Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Growth of N-doped BiOBr nanosheets on carbon fibers for photocatalytic degradation of organic pollutants under visible light irradiation



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ARTICLE INFO

Article history: Received 12 January 2014 Received in revised form 14 February 2014 Accepted 1 April 2014 Available online 12 April 2014

Keywords: Carbon fibers Photocatalysis Visible light irradiation Organic pollutants

1. Introduction

The photocatalytic technology has attracted extensive interest in the past decades due to its wide potential application in environmental protection procedures such as air purification, water disinfection, hazardous waste remediation and water purification [1,2]. Compared with other photocatalysts, semiconductor photocatalytic process has shown great potential as a low cost, environmentally friendly and sustainable treatment technology for the treatment of wastewater. The ability of this advanced oxidation technology has been widely demonstrated to remove persistent organic compounds and microorganisms in water [3,4]. For example, TiO₂ powders are usually utilized in suspension for water treatment, which is helpful to increase the photocatalytic performance with the decrease in particles size of powder due to the smaller particles having larger specific surface [5, 6]. However, conventional TiO₂ photocatalyst can only utilize the light with wavelengths shorter than 388 nm (UV range) due to its wide band gap (e.g., $E_g \approx 3.2$ eV for anatase), which limits its application with solar light [7]. Many efforts have been made in the last two decades in order to overcome this limitation. The two main approaches are dye sensitization [8] and doping with impurities [7,9,10]. On the other hand, the separation of TiO₂ powders from the treated wastewater prior to discharge is a time-consuming and expensive process, which limits the development and application of TiO₂ photocatalysis in

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ABSTRACT

Aiming at effectively utilizing visible light and convenient separation of the photocatalysts from the water treatment system, the N-doped BiOBr photocatalysts with nanosheets structure and visible light photocatalytic properties have been immobilized on the surface of carbon fibers (CFs) by a facile solvothermal route. The morphology and structural properties of the resultant N-doped BiOBr/CFs hybrid structures were investigated by scanning electron microscopy (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The as-prepared N-doped BiOBr/CFs hybrids exhibited excellent photocatalytic activities for the degradation of organic pollutants (rhodamine B and methanol) under visible light irradiation.

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water treatment. Therefore, the exploitation of visible light-driven photocatalysts is indispensable for the practical application of the photocatalytic system [11–13].

As a group of V–VI–VII semiconductors, bismuth oxyhalide compounds have attracted considerable attention due to their remarkable photocatalytic activities under visible light irradiation [5]. Among the bismuth oxyhalides, BiOBr, which crystallizes, possess the tetragonal matlockite structure, a layered structure composed of $[Bi_2O_2]^{2+}$ layers interleaved with double Br layers among the bismuth oxyhalides receives remarkable attentions owing to its stability, suitable band gaps and relatively superior photocatalytic abilities. So far, a variety of BiOBr nano- and micro-structures, including nanoplates, nanobelts and microspheres prepared by numerous methods, have been used as photocatalysts to degrade organic contaminant. The photocatalytic properties of BiOBr crystals can be improved by the incorporation of the highly reactive component, such as cation, anion and metal oxides [14–17].

Aiming at effectively utilizing visible light and convenient separation of the photocatalysts from the photocatalytic water treatment system, an ideal way is to grow visible light responsive photocatalysts on certain substrates to form an ordered film without agglomeration. Carbon fibers (CFs) are long, thin strand materials and composed mostly of carbon atoms that offer advantages for advanced materials, such as lightweight, high-tensile strength, manufacturing flexibility and heat resistance. Moreover, CFs are flexible, conductive and stable in corrosive conditions, and they also can supply a large surface area [18,19]. On the one hand, the micropore surface of CFs greatly enhances the efficiency of pollutant adsorption. On the other hand, CFs can be regenerated in situ, when the pollutants adsorbed on the surface were migrated to



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the surface of catalysts and degraded [20,21]. Therefore, CFs are ideal substrate materials for applications in photocatalysis of pollutants. Although CFs have been used as substrate for preparation of photocatalysts, most cases are limited to immobilize of TiO₂ particles [18–24]. Here we introduced a facile solvothermal route to immobilize N-doped BiOBr nanosheets on surface of CFs. The prepared hybrids showed excellent photocatalytic activity for degradation of organic pollutants under visible light irradiation.

2. Experimental

2.1. Growth of N-doped BiOBr nanosheets on carbon fibers

First, CFs are activated by strong acid treatment. Then N-doped BiOBr nanosheets are immobilized on surface of CFs by a solvothermal route. In a typical synthesis, Bi(NO₃)₃•5H₂O (1.27 g) was added to 60-mL 2-methoxyethanol. Then urea (0.34 g) and CTAB (0.60 g) were added and stirred until a homogeneous solution obtained. The solution was transferred to a Teflon-lined stainless steel autoclave. The acid treated CFs were immersed in the above solution. The solvothermal treatment was conducted at 160 °C for 48 h. After cooling, the as-prepared sample was washed by water and dried at 60 °C for 12 h to get the fine N-doped BiOBr/CFs products.

2.2. Characterization

The microstructures and crystal phase of the as-prepared samples were analyzed with a Siemens Diffraktometer D5000 X-ray diffractometer with Cu K α radiation source at 35 kV, with a scan rate of 10° s⁻¹ in the 2θ range of 10° – 80° . The ULTRA-55 field emission scanning electron microscopy (FE-SEM) at an accelerating voltage of 10 kV and the JSM-2100 transmission electron microscopy (TEM) were used to characterize the morphologies of the as-prepared samples. The Brunauer-Emmet-Teller (BET)-specific surface area was measured using a specific surface and pore size analysis instrument (3H-2000PS1/2 static volume method, China). The UV-vis diffuse reflectance spectra were obtained for the dry-pressed disk samples using a UV-vis spectrometer (U-3010, Hitachi). X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation. The base pressure was about 3 \times 10⁻⁹ mbar. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon.

2.3. Measurement of photocatalytic activity

The photocatalytic activity of N-doped BiOBr/CFs product was investigated by the photodegradation of RhB and methanol. The photodegradation experiments were carried out in a closed box. The radiation source was 500 W high-pressure Xenon lamp equipped with UV cutoff filter to provide visible light ($\lambda \ge 400 \text{ nm}$) (model BL-GHX-V, Shanghai Bilon Instruments Factory, China). For the photocatalytic degradation of RhB, 0.03 g of the as-prepared catalysts (pure CFs or N-doped BiOBr/CFs) were suspended in 50 mL RhB $(C_0 = 10 \text{ mg} \cdot \text{L}^{-1})$ aqueous solution with constant stirring. Prior to irradiation, the suspensions were stirred in the dark for 3 h to ensure the adsorption-desorption equilibrium. The concentration of RhB was measured by JASCO V-570 UV-vis-NIR spectrophotometer (Japan). For the comparison, a blank experiment (without any catalysts) and a parallel test in the dark (with N-doped BiOBr/CFs) were carried out for indicating the adsorption of RhB under the same conditions. For the photocatalytic degradation of methanol, 0.03 g of the as-prepared catalysts (N-doped BiOBr/CFs) were suspended in 50 mL methanol $(C_0 = 5.0 \%, v/v)$ aqueous solution. The obtained mixture was sealed in a photo-catalytic degradation system (100 mL glass tube) with constant stirring. The temperature of the reactant solution was maintained around 300 K by a flow of cooling water during the reaction. The amount of methanol in the solution was analyzed by high-performance liquid chromatography (HPLC, Agilent 1260) using high purity water as mobile phase. The conversion ratio (CR, %) can be calculated by the following formula: CR% = $(A_0 - A_t)^*100\% / A_0$, where A_0 and A_t are the integral area of methanol peak with the photo-catalytic degradation time at 0 and t min, respectively. The component and the concentration of resulting gases after photodegradation were analyzed by gas chromatography (GC, Agilent 6890) equipped with HP-5 (5% Ph Me Siloxane, 30 m · 0.32 mm · 0.25 lm film thickness) capillary column and detected by using thermal conductivity detector [25]. The concentration of CO₂ (ppm) equaled the difference value between the measured value obtained from GC and the actual concentration of CO₂ in the atmosphere (395 ppm).

3. Results and discussion

Fig. 1A shows the SEM image of the products. The CFs substrates are uniformly and compactly covered by a large number of nanosheets to form a rough surface, as shown in Fig. 1B and C, compared with the smooth surface of pure CFs (Fig. 1E). The thickness of these nanosheets is around 400 nm (Fig. 1D). These nanosheets interweave together to form an open porous structure. A small quantity of flower-like microspheres, which actually are composed of many nanosheets as the petals, also can be found on the surface of composite fibers. It has been reported that such small sizes of these nanosheets may be indicative of a possible quantum confinement effect for the properties of such structures [26]. TEM characterization may provide additional information regarding the interior structure of these architectures. A typical TEM image is shown in Fig. 1H, which further confirms that the N-doped BiOBr layer is around 400 nm in thickness. This observation suggests that the continuous nanosheets are immobilized simultaneously on CFs and connected together as they continued to grow. A selectedarea electron diffraction (SAED) pattern taken from the edge of the composite fibers is shown in Fig. 1I. The SAED pattern from the border area of the CFs and nanosheets exhibits the combination of bright ring and single crystalline spot which is shown in Fig. 1J. These SAED patterns indicate the single crystalline nature of the nanosheets. The HR-TEM image of N-doped BiOBr layer in Fig. 1K and L show a welldefined crystallinity with lattice spacing of 0.292 nm and 0.248 nm, which are close to the d-spacing of the [012] (0. 28 nm) and [111] (0.26 nm) reflections of pure BiOBr [14]. The slight difference in lattice spacing is deviation due to the presence of nitride dopant. To investigate the formation process for the N-doped BiOBr nanosheets growth on CFs, the surface morphology of a sample at the intermediate state that obtained by reaction only 1 h is inspected by the SEM measurement. Many isolated flower-like structure can be found on the surface of CFs (Fig. 1F, G). This observation possible suggests that the growth of Ndoped BiOBr layer is originated from the active sites of CFs. These active sites are produced by break the C-C bonds in a strong acid treatment and created oxidation for immobilization of N-doped BiOBr nanosheets. With the prolonging reaction time, the nanosheets are growth and compacted each other to form three-dimensional (3D) interweave hybrid structure (see Fig. S1).

Fig. 2A shows the XRD patterns of pristine CFs, N-doped BiOBr and N-doped BiOBr/CFs. It can be found that the pristine CFs exhibit a broad peak located between 20° and 30° assigned as the d_{002} layers, representing the presence of integral graphite crystal structure [27]. No detectable dopant-related peaks can be observed in N-doped BiOBr except the typical tetragonal structure of BiOBr crystal (JCPDS No. 73-2061) due to the low content and high dispersity of dopants. The N-doped BiOBr/CFs exhibit the typical diffraction peaks of pristine CFs and N-doped BiOBr.

XPS analysis can provide a valuable insight into the surface structure of carbon fiber supported N-doped BiOBr photocatalyst. The XPS survey spectrum of the photocatalyst exhibit prominent peaks of carbon, oxygen, bismuth and relatively feeble peaks of nitrogen, as shown in



Fig. 1. SEM images of N-doped BiOBr/CFs at low and high magnifications (A–D), SEM images of CFs (E), SEM images of N-doped BiOBr/CFs (1 h) at low and high magnifications (F, G), TEM image of N-doped BiOBr composites (H), selected-area electron diffraction (SAED) patterns (I, J) and the d-spacing between the lattice planes (0.292 nm and 0.246 nm) corresponds to the (012) and (111) planes for BiOBr (K, L).

Fig. 2B. The high-resolution XPS spectrum of C1s on the composite photocatalyst is shown in Fig. 2C, which can be fitted as three peaks at binding energies of 289.4, 286.2, and 284.6 eV, respectively. It implies that three different chemical environments of carbon existed in the products. The weak peaks at 286.2 eV and 289.4 eV are usually assigned to the oxygen bound species C-O and C(O)O, and the strong peak at 284.6 eV is ascribed to the elemental carbon [28-30]. Due to the surface oxidation during the preparation process, the oxidized active sites on CFs surface can be contributed to the deposition and growth of N-doped BiOBr. The presence of nitride dopant is confirmed from N1s core level. Two peaks at binding energies of 399.5 eV and 402.5 eV are observed, as shown in Fig. 2D. The peak at 399.5 eV is ascribed to Bi-N bound in nitride layers and the peak at 402.5 eV is assigned to the substitutional N in the BiOBr lattice [31-33]. Furthermore, nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves are carried to investigate the porous structure of the as-prepared samples. The as-prepared samples exhibit the type IV isotherms characteristic of mesoporosity (see Fig. S2). The asprepared N-doped BiOBr/CFs products show the higher surface area $(6.0266 \text{ m}^2/\text{g})$ than that of pure CFs $(0.3268 \text{ m}^2/\text{g})$ due to the covering N-doped BiOBr nanosheet on the surface of CFs. The mean pore diameter of N-doped BiOBr/CFs (3.63 nm) is lower than that of pure CFs (3.99 nm). However, the total pore volume of N-doped BiOBr/CFs (0.0366 mL/g) is larger than that of pure CFs (0.0145 mL/g) owing to the more pores produced by the association of the smaller nanosheets. The absorption edge and band-gap energies of the as-prepared samples are determined by UV-vis diffuse reflectance spectra (see Fig. S3). It can be found that N-doped BiOBr products have stronger absorption under the visible light region compared with pure BiOBr. The N-doped BiOBr/CFs exhibit the stronger absorption in the visible light range due to the black color of CFs and inherent optical performance of N-doped BiOBr products.

The photoactivity of the N-doped BiOBr/CFs samples is evaluated by degradation of RhB ($C_0 = 10 \text{ mg}\cdot\text{L}^{-1}$) under the visible light irradiation and room temperature (T = 300 K), as shown in Fig. 3A. For the comparison, a blank experiment is firstly carried out for indicating the self-photodegradation of RhB. It can be found that RhB self-photodegradation is almost negligible under light irradiation without any catalysts. Compared with the blank experiment, the decolorization rate of RhB can be accelerated in the presence of pure CFs and N-doped BiOBr/CFs in the dark, which can be ascribed to adsorption action of pure CFs or N-doped BiOBr/CFs. The adsorption of RhB on pure CFs or N-doped BiOBr/CFs becomes saturated after 3 h for adsorption and desorption equilibrium in the dark, after which the concentration of



Fig. 2. XRD patterns of original CFs, N-doped BiOBr and N-doped BiOBr/CFs (A), XPS spectrum of the as-prepared N-doped BiOBr/CFs (B) and high-resolution XPS spectra of C1s (C) and N1s (D) over N-doped BiOBr/CFs.

RhB decrease slightly with prolonging time. However, the adsorption amount of RhB with N-doped BiOBr/CFs is higher than that of pure CFs due the higher surface area of the former. Under the light irradiation, the decolorization rate of RhB can be accelerated in presence of pure CFs, which can be ascribed to the dual actions of photolysis and adsorption [28]. The decolorization rate of RhB is further accelerated



Fig. 3. Photocatalytic degradation of RhB (A) and cycling runs for the photodegradation of RhB over as-prepared N-doped BiOBr/CFs (B), SEM image of the N-doped BiOBr/CFs (C) and XRD patterns of N-doped BiOBr/CFs after five cycles (D).

in the presence of the N-doped BiOBr/CFs (see Fig. S4). There is no doubt here that photocatalysis plays an important role to decolor RhB besides photolysis and adsorption. The appearance of N-doped BiOBr on the surface of CFs enlarge its specific surface area, thus increasing the RhB adsorption capacity for N-doped BiOBr/CFs. Meanwhile, the preenriched RhB molecules can be excited by light, and then the photoinduced electrons inject into the conduction band of N-doped BiOBr, triggering the photo-degradation reactions [34,35]. Although the N doping narrows the band gap and shifts up the CB edge due to the strain effects, it is still hard for adjusting the conductive band (CB) of N-doped BiOBr/CFs to the level of RhB due to the broad potential distance between the RhB (-1.12 eV) and BiOBr (0.17 eV) [35,36].

In order to test the re-use performances of composite photocatalysts, the recycle experiment on the photocatalytic decoloration of RhB solution is carried out. As shown in Fig. 3B, the efficiency of photocatalytic decoloration is still maintained without significant decline even after the five cycles. The excellent reuse performance of the N-doped BiOBr/CFs may be resulted from the good binding property between N-doped BiOBr layer and CFs. Only a small numbers of N-doped BiOBr nanosheets is flaked away from CFs after five cycles, as the arrows shown in Fig. 3C. The results of XRD pattern of N-doped BiOBr/CFs show no detectable difference after five cycles which further indicating the stability of N-doped BiOBr/CFs (Fig. 3D).

The photo-catalytic degradation property of colorless methanol a liquid-solid system (5%, v/v) over the N-doped BiOBr/CFs is also investigated under similar conditions. The concentration change of methanol in the photo-catalytic degradation system is evaluated by the highperformance liquid chromatography (HPLC), as shown in Fig. 4A. Before the photo-catalytic degradation, the elution time for the methanol is around 5.7 min, where shows the strongest peak. With the development of photo-catalytic degradation, the intensity of peak decreases gradually which implies the falling of the methanol concentration in the solution. After irradiation for 150 min, the peak at elution time around 5.7 min is almost disappeared completely. Furthermore, no other peaks can be found in the curves, which indicate no intermediate products are formed during the photocatalytic degradation process and the methanol might be degraded directly into CO₂ and H₂O. Calculating the integral area of methanol peak at different reaction time, the conversion ratio of methanol can be obtained, as shown in the inset of Fig. 4A. After irradiation for 2.5 h in the presence of N-doped BiOBr/CFs, more than 90% of methanol has been degraded. The photocatalytic degradation of methanol also can be evaluated by the CO₂ concentration in the gas above liquid surface in a sealed photocatalytic degradation system using gas chromatography (GC) measurement. In the resulting gaseous sample after photodegradation, methanol was found to be decomposed to CO₂ and H₂O from GC analysis, and there are no intermediate products such as hydrocarbons. Fig. 4B shows the concentration of CO₂ generated during the photodegradation of methanol after light irradiation for 2 h under the different conditions. It can be found that the concentration of CO₂ is around 10 ppm without CFs or N-doped BiOBr/CFs in the dark. Under irradiation of light, the concentration of CO₂ is increased to ~ 40 ppm which indicates the self-photodegradation of methanol is negligible. However, the concentration of CO₂ can be achieved to around 420 ppm with presence of N-doped BiOBr/CFs. The concentration of CO₂ increases slightly in the presence of CFs compared with the blank experiment. These phenomena indicate that the selfphotodegradation of methanol is weak and pure CFs do not possess photocatalytic activity. The degradation rate of methanol can be accelerated using the N-doped BiOBr/CFs as catalyst under light irradiation. In addition, there is no doubt here that photocatalysis played an important role to photodegradation methanol besides photolysis and adsorption.

For investigation of plausible reaction mechanism for the superior photocatalytic activity of N-doped BiOBr/CFs and detecting the active species during photocatalytic reactivity, hydroxyl radicals (•OH), the superoxide radical $(0^{\bullet-}_2)$ and holes (h^+) are investigated by adding 1.0 mM isopropyl alcohol (IPA, a guencher of •OH), p-benzoguinone (BQ, a quencher of $O_2^{\bullet-}$) and triethanolamine (TEOA, a quencher of h⁺), respectively [37,38]. The trapping experiments are similar to the photocatalytic activity test above. It can be found that the photocatalytic decoloration of RhB is declined slightly by the addition of 1 mM IPA (a quencher of •OH). However, addition of 1 mM BQ (a quencher of $O_2^{\bullet-}$) or 1 mM TEOA (a quencher of h^+) into the reaction system, the decolorization rate of RhB were decelerated significantly. Therefore, it can be concluded that O_2^{-} and h^+ are the main active species for degradation of organic pollutants solution under visible light irradiation, rather than •OH, as shown in Fig. 5. On the basis of our experiment results, the plausible reaction mechanism for the superior photocatalytic activity of N-doped BiOBr/CFs samples is proposed (Scheme 1). The UVvisible light irradiation activates N-doped BiOBr/CFs to generate strongly oxidative holes (h^+) in valence band and reductive electrons (e^-) in conduction band. Then these photo-induced electrons are trapped by molecular oxygen (O_2) to form superoxide ions $(O_2^{\bullet-})$. On the other hand, the electron transfer between N-doped BiOBr and CFs will greatly retard the recombination of photo induced charge carriers and prolong electron lifetime, which may be an important role for the excellent photoactivity of N-doped BiOBr/CFs samples [18,19,39,40].



Fig. 4. Photocatalytic degradation of methanol using N-doped BiOBr/CFs as catalyst under the light irradiation (A) and the relationship between the amount of CO₂ evolved over different photocatalytic materials (C).



Fig. 5. Trapping experiment of active species during the photocatalytic degradation of RhB reaction.

4. Conclusion

In summary, the N-doped BiOBr nanosheets with visible light photocatalytic properties have been immobilized on the surface of CFs by a facile solvothermal route. The morphologies, structural properties and photocatalytic activities of the resultant N-doped BiOBr/CFs hybrid structure were investigated. At the same time, it also proves that the final removal of organic pollutants from solutions is caused by photocatalytic degradation rather than by sorption. Furthermore, the threedimensional (3D) N-doped BiOBr/CFs hybrid structure can capture light from all directions, thus showing potential for application in places with high albedo (high fraction of reflected radiation). This work may provide new insights into preparing other inorganic photocatalytic fibers and may extend their potential applications for degradation of organic pollutants.

Acknowledgments

This work was financially supported by the "521 Talents Training Plan" in ZSTU, the Scientific Research Foundation for the Returned Overseas Chinese Scholars, the State Education Ministry (1001603-C) and the National Natural Science Foundation of China (51373155, 51133006). X. L. thanks the Innovative Program for Graduate Students of Zhejiang Sci-Tech University through grant YCX12013 and Training Plan for Excellent Master's Thesis through grant 2013YSPY14.



Scheme 1. Schematic illustration of the photocatalytic mechanism of organic pollutants degradation over N-doped BiOBr/CFs photocatalyst.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.powtec.2014.04.005.

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