Efficient visible light photocatalytic NO_x removal with cationic Ag clusters-grafted (BiO)₂CO₃ hierarchical superstructures

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HIGHLIGHTS

- Microstructural optimization and surface cluster-grafting were firstly combined.
- Cationic Ag clusters were grafted on the surface of (BiO)₂CO₃ superstructures.
- The Ag clusters-grafted BHS displayed enhanced visible light photocatalysis.
- Direct interfacial charge transfer (IFCT) from BHS to Ag clusters was proposed.
- The charge transfer process and the dominant reactive species were revealed.

GRAPHICAL ABSTRACT

The cationic Ag clusters-grafted (BiO)₂CO₃ hierarchical superstructures exhibits highly enhanced visible light photocatalytic air purification through an interfacial charge transfer process induced by Ag clusters.

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ABSTRACT

A facile method was developed to graft cationic Ag clusters on (BiO)₂CO₃ hierarchical superstructures (BHS) surface to improve their visible light activity. Significantly, the resultant Ag clusters-grafted BHS displayed a highly enhanced visible light photocatalytic performance for NO_x removal due to the direct interfacial charge transfer (IFCT) from BHS to Ag clusters. The chemical and coordination state of the cationic Ag clusters was determined with the extended X-ray absorption fine structure (EXAFS) and a theoretical structure model was proposed for this unique Ag clusters. The charge transfer process and the dominant reactive species ([•]OH) were revealed on the basis of electron spin resonance (ESR) trapping. A new photocatalysis mechanism of Ag clusters-grafted BHS under visible light involving IFCT process was uncovered. In addition, the cationic Ag clusters-grafted BHS also demonstrated high photochemical and structural stability under repeated photocatalysis runs. The perspective of enhancing

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photocatalysis through combination of microstructural optimization and IFCT could provide a new avenue for the developing efficient visible light photocatalysts.

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1. Introduction

To utilize the abundant visible light in solar light (about 48% fraction of sunlight) or indoor light for environmental remediation, it is urgent and highly desirable to develop visible light responsive photocatalysts with high activity and stability [1–3]. It can be achieved by either development of photocatalysts with narrow band gap or modification with photocatalysts with large band gap.

Up to now, bismuth-containing materials such as Bi_2WO_6 , Bi_2MoO_6 , BiVO_4 , BiOX ($X = \text{Cl}, \text{Br}, \text{I}$), BiFeO_3 , $\text{Bi}_2\text{Ti}_2\text{O}_7$, $\text{Bi}_2\text{Sn}_2\text{O}_7$, have attracted much research interests as they could respond to visible light [4–12]. Of particular interest, the emergent $(\text{BiO})_2\text{CO}_3$ has demonstrated high visible light photocatalytic activity in degradation of pollutants. Recently, Xiong et al. have fabricated $(\text{BiO})_2\text{CO}_3$ hierarchical microspheres with efficient visible light photocatalytic activity in comparison with the $(\text{BiO})_2\text{CO}_3$ nanosheets, which can be ascribed to the surface scattering and reflecting (SSR) effect resulting from the special 3D hierarchical structure [13,14]. To further extend the light absorption spectra of $(\text{BiO})_2\text{CO}_3$ into visible light region, diverse approaches have been developed, such as surface metal decoration, doping and heterojunction construction [15–22].

Apart from the visible light absorption, the electron/hole separation efficiency is another dominant factor. Recently, cationic clusters-grafting as a new strategy has been applied to promote the visible light photocatalysis via interfacial charge transfer [23–28]. For example, Cu(II) , Cr(III) , Fe(III) and Ce(III) nanoclusters have been grafted on the surface of TiO_2 [23–28], which could increase the photocatalysis efficiency via increasing the visible-light absorption without inducing impurity levels in the band gap. Under visible-light irradiation, electrons in the valence band of TiO_2 can be excited and directly transfer to the surface nanoclusters through an interfacial charge transfer (IFCT) process [23–28]. This concept is also applicable to other semiconductors besides TiO_2 [29–31]. However, to the best of our knowledge, there is no report on grafting clusters on $(\text{BiO})_2\text{CO}_3$ hierarchical superstructures to achieve enhanced visible light photocatalysis.

In this study, microstructural optimization and surface clusters modification were combined. The cationic Ag clusters were firstly grafted on the surface of $(\text{BiO})_2\text{CO}_3$ hierarchical superstructures (BHS) by soaking the BHS in AgNO_3 aqueous solution. The chemical and coordination state of the Ag clusters ($\text{Ag}_n^{\delta+}$ and Ag_n^0) was determined with EXAFS. A theoretical structural model for this unique Ag clusters was proposed, which could provide new insight into the understanding of the key role of Ag clusters in enhancing photocatalysis. A new visible light photocatalysis mechanism of cationic Ag clusters-grafted BHS involving IFCT process was uncovered, which was totally different from that of Ag metal-deposited $(\text{BiO})_2\text{CO}_3$ [19]. The present work demonstrated the efficient visible light photocatalytic NO_x removal with cationic Ag clusters-grafted $(\text{BiO})_2\text{CO}_3$ hierarchical superstructures. NO is a typical air pollutant that causes secondary smog and $\text{PM}_{2.5}$. With the as-prepared Ag clusters-grafted $(\text{BiO})_2\text{CO}_3$, the NO in air can be photocatalytically converted into final less harmful products (NO_3^-) [12]. The various characterizations were applied to gain insight in the structure-performance relationship in NO removal and propose the photocatalysis mechanism with Ag clusters-grafted $(\text{BiO})_2\text{CO}_3$. Most importantly, the Ag clusters-grafted BHS exhibited high photochemical stability and durability in NO_x removal, which was significant for its practical application. This work has demonstrated a facile strategy for promoting the visible light photocatalysis efficiency via cationic clusters modification. This concept can be extended to other photocatalytic systems to advance the overall photocatalysis efficiency.

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2. Experimental

2.1. Synthesis of Ag clusters-grafted $(\text{BiO})_2\text{CO}_3$ hierarchical superstructures

All chemicals used in this study were analytical grade. The synthesis of $(\text{BiO})_2\text{CO}_3$ hierarchical superstructures (BHS) was reported in our previous work [22]. In a typical process, 0.75 g of $(\text{BiO})_2\text{CO}_3$ was added into 60 mL distilled water, and then ultrasound dispersed for 30 min. The aqueous suspension was put into thermostat water bath at 60°C and stirred for 30 min. Then the 40 mL of AgNO_3 aqueous solution was added to the above solution under continuous stirring for another 2 h. The sample obtained was filtered, washed with deionized water and ethanol for three times and dried at 60°C for 12 h to get the final products. The molar ratio of AgNO_3 to $(\text{BiO})_2\text{CO}_3$ was controlled at 0.10, 0.20 and 0.50, respectively. Accordingly, the simplified sample name was BHS-Ag-X, with X representing the molar ratio of AgNO_3 to $(\text{BiO})_2\text{CO}_3$.

2.2. Characterization

The crystal phases of the sample were analyzed by X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA in a 2θ range of 5° – 80° at room temperature (model D/max RA, Rigaku Co., Japan). Before the XRD test, a certain amount of powder sample was pressed into a disk by a piece of smooth glass directly. The morphological structure were examined by scanning electron microscopy (SEM: JEOL model JSM-6490, Japan), transmission electron microscopy (TEM: JEM-2010, Japan). X-ray photoelectron spectroscopy with $\text{Al K}\alpha$ X-rays ($h\nu = 1486.6 \text{ eV}$) radiation operated at 150W (XPS: Thermo ESCALAB 250, USA) was used to investigate the surface properties. The shift of the binding energy due to relative surface charging was corrected using the $\text{C}1s$ level at 284.8 eV as an internal standard. The Brunauer–Emmett–Teller (BET) surface area and the pore size distribution of the products were identified by a Micromeritics ASAP 2020 apparatus. All the samples were degassed at 150°C prior to measurements. The UV–vis diffuse reflection spectra were obtained for the dry-pressed disk samples using a UV–vis spectrophotometer (UV–vis DRS: UV-2450, China) equipped with an integrating sphere assembly, using 100% BaSO_4 as reflectance sample. The solid-state photoluminescence (PL) spectra were measured with fluorescence spectrophotometer (PL: FS-2500, Japan) using a Xe lamp as an excitation source with optical filters. The EXAFS of Ag–K edges were measured in transmission mode at room temperature on the NW10A beamline, Photon Factory, Advanced Ring for pulse X-rays (PFAR), Institute of Materials Structure Science, High Energy Accelerator Research Organization (IMSS-KEK), Japan. EXAFS data were analyzed by the REX2000 program (Rigaku Co.) and were normalized with edge height and then the first order derivatives were taken to compare the variation of absorption edge energies. The spin trapping electron spin reso-

Fig. 1. Visible light photocatalytic activity of pure BHS and BHS-Ag-X with different Ag contents for NO removal (a) and evolution of NO_2 in the outlet (b).

nance (ESR) measurements were performed on a Bruker JES FA200 ESR spectrometer with a xenon lamp with an optical filter as the visible light source. DMPO (5,5'-dimethyl-1-pyrroline-N-oxide) was used as a spin-trap reagent to trap the reactive radicals of hydroxyl radicals ($\bullet OH$) and radicals.

2.3. Photocatalytic application of BHS-Ag in air purification

The photocatalytic activity of the resulting samples was investigated by removal of NO at ppb level in a continuous flow reactor at ambient temperature. The volume of the rectangular reactor was 4.5 L (30 cm $\times$ 15 cm $\times$ 10 cm). A commercial tungsten halogen lamp (150 W) was vertically placed 20 cm above the reactor, and the average light intensity was 0.16 W/cm². For the visible light photocatalytic activity test, UV cutoff filter (420 nm) was adopted to remove UV light. The photocatalyst samples were prepared by coating an aqueous suspension of the glass dish in which the weight was kept at 0.10 g and then dried at 60 °C. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N_2 balance). The initial concentration of NO was diluted to 550 ppb by the air stream supplied by purified air. The desired relative humidity (RH) level of the NO flow was controlled at 60% by passing the zero air streams through a humidification chamber. The gas streams were premixed completely by a gas blender, and the flow rate was controlled at 3.3 L/min by a mass flow controller. After the adsorption–desorption equilibrium was achieved, the lamp was turned on. The concentration of NOx was continuously measured by a chemiluminescence NOx analyzer (Thermo Environmental Instruments Inc., 42i-TL), which monitors NO, NO_2 , and NOx (NOx represents NO + NO_2) with a sampling rate of 1.0 L/min. The NO removal ratio (η) was calculated as $\eta(\%) = (1 - C/C_0) \times 100\%$, where C and C_0 are concentrations of NO in the outlet steam and the feeding stream, respectively.

2.4. Measurement of electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy measurement was used to indicate the charge separation efficiency over the samples. It was conducted using a three-electrode quartz cell equipped on CHI-660B electrochemical system. The saturated calomel electrode (SCE) was used as the reference electrode, and platinum wire serves as counter electrode. Potentials are given with reference to the SCE, and the voltage was set as 0.0 V. The working electrodes were BHS and BHS-Ag-0.20 films, which were coated on ITO glass. The electrolyte was 0.1 M of Na_2SO_4 solution. All the electrochemical impedance spectroscopy measurement was carried out under visible light irradiation emitted from a 500 W Xe

Fig. 2. XRD patterns of as-prepared BHS and BHS-Ag-X with different $AgNO_3$ contents.

lamp with a 420 nm cut-off filter. The average power of visible light was controlled at 45 mW/cm².

3. Results and discussion

3.1. Visible light photocatalytic NO removal with Ag clusters grafted $(BiO)_2CO_3$ hierarchical superstructures

NO with concentration at ppb level is one of the dominant air pollutants and cannot be easily removed under ambient conditions. NO could transform to secondary smog and PM_{2.5} with higher toxicity to human [12]. When the NO was converted to less harmful nitrate ions with photocatalysis, the nitrate ions can be easily washed away with water/rain washing and photocatalysts can be well-regenerated [17]. Fig. 1a shows the variation of NO concentration (C/C_0 %) with irradiation time over the as-prepared samples under visible light irradiation. All the samples exhibit decent visible light photocatalytic activity for NO removal. According to previous reports, the main product of NO photooxidation is NO_3^- ions [12,17]. As previous reported, $(BiO)_2CO_3$ nanosheets exhibits no visible light activity due to the large band gap and the pure BHS has a decent NO removal ratio of 22.0% under visible light irradiation [13,14]. Xiong et al. propose that the decent visible light activity of pure BHS is related to its special hierarchical structures, which could induce the effects of multiple light surface scattering

Fig. 3. The SEM images of $(\text{BiO})_2\text{CO}_3$ hierarchical superstructures (a, b).

Table 1

The S_{BET} , pore volume, peak pore diameter, NO removal ratio of the samples.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Peak pore diameter (nm)	NO η (%)
BHS	45.9	0.121	3.2/8.9	21.5
BHS-Ag-0.10	43.7	0.127	3.6/7.4	48.6
BHS-Ag-0.20	45.6	0.134	3.6/7.4	52.8
BHS-Ag-0.50	42.7	0.123	3.6/7.4	48.1

and reflecting (SSR effect) and increase the optical path-length of a photon and absorption [13].

When the BHS is soaked in AgNO_3 aqueous solution, the resulted Ag-modified BHS shows a significantly increased NO removal ratio. When the molar ratio of AgNO_3 to BHS is increased to 0.20, the removal ratio is increased unprecedentedly to 52.8%, which is comparable to that of Ag metal-decorated $(\text{BiO})_2\text{CO}_3$ [19]. The high performance of Ag clusters-grafted $(\text{BiO})_2\text{CO}_3$ (52.8%) for NO removal outperforms that of the decent BiOBr (21.3%), C-doped TiO_2 (21.8%) and porous $\text{g-C}_3\text{N}_4$ (32.7%) [32,33]. Further increasing the molar ratio of AgNO_3 to BHS to 0.50, the NO removal ratio is decreased slightly as the excessive Ag clusters would cover the active sites of BHS, which could shield the substrate $(\text{BiO})_2\text{CO}_3$ from incident light and diminish the active sites for photocatalysis reaction [30,31]. The concentration of reaction intermediate of NO_2 is continuously monitored (Fig. 1b). Based on these data and final oxidation product, the selectivity of NO to NO_2 and NO_3^- can be determined. The selectivity of NO to NO_3^- increases from 83.1% for BHS to 90.0% for BHS-Ag-0.20. This result implies that the Ag clusters could not only enhance the photocatalytic NO removal ratio, but also increase the selectivity of NO to NO_3^- . This is beneficial for environmental applications. The formation of cationic Ag clusters can be ascribed to the interaction of Ag^+ ions with the adjacent O atoms (discuss later). When different amount of AgNO_3 is added, the cationic Ag clusters with different loading would be formed. In this sense, the amount of AgNO_3 could reflect the content of Ag clusters on the surface of BHS.

Obviously, Ag metal should not be generated as no reductant is used in the synthesis process, which indicates a different mechanism from Ag metal-decorated $(\text{BiO})_2\text{CO}_3$. What is the true chemical state of Ag in the BHS-Ag samples? What is the mechanism of the activity enhancement? In the next study, a systematic investigation is focused on these issues.

3.2. Phase structure

Fig. 2 presents the XRD patterns of pure BHS and BHS-Ag-X with different AgNO_3 contents. All the diffraction peaks detected can be indexed to tetragonal $(\text{BiO})_2\text{CO}_3$ (JCPDS-ICDD Card No. 41-1488).

No peaks of any other phases (such as Ag_2CO_3) or impurities can be observed. The position of diffraction peaks of BHS-Ag-X does not change in comparison with BHS, which suggests that the Ag clusters is highly dispersed on the surface of BHS instead of entering into the lattice. According to Li's report, Ag^+ would be reduced to metal Ag by citrate ion in bismuth citrate under hydrothermal treatment [19]. In our case, the process was conducted at 60°C without supplying any reductive agents. Therefore, the Ag metal would not be generated. In addition, Ag^+ would not combine with carbonate ions to form Ag_2CO_3 because the solubility constant (K_{sp}) of Ag_2CO_3 (1×10^{-11}) is much higher than that of $(\text{BiO})_2\text{CO}_3$ (3.98×10^{-36}).

3.2. Morphological structure

The morphology and microstructure of the obtained samples were characterized by SEM, TEM and HRTEM. Fig. 3a and b show that the pure BHS sample consists of many three-dimensional (3D) flower-like hierarchical superstructures self-assembled with two-dimensional (2D) nanosheets. These microspheres are in different sizes ranging from 0.9 to $1.5 \mu\text{m}$. As shown in Fig. 4a and b, the BHS-Ag-0.20 has similar morphology in comparison with pure BHS, which indicates that the Ag clusters modification does not change the morphological structure of BHS. As the Ag clusters is too small that it cannot be observed directly in the SEM image.

Fig. 5b shows the energy dispersive spectrometer (EDS) spectra recorded on several microspheres in Fig. 5a. The C, O, Bi and Ag elements can be detected. The elemental mapping (Fig. 5c–f) of the microspheres in Fig. 5a indicates that the Ag clusters are uniformly distributed on the $(\text{BiO})_2\text{CO}_3$ superstructures.

In order to further elucidate the structure of the Ag species, TEM and HRTEM was performed. Fig. 6a shows the TEM image of BHS-Ag-0.20, which is solid in center. Fig. 6b shows the typical HRTEM image of a single nanosheet on the edge of the microsphere. The lattice spacing is determined to be 0.294 nm, corresponding to the (013) crystal plane of $(\text{BiO})_2\text{CO}_3$. The lattice spacing of Ag metal cannot be observed. Instead, some amorphous Ag clusters less than 10 nm can be observed on the surface. The existence of Cu(II) , Cr(III) , Fe(III) and Ce(III) nanoclusters on the surface of TiO_2 have also been observed with HRTEM in previous reports [23–28]. With the results of Ag mapping in Fig. 5f and HRTEM observation in Fig. 6b, we can conclude that the small Ag clusters are evenly distributed on the surface of $(\text{BiO})_2\text{CO}_3$ superstructures.

3.4. BET surface areas and pore structure

N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves of BHS-Ag-X with different Ag contents are shown in Fig. 7. As displayed in Fig. 7a, all the samples have an isotherm of type IV and type H3 hysteresis loops ($P/P_0 > 0.4$),

Fig. 4. The SEM (a, b) of Ag clusters-grafted $(\text{BiO})_2\text{CO}_3$ hierarchical superstructures (BHS-Ag-0.20).

Fig. 5. The SEM image (a), EDS spectra (b) and elemental mapping (c–f) of BHS-Ag-0.20.

Fig. 6. TEM (a) and HRTEM (b) images of BHS-Ag-0.20.

which indicates the presence of mesopores (2–50 nm) in all the samples. The hysteresis loops of BHS-Ag is the same as pure BHS, indicating that the Ag clusters just exist on the surface of BHS without modifying the pore structure. The BHS-Ag-0.20 samples have a slightly higher N_2 absorption at the relatively high pressure, indicating the presence of more mesopores [17]. Fig. 7b shows that the three samples have peak pore sizes at 3.6 and 7.4 nm. The small

mesopores can be ascribed to the pores formed with the microspheres, while the large mesopores are originated from the porosity formed among the stacked microspheres [19]. The S_{BET} , pore volume and peak pore diameter are summarized in Table 1. The catalyst with high surface areas and abundant mesopores would facilitate the exposure of active sites and promote the photocatalysis efficiency. The Ag clusters are very small (less than 10 nm) and

Fig. 7. N₂ adsorption-desorption isotherms (a) and pore size-distribution curves (b) of BHS-Ag-X with different AgNO₃ contents.

the amount of Ag clusters on the surface is not high. Therefore, the grafting of these small Ag clusters on the microspheres would exert little influence on the S_{BET} of the microspheres.

3.5. Local chemical structures of Ag clusters by XPS and EXAFS

In order to reveal the chemical state of the elements in the BHS and BHS-Ag-2.0 sample, XPS measurement was carried out. In Fig. 8a, we can observe two strong peaks at 164.2 and 158.9 eV that are corresponded to Bi4f_{5/2} and Bi4f_{7/2} of Bi³⁺ in BHS. Compared with pure BHS, a positive chemical shift of 0.20 eV can be observed for Ag clusters grafted BHS, that indicates the interfacial interaction between (BiO)₂CO₃ and grafted Ag clusters, which has also been confirmed with HRTEM (Fig. 6b) [30,31]. Fig. 8b shows the XPS spectra for Ag3d_{3/2} and Ag3d_{5/2}. The binding energy of Ag3d_{5/2} and Ag3d_{3/2} appears at around 368.2 and 374.5 eV, which indicate that the Ag species on the surface should be in the oxidized state [34–38]. From the C1s spectra in Fig. 8c, the peaks in BHS and BHS-Ag-0.20 centered at 284.8, 287.6, and 288.7 eV can be attributed to C–C, C=O and O=C–O groups, respectively. The O1s spectra (Fig. 8d) are also recorded. The binding energies around 530.9 eV is the characteristic peak of Bi–O binding energy in (BiO)₂CO₃ [19]. The shifting of the Bi–O binding energy in BHS-Ag-0.20 can be also ascribed to the interfacial interaction between (BiO)₂CO₃ and Ag clusters.

It is well-known that it is difficult for XPS to reveal the precise chemical state of Ag species. Thus, EXAFS technique was used to determine the chemical state and coordination structure of Ag clusters on BHS-Ag-0.20. The curve fitting was performed as shown in Fig. S1. Fig. 9a were plotted as radial function of BHS-Ag-0.20. The Ag–K absorption oscillation curves are processed via removal background, normalizing and fourier transformation by multiple K^3 to make good the decay at high K range. The x-coordinate ($R/\text{\AA}$) means the distance around the center atom of silver (Ag), and the y-coordinate (FT) means the chemical coordination number around center atom silver. It can be determined from Fig. 9a that the Ag–O bond distance and coordination number are 2.40 $\text{\AA}$ and 2.88–3.0, which means the average silver local structure are surrounded by almost 30 atoms [39]. The Ag–Ag shell with bond distance of 2.91 $\text{\AA}$ and coordination number of 4.69 can be determined, thus we deduce the average silver local structure also bonded with other 5 Ag atoms [40]. He and Deng reported the presence of silver clusters (Ag_n^{δ+} and Ag_n⁰) in Ag/Al₂O₃ catalyst [39]. Yoon et al. revealed that the presence of cationic silver clusters (Ag_n^{δ+} and Ag_n⁰) could promote the partial oxidation of hydrocarbons and production of active oxygenated species [40]. Based on EXAFS measurement, a theoretical model for the Ag clusters is proposed as shown in Fig. 9b. Obviously, the Ag clusters have coordinated with the surface oxy-

gen atoms of (BiO)₂CO₃, which is crucial for the highly enhanced visible light photocatalytic activity of BHS-Ag.

3.6. Light absorption and charge separation

The pure BHS has a white color. The BHS-Ag samples with the increased amount of Ag clusters show a pale grey color. From the UV–vis DRS spectra (Fig. 10a), we can see that the pure BHS displays the absorption edge around 375 nm. The low visible light absorption can be attributed to the special 3D hierarchical structure of BHS (showed in SEM Fig. 3). According to the UV–vis DRS spectra shown in Fig. 10a, it can be found that the visible light response of BHS is exactly increased with the increase in Ag loading amount. This interesting observation can be owing to the presence of Ag clusters. As we know, Ag metal nanoparticles could exhibit a surface plasmon resonance (SPR) absorption peak centered at 415–450 nm. However, the SPR absorption peak of Ag metal or the characteristic absorption of Ag₂O cannot be observed, which further confirms the role of Ag clusters in the contribution to enhance absorption spectra from 400 to 700 nm. This absorption can be attributable to the IFCT process involving electrons transfer from the valence band to the Ag clusters attached to the surface of (BiO)₂CO₃, which is also consistent with previous reports [31].

To measure the recombination rate of photogenerated electron-hole pairs, PL spectra was applied. A low PL intensity indicates a high charge separation efficiency. As can be seen in Fig. 10b, pure BHS gives the highest peak intensity. With increased Ag content, the intensity of PL peak is significantly decreased, which indicates a largely depressed recombination of photoinduced electron-hole pairs.

To evaluate the electronic interaction between Ag clusters and (BiO)₂CO₃ microspheres, photocurrent generation was carried out for BHS and BHS-Ag-0.20 electrodes as shown in Fig. 11a. It can be seen that prompt photocurrent generation is obtained during on and off cycles under visible light illumination. The photocurrent is gradually decayed with increasing the cyclic test probably due to the loss of the sample in the solution. The BHS shows certain photocurrent under visible light due the SSR effects, consistent with the photocatalytic activity (Fig. 1a). It is significant to observe that the photocurrent of the BHS-Ag-0.20 electrode is much higher than that of the BHS electrode. The photocurrent enhancement of BHS-Ag-0.20 can be ascribed to the enhanced charge separation efficiency due to the presence of Ag clusters, as confirmed with the PL result (Fig. 10b).

Furthermore, electrochemical impedance spectroscopy (EIS) was used to investigate the separation efficiency of electrons/holes pairs. The EIS Nyquist plots for BHS and BHS-Ag-0.20 electrodes

Fig. 8. The XPS spectra of BHS and BHS-Ag-0.20, Bi4f (a), Ag3d (b), C1s (c) and O1s (d).

Fig. 9. EXAFS spectra of BHS-Ag-0.20 (a) and the theoretical model of the Ag clusters (b).

under visible light irradiation are shown in Fig. 11b. The radius of the arc on the EIS spectra indicates the rate of reaction occurring at the surface of the electrode [19]. The smaller arc radius on the EIS Nyquist plot of BHS-Ag-0.20 under visible light irradiation implies that an efficient separation of electron/hole pairs has been achieved. The photoelectrochemical measurements suggest that cationic Ag clusters grafting is a powerful modifier to enhance separation of photogenerated electron/hole pairs and thus enhance the photocatalytic performance.

3.7. Photocatalysis mechanism on cationic Ag clusters-grafted BHS

Recently, Ag clusters have been supported on Al_2O_3 and utilized to enhance the catalytic reduction of NO_x [39]. The supported silver species attached to surface oxygen atoms are predominantly in +1 oxidation state ions. The Ag clusters can ionically bond with adsorbates, forming Ag–O–Al ionic bond [39]. Hellman and co-workers proposed that the Ag clusters incorporated into the alumina matrix would be in an oxidized state, which was beneficial for the NO_x adsorption [41]. These examples imply that the Ag clusters could

Fig. 10. UV-vis DRS spectra (a) and PL (b) of BHS and BHS-Ag-X with different Ag clusters contents.

Fig. 11. Photocurrent generation (a) and Nyquist plots (b) for BHS and BHS-Ag-0.20 electrodes under visible light irradiation ($\lambda > 420$ nm, $[\text{Na}_2\text{SO}_4] = 0.5$ M).

coordinate with surface oxygen atoms in a stable chemical state. In our case, the $(\text{BiO})_2\text{CO}_3$ has a typical layered structure with alternative stacking of $(\text{BiO})_2^{2+}$ layers interleaved by CO_3^{2-} groups [42,43]. The special crystal structure could behave as an excellent host substrate. So, it is highly possible that the Ag clusters can bond with $(\text{BiO})_2^{2+}$ layers to form cationic Ag clusters as also evidenced with EXAFS (Fig. 9).

To reveal the reactive species and the mechanism accounting for the photocatalytic oxidation of NO, an ESR spin-trap technique with DMPO for $\cdot\text{OH}$ radicals (Fig. 12a) was employed. As displayed in Fig. 12, no signal can be observed in the dark. Under visible light illumination (420 nm), the signals indexed to $\cdot\text{OH}$ radicals appear. The intensity of the peaks is increased as the irradiation time is prolonged. These results imply that the $\cdot\text{OH}$ radicals are responsible for the photocatalytic oxidation of NO in air. Because the potential of $(\text{BiO})_2\text{CO}_3$ conduction band (0.20 eV) and Ag^+/Ag (0.779 eV) is more positive than that of $\text{O}_2/\cdot\text{O}_2^-$ (−0.33 eV), the $\cdot\text{O}_2^-$ radicals would not be generated.

On the basis of the systematic investigation, we propose a new visible light photocatalysis mechanism of Ag clusters-grafted BHS as shown in Fig. 12b. Under visible light irradiation, the excited electrons in the valence band of $(\text{BiO})_2\text{CO}_3$ can be directly transferred to Ag clusters through an interfacial charge transfer (IFCT) process as the conduction band potential of $(\text{BiO})_2\text{CO}_3$ (0.20 eV) is lower than the redox potential of Ag^+/Ag (0.779 eV). The Ag^0 would be temporarily formed, which is capable of reducing O_2 , while the photogenerated holes remain in the valence band. As the potential of the Ag^+/Ag (0.779 eV) is higher than that of lower than

that of $\text{O}_2/\text{H}_2\text{O}_2$ (0.68 eV) and lower than that of $\text{O}_2/\text{H}_2\text{O}$ (1.23 eV), the electrons on Ag could reduce O_2 through a four electron process ($\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$). Although the actual mechanism needs further investigation, these results suggest that Ag clusters grafted BHS result in a significant activity enhancement. The use of multielectron-reduction clusters for oxygen reduction (such as Cu (II) and Fe(III)) has also been demonstrated to enhance the photocatalytic performance of other photocatalysts (TiO_2 and Bi_2O_3) [28–31].

The IFCT process is beneficial for charge separation as observed with PL and photocurrent generation (Figs. 10 and 11). As the potential of the holes at the valence band of $(\text{BiO})_2\text{CO}_3$ (3.53 eV) is more positive than the redox potential of $\text{OH}^-/\cdot\text{OH}$ (1.99 eV) [17], the holes can directly oxidize OH^- to $\cdot\text{OH}$ radicals ($\text{OH}^- + \text{h}^+ \rightarrow \cdot\text{OH}$, Fig. 12a), which could act as major reactive species for the photooxidation of NO to final NO_3^- product ($\text{NO} + 2\cdot\text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$, $\text{NO}_2 + \cdot\text{OH} \rightarrow \text{NO}_3^- + \text{H}^+$) [19,44]. Considering the similar surface areas, the highly enhanced visible light photocatalysis of Ag clusters-grafted BHS can be ascribed to the light reflecting and scattering effects benefited from hierarchical superstructure, and promoted charge separation benefited from IFCT process. Significantly, this photocatalysis mechanism is different from the Ag-metal deposited $(\text{BiO})_2\text{CO}_3$, where the surface plasmon effect is a dominant reason [19]. Therefore, the present work could open up a new scope for developing strategies in enhancing photocatalysis.

Fig. 13 The photochemical stability of a photocatalyst under repeated irradiation should be considered for practical applications [44,45]. An excellent photocatalyst should maintain stable activ-

Fig. 12. DMPO spin-trapping ESR spectra of BHS-Ag-0.20 in an aqueous dispersion for DMPO•OH (a), schematic illustration of the photocatalysis mechanism of Ag clusters-grafted BHS under visible light involving interfacial charge transfer (IFCT) processes (b).

Fig. 13. The repeated visible light photocatalytic activities of BHS-Ag-0.20 for the removal of NO in air.

ity and structure so that the catalyst can be used repeatedly. To test the stability, we conduct multiple photocatalytic runs for NO_x removal. Although C/C_0 for BHS-Ag-0.20 is gradually increased with increasing the cyclic test (Fig. 13), BHS-Ag-0.20 exhibits a decent stability in activity without obvious deactivation under five consecutive runs. Fig. S2a shows the XRD patterns of BHS-Ag-0.20 before and after irradiation and indicates the absence of any peaks of Ag or another Ag-based compounds except for the diffraction peaks of BHS after irradiation. The UV–vis DRS spectra of the BHS-Ag-0.20 before and after irradiation are shown in Fig. S2b. Also, the SPR absorption peak of Ag could not be detected. These results imply that the Ag clusters could be well-maintained after repeated irradiations, which is responsible for the high photocatalytic stability.

By combining the analysis results, we can conclude that the unique Ag clusters are very stable and superior to the Ag metal. Therefore, Ag clusters can be utilized to modify the surface semiconductor photocatalysts via an IFCT process for enhanced activity and stability. Also, considering the facile preparation process for cationic Ag clusters-grafted $(\text{BiO})_2\text{CO}_3$ hierarchical superstructures with highly enhanced visible light photocatalysis, the present method could be envisioned to be extended to other types of semiconductor photocatalysts.

4. Conclusion

The pure $(\text{BiO})_2\text{CO}_3$ hierarchical superstructures exhibits decent visible light photocatalytic performance because of the multiple light reflecting and scattering effects endowed with the 3D hierarchical architectures. With the addition of AgNO_3 , the cationic Ag clusters-grafted $(\text{BiO})_2\text{CO}_3$ hierarchical superstructures can be readily produced and exhibit highly enhanced visible light photocatalytic activity and photocurrent generation through an interfacial charge transfer process induced by Ag clusters. A theoretical structural model for this unique cationic Ag clusters is proposed based on the chemical and coordination state of the cationic Ag clusters ($\text{Ag}_n^{\delta+}$ and Ag_n^0) with EXAFS. The optimized BHS-Ag-0.20 exhibits an unprecedented photocatalytic NO removal ratio of 52.8%. A new visible light photocatalysis mechanism of Ag clusters-grafted BHS is proposed based on IFCT and reactive species trapping. The Ag clusters are stable under repeated irradiation, which enables the high photochemical activity and structural stability of Ag clusters-grafted $(\text{BiO})_2\text{CO}_3$ superstructures. Both the hierarchical superstructures and the Ag clusters co-contributed to the enhancement of the visible-light photocatalysis. The concept of promoting visible-light photocatalysis through interfacial charge transfer with cationic nanoclusters could also be extended to other semiconductor photocatalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.05.007>.

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