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The Effect of the Hydrothermal Time and Temperature in the Synthesis to the Properties of Nitrogen-doped TiO_2

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ABSTRACT

Nitrogen-doped TiO_2 (N-TiO_2) has been synthesized through hydrothermal method by reacting the ethanolic solution of ethylene diamine with titanium precursor. The acidic contition was adjusted by the addition of glacial acetic acid. The hydrolysis process was done using hydrothermal process at various hydrothermal time and temperatures. The resulting materials were characterised FTIR, XRD, and Diffuse Refflectance UV/VIS Spectroscopy. The result showed that the increase of hydrothermal temperature lead to increase of particle size, but decreasing the band gap energy. However, the longer the hydrothermal time provided the decrease of particle size with no sugnificantly effect to the band gap energy.

Keyword: N-doped TiO_2, hydrothermal, nanoparticle

1. INTRODUCTION

The photocatalytic process has many benefits in solving environmental problems. The use of photocatalysts is considered as an efficient method for separating pollutant compounds, degrading organic pollutants, decomposing dangerous chemicals in water and air. Photocatalysts have several advantages, such as it has strong oxidation-reduction properties, insoluble in water, and its chemical bonds are stable to light exposure (Aliah, et al, 2012). The application of photocatalysis in Indonesia is being a very promising method because it is supported by tropical climate with high amount of sunlight throughout the year with an effectiveness of 50-80%, an average humidity of 60-90% and rainfall for 150-220 days a year (Aristanto, 2009). Photocatalyst material or semiconductor is one of the materials that utilizes the photocatalytic process, as a combination process between photochemistry and catalysis. Semiconductor materials that usually used as photocatalyst under sunlight irradiation include TiO_2, ZnO, CdS, and Ag_3PO_4 (Han, et al, 2017).

TiO_2 material is widely used as a photocatalyst because of the advantages of TiO_2 compared to other semiconductor materials such as non-toxic, relatively inexpensive, excellent chemical stability, high thermal stability, and high photocatalytic activity (Choi, Park, & Hoffmann, 2009). Researchers have made many attempts to modify TiO_2 photocatalysts to produce a more active material in visible light. Among the efforts made was inserting dopants on the TiO_2 crystal matrix (Lestari, 2009).

Azami et al. (2017) reported that the doping nitrogen on TiO_2 resulted in an increased response to visible light. Furthermore, it was said that the nanoscale of N-doped titanium dioxide has an improving performance like stronger material, resistant to corrosion, and has better thermal insulation (Anggraita & Pramudita, 2006). Nitrogen is being an effective dopant for TiO_2 because of

its atomic size which is similar to oxygen, good stability, and low ionization energy (Kusumawardani, Kartini & Narsito, 2012).

TiO_2 nanostructures has been developed in various fields, for example in the energy sector, include nanotubes, nanoparticles, and nanofibers (Camposeco, et al, 2016). Various methods can be used to synthesize TiO_2 nanotubes such as sol-gel, hydrolysis, hydrothermal, and anodization (Ramadhy, Rahmalia & Usman, 2020). The advantages of the hydrothermal synthesis method compared to other methods include saving energy, simple process, pollution-free (because it is carried out in a closed system), quite efficient cost, higher dispersion rate, and lower operating temperature with the right solvent, as well as an ease of structure tunning (Pujianto, 2020).

The character of TiO_2 synthesized by the hydrothermal method is strongly influenced by hydrothermal conditions such as temperature, concentration, and duration of hydrothermal in the sample preparation process (Liu, et al, 2012). Wu et al. (2010) stated that the absorption of N-TiO_2 photocatalyst increased in response in the visible light region with increasing hydrothermal temperature and showed higher photocatalytic activity. Therefore, it is a need to studi the synthesis of N-doped TiO_2 through hydrothermal process with variation of hyfothermal time and temperature.

2. RESEARCH METHOD

2.1 Materials

Titanium tetraisopropoxide (TTIP/$C_{12}H_{28}O_4Ti$), ethylene diamine ($C_2H_8N_2$), ethanol, and glacial acetic acid were used as recieved without further purification.

2.2 Procedure

Synthesis of N-TiO_2 nanoparticle was carried out by dissolving 6.7 ml ethylene diamine in ethanol and stirred for 60 minutes. Then 3 ml of TTIP and 5 ml of acetic acid were added. After all homogeneous, the mixture was put into a Teflon chamber to be hydrothermally at a temperature of 100^{o}C for one day. After the hydrothermal process, the resulted material was dried in oven at 80^{o}C, then calcined at 500^{o}C for 4 hours to get N-TiO_2 nanoparticles. The procedure was repeated at the hydrothermal temperature of 140 and 180^{o}C. The variation of hydrothermal time was done at 2 and 3 days. The resulting N-TiO_2 nanoparticles were characterized using XRD, UV-VIS DRS, and FTIR.

3. RESULTS AND ANALYSIS

The N-doped TiO_2 has been successfully synthesized through hydrothermal method resulting in a yellowish powder. Several characterization was done to study the effect of synthesis parameter to the properties of resulted N-doped TiO_2.

3.1 Crystal Analysis

To study the effect of synthesis parameter to the crystal structure, the synthesized N-doped TiO_2 were characterized using X-Ray Diffractometer with radiation source of Cu Kα (1.54060 Å) at 2θ range of 20-80º. The XRD analysis results of hydrothermal temperature variation were shown in Figure 1, while the hydrotermal time variation were shown in Figure 2.

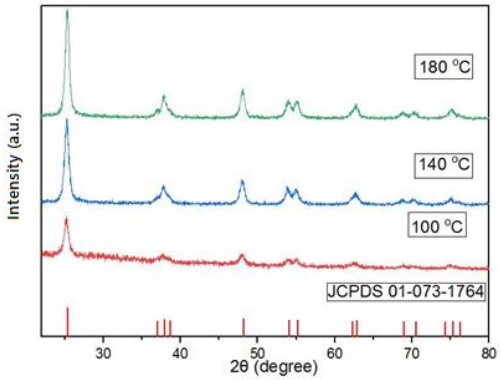

Figure 1. Diffractogram of N-doped TiO_2 at hidrothermal temperature variation

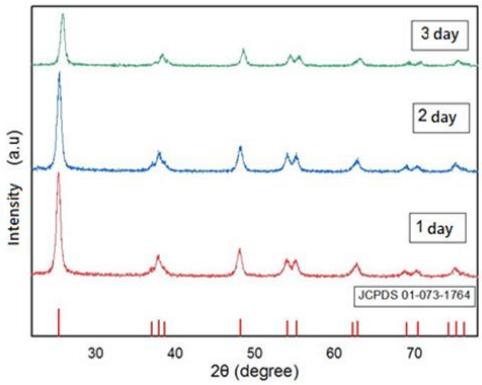

Figure 2. Diffractogram of N-doped TiO_2 at hydrothermal time variation

The diffractogram in both Figures showed only peaks characteristic of anatase TiO_2 crystal structure as confirmed by the JCPDS data No. 01-073-1764. There is no rutile and brookite peaks found in all diffractogram. It is indicated that hydrothermal method is being a proper method to produce the anatase crystal type. The same result was also reported by many researchers (Kusumawardani, Kartini & Narsito, 2012; Liu, et al, 2002; Wu, el al, 2010) since the presence of acidic condition will avoid the fast hydrolysis and tend to the formation of anatase structure, which found as the most active structure as photocatalyst material.

The refinement method was applied to the XRD result using Rietica program to study the crystallinity of prepared N-doped TiO_2 with hydrothermal time and temperature variation. The refinement results are listed in Table 1 for temperature variation and Table 2 for time variation. Based on the refinement result, the increase of hydrothermal temperature lead to the lower crystal cell volume with a shorter *c* axis direction. The same trend was found at the longer hydrothermal time.

Table 1. Crystal Parameter of N-doped TiO_2 synthesized at temperature variation

Parameters	Temperature (°C)			
	100	140	180	JCPDS
Crystal System	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space Group	141/AMD	141/AMD	141/AMD	141/AMD
$a = b$ (Å)	3.77941	3.79274	3.78921	3.77620
c (Å)	9.58029	9.51909	9.53720	9.48862
Cell volume (Å^3)	138.296	136.931	136.932	135.254

Table 2. Crystal Parameter of N-doped TiO_2 synthesized at hydrothermal time variation

Parameters	Hydrothermal time (day)			
	1	2	3	JCPDS
Crystal System	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space Group	141/AMD	141/AMD	141/AMD	141/AMD
$a = b$ (Å)	3.78920	3.82942	3.76231	3.77620
c (Å)	9.58371	9.64952	9.03630	9.48862
Cell volume (Å^3)	136.932	133.304	127.907	135.254

The crystallite of synthesized materials were calculated based on FWHM values using Debrye-Scherrer formulation and the result are listed in Table 3. Based on the diffraction pattern and the data obtained, it is known that the average crystal size tends to increase due to the increase in hydrothermal temperature. In general, the crystallinity will increase with the increase in hydrothermal temperature and the optimal temperature is in the temperature range of 100 to 200 °C (Liu, et al, 2002). It was also found that the average yield of the crystal size becomes smaller the longer it is synthesized using the hydrothermal method. Based on their size, anatase are thermodynamically stable at crystal sizes less than 11 nm, brookite between 11-35 nm and rutile more than 35 nm (Licciulli, 2002). Based on the results of the average crystal size on the variation of hydrothermal time, it is concluded that the longer of hydrothermal time lead to the more thermodynamically stable of the anatase structure in the sample.

Table 3. Average crystallite size

Variation	Average D (nm)
100° C (1 day)	8.1766
140° C (1 day)	8.6548
180° C (1 day)	14.6654
180° C (2 day)	11.0063
180° C (3 day)	10.9234

3.2 Analysis of Electronic Structure

The electronic structure was studied using diffuse reflectance spectrocopy at the wavelength of 200-800 nm (Figure 3). The reflectance data was used to obtained the bad gap energy value which determined using Tauc Plot.

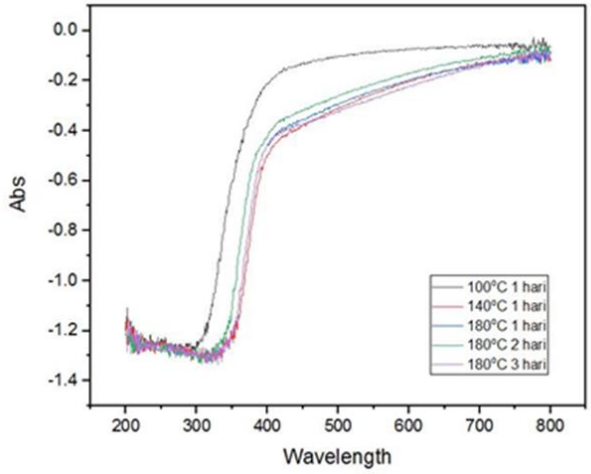

Figure 3. DRUV Spectra Analysis of N-doped TiO_2 synthesized at various concentration

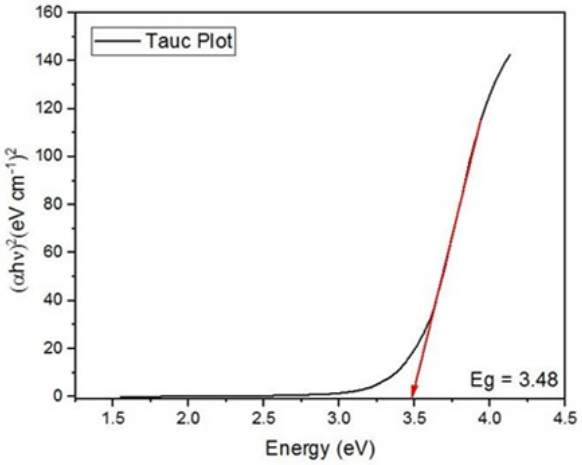

Figure 4. Tauc Plot of N-doped TiO2 prepared at 100o for 1 day

Table 3. Eg Values at any variation

Variation	E_g (eV)
100° C (1 day)	3.48
140° C (1 day)	2.96
180° C (1 day)	2.91
180° C (2 day)	2.96
180° C (3 day)	2.98

The results of the analysis using UV Vis Spectroscopy indicates the effect of hydrothermal variation to the electronic structure of N-doped TiO_2. The increase of the temperature resulted in a more red shift with the lower band gap value. It means that the higher hydrothermal temperature tend to the increase of material response toward visible light. The different trend was found from the effect of hydrothermal time where the longer of hydrothermal time resulted in the higher band gap energy, but the change in Eg is just slightly significant.

3.3 Analysis Organic Functional Group

The FTIR analysis were performed to the prepared N-doped TiO_2 before and after calcination. The results showed that the calcination process was properly removed the ethylenediamine compounds from the calcined powder. Some nitrogen left in the material, since it resulted a yellowish powder as characteristic of N-doped TiO_2. Characterization using FTIR also aimed to determine the functional groups that make up the framework of N-doped TiO_2, and to identify the presence of Ti-N vibrations as an indication of the formation of bonds between N and Ti, as a result of the addition of nitrogen dopants. Changes in functional groups that occur during the calcination process can be seen in Figure 5, it shows the measured wave numbers as an indication of the formation of bonds between N and Ti. In the 1000-1700 cm^{-1} wavenumber region, it shows the presence of N-Ti bonds. The absorption band in the wave number region of 650 cm^{-1} shows Ti-O-Ti bonding which indicates an interstitial N-doped TiO_2 bond model (nitrogen binds to oxygen), which indicates the presence of nitrogen in TiO_2.

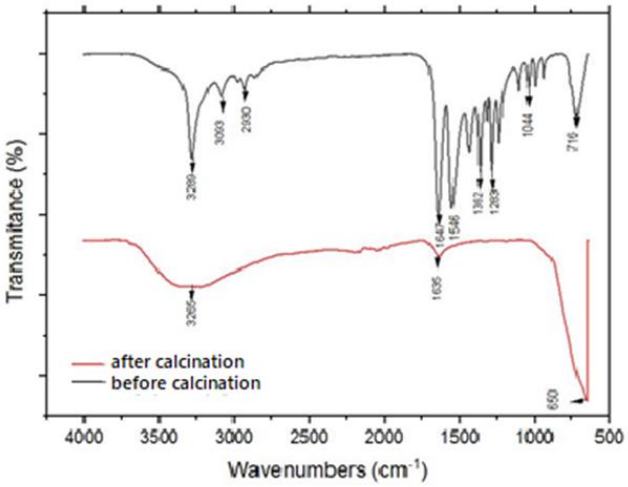

Figure 5. FTIR Spectra of N-doped TiO_2 before and after calcination

4. CONCLUSION

The increase in hydrothermal temperature and time during the synthesis has affected the properties of prepared N-doped TiO_2 nanoparticles, resulting in a band gap energy value that is smaller than the band gap energy value comparing to the pure TiO_2 except for a hydrothermal temperature variation of 100°C. It also affected the crystallinity of prepared N-doped TiO_2 where an increase in nanoparticle size at increasing temperature and a decrease in nanoparticle size at hydrothermal time.

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