Electronic Supplementary Material

Cu-doped Bi/Bi_2WO_6 catalysts for efficient N_2 fixation by photocatalysis

Xiaojing Li[1]*, Chunran Zhao[1]*, Junfeng Wang[1], Jiayu Zhang[3], Ying Wu (✉)[3], Yiming He (✉)[1,2]

1 Department of Materials Science and Engineering, Zhejiang Normal University, Jinhua 321004, China

2 Key Laboratory of Solid State Optoelectronic Devices of Zhejiang province, Zhejiang Normal University, Jinhua 321004, China

3 Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China

E-mails: hym@zjnu.cn (He Y); yingwu@zjnu.cn (Wu Y)

* These authors contributed equally to this work.

1. Photocatalytic N_2 fixation reaction

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. When the reaction was implemented under visible light, it is equipped with a UV cut-off filter (λ>420 nm). Before light irradiation, 0.1 g of solid catalyst was added into a 200 mL methanol solution (containing 10 mL methanol and 190 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 in a similar way. Only the scavenger is changed. For the reaction 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 is evacuated. The relative pressure to the outside world is -97kPa (the real pressure is about 4.3kPa).

2. Determination of NH_3 content by the NMR method

After photocatalytic reaction for 2.5 h, the obtained NH_4^+ content was also quantitatively determined by ^1H nuclear magnetic resonance (NMR, 600 MHz, Bruker AV600) with external standards, which takes maleic acid ($C_4H_4O_4$) as a reference. The calibration curve was created as follows. First, a series of NH_4^+ solutions with known concentration were prepared in 0.01 M HCl as standards; second, 24.5 mL of the NH_4^+ standard solution was mixed with 0.5 mL maleic acid (25 μg

mL^{-1}); third, the mixture was concentrated to approximately 1 mL and then identified using ^1H NMR spectroscopy (50 μL deuterium oxide (D_2O) was added in 0.45 mL concentrated solution before NMR detection); fourth, 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 by this method.

3. Characterizations of Cu-doped Bi_2WO_6 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 Cu-Bi_2WO_6 catalysts were recorded on a RM1000 spectrometer (Renishaw) via an excitation source of an Ar ion laser (514.5 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, electrochemical impedance spectroscopy (EIS), 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 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.

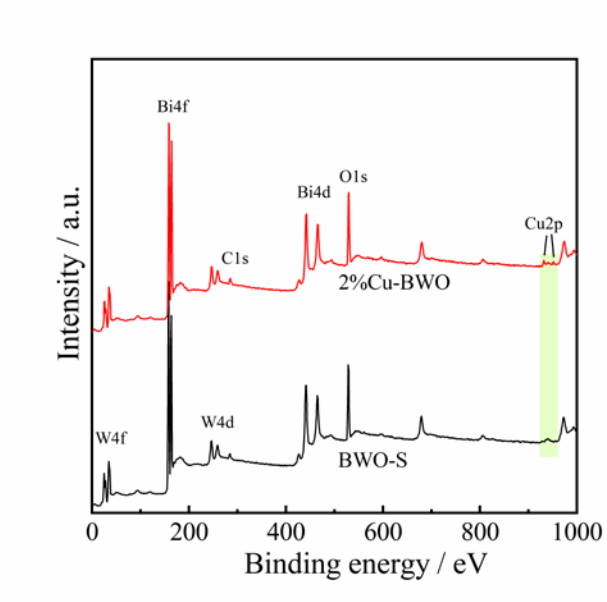

Figure S1 Survey XPS spectra of BWO-S and 2% Cu-BWO samples.

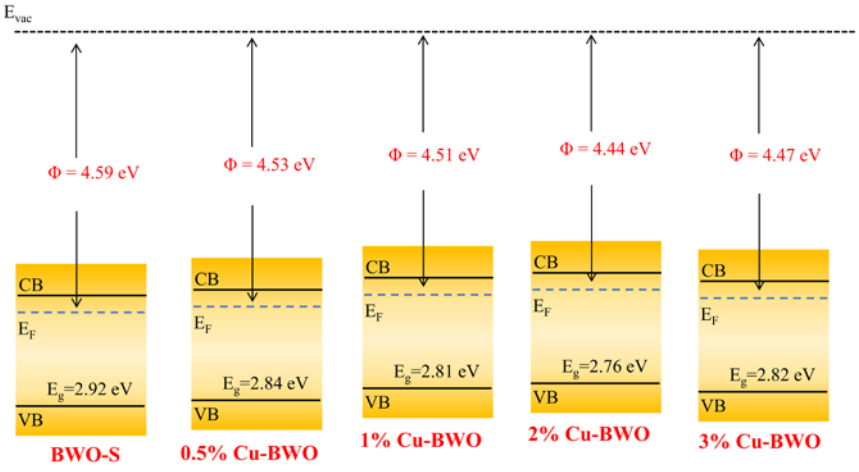

Figure S2 The estimated work functions (Φ) of BWO and Cu-BWO photocatalysts.

Note: The potential of standard hydrogen electrode is 4.5 eV (Vs vacuum level)

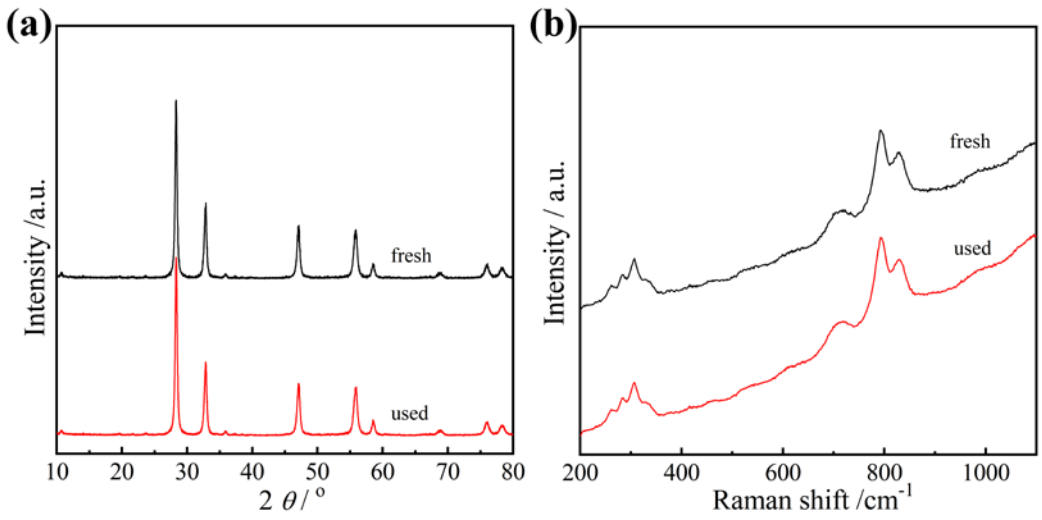

Figure S3 XRD patterns (a) and Raman spectra (b) of 2% Cu-BWO before and after photocatalytic reaction

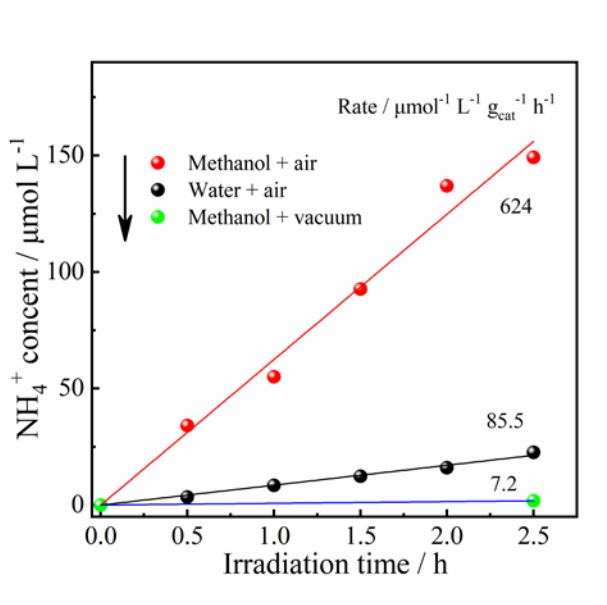

Figure S4 Photocatalytic activity of 2% Cu-BWO in different reaction conditions.

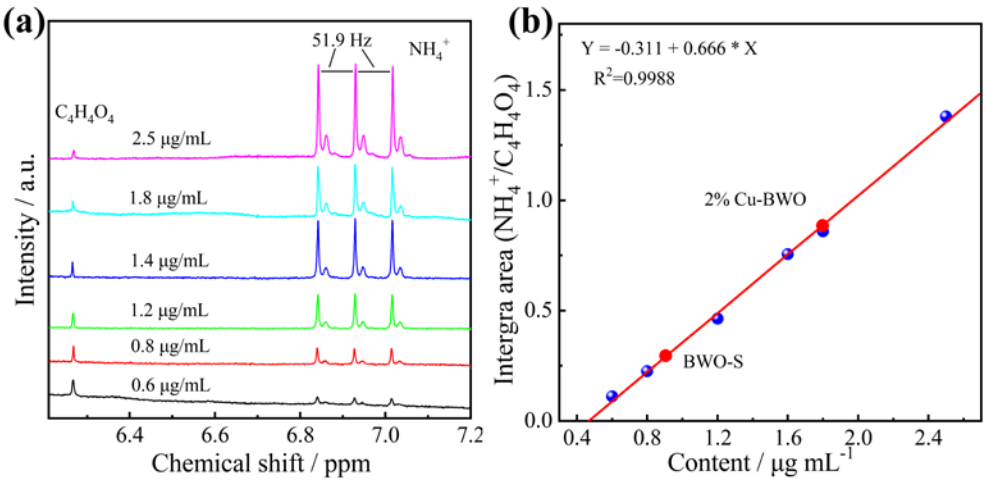

Figure S5 ^{1}H NMR spectra (600 MHz) of various $^{14}NH_4^+$ solutions (a) and the standard curve line obtained via an external standard method (b).

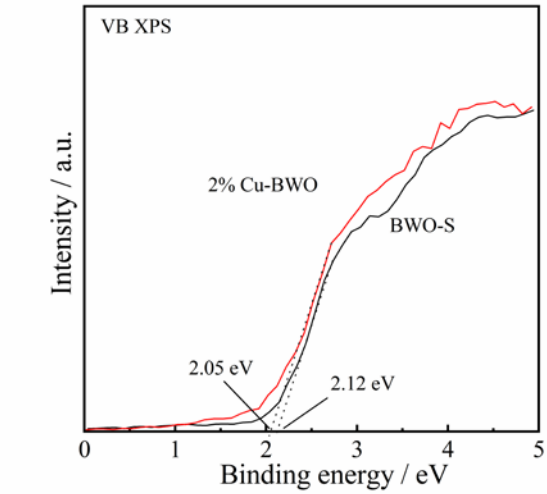

Figure S6 VB XPS spectra of BWO-S and 2% Cu-BWO.

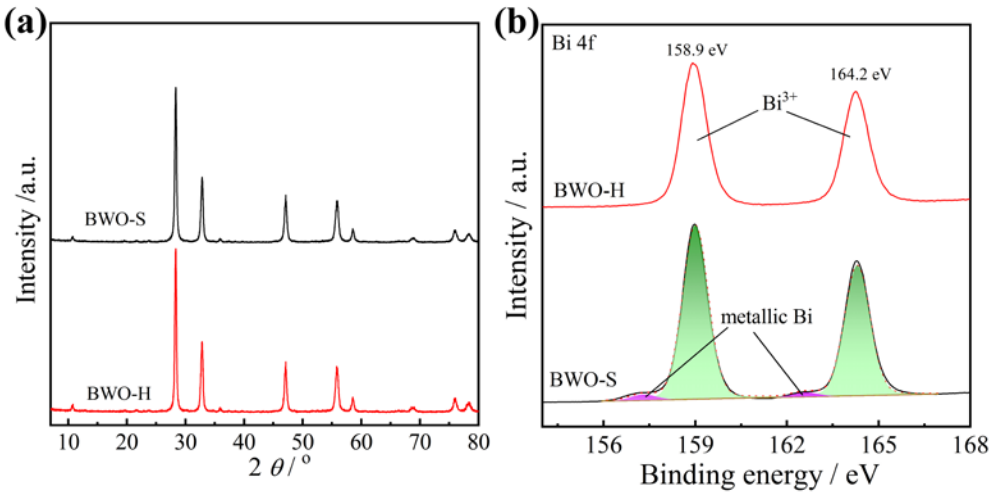

Figure S7 XRD patterns (a) and Bi 4f XPS spectra (b) of BWO-S and BWO-H samples.

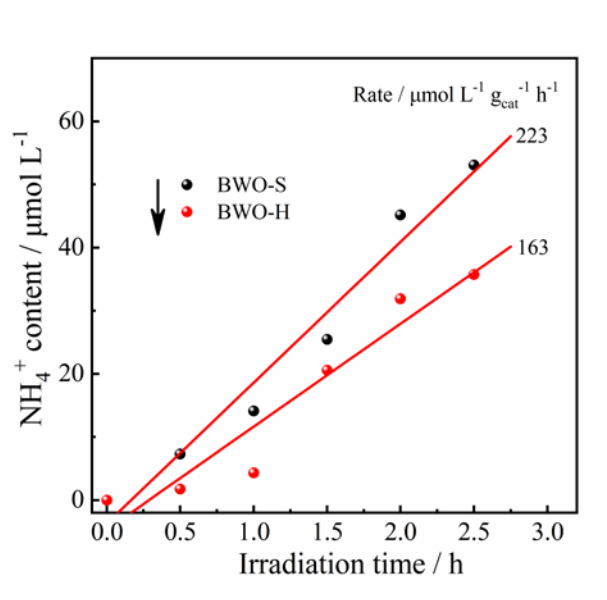

Figure S8 Photocatalytic N_2 fixation activity of BWO-S and BWO-H samples under simulated sunlight.

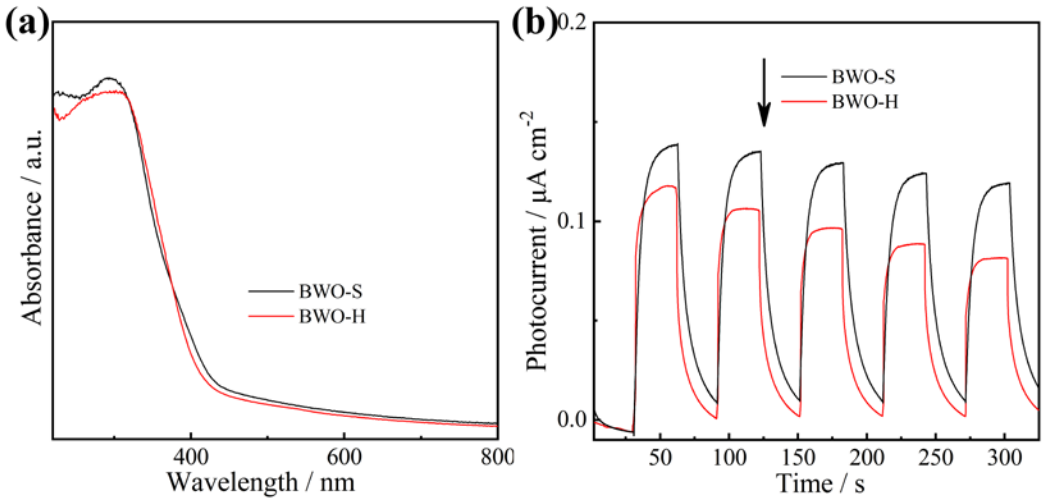

Figure S9 DRS spectra (a) and transient photocurrent response profiles (b) of BWO-S and BWO-H samples.