Electronic Supplementary Information

Controllable synthesis of conical BiVO₄ for photocatalytic water oxidation

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Experimental Section

Preparation of BiVO₄ crystals with six different morphologies. The monoclinic BiVO₄ crystals with a conical morphology were obtained by a two phase method using oleic acid (OA), oleylamine (OLA) and 1-octadecene (1-ODE) as the oil phase and aqueous nitric acid as the liquid phase. First, in a three-neck flask, a solution containing Bi(NO₃)₃·5H₂O (1.25 mmol), OA (2.5 mL), OLA (2.5 mL) and ODE (25 mL) was sonicated until it became a white suspension. Then the flask was heated to 170 °C under the N₂ atmosphere and maintained this temperature for different minutes (20, 30, 40, 60 and 120 min). Subsequently, NH₄VO₃ (2.5 mmol) was dissolved in a mixture of HNO₃ (5 mL) and H₂O (25 mL) to form a transparent yellow solution. And then, the above solution was injected into the above flask containing $Bi(NO_3)_3 \cdot 5H_2O$ when the temperature was decreased to 60 °C. Then the temperature was raised to 100 °C and kept for different minutes (40, 60, 90, and 120 min) under the N₂ atmosphere. The reaction solution was naturally cooled to room temperature. After the addition of n-hexane and ethanol, the solution was stratified. Afterward, the upper organic solution was taken out and centrifuged. The obtained solid products were collected by centrifugation, washed several times with n-hexane and ethanol, and then dispersed in n-hexane for further characterization.

Preparation of decahedron BiVO₄ (D-BiVO₄). The D-BiVO₄ was synthesized by the aqueous process. A mixture of K_2CO_3 and V_2O_3 was calcined in air at 450 °C for 5 h to form layered $K_3V_5O_{14}$. Bi(NO₃)₃·5H₂O reacted with distilled water to form slightly soluble BiONO₃. A suspension of $K_3V_5O_{14}$ powder and BiONO₃ solution was stirred mildly at room temperature for 3 days. The resulting BiVO₄ was collected by filtration and washed with distilled water, and then dried overnight in vacuum at 60 °C.

Preparation of sheet-like BiVO₄ (S-BiVO₄). BiVO₄ samples were synthesized by the addition of an appropriate amount of TiCl₃ (directing agent, Ti/Bi=1.2 at.%) to a solution of NH₄VO₃ (6.0 mM) and Bi(NO₃)₃·5H₂O (6.0 mM) in nitric acid (30 mL, 2.0 M) at room temperature. The pH value of the reaction mixture was adjusted to 2 with ammonia solution (25-28 wt.%) under vigorous stirring. After stirring for 0.5 h at room temperature, 1.5 g of organic citric acid (CA) was added to the reaction mixture, and then transferred into a Teflon-lined stainless steel autoclave and aged at 180 °C

for 18 h. Centrifugation and washing with plenty of water afforded vivid yellow powder, which was then dried at 80 °C.

Characterization of photocatalysts. The crystal structure of the as-prepared samples was characterized by X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer with Cu Ka radiation). The morphologies and structures were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S4800), transmission electron microscopy (TEM, JEM 2100, 200 kV) and a high-resolution transmission electron microscope (HRTEM, JEM 3010, 300 kV). Ultraviolet-visible (UV-vis) diffuse reflectance spectra were measured by using a UV-vis spectrophotometer (CARY 500). To test the recombination of photoinduced electron-hole pairs, PL spectra were obtained by an Edinburgh Instruments (FLSP 920) system operated at room temperature with an excitation wavelength of 350 nm. The surface elements content and valence were studied by X-ray photoelectron spectroscopy (XPS) measurements (ESCALAB 250Xi). The XPS spectrum was calibrated with respect to the binding energy of the adventitious C1s peak at 284.6 eV. X-ray absorption fine structure spectroscopy (XAFS) measurement and data analysis: XAFS spectra at the Bi L₃-edge and V K-edge were performed on the 1W1B beamline station of the Beijing Synchrotron Radiation Facility (BSRF), China. All the XAFS data were recorded in a fluorescence mode. The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages.¹ The valence band energy was investigated by ultraviolet photoelectron spectroscopy (UPS, ESCALAB 250Xi). Fourier transform infrared spectroscopy (FTIR) was carried out using a Jasco FTIR-4100 (Japan) spectrometer. The contents of elements Bi and V in the sample were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent 725). Brunauer-Emmett-Teller (BET) surface area measurement was performed at 180 °C on a Micromeritics ASAS 2460 adsorption analyzer in N₂-adsorption mode.

Photocatalytic tests. The photocatalytic O_2 -evolution reaction operated to estimate the activity of the photocatalyst was carried out in a glass gas-closed circulation system (CEL-SPH2N, CEAULight, China) under irradiation with a 300-W xenon lamp (CEL-HXBF 300). Typically, 35 mg photocatalyst was dispersed in 50 mL of aqueous solution containing AgNO₃ (0.025 M) as electron scavenger. The reactant solution was dispersed by mechanical stirring and maintained at 10 °C by the flow of cooling water during the test. After evacuation by vacuum pump, air could be hardly detected in the system. The amount of O_2 was determined by an online gas chromatograph (GC 2060, TCD detector and Ar carrier) and monitored every 30 min in order to determine the O_2 evolution rate.

Preparation of electrochemical working electrodes. 2 mg of catalyst powders was dispersed into 40 μ L of a mixture with a volume ratio of V_{water}/V_{isopropanol}=4:1 and 20 μ L of 5 wt% Nafion solution. After ultrasonication for 0.5 h, 5 μ L of the dispersion was deposited onto the glassy carbon electrode. Finally, the as-prepared catalyst electrode was dried in air at room temperature.

Electrochemical measurements. Electrochemical measurements were performed using an electrochemical station (CHI 660E) in a three-electrode electrochemical cell with a Pt mesh counter electrode (1×2 cm) and saturated Ag/AgCl reference electrode in 1.0 M phosphate buffer solution (PBS, pH=7, 145 mL) electrolyte. All potentials measured were calibrated to the reversible hydrogen electrode (RHE) using the following equation: $E_{RHE}=E_{Ag/AgCl}+0.059\times pH+0.205$. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 10⁵ to 0.1 Hz with a sinusoidal voltage amplitude of 5 mV. The ECSA was estimated from the electrochemical double-layer capacitance (C_{dl}).²⁻⁴ First, a series of cyclic voltammetry (CV) curves were measured at different scan rates (40, 80, 120, 160 and 200 mV s⁻¹) in a non-Faradaic region (-0.5 to 0.6 V *vs.* RHE).

Concentration of Bi ions test. The concentration of Bi ions dissolved in the oil phase was tested by ICP-atomic emission spectroscopy (Agilent 725 ICP-OES). Typically, the sampling was taken with an equal amount of oil phase solution containing $Bi(NO_3)_3 \cdot 5H_2O$ (1 mL) heated at 170 °C for 10 minutes, 40 minutes, and 120 minutes. Since $Bi(NO_3)_3 \cdot 5H_2O$ was insoluble in water, we thoroughly mixed the above oil phase solution with a certain amount of deionized water (l00 mL) for the same time and then centrifuged. We had taken an equal amount of clear aqueous solution to test ICP in order to determine the concentration of dissolved Bi^{3+} at different $Bi(NO_3)_3 \cdot 5H_2O$ dissolution time.



Fig. S1 The height and diameter distribution of C-BiVO₄ crystals.



Fig. S2 FE-SEM images and corresponding EDS elemental mapping of BiVO₄ with different morphologies (red: Bi, green: O, blue: V). (a) NS-BiVO₄; (b) NS-C-BiVO₄; (c) NP-C-BiVO₄; (d) C-BiVO₄; (e) SC-BiVO₄; (f) IR-BiVO₄.

Table S1. Dissolved Bi³⁺ concentration of oil phase in different dissolution conditions determined by ICP analysis.

Dissolution Conditions	170 °C, 10 min	170 °C, 40 min	170 °C, 120 min
Bi (mg/L)	0.45	1.2	2.9

Notes: The results confirmed that as the increase of dissolution time, the dissolved amount of Bi^{3+} showed an upward trend, and the difference in Bi^{3+} concentration would lead to morphology changes from nanosheets to conical and then irregular bulk. This value might not the real difference of Bi^{3+} dissolved concentration in oil phase that could lead to morphology changes, since the time of water extraction would significantly affect the actual Bi^{3+} concentration that dissolved in water.



Fig. S3 XRD patterns of the as-synthesized BiVO₄ crystals with different morphologies. Curves 1–6 correspond to NS-BiVO₄, NS-C-BiVO₄, NP-C-BiVO₄, C-BiVO₄, SC-BiVO₄, IR-BiVO₄, respectively.



Fig. S4 Crystal structures of the BiVO₄ samples synthesized with different $Bi(NO_3)_3 \cdot 5H_2O$ dissolution time. (a) Expanded XRD patterns showing the hyperfine structures of the (-121) and (040) diffraction peaks. (b) The correlations of the $Bi(NO_3)_3 \cdot 5H_2O$ dissolution time with the intensity ratios of (040)/(110) in the XRD patterns of the corresponding $BiVO_4$ samples, and the intensity was normalized using the (110) diffraction peak as an internal standard.

Notes: The normalization of the XRD intensity for comparison was performed using the (110) peak as the internal standard. Fig. S4a and b showed the correlations of the intensity ratios of (040)/(110) for the BiVO₄ samples synthesized with different Bi precursor dissolution time. It was worth noting that the corresponding nanosheets (NS-BiVO₄) of black curve featured with the highest exposed (040) crystal facet. Since the appearance of the conical structure, the BiVO₄ crystals mainly grew toward the (-121) facet instead of the (040) facet. Thus, the intensity of (040) began to decrease and was minimized as the nanosheets disappeared, and then increased slightly with the aggregation of the cones.

Table S2. Surface energy of (040), (110) and (-121) facet of monoclinic BiVO₄.

Facet	(040)	(110)	(-121)
Surface energy (J/m ²)	0.6112	0.6853	0.7064



Fig. S5 Schematic representation of atomic structures of (a) (040), (b) (110) and (-121) facet of monoclinic $BiVO_4$.



Fig. S6 Bi L₃-edge (a) XANES, (b) FT-EXAFS and V K-edge (c) XANES and (d) FT-EXAFS profiles of C-BiVO₄, NS-BiVO₄ and IR-BiVO₄.



Fig. S7 Optical properties of the $BiVO_4$ samples synthesized with different $Bi(NO_3)_3 \cdot 5H_2O$ dissolution time. (a) UV-vis spectra and (b) the corresponding Tauc plots.

Notes: The UV-vis spectra and the corresponding Tauc plots of $BiVO_4$ samples proved the similar tendency with the XRD intensities. Compared with other morphological $BiVO_4$, C- $BiVO_4$ exhibited an additional expanded visible light absorption region, and thus led to a narrower band gap. These results revealed that the method was very effective and favorable for the controlled synthesis of $BiVO_4$ crystals with different facets. Furthermore, all these results confirmed that a comprehensive understanding of the band gap structure of semiconductors was highly desirable to reveal the effects of morphology controlling.



Fig. S8 (a) PL spectra of D-BiVO₄ and C-BiVO₄. (b) EIS for D-BiVO₄ and C-BiVO₄ measured at phosphate buffer solution.

Name	Bi (mg/L)	V (mg/L)	n(Bi):n(V)
C-BiVO ₄	330	74	1:0.92

Table S3. Composition of C-BiVO₄ determined by ICP-OES.



Fig. S9 XPS spectra of C-BiVO₄ for (a) survey, (b) Bi 4f, (c) V 2p and (d) O 1s, respectively.



Fig. S10 FTIR spectra of (a) C-BiVO₄ has (red line) and has not (black line) been completely washed by ethanol and n-hexane; (b) as-synthesized $BiVO_4$ with different morphologies completely washed by ethanol and n-hexane.

Notes: The absorption peaks at 830, 731 and 610 cm⁻¹ was attributed to the antisymmetric stretching and symmetric stretching mode of V-O-V units of monoclinic BiVO₄.⁵ Only broad peaks of about 3400 and 1627 cm⁻¹ were due to the stretching vibration and bending vibration of adsorbed H₂O molecules.⁶ There was no extra peak belonging to organic ligands (OA or OLA). In contrast, peaks belonging to the stretching vibration and bending vibration of NH₂ (1690 cm⁻¹), and the asymmetric stretching vibration, symmetric stretching vibration and bending vibration of CH₂ (2930, 2860, and 1465 cm⁻¹) could be found in black line obviously.⁷ Therefore, it could be concluded that ethanol and n-hexane can thoroughly clean OLA and OA on the surface of BiVO₄.



Fig. S11 Photocatalytic activity of BiVO₄ crystals synthesized with 10, 20, 30, 40, 60 and 120 min of Bi(NO₃)₃·5H₂O dissolution time from aqueous AgNO₃ solutions (0.025 M, 50 mL) under illumination (λ >400 nm).

Table S4. BET surface area values of D-BiVO₄ and C-BiVO₄.

Samples	D-BiVO ₄	C-BiVO ₄
Surface area (m ² g ⁻¹)	2.8817	0.8911



Fig. S12 Nitrogen adsorption-desorption isotherm curves for (a) D-BiVO₄ and (b) C-BiVO₄.



Fig. S13 Linear fitting of Δ (current density) *versus* scan rates of D-BiVO₄ and C-BiVO₄ at 0.05 V vs. Ag/AgCl.

Notes: Δ (current density) was plotted against corresponding scan rates for both D-BiVO₄ and C-BiVO₄ and half of the slope of the linear fitted plots was taken as the double layer capacitance (C_{dl}). The ECSA values were usually accepted as proportional to the corresponding C_{dl} values. Here, the obtained C_{dl} values for D-BiVO₄ and C-BiVO₄ electrodes were 18.55 μ F cm⁻² and 12.875 μ F cm⁻².



Fig. S14 (a) XRD patterns, (b) UV-vis spectra, (c) Tauc plots and (d) photocatalytic activity of C-BiVO₄ and S-BiVO₄. Photocatalytic reaction conditions: 50 mg sample dissolved into 50 mL AgNO₃ solutions (0.025 M) and reacted under λ >400 nm illumination.

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