

## Electronic Supplementary Information

Boosting the visible-light photoactivities of BiVO<sub>4</sub> nanoplates by doping Eu and coupling CeO<sub>x</sub> nanoparticles for CO<sub>2</sub> reduction and organic oxidation

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### **Characterization.**

The composition of the materials was determined by a Rigaku (Japan) D/MAX-rA X-ray diffraction meter (XRD) equipped with graphite monochromatized Cu K $\alpha$  radiation ( $\gamma = 1.541874\text{\AA}$ ). The size and morphology of the final products were investigated by scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JEOL, JEM-2100). UV-visible absorption spectroscopy was recorded using a UV-visible spectrophotometer (SHIMADZU UV-2550). X-ray Photoelectron Spectroscopy (XPS) analysis were carried out using a Kratos-AXIS ULTRA DLD apparatus with Al (Mono) X-ray source and the binding energies of the samples were calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV). The photoluminescence (PL) spectra were recorded with a Hitachi F-4600 fluorescence spectrophotometer at room temperature. The Raman spectra were measured by a HORIBA JOBIN YVON LabRam-HR 800 micro-Raman spectrometer. The laser beam was focused with a 50 $\times$  objective lens to a ca. 1  $\mu\text{m}$  spot on the surface of the sample.

### **Photoelectrochemical measurements.**

For the synthesis of thin film electrodes, conductive fluorine-doped tin oxide (FTO)-coated glasses were used as substrates. Prior to use, the FTO glasses were washed with deionized water under sonication for 30 min and then washed with ethanol followed by deionized water and finally annealed at 450  $^{\circ}\text{C}$  for 30 min. The corresponding pastes for the samples were prepared as follows: 0.1 g of the resulting sample powder was dispersed in 1 ml of isopropyl alcohol under vigorous stirring, and then 0.05 g of Macrofol-2000 were added to the mixture, followed by an

ultrasonic treatment for 10 min and then kept under vigorous stirring for 30 min. Finally, 0.15 mL of acetyl acetone was added to it, and the mixture was kept under continuous stirring for 7 days. The films were prepared by doctor blade method and Scotch tape was used as the spacer. After drying naturally, the film was annealed at 450 °C for 30 min and then cooled to room temperature. Finally, the film was cut into 1.0×1.5 cm<sup>2</sup> pieces. The working geometric surface area of the samples film was 1 cm×1 cm.

Photoelectrochemical (PEC) measurement for samples was performed in a quartz cell of 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution using a xenon light (500 W) with a stabilized current power supply as the illumination source. The as-prepared films were used as working electrodes illuminated with illumination area of about 1×1 cm<sup>2</sup>. Platinum wire (99.9%) was used as the counter electrode, and a saturated KCl Ag/AgCl electrode (SSE) was used as the reference electrode. All the potentials in this work were referred to SSE at 298 K and applied potentials were controlled by a commercial computer-controlled potentiostat (AUTOLAB PG STAT 101). High-purity N<sub>2</sub> gas was employed to bubble through the electrolyte before the experiments. For comparison, the related current was also measured in the dark. TPD studies were performed using a CHEMBET-3000 (Quantachrome, U.S.A.) instrument in the temperature range of 313-1073 K.

#### **Measurement of photocatalytic activity for the degradation of 2,4-dichlorophenol (2,4-DCP).**

The photocatalytic activities of XC/BVO-X photocatalysts under visible light was evaluated by degrading 10 mmol·L<sup>-1</sup> of 2,4-DCP. A 400 W Xe lamp with a visible light-cutoff filter ( $\lambda > 420$  nm) as a light source was set at about 10 cm apart from the reactor. About 40 mg of each

photocatalyst was dispersed in 40 mL of 2,4-DCP solution followed by stirring for half an hour in dark to achieve the adsorption desorption before light irradiation. During the irradiation, the reaction samples were collected and centrifuged after regular interval of 30 min to remove the photocatalyst particles. The ratios ( $C/C_0$ ) of the 2,4-DCP concentration were adopted to evaluate the degradation efficiency ( $C_0$  is the initial concentration and  $C$  is the concentration at a certain time) by checking the absorbance values at 270 nm using a UV-vis spectrophotometer.

The stability of the photocatalysts was examined using repeated photocatalytic cycles for 2,4-DCP degradation for 3 h. After each cycle, the solution was extracted to measure the concentration of 2,4-DCP whereas the reacted photocatalysts were collected and dried for the next cycle.

#### **Evaluation of photocatalytic activities for CO<sub>2</sub> reduction.**

In the photocatalytic reduction of CO<sub>2</sub>, for each experiment, 0.02 g of powder sample was dispersed in 4 ml water contained in a 100 mL volume of cylindrical steel reactor with an area of 3.5 cm<sup>2</sup>. A 300 W Xenon arc lamp was used as the light source with a cut off filter of 420 nm for the photocatalytic reaction. Highly pure CO<sub>2</sub> gas was passed from the water and followed into the reaction setup to reach an ambient pressure. The used photocatalyst was allowed to equilibrate in the CO<sub>2</sub>/H<sub>2</sub>O system for 1h. During the irradiation, about 0.5 mL of the produced gas was taken from the reaction cell at a given time interval for the concentration analysis of main products such as CO and CH<sub>4</sub> using a gas chromatograph (GC-2002 with TCD detector; Ke Chuang, China).

#### **Hydroxyl radical measurement.**

Hydroxyl radical measurement was carried out in 0.001 M coumarin aqueous solution in a quartz reactor of 40 mL containing 0.05 g of sample powder. Prior to irradiation, the reactor was magnetically stirred for 10 min to attain an adsorption-desorption equilibrium. After irradiation for 1 h with a 300 W PLS-SXE300 Xenon lamp (made in China), the sample was centrifuged and a certain volume of solution was transferred into a Pyrex glass cell for the fluorescence measurement of 7-hydroxycoumarin at 390 nm excitation and 446 nm emission wavelength through a Hitachi F-4500 fluorescence spectrophotometer.

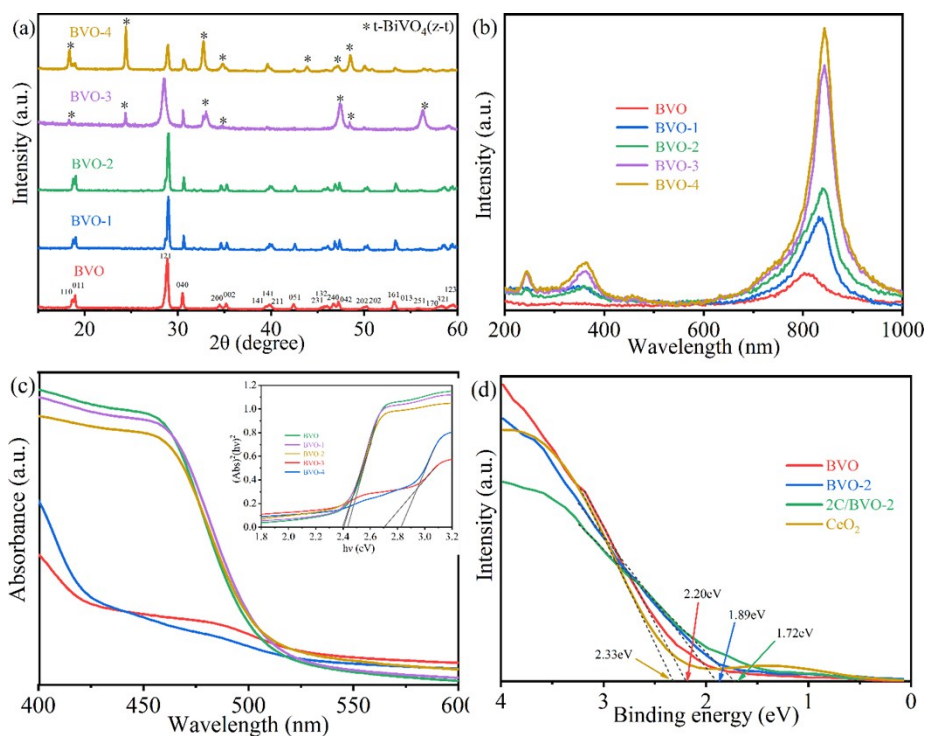
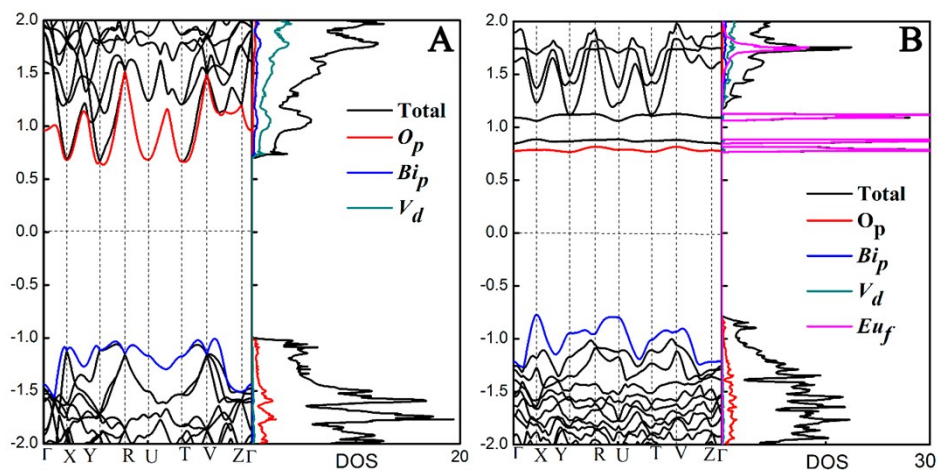


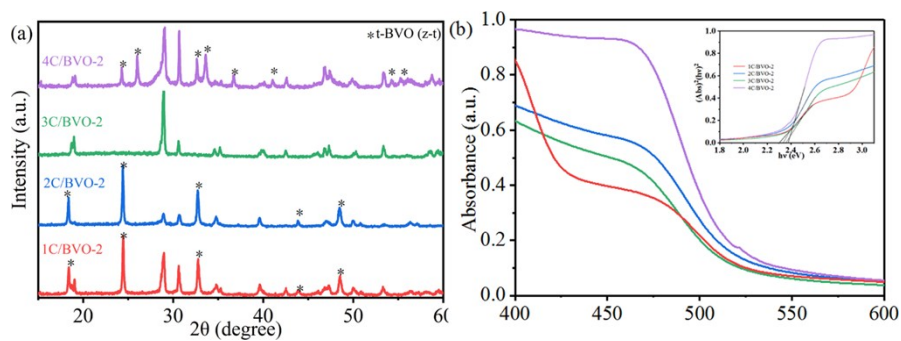
Figure S1 XRD patterns (a), Raman spectrum (b), UV-Vis DRS spectra (c) and valence band XPS spectra (d) of BVO and BVO-X samples.

**Table 1** Band gap energy of the pure BVO and BVO-X samples.

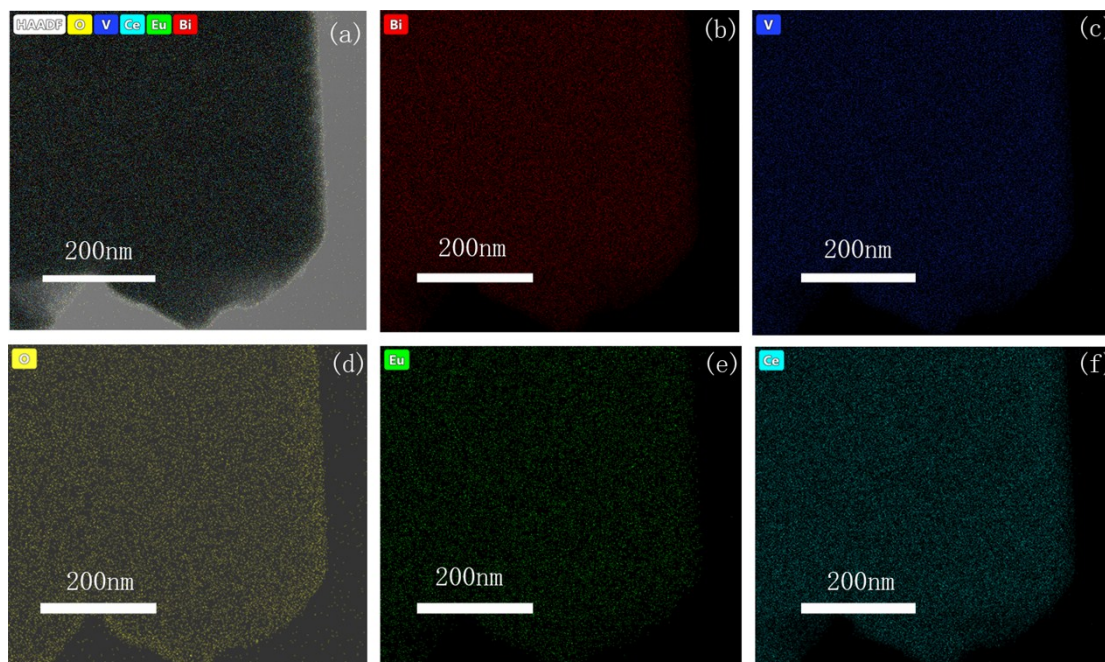
Sample	BVO	BVO-1	BVO-2	BVO-3	BVO-4
$E_g$ (eV)	2.42	2.41	2.39	2.70	2.82



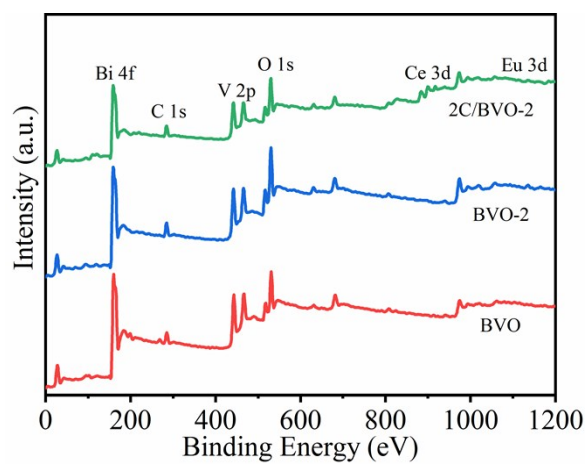
**Figure S2** Density of states of BVO (a) and BVO-2 (b).



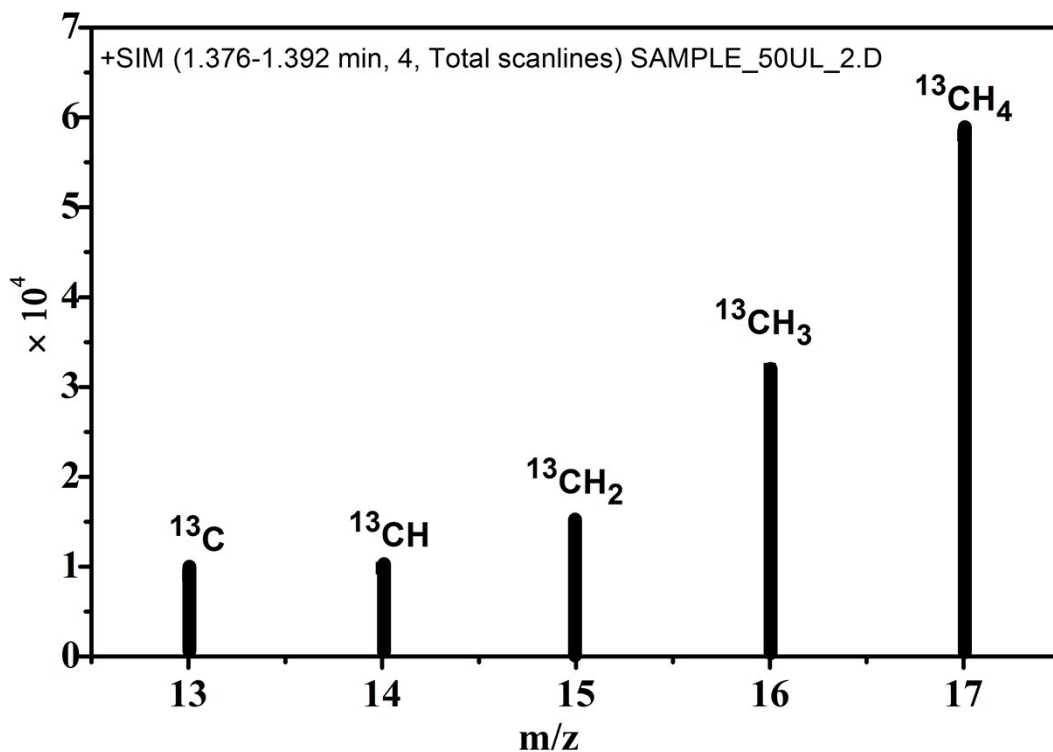
**Figure S3** XRD patterns (a) and UV-Vis DRS spectra (b) of XC/BVO-2. The inset displays the plot of the transformed Kubelka-Munk function versus energy of light.



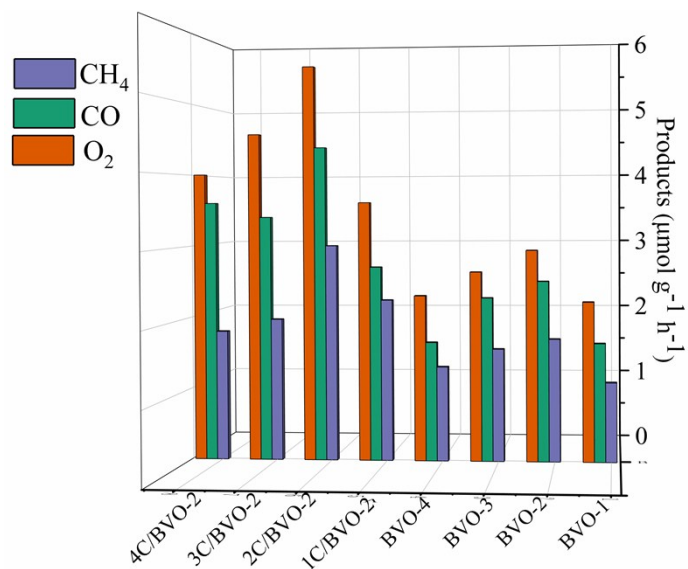
**Figure S4** HRTEM-EDX elemental mapping for 2C/BVO-2 sample.



**Figure S5** XPS survey spectra of BVO, BVO-2 and 2C/BVO-2 samples.



**Figure S6** The ion fragments of the products from the isotopic experiment using  $^{13}\text{CO}_2$  under the identical photocatalytic reaction condition.

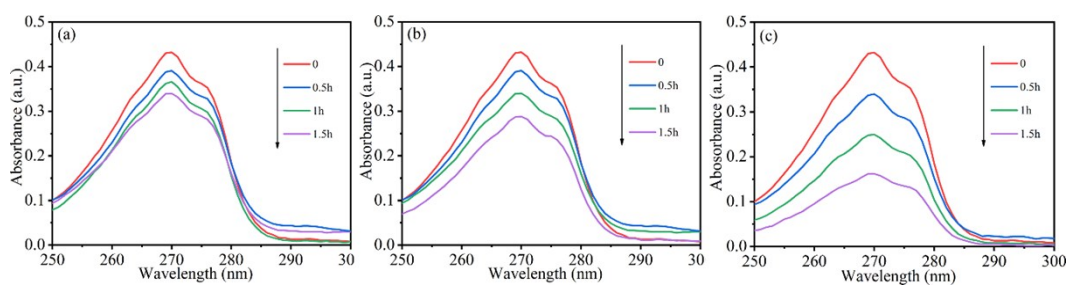


**Figure S7** The production rates of  $\text{CH}_4$  and  $\text{CO}$  during the photocatalytic  $\text{CO}_2$  reduction with  $\text{H}_2\text{O}$  on BVO-X and XC-BVO-2.

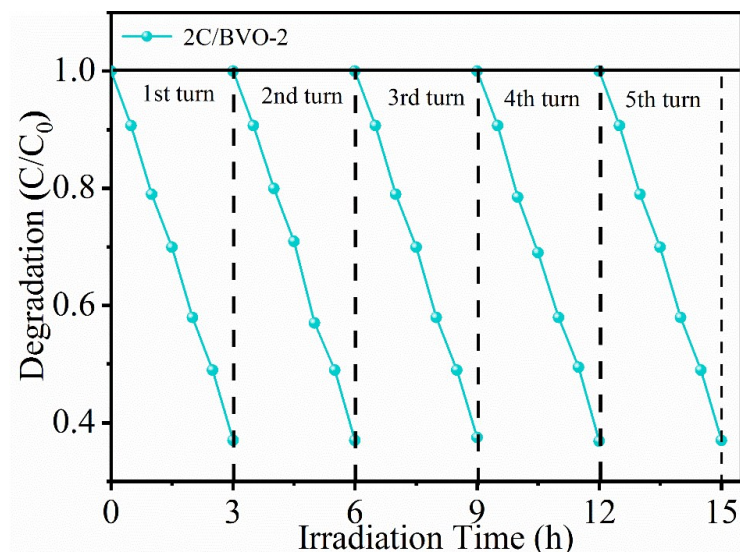


**Table S2** The production rates of CH<sub>4</sub> and CO during the photocatalytic CO<sub>2</sub> reduction with H<sub>2</sub>O on BVO-X and XC-BVO-2.

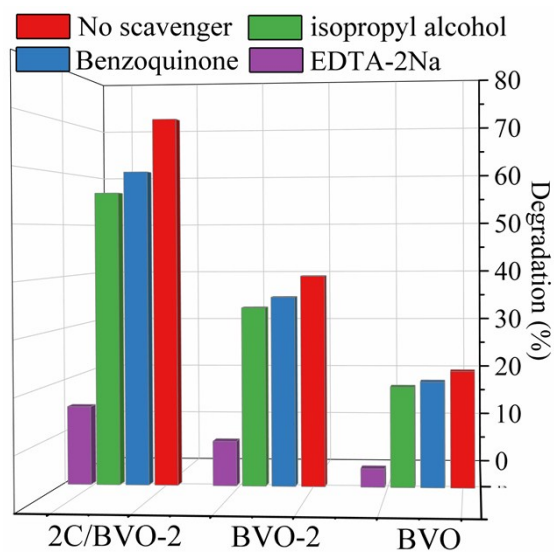
Photocatalytic	CH <sub>4</sub> / μmol.g <sup>-1</sup> .h <sup>-1</sup>	CO/ μmol.g <sup>-1</sup> .h <sup>-1</sup>	O <sub>2</sub> / μmol.g <sup>-1</sup> .h <sup>-1</sup>
BVO-1	1.1	1.64	2.21
BVO-2	1.7	2.5	2.93
BVO-3	1.55	2.27	2.63
BVO-4	1.31	1.65	2.3
1C-BVO-2	2.24	2.7	3.6
2C-BVO-2	3	4.37	5.5
3C-BVO-2	1.97	3.4	4.56
4C-BVO-2	1.8	3.6	4



**Figure S8** Time-dependent UV-vis absorption spectra of 2,4-DCP in the presence of various photocatalysts: BVO (a), BVO-2 (b), and 2C/BVO-2 (c).



**Figure S9** Stability and recyclability test for photocatalytic degradation of 2,4-DCP over 2C/BVO-2 sample.



**Figure S10** Photocatalytic degradation rates for 2,4-DCP in the presence of different scavengers under visible-light irradiation for 90 min on BVO, BVO-2 and 2C/BVO-2.