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Synthesis of Ni/NiO-TiO₂ using sol-gel method and its activity in blue methylene degradation

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Abstract. The synthesis of Ni-TiO₂ and NiO-TiO₂ with titanium isopropoxide and (Ni(NO₃)₂·6H₂O precursors using the sol gel method has been done. The calcination process was carried out by varying the order of the oxidation-reduction process and the temperature of calcination. The oxidation-reduction process produced Ni-TiO₂ material. XRD analysis (X-Ray Diffraction Spectrophotometer) showed the smallest size of Ni-TiO₂ particles was 7.44 nm and NiO-TiO₂ was 8.53 nm. The addition of dopants caused the TiO₂ band gap to become smaller. The smallest band gap due to Ni dopant was 2.68 eV while the smallest band gap due to the addition of NiO dopants was 2.81eV. SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-ray) results showed that the TiO₂ surface which was doped with Ni and NiO had small and smooth surface compared to TiO₂ without dopant. The synthesized material was then used for the photocatalytic activity test, that was the degradation of methylene blue. The highest degradation of methylene blue was in TiO₂ doped with Ni was 76.93%, while in TiO₂ doped with NiO was 80.63%.

1. Introduction

Titanium dioxide (TiO₂) is a widely applied material in various aspects. In recent decades, TiO₂ has been used as an anti-bacterial material, water decomposition, of methylene blue degradation, and many other applications. Titanium dioxide (TiO₂) is a high photoactive semiconductor that have chemical stability, non-toxic and has redox properties, which is able to oxidize organic pollutants and reduce a number of metal ions in solution. TiO₂ also has inert properties, stable to corrosion caused by light or chemicals, and abundantly available in nature [2]. As a semiconductor material, TiO₂ has a band gap energy about 3.2 eV-3.8 eV [3]. The size of this band gap will affect the excitation process of electrons from the valence band to the conduction band [4].

Titanium dioxide photocatalyst is a very strong oxidizing agent when exposed by 365-385 nm UV light wavelength. This photocatalysts is more advantageous than adsorbents such as activated charcoal in terms of reducing the concentration of dyes that may contaminate the aquatic environment due to TiO₂ photocatalysts can break down harmful dyes into simpler and relatively less dangerous substances. Meanwhile, activated charcoal only adsorbs the dye without breaking down the dye's compound [5]. The application of Ni and NiO dopants to TiO₂ expected to be increasing the photocatalytic activity of TiO₂ nanomaterials so that it can be applied to degrade dyes such as methylene blue. In this study, the difference in photocatalytic activity of Ni and NiO dopants in reducing the methylene blue color was tested. Methylene blue was chosen as the test material because this compound is quite harmful to



humans, which can cause nausea, vomiting, diarrhea, and difficulty in breathing. Methylene blue compound has a benzene structure that is difficult to decompose, toxic, carcinogenic and mutagenic [6].

2. Experimental Method

The equipment used in this research was magnetic stirrer, oven, furnace, XRD Shimadzu 6000, DR-UV-Vis (DR 6000), UV-Vis Spectrophotometer, SEM-EDX Hitachi S-4500. While the materials used include: methylene blue, titanium isopropoxide (Sigma Aldrich), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (E-Merck), HNO_3 (E-Merck), absolute ethanol (E-Merck) and aqua demineralization.

Both Ni-TiO₂ and NiO-TiO₂ materials were synthesized using the sol gel method. A total of 21.15 mL of titanium isopropoxide precursor were mixed into 45 mL of ethanol. Afterwards, 0.549 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in a mixture of 75 mL ethanol, 4.5 mL HNO_3 and 24 mL aquademin. This mixture then slowly added to the titanium isopropoxide solution until the sol was green, and aging for 48 hours. The results of the aging were then heated at 100 °C for 6 hours. The resulting solid was calcined at temperatures: 400, 450, and 500 °C with oxygen gas flowing at a flow rate of 2 mL/second for 2 hours, followed by hydrogen gas flowing at 300, 350, 400 °C calcination temperatures for 2 hours with the same flow rate [7]. On the other hand, the NiO-TiO₂ photocatalyst was synthesized in the same way as the Ni-TiO₂ synthesis, but the gas used sequence at calcination was reversed. As a comparison, TiO₂ without dopant was also synthesized with the same method without the addition of dopants.

Photocatalytic activity was tested against the degradation of methylene blue by weighing 0.1 gram of the synthesized material sample then added to 25 mL of 5 ppm methylene blue solution. The mixture was stirred while being illuminated by 6000K Xenon lamp visible light for 20 minutes. Periodically every 5 minutes, 5 mL of the solution were taken and then centrifuged to separate the solution from the solids and the absorbance was measured using a UV-Vis spectrophotometer [6].

3. Results and Discussion

The synthesis of Ni-TiO₂ and NiO-TiO₂ was carried out based on the difference in calcination temperature and the sequence of the oxidation-reduction process. The materials of photocatalyst Ni-TiO₂ and NiO-TiO₂ were synthesized using the sol gel method, where solution A containing titanium isopropoxide dissolved in absolute ethanol was mixed with solution B containing concentrated HNO_3 , absolute ethanol, a number of Ni precursors and aquademineral. The mixture turns green as a result of the addition of the compound ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). solution A and solution B are mixed and stirred slowly and gradually so that the solution does not form a gel too quickly and the solution can be mixed homogeneously. The formed sol is then aged for 48 hours to form into a gel. To get the desired powder, the gel then heated for 6 hours at 100 °C. The powder then calcined using a furnace accompanied by the addition of hydrogen-oxygen flow gas with various calcination temperature.

The calcination process was carried out by varying the sequence of the oxidation-reduction process and the calcination temperature. The first sample was calcined at a temperature at a certain temperature while flowing the oxygen gas. After cooling, the second calcination process was continued with hydrogen gas flow at a certain temperature with the same flow rate gas. The addition of hydrogen gas aims to remove the oxides present in the sample to produce Ni-TiO₂ sample. The second and third samples were calcined with the same treatment, but with different using temperature. The second sample was carried out at 500 °C for oxygen flow gas followed by hydrogen flow gas at 350 °C, while third sample was carried out at 550 °C for oxygen flow gas followed by hydrogen gas flow at 400 °C.

The second calcination process was the reduction-oxidation process. The sample was calcined with the addition of hydrogen flow gas at first, then followed by oxygen flow gas for 2 hours each. The first sample is calcined at a certain temperature while flowing the hydrogen gas, then followed by oxygen gas with the same gas flow rate, at a certain temperature. Second and third samples were calcined with the same treatment but different temperature. The second sample was carried out at 350 °C for hydrogen flow, followed by oxygen flow at 500 °C for 2 hours. Whereas third sample was carried out at 400 °C for hydrogen flow gas, followed by oxygen flow gas at 550 °C for 2 hours. This calcination aimed to remove the remaining solution and impurities.

The synthesized samples were coded A, B, C for NiO-doped TiO₂ samples, and D, E, F codes for NiO-doped TiO₂. TiO₂ without dopant was white color, Ni-TiO₂ material was light green, while NiO-TiO₂ material was blackish brown. This blackish brown color indicates the presence of oxides in Ni which form the NiO-TiO₂ material [7].

Figures 1 and 2 show the XRD patterns of TiO₂ without dopant, TiO₂ with Ni and NiO. The TiO₂ without dopants has crystalline phase dominated by anatase phase more than TiO₂ doped Ni. The anatase phase can be seen at the peaks 2θ 25,325°; 37,84°; 53,952°; 68,842°; dan 74,155° with each in [101], [004], [105], [116] and [107] planes. The rutile phase grew at a peak of 2θ 37,700° at [101] plan and 61,188° at [002] planes. The brucite phase was seen at the peak intensity of 42,560° at 410 field and 47,840° at [321] plane. The NiO-doped TiO₂ was also dominated by the anatase phase. Rutile and brucite phases are also seen in NiO-TiO₂ material. This is in accordance with the JCPDS Card no 84-1286.

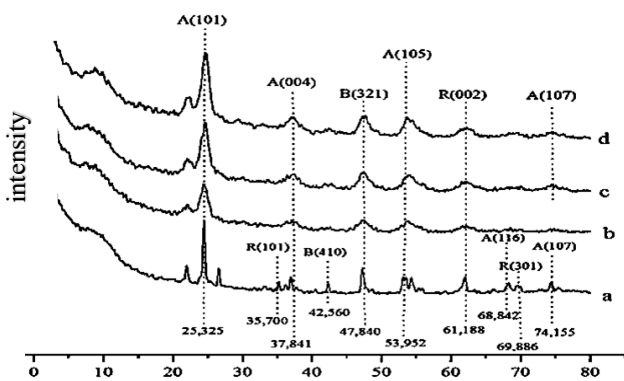


Figure 1. XRD diffractogram: a. TiO₂; b. Ni-TiO₂ A (450 °C O₂-300 °C H₂); c. Ni-TiO₂ B (500 °C O₂-350 °C H₂) and d. Ni-TiO₂ C (550 °C O₂-400 °C H₂)

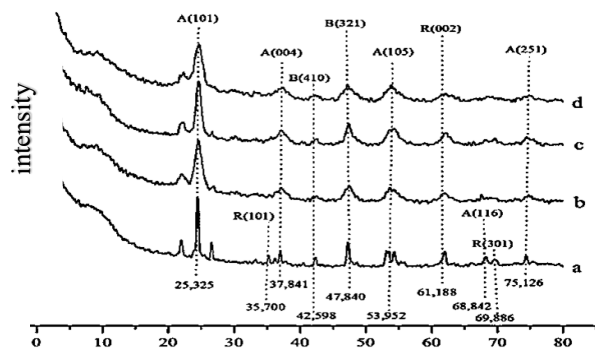


Figure 2. XRD diffractogram: a. TiO₂; b. NiO-TiO₂ D (300 °C H₂-450 °C O₂); c. NiO-TiO₂ E (350 °C H₂-500 °C O₂) and d. NiO-TiO₂ F (400 °C H₂-550 °C O₂)

There is a difference in peak intensity due to differences in calcination temperature (Figure 1 and Figure 2). The higher the calcination temperature causes the peaks of the diffractogram be sharper. The sharpness of diffractogram peak indicates that TiO₂ is crystalline. The presence of Ni and NiO dopants in TiO₂ lead the crystal growth inhibited in TiO₂ proves that the variations in calcination temperature and the presence of Ni and NiO dopants have an effect on crystallinity and material growth [8, 9].

Table 1. The λ value, band gap and particle size of TiO₂ without dopants and TiO₂ with Ni and NiO

Sample	λ (nm)	Band Gap (eV)	Particle size (nm)
TiO ₂	383.79	3.23	22.4507
Ni-TiO ₂ A	413.53	3.00	11.2453
Ni-TiO ₂ B	463.33	2.68	7.4437
Ni-TiO ₂ C	438.39	2.83	9.2068
NiO-TiO ₂ D	393.18	3.15	8.5851
NiO-TiO ₂ E	438.62	2.83	8.5345
NiO-TiO ₂ F	441.14	2.81	10.2259

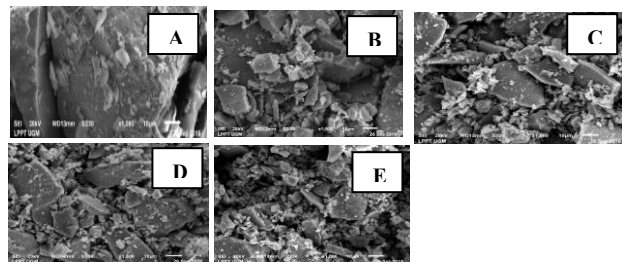


Figure 3. SEM analysis results a) TiO₂, b)Ni-TiO₂ B (500 °C O₂-350 °C H₂), c)Ni-TiO₂ C (550 °C O₂-400 °C H₂), d)NiO-TiO₂ E (350 °C H₂-500 °C O₂), and e) NiO-TiO₂ F (400 °C H₂-550 °C O₂) at 1000x magnification

TiO₂without Ni and NiO dopants had a particle size of 22.4507 nm (Table 1). The addition of Ni and NiO dopants with various calcination temperature caused the TiO₂ particle size became smaller. When TiO₂ was doped with Ni or NiO, the growth of TiO₂ crystals was inhibited so that the crystal size become

smaller. The results of this study are in accordance with the report of Liu et al. [10] and Townsend et al. [11] who stated that the TiO_2 particle size became smaller after the addition of dopants.

The semiconductor bandgap value affects the semiconductor's performance in exciting electrons from the valence band region to the conduction band and the recombination process occurred. TiO_2 without calcined dopant at 500 °C has a band gap of 3.23 eV (Table 1). The results of this study are similar to the measurements made by Elbushra et al. [12] who reported the synthesized TiO_2 band gap of 3.2 eV. This TiO_2 band gap value is less effective because it can only absorb UV rays. Too large Band gap makes the movement of electrons difficult so that it can inhibit the work of electrons which lead the flow of electrons to be also inhibited [13].

The application of Ni and NiO dopants into the TiO_2 bulk structure decreased the band gap value. This is supported by research conducted by Priatmoko et al. [3] who stated that the addition of Ni and NiO dopants lead the band gap value of TiO_2 become smaller. This is due to the presence of Ni or NiO which enters the TiO_2 structure so that it can cause the excitation of Ni's 3d electrons to the TiO_2 conduction band. Sim et al. [14] reported that absorption increasing in the visible light region was also caused by the formation of dopant energy levels in the TiO_2 band gap. The 3d electrons are excited from the dopant energy level to the TiO_2 conduction band. However, too small a band gap value will also affect the performance of the photocatalyst. Too small band gap leads a too fast jump of electrons from the valence band to the conduction band so that it is less effective as an oxidizer [15].

Figure 3 is the topographic shape of the SEM-EDX results of the photocatalyst sample. TiO_2 without dopants has a topographical shape in the form of a rough and large surface similar to boulders (Figure 3). In contrast to TiO_2 which is doped with Ni and NiO, the topographic structure is smaller and smoother than TiO_2 without dopants due to the addition of Ni and NiO at the time of synthesis. Dopant ion is evenly and homogeneously distributed on the TiO_2 surface with different sizes. Rielda et al. [4] stated that the addition of dopants to TiO_2 caused the morphological structure of TiO_2 become smaller and smoother and has more regular distribution.

EDX analysis (Energy Dispersive X-ray Spectroscopy) was used to determine how much Ni and NiO were entered into the pores of TiO_2 . Based on the results of EDX analysis on Ni- TiO_2 B material, the Ni entered the TiO_2 pores was 1.39% from 2.5% during the initial synthesis. The Ni- TiO_2 C, Ni material entered the TiO_2 pores was 1.52%. The EDX analysis result of NiO- TiO_2 E material showed that the NiO entered the TiO_2 pores was 1.34%, while the NiO- TiO_2 F NiO material entered the TiO_2 pores was 1.31%. The reduced percentage of Ni or NiO that enter the TiO_2 pores is probably due to the oxidation reduction process during calcination. The addition of oxygen and hydrogen gases flow during the calcination process allows Ni or NiO materials carried by the gas.

The photocatalytic activity test of TiO_2 without dopant, Ni- TiO_2 doped Ni, and TiO_2 doped NiO was carried out by applying them to the degradation of methylene blue dye. The materials used to degrade the methylene blue dye were 0.1 g and 25 mL of 5 ppm methylene blue dye. Before measuring the absorbance, a centrifuge was performed for 7 minutes to separate the solution from the solid. The test was carried out every 5 minutes for 5 times using a UV-Vis spectrophotometer at 663 nm wavelength. The 663 nm wavelength was the optimum wavelength of methylene blue dye measured by UV-Vis spectrophotometer at 700-500 nm range.

The decreasing concentration of methylene blue dye was indicated by a decrease in absorbance after adding TiO_2 without dopant, TiO_2 doped Ni, and TiO_2 doped NiO. The measurement results for treatment using TiO_2 can be seen in Figure 4a.

There was a decrease in the concentration of methylene blue with treatment using TiO_2 material without dopants (Figure 4a). In the 0th minute before the light irradiation, there was a decrease in the concentration of methylene blue dye by 0.28% that indicates TiO_2 has the ability to absorb methylene blue even without light. The longer the radiation is carried out, the more the concentration decreases. In this study, at the 20th minute of exposure, there was a decrease in the concentration of the dye methylene blue by 30%. Mustaq et al. [16] reported that the long exposure time affected the degradation of methylene blue.

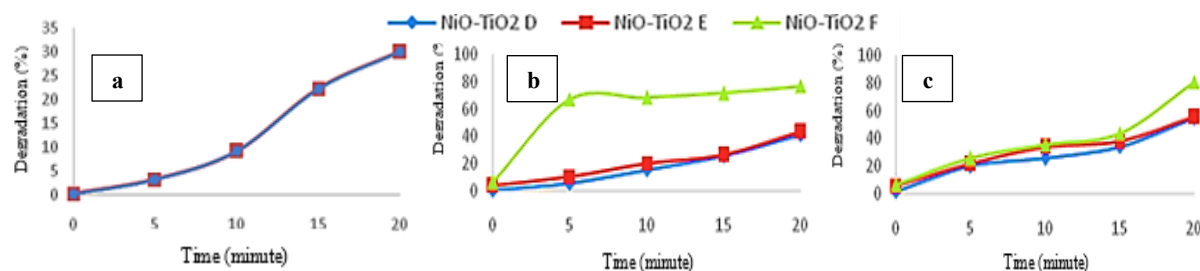


Figure 4. Degradation of methylene blue by treating TiO₂ (a) material without dopants, (b) TiO₂ doped Ni treatment, (c) TiO₂ doped NiO treatment

There was a decrease in the concentration of the dye methylene blue with TiO₂ doped NiO treatment with various calcination temperature (Figure 4b and Figure 4c). The presence of NiO dopants on TiO₂ leads the band gap of TiO₂ become smaller [17,18]. The smaller band gap leads the increasing of photocatalyst activity and makes it easier for the photocatalyst to absorb photons. While the calcination temperature affects the particle size and the growth of the crystal lattice. The higher the calcination temperature, the smaller the particle size and the sharper the peak intensity. The smaller material leads the bigger particle pores so that the absorption of light was maximized. Meanwhile, the anatase phase increased more in the presence of the calcination temperature. The anatase phase has advantages in terms of photocatalytic activity [19,20]. In the 0th minute, the highest decrease in methylene blue concentration occurred in TiO₂ dopant Ni treatment with a calcination temperature variation of 550 °C-400 °C (oxygen-hydrogen flow gas) at 6.10%. Then the Ni-TiO₂ B sample was 3.60% and the Ni-TiO₂ C sample was 6.10%. The degradation of methylene blue was increasing in the presence of visible light irradiation. The longer the exposure, the higher the degradation of methylene blue that occurs.

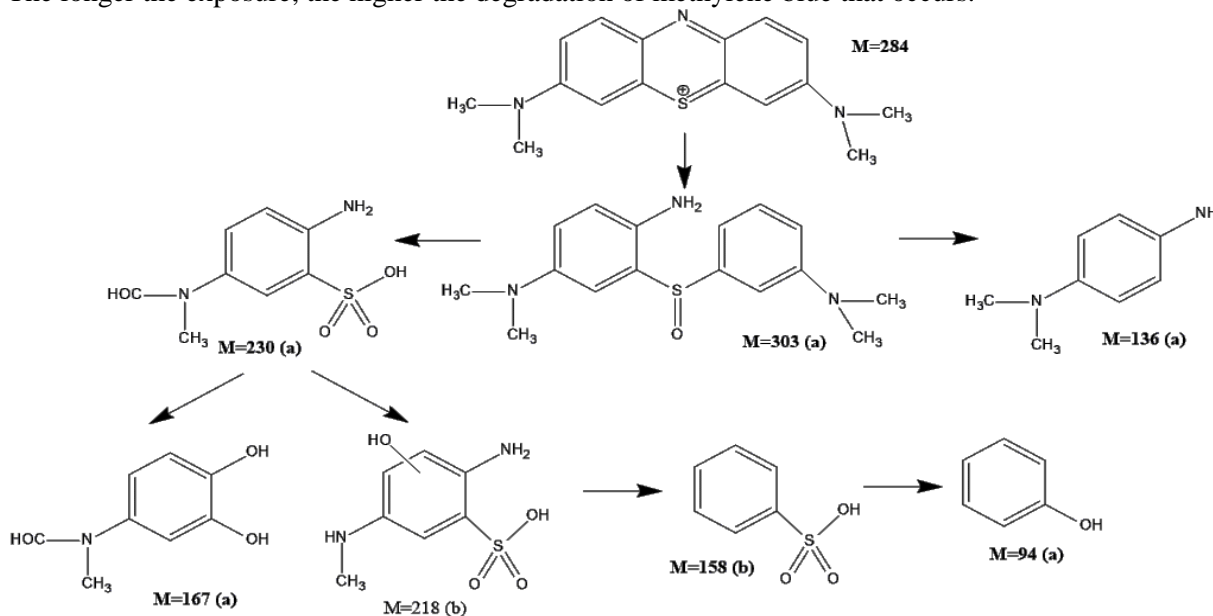


Figure 5. Photocatalytic degradation pathway of methylene blue

The results of the analysis of methylene blue degradation products using photocatalytic on the basis of TiO₂ as carried out some research showed that the final products of degradation of methylene blue are nitrate, sulphate, ammonium and CO₂ gas [21,22,23]. Based on the evidence of GC-MS and LC-MS analysis, it was found that there were intermediate compounds before becoming the final product. At the beginning of the photocatalytic reaction, hydroxyl radicals, as a result of the interaction between

solid TiO₂ nanomaterials and light with a certain energy, first attacked the conjugate structure of the N-S heterocycle groups. This group is a target for hydroxyl because of the higher electron density of sulfhydryl. Methylene blue is then degraded to 2-amino-5-dimethylamino-benzenesulfonic and Dimethyl-(4-nitro-phenyl)-amine acid anions.

The dimethyl-(4-nitro-phenyl)-amine compound then reacts with the hydroxyl radical to form p-dihydroxy-benzene. While the 2-amino-5-dimethylamino-benzenesulfonic acid anion then undergoes breakdown into 4-amino-benzenesulfonic acid and 2-amino-5-dimethylamino-benzenesulfonic acid. The intermediate 4-Amino-benzenesulfonic acid will then be oxidized to 4-Nitro-benzenesulfonic anion. The series of reactions will continue and the degradation process will stop after CO₂ and H₂O, NO₃⁻, SO₄²⁻ and NH₄⁺ are formed. In detail, the reaction mechanism is described in the Figure 5 [23].

4. Conclusion

Based on the research results, it can be concluded that the TiO₂ particle size and band gap size are smaller due to heating with various calcination temperature and the presence of Ni and NiO dopants entered the TiO₂ structure. The increasing in size is not directly proportional to the increasing of the calcination temperature in both the particle size and the band gap size. The smallest particle sizes of Ni-TiO₂ and NiO-TiO₂ were 7.44 and 8.53 nm, respectively. The smallest band gap sizes are Ni-TiO₂ and NiO-TiO₂, at 2.68 and 2.81 eV. The presence of Ni and NiO dopants in the TiO₂ catalyst can accelerate the photocatalytic activity due to the addition of Ni and NiO dopants to TiO₂ leads the TiO₂ the smaller particle size, the increasing crystallinity, and the smaller band gap size so that the photocatalytic activity of TiO₂ increases. The increased photocatalytic activity of TiO₂ leads greater degradation of methylene blue. The largest degradation of methylene blue was in TiO₂ doped with Ni by 76.93%, while the largest degradation of methylene blue was in TiO₂ doped with NiO by 80.63%.

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