Effect of Crystallite Structure and Graphene Incorporation on Photocatalytic Performance of LaFeO₃

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Abstract. In this study, LaFeO₃ photocatalysts were synthesized by using co-precipitation method at different calcination temperatures of 600 °C, 700 °C, and 800 °C. Graphene was also introduced into LaFeO₃ to improve the photocatalytic performance. The photocatalysts were characterized by using X-Ray Diffraction (XRD), Brunauer-Emmet-Teller (BET) surface area analysis, and Fourier Transform Infrared (FTIR) spectroscopy. The prepared photocatalysts were also evaluated to determine their photocatalytic degradation activities against methylene blue (MB) under visible light irradiation. LaFeO₃ with the calcination temperature of 800 °C with graphene supported showed orthorhombic structure and the highest photocatalytic performance. The different structure might affect the photocatalytic performance of samples, while the role of graphene on the nanocomposite could act as an electron transport layer and inhibited the recombination of photogenerated electron-hole pairs. The stability of the catalyst on the photocatalytic process was also studied.

Keywords: Graphene, photocatalytic, LaFeO₃.

1. Introduction
LaFeO₃ with the multifunctional properties has received considerable attention due to its promising application in advanced technology such as fuel cells, gas sensor, solid electrolytes, superconductors, and catalyst [1-2]. As a catalyst, LaFeO₃ exhibits strong catalytic abilities due to its unique optoelectronic properties and its narrow optical gap which can be exploited as a highly effective catalyst in the visible light region [3]. The photocatalytic activity of LaFeO₃ nanoparticles has been reported in several studies [3-4]. However, there are few reports about the effect of calcination temperature on the crystal structure and photocatalytic activity of LaFeO₃ nanoparticles.

The photocatalytic activity of LaFeO₃ nanoparticles calcined at 800 °C has been reported in our previous work [5]. However, LaFeO₃ nanoparticles can not completely degrade MB pollutant due to its high electron and hole recombination. Therefore, to enhance the photocatalytic performance, graphene with electron transport layer capacity is introduced to LaFeO₃ to inhibit the electron and hole recombination.
recombination and enhance the photocatalytic performance. Graphene with its large surface area also can increase the photocatalytic performance by increasing the number of the active site involves in the degradation process [6-7]. The aim of this work is to study the effect of crystal structure and graphene incorporation on the photocatalytic performance of LaFeO$_3$ nanoparticles. The stability of the catalyst on the photocatalytic experiment is also checked for four-times cycling processes.

2. Experimental Method

2.1 Catalyst preparation

All chemicals are analytical grade and were used without further purification. LaCl$_3$·7H$_2$O, FeCl$_2$·4H$_2$O, and sodium hydroxide (NaOH) were used to synthesize LaFeO$_3$ nanoparticles based on our previous work [5]. The LaFeO$_3$ nanoparticles were calcined at a different temperature of 600, 700, and 800 °C for 2 h under vacuum condition. The obtained LaFeO$_3$ (untreated, 600, 700, and 800 °C) were then mixed with graphene, purchased from Angstrøm Materials, to obtain the LaFeO$_3$/graphene composites. In the typical procedure, graphene was dissolved into distilled water and ethanol through ultrasonic treatment for 2 h. Then, LaFeO$_3$ nanoparticles were added to the graphene solution, followed by stirring for 2 h. The suspension was then centrifuged and dried at 70 °C for 12 h. The weight ratio of graphene to LaFeO$_3$ was held constant at 5 wt%.

2.2 Characterization

The samples were characterized by using X-Ray Diffraction (XRD), Brunauer-Emmet-Teller (BET) surface area analysis, and Fourier Transform Infrared (FT-IR) spectroscopy.

2.3 Photocatalytic

The photocatalytic activities of prepared samples were measured by observing the degradation of MB under visible light irradiation. First, the catalyst was dissolved into MB solution. Then, the mixture was stirred in the dark for 30 min to allow it to reach absorption–desorption equilibrium. After that, the suspension was irradiated under visible light irradiation for 2 h. The degradation of MB was monitored by using a Hitachi UH5300 UV-visible spectrophotometer at regular intervals. The percentage degradation of MB was recorded as $C_t/C_0$, where $C_t$ is the concentration of MB at each measurement interval during irradiation and $C_0$ is the initial concentration of MB after reaching adsorption–desorption equilibrium. The stability of the catalyst was also checked in this research by reusing the catalyst for four-times cycling processes.

3. Results and Discussion

Figure 1a shows the XRD patterns of LaFeO$_3$ for different calcination temperatures. For comparison, the XRD patterns of untreated LaFeO$_3$ is also shown in the figure. The result showed that the XRD pattern for untreated LaFeO$_3$ exhibited mixed phases of La$_2$O$_3$, Fe$_2$O$_3$, and Fe$_3$O$_4$, respectively [8-9]. After being calcined at 800 °C, the XRD pattern of the sample exhibited a single perovskite phase with orthorhombic structure [4, 10]. However, the secondary phase of La$_2$O$_3$ was still detected at 600 °C. The effect of graphene incorporation in the untreated and treated LaFeO$_3$ XRD pattern is also shown in Figure 1b. The result showed that the incorporation of graphene in the composite did not change the untreated and treated LaFeO$_3$ structure. The lattice parameter, crystallite size $<D>$, and specific surface area values of the samples are also summarized in Table 1. The lattice parameter values were obtained by MAUD Rietveld refinement method, while the crystallite size $<D>$ and specific surface area values were calculated by using Scherrer’s equation [11], and BET method, respectively.
The XRD patterns of LaFeO$_3$ with different calcination temperature without (a), and with additional graphene (b).

**Figure 1.** The XRD patterns of LaFeO$_3$ with different calcination temperature without (a), and with additional graphene (b).

**Table 1.** The lattice parameter, grain size $<D>$, and surface area of LaFeO$_3$ with different calcination temperature without and with additional graphene.

| Sample                  | Lattice Parameter | $<D>$ (nm) | Surface Area (m$^2$/g) |
|-------------------------|-------------------|------------|------------------------|
| LaFeO$_3$ - 600°C      | 5.5647            | 7.8551     | 5.5560                 | 22 | 47 |
| LaFeO$_3$ - 700°C      | 5.5355            | 7.8513     | 5.5553                 | 24 | 38 |
| LaFeO$_3$ - 800°C      | 5.5436            | 7.8456     | 5.5528                 | 58 | 31 |
| LaFeO$_3$ - 600°C/graphene | 5.4351            | 7.8144     | 5.5586                 | 20 | 137 |
| LaFeO$_3$ - 700°C/graphene | 5.4592            | 7.8340     | 5.5556                 | 24 | 129 |
| LaFeO$_3$ - 800°C/graphene | 5.4934            | 7.8403     | 5.5590                 | 26 | 123 |

**Figure 2.** FTIR spectra of pure graphene and LaFeO$_3$ - 800 °C/graphene composite.
The incorporation of graphene in the composite could be confirmed by using FT-IR measurements. Figure 2 shows the FT-IR spectra of pure graphene and the LaFeO$_3$-800 °C/graphene composite. The FT-IR spectra of graphene and its composites show a strong absorption at wavenumber 3440 cm$^{-1}$, which corresponds to the O–H stretching vibration [12]. The C=O and C-OH stretching vibrations of graphene are also observed at 1460–1750 cm$^{-1}$ and 1236 cm$^{-1}$, respectively, indicate the formation of graphene in the composite [12-13]. In addition, the presence of LaFeO$_3$ also could be detected with the existence of the Fe–O stretching vibration at wavenumber of 555 cm$^{-1}$ [14]. The 555 cm$^{-1}$ band was due to the Fe–O stretching vibration of octahedral FeO$_6$, which is the characteristic of the perovskite LaFeO$_3$[14-15].

Figure 3a shows the photocatalytic activity of LaFeO$_3$ with different calcination temperature. In comparison, the photocatalytic activity of untreated LaFeO$_3$ is also shown in the figure. The results showed that the photocatalytic performance of LaFeO$_3$ increased with the increasing calcined temperature. It indicates that the higher crystallinity of the samples could improve the photocatalytic performance of LaFeO$_3$. It was reported that the higher crystallinity could induce the higher carrier mobility, thus providing more exposed polar faces for hydroxyl radicals formation. These radicals were responsible for the degradation of organic pollutant which could increase the photocatalytic performance [16]. The effect of graphene incorporation on the photocatalytic activities of the untreated and treated LaFeO$_3$/graphene composites are also shown in the Figure 3b. The result showed that the incorporation of graphene could further increase the degradation efficiency. Graphene with the large surface area could increase the photocatalytic performance by increasing the surface active site that plays an important role in the degradation process. Moreover, its electron transport layer capacity could inhibit the photo-generated of electron-hole pair recombination. Thus it increased the photocatalytic performance [6-7]. The degradation of MB using the untreated and treated with LaFeO$_3$ nanoparticles and LaFeO$_3$/graphene composites followed the pseudo-first-order kinetic rate equation [17]. The obtained results presented in the Figure 4a that shows the higher crystallinity by increasing calcined temperature could increase the photocatalytic performance. In addition, the incorporation of graphene in the composite exhibited better photocatalytic performance. The stability of the catalyst was also evaluated for four-times repetitions. The results are shown in Figure 4d is indicating that the catalyst has good stability after four cycling processes in the photocatalytic experiment.

![Figure 3](image_url)

**Figure 3.** The photocatalytic activity of LaFeO$_3$ with different calcination temperature without (a) and with additional graphene (b).
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4. Conclusion
The photocatalytic activities of the untreated and treated with LaFeO$_3$ nanoparticles and LaFeO$_3$/graphene composites have been investigated under visible light irradiation. The effect of crystallinity of the catalyst improve the photocatalytic performance of LaFeO$_3$. We also obtained that the incorporation of graphene in the composite exhibited better photocatalytic performance. The prepared catalyst also has good stability in the photocatalytic experiment.

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Figure 4. (a) The rate constant of LaFeO$_3$ with different calcination temperature without and with additional graphene; and (b) The stability of the catalyst in photocatalytic process.