SPECIAL TOPIC: Advanced Photocatalytic Materials

Flower-like Bi⁰/CeO_{2-δ} plasmonic photocatalysts with enhanced visible-light-induced photocatalytic activity for NO removal

Junli Nie¹, Jianzhi Gao¹, Qian Shen^{2*}, Weibin Zhang³, Fei Rao¹, Mirabbos Hojamberdiev⁴ and Gangqiang Zhu^{1*}

ABSTRACT Plasmonic bismuth (Bi⁰) nanoparticle-decorated flower-like CeO_{2-δ} (Bi⁰/CeO_{2-δ}) photocatalysts with abundant oxygen vacancies (OVs) were synthesized *via* a solvothermal method. The OVs can not only improve the separation of electron-hole pairs, but also facilitate the adsorption and activation of gas molecules (NO/O₂). In addition, the Bi⁰ nanoparticles can enhance the visible light response and prevent the recombination of charge carriers by virtue of the surface plasmon resonance (SPR) effect, achieving an excellent ability for NO elimination and NO₂ inhibition under visible light irradiation. Density functional theory (DFT) calculations confirm that the Schottky barrier between Bi⁰ and CeO_{2-δ} accompanied with the OVs are pivotal for the migration of photogenerated charge carriers to involve in the photocatalytic NO removal. Trapping experiments and *in situ* FTIR spectroscopy were conducted to explore the mechanism of the photocatalytic NO removal, suggesting that the photocatalytic NO removal can be significantly enhanced by introducing abundant OVs and the involvement of Bi⁰ metal nanoparticles.

Keywords: cerium oxide, bismuth nanoparticles, oxygen vacancy, surface plasmon resonance, Schottky barrier, NO removal

INTRODUCTION

The nitric oxide (NO) pollutants emitted from vehicles and industries are pernicious to the environment and human health [1,2]. Semiconductor-based photocatalytic oxidation technology has recently drawn much attention in NO removal owing to its high efficiency, less energy

consumption, and eco-friendliness nature [3]. Much efforts have been done to explore various photocatalysts with excellent photocatalytic activities, such as TiO₂ [4], Bi₅O₇I [5], g-C₃N₄ [6], etc. Among them, CeO₂, a promising metal oxide semiconductor, has been extensively applied in various applications, including photocatalysis [7], gas detection [8], and pharmaceuticals [9]. The Ce⁴⁺/Ce³⁺ redox couple in CeO_{2-δ} induces the formation of oxygen vacancies (OVs), decreasing the band gap energy and enhancing the visible light response [10]. The OVs as anchor centers can limit the recombination of electron-hole pairs [11]. Moreover, it is also reported that OVs are beneficial to the adsorption and activation of molecular O₂, which facilitates the generation of superoxide radicals (·O₂⁻ and O₂⁻) in the dark [12]. In addition, OVs are convenient for the conversion of NO to NO₃⁻ and NO₂ to NO₂⁻, hindering the generation of toxic intermediates NO₂ [13]. Thus, CeO_{2-δ} is believed to be an excellent photocatalyst for NO removal owing to its sufficient redox ability and OV-rich surface. However, CeO_{2-δ} with a wide band gap shows a low visible-light photocatalytic activity, and its efficiency is hindered by the inadequate separation of charge carriers [14,15].

Among various approaches toward ameliorating the poor efficiency of photogenerated charge carriers, a semimetal Bi⁰/semiconductor composite is believed to be an excellent photocatalytic system. It is documented that the semimetal Bi⁰ nanoparticles endowed with the surface plasmon resonance (SPR) effect can extend the visible light response and accelerate the separation of charge

¹ School of Physics and Information Technology, Shaanxi Normal University, Xi'an 710062, China

² Key Laboratory of Flexible Electronics (KLOFE) and Institute of Advanced Materials (IAM), Nanjing Tech University, Nanjing 211816, China

³ School of Physics and Optoelectronic Engineering, Yangtze University, Jingzhou 434023, China

⁴ Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

* Corresponding authors (emails: zgq2006@snnu.edu.cn (Zhu G); iamqshen@njtech.edu.cn (Shen Q))

carriers, resulting in a superior photocatalytic activity. Chen *et al.* [16] reported that Bi⁰-decorated Bi₂O₃ exhibited a significantly improved photocatalytic activity for NO abatement. Li *et al.* [17] elucidated that the Bi⁰-loaded composites displayed an appreciable performance for NO removal and NO₂ inhibition. More importantly, the Bi⁰ can substitute noble metals (e.g., Au [18], Pt [19], Pd [20], etc.) to construct the Schottky barrier with a semiconductor. It further improves the visible light response and boosts the separation of photogenerated charge carriers [21], inducing the formation of active species to degrade the pollutants [22]. Hence, the amalgamation of Bi⁰ nanoparticles onto a semiconductor can bring an extraordinary efficiency to NO purification and the suppression of harmful products. Inspired by the above-mentioned merits, it is reliable to couple Bi⁰ with CeO_{2-δ} for achieving high efficiency in NO removal and NO₂ inhibition.

In this study, the semimetal Bi⁰ nanoparticles were loaded on the flower-like CeO_{2-δ} *via* a solvothermal method. It is expected that the Schottky junction formed between the Bi⁰ and CeO_{2-δ} can trigger the separation of charge carriers. Furthermore, OV_s are helpful to enhance the absorption of light and the activation of molecules. Thus, the Bi⁰/CeO_{2-δ} photocatalysts show an excellent photocatalytic activity for NO removal due to the synergistic effect of OV_s and the SPR effect of the Bi⁰ nanoparticles. More importantly, the Bi⁰/CeO_{2-δ} photocatalyst was treated by H₂O₂ for investigating the indispensable roles of OV_s in NO₂ elimination. Density functional theory (DFT) calculations were also involved to analyze the improved interfacial charge separation caused by the OV_s and Bi⁰ nanoparticles. The underlying mechanism of the photocatalytic NO removal by the Bi⁰/CeO_{2-δ} photocatalyst was studied by trapping experiments and *in situ* FTIR spectroscopy.

EXPERIMENTAL

Synthesis of Bi⁰-decorated CeO_{2-δ}

All chemical reagents were of analytical grade and used without further purification. The flower-like CeO_{2-δ} powders were synthesized by a hydrothermal method followed by thermal treatment under N₂ and air. The detailed synthetic procedure was given in Supplementary information (SI). The Bi⁰-decorated CeO_{2-δ} photocatalysts were prepared by a solvothermal method. Firstly, 3 mmol of CeO_{2-δ} powder was dispersed in 50 mL of ethylene glycol, and then Bi(NO₃)₃·5H₂O was added with different amounts (2%, 6%, 10% and 14%). After stirring

for 30 min, the mixture was transferred into a 100-mL Teflon-lined stainless steel autoclave and maintained at 160°C for 12 h. The resulting precipitate was collected, washed with deionized water, and dried at 60°C for 12 h. The samples were denoted as x% Bi⁰/CeO_{2-δ} (x = 2, 6, 10, and 14) according to the amount of Bi⁰ nanoparticles.

Characterization

The crystal phase information of the powders was confirmed by X-ray powder diffraction (XRD, Bruker D8 Advance). X-ray photoelectron spectroscopy (XPS) was carried out on a Theta Probe AR-XPS System (Thermo Fisher Scientific, USA). The UV-vis absorption spectra of the samples were recorded on a Cary 5000 (Agilent) UV-vis-NIR spectrophotometer. The microstructures and nanostructures were observed on scanning electron microscope (SEM, Nova NanoSEM 450, FEI) and transmission electron microscope (TEM, JEM-2100F, JEOL). The elemental mapping images of the samples were investigated by an energy-dispersive X-ray spectrometer (EDX) attached to the TEM. The detailed evaluation of photocatalytic activity for NO removal, *in-situ* FTIR analyses of the photocatalytic NO removal process, trapping experiments and computational studies were given in SI.

RESULTS AND DISCUSSION

Crystal structure and morphology

The XRD patterns of the as-synthesized samples are displayed in Fig. 1a. The identifiable diffraction peaks at 2θ = 28.6°, 33.1°, 47.5° and 56.3° belong to the crystallographic planes of cubic phase CeO₂ (ICDD PDF# 34-0394). In the XRD patterns of the Bi⁰/CeO_{2-δ} photocatalysts, the predominant diffraction peaks are in good agreement with that of the cubic phase CeO₂, while minor diffraction peaks can be assigned to the crystallographic planes of the hexagonal phase of Bi⁰ (ICDD PDF# 44-1246). Clearly, the intensity of the diffraction peaks of the hexagonal phase Bi increased with the increasing amount of Bi⁰ content, indicating the successful synthesis of the Bi⁰/CeO_{2-δ} photocatalysts.

The surface chemical compositions of CeO_{2-δ} and 10% Bi⁰/CeO_{2-δ} were determined by XPS. As shown in Fig. S1, the XPS survey spectrum of CeO_{2-δ} contains Ce, O, and C, while the Bi, Ce, O, and C are present in the survey spectrum of 10% Bi⁰/CeO_{2-δ}. The C signal observed at 284.6 eV is associated with adventitious carbon [23]. The peaks in the range of 875–920 eV are ascribed to the Ce 3d states of CeO_{2-δ} and 10% Bi⁰/CeO_{2-δ} (Fig. 1b). The

Figure 1 (a) XRD patterns of CeO_{2-δ} and Bi⁰/CeO_{2-δ} photocatalysts. High-resolution XPS spectra of (b) Ce 3d, (c) O 1s, and (d) Bi 4f of CeO_{2-δ} and 10% Bi⁰/CeO_{2-δ} samples. (e) UV-vis absorption spectra of all the samples. (f) EPR spectrum of CeO_{2-δ} and 10% Bi⁰/CeO_{2-δ} photocatalyst.

peaks labeled as *a*, *c* and *d* can be assigned to the Ce⁴⁺ 3d_{5/2} states, and other three peaks of *a'*, *c'* and *d'* are attributed to the Ce⁴⁺ 3d_{3/2} states, confirming a +4 oxidation state of cerium in the photocatalysts [24]. The peaks of *b* and *b'* are associated with a +3 oxidation state of cerium, indicating the coexistence of Ce⁴⁺/Ce³⁺. The emergence of Ce³⁺ implies the defects, while Ce⁴⁺ represents numerous sites of electron trapping, leading to an appreciable photocatalytic activity [25]. The O 1s signals at 529.0, 530.8 and 531.4 eV are assignable to the Ce–O bond, oxygen vacancies, and adsorbed oxygen, respectively (Fig. 1c). The two obvious peaks centered at 157.1 and 162.3 eV can be indexed to the Bi⁰ 4f_{7/2} and Bi⁰ 4f_{5/2} of 10% Bi⁰/CeO_{2-δ} (Fig. 1d), respectively. The corresponding peaks of Ce 3d and O 1s in 10% Bi⁰/CeO_{2-δ} were slightly shifted towards higher binding energy after loading Bi⁰ nanoparticles, implying an intimate contact between Bi⁰ and CeO_{2-δ}.

The UV-vis absorption spectra of the as-synthesized photocatalysts are demonstrated in Fig. 1e. Clearly, the absorption edge of CeO_{2-δ} is located at 460 nm, indicating a weak visible light response. As a direct semiconductor, the estimated band gap energy of CeO_{2-δ} is 2.88 eV according to the equation: $(\alpha h\nu)^2 = h\nu - E_g$, where $h\nu$ is the incident photon energy, E_g is the optical band gap, and α is the absorption coefficient, which is obtained near the absorption edge from the transmittance [26]. In com-

parison with CeO_{2-δ}, the Bi⁰/CeO_{2-δ} photocatalysts exhibit an enhanced light absorption extending from visible to near infrared (NIR) region, and the absorption intensity increases with the increasing Bi⁰ content. This obvious harvest of light absorption in the Bi⁰/CeO_{2-δ} photocatalysts may mainly result from the SPR effect of Bi⁰ nanoparticles [17]. The electron paramagnetic resonance (EPR) spectra of the samples are shown in Fig. 1f. Clear EPR signals centered at $g = 2.003$ indicate a high concentration of OV in the CeO_{2-δ} and 10% Bi⁰/CeO_{2-δ} photocatalysts. It is expected that the OV in the photocatalysts can promote the electron mobility and enhance the visible light absorption.

As shown in Fig. S2a, b, the three-dimensional flower-like architectures of CeO_{2-δ} with a diameter of 1.5–3 μm were assembled by nanosheets. The TEM images in Fig. S2c, d reveal that the CeO_{2-δ} nanosheets were formed by the agglomeration of nanoparticles. The high-resolution TEM (HRTEM) image in Fig. S2e illustrates a lattice spacing of 0.311 nm, which is in agreement with the (111) crystal plane of CeO₂. In the selected area electron diffraction (SAED) pattern in Fig. S2f, the lattice spacings of 0.313, 0.188, and 0.153 nm are indexed to the (111), (220) and (222) crystallographic planes of CeO₂, confirming the high crystallinity of the flower-like CeO_{2-δ} architectures. After loading the Bi⁰ nanoparticles, the 10% Bi⁰/CeO_{2-δ} photocatalyst still retains its flower-like morphology

Figure 2 (a, b) SEM images, (c) TEM and (d, e) HRTEM images, (f) Scanning TEM image, and (g) EDX element mapping images of 10% Bi⁰/CeO_{2-δ}.

(Fig. 2a). The Bi⁰ nanoparticles in different sizes are embedded on the flower-like architectures of CeO_{2-δ} (Fig. 2b, c). Fig. 2d, e show that the lattice spacings of 0.310 and 0.327 nm can be assigned to the (111) and (012) crystallographic planes of CeO_{2-δ} and Bi⁰, respectively. The EDX element mapping images in Fig. 2f, g confirm that the Ce and O are homogeneously dispersed and Bi⁰ mainly appears on the surface of Bi⁰/CeO_{2-δ}. The combination of CeO_{2-δ} and Bi⁰ is beneficial to the migration of photoinduced charge carriers, resulting in high photocatalytic performance [27].

Generally, a photocatalyst with a high specific surface area exhibits much more active sites for photocatalysis. Table S1 indicates that the specific surface areas of CeO_{2-δ}, 2% Bi⁰/CeO_{2-δ}, 6% Bi⁰/CeO_{2-δ}, 10% Bi⁰/CeO_{2-δ} and 14% Bi⁰/CeO_{2-δ} are 135.95, 94.69, 84.76, 77.74, and 71.49 m² g⁻¹ (Fig. S3), respectively. Although the specific surface area decreases after loading excess Bi⁰ nanoparticles, the 10% Bi⁰/CeO_{2-δ} photocatalyst still demonstrates higher specific surface area than many other photocatalysts provided in Table S2, contributing to the high photocatalytic activity.

The band structures and the density of states were investigated by DFT calculations to understand the influ-

ence of OV's (Fig. S4). The band gap energies of CeO₂ and CeO_{2-δ} are 2.74 and 2.58 eV, respectively, indicating an enhanced light absorption in CeO_{2-δ}. Moreover, the CeO_{2-δ} with a lower hybrid electron density is conducive to the migration of photoinduced charge carriers. Therefore, the OV's in CeO_{2-δ} ensure an enhanced light responsiveness and superior performance for the separation of photoinduced charge carriers.

Photocatalytic activity for NO removal

The photocatalytic activities for NO removal of the samples were evaluated under visible light irradiation. Fig. 3a displays that the NO concentration changed with the prolonging reaction time. The NO removal efficiency of CeO_{2-δ} was only 27.0% after 30 min light irradiation, and the Bi⁰ demonstrated negligible NO removal ability. It is clear that the photocatalytic activity of Bi⁰/CeO_{2-δ} surpasses that of pure CeO_{2-δ} and Bi⁰. As shown in Fig. 3b, the NO removal rates of 36.2%, 40.5%, 43.7%, and 41.2% were achieved by loading 2%, 6%, 10%, and 14% Bi⁰ nanoparticles on CeO_{2-δ} photocatalyst, respectively. The photocatalytic activity for NO removal of the Bi⁰/CeO_{2-δ} photocatalyst was gradually improved by loading Bi⁰ nanoparticles up to 10% and then decreased at 14%.

Figure 3 (a) The change of NO concentration versus visible light irradiation time. (b) The NO removal rate of the samples. (c) The generation of NO_2 over different samples. (d) The photocatalytic NO removal under light irradiation with different wavelength-filters (420, 500, 550, and 600 nm). (e) *In situ* FTIR spectra measured during the adsorption of $\text{NO}+\text{O}_2$ in the dark. (f) NO oxidation under visible light irradiation over 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalyst.

This is because the formed heterojunction enhanced the light absorption and the separation of charge carriers, leading to an improved photocatalytic activity. However, an excess amount of Bi^0 nanoparticles occupy the active sites for photocatalytic reaction, causing a decrease in the photocatalytic activity for NO removal [28]. The evolution of NO_2 produced during the photocatalytic process was monitored. As shown in Fig. 3c, the pure $\text{CeO}_{2-\delta}$ generates a relatively high fraction of NO_2 with a yield of 12.14 ppb, while the $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalysts release limited contents of NO_2 . The concentrations of NO_2 generated by 2% $\text{Bi}^0/\text{CeO}_{2-\delta}$, 6% $\text{Bi}^0/\text{CeO}_{2-\delta}$, 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ and 14% $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalysts are 3.64, 3.56, 2.96 and 4.16 ppb, respectively. It is clear that the loading of Bi^0 nanoparticles can suppress the generation of NO_2 , implying that the $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalyst is an appropriate candidate for NO removal.

According to previous studies [17,29], Bi^0 /semiconductor systems show an excellent photocatalytic ability on account of the SPR effect of Bi^0 nanoparticles. To investigate the SPR effect of Bi^0 nanoparticles, $\text{CeO}_{2-\delta}$ and 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalyst were irradiated by light with cut-off filters of 420, 500, 550, and 600 nm to evaluate the photocatalytic performance for NO removal. Fig. 3d and Fig. S5a exhibit that NO removal efficiency

was modulated by light irradiation with different wavelengths and gradually decreased with increasing wavelength of light. NO could not be removed by $\text{CeO}_{2-\delta}$ under light irradiation with 550 and 600 nm cut-off filters. However, the NO removal rates of 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ under light irradiation with 500, 550, and 600 nm cut-off filters are about 22.3%, 8.30%, and 4.30%, respectively. It indicates that the low energy photons with the wavelengths of 550 and 600 nm in 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ still can generate some active radicals. The photocatalysis can be initiated by plasmonic hot electrons generated by the SPR effect of Bi^0 . Hence, the $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalysts still show a photocatalytic property for NO removal irradiated by light with longer wavelengths. The stability and reusability of the 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalyst were evaluated and shown in Fig. S5b. The NO removal efficiency and the generated concentration of NO_2 slightly change after five repeated runs, which represents outstanding stability of 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$. In addition, the XRD patterns (Fig. S5c) and XPS spectra (Fig. S5d–f) of the 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalysts show no significant change in crystallinity and surface chemical composition before and after the photocatalytic reaction, implying that the prepared photocatalyst has an excellent structural and chemical stability.

In situ FTIR spectroscopy was used to monitor the formed intermediates and final products during the photocatalytic process. During the adsorption process in Fig. 3e, the peaks associated with NO at 1541 cm^{-1} were remarkably intensified as the irradiation time was prolonged [30]. Moreover, the OV promoted the formation of many active radicals, including O_2^- and $\cdot\text{O}_2^-$ [31], which would further oxidize NO to form bridging nitrate (NO_2^-), with the peaks at 1059 and 1457 cm^{-1} [32,33]. Part of NO_2^- was further converted into nitrite (NO_3^-) and adsorbed at 1025 , 1225 , and 1641 cm^{-1} [34,35]. Some peaks of nitrosyls adsorbed on the surface of photocatalysts can also be observed at 1717 cm^{-1} [32,36]. Therefore, the change of the *in situ* FTIR spectra in the dark resulted from the physical adsorption and oxidation of NO.

The photolysis of NO was initiated under visible light irradiation (Fig. 3f), resulting in that some products vanished by means of the effects of active species. Except the bands at 1059 and 1641 cm^{-1} , all other vibrations ascribed to the NO_3^- , NO_2^- , and NO_2 were also generated. The peak assignable to the preliminary product (NO_2) at 1365 cm^{-1} was intensified due to the direct oxidation of NO [37]. The new peaks at 857 and 1186 cm^{-1} were assigned to NO_2^- [32,38], while the peaks at 933 , 1030 , and 1557 cm^{-1} could be ascribed to the monodentate/bidentate NO_3^- [34,39]. Besides, part of the products tended to be converted into the most stable nitrate and enwrapped the active sites, reducing the photocatalytic activity.

It is well known that OVs can boost the separation of photogenerated charge carriers, further inducing more reactive oxygen species throughout the whole reaction [31]. Also, the adsorption and photocatalytic activation of NO/ O_2 are attributed to the OVs on the surface of photocatalysts [12]. To investigate the role of OVs during the photocatalytic NO removal, the photocatalysts were treated by hydrogen peroxide (H_2O_2) to oxidize Ce^{3+} to form Ce^{4+} , efficiently reducing the concentrations of the OVs in the 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalyst [40]. Fig. S6a, b show that the photocatalytic NO removal rate of 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ treated with H_2O_2 apparently dropped, and the generation of NO_2 was significantly increased from 2.96 to 11.6 ppb. Thus, it indicates that the OVs are beneficial to the photocatalytic oxidation of NO and can hinder the formation of NO_2 during the photocatalytic process.

Mechanism

The photoelectrochemical and photoluminescence properties of $\text{CeO}_{2-\delta}$ and 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalyst are

shown in Fig. S7a–c to illustrate the influence of Bi^0 and OVs on the photocatalytic activity of $\text{CeO}_{2-\delta}$. The 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ electrode shows a higher photocurrent response (Fig. S7a), indicating an efficient separation of photogenerated charge carriers. Clearly, the electrochemical impedance spectroscopy (EIS) Nyquist plot of the 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ electrode (Fig. S7b) displays a smaller radius in comparison to that of $\text{CeO}_{2-\delta}$, confirming a higher-efficiency transfer of photogenerated charge carrier [41]. The photoluminescence spectra of $\text{CeO}_{2-\delta}$ and 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalyst further reveal an efficient transfer efficiency of photogenerated charge carrier in 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ (Fig. S7c). Thus, the synergistic effects of Bi^0 and OVs facilitate the separation of photogenerated electron and holes, leading to a desirable photocatalytic oxidation activity for NO removal.

As shown in Fig. S7d, the additional photocatalytic experiments were performed using various radical scavengers to insight into the roles of the involved active species during the photocatalytic process of the 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalyst [42]. It was found that e^- , h^+ , $\cdot\text{O}_2^-$, and $\cdot\text{OH}$ were involved in the photocatalytic NO removal. Particularly, e^- showed a pronounced effect throughout the photocatalytic reaction. Furthermore, the electron spin resonance (ESR) measurements were conducted using $\text{CeO}_{2-\delta}$ photocatalyst (Fig. S7e, f), confirming that reactive $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ species were involved in the photocatalytic NO removal. Therefore, it can be inferred that the generated active species (e^- , h^+ , $\cdot\text{O}_2^-$ and $\cdot\text{OH}$) have a significant influence on the overall photocatalytic process.

When $\text{CeO}_{2-\delta}$ is in contact with Bi^0 , a Schottky barrier will be constructed due to the imbalance between the Fermi levels (Fig. 4a and Fig. S8a–c) [43]. This process can hinder the recombination and attain abundance of photoinduced charge carriers. It is observed from the charge difference distribution (CDD) of the 10% $\text{Bi}^0/\text{CeO}_{2-\delta}$ system that a number of electrons are accumulated and depleted around the Bi and Ce atoms, respectively (Fig. 4b). The electrons escape from the Ce atoms and move to the Bi atoms, creating a channel for the transfer of charge carriers and forming a covalent bonding between the Bi and Ce atoms [44]. As an electron acceptor, the Bi^0 prevents the recombination of photoinduced charge carriers. Therefore, the photoquantum efficiency of $\text{Bi}^0/\text{CeO}_{2-\delta}$ photocatalysts was improved, displaying an outstanding photocatalytic activity.

The Mott-Schottky plot in Fig. 4c shows that the $\text{CeO}_{2-\delta}$ is featured as a typical n-type semiconducting nature, and the flat band potential is at -0.75 V vs. saturated calomel electrode (SCE). The position of con-

Figure 4 (a) The Schottky barrier formed between Bi⁰ and CeO_{2-δ}, and (b) the charge difference distribution of the 10% Bi⁰/CeO_{2-δ} interface (red and blue represent charge accumulation and depletion, respectively). (c) Mott-Schottky plot of CeO_{2-δ} and (d) the proposed mechanism for the photocatalytic NO removal by the Bi⁰/CeO_{2-δ} photocatalyst.

duction band (CB) is nearly similar to that of flat band potential (-0.51 V vs. normal hydrogen electrode (NHE)) [14]. Therefore, the position of valence band (VB) of CeO_{2-δ} is 2.37 V vs. NHE based on the formula: $E_{VB} = E_{CB} + E_g$ [14]. According to the above-presented results, the proposed mechanism for the photocatalytic NO removal by the Bi⁰/CeO_{2-δ} photocatalysts is shown in Fig. 4d. The OV level and the introduction of Bi⁰ nanoparticles significantly enhance the light absorption of the Bi⁰/CeO_{2-δ} photocatalysts, showing an excellent photo-absorption property [17]. Under visible light irradiation, the photo-induced electrons of CeO_{2-δ} move to the impurity level and then to the CB, while part of the photogenerated electrons in the impurity level are injected to the Bi⁰. Subsequently, hot electrons formed from the SPR effect of Bi⁰ along with the injected electrons overcome the Schottky barrier and accumulate on the CB of CeO_{2-δ}. Thus, the construction of the Schottky barrier considerably promotes the transfer of interfacial charge carriers [1]. Both Bi⁰ and OV can serve as electron acceptors to impede the recombination of photoinduced electrons and holes [28]. The photocatalytic system with high redox capacity induces the formation of a sufficient number of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, which will participate in the direct oxida-

tion of NO. Besides, the large specific surface area and an adequate concentration of OV further increase the possibility of molecular (O₂, NO, and NO₂) adsorption and conversion. As a result, the synergistic effects of OV and Bi⁰ significantly enhance the photocatalytic NO removal efficiency.

CONCLUSIONS

In this work, the plasmonic Bi⁰ nanoparticle-decorated flower-like CeO_{2-δ} photocatalysts with abundant OV were prepared by a solvothermal method. The OV and deposited Bi⁰ nanoparticles improved the visible light utilization and accelerated the migration of photoinduced charge carriers, which engendered abundance of active species involving in the photocatalytic NO removal. The DFT calculations further confirmed the importance of the formed Schottky barrier in improving the photocatalytic activity for NO removal. The results of trapping experiments and *in situ* FTIR spectroscopy analyses allowed gaining more insights into photocatalytic mechanism and reaction pathway. Particularly, the dominating role of active species throughout the photocatalytic NO removal and in suppression of NO₂ generation was identified. This study shows that the photocatalytic NO removal can be

significantly enhanced by introducing abundant OV's and involving plasmonic metal nanoparticles.

Received 25 May 2020; accepted 21 July 2020;

published online 23 September 2020

- Dong F, Zhao Z, Sun Y, *et al.* An advanced semimetal-organic Bi spheres-g-C₃N₄ nanohybrid with SPR-enhanced visible-light photocatalytic performance for NO purification. *Environ Sci Technol*, 2015, 49: 12432–12440
- Bui PD, Tran HH, Kang F, *et al.* Insight into the photocatalytic mechanism of tin dioxide/polyaniline nanocomposites for NO degradation under solar light. *ACS Appl Nano Mater*, 2018, 1: 5786–5794
- Signoretto M, Ghedini E, Trevisan V, *et al.* TiO₂-MCM-41 for the photocatalytic abatement of NO_x in gas phase. *Appl Catal B-Environ*, 2010, 95: 130–136
- Xiao F, Zhou W, Sun B, *et al.* Engineering oxygen vacancy on rutile TiO₂ for efficient electron-hole separation and high solar-driven photocatalytic hydrogen evolution. *Sci China Mater*, 2018, 61: 822–830
- Zhang J, Zhu G, Li S, *et al.* Novel Au/La-Bi₅O₇I microspheres with efficient visible-light photocatalytic activity for NO removal: synergistic effect of Au nanoparticles, La doping, and oxygen vacancy. *ACS Appl Mater Interfaces*, 2019, 11: 37822–37832
- Guo Y, Chang B, Wen T, *et al.* A Z-scheme photocatalyst for enhanced photocatalytic H₂ evolution, constructed by growth of 2D plasmonic MoO_{3-x} nanoplates onto 2D g-C₃N₄ nanosheets. *J Colloid Interface Sci*, 2020, 567: 213–223
- Channei D, Nakaruk A, Phanichphant S. Influence of graphene oxide on photocatalytic enhancement of cerium dioxide. *Mater Lett*, 2017, 209: 43–47
- Wang J, Li Z, Zhang S, *et al.* Enhanced NH₃ gas-sensing performance of silica modified CeO₂ nanostructure based sensors. *Sens Actuat B-Chem*, 2018, 255: 862–870
- Al-Hetlani E, Amin MO, Madkour M, *et al.* CeO₂-CB nanocomposite as a novel SALDI substrate for enhancing the detection sensitivity of pharmaceutical drug molecules in beverage samples. *Talanta*, 2018, 185: 439–445
- Wang Z, Jiang S, Li Y, *et al.* Highly active CeO₂ hollow-shell spheres with Al doping. *Sci China Mater*, 2017, 60: 646–653
- Li X, Zhang W, Cui W, *et al.* Reactant activation and photocatalysis mechanisms on Bi-metal@Bi₂GeO₅ with oxygen vacancies: A combined experimental and theoretical investigation. *Chem Eng J*, 2019, 370: 1366–1375
- Ran M, Wang H, Cui W, *et al.* Light-induced generation and regeneration of oxygen vacancies in BiSbO₄ for sustainable visible light photocatalysis. *ACS Appl Mater Interfaces*, 2019, 11: 47984–47991
- Zhao Z, Cao Y, Dong F, *et al.* The activation of oxygen through oxygen vacancies in BiOCl/PPy to inhibit toxic intermediates and enhance the activity of photocatalytic nitric oxide removal. *Nanoscale*, 2019, 11: 6360–6367
- Wen XJ, Niu CG, Huang DW, *et al.* Study of the photocatalytic degradation pathway of norfloxacin and mineralization activity using a novel ternary Ag/AgCl-CeO₂ photocatalyst. *J Catal*, 2017, 355: 73–86
- Mittal M, Gupta A, Pandey OP. Role of oxygen vacancies in Ag/Au doped CeO₂ nanoparticles for fast photocatalysis. *Sol Energy*, 2018, 165: 206–216
- Chen M, Li Y, Wang Z, *et al.* Controllable synthesis of core-shell Bi@amorphous Bi₂O₃ nanospheres with tunable optical and photocatalytic activity for NO removal. *Ind Eng Chem Res*, 2017, 56: 10251–10258
- Li X, Zhang W, Li J, *et al.* Transformation pathway and toxic intermediates inhibition of photocatalytic NO removal on designed Bi metal@defective Bi₂O₃/SiO₂. *Appl Catal B-Environ*, 2019, 241: 187–195
- Huang Y, Liu J, Cao D, *et al.* Separation of hot electrons and holes in Au/LaFeO₃ to boost the photocatalytic activities both for water reduction and oxidation. *Int J Hydrogen Energy*, 2019, 44: 13242–13252
- Hu H, Qian D, Lin P, *et al.* Oxygen vacancies mediated *in-situ* growth of noble-metal (Ag, Au, Pt) nanoparticles on 3D TiO₂ hierarchical spheres for efficient photocatalytic hydrogen evolution from water splitting. *Int J Hydrogen Energy*, 2020, 45: 629–639
- Huang Z, Zhang Y, Dai H, *et al.* Highly dispersed Pd nanoparticles hybridizing with 3D hollow-sphere g-C₃N₄ to construct 0D/3D composites for efficient photocatalytic hydrogen evolution. *J Catal*, 2019, 378: 331–340
- Zhang W, Wang B, Hao C, *et al.* Au/Cu₂O Schottky contact heterostructures with enhanced photocatalytic activity in dye decomposition and photoelectrochemical water splitting under visible light irradiation. *J Alloys Compd*, 2016, 684: 445–452
- Wang M, Zhang Y, Jin C, *et al.* Fabrication of novel ternary heterojunctions of Pd/g-C₃N₄/Bi₂MoO₆ hollow microspheres for enhanced visible-light photocatalytic performance toward organic pollutant degradation. *Separ Purific Tech*, 2019, 211: 1–9
- Xia Y, Cheng B, Fan J, *et al.* Near-infrared absorbing 2D/3D ZnIn₂S₄/N-doped graphene photocatalyst for highly efficient CO₂ capture and photocatalytic reduction. *Sci China Mater*, 2020, 63: 552–565
- Ding H, Yang J, Ma S, *et al.* Large dimensional CeO₂ nanoflakes by microwave-assisted synthesis: lamellar nano-channels and surface oxygen vacancies promote catalytic activity. *ChemCatChem*, 2018, 10: 4100–4108
- Yang Y, Xing L, Ren W, *et al.* Oxygen activation through β-Bi₂O₃ and ultrafine CeO₂ interactions to promote catalytic soot combustion. *Ind Eng Chem Res*, 2019, 58: 22006–22014
- Hu J, Chen D, Li N, *et al.* Fabrication of graphitic-C₃N₄ quantum dots/graphene-InVO₄ aerogel hybrids with enhanced photocatalytic NO removal under visible-light irradiation. *Appl Catal B-Environ*, 2018, 236: 45–52
- Behera A, Kandi D, Martha S, *et al.* Constructive interfacial charge carrier separation of a p-CaFe₂O₄@n-ZnFe₂O₄ heterojunction architect photocatalyst toward photodegradation of antibiotics. *Inorg Chem*, 2019, 58: 16592–16608
- Zhao Z, Zhang W, Sun Y, *et al.* Bi cocatalyst/Bi₂MoO₆ microspheres nanohybrid with SPR-promoted visible-light photocatalysis. *J Phys Chem C*, 2016, 120: 11889–11898
- Zhu G, Hojamberdiev M, Zhang S, *et al.* Enhancing visible-light-induced photocatalytic activity of BiOI microspheres for NO removal by synchronous coupling with Bi metal and graphene. *Appl Surf Sci*, 2019, 467–468: 968–978
- Underwood GM, Miller TM, Grassian VH. Transmission FT-IR and Knudsen cell study of the heterogeneous reactivity of gaseous nitrogen dioxide on mineral oxide particles. *J Phys Chem A*, 1999, 103: 6184–6190
- Rao F, Zhu G, Hojamberdiev M, *et al.* Uniform Zn²⁺-doped BiOI microspheres assembled by ultrathin nanosheets with tunable

oxygen vacancies for super-stable removal of NO. *J Phys Chem C*, 2019, 123: 16268–16280

- 32 Hadjiivanov K, Avreyska V, Klissurski D, *et al.* Surface species formed after NO adsorption and NO + O₂ coadsorption on ZrO₂ and sulfated ZrO₂: An FTIR spectroscopic study. *Langmuir*, 2002, 18: 1619–1625
- 33 Hu H, Cai S, Li H, *et al.* *In situ* DRIFTS investigation of the low-temperature reaction mechanism over Mn-doped Co₃O₄ for the selective catalytic reduction of NO_x with NH₃. *J Phys Chem C*, 2015, 119: 22924–22933
- 34 Martirosyan GG, Azizyan AS, Kurtikyan TS, *et al.* *In situ* FT-IR and UV-vis spectroscopy of the low-temperature NO disproportionation mediated by solid state manganese(II) porphyrinates. *Inorg Chem*, 2006, 45: 4079–4087
- 35 Wu J, Cheng Y. *In situ* FTIR study of photocatalytic NO reaction on photocatalysts under UV irradiation. *J Catal*, 2006, 237: 393–404
- 36 Hadjiivanov K, Knözinger H. Species formed after NO adsorption and NO + O₂ co-adsorption on TiO₂: an FTIR spectroscopic study. *Phys Chem Chem Phys*, 2000, 2: 2803–2806
- 37 Feng X, Zhang W, Sun Y, *et al.* Fe(III) cluster-grafted (BiO)₂CO₃ superstructures: *in situ* DRIFTS investigation on IFCT-enhanced visible light photocatalytic NO oxidation. *Environ Sci-Nano*, 2017, 4: 604–612
- 38 Wang H, Sun Y, Jiang G, *et al.* Unraveling the mechanisms of visible light photocatalytic NO purification on earth-abundant insulator-based core-shell heterojunctions. *Environ Sci Technol*, 2018, 52: 1479–1487
- 39 Huang SJ, Walters AB, Vannice MA. Adsorption and decomposition of NO on lanthanum oxide. *J Catal*, 2000, 192: 29–47
- 40 Shang H, Li M, Li H, *et al.* Oxygen vacancies promoted the selective photocatalytic removal of NO with blue TiO₂ via simultaneous molecular oxygen activation and photogenerated hole annihilation. *Environ Sci Technol*, 2019, 53: 6444–6453
- 41 Li H, Wu T, Cai B, *et al.* Efficiently photocatalytic reduction of carcinogenic contaminant Cr (VI) upon robust AgCl:Ag hollow nanocrystals. *Appl Catal B-Environ*, 2015, 164: 344–351
- 42 Cui YL, Guo XN, Wang YY, *et al.* Visible-light-driven photocatalytic N-arylation of imidazole derivatives and arylboronic acids on Cu/graphene catalyst. *Sci Rep*, 2015, 5: 12005–12013
- 43 Chang L, Zhu G, Hassan QU, *et al.* Synergetic effects of Pd⁰ metal nanoparticles and Pd²⁺ ions on enhanced photocatalytic activity of ZnWO₄ nanorods for nitric oxide removal. *Langmuir*, 2019, 35: 11265–11274
- 44 Lei B, Cui W, Sheng J, *et al.* Synergistic effects of crystal structure and oxygen vacancy on Bi₂O₃ polymorphs: intermediates activation, photocatalytic reaction efficiency, and conversion pathway. *Sci Bull*, 2020, 65: 467–476

Acknowledgements This work was supported by the National Natural Science Foundation of China (51772183, 21673118 and 21972067), the Key Research and Development Program of Shaanxi Province (2018ZDCXL-SF-02-04), the Natural Science Foundation of Hubei Province (2019CFB225), and the Fundamental Research Funds for the Central Universities (GK201903023 and GK201801005).

Author contributions Zhu G and Shen Q designed the project; Nie J and Rao F performed the experiments; Nie J, Zhang W and Rao F performed the data analysis; Zhu G, Zhang W and Gao J contributed to the theoretical analysis; Nie J, Zhu G, Shen Q and Hojamberdiev M

wrote the paper. All authors contributed to the general discussion.

Conflict of interest The authors declare no competing financial interest.

Junli Nie is now pursuing her Master degree in the School of Physics and Information Technology, Shaanxi Normal University. Her current research interest mainly lies in the preparation of photocatalytic materials and their photocatalytic activity for NO removal.

Gangqiang Zhu is now a professor in the School of Physics and Information Technology, Shaanxi Normal University. He received his PhD from Xi'an Jiaotong University (XJTU) in 2012. His research interests mainly focus on the high-performance photocatalytic materials and their photocatalytic mechanisms for environmental purification. He has published more than 100 peer-reviewed papers with over 3000 citations and his H-index is 29.

Qian Shen received her BSc in chemistry from China Agriculture University in 2008 and her PhD in physical chemistry from Peking University in 2013. She was a research fellow at National University of Singapore from 2013 to 2015. She is currently an associate professor at the Institute of Advanced Materials (IAM), Nanjing Tech University. Her current research interest is mainly about surface chemistry.

花型Bi⁰/CeO_{2-δ}等离子体光催化剂增强可见光光催化去除NO

聂俊丽¹, 高健智¹, 申茜^{2*}, 张伟斌³, 饶斐¹,
Mirabbos Hojamberdiev⁴, 朱刚强^{1*}

摘要 本文利用溶剂热法合成了Bi⁰纳米颗粒修饰的富氧空位(OVs)花型CeO_{2-δ} (Bi⁰/CeO_{2-δ})光催化剂。OVs不仅能够加速电子-空穴对的分离,而且有利于气体分子(NO/O₂)的吸附和活化。此外,Bi⁰纳米颗粒具有表面等离子体共振效应,它能够提高催化剂的可见光响应、减少光生载流子的复合。Bi⁰/CeO_{2-δ}光催化剂在可见光下具有优异的一氧化氮(NO)去除活性,并可有效抑制NO₂生成。密度泛函理论(DFT)计算证实,Bi⁰与CeO_{2-δ}界面处的肖特基势垒以及OVs的存在促进了载流子的分离,进而参与NO的光催化去除。通过捕获实验和原位红外光谱分析了Bi⁰/CeO_{2-δ}催化剂光催化去除NO的机理,研究表明丰富的OVs和金属纳米颗粒负载能够显著提高材料光催化去除NO的性能。