A novel efficient boron-doped LaFeO$_3$ photocatalyst with large specific surface area for phenol degradation under simulated sunlight

Haitao Wu, Ruisheng Hu,* Tingting Zhou, Chun Li, Wanwan Meng and Jun Yang

Boron-doped LaFeO$_3$ photocatalysts were successfully synthesized by a facile sol-gel method using glucose as a novel complexing agent. The photocatalysts were characterized by XRD, SEM, TEM, UV-vis DRS, BET, XPS and O$_2$-TPD techniques. The results show that the catalysts formed pure orthorhombic perovskite structures when the boron-doped content was less than 7.5%. The specific surface area of 3.5% B-doped catalysts reached 62.3 m$^2$ g$^{-1}$, but pure LaFeO$_3$ achieved just 6.4 m$^2$ g$^{-1}$. The content of absorbed oxygen increased to 61.28% for 3.5% B-doped LaFeO$_3$ from 38.2% for undoped LaFeO$_3$. Compared with undoped and other boron-doped LaFeO$_3$ photocatalysts, the 3.5% B-doped LaFeO$_3$ catalyst exhibits the best photocatalytic activity for phenol degradation after 300 min of simulated sunlight irradiation. The superior photocatalytic activity of B-doped LaFeO$_3$ is ascribed to these factors: first, the large specific surface area; second, the efficient separation of photogenerated electrons and holes on the surface of the catalyst; third, the increase in oxygen centers for photocatalytic activity.

1 Introduction

All kinds of phenol wastewater have increased with the rapid development of petrochemicals, plastics, synthetic fibers and the coking industry. Phenolic wastewater has a toxic potential for carcinogenic, teratogenic and mutagenic influences on the growth and reproduction of aquatic organisms and contaminates drinking water sources. Therefore, the treatment of wastewater containing phenol is one of the most major problems to be solved. Photocatalytic oxidation is an effective method for phenol degradation and has caught the attention of many researchers in recent years. Photocatalytic oxidation has the advantages of high efficiency and stability for the treatment of phenolic wastewater, and can oxidize organic contaminants to carbon dioxide and water, completely, without secondary pollution to the environment.

Perovskite-type oxides have attracted growing interest due to their special crystal structure, electric conductivity, optical properties, catalytic activity etc. The applications of perovskite-type oxides in methane combustion$^{1,2}$, photoelectric conversion$^{3,4}$ and photocatalysis$^{5}$ have been researched for decades. As a multifunctional material, LaFeO$_3$ also has great application potential in the field of photocatalysis.$^{6-8}$ Metal doping of LaFeO$_3$ has been reported to enhance the photocatalytic activity$^{6,9}$ and to improve the decomposition speed of hydrogen peroxide.$^{10}$ In recent years, research efforts have been mainly focused on the perovskite-type oxide LaFeO$_3$ with partial substitution of La by rare earth metals (e.g. Ce),$^4$ alkaline earth metals (e.g. Ca, Sr, Ba)$^{11,12}$ and alkali metals (e.g. Li).$^9$ The partial substitution of Fe by transition metals (e.g. Ni, Cr, Mn)$^{10,13,14}$ and semiconductor metals (e.g. Al)$^{15}$ has also been studied. Some references reported$^{16,17}$ doping of the non-metallic atom, boron, in composite oxides such as TiO$_2$ and BiVO$_4$ in order to increase the photocatalytic activity. However, there are only rare reports of LaFeO$_3$ with non-metal doping to improve the photocatalytic activity for the degradation of phenol.

In this work, undoped and B-doped LaFeO$_3$ catalysts were synthesized by the sol-gel method using glucose as a complexing agent. The structure, the physical and chemical properties and the photocatalytic activities of the samples for phenol degradation have been investigated in detail.

2 Experimental section

2.1 Chemicals and materials

All the reagents were of analytical grade and were used without further purification. Lanthanum nitrate hexahydrate (La(NO$_3$)$_3$·6H$_2$O) was obtained from Tainjin Fengchuan Chemical Reagent Technologies Co., Ltd, China. Iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O), boric acid (HBO$_3$), phenol and glucose were obtained from Sinopharm Chemical Reagent Co., Ltd, China.
2.2 Preparation of catalysts

B-doped LaFeO$_3$ powders of different concentrations were prepared by the sol–gel method using glucose as the complexing agent, B:Fe:La = x:(1-x):1, x = 0, 0.03, 0.05, 0.07, 0.1, 0.15, corresponding to molar ratios of 0%, 1.5%, 2.5%, 3.5%, 5%, 7.5%, respectively. Stoichiometric amounts of La(NO$_3$)$_3$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and HBO$_3$ were dissolved in deionized water and mixed with an appropriate amount of glucose. The mixed solution was placed in a thermostatic water bath at 70 °C with magnetic stirring until it formed a viscous gel. The xerogel was obtained after the viscous gel had been dried in an oven at 100 °C. Finally, the xerogel was calcined at 500 °C for 3 h in a muffle furnace, then at 700 °C for 3 h.

2.3 Catalyst characterization

The obtained catalysts were characterized by different techniques. The X-ray powder diffraction (XRD) data was recorded using an Empyrean diffractometer (Netherlands). Scanning Electron Microscope (SEM) and High-Resolution Transmission Electron Microscope (HRTEM) analysis was performed on a Hitachi S-4800 (Japan). Nitrogen adsorption–desorption isotherms were conducted in an ASAP2020 tester (America). The optical properties were tested by UV–vis spectrophotometry (UV-3600 Shimadzu, America). The shapes and positions of the diffraction peaks of the B-doped catalysts are similar to that of undoped LaFeO$_3$ catalyst, indicating that the boron atoms are uniformly dispersed within the LaFeO$_3$ structure, which is consistent with previous reports. The XRD patterns of the boron-doped catalysts (>7.5%) are shown in Fig. 1(b). We can see that an impurity phase (LaBO$_3$) is formed, which indicates that 7.5% doping concentration is optimal to the crystallization and to obtaining the pure phase of LaFeO$_3$. The cell parameter data of the catalysts were obtained from XRD powder diffraction by computation, and are shown in Table 1. The cell parameters of the B-doped catalysts have changed slightly, and the cell volumes of the B-doped catalysts are smaller than the undoped catalyst (242.9 Å$^3$), which suggests that the boron atoms are incorporated into the crystal lattice of LaFeO$_3$ and partially replace the iron atoms, since the radius of boron atoms ($r_{\text{B}^{3+}} = 0.23$) is smaller than iron atoms ($r_{\text{Fe}^{3+}} = 0.65$). The XRD patterns of the boron-doped LaFeO$_3$ catalysts with different molar concentrations are shown in Fig. 1. From Fig. 1(a), we observe that the B-doped catalysts (<7.5%) are well crystallized and have intensive diffraction peaks at 2θ values of 22.6°, 32.2°, 39.7°, 46.1°, 57.4°, 67.3° and 76.6°. Those peaks are indexed to the orthorhombic phase of LaFeO$_3$ and are consistent with the standard pattern of JCPDS card no. 88-0641 for LaFeO$_3$, without any impurity phases. According to Hiddeki Kato,$^{18}$ the orthorhombic phase can transfer the excited energy of the photogenerated-electron/hole pairs highly efficiently. In other words, the orthorhombic structure of the as-prepared samples is favorable for the separation of electrons and holes, which is beneficial for photocatalytic reactivity.

2.4 Photocatalytic activity evaluation

Photocatalytic activities of the catalysts were investigated by the degradation of phenol under simulated sunlight irradiation. The photocatalytic process was carried out in a SGY-I multifunctional photochemical reactor with 250 mg of photocatalyst and 250 ml of aqueous phenol solution (20 mg L$^{-1}$). The reaction was kept air ventilated and was magnetically stirred throughout. In order to reach the adsorption–desorption equilibrium, the catalysts were kept in dark for 30 minutes. Then the suspension was irradiated by a 300 W halogen lamp for 5 h. Sampling was performed every 30 min and the phenol concentration was determined by using an ultraviolet spectrophotometer (UV-7504PC) at a wavelength of 270 nm after centrifugation. The temperature of the reaction system was maintained at room temperature by providing cooling water during the whole process. The degradation ($D$) was calculated by the equation: $D = (C_0 - C_t)/C_0 \times 100\%$, where $C_0$ is the absorbance intensity of the phenol solution after the dark reaction and $C_t$ is the absorbance intensity after irradiation. For comparison, a blank experiment using a sample of phenol irradiated without any catalysts was also performed.

3 Results and discussion

3.1 Structural characterization

The XRD patterns of the boron-doped LaFeO$_3$ catalysts with different molar concentrations are shown in Fig. 1. From Fig. 1(a), we observe that the B-doped catalysts (<7.5%) are well crystallized and have intensive diffraction peaks at 2θ values of 22.6°, 32.2°, 39.7°, 46.1°, 57.4°, 67.3° and 76.6°. Those peaks are indexed to the orthorhombic phase of LaFeO$_3$ and are consistent with the standard pattern of JCPDS card no. 88-0641 for LaFeO$_3$, without any impurity phases. According to Hiddeki Kato,$^{18}$ the orthorhombic phase can transfer the excited energy of the photogenerated-electron/hole pairs highly efficiently. In other words, the orthorhombic structure of the as-prepared samples is favorable for the separation of electrons and holes, which is beneficial for photocatalytic reactivity.

The XRD patterns of the boron-doped catalysts (>7.5%) are shown in Fig. 1(b). We can see that an impurity phase (LaBO$_3$) is formed, which indicates that 7.5% doping concentration is optimal to the crystallization and to obtaining the pure phase of LaFeO$_3$. The cell parameter data of the catalysts were obtained from XRD powder diffraction by computation, and are shown in Table 1. The cell parameters of the B-doped catalysts have changed slightly, and the cell volumes of the B-doped catalysts are smaller than the undoped catalyst (242.9 Å$^3$), which suggests that the boron atoms are incorporated into the crystal lattice of LaFeO$_3$ and partially replace the iron atoms, since the radius of boron atoms ($r_{\text{B}^{3+}} = 0.23$) is smaller than iron atoms ($r_{\text{Fe}^{3+}} = 0.65$).
Undoped and 3.5% B-doped catalysts were used to analyze the morphology. Obviously, the morphology of undoped LaFeO₃ is different from 3.5% B-doped LaFeO₃, as demonstrated in Fig. 2. Undoped catalyst (Fig. 2(a)) shows a stacked reticular morphology that consists of short nanorods which are connected to each other. 3.5% B-doped catalyst (Fig. 2(b)) displays small block-shaped particles and no bonding phenomena. The particle size distributions of the catalysts are uniform. Fig. 3 shows the TEM and HRTEM images. It can be seen that the particle size of undoped LaFeO₃ is obviously larger than that of B-doped LaFeO₃, which reveals that boron atoms have an effect on diminishing the particle size. The catalysts are a hexagonal shape, as shown by the red trace in the figure, which is consistent with the result of XRD analysis. The (101) interplanar spacing is 0.41 nm measured by HRTEM for LaFeO₃. However, the (101) lattice spacing of the 3.5% B-doped catalyst is only 0.38 nm which, when combined with the previously obtained cell parameters, indicates that the boron atoms have been doped into the structure of LaFeO₃. To further prove the element distribution of the B-doped catalyst, the elemental mapping images of 3.5% B-doped LaFeO₃ were tested and are shown in Fig. 4. Different colors show the distribution of different elements, hence it can be confirmed that the boron atoms are well dispersed among La and Fe atoms.

### 3.2 Nitrogen adsorption–desorption isotherms

To further investigate the effect of boron doping on the structure, the nitrogen adsorption isotherms were tested, and analyzed using the desorption data. Table 2 shows the specific surface area, the average pore size and the pore volume measurement data of the as-prepared samples. We find from Table 2 that the specific surface areas of the B-doped catalysts are enlarged tenfold at least, which is much larger than those previously reported for metal doped LaFeO₃ (ref. 6, 10, 21) and pure LaFeO₃ (6.38 m² g⁻¹). Meanwhile, it is worth noting from Table 2 that the pore volume of the 3.5% B-doped catalyst is the largest, which suggests that the catalyst possesses more pores. More pores provide more activity sites and a larger specific surface area creates more reaction sites. These factors give rise to a better photocatalytic activity. The pore size distributions of the catalysts are shown in Fig. 5. The pore diameter of B-doped catalysts is evidently smaller and the pore volume is significantly larger, which explains why the specific surface area of B-doped catalysts is enlarged and indicates that boron atoms have a significant impact on the structure of the catalysts. In Fig. 5, we can see that the pore size of all the boron-doped catalysts have peaks at about 4 nm and about 12 nm, but undoped LaFeO₃ has a

### Table 1  The cell parameters and grain diameters of the catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>D (nm)</th>
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<tr>
<td>LaFeO₃</td>
<td>5.56</td>
<td>7.86</td>
<td>5.56</td>
<td>242.9</td>
<td>34.3</td>
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<tr>
<td>1.5% B-doped LaFeO₃</td>
<td>5.56</td>
<td>7.86</td>
<td>5.56</td>
<td>242.8</td>
<td>24.9</td>
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<tr>
<td>2.5% B-doped LaFeO₃</td>
<td>5.56</td>
<td>7.85</td>
<td>5.55</td>
<td>242.2</td>
<td>18.7</td>
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<td>3.5% B-doped LaFeO₃</td>
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<td>7.83</td>
<td>5.53</td>
<td>242.3</td>
<td>17.9</td>
</tr>
<tr>
<td>5.0% B-doped LaFeO₃</td>
<td>5.56</td>
<td>7.85</td>
<td>5.56</td>
<td>242.5</td>
<td>26.9</td>
</tr>
<tr>
<td>7.5% B-doped LaFeO₃</td>
<td>5.55</td>
<td>7.87</td>
<td>5.54</td>
<td>242.2</td>
<td>26.5</td>
</tr>
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</table>

Fig. 2 SEM images of the catalysts, (a) undoped LaFeO₃, (b) 3.5% B-doped LaFeO₃.

Fig. 3 TEM (left) and HRTEM (right) images of the catalysts, (a) undoped LaFeO₃, (b) 3.5% B-doped LaFeO₃.

Fig. 4 Elemental mapping images of partial 3.5% B-doped LaFeO₃ catalyst. (a) La, (b) Fe, (c) B, (d) detecting range of elemental mapping.
peak about 35 nm. The enlarged view of the 1.5% boron-doped sample is shown in the inset of Fig. 5. These results show that boron doping has a significant impact on the grain, pore size and specific surface area, consistent with the XRD, SEM and TEM before.

The nitrogen adsorption–desorption isotherms of the samples are shown in Fig. 6. The adsorption isotherms of all the samples present are typical type IV, indicating that the catalysts are mesoporous in structure. However, repeated experiments show there are two types of hysteresis loop for B-doped catalysts at different concentrations. One type is a H2 hysteresis loop with a large area, as shown in Fig. 6(a). The H2 loop is especially difficult to interpret; but is attributed to the formation of H2 hysteresis loop is the result of holes formed by accumulation of uniform particles. Another type is the H1 hysteresis loop, which demonstrates that the catalysts possess an even, ordered mesoporous structure, as shown in Fig. 6(b). The results imply that photocatalytic activity is closely connected with the shape and size of the pores. A pore size of about 10 nm is supposed to be most appropriate for phenol to enter the interior of a catalyst, but at the same time it is conducive to the separation of the reaction product from the catalyst in the photocatalytic reaction.

### Table 2 The phase, grain diameter and specific surface area of catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>( S_{\text{BET}} ) (m² g⁻¹)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm³ g⁻¹)</th>
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<tr>
<td>LaFeO₃</td>
<td>6.4</td>
<td>38.8</td>
<td>0.077</td>
</tr>
<tr>
<td>1.5% B-doped LaFeO₃</td>
<td>48.4</td>
<td>16.3</td>
<td>0.204</td>
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<tr>
<td>2.5% B-doped LaFeO₃</td>
<td>111.9</td>
<td>7.7</td>
<td>0.172</td>
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<tr>
<td>3.5% B-doped LaFeO₃</td>
<td>62.3</td>
<td>11.9</td>
<td>0.221</td>
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<tr>
<td>5.0% B-doped LaFeO₃</td>
<td>116.1</td>
<td>7.4</td>
<td>0.137</td>
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<tr>
<td>7.5% B-doped LaFeO₃</td>
<td>104.6</td>
<td>12.0</td>
<td>0.167</td>
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</table>

### 3.4 X-ray photoelectron spectroscopic analysis of the catalysts

Fig. 8 shows the XPS spectra of La 3d, Fe 2p, O 1s and B 1s in the undoped sample and in the B-doped LaFeO₃ catalysts and the results are summarized in Table 3. The binding energies of 849.9 eV and 533.0 eV are ascribed to La 3d₃/₂ and La 3d₅/₂, which are characteristic peaks for La 3d in pure LaFeO₃ as shown in Fig. 8(a). The H2 loop is especially difficult to interpret; but is attributed to the formation of H2 hysteresis loop is the result of holes formed by accumulation of uniform particles. Another type is the H1 hysteresis loop, which demonstrates that the catalysts possess an even, ordered mesoporous structure, as shown in Fig. 6(b). The results imply that photocatalytic activity is closely connected with the shape and size of the pores. A pore size of about 10 nm is supposed to be most appropriate for phenol to enter the interior of a catalyst, but at the same time it is conducive to the separation of the reaction product from the catalyst in the photocatalytic reaction.

### 3.3 UV-visible diffuse reflectance spectroscopy

The catalysts were characterized by UV-visible diffuse reflectance spectroscopy in order to explore their optical properties, as shown in Fig. 7. It can obviously be seen that undoped LaFeO₃ and B-doped LaFeO₃ catalysts have visible light and ultraviolet absorption in the region of 250–550 nm, which is similar to that of reported references. The band gaps of B-doped catalysts vary from 2.23 to 1.71 eV, which is estimated from \( E_g = 1240/\lambda_g \) (eV). It is deemed that boron doping results in a narrowed band gap. There are different opinions about the reason for absorption bands changing for B-doped catalysts. Some researchers propose that the change is caused by localized states and some believe that it is caused by the nanometer size effect. However, some studies suggest that catalysts form oxygen defects by boron substituting oxygen. However, it is obvious that the performance of visible light absorption is improved and that the photocatalytic activity of the catalysts is enhanced as a result of doping boron atoms.

![Fig. 5](image-url) The enlarged image of pore size distribution of 1.5% B-doped LaFeO₃ catalyst.

![Fig. 6](image-url) The adsorption and desorption isotherms of undoped and B-doped catalysts, (a) 2.5% and 5.0% B-doped catalysts, (b) 1.5%, 3.5% and 7.5% B-doped catalysts.
The peak fitting analysis data of the adsorbed oxygen content and the lattice oxygen for the B-doped and undoped catalysts are shown in Table 3. The adsorbed oxygen content of the B-doped catalysts is significantly greater than the undoped catalyst (38.2%), which is closely related to the photocatalytic activity. More adsorbed oxygen means that more active species are generated in the photocatalytic reaction. The active species play an important role in the photocatalytic reaction and are favorable for photocatalytic activity.

Fig. 8(d) shows the binding energy of B 1s. The standard binding energy of B 1s is 193.0 eV (B–O). Here, the binding energy of B 1s is 195.8 eV (for the 3.5% B-doped catalyst) and 195.9 eV (for the 1.5%, 2.5% and 5.0% catalysts), which is a shift of about 2.8 eV to a higher binding energy. The XPS spectrum of N 1s was tested to see whether there was some N doping, since the catalysts were synthesized by calcinations at 700 °C in an air atmosphere. As shown in the inset of Fig. 8(d), no distinctive peaks appeared in the spectrum. According to this XPS result, it is deemed that the presence of N doping in the catalysts is impossible. The change in binding energy should arise from the result of the interactions between La, Fe and B, since lanthanum and iron atoms have an electronic shielding effect on the boron atoms. Boron doping also had an effect on the binding energies of La 3d, Fe 2p and O 1s.

3.5 Temperature programmed desorption of oxygen

The O2-TPD spectra are shown in Fig. 9. Two oxygen desorption peaks are observed in LaFeO3 and the 3.5% B-doped LaFeO3 catalyst. A large and sharp desorption peak centered at 596 °C and a small shoulder peak centered at 671 °C appear for the 3.5% B-doped LaFeO3, and the undoped LaFeO3 has two weak peaks (606 °C and 662 °C). The peak area correlates to the number of oxygen-supplying centers. From the figure, we find the peak area of the B-doped catalyst at 596 °C is considerably larger than the undoped, indicating that the number of desorption centers at low temperature in B-doped LaFeO3 is significantly more than in the undoped. That is to say, compared with the undoped catalyst, the oxygen adsorption capacity of the B-doped catalyst is better. This is an important factor to improve the photocatalytic activity of B-doped LaFeO3.

3.6 Photocatalytic activities of catalysts

First, we carried out a blank experiment (in the presence of sunlight irradiation without any catalyst) in order to better illustrate the photocatalytic activities of the catalysts and their enhanced activities, as shown in Fig. 10(a) and (b). It is found that phenol degradation hardly occurred in this blank experiment.

The photocatalytic activities of undoped LaFeO3 and 3.5% B-doped LaFeO3 were investigated by phenol degradation under simulated sunlight irradiation, as shown in Fig. 10(a). The degradation of 3.5% B-doped LaFeO3 reached 87.9% after 300 min of simulated sunlight irradiation, which is evidently higher than that of LaFeO3 (30.9%). Fig. 10(b) shows

**Table 3** La 3d, Fe 2p, O 1s, B 1s and C 1s binding energies for the catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>La 3d_{3/2} (eV)</th>
<th>La 3d_{5/2} (eV)</th>
<th>Fe 2p_{1/2} (eV)</th>
<th>Fe 2p_{3/2} (eV)</th>
<th>B 1s (eV)</th>
<th>O 1s (eV)</th>
<th>Area (%)</th>
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<tbody>
<tr>
<td>5.0% B-doped LaFeO3</td>
<td>854.6, 851.4</td>
<td>837.7, 834.6</td>
<td>724.0</td>
<td>711.4</td>
<td>195.9</td>
<td>532.0, 530.3</td>
<td>40.1</td>
</tr>
<tr>
<td>3.5% B-doped LaFeO3</td>
<td>854.4, 851.2</td>
<td>837.9, 834.3</td>
<td>723.9</td>
<td>711.1</td>
<td>195.8</td>
<td>530.0, 532.0</td>
<td>61.3</td>
</tr>
<tr>
<td>2.5% B-doped LaFeO3</td>
<td>854.1, 851.0</td>
<td>837.4, 834.1</td>
<td>724.6</td>
<td>711.0</td>
<td>195.9</td>
<td>529.9, 531.2</td>
<td>62.7</td>
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<tr>
<td>1.5% B-doped LaFeO3</td>
<td>854.9, 851.4</td>
<td>838.3, 834.8</td>
<td>724.7</td>
<td>710.6</td>
<td>195.9</td>
<td>529.9, 531.9</td>
<td>43.5</td>
</tr>
<tr>
<td>LaFeO3</td>
<td>854.2, 849.9</td>
<td>837.4, 833.0</td>
<td>724.4</td>
<td>710.1</td>
<td>—</td>
<td>529.7, 531.8</td>
<td>38.2</td>
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</table>
the photocatalytic activities of B-doped LaFeO$_3$ catalysts with different concentrations after 300 min of simulated sunlight irradiation. Obviously, the photocatalytic activities of B-doped catalysts are largely enhanced and achieved 71.9%, 82.2%, 87.9%, 83.9% and 78.2%, corresponding to 1.5%, 2.5%, 3.5%, 5% and 7.5% of B-doping, respectively. We also find from Fig. 10(b) that the photocatalytic activities of the catalysts are initially enhanced with B-doping, and then the photocatalytic activities weaken. It can be observed that the optimum doping content of boron is 3.5%. In addition, we analyzed the UV absorbance of phenol with different irradiation times, and this is shown in Fig. 10(c). It can be seen that the intensities of absorbance gradually diminishes with increasing time (from 0 min to 300 min). The maximum absorption wavelength of phenol does not shift and is always 270 nm, and there is also no other absorption peak, which demonstrates that the concentration of phenol decreases with time. In addition, the degradation rate of phenol with time demonstrates that the photocatalytic reaction follows first order kinetics and the apparent rate constants can be obtained from Fig. 10(d). Furthermore, the phenol degradation rates of B-doped catalysts are clearly larger than the undoped sample.

To further explore the performance and enhanced photocatalysis of the catalysts, the absorption activities of the catalysts were investigated, as shown in Fig. 11(a), by mixing 1 g L$^{-1}$ of catalyst and 20 mg L$^{-1}$ of phenol with magnetic stirring. We found that the concentration of phenol kept steady after 30 min, demonstrating that the reaction system had achieved absorption equilibrium. The absorption amounts of the catalysts were about 7%, 10%, 32%, 21%, 30% and 27%, corresponding to specific surface areas of 6.4 m$^2$ g$^{-1}$, 48.4 m$^2$ g$^{-1}$, 111.9 m$^2$ g$^{-1}$, 62.3 m$^2$ g$^{-1}$, 116.1 m$^2$ g$^{-1}$ and 104.6 m$^2$ g$^{-1}$, respectively. From Fig. 11(a), we observed that the best absorption activity of B-doped catalysts does not correspond to the biggest specific surface area, but the absorption activity of the catalyst with the smallest specific surface area is the lowest. Meanwhile, the absorption activities of the B-doped catalysts are higher than that of the undoped catalyst and a larger specific surface area generally corresponds to a higher absorption activity. Therefore, it is considered that increasing the specific surface area facilitates enhanced activity. The photocatalytic activity tests of the catalysts were performed under visible light irradiation and a 300 W xenon lamp was used as a visible light source with a 420 nm cut-off filter. The results, shown in Fig. 11(b), show that the photocatalytic activity of the catalysts under visible light irradiation is slightly poorer than that when irradiated by simulated sunlight. The catalysts have absorption activity under both UV...
and visible light irradiation. Because the simulated sunlight contains a UV-light component, the photocatalytic activities under simulated sunlight are superior to those under visible light. In a word, the B-doped LaFeO$_3$ catalysts for phenol degradation are more efficient than undoped LaFeO$_3$ under both visible light and simulated sunlight, demonstrating that boron doping helps to enhance the photocatalytic activity of LaFeO$_3$ for phenol degradation.

4 Conclusions

In this work, we prepared boron doped orthorhombic perovskite catalysts by the sol-gel method using glucose as a novel complexing agent. We improved the photocatalytic activity by boron doping and obtained the optimal doping concentration. Most important of all is that the photocatalytic activities of all the B-doped catalysts are evidently improved under both visible light and simulated sunlight. In particular, the 3.5% B-doped LaFeO$_3$ catalyst achieved 87.9% phenol degradation in simulated sunlight. Doping boron is a new avenue for perovskite research in the field of photocatalytic materials. A schematic diagram was designed to illustrate the reaction route of photocatalysis on the catalysts, as shown in Fig. 11(c).

Acknowledgements

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Notes and references