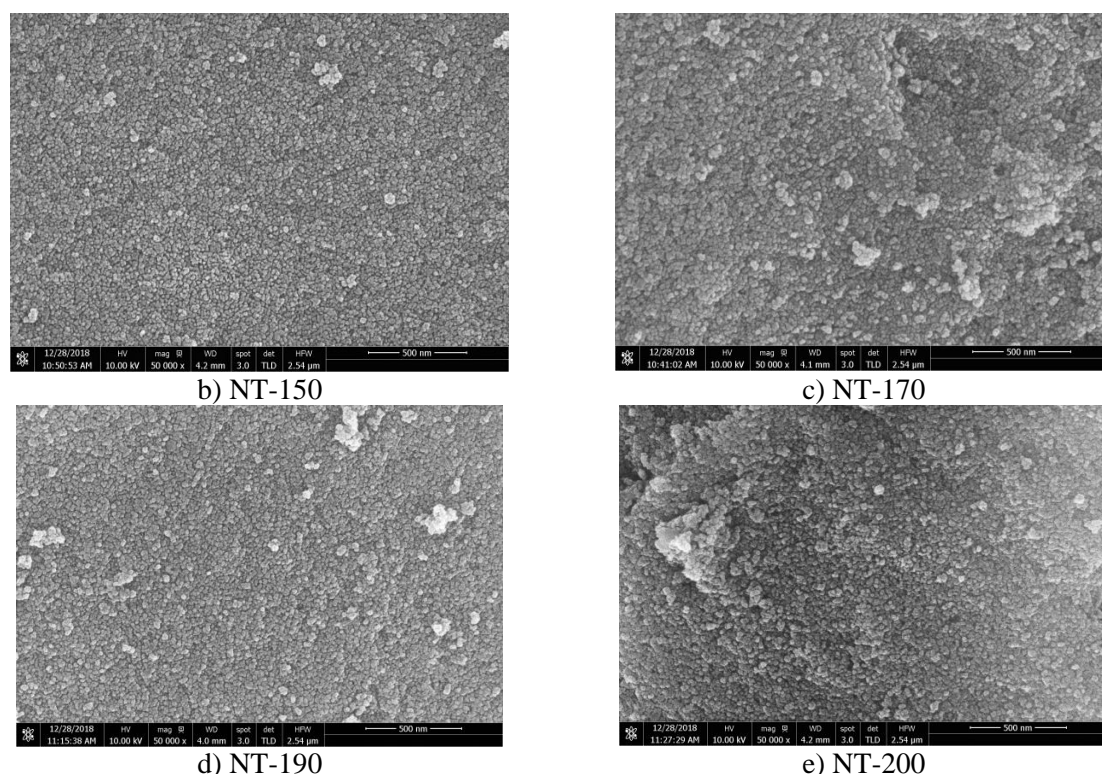


Figure 2. SEM images N-doped TiO₂ and undoped TiO₂ prepared by solvothermal with different synthesized temperatures.

3.3. Porosity

The specific surface area, total pore volume and average pore diameter of N-doped TiO₂ 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 TiO₂ samples were significantly increased when compared with the undoped TiO₂. This is caused by the incorporation of nitrogen in anatase TiO₂ structure. Nitrogen atoms could interfere the growth of anatase TiO₂ 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 N₂ adsorption-desorption isotherms of N-doped TiO₂ which are identified as type IV isotherms according to the IUPAC classification [16]. It was indicated that N-doped TiO₂ 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 TiO₂ and undoped TiO₂ 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

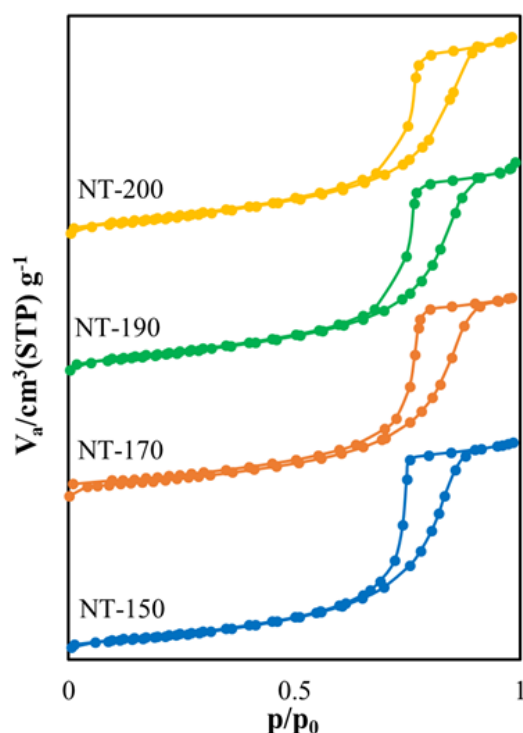


Figure 3. N_2 adsorption-desorption isotherm of N-doped TiO_2 prepared by solvothermal with different synthesized temperatures.

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.

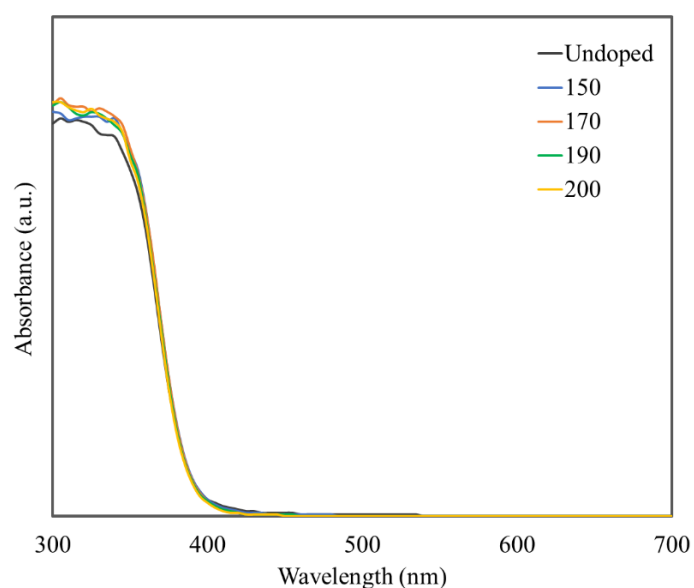


Figure 4. UV-vis absorption spectra N-doped TiO_2 and undoped TiO_2 prepared by solvothermal with different synthesized temperatures.

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_2O) in atmosphere to produce super dioxide (O_2^-) and hydroxyl radical ($\cdot\text{OH}$). The super dioxide and hydroxyl radical can oxidize the molecules of MB. Finally, carbon dioxide (CO_2), water and intermediate product are formed.

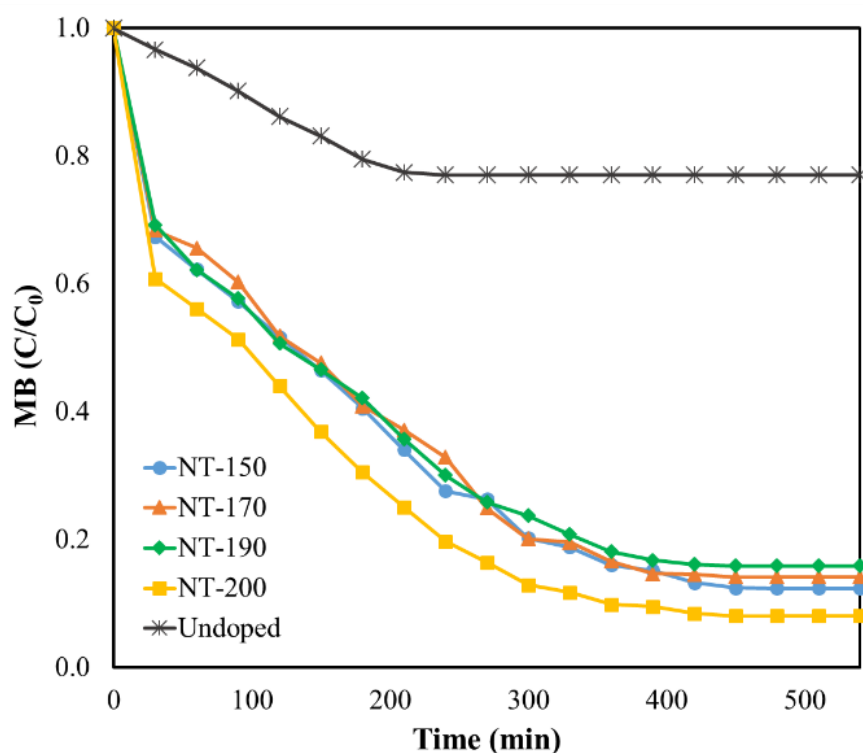


Figure 5. MB decolorization under visible light irradiation by N-doped TiO_2 and undoped TiO_2 prepared by solvothermal with different synthesized temperatures.

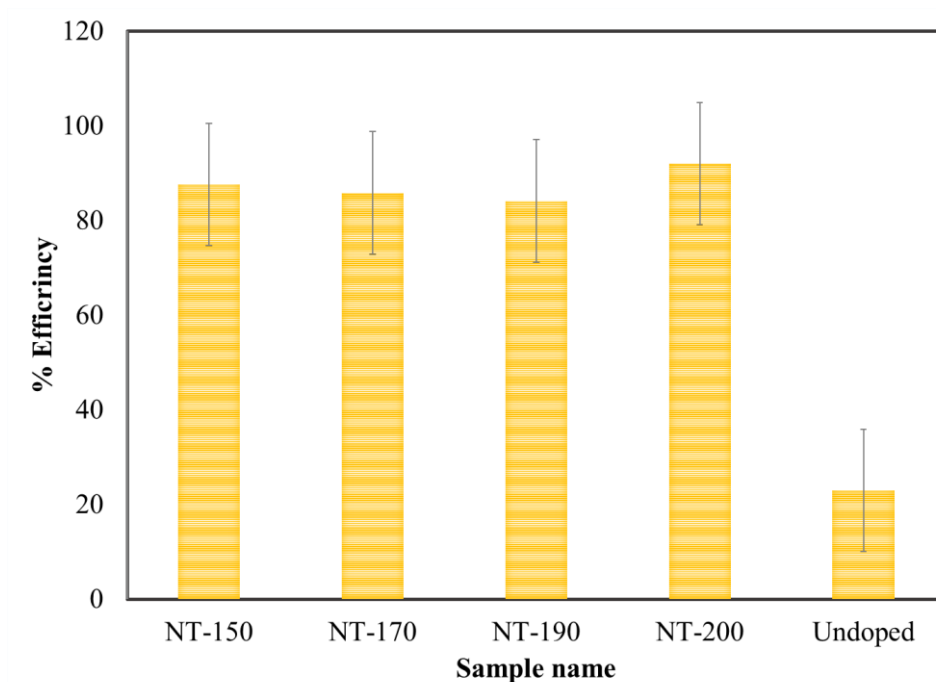


Figure 6. MB decolorization efficiency of N-doped TiO_2 and undoped TiO_2 prepared by solvothermal with different synthesized temperatures under visible light.

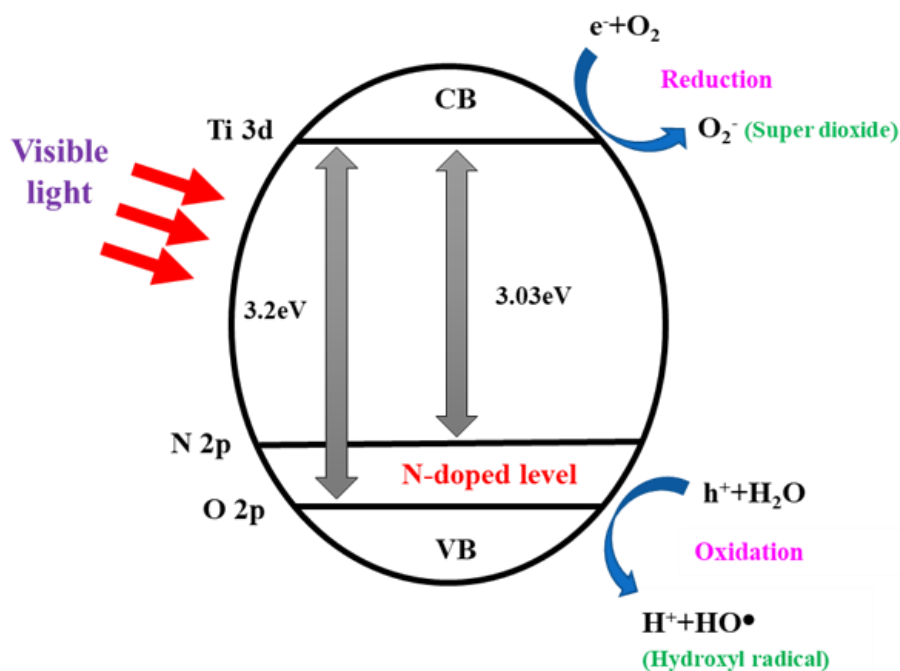


Figure 7. The mechanism of photocatalytic reaction of N-doped TiO_2 .

4. Conclusion

The photocatalytic reactivity of TiO₂ 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 TiO₂. N dopant could reduce the band gap energy, decrease crystallite size and increase surface area of TiO₂.

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