Enhancement of photocatalytic activities of perovskite LaFeO₃ composite by incorporating nanographene platelets

N Afifah¹,² and R Saleh¹,²
¹Department of Physics, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia
²Integrated Laboratory of Energy and Environment, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

Corresponding author’s e-mail: rosari.saleh@gmail.com

Abstract. LaFeO₃/NGP composites with several concentrations of NGP by weight percent were prepared using co-precipitation methods. The ferromagnetic behavior of LaFeO₃/NGP composites was characterized by vibrating sample magnetometer (VSM), while the structural properties were investigated using X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and Brunauer–Emmett–Teller (BET) surface area analysis. The LaFeO₃ nanoparticles with and without NGP show orthorhombic structure and ferromagnetic behavior. The samples were used to degrade methylene blue using visible light irradiation. The obtained results revealed that the photocatalytic performance of LaFeO₃/NGP composites increased with increasing NGP from 3 wt.% up to 5 wt.%. The main factors influencing the photocatalytic activity were studied and are discussed herein.

1. Introduction
The carbon-based material graphene has attracted much attention because of its large specific surface area, flexible structure, excellent mobility of charge carriers, and good electrical and thermal conductivity [1-3]. Graphene, with its unique properties, could serve as a support material and dispersion medium for catalysts, which could inhibit the aggregation of catalyst while it is dissolving into aqueous organic dye [4-5]. The photocatalytic activity of graphene as a supporting material has been reported by several studies. Li et al. (2013) [6] and Morales-Torres et al. (2013) [2] reported the photocatalytic degradation of organic pollutants in wastewater by P25-graphene composite. Their results showed that the photocatalytic activity of P25-graphene composite is better than that of pure P25. Xiang et al. (2012) [7] and Tu et al. (2009) [8] also reported the photocatalytic activity of a graphene/TiO₂ composite. The role of graphene in their composite is an electron transport channel, which could inhibit electron–hole recombination and enhance catalytic performance.

Graphene could support lanthanum ferrite (LaFeO₃) nanoparticles as well as TiO₂. LaFeO₃ is an ABO₃ perovskite type-oxide that is widely used as a catalyst due to its unique optoelectronic properties and narrow optical band gap, making it suitable for application as a visible light photocatalyst [9, 10]. The photocatalytic activity of LaFeO₃ nanoparticles was reported in our previous work [11]. However, in our previous studies, LaFeO₃ nanoparticles could not completely degrade organic pollutants in the photocatalytic process. Therefore, in this research we combined nanographene platelets (NGP) with LaFeO₃ in composite form to increase the photocatalytic performance. LaFeO₃/NGP with various weight percent (wt.%) of NGP were synthesized using the co-precipitation method. The photocatalytic activity of all samples was evaluated under visible light irradiation. Methylene blue (MB) was used as
a model organic pollutant. The stability of the catalyst and the main active species playing an important role in the photocatalytic process were also studied.

2. Experimental details

Catalyst preparation: \(\text{LaCl}_3\cdot7\text{H}_2\text{O}, \text{FeCl}_2\cdot4\text{H}_2\text{O},\) and sodium hydroxide (NaOH) were purchased from Merck (Kenilworth, NJ, USA). The chemical reagents were used to synthesis \(\text{LaFeO}_3\) nanoparticle based on our previous work [11]. Nanographene platelets (NGP), purchased from Angstron Materials (Dayton, OH, USA), were then used to synthesis \(\text{LaFeO}_3/\text{NGP}\) composites using the co-precipitation method. The weight ratio of NGP to \(\text{LaFeO}_3\) varied at 3, 5, and 10 wt.%. Briefly, NGP was dissolved into 80 mL distilled water and 40 mL ethanol through ultrasonic treatment for 2 h. Then, \(\text{LaFeO}_3\) nanoparticles were added to the NGP solution, followed by stirring for 2 h. The suspension was then centrifuged and dried at 70°C for 12 h.

Characterization: The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), vibrating sample magnetometer (VSM), and Brunauer–Emmett–Teller (BET) surface area analysis spectroscopy.

Photocatalytic activity: The photocatalytic activity was determined by observing the degradation of MB under visible light irradiation. First, 0.4 g/L catalyst was dissolved into 100 mL of 20 mL/g MB. The resulting solution was stirred in the dark for 30 min to allow it to reach absorption–desorption equilibrium. Then, the suspension was irradiated using a 40 W Xe lamp as the visible light source for 2 h. The degradation of MB was monitored using a Hitachi (Tokyo, Japan) UV5300 UV-visible spectrophotometer. The degradation of MB was plotted as \(\text{C}_t/\text{C}_0\), where \(\text{C}_t\) is the concentration of MB at each measurement interval during irradiation and \(\text{C}_0\) is the initial concentration of MB after reaching absorption–desorption equilibrium. The stability of the catalyst was also checked in this research by reusing the catalyst for four times cycle processes. The main active species involved in the catalytic degradation of MB were studied using sodium sulfate, di-ammonium oxalate and tert-butyl alcohol, which are recognized as scavengers for electrons, holes, and hydroxyl radical species, respectively.

3. Results and discussion

The structural properties of all samples were characterized using XRD. Figure 1(a) shows the XRD pattern of the \(\text{LaFeO}_3/\text{NGP}\) composites with different wt.% NGP. The XRD pattern of \(\text{LaFeO}_3\) nanoparticles is also shown as a comparison. The diffraction peak at 2θ of 26.4° confirmed the graphite structure of NGP. The obtained diffraction peak of NGP increased with increasing wt.% NGP. The orthorhombic structure of \(\text{LaFeO}_3\) could also be found in the XRD pattern of all composites. No other phases or impurities were found, indicating that the desired synthesized sample was obtained. Along with XRD measurements, the crystal size value could also be calculated using Scherrer’s formula [12]. The crystal size and lattice parameters of all samples are summarized in table 1.

The incorporation of NGP into the composite was confirmed by FT-IR measurements. Figure 1(b) shows the FT-IR spectra of the \(\text{LaFeO}_3/\text{NGP}\) composites with various wt.% NGP. The FT-IR spectrum of pure NGP is also shown for comparison. The strong absorption at wavenumber 555 cm\(^{-1}\) is the \(\text{Fe}–\text{O}\) stretching vibration of octahedral \(\text{FeO}_6\), which was characteristic of the material forming the perovskite \(\text{LaFeO}_3\) [12-14], while the \(\text{C}=\text{O}\) stretching vibration at 1460-1750 cm\(^{-1}\) confirmed the presence of NGP in the sample [15-16]. The \(\text{O}–\text{H}\) stretching vibration was also found at wavenumber 3440 cm\(^{-1}\) [16].

Magnetic saturation of the \(\text{LaFeO}_3\) nanoparticles and \(\text{LaFeO}_3/\text{NGP}\) composites with various wt.% NGP can also be seen in figure 1(c). All samples showed ferromagnetic behavior at room temperature. The magnetic saturation of the composite increased as the wt.% of NGP increased up to 5 wt.% and then decreased with the addition of 10 wt.% NGP. The degradation rate of MB was also calculated using the pseudo-

---

2

---

International Symposium on Current Progress in Functional Materials
IOP Conf. Series: Materials Science and Engineering
IOP Publishing
IOP Conf. Series: Materials Science and Engineering 188 (2017) 012054
doi:10.1088/1757-899X/188/1/012054
first-order kinetic rate equation [17]. The obtained result (shown in figure 2(b)) revealed that LaFeO$_3$

![XRD pattern](image1)

![FTIR spectra](image2)

![VSM spectra](image3)

**Figure 1.** (a) XRD pattern; (b) FTIR spectra; and (c) VSM spectra of LaFeO$_3$/NGP composites with different wt.% NGP.

| Sample                  | Lattice Parameter (Å) | <D> (nm) | M-S (emu/g) | Surface area (eV) |
|-------------------------|-----------------------|----------|-------------|------------------|
| LaFeO$_3$               | a: 5.5436, b: 7.8456, c: 5.5528 | 58       | 12.08       | -                |
| LaFeO$_3$/3 wt.% NGP    | a: 5.5326, b: 7.8376, c: 5.5592 | 28       | 12.41       | 43               |
| LaFeO$_3$/5 wt.% NGP    | a: 5.5632, b: 7.8687, c: 5.5727 | 27       | 13.38       | 76               |
| LaFeO$_3$/10 wt.% NGP   | a: 5.5703, b: 7.8782, c: 5.5743 | 28       | 13.06       | 90               |

**Table 1.** The lattice parameter, grain size <D>, magnetic saturation (M-S) and surface area of LaFeO$_3$/NGP composites.
with added NGP shows more rapid degradation of MB than LaFeO$_3$ without NGP. It has been suggested that the photocatalytic efficiency depends on several factors, one of which is surface area. A large surface area may increase the opportunity for contact between the catalyst and light, thereby increasing the rate at which the oxidation process happens [18]. The surface area of the LaFeO$_3$/NGP composites is summarized in table 1. The results show that increasing the NGP content increased the surface area of the catalyst. However, the highest photocatalytic activity was observed with 5 wt.% added NGP. This indicates that the photocatalytic degradation efficiency of the composite was more influenced by the capacity of the electron transport layer of NGP, which could inhibit electron–hole recombination and enhance photocatalytic performance [18-20].

After determining the catalyst with the maximum degradation rate, the stability of the catalyst was also observed. MB solutions were degraded using the same catalyst four times under the same treatment conditions. The results of reusing the LaFeO$_3$/NGP composite (5 wt.%) as a catalyst can be seen in figure 3(a). After four repetitions, the catalyst did not show a significant decrease in activity, indicating that the catalyst has good stability.

To study the main active species in the process of MB degradation using the LaFeO$_3$/NGP composite (5 wt.%), the experiment was repeated with the addition of active species like electrons, holes, and...
hydroxyl radicals. Na$_2$S$_2$O$_8$ and di-ammonium oxalate were used as electron and hole scavengers, while tert-butyl alcohol was used as a hydroxyl radical scavenger. The influence of these scavengers on the photocatalytic activity of LaFeO$_3$/NGP composites (5 wt.%) is shown in figure 3(b). The presence of scavengers decreased the degradation rate of MB; the largest decrease was obtained with di-ammonium oxalate. This result indicates that the holes pay the most important role in the photocatalytic activity.

4. Conclusions
The photocatalytic activity of LaFeO$_3$/NGP composites with various wt.% NGP has been investigated under visible light irradiation. The composite with incorporated NGP shows better photocatalytic performance than the LaFeO$_3$ nanoparticles. The LaFeO$_3$/NGP composites also showed stability as they were able to degrade MB through four photocatalytic cycles without a decrease in efficiency. The role of NGP in composites could inhibit electron–hole recombination and enhance catalytic performance.

References
[1] Aleksandrzak M, Adamski P, Kulkulka W, Zielinska B and Mijowska E 2015 Appl. Surf. Sci. 331 193-9
[2] Morales-Torres S, Pastrana-Martínez L M, Figueiredo J L, Faria J L and Silva A M 2013 Appl. Surf. Sci. 275 361-8
[3] Machado B F and Serp P 2012 Catal. Sci. Technol. 2 54-75
[4] Zhou K, Zhu Y, Yang X, Jiang X and Li C 2011 New J. Chem. 35 353-9
[5] Liang D, Cui C, Hu H, Wang Y, Xu S, Ying B, Li P, Lu B and Shen H 2014 J. Alloy. Compd. 582 236-40
[6] Li J, Zhou S, Hong G and Chang C 2013 Chem. Eng. J. 219 486-91
[7] Xiang Q, Yu J and Jaroniec M 2012 Chem. Soc. Rev. 41 782-96
[8] Tu W, Zhou Y, Liu Q, Yan S, Bao S, Wang X, Xiao M and Zou Z 2009 Adv. Funct. Mater. 19 894-904
[9] Grabowska E 2016 Appl. Catal. B: Environ. 186 97-126
[10] Tang P, Tong Y, Chen H, Cao F and Pan G 2013 Curr. Appl. Phys. 13 340-3
[11] Afifah N and Saleh R 2016 J. Phys. Conf. Ser. 710 012030
[12] Abazari R and Sanati S 2013 Superlattice. Microst. 64 148-57
[13] Noroozifar M, Khorasani-Motlagh M, Ekrami-Kakhki M S and Khaleghian-Moghadam R 2014 J. Power Sources 248 130-9
[14] Kaiwen Z, Xuehang W, Wenwei W, Jun X, Siqi T and Sen L 2013 Adv. Powder Technol. 24 359-63
[15] Fujii T, Matsusue I, Nakatsuka D, Nakaniishi M and Takada M 2015 Mater. Chem. Phys. 129 805-9
[16] Taufik A and Saleh R 2016 AIP Conf. Proc. 1725 020089
[17] Saleh R and Djaja N F 2014 Superlattice. Microst. 74 217-33
[18] Kim T W, Park M, Kim H Y and Park S J 2016 J. Solid State Chem. 239 91-8
[19] Hu J, Men J, Ma J and Huang H 2014 J. Rare Earth. 32 1126-34
[20] Hu J, Ma J, Wang L and Huang H 2014 J. Alloy. Compd. 583 539-45