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Article

Influence of lanthanum-doping on photocatalytic properties of BiFeO₃ for phenol degradation

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ABSTRACT

A series of BiFeO₃ and lanthanum-doped BiFeO₃ photocatalysts were synthesized by a facile sol-gel method using citric acid as complexing agent, and used to remove phenol in industrial wastewater under simulated sunlight irradiation. The samples were characterized by X-ray diffraction, energy dispersive spectroscopy, X-ray photoelectron spectroscopy, UV-Vis diffuse reflectance spectroscopy and photoluminescence spectroscopy. The introduction of La effectively suppressed the generation of an impurity phase. All the metals (La, Bi and Fe) are well distributed. Under simulated sunlight irradiation, the La-doped BiFeO₃ photocatalysts exhibited superior photocatalytic activity to pure BiFeO₃. The 15% La-doped BiFeO₃ photocatalyst exhibited the best activity, with a degradation rate of 96% and COD removal rate of 81.53% after irradiation for 180 min, and it showed good recycling stability. The enhanced photocatalytic ability of 15% La-doped BiFeO₃ was attributed to the increase of adsorbed surface hydroxyl groups, enhancement of visible light absorption and reduction of electron-hole recombination. We confirmed that the primary active species was •OH by adding different scavengers during the photodegradation of phenol and proposed a reaction mechanism based on these experiments.

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1. Introduction

The discharge of wastewater containing organic pollutants leads to serious environmental hazards. Phenolic compounds are one of the most toxic industrial pollutants. They are more degradation-resistant than other organic dyes, such as methyl orange (MO) and rhodamine B (RhB) [1,2]. Therefore, attention is paid to developing effective removal methods for phenolic compounds in industrial wastewater. An advanced oxidation process (AOP) has attracted attention. TiO₂ is a promising photocatalyst widely applied in the degradation of organic pollutants. However, the wide band gap (3.2 eV) photocatalyst can be only driven by ultraviolet light, which limits its application

due to the low utilization of solar energy [3,4]. To utilize solar energy effectively, researchers considered two aspects: modification of TiO₂ to extend its response to the visible light region [4–6] and development of new photocatalysts with a narrow band gap [7–9].

Bismuth ferrite (BiFeO₃) is a potential photocatalyst due to its narrow band gap (2.2–2.5 eV), chemical stability and low cost [10]. However, the photocatalytic performance of pure BiFeO₃ is poor due to the high recombination rate of photogenerated electron-hole pairs, and impurity phases are formed easily during its preparation, which restrict its practical application in the photocatalytic field [11]. So far, the modifications of BiFeO₃ are focused on the preparation method [12], noble

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metal deposition [13], and the construction of a heterojunction [10]. The photocatalytic performance of BiFeO₃ has been improved to some degree, while a simple and low cost method is always required. It is known that ion doping as a simple and effective method to enhance the photocatalytic performance by introducing an impurity level or tailoring the band gap and promoting the separation of photo-generated electrons and holes. However, studies on ion-doped BiFeO₃ are mainly concentrated on the enhancement of optical properties [14], multiferroic properties [15], ferromagnetism [16] and photovoltaics [17]. Studies on the photocatalytic degradation of refractory organics are few. There are scarce reports on the study of the photocatalytic reaction mechanism of La-doped BiFeO₃, effect of lanthanum on the phase, surface oxygen species and photocatalytic activity for phenol degradation. Therefore, it is necessary to systematically explore the influence of La³⁺ on the photocatalytic behavior of BiFeO₃ and the reaction mechanism.

There are no reports on La-doped BiFeO₃ photocatalysts prepared by the sol-gel method for phenol degradation. Here, we first prepared a series of photocatalysts Bi_{1-x}La_xFeO₃ (mole fraction $x = 0, 0.10, 0.15, 0.20$) by a one-step sol-gel method using citric acid as complexing agent. The effects of lanthanum doping on the phase, surface oxygen species and photocatalytic activity were studied. A reaction mechanism was proposed.

2. Experimental

2.1. Reagents

All of the reagents were analytical grade and used without further purification. Lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O) and citric acid were obtained from Tianjin Fengchuan Chemical Reagent Technology Co., Ltd, China. Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O), phenol (C₆H₅OH) and nitric acid (HNO₃, 65 wt%) were obtained from Sinopharm Chemical Reagent Co., Ltd, China. Distilled water was used throughout this study.

2.2. Catalyst preparation

The Bi_{1-x}La_xFeO₃ samples were prepared by a one-step sol-gel process. Stoichiometric amounts of La(NO₃)₃·6H₂O, Bi(NO₃)₃·5H₂O and Fe(NO₃)₃·9H₂O were dissolved in 100 mL deionized water mixed with 10 mL HNO₃ and an appropriate amount of citric acid. The solution in a thermostatic water bath at 70 °C was stirred with a magnet until the solution became a viscous crimson gel. An orange red xerogel was obtained after the viscous gel was dried in an oven at 100 °C under air atmosphere. The xerogel was calcined at 500 °C for 2 h and then at 600 °C for 1 h in a muffle furnace with a heating rate of 5 °C/min. Brick red Bi_{1-x}La_xFeO₃ samples were obtained. Undoped BiFeO₃ powders were prepared as in the above but without adding La(NO₃)₃·6H₂O.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded

with an Empyrean X-ray diffractometer (Panalytical, Holland) using Cu K α radiation ($\lambda = 0.1542$ nm, scanning step = 0.0667°/s), scanning over the range of $2\theta = 10^\circ$ – 60° and operating at 40 kV and 40 mA. Scanning electron microscopy (SEM) used an S-4800 microscope (Hitachi, Japan) with acceleration voltage of 20 kV. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HR-TEM) analyses were carried out on a G2F20S-TWI (Tecnai, American) at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 spectrometer (Thermo, American). The binding energy positions were calibrated against C 1s at 284.6 eV. The optical property was characterized by UV-Vis diffuse reflectance spectroscopy on a UV-3600 Spectrophotometer (Shimadzu, Japan) over the wavelength range of 200 to 800 nm. BaSO₄ was used as a reflectance standard. Fluorescence emission (PL) spectra were measured on a FLS920-type fluorescence spectrophotometer (Edinburgh Instruments, England) with light source of 450 W xenon lamp and excitation wavelength of 375 nm. Chemical oxygen demand (COD) was determined by a 5B-3F instrument (Lianghua, China), and COD removal rate was calculated by the equation: COD removal rate = (COD_{initial} – COD_{final})/COD_{initial} × 100%, where COD_{initial} is the COD of the phenol solution after the dark reaction and COD_{final} is that after irradiation.

2.4. Photocatalytic activity measurement

The photocatalytic performance of the catalysts was evaluated by the photodegradation of phenol in aqueous solution. The photocatalytic experiments were carried out on a CEL-LAB500 multibit photochemical reaction instrument (AULTT, China). A 300 W halogen lamp was used to simulate solar irradiation. A constant room temperature was maintained by replenishing the cooling water during the reaction. In a typical photocatalytic reaction, 30 mg photocatalyst was added into a 30 mL phenol aqueous solution (20 mg/L) with air ventilation and magnetic stirring. Before the illumination was turned on, the catalyst was placed in the dark for 30 min to reach adsorption equilibrium. The sampling during the photocatalytic reaction was taken every 30 min and the suspension was irradiated for 180 min. The phenol concentration was measured by an ultraviolet spectrophotometer (UV-7504PC) at the wavelength of 270 nm after centrifugation. Phenol degradation (D) was calculated by formula $D = (A_0 - A_t)/A_0 \times 100\%$, where A_0 is the absorbance of the phenol solution before the light source was turned on, and A_t was after irradiation. A blank test of phenol solution irradiated without any catalyst was also performed for comparison.

2.5. Detection of hydroxyl radicals ($\cdot\text{OH}$)

In this experimental procedure, terephthalic acid (TA) as a probe molecule readily reacts with $\cdot\text{OH}$ to produce a highly fluorescent product, 2-hydroxyterephthalic acid (excitation, $\lambda_{\text{exc}} = 315$ nm; emission, $\lambda_{\text{em}} = 425$ nm) [18]. The 15% La-doped BiFeO₃ sample (0.1 g) was dispersed in 100 mL of a 0.5 mmol/L TA aqueous solution with 2 mmol/L concentration of NaOH at

room temperature. The resulting solution was magnetically stirred and the suspension was exposed to simulated sunlight. At 10 min intervals, the suspension was sampled and centrifuged to measure the maximum PL intensity using a fluorescence spectrophotometer with an excitation wavelength of 315 nm.

3. Results and discussion

3.1. Phase analysis

The phase composition of the samples is exhibited in Fig. 1. For the BiFeO₃ sample without La doping, not only the rhombohedral phase of BiFeO₃ (JCPDS No. 86-1518) but also Bi₂₅FeO₄₀ (JCPDS No. 02-2190) at 28° and 33° were detected. Along with the increase of lanthanum doping, the characteristic peaks of Bi₂₅FeO₄₀ disappeared. However, when the mole fraction of lanthanum was increased to 20%, the characteristic peaks of Bi₂₅FeO₄₀ appeared again. This was derived from the tilt and twist of FeO₆ octahedra and the collapse of the structure around the Bi atoms resulting from the smaller radius of the La ions [19]. This phenomenon indicated that an appropriate amount of La³⁺ doping can suppress the generation of the impurity Bi₂₅FeO₄₀ phase. Enlarged views of the strongest peak are shown in the inset of Fig. 1. It clearly can be seen that the (104) diffraction peak shifted to a higher angle with the increase of La content, suggesting that the La ions were incorporated into the perovskite structure. More importantly, it was also observed that the (110) and (104) diffraction peaks of BiFeO₃ were more split compared to those of Bi_{1-x}La_xFeO₃, further demonstrating that La ions were successfully doped into the BiFeO₃ lattice [20].

Table 1 shows the cell parameters of the catalysts computed by the X'Highscore plus software. The average crystallite size was calculated with the full width at half maximum using the (110) plane of BiFeO₃ peaks using the Scherrer formula [21]. The crystallite size decreased from 79.2 nm (La = 0%) to 46.1 nm (La = 20%) with an increase of La³⁺ dopant concentration, implying that the lanthanum ion could restrict the grain size of BiFeO₃. Besides, the radius of the lanthanum atom ($R_{\text{La}^{3+}} =$

Fig. 1. XRD patterns of as-prepared BiFeO₃ samples with different La dopings.

Table 1

Cell parameters and crystallite size of the BiFeO₃ catalysts with different La dopings.

La doping (%)	<i>a</i> = <i>b</i> (nm)	<i>c</i> (nm)	Cell volume (nm ³)	Crystallite size ^a (nm)
0	0.558	1.387	0.3738	79.2
10	0.557	1.381	0.3721	78.3
15	0.557	1.378	0.3713	56.0
20	0.557	1.376	0.3712	46.1

^a Calculated using Scherrer equation with the diffraction peaks of (110) plane.

0.116 nm) is smaller than that of the bismuth atom ($R_{\text{Bi}^{3+}} = 0.117$ nm), so the shrinkage of the cell volume further proved the incorporation of lanthanum atoms into the crystal lattice of BiFeO₃.

3.2. SEM and TEM analysis

The SEM images of the samples are shown in Fig. 2. Obviously, the particle size of undoped BiFeO₃ was different from 15% La-doped BiFeO₃. Undoped BiFeO₃ was composed of a number of elongated and massive particles with the size of 210–400 nm, which adhered to each other. Besides, the morphology of 15% La-doped BiFeO₃ exhibited irregular spherical particles with the size of 60–150 nm. Clearly, the particle size of the 15% La-doped BiFeO₃ sample was smaller than that of undoped BiFeO₃, which further illustrates that the incorporation of La³⁺ could decrease the catalyst particle size. The smaller size is beneficial to the transfer of photo-generated electrons and the enhancement of the photocatalytic performance [22].

The TEM images of undoped BiFeO₃ and 15% La-doped BiFeO₃ are shown in Fig. 3. It can be seen that the particle size of undoped BiFeO₃ was larger than that of the La-doped BiFeO₃ catalyst, which is in agreement with the SEM results. The fringe interval with a distance of 0.40 nm corresponded to the (012) crystal plane of undoped BiFeO₃ as shown in Fig. 3(a), while the interplanar distance of 0.38 nm matched the same (012) crystallographic plane of 15% La-doped BiFeO₃. The smaller interplanar spacing indicated that La³⁺ was partly incorporated into the structure of BiFeO₃ [23].

Energy dispersive spectroscopy (EDS) analysis was carried out to examine the element distribution of the 15% La-doped BiFeO₃ catalyst. This is shown in Fig. 4. Clearly, the rare earth lanthanum atoms were highly dispersed among the bismuth and iron atoms. Moreover, Fig. 4(e) further confirmed that the atomic ratio of La:Bi:Fe was 7.16:42.84:50.00, which indicated that the atomic ratio of La/(La + Bi) was 0.1432, close to the

Fig. 2. SEM images of (a) undoped BiFeO₃ and (b) 15% La-doped BiFeO₃ catalysts.

Fig. 3. TEM and HRTEM images of (a) undoped BiFeO_3 and (b) 15% La-doped BiFeO_3 catalysts.

0.15 in 15% La-doped BiFeO_3 catalyst. Therefore, from this analysis results, it is reasonable to believe that rare earth La atoms were successfully incorporated into BiFeO_3 and dispersed uniformly.

3.3. XPS analysis

The XPS spectra of BiFeO_3 and La-doped BiFeO_3 were further used to investigate the chemical composition and surface state. These are shown in Fig. 5. Fig. 5(a) shows the survey spectra of the undoped BiFeO_3 and 15% La-doped BiFeO_3 catalysts. Clearly, the spectrum of the La-doped BiFeO_3 was almost the same as that of undoped BiFeO_3 except for the weaker spectral features of La 3d. Fig. 5 (b), (c) and (d) show the high resolution La 3d, Bi 4f and Fe 2p XPS spectra of the samples, respectively. For the spectra of La 3d, it can be seen that two binding energy peaks appeared at 835.1 and 851.6 eV, corresponding to La 3d_{5/2} and La 3d_{3/2}, respectively, which were attributed to La³⁺ [24]. Besides, as shown in Fig. 5(c), the binding energies at 158.8 and 163.9 eV were Bi 4f_{7/2} and Bi 4f_{5/2}, respectively, which were assigned to Bi³⁺ [25]. Fig. 5(d) shows the high resolution spectra of Fe 2p. For undoped BiFeO_3 , the peaks corresponding to the Fe 2p_{3/2} and Fe 2p_{1/2} of Fe³⁺ appeared at 714.5 and 728.0 eV, respectively. The Fe 2p_{3/2} spectra of La-doped BiFeO_3 were shifted towards lower binding energy, which was near 710 eV, which suggested the presence of Fe²⁺ [26,27]. The slight shift of the XPS spectra of Bi 4f and Fe 2p indicated that the chemical environment of Fe and Bi in BiFeO_3 was changed because of La doping. Notably, the presence of Fe ions of various valence states will be conducive to the formation of more oxygen vacancies [28,29], which is beneficial to the surface adsorption on BiFeO_3 of organic and oxygen species.

A photocatalytic reaction involves a series of redox reac-

Fig. 4. EDS of 15% La-doped BiFeO_3 catalyst. (a) Area of elemental mapping; (b) Fe (green); (c) Bi (red); (d) La (light blue); (e) EDS spectrum.

tions and the surface oxygen species play an important role in the photocatalytic process, so the O 1s XPS spectra were analyzed. This is depicted in Fig. 6. All the O 1s XPS peaks can be well-fitted by three Lorentzian-Gaussian lines, which indicated that there were three kinds of surface oxygen species. The binding energy at 529–530 eV was due to lattice oxygen atoms (O_{lat}). The main peak at 531 eV can be assigned to hydroxyl oxygen (O_{OH}). The binding energy of 532–533 eV was assigned to surface adsorbed oxygen (O_{O_2}) [30,31]. The peak fitting and analysis data of the three oxygen species are shown in Table 2. It can be seen that the hydroxyl oxygen of the La-doped BiFeO_3 was more than that of undoped BiFeO_3 , especially that the surface hydroxyl oxygen content of 15% La-doped BiFeO_3 reached 51.89%. In a photocatalytic reaction, a higher content of surface hydroxyl groups can produce more reactive oxygen species (hydroxyl radical, $\cdot\text{OH}$), which is beneficial to the photocatalytic reaction [32].

3.4. Optical property analysis

To examine the optical properties of the photocatalysts, the UV-Vis DRS and PL spectra were investigated. These are shown in Fig. 7. As can be seen in Fig. 7(a), all the samples exhibited a wide absorption ranging from 300 to 600 nm. The optical intensities of the La-doped BiFeO_3 were enhanced and the absorption edges have an obvious red shift to different degrees. Especially, the 15% La-doped BiFeO_3 exhibited the strongest absorption property. The band gaps of the samples were further studied using the Kubelka-Munk (K-M) formula [33]. The plot of $[F(R_\infty)h\nu]^2$ versus $h\nu$ (photon energy) is in the inset in

Fig. 5. (a) XPS survey spectra of undoped BiFeO₃ and 15% La-doped BiFeO₃ catalysts and high resolution spectra of (b) La 3d, (c) Bi 4f and (d) Fe 2p.

Fig. 7(a). The band gaps of the BiFeO₃ and Bi_{1-x}La_xFeO₃ ($x = 0.10, 0.15, 0.20$) samples were estimated to be 2.10, 2.15, 2.06, and 2.07 eV, respectively, suggesting that lanthanum doping narrowed the band gap. The changes of band gaps may be attributed to the formation of an impurity level due to the incorporation of La [34], which will be beneficial for the photocatalytic performance.

PL conducted at the excitation wavelength of 375 nm can provide information about surface defects, oxygen vacancies and electron-hole recombination. As shown in Fig. 7(b), 0% and 15% La-doped BiFeO₃ show the obvious PL signals at the wavelength of 510 nm, which was attributed to the electronic transition from the conduction band of BiFeO₃ to its valance band [10]. Generally speaking, a lower PL intensity indicates a lower recombination of charge carriers. The lower PL intensity of 15% La-doped BiFeO₃ suggested the better separation of the charge carriers, and thus interfacial charge-transfer efficiency was enhanced after the incorporation of lanthanum.

3.5. Photocatalytic performance

The photocatalytic performance of the samples was evaluated by the degradation of phenol (20 mg/L) under simulated solar light irradiation (300 W halogen lamp) for 180 min. The results are illustrated in Fig. 8. As shown in Fig. 8(a), the pho-

tocatalytic performance of BiFeO₃ was enhanced by the incorporation of an appropriate amount of lanthanum. Especially, the degradation rate of 15% La-doped BiFeO₃ reached 96%, which was much higher than that of undoped BiFeO₃. Moreover, the COD measurement was further conducted to investigate the mineralization degree of phenol, which was quantified by the COD removal rate. This is shown in Fig. 8(b). The COD removal rate of 15% La-doped BiFeO₃ was 81.53%, which was much higher than that of undoped BiFeO₃ (14.81%). Obviously, the higher COD removal rate indicated the higher mineralization rate of the organic material in the photocatalytic degradation. In addition, the plot of $\ln(C_0/C_t)$ versus time demonstrated that the photocatalytic reaction followed first order kinetics. The apparent rate constants were obtained from Fig. 8(c). Furthermore, the phenol degradation rates of the La-doped catalysts were clearly higher than that of the undoped sample.

The stability of the catalyst is an important issue in the photo-degradation reaction, so the stability of the 15% La-doped BiFeO₃ catalyst was investigated. As shown in Fig. 8(d), 15% La-doped BiFeO₃ exhibited excellent photocatalytic stability in the degradation of phenol. At the third recycle test, the degradation rate of phenol was still 89.47%, which was similar to that of the first run (95.06%). Besides, Fig. 8(d) shows the XRD patterns of the fresh and used 15% La-doped BiFeO₃ catalyst. There was no diffraction peak of an impurity

Fig. 6. O 1s spectra of BiFeO₃ catalysts with different La dopings.

Fig. 7. (a) UV-Vis DRS and (b) PL spectra of 0% and 15% La-doped BiFeO₃ catalysts. The inset in Fig. 7(a) is the plots of the band gap energy.

phase that can be detected. The difference was the intensity of the corresponding peaks, which further confirmed the stability of the 15% La-doped BiFeO₃ photocatalyst.

3.6. Trapping experiment

In the photocatalytic process, the active species mainly involve the hole (h^+), hydroxyl radical ($\cdot OH$) and superoxide radical ($O_2^{\cdot -}$). So what active species is the key in the photo-degradation reaction? Free radical capture experiments were conducted by adding different active species scavengers

using phenol photo-degradation as the model reaction. Briefly,

Table 2

Oxygen composition and their fractions on the surface of the La-doped BiFeO₃ catalysts derived from the curve fitting of the O 1s spectra.

La doping (%)	O _{lat}		O _{OH}		O _{O2}	
	B.E. (eV)	Fraction (%)	B.E. (eV)	Fraction (%)	B.E. (eV)	Fraction (%)
0	529.6	62.12	530.9	28.39	532.3	9.49
10	529.1	42.84	530.6	48.51	533.2	8.65
15	529.4	29.96	530.8	51.89	532.8	18.15
20	529.0	44.68	530.6, 531.7	49.12	533.2	6.20

Fig. 8. (a) Photocatalytic activity and (b) COD removal rate of phenol solution with $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ catalysts and without a catalyst (blank experiment) under simulated sunlight irradiation after 180 min; (c) $\ln(C_0/C_t)$ versus time for La-doped BiFeO_3 catalysts; (d) Recycling tests of 15% La-doped BiFeO_3 catalyst and XRD patterns before and after recycling.

the phenol photo-degradation was repeated by adding benzoquinone (BQ) as a superoxide radical scavenger ($\text{O}_2^{\cdot-}$), *tert*-butyl alcohol (TBA) as a hydroxyl radical scavenger ($\cdot\text{OH}$) and ethylene diamine tetraacetic (EDTA) as a hole (h^+) scavenger [35–37]. As shown in Fig. 9(a), the photo-degradation of phenol was inhibited when EDTA and TBA were added, while there was no obvious photo-degradation reduction with the

addition of BQ. This gave the evidence that the degradation of phenol was dominated by the oxidation reaction of hydroxyl radicals and direct hole oxidation.

3.7. Hydroxyl radical generation

To probe the generation of the $\cdot\text{OH}$ radical in the simulated

Fig. 9. (a) Photocatalytic activity of 15% La doped- BiFeO_3 nanoparticles with various additives (4 mmol/L) under simulated sunlight irradiation; (b) $\cdot\text{OH}$ trapping PL spectra of 15% La doped- BiFeO_3 nanoparticles with terephthalic acid solution under simulated sunlight irradiation. Excitation wavelength was 315 nm.

sunlight irradiated suspension of the La-doped BiFeO₃ sample, the photoluminescence (PL) spectra with terephthalic acid (TA) as a probe molecule were carried out [38]. A maximum intensity peak in the PL spectra was observed at 425 nm with an excitation wavelength of 315 nm as shown in Fig. 9(b). It was also observed that the PL intensity increased gradually with increasing irradiation time, showing a markedly enhanced production of 2-hydroxyterephthalic acid. This demonstrated that •OH was indeed generated on the irradiated surface of La-doped BiFeO₃. The formation of •OH on the surface of the La-doped BiFeO₃ photocatalyst would lead to enhanced photocatalytic activity for the degradation of phenol under simulated sunlight irradiation.

3.8. Proposed mechanism for photocatalytic activity enhancement

The generation of the active species is closely related to the potential energy of the conduction band (CB) and valence band (VB) of the semiconductor. The potentials of the CB and the VB edges of BiFeO₃ were obtained using Mulliken electronegativity theory [37,39]. This is shown as follow:

$$E_{VB} = X - E^e + 0.5E_g \quad (1)$$

$$E_{CB} = E_{VB} - E_g \quad (2)$$

where E_{VB} is the VB potential, X is the electronegativity of the semiconductor ($X = [\chi(A)^a\chi(B)^b\chi(C)^c]^{1/(a+b+c)}$, χ is the electronegativity of the elements), E^e is the standard hydrogen electrode potential (~4.5 eV), E_g is the semiconductor band gap obtained from Fig. 6(a), and E_{CB} is the CB potential. From the above, the VB potential of the BiFeO₃ semiconductor photocatalyst was calculated to be 2.55 eV and the CB potential was 0.45 eV.

When solar light irradiates La-doped BiFeO₃, BiFeO₃ is activated to produce h^+ and e^- as described in Eq. (1). The electrons at the CB of BiFeO₃ cannot reduce O₂ to O₂^{•−} because the CB edge potential of BiFeO₃ (0.45 eV vs. NHE) is more positive than the standard redox potential E^0 (O₂/O₂^{•−}) (−0.33 eV vs. NHE), which is consistent with the result of the free radical capture test. So the superoxide radicals are not the active species. However, the CB edge potential of BiFeO₃ is more negative than the standard redox potential E^0 (O₂/H₂O₂) (0.685 eV vs. NHE) [40], suggesting that oxygen adsorbed on the surface of the composite semiconductor can react with two electrons to form H₂O₂ as shown in Eq. (4). Subsequently, H₂O₂ combines with one electron to further form •OH as described in Eq. (5) and Eq. (6). •OH has a strong oxidation characteristic to participate in the photocatalytic reaction as shown in Eq. (8). Furthermore, the VB edge potential of BiFeO₃ (2.55 eV vs. NHE) is more positive than the standard redox potential of E^0 (•OH/OH[−]) (1.99 eV vs. NHE) [31], suggesting that the accumulated holes on the VB of BiFeO₃ can oxidize OH_{ads}[−] to form •OH as shown in Eq. (7). The XPS results showed a large amount of hydroxyl oxygen adsorbed on the surface of the La-doped BiFeO₃, which provided a reliable basis for the inference. Some of the holes may be directly involved in the oxidation of organic compounds according to the above free radical capture experiment. Moreover, for the substitution lanthanum, the band gap

Fig. 10. Schematic of the phenol degradation mechanism over 15% La-doped BiFeO₃.

was narrowed from 2.10 to 2.06 eV and a dopant energy level (La³⁺ impurity level) was formed below the conduction to enhance the absorption of visible light [41]. Consequently, the transmission distance of the charge carriers would be shortened, which is beneficial to the transfer of electrons to promote the photodegradation of phenol [42]. Based on the above discussion, a photocatalytic degradation mechanism was proposed as shown in Fig. 10. The phenol degradation is as follows:

4. Conclusions

We prepared BiFeO₃ perovskite catalysts with different lanthanum dopant concentration by the sol-gel method using citric acid as a complexing agent. Incorporation of lanthanum suppressed the formation of Bi₂₅FeO₄₀ and improved the photocatalytic performance of BiFeO₃. The photocatalytic activity of the 15% La-doped BiFeO₃ catalyst was 3.4 times that of undoped BiFeO₃ in the degradation of phenol under simulated sunlight irradiation for 180 min. The COD removal rate reached 81.53%. The smaller particles, stronger light absorption, lower electron-hole recombination rate and more hydroxyl groups on the catalyst surface were responsible for the excellent catalytic activity of 15% La-doped BiFeO₃.

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Graphical Abstract

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Lanthanum-doped BiFeO₃ catalysts showed superior photocatalytic activity in phenol degradation because of the efficient separation of electron-hole pairs. •OH was the main active species.

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La 掺杂 BiFeO₃ 对苯酚光催化降解性能的影响

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摘要: 苯酚是一种稳定、毒性大且难降解的有机物, 对人类和生态环境产生很大威胁, 因此急需研发出能有效移除工业废水中苯酚污染物的方法. 其中, 绿色、高效的光催化氧化技术得到研究人员青睐. 在半导体光催化剂中, BiFeO₃ 具有带隙窄 (2.2–2.5 eV)、化学稳定性好及成本低等优点, 被看作是最有潜力的光催化剂. 但是, BiFeO₃ 存在光生电子空穴对复合率高, 制备过程中易形成杂质相的缺点, 使得其光催化活性很差, 限制了 BiFeO₃ 在光催化领域的应用. 异种离子的引入能产生杂质能级或裁剪半导体带隙, 同时促进光生载流子分离, 故可考虑采用离子掺杂改性 BiFeO₃ 的手段来抑制杂质相生成, 提高载流子分离, 从而提高 BiFeO₃ 的光催化性能.

本文以柠檬酸为络合剂, 通过一步溶胶凝胶法合成了系列样品 Bi_{1-x}La_xFeO₃ (摩尔分数 $x = 0, 0.10, 0.15, 0.20$). 通过 X 射线衍射 (XRD)、扫描电镜 (SEM)、能谱 (EDS)、透射电镜 (TEM)、X 射线光电子能谱 (XPS)、紫外可见漫反射 (UV-Vis DRS) 及荧光光谱 (PL) 等手段对不同样品的物相、形貌、表面价态和光学性能进行了表征. 并通过活性物种捕获实验和羟基自由基 ($\cdot\text{OH}$) 产生实验分析了 Bi_{0.85}La_{0.15}FeO₃ 样品在苯酚降解过程中的主要活性物种和降解机理. 相对于单相 BiFeO₃, La 改性 BiFeO₃ 催化剂的光降解苯酚性能均有提高, 其中 La 最佳掺杂量为 0.15. 在模拟太阳光下照射 180 min 后, Bi_{0.85}La_{0.15}FeO₃ 的光催化活性达到 96%, 同时 COD 去除率达到 81.53%, 并表现出好的循环使用活性和稳定性. 研究发现, 该光催化过程中主要的活性物种为 $\cdot\text{OH}$.

XRD, SEM, TEM 和 EDS 结果表明, La 元素掺杂进 BiFeO₃ 结构中, 且各元素分布均匀, 同时, 适量 La 元素掺杂能有效抑制杂质相 Bi₂₅FeO₄₀ 的形成, 而且 La 掺杂 BiFeO₃ 样品的颗粒尺寸略有减小, 有利于电子空穴转移. XPS 显示, La 改性 BiFeO₃ 样品的表面有氧空位形成, 将有利于有机物的吸附和降解; 另外, 羟基氧和吸附氧含量增大, 有利于活性氧物种形成. UV-Vis DRS 和 PL 测试证明, La 改性后的样品对可见光的响应增强, 样品带隙变窄, 产生杂质能级, 抑制了光生载流子复合, 有利于产生更多载流子来促进活性物种形成, 从而提高光催化活性. 氧物种捕获实验说明, 在 Bi_{0.85}La_{0.15}FeO₃ 参与的苯酚降解过程中的主要活性物种是 $\cdot\text{OH}$, 同时 $\cdot\text{OH}$ 的产生实验也证明了在光照下 $\cdot\text{OH}$ 在 Bi_{0.85}La_{0.15}FeO₃ 光催化剂表面持续产生, 并提出了光催化降解机理.

关键词: 溶胶-凝胶法; 镧掺杂; BiFeO₃; 光催化; 苯酚

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