Morphology and Degradation Kinetics of N-Doped TiO_2 Nano Particle Synthesized Using Sonochemical Method

Eko Hidayanto[a], Heri Sutanto[b], Mukholit[c], Singgih Wibowo[d]
and Muhammad Irwanto[e]

Departement of Physics, Faculty of Sciences and Mathematics, Diponegoro University
Jalan Prof. Soedarto, SH Tembalang-Semarang, Indonesia - 50275

[a]ekohidayanto@fisika.undip.ac.id, [b]herisutanto@fisika.undip.ac.id, [c]mukholit@st.fisika.undip.ac.id,
[d]singgih@st.fisika.undip.ac.id, [e]muhammad.irwanto@st.fisika.undip.ac.id

Abstract. Nano particle of N-doped TiO_2 with the size of 21.42 nm was successfully created using sonochemical method. Concentration of Nitrogen (N) doping on TiO_2 was calculated using mole ratio of Urea and TTiP. Doping variations were performed by doping 5% to 9% N, and did not change the crystallite size and strain. The nano particle produced has a polycrystalline structure with a dominant diffraction peak (101). Doping N into TiO_2 affects the morphology of particle surface, thus tending to shrink. Results of photo catalysis on liquid samples of MB 20 ppm dye indicate that the addition of N improves the degradation ability of TiO_2, with the highest value on sample T5 of 85% and with a rate of degradation kinetics of 0.024 ppm/minute.

Introduction

Photo catalytic materials such as TiO_2 are well known to oxidize and reduce harmful organic pollutants [1]. In a photo catalysis process, TiO_2 material with the band gap energy of 3.0 eV to 3.2 eV is active when irradiated with ultraviolet light [2]. The problem is the presence of ultraviolet light in nature is very limited. From the total solar energy received by the earth, the amount of ultraviolet light is only about 4% [3]. Therefore, various methods have been tried to modify the TiO_2 material in order to make it work in visible light so that sunlight can be optimally used and purification processes can be effectively carried out [4]. One method to activate TiO_2 in visible light is by planting several types of ions, both of transition metal ions such as Cu, Co, Ni, Cr, Mn, Mo, Nb, V, Fe, Ru, Au, Ag, and Pt, and of non-metallic ions such as N, S, C, B, P, I, and F [5]. Based on previous researches, ion implantation of nitrogen to produce a photo catalyst that work on visible light is the most effective method compared to the other techniques [6].

Research on TiO_2 material has been performed using various methods, including precipitation, sol-gel, hydrolysis, sputtering, and Chemical Vapor Deposition (CVD) [5]. Among these methods, sol-gel and hydrolysis are in great demand and have been widely used. However, these methods do have drawbacks. Sol-gel method usually produces TiO_2 with high content of impurities, whereas Hydrolysis method takes too long to produce TiO_2 crystals at low temperatures [7].

N-doped TiO_2 can also be made using another method, the sonochemical method. Sonochemical method is very easy and can be carried out by utilizing ultrasonic vibration bath [8]. Kim et al reported that the sonochemical method is superior for the preparation of nanoscale materials and amorphous crystals [9-10]. In addition, the sonochemical method is also environmentally friendly and safe [7, 11]. This paper reports the results of a research on varied Nitrogen doping on the microstructure and morphology of N-TiO_2 nano particle surface against the rate of degradation kinetics on methylene blue (MB) liquid colorant sample.

Materials and Method

Synthesis of N-doped TiO_2 was initiated by mixing 5 ml Ti $[(CH_3)_2CHO]$ (TTIP, Aldrich), 1 ml CH_3COCH_3, and 1 ml CH_3OH (Merck Chemical) as the solvent. Urea (CH_4N_2O) as a source of nitrogen was added to the solution with mole ratios of Urea and TTIP 0%, 5%, 7% and 9%

respectively, labeled as T, T5, T7 and T9. Then, the solution was irradiated with ultrasonic bath at 40 kHz for 40 minutes. After that, the solution was stirred using a magnetic stirrer hot plate at 60 °C for 170 minutes to produce powder and then the resulting powder was calcinated using a furnace at 500 °C for 2 hours. Furthermore, the powders were characterized using Shimadzu XRD 7000 Maxima at a wavelength of 1.5405 Å, to determine the crystal structure, and using SEM JEOL 6510-LA to determine the morphology. The photo catalytic activity was tested using Methylene Blue (MB) solution with a concentration of 20 mg/L of water under solar radiation.

Results and Discussion

Structure Characterization. XRD test of N-doped TiO_2 and TiO_2 (T9) were synthesized by sonochemical method. There resulting polycrystalline structure is shown in Fig. 1. The XRD figure of the N-doped TiO_2 shows that there are peaks at 2θ in 25.42^0; 38.02^0; 48.10^0; 55.12^0; 63.18^0; 70.40^0; and 76.00^0. Results from MATCH program data processing can be seen in Fig. 2. It is observable that diffraction peaks of TiO_2 are at (101), (004), (200), (211), (220) and (301).
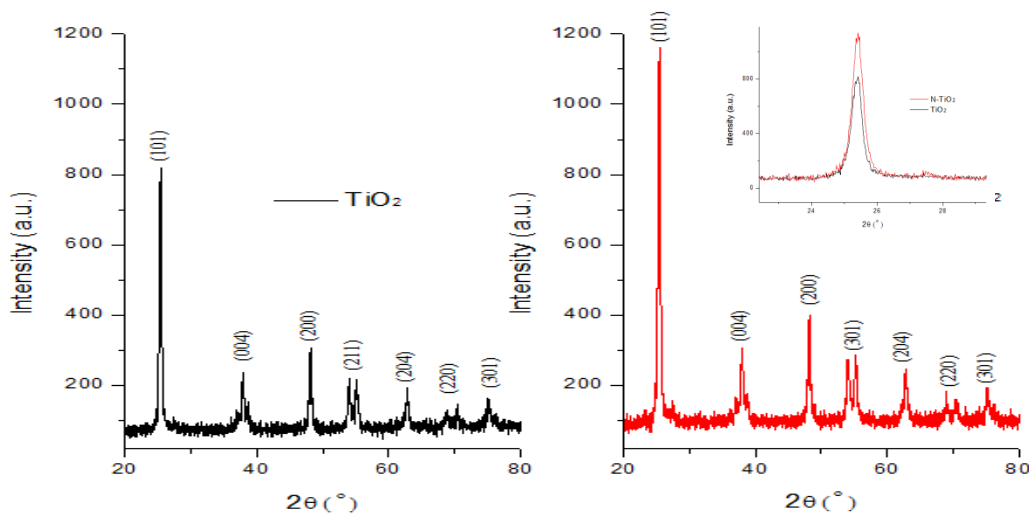

Fig. 1. XRD spectra of TiO_2 and N-doped TiO_2 (T9).

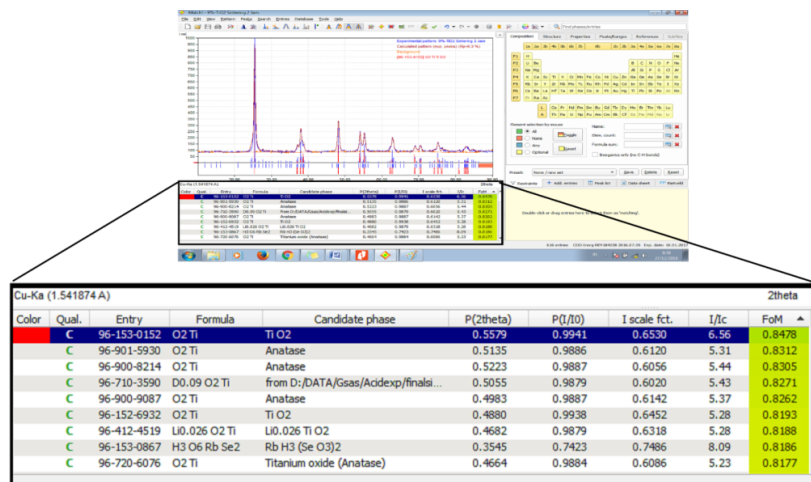| Cu-Ka (1.541874 A)							2theta
Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM
C	96-153-0152	O2 Ti	Ti O2	0.5579	0.9941	0.6530	6.56	0.8478
C	96-901-5930	O2 Ti	Anatase	0.5135	0.9886	0.6120	5.31	0.8312
C	96-900-8214	O2 Ti	Anatase	0.5223	0.9887	0.6056	5.44	0.8305
C	96-710-3590	D0.09 O2 Ti	from D:/DATA/Gsas/Acidexp/finalsi...	0.5055	0.9879	0.6020	5.43	0.8271
C	96-900-9087	O2 Ti	Anatase	0.4983	0.9887	0.6142	5.37	0.8262
C	96-152-6932	O2 Ti	Ti O2	0.4880	0.9938	0.6452	5.28	0.8193
C	96-412-4519	Li0.026 O2 Ti	Li0.026 Ti O2	0.4682	0.9879	0.6318	5.28	0.8188
C	96-153-0867	H3 O6 Rb Se2	Rb H3 (Se O3)2	0.3545	0.7423	0.7486	8.09	0.8186
C	96-720-6076	O2 Ti	Titanium oxide (Anatase)	0.4664	0.9884	0.6086	5.23	0.8177

Fig. 2. XRD data processing using MATCH program.

MATCH program data processing results do not show nitrogen (N) atom increasing in number because nitrogen concentration embedded within the framework of TiO_2 is still too small. Successful Nitrogen doping can be measured by observing shifts in diffraction peak field (101) N-doped TiO_2 and TiO_2 without doping, as shown in Fig. 1 (insert). Complete results of microstructure tests and calculations are given in Table 1.

Table 1. Peak diffraction (2θ), FWHM, and crystallite size of T-T9 samples.

Sample	FWHM (rad)	$2\,\theta(°)$	D (nm)	$\overline{D}$ (nm)
T	0.00607	25.37938	23.40790	
	0.00668	37.89363	21.93837	
	0.00654	48.11365	23.21011	21.42840
	0.00771	54.00921	20.16190	
	0.00813	55.13067	19.23297	
	0.00787	62.78555	20.61914	
T5	0.00607	25.37938	23.40798	
	0.00668	37.89363	21.93811	
	0.00654	48.11365	23.21015	21.42858
	0.00771	54.00920	20.16232	
	0.00813	55.13067	19.23379	
	0.00787	62.78555	20.61912	
T7	0.00607	25.37938	23.40795	
	0.00668	37.89363	21.93711	
	0.00654	48.11365	23.21005	21.42824
	0.00771	54.00919	20.16522	
	0.00813	55.13066	19.23009	
	0.00787	62.78555	20.61901	
T9	0.00607	25.37938	23.40797	
	0.00668	37.89364	21.93023	
	0.00654	48.11365	23.20999	21.42725
	0.00771	54.00920	20.16336	
	0.00813	55.13067	19.23356	
	0.00787	62.78555	20.61836	

Table 1 shows that N doping in TiO_2 does not significantly affect crystallite size (D). Doping 5% Nitrogen (T5) increases crystal size and hence affects shift grating. While on doping 7% (T7) and 9% (T9) nitrogen, decreases crystal size as element O is replaced by N, which increases internal contraction in TiO_2 crystals. Resulting plots using the classic Williamson-Hall equation to determine the strain of the samples indicate no change of strain on both TiO_2 and N-TiO2. Calculated strain for all samples is 0.049.

Scanning Electron Microscopy (SEM) Characterization. Fig. 3 shows SEM images of all prepared samples. The grains of pure TiO_2 (T) are higher than N-doped TiO_2. There are significant numbers of particles on the surfaces of N-doped TiO_2 grains. In the last image, N-doped TiO_2 has the highest dopant concentration. The whole surface is covered with homogeneous small particles. Therefore, it is fair to say that nitrogen reduces the size of TiO_2 particles and creates wider surface area. This result is good for photo catalysis applications. Earlier researches showed that wide surface area of TiO_2 increases its photo catalytic activity.

Degradation kinetics of TiO_2-N for 20 ppm Methylene Blue (MB). Photo catalytic test was carried out under the sunlight using 20 ppm methylene blue. Visually, successful rate of degradation is marked color change of methylene from blue to transparent. The clarity of a solution can be represented in the absorbance data by testing using UV-Vis spectrophotometer and results of degradation are shown in Fig. 4. Absorbance of Methylene blue (MB) exposed to sunlight without N-doped TiO_2 was not significantly reduced (Fig. 4b). There are two reactions that may occur with the addition of N-doped TiO_2 powder; adsorption and photo catalysis. Adsorption reaction is influenced by the absorption field, while photo catalytic reaction is influenced by light existence. In the process MB solution color degradation, information concerning the role of this reaction is very

important because it relates to the continuity of degradation process. Adsorption reaction will stop when it reaches saturation, while photo catalytic reaction will continue as long as there is no source of light as a trigger. In order to determine reaction that plays an important role in MB solution color degradation, testing was performed in dark condition to know the level of degradation caused by the adsorption reaction of N-doped TiO_2 powder. The results of MB solution test added with N-doped TiO_2 powder in dark conditions are shown in Fig. 4 (a).
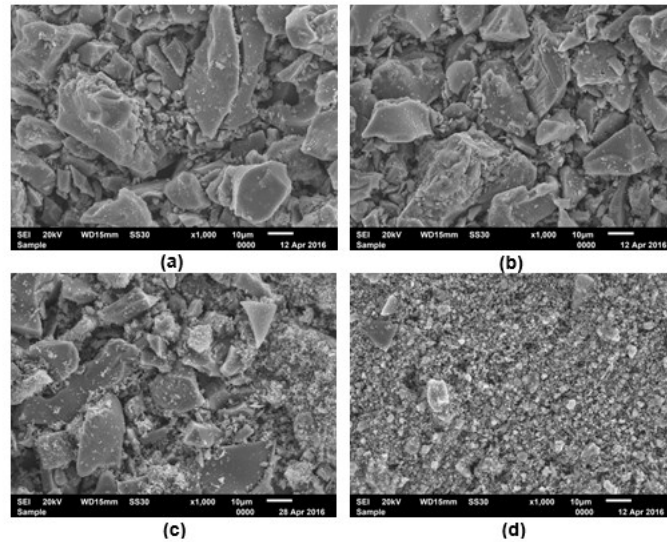
Fig. 3. SEM images of (a) T, (b) T5, (c) T7, and (d) T9.

(a)   (b)   (c)
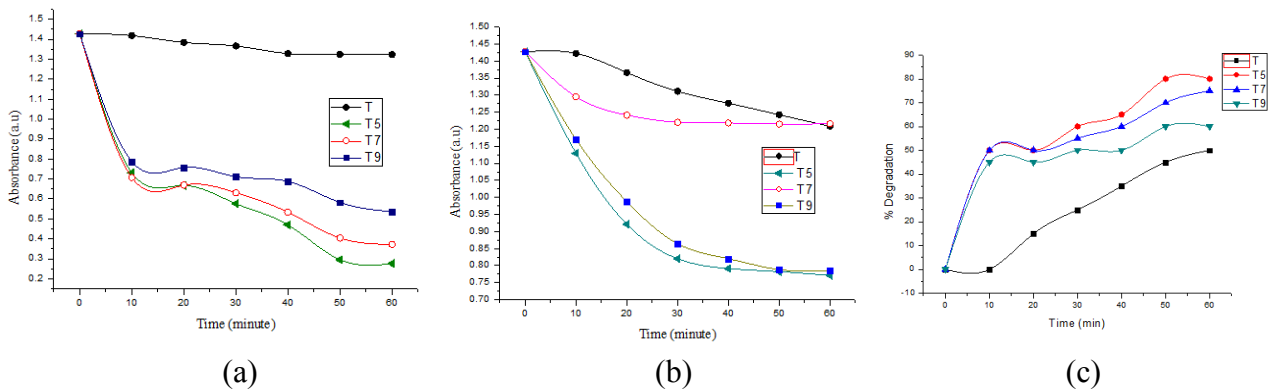
Fig. 4. Photo catalytic tests of 20 ppm MB: (a) dark condition, (b) sunlight irradiation,
(c) N-TiO$_2$ degradation graph.

MB degradation test for 5% N-doped TiO_2 (T5) showed the most optimum result. This is marked by decreasing MB absorbance value (Fig. 4 c). Samples T7 and T9 also showed the contribution of N doping in accelerating degradation. The decline rate of absorbance value is influenced by several factors; crystal size, band gap energy, adsorption capacity, and light intensity. The smaller the crystal size, the greater the interaction extent is. Therefore, photo catalytic activity and decrease in absorbance values are also magnified. Adsorption capacity is directly proportional to decreasing MB absorbance value. The higher the adsorption power, the greater the decrease of absorbance value is. Light intensity is also proportional to the rate of decrease in MB absorbance value. High light intensity indicates the amount of energy, so the process of photo catalytic reaction is more optimum in this condition. The presence of the light affects the photo catalytic reaction as well as photolysis process.

To determine the rate of degradation of a material, it is necessary to calculate the degradation rate by finding the gradient of the graph ln Co/Ct against time. Plotting results of degradation rate are shown in Fig. 5. From the kinetic curve of MB degradation in sample T5, a linear equation of $y = 0,024x + 0.179$ with R2 = 0.936 is obtained. The constant of reaction rate (k) is indicated by the slope, which is 0,024 ppm/min. Constants of reaction rate from all other samples can be obtained in the same way, as shown in Table 2.
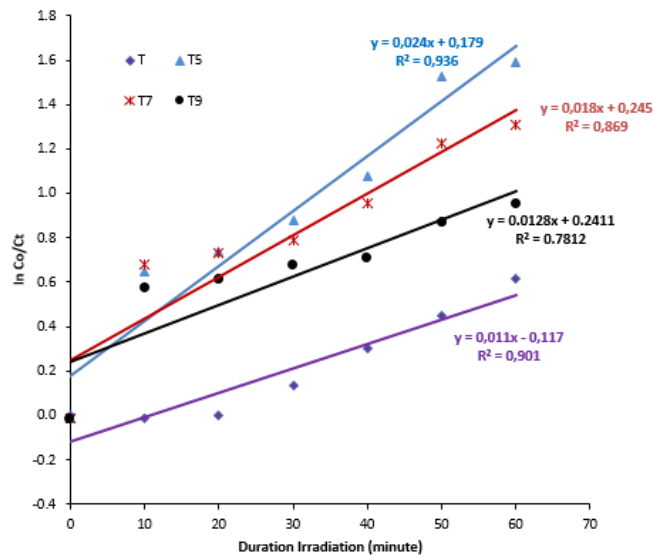
Fig. 5. Degradation kinetics of Methylene Blue under sunlight irradiation.

Table 2. Degradation rate of N-doped TiO_2.

Sample	Degradation kinetics (ppm/minute)
T	0.011
T5	0.024
T7	0.018
T9	0.012

Conclusion

N-doped TiO_2 nano particle of 21.42 nm size has been successfully created by sonochemical method at 24 kHz frequency. Synthesis with N doping variations of 5% to 9% did not change the crystallite size and strain. The produced nano particle has a polycrystalline structure with a dominant diffraction peak (101). N doping into TiO_2 causes the surface morphology of the nano particle to tend to shrink. Photo catalysis test results on liquid samples of 20 ppm MB dye indicate that N doping improved degradation ability of TiO_2. In dark conditions without light, degradation is decreased because reaction between the surface and the catalyst is not significant. The highest accelerated degradation occurred in sample T5 with a degradation rate of 0.024 ppm/minute.

Acknowledgment

References

[1] P. Kajitvichyanukula, J. Ananpattarachaia, S. Pongpomb, Sol–gel preparation and properties study of TiO_2 thin film for photocatalytic reduction of chromium(VI) in photocatalysis process, Science and Technology of Advanced Materials, 6 (2005), 352–358.

[2] K. Eufinger, D. Poelman, H. Poelman, R. D. Gryse, G. B. Marin, TiO_2 thin film for photocatalytic applications, Thin Solid Film Process and Application, (2008), 189-127.

[3] G. Yang, Z. Jiang, H. Shi, T. Xiao, Z. Yan, Preparation of highly visible-light active N-doped TiO_2p Photocatalyst, Journal of Materials Chemistry, 20 (2010), 5301-5309.

[4] S. Buzby, M. A. Barakat, H. Lin, C. Ni, S. A. Rykov, J. G. Chen, S. I. Shah, Visible light photocatalysis with nitrogen-doped titanium dioxide nanoparticles prepared by plasma assisted chemical vapor deposition, J. Vac. Sci. Technol. B, 24(3) (2006), 1020-1025.

[5] D. S. Tsoukleris, C. Fratti, E. A. Plavatou, I. Deligkiozi, K. Hrissagis, Influence of annealing process on N-doped TiO₂ nanocrystalline powders prepared by sol-gel method, Σχολή Χημικών Μηχανικών, Ε.Μ.Π., (2013).

[6] C. Chen, H. Bai, S. Chang, C. Chang, W. Den, Preparation of N-doped TiO2 photocatalyst by atmospheric pressure plasma process for VOCs decomposition under UV and visible light sources, Journal of Nanoparticle Research, 9 (2007), 365–375.

[7] I. Hernández-Perez, A. M. Maubert, L. Rendón, P. Santiago, H. Herrera-Hernández, L. D. Arceo, V. G. Febles, E. D. González, L. González-Reyes, Ultrasonic synthesis: structural, optical and electrical correlation of TiO₂ nanoparticles, International Journal of Electrochemical Science, 7 (2012), 8832-8847.

[8] H. Sutanto, E. Hidayanto, Mukholit, S. Wibowo, I. Nurhasanah, Hadiyanto, The physical and photocatalytic properties of N-doped TiO₂ polycrystalline synthesized by a single step sonochemical methode at room temperature, Material Science Forum, 890 (2017), 121-126.

[9] T. Kim, V. Hernández-Perez, G. Gyawali, S. Cho, T. Sekino., S. Lee, Synthesis of solar light responsive Fe, N co-doped TiO₂ photocatalyst by sonochemical method, Catalysis Today, 212 (2012), 75-80.

[10] L. Zhu, J.D Chung, W.C. Oh, Rapid sonochemical synthesis of novel PbSe–graphene–TiO2 composite sonocatalysts with enhanced on decolorization performance and generation of ROS, Ultrasonics Sonochemistry, 27 (2015), 252-261.

[11] C. Kahatthaa, N. Wongpisutpaisana, N. Vittayakorna, W. Pecharapa, Physical properties of V-doped TiO2 nanoparticles synthesized by sonochemical-assisted process, Ceramics International, 39 (2013), S389-S393.