Electronic Supplementary Material

Enhanced photocatalytic N_2 fixation using $KNbO_3/Bi_4O_5Br_2$ type II heterojunction

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1. Photocatalytic N_2 fixation reaction

The photocatalytic nitrogen fixation experiments were conducted in a self-built photochemical reactor. A 300W Xe lamp (PLS-SXE300C, Beijing ProfectLight Co. Ltd., China) was used as the simulated sunlight source. When implementing the photocatalytic reaction under visible light, a UV-cut filter (λ>420 nm) was installed. Prior to light irradiation, 0.1 g of solid catalyst was added into a 100 mL methanol solution (containing 5 mL methanol and 95 mL deionized water) and stirred for 1 h in the dark to ensure an adsorption–desorption equilibrium. During light exposure, 7 mL of the liquid was extracted from the solution every one-hour interval for ammonia detection. The sample solution was centrifuged to obtain the supernatant, and then 30 μL of sodium tartrate and 30 μL of Nessler's reagent were added successively. After 12 min of reaction, the ammonia concentration was analyzed by measuring the absorbance at 420 nm with a UV-vis spectrophotometer (Figure S1). The photocatalytic N_2 fixation in the presence of different scavengers was conducted similarly, except that the scavenger was changed. For the reaction performed in the presence of N_2, the bubbling N_2 flow rate was controlled to 50 mL · min^{-1}. For the reaction under vacuum, the reactor was replaced with a closed quartz reactor. After the reaction solution and catalyst were added, the air in the reactor was evacuated, and the relative pressure to the outside world was maintained at －97 kPa (the actual pressure was about 4.3 kPa).

2. Determination of NH_3 content by the NMR method

After 5-hour photocatalytic reaction, the NH_4^+ content was quantitatively determined by ^1H nuclear magnetic resonance (NMR) (600 MHz, Bruker AV600) with external standards, taking maleic acid ($C_4H_4O_4$) as a reference. To create the calibration curve, a series of NH_4^+ solutions with known concentration were prepared in 0.01 M HCl as standards. Next, 24.5 mL of the NH_4^+ standard solution was mixed with 0.5 mL maleic acid (25 μg/mL). The mixture was then concentrated to approximately 1 mL and identified using ^1H NMR spectroscopy (50 μL deuterium oxide (D_2O) was added in 0.45 mL concentrated solution before NMR detection). The calibration was achieved using the peak area ratio between NH_4^+ and tris-maleate because the NH_4^+ concentration and the area ratio are positively correlated. Similarly, the NH_4^+ concentration after photocatalytic reaction was quantitatively determined using this method.

4. Characterizations of $KNbO_3/Bi_4O_5Br_2$ photocatalysts

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

$KNbO_3/Bi_4O_5Br_2$ catalysts were recorded on an RM1000 spectrometer (Renishaw) via an excitation source of an Ar ion laser (514.5 nm). Brunner−Emmet−Teller (BET) surface area analysis was performed by N_2 adsorption at 77 K on a 3H-2000PS2 apparatus (Beishide Instrument). 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 an 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, electrochemical impedance spectroscopy (EIS), 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 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 used as the light source. photoluminescence (PL) spectra of the photocatalyst were recorded on an FLS-920 fluorescence spectrometer manufactured by Edinburgh-Instrument, UK.

Figure S1 UV-vis curves of various NH_3 concentrations after incubation for 12 min at room temperature and the (b) calibration curve used for the estimation of the NH_3 concentration

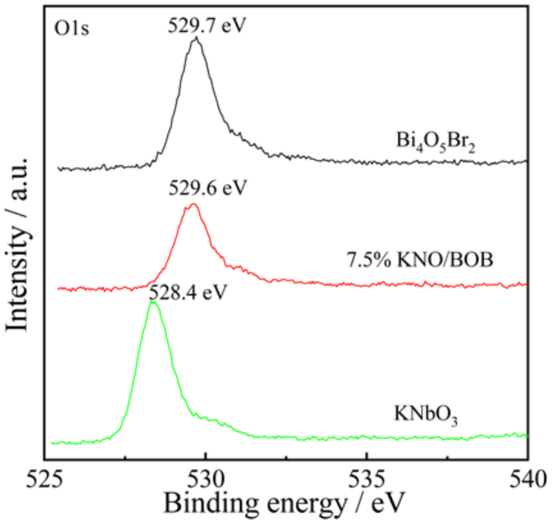
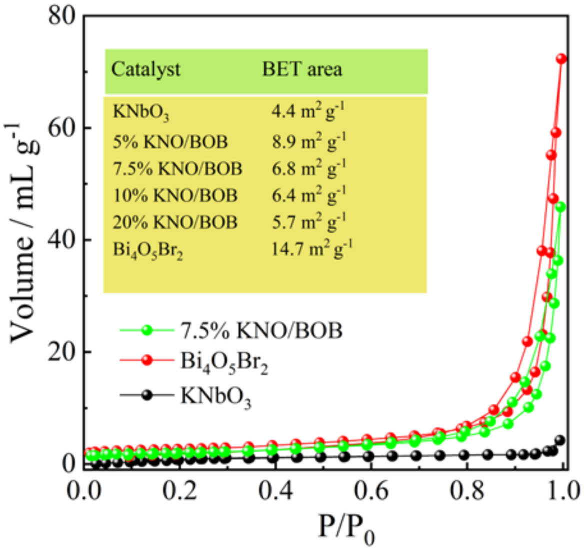


Figure S2 O1s XPS spectra of $KNbO_3$, $Bi_4O_5Br_2$, and 7.5% KNO/BOB



Catalyst	BET area
$KNbO_3$	4.4 $m^2\ g^{-1}$
5% KNO/BOB	8.9 $m^2\ g^{-1}$
7.5% KNO/BOB	6.8 $m^2\ g^{-1}$
10% KNO/BOB	6.4 $m^2\ g^{-1}$
20% KNO/BOB	5.7 $m^2\ g^{-1}$
$Bi_4O_5Br_2$	14.7 $m^2\ g^{-1}$

Figure S3 N_2 adsorption-desorption isotherms of $KNbO_3$, $Bi_4O_5Br_2$, and 7.5% KNO/BOB

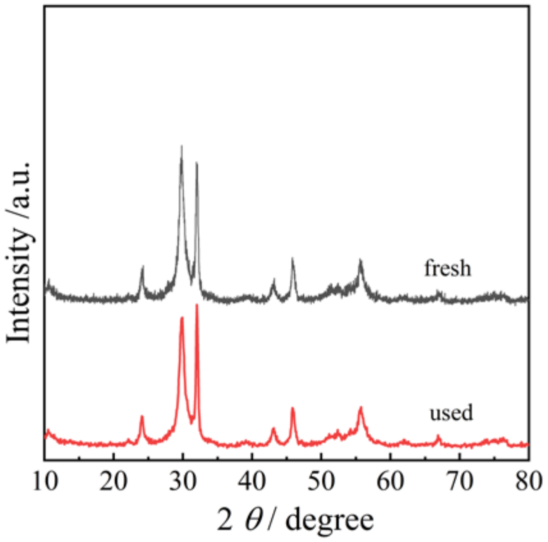


Figure S4 XRD patterns of 7.5% KNO/BOB composite before and after reaction

Figure S5 ^{1}H NMR spectra of various $^{14}NH_4^+$ solutions (a) and the standard curve line obtained via the external standard method (b).