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A simple preparation of carbon doped porous Bi₂O₃ with enhanced visible-light photocatalytic activity



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ABSTRACT

Carbon doped bismuth oxide (Bi₂O₃) with a porous structure is obtained by a simply calcination of bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) in glycol solution. The as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and UV–Vis absorption spectroscopy. The photocatalytic activity was evaluated by the photocatalytic degradation of methyl orange (MO) in an aqueous solution under visible-light radiation ($\lambda > 420$ nm). The results show that carbon was incorporated into the lattice of Bi₂O₃. The absorption intensity of C-doped Bi₂O₃ increases in the region of 450–530 nm and the absorption edge has an obvious shift to long wavelength. The C-doped Bi₂O₃ exhibited much higher photocatalytic activity than the pure one due to the synergetic effects of the porous structure and the improved absorption in the visible-light region.

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1. Introduction

Degradation of aqueous organic pollutants in wastewater through photocatalysis has received increasing attention over the last decades [1–3]. Although conventional TiO₂ possesses excellent photocatalytic activity and stability, it can only function under UV light (ca. 4% of the solar spectrum). Therefore, many efforts have been dedicated to develop visible light photocatalytic materials for the better utilization of solar light [4–7]. One noteworthy strategy is the development of the narrow band gap semiconductors as visible light photocatalytic materials [8–11]. Among the various narrow band gap semiconductors, bismuth oxide (Bi₂O₃) with band gap varying from 2.1 to 2.8 eV is a prospective candidate [12–16]. The visible light photocatalytic activity of Bi₂O₃ has been widely studied [12–18]. For example, Cheng et al. found that Bi₂O₃ displays much higher photocatalytic activity than N-doped P25 for the degradation of methyl orange and 4-chlorophenol under visible irradiation [16]. Muruganandham et al. reported the synthesis of the honeycomb brushlike Bi₂O₃, which showed superior photocatalytic performance [17]. Wang et al. synthesized 3D flower-like Bi₂O₃ microspheres with excellent visible-light-driven photocatalytic activities for the degradation of Rhodamine B [18]. However, the application of pure Bi₂O₃ is still limited due to its high electron-hole recombination rate in the process of photocatalytic reaction. Therefore, it is necessary to develop strategies to improve the visible-light photocatalytic reactivity and efficiency of Bi₂O₃ for the decomposition of organic pollutants.

Recently, it was reported that the doped Bi₂O₃ with other elements showed enhanced photocatalytic activity [19-22]. Li et al. reported that dysprosium-doped Bi₂O₃ displays enhanced visiblelight photocatalytic performance due to the improved photoinduced charge separation rate [19]. Dai and co-workers reported the fabrication of low Fe-doped Bi₂O₃ and its visible-light photocatalytic activity for the decolorization of chlorophenol [21]. Wu et al. found that separation efficiency for electron-hole and visible-light photocatalytic activity were enhanced when Bi₂O₃ was doped with praseodymium [22]. In this study, carbon doped Bi_2O_3 was prepared via a simple calcination of $Bi(NO_3)_3$, $5H_2O$ in glycol solution. The prepared samples show high visible-light photocatalytic activity for the photodegradation of methyl orange (MO) aqueous solution. To the best of our knowledge, this is the first report on the preparation and visible-light photocatalytic activity of C-doped Bi₂O₃.

2. Experimental

2.1. Sample preparation

All reagents used in this study were of analytical grade and were purchased from Shanghai Chemical Regent Factory of China without further purification. C-doped Bi₂O₃ was prepared by a calcination method using Bi(NO₃)₃·5H₂O and glycol as precursor. In a typical synthesis procedure, 1.5 g of Bi(NO₃)₃·5H₂O was dissolved

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in 20 mL of glycol under magnetic stirring. Subsequently, the above solution was transferred into an semi-closed alumina crucible with a cover, and then annealed at 500 °C for 3 h with a heating and cooling rate of 10 °C min⁻¹ to decompose Bi(NO₃)₃ into Bi₂O₃. The reference sample, pure Bi₂O₃ without carbon doping, was also prepared by a calcination method only using Bi(NO₃)₃·5H₂O as precursor and all other experimental conditions were kept the same.

2.2. Characterization

The X-ray diffraction (XRD) patterns, which were used to characterize the crystalline phases, were carried out on an X-ray diffractometer (D/MAX-RB, Rigaku, Japan) using Cu K\alpha radiation at a scan rate of 0.05° 2θ s⁻¹. The accelerating voltage and the applied current were 40 kV and 80 mA, respectively. The morphology of the sample was observed on a field emission scanning electron microscope (SEM) (Hit-achi, Japan) with an acceleration voltage of 10 kV. X-ray photoelectron spectroscopy (XPS) measurements were done on a VG ESCALAB 210 electron spectrometer using Mg K\alpha radiation. All the binding energies were referenced to the C1s peak at 284.8 eV of the surface carbon. The UV-visible diffuse reflectance spectra of the samples were obtained for the dry-pressed film samples using a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). BaSO₄ was used as a reflectance standard in the UV-visible diffuse reflectance experiments.

2.3. Evaluation of photocatalytic activity

The photocatalytic activity of the samples was measured for the photocatalytic oxidation of MO aqueous solution under visible-light at ambient temperature. In detail, 0.1 g of the as-prepared catalyst powders was dispersed in a 25 mL of 4×10^{-5} M MO aqueous solution in a 7.0 cm culture dish. Prior to illumination, the resulting mixture was allowed to reach the adsorption-desorption equilibrium. A 200 W xenon lamp with a 420 nm cutoff filter positioned 25 cm above the dish was used as a visible-light source to trigger the photocatalytic reaction. The concentration of MO was determined by an UV-visible spectrophotometer (UV-2550, Shimadzu, Japan).

3. Results and discussion

3.1. Phase structures and morphology

XRD was used to identify and determine the phase structure of the as-prepared C-doped Bi₂O₃ powder. Fig. 1 shows a comparison of the XRD patterns of the pure and C-doped Bi₂O₃ samples. As can be seen from this figure, the diffraction patterns of both samples can be well indexed to the single monoclinic phase of well-crystalline α -Bi₂O₃ according to the JSPDS file (No. 65-2366), and no other diffraction peaks were found, indicating that the C-doped sample maintains the crystal structure as pure Bi₂O₃. It can be seen that there is no significant shift of XRD peak position after carbon doped in the Bi₂O₃, but all diffraction peaks became broadening in comparison with pure Bi₂O₃, and the peak intensity decreases obviously, probably owing to the shield effect



Fig. 1. XRD patterns of pure (a) and C-doped Bi₂O₃ (b) samples.

of doped carbon species [23] or the distortion of lattice induced by the incorporation of carbon atoms into the surface and bulk of Bi_2O_3 [24–26]. The average crystallite sizes of the pure and C-doped Bi_2O_3 calculated by the Scherrer equation are 56.3 and 29.9 nm, respectively.

The morphologies of the as-prepared samples were investigated using SEM. In contrast to the as-prepared pure Bi₂O₃ with smooth surface (Fig. 2a), many porous appear on the surface of C-doped Bi₂O₃ (Fig. 2b), suggesting that the presence of ethylene glycol has a strong effect on the morphology of C-doped Bi₂O₃. The formation mechanism of the porous Bi₂O₃ is investigated by SEM analysis of the products maintained at 550 °C for various times (Fig. 3). After calcination for 20 min, Bi(NO₃)₃-glycol system burnt strongly in the semi-closed alumina crucible (a quasi-closed system). An extremely high temperature can be achieved within a very short duration [27]. Then, $Bi(NO_3)_3$ was decomposed into Bi_2O_3 rapidly and a part of glycol was sealed inside it. Thus, the surface of Bi₂O₃ particles shows smooth and no holes can be observed as well. After calcination for 40 min, the sealed glycol was decomposed into carbon dioxide and water vapor, resulting in the formation of holes on the surface of Bi₂O₃. With the increase of the time, more holes formed, leading to the formation of porous C-doped Bi₂O₃ after calcination for 3 h. In contrast, in the absence of glycol, little gas released and no holes formed in the pure Bi₂O₃.

The porous structure of C-doped Bi₂O₃ sample observed by SEM was further studied by N₂ adsorption/desorption analysis. Fig. 4 shows the N₂ adsorption/desorption isotherms of the pure and C-doped Bi₂O₃ samples. For C-doped Bi₂O₃, the physioadsorption isotherms can be classified as type IV in the IUPAC classification with a distinct hysteresis loop observed in the range of $0.5-1.0P/P_0$, which was characteristic of porous materials [28]. The BET surface areas of the pure and C-doped Bi₂O₃ samples are 5.9 and 1.7 m²/g, respectively.

3.2. XPS analysis

The surface chemical composition and chemical states of the samples studied were investigated by XPS. Fig. 5 exhibits the high-resolution XPS spectra of the C 1s and Bi 4f regions of pure and C-doped Bi₂O₃. In the case of the C-doped Bi₂O₃, the XPS peak of C1s can be decomposed into three Gaussian peaks which centered at 280.7, 285, 288.9 eV, respectively. While, for pure Bi₂O₃ sample, only two Gaussian peaks were adopted to fit the profile. The binding energy of 288.9 eV is associated with the carboxyl C (O–C=O) groups. For the peak located at 285 is usually assigned to elemental carbon. One of the greatest differences in the XPS spectra is that the third fitted peaks at 280.7 eV for C-doped Bi_2O_3 sample. The binding energy peak at 280.7 eV can be ascribed to the formation of Bi-C bond [29], indicating that C substitutes oxygen in the lattice of Bi₂O₃. Similar metal-C bonds were also observed in C-doped ZnO and C-doped TiO₂, in which the binding energy located 282.7 eV and 281 eV, respectively [30,31]. Fig. 5B shows the Bi 4f spectrum of pure Bi₂O₃ and Cdoped Bi2O3. The binding energies of Bi 4f peaks (164.3 and 159.1 eV) in C-doped Bi₂O₃ increased to a higher value compared with those of pure Bi₂O₃ (163.9 and 158.7 eV), suggesting that some of the lattice oxygen atoms were replaced by carbon atoms and doping C can lead to a decrease of electron density on Bi due to the lower electronegativity of carbon compared to that of oxygen [32,33].

3.3. UV-Vis diffuse reflectance spectra

To study the optical response of pure and carbon doped Bi_2O_3 samples, the UV–Vis diffuse reflectance spectra were measured (Fig. 6). Compared with the pure Bi_2O_3 , the absorption edge of



Fig. 2. SEM images of pure (a) and C-doped Bi₂O₃ (b) samples.



Fig. 3. SEM images of C-doped Bi₂O₃ obtained by a calcination of Bi(NO₃)₃ in glycol solution at 500 °C for 20, 40 min, 1, and 3 h.



Fig. 4. N_2 adsorption and desorption isotherms for pure (a) and C-doped $Bi_2O_3\left(b\right)$ samples.

the C-doped Bi_2O_3 has an obvious red-shift,¹ and a conspicuous visible-light absorption shoulder around 450–530 nm can be observed, which is consistent with yellow color characteristic of the C-doped Bi_2O_3 sample (inset in Fig. 6). Furthermore, the photo-response of the C-doped Bi_2O_3 can expand to 800 nm with constant absorbance, which is important for the solar energy application.

3.4. Photocatalytic activity

The photocatalytic performances of the pure and C-doped Bi₂O₃ samples were investigated by the decomposition of MO aqueous solution under visible light irradiation. Under dark conditions (no light irradiation), the concentration of MO did not change for measurements on the Bi₂O₃ samples studied. Also, irradiation in the absence of photocatalysts did not result in the photocatalytic decolorization of MO. Therefore, the presence of both irradiation and Bi₂O₃ sample is necessary for the efficient degradation of MO. These results suggest that the decomposition of MO aqueous solutions is caused by photocatalytic reactions on the Bi₂O₃ surface under the visible light irradiation. The ratio of MO concentration C and initial MO concentration C₀ versus the degradation time was shown in Fig. 7. It can be observed that commercial P25 exhibited inefficient photocatalytic degradation with MO photodegradation efficiency of 19% within 150 min. And approximately 42% of the dye was removed by the pure Bi₂O₃, which is much slower than that of C-doped sample. The enhanced photocatalytic activity of C-doped Bi₂O₃ can be attributed to the synergetic effects of porous structure, enhanced light-absorption and extended light-response range caused by carbon-doping within the Bi₂O₃ lattice. The porous materials possess larger specific surface area, which contributes to more possible reaction sites on the photocatalyst surface, resulting in the higher photocatalytic activity [34,35]. On the other hand,

 $^{^{1}\,}$ For interpretation of color in Fig. 6, the reader is referred to the web version of this article.



Fig. 5. XPS spectra for the (A) C 1s and (B) Bi 4f of pure (a) and C-doped $Bi_2O_3\ (b)$ samples.



Fig. 6. UV-visible diffuse reflectance spectra of pure (a) and C-doped Bi_2O_3 (b) samples; the inset shows corresponding colour of these samples.

porous structure facilitates the rapid diffusion of ions and molecules within the material so that the rate of photocatalytic reactions is substantially improved. The other cause of the enhanced photocatalytic activity of C-doped Bi₂O₃ is the enhanced lightabsorption. The number of excited electrons and holes created by light irradiation plays an important role in affecting the photocatalytic efficiency. The higher the number of carriers, the better the photocatalyst is. Thus, a better photocatalytic activity for C-doped Bi₂O₃ is achieved as a result of enhanced absorption capacity and extended light-response region.



Fig. 7. Photocatalytic activity of Degussa P25 (a), pure (b) and C-doped $Bi_2O_3\ (c)$ samples.

4. Conclusions

C-doped Bi₂O₃ with porous structure have been successfully synthesized by a simply calcinations of Bi(NO₃)₃ in glycol solution. The C-doped Bi₂O₃ exhibits an obvious red-shift which occurs in the absorption edge and presents significantly enhanced absorption in the visible-light region. The C-doped Bi₂O₃ exhibits excellent photocatalytic activity for the photodegradation of MO under the irradiation of visible light. This study provides a simple one-step method to fabricate a high-performance photocatalyst, which may open new possibilities to design semi-conductor materials for future applications.

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References

- [1] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69–96.
- [2] X.B. Chen, S.S. Mao, Chem. Rev. 107 (2007) 2891–2959.
- [3] Z.J. Zou, C.S. Xie, S.S. Zhang, X.L. Yu, T. Zou, J. Li, J. Alloys Comp. 581 (2013) 385– 391.
- [4] G.P. Dai, S.Q. Liu, Y. Liang, H.J. Liu, Z.C. Zhong, J. Mol. Catal. A: Chem. 368–369 (2013) 38–42.
- [5] D.F. Wang, T. Kato, J.H. Ye, J. Am. Chem. Soc. 130 (2008) 2724–2725.
- 6] J.G. Yu, Q. Li, S.W. Liu, M. Jaroniec, Chem. Eur. J 19 (2013) 2433-2441.
- 7] H.Y. Feng, D.F. Hou, Y.H. Huang, X.L. Hu, J. Alloys Comp. 592 (2014) 301–305.
- [8] W.D. Shi, J.Q. Shi, S. Yu, P. Liu, Appl. Catal., B 138–139 (2013) 184–190.
- [9] J. Wang, B. Li, J.Z. Chen, L. Li, J.H. Zhao, Z.P. Zhu, J. Alloys Comp. 578 (2013) 571– 576.
- [10] B.C. Pan, Y.M. Xie, S.J. Zhang, L. Lv, W.M. Zhang, ACS Appl. Mater. Interfaces 4 (2012) 3938–3943.
- [11] H. Liu, Y. Su, P. Chen, Y. Wang, J. Mol. Catal. A: Chem. 378 (2013) 285–292.
- [12] A. Hameed, T. Montini, V. Gombac, P. Fornasiero, J. Am. Chem. Soc. 130 (2008) 9658–9689.
- [13] L.J. Cheng, Y. Kang, J. Alloys Comp. 585 (2014) 85-93.
- [14] W.C. Hao, Y. Gao, X. Jing, W. Zou, Y. Chen, T.M. Wang, J. Mater. Sci. Technol. 30 (2014) 192–196.
- [15] L. Leontie, M. Caraman, M. Delibas, G.I. Rusu, Mater. Res. Bull. 36 (2001) 1629– 1637.
- [16] H.F. Cheng, B.B. Huang, J.B. Lu, Z.Y. Wang, B. Xu, X.Y. Qin, X.Y. Zhang, Y. Dai, Phys. Chem. Chem. Phys. 12 (2010) 15468–15475.
- [17] M. Muruganandham, R. Amutha, G.J. Lee, S.H. Hsieh, J.J. Wu, M. Sillanpäa, J. Phys. Chem. C 116 (2012) 12906–12915.
- [18] J.L. Wang, X.D. Yang, K. Zhao, P.F. Xu, L.B. Zong, R.B. Yu, D. Wang, J.X. Deng, J. Chen, X.R. Xing, J. Mater. Chem. A 1 (2013) 9069–9074.
- [19] J.Z. Li, J.B. Zhong, J. Zeng, F.M. Feng, J.J. He, Mater. Sci. Semicond. Process. 16 (2013) 379–384.

- [20] P. Malathy, K. Vignesh, M. Rajarajan, A. Suganthi, Ceram. Int. 40 (2014) 101-107.
- [21] Y.R. Dai, L.F. Yin, J. Alloys Comp. 563 (2013) 80–84.
 [22] S.X. Wu, J.Z. Fang, W.C. Xu, C.P. Cen, J. Chem. Technol. Biotechnol. 88 (2013) 1828-1835.
- [23] A. Hagfeld, M. Grätze, Chem. Rev. 95 (1995) 49–68.
 [24] X.X. Lin, F. Rong, X. Ji, D.G. Fu, Microporous Mesoporous Mater. 142 (2011) 276-281.
- [25] J. Yang, H.Z. Bai, Q. Jiang, J.S. Lian, Thin Solid Films 516 (2008) 1736-1742.
- [26] K.R. Wu, C.H. Hung, Appl. Surf. Sci. 256 (2009) 1595-1603.
 [27] Y. Cai, H.Q. Fan, M.M. Xu, Q. Li, Colloids Surf., A 436 (2013) 787–795.
- [28] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Sieminewska, Pure Appl. Chem. 57 (1985) 603.
- [29] J.H. Yu, B. Wei, L. Zhu, H. Gao, W.J. Sun, L.L. Xu, Appl. Surf. Sci. 284 (2013) 497-502.
- [30] H. Pan, J. Yi, L. Shen, R. Wu, J. Yang, J. Lin, Y. Feng, J. Ding, L. Van, J. Yin, Phys. Rev. Lett. 99 (2007) 127201.
- [31] S.W. Liu, C. Li, J.G. Yu, QJ. Xiang, CrystEngComm 13 (2011) 2533–2541.
 [32] H.Q. Jiang, C.Y. Wang, P. Wang, J.S. Li, Z.Y. Lu, J. Mater. Sci. Eng. 29 (2011) 161–
- 166. [33] M. Wang, Q. Liu, Y.S. Che, L.F. Zhang, D. Zhang, J. Alloys Comp. 548 (2013) 70-76.
- [34] K. Xia, D. Ferguson, Y. Djaoued, J. Robichaud, N. Tchoukanova, R. Brüning, E. McCalla, Appl. Catal. A 387 (2010) 231–241.
- [35] S.C. Han, L.F. Hu, N. Gao, A.A. Al-Ghamdi, X.S. Fang, Adv. Funct. Mater. (2014), http://dx.doi.org/10.1002/adfm.201400012.