

Supplementary Material

Polyoxometalates tailoring of frustrated Lewis pairs on Ce-doped Bi₂O₃ for boosting photocatalytic CO₂ reduction

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1. Experimental section

1.1. Materials and reagents

All salts and other chemicals were of the highest purity available from commercial sources without further purification. DI water (18.25 MΩ·cm) applied in all the experiments was attained from a Molecular Lab Water Purifier.

1.2. Synthesis of Bi₂O₃

Bi₂O₃ was synthesized via a reported synthetic method.¹ 1.02 g of benzenetetracarboxylic acid (BTA) was dissolved in 75 mL ethanol as solution A, 2 mmol Bi(NO₃)₃·5H₂O was dissolved in 75 mL deionized water as solution B. Then, solution A was mixed with solutions B in a three necked flask and kept at 80 °C for 1 h, and naturally cooled to room temperature. The obtained white precipitates were washed with water and ethanol for several times, and then placed in a vacuum drying apparatus overnight for further use. The obtained white precipitates were directly

annealed in air at 600 °C for 3 h, and then cooled to room temperature.

1.3. Synthesis of $CeBiO_x$

$CeBiO_x$ was synthesized via a reported synthetic method.¹ 1.02 g of benzenetetracarboxylic acid (BTA) was dissolved in 75 mL ethanol, named as solution A. X mmol $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 75 mL deionized water as solution B, and Y mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 75 mL deionized water as solution C. Then, solution A was mixed with solutions B and C in a three necked flask and kept at 80 °C for 1 h, and naturally cooled to room temperature. The obtained white precipitates were washed with water and ethanol for several times, and then placed in a vacuum drying apparatus overnight for further use. The obtained white precipitates were directly annealed in air at 600 °C for 3 h, and then cooled to room temperature. By controlling the molar amount of added $Ce(NO_3)_3 \cdot 6H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$, the Ce-doping contents were controlled. The molar ratios of $Ce(NO_3)_3 \cdot 6H_2O$ to $Bi(NO_3)_3 \cdot 5H_2O$ are 1:1, 1:2 and 2:1, respectively.

1.4. Synthesis of $Na_{16}[Cu_4(H_2O)_2(\alpha-P_2W_{15}O_{56})_2] \cdot 42H_2O$ (**Cu₄**)

The **Cu₄** POM was prepared according to the reported method.² In a 100 mL beaker, a solution of $CuCl_2 \cdot 2H_2O$ (0.43 g, 2.50 mmol) and NaCl (2.92 g dissolved in 50 mL distilled water) was charged. Solid $Na_{12}[\alpha-P_2W_{15}O_{56}] \cdot 18H_2O$ (5.00 g, 1.25 mmol) was added in one portion, and the mixture was stirred and heated to boiling. The color was changed from blue to bright lime green. The hot, turbid solution was filtered. The crystals were produced from the clear yellow-green solution within a few minutes. The filtrate was cooled to room temperature, stoppered, and placed in a refrigerator at 5 °C overnight. The resulting lime green crystals were collected by filtration, washed with absolute ethanol (3×10 mL), and then with absolute ether (3×10 mL). The **Cu₄** POM was obtained as a lime green powder.

1.5. Synthesis of $(NH)_4[H_6CuMo_6O_{24}] \cdot 4H_2O$ (**CuMo₆**)

The **CuMo₆** POM was synthesized according to the literature.³ 2.65 g ammonium molybdate was weighed and dissolved in an 80 mL of deionized water. The solution was heated to boiling named as solution A. Then, 0.749 g $CuSO_4 \cdot 5H_2O$ was dissolved

in 29 mL of deionized water to obtain solution B. Solution B was dropped into solution A slowly and then cooled to room temperature. The mixture was evaporated to 30 mL by a rotary evaporator. The mixture was then filtered immediately, and the filtrate was allowed to stand for crystallization. Finally, the crystals were collected after washing with ethanol and drying under vacuum.

*1.6. Synthesis of $\text{Na}_{12}[(\alpha\text{-SbW}_9\text{O}_{33})_2\text{Cu}_3(\text{H}_2\text{O})_3]\cdot 46\text{H}_2\text{O}$ (**Cu₃**)*

The **Cu₃** POM was synthesized according to the literature.⁴ Dissolving $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (1.0 g, 5.8 mmol) using 50 mL of ultrapure water, then $\text{Na}_9[\alpha\text{-SbW}_9\text{O}_{33}]\cdot 19.5\text{H}_2\text{O}$ (10 g, 3.5 mmol) was added. The solution was refluxed for 1 hour at pH 6.2. Then, the solution was cooled and filtered. Finally, the filtrate was slowly evaporated at room temperature to obtain large green crystals of **Cu₃** POM.

*1.7. Synthesis of $\text{Na}_{16}[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_2]\cdot 58\text{H}_2\text{O}$ (**Ni₄**)*

The **Ni₄** POM was prepared according to a reported method.² In a 100 mL beaker, a solution of $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.73 g, 2.50 mmol) and NaCl (2.93 g dissolved in 50 mL distilled water, 1 M) was prepared. Solid $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ (5.00 g, 1.25 mmol) was added all at once, and the mixture was stirred. The color of the solution changed from fluorescent olive green to bright green. The solution was heated to 50 °C, cooled to room temperature, covered, and placed in a refrigerator at 5 °C overnight. The resulting green crystalline product was filtered, washed with anhydrous ethanol for three times (3×10 mL), followed by washing with anhydrous ether (3×10 mL), and dried in an oven at 50°C to obtain the green powder of **Ni₄** POM.

*1.8. Synthesis of $\text{Na}_{16}[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_2]\cdot 58\text{H}_2\text{O}$ (**Co₄**)*

The **Co₄** POM was prepared according to a reported method.² In a 100 mL beaker, a solution of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (1.83 g, 2.50 mmol) and NaCl (2.93 g dissolved in 50 mL distilled water, 1 M) was prepared. Solid $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ (5.00 g, 1.25 mmol) was added all at once, and the mixture was stirred. The color of the solution changed from fluorescent olive green to dark reddish-brown, eventually turning wine red with a green hue. The solution was heated to 50°C, cooled to room temperature, covered, and placed in a refrigerator at 5 °C overnight. The resulting brownish-green crystalline

product was filtered, washed with anhydrous ethanol for three times (3×10 mL), followed by washing with anhydrous ether (3×10 mL), and dried in an oven at $50\text{ }^{\circ}\text{C}$ to obtain the brownish-green powder of **C₀₄** POM.

1.9. Synthesis of $\text{Na}_{16}[\text{Zn}_4(\text{H}_2\text{O})_2(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 16\text{H}_2\text{O}$ (**Zn₄**)

The **Zn₄** POM was prepared according to a reported method.² In a 100 mL beaker, a solution of ZnCl_2 (0.34 g, 2.50 mmol) and NaCl (2.92 g dissolved in 50 mL distilled water, 1 M) was prepared. Solid $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ (5.00 g, 1.25 mmol) was immediately added with vigorous stirring and heating. The solution was heated to $80\text{ }^{\circ}\text{C}$ to generate a turbid solution, followed by hot filtration. The clear filtrate was collected in a preheated 100 mL beaker and placed in a refrigerator at $5\text{ }^{\circ}\text{C}$ overnight. The product was recovered on a suction filter funnel, washed with anhydrous ethanol for three times (3×10 mL), followed by washing with anhydrous ether (3×10 mL), and dried in an oven at $50\text{ }^{\circ}\text{C}$ to obtain a white powder of **Zn₄** POM.

1.10. Synthesis of POMs/CeBiO_x

20 mg of CeBiO_x was dispersed in 25 mL beaker with 10 mL of water and sonicated for uniform dispersion. The POMs (**Cu₃**, **Cu₄**, **Ni₄**, **Co₄**, **Zn₄**, **CuMo₆**) were added to the CeBiO_x dispersion and stirred. The dispersion was stirred overnight at room temperature. After overnight stirring, the POMs/ CeBiO_x product was separated by centrifugation, followed by water washing. The products were then dried in a vacuum oven and used for various characterization and catalytic experiments. The resulting samples were named as **Cu₃**/ CeBiO_x , **Cu₄**/ CeBiO_x , **Ni₄**/ CeBiO_x , **Co₄**/ CeBiO_x , **Zn₄**/ CeBiO_x and **CuMo₆**/ CeBiO_x .

1.11. Synthesis of X wt.% **Cu₃**/ CeBiO_x

20 mg of CeBiO_x was dispersed in 25 mL beaker with 10 mL of water and sonicated for uniform dispersion. Different X wt.% **Cu₃** (X = 0, 1 wt.%, 3 wt.%, 5 wt.% and 7 wt.%) were added to the CeBiO_x dispersion and stirred. The dispersion was stirred overnight at room temperature. After overnight stirring, the X wt.% **Cu₃**/ CeBiO_x products were separated by centrifugation, followed by water washing. The products were then dried in a vacuum oven. The mass fractions of **Cu₃** in different samples were

0, 1 wt.%, 3 wt.%, 5 wt.% and 7 wt.%, and the resulting samples were named as 1% $\text{Cu}_3/\text{CeBiO}_x$, 3% $\text{Cu}_3/\text{CeBiO}_x$, 5% $\text{Cu}_3/\text{CeBiO}_x$ and 7% $\text{Cu}_3/\text{CeBiO}_x$.

1.12. Synthesis of 5% $\text{Cu}_3/\text{Bi}_2\text{O}_3$

In a typical electrostatic adsorption process, 20 mg of CeBiO_x was dispersed in 25 mL beaker with 10 mL of water and sonicated for uniform dispersion. X wt.% Cu_3 was added to the CeBiO_x dispersion and stirred. The dispersion was stirred overnight at room temperature. After overnight stirring, the 5 wt.% $\text{Cu}_3/\text{CeBiO}_x$ product was separated by centrifugation, followed by water washing. The product was then dried in a vacuum oven.

1.13. Characterization

Ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$) for the preparation of solutions was attained from a Molecular Lab Water Purifier. X-ray photoelectron spectroscopy (XPS) spectra were measured by Shimadzu Axis Supra with X-ray monochromatisation. The binding energy of each element was corrected by C 1s peak (284.6 eV) from residual carbon. Infrared transmission spectra were collected using a Fourier Transform infrared (FT-IR) spectrophotometer (Nicolet iS5, Thermo Fisher SCIENTIFIC, America). XRD patterns were recorded on a Rigaku Ultima IV diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a graphite monochromator from 5° to 50° at a scanning rate of $5^\circ/\text{min}$. UV-vis diffuse absorption spectra were recorded on an UV-2600 UV-vis spectrophotometer (Shimadzu Corp.) equipped with an integrating sphere using BaSO_4 as the reference. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and the corresponding EDX mapping images were collected on a Tecnai F30 operating at a 200 kV accelerating voltage. Raman measurements were acquired using a Lab RAM HR Evolution Reflex Raman confocal microscope (HORIBA FRANCE SAS, France), equipped with a diode laser emitting at 532 nm. The liquid product was confirmed by a Liquid Nuclear Magnetic Resonance Spectrometer (NMR, JNM-ECS 400M, JEOL, Japan). Mott-Schottky measurements, electrochemical impedance spectroscopy (EIS), and time-resolved photocurrent behaviors were performed on the electrochemical workstation (CH Instruments Ins.) in

a 3-electrode configuration with the assembled photoelectrodes (as-prepared materials on FTO glass) as the working electrode, the Pt slice as the counter electrode and the Ag/AgCl as the reference electrode. 0.5 M Na₂SO₄ solution was used as the electrolyte.

1.14. Photocatalytic CO₂ reduction measurement

The photocatalytic CO₂ reduction reaction was carried out in a 50 mL quartz reaction vessel with a top illumination design.

Accurately weigh 5.00 mg of catalyst and place it in the reaction vessel. Add the reaction solution, which consists of water (H₂O), acetonitrile (CH₃CN) and the sacrificial electron donor triethanolamine (TEOA), in a volume ratio of V(TEOA) : V(H₂O) : V(CH₃CN) = 1 : 2 : 3. Before illumination, perform a gas displacement operation by continuously passing ultra-pure CO₂ (≥ 99.999%) gas through the reaction vessel for 20 min to remove the air from the reaction vessel.

The top of the reaction vessel is equipped with a 300 W xenon lamp (100 mW cm⁻²) as the light source. During the irradiation process, approximately 1 mL of gas sample is taken from the stainless steel reactor and injected into a gas chromatograph GC9790 Plus. The products are sequentially quantitatively analyzed every 1 hour, with CH₄, CO and H₂ being detected. The gas chromatograph is equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The production rate is derived based on the calibration curve. Throughout the measurement process, the temperature of the entire reaction chamber is maintained at around 25 °C. The liquid products are studied using nuclear magnetic resonance spectroscopy. A mixture of 0.5 mL of the reaction solution and 0.1 mL of D₂O (containing 0.05 μL of dimethyl sulfoxide (DMSO) as an internal standard) is prepared to obtain the NMR signal.

Cyclic tests: The cyclic experimental testing is conducted as follows: After the first reaction, the catalyst is washed and recovered by rinsing with acetonitrile, ethanol, and water, followed by centrifugation. Then, the catalyst is used for the second reaction experiment. After the second reaction, the catalyst is washed and recovered again by rinsing with acetonitrile, ethanol, and water, followed by centrifugation for the third experiment, and so on. This process is repeated for a total of five tests.

1.15. Photoelectric performance evaluation

Preparation of FTO Working Electrodes: Add 5.00 mg of catalyst to 1 mL of anhydrous ethanol and a mixture solution composed of 5 μ L of 5% Nafion. Sonicate the suspension for half an hour, then use a pipette to evenly drop the solution onto the FTO substrate. Dry the coated substrate under an infrared lamp, and finally, dry it at 60 °C for 1 h in a convection oven.

Mott-Schottky test is performed at frequencies of 500 Hz, 1000 Hz and 1500 Hz with a step size of 5 mV. Electrochemical Impedance Spectroscopy (EIS) test is conducted over a frequency range of 10^{-2} to 10^5 Hz with an amplitude of 10 mV. Photocurrent measurement involves periodically switching between dark and illuminated conditions every 40 s to obtain the current density under dark and illuminated conditions.

The conversion relationship between the working voltage relative to the reference electrode (Ag/AgCl) and the standard hydrogen electrode (NHE) is given by: $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197$ (V vs. NHE).

2. Figures

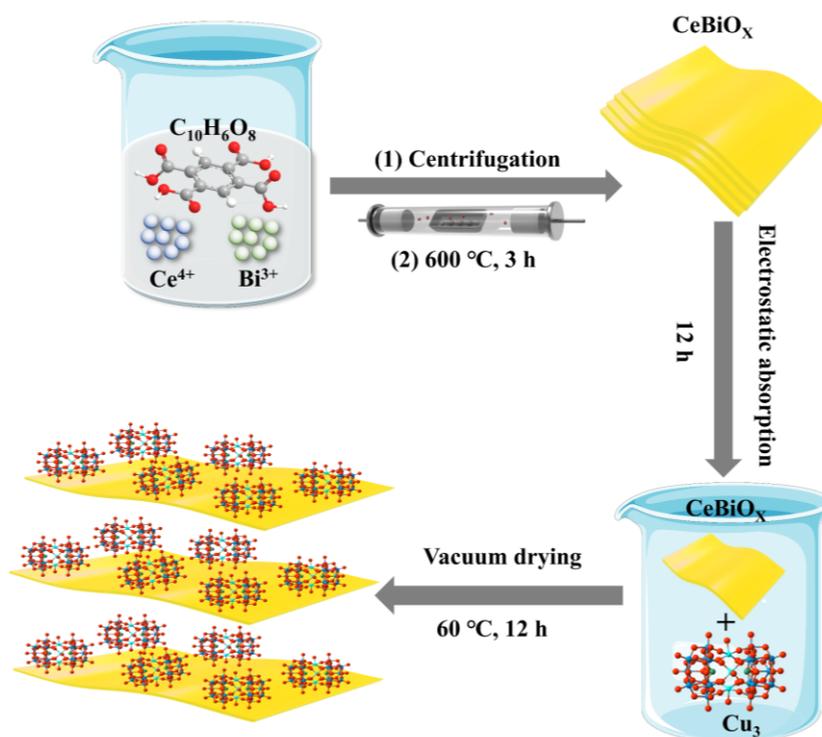


Fig. S1 Schematic illustration for the synthesis of $CeBiO_x$ and the $Cu_3/CeBiO_x$ composite.

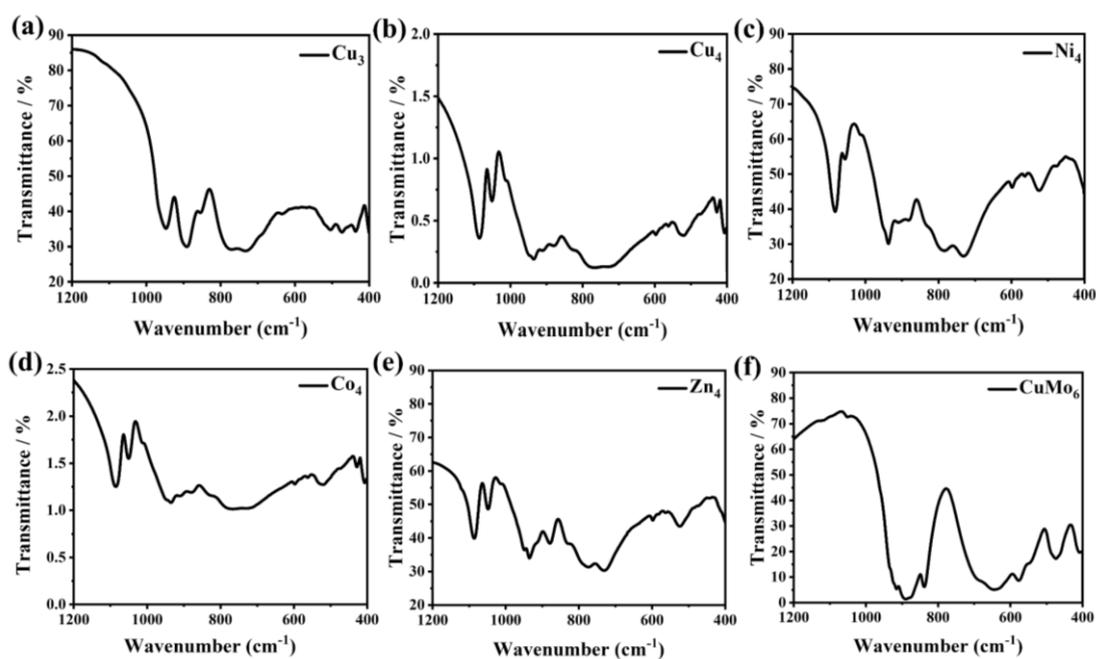


Fig. S2 FT-IR spectra of Cu_3 , Cu_4 , Ni_4 , Co_4 , Zn_4 and $CuMo_6$.

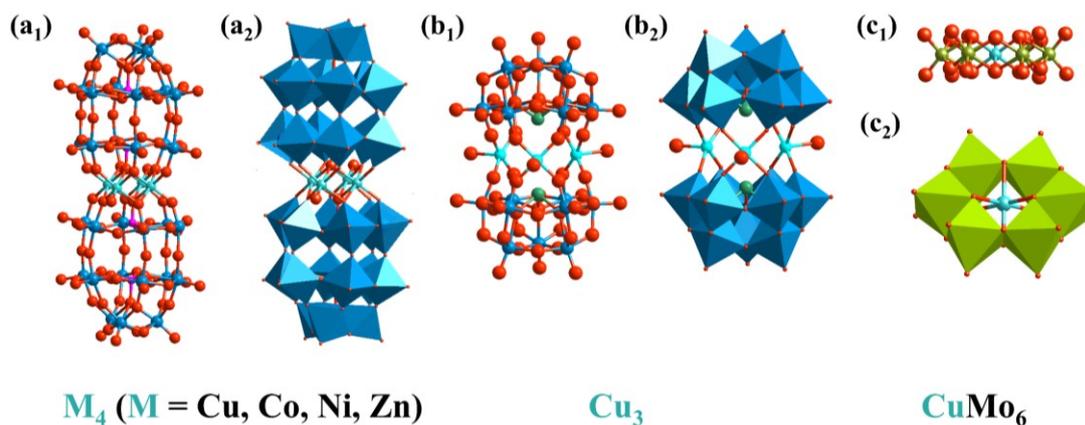


Fig. S3 (a) Combined polyhedral/ball-and-stick representations of the structures of M_4 ($M = \text{Cu, Co, Ni, Zn}$), (b) Combined polyhedral/ball-and-stick representations of the structure of Cu_3 , (c) Combined polyhedral/ball-and-stick representations of the structure of CuMo_6 .

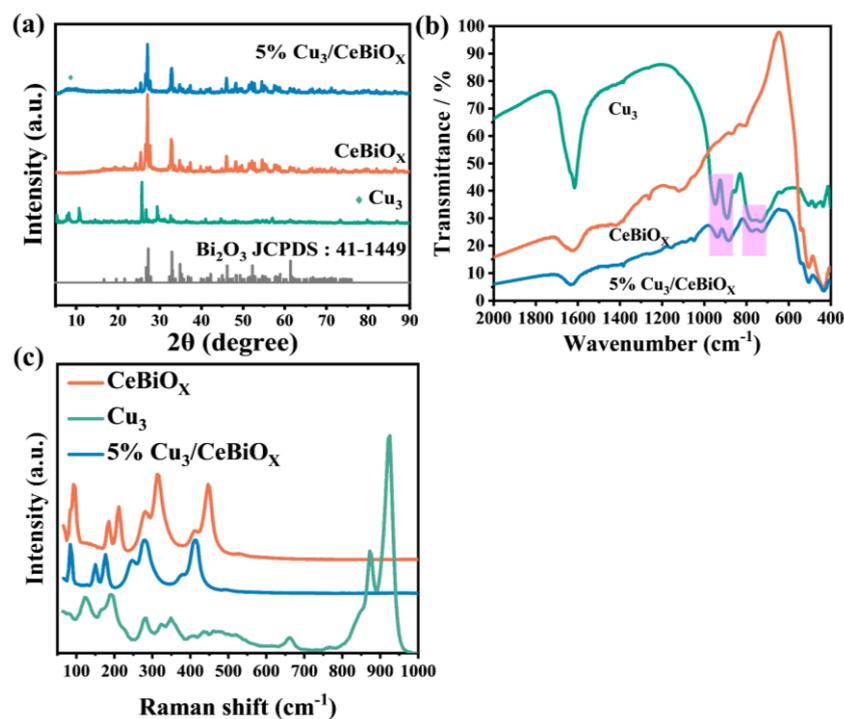


Fig. S4 (a) The XRD patterns of CeBiO_x , 5% $\text{Cu}_3/\text{CeBiO}_x$ and Cu_3 , (b) FT-IR spectra of CeBiO_x , 5% $\text{Cu}_3/\text{CeBiO}_x$, (c) Raman spectra of CeBiO_x and 5% $\text{Cu}_3/\text{CeBiO}_x$.

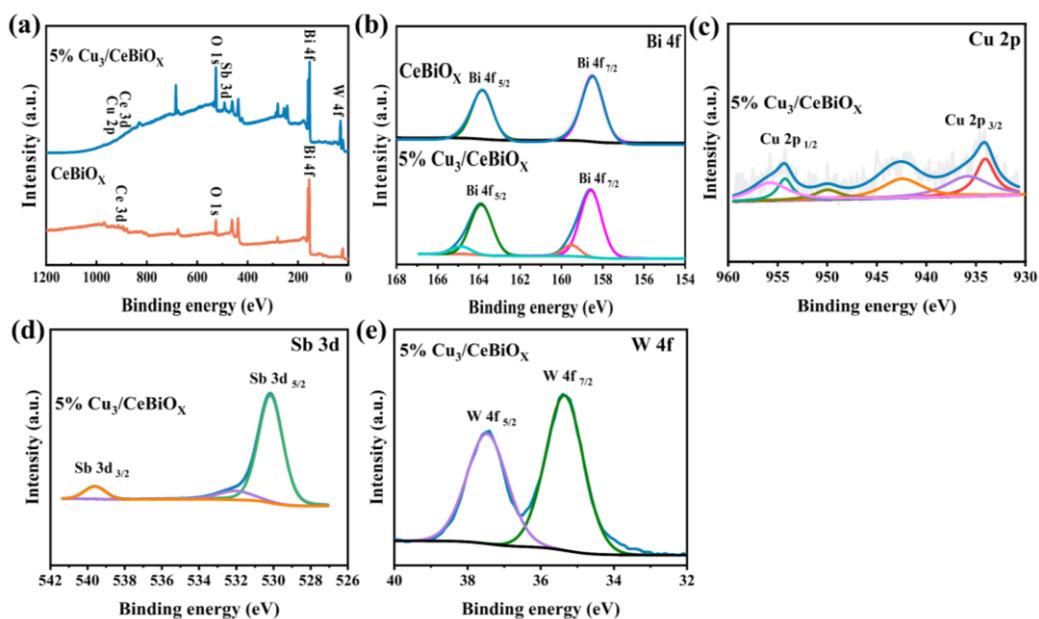


Fig. S5 (a) Full-scan XPS spectrum of CeBiO_x and 5% $\text{Cu}_3/\text{CeBiO}_x$, High-resolution XPS spectra of (b) Bi 4f, (c) Cu 2p, (d) Sb 3d and (e) W 4f for 5% $\text{Cu}_3/\text{CeBiO}_x$.

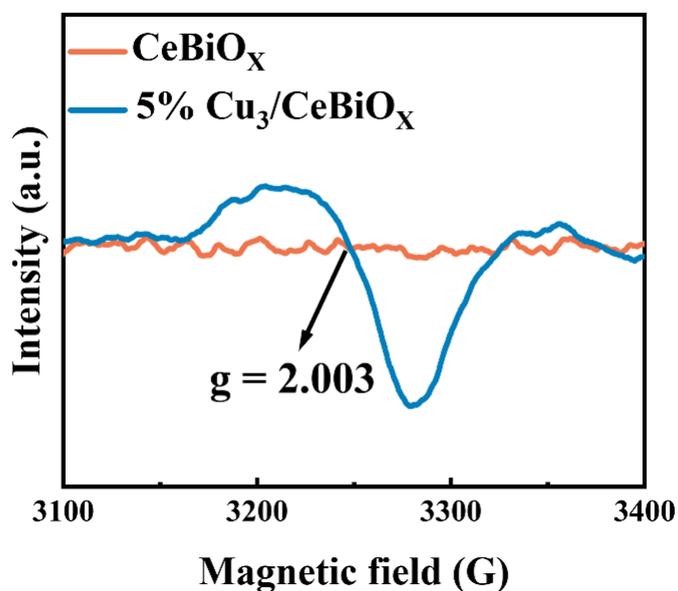


Fig. S6 ESR spectra of CeBiO_x and 5% $\text{Cu}_3/\text{CeBiO}_x$, the fluctuations in the ESR spectrum of CeBiO_x are attributed to the instrument baseline fluctuations.

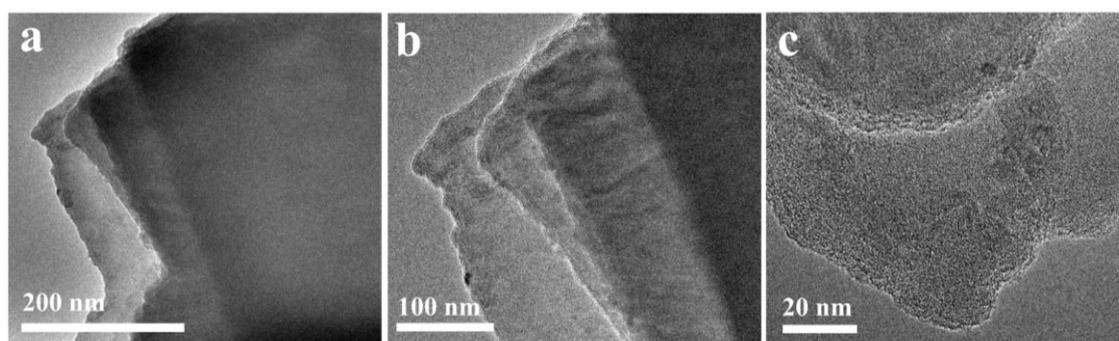


Fig. S7 (a-c) TEM images of 5% $\text{Cu}_3/\text{CeBiO}_x$.

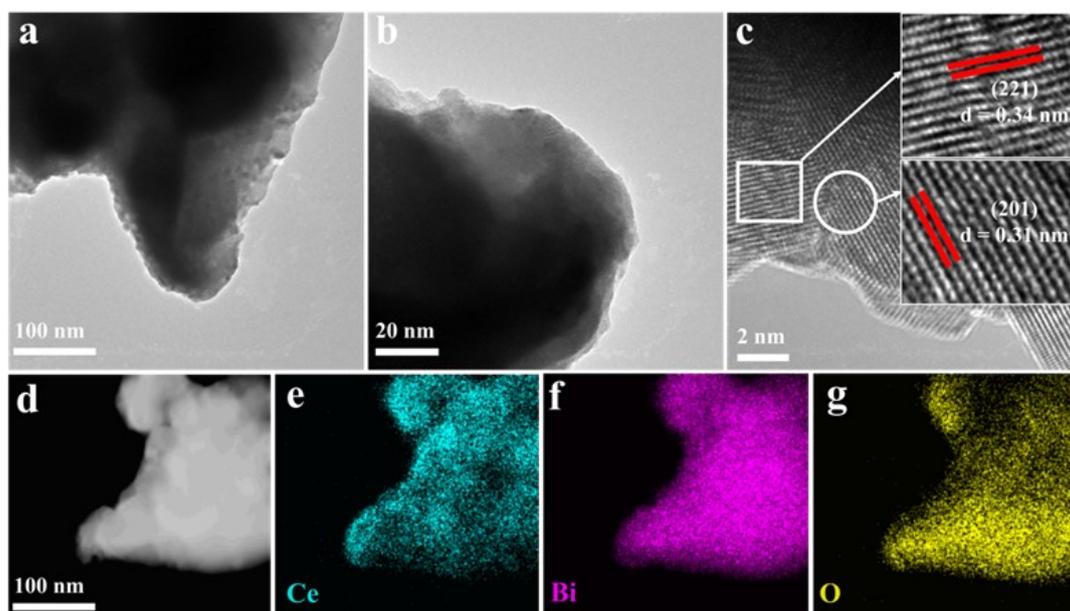


Fig. S8 (a) and (b) TEM images of CeBiO_x , (c) HR-TEM images of CeBiO_x , (d) STEM and (e-g) the corresponding EDX mapping images of CeBiO_x .

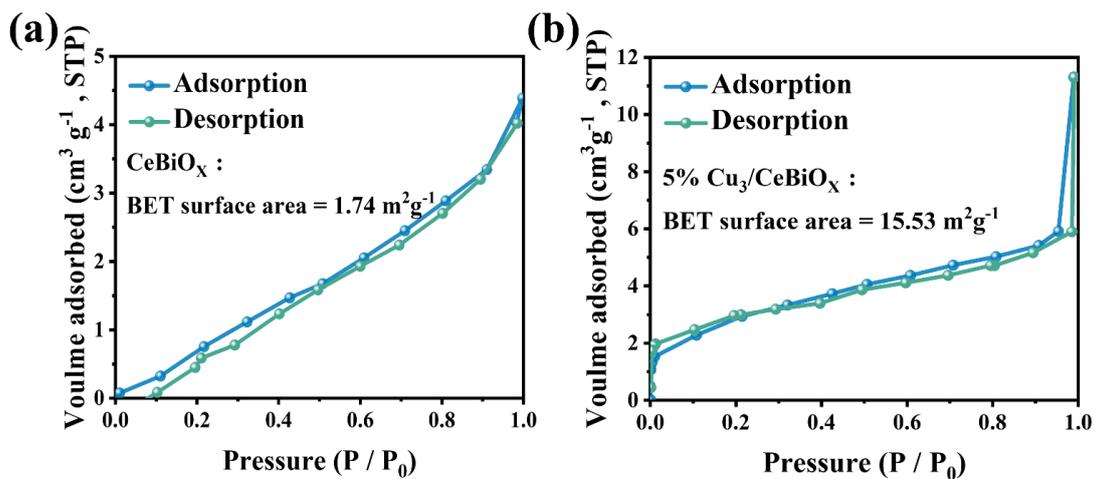


Fig. S9 N_2 adsorption-desorption isotherms of (a) $CeBiO_x$ and (b) $5\% Cu_3/CeBiO_x$.

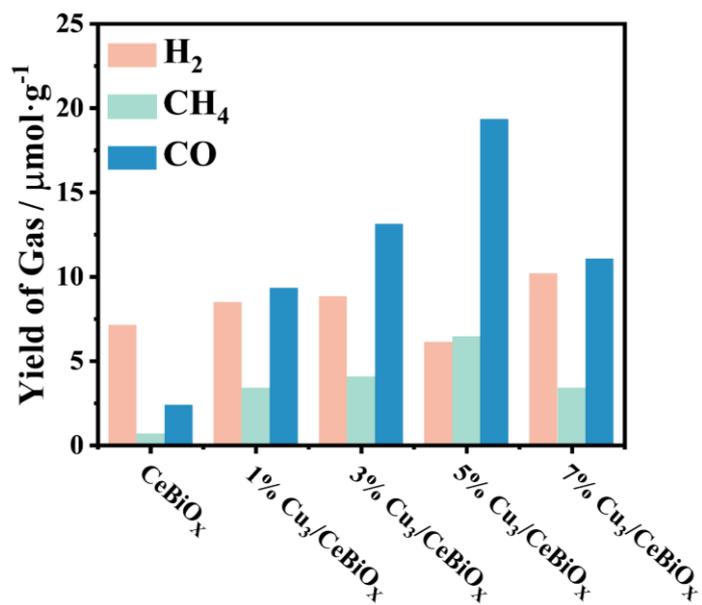


Fig. S10 Production rates of H_2 , CO and CH_4 on $CeBiO_x$ and $Cu_3/CeBiO_x$ with various loading amounts.

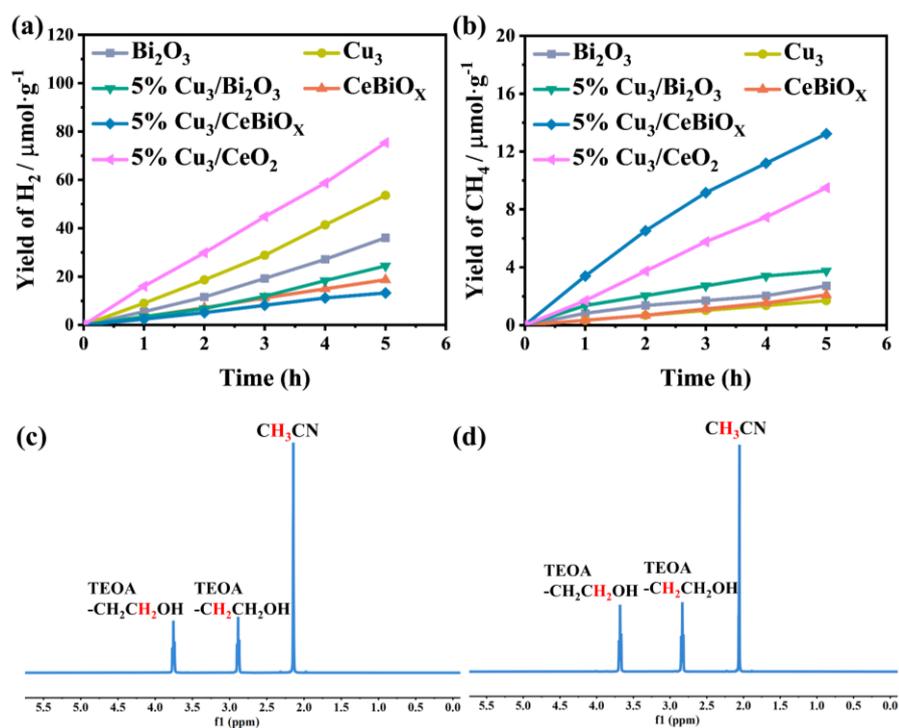


Fig. S11 (a) H₂ and (b) CH₄ yields as function of the irradiation time with Bi₂O₃, Cu₃, CeBiO_x, 5% Cu₃/CeO₂, 5% Cu₃/Bi₂O₃ and 5% Cu₃/CeBiO_x as catalysts, ¹H-NMR spectra of the organic solutions formed after the reaction of (c) CeBiO_x and (d) 5% Cu₃/CeBiO_x.

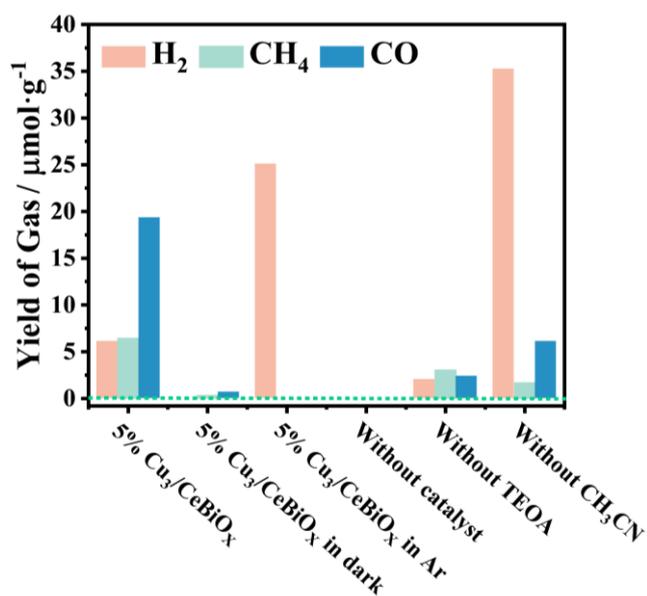


Fig. S12 Control experiments of photocatalytic CO₂ reduction under different conditions.

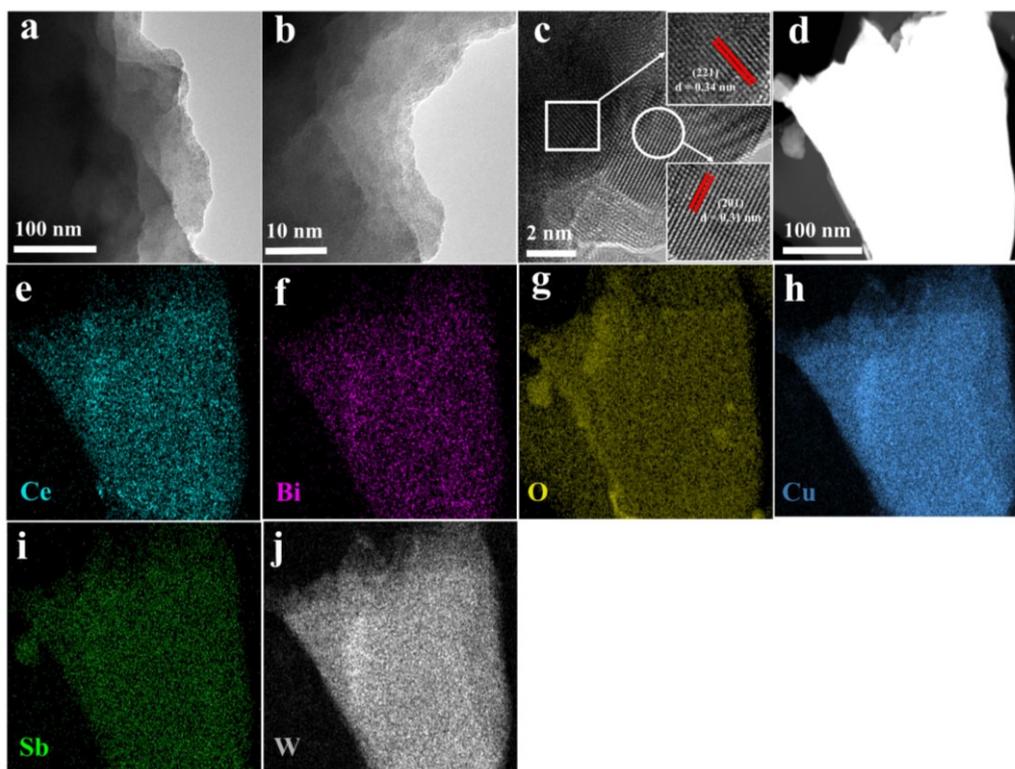


Fig. S13 (a) and (b)TEM images, (c) HR-TEM images, (d) STEM and (e-j) the corresponding EDX mapping images of 5% $\text{Cu}_3/\text{CeBiO}_x$ before and after 5 cycles of photocatalytic reactions.

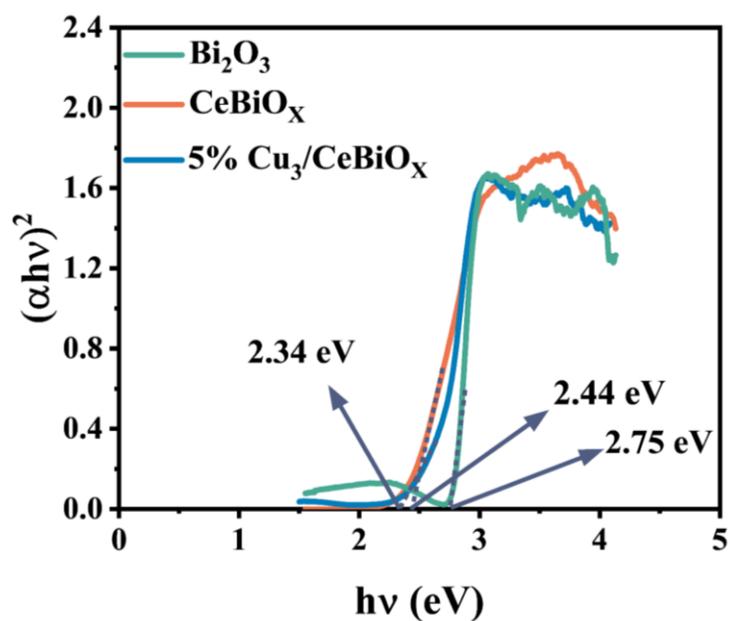


Fig. S14 Tauc plots of Bi_2O_3 , CeBiO_x and 5% $\text{Cu}_3/\text{CeBiO}_x$.

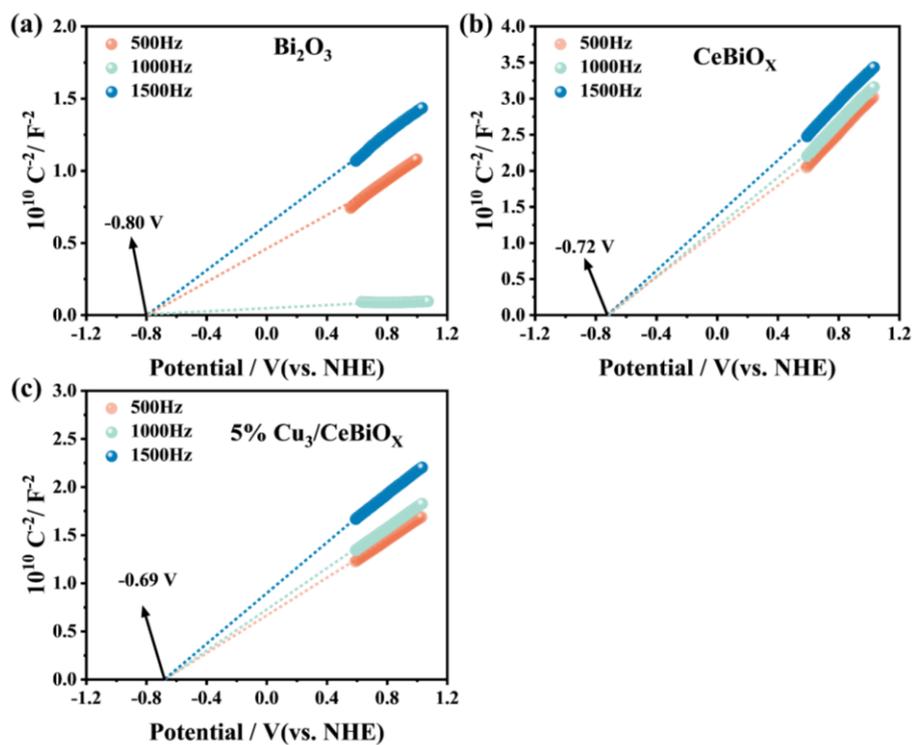


Fig. S15 Mott-schottky curves of (a) Bi_2O_3 , (b) CeBiO_x and (c) 5% $\text{Cu}_3/\text{CeBiO}_x$.

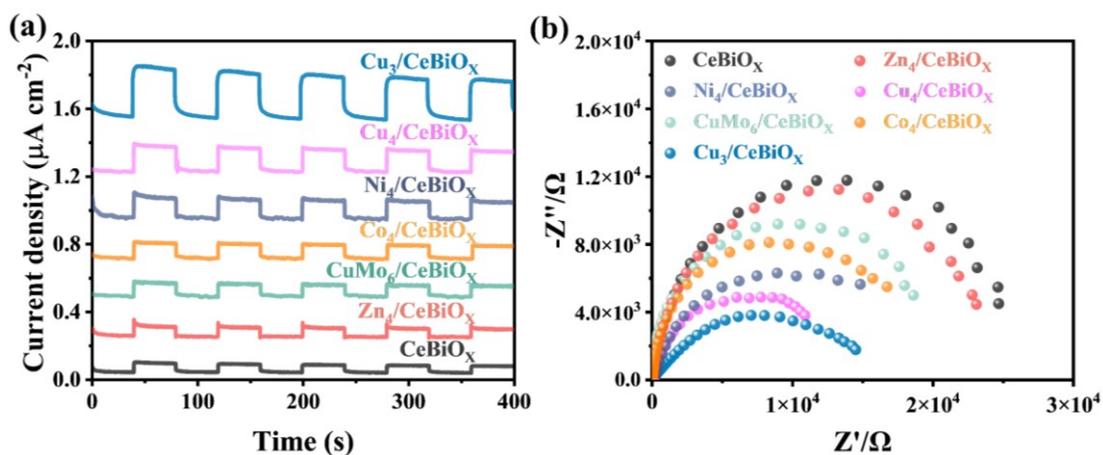


Fig. S16 Photocurrent curves and Nyquist plots of CeBiO_x and POMs/ CeBiO_x .

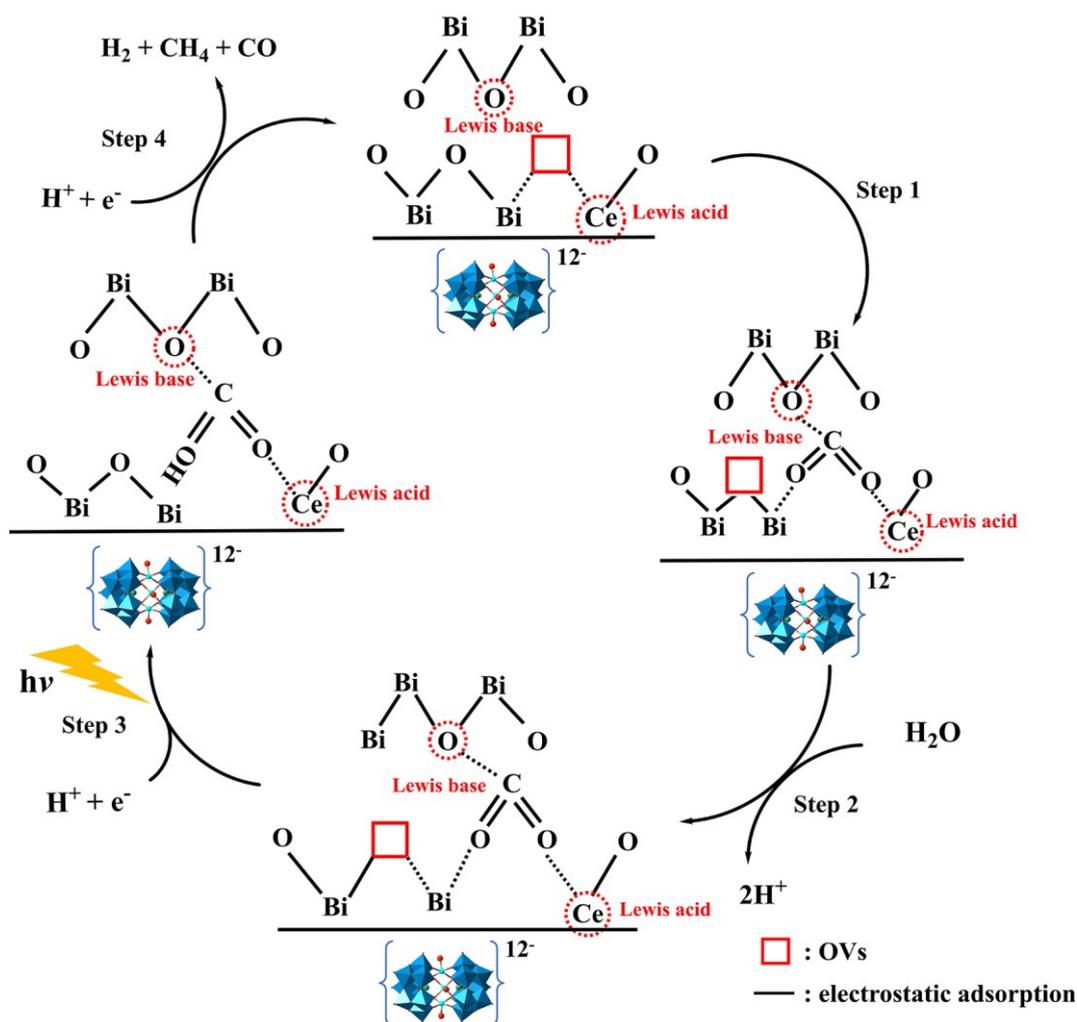


Fig. S17 Possible frustrated Lewis pairs and photocatalytic mechanism for 5% $\text{Cu}_3/\text{CeBiO}_x$.

Table S1 Zeta Potential of CeBiO_x and Cu₃ samples.

Sample	Zeta Potential (mV)	Mean (mV)
CeBiO _x	22.8	24.4
	21.8	
	28.5	
Cu ₃	-28.5	-29.2
	-25.4	
	-33.7	

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