The influence of calcination temperature on the optical, morphological properties and photocatalytic activity of lanthanum orthoferrite

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Abstract. In this study, the effect of calcination temperature towards the optical, morphological properties and photocatalytic degradation performance of the synthesized LaFeO\textsubscript{3} were investigated. The precursor and synthesized LaFeO\textsubscript{3} calcined at 500-900 °C were characterized using X-ray diffractometer (XRD), Thermogravimetric analysis (TGA), UV-Vis spectrophotometer, Fourier Transform Infrared Spectroscopy (FTIR) and BET. The photocatalytic activity of the synthesized LaFeO\textsubscript{3} was performed on oily wastewater. The photocatalytic degradation performance of LaFeO\textsubscript{3} was 67%, 72% and 63% for 1000ppm, 10000ppm and 20000ppm respectively. This study verified that calcination temperatures have a major impact on the optical, structural and morphological properties of nanoparticles.

1. Introduction

Countless harmful hydrocarbon mixture, chemical components and heavy metal present in oily wastewater [1]. There is a typical limit for oil and grease discharges depend on the types of the oils. For instance, the discharge limits for mineral and synthetic oils are 10-15 mg/L while for those of vegetable and animal based from 100-150 mg/L. Oily wastewater need to be treated because it can affect drinking water and groundwater resources, endangering aquatic resources and human health, affecting crop production and destructing the natural landscape [2].

Various semiconductors have been applied as photocatalysts for photo-degradation of organic and inorganic contaminants such as TiO\textsubscript{2}, WO\textsubscript{3}, ZnO, CuS, BiOBr, and BiFeO\textsubscript{3} [3-5]. Among them, titanium dioxide (TiO\textsubscript{2}) is the most widely studied since it is non-toxic, chemically stable, commercially available and inexpensive [6]. However, TiO\textsubscript{2} can only be activated using ultraviolet light (<390nm) as it cannot be activated by visible light because of the high band gap (3.2eV) [7]. The other barrier using TiO\textsubscript{2} as the photocatalyst is the rapid recombination of electron-hole pair. Due to this limitations, this method is still not practically being used in large industry [8]. In order to activate photocatalyst using visible light, various ways and solution came out such as altering the photocatalyst band gap using dye sensitization, metal, non-metal doping and synthesizing new narrow band gap photocatalyst [4, 7, 9, 10].

Perovskite with typical ABO\textsubscript{3} formula such as NaTaO\textsubscript{3}, KTaO\textsubscript{3}, LaFeO\textsubscript{3} have a higher photocatalytic activity due to its narrow band gap, unique crystal structure and electronic properties [11]. Citric acid and glucose based sol-gel method were used in previous studied and successfully synthesized LaFeO\textsubscript{3}. Glucose is more favorable as complexing agents as it is eco-friendly nature, low cost, facile and reproducibility. The use of glucose as a chelating agent often leads to convenience that requires less energy to synthesize high-purity nanoparticles. Based on previous studies, the
temperature used in calcining while synthesizing was undoubtedly affected the structure, particle size and properties of the end product but rarely explored and reported [12, 13].

In this study, lanthanum based photocatalyst, Lanthanum Orthoferrite (LaFeO₃) with narrow bandgap has been synthesized via sol-gel method in order to be activated under visible light irradiation. Study on the effect of calcination temperature towards the physicochemical properties and photocatalytic degradation performance of the synthesized LaFeO₃ were investigated.

2. Experimental
2.1 Materials
In the typical synthesis of perovskite LaFeO₃, lanthanum nitrate, La (NO₃)₃.6H₂O, iron (III) nitrate nonahydrate, Fe(NO₃)₃.9H₂O, glucose C₆H₁₂O₆ were used as starting materials to prepare LaFeO₃ nanostructures by sol-gel route. Oil-in-water emulsion was made using Bagus cooking oil together with sodium dodecyl sulphate (SDS) for photocatalytic activity test.

2.2 Preparation of photocatalyst
Perovskite type of lanthanum orthoferrite (LaFeO₃) nanoparticles materials was synthesized according to a method which has been described elsewhere (T. Liu & Xu, 2011). Glucose solution with 80% concentration was prepared using 500ml beaker. 150ml of distilled water then was added into the beaker with stirrer bar. Bear in mind that glucose powder must be added after adding water in the beaker to avoid rock candy. Put the beaker on the hot plate and heat the water to become warm water using the temperature of 50-60°C. While waiting for the water, weight the glucose powder, 80% from 500ml, 400g glucose solution was mixed together in the 250ml beaker with stirrer bar. Bear in mind that glucose powder must be stirred each time before use.

La (NO₃)₃.6H₂O and glucose solution was mixed together in the 250ml beaker on the hot plate with magnetic stirrer in it and at 55-65°C. Using the mol ratio of glucose to metal ions of 3:5, Fe (NO₃)₃.9H₂O was added to the solution under constant stirring and temperature around 70°C until it dissolves completely. Decomposition of ions nitrate gave out brownish gas after dissolving Fe (NO₃)₃.9H₂O. The sample then was removed from hot plate and heated in the oven at 250°C for 2 hours. After 2 hours, the sample was let to cool down and out of the oven. The sample was then be ground into slightly ground powder and precursor was obtained. Precursor was then be calcined at various temperatures ranging from 500-900°C for 2 hours. Final product should be ground again to get finer powder.

2.3 Characterization
The precursor and calcined samples were characterized using various characterization techniques. The TGA analysis is conducted to determine the weight loss and the phase change of the sample precursor and calcined samples. Crystallite phase and size were analyzed by X-ray diffraction (XRD) that were performed on a X’Pert PRO PANanalytica from from 10° to 90° using Cu Kα radiation of λ=0.1540nm. UV-Vis absorption spectrophotometer using Perkin Elmer Lambda 25 were used in this study to analyzed the optical properties of synthesized samples. The morphology of the synthesized samples was observed using Low Voltage FE-SEM (Hitachi FE-SEM SU8000 EDX (Bruker) with an acceleration voltage of 3.0 kV. Specific surface area and pore volume were measured and calculated by N₂ adsorption using Brunauer, Emmet and Teller (BET) (Micromeritics Instrument Corporation TriStarII 3020) analyzer based on nitrogen gas adsorption.

2.4 Photocatalytic activity
The synthetic oily wastewater was prepared using cooking oil brand Bagus, by Sime Darby. The synthetic oil-in-water emulsion was prepared according to method by Gohari et al., (2014) in which the synthetic oil of different concentrations, i.e. 10, and 2000 ppm, was mixed with DI water under vigorous stirring at 250 rpm for about 30 min at room temperature while adding sodium dodecyl sulphate (SDS) to produce homogenous mixture between oil and water. Once the process was completed, a solution with uniform yellowish colour was obtained. Considering coalescence of oil droplets that may happen during an extended period of storage, synthetic oily wastewater was prepared a day before experiment to keep the feed characteristics consistent.
The photocatalytic degradation of oily wastewater using synthesized LaFeO$_3$ as photocatalyst was conducted in a closed stainless-steel box as a batch reactor. 300 mL synthetic oil emulsion were put in the beaker. 0.3g of LaFeO$_3$ calcined at 600°C was added into the beaker. The mixture then was being stirred for 30 minutes for adsorption process in a dark place with continuous stirring. After 30 minutes of adsorption process, the photocatalytic activity was then tested under visible-light irradiation for 150 minutes. 10mL of the mixture was aliquot using 10mL syringe and was filtered using syringe filter (brand, size) at 30 minutes interval for 2 hours and 30 minutes.

Stir the mixture for another 30 minutes under visible light irradiation (100 watt). After 30 minutes, an aliquot was taken again. This activity continues for 2 hours and 30 minutes, for every 30 minutes 10mL aliquot was taken as sample and stored in dark place to avoid further photocatalytic activity. The concentration of the synthetic oil was varied for 1000 ppm, 10 000 ppm, 20 000 ppm.

3. Results and Discussion

3.1 Thermal decomposition analysis
The TGA analysis is conducted to determine the weight loss and the phase change of the sample precursor and calcined samples. Figure 1 shows the thermal decomposition curves of the LaFeO$_3$ precursor and nanoparticles that can be described as follows. The weight loss for precursor shows two weight loss segments. The first segment is attributed to the elimination of water molecules and the crystallization process of the materials. The second significant weight loss observed between 360-629.5°C mainly due to the decomposition of organic compound.

The weight loss for LaFeO$_3$ calcined at 500°C shows only a segment and there’s no further weight loss was observed after that. The segment observed between 59.5 - <629.5 °C is due to the decomposition remaining organic compound and formation of the disordered La$_2$O$_3$ [14]. There is no weight loss observed for sample calcined at 600°C-900°C confirmed that all organic matter has been burnt out and there is no change in phase [15]. This finding shows that LaFeO$_3$ precursor and nanoparticles calcined at 500°C were completely in crystal form after 630°C. On the other hand, LaFeO$_3$ calcined at 600°C-900°C were thermally stable and completely crystallized.

![Figure 1 TGA Curves of precursor and LaFeO$_3$ calcined at 500 – 900 °C](image-url)
3.2 Crystallinity properties

Figure 2 shows the pXRD pattern of LaFeO$_3$ calcined at various temperatures range between 500°C and 900°C for 2h in air. Lattice parameter for LaFeO$_3$ synthesized by sol-gel route is $\alpha=3.926$. The observed patterns all indexed with JCPDS card no.37-1493. The precursor and sample synthesized at 500°C is in amorphous structure as it can be seen by wide and broad continuum. LaFeO$_3$ was completely crystallized into perovskite phase at calcination temperature of 600°C. Further calcined the precursor at 700°C to 900°C for 2h yield more crystalline pure LaFeO$_3$ with orthorhombic structure.

Increasing the calcination temperature will result in sharper and stronger peaks indicating greater crystallization. The average crystallite size of all samples was calculated from X-ray line broadening of the (1 1 0) diffraction peak using Debye-Scherrer’s equation. The crystallite size of particles has been determined according to the x-ray line-broadening at (1 1 2). Crystallite size of 23.82 nm, 31.17 nm, 32.0 nm, and 38.3 nm were obtained for the samples calcined at 600°C, 700°C, 800°C, 900°C respectively. It can be seen clearly that crystallite size of each sample gradually increases with the increasing of the calcination temperature (T. Liu & Xu, 2011). Narrow band gap is needed to ensure the photocatalyst can be activated by visible light to carry the photocatalytic activity. Crystallite size of the particle gives strong influence to the value of the band gap as smaller crystallite size give rise to the band gap value [16]. This result is consistent with the band gap value as shown in Table 2.

3.3 Morphological properties

The surface morphology of the precursor and pure LaFeO$_3$ were analysed by field emission scanning electron microscopy (FESEM). FESEM micrographs of LaFeO$_3$ precursor and powders calcined at various temperature ranges from 500°C-900°C are presented in Figure 3. Powder calcined at 500°C consists of agglomerated particles but porous. At 600°C, the nanoparticle seems to be in regular porous morphology and connect with each other to form a large network system. Further calcined the
precursor to 700°C-900°C, changes the particle morphology. From FESEM images, it can clearly be seen that the particle size increase with the calcination temperature. The formation of sponge-like structure and “chess-like” structure can be observed in Figure 3(b) and 3(c) for samples calcined at 500°C and 600°C. Figure 3(d) and 3(e) are the images of LaFeO₃ calcined at 700°C and 800°C shows the pseudohexagonal-like structure of nanoparticles. While uniform nano-hexagonal shape for the powder calcined at 900°C can be seen through the FESEM image. All sample calcined at 500-900°C exhibit porous morphology, due to the charring reaction causing the evaluation of a large amount of gasses (Feng et al., 2011). It is well known that smaller particles size with higher surface area will provide more active sites thus promising for photocatalytic activity. It is also understood that the particle size and surface area are inversely related to each other. The surface area for each particle will be discussed in next section. As the particle size increase with calcination temperature, LaFeO₃ nanoparticles calcined at 600°C exhibit more favorable condition with smaller particle size and high surface area.

![FESEM micrographs of LaFeO₃ (a)precursor and sample calcined at (b)500°C, (c)600°C, (d)700°C, (e)800°C, (f) 900°C for 2h.](image)

3.4 Structural Analysis
FTIR spectra of LaFeO₃ precursor and the powder calcined at different temperatures are illustrated in Figure 4. It can be observed that all spectra exhibit two dominant absorption regions at 500-600cm⁻¹ and at band ~3500cm⁻¹. All the calcined samples show a peak around 550-570 cm⁻¹ are attributed to Fe-O stretching vibrational [17-20]. This new band appeared at nearly 600 cm⁻¹ is the band for the formation of LaFeO₃ attributed to the Fe-O stretching band and being characteristic of the octahedral FeO₆ group in LaFeO₃ [20-22]. The O-Fe-O deformation vibration (V₂ mode) obviously can be seen
by the strong absorption band less and near 500 cm\(^{-1}\) for all the calcined samples except for sample calcined at 500°C and precursor [12, 17, 23].

The smaller peak exists at 850 and 1080 cm\(^{-1}\) were resemble to the principal vibration of CO\(_3\)^{2-} group due to the contact to the ambient atmosphere, demonstrating that La-Carbonate exist at the surface of LaFeO\(_3\) nanoparticles. Two vibrational bands can also be observed at 1570 cm\(^{-1}\) and 1385 cm\(^{-1}\) that are assigned to the splitting of the asymmetric stretching of metal carbonate (T. Liu & Xu, 2011). Almost complete disappearance of this band for the sample calcined 600°C and complete disappearance for the samples calcined at 700-900°C showing that the CO\(_3\)^{2-} group were completely removed leaving behind only La. The wide band observed at ~3400 cm\(^{-1}\) was assigned for O-H stretch for precursor and 500-700°C samples (Lebid & Omari, 2013)(T. Liu & Xu, 2011). The reduction or disappearance of all the stated peaks (1080 cm\(^{-1}\), 1570 cm\(^{-1}\) and 1385 cm\(^{-1}\), 3400 cm\(^{-1}\)) indicating relatively pure phase formation for the samples calcined at 600-900°C.

Figure 4 FTIR spectra of LaFeO\(_3\) precursor and the powder calcined at different temperature

Based on the above FTIR results, Figure 5 shows the expected molecular structure of the metal ions and glucose complex. The formation of the chelation process can be described during the hydrolysis and condensation phase, in which the xerogel was fully formed. The chelation mechanism could be further explained from the structure of glucose, which consists of five hydroxyl groups (OH-) that can chelate to form metal complexes with metal ions.
Figure 5 Possible complex of metal ions and glucose in gel precursor of LaFeO₃ nanoparticles

3.5 Surface area analysis

In this study, BET surface area and pores size distribution were analyzed to determine the specific surface area of the synthesized LaFeO₃ at different calcination temperature. For the photocatalysis process where the reaction happens on the surface of the catalyst, surface areas of the nanoparticles are the main concern. In general, small particle size is more favorable as its lead to higher surface area. The surface area values for the calcined samples are tabulated in Table 1. It can be seen that the surface area values were decreasing with the calcination temperature except for the sample calcined at 600°C. Besides, this result is also in agreement with the crystallite size and particles size of LaFeO₃ that can be observed in XRD pattern and SEM images, respectively. For LaFeO₃-500, lower surface area could be related to the agglomeration of the particles.

Comparison our results with those reported in the literature is shown in Table 1. Based on this table, it can be concluded that our photocatalyst surface area is comparable with others at 600°C calcination temperature. Besides, it is clear that calcination time and complexing agents does have significant effects on the surface area of the photocatalyst. The surface area of the LaFeO₃ nanoparticles was found to be 15.68m²/g for sample calcined at 600°C which is higher than the reported value 8.5m²/g [19] and 14.1 m²/g [24]. This result shows that LaFeO₃ synthesized in this study have enough surface area to promote the degradation of oily wastewater. Even tough samples prepared using PVP K-30 have high surface area, their calcination time is longer which is not favorable as it is time and energy consuming. For citric acid, a lot study has demonstrated that the used of citric acid as complexing agents leads to less purity photocatalyst.

Table 1 Surface areas of LaFeO₃ synthesized using different complexing agents and calcination temperature

| Sample | Calcination temperature (°C) | Calcination time (h) | Complexing agents | Surface area (m²/g) | References |
|--------|-----------------------------|---------------------|-------------------|---------------------|------------|
| 1      | 500                         | 2                   | Glucose           | 3.89                | This study |
| 2      | 600                         | 2                   | Glucose           | 15.68               |            |
| 3      | 700                         | 2                   | Glucose           | 6.43                |            |
| 4      | 800                         | 2                   | Glucose           | 4.63                |            |
| 5      | 900                         | 2                   | Glucose           | 2.40                |            |
| 6      | 600                         | n/a                 | Glucose           | 8.5                 | [19]       |
| 7      | 600                         | n/a                 | Glucose           | 14.1                | [24]       |
| 8      | 600                         | 5                   | Citric acid       | 5.37                | [24]       |
| 9      | 600                         | 2                   | Citric acid       | 22.55               | [25]       |
| 10     | 600                         | 3                   | PVP K-30          | 26.62               | [26]       |

3.6 UV–vis diffuse reflectance spectra

Figure 6 represents the UV-Vis absorption spectrum of LaFeO₃ calcined at 500-900°C in the wavelength range from 200-800 nm. Lambda max from UV-Vis analysis should have peak more than
400nm and above to show the active photocatalytic activity in visible wavelength region. The absorption of LaFeO$_3$ precursor and LaFeO$_3$ calcined at 600-900°C was characterized with a sharp absorption edge at about 600-700 nm with band gap range 1.63-2.15 eV. The absorption edge in this region indicates that LaFeO$_3$ nanoparticles prepared by sol-gel method could serve as a potential visible-light-driven photocatalytic material. Figure 7 shows the results of band gap obtained by applying the Kubelka-Munk method to LaFeO$_3$ powder samples calcined at the temperature of 500-900°C whose values are tabulated in the Table 2.

Figure 6 UV-Vis spectrum of the perovskite LaFeO$_3$ calcined at different temperature, 600-900°C
According to Figure 7, the estimated value of band gap using Kubelka-Munk Function for LaFeO$_3$ calcined at 500°C is ~1.63 eV, which is relatively lower than P25 at 3.24 eV. The low band gap value of LaFeO$_3$ supported the visible light-driven characteristics of the synthesized photocatalyst. In Table 2 shows all the criteria that outstandingly has been encountered to find the finest sample calcined. The band gap value is increasing with the crystal size of nanoparticles. This is related to the quantification effect obtained due to morphological variations in the nanoparticles. As noted in the FESEM images (see Figure 3), the calcination treatment of LaFeO$_3$ material results in the formation of sponge-like structure, "chess-like" structure, pseudohexagonal-like structure, and hexagonal-like structure. The development of the structure of variance is responsible for quantum confinement.

Table 2 The value of the band gap, surface area and crystal size for LaFeO$_3$ calcined at 500-900°C.

| Samples   | Band gap (eV) | Surface area (m$^2$/g) | Crystal Size (nm) |
|-----------|---------------|------------------------|-------------------|
| LaFeO$_3$-500 | 1.63          | 3.89                   | Amorphous         |
| LaFeO$_3$-600 | 1.88          | 15.68                  | 7.29              |
| LaFeO$_3$-700 | 1.95          | 6.43                   | 11.55             |
| LaFeO$_3$-800 | 2.13          | 4.63                   | 12.60             |
| LaFeO$_3$-900 | 2.15          | 2.40                   | 15.43             |

The finest photocatalyst among sample in this study is LaFeO$_3$-600 because of its properties. This LaFeO$_3$-600 has the outstanding surface area (15.68m$^2$/g) with low band gap value (1.88 eV) and small crystal size (7.29 nm). This LaFeO$_3$-600 were served as a potential visible-light-driven photocatalytic material and has been chosen to undergo photocatalytic activity to treat synthetic oily wastewater.
3.7 Photocatalytic activity

UV-Vis spectrometer analysis on the degradation of the synthetic oily wastewater in dark (adsorption) and under visible light irradiation are shown in Figure 8. The photocatalytic activity of LaFeO$_3$ samples was evaluated by observing the degradation of synthetic oily water driven by visible light as the model pollutant. Only LaFeO$_3$-600C was selected to study the photocatalytic activity due to its large surface area. It is clearly shown that LaFeO$_3$ powder calcined at 600°C exhibit strong visible light absorption and more stable than the others. After absorption and desorption time have passed, at t=0s, the photocatalytic activity was proceeded under visible light irradiation and constant aeration. After half (0.5) hour adsorption equilibrium, we can find initial characteristic peak of synthetic oily wastewater decreased different from each other, which indicate the adsorption effect of each sample with an adsorption amount of 20% (1000ppm), 27% (10000ppm) and 55% (20000ppm). This results is comparable with previous study (Moslehyani et al., 2015). Under the irradiation of visible light for the next 150 minutes, the removal efficiency increases up to 67%, 72% and 63% for 1000ppm, 10000ppm and 20000ppm respectively. It was also showed that without any photocatalyst (photolysis) the degradation of synthetic oily wastewater was low, where removal efficiency of less than 5% was observed proving the stability of the pollutant under visible light irradiance.

![Figure 8](image.png)

Figure 8 Degradation of synthetic oily wastewater using LaFeO$_3$-600 for different initial concentration

Figure 9 illustrates the possible photocatalytic process at different initial concentrations. Limited interaction between oil droplet and photocatalyst result in less degradation for 1000 ppm initial concentration. 10 000 ppm is considered as optimum initial concentration for 1g/L of LaFeO$_3$ photocatalyst. Possibility of oil interact and absorb on the surface of photocatalyst was increased thus, increasing the degradation rate. Turbidity is high at 20 000 ppm, which leads to less light penetration and therefore less hydroxyl radical production, which reduces degradation. Besides, the excessive
contaminant adsorbed on the surface of the photocatalyst is believed can block the active sites from receiving light for photoactivation and lead to low photocatalytic performance.

![Schematic diagram of photocatalytic process with different initial concentration.](image)

**Figure 9** A schematic diagram of photocatalytic process with different initial concentration.

### 4. Conclusions

In summary, LaFeO$_3$ perovskite has been successfully synthesized using sol-gel method with varied calcination temperature between 500-900°C. XRD analysis confirmed that LaFeO$_3$ fully crystallized for calcination temperature of 600°C and above. The crystallite size of 23.82 nm, 31.17 nm, 32.0 nm, and 38.3 nm were obtained for the samples calcined at 600°C, 700°C, 800°C, 900°C respectively. The LaFeO$_3$ photocatalyst with the highest surface area is LaFeO$_3$-600 with a surface area of 15.68 m$^2$/g. The synthesized LaFeO$_3$-600 able to degrade oily wastewater up to 72% in 150 min. This study confirmed that the calcination temperatures significantly affects the optical, structural and morphological properties of nanoparticles.

### Acknowledgement

This work was supported by the Malaysia Ministry of Education (MOE) under FRGS (Grant No. R.J130000.7851.5F007) and MRUN (Grant no: R.J130000.7813.4L874). The authors would also like to acknowledge Universiti Teknologi Malaysia for financial support and instruments used for characterizations of samples within this study.

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