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Effect of Annealing Temperature on Optical Properties and Photocatalytic Properties of TiO_2:N 8% Thin Film for Rhodamine B Degradation

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Abstract

Titanium dioxide (TiO_2) is a widely studied photocatalyst for the degradation of organic pollutants from wastewater. This semiconductor is more potential than other semiconductors because of its stability, non-toxic, low cost, and commercial availability. A thin film of TiO_2:N 8% was deposited on a glass substrate using a sol-gel method with a spray coating deposition at a temperature of 450 °C. Precursors used in the synthesis of TiO_2:N 8% are titanium (IV) isopropoxide (TTiP), 2-propanol, acetic acid, methanol, and urea as the source of nitrogen doping. Thin film TiO_2:N 8% of subsequent deposition results at annealing at temperatures 400 °C, 500 °C, and 600 °C. Optical properties of TiO_2:N 8% were tested using a UV-Vis spectrophotometer at 200-500 nm wavelength range. The photocatalytic properties of TiO_2:N 8% thin films were tested by degradation of a solution of Rhodamine B (RhB) 10 ppm using sunlight and UV C light for 3 hours. The energy gap in thin film TiO_2:N 8% sequentially from Without Annealing, Annealing 400 °C, Annealing 500 °C, Annealing 600 °C has a value of 3.28 eV; 3.26 eV; 3.08 eV; and 2.95 eV, respectively. The material TiO_2:N 8% without annealing has a grain shape having a diameter of 0.5 μm to 1 μm, while for TiO_2:N 8% annealing 400 °C has the same grain shape without annealing. The composition of nitrogen atoms in the TiO_2:N sample of 8% by 0.2%. The efficiency of degradation shows the properties of TiO_2:N 8% photocatalyst with annealing for the better. The degradation process using 400 °C annealing temperature yields a thin film TiO_2:N 8% with better properties under UV C lamp of 89.22% in 180 minutes. Annealing temperature increase yields TiO_2:N 8% thin film with improved photocatalyst properties in sunlight with an annealing temperature of 600 °C at 79.30% in 180 minutes.

Keywords: Thin Film, TiO_2:N, Annealing, Rhodamine B

1. Introduction

Water has become a necessity in everyday life. Almost all aspects of life require a lot of clean water such as for drinking, cooking, bathing, and washing. However, the availability of clean water at this time has begun to decrease due to the declining quality and quantity of water in our environment. Currently, various efforts have been made to obtain clean water free from contamination as a result of a large number of human activity. In general, there are 4 activities in water cycle associated with human activities such as water exploration, water consumption, wastewater production and wastewater purification. In wastewater purification activities, there are several process activities such as filtration, sedimentation, and disinfectant. Although the purification system is quite effective, it is still quite expensive due to the filtration system and the use of filtration materials [1]. One of the alternative water purifications that can be used is by using photocatalyst method.

The photocatalyst is a process of combination of the photochemical process with catalyst, for the chemical process can be generated by using light and the presence of the catalyst as a reaction accelerator of the photocatalyst. Usually to get a photocatalyst process using a semiconductor material. The semiconductor material is a useful material for the environment because it can decompose pollutants such as harmful chemical compounds. For photocatalyst process, when the semiconductor material absorbs light with energy equal to or greater than its energy gap there will be charge separation or photoexcitation inside a semiconductor material. The electron (e) will excite to the conduction band and leave the positive hole (h^+) in the valence band [2]. When h+ interacts with water molecules will produce a hydroxyl radical compound (HO*). HO* compound is oxidizing agents for organic compounds [3].

TiO_2 oxide is a white solids-semiconductor material with a molecular weight of 79.90 and melting point of 1185 °C. This compound is not dissolved in water, hydrochloric acid, and nitric acid, but soluble in concentrated sulfuric acid [4]. TiO_2 has a very wide energy gap between (3.2 eV-3.4 eV), for pure TiO_2 has a photocatalytic efficiency of 5% from solar energy in the ultraviolet (<380 nm) range, in this range can activate pure TiO_2 photocatalytic reaction. To utilize solar energy, the effort to widen the spectrum of sunlight absorption into visible light range (<400 nm- 700 nm) become important, because about 45% of solar energy will be used in the photocatalytic process. In order for the use of solar energy to be effective, it is necessary to do a method to minimize the energy gap and increase the light absorption by using an additional material as doping [5]. Nitrogen is an effective doping material because its size is not much different from oxygen and its small ionization energy. In addition, nitrogen can reduce the TiO_2 energy gap so as to improve the quality of TiO_2 thin film [6].

RhB (Rhodamine B) is a synthetic dye commonly used as a textile dye. The market name of the RhB is Briliant Pink B, Food Red 15, and Basic Violet 10 with the chemical formula $C_{28}H_{31}ClN_2O_3$, and having a molecular weight of 479.02 gr/mol. RhB is one of the dyes used in the textile industry because it is more economical and easy to obtain. Then, RhB is one of the dyes used for paint, textile, and paper industries. In addition, RhB has a very dangerous content for health [7].

Lin et al made a TiO_2:N thin film using spin coating method by varying the annealing temperature. The maximum annealing temperature is 400 °C and used to degrade methylene blue dyes using UV light. The results showed that the annealing temperature increase impacted the decreased of the energy gap, thus increasing the photocatalytic effect [8]. Zheng et al reported photocatalytic activity TiO_2:N by varying the annealing temperature to degrade the Rhodamine B (RhB) dye. These results indicate that the annealing temperature of 500 °C has a better degradation efficiency [9]. In addition, Indriyani et al made thin films TiO_2 and TiO_2:N with N doping of 8% without annealing to degrade Direct Blue 71 dye. The results show that TiO_2:N 8% thin film has much better photocatalytic properties than using TiO_2 thin film when exposed by UV light [10].

In this research will be made thin film TiO_2:N 8% by varying annealing temperature using the sol-gel method with spray coating technique. Then, a thin film of TiO_2:N 8% with annealing temperature variation was used to degrade Rhodamine B (RhB) dye using sunlight and UV C light.

2. Material and Method

2.1. Experiment Method

In this research uses a variety of materials such as Titanium (IV) Isopropoxide ($Ti[OCH(CH_3)_2]_4$) (Sigma Aldrich, 97%), Urea ($CO(NH_2)_2$) (Merck, 99%), Acetic Acid (CH_3COOH) (Merck, 100%), 2-propanol (IPA) ($CH_3CH(OH)CH_3$) (Merck, 99,5%), Aseton (CH_3COCH_3) (Merck, 99,5%), Methanol (CH_3OH) (Merck, 99,9%), Rhodamine B ($C_{28}H_{31}ClN_2O_3$).

The equipment used in this research are Hotplate Magnetic Stirrer (Yellow Line, Yellow MAG HS 7), Spray-gun (Krisbow HS-80), Compressor (Krisbow), Digital Balance (VMC (Virtual Measurements & Control)), UV C lamp (Electronic ballast), UV-Vis spectrophotometer (Shimadzu).

The synthesis of precursor TiO_2:N 8% 0,2 M was prepared using a sol-gel method by dissolving 3.17 ml of TTIP into 9.5 ml of 2-propanol at a temperature of 27 °C and stirred using a magnetic stirrer for 60 minutes. 10.3 ml of acetic acid was added to precursor and stirred again for 15 minutes, then 24 ml of methanol was added and stirred for 15 minutes. The urea as a source of nitrogen was added into the solution with the total amount of 4.13 gram and stirring for 30 minutes under closed conditions to obtain a homogeneous solution. To determine the content of nitrogen doping using the mole fraction by the first step calculate the mole value of the solution, then calculate the mass value of urea and calculate the doping mass of Nitrogen from 8% urea mass, so that the mass of Nitrogen 8% was obtained.

The TiO_2:N 8% solution was deposited on a glass substrate using a spray coating method. Glass substrate was cleaned using methanol, acetone, and aquades to remove impurities particles. Glass substrate was dried for 5 minutes in open space, and heated using hotplate at 450 °C for 30 minutes. Meanwhile, the preparation of TiO_2:N 8% solution was inserted into the sprayer bottle to be deposited. After the glass substrate was ready for deposition, the solution begins to deposited with deposition distance of 30 cm above the glass substrate using a sprayer. For the process of thin film annealing TiO_2:N 8% was done using a furnace with the temperature variation of 400 °C, 500 °C, and 600 °C, respectively. Each sample (400 °C, 500 °C, and 600 °C) was annealed for 1 hour.

2.2. Characterization of TiO_2:N 8% thin film using UV-Vis Spectrophotometer

The optical properties of TiO_2:N 8% thin film was tested using a UV-Vis spectrophotometer, and will produce an absorbance spectrum of TiO_2:N 8% in the wavelength range of 200-500 nm. The data was obtained used to determine the energy gap value using the tauc's plot method with indirect transition equation as follows:

$$(\alpha h\vartheta)^{1/2} = B(\alpha\text{hv} - E_g) \qquad (1)$$

with α is absorption coefficient, hv is the photon energy, B is constants, E_g is energy gap, $n = 2$ for the direct energy gap, and $n = 1/2$ for indirect energy gap. The energy gap can be obtained by extrapolating the linear portion of the curve $(\alpha hv)^n \sim hv$ on $(\alpha hv)^n = 0$ [11]. The value of the absorption coefficient (α) was calculated with the following equation:

$$\alpha = \frac{2.303 * A}{t} \qquad (2)$$

with t is the thickness of the thin film and A is the absorbance of the sample obtained from the characterization [12].

2.3. Rhodamine B (RhB) degradation test

The degradation of 10 ppm RhB solution was performed using a photocatalyst of TiO_2:N 8% into 1 liter of water as solvent under the sun and UV C light as a source of degradation. The degradation process using sunlight and UV C was done simultaneously. The degradation of the solution was carried out for 3 hours for each samples starting at 09.48-12.48 WIB (Western Indonesia Time) with taking solution every 30 minutes. All of the samples were tested absorbance using a UV-Vis spectrophotometer, and the efficiency of RhB degradation was calculated using the following equation:

$$\eta\ (\%) = \left(1 - \frac{C_t}{C_o}\right) \text{x}\ 100 \qquad (3)$$

with C_0 and C_t is initial concentration and final concentration of the RhB solution.

3. Results and Discussion

3.1. Effect of Annealing Temperature on Optical Properties Thin Film TiO_2:N 8%

The thin film TiO_2:N 8% can be distinguished by analyzing optical properties using a UV-Vis spectrophotometer. The results obtained are absorbance and energy gap width. The absorbance spectrum in the wavelength range 200-500 nm can be seen in Figure 1. From all samples, it can be seen that a thin film TiO_2:N 8% with the annealing temperature of 600 ^{o}C has a greater absorbance, for the thin film of TiO_2:N 8% with an annealing temperature of 400 ^{o}C has a smaller absorbance. Based on Figure 1, it can be seen that the sequence of a thin film with the ability of light absorption from the largest to the smallest is annealing 600 ^{o}C, annealing 500 ^{o}C, without annealing, and annealing 400 ^{o}C.

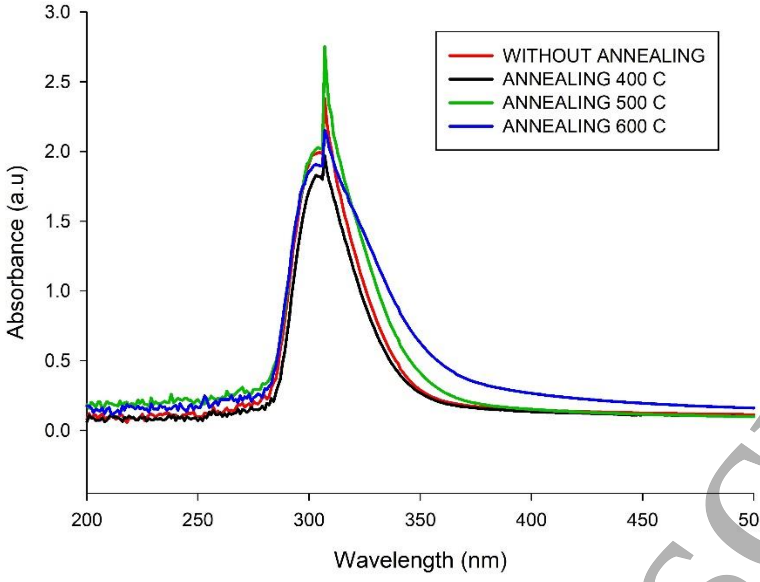
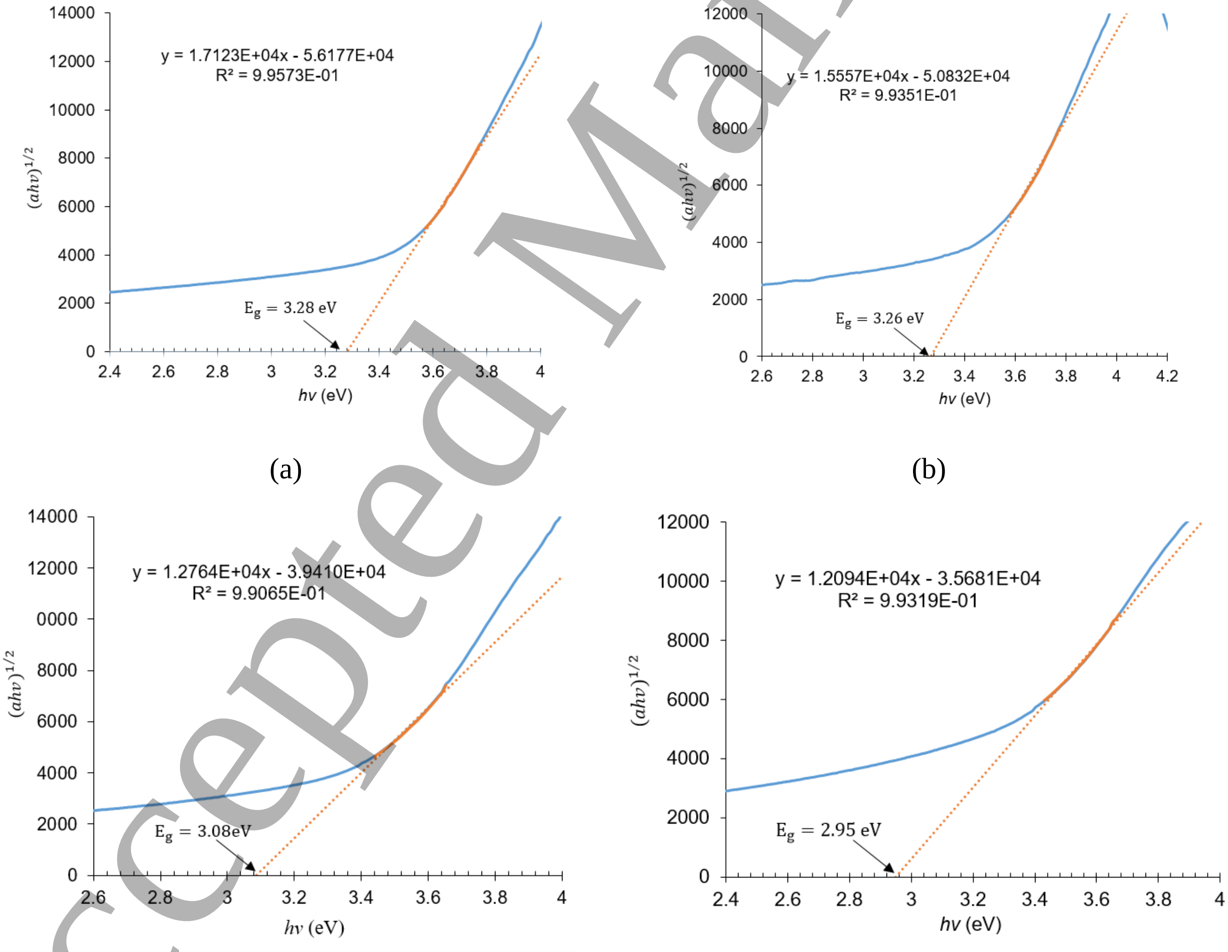


Figure 1. Spectrum absorbance of thin film TiO_2:N 8%

Energy gap value was calculated using the tauc's plot method. This method was determined using the absorbance value generated by UV-Vis spectrophotometer at the linear region of the relationship graph between *hv* dan $(\alpha hv)^{1/2}$. The energy gap using indirect transition with $n = {}^{1}/_{2}$ and the result can be seen in Figure 2.



(a) (b)

(c) (d)

Figure 2. Graph of energy gap TiO_2:N 8% (a) Without Annealing, (b) Annealing 400 ºC, (c) Annealing 500 ºC (d) Annealing 600 ºC

The energy gap in Figure 2 shows the energy gap decreases as the annealing temperature increases in TiO_2:N 8% thin film. Blanco et al showed the same results by producing a slight decrease in band gap energy when the annealing temperature was above 300 °C [13]. The decrease in energy gap is caused by the presence of a new energy level between the valence band and the conduction band. The resulting energy gap by the sample by using annealing process is lower from pure TiO_2 without annealing process. This is due to the maximum shift of the valence band and the oxidizing power of the hole in the TiO_2: N material becomes more increased [14]. The energy gap in thin film TiO_2:N 8% sequentially from Without Annealing, Annealing 400 °C, Annealing 500 °C, Annealing 600 °C has a value of 3.28 eV; 3.26 eV; 3.08 eV; and 2.95 eV, respectively.

The surface state present in all materials due to the sharp transition of the solid material occurring at the nearest atomic film to the surface. The surface state was caused by an incomplete covalent bonding on the semiconductor surface [14] and produces an energy level of electrons in the energy gap. The surface state of a semiconductor material can provide an important role in influencing photocatalytic activity. When the electrons and holes are trapped in the surface state, the spatial overlap of the load carrier becomes reduced, then slows the recombination process due to the local nature of the surface state [15]. Therefore, the surface state with abundant amounts can greatly encourage the separation of electron-hole photoexcitation pairs. The abundance of surface state in a semiconductor photocatalyst was determined by the semiconductor surface atomic structure. Morphology and dopant are important factors affecting the atomic structure of thin film surfaces [14].

TiO_2 has three crystalline structures such as anatase (3,2 eV), rutile (3,0 eV) dan brookite (3,4 eV). Thin film of TiO_2:N 8% formed in this study is rutile structure. These results are supported from the results of analyzing XRD patterns of TiO_2:N 8% thin film and can be seen in Figure 3 with the crystal orientation.

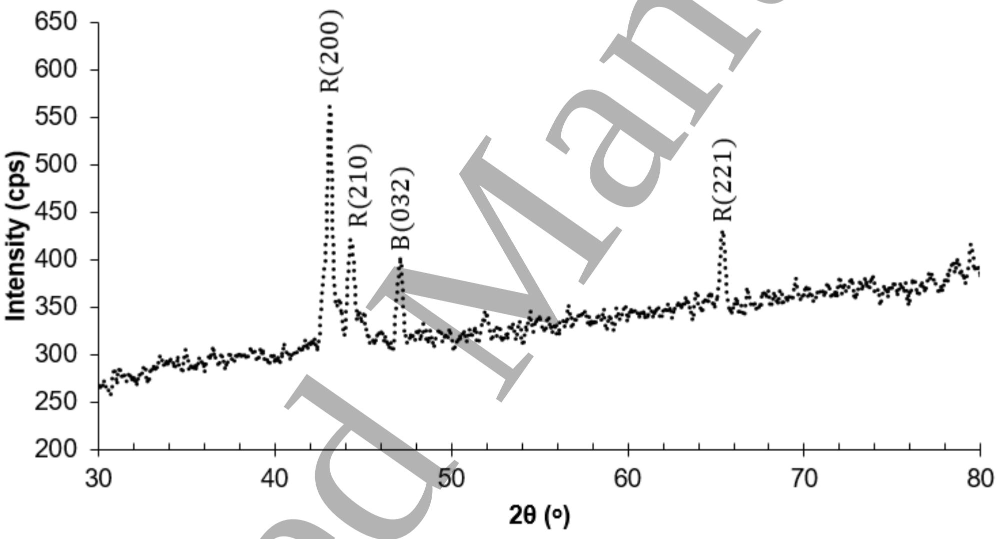
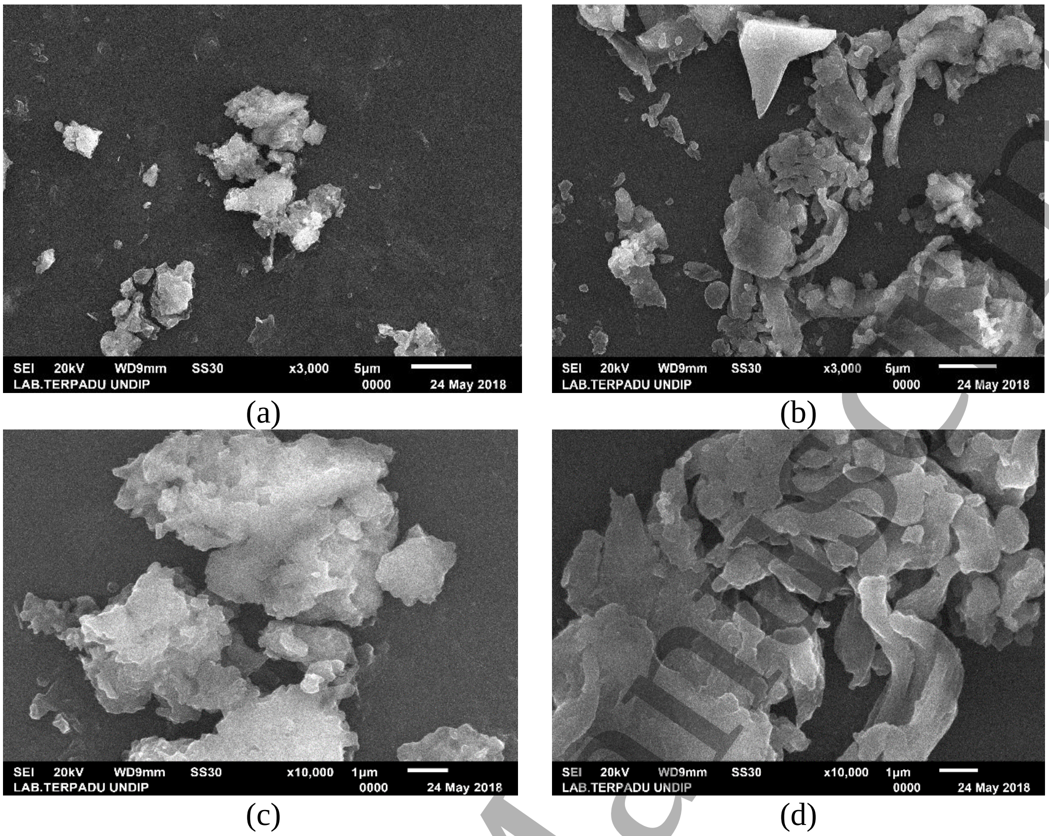


Figure 3. XRD thin film pattern of TiO_2:N with the field of crystal orientation

It can be seen that the thin film TiO_2: N 8% has four diffraction peaks at 43.00°, 44.21°, 65.24° and 82.53° indicating the rutile crystal structure with orientation plane 200, 210 and 221 according to JCPDS data No. 21-1276, and 46.98° (032) which refers to the brookite crystal structure according to JCPDS data No. 18-0875. The results of this study have different results with research conducted Nugroho [16] shows that TiO_2 has an anatase crystal structure with orientation plane 101 and 104 according to JCPDS No. 21-1272 with a crystallite size of 25.72 nm. The crystal size of TiO_2:N in this study was 20.13 nm, the crystallite size is one of the factors that influence degradation activity [17].

The SEM characterization was performed to determine the surface morphology of TiO_2:N 8% thin film of deposition result. The morphological differences generated by TiO_2: N 8% thin films can be seen in Figure 4. Based on Figures 4 (a) and 4 (c) shows that the grain of TiO_2:N 8% without annealing has a flat shape and tends to converge at a certain point so that there is more free space on the surface of the thin film. For Figure 4 (a) and 4 (c) with annealing 400 °C having a cylindrical shape. These results indicate the presence of varying thicknesses on the surface of the thin film, so that surface film TiO_2:N 8% annealing 400 °C more rough than surface film TiO_2:N 8% without annealing. Roughness rates of TiO_2:N 8% can be seen based on Figures 4 (b) and 4 (d) having a more rigid shape compared with the form TiO_2:N without annealing. Lin et al. (2013)

reported that surface roughness is directly proportional to annealing temperatures. This suggests that the grain shape becomes more euhedral (having a shape) with increasing annealing temperatures.



(a) (b)

(c) (d)

Figure 4. The surface of morpohology TiO_2:N 8% thin film (a) Without Annealing with magnification of 3.000x, (b) Annealing 400 °C with magnification of 3.000x, (c) Without Annealing with magnification of 10.000x, (d) Annealing 400 °C with magnification of 10.000x

For the measurement results of the TiO_2:N 8% thin film grain distribution shown in Figure 5. Based on Figure 5 shows that the grain size diameter distribution TiO_2:N 8% has a variety of sizes and can be seen based on the frequency difference in each sample. In general, the material TiO_2:N 8% without annealing has a grain shape having a diameter of 0.5 μm to 1 μm, while for TiO_2:N 8% annealing material 400 °C has the same grain shape without annealing.

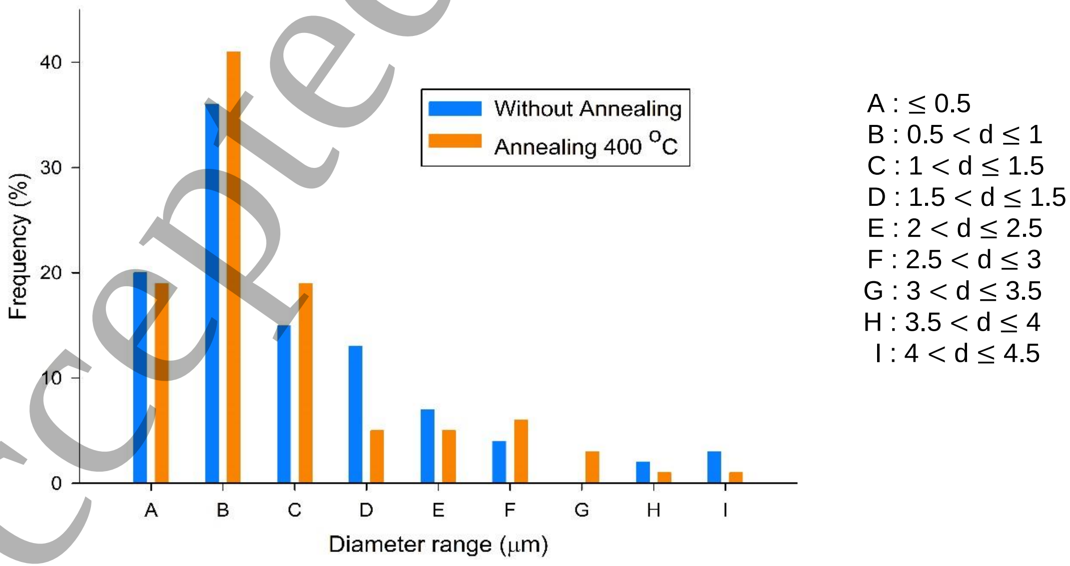


Figure 5. The grain size diameter distribution of TiO_2:N 8%

The determination of nitrogen content using ZAF method with SEM-EDX equipment type JEOL 6510 (LA). The results of composition testing (shown in Figure. 6 and Table 1) show that the composition of the nitrogen atoms in the TiO_2:N 8% film sample is 0.2%. The composition of nitrogen deposited with this small percentage indicates a shift in the crystal structure of Figure 3. Doping nitrogen into the TiO_2 matrix to create an oxygen-deficient site is important to stop reoxidation [18].

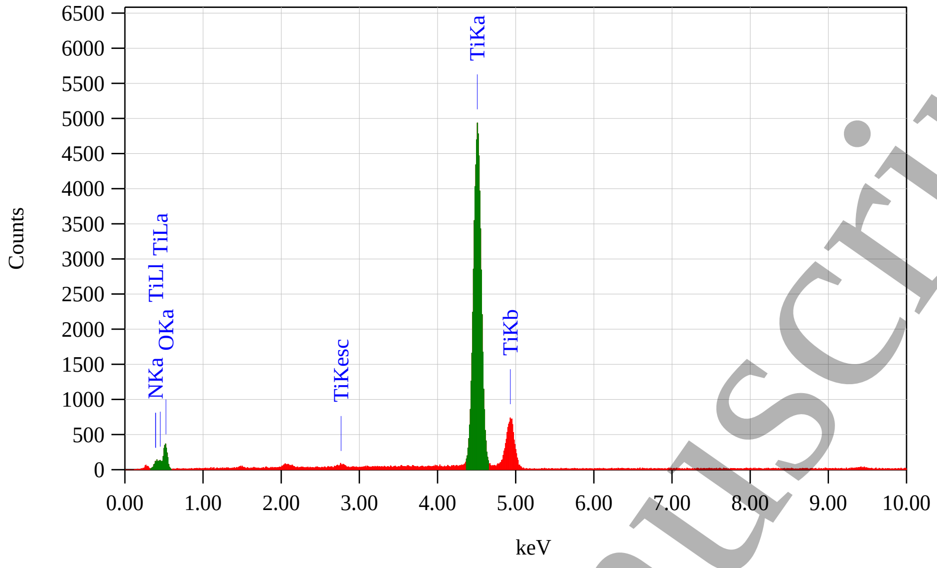


Figure 6. EDX Spectra of TiO_2:N 8%

Table 1. Thin film atomic composition TiO_2:N 8%

Element	KeV	Atom%
N	0.392	0.20
O	0.525	57.13
Ti	4.508	42.67

3.2. Effect of Annealing Temperature on Thin Film Photocatalyst Properties TiO_2:N 8%

The properties of TiO_2:N 8% thin film photocatalysts were tested by degradation of the Rhodamine B (RhB) dye solution of 10 ppm. Figure 7 shows the results of a degraded solution of RhB using sunlight (a) starting at 09.48-12.48 WIB and UV light C (b) for 3 hours. The measurement of the intensity of sunlight using lux meters during the degradation process takes place, for the measurement results can be seen in Table 2.

Table 2 The intensity of sunlight when the degradation process takes place

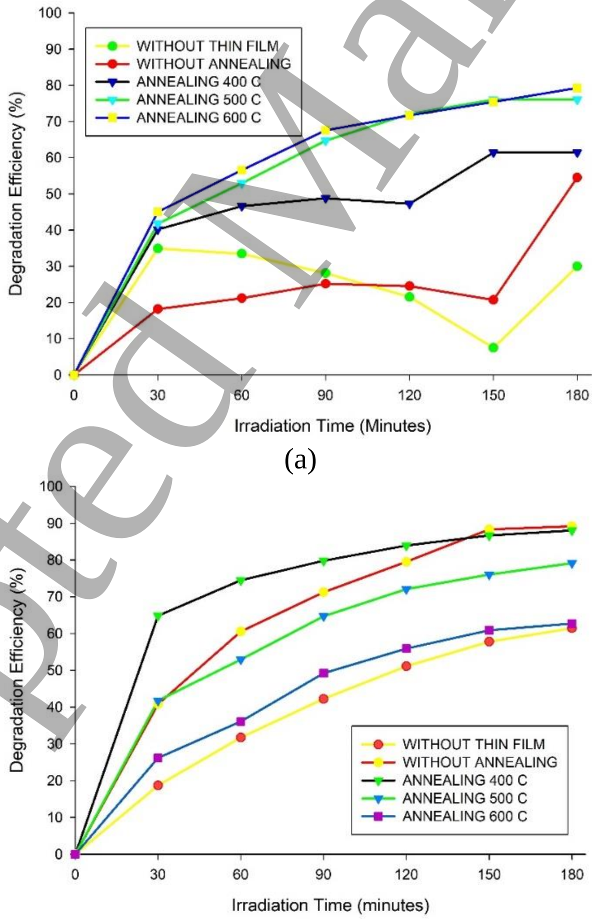
Time (minute)	Intensitas (lux)
09.48-10.18	634
10.18-10.48	675
10.48-11.18	479
11.18-11.48	409
11.48-12.18	668
12.18-12.48	721

It can be seen that the color changes that occur the longer the time of irradiation produces a clearer color change. The color change results are not the same for each annealing temperature treatment. The results showed that the process of degradation with sunlight is less effective than UV C lamp, this is because the intensity of sunlight is not constant.

(a) (b)

Figure 7. RhB solution after degradation below (a) sunlight (b) UV light lamp C

The efficiency of the degradation of the RhB solution can be seen in Figure 8 which shows the percentage of the graph every 30 minutes. The degradation was performed for a non-abrasive thin film of RhB solution, without annealing, 400 °C, 500 °C, and 600 °C. Figure 8 (a) shows the graph of the degradation efficiency of the RhB solution under sunlight. The efficiency of TiO_2:N 8% thin film degradation was not linear for without thin film, without annealing and annealing 400 °C. For the efficiency that is linearly owned by annealing 500 °C and annealing 600 °C. The best photocatalytic efficiency is annealing 600 °C and the lowest is without using a thin film. The degradation graph efficiency under UV C lamp (Figure 8b) shows the efficiency percentage of overall RhB solution. The best photocatalytic efficiency under UV C light is annealing at 400 °C and the lowest is without using a thin film. This is because the anatase energy gap (3.2 eV) has an improved photocatalytic effectiveness under UV light [13]. When compared to the use of sunlight for degradation requires photocatalysts with energy gaps <3.0 eV [10].



(a)

(b)

Figure 8. The efficiency of degradation of the RhB solution under (a) sunlight (b) UV light lamp C

The percentage degradation of the RhB solution with TiO_2:N 8% thin film can be seen in Table 3. These results indicate degradation using sunlight with 600 °C annealing is more effective than using UV light C. For annealing 400 °C it is more effective to use UV light than using sunlight.

Table 3. The efficiency of TiO_2:N 8% thin film degradation

RhB Solution	The Ability of Degradation (%)	
	Visible Light	**Lamp UV C**
Without Thin Film	30,01	61,47
Without Annealing	54,56	89,22
Annealing 400 °C	61,44	88,06
Annealing 500 °C	76,05	79,15
Annealing 600 °C	79,30	62,72

4. Conclusions

A thin film of TiO_2:N 8% is deposited on a glass substrate using a sol-gel method with a spray coating deposition technique at a without annealing, temperatures 400 °C, 500 °C and 600 °C. The annealing process causes a narrowing of the thin film energy gap TiO_2:N 8%. The higher the annealing temperature the smaller the energy gap is 3.28 eV; 3.26 eV; 3.08 eV; and 2.95 eV. In general, the material TiO_2:N 8% without annealing has a grain shape having a diameter of 0.5 μm to 1 μm, while for TiO_2:N 8% annealing material 400 °C has the same grain shape without annealing. The composition of nitrogen atoms in the TiO2: N sample of 8% by 0.2%. The efficiency of degradation shows the properties of TiO_2:N 8% photocatalyst with annealing for the better. The degradation process using 400 °C an annealing temperature yields a thin film TiO_2:N 8% with better properties under UV C lamp of 89.22% in 180 minutes. Annealing temperature increase yields TiO_2:N 8% thin film with improved photocatalyst properties in sunlight with annealing temperature of 600 °C at 79.30% in 180 minutes.

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References

[1]. Sutanto, H., Hidayanto, E., Subagio, A., Widiyandari, H., Nugroho, I.A., dan Rahmawati, Z., 2011, Pembuatan Sistem Pengolah Air Bersih Menggunakan Material Fotokatalis Titania (TiO_2), ResearchGate, Prosiding Seminar Nasional Sains dan Teknologi Ke-2, Semarang : Fakultas Teknik, Universitas Wahid Hasyim.

[2]. Gerischer, H. 1993. Photoelectrochemical Catalysis of The Oxidation of Organic Molecules by Oxygen on Small Semiconductor Particles with TiO_2 An Examples, Electrochemica Acta 38 (1), pp. 3-9.

[3]. Rilda, Y., Dharma, A., Arief, S., Alief, A., and Shaleh, B. 2010. Efek Doping Ni(II) pada aktifitas fotokatalitik dari TiO_2 untuk inhibisi bakteri patogenik, Jurnal Makara 14 (1), pp.7-14.

[4]. Cotton, F. A., and Wilkinson, G. 1999. Advanced Inorganic Chemistry 6th ed, John Willey and Sons Inc, Van Couver.

[5]. Nurmawarti, I., Abdullah, M., and Khairurrijal, K. 2009. Distribusi Celah Pita Energi Titania Kotor, Jurnal Nanosains dan Nanoteknologi, pp. 38-42.

[6]. Yin, W.J., Chen, S., Yang, J.H., Gong, X.G., Yan, Y., and Wei, S.H. 2010. Effective Band Gap Narrowing of Anatase TiO_2 by Strain Along a Soft Crystal Direction, Applied Physics Letter 96, pp. 1-3.

[7]. Subramani, A, K., Bryappa, K., Ananda, S., Ray, K. M. L., Ranganathaiah, C., Yoshimura, M. 2007. Photocatalytic Degradation of Indigo Carmine Dye Using TiO_2 Impregnated Activated Carbon, Bull, Mater Sci 31, Indian Academy of Sciences, pp. 37-41.

[8]. Lin, C. P., Chen, H., Nakaruk, A., Koshy, P., and Sorrel, C.C. 2013. Effect of Annealing Temperature on the Photocatalytic Activity of TiO_2 Thin Films, Energy Procedia 34, 627-636.

[9]. Zheng, S.K., Wang, T.M., Xiang, G., and Wang, C. 2001. Photocatalytic Activity of Nanostructured TiO_2 Thin Films Prepared by dc Magnetron Sputtering Method, Vacuum 62, pp. 361-366.

[10]. Indriyani, Y., Sutanto, H., and Nurhasanah, I. 2017. Analisis Sifat Optis Lapisan Tipis TiO_2:N untuk Fotodegradasi Direct Blue 71, JurnalIlmiah Teknosains 3 (2), pp. 98-103.

[11]. Ilican, S., Caglar, M. dan Caglar, Y., 2007, Determination of The Thickness and Optical Constants of Transparent Indium-doped ZnO Thin Films by The Envelope Method, Materials Science-Poland, 25, 709-718

[12]. Yakuphanoglu, F. Ilican, S. and Caglar, Y. 2007. The determination of the optical band and optical constant of non-crystalline and crystalline ZnO thin film deposited by spray pyrolysis, Journal of Optoelectronics and Advanced Materials 9 (7), pp. 2180-2185.

[13]. Blanco, E., Gonzalez-Leal, J.M., and Ramirez-del Solar, M. 2015. Photocatalityc TiO_2 Sol-gel Thin Films: Optical and Morphological Characterization, Solar Energy 122, pp. 11-23

[14]. Liu, G., wang L., Yang H.G., dan Lu, G.Q., 2009, Titania Based Photocatalyst Crystal Growth, Doping, and Heterostructuring, J. Mater, Chem. 20, 831-843.

[15]. Daude, N., Gout, C., and Jouanin, C., 1977, Electronic Band Structure of Titanium Dioxide, Physical Review B, 15, 3229-3235.

[16]. Nugroho, I.A., 2011, Deposisi Lapisa Tipis Titania dan Pembuatan Sistem Pengolah Air Limbah organic Menggunakan Material Fototokatalis Titania (TiO_2), Skripsi, Fakultas Sains dan Matematika, Universitas Diponegoro, Semarang.

[17]. Aziz, A.A., Cheng, C.K., Ibrahim, S., Matheswaran, M. dan Saravanan, P., 2012, Visible Light Improved, Photocatalytic Activity of Magnetically Separable Titania Nanocomposite, Chemical Engineering Journal, 183, 349-356.

[18]. Zaleska, A., 2008, Doped-TiO_2: A Review, Recent Patents on Engineering, Bentham Science Publishers Ltd, 2, 157-164