Enhancement of Sonocatalytic Activity and Stability of Magnetic LaFeO$_3$/Fe$_3$O$_4$ Nanocomposites

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Abstract. Recyclable catalyst using magnetic LaFeO$_3$/Fe$_3$O$_4$ nanocomposite has been successfully synthesized using co-precipitation method. The structural and magnetic properties of the samples were investigated using X-Ray Diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, and Vibrating Sample Magnetometer (VSM) Spectroscopy. The XRD results revealed that the LaFeO$_3$/Fe$_3$O$_4$ nanocomposite shows orthorhombic and cubic spinel structure from LaFeO$_3$ and Fe$_3$O$_4$, respectively. The saturation magnetization of LaFeO$_3$ increases with the increasing of Fe$_3$O$_4$ content in the nanocomposite. The sonocatalytic performance and recyclability of the sample were evaluated by degrading methylene blue (MB) as a model of organic pollutant. Compared to LaFeO$_3$ nanoparticles, the sonocatalytic activity of LaFeO$_3$/Fe$_3$O$_4$ nanocomposite showed better performance. The stability of the catalyst was also checked by removing the catalyst from the MB solution simply using an external magnetic field. The result shows that the sample has good stability.

1. Introduction

Since 1990, the use of ultrasonic irradiation to destroy organic contaminant in wastewater has drawn special attention which offers several advantages such as safety, cleaness, high penetrability in an aqueous medium, high degradation efficiency and energy conversion without generating any secondary pollutant [1–4]. However, the use of ultrasonic irradiation alone may not be suitable for all kinds of pollutant and various variables such as the power of ultrasonic, the chemical structures, and the size of pollutant molecules. In addition, the ultrasonic process consumes a high amount of energy and time that makes it expensive [5]. Applying the catalyst in the sonocatalytic process is one of the promising ways to improve the performance of the ultrasonic irradiation in degrading the pollutants. The sonocatalytic process can be explained by the mechanism of sonoluminescence and hot spot. When an ultrasonic irradiates a catalyst, electron in the valence band of catalyst are excited to the conduction band by the sonoluminescence and hot spot, leaving the holes in the valence band. The sono-excited electrons and holes are participated in a redox reaction to degrade organic pollutant, which makes catalyst behave like photocatalyst. Therefore, in sonocatalytic activity, ultrasonic irradiation not only induces sonolysis but also generates electron and hole pairs in the catalyst which could enhance the catalytic performance by providing additional nucleation sites for development of cavity microbubble and subsequently increase the pyrolytic degradation and reactive radical generation [6].
LaFeO$_3$ with unique optoelectronic and a narrow optical gap has received intensive attention because of its strong catalytic activity [7]. The sonocatalytic activities of LaFeO$_3$ nanoparticles have been reported in our previous work [8]. The results showed that LaFeO$_3$ nanoparticles had good sonocatalytic performance and stability. However, the stability experiment could not be carried out easily by an applied external magnetic field. Therefore, in this work magnetite (Fe$_3$O$_4$) that has strong magnetic property is introduced to LaFeO$_3$ to enhance the sonocatalytic performance and the stability of the catalyst. The samples were synthesized using the co-precipitation method and were characterized by several measurements. The sonocatalytic performance and stability were also checked using methylene blue (MB) as a model of organic pollutant.

2. Experimental details

2.1. Synthesis of the Nanoparticles

Lanthanum (III) chloride heptahydrate (LaCl$_3$·7H$_2$O), Iron (II) chloride tetrahydrate (FeCl$_2$·4H$_2$O), and sodium hydroxide (NaOH) were used to synthesize LaFeO$_3$ nanoparticle using the co-precipitation method based on our previous work [8]. Iron (II) sulfate heptahydrate (FeSO$_4$·7H$_2$O), sodium hydroxide (NaOH), ethanol, ethylene glycol, and acetic acid (20%) were used to prepare Fe$_3$O$_4$ nanoparticles using the sol-gel method [9].

2.2. Synthesis of the Nanocomposites

The prepared LaFeO$_3$ and Fe$_3$O$_4$ nanoparticles were then used to synthesize the LaFeO$_3$/Fe$_3$O$_4$ nanocomposite with the variation of the molar ratio of 1:0.1, 1:0.3, 1:0.5, and 1:1, respectively. The synthesized nanocomposite was obtained through the following steps: first, the LaFeO$_3$ nanoparticle was dissolved in distilled water, while Fe$_3$O$_4$ was dissolved in ethanol. Then, these two solutions were mixed and ultrasonicated for two hours. The obtained mixtures were then centrifuged to separate the precipitations and solutions. Thereafter, the precipitations obtained were allowed to stand at room temperature and then heated 100°C for one hour under vacuum conditions.

2.3. Characterization

The samples were characterized by X-Ray Diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, and Vibrating Sample Magnetometer (VSM).

2.4. Sonocatalytic Activity

The detailed sonocatalytic procedure have been reported in our previous work [8]. Methylene blue (MB) was selected as a model of organic pollutant and the sonocatalytic activity were carried out under ultrasonic irradiation. The degradation of MB was monitored using a Hitachi (UH5300) UV-visible spectrophotometer. 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. To further study the recyclability of the catalyst, LaFeO$_3$/Fe$_3$O$_4$ nanocomposite was used repeatedly for four-times. In the each run, the catalyst could be easily separated by an applied magnetic field.

3. Results and Discussion

The magnetic separation process in the sonocatalytic is a very important issue for its practical application. The catalyst is expected to be easy recovering from the aqueous organic dyes and recycling for several times. Therefore, to study the magnetic properties of the samples, Figure 1a presents the magnetic hysteresis curves of LaFeO$_3$/Fe$_3$O$_4$ nanocomposite with different molar ratio of Fe$_3$O$_4$. The magnetic hysteresis curves of LaFeO$_3$ and Fe$_3$O$_4$ nanoparticles are also shown as a comparison. The results show that all samples exhibit ferromagnetic behavior at room temperature. The corresponding saturation magnetization values are also summarized in Table 1. The saturation magnetic values of LaFeO$_3$/Fe$_3$O$_4$ nanocomposite increase with the increasing of Fe$_3$O$_4$ contents. It indicates that LaFeO$_3$/Fe$_3$O$_4$ nanocomposite could be further applied for the separation process. It can
Figure 1. (a) VSM spectra; (b) XRD pattern of LaFeO$_3$/Fe$_3$O$_4$ nanocomposites with different molar ratio of Fe$_3$O$_4$.

Table 1. The lattice parameter, grain size <D>, magnetic saturation (M-S) and surface area of LaFeO$_3$/Fe$_3$O$_4$ nanocomposite.

| Sample                      | Lattice Parameter LaFeO$_3$ | Lattice Parameter Fe$_3$O$_4$ | <D> LaFeO$_3$ (nm) | <D> Fe$_3$O$_4$ (nm) | M-S (emu/g) | Surface Area (m$^2$/g) |
|-----------------------------|------------------------------|-------------------------------|-------------------|----------------------|-------------|------------------------|
| LaFeO$_3$                   | 5.5436 7.8456 5.5528        | -                             | 58                | -                    | 12.08       | 31                     |
| Fe$_3$O$_4$                 | -                             | 8.3638                        | 45                | 82.13                | 3           | 9                      |
| LaFeO$_3$/0.1Fe$_3$O$_4$    | 5.5692 7.8564 5.5623        | 8.3258                        | 24                | 20.87                | 24          | 19                     |
| LaFeO$_3$/0.3Fe$_3$O$_4$    | 5.5324 7.8497 5.5660        | 8.3288                        | 30                | 28.93                | 19          | 13                     |
| LaFeO$_3$/0.5Fe$_3$O$_4$    | 5.4580 7.8126 5.5550        | 3.3299                        | 34                | 41.96                | 13          | 9                      |
| LaFeO$_3$/Fe$_3$O$_4$       | 5.4312 7.8096 5.5509        | 8.3307                        | 36                | 55.58                | 9           | 9                      |

be seen in the inset of Figure 1a, the catalyst could be easily separated by an applied external magnetic field.

Figure 1b displays the XRD pattern of LaFeO$_3$/Fe$_3$O$_4$ nanocomposite with different molar ratio of Fe$_3$O$_4$. As a comparison, the XRD pattern of LaFeO$_3$ and Fe$_3$O$_4$ nanoparticles are also shown in the figure. For LaFeO$_3$/Fe$_3$O$_4$ nanocomposites, the diffraction peaks at 2θ = 22.6°, 32.2°, 39.8°, 46.2°, 57.5°, 67.4°, and 76.7° which index to the (101), (121), (220), (202), (240), (242), and (204), planes, respectively, are corresponded to the orthorhombic structure of LaFeO$_3$ [10]. While the existence of diffraction peaks at 2θ = 35.5° which represent to the (311) planes correspond to the cubic spinel structure of Fe$_3$O$_4$[9]. No other segregation of phase was found, indicating that the desired synthesized sample was obtained. The lattice parameter and crystal size <D> of the samples, obtained by Rietveld refinement method using MAUD program and calculated using the Scherrer’s formula [11], are summarized in Table 1. The specific surface area measured using BET method is also tabulated in Table 1.

The sonocatalytic degradation of methylene blue (MB) using LaFeO$_3$ nanoparticles as a catalyst is shown in Figure 2a. The effect of Fe$_3$O$_4$ incorporation on the sonocatalytic performance of LaFeO$_3$/Fe$_3$O$_4$ nanocomposites is also illustrated in the figure. It can be seen that MB degradation in the presence of LaFeO$_3$/Fe$_3$O$_4$ nanocomposites increases with the increasing nanocomposites molar ratio up to 1:0.5 and decreases when the nanocomposites molar ratio further increase. However, all nanocomposites samples still show better performance than LaFeO$_3$ nanoparticles. The
sonodegradation of MB using LaFeO$_3$/Fe$_3$O$_4$ nanocomposite obeys pseudo-first order kinetics with respect to the concentration of MB: $\ln(C_t/C_0) = k_{app} t$, where $k_{app}$ is the apparent reaction constant for catalysis used as the basic parameter for different catalysts [12]. The apparent reaction constant of LaFeO$_3$/Fe$_3$O$_4$ nanocomposites was calculated and the results are presented in the inset of Figure 2a. It can be seen clearly in the figure, the LaFeO$_3$/Fe$_3$O$_4$ nanocomposite with a molar ratio of 1:0.5 exhibits maximum sonocatalytic performance for degrading MB.

In the sonocatalytic process, it is known that ultrasonic irradiation not only induces sonolysis but also generate electron and hole pairs in the catalyst [6]. The present of Fe$_3$O$_4$ in the nanocomposite could improve the sonocatalytic performance by trapping the photo-generated electrons from the conduction band of LaFeO$_3$ [13]. The photo-generated electrons could then react with Fe$^{3+}$ ions to form Fe$^{2+}$ ions. After that, Fe$^{2+}$ ions would react with molecular oxygen (O$_2$) to yield Fe$^{3+}$ ions and superoxide radical (•O$_2$) as following this equation: Fe$^{2+} + O_2 \rightarrow Fe^{3+} + •O_2$ [14]. The produced superoxide radicals are known as one of the strong reduction and oxidation agents that could destroy the complex chemical bonds of organic pollutants such as MB [15].

The stability of the catalyst was also checked using LaFeO$_3$/Fe$_3$O$_4$ nanocomposites with maximum degradation rate. The removed catalyst as depicted in the inset of Figure 2b, was used to degrade MB solutions four-times under the same treatment conditions. After four repetitions (as showed in the Figure 4b), insignificant losses of activity were observed, indicating that the catalyst has excellent stability and recyclability in the sonocatalytic process.

4. Conclusion
The orthorhombic and cubic spinel structure of LaFeO$_3$/Fe$_3$O$_4$ nanocomposites show better sonocatalytic performance than LaFeO$_3$ nanoparticles. The 1:0.5 of LaFeO$_3$/Fe$_3$O$_4$ nanocomposite exhibits maximum sonocatalytic performance for degrading MB. The samples also show ferromagnetic behavior at room temperature which makes the separation process in the stability experiment become easier. The results show that the catalyst has excellent stability and recyclability in the sonocatalytic process.

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