Electronic Supplementary Information (ESI) for

**Oxygen vacancy induced Bi\textsubscript{2}WO\textsubscript{6} for the realization of photocatalytic CO\textsubscript{2} reduction over the full solar spectrum: from the UV to the NIR region**

by

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(1) Detailed Experimental Procedures

Chemical reagents

All chemicals reagents were of analytical grade and were used as received without any further purification. Bismuth (III) nitrate pentahydrate, Bi(NO$_3$)$_3$·5H$_2$O (≥ 98.0%) and ethylene glycol, EG (≥ 99.0%) were purchased from Sigma Aldrich; sodium tungstate dihydrate, Na$_2$WO$_4$·2H$_2$O (≥ 99.0%) was supplied by Merck and ethanol, C$_2$H$_5$OH (Grade AR 96.0%) was procured from Friendemann Schmidt Chemical. Deionized (DI) water with resistivity ≥ 18 MΩ cm was utilized throughout the experiment.

Synthesis of photocatalysts

Bi$_2$WO$_6$ with oxygen vacancies was prepared via a highly facile one-step ethylene glycol-assisted solvothermal process. In brief, 2 mmol of Na$_2$WO$_4$·2H$_2$O was dissolved in 30 mL of EG and the homogenous solution was added dropwise into 70 mL of EG solution containing 4 mmol of Bi(NO$_3$)$_3$·5H$_2$O. The colourless solution was vigorously stirred for 1 h at room temperature, and then transferred to a 125mL Teflon-lined stainless steel autoclave, which was maintained at 180°C for 20 h under autogenous pressure. After completion of the reaction, the autoclave was air-cooled to room temperature and the resulting precipitate was collected and washed with ethanol and DI water for several times to remove residual ions. The final product was dried at 60°C for overnight and was designated as Bi$_2$WO$_6$-OV. On another note, pristine Bi$_2$WO$_6$ without oxygen vacancy defects was obtained by annealing Bi$_2$WO$_6$-OV at 400°C in air-rich atmosphere for 4 h to reoxidize the surface. The sample collected was denoted as Bi$_2$WO$_6$-P.

Material characterization

The surface morphology of the as-synthesized samples was investigated using a Hitachi SU8010 field emission scanning electron microscopy (FESEM). High resolution transmission electron microscopy (HRTEM) images were acquired by TECNAI G2 F20 transmission electron microscope at an accelerating voltage of 200 kV. The sample for TEM analysis was prepared by depositing the sample suspension in ethanol onto carbon-coated copper grid. The electron spin resonance (ESR) spectra of the samples were obtained by a JEOL JES-FA200 ESR spectrometer. Powder X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Discover X-Ray diffractometer with Cu K$_\alpha$ radiation (λ = 0.15406 nm) at a scan rate of 0.02 s$^{-1}$ with applied current and accelerating voltage of 40 mA and 40 kV, respectively. The Raman Spectra were obtained using a micro Raman spectrometer (Horiba LabRAM HR Evolution) at room temperature with 514 nm laser excitation. The high resolution X-ray photoelectron spectroscopy
(XPS) spectra were attained on a scanning X-ray microprobe PHI Quantera II (Ulvac-PHI, INC.) equipped with an monochromatic Al-\(K_x\) (\(h\nu = 1486.6\) eV) X-ray source and analysed under ultra-vacuum (2.4 x 10\(^{-6}\)) environment. All binding energies were charged corrected by adventitious carbon signal (C 1s peak) at 284.6 eV. The absorbance spectra of the photocatalysts were measured using Agilent Cary 100 ultraviolet-visible (UV-vis) spectrophotometer within the range of 200–800 nm and the bandgap energies were determined from Kubelka-Munk (KM) function, \(F(R)\) and extrapolation of Tauc plots, \([F(R)\cdot h\nu]^{1/2}\) vs. \(h\nu\).

**Evaluation of photocatalytic CO\(_2\) reduction**

The photocatalytic activity of the as-prepared samples was evaluated by photoreduction of CO\(_2\) into CH\(_4\). The experiment was conducted at ambient temperature and atmospheric pressure in a custom-made, continuous gas flow reactor, as reported in our previous works.\(^1\)\(^6\) A 500 W Xenon arc lamp (CHF-XM-500W) equipped with different cut-off filters was employed to provide multiple light source, including UV (\(\lambda < 400\) nm), Vis (\(\lambda > 400\) nm), NIR (\(\lambda > 700\) nm) and simulated solar light (AM 1.5 filter). In a typical CO\(_2\) photoreduction experiment, the photocatalysts were uniformly coated on glass rods and were placed into quartz columns. The CO\(_2\) source of high purity (99.999%) was bubbled through H\(_2\)O to provide a gas mixture of CO\(_2\) and water vapour (reactant gas), which was directed to the quartz columns to allow intimate contact between the reactant gas and photocatalysts. Prior to photoreaction, the reactant gas was purged through the reactor at a flowrate of 50 mL/min for 30 min to remove any excess air from the system and also to ensure reactant gas molecules were completely adsorbed on the surface of photocatalysts. Henceforth, the reactant gas flow rate was reduced to 5 mL/min and it was maintained for 8 h under different light irradiation to evaluate the photocatalytic activity of the as-prepared samples. The product gas was collected at every 1 h interval and analyzed by using a gas chromatography (Agilent 7820A GC), equipped with flame ionized detector (FID) and thermal conductivity detector (TCD). The experiment set-up is illustrated in Fig. S1 and this set-up was enclosed in a black box to avoid any light interference from the surroundings to the reaction environment. The CH\(_4\) yield was quantified using Eq. S1.

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\text{Yield (\(\mu\text{mol g}^{-1}\text{h}^{-1}\))} = \frac{(C_{\text{final CH}_4} - C_{\text{initial CH}_4}) \times \text{volumetric flowrate of product gas}}{\text{Amount of photocatalyst used}}
\]  
\[(S1)\]
Experimental set-up for photocatalytic CO₂ reduction

**Figure S1** Schematic diagram of the set-up of photocatalytic CO₂ reduction experiment.

Control measurements of photocatalytic CO₂ reduction

To validate the indispensable role of Bi₂WO₆-OV and Bi₂WO₆-P as photocatalysts to drive the reduction of CO₂ to CH₄, a number of control experiments were performed, including: (1) under CO₂/H₂O vapour flow and light irradiation but without photocatalyst; (2) under CO₂/H₂O vapour flow with photocatalyst but without light irradiation; (3) under light irradiation with photocatalyst but without CO₂ (under N₂/H₂O vapour flow) and (4) under light irradiation with photocatalyst but without H₂O (under CO₂ flow only). In all these cases, negligible-to-none of CH₄ products was generated. Therefore, the product yields detected in the reactions could be confidently assigned to stem from photocatalytic CO₂ reduction and the possibility of the source of carbon residuals and photolysis could be ruled out. In addition, it was proven that photocatalyst, light source and CO₂/H₂O vapour flow are the several prerequisites for CO₂ photoreduction to take place.
(2) Structural Features of Bi$_2$WO$_6$-P

**Figure S2** (A) TEM image and (B) HRTEM image of the as-developed Bi$_2$WO$_6$-P.
(3) High Resolution W 4f and O 1s XPS spectra

Figure S3 (A) High resolution W 4f and O 1s XPS spectra of Bi$_2$WO$_6$-P and Bi$_2$WO$_6$-OV.
(4) Stability Test of Bi$_2$WO$_6$-OV

Figure S4 Recycling runs of photocatalytic CO$_2$ reduction over Bi$_2$WO$_6$-OV under simulated solar light irradiation: (A) Time courses of CH$_4$ evolution and (B) total CH$_4$ evolution for each cycle.
References


