

Preparation, characterization and photocatalytic properties of REFeO₃ (RE = Sm, Eu, Gd)

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Received 16 October 2004; received in revised form 14 January 2005; accepted 14 January 2005

Abstract

Nanometer materials of rare earth mixed oxides REFeO₃ (RE = Sm, Eu, Gd) with the structure of perovskite-type were synthesized by the sol–gel method in the citric acid system. The structure and crystal phase of the powders were characterized using an X-ray diffractometer. The shape and size were analyzed using a JEM-100X transmission electron microscopy. The perovskite-type oxides were spherical with the mean grain size of 28, 20 and 21 nm, respectively. Their crystal structures showed a certain amount of lattice distortion due to the decrease of grain size and the increase of surface area. The photocatalytic activities of these three materials were studied for the degradation of various water-soluble dyes. The effect of catalyst loading on the photocatalytic activity was also investigated. SmFeO₃, EuFeO₃, GdFeO₃ exhibited high photocatalytic activities and the increase in catalyst loading could improve their photocatalytic activities.

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Keywords: Nanometer materials; Perovskite-type structure; REFeO₃; Sol–gel; Photocatalytic property

1. Introduction

Dyes and other toxic organic compounds found in textile wastewater would bring out serious pollution and must be removed or destroyed to an acceptable level before discharge to receiving waters. But the decomposition of these compounds is not easy through conventional approaches. Heterogeneous photocatalysis has been used successfully to solve this problem. When the catalyst is illuminated with light whose energy is equal to or greater than the bandgap, electrons are excited from the valence band to the conductor band, thus electron–hole pairs are generated. Separated electrons and holes diffuse to the surface of the catalyst and react with water, hydroxyl group and molecular oxygen adsorbed on the surface of the catalyst producing reactive radicals which can induce the mineralization of organic pollutants [1,2]. Of many semiconductor oxides such as Fe₂O₃, ZnO, TiO₂, SnO₂, TiO₂

has proven to be the benchmark photocatalyst for effective degradation of organic pollutants, primarily because of its optical and electronic properties, low cost, chemical stability and non-toxicity. However, it has been shown that the photocatalytic activity of TiO₂ is limited by fast charge–carrier recombination and low interfacial charge-transfer rates of photogenerated carriers [3,4]. On the other hand, since its bandgap is large ($E_g = 3.2$ eV), TiO₂ cannot absorb visible light and only makes use of 3–5% of the solar beam that can reach the earth. Therefore, the search for novel materials in heterogeneous photocatalysis with high performance has been a matter of interest in the last years.

RETO₃ perovskite-type oxides, with RE = rare earth and T = transition metal, are very important materials in advanced technologies such as solid oxide fuel cells [5], catalysts [6], materials for electrodes [7] and chemical sensors [8] because of their functional properties. In addition, these oxides show high photocatalytic activities. For example, Yang [9] has investigated systemically the photocatalytic activities of LaMO₃ (M = Cr, Mn, Fe, Co) in aqueous media

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for degradation of various water-soluble dyes. To the best of our knowledge, little attention has been paid to the research on photocatalytic properties of other rare earth mixed oxides.

In this paper, nanosized perovskite-type rare earth mixed oxides SmFeO_3 , EuFeO_3 and GdFeO_3 were prepared by the sol–gel method in the system of citric acid. These samples were used as catalysts in the photodegradation of water-soluble dyes. The results show that they are very promising due to their high photocatalytic activities.

2. Experimental

2.1. Preparation of SmFeO_3 , EuFeO_3 and GdFeO_3 nanometer powders

SmFeO_3 , EuFeO_3 and GdFeO_3 nanometer powders were prepared by the sol–gel method. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , nitric acid, citric acid were used as the starting materials. They are all A.R. grade reagents. A given amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in de-ionized water and Sm_2O_3 in nitric acid (1:1 volume fraction), respectively. Citric acid was dissolved in de-ionized water (0.5 mol dm^{-3}). A stoichiometric amount of Fe^{3+} and Sm^{3+} were thoroughly mixed, and then a certain amount of citric acid was introduced into the above mixture. The mole ratio of Fe^{3+} plus Sm^{3+} to citric acid is 1:2. The mixture was stirred and sol formed. The sol was evaporated on a water bath at 80°C then dried at 103°C in baking oven until xerogel formed. The xerogel was ground in agate mortar and turned into powder. The powder was slowly heated to 400°C and pre-calcined for 4 h to make the organic matter decompose completely, then calcined at 900°C for 4 h in muffle furnace. The product was cooled to room temperature and the SmFeO_3 nanocrystalline was obtained. In the same way, EuFeO_3 and GdFeO_3 powders were synthesized. The structure and crystal state of the powders were characterized using an X-ray diffractometer (Germany Bluker D8-Advance) with a Cu K α radiation (wavelength $\lambda = 0.15406 \text{ nm}$) operating at 20 mA and 40 kV. The shape and size of powders were analyzed using a JEM-100SX transmission electron microscopy.

2.2. Photocatalytic activity testing

The photocatalytic activities of REFeO_3 catalysts were evaluated by the degradation of four types of water-soluble dyes which include Reactive Turquoise Blue KGL, Reactive Brilliant Blue KGR, Reactive Brilliant Red X-3B, Reactive Brilliant Orange K3N. Experiments were performed in the SGY-1 multifunctional photochemical reactor with a 300-W high-pressure mercury lamp ($\lambda_{\text{max}} = 365 \text{ nm}$). Running water was passed through the double wall to cool the reaction solution and remove the IR fraction of the beam. The suspensions for the photochemical reactor were prepared by adding

various REFeO_3 nanopowders to a known concentration of dye solution. All experimental conditions were kept constant as follows: 250 ml of the suspension, 20 mg l^{-1} of initial dye concentration, 0.15 g of photocatalyst and magnetic stirring. The photocatalytic reaction lasted 2 h. Samples ($\sim 10 \text{ ml}$) for analysis were withdrawn through pipettes every 20 min, and immediately centrifuged. Absorbance of the supernatant solution and initial solution was determined, respectively, using a 722 UV-vis spectrophotometer at the maximum absorption wavelength of various dyes. Degradation rate D_e was calculated as $D_e = (A_0 - A)/A_0$ where A_0 shows initial absorbance and A shows final absorbance. Two comparison experiments were carried out under the same condition, but one was done without catalyst, and another was in the dark. At least three photocatalytic experiments were carried out for each condition, averaging the results. The degradation of dyes was studied by a Bio-Rad FTS-40 Fourier transform infrared spectrograph and a Perkin-Elmer Lambda-17 UV-vis spectrophotometer.

3. Results and discussion

3.1. Structural characteristics of SmFeO_3 , EuFeO_3 and GdFeO_3 powders

XRD patterns of SmFeO_3 , EuFeO_3 and GdFeO_3 powders are shown in Fig. 1. It is found that all the powders are perovskite phases with orthorhombic structure. The lattice parameters of SmFeO_3 , EuFeO_3 and GdFeO_3 were calculated by virtue of the (h, k, l) of every peak, the value of interplanar distance provided by X-ray diffractometer, and the formula: $d = (h^2/a^2 + k^2/b^2 + l^2/c^2)^{-1/2}$ where (h, k, l) is the indices of crystallographic plane, d is the interplanar distance, (a, b, c) is the lattice parameters. The mean grain size was calculated by Deby–Scherrer equation: $D = 0.89\lambda/\beta \cos \theta$, where D is the mean grain size, λ is the wavelength, β is the full width at half maximum, θ is the scanning angle. Both of them are listed in Table 1.

The TEM photographs of SmFeO_3 , EuFeO_3 and GdFeO_3 (Fig. 2) indicate that the sample particles are uniform spheri-

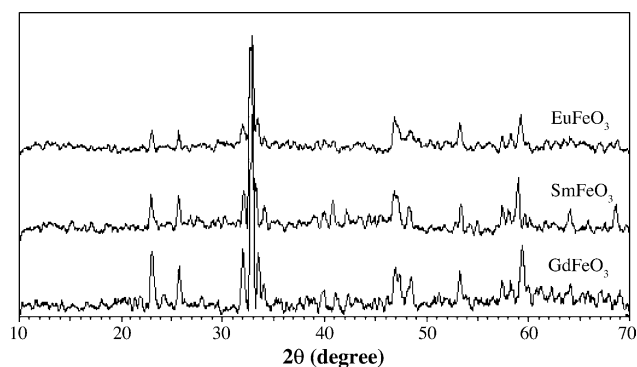


Fig. 1. XRD patterns of SmFeO_3 , EuFeO_3 and GdFeO_3 powders.

Table 1
Lattice parameters and mean grain size of SmFeO₃, EuFeO₃ and GdFeO₃ powders

Compound	Lattice constant (Å)			Cell volume (Å ³)	Mean grain size
	<i>a</i>	<i>b</i>	<i>c</i>		
SmFeO ₃	5.39	5.58	7.71	231.89	25
EuFeO ₃	5.37	5.63	7.66	231.59	23
GdFeO ₃	5.35	5.59	7.68	229.68	24

cal grains. The average grain size calculated in proportion to the photos is about 28, 20 and 21 nm, which are in consistent with the results obtained from XRD. The values of lattice distortion were calculated by the following formula [10]:

$$(2\omega)^2 \cos^2\theta = 4/\pi^2(\lambda/D)^2 + 32\langle\varepsilon^2\rangle \sin^2\theta$$

where 2ω is the full width at half maximum, θ is scanning angle, D is the mean grain size and $\langle\varepsilon^2\rangle^{1/2}$ is lattice distortion.

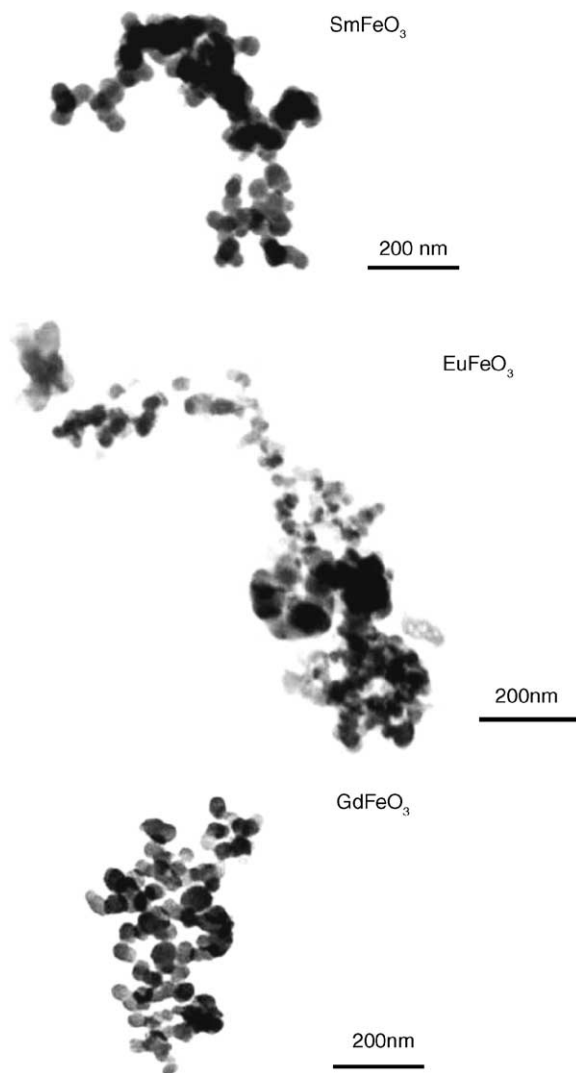


Fig. 2. TEM of nanosized SmFeO₃, EuFeO₃ and GdFeO₃ (enlarged 50,000 times).

The lattice distortions of SmFeO₃, EuFeO₃ and GdFeO₃ are estimated as 2.41×10^{-3} , 2.55×10^{-3} and 2.50×10^{-3} , respectively. Because the products are nanometer materials with smaller grain size and larger surface area that is extremely disorderly, the crystal structures deviate from its bulk and show a certain amount of lattice distortion. It is the smaller grain size and the larger surface area that benefits the contact between dyes and catalysts. Catalysts can absorb larger numbers of dyes and increase their photoactivities.

3.2. Photocatalytic activity measurement

The photocatalytic degradation of various dyes over SmFeO₃, EuFeO₃ and GdFeO₃ samples was investigated and the results are shown in Table 2. It is clear from Table 2 that after 2 h irradiation, various dyes have been degraded to a certain extent over three catalysts and the photocatalytic activities of the three samples increase in the sequence of SmFeO₃ < EuFeO₃ < GdFeO₃. The suspensions after irradiation were filtered and the catalysts were dried at ambient temperature. Comparing the IR spectra of initial dyes with that of the catalysts before and after irradiation, it can be seen that there are no absorption peaks of dyes in the IR spectra of the catalysts after irradiation, which proves that the degradation of dyes is not caused by adsorption of the substrates onto the catalysts, but by photocatalytic reaction. Fig. 3 shows the UV–vis absorption spectra of Reactive Turquoise Blue KGL solution of initial and after 2 h reaction in the system of GdFeO₃. The results show that for initial Reactive Turquoise Blue KGL solution, three absorption bands at $\lambda = 604.8$, 264.0 and 213.6 nm are observed. A small decrease in the absorbance of the substrate is found after 2 h in the presence of GdFeO₃ in the dark, which is attributed to the adsorption of the substrate onto the catalyst. In contrast, the main absorption peaks of the substrate almost completely disappear at all wavelengths in the presence of GdFeO₃ after 2 h irradiation, indicating that the dye is surely mineralized by photocatalytic action.

It is well known that REFeO₃ belong to the structure of perovskite-type. In the process of synthesis, because of the deviation of the mole ratio of RE/Fe from chemical stoichiometric proportion, they lost the metal atoms at the crank points of the cells and produced metal vacancies. To maintain the charge balance, oxygen vacancies should form resulting in the increase of oxygen absorbed. The densities of reactive OH[•] become higher when oxygen absorbed is increased, which facilitates the photocatalytic reaction. In addition, according to Shui et al. [11], the compounds which possess bigger lattice distortion have higher photocatalytic activities by virtue of increasing the additional routes of trapping holes and decreasing the recombination rate of electron–hole pairs. In REFeO₃ oxide, big lattice distortion is probably another reason of high photocatalytic activities of such kinds of compounds.

Table 2
Degradation rate of various dyes after 2 h of irradiation over SmFeO₃, EuFeO₃ and GdFeO₃

	Reactive Turquoise Blue KGL (%)	Reactive Brilliant Blue KGR (%)	Reactive Brilliant Red X-3B (%)	Reactive Brilliant Orange K3N (%)
SmFeO ₃	49.0	55.8	97.4	97.6
EuFeO ₃	68.8	72.9	96.4	97.9
GdFeO ₃	74.9	79.9	96.5	98.2

The photocatalytic activities of three oxides for decomposing dyes are dependent on lanthanoids, increasing in the sequence of SmFeO₃ < EuFeO₃ < GdFeO₃. The reason has not been well understood. One explanation is possibly the structure of REFeO₃. It is generally believed that in perovskite-type oxides, A-site cations are catalytically inert components whose effect on photocatalytic process is negligibly small compared to that of B-site cations which are the catalytically active centers, because the conduction band and the valence band mainly consist of B_d orbitals and the O_p orbitals, respectively [12,13]. The band structure is not strongly affected by lanthanoids due to localized character of their 4f orbitals. In our study, the photodegradation increases in the sequence of Sm < Eu < Gd, suggesting that in perovskite-type oxides, A-site cations also affect the photocatalytic activity and that partly occupied 4f-levels of lanthanoids may have a key role in photocatalytic reactions [14–16]. The highest photocatalytic activity of GdFeO₃ is probably related to half-filled electronic structure of Gd and the smallest radius of Gd ion. The lowest photocatalytic activity of SmFeO₃ is possibly due to its smallest lattice distortion of the three materials and the biggest radius of Sm ion. Further studies are currently being carried out to elucidate these observations.

3.3. Comparison experiments

Fig. 4 shows the results of three comparison experiments carried out in the system of GdFeO₃ suspensions. As shown, a slight loss occurs after 2 h irradiation in the absence of GdFeO₃, indicating that the dye is photo-stable basically. In the presence of GdFeO₃ but without irradiation, the decrease in dye concentration rises quickly at start, then reaches a saturation value, which is due to the adsorption of dye molecule on the catalyst. In the presence of catalyst and light, the degrada-

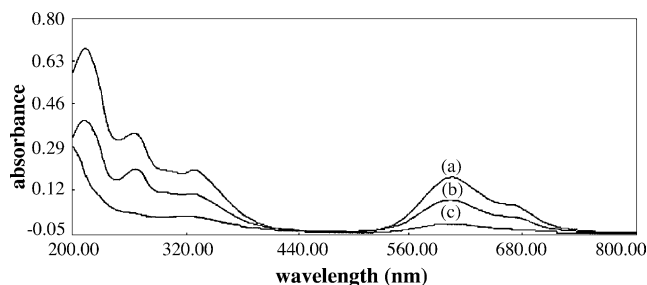


Fig. 3. UV-vis absorption spectra of Reactive Turquoise Blue KGL solution: (a) initial solution; (b) in the presence of GdFeO₃, without irradiation; (c) in the presence of GdFeO₃, with irradiation.

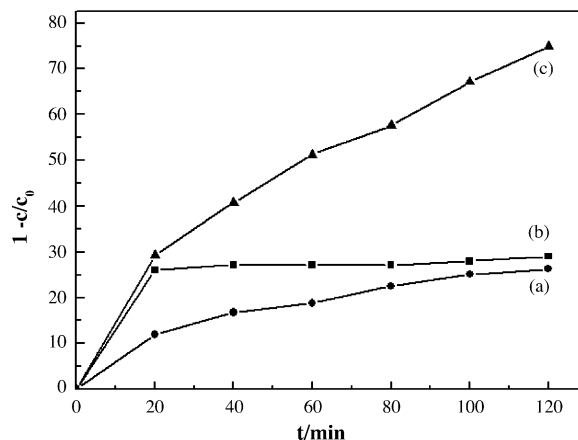


Fig. 4. The degradation of Reactive Turquoise Blue KGL: (a) in the absence of GdFeO₃, with irradiation; (b) in the presence of GdFeO₃, without irradiation; (c) in the presence of GdFeO₃, with irradiation.

tion of dye increases with irradiation time. Comparing curves (b) and (c), it is seen that up to 20 min, two curves are similar, implying that adsorption is responsible to the decrease of dye concentration in both cases. Then, the two curves separate sharply. In case 3, after 60 min of irradiation, the degradation comes up to 51.3% compared with 27.1% in case 2, suggesting that photocatalytic reaction leads to the degradation in case 3 and that GdFeO₃ has high photocatalytic activity. This also denotes that the presence of semiconductor as well as UV light irradiation are indispensable for the photocatalytic reaction to take place and the degradation of dyes occurs photocatalytically on the catalyst surface.

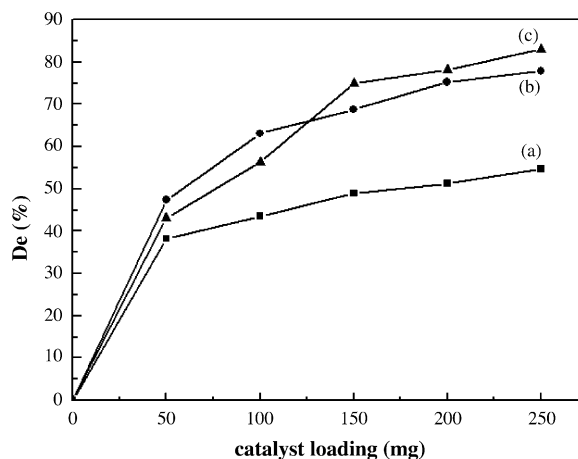


Fig. 5. The degradation of Reactive Turquoise Blue KGL as a function of catalyst loading: (a) SmFeO₃, (b) EuFeO₃, (c) GdFeO₃.

3.4. Influence of catalyst loading

The influence of catalyst loading on the photodegradation of dyes was investigated and illuminated in Fig. 5. As shown, with catalyst loading increasing, the photocatalytic reactivity increases but the increasing tendency lows down gradually. In the case of GdFeO₃, when the catalyst loading of GdFeO₃ is 50 mg, the degradation rate is 43.1%. While the loading reaches 150 mg, the degradation rate is 74.9%, but the degradation rate is only 83.0% when the loading is 250 mg. This phenomenon is similar to the one found in the study of other photocatalysts such as TiO₂ and ZnO [17–19], which could be explained as follows: when the catalyst loading is small, the photon absorbed by catalyst and utilized for the photocatalytic reaction is few. So the photocatalytic activity is low. With the increase of the catalyst loading, the number of photon absorbed and active centers on the surface of catalyst increase, resulting in the improvement of the activity. But as the catalyst loading becomes large, the number of photon tends to a saturation value. The larger catalyst loading probably brings about light blocking which has an impact on the photocatalytic efficiency and also results in the waste of catalyst.

4. Conclusions

SmFeO₃, EuFeO₃ and GdFeO₃ nanometer materials with the structure of perovskite-type were synthesized by sol–gel method in the citric acid system. Their mean grain size is about 28, 20 and 21 nm, respectively. These materials are promising candidates for the degradation of various water-soluble dyes with high photocatalytic activity. Further studies are necessary to put all the new materials into practice.

Acknowledgements

This work was supported by Henan Innovation Project for University Prominent Research Talents (2118) and Henan Key Project for Science and Technology (0424270073).

References

- [1] M.I. Litter, *J. Appl. Catal. B: Environ.* 23 (1999) 89.
- [2] H. Kisch, W. Macyk, *Chemphyschem* 3 (2002) 399.
- [3] S.T. Martin, H. Herrmann, W. Choi, M.R. Hoffmann, *Trans. Faraday Soc.* 90 (1994) 3315.
- [4] W.D. Ward, A.J. Bard, *J. Phys. Chem.* 86 (1982) 3599.
- [5] N.Q. Minh, *Ceramic full cells*, *J. Am. Ceram. Soc.* 76 (1993) 563.
- [6] K.J. Haralambous, Z. Loizos, N. Spyrellis, *Mater. Lett.* 11 (1991) 133.
- [7] C.B. Alock, R.C. Doshi, Y. Shen, *Solid State Ion.* 51 (1992) 281.
- [8] H. Aono, E. Traversa, M. Sakamoto, Y. Sadaoka, *Sens. Actuators B* 94 (2003) 132.
- [9] Q.H. Yang, *Photocatalytic oxidation and reduction activity of nanoperoxovskite ABO₃ oxides*, PhD Dissertation, Tianjin University, Tianjin, 2002.
- [10] G. Xiong, X.J. Yang, L.D. Lu, X. Wang, *J. Inorg. Mater.* 13 (1998) 613.
- [11] M. Shui, L.H. Yue, Z.D. Xu, *Acta. Phys. Chim. Sin.* 16 (2000) 459.
- [12] P.A. Cox, *Transition Metal Oxides*, Oxford University Press, Oxford, 1992, p. 105.
- [13] P.J.H. Voorhoeve, in: J.J. Burton, R.L. Garten (Eds.), *Advanced Materials in Catalysis*, Academic Press, New York, 1997, p. 129.
- [14] M. Machida, J. Yabunaka, T. Kijima, *Chem. Commun.* (1999) 1939.
- [15] M. Machida, J. Yabunaka, T. Kijima, *Chem. Mater.* 12 (2000) 812.
- [16] M. Machida, J. Yabunaka, T. Kijima, S. Matsushima, *Int. J. Inorg. Mater.* 3 (2001) 545.
- [17] M. Muruganandham, M. Swaminathan, *Sol. Energy Mater. Sol. C* 81 (2004) 439.
- [18] J. Feng, X. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, *Water Res.* 37 (2003) 3776.
- [19] S. Chakrabarti, B.K. Dutta, *J. Hazard. Mater. B* 112 (2004) 269.