Supporting information

Plasma-induced black bismuth tungstate as a photon harvester for photocatalytic carbon dioxide conversion

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Characterization

The X-ray diffraction (XRD) with Cu Kα (λ = 1.5418 Å) as a source is a Shimadzu XRD-6100 diffractometer, which was used to characterize phases structures of the as-prepared photocatalysts. The range of 2θ is from 10° to 80°, and the scan rate is 0.1167° s^{-1}. The photocatalyst morphology was observed by field emission scanning electron microscope (FE-SEM, JEOL-JSM-7001F, Japan) and transmission electron microscope (200 kV) with an accelerating voltage of 10kV. X-ray photoelectron spectroscopy (XPS) of the photocatalyst was obtained by using an ESCALab MKII spectrometer with 20 kV of Mg Kα radiation. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) was performed to measure the optical properties of the as-prepared photocatalysts by using a UV-vis spectrophotometer (Shimadzu UV-2450, Japan). A QuantaMaster and TimeMaster Spectrofluorometer was used to investigate photoluminescence (PL) spectroscopy. In-situ FTIR spectra were obtained by using a Thermo Scientific Nicolet iS50.

Photoelectrochemical measurement

An electrochemical workstation of 760B (CHI760B, Chenhua Instrument Company, Shanghai, China) was performed on for electrochemical measurement using a three-electrode system. Photocurrent and electrochemical impedance spectroscopy (EIS) measurements of samples were carried out on it. In the three-electrode system of electrochemical workstation, the reference electrode was a saturated calomel electrode (SCE), and the platinum wire was used as the counter electrode. The working electrode was prepared as follows: 5 mg photocatalyst powder dispersed in 1 mL ethanol solution,

then 20 μL suspended coated in 10 × 5 mm indium-tin-oxide (ITO) glass and dried for 60°C to remove ethanol for 12 h. Put above three electrodes into the electrolyte solution of 0.2 M Na_2SO_4. The light source is a 300 W Xe lamp (PLS-SXE3, Beijing Perfectlight). At room temperature, started electrochemical measurement applied no voltage between the electrodes.

Photocatalytic CO_2 reduction evaluation

Photocatalytic CO_2 reduction was carried out on a photoreaction system (Labsolar-6A, Beijing Perfectlight, Fig. S8). The powder (10 mg) catalyst was dissolved in a 300 mL reactor with a quartz glass cover, including 2 mL of TEOA as sacrificial electron donor, 4 mL of deionized water, and 6 mL of MeCN. Ultrasound the prepared solution at room temperature for 10 min. Connect the reactor to the photoreaction system. After the air in the reaction system was cleared away, high-purity CO_2 was introduced into the system until the pressure reached 70 kPa and circulated for 60 min to achieve uniform distribution of CO_2 gas. The temperature of photocatalytic CO_2 reduction was set at 5°C by the cooling water circulation system, promoting the adsorption of CO_2. A 300 W Xe lamp (PLS-SXE3, Beijing Perfectlight) was employed as the light source. A gas chromatograph (GC2002, KeChuang, Shanghai) equipped with thermal conductivity detector (TCD) and hydrogen flame ionized detector (FID) was used to determine the amount of the gas product.

Table S1. Comparison of the performances with other catalysts for photocatalytic CO_2 reduction

Light source	Catalyst	Reaction medium	Products	Activity	Reference
300 W Xe lamp	**Bi_2WO_6**	**Liquid-solid, water and TEOA**	**CO**	**56.5 μmol g^{-1} h^{-1}**	**This Work**
300 W Xe lamp	Ti_3C_2/ Bi_2WO_6	Liquid-solid, water	CH_4	1.78 μmol g^{-1} h^{-1}	[1]
300 W Xe lamp	BiOBr/ ACSs	Liquid-solid, water	CO	23.74 μmol g^{-1} h^{-1}	[2]
300 W Xe lamp	$BiOIO_3$	Liquid-solid, water	CO	6.30 μmol g^{-1} h^{-1}	[3]
300 W Xe lamp	$Bi_4O_5Br_2$	Gas-solid, water	CO	3.16 μmol g^{-1} h^{-1}	[4]
visible light ($\lambda > 420$ nm)	BVO/C /Cu_2O	Gas-solid, water	CO	3.01 μmol g^{-1} h^{-1}	[5]

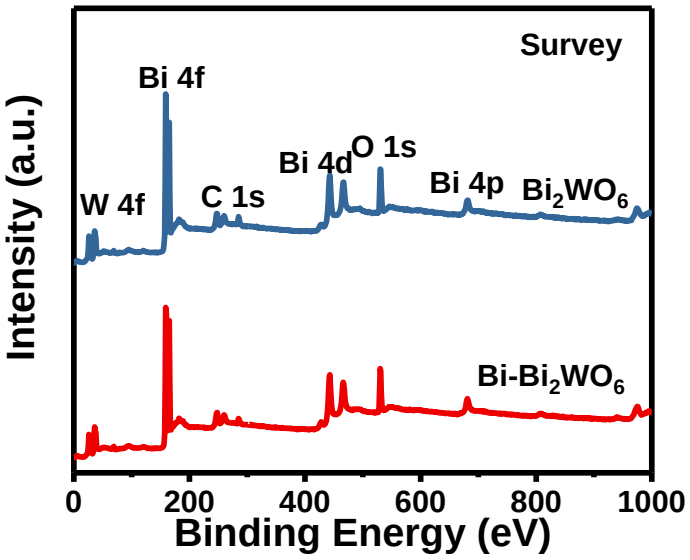

Fig. S1 XPS spectra of original Bi_2WO_6 and 6-BT.

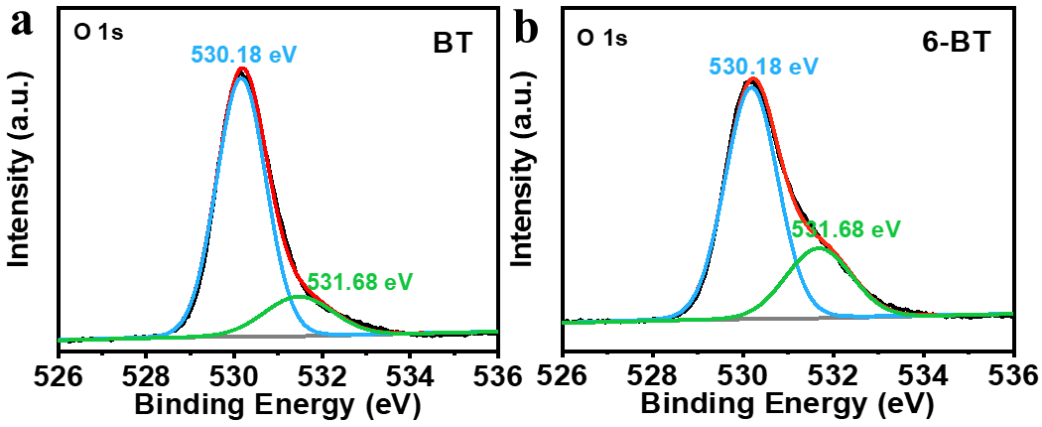

Fig. S2 XPS high-resolution spectra of (a) O 1s of BT and (b) O 1s of 6-BT.

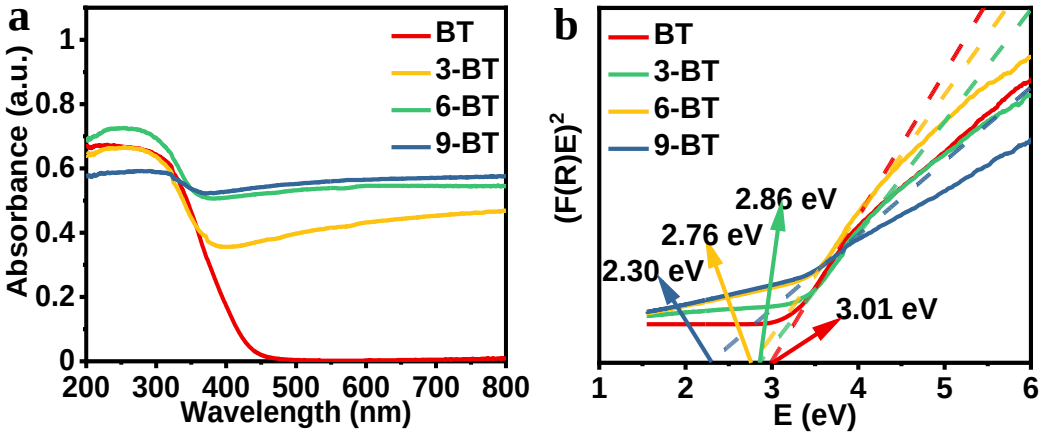

Fig. S3 (a) UV-vis diffuse reflection spectrum and (b) estimated bandgap of BT and X-BT (X=3, 6, 9).

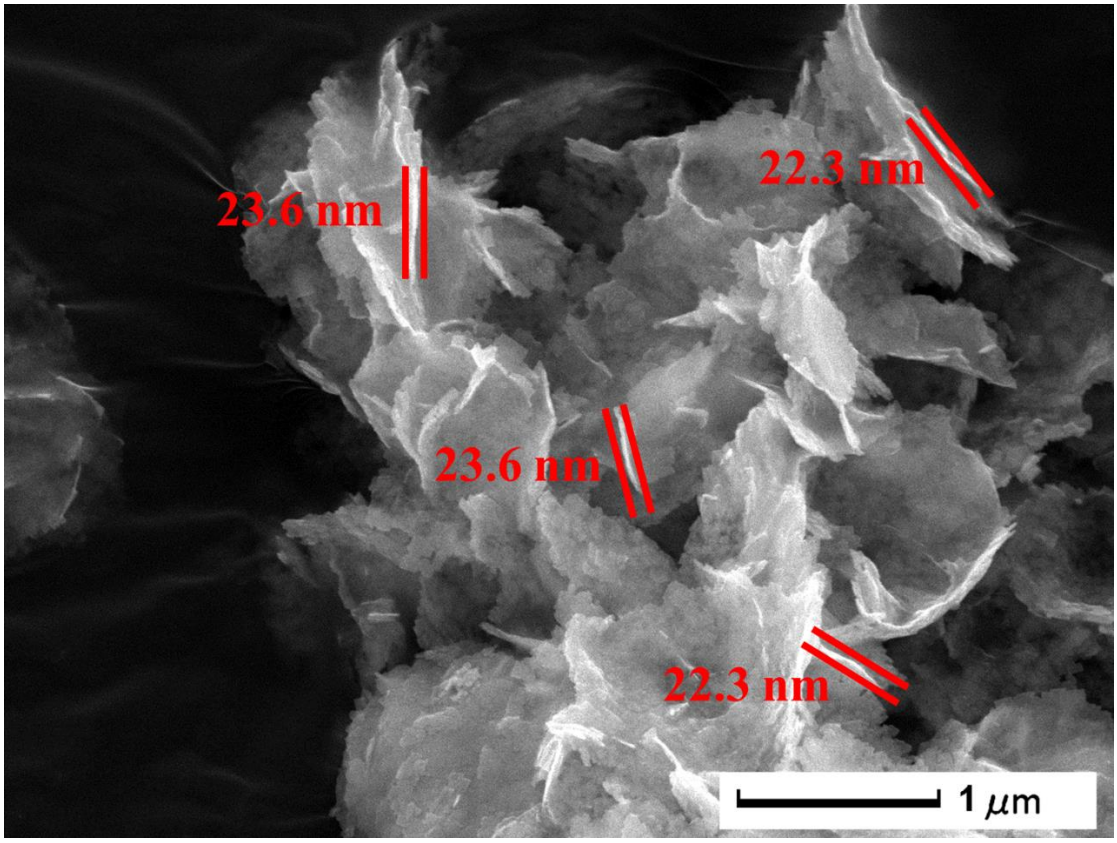

Fig. S4 SEM image of 6-BT.

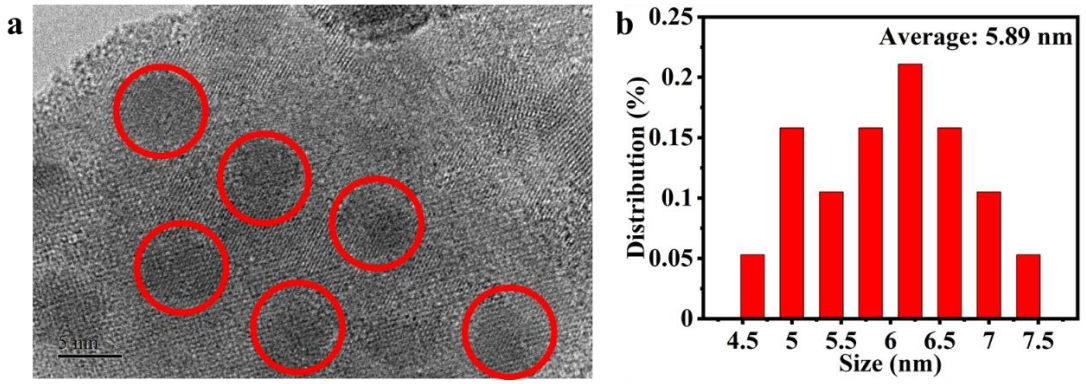

Fig. S5 HRTEM image (a) and Bi QDs size distribution (b) of 6-BT.

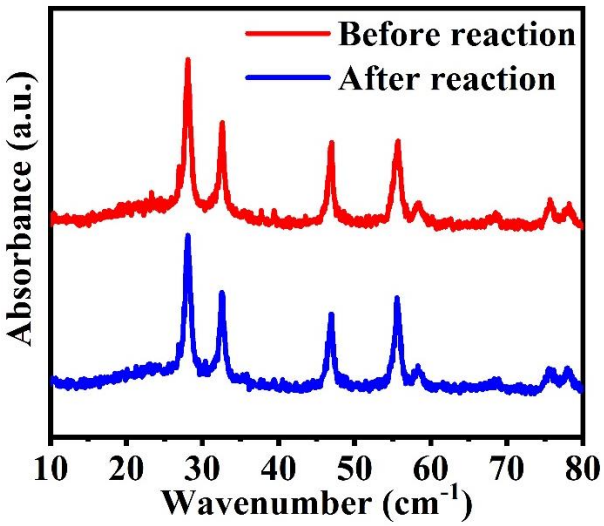

Fig. S6 XRD patterns of 6-BT before and after the photocatalytic CO_2 reduction reaction.

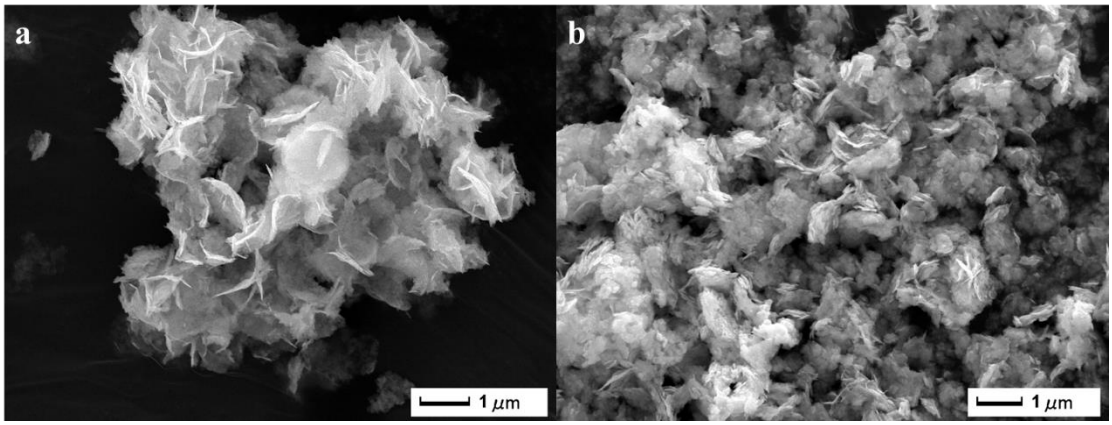

Fig. S7 SEM images of 6-BT before (a) and after (b) the photocatalytic CO_2 reduction reaction.

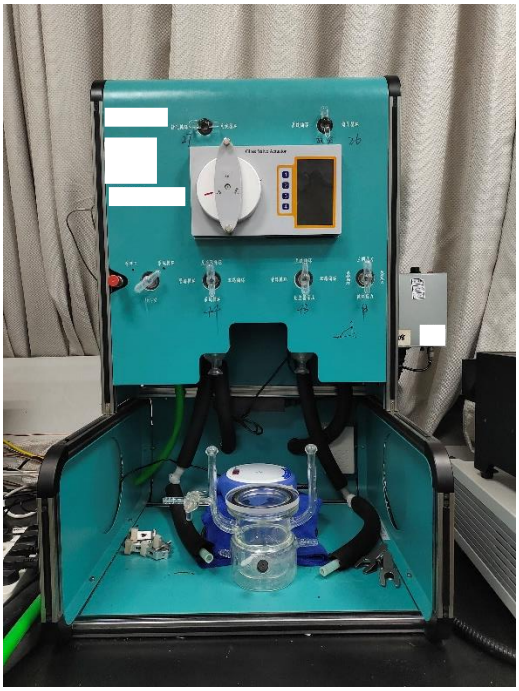

Fig. S8 Photo of photocatalytic reaction equipment.

Reference

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