Electronic Supplementary Information for

Semimetal bismuth element as a direct plasmonic photocatalyst

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• Experimental Section

1.1 Synthesis of Bi nanoparticles

All chemicals used in this study were analytical grade and were used without further purification. Distilled water was used in all experiments. In a typical synthesis, Bi nanoparticles were synthesized under an aqueous condition. In a typical synthesis, 0.1 g of $H_2C_4H_4O_6$, 0.5 g of NaOH and 40 mL of NaH₂PO₂ • H₂O (5 mol /L) were added to 75 ml of distilled water firstly at room temperature and stirred for 30 min. Then, 5 ml of 1 M Bi(NO₃)₃ • 5H₂O was added to the above solution and stirred for 10 min. Next, the resulted grey suspension was transferred to water bath of 60 °C and stirred for 6 h. The resulting black precipitate was filtered and washed with distilled water and absolute ethanol for three times to remove impurities, and then dried at 60 °C for 12 h to get final product.

1.2 Characterization

The crystal phases of the samples were analyzed by X-ray diffraction with Cu Karadiation (XRD: model D/max RA, Rigaku Co., Japan). A scanning electron microscope (SEM, JEOL model JSM-6490, Japan) were used to characterize the morphology of the obtained product. The morphology and structure of the sample were examined by transmission electron microscopy (TEM: JEM-2010, Japan). FT-IR spectra were recorded on a Nicolet Nexus spectrometer on samples embedded in KBr pellets. X-ray photoelectron spectroscopy with Al K α X-rays (hv= 1486.6 eV) radiation (XPS: Thermo ESCALAB 250, USA) was used to investigate the surface properties. The UV-vis diffuse reflection spectra were obtained for the dry-pressed disk samples using a Scan UV-vis spectrophotometer (UV-vis DRS: TU-1901, China) equipped with an integrating sphere assembly, using BaSO4 as reflectance sample. Nitrogen adsorption-desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA). The sample was degassed at 90 °C prior to measurements. The sample for ESR measurement was prepared by mixing Bi particles in a 50 mM DMPO solution tank (aqueous dispersion for DMPO-•OH and methanol dispersion for DMPO-•O2). UV light of 280 nm was used to irradiate the sample. All photoelectrochemical measurements were conducted in a three electrode system on a CH 660D electrochemical work station, using the FTO glass with Bi films as the working electrode, saturated calomel electrode as the reference electrode, and Pt wire as the counter electrode. All potentials are quoted with respect to saturated calomel electrode. For photoelectrochemical tests, the working electrode was irradiated from the Bi films (250 mg of as-prepared Bi nanoparticles were suspended in 0.5 mL of DMF, which was then dip coated on a 10 mm \times 10 mm FTO glass electrode. The electrode was then annealed at 170°C for 2h) side under a 300W Xe lamp. Incident visible-light was obtained by utilizing a 420 nm cutoff filter. The photocurrent-time dependence of Bi films at open circuit potential was measured in 0.5 M Na₂SO₄ under chopped illumination with 40s light on/off cycles.

1.3 Evaluation of photocatalytic activity

The photocatalytic activity was investigated by removal of NO at ppb levels in a continuous flow reactor at ambient temperature. The volume of the rectangular reactor, made of stainless steel and covered with Saint-Glass, was 4.5 L (30 cm \times 15 cm \times 10 cm). A 150 W commercial tungsten halogen lamp was vertically placed outside the reactor. A UV cutoff filter (420 nm) and (510 nm) were adopted to remove UV light in the light beam, respectably. For activity test under 254 nm, 280 nm and 360 nm, UV lamps (15 W, 8 W and 6 W) were used, respectively. For each photocatalytic activity test, two sample dishes (with a diameter of 12.0 cm) containing photocatalyst powders were placed in the center of the reactor. The weight of the photocatalyst used for each dish was kept at 0.1 g. The 0.1 g sample was added into 30 mL of H₂O and ultrasonicated for 10 min. Then the aqueous suspension was coated onto the glass dishes. The coated dish was pretreated at 60 °C to remove water in the suspension and then cooled to room temperature before photocatalytic testing. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N₂ balance, standard gas). The initial concentration of NO was diluted to about 600 ppb by the air stream. The desired relative humidity (RH) level of the NO flow was controlled at 50% 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 2.4 L/min by a mass flow controller. After the adsorption desorption equilibrium was achieved, the lamp was turned on. The concentration of NO was continuously measured by a chemiluminescence NO analyzer (Thermo Environmental Instruments Inc., 42i-TL), which monitors NO, and NO₂ with a sampling rate of 1.0 L/min. The removal ratio (η) of NO was calculated as $\eta(\%) = (1 - C/C_0) \times 100\%$, where C and C₀ are concentrations of NO in the outlet steam and the feeding stream, respectively.



Fig.S1 Bi 4f XPS spectra of Bi nanoparticles (a) and Bi nanoparticles after sputtering for 15nm thickness of the surface (b).



Fig.S2 N₂ adsorption-desorption isotherm (a) and the corresponding pore distribution of Bi nanoparticles (b).



Fig. S3 UV-vis DRS of the Bi (III) species and Bi nanoparticles.



Fig. S4 Photocurrent-time curves under UV-vis and visible light (>420 nm) irradiation with 40 s light on/off cycles.



Fig. S5 Monitoring of the fraction of NO_2 intermediate over Bi nanoparticles (a), and Long-term photocatalytic activity of Bi nanoparticles (b).



Fig. S6 Tentative illustration of the reduction and oxidation potential of active species and NO, and the excitation of electron-hole pairs from different bands under different irradiation wavelengths: 280 nm, 360 nm, and 420-820 nm. (The electrons and holes produced by the excitation of the light with wavelength at 280 nm are able to induce the production of active species ($\cdot O_2^-$ and $\cdot OH$), but the electrons and holes produced by the excitation of the light with wavelength exceeding 360 nm cannot induce the production of $\cdot O_2^-$ and $\cdot OH$. Obviously, the wavelength of the light determines the reduction and oxidation power of the electrons and holes. When the Bi nanoparticles are irradiated by the light with different wavelength, electrons located at different bands (e.g., conduction band or d-bands) can be excited to SPR states, leaving the holes. The shorter the wavelength (higher energy), electrons located at lower bands can be excited to SPR states with higher reduction potential, leaving holes with higher oxidation potential as shown in Fig. S6.)



Fig. S7 Photocatalytic removal ratio (left axis, black line) of NO (The NO removal ratio from direct UV pyrolysis was deducted from the overall NO removal ratio) and optical absorbance (right axis, blue line) of Bi nanoparticles.