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Supplementary Materials

Fabrication of Z-scheme $AgBr/Bi_4O_5Br_2$ nanocomposite and its high efficiency in photocatalytic N_2 fixation and dyes degradation

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1. Photocatalytic N_2 fixation

The photocatalytic nitrogen fixation experiments were also performed in the self-build photochemical reactor. A 300W Xe lamp (PLS-SXE300C, Beijing ProfectLight Co. Ltd., China) was used as the simulated sunlight sources. Before light irradiation, 0.05 g of solid catalyst was added into a 100 mL ethanol solution (containing 5 mL ethanol and 95 mL deionized water) and stirred for 1 h in the dark to ensure an adsorption–desorption equilibrium. When the light is on, 3 mL portion of liquid was taken out from the solution every one hour intervals for ammonia detection. The sample solution was centrifuged to obtain a supernatant. Then, 20 μl of sodium tartrate and 30 μl of Nessler's reagent were added dropwise successively. After 12 min of reaction, the ammonia concentration was analyzed by the absorbance at 420 nm measured by a UV-vis spectrophotometer. The photocatalytic N_2 fixation in the presence of different scavengers was performed as the same way. The concentration of methanol and isopropanol (IPA) is as same as that of ethanol (5 vol%). For benzoquinone (BQ) and ammonium oxalate (AO), the concentration was controlled to be 0.001M. The flow rate of N_2 is 50 mL/min.

2. Photocatalytic dyes degradation

The photocatalytic degradation experiments were performed in a self-build photochemical reactor equipped with a 350W Xe lamp which was combined with two filters to cut off UV and IR light. All photocatalytic reactions were performed using the same initial conditions. Methylene blue (MB) solution was chosen as a model pollutant to evaluate the photocatalytic activity of $AgBr/Bi_4O_5Br_2$. The concentration of MB dye in the reaction was 2×10^{-5} mol/L, and the

photocatalyst amount is 0.1 g. Before the light irradiation, the suspension was magnetically stirred for 60 min in dark to obtain a good dispersion and establish adsorption–desorption equilibrium between the organic molecules and the catalyst surface. The concentration of MB solution was analyzed by measuring the maximum absorbance at 663 nm using a UV–vis spectrophotometer. During the photocatalysis, 6 mL of the suspension was extracted at an interval of 10 min for analysis. The degradation procedures were as same as that of MB. Trapping experiments were also performed to determine the reactive species during the photodegradation of MB. The photocatalytic degradation of rhodamine B (RhB) and methyl orange (MO) were performed via the same way. The concentration of RhB and MO are controlled to be 20ppm.

3. Characterizations of AgBr/$Bi_4O_5Br_2$ photocatalysts

Brunner−Emmet−Teller (BET) surface area analysis was performed by N_2 adsorption at 77 K on a 3H-2000PS2 apparatus (Beishide Instrument). X-ray diffraction (XRD) analysis was performed on a D8 Advance (BRUKER AXS GMBH, Germany) X-ray diffractometer using Cu Kα radiation (40 kV/40 mA). The Raman spectra of the catalysts were recorded on a RM1000 spectrometer (Renishaw). The excitation laser wavelength is 785 nm. Scanning electron microscopy (SEM) was carried out on a Field emission scanning electron microscope (Hitachi S-4800) with the accelerating voltage of 5 kV. Transmission electron microscopy (TEM) was employed on a JEM-2010F transmission electron microscope via the accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) spectra of the catalysts were obtained via using a Thermo Scientific ESCALAB 250Xi Microprobe instrument using Al-Kα as a ray source. The C 1s signal was adjusted in the location of 284.6 eV. UV-visible diffuse reflection spectroscopy

(DRS) was actualized on a UV-visible spectrophotometer (Agilent Cary5000) and the reference sample was $BaSO_4$. A CHI 660E electrochemical workstation with a standard three-electrode cell was employed to perform the photocurrent (PC) responses, the electrochemical impedance spectroscopy (EIS), the linear sweep voltammetry (LSV) and Mott-schottky measurements. The test was operated at room temperature. The photocatalyst, Ag/AgCl (saturated KCl), and a Pt wire were used as the working electrode, the reference electrode, and the counter electrode, respectively. The preparation of working electrode refers to the previous literature [1]. The coated area of the photocatalyst on the ITO glass was 1×1 cm and Na_2SO_4 (0.5 M) aqueous solution was used as the electrolyte. For PC measurement, a 300 W Xe lamp was served as the light source.

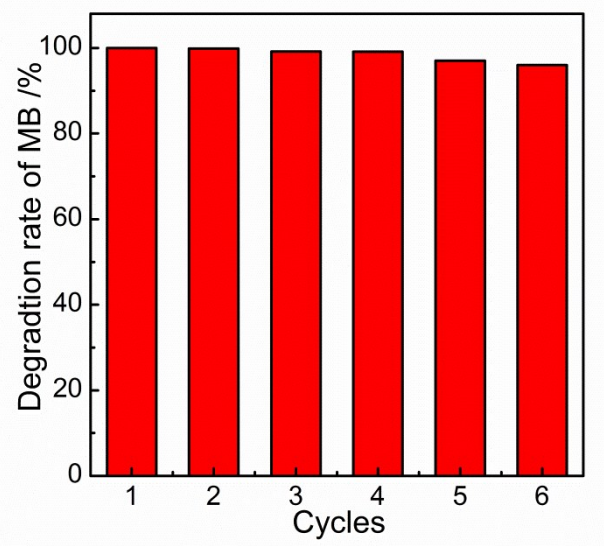

Fig. S1 Cycling test of 5.0wt.% AgBr/$Bi_4O_5Br_2$ composite in MB degradation under visible light irradiation.

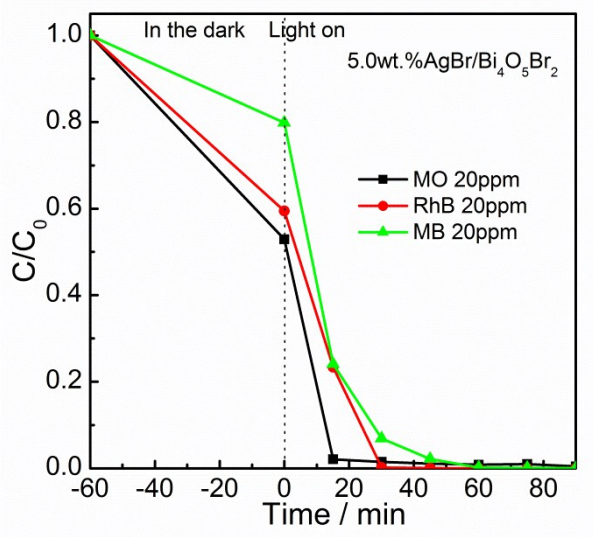

Fig. S2 Photocatalytic activity of 5.0wt.% AgBr/$Bi_4O_5Br_2$ composite under visible light irradiation.

Table S1 Atomic content of different elements in 5.0 wt.% $AgBr/Bi_4O_5Br_2$ samples.

Photocatalyst		Atomic content				Atomic ratio
		Bi	O	Br	Ag	$Ag^0 : Ag^+$
5.0wt.%$AgBr/Bi_4O_5Br_2$	Theoretical	35.5%	44.2%	17.8%	2.5%	-
	XPS	29.8%	49.0%	20.0%	1.2%	1:4

References:

[1] Y.M. He, L.H. Zhang, M.H. Fan, X.X. Wang, M.L. Walbridge, Q.Y. Nong, Y. Wu, L.H. Zhao, Z-scheme $SnO_{2-x}/g\text{-}C_3N_4$ composite as an efficient photocatalyst for dye degradation and photocatalytic CO_2 reduction. Sol. Energy Mat. Sol. C. 137 (2015) 175–184.