The Influence of TiO2 Nanoparticles on LaFeO3/TiO2 Nanocomposites for Reduction of Aqueous Organic Dyes

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Abstract. A series of Lanthanum ferrite (LaFeO3) nanoparticles over titanium dioxide (TiO2) were synthesized using sol-gel method at room temperature by varying the loading of LaFeO3 on TiO2. The magnetic properties of samples were measured using vibrating sample magnetometer and photosonocatalytic activity towards the degradation of methylene blue under light (UV or visible) and ultrasound irradiation was also evaluated. The morphology and structure of the samples were characterized by field emission scanning electron microscope, energy dispersive analysis and X-ray diffraction. Furthermore the optical properties were also characterized by UV-visible diffuse reflectance. The experimental results showed that the prepared perovskites had sphere-like shape and strong visible light absorption. LaFeO3 demonstrated ferromagnetic properties and the magnetization decreased with the incorporation of TiO2 in the samples. However, the incorporation of TiO2 increased the photosonocatalytic activity and extended the photosensitivity to UV light.

1. Introduction
One of methods to degrade organic pollutant in wastewater commonly applied by researchers was the photocatalytic process. The photocatalytic process was the process of degrading organic pollutant using light as the irradiation source assisted by catalyst. However, in line with its development, the researchers found that the photocatalytic test greatly depends on the amount of light penetration into the water, so that the light could be absorbed by the catalyst, and then the photodegradation process could take place. Unfortunately, the organic pollutant in environment oftentimes had quite high density and not transparent. Consequently, light only could travel into the water by several millimeters hence inhibiting degradation of organic pollutant [1-2]. Recently researchers found that use of ultrasonic radiation was able to settle the above problem. The ability of ultrasonic irradiation penetration was very high for all water media that could reach depths of up to 15-20 cm [3]. In addition, ultrasonic irradiation was uniformly dispersed in the water medium so that it could reduce the agglomeration of particles that commonly occurred in the catalytic process [4]. The sonolysis process could actually be performed without catalyst, but its low efficiency required semiconductor that was applied as a catalyst [5]. In the sonocatalytic process, semiconductor could also play an active role as catalyst by utilizing sonoluminescence that appeared due to implosion of acoustic bubbles at the high local temperature of 5000 K and pressure of 1000 atm. This caused not only sonocatalytic process but also photocatalytic process occurred simultaneously [1]. Based on the above-mentioned process, the synergy effect might arise if the photocatalytic and sonocatalytic processes were done simultaneously...
namely the photosonocatalytic process that might draw the attention of researchers. Considering the result to be obtained, the combination of both catalytic processes was predicted to produce better efficiency than if each process was done separately.

One of semiconductors that frequently used as catalyst was TiO2. Its relatively low price, non-toxic and its high catalytic capability drew the attention to use it as a catalyst [6]. This is because solar energy contains around ~46% visible light and only around 4-5% ultraviolet light [7]. Therefore, to maximize used of solar energy as an energy source, a new type of catalyst that could play an active role in visible light was interesting to be developed [8-9]. LaFeO3 was one of catalysts that could be active in visible light. In addition, its stability, environmental friendless, and multi functions were the added value of utilization of this material [10]. The photocatalytic process highly depended on the recombination of electron and hole pairs from catalyst materials such as LaFeO3. For that purpose, to prepare LaFeO3 in the form of nanocomposites for example by using TiO2 was known to be able to inhibit the recombination of electron and hole pairs so that its catalytic performance could increase [9, 11]. Several researchers have reported photocatalytic activities using LaFeO3/TiO2 nanocomposites as catalyst [11]. However, photosonocatalytic activities performed using the nanocomposites are rarely found.

Hence, in this study several series of LaFeO3/TiO2 nanocomposites with variation of molar ratios have been successfully synthesized using the sol-gel method. The morphology, structure, magnetic properties and optical properties of the samples would be studied. Photosonocatalytic activities would also be performed using methylene blue (MB) as the model of organic pollutant. The influences of TiO2 on the photosonocatalytic activity of LaFeO3/TiO2 were carried out under different light sources (UV or visible).

2. Experimental details

**Materials:** LaCl3.7H2O, FeCl2.4H2O, titanium dioxide (TiO2) and sodium hydroxide (NaOH) were purchased from Merck. All chemical reagents were analytical grade and used without further purification.

**Catalyst preparation:** LaFeO3 nanoparticles were synthesized using co precipitation method based on our previous work [12]. Subsequently, several series of LaFeO3/TiO2 nanocomposites with different molar ratio 1:0.1, 1:0.3, and 1:0.5 were prepared using sol-gel method [13]. In brief, 0.00125 mol of TiO2 was dissolved into 30 ml of distilled water under magnetic stirrer. Then, 0.00125 of NaOH that had been dissolved into 65 ml of distilled water was added into the mixture. This mixture was designated as solution A. Afterward solution A was stirred and heated at the temperature of 80°C. Meanwhile, the above synthesized LaFeO3 were dissolved into 30 ml of distilled water and were designated as solution B. Subsequently, solution B was introduced into solution A and the mixtures were continuously stirrer at 80°C for 2h. The obtained mixtures were centrifuged and washed for several times with ethanol and distilled water. Afterward, the final product was allowed to stand overnight at the room temperature and then heated at 100°C for 1h under vacuum condition.

**Characterization:** The morphology and elemental analyses of samples were studied using LEO 420 field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) spectroscopy. XRD pattern was obtained using a Rigaku Miniflex 600 with Cu-Kα (λ = 1.54060 Å) as a radiation source operated at 40 kV and 20 mA in the range of 20° up to 90°. The magnetic properties were measured using the Oxford Type 1.2 T vibrating sample magnetometer (VSM). The measurement was carried out from 0 to ± 1 Tesla. Then, the optical properties were measured using UV-Vis diffuse reflectance spectrophotometer.

**Catalytic activity:** Methylene blue (MB) was selected as the model of organic pollutant in this study. The photosonocatalytic processes were conducted in a cylindrical glass vessel equipped with a magnetic stirrer under light and ultrasonic irradiation simultaneously. The ultrasonic irradiation was carried out using a commercially ultrasonic bath operated at fixed frequency and power of 40 kHz and 150 W. While, the different light of 40 W- UV lamp and 40 W- Xe lamp were used as the UV and
Visible light irradiation source. The solution was analyzed using Hitachi UH5300 UV-visible spectrophotometer. The percentage degradation of MB was recorded as $C_t/C_0$, where $C_t$ is the concentration of organic pollutant in each irradiated time interval and $C_0$ is the initial concentration of organic pollutant after adsorption-desorption equilibrium was reached. In order to study the main active species that play important role in the degradation of MB, different substance such as di-ammonium oxalate, sodium sulfate, and tert-butyl alcohol were used as holes, electrons and hydroxyl radicals scavengers. The stability of catalyst was also checked by reusing the catalyst four times cycle processes.

3. Results and Discussion
The morphology of the samples was investigated using FESEM image. Figure 1 showed FESEM image from (a) LaFeO$_3$ nanoparticles, (b) TiO$_2$ nanoparticles, and (c) LaFeO$_3$/TiO$_2$ nanocomposites with the molar ratio of 1:0.3. As can be seen from Figure 1a, the synthesized LaFeO$_3$ nanoparticles consist of agglomerated particles, while the individual particles appeared to be spherical [12]. The spherical-like shape of TiO$_2$ nanoparticles was also shown in Figure 1b. Hence in Figure 1c, the morphology of LaFeO$_3$/TiO$_2$ nanocomposites showed spherical-like shape from both nanoparticles and agglomerated particles originating from LaFeO$_3$ nanoparticles. Elemental analysis of the samples has also been studied using EDX measurement. Figure 2a showed the EDX spectra of TiO$_2$ nanoparticles, LaFeO$_3$ nanoparticles, and LaFeO$_3$/TiO$_2$ nanocomposites with the molar ratio of 1:0.3. The presence of La, Fe, Ti, and O in EDX spectrum confirmed the formation of LaFeO$_3$/TiO$_2$ in the form of nanocomposites.

The crystal structure of the samples was studied using XRD spectroscopy. Figure 2b showed the XRD pattern of the LaFeO$_3$/TiO$_2$ sample with the molar variation ratio of 1:0.1, 1:0.3, and 1:0.5. As comparison, the XRD pattern of TiO$_2$ nanoparticles and LaFeO$_3$ nanoparticles were also shown in this figure. The XRD pattern of TiO$_2$ nanoparticles showed tetragonal structure with the anatase phase. While the XRD pattern of LaFeO$_3$ nanoparticles showed orthorhombic structure. No additional phase or impurity found in the diffraction pattern of each nanoparticle. For LaFeO$_3$/TiO$_2$ nanocomposites, the diffraction peaks at $2\theta$ 22.6°, 32.2°, 39.8°, 46.2°, 57.5°, 67.4°, and 76.7° which represent planes (101),(121), (220), (202), (242), and (204) respectively are known to be the diffraction pattern from the orthorhombic structure of LaFeO$_3$ [14]. Meanwhile the diffraction peak at 2$\theta$ 25.2° which represent plane (101) constitutes the diffraction pattern of the anatase phase from TiO$_2$ [11]. The dominant XRD pattern of LaFeO$_3$ might be caused by the molar ratio between LaFeO$_3$ and TiO$_2$ which is relatively small. No other segregation of phase was also found in the diffraction pattern of LaFeO$_3$/TiO$_2$ nanocomposites. The lattice parameter obtained by Rietveld refinement method using MAUD program and crystallite size $<D>$ calculated using the Scherrer’s formula have been summarized in Table 1.

![Figure 1. FESEM image of (a) LaFeO$_3$ nanoparticles; (b) TiO$_2$ nanoparticles; and (c) LaFeO$_3$/TiO$_2$ nanocomposites with molar ratio of 1:0.3. All images are at 20.000× magnification (scale bar = 5µm).](image-url)
Figure 2. (a) EDX spectra; and (b) XRD pattern of LaFeO3/TiO2 nanocomposite.

Figure 3. (a) VSM and (b) UV-vis spectra of LaFeO3/TiO2 nanocomposites.

Table 1. The lattice parameter, grain size <D>, magnetic saturation (M-S) and band gap of LaFeO3/TiO2 nanocomposite.

| Sample          | Lattice Parameter | Lattice Parameter | <D>  | <D> | M-S (emu/g) | Band Gap (eV) |
|-----------------|-------------------|-------------------|------|-----|-------------|--------------|
|                 | a (Å)             | b (Å)             | c (Å) | a=b (Å) | c (Å) (nm) | (nm)         | (eV)         |
| LaFeO3          | 5.5436            | 7.8456            | 5.5528 | -  | -           | 58           | 12.08        | 2.45         |
| LaFeO3/0.1TiO2  | 5.5440            | 7.7794            | 5.5500 | 3.8355 | 9.6407    | 28           | 36           | 2.91         | 2.49         |
| LaFeO3/0.3TiO2  | 5.5590            | 7.7140            | 5.6540 | 3.7822 | 9.5023    | 27           | 30           | 1.62         | 2.53         |
| LaFeO3/0.5TiO2  | 5.5222            | 7.6865            | 5.6533 | 3.7860 | 9.4950    | 23           | 29           | 0.55         | 2.58         |

The influence of TiO2 on the magnetic properties of LaFeO3/TiO2 nanocomposites was also studied using VSM measurement. Figure 3a showed the VSM spectra of LaFeO3 nanoparticles and LaFeO3/TiO2 nanocomposites with different molar ratio. As can be seen in the figure, all samples showed ferromagnetic behaviour under room temperature. With the increasing of TiO2 content the magnetic saturation (Table 1) of LaFeO3/TiO2 nanocomposites decreases respectively. The reduced mass of LaFeO3 in the presence of non-magnetic TiO2 might cause the decrease of magnetic saturation on the samples [13].

The optical property of the samples was performed using UV-Vis diffuse reflectance spectroscopy measured at the room temperature in the range of 200-800 nm. Figure 3b showed UV-Vis reflectance spectra of LaFeO3 nanoparticles and LaFeO3/TiO2 nanocomposites with different molar ratio. By extrapolating the spectra using Kubelka-Munk analysis with following equation: \( F(R) = (1-R)^2/2R \) [15], with R as diffuse reflectance, the optical gap of each sample could be known. Based on this function, the band gap was obtained by plotting the value of \( F(R)^2 \) vs. the energy in electron volts. The
linear part of the curve was then extrapolated to become \( F(R)^2 = 0 \) and subsequently the optical gap could be known. The optical gap of the samples have been summarized in Table 1. The result showed that all samples have optical gap values in the visible light region. However, the optical gap of the nanocomposites increased with the increasing of TiO2 molar ratio. It indicated that the nanocomposites also have good response to UV light. Therefore, in the photosonocatalytic test both UV and Visible light were used as an irradiation sources.

![Figure 4](image)

**Figure 4.** (a) The degradation of methylene blue by using LaFeO3/TiO2 nanocomposite with various molar ratio; (b) The effect of various scavengers on photosonocatalytic degradation of methylene blue by using LaFeO3/TiO2 nanocomposite with molar ratio of 1:0.5; and (c) The reusability on the photosonocatalytic degradation of methylene blue by using LaFeO3/TiO2 nanocomposite with molar ratio of 1:0.5 under visible light irradiation.

Figure 4a showed the photosonocatalytic activity of LaFeO3/TiO2 nanocomposites under UV and visible light irradiation. As a comparison the photosonocatalytic activities of LaFeO3 nanoparticles could also be observed. The degradation of MB increased with the increasing of TiO2 molar ratio and showed better performance than LaFeO3 nanoparticles. LaFeO3/TiO2 nanocomposites with the molar ratio of 1:0.5 showed highest degradation both under UV and visible light irradiation. The MB degradation obtained in the photosonocatalytic follow the equation of pseudo-first order kinetics model: \( \ln \left( \frac{C_t}{C_0} \right) = k_{\text{app}} t \), where \( k_{\text{app}} \) is the apparent reaction constant for catalysis used as the basic parameter to compare different catalysts. The reaction constant of different catalysts has been examined in this study and the result could be observed in inset Figure 4a. The result indicated that the photosonocatalytic activity using visible light was faster than using UV light irradiation. In addition, the main active species that play the important role in the photosonocatalytic activity was also examined in this study. Degradation of methylene blue with the existence of Na2S2O8, di-ammonium oxalate and tert-butyl alcohol as electrons, holes, and hydroxyl radicals scavenger, could be observed in Figure 4b. The presence of di-ammonium oxalate as holes scavenger inhibited the degradation of MB. This result confirmed that holes play an important role in degrading of MB. Figure 4c showed the stability of catalyst four times cycle processes. The result indicated that LaFeO3/TiO2 nanocomposites showed good stability for degrading MB in the photosonocatalytic activity.

High photosonocatalytic activities of LaFeO3/TiO2 nanocomposites under visible light irradiation compared to using UV light could be explained as follows: In the photosonocatalytic process, the
catalyst interacted with light and ultrasonic wave. Interaction between the catalyst and the light produced the separation process of electron and hole. While interaction between catalyst and ultrasonic wave could increase formation of hydroxyl radicals (•OH) and formation of electron and hole pairs at the same time. Formation of electron, hole and •OH in the photosonocatalytic processes play an important role on the degradation process. LaFeO3 nanoparticles is a catalyst that has optical gap in the range of visible light irradiation, and based on the result of UV-Vis measurement, the optical gap of LaFeO3/TiO2 nanocomposites also showed the absorption in the visible light region. Hence, the possibility of LaFeO3/TiO2 nanocomposites to produce electron and hole pairs was higher if it was conducted using visible light irradiation. In the photosonocatalytic activity using visible light source, TiO2 could be serve as electron transport layer. When visible light was given to the catalyst, the electron that was excitated to the conduction band of LaFeO3 did not directly return to the valence band but first transferred to the conduction band of TiO2. Conversely, when a photosonocatalytic activity was conducted on UV light, the excitated electron in conduction band of TiO2 would first be transferred to the conduction band of LaFeO3. The variation of TiO2 molar ratio in the sample caused the different degradation of MB. Under UV radiation, the higher content of TiO2 was known to be able to increase absorption of UV light, hence LaFeO3/TiO2 nanocomposites with the molar ratio of 1:0.5 indicated a more dominant result compared to with other molar ratio. While in visible irradiation, TiO2 only served as an electron transport layer that could inhibit the recombination of electrons and holes pairs. When an electron was transferred in the conduction band of TiO2 or LaFeO3, at the same time, the hole left in the valence band could move freely to be able to react with OH-, resulting the total hydroxyl radicals (•OH) obtained in the photosonocatalytic process increase. Hence, this result confirmed that hole play important role in the degradation of MB.

4. Conclusion
Photosonocatalytic activity of LaFeO3/TiO2 nanocomposites for degrading MB was successfully performed under UV or visible light irradiation. The incorporation of TiO2 on LaFeO3/TiO2 nanocomposites showed faster degradation on the photosonocatalytic processes than LaFeO3 nanoparticles both under UV or visible light irradiation. The formed LaFeO3/TiO2 nanocomposites played an important role in inhibiting recombination of electron and hole pairs that further improved the degradation of MB in the photosonocatalytic process.

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