Photocatalytic activity of hydrothermally synthesized Al₂O₃-graphene nanocomposite

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Abstract. In this study, Al₂O₃-graphene nanoplatelets (GNP) nanocomposite was evaluated on its properties and performance towards methyl orange (MO) dye. Al₂O₃-GNP nanocomposite was prepared by conventional hydrothermal at 200°C for 24 h. The result showed the crystallite size of Al₂O₃ is decreased and internal strain increased with the increased GNP content. The particle size of nanocomposite becomes larger with the increment GNP amount in the nanocomposite. Nanocomposite with lower graphene contents (20 wt%) and higher Al₂O₃ contents performed (80 wt%) the optimum for the MO absorption with efficiency of 75% in visible light.

1. Introduction

Al₂O₃ is the most widely used ceramic matrix to produce composite due to low price, high hardness and chemical stability [1]. Al₂O₃ also possess high thermal conductivity, melting point and thermal expansion making it possible for high temperature application [2]. However, Al₂O₃ suffers from low fracture toughness [3-4]. Therefore, Al₂O₃ is reinforced with nanoparticles such as carbon nanotube [5], titanium dioxide nanoparticles [6] and silver nanoparticles [7]. Al₂O₃ also has potential to be functionalized in environmental application as it has properties that could reduce the band gap of the materials [8]. However, Al₂O₃ is seldom reinforced with graphene for the used as photocatalytic materials for degradation of dyes.

Reinforcement of the composite is defined as binder that combines the two materials together. Reinforcement usually carries the load of the composite for about 70 to 90% by fibers. The reinforced materials provide structural properties such as stiffness, strength and thermal stability to the composite. The examples of the reinforcement materials used as reinforced phase in Al₂O₃ are silicon nitride (Si₃N₄) [9], carbon nanotube (CNT) [10] and silver nanoparticles [7].

Al₂O₃-based nanocomposite has been found mostly on high temperature application. However, there is limited information regarding the performance of Al₂O₃-based nanocomposite in waste water application. Recently, graphene gains the interest of the most researchers to become reinforcement in
the nanocomposite [11]. Graphene with structure of two-dimensional (2D) honeycomb lattice is also an ideal candidate to be reinforced with Al₂O₃. This is because graphene exhibits excellent electrical and mechanical properties [11]. Graphene displays a good compatibility with Al₂O₃ nanocomposite that can enhanced the mechanical properties of nanocomposite [12]-[14] so that it can be used for waste water application. Therefore, this study used Al₂O₃-graphene nanocomposite to degrade the dyes in wastewater treatment. The aim of the research is to evaluate the characteristics of using different content of graphene in Al₂O₃-graphene nanocomposite produced by hydrothermal method. The performance of Al₂O₃-graphene nanocomposite towards the degradation of dyes for environmental application potential will be discussed.

2. Experiment

2.1 Preparation of Al₂O₃-GNP nanocomposite

The raw materials used in this study were graphene powder (>99% purity, average particle size >20 nm) and Al₂O₃ powder (>99.9% purity, average particle size >20 μm) and were purchased by Sigma Aldrich. Al₂O₃ and graphene nanocomposite was prepared according to Table 1. Prior to performing hydrothermal method, the sample was premixed using ball milling for an hour. Then, 100 ml aqueous solution consisted of 1M NaOH and water was added to the mixture. The mixture was stirred for 30 minutes and subjected to hydrothermal treatment at 200°C for 24 h in an autoclave. Then, the sample was washed with 100 ml 0.1 M HCl and distilled water. The sample was dried in an oven at 80°C for 24 h.

Table 1. Nanocomposite composition for hydrothermal process

| Nano composite | Al₂O₃ (wt%) | GNP (wt%) |
|---------------|------------|----------|
| AG80          | 80         | 20       |
| AG70          | 70         | 30       |
| AG60          | 60         | 40       |
| AG50          | 50         | 50       |
| A100          | 100        | 0        |

2.2 Characterization

The determination of phase identification of Al₂O₃-graphene nanocomposite was performed by X-Ray Diffraction (XRD) using Bruker D2 Phaser. The step size was 0.02° and the range of 2θ angle between 20° to 90°. Morphology of nanocomposite was studied using scanning electron microscope (SEM) JSM-IT100. Fourier Transformation Infrared Spectrophotometer (FTIR) was used to determine the specific functional groups of Al₂O₃-GNP nanocomposite using Nicolet IS5 Spectrometer. Thermo Scientific OMNIC Specta software was used to analyse the functional group of the composite.

2.3 Photocatalytic performance

The performance of nanocomposite on photocatalytic degradation of methyl orange (MO) was studied. 0.1 g of samples was added into 100 ml of 20 ppm MO dye solution. The aqueous suspension was magnetically stirred throughout the experiment. The suspension was subjected to visible light irradiation start from 1, 2, 3 and 4 h and any discoloration was recorded by UV-vis.

UV-Vis spectrometer HACR DR 5000 with specification wavelength range of 190 to 1100 nm, accuracy of ±1 nm in wavelength range 200 to 900 nm and resolution of 0.1 nm was used to record the absorption spectra. The wavelength was 457 nm and the original absorbance value of MO was taken 1.9. The percentage of the MO degradation was calculated using the following equations:

\[
MO\ absorption\ (%) = \frac{A_0 - A_t}{A_0} \tag{1}
\]
where $A_0$ is original absorbance value of MO and $A_I$ is absorbance value of compositions with MO.

3. Results and Discussion

Phase identification of Al$_2$O$_3$-GNP nanocomposite was characterized using XRD is shown in Figure 1. Peak pattern of raw Al$_2$O$_3$ and after hydrothermal process shows no significant difference between these two patterns. This is because at temperature setup 200°C of hydrothermal was not enough to form new or change structure in Al$_2$O$_3$. This is in agreement with Shehata et al., 2011 [15] that even though at thermal treatment of 975°C it still could not change Al$_2$O$_3$ form as the Al$_2$O$_3$ were uniformly dispersed. In Al$_2$O$_3$-graphene nanocomposite, the intensity of Al$_2$O$_3$ become sharp with decreasing GNP content indicating this composite is a polycrystalline material. While, peak of GNP was maintained since the amount GNP was higher. In the nanocomposite containing higher Al$_2$O$_3$ content, small shift to the right can be detected indicating the presence of graphene affects the Al$_2$O$_3$ lattice structure. Moreover, as the Al$_2$O$_3$ content increased, the crystal structure of the nanocomposites also changes. The intensity of Al$_2$O$_3$ becomes narrower which is due to hexagonal lattice of graphene changes to tetragonal after it is dispersed in Al$_2$O$_3$. This indicates that the introduction of graphene to the Al$_2$O$_3$ matrix changed the crystal structure of the nanocomposite.

![Figure 1. XRD pattern of a) as-received GNP, b) as-received Al$_2$O$_3$, c) AG50, d) AG60, e) AG70 and f) AG80 g) A100 nanocomposites](image-url)

The calculated crystallite size and internal strain of Al$_2$O$_3$ is presented in Table 2. It can be observed that as the graphene content decreased, the crystallite size of Al$_2$O$_3$ decreased and the internal strain increased. This result also was found similar to the study of Lee and Kale (2008) [16].
Table 2. The crystallite size and internal strain of Al$_2$O$_3$-GNP nanocomposite

| Nanocomposite | Crystallite size (nm) | Internal strain |
|---------------|----------------------|-----------------|
| AG50          | 20.3                 | 0.0050          |
| AG60          | 19.0                 | 0.0096          |
| AG70          | 14.6                 | 0.0195          |
| AG80          | 14.3                 | 0.0206          |

Figure 2 shows the SEM images of different compositions of Al$_2$O$_3$-GNP nanocomposite. In the equal amount of Al$_2$O$_3$ and GNP particles, it is obtained that Al$_2$O$_3$ particles are distributed in GNP particles. As shown in Figure (b), the Al$_2$O$_3$ particles are clearly distributed as a result of increasing Al$_2$O$_3$. This implies that hydrothermal with 200°C was enough to homogenously distribute the GNP particles in Al$_2$O$_3$ particles.

Figure 3 presents the FTIR spectra of as-received GNP, hydrothermally Al$_2$O$_3$ (A100) and Al$_2$O$_3$-GNP nanocomposites. The significant absorption peak located at 1850 to 2250 cm$^{-1}$ were observed similar absorption at 2104 cm$^{-1}$ to that of as-received GNP which corresponding to the triple bond of carbon stretching vibrations. The percentage transmittance of A100 and as-received GNP was quite far from each other. This means that the intensity of Al$_2$O$_3$ is greater than GNP because Al$_2$O$_3$ absorbed more amount of radiation than GNP [17]. Moreover, other peak absorptions are observed at 3291 and 3378 cm$^{-1}$ attributed to the OH vibrations of adsorbed water molecules of A100 (OH stretching–Al–OH) [18][19]. The peak located at 1649 cm$^{-1}$ is due to –OH bending. This could be explained that after hydrothermal process, the OH bond was developed inside the Al$_2$O$_3$ particles.

The performance of Al$_2$O$_3$-GNP nanocomposite on percentage of MO absorption in visible light is given in Figure 4. It can be observed that as the Al$_2$O$_3$ content became higher, the absorbance of MO became higher. The highest percentages of MO absorption are AG60 and AG80 with more than 80%. This showed that the photocatalytic efficiencies of Al$_2$O$_3$-GNP nanocomposite are influenced by the introduction of GNP as supported by Yan et al., 2013 [20]. It can be seen that AG70 absorbed the lowest MO. AG100 also absorbed MO better with slightly increased percentage in 4 h. This is the same result as reported by Hassena et al., 2008 [21] that Al$_2$O$_3$ itself also better in degradation of MO. Ahmad et al., (2017) also proved that nanocomposite shows higher MO adsorption rate [22]. At 3 h, the MO absorption of all the compositions has increased but after that began to decreased gradually. This might due to the surrounding environment factor that could affect the reading such as light intensity and temperature.
Figure 3. FTIR spectra of a) A100 b) as-received GNP c) AG70 d) AG50 nanocomposites

Figure 4. The absorption of MO for a) 1 b) 2 c) 3 and d) 4 h of Al₂O₃-GNP nanocomposites

4. Conclusion
Al₂O₃-GNP nanocomposite was successfully prepared by hydrothermal method. The performance of Al₂O₃ with lower graphene contents shows MO absorption with efficiency nearly 75% in visible light. The decreased of crystallite size and internal strain increased with the increased GNP content which also proportionate with the increment of particle size of the nanocomposite. Al₂O₃-GNP nanocomposite can be an alternative of metal oxide photocatalyst with graphene and may carry a great potential in environmental application.
5. Reference
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