Optimization of Energy and Time Variations for Synthesis of N doped TiO_2 Nanotube using Microwave-Asssisted Hydrothermal Method

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ABSTRACT

This study aimed to determine the effect of energy and time hydrothermal microwave time variations on the crystal structure and N-TiO_2 nanotube photocatalytic activity. The synthesis of N-TiO_2 nanotube was performed with the hydrothermal microwave method. The N-TiO_2 preparationwas carried out by dissolving ethylenediamine precursor in 80 ml of 96% ethanol and 3 ml TTIP which was reacted at 70 °C for 4 hours. The obtained N-TiO_2 was formed into nanotubes used the hydrotermal microwave method in low temperature (180W), medium temperature (360 W), and high temperature (720 W) with time variations of 30 minutes, 1 hour, and 2 hours. The microwave hydrothermal process in this study used 10 M NaOH to form a tubular structure and 0.5 M HCl as an ion exchange. The characterization analysis performed by X-Ray Diffraction, UV-Diffuse Reflectance Spectroscopy, and blue methylene degradation. The results of this study indicate that the variations of time and energy of the microwave hydrothermal method affect the crystal structure of the N-TiO2 nanotubes. The nanotubes structure has been formed at a variety of low energy 2 hours, medium energy 0.5 hours, 1 hour and 2 hours, and high energy 2 hours. Energy and time variations of hydrothermal microwave affect the photocatalytic activity of N-TiO_2 nanotubes showed second-order kinetics. The best percentage of degradation produced in the T2 variation is the photocatalyst reaction of 71.89% and the adsorbs reaction of 64.81%.

Keyword: *: N-TiO_2 Nanotube, microwave, hydrothermal, time variation, energy variation*

1. INTRODUCTION

More sunlight is emitted in the visible area than UV light, which is only about 5% of all sunlight that reaches the earth's surface. Utilization of sunlight both in the photovoltaic and photocatalyst fields becomes ineffective when only using UV light, while ~43-52% of the sunlight spectrum is emitted in the visible region (Zong, Lu, and Wang, 2013). The oxide semiconductor material has good chemical stability under UV and visible light, so that the oxide semiconductor can be used as a catalyst. The oxide semiconductors commonly used by researchers are ZnO (Lam et al., 2015), TiO_2 (Wang et al., 2018), and Fe_2O_3 (An et al., 2015). Titanium dioxide (TiO_2) is one of the most widely used oxide semiconductor materials because it has advantages such as non-toxicity, high physical and chemical stability, low price (Singh et al., 2016), corrosion resistance, and very abundant quantities (Yan et al., 2011).

Dopants inserted into TiO_2 crystals can be in the form of non-metallic materials such as F, P, I, N (Ansari, Khan, and Ansari, 2016), C and S (Zong, Lu, and Wang, 2013) or metallic materials, namely Cr, Fe , Al, Sn, V and Co (Chen and Mao, 2007). The dopant that is widely studied by researchers is nitrogen dopant because it has a metastable center and atomic size that is proportional to oxygen (Y. Gao et al., 2013). In Azami et al's research (2017) showed that nitrogen-doped TiO2 showed an increased response under visible light radiation.

Nitrogen-doped titanium dioxide is made on a nanoscale because it can improve performance so that it is stronger, resistant to corrosion, good thermal insulation (Anggraita, 2006) has a specific surface area and high interaction (Slamet, 2012). The nano form used in this research is nanotubes. The synthesis of nitrogen-doped TiO2 in the form of nanotubes can be carried out by several methods including sol-gel (Lim et al., 2018), hydrothermal (Lee et al., 2011), anodization (Yoriya, 2014), and microwave hydrothermal (Huy et al., 2011 and Gyawali, 2016).

The synthesis of nitrogen-doped TiO_2 in the form of nanotubes can be carried out by a popular and widely used method, namely hydrothermal, besides being cheap, it can also increase surface area, crystallinity, thermal stability and photocatalytic activity (Kim and Kwak, 2007). The hydrothermal method can be assisted by microwave irradiation because it can achieve high power and pressure in a short time with a closed system and is very energy efficient (Meng et al., 2016). This method is called microwave hydrothermal which can be a new method in materials science because of its fast volumetric heating, low thermal gradient and high yield (Roy and Prasad, 2018).

This research uses a photocatalyst method for the degradation of methylene blue. Methylene blue was chosen as the material for degradation because it is easy to obtain and cheap. Methylene blue is a waste that comes from organic materials and is difficult to decompose, so methylene blue is used in photocatalysts to decompose hazardous compounds (Chandra et al., 2019). The precursor used in this study was TTIP with ethanol as a solvent. The temperature variations used are low, medium, and high with variations in time of 30 minutes, 1 hour and 2 hours. The purpose of this study was to determine the effect of microwave hydrothermal temperature and time variations on the photocatalytic activity and crystal structure of nitrogen-doped TiO_2 nanotubes.

2. RESEARCH METHOD

2.1 Synthesis of N-TiO_2

Ethylenediamine as much as 6.7 ml was dissolved in 80 ml of 96% ethanol then stirred for 30-60 minutes until homogeneous (forming micelles). After being homogeneous, 3 ml of Titanium (IV) Isopropoxide (TTIP) was added dropwise and stirred again for 1 hour. Then refluxed at 70 °C for 4 hours, then allowed to stand at room temperature, then added 4 ml of glacial acetic acid and 8 ml of deionized water and stirred for 24 hours and let stand for 2 days. The solution that had been left for 2 days was cloudy yellow then added deionized water and 1:1 ethanol and then centrifuged so that the solvent and solids could be separated. The solids were dried in an oven at 90 °C and calcined at 450 °C for 4 hours.

2.2 Synthesis of N-TiO_2 Nanotube through Hydrothermal Microwave

The synthesis of N-TiO_2 nanotubes was carried out by dissolving 0.3 g of N-TiO_2 into 30 ml of 10 M NaOH, stirring for 2 hours. Then hydrothermally with the help of microwaves with low, medium and high power variations and time variations for 0.5 hours, 1 hour, and 2 hours. Washed with 0.5M acid solution (HCl) for 24 hours, then washed again using a 1:1 mixture of water and ethanol and centrifuged to collect the solids. The solid was dried in an oven at 90°C for 4 hours and calcined at 500° for 4 hours.

2.3 Photocatalytic Activity Test

Standard methylene blue solution was made by dissolving 0.03 g of methylene blue in 100 ml of distilled water and put it in a 100 ml volumetric flask. 1 ml was taken to be redissolved in 100 ml of distilled water to obtain a concentration of 10^{-5} M. The adsorption and photocatalyst reactions were carried out by inserting 0.05 g N-TiO_2 nanotubes in 10 ml of methylene blue solution placed in a shaker. The absorbance was measured with a wavelength of 663.5 nm using Spectronic 20. The adsorption was measured under dark condition and illuminated by 5 watt fluorescent lamp at the time 0, 1, 2, 5, 10, 15, 20, 40, 60, and 90 min, and absorbance is measured according to the concentration at a predetermined time. The sample code are listed in Table 1.

Table 1. Code sample of resulted N-TiO_2 nanotube

Code	Microwave power	Microwave time (h)
R 2	Low (180 watt)	2
S0,5	Medium (360 watt)	0.5
S 1	Medium (360 watt)	1
S 2	Medium (360 watt)	2
T 2	High (780 watt)	2

3. RESULTS AND DISCUSSION

X-ray Diffraction technique was used to study the crystallinity of the resulted N-TiO_2 nanotube. The results of XRD characterization at low power within 2 h microwave time (Figure 1) showed peaks at anatase and brookite, anatase diffraction angle at 28.93° (101), brookite at 41.44° (130) and 44.35° (012). The appearance of brookite can be caused by over washing with HCl. The optimum time for washing HCl is 4 hours (Kusumawardani, 2012). XRD results at low power (180 watts) within 2 hours can be stated to have very low crystallinity with the presence of an anatase peak in the shifted plane (101) and has a weak peak.

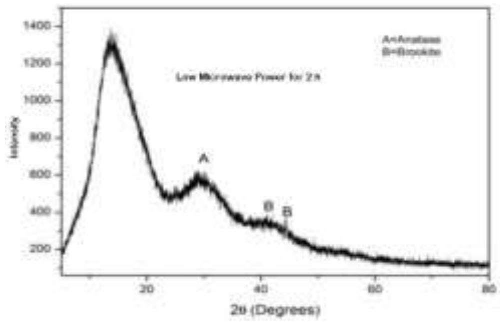

Figure 1. XRD Result of n-TiO_2 nanotube synthesized at low MW power for 2 hours

XRD results for hydrothermal time variations at medium power (360 watts) are presented in a diffractogram (Figure 2) which has been analyzed using U-Fit Software. The diffraction peaks of the anatase phase at S0.5 were 57.48° and 75.20°, S1 at 28.93° and 57.69°, S2 at 52.13°, 54.87°, and 57.12° and T2 at 37.58°, 52.27°, 57.62°, and 78.71°. The results of the diffraction peak were in accordance with the characteristic peak of the anatase phase at 2θ 25.43°; 37.24°; 38.18°; 48.24°; 54.40°; 55.31°; 63.13°; 70.61° and 75.63° (Fauriani, 2019; Wu, 2005) but there are some shifting diffraction peaks. This indicates a change in the structure of an anatase crystal.

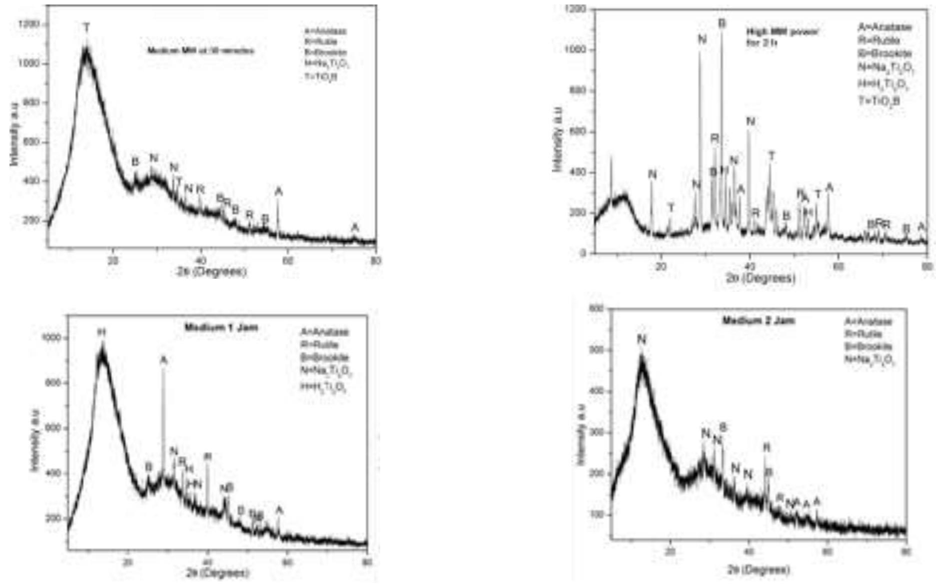

Figure 2. XRD Result of N-TiO_2 nanotube synthesized at MW power and time variation

The characteristic peak of rutile is at 2θ 27.44°; 35.6°; 40,80°; 41.18°; 44°; 54.29° (Azami et al., 2017; Kasuga et al., 1999; Li et al., 2014). The diffraction peaks at S0.5 were at 28.93°, 45.38°, and 51.14°, the diffraction peaks S1 at 33.71°, 39.83° and 52.42°, S2 at 43.97° and 47.91°, and T2 diffraction peaks at 32.02°, 45.38°, 51.14°, 68.16° and 70.69°. The diffraction angle shift occurs in the rutile phase so that there is a change in structure or agglomeration in a crystal. The rutile phase can appear significantly without the anatase phase due to acid washing for 2 hours in the conventional hydrothermal process and microwave hydrothermal washing for 0.5 hours (Morishima et al, 2007) this can be seen in samples T2 and S1 the presence of a rutile phase with high intensity.

The brookite phase also appears in the R2 variation; S0.5; S1; S2 and T2 which according to research by Morishima et al (2007) stated that brookite can be formed usually on hydrolysis using alcohol and acid solution (HCl) for too long. The brookite phase can be formed in microwave hydrothermal synthesis since it was detected as a secondary phase, during the microwave heating process for a long time. According to Peng et al (2010) to find out if a crystal has formed a nanotube structure, it can be seen through the XRD diffractogram, namely the peak appeared at 2θ 9.58°; 24.01°; 28.68°; and 48.23°. In this study it can be assumed that the nanotube structure has been formed in the T2 variation which has diffraction peaks of 28.78° and 48.05°; S2 at the diffraction peak 28.51°; S1 is found at the diffraction peaks of 28.93° and 48.05°; S0.5 at a diffraction peak of 28.93° and L2 at a diffraction peak of 28.93°. N-TiO_2 in each variation based on XRD results has shown the occurrence of nanotube structures. The nanotube structure occurs due to the addition of NaOH solution. NaOH bound in crystals can be determined by XRD at a diffraction peak around 28.68° (Peng et al., 2010).

The five variations of nanocrystals (T2, S2, S1, S0, 5, and R2) were found to have an impurity phase. According to Huy and Gyawali (2016) that the peak in N-TiO_2 nanotubes contained an impurity phase, namely titanate which can appear at a diffraction angle of 9°; and 24.3°. The exchange of Na+ ions with Cl- in N-TiO_2 nanotubes that occurs imperfectly can be possible that there is excessive Na+ intercalation between the crystal chambers, other phases such as $H_2Ti_3O_7$, $Na_2Ti_3O_7$, lepidocrocite $H_xTi_{2-x}/4X_x/4O_4(H_2O)$ will appear with orthorhombic shape or TiO_2 B (H. Ou and Lo, 2007).

Characterization of N-TiO_2 Nanotubes with UV-DRS (Diffuse Reflectance Spectroscopy) was used to measure absorption at UV to visible wavelengths (200-800 nm) and measure band gap energy. The theory used to determine the band gap value in powdered semiconductor materials is Kubelka Munk (Morales, Mora and Pal, 2007). Mathematically the Kubelka Munk function can be derived by the equation K/S = (1-R)2/2R. K and S are the absorption and backscatter coefficients. The relationship between Kubelka Munk and energy gap shows the effectiveness of microwave hydrothermal power and time on absorption in the visible light region.

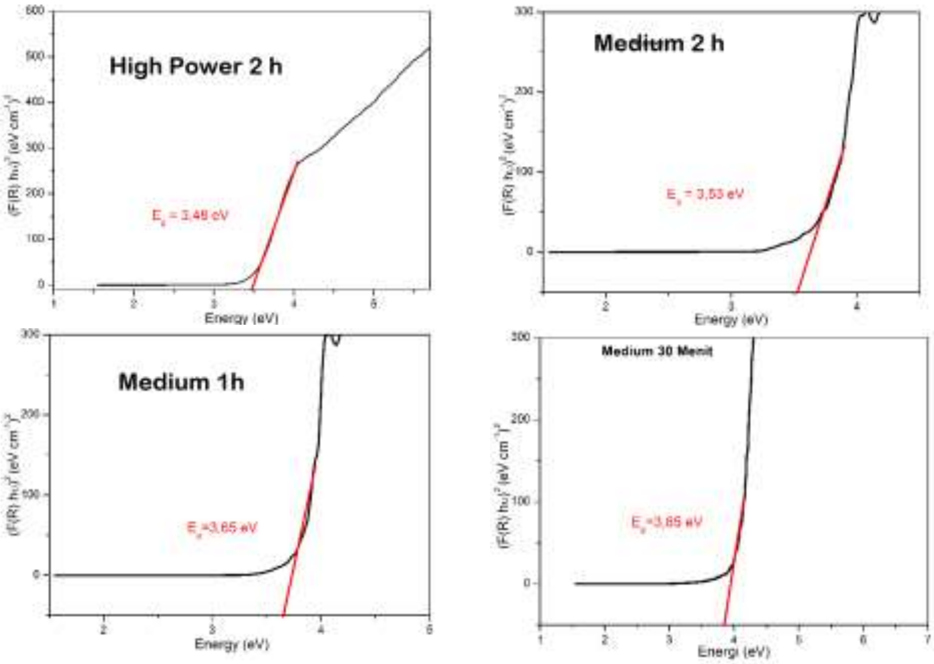

Figure 3. Kubelka-Munk Graph of N-TiO_2 nanotube with MW power and time variation

The band gap energy will affect the photocatalyst activity test, because the low band gap energy will increase the good photocatalyst activity. When reducing the band gap energy, it can shift the absorption to the visible light region (Zong, Lu, and Wang, 2013). N-TiO2 nanotube crystals that have shown band gap energy are close to the theory of 3.0–3.4 eV, namely the variation of T2 with a value of 3.48 eV. Sample S0.5; S1; and the resulting S2 has a larger band gap energy than the T2 sample. If the resulting band gap energy is large, the resulting surface area will be small (Slamet, 2012).

Photocatalyst activity

Degradation of methylene blue organic compounds using spectronic 20 at a wavelength of 663.5 nm. Methylene blue is used for degradation because it is a waste that is difficult to decompose, so it requires various methods to be able to decompose these compounds in the environment.

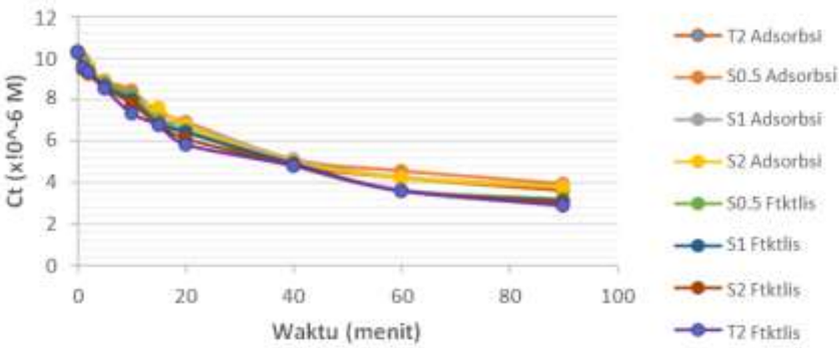

Figure 4. Photodegradation of Methylene Blue

N-TiO_2 has good photocatalytic activity and leaves a small amount of methylene blue at light T2 (Figure 4). The best % degradation obtained was shown in T2 photocatalyst reaction and adsorption reaction with 71.89% and 64.81% gains, respectively. According to Burda et al (2003) that nitrogen-doped nanoparticles will show increased photocatalytic activity under visible light radiation, compared to undoped TiO_2 nanoparticles, these nanoparticles show little photocatalytic activity. According to Geng et al (2009) that the photocatalytic activity for the degradation of methylene blue using an N-TiO_2 catalyst showed 95.1%.

4. CONCLUSION

Variations in time and power of the microwave hydrothermal method affect the characteristics of the crystal structure of N-TiO_2 nanotubes. The nanotube structure has been formed at low power variations of 2 hours, medium power 0.5 hours, 1 hour, and 2 hours, and high power 2 hours. Variations in time and microwave hydrothermal power affect the photocatalytic activity of N-TiO_2 nanotubes showing order 2 kinetics. The best percentage of degradation of methylene blue is produced in the T2 variation, namely the photocatalyst reaction of 71.89% and the adsorption reaction of 64.81%.

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