available at www.sciencedirect.com

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

Article

Microspheres of graphene oxide coupled to N-doped $\text{Bi}_2\text{O}_3\text{CO}_3$ for visible light photocatalysis

Ruiben Jin*, Xiaojia Jiang, Yangyuan Zhou, Jianfu Zhao

College of Environmental Science and Engineering, State Key Laboratory of Pollution Control and Resources Reuse, Tongji University, Shanghai 200092, China

ARTICLE INFO

Article history:

Received 26 November 2015

Accepted 26 February 2016

Published 5 May 2016

Keywords:

Graphene oxide

Nitrogen-doped bismuth subcarbonate

Hydrothermal approach

Activity enhancement

Nitrogen oxide removal

ABSTRACT

Hierarchical microspheres of a graphene oxide (GO) coupled to N-doped $(\text{BiO})_2\text{CO}_3$ composite (N-BOC-GO) was synthesized by a simple hydrothermal approach. The N-BOC-GO composite gave enhancement in photocatalytic activity compared to the pure BOC and N-BOC samples. With 1.0 wt% GO, 62% NO removal was obtained with N-BOC-GO. The factors enhancing the photocatalytic performance were the high electron-withdrawing ability and high conductivity of GO and improved visible light-harvesting ability of N-BOC-GO with a 3D hierarchical architecture due to the surface scattering and reflecting (SSR) effect. An effective charge transfer from N-BOC to GO was demonstrated by the much weakened photoluminescence intensity of the N-BOC-GO composite. This work highlights the potential application of GO-based photocatalysts in air purification.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

The increasing demand for clean energy and increasing environmental pollution are severe issues around the world. Many strategies and solutions have been adopted to solve the problems [1,2]. Among these, photocatalysis pioneered by Fujishima et al. [3] has long been regarded as a highly efficient technology and has great potential for solving the current energy crisis and environmental deterioration. Many photocatalytic materials have been developed [4–8]. Since the first report was published in 1972 of photocatalytic splitting of water on TiO_2 electrodes, TiO_2 as a photocatalyst with chemical stability, non-toxicity and low cost has been demonstrated in areas such as energy conversion and contaminants degradation, and in solar cells [9–13]. However, it notoriously suffers from the

rapid recombination rate of photogenerated electron-hole pairs and the low utilization of solar energy (it can only be excited by UV light) and thus has inferior photocatalytic activity, which inhibited its applications in photocatalysis. In addition to the urgent demand for exploring visible light photocatalysts, the development of innovative strategies to improve the photocatalytic activity of known photocatalysts is also indispensable for applications. Therefore, it is a great challenge to develop a visible light-driven photocatalyst with superior photocatalytic activity.

Among the various semiconductors, $(\text{BiO})_2\text{CO}_3$ is a promising photocatalyst because of its attractive morphology, exceptional photochemical stability and high photocatalytic efficiency [14]. However, the photocatalytic performance of $(\text{BiO})_2\text{CO}_3$ is limited by the following two reasons. (1) The wide band gap

* Corresponding author. Tel/Fax: +86-021-65135472; E-mail: beny1224@163.com

This work was supported by the National Natural Science Foundation of China (21277097) and the Key Projects in the National Science & Technology Pillar Program during the 12th Five-Year Plan Period (2012BAJ21B01).

DOI: 10.1016/S1872-2067(15)61079-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 5, May 2016

of $(\text{BiO})_2\text{CO}_3$ means it has poor visible light harvesting ability. Anion doping as an efficient strategy is most widely investigated because of its effectiveness in broadening the light responsive range of wide bandgap semiconductors. Recently, Dong et al. [15,16] reported N-doped $(\text{BiO})_2\text{CO}_3$ hierarchical microspheres made by an in situ method with efficient and durable visible light driven photocatalytic activity. (2) The photocatalytic generated electron-hole pairs have a rapid recombination rate in $(\text{BiO})_2\text{CO}_3$, which results in low photocatalytic reactivity. Therefore, it is still a problem to enhance the photocatalytic efficiency of $(\text{BiO})_2\text{CO}_3$. One efficient way to improve the photocatalytic performance is to reduce electron-hole recombination by hybridizing with graphene or graphene oxide (GO) [17–22]. For example, Zhang et al. [23] synthesized graphene-wrapped $(\text{BiO})_2\text{CO}_3$ core-shell structures with high photocatalytic activity for carbamazepine degradation. Madhusudan et al. [24] prepared novel hierarchical graphene- $(\text{BiO})_2\text{CO}_3$ composites with enhanced photocatalytic performance for the degradation of rhodamine B under visible light. However, no research on GO wrapped N-doped $(\text{BiO})_2\text{CO}_3$ has been reported.

In the present study, to solve the drawbacks of $(\text{BiO})_2\text{CO}_3$ of a narrow visible light response range and high charge carrier recombination rate, a combined strategy based on the simultaneous introducing of anion doping (i.e. N-doping) and hybridization with GO was developed. A one-step hydrothermal method was further developed to produce the GO coupled N-doped $(\text{BiO})_2\text{CO}_3$ microsphere composite, which achieved a high visible light photocatalytic activity of NO removal ratio of 62%. Furthermore, this work highlights the mechanism for enhancing the photocatalytic performance after the introduction of only 1.0 wt% GO.

2. Experimental

2.1. Sample preparation

The GO coupled N-doped $\text{Bi}_2\text{O}_2\text{CO}_3$ microspheres (N-BOC-GO) was prepared by a hydrothermal method. All the reagents used in this research were analytical grade and were utilized without further purification. Deionized (DI) water was used in all experiments. GO was purchased from Nanjing Xianfeng Chemical Factory, China. In a typical synthesis, an amount of bismuth citrate (1.60 g) was dissolved in a concentrated ammonia solution (28%, 3.8 mL). The light yellow solution was stirred for 5 min. Deionized water (46 mL) was added into the solution. GO (0.01 g) was then added, and the resulting solution was subjected to ultrasonic sonication for 30 min. Next, the mixture was further vigorously stirred for 15 min to ensure it was homogeneous. After that, the solution was transferred into a 100 mL Teflon-lined autoclave and held at 180 °C for 24.5 h. After reaction, the precipitate was collected by centrifugation, and then rinsed with deionized water and ethanol several times to remove the impurity. The final product (labeled as N-BOC-GO) was dried in an oven at 70 °C overnight. Pure $\text{Bi}_2\text{O}_2\text{CO}_3$ without N-doping or GO and N-doped $\text{Bi}_2\text{O}_2\text{CO}_3$ without any GO were prepared using the same experimental

conditions for the purpose of comparison and were labeled as BOC and N-BOC, respectively.

2.2. Characterization

The crystal phase of the samples was investigated by an X-ray diffractometer (XRD, model D/max RA, Japan). X-ray photoelectron spectroscopy (XPS) with Al K_α X-rays (Thermo ESCALAB 250, USA) was used to investigate the surface properties. The morphology and microstructure of the samples were characterized by scanning electron microscopy (SEM-EDX, JEOL model JSM-6490, Japan), transmission electron microscopy (TEM, JEM-2010, Japan) and high resolution transmission electron microscopy (HRTEM). Fourier transform infrared spectroscopy (FT-IR) was recorded on a Nicolet Nexus spectrometer on samples embedded in KBr pellets, which was used to detect the functional groups on the samples. Raman spectra were recorded at room temperature using a micro-Raman spectrometer (Renishaw InVia) in the backscattering geometry with a 514.5 nm Ar⁺ laser excitation source. Nitrogen adsorption and desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA). The sample was degassed at 110 °C prior to the measurement. The optical properties of the samples were obtained by a Scan ultraviolet-visible spectrophotometer (UV-vis DRS, UV-2450, Shimadzu, Japan) equipped with an integrating sphere assembly, using BaSO_4 as the reflectance sample. The photoluminescence (PL) spectra of the samples were obtained using a fluorescence spectrophotometer (FS-2500, Japan) with an Xe lamp with an optical filter as the excitation source, which was used to investigate the recombination and separation of photogenerated electrons and holes in the samples.

2.3. Visible light photocatalytic activity

The photocatalytic activity was evaluated by the oxidation of NO at the ppb level in a continuous flow reactor at ambient temperature. The volume of the rectangular reactor made of stainless steel and covered with Saint-Glass was 4.5 L (30 cm × 15 cm × 10 cm). A 150-W commercial tungsten halogen lamp was vertically placed above the reactor. A UV cutoff filter (420 nm) was adopted to remove UV light in the light beam. The photocatalyst (0.2 g) was coated onto two dishes with a diameter of 12.0 cm. The coated dish was then pretreated at 70 °C to remove water in the suspension. The NO gas was from a compressed gas cylinder at a concentration of 100 ppm of NO (N_2 balance). The initial concentration of NO was diluted to 600 ppb by an air stream. The desired relative humidity (RH) level of the NO flow was controlled at 50% by passing the zero air stream through a humidification chamber. The gas streams were premixed by a gas blender. The flow rate was controlled at 2.4 L/min by a mass flow controller. After adsorption equilibrium was achieved, the lamp was turned on. The concentration of NO was continuously measured by a chemiluminescence NO analyzer (Thermo Environmental Instruments Inc., 42i-TL), which monitors NO, NO_2 , and NO_x (NO_x represents NO + NO_2) with a sampling rate of 1.0 L/min. The removal ratio (η) of NO

was calculated as $\eta = (1 - C/C_0) \times 100\%$, where C and C_0 are the concentrations of NO in the outlet steam and the feed stream, respectively.

3. Results and discussion

3.1. Chemical composition

XRD patterns were recorded for the N-BOC samples to confirm the crystallographic phase of N-BOC in the composite and investigate the influence of GO on the crystallinity of the N-BOC microspheres. Figure 1(a) shows the XRD patterns of the N-BOC-GO microspheres prepared with only 1.0 wt% of GO as compared to that of the N-BOC. The diffraction peaks of the N-BOC showed that it was a tetragonal $\text{Bi}_2\text{O}_2\text{CO}_3$ phase (JCPDSICDD 41-1488). For N-BOC-GO, no characteristic diffraction peak for the carbon species was detected, which was attributed to the small amount and relatively low diffraction intensity of GO as well as its high dispersion in the hybrid composite. Notably, no changes in the diffraction peaks and lattice parameters of $\text{Bi}_2\text{O}_2\text{CO}_3$ in the N-BOC-GO composite were observed, indicating that the GO was on the surface and did not distort the lattice of $\text{Bi}_2\text{O}_2\text{CO}_3$ [25,26]. Figure 1(a) indicated that the peak intensity of the (110) peak was stronger than that of the (103) peak, suggesting that the samples have a perpendicular growth along the (110) crystallographic plane [27], which was further demonstrated by HRTEM (Fig. 5(b)). Figure 1(b) shows the enlarged (103) and (110) diffraction peak region. It can be seen that the peak intensity of N-BOC-GO was stronger while the peak width at half-height was narrower than those of N-BOC, which imply an enhanced crystallinity nature of the composite after introducing 1.0 wt% of GO.

The interaction between N-doped $\text{Bi}_2\text{O}_2\text{CO}_3$ and GO in the composite was investigated by XPS as shown in Fig. 2. The peaks with the binding energies at 164.7 and 159.3 eV corresponding to Bi $4f_{5/2}$ and Bi $4f_{7/2}$ can be assigned to the Bi^{3+} oxidation state (Fig. 2(a)) [15]. Compared to N-BOC, these peaks in N-BOC-GO were shifted to lower binding energy, indicating the presence of a strong interaction between the N-doped $\text{Bi}_2\text{O}_2\text{CO}_3$ microsphere and graphene oxide. For N-BOC, the O 1s spectrum could be fitted to three peaks at 532.5, 531.26 and 530.14 eV. The peak at 530.14 eV was ascribed to the Bi–O bond in

$\text{Bi}_2\text{O}_2\text{CO}_3$, and the other two peaks at 532.5 and 531.26 eV can be identified as due to H_2O adsorbed on the surface and a carbonate species (Fig. 2(b)). The C 1s peaks at 284.8, 286.3 and 287.8 eV were assigned to adventitious carbon species, while the peak at 288.8.0 eV was assigned to the carbonate ion in $\text{Bi}_2\text{O}_2\text{CO}_3$ (Fig. 2(c)) [28]. In contrast to N-BOC, the O 1s and C 1s peaks for the carbonate species and adventitious carbon species were stronger with N-BOC-GO. This was because GO contains oxygen-containing and carbon-containing functional groups [29]. The high resolution N 1s peak located at 400 eV can be observed for N-BOC and N-BOC-GO, as shown in Fig. 2(d), indicating that elemental N was successfully doped into the samples.

FT-IR was used to investigate the existence of GO in N-BOC-GO composite because GO displays the characteristic IR spectra for the oxygen-containing functional groups on its surface. As illustrated in Fig. 3(a), the absorption bands of the samples are similar, but the peak intensity of the two absorption bands (i.e. 1051 and 1405 cm^{-1}) for N-BOC-GO were increased by the coupling with 1.0 wt% GO as compared to that of N-BOC. The two characteristic absorption bands corresponded to the alkoxy C–O stretching and the carboxyl O–H stretching of GO [30]. The broad peaks in the range of 1495–1700 and 3200–3600 cm^{-1} were assigned to the vibrations of surface hydroxyl groups and molecular water. It is worthwhile to note that the peaks of the hydroxyl groups in the range of 1495–1700 cm^{-1} became obscured, which was attributed to the influence of the surface hydroxyls on GO. In particular, the peaks of the hydroxyl groups were vanished by introducing GO, resulting in the enhanced crystallinity of N-BOC-GO [31]. This result is in good agreement with the XRD data.

Raman spectroscopy is often used to characterize the disorder and defect structures of GO. Figure 3(b) shows the Raman spectra of N-BOC and N-BOC-GO. Compared with N-BOC, two characteristic prominent broad Raman bands were observed with N-BOC-GO at 1600 and 1359 cm^{-1} , which were due to the G and D bands of GO, respectively [32]. The G band corresponds to the C–C stretching vibrations of sp^2 hybridized carbon atoms. The D band is associated with sp^3 defects in carbon. FT-IR combined with Raman revealed the presence of GO in the composite.

Fig. 1. XRD patterns (a) and the (103) and (110) diffraction region (b) of N-BOC and N-BOC-GO samples.

Fig. 2. XPS spectra of the N-BOC and N-BOC-GO samples. (a) Bi 4f; (b) O 1s; (c) C 1s; (d) N 1s.

Fig. 3. FT-IR spectra (a) and Raman spectra (b) of the samples.

3.2. Microstructure

The morphology of the samples was analyzed by SEM to directly observe the microstructure of 1.0 wt% GO decorated N-BOC microspheres, and to specifically investigate the influence of GO on the morphology of the N-BOC microspheres. The SEM image of N-BOC-GO (Fig. 4(a)) showed that the composite sample comprised irregularly agglomerated approximately spherical microspheres. The size of the prepared N-BOC-GO microspheres has an average diameter of 1.5 μm . After the addition of GO, the N-BOC-GO microspheres were anchored to GO with a wrinkled and ultrathin surface, indicating that GO inter-

acted with the N-BOC microspheres by physisorption or electrostatic binding or charge transfer interaction rather than by a chemical reaction. The SEM micrograph at higher magnification provided in Fig. 4(b) revealed that the N-BOC-GO microspheres with a 3D hierarchical architecture were composed of a large number of 2D nanoplates with a thickness of approximately 10 nm. Evidently, the N-BOC microspheres were wrapped in GO nanosheets, which suggested that the GO nanosheets were not incorporated into the lattice of N-BOC and have no effect on the morphology of the N-BOC-GO composite. This result was consistent with the XRD data.

The microstructure of N-BOC-GO was investigated in further detail by TEM, HRTEM and EDX elemental mapping. As can

Fig. 4. SEM images of the N-BOC-GO sample.

from Fig. 5(a), the TEM images of N-BOC-GO showed that N-BOC-GO microspheres were present on the surface of GO, which has a characteristic wrinkle on the edge. The result further confirmed the combination of GO and N-BOC microspheres, which was also in agreement with the SEM results (Fig. 4). More important, because the N-BOC microspheres interacted with the GO through physisorption or a charge transfer or electrostatic interaction, the interaction between the N-BOC microspheres and GO can be beneficial for electron transfer from the N-BOC microspheres to GO in the photoexcitation process. The corresponding HRTEM image of N-BOC-GO (Fig. 5(b)) revealed the well-defined crystallinity of the N-BOC microspheres. The lattice fringes of individual N-BOC microspheres with d spacing of 0.271 nm can be ascribed to the (110) crystal plane of crystalline BOC. The result further confirmed that the N-BOC-GO microspheres grew along the (110) direction, which agreed with the XRD patterns. To further confirm the presence of GO, EDX mapping of O, Bi and C elements were conducted (Fig. 5(c)–(e)). One can see that the C element was homogeneously distributed on the N-BOC-GO sample, and also further confirming the formation of a N-BOC-GO composite.

Nitrogen adsorption isotherms (Fig. 6(a)) for these two samples were used for a further investigation of their morphology. They gave a type IV isotherm with a typical H3 hysteresis loop characteristic of mesoporous solids [33]. Their corresponding pore size distributions are displayed in Fig. 6(b). An obvious bimodal pore size distribution was observed, which showed medium mesopores with a pore diameter of 3.7 nm, and large mesopores and macropores in a wide range of 10–100 nm. This further confirmed the formation of mesopores and macropores. These pores were created by the aggregated

Fig. 5. TEM (a), HRTEM (b) images and EDX mapping ((c)–(e)) of N-BOC-GO.

nanoplates. The specific BET surface areas were calculated to be 46 and 42 cm^3/g , for N-BOC and N-BOC-GO, respectively, indicating that GO had little influence on the microstructure.

3.3. Optical properties and charge transfer

It is well known that the optical properties of semiconductor photocatalysts are important factors in their photocatalytic activity. A comparison of the UV-vis DRS of BOC, N-BOC and N-BOC-GO is displayed in Fig. 7. Compared with BOC, N-BOC shows an increased light absorption range from 360 to 500 nm caused by N doping. The combination of GO with the N-BOC microspheres gave a change in the optical absorption. There was an obvious significantly enhanced absorption intensity of visible light after a small amount of GO was introduced into the N-BOC microspheres. This result showed that the absorption ability of N-BOC could be greatly improved by the addition of GO. Xiong et al. [34] reported that hierarchical nanostructures could create multiple light reflecting and scattering to enhance the light absorption probability (the SSR effect). This means that the 3D hierarchical architecture endowed the N-BOC-GO microspheres with enhanced light absorption by the SSR effect, and a more efficient utilization of solar energy can be obtained

Fig. 6. N_2 adsorption isotherms (a) and the pore diameter distribution (b) of N-BOC and N-BOC-GO.

Fig. 7. UV-vis diffuse reflectance spectra of BOC, NBOC, and N-BOC-GO photocatalysts.

accordingly. The band gap values (E_g) of the three samples based on the UV-vis DRS data were calculated. The band gaps of BOC, N-BOC, and N-BOC-GO were 3.42, 3.27, and 3.08 eV, respectively [35]. The band edges show an evident red shift, which indicated that the optical property of N-BOC-GO was successfully improved by the introduction of GO.

PL spectra have been extensively used to see the efficiency of charge carrier trapping, migration, and separation and to investigate the fate of photogenerated electron-hole pairs [36]. As seen in Fig. 8, GO exhibited a significant influence on this optical property. The PL intensity of the N-BOC-GO composite was noticeably decreased by the addition of only 1.0 wt% GO as compared with N-BOC. The result implied that the N-BOC-GO composite can dramatically suppress the recombination of electrons and holes under visible light irradiation and lead to improved photocatalytic performance. This was ascribed to the fact that in the transport of photogenerated electrons from N-BOC to GO under visible light illumination, GO can serve as an acceptor of the generated electrons of N-BOC, which effectively decrease charge recombination and leaving more photogenerated charges to participate in the chemical reaction.

3.4. Visible light photocatalytic activity and stability

Recently, Li et al. [37] synthesized mesoporous $g\text{-C}_3\text{N}_4$ with a graphene oxide nanocomposite and also applied it as the

Fig. 8. PL emission spectra of N-BOC and N-BOC-GO.

photocatalyst in the removal of NO under visible light irradiation. They obtained a maximum NO removal rate of 60.7%. Steng et al. [38] prepared TiO_2 -graphene oxide nanocomposite and applied it in the photocatalytic degradation of butane in the gas phase. This gave excellent photocatalytic activity under both UV and visible light irradiation. These results convincingly demonstrate that GO is a very promising candidate for developing photocatalysts with high performance. Therefore, a simple combined strategy was employed by hybridizing only 1.0 wt% GO with N-BOC in order to get an expected significant improvement in photocatalytic activity. For BOC and N-BOC, relatively low photocatalytic removal rates of NO (17% and 28%, respectively) were observed due to the rapid recombination of photogenerated electron-hole pairs under visible light irradiation (Fig. 9(a)). After the introduction of 1.0 wt% of GO, as we expected, the photocatalytic activity of N-BOC-GO was greatly enhanced to 62% after 30 min visible light illumination. This was attributed to two main factors. First, as compared to pure BOC, the reduced band gap of the N-BOC-GO microspheres caused by N doping and the introducing of GO, and the SSR effect from its 3D hierarchical architecture allowed solar energy to be utilized more efficiently. Second, when compared with N-BOC, in the N-BOC-GO system, GO can work as an acceptor of the photogenerated electrons of N-BOC and the recombination between the photoinduced charge carriers can be much suppressed, leading to the high efficiency of NO removal. Note that the initial NO_x removal over N-BOC-GO was slightly slower than that of BOC and N-BOC, probably because the GO was first converted into reduced GO (rGO) with better conductivity by photo-generated electrons.

In particular, the stability of a photocatalyst is crucial for practical application [39,40]. To evaluate the stability of the N-BOC-GO photocatalyst for removal of NO under irradiation of visible light, recycling experiments under the same conditions were conducted. As seen in Fig. 9(b), the removal rate of NO for N-BOC-GO continued steadily without noticeable deactivation after five runs, which indicated the stability of N-BOC-GO.

3.5. Formation process and mechanism of activity enhancement

On the basis of the above analysis, a formation mechanism of the N-BOC-GO microspheres is depicted in Fig. 10. In the hydrothermal process, N-BOC self-assembles into a hierarchical conglomeration through molecular interaction, which is then transformed into 3D microspheres driven by the minimization of surface energy. After adding a small amount of GO, the N-BOC microspheres interact with GO through physisorption or electrostatic binding or charge transfer interaction and homogeneously disperse on the surface of GO. Eventually, the morphology of the final composite (i.e. N-BOC-GO) was like that of roses (N-BOC) with leaves (GO).

Besides the important role of the formation process of N-BOC-GO, it is interesting to study the mechanism of enhanced photocatalytic activity by N-BOC-GO. As illustrated in Fig. 10, under visible light irradiation, photogenerated electrons and holes are created over N-BOC, and electrons are transferred from N-BOC to the surface of GO. This can be explained by the

Fig. 9. Photocatalytic removal of NO in a single pass flow of air over BOC, N-BOC and N-BOC-GO samples (a) and stability of N-BOC-GO in multiple runs of photocatalytic removal of NO (b) under visible light irradiation (continuous reactor, NO concentration: 600 ppb).

Fig. 10. Schematic of the formation process of N-BOC-GO microspheres and the mechanism of photocatalytic activity enhancement.

fact that GO can serve as an electron collector and transport medium to efficiently separate the photogenerated electron-hole pairs, which prolong the lifetime of the charge carriers. This result also is in accordance with the variation of the PL intensity (Fig. 8). Holes in the valence band (VB) of N-BOC can directly oxidize NO or induce the production of $\cdot\text{OH}$ to oxidize NO to produce NO_3^- and small amounts of NO_2 and NO_2^- [15]. Furthermore, the unique characteristics of GO allows photocatalytic reactions to take place not only on the surface of the N-BOC photocatalyst, but also on the GO sheets and thus greatly enlarge the reaction space. In summary, the introduction of GO into the N-BOC system efficiently separates the photogenerated carriers and increases the reaction active sites.

4. Conclusions

A N-BOC-GO composite was prepared by a simple hydrothermal method. N-BOC-GO was uniformly dispersed on the surface of GO, which facilitated the transfer of photogenerated charge carriers from N-BOC to GO. The effects of 1.0 wt% GO on the crystallinity, morphology, light absorbance property and PL intensity of N-BOC were systematically investigated. N-BOC-GO microspheres with a 3D hierarchical architecture favored the efficient utilization of solar energy, and the addition of GO

promoted the rapid separation of photogenerated electron-hole pairs. The composite with a high photocatalytic activity will help extend applications in the environmental and energies areas.

References

- [1] W. A. Jury, H. Vaux Jr, *Proceed. Nat. Acad. Sci. USA*, **2005**, 102, 15715–15720.
- [2] J. C. Swarbrick, U. Skyllberg, T. Karlsson, P. Glatzel, *Inorg. Chem.*, **2009**, 48, 10748–10756.
- [3] A. Fujishima, K. Honda, *Nature*, **1972**, 238, 37–38.
- [4] G. H. Dong, W. K. Ho, Y. H. Li, L. Z. Zhang, *Appl. Catal. B*, **2015**, 174–175, 477–485.
- [5] X. X. Xu, C. Randorn, P. Efstathiou, J. T. S. Irvine, *Nat. Mater.*, **2012**, 11, 595–598.
- [6] D. J. Martin, N. Umezawa, X. W. Chen, J. H. Ye, J. W. Tang, *Energy Environ. Sci.*, **2013**, 6, 3380–3386.
- [7] S. X. Ouyang, H. Tong, N. Umezawa, J. Y. Cao, P. Li, Y. P. Bi, Y. J. Zhang, J. H. Ye, *J. Am. Chem. Soc.*, **2012**, 134, 1974–1977.
- [8] J. Jiang, K. Zhao, X. Y. Xiao, L. Z. Zhang, *J. Am. Chem. Soc.*, **2012**, 134, 4473–4476.
- [9] J. W. Tang, J. R. Durrant, D. R. Klug, *J. Am. Chem. Soc.*, **2008**, 130, 13885–13891.
- [10] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.*, **1995**, 95, 69–96.

Graphical Abstract

Chin. J. Catal., 2016, 37: 760–768 doi: 10.1016/S1872-2067(15)61079-8

Microspheres of graphene oxide coupled to N-doped $\text{Bi}_2\text{O}_2\text{CO}_3$ for visible light photocatalysis

Ruiben Jin*, Xiaojia Jiang, Yangyuan Zhou, Jianfu Zhao
Tongji University

Microspheres of graphene oxide (GO) coupled to N-doped $(\text{BiO})_2\text{CO}_3$ showed improved photocatalytic activity compared to pure BOC and N-BOC, which was due to the high electron-withdrawing ability and conductivity of GO and improved visible light harvesting ability of the 3D hierarchical architecture.

- [11] A. Fujishima, X. T. Zhang, C. R. Chim., **2006**, 9, 750–760.
- [12] A. Fujishima, X. T. Zhang, D. A. Tryk, *Int. J. Hydrogen Energy*, **2007**, 32, 2664–2672.
- [13] A. J. Frank, N. Kopidakis, J. van de Lagemaat, *Coord. Chem. Rev.*, **2004**, 248, 1165–1179.
- [14] F. Dong, W. K. Ho, S. C. Lee, Z. B. Wu, M. Fu, S. C. Zou, Y. Huang, *J. Mater. Chem.*, **2011**, 21, 12428–12436.
- [15] F. Dong, Y. J. Sun, M. Fu, W. K. Ho, S. C. Lee, Z. B. Wu, *Langmuir*, **2012**, 28, 766–773.
- [16] F. Dong, R. Wang, X. W. Li, W. K. Ho, *Appl. Surf. Sci.*, **2014**, 319, 256–264.
- [17] Q. J. Xiang, J. G. Yu, M. Jaroniec, *Chem. Soc. Rev.*, **2012**, 41, 782–796.
- [18] Q. J. Xiang, B. Cheng, J. G. Yu, *Angew. Chem. Int. Ed.*, **2015**, 54, 11350–11366.
- [19] B. Yuan, J. X. Wei, T. J. Hu, H. B. Yao, Z. H. Jiang, Z. W. Fang, Z. Y. Chu, *Chin. J. Catal.*, **2015**, 36, 1009–1016.
- [20] Y. H. Zhang, B. Shen, H. W. Huang, Y. He, B. Fei, F. Z. Lv, *Appl. Surf. Sci.*, **2014**, 319, 272–277.
- [21] W. D. Zhang, F. Dong, W. Zhang, *Appl. Surf. Sci.*, **2015**, 358, 75–83.
- [22] Q. Li, X. Li, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, *Adv. Energy Mater.*, **2015**, 5, 1500010–1500037.
- [23] Y. L. Zhang, D. Y. Li, Y. G. Zhang, X. F. Zhou, S. J. Guo, L. B. Yang, *J. Mater. Chem. A*, **2014**, 2, 8273–8280.
- [24] P. Madhusudan, J. G. Yu, W. G. Wang, B. Cheng, G. Liu, *Dalton Trans.*, **2012**, 41, 14345–14353.
- [25] F. Dong, S. C. Lee, Z. B. Wu, Y. Huang, M. Fu, W. K. Ho, S. C. Zou, B. Wang, *J. Hazard. Mater.*, **2011**, 195, 346–354.
- [26] F. Dong, H. T. Liu, W. K. Ho, M. Fu, Z. B. Wu, *Chem. Eng. J.*, **2013**, 214, 198–207.
- [27] F. Dong, T. Xiong, Z. W. Zhao, Y. J. Sun, M. Fu, *CrystEngComm*, **2013**, 15, 10522–10532.
- [28] W. L. Cen, T. Xiong, C. Y. Tang, S. D. Yuan, F. Dong, *Ind. Eng. Chem. Res.*, **2014**, 53, 15002–15011.
- [29] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.*, **2010**, 39, 228–240.
- [30] T. Szabó, E. Tombač, E. Illés, I. Dékány, *Carbon*, **2006**, 44, 537–545.
- [31] Q. Y. Li, H. T. Liu, F. Dong, M. Fu, *J. Colloid Interface Sci.*, **2013**, 408, 33–42.
- [32] K. N. Kudin, B. Ozbas, H. C. Schniepp, R. K. Prud'homme, I. A. Aksay, Roberto Car, *Nano Lett.*, **2008**, 8, 36–41.
- [33] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniowska, *Pure Appl. Chem.*, **1985**, 57, 603–619.
- [34] T. Xiong, F. Dong, Z. B. Wu, *RSC Adv.*, **2014**, 4, 56307–56312.
- [35] A. B. Murphy, *Sol. Energy Mater. Sol. Cells*, **2007**, 91, 1326–1337.
- [36] G. G. Zhang, M. W. Zhang, X. X. Ye, X. Q. Qiu, S. Lin, X. C. Wang, *Adv. Mater.*, **2014**, 26, 805–809.
- [37] F. Dong, Y. H. Li, Z. Y. Wang, W. K. Ho, *Appl. Surf. Sci.*, **2015**, 358, 393–403.
- [38] V. Štengl, S. Bakardjieva, T. M. Grygar, J. Bludská, M. Kormunda, *Chem. Cent. J.*, **2013**, 7, 41–52.
- [39] F. Dong, T. Xiong, Y. J. Sun, H. W. Huang, Z. B. Wu, *J. Mater. Chem. A*, **2015**, 3, 18466–18474.
- [40] T. Xiong, H. W. Huang, Y. J. Sun, F. Dong, *J. Mater. Chem. A*, **2015**, 3, 6118–6127.

耦合氧化石墨烯的 N 掺杂 $\text{Bi}_2\text{O}_2\text{CO}_3$ 微球光催化性能增强机制

金瑞奔*, 蒋孝佳, 周仰原, 赵建夫

同济大学环境科学与工程学院污染控制与资源化国家重点实验室, 上海 200092

摘要: 光催化作为一种环境友好技术, 在解决环境污染和能源匮乏问题方面展现出巨大应用潜力。TiO₂ 因其化学稳定性、无毒和低成本被广泛应用于能源转换和污染物降解等领域, 但其快速的电子-空穴复合与低太阳能利用率等限制了其在光

催化中的潜在应用. 因此, 寻找新的有优越可见光活性的催化剂是一个挑战. 最近, $(\text{BiO})_2\text{CO}_3$ 因其独特的形貌、化学稳定性和较高的催化效率成为有前景的光催化剂. 然而, $(\text{BiO})_2\text{CO}_3$ 较大的带隙限制了对太阳光的利用, 快速的电子-空穴复合阻碍了光催化性能的提高. 因此, 提高 $(\text{BiO})_2\text{CO}_3$ 的光催化效率是当务之急.

近期研究表明, 通过与氧化石墨烯杂交提高载流子的分离能力, 可有效增强光催化性能. 基于此, 我们设计并合成了一种氮掺杂的 $(\text{BiO})_2\text{CO}_3$ 与氧化石墨烯(GO)耦合的新型光催化剂(N-BOC-GO). 首先, 通过一步水热法合成了 N-BOC-GO 微球. N-BOC-GO 光催化剂对 NO 可见光光催化去除性能达到 62%. 采用 X 射线衍射(XRD)、X 射线光电子能谱(XPS)、扫描电子显微镜(SEM)、紫外-可见漫反射光谱(UV-Vis)和光致发光光谱(PL)等表征手段研究了 N-BOC-GO 的光催化性能增强机制. 从 N-BOC-GO 的 XRD 谱中没有发现 GO 的衍射峰, 说明加入的 GO 分散度高; N-BOC-GO 中的 BOC 晶格参数没有发生变化, 说明 GO 没有进入 BOC 晶格, 但加入 GO 增强了 N-BOC 的结晶度. XPS 结果表明, 与 N-BOC 相比, N-BOC-GO 的峰位置发生了明显位移, 表明 N-BOC 和 GO 之间存在强相互作用. 此外, FT-IR 和拉曼光谱证明了在复合物中存在 GO. SEM 表明, N-BOC 规则地团聚成微球, 且微球被固定在有褶皱的 GO 片上. 这说明 GO 与 N-BOC 的作用是静电作用或物理作用, 在光激发过程中有利于 N-BOC 微球上的电子转移到 GO 片上. UV-Vis 图谱中, N-BOC-GO 表现出明显增强的可见光吸收, 说明加入 GO 会明显提高 N-BOC 的吸收能力. 此外, 3D 分层结构会通过 SSR 效应提高光吸收. 从 PL 图可以发现, N-BOC-GO 的电子-空穴复合明显下降, 说明 GO 可以转移电子从而提高光催化性能.

结合前面的分析, 我们提出了 N-BOC-GO 光催化剂 3D 分层结构的形成和性能增强机制. 在水热过程中, 通过分子间相互作用使 N-BOC 自组装成块, 随后在表面能最小化的作用下转化成 3D 微球. 加入 GO 后, N-BOC 和 GO 通过物理吸附使得 N-BOC 微球均匀分散在 GO 上, 最后 N-BOC-GO 的形貌类似于玫瑰花和其叶子的组合. 在可见光照射下, N-BOC 产生电子-空穴对, 电子从 N-BOC 表面转移到 GO 表面, 表明 GO 可作为电子的收集者和传递者以有效分离电子-空穴对, 延长载流子寿命. N-BOC 价带上的空穴可以直接氧化 NO 或产生 $\cdot\text{OH}$ 氧化 NO. 此外, 由于 GO 独特的特征, 光催化反应发生在 N-BOC 催化剂表面和 GO 片上, 从而提高了反应空间位点. 故引入 GO 于 N-BOC 体系中可有效分离光生载流子和提高反应活性位点, 从而显著提高可见光催化性能.

关键词: 氧化石墨烯; 氮掺杂 $(\text{BiO})_2\text{CO}_3$; 水热法; 活性增强; NO 去除

收稿日期: 2015-11-26. 接受日期: 2016-02-26. 出版日期: 2016-05-05.

*通讯联系人. 电话/传真: (021)65135472; 电子信箱: beny1224@163.com

基金来源: 国家自然科学基金(21277097); “十二五”国家科技支撑计划重点项目(2012BAJ21B01).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).