

Fabrication of La-Doped Bi_2O_3 Nanoparticles with Oxygen Vacancies for Improving Photocatalytic Activity

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Abstract

La-doped Bi_2O_3 were prepared via a simple sol-gel method following a facile low temperature calcination process, and citric acid as an organic complexing agent. La^{3+} doping could not only create oxygen vacanices (OVs) on the surface of Bi_2O_3 , but also as the efficient scavenger to capture photogenerated electrons. The novel x% $La-Bi_2O_3$ photocatalysts exhibited oxidation capacities for degrading azo dye methyl orange (MO) and colorless pollutant phenol, and 2% $La-Bi_2O_3$ sample showed the highest photocatalytic activity. The enhanced photocatalytic activity in MO and phenol photo-degradation were attributed to the strong synergistic effects of La^{3+} -doping and oxygen vacancies (OVs), which La^{3+} ions capture, transfer, and release the photo-generated electrons for conversion from O_2 to O_2^- to prevent the hot e^- of CB to jump into the level of OVs, thereby increase separation efficiencies of photo-generated electrons and holes. The present study may present a new perspective for the utilization of rare earth ion doping to improve the performance of other photocatalytic materials.

Graphic Abstract



Keywords $Bi_2O_3 \cdot La^{3+}$ doped \cdot Oxygen vacancies $\cdot O_2$ -TPD \cdot Photocatalytic activity

1 Introduction

Bismuth oxide (Bi_2O_3) , as the most industrially important compound of bismuth with non-toxicity, chemical stability to light illumination, and strong oxidizing ability of holes in the valance band (VB) [1, 2], has been emerged as a

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promising photocatalytic material in the decomposition of various organic contaminants in waste water [3, 4]. However, Bi₂O₃ is now confronted with greater recombination rate of the e^{-}/h^{+} pairs, which decrease the degradation efficiency of organic pollutants [5]. To improve the photocatalytic performance of Bi₂O₃, the coupling with other semiconductors to construct heterojunctions have been extensively studied such as Bi₂O₃/ZnO [6], Bi₂O₃/TiO₂ [7], Bi₂O₃/Bi₂WO₆ [8], Bi₂O₃/BiPO₄ [9], Bi₂O₃/g-C₃N₄ [10], Bi₂O₃/NaBiO₃ [11], Bi₂O₃/BiVO₄ [12], and Bi₂O₃/ Bi_3O_4Br [13]. All of the results show that phototcatalytic activity has been improved to the extent due to efficient separation of photoinduced carriers. In addition, doping is another strategy adopted to improve the photocatalytic activity. Doing metal [14, 15] or non-metal elements [16, 17] have been proven to be effective method to extent the absorption regime to visible. Recently, doping with lanthanide ions are of technological interest due to particular electronic structures [18, 19]. Lanthanide ions could capture photoelectrons as electron scavengers to inhibit the recombination, and improve the separation of the photogenerated carrier [20, 21]. Doping TiO₂ with La $(La-TiO_2)$ can enhance the visible light absorption by adjusting the electronic structure, and exhibited an excellent photocatalytic performance for acetone and NO removal [22, 23]. An optimal amount of La^{3+} doping in MgO can remarkably increase the photocatalytic degradation of flumequine antibiotic (FLQ), which is attributed to the crystalline defect [24]. M. Bilal Tahir et al. fabricate RM-doped WO₃ (RM = La, Gd, Er) nanostructures, which show excellent photocatalytic performance with 2% Gd-doping WO₃, which could be accredited to suppressed recombination of charge-carriers [25]. In fact, doping is also considered to be an effective approach to create oxygen vacancies [26–28]. The introduction of oxygen vacancies (OVs) has been extensively investigated to enhance the photo-absorption and photocatalytic activity [29-33]. La-doped CeO₂ has shown to improved the catalytic efficiency for combustion of methane, and the substitution of La enhance the oxygen vacancy concentration and promote the migration of the surface oxygen, leading to improve the catalytic activity of CeO_2 [34].

In this work, La doped Bi_2O_3 samples were prepared by a simple sol–gel method, and oxygen vacancies are introduced via calcining in inert gas. The content of oxygen vacancies can be effectively changed by the amount of La^{3+} used in the synthesis process. The photocatalytic activities of as-prepared samples were evaluated by degradation of MO/Phenol. La-doped Bi_2O_3 sample exhibited excellent photocatalytic performance than pure Bi_2O_3 , and the possible photodegradation mechanisms for MO/phenol removal by La-doped Bi_2O_3 with oxygen vacancies were proposed in detail.

2 Experimental

2.1 Chemicals and Catalysts Synthesis

Bismuth nitrate pentahydrate $(Bi(NO_3)_3 \cdot 5H_2O)$, nitric acid, and citric acid were purchased from Guangdong xilong Chemical Co., Ltd., P.R. China. Lanthanum nitrate hexahydrate $(La(NO_3)_3 \cdot 6H_2O)$ was purchased from Tianjin Guangfu Fine Chemical Research Institute. The organic pollutants were obtained from Beijing Chemical Reagents Company. All reagents used are of analytically grade without further purification. Deionized water was used throughout the whole research process.

La-doped Bi₂O₃ catalysts were synthesized via a simple sol-gel-calcination method (a facile low temperature calcination method) with citric acid as organic complexing agent. In the typical procedure, firstly 5 mmol of Bi(NO₃)₃·5H₂O was dissolved in 10 mL of 1.5 M dilute nitric acid, while the expected stoichiometric La(NO₃)₃·6H₂O was dissolved 20 mL deionized water; Secondly $La(NO_3)_3$ solution was added into the $Bi(NO_3)_3$ solution under stirring conditions. Next, 10 mL of citric acid (6 M) was slowly dropped into the above solution with vigorous magnetic stirring for 40 min and continuously heated to 70 °C until it became gel. The resulting gel was dried at 80 °C for 12 h, and then ground into powders. Finally, the powder was calcined at 400 °C in a flow of 5% H_2/N_2 atmosphere for 1 h with a heating rate of 2 °C/min. In this way, we obtained a series of x% Ladoped Bi₂O₃ nanoparticles with different molar ratios of $La(NO_3)_3/Bi(NO_3)_3(x = 1, 2 \text{ and } 3)$, which were marked as 1% La-Bi₂O₃, 2% La-Bi₂O₃ and 3% La-Bi₂O₃, respectively. For comparison, the pure Bi₂O₃ was prepared in the same method without adding $La(NO_3)_3$.

2.2 Catalyst Characterization

X-ray diffraction (XRD) pattern of pure Bi_2O_3 and Ladoped Bi_2O_3 catalyst were carried out on SuperNova X-ray diffraction system with Cu K α radiation($\lambda = 0.15406$ nm). The surface morphology of the sample was characterized with a FEI QUANTA 250 FEG scanning electron microscope (SEM) attached with energy-dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analysis were conducted on Tecnai G2 F20 to observe the microstructure and the inter planar spacings of the catalysts. The chemical states of La-doped Bi_2O_3 nanoparticles were investigated using X-ray photoelectron spectroscopy (XPS) studies (Thermo Scientific X-ray photoelectron spectrometer: K-ALPHA surface analysis) with Al k α radiation. The BET specific surface areas of the asprepared samples were recorded on nitrogen-adsorption system (ASAP-2020) through the nitrogen adsorption–desorption isotherms at 77 K. The electron paramagnetic resonance (EPR) spectra were carried out on a JES-FA200 ESR spectrometer at 100 K in liquid N₂. Photoluminescence spectra were tested by fluorescence spectrometer (HITACHI F-4600) at 25 °C. Photocurrent studies were obtained by CHI660D electrochemical workstation. A PCA-1200 chemisorption analyzer (Beijing BUILDER, China) was used to perform the O₂ temperature programming desorption (O₂-TPD) experiment.

2.3 Photocatalytic Activity Tests

The photocatalytic activities of the as-prepared samples were evaluated by degrading methyl orange (MO, 10 mg/L) and phenol (50 mg/L). To investigate methyl orang/phenol degradation performance of the as-prepared samples, batch experiments were carried out. Typically, 100 mg of photocatalysts were added into 100 mL of the methyl orange/phenol solution and well dispersed under ultrasonic treatment for 30 s. Then the mixture was stirred in darkness for 1 h to reach the adsorption/desorption equilibrium. Finally the mixture was irradiated by a 300 W Xe lamp (CEAULIGHT,

CEL-HXF300D2) with a 420 nm cut-off filter. During the degradation process, an aliquot of 2 mL was withdrawn at fixed time intervals and centrifuged to monitor the pollutant concentrations by a UV–Vis spectrophotometer (PER-SEE, TU-1950) at their maximum absorption wavelengths. To identify the active species in the photocatalytic process, isopropanol (IPA, 10 mmol/L), disodium ethylenediamine-tetraacetate (EDTA-2Na, 1 mmol/L), benzoquinone (BQ, 6 mmol/L), was added into the MO/phenol degradation system as a quencher of hydroxyl radicals ('OH) [35], holes (h⁺) [36], and superoxide radicals (' O_2^-) [37] respectively.

3 Results and Discussion

3.1 Morphology, Structure, and Physical Properties

The morphology of as-prepared pure Bi_2O_3 and La-doped Bi_2O_3 samples were investigated with SEM, TEM, and HRTEM analysis. Figure 1a displayed SEM image of undoped Bi_2O_3 particles, which were irregular, and aggregated to form a larger particle. The surface of undoped Bi_2O_3 particles were relatively smooth and flat. After La doping (Fig. 1b–d), the particles were also irregular, and the particle size was found to be gradually decreased with the increment



 $\label{eq:Fig.1} \mbox{Fig.1} \mbox{ SEM images of } Bi_2O_3\ (a), 1\% \ La-Bi_2O_3\ (b), 2\% \ La-Bi_2O_3\ (c) \mbox{ and } 3\% \ La-Bi_2O_3\ (d) \ A-Bi_2O_3\ (d) \ A-Bi_2O_3\$

of La content from 1 to 3%. The surface of La-doped Bi_2O_3 particles were relatively rough. The morphology change of the La-doped samples could be ascribed to the substitution of the smaller sized of La^{3+} ions for Bi^{3+} ions in Bi_2O_3 . The decrease with increasing La content could be attributed to. The smaller particle size in most cases would give rise to a larger surface area and higher adsorption capacity, which is usually beneficial for photocatalytic activity [38].

Figure 2 shows the TEM and high resolution TEM (HRTEM) images of 2% La–Bi₂O₃ sample. As shown, 2% La–Bi₂O₃ sample (Fig. 3a–c) were irregular particles, which was in consistent with the SEM results. The HRTEM image for the 2% La–Bi₂O₃ sample (Fig. 3d) identifies the crystal lattice fringes with two different interplanar distances of 2.68 nm and 3.24 nm, which could be assigned to the

(202) and (121) crystal planes of Bi_2O_3 , respectively. The lattice fringe of crystal phase corresponds to La species is not observed, confirming that most of the La species in La-Bi₂O₃ enter into Bi₂O₃ lattice to form Bi–La oxides solid solution [34].

The chemical composition is tested by EDS attached with SEM. Figure 2e exhibited the EDS spectrum of as-prepared 2% La–Bi₂O₃ sample, and the peaks of Bi, O and La elements are detected. The atomic percentage was about 34.53 and 64.50% of Bi and O in the EDS spectrum, while the La concentration was ca. 1.57 wt%.

X-ray powder diffraction patterns of the prepared samples are shown in Fig. 3a. Obviously, the XRD pattern of the pure Bi_2O_3 exhibited the monoclinic α - Bi_2O_3 (JCPDS PDF-76-1730). The main diffraction peaks at $2\theta = 27^\circ$, 27.5°, 31.1°,



Fig. 2 TEM images of 2% La– Bi₂O₃ (**a**–**c**), HRTEM 2% La– Bi₂O₃ (**d**), and EDS spectrum of 2% La–Bi₂O₃ (**e**)



Fig. 3 XRD patterns (a) and FTIR spectra (b) of Bi₂O₃ powders with different La contents

and 33.4° could be attributed to the lattice planes (112), (121), (122), and (202), respectively. After low content of La doping, the crystal structure of Bi₂O₃ did not change, and no characteristic peaks of La₂O₃ and other phase of La were observed, indicating the formation of Bi–La oxides solid solution. However, the extra diffraction peaks emerge after La-doping increase to 3% molar fraction of La³⁺. The phenomena would be attributed to the fact that the ionic radius of La³⁺ (1.030 Å) was greatly close to the Bi³⁺ (1.062 Å) [39], and La³⁺ was easily to replace Bi³⁺ and occupied the regular lattice site in Bi₂O₃ crystal lattice.

To identify the presence of various bonds in the samples, the FTIR spectra of the as-prepared samples were carried out shown in Fig. 3b. It could be seen that all as-prepared samples had similar profiles of FTIR spectrum. Two peaks at 424 and 503 cm⁻¹ were attributed to the vibrations of the Bi–O bond of BiO₆ octahedron, and the Bi–O–Bi bond stretching peak was present at 845 cm⁻¹ [40]. In addition, the O–H stretching vibration of adsorbed water corresponded to 3425 cm⁻¹, and the peak at 1380 cm⁻¹ was the characteristic peak of the nitrate group. However, no La–O bonds were detected in La–Bi₂O₃ as a result of the relatively low content of La³⁺, which is accordance with the XRD results.

The average crystallite size (D) was estimated according to the following classical Scherrer equation [41]:

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

where D is the average crystallite size, *K* is a shape factor (0.89), λ is the wavelength of the X-ray radiations (Cu K α =0.15418 nm), β is the full width at half maximum (FWHM) intensity, and θ is the Bragg angle. Table 1 shows the calculated results. It can been seen La³⁺ doping could decrease the crystallite size of the Bi₂O₃, consistent with the fact that the ionic radius of La³⁺ (1.030 Å) was smaller than

 Table 1
 Physical properties of the prepared samples

Samples	Crystallite size (nm)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Band gap (eV)
Bi ₂ O ₃	39.5	2.54	0.0308	2.853
1% La–Bi ₂ O ₃	25.7	8.65	0.0987	2.855
2% La-Bi ₂ O ₃	22.8	12.6	0.1321	2.849
3% La–Bi ₂ O ₃	21.7	5.68	0.0538	2.838

that of Bi^{3+} (1.062 Å). Catalysts with smaller crystallites were generally known to exhibit better catalytic properties [42].

The BET surface areas and pore parameters of the prepared samples were tested and analyzed by N₂ adsorption/ desorption method. The isotherms of Bi_2O_3 , 1% La $-Bi_2O_3$, 2% La $-Bi_2O_3$ and 3% La $-Bi_2O_3$ samples were presented in Fig. 4. It could be concluded all the isotherms were identified as a combination of types IV. A distinct H3 hysteresis loop was observed in the range of 0.8–1.0 P/P₀, indicating that these samples had a porous structure.

The detail information of BET surface areas and Pore Volume of the prepared samples are listed in Table 1. The 1% La–Bi₂O₃ and 2% La–Bi₂O₃ composites had BET surface areas of 12.6 m²/g and 8.65 m²/g, respectively, which were higher than that of Bi₂O₃ (2.54 m²/g) and 3% La–Bi₂O₃ (5.68 m²/g). The total pore volumes of 1% La–Bi₂O₃ and 2% La–Bi₂O₃ composites were 0.0987 cm³/g and 0.0471 cm³/g, respectively, which were higher than that of Bi₂O₃ (0.0308 cm³/g) and 3% La–Bi₂O₃ (0.0538 m²/g). The higher BET surface areas and porous structure would provide more active sites and transport paths for reactant molecules and products, which was extremely useful in photocatalytic process.



Fig. 4 Nitrogen adsorption-desorption isotherms of Bi₂O₃ and La-Bi₂O₃



Fig. 5 a UV–Vis diffuse reflectance absorption spectra for Bi_2O_3 and La doped Bi_2O_3 , b determination of the band gap energies for Bi_2O_3 and La doped Bi_2O_3

The UV–Vis DRS spectrum was used to investigate the optical adsorption properties of the prepared samples, and recorded in Fig. 5. It is observed that La doping lead to an increase in absorption intensity in the region of 250–450 nm and the absorption band edge a little bit red shift. These changes might be ascribed to the oxygen vacancy in the La–Bi₂O₃ introduces shallow-trap levels in the band gap of the Bi₂O₃ which could trap the excited electrons [43].

The band gap of the prepared photocatalysts were estimated from reflectance data using the following formula: $\alpha hv = A(hv - E_g)^{n/2}$, where α , h, v, A and Eg represents absorption coefficient, Planck constant, light frequency, a constant, and band gap energy, respectively. And the n depend on the transition in a semiconductor (n = 1 for direct transition and n = 4 for indirect transition). The value of n for Bi₂O₃ were reported to be 1 [44].

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The plot of $(\alpha hv)^2$ versus (hv) shown in Fig. 5b, the band gaps were estimated to be 2.853, 2.855, 2.849 and 2.838 eV for Bi₂O₃, 1% La–Bi₂O₃, 2% La–Bi₂O₃, and 3% La–Bi₂O₃, respectively. The results indicated that the band gaps of 2% La–Bi₂O₃ sample were slightly narrowed.

3.2 Chemical States

To elucidate the surface chemical environments of Bi, La and O elements the prepared catalysts were characterized by X-ray photoelectron spectroscopy (XPS). The O 1s XPS spectra of prepared samples (shown in Fig. 6a) are deconvoluted into three peaks located at 529.48 ± 0.2 eV, 530.88 ± 0.2 eV, 531.58 ± 0.2 eV, which corresponds to lattice oxygen (O_L) [45], oxygen vacancies (O_V) [46] and surface chemisorbed oxygen (O_a) [47, 48], respectively. With



Fig. 6 High-resolution XPS spectra of as-prepared samples: a O 1s; b La 3d with peak fitting

the addition of La, the O_V/O 1s molar ratio increases from 17.8 to 39.7%, and then decreases to 25.4%, indicating the O_V concentration on the catalysts 2% La-Bi₂O₃ surface is higher than that of other catalysts. The oxygen vacancies on the catalyst surface can serve as photoinduced electron traps as well as adsorption sites where the electrons in oxygen vacancy states can reduce the absorption of oxygen on the surface of the samples and produce O_2^- , which is benefit to the enhancement of photocatalytic activity [49, 50]. The results demonstrates the oxygen vacancies can be generated via annealing treatment under inert gases atmosphere. Generally, oxygen vacancies (Vo) in metal oxides can be formed by remove oxygen atoms in the lattice sites (O_0) to the gaseous state (O_2) at a non-oxidizing condition [51, 52].

$$O_o \leftrightarrow V_o + 1/2O_2(gas) + 2e^{-1} \tag{2}$$

In addition, the La 3d XPS spectrum of La-doping samples presented in Fig. 6b.

For 1% La–Bi₂O₃ sample, two peaks located at 834.4 eV and at 851.2 eV are ascribed to $3d_{5/2}$ and $3d_{3/2}$, respectively. The rest of the two binding energies at the high binding energy side of the $3d_{5/2}$ and $3d_{3/2}$ belong to the satellite peaks of La³⁺. With the increase of La content, the intensity of $3d_{5/2}$ and $3d_{3/2}$ peaks increases and the peak gradually shifts to higher binding energy, which may attribute to the changes of the crystal structure or electronic properties due to Ladoing. These results demonstrate La is in the +3 oxidation state in all La-doping samples, and La³⁺ ions were successfully doped into the surface lattice of Bi₂O₃ nanoparticles [53]. These results were in good agreement with the standard binding energy of La [54].

3.3 Photocatalytic Activity

The photocatalytic activity of as-prepared samples was evaluated by degradation of MO/phenol under visible light



Fig. 7 Photodegradation of a 10 mg/L of MO, b 50 mg/L of phenol over prepared samples

 $(\lambda \ge 420 \text{ nm})$ irradiation. Figure 7 presents the time-dependent degradation profile of MO (Fig. 7a) and phenol (Fig. 7b) over the as-prepared samples. For comparison, dark adsorption and the direct photolysis were also examined. The adsorption-desorption equilibriums between photocatalysts and MO/phenol molecules could establish in 60 min under the dark with continuous stirring. La-doping enhances the adsorption properties of the catalysts, which is ascribed to the result of the slightly increased surface areas than of pure Bi_2O_3 , arising from the rough surface of La-doping Bi_2O_3 . In the direct photolysis process, the MO/phenol solution was only undergone the photo irradiation without any photocatalysts. It was found that, the direct photolysis of MO and phenol were almost negligible. Figure 7a depicts the variation of MO concentration (C_t/C_0) over as-prepared samples against reaction time. It was obvious that the photocatalytic activity was significantly enhanced after the appropriate content of La³⁺ doping. After 100 min irradiation, 89%, 98%, and 79% of MO dye solution was degraded by 3% La-Bi₂O₃, 2% La-Bi₂O₃ and 1% La-Bi₂O₃ respectively, while only 27% degradation rate by Bi₂O₃. Furthermore, the photocatalytic performance for degradation of phenol over as-prepared samples was also studied (Fig. 7b). The photodegradation rates of phenol over Bi₂O₃, 1% La-Bi₂O₃, 2% La-Bi₂O₃ and 3% La-Bi₂O₃ were 31%, 63%, 73%, and 59%, respectively.

Additionally, the apparent reaction rate constant k is calculated by the pseudo-first-order rate equation: $\ln(C_0/C_t) = k$, and is summarized in Table 2. Obviously, the apparent reaction rate constant k of 2% La–Bi₂O₃ sample was larger than that of the other samples. The results demonstrated that appropriate content of La doping could greatly enhance the photocatalytic activity for both MO and phenol degradation.

3.4 Separation Efficiency of Charge Carriers

In order to clarify the separation efficiency and transfer rate of photogenerated electron and hole, a series of experiments for charge carrier separation are performed. Photoluminescence emission intensity was related to the recombination rate of photogenerated electrons and holes after excitation process. The lowest the emission intensity, the lower recombination rate of photogenerated electrons and holes will be

Table 2 Reaction rate constants (k) of MO and phenol

Sample	MO k/min^{-1} (× 10 ⁻³)	Phenol k/h ⁻¹
Bi ₂ O ₃	3.2	0.0872
1% La–Bi ₂ O ₃	14.3	0.203
2% La-Bi ₂ O ₃	37.1	0.288
3% La–Bi ₂ O ₃	19.8	0.223

Reaction conditions: [catalyst] = 100 mg; [MO] = 10 mg/L; [phenol] = 50 mg/L

occurred in photocatalytic process [55]. Photoluminescence spectra of as-prepared samples are carried out and the result was provided in Fig. 8a. As can be seen, the PL spectra intensity of 2% La–Bi₂O₃ is much lower than that of the other prepared samples, indicating that 2% La–Bi₂O₃ has a relatively low rate of recombination of photogenerated electrons and holes. The recombination of e^- and h^+ on 2% La–Bi₂O₃ should be suppressed by the oxygen vacancies, which is helpful for the transfer and separation of photogenerated electron–hole pairs.

Additionally, transient photocurrent responses (Fig. 8b) and electrochemical impedance spectroscopy (EIS) (Fig. 8c) were performed to reveal the separation and transfer of photogenerated electron–hole pairs during the photocatalytic reaction. The higher photocurrent density means a longer lifetime of the photogenerated charge carriers and a higher photocatalytic activity [56].

As shown in Fig. 8b, all the prepared samples show a stable photocurrent response in intermittent 30 s switch-on and -off cycles under irradiation of visible light, and La-doping produce more photocurrent response. 2% La-Bi₂O₃ sample exhibited the strongest photocurrent intensity compared to other samples, which was 2.8, 1.9, and 1.2 folders than those of Bi₂O₃, 1% La-Bi₂O₃, and 3% La-Bi₂O₃, indicating that more photogenerated electrons and holes are efficiently separated in 2% La-Bi₂O₃ sample. Simultaneously, 2% La-Bi₂O₃ has the lowest arc radius in the electrochemical impedance spectroscopy (EIS) Nyquist plot in Fig. 8c, which means a lower resistance of electron transfer and an effective separation of photo-generated electron-hole pairs in 2% La-Bi₂O₃ sample [57-59]. These results declared more oxygen vacancies could bring about a more efficient separation efficiency and lower recombination rate for photogenerated electron-hole pairs, which were in accordance with the change of photocatalytic activity.

3.5 Mechanism for Photo-Degradation of MO/ Phenol

To clarify the mechanism of the photo-degradation of MO and phenol over the as-prepared samples, trapping experiments were carried out to capture the major active species generated in photocatalytic process, such as superoxide radicals (O_2^-), hydroxyl radicals(OH) and h⁺ [60]. Herein, isopropanol (IPA), benzoquinone (BQ) and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) were chosen as the scavenger for OH, O_2^- and h⁺/ O_2^- , respectively. As shown in Fig. 9a, the addition of isopropanol (IPA) didn't show significant change on the degradation of MO, suggesting that hydroxyl radicals (OH) played a negligible role during the photo-degradation process. However, an obvious decrease in the photoactivity upon the addition of BQ indicated that the O_2^- had some contribution to the photo-degradation of MO.



Fig.8 a PL spectra, b transient photocurrent responses, c electrochemical impedance spectroscopy of as-prepared samples

In addition, the degradation rate of MO further decreased with the addition of EDTA-2Na. The above results could demonstrate that the photo-generated h⁺ was the most critical species, and O_2^- served as a secondary active species during photocatalytic degradation of MO.

Figure 9b presents the effect of scavengers on photocatalytic activity of as-prepared samples with addition of EDTA-2Na, IPA and BQ, respectively. The addition of IPA and BQ had negligible effect on the photocatalytic activity, while, photocatalytic activity was tremendously reduced in case of EDTA-2Na. The scavenging experiment identified holes (h⁺) as main oxidizing species.

In order to further confirm the generation of O_2^- radicals in the photocatalytic process, we employed the electron spin-trap technique (ESR technique) to probe the active oxygen species based on the fact that O_2^- can be trapped by 5,5-dimethyl-L-pyrroline-N-oxide (DMPO) [61]. Figure 9c shows no DMPO- O_2^- signal was observed when the photocatalytic reaction was performed with pure Bi₂O₃. The characteristic ESR signals of DMPO- O_2^- appeared in the presence of 2% La-Bi₂O₃ sample, which provide evidence of O_2^- formed.

 O_2 temperature programming desorption (O_2 -TPD) experiment were performed with Bi_2O_3 and 2% La- Bi_2O_3 to investigate the O_2 desorption behavior on the surface of photocatalysts, which is shown in Fig. 9d. As known, the low temperature peak below 700 °C is referred to as the α -oxygen desorption and stemmed from the oxygen species adsorbed on the surface of the catalyst during calcination [62]. It is clear that the desorption peak of O_2 from 2% La- Bi_2O_3 surface is the most intense one, indicating that 2% La- Bi_2O_3 can adsorb more O_2 than Bi_2O_3 . This significant enhancement of adsorbed α -oxygen is likely related to the existence of surface oxygen vacancies.

To further identify whether surface oxygen vacancy is the main factor of O₂ adsorption, the electron paramagnetic resonance (EPR) spectra of 2% La–Bi₂O₃ and Bi₂O₃ were conducted on a JES-FA200 ESR spectrometer at 100 K in liquid N₂. The comparison of the ESR spectra of Bi₂O₃ and 2% La–Bi₂O₃ were illustrated in Fig. 9e. The typical ESR signal at g = 2.001 (calculated by g = h ν/β H) emerged in 2% La–Bi₂O₃ sample, which proves the existence of oxygen vacancies. The results indicated the La doping and low temperature calcination could largely



Fig. 9 Trapping experiments of the photodegradation of MO (**a**) and phenol (**b**) over 2% La–Bi₂O₃ sample; **c** DMPO-ESR spectra of Bi₂O₃ and 2% La–Bi₂O₃ samples; **d** O₂-temperature programmed desorption



Fig. 10 A proposed schematic photodegradation mechanisms for MO over 2% La–Bi₂O₃ sample under visible light irradiation

induce the formation of oxygen vacancies, which can adsorb atmospheric oxygen.

Based on a series of experiments mentioned above, a proposed photocatalytic mechanism for the enhanced photocatalytic activity of x% La–Bi₂O₃ was shown in Fig. 10, and the main degradation processes of MO/phenol are as follows:

profiles of Bi_2O_3 and 2% La–Bi_2O_3 samples; $e\ EPR$ signals of Bi_2O_3 and 2% La–Bi_2O_3 samples

$$La - Bi_2O_3 + hv \to e^{-1}(CB) + h^+ \tag{3}$$

$$La - Bi_2O_3 + hv \to e^{-1}(OVs) + h^+ \tag{4}$$

$$La^{3+}(5d^{0}6s^{0}) + e^{-1}(OVs) \to La^{2+}(5d^{0}6s^{1})$$
(5)

$$O_2 + La^{2+}(5d^06s^1) \to \cdot O_2^- + La^{3+}(5d^06s^0)$$
 (6)

$$MO/Phenol + O_2^-/h^+ \to CO_2 + H_2O + \dots$$
(7)

The enhanced photocatalytic activity of 2% La-Bi₂O₃ samples could be ascribed to several factors. Firstly, the formed OVs states located between the CB and VB as an impurity level due to the La doping. The OVs states would take part in a new photoexcitation process, which the photogenerated e⁻ transferred from the VB to the OVs levels and left h⁺ in the VB. As a result, more photoinduced h⁺ with high oxidizing ability would participate in the photodegradation process. Secondly, due to particular electronic structure of La^{3+} (5s²5p⁶5d⁰6s⁰), La^{3+} ions have exceptional electron searching ability [63]. La³⁺ ions doped into Bi₂O₃ crystal lattice might act as the efficient scavengers to capture electrons to be reduced to La^{2+} ions $(5s^25p^65d^06s^1)$, preventing the hot e⁻ of CB to jump into the level of OVs. While, La^{2+} ions easily return to original state by releasing electrons, the released electron could quickly transfer to the oxygen molecules adsorbed on the surface of the La-Bi₂O₃

photocatalyst and reduce the oxygen molecules to O_2^- , i.e. superoxide radical, which could further degrade MO/phenol. Obviously, the synergistic effects of La³⁺-doping and oxygen vacancies (OVs) play an important role in photodegradation processes of MO/phenol.

4 Conclusions

La doping Bi_2O_3 photocatalyst has been successfully synthesized via a facile sol–gel method following a facile low temperature calcination. 2% La– Bi_2O_3 exhibited excellent photocatalytic activity in degradation of MO/phenol. The content doping of La³⁺ and the amount of oxygen vacancies of 2% La– Bi_2O_3 plays a crucial role in promoting the separation of photogenerated electrons and holes, and their synergistic effect brings about the improved photocatalytic performance. In this research, the amount of oxygen vacancy could be controlled by the temperature, atmosphere, and time in calcining process. Optimization of these experimental condition will be the way to increase and control concentration of oxygen vacancy. Besides, the present work would be useful to explore oxygen vacancies induced photocatalytic activity in rare earth ion doped semiconducting oxides.

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