Multifunctional Photocatalytic Degradation of Methylene Blue Using LaMnO$_3$/Fe$_3$O$_4$ Nanocomposite on Different Types of Graphene

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Abstract. This study added different types of graphene (GN-1 and GN-2) into LaMnO$_3$/Fe$_3$O$_4$ nanocomposite to degrade MB as an organic pollutant. LaMnO$_3$/Fe$_3$O$_4}$/GN-1 and LaMnO$_3$/Fe$_3$O$_4}$/GN-2 composites were synthesized using the co-precipitation method in a constant 5 wt% of GN. The as-prepared samples were characterized using XRD and TGA. The LaMnO$_3$/Fe$_3$O$_4}$/GN-1 and LaMnO$_3$/Fe$_3$O$_4}$/GN-2 composites showed the orthorhombic structure of LaMnO$_3$ nanoparticles and the cubic spinel of Fe$_3$O$_4$ nanoparticles, as well as of GN-1 and GN-2. The graphite structure of NGP in LaMnO$_3$/Fe$_3$O$_4}$/GN-1 composites was confirmed. However, the peak of graphene in LaMnO$_3$/Fe$_3$O$_4}$/GN-2 could not be identified. The photocatalytic efficiency of the LaMnO$_3$/Fe$_3$O$_4}$/GN-2 was higher than that of LaMnO$_3$/Fe$_3$O$_4}$/GN-1. The enhancement of the photocatalytic light activity can be attributed to the high separation efficiency of electron-hole recombination and to the large surface contact between LaMnO$_3$/Fe$_3$O$_4$ and graphene, which can improve the transfer efficiency of the photocatalytic process. In addition, the effects of catalyst dosage, rate constant, and scavengers were investigated and discussed.

1. Introduction

Organic dyes are produced from textile and other industrial processes that are known to be one of the major of pollutants in wastewater. Removal of organic dyes from wastewater has become priority for researchers recent decades. There are many effective removal methods in wastewater. One method that refers to the removal of organic pollutants in wastewater is photocatalytic activity.

Semiconducting photocatalyst TiO$_2$ has been widely used because of its good performance as a nanoparticle powder [1-2]. However, TiO$_2$ can only absorb ultraviolet (UV) light due to its wide band gap (3.2 eV) and high photogenerated electron-hole pairs [3-5]. To overcome this problem, perovskite oxide has been used as a good photocatalyst in the visible light region because of its environment friendliness, high electron mobility, non-toxicity, and high chemical stability [6-7]. The perovskite oxide that has been used to degrade organic pollutants contained in wastewater is LaMnO$_3$ nanoparticles. However, LaMnO$_3$ nanoparticles have showed some limitations in their practical application such as separating materials from liquid. Adding content of Fe$_3$O$_4$ to the LaMnO$_3$ overcame the separation problem. The presence of Fe$_3$O$_4$ in LaMnO$_3$ shows an easily-composited photo-generated electron-hole pairs and a small surface area that may reduce catalytic efficiency. Therefore, to overcome several problems associated with this material, many efforts have been...
introduced to improve their photocatalytic efficiencies, such as growing LaMnO$_3$/Fe$_3$O$_4$ on the layers of carbon-based materials. Graphene is a type of ultra-thin two dimensional two layered of carbon-based material that has attracted considerable attention because of its excellent electronic conductivity, high specific surface area, high stability and large surface to volume ratio [8]. Thus compounding different types of graphene (GN-1 and GN-2) in a semiconductor photocatalyst has the potential to enhance photocatalytic performances. The present work investigates the addition of different types of graphene (GN-1 and GN-2) in LaMnO$_3$/Fe$_3$O$_4$ nanocomposites affects methylene blue (MB) degradation as a model for an organic pollutant under a visible light source.

2. Experimental details

2.1. Chemicals

All the chemicals used in this work are of analytical grade. The chemicals used in the synthesis process of the LaMnO$_3$/Fe$_3$O$_4$ with the addition of different types of graphene are lanthanum (III) chloride heptahydrate (LaCl$_3$.7H$_2$O, Merck, 99%), manganese (II) chloride tetrahydrate (MnCl$_2$.4H$_2$O, Merck, 99%), sodium hydroxide (NaOH, Merck, 99%), iron (II) sulphate heptahydrate (FeSO$_4$.7H$_2$O, Merck, 99%), acetic acid (20%), ethanol and ethylene glycol. They are commercially available from Merck and were used in this study without further purification. Furthermore, different types of graphene (NGP and graphene) were available from Angstrom materials.

2.2. Catalyst preparation

LaMnO$_3$ and Fe$_3$O$_4$ nanoparticles were synthesized using the co-precipitation [9] and the sol gel [10] method, respectively as described in our previous study. Briefly, LaMnO$_3$ nanoparticles were dissolved into 100 ml distilled water and Fe$_3$O$_4$ nanoparticles were dissolved into 50 ml ethanol. Both solutions were mixed until blended. Then, the mixed solutions were ultrasonicated for 2 hour and allowed to stand at a room temperature for a few minute to get thermal equilibrium. After that, the mixed solutions were centrifuged to separate materials from residual reaction. The obtained materials were allowed to stand at a room temperature to have an aging process overnight. The LaMnO$_3$/Fe$_3$O$_4$ nanocomposites were obtained after being dried at a temperature 100 °C under vacuum conditions for an hour. The molar ratio of LaMnO$_3$/Fe$_3$O$_4$ that will be used to synthesize the sample on different types of graphene is 1:0.5.

The NGP and graphene amount was added to LaMnO$_3$/Fe$_3$O$_4$ in a constant 5 wt%. The LaMnO$_3$/Fe$_3$O$_4$ with the addition of NGP and graphene were also synthesized using the co-precipitation method. Briefly, 100 mg of NGP were dissolved in 80 ml water and 40 ml ethanol using an ultrasonic treatment for two hours. Next, 2 g of LaMnO$_3$/Fe$_3$O$_4$ were added to the NGP solution. Then, the mixed solution was stirred for two hours to achieve a homogeneous solution. The suspension was heated at 120°C for three hours to affect the deposition of the LaMnO$_3$/Fe$_3$O$_4$ on the graphene sheets. Then, the solution was centrifuged to separate the materials from the residual reaction. It also performed the same way to synthesize LaMnO$_3$/Fe$_3$O$_4$ with the addition of graphene. The LaMnO$_3$/Fe$_3$O$_4$/GN-1 and LaMnO$_3$/Fe$_3$O$_4$/GN-2 composites were obtained after being dried under vacuum conditions over night. The LaMnO$_3$/Fe$_3$O$_4$ with the addition NGP was labeled LaMnO$_3$/Fe$_3$O$_4$/GN-1 and the LaMnO$_3$/Fe$_3$O$_4$ with the addition of graphene was labeled LaMnO$_3$/Fe$_3$O$_4$/GN-2.

2.3. Characterization

The synthesized catalysts were characterized employing standard analytical techniques such as XRD. A crystal structure analysis was carried out on a Rigaku Miniflex 600 with Cu-K$_\alpha$ ($\lambda = 1.54060$) radiation operated in 40 kV and 20 mA. Thermogravimetric analysis (TGA) was conducted to estimate the amount of GN in the samples.
2.4. Catalytic activity
The catalytic activity was examined by observing the degradation rate of MB in the presence of LaMnO$_3$/Fe$_3$O$_4$/GN-1 and LaMnO$_3$/Fe$_3$O$_4$/GN-2. The degradation of MB was tested in an alkaline condition (pH 13). A 40 W Xe lamp light was used as a visible light source. The suspensions were placed in a dark condition for 30 minutes to achieve absorption and desorption equilibrium. Then, the suspensions irradiated under visible light for two hours. The suspension was analyzed at regular 15 minute using a Hitachi UH5300 UV-visible spectrophotometer. The MB degradation rate was also analyzed by adding some scavengers, sodium sulfate as an electron scavenger, di-ammonium oxalate as a holes scavenger and tert-butyl alcohol as a hydroxyl radical scavenger. The catalyst’s stability was also checked four times.

3. Results and Discussion
The XRD patterns of LaMnO$_3$/Fe$_3$O$_4$ with different types of graphene (GN-1 and GN-2) have been analyzed. Figure 1.a shows the XRD pattern of graphene in different types (GN-1 and GN-2), LaMnO$_3$/Fe$_3$O$_4$, LaMnO$_3$/Fe$_3$O$_4$/GN-1 and LaMnO$_3$/Fe$_3$O$_4$/GN-2. The observed diffraction peaks at ($2\theta = 22.12^\circ, 22.96^\circ, 25.06^\circ, 31.08^\circ, 32.21^\circ, 33.2^\circ, 38.94^\circ, 40.05^\circ, 45.4^\circ, 47.07^\circ, 56.19^\circ, 57.6^\circ, 58.56^\circ, 67.68^\circ, and 75.68^\circ$) shows the orthorhombic structure of LaMnO$_3$ nanoparticles[11-12] and ($2\theta = 30.36^\circ, 35.76^\circ, 43.47^\circ, 53.94^\circ, 57.51^\circ, and 63.74^\circ$) shows the cubic spinel of Fe$_3$O$_4$ nanoparticles.

Figure 1. (a) XRD pattern; (b) TGA curves of LaMnO$_3$/Fe$_3$O$_4$, LaMnO$_3$/Fe$_3$O$_4$/GN-1 and LaMnO$_3$/Fe$_3$O$_4$/GN-2.

**TABLE 1.** The lattice parameter and grain size <$D>$ of LaMnO$_3$/Fe$_3$O$_4$ and LaMnO$_3$/Fe$_3$O$_4$/GN composites.

| Sample                  | Lattice Parameter | Lattice Parameter | <D> LaMnO$_3$ | <D> Fe$_3$O$_4$ |
|-------------------------|------------------|------------------|---------------|-----------------|
| LaMnO$_3$/Fe$_3$O$_4$   | a (Å)            | b (Å)            | c (Å)         | (nm)            |
|                         | 5.731            | 7.705            | 5.538         | 8.367           |
| LaMnO$_3$/Fe$_3$O$_4$/GN-1 | 5.518            | 7.669            | 5.713         | 8.340           |
| LaMnO$_3$/Fe$_3$O$_4$/GN-2 | 5.512            | 7.658            | 5.722         | 8.339           |
After NGP was introduced to the LaMnO$_3$/Fe$_3$O$_4$ for photocatalysis, the XRD pattern showed a peak at $2\theta = 26.4^\circ$ and its diffraction peaks reveal the presence of graphite structure. The graphite structure of NGP in LaMnO$_3$/Fe$_3$O$_4$/GN-1 composites was confirmed. Furthermore, the peaks of graphene in LaMnO$_3$/Fe$_3$O$_4$/GN-2 cannot be identified by XRD measurements because of its broad peak. There were no peaks of graphene observed in the LaMnO$_3$/Fe$_3$O$_4$/GN-2 composite because of the small graphene content (5wt%). The crystallite size of the samples which was calculated by the scherrer equation [14-15] and the unit cell parameter was tabulated in Table 1.

To estimate the amount graphene (GN-1 and GN-2) in the LaMnO$_3$/Fe$_3$O$_4$/GN-1 and LaMnO$_3$/Fe$_3$O$_4$/GN-2 composites, thermogravimetric analysis (TGA) was carried out in an air flux. Figure 1.b shows the TGA curve of LaMnO$_3$/Fe$_3$O$_4$ nanocomposite and LaMnO$_3$/Fe$_3$O$_4$ with the addition of different types of graphene (GN-1 and GN-2). The results indicate that LaMnO$_3$/Fe$_3$O$_4$ has...
the lowest weight loss percentage and that it is the more stable sample. However, LaMnO$_3$/Fe$_3$O$_4$ with the addition of nanographene platelets and graphene has the weight loss for about 5%. The differences in weight loss between LaMnO$_3$/Fe$_3$O$_4$, LaMnO$_3$/Fe$_3$O$_4$/GN-1 and LaMnO$_3$/Fe$_3$O$_4$/GN-2 with the addition of different types of graphene (GN-1 and GN-2) after the oxidation could be directly translated to the amount of NGP and graphene in the LaMnO$_3$/Fe$_3$O$_4$/GN-1 and LaMnO$_3$/Fe$_3$O$_4$/GN-2 [16].

Figure 2.a shows the photocatalytic activity of LaMnO$_3$/Fe$_3$O$_4$ and LaMnO$_3$/Fe$_3$O$_4$ with the addition of different types of graphene (GN-1 and GN-2). As can be seen from the figure, LaMnO$_3$/Fe$_3$O$_4$ with the addition of NGP and graphene has better photocatalytic activity than that LaMnO$_3$/Fe$_3$O$_4$ nanocomposite. LaMnO$_3$/Fe$_3$O$_4$/GN-2 also has the highest photocatalytic performances among other samples. Compared with LaMnO$_3$/Fe$_3$O$_4$ and LaMnO$_3$/Fe$_3$O$_4$/GN-1, the addition of graphene expands the LaMnO$_3$ light response range, high separation efficiency of electron-hole recombination and it also shows that graphene can act as an electron acceptor and transporter in
the LaMnO$_3$/Fe$_3$O$_4$/GN-2 composite [17]. In the LaMnO$_3$/Fe$_3$O$_4$/GN-2, the excited electrons can transfer from the conduction band to graphene. Thus, graphene can act as an acceptor of the generated electrons. Both the graphene’s electrons accepting and transporting can achieve a higher photocatalytic performances for LaMnO$_3$/Fe$_2$O$_4$/GN-2. Furthermore, the large surface contact between graphene and LaMnO$_3$/Fe$_2$O$_4$ was also able to increase its photocatalytic performance. The first-order kinetics of photocatalytic degradation for LaMnO$_3$/Fe$_2$O$_4$, LaMnO$_3$/Fe$_2$O$_4$/GN-1 and LaMnO$_3$/Fe$_2$O$_4$/GN-2 are shown in figure 2.b. The figure plotted the function of $\ln (C/C_0)$ vs. irradiation time ($t$) and the photodegradation of the MB can be formulated using the first-order kinetic equation. $\ln (C/C_0) = -k.t$ is used to fit experimental data, where $C_0$ is the concentration of MB at $t=0$ and $C_t$ is the concentration of MB at ($t$), respectively, and $k$ is the first order rate constant. The figure also showed that LaMnO$_3$/Fe$_2$O$_4$ with the addition of graphene has the maximum values of the apparent rate. The absorption peak of MB was almost eliminated using LaMnO$_3$/Fe$_2$O$_4$/GN-2 after irradiating for about 75 minutes. As shown in figure 3, graphene to LaMnO$_3$/Fe$_2$O$_4$ made the decoloration rate of the dye 99.96%.

The effect of catalyst dosage in LaMnO$_3$/Fe$_2$O$_4$/GN-2 is shown in Figure 4.a. increasing the amount of catalyst dosage to approximately 0.1g/L-0.4g/L can increase, the photocatalytic activity in the MB degradation as a model for organic pollutants. This is due to the increase of active species on the photocatalytic activity, which increases a group of ($\bullet$OH) to degrade MB as a model for organic pollutants. The main active species in the photocatalytic activity of LaMnO$_3$/Fe$_2$O$_4$/GN-2 could be determined by adding some scavengers as shown in Figure 4.b. The addition of tert-butyl alcohol as a hydroxyl radical scavenger, di-amonium oxalate as a holes scavenger and sodium sulfate (Na$_2$SO$_4$) as an electron scavengers was able to inhibit the degradation rate. This demonstrates that the main active species in the photocatalytic activity of LaMnO$_3$/Fe$_2$O$_4$ was holes$>$ electron $>$ hydroxyl radical ($\bullet$OH). The samples’ stability was also checked in four cycle processes by using the highest dosage concentration (0.4 g/L) as shown in Figure 5. The results show that, the samples have good stability and reusability even after the four cycle processes.

4. Conclusion
LaMnO$_3$/Fe$_2$O$_4$ with the addition of different types of graphene has been successfully synthesized using the co-precipitation method. The photocatalytic activity of LaMnO$_3$/Fe$_2$O$_4$ nanocomposites was evaluated under visible light irradiation. The results show that LaMnO$_3$/Fe$_2$O$_4$/GN-2 demonstrates superior photocatalytic activity to LaMnO$_3$/Fe$_2$O$_4$/GN-1 because the addition of graphene in LaMnO$_3$/Fe$_2$O$_4$/GN-2 expands the LaMnO$_3$ light response range, high separation efficiency of electron-hole recombination and it also shows that graphene can act as an electron acceptor and transporter in the LaMnO$_3$/Fe$_2$O$_4$/GN-2 composite. Furthermore, adding a dosage concentration up to 0.4 g/L in the photocatalytic activity increases MB degradation. The samples have good stability and reusability even after the four cycle processes after the additional of NGP and graphene. Furthermore, the main active species with the addition of some scavenger were holes $>$ electrons $>$ hydroxyl radical ($\bullet$OH).

5. References
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