Supporting Information

Efficient charge separation of a Z-scheme $Bi_5O_{7-\delta}I/CeO_{2-\delta}$ heterojunction with enhanced visible light photocatalytic activity for NO removal

Ziyi Yao^a, Junli Nie^a, Qadeer Ul Hassan^a, Guian Li^a, Jiabin Liao^b, Weibin Zhang^c, Lujun Zhu^{a*}, Xianjin Shi^d, Fei Rao^a, Jun Chang^a, Yu Huang^d, and Gangqiang Zhu^{a*}

^aSchool of Physics and Information Technology, Shaanxi Normal University, Xi'an 710061, PR China

^bInstitute of Nanomaterials, Amer International Group Co. Ltd, Weinan, 715100, PR China

^cInstitute of Physics and Electronic Information, Yunnan Normal University, Kunming 650500, P.R. China

^dKey Laboratory of Aerosol Chemistry and Physics, State Key Laboratory of Loess and Quaternary Geology (SKLLQG), Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, 710061, China

*To whom correspondence should be addressed: Tel./Fax: +86-29-81530750 Email address: zhulujun@snnu.edu.cn , zgq2006@snnu.edu.cn (G. Zhu)

Contents

I. Methods

II. Supplementary Figures

Supplementary Figure S1. (a,b) N₂ adsorption-desorption isotherms and corresponding pore-size distribution curves of CeO_{2- δ}, Bi₅O_{7- δ}I and 20% Bi₅O_{7- δ}I/CeO_{2- δ} samples.

Supplementary Figure S2. (a) PL spectra, (b) EIS Nyquist spectra, (c) transient photocurrent responses (I–t), (d) SPS spectra of $CeO_{2-\delta}$, $Bi_5O_{7-\delta}I$ and 20% $Bi_5O_{7-\delta}I$ /CeO_{2-\delta}.

Supplementary Figure S3. (a, b) schematic diagram of Type-II and Z-scheme schematic diagram of photocatalytic NO removal by the $Bi_5O_{7-\delta}I/CeO_{2-\delta}$.

I. Methods

Synthesis of CeO_{2-δ}

All chemical reagents purchased from Aladdin Reagent Co. Ltd. (China) were analytically pure and were used without further purification. 5 mmol Ce(NO₃)₃•6H₂O, 15 mmol C₃H₅NO and 10 mmol C₆H₁₂O₆ were completely dissolved in 50 ml deionized water under a magnetic stirring. The pH value of the solution was adjusted to ~10 by adding ammonia. The solution was continuously stirred for 60 minutes, then transferred the solution to the polytetrafluoroethylene stainless steel reactor, after that put at 180°C for 72 hours. Then, the resulting precipitate was collected and washed with deionized water for several times. Three-dimensional CeO_{2-δ} architecture was finally obtained by a heat treatment of hydrothermally synthesized precursor at 600°C for 6 h under N₂ and at 400°C for 4 h in air.

Trapping experiments

Trapping experiments using various scavengers were performed to identify the roles of active species generated during the photocatalytic reaction pathway. Potassium dichromate (K₂Cr₂O₇), potassium iodide (KI), isopropanol alcohol (IPA, C₃H₈O), and p-benzoquinone (PBQ) were used as scavengers for e⁻, h⁺, \cdot OH and \cdot O₂⁻, respectively. The Bi₅O_{7- δ}I/CeO_{2- δ} composite photocatalyst with different scavengers (0.02 g) was ultrasonically dispersed in water for 30 min and deposited onto the glass substrate. After drying, the photocatalytic activities of the sample were evaluated under visible light.

In situ FTIR investigation

In situ FTIR of samples was analyzed in order to check the possible products during the photocatalytic reaction. It was recorded on a VERTEX 70 spectrometer (Bruker, Germany) equipped with

pretreatment equipment, *in situ* reaction cell, gas system, and light source. The FTIR spectrum after heat treatment (150 °C) was selected as the background, the NO+O₂ was introduced in the *in situ* reaction cell and absorbed on 0.1 g photocatalyst. The sample was subjected to dark environment for 20 min to achieve the adsorption-desorption equilibrium. Afterward, a 300W Xenon lamp with a UV cut off filter (λ =420 nm) was served as visible light source. The real-time *in situ* FTIR spectra were detected at every one and three minutes in dark and under light illumination, respectively.

Photocatalytic NO removal experiments

The photocatalytic activity of the synthesized samples was evaluated by recording the concentration variations of NO in a quartz reactor with the volume of 4.5 L (L=30 cm × W=15 cm × H=10 cm) at room temperature. Typically, 0.1 g of the photocatalyst powder was dispersed in 15 mL of deionized water under sonication and deposited onto the glass substrate (d = 10 cm) and dried at 70 °C for 4 h. The photocatalyst-deposited glass substrate was placed in the reactor and exposed to 430 ppb diluted NO (50 ppm NO feed stream + zero air) for achieving the adsorption-desorption equilibrium. A 300 W Xenon lamp (Perfect light, microsolar 300, Beijing, China) with a UV cut-off filter (λ =420 nm) was used as a visible light source and vertically placed 20 cm above the glass substrates. The entire measurement was conducted at ambient conditions with relative humidity of 30±5%. When the adsorption-desorption equilibrium was achieved, the sample was irradiated by visible light. The concentration of NO was continuously detected and measured every one minute using a NO-NO₂-NO_x analyzer (42i, Thermo Scientific). The removal rate (η) of NO was calculated using the following equation:

$$\eta = 1 - \binom{c}{c_0} \times 100\%$$

where C and C_0 refer to the NO concentration at a given time and initial concentration of NO,

respectively.

DFT calculations

The DFT calculations were implemented using the Cambridge Sequential Total Energy Package (CASTEP) code. The generalized gradient approximation with the Perdew-Burke-Ernzerh of (PBE) exchange-correlation density functional was used to account for exchange correlation potentials and electron-electron interactions. The work functions were carried out in a plane-wave basis set with the cut-off energy at 380 eV. For the calculations of structural and electronic properties, the Brillouin zone was sampled with a $3 \times 3 \times 4$ Monkhorst-pack *k*-point grid geometry optimization and estimated by Hybrid functional based on the Heyd-Scuseria-Ernzerh of (HSE06) method. Moreover, the self-consistent field convergence criterion was set to 2.0×10^{-6} eV/atom, the maximum force was 0.05 eV/Å, the maximum pressure was 0.1 GPa, and the maximum displacement was 0.002 Å. In addition, the electron density difference (EDD) map was conducted using a $2 \times 4 \times 2$ mesh to explicate the charge transfer.

II. Supplementary Figures



Supplementary Figure S1. (a) N₂ adsorption-desorption isotherms of CeO_{2- δ}, Bi₅O_{7- δ}I and 20% Bi₅O_{7- δ}I/CeO_{2- δ} samples, (b) pore-size distribution curves of CeO_{2- δ}, Bi₅O_{7- δ}I and 20% CeO_{2- δ}/Bi₅O_{7- δ}I samples.



Supplementary Figure S2. (a) PL spectra, (b) EIS Nyquist spectra, (c) transient photocurrent responses (I–t), (d) SPS spectra of $CeO_{2-\delta}$, $Bi_5O_{7-\delta}I$ and 20% $Bi_5O_{7-\delta}I$ /CeO_{2-\delta}.



Supplementary Figure S3. (a, b) schematic diagram of Type-II and Z-scheme schematic diagram of photocatalytic NO removal by the $Bi_5O_{7-\delta}I/CeO_{2-\delta}$.