Supplementary Material

Three-dimensionorderedmacroporousbismuthvanadates:PMMA-templatingfabricationandexcellentvisible-light-drivenphotocatalytic performance for phenol degradation

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Catalyst characterization procedures:

X-ray diffraction (XRD) patterns of the as-fabricated BiVO₄ catalysts were recorded on a Bruker/AXS D8 Advance X-ray diffractometer operated at 40 kV and 35 mA with a Cu $K\alpha$ X-ray irradiation source ($\lambda = 0.15406$ nm). Laser Raman spectra of the BiVO₄ catalysts were measured on a Bruker RFS/100 Raman spectrometer equipped with a Nd:YAG laser (1064 nm) and an InGaAs detector; the laser power was 100 mW. The powdered catalyst was placed in a sample holder, and the spectrum of each sample was recorded from 200 to 1000 cm^{-1} with a resolution of 4 cm^{-1} in ambient atmosphere. Fourier transform infrared (FT-IR) spectra of the catalysts (1 wt% sample + 99 wt% KBr) were obtained in the 400-4000 cm⁻¹ range with a resolution of 0.4 cm⁻¹ on a Bruker Vertex 70 spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis were conducted on a SDT Q600 (TA) apparatus in an air flow of 100 mL/min from room temperature to 700 °C (heating rate: 10 °C/min). Surface areas of the catalysts were determined via N₂ adsorption at -196 °C on a Micromeritics ASAP 2020 adsorption analyzer. Before measurement, each of the catalysts was degassed at 250 °C for 3 h. The surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. The investigation by means of scanning electron microscope (SEM) was conducted on a Gemini Zeiss Supra 55 apparatus operated at 10 kV. Transmission electron microscopic (TEM) and high-resolution TEM images of the typical samples were obtained using a JEOL JEM-2010 instrument. The X-ray photoelectron spectroscopy (XPS) was used to determine the Bi 4f, V 2p, and O 1s binding energies (BEs) of surface bismuth, vanadium, and oxygen species, respectively, with Mg K α (hv = 1253.6 eV) as the excitation source. Before XPS measurement, the catalyst was pretreated in an O₂ flow

of 20 mL/min at 450 °C for 1 h. After being cooled to room temperature, the pretreated catalyst was transferred to a holder in a Glove Bag (Instruments for Research and Industry, USA) that was filled with helium, and then the holder was transferred into the spectrometer chamber under helium. Before being analyzed in the analysis chamber, the pretreated catalyst was degassed in the preparation chamber for 0.5 h. The C 1s signal at BE = 284.6 eV was taken as a reference for BE calibration. The ultraviolet-visible (UV-Vis) diffuse reflectance spectra of the catalysts in the range of 200–800 nm were measured on a Shimadzu UV-2450 UV-Vis spectrophotometer using BaSO₄ as standard.



Fig. S1. Laser Raman spectra of (a) BiVO₄-AA-1, (b) BiVO₄-AA-2, (c) BiVO₄-CA-1, and (d) BiVO₄-CA-2.

Laser Raman results:

Fig. S1 illustrates the laser Raman spectra of the four BiVO₄ samples obtained under different conditions. It is observed that there are six Raman bands at 210, 327, 367, 633, 702, and 826 cm⁻¹ for each of the BiVO₄ samples. The signals are Raman bands characteristic of monoclinic BiVO₄.¹⁻³ The Raman band at 210 cm⁻¹ is assignable to the rotation/translation modes of BiVO₄; the ones at 327 and 367 cm⁻¹ are attributable to the asymmetric and symmetric deformation modes of the VO₄³⁻ tetrahedron, respectively; the one at 633 cm⁻¹ is

ascribable to the asymmetric stretching vibration of the V–O bond; and the ones at 702 and 826 cm⁻¹ are due to the stretching vibrations of two different types of V–O bonds. The shifts of Raman bands at 633 and 702 cm⁻¹ (V–O stretching vibration) suggest that the lower frequency of the Raman stretching bands is corresponding to a longer bond length. Such a suggestion was confirmed by the well-established functional relationship between the Raman stretching frequency and the metal–oxygen bond length in the local structure.⁴ It is also seen from Figure S1 that discrepancy in Raman band intensity of these samples is insignificant, indicating that the BiVO₄ samples are of similar crystallinity.

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Fig. S2. FT-IR spectra of (a) uncalcined BiVO₄-AA-1, (b) calcined BiVO₄-AA-1, (c) uncalcined BiVO₄-CA-1, and (d) calcined BiVO₄-CA-1.

FT-IR RESULTS:

Fig. S2 shows the FT-IR spectra of the BiVO₄-AA-1 and BiVO₄-CA-1 samples before and after calcination at 450 $^{\circ}$ C for 4 h. The absorption band below 750 cm⁻¹ is characteristic of the

 v_3 asymmetric stretching mode of VO₄³⁻, the absorption band at 830 cm⁻¹ is due to the v_1 symmetric stretching vibration of VO_4^{3-1} . There are three weak absorption bands at 3430, 3563, and 1627 cm^{-1} , attributable to the bending and stretching vibrations of adsorbed water molecules¹. The absorption bands at 2870, 2964, and 3010 cm^{-1} are assignable to the symmetric and asymmetric stretching vibrations of the CH₂ groups and the terminal CH₃ group of residual organic species (from organic compounds used in the synthesis). The absorption band at 1387 cm⁻¹ is due to the residual NO₃⁻¹ ions of the samples.² The absorption bands at 1292, 1456, and 1741 cm^{-1} are due to the symmetric and asymmetric stretching vibrations of COO^{-3-5} The absorption band at 1645 cm⁻¹ is due to the stretching vibration of C=O bonds,⁴ the ones at 1097, 1157, and 1243 cm⁻¹ are due to the stretching vibrations of C–O (ester bonds),^{3,6} and the ones at 755, 844, and 985 cm⁻¹ are due to the bending vibrations of C-H bonds.³ According to the FT-IR spectra, one can realize that there was the presence of adsorbed H₂O, EG, and ascorbic acid or citric acid as well as PMMA template on the uncalcined BiVO₄ samples (Fig. S2a and c), but all of the organics were completely removed after these samples were calcined at 450 °C for 4 h (Figure S2b and d). Therefore, the FT-IR results clearly indicate that after the thermal treatments adopted in the present study, there was complete elimination of the organics from the BiVO₄ samples.

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Fig. S3. TGA/DSC profiles of (A) BiVO₄-AA-1 and (B) BiVO₄-CA-1 samples before

calcination at 450 °C for 4 h.

TGA/DSC results:

Fig. S3 illustrates the TGA/DSC profiles of the uncalcined BiVO₄-AA-1 and BiVO₄-CA-1 samples. From Fig. S3A, one can see that there are two weight losses (totally 10.4 wt%)

below 186 °C (attributable to the removal of physically adsorbed methanol,¹ water,¹ and nitrate ions²) accompanying with two weak endothermic signals at 107 and 154 °C. A big weight loss (79.4 wt%) can be seen in the temperature range of 186–408 °C, together with the appearance of a strong endothermic peak at 365 °C, which can be attributed to the oxidative elimination of the residual ascorbic acid³ and EG and the PMMA template.⁴ There are no weight losses above 408 °C. For the uncalcined BiVO₄-CA-1 sample (Fig. S3B), there are three weight losses (totally 15.3 wt%) below 177 °C, attributable to the removal of physically adsorbed methanol,¹ water,¹ and nitrate ions,² accompanying with three weak endothermic signals at 50, 109 and 140 °C. There is a big weight loss (76.1 wt%) in the temperature range of 177–409 °C, with the corresponding strong endothermic peak appearing at 367 °C; such a big weight loss can be ascribed to the oxidative removal of the residual citric acid⁵ and EG⁴ and the PMMA template.⁴ Above 409 °C, there is no detection of weight losses. The above results indicate that calcining the BiVO₄ precursors at 450 °C could guarantee the complete removal of organic solvent and PMMA template, as also substantiated by the results of FT-IR investigation.

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Fig. S4. (A) Nitrogen adsorption-desorption isotherms and (B) pore size distributions of (a) BiVO₄-AA-1, (b) BiVO₄-AA-2, (c) BiVO₄-CA-1, and (d) BiVO₄-CA-2.

BET results:

Shown in Fig. S4 are the N₂ adsorption-desorption isotherms and pore size distributions of the four BiVO₄ samples. It is observed from Fig. S4A that each of the BiVO₄ samples shows a type III isotherm with a H3 hysteresis loop,¹ implying the generation of slit-shaped pores in the aggregates of nano- or microparticles. The absence of an adsorption plateau at a p/p_0 of *ca*. 1.0 suggests the presence of macropores.^{2,3} Apparently, all of the BiVO₄ samples have macropores, and the appearance of a quite narrow H1 hysteresis loop in the p/p_0 range of 0.1–0.8 implies the presence of nanovoids or nanopores,^{1,3} in good agreement with the SEM and TEM observations (Figs. 2 and 3). The BiVO₄ samples display a narrow pore size distribution in the 2–10 nm range (Fig. S4B); furthermore, the dV/dD value decreases with an increase in pore size around 2 nm, suggesting that there might be the presence of micropores in the four BiVO₄ samples. These micropores are mostly originated from the skeletons of the macropores of BiVO₄.

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Fig. S5. (A) Bi 4f, (B) V 2p_{3/2}, and (C) O 1s XPS spectra of (a) BiVO₄-AA-1, (b) BiVO₄-AA-2, (c) BiVO₄-CA-1, and (d) BiVO₄-CA-2.



Fig. S6. The absorbance versus wavelength of sampled solutions over BiVO₄-AA-1 photocatalyst before and after reaction (0–180 min) in the presence of 0.6 mL H₂O₂ for the degradation of phenol aqueous solution ($C_0 = 0.2 \text{ mmol/L}$) under visible-light ($\geq 400 \text{ nm}$) illumination.