available at www.sciencedirect.com

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

Article

Enhanced plasmonic photocatalysis by SiO₂@Bi microspheres with hot-electron transportation channels via Bi–O–Si linkages

Zilin Ni ^a, Wendong Zhang ^b, Guangming Jiang ^a, Xiaoping Wang ^a, Zhenzhen Lu ^c, Yanjuan Sun ^{a,*}, Xinwei Li ^a, Yuxin Zhang ^d, Fan Dong ^{a,#}

^a Chongqing Key Laboratory of Catalysis and New Environmental Materials, Engineering Research Center for Waste Oil Recovery Technology and Equipment of Ministry of Education, College of Environment and Resources, Chongqing Technology and Business University, Chongqing 400067, China

^b Department of Scientific Research Management, Chongqing Normal University, Chongqing 401331, China

^c College of Civil Engineering, Chongqing JiaoTong University, Chongqing 400074, China

^d College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China

ARTICLE INFO

Article history:

Received 1 May 2017

Accepted 3 May 2017

Published 5 July 2017

Keywords:

SiO₂@Bi metal

Bi–O–Si bond

Electron transfer

In situ diffuse reflectance infrared

Fourier transform spectroscopy

Photocatalytic nitric oxide removal

ABSTRACT

The semimetal Bi has received increasing interest as an alternative to noble metals for use in plasmonic photocatalysis. To enhance the photocatalytic efficiency of metallic Bi, Bi microspheres modified by SiO₂ nanoparticles were fabricated by a facile method. Bi–O–Si bonds were formed between Bi and SiO₂, and acted as a transportation channel for hot electrons. The SiO₂@Bi microspheres exhibited an enhanced plasmon-mediated photocatalytic activity for the removal of NO in air under 280 nm light irradiation, as a result of the enlarged specific surface areas and the promotion of electron transfer via the Bi–O–Si bonds. The reaction mechanism of photocatalytic oxidation of NO by SiO₂@Bi was revealed with electron spin resonance and in situ diffuse reflectance infrared Fourier transform spectroscopy experiments, and involved the chain reaction NO → NO₂ → NO₃[−] with •OH and •O₂[−] radicals as the main reactive species. The present work could provide new insights into the in-depth mechanistic understanding of Bi plasmonic photocatalysis and the design of high-performance Bi-based photocatalysts.

© 2017, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Photocatalysis has become one of the most promising energy technologies on account of its potential to provide sustainable solutions to environmental and energy problems [1–6]. Semiconductor photocatalysis has been widely applied in various fields, such as environmental remediation, clean energy

production, carbon fixation and chemical synthesis [1–6]. Alternatively, the newly emerging class of plasmonic photocatalysts based on noble metals has the potential to significantly boost the photocatalytic performance of semiconductors. When the incident frequency of the photons matches the oscillating frequency of the conduction-band electrons in metallic nanoparticles, the nanoparticles undergo the localized surface

* Corresponding author. Tel/Fax: +86-23-62769785-605; E-mail: syhsyj@163.com

Corresponding author. Tel/Fax: +86-23-62769785-605; E-mail: dfctbu@126.com

This work is supported by the National Natural Science Foundation of China (21501016, 51478070, 21406022, 21676037), the National Key R&D Project (2016YFC0204702), the Innovative Research Team of Chongqing (CXTDG201602014), the Natural Science Foundation of Chongqing (cstc2016jcyjA0481, cstc2015jcyjA0061), the Science and Technology Project of Chongqing Education Commission (KJ1600625, KJ1500637), the Application and Basic Science Project of Ministry of Transport of People's Republic of China (2015319814100), and the Innovative Research Project from CTBU (yjscxx2016-060-36).

DOI: 10.1016/S1872-2067(17)62849-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 7, July 2017

plasmon resonance (LSPR) effect. This enhances the local electromagnetic fields around the metal surface to improve its optical trapping capability and photoelectric conversion rate, thus enabling some metals to perform as photocatalysts [7–10]. Both noble metals (Au, Ag, Pd) and non-noble metals (Cu) exhibit LSPR characteristics under visible-light excitation [8,11–13]. It has been found that the optical response of some non-noble metals (Bi and Al) can be tuned from ultraviolet (UV) light to the visible-light region [14,15].

Bismuth, the most abundant non-precious semimetal element on earth, has recently been found to demonstrate impressive and stable photocatalytic activity towards the removal of NO under 280 nm light irradiation, representing a new, direct plasmonic photocatalyst [14]. In combination with appropriate semiconductors such as C_3N_4 and $(\text{BiO})_2\text{CO}_3$, metallic Bi as a cocatalyst can promote their photocatalytic activity by surface plasmon resonance (SPR)-based enhancement of their light-harvesting ability, and by the SPR-mediated formation of electromagnetic fields, promoting the separation of photogenerated charge carriers. In addition, Bi can perform as an electron trap to facilitate charge-carrier separation, similar to the role of noble metals in metal/semiconductor composites [16–18].

However, no study has yet been reported concerning the use of pristine elemental Bi to enhance the efficiency of plasmonic photocatalysis. Naked SiO_2 is not a viable photocatalyst because of its large band gap, which only enables it to absorb shortwave ultraviolet light [19,20]. Based on its stability and high specific surface area, SiO_2 is usually employed as a support or composite component to enhance the thermal stability of the photocatalyst or elevate its adsorption capacity for reactants [21–23]. To date, there has been no report on the use of SiO_2 to enhance the plasmonic photocatalytic ability of metallic Bi. Moreover, the reaction pathway of the photocatalytic oxidation of NO by $\text{SiO}_2\text{@Bi}$ remains unknown.

Herein, Bi spheres modified by SiO_2 nanoparticles were developed for the first time by a facile method. The addition of SiO_2 considerably enhanced the plasmonic photocatalytic activity of metallic Bi towards the removal of NO under 280 nm light irradiation, and ensured high chemical stability. The enlarged surface area and the formation of Bi–O–Si bonds played key roles in improving the photocatalytic performance of $\text{SiO}_2\text{@Bi}$. Using the Bi–O–Si bonds as a transportation channel, the photogenerated electrons in metallic Bi were rapidly transferred to the surface of $\text{SiO}_2\text{@Bi}$, promoting the separation and transfer of photoexcited carriers, as well as the formation of reactive radicals for oxidation. The reaction mechanism of photocatalytic NO oxidation by $\text{SiO}_2\text{@Bi}$ was revealed with electron spin resonance (ESR) and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and involved the chain reaction $\text{NO} \rightarrow \text{NO}_2 \rightarrow \text{NO}_3^-$ with $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ radicals as the main reactive species. A new mechanism for plasmonic photocatalysis by $\text{SiO}_2\text{@Bi}$ composites involving Bi–O–Si bonds as transportation channels was also proposed.

2. Experimental

2.1. Synthesis of Bi microspheres and $\text{SiO}_2\text{@Bi}$ microspheres

All chemicals used in this study were analytical grade and were used without further purification. In a typical synthesis, 0.364 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was first dissolved in 10 mL of HNO_3 (1 mol/L). The mixture was then transferred into a Teflon-lined autoclave (100 mL) with stirring for 30 min. After dissolution, ethylene glycol (55 mL) was added and stirred for 30 min. 0.6 g of polyvinylpyrrolidone (PVP, molecular weight 24000) was subsequently added into the solution and stirred until dissolution. Next, 0.011 g of commercial SiO_2 nanoparticles was added into the above solution and stirred for 10 min. The aqueous suspension was then heated to 160 °C for 24 h. After the reaction, the black solid product was filtered, washed three times with distilled water and absolute ethanol to remove impurities, and then dried at 60 °C for 12 h to obtain the final $\text{SiO}_2\text{@Bi}$ products. For comparison, Bi spheres were prepared according to the above method without the addition of SiO_2 nanospheres.

2.2. Characterization

The crystal phases of the samples were analyzed by X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation (model D/max RA, Rigaku Co., Japan). X-ray photoelectron spectroscopy (XPS) with Al $\text{K}\alpha$ X-rays (Thermo ESCALAB 250, USA) was used to investigate the surface properties. The microstructure of the samples was examined with a scanning electron microscope (SEM, JEOL model JSM-6490) and a transmission electron microscope (TEM, JEM-2010, Japan). The UV-vis diffuse-reflectance spectra were obtained for the dry-pressed disk samples utilizing a scanning UV-vis spectrophotometer (UV-vis DRS, UV-2450, Shimadzu, Japan) equipped with an integrating sphere assembly. Photoluminescence (PL) spectroscopy (F-7000, HITACHI) was employed to probe the charge-separation properties of the samples. Nitrogen adsorption-desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA). The samples were degassed at 90 °C prior to measurements. Time-resolved fluorescence decay spectra were taken with a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920). ESR signals of radicals spin-trapped by 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were recorded on a JES FA200 spectrometer. Samples for ESR measurement were prepared by mixing the samples in a DMPO solution (40 mmol/L) tank and irradiation with UV light at 280 nm. The aqueous dispersion was used for DMPO- $\bullet\text{OH}$ detection and the methanol dispersion for DMPO- $\bullet\text{O}_2^-$ detection.

2.3. Photocatalytic activity in NO removal

The photocatalytic activity of the samples was investigated by the removal of NO at 1×10^{-3} $\mu\text{g/mL}$ in a continuous-flow reactor at room temperature. The detailed specifications of the reactor system can be found in our previous publications [16–18]. For photocatalytic activity testing, the light source was an 8-W ultraviolet (280 nm) lamp placed vertically outside the reactor.

Scheme 1. Reaction apparatus for the in situ DRIFTS measurements.

2.4. In situ DRIFTS study of photocatalytic NO oxidation process

In situ DRIFTS measurements were conducted using a Bruker Tensor II Fourier transform infrared spectroscopy (FTIR) equipped with an in situ diffuse-reflectance cell (Harrick) as shown in Scheme 1 and Fig. 1. Photocatalyst samples were put into the cell. First, He gas (50 mL/min) was used to remove residual hydrocarbons, H₂O and CO₂. The real-time FTIR spectrum obtained after ventilation was utilized as the background. Then, the reaction mixtures (25 mL/min NO, 25 mL/min O₂) were introduced into the cell. The NO was allowed 20 min to adsorb onto the catalysts. Next, the photocatalysts were illuminated by the UV light source (MUA-165) for 40 min. The real-time FTIR spectra were recorded at intervals of 8 min. The gas fluxes were kept constant throughout (25 mL/min NO, 25 mL/min O₂). Finally, after turning off the light source, the FTIR spectra were recorded at intervals of 2 min with the same gas fluxes. The full IR scanning range was 4000–600 cm⁻¹. To analyze the photocatalytic oxidation process on SiO₂/Bi, the relevant section of this range was 1900–1200 cm⁻¹.

3. Results and discussion

3.1. Microstructural features

In the XRD patterns of SiO₂@Bi shown in Fig. 2(a), all the

Fig. 1. Experimental setup for in situ DRIFTS under light irradiation.

diffraction peaks can be exactly indexed to the rhombohedral phase of elemental Bi (JCPDS PDF card 85–1329). The signature diffraction peaks for SiO₂ cannot be detected because of the low content of SiO₂ in the composites. In Fig. 2(b), the peak around 582 cm⁻¹ can be ascribed to the Bi–O bond, as elemental Bi is easily oxidized by O₂ in air [14]. The resulting bismuth oxide layer on the surface protects Bi from further oxidation. In the XRD patterns (Fig. 2(a)), only the diffraction peaks of rhombohedral metallic Bi can be detected, which implies that the bismuth oxide layer on the surface is amorphous [14]. For the SiO₂@Bi composites, the peak arising from the Bi–O bond disappears. However, a new peak at 783 cm⁻¹ appears. The peaks at 466 and 1095 cm⁻¹ can be assigned to the symmetrical stretching vibration and anti-symmetrical stretching vibration,

Fig. 2. XRD patterns (a) and FTIR spectra (b) of the as-prepared Bi spheres and SiO₂@Bi samples.

Fig. 3. SEM (a, b) and TEM (c, d) images of the SiO₂@Bi sample.

respectively, of Si–O–Si [24–26]. The peak at 1614 cm^{−1} is from the bending vibration of O–H bonds in H₂O. Considering the composition of the catalyst, the new peak at 783 cm^{−1} can probably be assigned to the Bi–O–Si bond in the SiO₂@Bi composites.

The SEM images in Fig. 3(a) and (b) show that the overall morphology of the SiO₂@Bi sample consists of microspheres and nanoparticles. The microspheres, of about 1–2 μm in size, are formed of Bi, and are surrounded by a large amount of SiO₂ nanoparticles, as shown in Fig. 3(c). Fig. 3(d) exhibits an HRTEM image of SiO₂@Bi at one edge. The lattice spacing of 0.227 nm corresponds to the (110) plane of rhombohedral Bi (JCPDS 85-1329). The lattice spacing of 0.386 nm can be ascribed to the (111) plane of SiO₂ (JCPDS 85-0419). The intimate contact between SiO₂ and Bi can be clearly observed in the SiO₂@Bi samples, which provides further evidence for the formation of Bi–O–Si linkages. The successful construction of SiO₂@Bi can also be confirmed by the EDX mapping in Fig. 4, demonstrating the uniform distribution of Bi and Si elements in the sample.

The addition of SiO₂ enlarges the specific surface area of the

Fig. 4. EDX mapping of SiO₂@Bi sample (a) and the corresponding maps for the elements C (b), O (c), Bi (d) and Si (e).

Bi spheres from 16 to 27 m²/g, as determined from the N₂ adsorption-desorption isotherms (Fig. 5(a)). The pore volumes are also increased upon the addition of SiO₂ (Table 1). The mesopores in SiO₂@Bi allow light to be scattered within their pore channels, and thus enhance the light-harvesting efficiency (Fig. 5(b)). The enlarged specific surface area of SiO₂@Bi increases the material's adsorption capacity for NO and thus promotes its photocatalytic activity. The specific surface area (*A*_{BET}), pore volume, peak diameter and NO removal ratio of the Bi spheres and SiO₂@Bi samples are shown in Table 1.

3.2. Chemical composition

XPS was used to investigate the chemical state of SiO₂@Bi.

Fig. 5. N₂ adsorption-desorption isotherms (a) and the corresponding pore-size distribution curves (b) of the samples.

Table 1

Specific surface area (A_{BET}), pore volume, peak diameter and NO removal ratio (η) of Bi microspheres and $\text{SiO}_2\text{@Bi}$ samples.

Sample	A_{BET} (m^2/g)	Pore volume (cm^3/g)	Peak diameter (nm)	η (%)
Bi sphere	16	0.11	3.7/30.1	36.9
$\text{SiO}_2\text{@Bi}$	27	0.14	3.6/23.0	53.6

Fig. 6 depicts the XPS spectra of the elements C, O, Bi and Si, which are consistent with the EDX results (Fig. 4). The peak of C is ascribed to adventitious carbon (Fig. 6(a)). Before etching, the O 1s peaks centered at 529.6 and 530.8 eV (Fig. 6(b)) can be assigned to the binding energies of Bi–O–Si and Si–O, respectively [27]. In comparison with the Si–O bond, the binding energy of Bi–O–Si is lower, so the shift of O 1s to lower energy after etching indicates that Bi–O–Si is present. After etching, an additional peak of O 1s around 533.1 eV (Fig. 6(b)), arising from SiO_2 , can also be observed, indicating that some of the SiO_2 particles are incorporated into the interior of $\text{SiO}_2\text{@Bi}$ [28,29]. The Bi 4f spectra before and after etching have distinct differences, as shown in Fig. 6(c). The characteristic peaks centered at 156.8 and 162.1 eV can be attributed to metallic Bi, suggesting the presence of Bi–Bi bonds. The peaks around 158.9 and 164.2 eV are the characteristic peaks of Bi^{3+} ions, originating from the bismuth oxide layer formed on the surface of the $\text{SiO}_2\text{@Bi}$ composites [18]. For comparison, the intensity of the Bi–Bi peaks is significantly increased after etching, which demonstrates that the surface of the elemental Bi is easily oxi-

dized by O_2 in air, forming a thin, amorphous bismuth oxide layer that protects Bi from further oxidation. As depicted in Fig. 6(d), the intensity of the Si 2p peak is increased after etching, which further confirms the presence of SiO_2 particles in the interior of $\text{SiO}_2\text{@Bi}$.

3.3. Optical properties

The UV-vis DRS results of the Bi and $\text{SiO}_2\text{@Bi}$ samples are shown in Fig. 7(a). Both the samples show strong UV light absorption (250–290 nm), which can be mainly assigned to the characteristic SPR absorption of metallic Bi. The light-harvesting ability of $\text{SiO}_2\text{@Bi}$ is enhanced in the range from 290 to 400 nm after the addition of SiO_2 . The photophysical properties of the photoexcited charge carriers in Bi and $\text{SiO}_2\text{@Bi}$ were further analyzed using ns-level time-resolved fluorescence decay spectroscopy, as illustrated in Fig. 7(b) and (c). The decay spectra can be fitted to obtain the radiative lifetime of the samples. The fitting results are given in Table 2, showing the lifetime components (τ_1) and the corresponding relative percentages of charge carriers. The lifetime (τ_1) of metallic Bi is 7.76 ns. After the addition of SiO_2 , the lifetime increases to 8.34 ns, i.e., the carrier lifetime is increased by the formation of $\text{SiO}_2\text{@Bi}$. The prolonged lifetime of the charge carriers can be attributed to the formation of Bi–O–Si bonds. Benefiting from SPR, the photogenerated electrons in metallic Bi are rapidly transferred to the surface of SiO_2 via the Bi–O–Si bonds, which serve as hot-electron transportation channels. This promotes

Fig. 6. C 1s (a), O 1s (b), Bi 4f (c) and Si 2p (d) XPS spectra for $\text{SiO}_2\text{@Bi}$ before and after etching.

Fig. 7. UV-vis DRS of the samples (a), and ns-level time-resolved fluorescence spectra for Bi spheres (b) and SiO₂@Bi (c), respectively.

Table 2

Kinetics of emission decay parameters of Bi and SiO₂@Bi.

Sample	Component	Lifetime (ns)	Relative percentage (%)	χ^2
Bi	τ_1	7.76	100	1.031
SiO ₂ @Bi	τ_1	8.34	100	1.059

the separation and transfer of the photoexcited carriers, as well as the formation of reactive radicals for oxidation [30]. The prolonged lifetime of the charge carriers increases their probability of participating in photocatalytic reactions before recombination. Moreover, the increased formation of radicals enhances the photocatalytic oxidation strength of the material.

3.4. Investigation of photocatalytic NO oxidation process by ESR and in situ DRIFTS

To determine which reactive radical species take part in photocatalysis, trapping experiments for superoxide ($\bullet\text{O}_2^-$) and hydroxyl radicals ($\bullet\text{OH}$) were performed. As depicted in Fig. 8, for both $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals, the signals of SiO₂@Bi are much stronger than those of Bi spheres under 280 nm light irradiation. This indicates that the addition of SiO₂ enhanced the production of both species of active radicals, presumably by increasing the charge separation via the formation of Bi–O–Si bonds.

In situ DRIFTS was then performed to further study the mechanism of photocatalytic NO oxidation by SiO₂@Bi. Fig. 9 shows the time evolution of the IR spectra during 40 min of photocatalytic treatment of NO over SiO₂@Bi with UV-light irradiation. The spectra obtained before switching the light source on and after switching it off are also presented for comparison. Table 3 summarizes the assignments of the observed bands. After introducing the mixture of NO and O₂, the NO interacted with reactive sites on the surface of SiO₂@Bi, generating surface nitrosyl species. At the same time, the surface reactions of NO with oxidative species ($\bullet\text{O}_2^-$ and $\bullet\text{OH}$) resulted in the production of nitrates [31]. The main IR peaks of the adsorbed NO₃[−] species can be found in the regions of 1507–1576, 1636 and 1749 cm^{−1}. The IR absorptions of NO₂[−] are located at 1419–1473, 1653 and 1684 cm^{−1} [31–37]. After 8 min of UV-light illumination, the IR peaks in the regions corresponding to NO₂[−] and NO₃[−] become markedly stronger, which can be attributed to the fast electron transfer induced by the Bi–O–Si bonds. Fast electron transfer promotes the formation of greater amounts of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals, generating nitrate/nitro species ($\text{NO} + \bullet\text{O}_2^- \rightarrow \text{NO}_3^-$, $\text{NO} + 2\bullet\text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$, $\text{NO}_2 + \bullet\text{OH} \rightarrow \text{NO}_3^- + \text{H}^+$). From 16 to 24 min, the peaks of both NO₂[−] and NO₃[−] species decline slightly, which is related to the increasing saturation of the active sites. From 32 to 40 min, the bands corresponding to the final product NO₃[−] are stronger than those of the other nitrate species. The peaks for NO₂[−] can be formed

Fig. 8. DMPO spin-trapping ESR spectra of Bi spheres and SiO₂@Bi composites in a methanol dispersion for DMPO- $\bullet\text{O}_2^-$ (a) and in an aqueous dispersion for DMPO- $\bullet\text{OH}$ (b).

Fig. 9. In situ DRIFTS spectra of NO adsorption followed by photocatalytic NO oxidation over SiO₂@Bi under ultraviolet light irradiation, and after turning off the light source.

by two routes ($\text{NO}_3^- + \text{O}^{2-} + 2\text{NO} \rightarrow 3\text{NO}_2^-$ and $\text{NO}_3^- + 2\text{NO} \rightarrow \text{NO}^+ + 2\text{NO}_2^-$) [35]. A trace amount of NO (with peaks at 1772 and 1869 cm^{-1} from 32 to 40 min) is formed by the desorption and decomposition of the main adsorbed nitrates [34–36,38]. After turning off the light for 8 min, the IR intensities for the NO_2^- and NO_3^- species decline because of the cessation of the photocatalytic reaction.

3.5. Photocatalytic activity, stability and mechanisms

The photocatalytic activity of SiO₂@Bi was evaluated for the removal of NO in air under UV light irradiation. Fig. 10(a) shows the time evolution of the NO concentration (C/C_0) during irradiation over elemental Bi and SiO₂@Bi. C_0 and C are the initial and real-time concentration, respectively. The figure also shows the corresponding data for SiO₂, which, as an insulator, shows no photocatalytic activity for NO removal under light irradiation. Significantly, a high NO removal ratio of 53.6% is achieved in the presence of SiO₂@Bi photocatalyst, whereas Bi exhibits a relatively low NO removal ratio of 36.9%. Note that the amorphous bismuth oxide is inactive under light irradiation

Table 3

Assignments of the IR bands observed during NO adsorption, during the photocatalytic treatment of NO and after turning off the light.

Wavenumber (cm ⁻¹)	Assignment	Ref.
1419	NO_2^- surface species	[31]
1457	NO_2^- (monodentate nitrates), $\nu(\text{N}=\text{O})$	[32]
1473	NO_2^- vibration modes	[33]
1507	NO_3^- (monodentate nitrates), $\nu_{\text{as}}(\text{NO}_2)$	[34]
1522	NO_3^- , $\nu_{\text{as}}(\text{NO}_3^- \text{ split})$	[32]
1541	NO_3^- , $\nu_{\text{as}}(\text{NO}_3^- \text{ split})$	[32]
1558	bidentate nitrates	[35]
1576	NO_3^- , $\nu_{\text{as}}(\text{NO}_3^- \text{ split})$	[32]
1617	H_2O , $\delta(\text{HOH})$	[32]
1636	NO_3^- vibration modes	[31]
1653	NO_2^- vibration modes	[36]
1684	NO_2^- (monodentate nitrates), $\nu(\text{N}=\text{O})$	[37]
1749	NO_3^- (bidentate nitrates), $\nu_s(\text{NO}_2) + \delta(\text{ONO})$	[37]
1772	NO absorbed on SiO ₂ @Bi	[36]
1840–1869	monodentate nitrates, $\nu(\text{NO})$	[34,35]

[14,18]. The photoinduced electrons can pass through the thin layer of amorphous bismuth oxide via the well-known quantum tunneling effect [18]. The ability of SiO₂@Bi and elemental Bi to remove NO under photocatalytic conditions can be ascribed to the direct plasmonic photocatalytic effect of the semimetal Bi [14,39–41]. The greatly enhanced activity of SiO₂@Bi can be attributed both to the enlarged surface areas and to the increased production of active species, benefiting from the presence of polar Bi–O–Si bonds [30]. It is noteworthy that the photocatalytic activity of SiO₂@Bi under UV light irradiation actually increases slightly after five cycles (Fig. 10(b)). Its high photocatalytic activity and photochemical stability indicate the great potential of SiO₂@Bi as a novel Bi-metal-based plasmonic photocatalyst.

The mechanism of photocatalytic NO oxidation over metallic Bi is shown in Fig. 11(a). Through surface plasmon resonance in metallic Bi, $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ radicals are produced together with hot holes and hot electrons. These two species of reactive radicals are responsible for the oxidation of NO [14]. However, further improvement is necessary to suppresses the recombination of holes and electrons, which terminates the photocata-

Fig. 10. Photocatalytic removal of NO under 280 nm light for all three samples (a) and cycling efficiency of photocatalysis over SiO₂@Bi (b).

Fig. 11. Mechanism of photocatalytic NO oxidation over metallic Bi (a) and illustration of the hot-electron transportation channels formed by Bi–O–Si bonds in SiO₂@Bi composites (b).

lytic activity. The hybridization of metallic Bi with SiO₂ results in the formation of Bi–O–Si bonds. As indicated by the HRTEM and time-resolved PL results, the Bi–O–Si bonds are beneficial for charge separation and electron transfer, thus promoting the production of •OH and •O₂^{•−} radicals, leading to enhanced photocatalytic efficiency of metallic Bi (Fig. 11(b)).

4. Conclusions

The first plasmonic photocatalyst to be based on SiO₂@Bi microspheres was developed by a facile method. The SiO₂@Bi nanohybrid exhibited an impressive and stable activity for the direct plasmonic photocatalytic removal of NO in air under UV light irradiation. The enhanced activity of SiO₂@Bi can be ascribed to the enlarged specific surface area and to the promotion of electron transfer by the Bi–O–Si bonds. The mechanism of plasmonic photocatalytic NO oxidation was revealed with in situ DRIFTS and ESR trapping, and involved the chain reaction

NO → NO₂ → NO₃^{•−}. The present work provides new insights into the mechanistic understanding of plasmonic photocatalysis using metallic Bi and may aid the design of high-performance Bi-based plasmonic photocatalysts.

References

- [1] Y. Zheng, L. H. Lin, B. Wang, X. C. Wang, *Angew. Chem. Int. Ed.*, **2015**, 54, 12868–12884.
- [2] X. P. Liu, H. Qin, W. L. Fan, *Sci. Bull.*, **2016**, 60, 645–655.
- [3] R. Y. Zhang, W. C. Wan, D. W. Li, F. Dong, Y. Zhou, *Chin. J. Catal.*, **2017**, 38, 313–320.
- [4] Z. L. Ni, Y. J. Sun, Y. X. Zhang, F. Dong, *Appl. Surf. Sci.*, **2016**, 365, 314–335.
- [5] L. Chen, J. He, Y. Liu, P. Chen, C. T. Au, S. F. Yin, *Chin. J. Catal.*, **2016**, 37, 780–791.
- [6] T. Xiong, H. J. Zhang, Y. X. Zhang, F. Dong, *Chin. J. Catal.*, **2015**, 36, 2155–2163.

Graphical Abstract

Chin. J. Catal., 2017, 38: 1174–1183 doi: 10.1016/S1872-2067(17)62849-3

Enhanced plasmonic photocatalysis by SiO₂@Bi microspheres with hot-electron transportation channels via Bi–O–Si linkages

Zilin Ni, Wendong Zhang, Guangming Jiang, Xiaoping Wang, Zhenzhen Lu, Yanjuan Sun*, Xinwei Li, Yuxin Zhang, Fan Dong*
 Chongqing Technology and Business University;
 Chongqing Normal University;
 Chongqing JiaoTong University;
 Chongqing University

Bi–O–Si bonds in SiO₂@Bi are beneficial for charge separation and electron transfer, thus promoting the production of •OH and •O₂^{•−} radicals, leading to enhanced photocatalytic efficiency of metallic Bi.

- [7] Q. Hao, C. X. Wang, H. Huang, W. Li, D. Y. Du, D. Han, T. Qiu, P. K. Chu, *Sci. Rep.*, **2015**, 5, 15288.
- [8] M. B. Gawande, A. Goswami, F. X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril, R. S. Varma, *Chem. Rev.*, **2016**, 116, 3722–3811.
- [9] M. J. Kale, T. Avanesian, P. Christopher, *ACS Catal.*, **2013**, 4, 116–128.
- [10] X. J. Lang, X. D. Chen, J. C. Zhao, *Chem. Soc. Rev.*, **2014**, 43, 473–486.
- [11] X. Chen, H. Y. Zhu, J. C. Zhao, Z. F. Zheng, X. P. Gao, *Angew. Chem. Int. Ed.*, **2008**, 120, 5433–5436.
- [12] P. Christopher, H. L. Xin, S. L. Linic, *Nat. Chem.*, **2011**, 3, 467–472.
- [13] P. S. Archana, N. Pachauri, Z. C. Shan, S. L. Pan, A. Gupta, *J. Phys. Chem. C*, **2015**, 119, 15506–15516.
- [14] F. Dong, T. Xiong, Y. J. Sun, Z. W. Zhao, Y. Zhou, X. Feng, Z. B. Wu, *Chem. Commun.*, **2014**, 50, 10386–10389.
- [15] L. N. Zhou, C. Zhang, M. J. McClain, A. Manjavacas, C. M. Krauter, S. Tian, F. Berg, H. O. Everitt, E. A. Carter, P. Nordlander, N. J. Halas, *Nano Lett.*, **2016**, 16, 1478–1484.
- [16] F. Dong, Q. Y. Li, Y. J. Sun, W. K. Ho, *ACS Catal.*, **2014**, 4, 4341–4350.
- [17] Y. J. Sun, Z. W. Zhao, F. Dong, W. Zhang, *Phys. Chem. Chem. Phys.*, **2015**, 17, 10383–10390.
- [18] F. Dong, Z. W. Zhao, Y. J. Sun, Y. X. Zhang, S. Yan, Z. B. Wu, *Environ. Sci. Technol.*, **2015**, 49, 12432–12440.
- [19] I. Aharonovich, Y. Lifshitz, S. Tamir, *Appl. Phys. Lett.*, **2007**, 90, 263109/1–263109/3.
- [20] D. E. Zhang, J. B. Wu, B. P. Zhou, Y. Y. Hong, S. B. Li, W. Wen, *Nanoscale*, **2013**, 5, 6167–6172.
- [21] J. Chen, S. H. Shen, P. H. Guo, M. Wang, J. Z. Su, D. M. Zhao, L. J. Guo, *J. Mater. Res.*, **2014**, 29, 64–70.
- [22] C. Liu, D. Yang, Y. Jiao, Y. Tian, Y. G. Wang, Z. Y. Jiang, *ACS Appl. Mater. Interfaces*, **2013**, 5, 3824–3832.
- [23] R. Fateh, R. Dillert, D. Bahnemann, *Langmuir*, **2013**, 29, 3730–3739.
- [24] X. X. Zhu, J. J. Xie, D. B. Lin, Z. Q. Guo, J. Xu, Y. Shi, F. Lei, Y. L. Wang, *J. Alloys Compd.*, **2014**, 582, 33–36.
- [25] X. M. Zhu, C. L. Mai, M. Y. Li, *J. Non-Cryst. Solids*, **2014**, 388, 55–61.
- [26] Y. P. Zhang, Y. X. Yang, Y. W. Ou, W. Hua, J. H. Zheng, G. R. Chen, *J. Am. Ceram. Soc.*, **2009**, 92, 1881–1883.
- [27] Q. F. Han, J. Zhang, X. Wang, J. W. Zhu, *J. Mater. Chem. A*, **2015**, 3, 7413–7421.
- [28] A. Thøgersen, J. H. Selj, E. S. Marstein, *J. Electrochem. Soc.*, **2012**, 159, D276–D281.
- [29] G. Hollinger, Y. Jugnet, P. Pertosa, T. M. Duc, *Chem. Phys. Lett.*, **1975**, 36, 441–445.
- [30] L. Pang, F. Teng, D. F. Yu, Y. X. Zhao, Q. Xu, J. Xu, Y. F. Zhai, *J. Phys. Chem. A*, **2016**, 120, 2657–2666.
- [31] A. Wojtaszek, I. Sobczak, M. Ziolk, *Catal. Today*, **2012**, 192, 149–153.
- [32] B. Azambre, L. Zenboury, A. Koch, J. V. Weber, *J. Phys. Chem. C*, **2009**, 113, 13287–13299.
- [33] Y. Liu, T. T. Gu, X. L. Weng, Y. Wang, Z. B. Wu, H. Q. Wang, *J. Phys. Chem. C*, **2012**, 116, 16582–16592.
- [34] M. Kantcheva, A. S. Vakkasoglu, *J. Catal.*, **2004**, 223, 352–363.
- [35] K. Hadjiivanov, H. Knozinger, *Phys. Chem. Chem. Phys.*, **2000**, 2, 2803–2806.
- [36] Z. X. Zhang, M. X. Chen, Z. Jiang, W. F. Shangguan, *J. Environ. Sci.*, **2010**, 22, 1441–1446.
- [37] M. Kantcheva, E. Z. Ciftlikli, *J. Phys. Chem. B*, **2002**, 106, 3941–3949.
- [38] M. Chen, Z. H. Wang, D. M. Han, F. B. Gu, G. S. Guo, *J. Phys. Chem. C*, **2011**, 115, 12763–12773.
- [39] X. F. Chang, L. Xie, W. E. I. Sha, K. Lu, Q. Qi, C. Y. Dong, X. X. Yan, M. A. Gondal, S. G. Rashid, Q. I. Dai, W. Zhang, L. Q. Yang, X. O. Qiao, L. Mao, P. Wang, *Appl. Catal. B*, **2017**, 201, 495–502.
- [40] F. Dong, T. Xiong, S. Yan, H. Q. Wang, Y. J. Sun, Y. X. Zhang, H. W. Huang, Z. B. Wu, *J. Catal.*, **2016**, 344, 401–410.
- [41] Y. H. Li, K. L. Lv, W. Ho, Z. W. Zhao, Y. Huang, *Chin. J. Catal.*, **2017**, 38, 321–329.

Bi–O–Si键作为热电子传输通道增强SiO₂@Bi微球的等离子体光催化效率

倪紫琳^a, 张文东^b, 蒋光明^a, 王小平^a, 鲁贞贞^c, 孙艳娟^{a,*}, 李欣蔚^a, 张育新^d, 董帆^{a,#}

^a重庆工商大学环境与资源学院, 重庆市催化与环境新材料重点实验室,

教育部废油资源化技术与设备工程研究中心, 重庆400067

^b重庆师范大学科研处, 重庆401331

^c重庆交通大学土木工程学院, 重庆400074

^d重庆大学材料科学与工程学院, 重庆400044

摘要: 具有等离子体效应的贵金属Au和Ag等常被用于修饰半导体光催化剂。非贵金属Bi成本低, 来源丰富, 最近被报道可以直接作为等离子体光催化剂应用于空气中NO净化。为了进一步提高Bi单质的光催化活性, 需对其进行改性。SiO₂的禁带宽度过大, 不能单独作为光催化剂, 但它的稳定性好, 比表面积大, 因而常作复合材料用于提高光催化剂的反应效率、稳定性及对反应物的吸附能力。目前, 尚未见SiO₂修饰Bi单质的相关报道。

本文通过溶剂热法制备了SiO₂@Bi微球, 并对其微结构进行了表征, 对光催化氧化NO的反应过程进行了原位漫反射红外光谱(DRIFTS)分析, 揭示了Bi–O–Si键在提升SiO₂@Bi光催化氧化NO性能中的作用机制。结果显示, 用SiO₂纳米颗粒修饰Bi球, 形成的Bi–O–Si键作为热电子传输通道, 能显著提高Bi单质光催化氧化去除NO的能力。

扫描电镜、透射电镜、傅里叶变换红外光谱和X射线光电子能谱等表征结果表明, SiO₂纳米颗粒负载于Bi球上, 且SiO₂@Bi内形成了Bi–O–Si键。作为光生热电子的传输通道, Bi–O–Si键能促进光生电子的转移和载流子的分离, 提高活性自由基·OH和·O₂⁻的产量, 增强SiO₂@Bi在紫外光下等离子体光催化氧化NO的能力。自由基捕获测试(ESR)表明, SiO₂@Bi

在光催化反应中产生的 $\cdot\text{OH}$ 和 $\cdot\text{O}_2^-$ 数量均明显高于单质Bi在反应中形成自由基的数量。原位DRIFTS发现, Bi–O–Si键能快速转移光生电子, 从而有利于 $\text{NO} \rightarrow \text{NO}_2 \rightarrow \text{NO}_3^-$ 反应的进行。此外, $\text{SiO}_2@\text{Bi}$ 的比表面积变大, 因而对NO的吸附能力增强, 同时促进了光催化反应。本文揭示了 $\text{SiO}_2@\text{Bi}$ 等离子体光催化性能增强的微观机制和光催化氧化NO的反应机理, 为Bi基光催化剂的改性和应用提供了新的认识。

关键词: $\text{SiO}_2@\text{Bi}$ 金属; Bi–O–Si键; 电子传输; 原位漫反射红外光谱; 光催化去除一氧化氮

收稿日期: 2017-05-01. 接受日期: 2017-05-03. 出版日期: 2017-07-05.

*通讯联系人. 电话/传真: (023)62769785-605; 电子信箱: syhsyj@163.com

#通讯联系人. 电话/传真: (023)62769785-605; 电子信箱: dfctbu@126.com

基金来源: 国家自然科学基金(21501016, 51478070, 21406022, 21676037); 国家重点研发计划(2016YFC0204702); 重庆市高校创新团队建设计划(CXTDG201602014); 重庆市自然科学基金(cstc2016jcyjA0481, cstc2015jcyjA0061); 重庆市教委科技项目(KJ1600625, KJ1500637); 交通运输部应用和基础科学项目(2015319814100); 重庆工商大学创新型科研项目(yjscxx2016-060-36). 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>).

《催化学报》2016 年 SCI 影响因子公布

据美国汤森路透 (Thomson Reuters) 近日公布的2016年度《期刊引证报告》(Journal Citation Reports, JCR), *Chinese Journal of Catalysis* (《催化学报》) 的最新SCI影响因子 (IF) 为2.813 (2015年为2.628), 在国内化学类期刊中名列前茅; 在国际应用化学学科72种期刊中排名第17位, 排名居前23.61%, 位居Q1区。《催化学报》在发文量和影响因子上已经与国际著名催化领域期刊*Catal. Lett.* (IF 2.799), *Top. Catal.* (2.486) 和*J. Mol. Catal. B* (IF 2.269) 相当。近年, 《催化学报》的学术质量及影响力不断提升, 这是中国化学会催化委员会委员、编委、审稿专家、作者和读者长期不懈努力和共同支持的结果。衷心感谢各位老师对期刊宣传、投稿原创性高质量稿件、学术质量把关以及组约优秀稿件、组办高水平专刊等方面所给予的持续和巨大的支持!

(《催化学报》编辑部 2017-06-15)