Synthesis, Characterization and Catalytic Properties of Perovskite LaFeO$_3$ Nanoparticles

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Abstract. Orthorhombic structure of rare earth perovskite-type oxide LaFeO$_3$ nanoparticles with light absorption properties in the visible range was prepared by co-precipitation method. The prepared nanoparticles was characterized by several measurements such as X-ray diffraction, energy dispersive X-ray, field emission scanning electron microscope, diffuse reflectance spectroscopy, vibrating sample magnetometer and electron spin resonance spectroscopy. Methylene blue was taken as the model pollutant to evaluate its photocatalytic, sonocatalytic, photosonocatalytic degradation in the presence of LaFeO$_3$ nanoparticles. The degradation of methylene blue followed the pseudo-first order model in all three processes. The observed rate constants indicate that the photosonocatalytic was faster than the respective individual. Radical scavenger experiments revealed that holes were the predominant oxidative species involved in all three processes.

1. Introduction

With an increase of the industrialization, environmental pollution problem are getting worse. Many contaminants are often discharged from industrial and wastewater treatment plants and contaminate groundwater and surface water. Therefore, it is urgent for the scientist to find solutions to mitigate the damage that is caused by these pollutants. Several studies using catalysts have been employed to decompose harmful organic and inorganic pollutant into harmless chemicals [1-3]. The remarkable progress of photocatalytic has been limited to ultraviolet light although visible light range is far more useful in the solar spectrum. Hence, the development of catalyst that can be activated in the visible region has become important topic research today [4-6].

Perovskite-type materials with the general formula of ABO$_3$ have attracted considerable attention in the field of catalysis [7-8]. It is reported that perovskite oxide exhibits high photocatalytic activity towards degradation of organic contaminant under visible light irradiation and stable in various environment [9]. Therefore, perovskite oxide with appropriate crystal structure, morphology and optical properties for improvement of photocatalytic efficiency is paid much attention by researchers [6-7].

Recently, it was also reported that ultrasonic bath is used for the degradation of organic contaminants. It is known that during the ultrasonic irradiation sonoluminescence, cavitational and hot spot were occurred, leads to the dissociation of water molecules and generated active radicals. These
active radicals have a higher reaction activity could completely decompose pollutant molecule structures in wastewaters [10]. Hence, based on the above reason, LaFeO$_3$ nanoparticles as a typical ABO$_3$-type perovskite structure were employed as catalysts under visible light and ultrasonic irradiation separately and simultaneously to degrade methylene blue as a model of organic contaminant. The combination of the ultrasonic with the visible light assisted photocatalytic technique is expected to enhance the catalytic performance and to reduce the operating cost needed for degradation of organic contaminants [10-12]. LaFeO$_3$ nanoparticles were synthesized by co-precipitation methods. The structural and morphological properties of synthesized LaFeO$_3$ nanoparticles were characterized by X-ray diffraction, energy dispersive X-ray spectroscopy, field emission scanning electron microscope, energy band gap was determined from diffuse reflectance spectroscopy, while magnetic properties were measured using vibrating sample magnetometer and electron spin resonance spectroscopy. The influence of several experimental parameters on the catalytic efficiency was evaluated. In order to understand the main active oxidative species responsible for the degradation of methylene blue the control experiment with added different types of scavenger were conducted.

Hence, perovskite LaFeO$_3$ nanoparticles can result in a promising catalyst for the removal the organic pollutants under the combination of both irradiations.

2. Experimental details

Chemicals: All chemicals were analytical grade and were used without further purification. For co-precipitation synthesis the following reagents were used LaCl$_3$.7H$_2$O (Merck), FeCl$_2$.4H$_2$O (Merck), and NaOH (Merck).

Preparation of LaFeO$_3$ nanoparticles: In a typical procedure, 0.2 mol L$^{-1}$ LaCl$_3$.7H$_2$O and 0.2 mol L$^{-1}$ FeCl$_2$.4H$_2$O were dissolved in 300 ml distilled water to form solution. The solution was sonicated using an ultrasonic cleaner operating at 57 kHz for 1 h and then stirred continuously for 0.5 h at 60 °C. Then, appropriate amounts of NaOH solution with 1.0 mol L$^{-1}$ concentration was added drop wise into the above solution under vigorous stirring at 80 °C for 2 h until the pH value of 13 was reached. The mixtures were allowed to stand at room temperature for 4 h and a large amount of precipitate was formed immediately. The precipitate was centrifuged and washed with distilled water and ethanol several times, then dried at 120°C overnight. Finally, LaFeO$_3$ nanoparticles was obtained after calcinated at 800°C for 2 h under vacuum condition.

Characterization: The crystal structure of LaFeO$_3$ nanoparticles was determined using X-ray diffraction (XRD) measurements using a monochromatic Cu-K$\alpha$ (λ = 1.54060 Å) radiation operated at 30 kV and 20 mA in the range of 10$^\circ$ to 80$^\circ$. The X-ray diffraction patterns were analyzed using the MAUD program and Rietveld whole profile fitting to determine the crystal structure and lattice parameters. Elemental analyses and the morphology of the samples were determined using energy dispersive X-ray (EDX) spectroscopy, and field emission scanning electron microscopy (FESEM). The optical characteristic was determined using UV-Vis diffuse reflectance spectrophotometer with an integrating sphere and a spectral reflectance standard over a wavelength range of 200 to 800 nm. Magnetic measurements were performed on vibrating sample magnetometer (VSM). Electron spin resonance (ESR) was performed at room temperature and an X-band spectrometer equipped with a 9.1 GHz field modulation unit.

Catalytic activity: The catalytic activity of LaFeO$_3$ nanoparticles was evaluated by measuring the degradation of methylene blue at room temperature under visible light (photocatalytic) and ultrasonic irradiation (sonocatalytic) separately and the combination between visible light and ultrasonic irradiation (photosonocatalytic) simultaneously. Photocatalytic study was conducted in a cylindrical glass vessel equipped with a magnetic stirrer under a 40 W Xe lamp light positioned horizontally 30 cm above the colloid surface. Sonocatalytic experiments were carried out using a commercially ultrasonic bath operated at fixed frequency and power of 40 kHz and 150 W, respectively. Prior to irradiation, the suspensions were sonicated in the dark for 30 min to obtain a colloidal suspension.
Under ambient conditions and with stirring, the solution in the glass vessel was exposed to light or/and ultrasonic wave. Subsequently, the solution was irradiated for 2 h at regular intervals. The solution was analyzed using UV-visible spectrophotometer. The percentage degradation of organic pollutants 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 is reached. In order to study the active species involved in catalytic degradation of organic pollutant, different substances such as ammonium oxalate, sodium sulfate, and tert-butyl alcohol, recognized as scavengers for holes, electrons and hydroxyl radical species, respectively were used.

3. Results and Discussion

Fig. 1a shows the XRD pattern of LaFeO$_3$ nanoparticles. The XRD peaks are well defined and it indicates that synthesized nanoparticles are well crystallized. The XRD reflections appeared are well indexed by an orthorhombic unit cell of LaFeO$_3$ without any impurity phases. The lattice parameters estimated from XRD pattern using the Rietveld refinement as well as crystallized size using the Scherrer’s formula [13] are tabulated in Table.1. The values of the lattice parameters and the crystallite sizes are in good agreement with that of orthorhombic LaFeO$_3$ published elsewhere [13-15]. In the inset of Fig. 1a shows the field emission scanning electron images of the synthesized LaFeO$_3$ nanoparticles. It is seen that the synthesized samples consist of agglomerated particles. The individual particles appear to be spherical. In Fig. 1b, the EDX spectra were plotted. The EDX analysis was employed to determine the element of the synthesized materials. As shown in the Fig.1b, the elements present are La, Fe and O with a mole ratio of 1:1:3 corresponding to the stoichiometric composition of LaFeO$_3$.

The magnetic properties of LaFeO$_3$ nanoparticles are investigated, as shown in Fig.2a. The nanoparticles show ferromagnetic behavior, with clear hysteresis loops. The saturation magnetization, remnant magnetization and coercive field are tabulated in Table. 2. This result is of great interest since bulk LaFeO$_3$ has antiferromagnetic behavior [16-17]. Compared with other nanoparticles, magnetization obtained in this study has a higher value with that from other synthesis methods [14, 18-22]. It is reported that the origin of ferromagnetism in LaFeO$_3$ nanoparticles could be due to several reason. The first possibility is due to the uncompensated canted spins from the surface as well as from internal canted spins of Fe$^{3+}$ as the source of magnetic moment [14]. The uncompensated surface spins can be generated due to the increase of surface area or the decrease of crystallite size [14]. This behavior has also been observed in other perovskites nanoparticles such as BiFeO$_3$ [23-24] and YFeO$_3$ [25]. Another possibility is due to clustering such as Fe, FeO and Fe$_2$O$_3$, since those have ferromagnetic materials. Finally, ferromagnetic behavior may be originated from double exchange interaction [14]. From our XRD result, it is seen that a secondary phase does not observed in our sample. Therefore, ferromagnetic origin from clustering can be excluded in our sample. In order to study the oxidation state Fe in our sample, ESR measurement was performed. The ESR spectrum of LaFeO$_3$ (Fig. 2b) showed a broad unsymmetry signal. We have carefully studied the signal and found that the spectra considered as a superposition of three overlapping signals, a line at a g value of 2.9978 attributed to La$^{3+}$ ions and another line at g value of 2.2288 and 2.0044 assigned to Fe$^{2+}$ and Fe$^{3+}$ ions. From the XRD and ESR measurements, it is suggested that the origin of ferromagnetism in our LaFeO$_3$ nanoparticles might be due to uncompensated canted spins or double exchange interaction. However, further study needs to clarify this effect quantitatively.

It is known that diffuse reflectance spectroscopy can give information about the electronic interaction near the optical band gap region. The band gap energy of LaFeO$_3$ nanoparticles was calculated from diffuse reflectance spectra by performing a Kubelka-Munk analysis using the following equation: $F(R) = (1-R)^2/2R$ [26], with R as the diffuse reflectance. According to this function the band gap energy can be obtained by plotting the $F(R)^2$ vs. the energy in electron volts.
Fig. 1. (a) XRD pattern of LaFeO$_3$ nanoparticles; and (b) EDX spectra of LaFeO$_3$ nanoparticles.

| Sample  | Lattice Parameter | Volume (Å$^3$) | <D> (nm) |
|---------|------------------|---------------|--------|
| LaFeO$_3$ | a (Å) = 5.5436 | b (Å) = 7.8456 | c (Å) = 5.5528 | 241.5072 | 58 |

Fig. 2. (a) VSM and (b) ESR spectra of LaFeO$_3$ nanoparticles.

| Sample  | M-S (emu/g) | Magnetic Remanent (emu/g) | Coercivity (Tesla) | Band Gap (eV) |
|---------|-------------|---------------------------|-------------------|---------------|
| LaFeO$_3$ | 12          | 2.12                      | 0.19              | 2.45          |
The linear part of the curve was extrapolated to \( F(R)^2 = 0 \) to calculate the direct band gap energy. The result is tabulated in Table 2. This value is closed to the value reported in the literature [26-28].

The influence of LaFeO\(_3\) nanoparticles on the degradation of methylene blue is illustrated in Fig. 3. It can be seen that methylene blue degradation in the presence of both nanoparticles increased with increasing irradiation time. As clearly seen, the degradation of methylene blue occurs appreciably faster under simultaneously irradiation of visible light and ultrasonic than under separately irradiation in a similar experiment condition. The maximum degradation of 100% is obtained for the...
simultaneously irradiation of visible light and ultrasonic within 2 h. The photo-, sono- and photosono-
catalytic degradation of methylene blue by LaFeO$_3$ nanoparticles obeyed pseudo-first order kinetics
with respect to the concentration of methylene blue: 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. The apparent reaction
constant for different catalyst was studied and the results are displayed in the inset of Fig. 3. The
methylene blue degradation under combination of visible light and ultrasonic irradiation exhibits faster
degradation rate compared to visible light or ultrasonic irradiation alone. In order to detect the main
active oxidative species responsible in the catalytic activity, control experiments with added different
type of scavengers for hydroxyl radicals, holes and electrons were conducted with light or/and
ultrasonic irradiation. The degradation of methylene blue in the presence of tert-butyl alcohol,
ammonium oxalate and Na$_2$S$_2$O$_8$ scavenger for hydroxyl radicals, holes and electrons, respectively, is
displayed in Fig. 4. It can be seen that the presence of ammonium oxalate scavenger for holes inhibits
the removal of methylene blue, which confirmed the indispensable role of holes in the degradation
process of methylene blue.

The method of visible light and ultrasonic irradiation combined with catalytic activity can generate
reactive oxygen species to degrade organic pollutant. It is known that sonocatalytic process is based on
the ultrasonic cavitation effect that can result in sonoluminescence (wide range of wavelength) and hot
spot. It is reported that hot spots can cause H$_2$O molecules to pyrolyze to form •OH radicals.
Moreover, sonoluminescence involves intense UV light, which makes LaFeO$_3$ nanoparticles behave
like photocatalyst during sonication. Therefore, in sonocatalytic activity ultrasonic irradiation not only
induces sonolysis but also generate electron and hole pairs in the catalyst. The photo-generated
electrons in the conduction band migrate to the surface where they are scavenged by molecular oxygen
O$_2$ to yield •O$_2^-$ superoxide radical. Meanwhile holes can react with hydroxyl groups (OH$^-$), and •OH
radicals are then formed. Under simultaneous excitation of ultrasonic and visible light, the catalytic
activities of LaFeO$_3$ nanoparticles were enhanced, due to the high efficiency charge separation. Since
the band gap of LaFeO$_3$ nanoparticles is in the visible range, electron in the conduction band and hole
in the valence band can be easily generated by visible light. However, not all photo-generated
electrons stay in the conduction band; some of the electrons will be transferred to electron-trapping
states, which effectively separate the electrons and holes and suppress the probability of electron–hole
recombination. From the ESR spectra, it is seen that there is a paramagnetic centers of La$^{3+}$, Fe$^{2+}$ and
Fe$^{3+}$. In this process, the electron collected in the paramagnetic centers can later react with the
absorbed molecular oxygen to yield O$_2$. Simultaneously, the photogenerated holes in the valence band
can then react with the hydroxyl group (OH$^-$) to form a hydroxyl radical, •OH. Thus, it is concluded
that holes play the most important role in the degradation of MB, which is in agreement with the
results of control experiments with added scavenger, as shown in Fig.4.

4. Conclusion

In conclusion, this study has shown that methylene blue as a model of organic pollutant can be
effectively degraded in the presence of LaFeO$_3$ nanoparticles by using visible light and ultrasonic
irradiation simultaneously (photosonocatalytic). The structural characterization of LaFeO$_3$
nanoparticles showed that the structure has an orthorhombic single phase structure with crystallite size
of 58 nm and the band edge of 2.45 eV. Study of magnetic property using vibrating sample
magnetometer showed that LaFeO$_3$ nanoparticles has ferromagnetic behavior with magnetization of 12
emu/gr at 0.19 Tesla. Based on XRD and ESR measurements we believed that the origin of
ferromagnetism in our LaFeO$_3$ nanoparticles is due to the uncompensated canted spin on the surface.

References

[1] R. Andreozzi, V. Caprio, A. Insola and R. Marotta, Advanced oxidation processes (AOP) for
water purification and recovery, Catalysis Today, vol. 53, pp. 51-59, 1999. Muhammad iqbal
farabi

[2] K. Pirkanniemi and M. Sillanpaa, Heterogeneous water phase catalysis as an environmental
application: a review, *Chemosphere*, vol. 48, p. 1047–1060, 2002.

[3] A. Srinivasan and T. Viraraghavan, Decolorization of dye wastewaters by biosorbents: A review, *Journal of Environmental Management*, vol. 91, pp. 1915-1929, 2010.

[4] P. Tang, Y. Tong, H. Chen, F. Cao and G. Pan, Microwave-assisted synthesis of nanoparticulate perovskite LaFeO$_3$ as a high active visible-light photocatalyst, *Current Applied Physics*, vol. 13, pp. 340-343, 2013.

[5] Q. Peng , B. Shan, Y. Wen and R. Chen, Enhanced charge transport of LaFeO$_3$ via transition metal (Mn, Co, Cu) doping for visible light photoelectrochemical water oxidation, *International Journal of Hydrogen Energy*, vol. 40, pp. 15423-15431, 2015.

[6] R. Abazari, S. Sanati and L. A. Saghatforoush, A unique and facile preparation of lanthanum ferrite nanoparticles in emulsion nano reactors: Morphology, structure, and efficient photocatalysis, *Materials Science in Semiconductor Processing*, vol. 25, p. 301–306, 2014.

[7] F. Li, Y. Liu, R. Liu, Z. Sun, D. Zhao and C. Kou, Preparation of Ca-doped LaFeO$_3$ nanopowders in a reverse microemulsion and their visible light photocatalytic activity, *Materials Letters*, vol. 64, p. 223–225, 2010.

[8] M. Yang, A. Xu, H. Du, C. Sun and C. Li, Removal of salicylic acid on perovskite-type oxide LaFeO$_3$ catalyst in catalytic wet air oxidation process, *Journal of Hazardous Materials*, vol. B139, p. 86–92, 2007.

[9] S. Thirumalairajan, K. Girija and I. Ganesh, Controlled synthesis of perovskite LaFeO$_3$ microsphere composed of nanoparticles via self-assembly process and their associated photocatalytic activity, *Chemical Engineering Journal*, vol. 209, p. 420–428, 2012.

[10] P. Sathishkumar, R. V. Mangalaraja and S. Anandan, Review on the recent improvements in sonochemical and combined sonochemical oxidation processes – A powerful tool for destruction of environmental contaminants, *Renewable and Sustainable Energy Reviews*, vol. 55, p. 426–454, 2016.

[11] M. Martín de Vidales, S. Barba , C. Sáez, P. Cañizares and M. Rodrigo, Coupling ultraviolet light and ultrasound irradiation with Conductive-Diamond Electrochemical Oxidation for the removal of progesterone, *Electrochim Acta*, vol. 140, pp. 20-26, 2014.

[12] K. Jyothi, S. Yesodharan and E. Yesodharan, Ultrasound (US), ultraviolet light (UV) and combination (US + UV) assisted semiconductor catalysed degradation of organic pollutants in water: oscillation in the concentration of hydrogen peroxide formed in situ, *Ultrason Sonochem*, vol. 21, pp. 1787-1796, 2014.

[13] R. Abazari and S. Sanati, Perovskite LaFeO$_3$ nanoparticles synthesized by the reverse microemulsion nanoreactors in the presence of aerosol-OT: Morphology, crystal structure, and their optical properties," *Superlattices and Microstructures*, vol. 68, p. 148–157, 2013.

[14] S. Phokha, S. Pinitsontorn, S. Maensiri and S. Rujirawat, Structure, optical and magnetic properties of LaFeO$_3$ nanoparticles prepared by polymerized complex method," *Journal of Sol-Gel Science and Technology*, vol. 71, pp. 333-341, 2014.

[15] M. Milanova, J. Zaharieva, R. Todorovska and D. Todorovsky, Polymetallic citric complexes as precursors for spray-pyrolysis deposition of thin LaFeO$_3$ films, *Thin Solid Films*, vol. 562, p. 43–48, 2014.

[16] W. Lee, H. J. Yun and J. Yoon, Characterization and magnetic properties of LaFeO$_3$ nanofibers synthesized by electrospinning, *Journal of Alloys and Compounds*, vol. 583, p. 320–324, 2014.

[17] D. Treves, Studies on Orthoferrites at the Weizmann Institute of Science, *Journal of Applied Physics*, vol. 36, p. 1033, 1965.

[18] Z. Kaiwen, W. Xuehang, W. Wenwei , X. Jun, T. Siqi and L. Sen, Nanocrystalline LaFeO$_3$ preparation and thermal process of precursor, *Advanced Powder Technology*, vol. 24, p. 359–363, 2013.

[19] A. Cristo´ bal , P. Botta, P. Bercoff and J. P. Lo´ pez, Mechanosynthes is and magnetic properties of nanocrystalline LaFeO$_3$ using different iron oxides, *Materials Research..."
[20] J. Huang, P. Su, W. Wu, Y. Li, X. Wu and L. Tao, Preparation of nanocrystalline BiFeO$_3$ and kinetics of thermal process of precursor, *Journal of Thermal Analysis and Calorimetry*, vol. 111, p. 1057–1065, 2013.

[21] X. Qi, J. Zhou, Z. Yue, Z. Gui and L. Li, Auto-combustion synthesis of nanocrystalline LaFeO$_3$, *Materials Chemistry and Physics*, vol. 78, pp. 25-29, 2002.

[22] D. Jia, J. Xu, H. Ke, W. Wang and Y. Zhou, Structure and multiferroic properties of BiFeO$_3$ powders, *Journal of the European Ceramic Society*, vol. 29, p. 3099–3103, 2009.

[23] R. Mazumder, S. Ghosh, P. Mondal, D. Bhattacharya, S. Dasgupta, N. Das, A. Sen, A. Tyagi, M. Sivakumar, T. Takami and H. Ikuta, Particle size dependence of magnetization and phase transition near TN in multiferroic BiFeO$_3$, *Journal of Applied Physics*, vol. 100, p. 033908, 2006.

[24] F. Gao, Y. Yuan, K. Wang, X. Chen, F. Chen, J. Liu and Z. Ren, Preparation and photoabsobtion characterization of BiFeO$_3$ nanowires, *Applied Physics Letter*, vol. 89, p. 102506, 2006.

[25] R. Maiti, S. Basu and D. Chakravorty, Synthesis of nanocrystalline YFeO$_3$ and its magnetic properties, *Journal of Magnetism and Magnetic Materials*, vol. 321, pp. 3274-3277, 2009.

[26] R. Köferstein, L. Jäger and S. G. Ebbinghaus, Magnetic and optical investigations on LaFeO$_3$ powders with different particle sizes and corresponding ceramics, *Solid State Ionics*, vol. 249–250, p. 1–5, 2013.

[27] J. Li, X. Pan, Y. Xu, L. Jia, X. Yi and W. Fang, Synergetic effect of copper species as cocatalyst on LaFeO$_3$ for enhanced visible-light photocatalytic hydrogen evolution, *International Journal of Hydrogen Energy*, vol. 40, p. 13918–13925, 2015.

[28] K. Parida, K. Reddy, S. Martha, D. Das and N. Biswal, Fabrication of nanocrystalline LaFeO$_3$: An efficient sol-gel auto-combustion assisted visible light responsive photocatalyst for water decomposition, *International Journal of Hydrogen Energy*, vol. 35, pp. 12161-12168, 2010.