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## Efficient visible light photocatalytic NO<sub>x</sub> removal with cationic Ag clusters-grafted (BiO)<sub>2</sub>CO<sub>3</sub> hierarchical superstructures

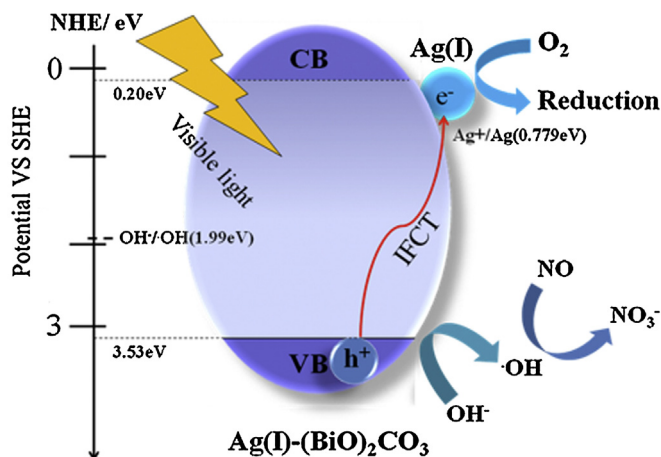
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### HIGHLIGHTS

- Microstructural optimization and surface cluster-grafting were firstly combined.
- Cationic Ag clusters were grafted on the surface of (BiO)<sub>2</sub>CO<sub>3</sub> 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)<sub>2</sub>CO<sub>3</sub> 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)<sub>2</sub>CO<sub>3</sub> 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<sub>x</sub> 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 (<sup>•</sup>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  $\text{Bi}_2\text{WO}_6$ ,  $\text{Bi}_2\text{MoO}_6$ ,  $\text{BiVO}_4$ ,  $\text{BiOX}$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ),  $\text{BiFeO}_3$ ,  $\text{Bi}_2\text{Ti}_2\text{O}_7$ ,  $\text{Bi}_2\text{Sn}_2\text{O}_7$ , 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,  $\text{Cu(II)}$ ,  $\text{Cr(III)}$ ,  $\text{Fe(III)}$  and  $\text{Ce(III)}$  nanoclusters have been grafted on the surface of  $\text{TiO}_2$  [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  $\text{TiO}_2$  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  $\text{TiO}_2$  [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  $\text{AgNO}_3$  aqueous solution. The chemical and coordination state of the Ag clusters ( $\text{Ag}_n^{\delta+}$  and  $\text{Ag}_n^0$ ) 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  $\text{NO}_x$  removal with cationic Ag clusters-grafted  $(\text{BiO})_2\text{CO}_3$  hierarchical superstructures.  $\text{NO}$  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  $\text{NO}$  in air can be photocatalytically converted into final less harmful products ( $\text{NO}_3^-$ ) [12]. The various characterizations were applied to gain insight in the structure-performance relationship in  $\text{NO}$  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 pho-

tochemical stability and durability in  $\text{NO}_x$  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.

## 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  $60^\circ\text{C}$  and stirred for 30 min. Then the 40 mL of  $\text{AgNO}_3$  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  $60^\circ\text{C}$  for 12 h to get the final products. The molar ratio of  $\text{AgNO}_3$  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  $\text{AgNO}_3$  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  $2\theta$  range of  $5^\circ$ – $80^\circ$  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  $150^\circ\text{C}$  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%  $\text{BaSO}_4$  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-

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