

# Supporting Information

## Dependence of the intrinsic phase structure of $\text{Bi}_2\text{O}_3$ catalysts on photocatalytic $\text{CO}_2$ reduction†

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## Experimental section

### Chemical reagents

Bismuth (III) nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ), sodium hydroxide ( $\text{NaOH}$ ), sodium borohydride ( $\text{NaBH}_4$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), citric acid, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), glacial acetic acid ( $\text{HAc}$ ) and nitric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water (18.25 M $\Omega$ , Molecular) was used for all instrument cleaning and solution preparation. All chemicals were used as receiving without any further purification.

### Preparation of different crystal phase of $\text{Bi}_2\text{O}_3$ photocatalysts

The different crystal phase of  $\text{Bi}_2\text{O}_3$  ( $\alpha$ -/ $\beta$ -/ $\gamma$ - $\text{Bi}_2\text{O}_3$ ) photocatalysts were synthesized according to previous reported with some modifications.<sup>1,2</sup> For the preparation of  $\alpha$ - $\text{Bi}_2\text{O}_3$  and  $\beta$ - $\text{Bi}_2\text{O}_3$ , 2 mmol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was dissolved in 10 ml  $\text{HNO}_3$  (1 mol L<sup>-1</sup>) aqueous solution, and then add 1.5 mmol citric acid to the above solution. After the mixed suspension was magnetically stirred for 10 min, the pH value of the solution was adjusted to 4 with a 2 mol L<sup>-1</sup>  $\text{NaOH}$  solution under stirring. The obtained white suspension was transferred to a Teflon-lined stainless-steel autoclave and kept at 180 °C for 24 h. After the reaction, it was cooled to room temperature, collected and washed repeatedly with deionized water and absolute ethanol, and collected by centrifugation. Drying in an oven at 70 °C overnight to obtain  $\text{Bi}_2\text{O}_2\text{CO}_3$  precursor. Furthermore, the dried  $\text{Bi}_2\text{O}_2\text{CO}_3$  precursor is ground, and then placed in the air for heat treatment at 500 °C or 360 °C for 3 h to obtain  $\alpha$ - $\text{Bi}_2\text{O}_3$  and  $\beta$ - $\text{Bi}_2\text{O}_3$  nanomaterials, respectively. To obtain  $\gamma$ - $\text{Bi}_2\text{O}_3$ , 1.5 mmol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was dissolved in 40 ml  $\text{HNO}_3$  (1 mol L<sup>-1</sup>) aqueous solution, then add 20 ml ethylene glycol solution and stir vigorously for 20 min to obtain a clear solution system. Then heat the mixed solution to 80 °C, then quickly pour 60 ml  $\text{NaOH}$  (1.5 mol L<sup>-1</sup>) solution into the above solution and keep it at 80 °C for 120 min, collect and wash the reaction product to remove the surface organic matter, and finally put it in an oven at 70 °C to obtain  $\gamma$ -  $\text{Bi}_2\text{O}_3$  powder with hexahedron structure.

### Characterization

Scanning electron microscopy measurements were carried out on a field-emission scanning electron microscope (SEM, JSM-6701F, JEOL) operated at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) measurements were performed by using a FEI TecnaiTF 20 microscope operated at 200 kV. The crystalline structures were identified by X-ray diffraction analysis (XRD,

Smartlab-SE) using Cu K $\alpha$  radiation at 50 kV and 50 mA. UV-visible diffuse reflectance spectra were performed on a UV-2550 (Shimadzu) spectrometer by using BaSO<sub>4</sub> as the reference and Raman spectra were carried out on LabRAM HR Evolution from French HORIBA Jobin Yvon S.A.S. The elemental composition and chemical valence states were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). Transient absorption spectra (TA) and TA kinetics were obtained with an Edinburgh LP 980 spectrophotometer. CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) was carried out on a ChemBET Pulsar TPR/TPD analyzer (Quantachrome Instruments U.S.) which coupled with a thermal conductivity detector. The <sup>13</sup>C-labeled isotope tracer experiment was performed and the products were analyzed using gas chromatography-mass spectrometry (7890A and 5975C, Agilent).

### **Photocatalytic CO<sub>2</sub> reduction experiment**

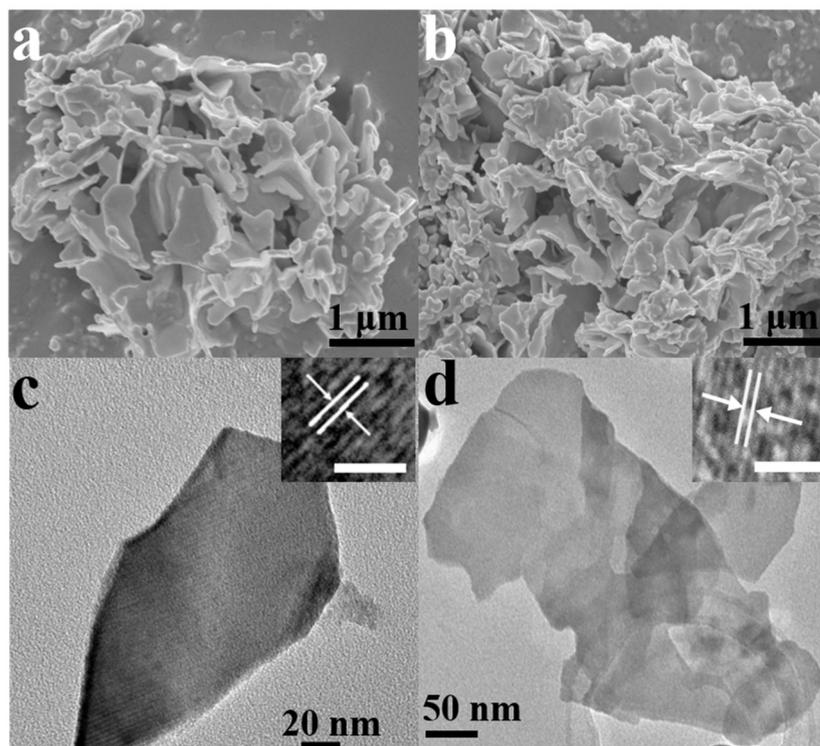
The experiments of CO<sub>2</sub> photoreduction with CO<sub>2</sub>/H<sub>2</sub>O solution on as-prepared Bi<sub>2</sub>O<sub>3</sub> samples were carried out in a closed evacuated system. Specifically, 5 mg of synthetic photocatalyst was ultrasonically dispersed in 2 ml deionized water, then the suspension was dispersed on a glass fiber membrane and dried. Suspend the glass fiber membrane in a 120 ml quartz glass reactor, and add 20 ml deionized water at the bottom of the reactor. Then the reactor was sealed and the air was removed by a water pump. After that the reactor was further purified with a high purity CO<sub>2</sub> flow through bubbling under continuous stirring for 15 min, and finally the reactor pressure was maintained at 0.02 MPa. Next, the reactor was fixed on a temperature-controllable continuous flow system to eliminate the influence of external ambient temperature. Simulated sunlight source from a 300W Xenon lamp cast from the top of the reactor. And the gaseous products were quantitatively and qualitatively monitored at fifteen-minute intervals by a gas chromatography on a basis of the standard curve. At the same time, the blank experiments without photocatalysts, and no light irradiation were carried out under the same conditions to confirm whether the carbon-based products were from the CO<sub>2</sub>. An isotope labeling experiment that using <sup>13</sup>CO<sub>2</sub> as a reactant was also performed to further check the carbon source of the products. And the products were verified by gas chromatography-mass spectrometry (GC-MS).

### **Photoelectrochemical measurements**

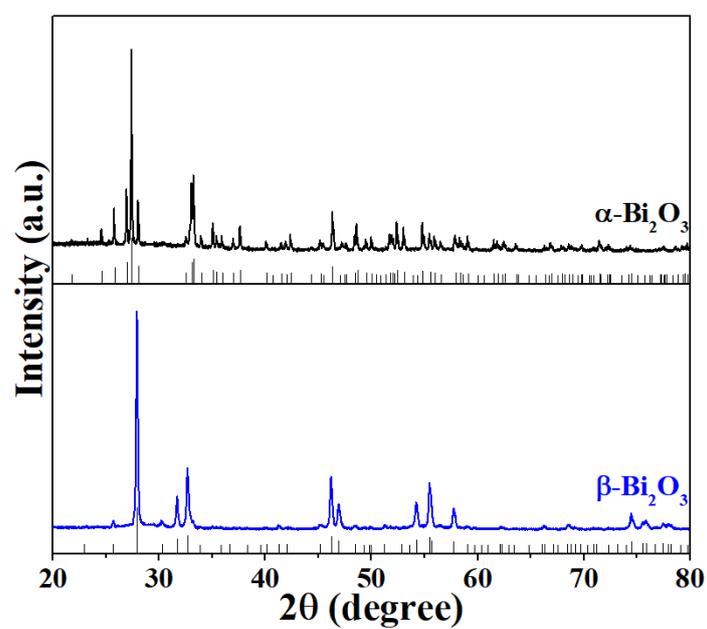
All the photoelectrochemical measurements were performed by a three-electrode cell with platinum foil (1.0 × 1.0 cm<sup>2</sup>) as a counter electrode, saturated potassium-chloride silver chloride electrode

(Ag/AgCl) as reference electrode, and the as-prepared sample as working electrode. The electrolyte was  $0.2 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ . A 300 W Xenon lamp was used to simulate light. Working electrodes were prepared as follows: 3 mg of the as-prepared catalysts and 20  $\mu\text{L}$  of Nafion solution (5 wt%) were dispersed in a 1 mL mixed solvent, which contains isopropanol and water (1:3 v/v) by sonication to form a homogeneous catalyst colloid. Then, 50  $\mu\text{L}$  of the catalyst colloid was spread on the pretreated FTO ( $1.0 \times 1.0 \text{ cm}^2$ ), and dried in air at room temperature to form photocatalysts modified FTO. Electrochemical impedance spectroscopy (EIS) and photocurrent measurements were determined at an AC voltage magnitude of 0.05 V with the frequency range of  $10^3$ -10 Hz.

## Additional Figures and Discussions



**Fig. S1** SEM and HR-TEM images of  $\alpha$ - $\text{Bi}_2\text{O}_3$  (a, c),  $\beta$ - $\text{Bi}_2\text{O}_3$  (b, d), respectively. (inset image: bar: 2 nm)



**Fig. S2** XRD pattern of as-prepared  $\alpha$ - $\text{Bi}_2\text{O}_3$ (a),  $\beta$ - $\text{Bi}_2\text{O}_3$ (b), respectively.

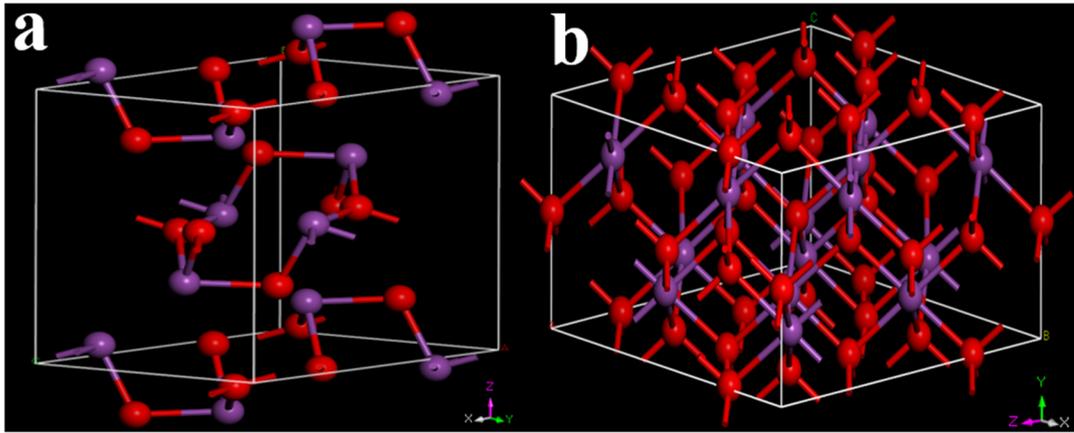


Fig. S3 The corresponding unit cell structure of  $\alpha$ - $\text{Bi}_2\text{O}_3$  (a),  $\beta$ - $\text{Bi}_2\text{O}_3$  (b), respectively.

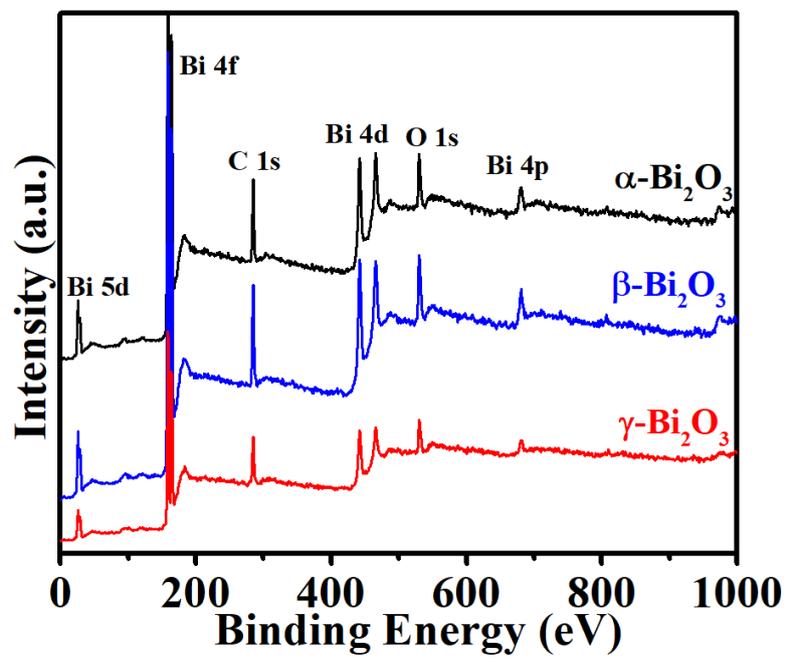


Fig S4. XPS spectra of as-prepared samples.

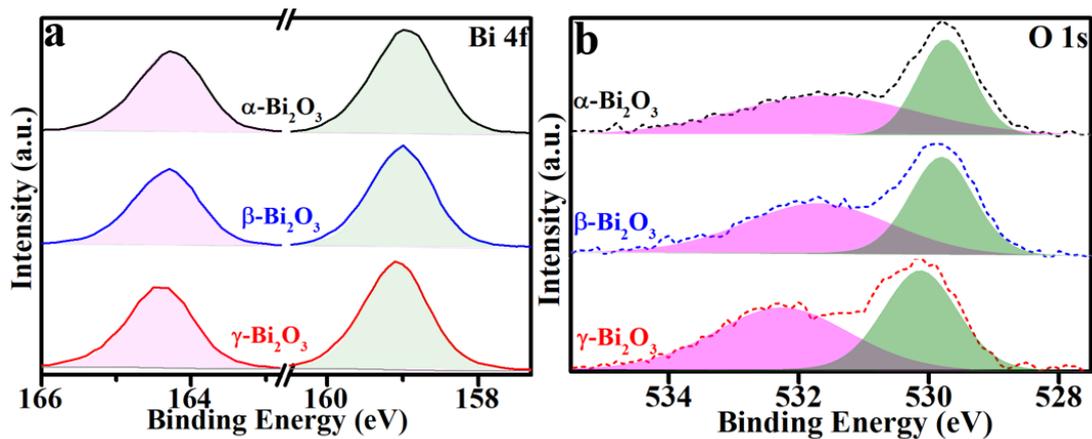


Fig. S5 XPS spectra of Bi 4f and O 1s in the as-prepared samples, respectively.

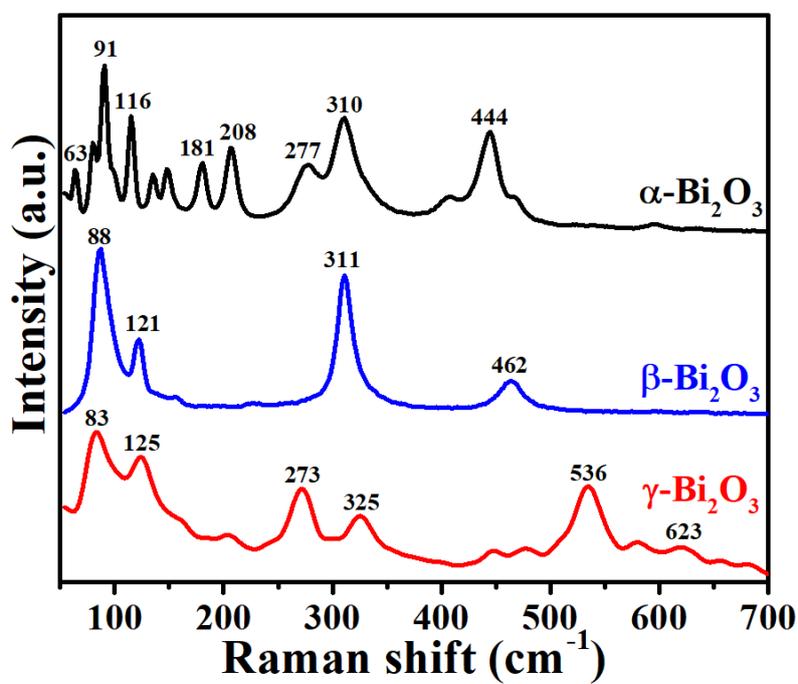


Fig. S6 Raman spectra of as-prepared samples.

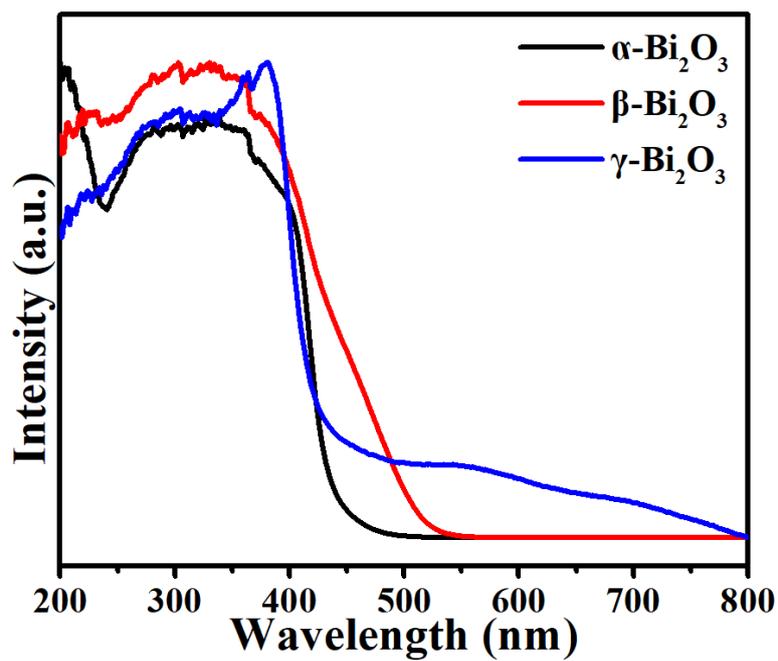


Fig.S7 UV-Vis DRS spectra of as-prepared samples.

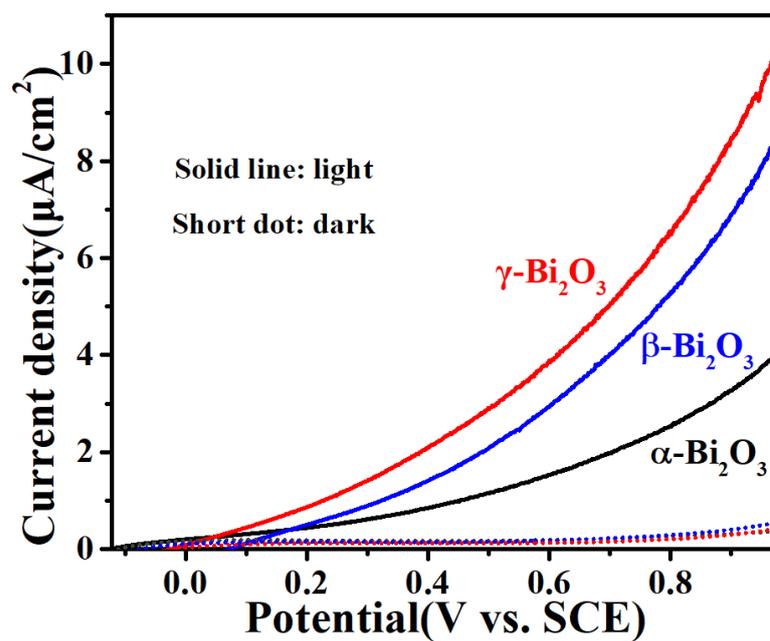


Fig. S8 Linear-sweep voltammograms curves of as-prepared Bi<sub>2</sub>O<sub>3</sub> photoanodes.

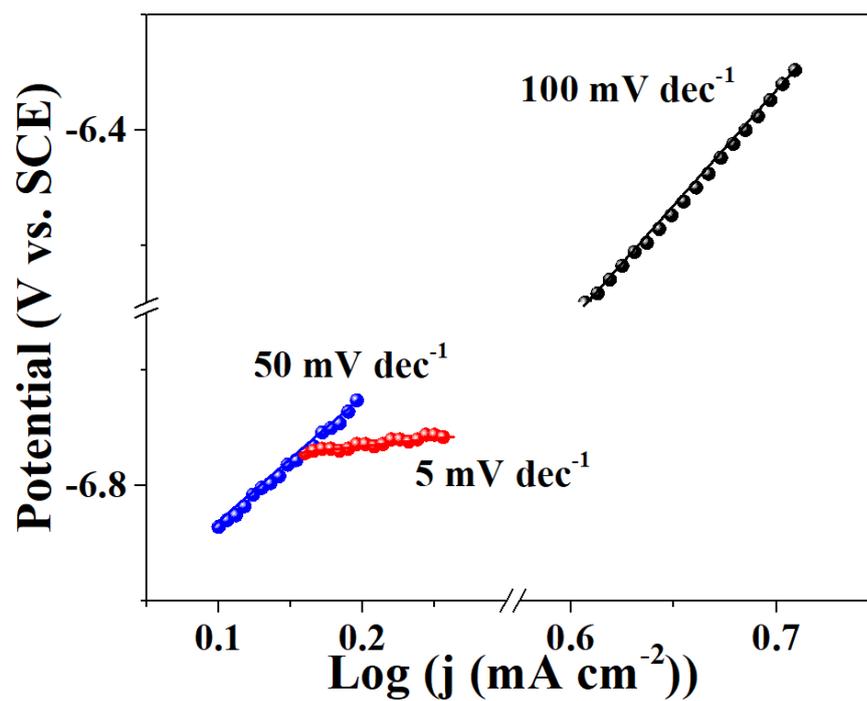


Fig. S9 Tafel plots of as-prepared Bi<sub>2</sub>O<sub>3</sub> samples.

## References

1. G. Zhu, W. Que and J. Zhang, *J. Alloy. Compd.*, 2011, 509, 9479-9486.
2. Y. Wang, Z. Li, H. Yu and L. Guo, *Mat.Sci. Semi. Proc.*, 2017, 64, 55-62.