Synthesis of ZnO/rGO/TiO₂ Composite and Its Photocatalytic Activity for Rhodamine B Degradation

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Abstract. Nowadays the growth of the textile industry in Indonesia is increasing. An example of dangerous textile waste is Rhodamine-B. Therefore, a method to treat Rhodamine B waste is needed. One method that can be used is photocatalysis. ZnO and TiO₂ semiconductors are known as good photocatalyst material because they have a small band gap energy. In addition, reduced graphene oxide (rGO) has a potential due to its good conductivity and large surface area. This study aims to synthesize ZnO/rGO/TiO₂ composite. Analysis of the composite shows peaks correspond to diffraction pattern of ZnO, TiO₂, and rGO. Based on scanning electron microscope analysis, the surface morphology of the composite was in the form of sheets (rGO), agglomerates (TiO₂), and hexagonal nanorod (ZnO). Further confirmation by EDX analysis shows elemental compositions of Zn, Ti, O, C (18.44, 7.44, 46.01, 28.11, respectively). FTIR analysis resulting in bands of C-O at 998 cm⁻¹, Ti-O-Ti at 506 cm⁻¹, and Zn-O at 497 cm⁻¹. Photocatalysis test using the composite gave the optimum value of Rhodamine-B degradation of 94.72 % under UV light irradiation for 5 hours.

1. Introduction

Today, the increasing number of textile industry in Indonesia indirectly increases the production of textile dye waste. The existence of this waste can cause environmental damage. This is because textile dyes are non-biodegradable organic substances that are easily accumulated in soils and waters [1]. One of the dyes that is usually used in the textile industry is Rhodamine B. This dye is a dangerous chemical that is not allowed to be mixed either in food, drinks, or cosmetics. If this molecule enters the human body, it can cause irritation of the skin, eyes, and liver cancer.

Various methods have been done to overcome this waste, for example catalytic ozonation [2], osmosis process [3], coagulation process [4], and etc. However, those several methods only transferred dye pollutants from one phase to another and unable to solve the problem [5]. A promising method to solve this problem is photocatalysis using semiconductor materials. With this method, dyes are broken down into compounds that are simpler and safer for the environment.

In this study, ZnO and TiO₂ semiconductors were used. ZnO was chosen because it has a small band gap of ~ 3.3 eV, chemically stable, and biodegradable [6]. TiO₂ was chosen because it has a high and stable photocatalyst activity and has the ability to absorb high energy with an energy gap value of 3.2 eV [7]. To increase the photocatalytic efficiency, graphene material can be added. This is because graphene is an extraordinary material with 2D structure and covalent bonds which make graphene has...
good properties including electron mobility of 200000 cm$^2$ V$^{-1}$ s$^{-1}$, surface area of 2630 m$^2$ g$^{-1}$, and thermal conductivity of 5000 W m$^{-1}$ K$^{-1}$ [8]. Thus, ZnO and TiO$_2$ semiconductors combined with reduced graphene oxide (rGO) to improve its photocatalytic properties for Rhodamine B degradation is investigated and discussed in this paper.

2. Experimental Details

2.1. Materials

All the chemicals used were of analytical grade without further purification. Graphite powder (>99 purity), H$_2$SO$_4$ 98%, Natrium Nitrate (NaNO$_3$), Kalium Permanganate (KMnO$_4$), Hydrogen Peroxide (H$_2$O$_2$), Zinc Powder, Titanium (III) Chloride (TiCl$_3$), Barium Chloride (BaCl$_2$), Natrium Chloride (NaCl), Ammonia (NH$_4$OH) 10% and Rhodamine B were obtained from SAP Chemicals.

2.1.1. Synthesis of Graphite Oxide.

The method used to oxidize graphite to graphite oxide in this study is the modification of the Hummer’s Method. Synthesis begins with stirring 2 grams of graphite with 80 ml of 98 % H$_2$SO$_4$ for 2 hours in an ice bath at temperature of around 5 °C. After that, 4 grams of NaNO$_3$ and 8 grams of KMnO$_4$ were added gradually for one hour. The addition process turns the solution to purplish green. Then the solution was stirred for one hour, resulting in homogeneous solution. The solution is was removed from the ice bath and stirred at 35 °C for 20 hours. In this process, the solution turn to dark brown and thickens. After that, the addition of 200 ml of distilled water is was carried out in stages. After 1 hour of stirring, 30 % H$_2$O$_2$ was added to the solution. The addition of H$_2$O$_2$ aims to stop the oxidation process and cause the color of the solution to turn yellow. The solution is was left in a stirring condition for 30 minutes, then the solution is was centrifuged to separate the precipitate. After that, 5 % HCl is was added to remove the remaining metal ions. Then it periodically washed until neutral pH is was obtained. To confirm the presence of sulfate ions, 1 M BaCl$_2$ titration was performed. If clean white precipitate appeared, it indicated that there were still sulfate ions left. During the washing process, the color of the solution would turn darker due to peeling of graphite to graphite oxide. The neutral solution was then dried at 120 °C for 12 hours to obtain graphite oxide sheet.

2.1.2. Synthesis of ZnO/rGO/TiO$_2$ composite.

Prior to composite synthesis, TiO$_2$ was firstly prepared using TiCl$_3$ precursor. The process was started by stirring 4.5 ml of TiCl$_3$ and 9 ml of NaCl for 30 minutes at 45 °C. Then, the solution was heated at 200 °C for 5 hours to produce a powder product. Meanwhile, the previously formed graphite oxide through the Hummer method with variations of 15 %wt was stirred for 1 hour so that the graphite oxide sheet was disintegrated and turned into smaller flakes. Then, it was cultivated for 2.5 hours so that the small debris dissolved in distilled water and graphene oxide compound was formed. After that, the stirring process was carried out simultaneously with the addition of 1 gram of Zn powder. After 1 hour stirring, 1 gram of powder product from the heating TiCl$_3$ solution was added into solution. Next, 8 ml of 10 % NH$_4$OH was added until precipitate was formed. The solution was then washed with distilled water and calcined at 700 °C for 4 hours to get the ZnO/rGO/TiO$_2$ composite.

2.1.3. Characterization and Testing

2.1.3.1. Characterization of ZnO/rGO/TiO$_2$ composite

To assess the characteristics of ZnO/rGO/TiO$_2$ composite, X-Ray Diffraction (XRD) (Philips Analytical) test was performed at 20 angle of 10°– 90° with λ Cu-Kα 1.54060 Å to determine the crystal structure. Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) Inspec S50 was used to observe the morphology and composition. Fourier Transform Infrared Spectroscopy (FTIR) (Scientific Nicolet iS10) test was done to determine the functional groups of the composite at wavenumber range 3500-500 cm$^{-1}$.
2.1.3.2 Photocatalysis testing of ZnO/rGO/TiO2 composite for Rhodamine B degradation

Firstly, Rhodamine B powder was weighed in 0.01 gram then dissolved into 100 mL of distilled water to obtain a solution of Rhodamine B with a concentration of 100 mg L⁻¹, then pipetted 2; 4; 6; 8; and 10 mL into a 100 mL measuring flask and diluted with distilled water to obtain a solution with a concentration of 2; 4; 6; 8; 10 mg L⁻¹. Then the maximum wavelength of rhodamine B and sample of 2; 4; 6; 8; 10 mg L⁻¹ is determined by using a UV-Vis spectroscopy. Next, 0.2 gram of ZnO, TiO₂, ZnO/TiO₂ (50:50 %wt), rGO/ZnO (15:85 %wt), rGO/TiO₂ (15:85 %wt), and ZnO/rGO/TiO₂ (42.5:15:42.5 %wt) were dissolved into Rhodamine B solution. The irradiation time was variate 1-5 hours with the help of UV Light 20 Watt, and the sample was taken every 1 hour. Next, Ultra-Violet Visible Spectroscopy (UV Vis) test was conducted to determine the optimum wavelength of all the sample and absorbance after degradation process. Then using equation 1 to calculate the % of degradation

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\% D = \frac{C_0 - C_t}{C_0} \times 100\% 
\]  

(1)

Where % D = % Degradation, \( C_0 \) = Initial concentration before irradiation, \( C_t \) = Concentration after \( t \) hour irradiation.

3. Results and Discussion

3.1. XRD Result

XRD analysis was used to determine the phases contained in the material. The XRD results of graphite, graphite oxide and rGO are shown in Figure 1. A sharp peak (002) and high intensity at 2θ = 26.43° with d-spacing of 3.37 Å correspond to a graphite peak with a hexagonal crystal structure (JCPDS 03-065-6212). The graphite crystallinity is very good, as indicated by the high intensity that shows better crystallinity.

Next, the graphite was oxidized to form graphite oxide which has a different peak (001) compared to that of graphite at 2θ of 12.45° with lower intensity but bigger d-spacing of 7.10 Å.

![Figure 1. XRD pattern of graphite, graphite oxide, and rGO.](image)

After the reduction process has been done, graphite oxide was converted to reduce graphene oxide (rGO). The rGO diffraction peak observed at peak (002) at 2θ of 24.04 ° with d-spacing of 3.38 Å, and lower intensity than graphite and graphite oxide, as well as broadening peaks. It indicates that the
structure is amorphous. The XRD results for graphite, graphite oxide and rGO are in accordance to the research conducted by Mishra [9].

The results of XRD for TiO$_2$, ZnO, and the composite are shown in Figure 2. TiO$_2$ samples formed diffraction peaks (110) at 2$\theta$ of 27.056°, (101) at 2$\theta$ of 35.988°, and (200) at 2$\theta$ of 38.636°, which shows that the dominant structure of TiO$_2$ formed is rutile (JCPDS 21-1276) [10].

In the TiO$_2$ samples, the highest peaks were formed at 31.75°, 34.44°, 36.25° that correspond to (100), (002) and (101), respectively. Based on these data, the formed ZnO structure is hexagonal wurtzite (JCPDS 79-2205) [11]. In addition, there is a new peak in rGO at 2$\theta$ of 23.9° [12] indicating that the composite has been successfully synthesized.

3.2. FTIR Result

In the ZnO samples, the highest peaks were formed at 31.75°, 34.44°, 36.25° that correspond to (100), (002) and (101), respectively. Based on these data, the formed ZnO structure is hexagonal wurtzite (JCPDS 79-2205) [11]. In addition, there is a new peak in rGO at 2$\theta$ of 23.9° [12] indicating that the composite has been successfully synthesized.

3.2. FTIR Result

![Figure 2. XRD diffraction pattern of ZnO, TiO$_2$ and ZnO/rGO/TiO$_2$ composite.](image1)

![Figure 3. FTIR spectra of graphite, graphite oxide, and rGO.](image2)
Figure 3 shows the results of FTIR analysis for graphite, graphite oxide, and rGO. Graphite has functional groups that display bands at 1577 cm\(^{-1}\) (C=C), and at 1003 cm\(^{-1}\) (C–O). Graphite oxidation produces graphite oxide structure, in which the new bonds with O and H are formed, such as C=O at 1830 cm\(^{-1}\), C–OH at 1233 cm\(^{-1}\), C–O–C at 1300 cm\(^{-1}\), and OH at 3293 cm\(^{-1}\). After that, the reduction of graphite oxide will eliminate the O and H bonding groups, so that the remaining functional groups are C=C and C–O. It indicates that the reduction occurs imperfectly. This result is in accordance with previous research conducted by Yan, et al [13].

Figure 4. FTIR spectra of ZnO, TiO\(_2\) and composite ZnO/ rGO/ TiO\(_2\).

The IR spectra of ZnO/rGO/ TiO\(_2\) composite are shown in Figure 4. There are C–O peak at 998 cm\(^{-1}\) and C=C peak at 1689 cm\(^{-1}\) indicating the formation of rGO. Moreover, the composite also has Ti–O–Ti peak at 506 cm\(^{-1}\) [14], and Zn–O peak at 497 cm\(^{-1}\) [15]. Based on the IR spectra of the composite, it can be said that the composite has been formed.

3.3. SEM and EDX Result

Figure 5 shows the SEM test results for graphite (A), Graphite Oxide (B) and rGO (C). Graphite has a thick morphology in the form of flakes. When graphite is oxidized, the flakes will turn to transparent sheets, which resembling the graphite oxide. Furthermore, the reduced graphite oxide will form a thin sheet structure, This mechanism is known as chemical exfoliation, which is the reduction in the number of layers of graphite, resulting in a thin structure in the form of a monolayer, or few layers of graphene in the form of rGO.

Figure 5. SEM images of graphite (A), graphite oxide (B), and rGO (C) mag 20000x.
Figure 6. SEM images of ZnO (A), TiO$_2$ (B) and ZnO/rGO/TiO$_2$ composite (C) mag 10000x.

Figure 6 shows the SEM result of ZnO (A), TiO$_2$ (B) and ZnO/rGO/TiO$_2$ composite (C). ZnO has morphology of hexagonal nanorods, while TiO$_2$ has a morphology of nearly spherical agglomerate. In the composite, it appears that there are structures in the form of hexagonal nanorods which is the characteristics of ZnO, agglomerated structure which shows TiO$_2$, and thin and transparent sheet which shows rGO. Thus, it can be summarized that the composite has been formed.

The EDX analysis results are shown in Figure 7. At ZnO, a comparison value of %At Zn:O is 62.18:37.82. The high value of %At of Zn is probably due to the fact that a small amount of Zn was left in the composite. The ratio value of %At Ti:O is 39.15:60.85, close to the atomic ratio of TiO$_2$. For the composite, the ratio of %At Zn:Ti:O:C is 18.44:7.44:46.01:28.11. The %wt of C is 12.81% from the addition of 15% graphene oxide. It can be concluded that the compound has been formed.

Figure 7. EDX result of ZnO (A), TiO$_2$ (B) and ZnO/rGO/TiO$_2$ composite (C).
3.4. UV VIS and Photocatalysis Result

From Figure 8 (A) it is observed that the highest absorbance of UV Light after 5 hours irradiation was shown by ZnO. This indicates that there are still many Rhodamine B that have not been degraded.

![Figure 8. (A) Absorption profile of ZnO, TiO$_2$, ZnO/TiO$_2$ (50:50 %wt), rGO/ZnO (15:85 %wt), rGO/TiO$_2$ (15:85 %wt), and ZnO/ rGO/ TiO$_2$ (42.5:15:42.5 %wt ) after 5 hours irradiation; (B) absorption profile of ZnO/rGO/TiO$_2$ in various irradiation time of 1-5 hours](image)

The lowest absorbance value was shown by ZnO/rGO/TiO$_2$ composite, which indicates that only small amount of Rhodamine-B remains. Figure 8 (B) shows the absorbance value of ZnO/rGO/TiO$_2$ composite in various irradiation time. As the irradiation time increases, the absorbance value decreases, indicating that more Rhodamine-B concentration was degraded.

![Figure 9. Percentage of degradation profile of Rhodamine-B by ZnO, TiO$_2$, ZnO/TiO$_2$ (50:50 %wt), rGO/ZnO (15:85 %wt), rGO/TiO$_2$ (15:85 %wt), and ZnO/rGO/TiO$_2$ (42.5:15:42.5 %wt) after 5-hours irradiation.](image)

The degradation percentage results in Figure 9, show that the lowest degradation value after 5-hours irradiation was 64.42 %, which is correspond to ZnO. In TiO$_2$, the degradation value was 72.41%. When ZnO and TiO$_2$ were combined, the degradation value was increased to 77.87%. The
interesting point is, when rGO was added to ZnO or TiO$_2$, it increases the degradation value, to 81.18% (rGO/ZnO) and to 84.11% (rGO/TiO$_2$). When the three catalysts were combined as ZnO/rGO/TiO$_2$, the degradation percentage reaches the highest value of 94.73%.

The addition of rGO, which has a wide active surface area, increases the formation of super anions and OH$. This addition can accelerate the process of degradation because it is able to narrow the band gap of both TiO$_2$ and ZnO semiconductors so that the electron mobility occurs faster [16]. When the photon light energy falls on the surface of the semiconductor, electrons in the valence band excited to the conduction band faster. Then the holes left in the valence band react with water to form hydroxyl radical, which is responsible for the degradation of Rhodamine B.

4. Conclusion
ZnO/rGO/TiO$_2$ composite has been successfully synthesized by using Zn, TiCl$_3$, and graphite oxide powder as precursors. The XRD analysis shows that the ZnO, TiO$_2$, and rGO has hexagonal wurtzite, rutile and amorphous structures, respectively. The morphologies of ZnO, TiO$_2$, and rGO were hexagonal-shaped nanorods, spherical agglomerates, and thin sheets, respectively. The results of photocatalysts test showed that the best degradation percentage using irradiation time of 5 hours was obtained by ZnO/rGO/TiO$_2$ composite with value of 94.73%. This shows that by adding reduced graphene oxide, the active surface area of the catalyst will be much greater because reduced graphene oxide has a large surface area. It also increases the formation of super anions and OH$, which can accelerate the process of degradation.

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