Enhanced Fenton-like degradation of refractory organic compounds by surface complex formation of LaFeO₃ and H₂O₂

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Abstract

Nanoscale LaFeO₃ was prepared via sol–gel method and characterized by XRD, FTIR and N₂ adsorption/desorption experiment. The results indicated that, LaFeO₃ had a typical perovskite structure with a BET area of 8.5 m²/g. LaFeO₃ exhibited excellent Fenton activity and stability for the degradation of pharmaceuticals and herbicides in water, as demonstrated with sulfamethoxazole, phenazone, phenytoin, acyclovir and 2,4-dichlorophenoxyacetic acid, 2-chlorophenol. Among them, sulfamethoxazole (SMX) could be completely removed in LaFeO₃–H₂O₂ system after reaction for 120 min at neutral pH. Based on the ATR–FTIR analysis, the surface complex of LaFeO₃ and H₂O₂ was formed, which was important and essential for the enhanced Fenton reaction by accelerating the cycle of Fe³⁺/Fe²⁺. Hence, more •OH and •O₂⁻/HO₂⁻ were then produced in LaFeO₃–H₂O₂ system, resulting in more efficient removal of refractory organic compounds. Based on the surface interaction of LaFeO₃ and H₂O₂, a heterogeneous Fenton reaction mechanism was proposed.

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1. Introduction

The increasing worldwide contamination of surface and ground waters caused by pharmaceuticals and pesticides is a...
2. Experimental

2.1. Chemicals and materials

Citric acid, La(NO$_3$)$_3$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O and H$_2$O$_2$ (30%, w/w) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of LaFeO$_3$ perovskite

LaFeO$_3$ perovskite was prepared via a previously reported sol–gel method [18]. In a typical procedure, 1.3 g La(NO$_3$)$_3$·6H$_2$O and 1.6 g Fe(NO$_3$)$_3$·9H$_2$O were dissolved in 20 mL solvent (ethanol: deionized water = 3:1) in order to control the hydrolysis process. Citric acid was added into the nitrate precursors as the chelating agent and the molar ratio of the citric acid and metal ions was 1:1. After stirring for 17 h, the solution was heated at 100 °C in open air under stirring constantly to achieve a viscous mixture, which was dried at 100 °C overnight and well ground. Finally, the obtained solids were calcined in a muffle furnace at 270 °C for 2 h firstly and then at 700 °C for 6 h, respectively.

2.3. Characterization

The powder X-ray diffraction pattern (XRD) of LaFeO$_3$ was recorded on a Scintag-XDS–2000 diffractometer with Cu Kα radiation (λ = 1.54059 Å). The generator voltage and tube current used were 40 kV and 40 mA, respectively. The 2θ ranged from 10° to 80°. The crystalline size was estimated via the Scherrer equation. The infrared spectrum was recorded on a Fourier transform infrared (FTIR) spectrophotometer (TENSOR 27). N$_2$ adsorption/desorption experiment of LaFeO$_3$ was carried out using a Micromeritics ASAP2020 analyzer (Micromeritics, Norcross, GA). H$_2$O$_2$ concentration was determined by using the spectrophotometrically titrated TiCl$_4$ method for [H$_2$O$_2$] ≤ 10$^{-3}$ mol/L [19]. Reactive oxygen species were detected with electron spin resonance (ESR) spectroscopy using BMPO as a spin trap agent. The ESR spectra were obtained using a Bruker A300-10/12 electron paramagnetic resonance spectrometer (center field: 3514.00 G; microwave frequency: 9.85 GHz; and power: 5.05 mW).

2.4. Procedures and analysis

The heterogeneous Fenton-like reaction was carried out under ambient conditions (at 30 °C without the aids of ultrasonic and/or UV light irradiation). In a typical experiment, 70 mg LaFeO$_3$ powders were dispersed in 50 mL SMX solution (3 mg/L, pH 6.48). Prior to the addition of H$_2$O$_2$, the suspension was magnetically stirred for about 15 min to establish the adsorption/desorption equilibrium. Then, 23 mmol/L H$_2$O$_2$ was added to the above suspension under continuous magnetic stirring. At given time intervals, 2 mL samples were withdrawn and filtered through a Millipore filter (pore size 0.45 μm) to remove LaFeO$_3$ for analysis. The concentration of each organic compound was analyzed using high-performance liquid chromatography (1200 series; Agilent, Santa Clara, CA) with an Eclipse XDB-C18 column (5 μm, 4.6 mm × 150 mm; Agilent). All of the experiments were repeated three times.

The LaFeO$_3$ film used for in-situ flow-cell ATR–FTIR measurement was prepared as the following procedure: 1 mL of diluted LaFeO$_3$ dispersion (0.1 g LaFeO$_3$ was dispersed in 10 mL ethanol) was spreaded on the ATR crystal surface and allowed to dry in an oven for 3 h. The deposited film was then rinsed gently with water and dried again for the uniform dispersity of LaFeO$_3$ on ATR crystal. The ATR–FTIR spectra were recorded using the Nicolet 8700 FTIR spectrometer equipped with a DTGS detector and
ATR accessory. Infrared spectra in the range of 4000–400 cm\(^{-1}\) were obtained by averaging 128 scans with a resolution of 4 cm\(^{-1}\) under ambient temperature in dark. After the equilibration of LaFeO\(_3\) with NaCl at a flow rate of 3.0 mL/min, a certain amount of H\(_2\)O\(_2\) stock solution was added to start the Fenton reaction. While the oxidation experiments were subsequently performed by adding H\(_2\)O\(_2\) and SMX simultaneously. Samples for GC–MS analysis were prepared by the following procedure. The suspension after 30 and 120 min reaction time was filtered to remove LaFeO\(_3\) particles. The solution was evaporated by adding H\(_2\)O\(_2\) and SMX simultaneously. While the oxidation experiments were subsequently performed at 353 K, ramped at 3.5 K/min–553 K.

3. Results and discussion

3.1. Characterization of LaFeO\(_3\)

As shown in Fig. 1, the XRD pattern of LaFeO\(_3\) showed a highly crystalline and single-phase orthorhombic structure (JCPDS 15-0148) and the main crystallite size was estimated using the XRD data evaluated with the Scherrer equation at 40 nm. The strong adsorption at 558 cm\(^{-1}\) was observed in the FTIR spectrum (inset of Fig. 1), indicating the Fe–O stretching of FeO\(_6\) groups in LaFeO\(_3\). Moreover, LaFeO\(_3\) showed isotherm of type V according to IUPAC classification with a BET area of 8.5 m\(^2\)/g (JCPDS 15-0148), which was totally different from the reported one (60–70 nm, 5.2 m\(^2\)/g, JCDPS 0148) and the main crystallite size was estimated using the XRD data evaluated with the Scherrer equation at 40 nm. The strong adsorption at 558 cm\(^{-1}\) was observed in the FTIR spectrum (inset of Fig. 1), indicating the Fe–O stretching of FeO\(_6\) groups in LaFeO\(_3\). Moreover, LaFeO\(_3\) showed isotherm of type V according to IUPAC classification with a BET area of 8.5 m\(^2\)/g (JCPDS 15-0148), which was totally different from the reported one (60–70 nm, 5.2 m\(^2\)/g, JCPDS 74-2494). Hence, LaFeO\(_3\) with the smaller particle size, larger BET area and different crystalline structure in our study should have a promising performance in Fenton-like degradation of refractory organic compounds.

3.2. Heterogeneous Fenton catalytic activity of LaFeO\(_3\)

The effects of concentrations of LaFeO\(_3\), organic pollutant (SMX) and H\(_2\)O\(_2\) on the catalytic activity of LaFeO\(_3\) were firstly investigated (Figs. S1 and S2). It was found that the SMX removal efficiency increased with the increase of catalyst load and then reached a steady value when the LaFeO\(_3\) concentration was above 1.4 g/L. While the reaction rate decreased with the increase of initial SMX concentration and increased with the increase of initial H\(_2\)O\(_2\) concentration. Moreover, the H\(_2\)O\(_2\) addition mode had almost no influence on the activity of LaFeO\(_3\) and the SMX removal efficiency was even inhibited to some extent when the same amount of H\(_2\)O\(_2\) was added by three times. Therefore, the catalyst load and initial SMX and H\(_2\)O\(_2\) concentration were selected at 1.4 g/L, 3.0 mg/L and 23 mmol/L, respectively.

As shown in Fig. 3, 46.3% of SMX was depleted only by H\(_2\)O\(_2\), but the complete degradation could be obtained in the presence of LaFeO\(_3\) and H\(_2\)O\(_2\) simultaneously. Besides, compared with H\(_2\)O\(_2\) alone in Fig. 4, LaFeO\(_3\) also exhibited much higher catalytic activity for the Fenton-like degradation of other typical pharmaceuticals (ACV, PhZ and PhT) and herbicides (2,4-D and CPh). Moreover, the reaction process above followed a pseudo first order reaction in kinetics and the reaction rate constants for SMX, ACV, PhZ, PhT, 2,4-D and CPh in LaFeO\(_3\)–H\(_2\)O\(_2\) system were 0.029, 0.006, 0.008, 0.016, 0.011 and 0.014 min\(^{-1}\), respectively. There was also almost no adsorption of the investigated organic pollutants on LaFeO\(_3\) except CPh (10%). Thus, the enhanced removal of organic pollutants was attributed to the heterogeneous Fenton-like process and the degradation process was mainly occurred in the solution.

SMX was then selected as the representative to investigate its degradation process in different reaction system. The intermediates were monitored by GC–MS analysis (all the identified compounds were unequivocally identified using the NIST98 library database and the degradation was only occurred in the presence of LaFeO\(_3\)–H\(_2\)O\(_2\) system. The main intermediates were identified by comparing with the reference samples.

Fig. 1. XRD pattern and FTIR spectrum (inset) of LaFeO\(_3\).
with fit values higher than 90%). As shown in Tables S1–S4, either in \( \text{H}_2\text{O}_2 \) alone or in LaFeO\(_3–\text{H}_2\text{O}_2 \) system, almost the same products were detected at different reaction time (30 and 120 min) such as phenol, benzoic acid and dihydroxylamine except that formic acid was further generated in LaFeO\(_3–\text{H}_2\text{O}_2 \) system at 120 min.

While the TOC removal of SMX in \( \text{H}_2\text{O}_2 \) alone and LaFeO\(_3–\text{H}_2\text{O}_2 \) system was zero and 22%, respectively. The results indicated that most of the co-existing anions have little effect on the reaction system. While the significant retardation caused by PO\(_4^{3–}\) and CO\(_3^{2–}\) may be due to their quencher for \( *\text{OH} \) radicals [22,23].

### 3.3. Reaction mechanism discussion

To ascertain the reaction mechanism, the involved reaction oxygen species (ROS) in LaFeO\(_3–\text{H}_2\text{O}_2 \) system were monitored by using DMPO spin-trap ESR. As shown in Fig. 8a, the both measured ESR spectra exhibited a 4-fold characteristic peaks of the typical DMPO–*OH adduct with an intensity ratio of 1:2:2:1, and the intensity in the LaFeO\(_3–\text{H}_2\text{O}_2 \) system was much higher than that of \( \text{H}_2\text{O}_2 \) alone, which indicated that more \( *\text{OH} \) radicals were generated in Table S5. Obviously, there were no leaching Fe and La ions at the tested pH except 0.292 mg/L of La ion at pH 5.5. The above results indicated that LaFeO\(_3 \) had an excellent long-term stability.

Fig. 7 exhibited the investigation of the effects of co-existing anions on LaFeO\(_3 \) performance. The addition of anions had a negative influence on the efficiency of the heterogeneous Fenton system and followed the order PO\(_4^{3–}\) > CO\(_3^{2–}\) > Cl\(^–\) > SO\(_4^{2–}\) > C\(_2\)O\(_4^{2–}\) > NO\(_3^{–}\). The corresponding pseudo first order reaction rate constants also decreased with the above order: 0.017/0.002 < 0.022–0.023 < 0.026 < 0.027 < 0.029 min\(^{-1}\) (without anion). The results indicated that most of the co-existing anions have little effect on the reaction system. While the significant retardation caused by PO\(_4^{3–}\) and CO\(_3^{2–}\) may be due to their quencher for \( *\text{OH} \) radicals [22,23].
the former system. Besides that, the formation of HO$_2^+$/O$_2^•$ radical was also detected and the results were shown in Fig. 8B. Obviously, no significant signals attributed to ROS were found only in the presence of H$_2$O$_2$, while the characteristic peaks of the typical DMPO–HO$_2^+$/O$_2^•$ adducts were observed in LaFeO$_3$ suspension with H$_2$O$_2$ [24]. The results indicated that H$_2$O$_2$ was decomposed into •OH and HO$_2^+$/O$_2^•$ and the both radicals were the reactive oxygen species involved in the heterogeneous Fenton reaction process.

The interaction of LaFeO$_3$, H$_2$O$_2$ and SMX was further examined with ATR–FTIR. As shown in Fig. 9A, the peak of 1637 cm$^{-1}$, characterized as O–H bending vibration ($\delta$(OH)) and stretching vibration ($\nu$(OH)), indicating the presence of hydroxyl groups on the surface of LaFeO$_3$ [25]. After the addition of H$_2$O$_2$, $\delta$(OH) was slightly widened, suggesting that H$_2$O$_2$ could be adsorbed on LaFeO$_3$ surface via either directly bound to the surface Fe or by hydrogen bonding to form the surface complex [26,27].

Moreover, the new peaks centered at 1400 cm$^{-1}$, 1195 cm$^{-1}$ and 1080 cm$^{-1}$ were observed and the intensity also increased with reaction time, which could be attributed to the $\nu$(O–O) frequency of superoxide [28]. While no single was detected for the O–O stretching frequency of free H$_2$O$_2$ at 880 cm$^{-1}$ [29]. These features indicated that H$_2$O$_2$ preferred to form surface complex with LaFeO$_3$ instead of direct adsorption on the catalyst. Furthermore, the FTIR spectra of LaFeO$_3$ (the $\nu$(O–O) peak intensity) did not change with the reaction time during the heterogeneous Fenton degradation of SMX (Fig. 9B), which implied that the formation of LaFeO$_3$–H$_2$O$_2$ complex was essential and stable for the Fenton reaction process.

Fig. S3 further depicted H$_2$O$_2$ decomposition over LaFeO$_3$ in presence of SMX. Obviously, only 12.4 mmol/L of H$_2$O$_2$ was consumed at the reaction time 120 min and 10.6 mmol/L of H$_2$O$_2$ was still remained in the reaction system due to the initial H$_2$O$_2$ concentration 23 mmol/L. It also indicated the formation of LaFeO$_3$–H$_2$O$_2$ complex during the reaction process. Based on the experimental results and a review of the literature [30–32], a heterogeneous Fenton catalytic mechanism of LaFeO$_3$ was proposed as follows:

$$\begin{align*}
2\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \equiv\text{Fe}^{3+} \cdots \text{O} - \text{O} - \equiv\text{Fe}^{3+} \equiv + 2\text{H}^+ \\
\text{Fe}^3\cdots\text{O} - \equiv\text{Fe}^{3+} & \equiv + \text{H}_2\text{O}_2 \rightarrow \equiv\text{Fe}^{2+} \cdots \text{O} - \equiv\text{Fe}^{2+} + \text{H}^+ \\
\equiv + \equiv\text{HO}_2^+ + 2\text{H}^+ & \equiv\text{HO}_2^+ \rightarrow \text{O}_2^• + \text{H}^+ \\
\equiv\text{Fe}^{2+} \cdots \text{O} - \equiv\text{Fe}^{2+} & \equiv + \text{H}_2\text{O}_2 \rightarrow \equiv\text{Fe}^{3+} \cdots \text{O} - \equiv\text{Fe}^{3+} + 2\text{H}^+ \\
\equiv + 2\text{HO}^+ + \equiv\text{HO}_2^+ & \equiv\text{Fe}^{3+} \cdots \equiv\text{Fe}^{3+} \equiv \equiv\text{O}_2^• \rightarrow \equiv\text{Fe}^{2+} \cdots \equiv\text{O}_2^• \equiv \equiv\text{Fe}^{2+} \equiv\text{O}_2^•
\end{align*}$$

SMX + •OH/•HO$_2^•$ → Intermediates → CO$_2$ + H$_2$O

Firstly, H$_2$O$_2$ was chemisorbed on the surface of LaFeO$_3$ and the LaFeO$_3$–H$_2$O$_2$ surface complex was then generated. The chemical environment of iron element in LaFeO$_3$ was changed [33], and the O–O bond in H$_2$O$_2$ was significantly weakened [14] due to the formation of LaFeO$_3$–H$_2$O$_2$ complex. Moreover, the complexed Fe$^{3+}$/Fe$^{2+}$ could decrease the Fe$^{3+}$/Fe$^{2+}$ redox potential significantly [34]. Hence, the Fe$^{3+}$/Fe$^{2+}$ cycle was greatly accelerated and more reactive oxygen species such as •OH and O$_2^•$/HO$_2^•$ were then produced according to the Haber–Weiss mechanism, which was responsible for the efficient degradation of aqueous organic pollutants at neutral pH. Hence, the role of H$_2$O$_2$ in the heterogeneous Fenton reaction process could be divided into three aspects: (1) chemically absorbed on the surface of catalyst and
form LaFeO₃–H₂O₂ complex, (2) to generate *OH and O₂*+/HO₂*/ radicals via radical mechanism, and (3) to enhance the Fe³+/Fe²⁺ cycle and convert into oxygen via the surface oxygen vacancies mechanism [35].

4. Conclusion

Nanoscale LaFeO₃ with a typical perovskite structure was prepared and exhibited excellent Fenton activity and stability for the degradation of typical pharmaceuticals and herbicides in water. The organic pollutants could be almost completely degraded at neutral pH after 120 min of reaction time. *OH and O₂*+/HO₂*/ were the main reactive oxygen species involved in the degradation process. The initial solution pH (5.5–8.05) and co-existing anions had no significant negative influence on the Fenton activity of LaFeO₃ except PO₄³⁻ and CO₃²⁻. The consumed H₂O₂ not only was decomposed into oxygen and *OH and O₂*+/HO₂*/ radicals, but also accelerated the cycle of Fe³+/Fe²⁺ by generating LaFeO₃–H₂O₂ complex. Moreover, the heterogeneous Fenton reaction was performed without the aids of external stimulants, such as ultrasonic and UV light irradiation, which would greatly decrease the operation cost and accelerate its application in practical wastewater treatment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2015.03.065.

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