

Degradation of Methyl Orange Using N-TiO₂ Synthesized via Hydrothermal Treatment

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ABSTRACT. In this work, urea (0.1 to 1.7 wt.%) is incorporated with TiO₂ using hydrothermal treatment for 3 hours at temperatures of 180°C. The influence of urea content on the crystalline TiO₂ and their photocatalytic activity are investigated. The samples are characterized by using X-ray diffraction (XRD), energy dispersive X-ray (EDX), field emission scanning electron microscope (FESEM) and UV-Visible spectroscopy (UV-Vis). XRD results indicate that all samples are anatase phase while FESEM images shows agglomeration with average grain size approximately of 30 to 46 nm. The photocatalytic activity shows that TiO₂ with 0.5 wt.% of urea give the highest performance with 67% degradation after 4 hours visible light irradiation.

Keywords: TiO₂, Hydrothermal, Photocatalytic activity, Methyl orange;

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1. INTRODUCTION

One of the biggest issues in the world nowadays is air pollution. The polluted air can contribute to the unhealthy environment resulting to chronic diseases such as heart disease, lung cancer, and both chronic and acute respiratory diseases, including asthma [1,2]. World health organization(WHO) reported that 92% of the world population was living in places where the WHO air quality guidelines levels were not met. Ambient (outdoor air pollution) in both cities and rural areas was estimated to cause 3 million premature deaths worldwide in 2012 [3]. In order to address this issue, many researches have been conducted such as the used of ozonation [4], bio-monitoring [5] advanced oxidation process (AOP) and others. Among these, AOP is an environmental friendly technology for air purification as it can degrade and recalcitrant organic compounds into harmless materials. AOPs are based on the production of highly reactive and oxidizing hydroxyl radical ([•]OH) with a potential oxidation of 2.85V [6]. Photocatalysis is one of AOP technology that are widely used to detoxify organic pollutants in air and water [7-9]. The complex organic compounds can be break down by the generation of potent oxidation radicals such as [•]OH and O₂^{•-} [10].

TiO₂ is widely used as photocatalyst as it has the highest stability, high ultraviolet absorption, commercial availability and cheap. Furthermore, TiO₂ has high photoactivity and very suitable to use for removing pollutants in water and air. Despite the promising properties, TiO₂ application is limited to the UV region which only 4% of the entire solar system whereas 45% of the solar energy corresponds to the visible light. More practical application can be possible if the photocatalytic active region can be expanded to the visible

light region (400-700 nm), and the photoenergy can be used more efficiently. TiO₂ doped with metal and nonmetal element within certain limits can prolong the lifetime charge carriers of TiO₂ and change the optical properties towards visible light region [11-13]. In general, the TiO₂ doped showed higher photocatalytic activities compared than the pure ones.

In this work, we introduces a novel ceramic processing technology for the preparation of photocatalytic materials. The process involves the use of urea with various content (0.1 to 1.7 wt.%) incorporated with TiO₂ via hydrothermal treatment to obtain a nanostructure product. In addition, this paper describes the characteristic of N-TiO₂ and their performance as photocatalysts to degrade methyl orange dye compound under visible irradiation.

2. MATERIALS AND METHODS

The N-TiO₂ was synthesized using a modification procedure in previous study [14]. A determined urea mass was dissolved in water and stirred until complete dissolution. Titanium isopropoxide was dissolved in isopropanol alcohol and distilled water to obtain a 1 M solution. A determined volume of urea solution was drop wise added to the mixture under vigorous stirring and subsequently followed by hydrothermal treatment for 3 hours at temperatures of 180°C. The obtained solid was separated and dried at 80°C overnight. TiO₂ without nitrogen was also synthesized by the same procedure without the presence of urea to produce the hydrolysis of the alkoxide. The X-ray diffraction (XRD) measurements were performed using Bruker D8 Advance with CuK α as the X-ray source. The crystallite sizes of samples were calculated using Debye-Scherrer equation with correction for instrumental line broadening. The morphologies of the samples were observed by using high resolution field emission environmental scanning electron microscope (FESEM, JSM-7600F). The optical properties of samples were measured on a Shimadzu UV-VIS spectrometer (UV-1800) in the wavelength of 300-800 nm.

The photocatalytic activity of as-prepared N-TiO₂ were evaluated by degradation of methyl orange (MO) under visible light. A metal halogen lamp was used as light source and a UV-filter was employed to eliminate spectral range radiation below 400 nm. 5 mg of the as-prepared sample were dispersed and stirred in 10 ppm MO in the dark. After that, the solutions were irradiated up to 4 hours and the aliquot samples were collected in every one hour interval time. The concentration of degraded MO was measured by means of its corresponding to absorption intensity.

3. RESULTS AND DISCUSSION

The phase structure and purity of the as-prepared samples are determined by using XRD. Fig. 1 shows the XRD patterns of TiO₂ and N-TiO₂ synthesized via hydrothermal treatment. From Fig. 1, all the peak at an angle 2 θ (20 < 2 θ < 90) are anatase phase, corresponding to no. JCPDS: 00-021-1272. The peaks are located at 25.3°, 37.8°, 48.1°, 53.9°, 55.1°, 62.7°, and 68.8°, corresponding to the plane (101), (004), (200), (105), (211), (204), (116), and (220), respectively. The size of the crystallites are summarized in Table 1 and calculated by using Debye-Scherrer equation as shown in Eq.1.

$$d = \frac{\lambda k}{\beta \cos \theta} \quad (1)$$

Where d is the crystallite size, θ is the Bragg angle, β is the diffraction peak width at half of the maximum intensity, λ is the X-ray wavelength which is 0.15406 nm and k represents as constant form factor which is 0.89. It is found that the crystallite size of TiO₂ was decreased from 25.3 nm to 8.5 nm. The crystallite size was decreased due to the incorporation of N with TiO₂ which is an agreement with other result in previous study [15]. Furthermore, the ionic radius of N³⁻ (0.171 nm) is close to that of O²⁻ (0.144 nm), so N³⁻ can be incorporated into the TiO₂ lattice by substitution of O²⁻.

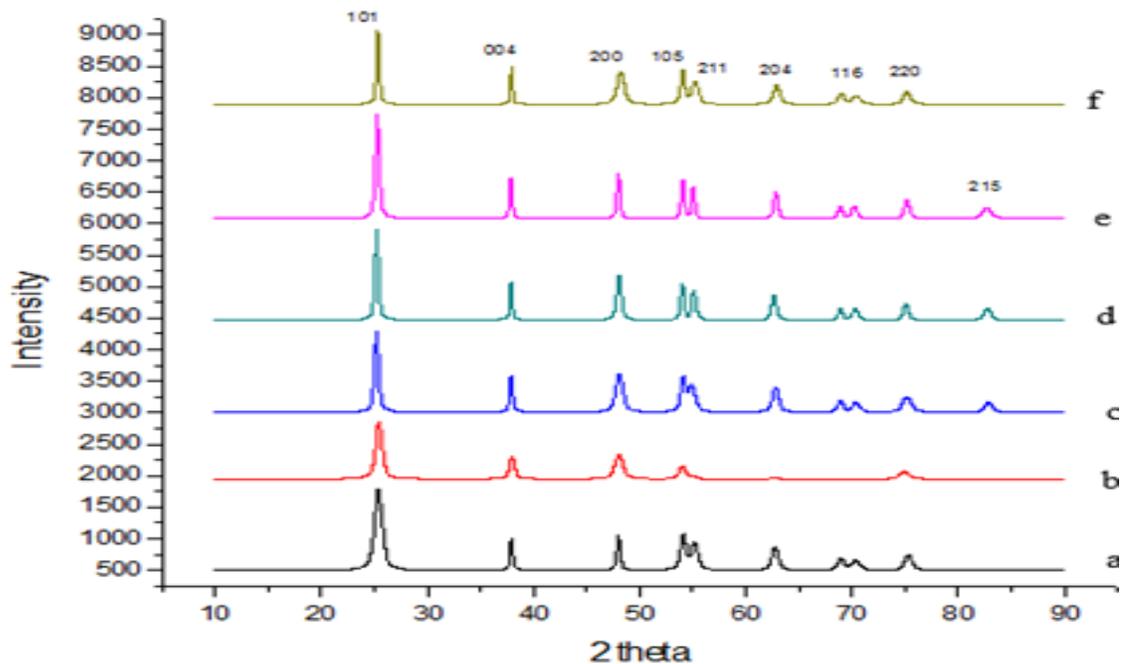


Fig. 1 XRD pattern for sample (a) 0.1 wt.% N-TiO₂, (b) 0.5 wt.% N-TiO₂, (c) 0.9 wt.% N-TiO₂, (d) 1.3 wt.% N-TiO₂, (e) 1.7 wt.% N-TiO₂ and (f) pure TiO₂

Table 1 Crystallite size pure TiO₂, 0.1 wt.%, 0.5 wt.%, 0.9 wt.%, 1.3 wt.%, and 1.7 wt.% N-TiO₂

Samples	Urea content (wt.%)	Crystallite size (nm)	Phases
Pure TiO ₂	0	25.3	Anatase
0.1 wt.% N-TiO ₂	0.1	10.0	Anatase
0.5 wt.% N-TiO ₂	0.5	11.4	Anatase
0.9 wt.% N-TiO ₂	0.9	8.5	Anatase
1.3 wt.% N-TiO ₂	1.3	15.5	Anatase
1.7 wt.% N-TiO ₂	1.7	14.3	Anatase

The morphology and size of the synthesized products are observed using FESEM. Fig. 2 shows the images of the synthesized samples prepared with various urea content. All samples are found to be agglomerated with grain size estimated from 32 to 46 nm. The agglomeration may due to several reasons such as the presence of capillary absorption, solid bridge, Van der Waals and hydrogen bond [16].

The photocatalytic performance of the as-prepared N-TiO₂ photocatalyst can be evaluated by degradation of MO solution under visible light irradiation. To achieve the adsorption equilibrium, the solution including MO and photocatalyst was stirred in dark for 30 min without light irradiation. Fig.3 shows the result

obtained after the photocatalytic activity conducted under visible light for 4 hours irradiation time. The photocatalytic activity was evaluated using the following (Eq. 2):

$$MO \text{ Degradation } (\%) = \frac{(C_0 - C)}{C_0} \times 100 \quad (2)$$

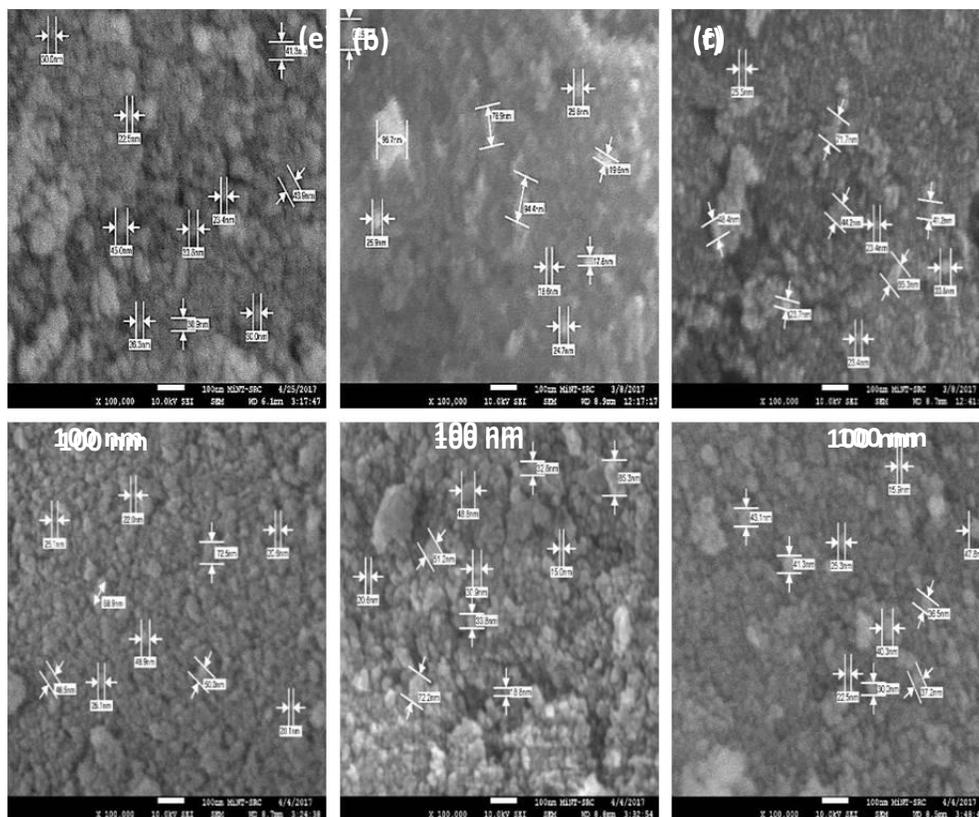


Fig.2 Grain size of (a) pure TiO₂, (b) 0.1 wt%, (c) 0.5 wt%, (d) 0.9 wt%, (e) 1.3 wt%, and (f) 1.7 wt% N-TiO₂

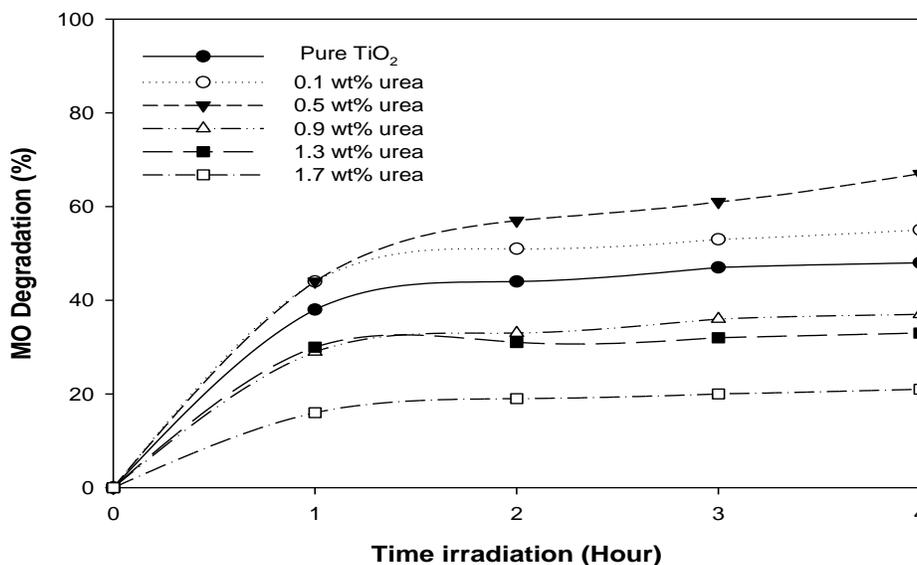


Fig. 3 MO degradation under visible light irradiation

Where C_0 is the original concentration of methyl orange and C is the concentration of methyl orange after irradiation. Based from Fig 3, it is found that the performance of photocatalytic activity from high to low is as follows: %, 0.5 wt.% N-TiO₂ > 0.1 wt.% N-TiO₂ > pure TiO₂ > 0.9 wt.% N-TiO₂ > 1.3 wt.% N-TiO₂ > 1.7 wt.% N-TiO₂. The highest photocatalytic activity is sample with 0.5 wt.% urea (67%) which is three times higher than 1.7 wt.% urea (21%). It is believe that the optimum amount of N in TiO₂ has reached the optimal value at 0.5 wt.% urea. In addition, the decreased of crystallite size may result to the increment of photocatalyst surface area. It is well known that materials with larger surface area can absorb more organic pollutants on their surface, leading to more reaction with electrons in photocatalytic process. It also resulted in higher efficiency in the photocatalytic activity. In another study, Kalantari et al. [15] suggested that the average transfer time of photocatalyst can be reduced by reducing the crystallite size N-TiO₂. Accordingly, there combination rate of photogenerated electron-hole pairs for N-TiO₂ is reduced and its photocatalytic activity increases.

4. SUMMARY

N-TiO₂ was successfully synthesized via hydrothermal treatment at 180 °C. It is found that the morphology, structural, optical property of the synthesized materials influence on the photocatalytic activity. The structural and morphological analysis showed that all samples have anatase framework and agglomerated. It is revealed that the photocatalytic activity of N-TiO₂ is greater compared to pure TiO₂ under visible light irradiation. The highest performance was contributed by 0.5 wt.% urea incorporation with TiO₂. Based on the results, N-TiO₂ can be regarded as an efficient visible-response photocatalyst which have a great significance in environmental purification including for air and wastewater treatment.

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