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Article

Sonocatalytic activity of LuFeO_3 crystallites synthesized via a hydrothermal route

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ABSTRACT

LuFeO_3 crystallites of different sizes and morphologies were synthesized via a hydrothermal route. The sonocatalytic properties of the as-synthesized samples were investigated by degrading various organic dyes, including acid orange 7 (AO7), rhodamine B (RhB), methyl orange (MO), and methylene blue (MB), under ultrasonic irradiation, revealing that they exhibit excellent sonocatalytic activity toward the degradation of these dyes. Particularly, the synthesized bar-like particles with lengths of $\sim 3 \mu\text{m}$ and widths of $\sim 1 \mu\text{m}$ have the highest sonocatalytic activity, and the degradation percentage of AO7 reaches 89% after 30 min of sonocatalysis. The effects of inorganic anions such as Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , and HCO_3^- on the sonocatalysis efficiency were investigated. Hydroxyl radicals ($\cdot\text{OH}$) detected by fluorimetry using terephthalic acid as a probe molecule were found to be produced over the ultrasonic-irradiated LuFeO_3 particles. The addition of ethanol, which acts as a $\cdot\text{OH}$ scavenger, leads to quenching of $\cdot\text{OH}$ radicals and a simultaneous decrease in the dye degradation. This suggests that $\cdot\text{OH}$ is the dominant active species responsible for the dye degradation.

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1. Introduction

Ultrasonic waves propagating in liquid can generate acoustic cavitation, which involves the processes of nucleation, growth, and implosion of cavitation bubbles. The violent implosion of cavitation bubbles results in the production of local high temperatures and pressures (i.e., hot spots) [1], during which the emission of light (i.e., sonoluminescences) is simultaneously brought about [2]. Under these local high-temperature and pressure conditions, water molecules can, to some extent, be thermally dissociated into hydroxyl radicals ($\cdot\text{OH}$) [3]. The $\cdot\text{OH}$ is a powerful oxidant that can attack organic pollutants, such as dyes, to make them decompose [4]. However, the degradation efficiency of dyes is extremely low because of the generation of a limited number of $\cdot\text{OH}$ under bare ultrasonic irradiation. The

dye degradation is expected to be greatly enhanced by adding semiconductor catalyst into the ultrasonic-irradiated dye wastewater. Various semiconductors have been studied as sonocatalysts in recent years, such as TiO_2 and TiO_2 -based composites [5,6], ZnO [7], Ag_3PO_4 [8], AgPO_3 [9], AgBr [10], $\text{MnO}_2/\text{CeO}_2$ [11], and $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ [12]. Semiconductor-based sonocatalysis can be understood in a similar way to semiconductor-based photocatalysis [13]. In a sonocatalytic system, electrons are excited from the valence band (VB) of the semiconductor to its conduction band (CB) by hot spots and/or sonoluminescences, thus creating electron-hole pairs. The sono-excited electrons and holes migrate to the catalyst particle surface and participate in redox reactions to produce active species like $\cdot\text{OH}$ radicals, which are responsible for the degradation of dye molecules. Compared with photocatalytic tech-

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nology, the semiconductor-based sonocatalysis offers an advantage in degrading nontransparent and highly concentrated dye wastewater because an ultrasonic wave has a strong penetrating ability for any water medium [14].

LuFeO₃ is a member of the rare-earth orthoferrite family and has been extensively studied because of its interesting magnetic structure, large dielectric constant, and multiferroic property [15–19]. LuFeO₃ is also an important semiconductor with a bandgap energy of ~2.14 eV [20,21], which makes it a potential sonocatalyst [22]. Generally, the sonocatalytic activity of a semiconductor highly depends upon its crystal size and morphology. Hence, it is important to investigate the sonocatalytic activity of LuFeO₃ with different sizes and morphologies of crystals, and their sonocatalytic mechanism. However, to date there has been little work on the hydrothermal synthesis of LuFeO₃ and their sonocatalytic activity or mechanism. Among various nanomaterial preparation techniques, the hydrothermal route offers an advantage in controlling the product size and morphology.

In this work, we synthesized LuFeO₃ crystallites via a hydrothermal route as described in Ref. [21], where the particle size/morphology was tailored by varying the NaOH concentration. The sonocatalytic activity of prepared samples was evaluated by the degradation of various organic dyes, including acid orange 7 (AO7), rhodamine B (RhB), methyl orange (MO), and methylene blue (MB), under ultrasonic irradiation. The sonocatalytic mechanism involved was systematically investigated and discussed.

2. Experimental

2.1. Catalyst preparation

LuFeO₃ crystallites were synthesized via a hydrothermal route as described elsewhere [21]. All raw materials and reagents were of analytical grade and used without further purification. H₂LuN₃O₁₀ (1 mmol) and Fe(NO₃)₃·9H₂O (1 mmol) were dissolved in 30 mL of distilled water. Then, 50 mL of NaOH solution with different concentrations was added dropwise into the mixture solution under magnetic stirring until all the metal ions were completely precipitated. The solution gradually turned into a dark-brown suspension. To make it mix homogeneously, the suspension was ultrasonically treated for 8 min and subsequently stirred vigorously for 30 min. The final mixture was transferred and sealed in a 100-mL Teflon-lined stainless steel autoclave and submitted to hydrothermal treatment at 200 °C for 24 h. After the reaction was completed, the autoclave was naturally cooled down to room temperature. The precipitates were collected and washed alternately with distilled water and absolute ethanol four times, and then dried in a thermostat drying oven at 80 °C for 10 h to obtain the final LuFeO₃ products. By varying the NaOH concentration to 0.625, 2.5, and 5 mol/L (final concentration in autoclave), three LuFeO₃ samples with different particle sizes and morphologies were prepared, and were termed as S1, S2, and S3, respectively.

2.2. Sample characterization

The phase purity and structure of the as-prepared LuFeO₃ samples were investigated by powder X-ray diffraction (XRD) with Cu K_α radiation ($\lambda = 0.15406$ nm). The size and morphology of the as-prepared LuFeO₃ particles were investigated by field emission scanning electron microscopy (SEM) operated at 5 kV. The ultraviolet-visible (UV-vis) diffuse reflectance spectrum of the samples was measured using a UV-visible spectrophotometer with an integrating sphere attachment.

2.3. Sonocatalytic performance evaluation

The sonocatalytic performance of the LuFeO₃ particles was evaluated by the degradation of organic dyes AO7, RhB, MO, and MB under ultrasonic irradiation. The ultrasonic source was a commercial ultrasonic clearing machine (BK-240), operating at an ultrasonic frequency of 60 kHz and output power of 240 W. The dye was dissolved in distilled water to make a dye solution (5 mg/L). The LuFeO₃ catalyst (0.08 g) was added to 20 mL of the dye solution, which was loaded in a glass beaker with an inner diameter of 32 mm and height of 75 mm. Before each sonocatalytic experiment, the mixture was magnetically stirred for 30 min in the dark to establish absorption-desorption equilibrium of the dye molecules on the catalyst particles, and then submitted to ultrasonic irradiation. During the sonocatalytic process, the ultrasonic bath temperature was maintained at 40 °C by circulating water through it. At a given time interval, 2 mL of the reaction solution was pipetted out and centrifuged at 4000 r/min for 10 min to remove the catalyst. The upper clear solution was then used for examination of the dye concentration, which was determined by measuring the absorbance of the solution at a fixed wavelength ($\lambda_{AO7} = 484$ nm, $\lambda_{RhB} = 554$ nm, $\lambda_{MO} = 464$ nm, and $\lambda_{MB} = 665$ nm) using a UV-vis spectrophotometer. The degradation percentage is defined as $(C_0 - C_t)/C_0 \times 100\%$, where C_0 and C_t are the dye concentrations before and after ultrasonic irradiation for time t , respectively.

The effects of inorganic anions Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻, and HCO₃⁻ on the sonocatalysis efficiency were investigated by separately adding NaCl, NaNO₃, Na₂SO₄, Na₃PO₄, and NaHCO₃ in 5 mmol/L to the reaction solution. Ethanol as a •OH scavenger was also added to the reaction solution to investigate its effect on the sonocatalytic degradation of the dye.

2.4. Hydroxyl radical analysis

Photoluminescence (PL) spectroscopy was used to examine the •OH radicals formed over the ultrasonic-irradiated LuFeO₃ catalyst using terephthalic acid (TPA) as a probe molecule. TPA tends to react with •OH to produce 2-hydroxyterephthalic acid (TAOH), which is a highly fluorescent compound [23]. The PL intensity of TAOH at around 429 nm is in proportion to the amount of produced •OH radicals. Hence, we can obtain information on the •OH radicals by detecting the PL intensity of the reacted solution. TPA was dissolved in NaOH solution (1.0 mmol/L) to make a 0.25 mmol/L TPA solution. The catalyst (0.08 g) was added to 20 mL of the TPA solution. After being magnetically stirred for 30 min in the dark, the mixed solution was ultrasonically irradiated. The reacted solution (2 mL) was

Fig. 1. XRD patterns of LuFeO_3 samples prepared at different NaOH concentrations. (1) S1 (0.625 mol/L); (2) S2 (2.5 mol/L); (3) S3 (5 mol/L).

pipetted out at a given reaction time interval, and then centrifuged at 4000 r/min for 10 min to remove the catalyst. The upper clear solution in the centrifuge tube was used for the PL measurements with a fluorescence spectrophotometer with an excitation wavelength of 315 nm. Ethanol in different volume fractions was added to the reaction solution to investigate its effect on the $\cdot\text{OH}$ yield.

3. Results and discussion

3.1. XRD results

Figure 1 shows the XRD patterns of LuFeO_3 samples prepared with different NaOH concentrations. It is seen that all of the reflection peaks can be indexed to the LuFeO_3 phase with orthorhombic space group (PDF 47-0071), and no traces of second phases are observed.

3.2. SEM analysis

Figure 2 shows SEM images of the as-prepared LuFeO_3 samples, revealing that the size and morphology of the LuFeO_3 particles are highly dependent on the NaOH concentration. It shows that the sample prepared at $C_{\text{NaOH}} = 0.625$ mol/L mainly consists of bar-like particles with lengths of ~ 3 μm and widths of ~ 1 μm . When the NaOH concentration is increased to 2.5

Fig. 3. UV-vis diffuse reflectance spectra of LuFeO_3 samples synthesized at different NaOH concentrations. The inset shows the corresponding first derivative spectra.

mol/L, the bar-like particles become longer and broader and have an average size of ~ 7 μm in length and ~ 2.5 μm in width. By further increasing the NaOH concentration up to 5 mol/L, the resulting particles become cube-like with an average size of ~ 2 μm . Among these samples, the one prepared at $C_{\text{NaOH}} = 0.625$ mol/L has the smallest particle size. In addition, the higher-magnification images in Fig. 2 reveal that the particles prepared in all cases are made up of small grains.

3.3. Optical properties

Figure 3 shows the UV-vis diffuse reflectance spectra of the LuFeO_3 samples. The inset in Fig. 3 shows the corresponding first derivative spectra, where the peak wavelengths are characterized as the absorption peaks of the samples. It is found that the samples exhibit a similar optical absorption property. The absorption peak at 579 nm is suggested to be attributed to the electron transition from the valence to conduction band, from which the bandgap energy, E_g , of the samples is 2.14 eV.

3.4. Sonocatalytic activity of different LuFeO_3 samples

Figure 4 shows the sonocatalytic degradation of A07 over LuFeO_3 samples as a function of ultrasonic time (t), along with the blank experimental result. It is seen that A07 appears to be stable under ultrasonic irradiation without catalyst, and its

Fig. 2. SEM images of LuFeO_3 particles synthesized at different NaOH concentrations. (a) S1; (b) S2; (c) S3.

Fig. 4. Sonocatalytic degradation of AO7 over different LuFeO_3 samples as a function of ultrasonic time, along with the blank experimental result.

degradation percentage is only 4% after 30 min of ultrasonication. In the absence of ultrasonic irradiation, LuFeO_3 samples show moderate adsorption of 8%–11% toward AO7. However, upon ultrasonic irradiation in the presence of the LuFeO_3 samples, the degradation of AO7 increases substantially with increasing irradiation time, implying that the samples exhibit excellent sonocatalytic activity. After irradiation for 30 min, the AO7 degradation percentage reaches 89%, 75%, and 86% over the S1, S2, and S3 samples, respectively. Among the three samples, S1 shows the highest sonocatalytic activity, which can be ascribed to its relatively small particle size. Generally, the recombination opportunity of the sonogenerated electron-hole pairs in the volume is expected to be reduced in small-sized particles, and the charge carriers can effectively migrate to the particle surface [24]. Furthermore, small-sized particles have a large surface area and thus can provide abundant surface active sites for the sonocatalytic reaction.

3.5. Sonocatalytic degradation of different dyes

Figure 5 shows the sonocatalytic degradation of AO7, RhB, MO, and MB over LuFeO_3 particles (S1) as a function of ultrasonic time (t), along with the corresponding blank experiment results.

Fig. 5. Sonocatalytic degradation of AO7, RhB, MO and MB over LuFeO_3 particles (S1) as a function of ultrasonic time (t), along with the corresponding blank experiment results.

MO, and MB over the LuFeO_3 particles (S1) as a function of ultrasonic time (t). The ultrasonic degradation of the four dyes without catalyst is also shown in Fig. 5, revealing that they appear to be stable under bare ultrasonic irradiation, and the highest degradation, observed for MB, is only 8% after 30 min of exposure to ultrasonic irradiation. In the absence of ultrasonic irradiation, these dyes show moderate adsorption of 8%–13% onto LuFeO_3 particles. Under the sonocatalysis over LuFeO_3 particles, all of the dyes undergo remarkable degradation. After 30 min of sonocatalysis, the degradation percentages of AO7, RhB, MO, and MB are about 89%, 82%, 73%, and 67%, respectively. Numerous factors are expected to collectively contribute to the differences between the degradation rates of the dyes, such as the molecular structure of the dye and the dye adsorption property on the catalyst particles.

3.6. Effect of inorganic anions on the sonocatalytic efficiency

Because inorganic anions such as Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , and HCO_3^- commonly exist in dye wastewaters, their influence on the sonocatalytic efficiency should be taken into consideration for practical wastewater treatment. Figure 6 shows the effect of inorganic anions on the sonocatalytic degradation of AO7 over LuFeO_3 particles (S1), where all the inorganic anions were added in a concentration of 5 mmol/L. It indicates that the addition of Cl^- anion has a negligible effect on the sonocatalytic degradation of AO7. However, inhibition of the sonocatalytic efficiency is observed when adding NO_3^- , SO_4^{2-} , PO_4^{3-} , and HCO_3^- to the reaction solution. One possible reason for this is that these inorganic anions can react with the sonogenerated holes and/or $\cdot\text{OH}$ radicals to produce $\cdot\text{NO}_3$, $\cdot\text{SO}_4$, $\cdot\text{H}_2\text{PO}_4$, and $\cdot\text{HCO}_3$ [25,26], which have an oxidation potential lower than that of $\cdot\text{OH}$ radicals. Moreover, the addition of the inorganic anions leads to a slight decrease in the AO7 adsorption onto LuFeO_3 particles due to their competitive adsorption against AO7 (Fig. 6), and this could also influence the sonocatalytic degradation of the dye. Although the inorganic anions have an inhibitive effect on the dye degradation, the sonocatalytic efficiency still maintains relatively high. After 30 min sonocatalytic reaction, the degradation percentage of AO7 reaches about

Fig. 6. Effect of Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , and HCO_3^- on the sonocatalytic degradation of AO7 over LuFeO_3 particles (S1).

88%, 74%, 57%, 62%, and 64% when adding Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , and HCO_3^- , respectively. This result reveals that LuFeO_3 can be used as a promising sonocatalyst for practical wastewater treatment.

3.7. Effect of ethanol on the sonocatalytic efficiency

It is noted that ethanol can be used as the scavenger of $\cdot\text{OH}$ radicals generated in the sonocatalytic process [27]. By investigating the effect of ethanol on the sonocatalytic efficiency, we can clarify the role of $\cdot\text{OH}$ radicals in the dye degradation reaction. Figure 7 shows the effect of ethanol on the sonocatalytic degradation of A07 over LuFeO_3 particles (S1). It shows that the degradation rate of the dye decreases with the increase of ethanol content. When 2% ethanol is added, only 7% of the dye is degraded after 30 min of sonocatalysis. This result implies that the sonocatalytic active species is quenched by ethanol, and hence $\cdot\text{OH}$ radicals are suggested to play an important role in the sonocatalysis. Moreover, the addition of ethanol leads to a slight decrease in the A07 adsorption, which is possibly due to the competitive adsorption of ethanol against A07 onto the catalyst.

3.8. Sonocatalytic reusability of LuFeO_3 particles

The sonocatalytic reusability of LuFeO_3 particles (based on S1) was examined by the recycling sonocatalytic experiment. After the first cycle of sonocatalysis was completed, the catalyst was collected by centrifugation, washed with distilled water, and dried at 60 °C for 10 h. The recovered catalyst was then introduced to a fresh A07 solution for the next cycle of the sonocatalytic experiment under the same conditions. This process was repeated three times. Figure 8 shows the time-dependent sonocatalytic degradation of A07 over LuFeO_3 particles during the four sonocatalytic cycles. It is seen that the sonocatalytic efficiency undergoes a slight decrease for cycled sonocatalytic degradation of the dye. One possible reason for the decreased sonocatalytic efficiency could be a slight loss of catalyst during the catalyst recycling process. Despite this, the catalyst still maintains a high sonocatalytic activity, and 65% of

Fig. 8. Four sonocatalytic degradation cycles of A07 using LuFeO_3 particles (S1).

the dye is observed to be degraded after 30 min of sonocatalysis for the fourth sonocatalytic cycle.

3.9. Detection of $\cdot\text{OH}$ radicals

Figure 9 gives the PL spectra of the TPA solution after reaction for 30 min over the ultrasonic-irradiated LuFeO_3 particles (S1) without ethanol, adding 2% ethanol, and the blank experiment results. The inset shows the locally enlarged PL spectra. It is observed that in the presence of LuFeO_3 particles, the ultrasonic-irradiated TPA reaction solution shows a strong PL signal at around 429 nm, but this is absent for the fresh TPA solution without irradiation. This implies the production of $\cdot\text{OH}$ radicals over the ultrasonic-irradiated LuFeO_3 particles. When adding an amount of ethanol to the TPA solution, the PL signal disappears, indicating quenching of the $\cdot\text{OH}$ radicals caused by ethanol. This result is consistent with the fact that the introduction of ethanol results in a drastic decrease in the sonocatalytic degradation of the dye, and hence $\cdot\text{OH}$ radicals are suggested to be the dominant active species in causing the dye degradation. In addition, a weak PL signal is visible for the ultrasonic-irradiated TPA solution without catalyst. This indicates the production of a small amount of $\cdot\text{OH}$ radicals under bare ultra-

Fig. 7. Effect of ethanol content (volume fraction) on the sonocatalytic degradation of A07 over LuFeO_3 particles (S1).

Fig. 9. PL spectra of the TPA solution after reaction for 30 min over the ultrasonic-irradiated LuFeO_3 particles without ethanol and adding 2% ethanol, along with the blank experiment results.

sonic irradiation, which come from the thermal dissociation of water molecules by the local high temperature and pressure [3]. However, the amount of $\cdot\text{OH}$ radicals produced without catalyst is negligible compared with the amount produced over the ultrasonic-irradiated LuFeO_3 particles.

3.10. Possible reaction mechanism

The sonocatalysis is initiated by exciting LuFeO_3 through hot spots and/or sonoluminescences, during which electrons are excited from the valence band of LuFeO_3 to its conduction band, thus creating electron-hole ($e_{\text{CB}}^- - h_{\text{VB}}^+$) pairs (Eq. (1)). The sonogenerated electrons and holes migrate to the LuFeO_3 particle surface and participate in a series of redox reactions to produce active species. Based on the experimental results and analysis, $\cdot\text{OH}$ radicals are suggested to be the main active species responsible for the dye degradation over the ultrasonic-irradiated LuFeO_3 particles. It is well known that the redox reaction to produce active species is highly dependent on the CB and VB edge potentials of the semiconductor. According to the Refs. [28–30], the CB and VB edge potentials of LuFeO_3 are calculated to be -0.08 and $+2.06$ V versus normal hydrogen electrode (NHE), respectively. Figure 10 schematically shows the band potentials of LuFeO_3 and its sonocatalytic mechanism toward the dye degradation. The redox potentials of $\text{H}_2\text{O}/\cdot\text{OH}$ and $\text{OH}^-/\cdot\text{OH}$ are $+2.72$ and $+1.89$ V versus NHE [31], which are positive and negative to the VB potential of LuFeO_3 , respectively. From a thermodynamic point of view, the sonogenerated h_{VB}^+ can react with OH^- (but cannot with H_2O) to produce $\cdot\text{OH}$ radicals (Eq. (2)). The redox potential of $\text{O}_2/\text{H}_2\text{O}_2$ is $+0.695$ V [32], which is positive relative to the CB potential of LuFeO_3 , indicating that $\cdot\text{OH}$ radicals can also be produced through Eqs. (3) and (4). $\cdot\text{OH}$ radicals attack the double bonds of dissolved dye molecules, thus destroying the dyes (Eq. (5)).

Fig. 10. Schematic illustration of the sonocatalytic mechanism of LuFeO_3 particles toward the dye degradation.

4. Conclusions

Bar- and cube-like LuFeO_3 particles were synthesized via a hydrothermal route. The as-synthesized particles exhibit good sonocatalytic activity toward the degradation of A07, RhB, MO, and MB under ultrasonic irradiation. The highest sonocatalytic activity is observed for the bar-like particles with lengths of ~ 3 μm and widths of ~ 1 μm , where the degradation percentage of A07 reaches 89% after sonocatalysis for 30 min. The inorganic anions Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , and HCO_3^- have an inhibitive effect on the sonocatalytic degradation of the dye, but the catalyst maintains a high sonocatalytic activity. The addition of ethanol leads to substantial suppression of the dye degradation. $\cdot\text{OH}$ radicals are found to be produced over the ultrasonic-irradiated LuFeO_3 particles and are quenched with the addition of ethanol. Based on the experimental results, it is suggested that $\cdot\text{OH}$ radicals are the primary active species in the sonocatalysis. LuFeO_3 particles also exhibit good sonocatalytic reusability.

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Graphical Abstract

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LuFeO_3 crystallites of different sizes and morphologies were synthesized via a hydrothermal route. The sonocatalytic property and mechanism of the as-synthesized samples were investigated by degrading organic dyes under ultrasonic irradiation.

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水热法制备的 LuFeO_3 晶粒的超声催化活性

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摘要: 超声波在水中传播时会产生大量空化气泡, 空化气泡经历成核、生长和瞬间崩塌等过程, 并在崩塌瞬间产生局部高温和高压, 过程中会发出瞬间闪光, 即声致发光。局部高温高压及声致发光可将半导体价带上的电子激发至导带, 形成电子/空穴对, 电子和空穴迁移至半导体颗粒表面, 参与一系列氧化还原反应致使有机污染物发生分解。由于超声波在各种液体中都具有很强的穿透能力, 因此与半导体光催化技术相比, 半导体超声催化技术在降解高浓度和不透明染料废水时具有明显优势。

LuFeO_3 是稀土正铁氧体中的一员, 具有独特磁结构、巨介电常数及多铁性, 近年来引起了人们极大的研究兴趣。同时, LuFeO_3 也是一种窄带隙半导体材料, 使其可以作为一种潜在的超声催化剂, 但相关报道很少。半导体材料的晶粒尺寸及形貌对其超声催化活性的影响非常大, 因此制备出不同晶粒尺寸及形貌的 LuFeO_3 颗粒并研究其超声催化性能具有重要意义。目前 LuFeO_3 的主要制备方法为传统的固相反应法, 该法需要反复研磨和高温煅烧使原料彻底反应, 而且制备出的颗粒尺寸较大, 相互粘连严重, 形貌难以控制。

在众多纳米材料制备方法中, 水热法在调控晶粒尺寸及形貌上具有巨大优势。本课题组曾采用水热法成功制备了单相的 LuFeO_3 颗粒, 通过改变 NaOH 浓度, 可以对产物的晶粒尺寸及形貌进行调控。基于此, 本文以酸性橙(AO7)、罗丹明B(RhB)、甲基橙(MO)和亚甲基蓝(MB)为目标降解物, 考察了水热法所制备的 LuFeO_3 颗粒在超声辐照下的超声催化性能, 并系统研究了晶粒尺寸及形貌、无机离子和乙醇对 LuFeO_3 颗粒超声催化活性的影响及 LuFeO_3 颗粒重复利用性能。以对苯二甲酸(TPA)为分子荧光探针, 采用光致发光(PL)技术检测在超声辐照下 LuFeO_3 反应液中产生羟基自由基($\cdot\text{OH}$)的情况, 探讨了 LuFeO_3 颗粒的超声催化机理。

超声催化反应结果表明, 采用水热法制备的 LuFeO_3 颗粒在超声辐照下表现出良好的超声催化活性。在 NaOH 浓度为0.625 mol/L时制备的 LuFeO_3 颗粒尺寸最小, 表现出最好的超声催化活性; 经过30 min超声催化反应后, AO7, RhB, MO和MB的超声降解率分别为89%, 82%, 73%和67%。加入 Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} 和 HCO_3^- 对 LuFeO_3 颗粒的超声催化活性有抑制作用。向反应液中加入2% (v/v)乙醇后, LuFeO_3 颗粒在超声辐照下对AO7几乎没有降解, 表明 $\cdot\text{OH}$ 在超声催化中起重要作用。重复回收实验结果表明, AO7的降解率随着循环次数增加有所下降, 这可能是由于催化剂回收时的损失所致。尽管如此, 催化剂仍能保持较高的催化活性, 经4次循环后, 反应30 min时AO7的降解率为65%。PL结果表明, LuFeO_3 颗粒在超声催化反应中产生了大量的 $\cdot\text{OH}$, 添加乙醇可以消

耗 $\cdot\text{OH}$ 并抑制染料的超声催化降解. 由此可见, $\cdot\text{OH}$ 是超声催化降解RhB的主要活性物种. 我们对 LuFeO_3 导带和价带的电位进行了估算, 从热力学角度对 LuFeO_3 颗粒超声催化降解染料的机理做出了初步解释.

关键词: 铁酸镨; 水热合成; 超声催化活性; 羟基自由基; 无机离子; 有机染料降解

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