

Supporting Information for

**Development of a novel $\text{Ba}_2\text{BiV}_3\text{O}_{11}$ photocatalyst with dual
functionality of water oxidation and proton reduction reactions**

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Materials:

BaCO₃ (99%), Bi₂O₃ (99.99%), V₂O₅ (99%), NaCl (99.8%), triethanolamine (98%), and NaOH (96%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. KCl (99.5%), HAuCl₄·4H₂O (Au 47.8%), and H₂PtCl₆·6H₂O (Pt 37%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Na₃RhCl·12H₂O (Rh 17.1%) and (NH₄)₂RuCl₆·6H₂O (Ru 28.4%) were purchased from Alfa-Aesar (China) Chemical Co., Ltd. H₂IrCl₆·6H₂O (Ir ≥ 35%) and AgNO₃ (99.85%) were obtained from Beijing InnoChem Science & Technology Co., Ltd. CH₄N₂S (AR) and Na₂SO₄ (99%) were offered by Tianjin Kermel Chemical Reagent Co., Ltd., China. All chemicals were used without purification.

Synthesis:

Preparation of BBVO: BBVO samples prepared via solid state and molten salt methods are denoted as BBVO-SSR and BBVO-Flux, respectively. In the solid state method, BaCO₃, Bi₂O₃, and V₂O₅ in a stoichiometric molar ratio of 2:1:3 are mixed and ground in a mortar for 1 h to form a homogeneous mixture. BBVO-Flux was synthesized under otherwise identical condition as BBVO-SSR except that the mixture was mixed with molten salt at a solute concentration of BaCO₃/KCl/NaCl=2:5:5 and ground for 20 min. The mixtures were then placed in 30 mL crucible and calcined in a muffle furnace at 1073 K for 10 h at a heating rate of 10 K/min. The BBVO-Flux sample was washed with deionized water and dried for further use.

Preparation of sulfur-doped BBVO (S-BBVO-Flux): Different mass ratios (0, 0.2, 0.33, 0.5, and 1) of BBVO-Flux and thiourea were ground in a mortar for 30 min to form a homogeneous mixture, which was then placed in a 30 mL crucible and calcined in a muffle furnace at 673 K for 4

h at a heating rate of 1 K/min to obtain the S-BBVO-Flux powder (Figure S1).

Photocatalytic reaction:

Photocatalytic water splitting reactions were carried out in a gas-closed circulation system (labsolar-6A, Beijing Perfectlight Technology Co, Ltd.) equipped with a top irradiation reaction vessel. For the oxygen evolution reaction, 50 mg photocatalyst was dispersed uniformly in 100 mL aqueous AgNO_3 solution (10 mM), sonicated for about 10 s, and irradiated under visible light. For the hydrogen evolution reaction, different kinds of proton reduction cocatalysts with a metal mass fraction of 1 wt% were loaded on the surface of photocatalyst. Then, 50 mg photocatalyst was dispersed in a 10 vol% triethanolamine aqueous solution and was irradiated under UV light. All reactions were evacuated for 20 minutes to ensure complete removal of air prior to illumination. The evolved gases are detected by on-line gas chromatography (GC-2014, Shimadzu Corporation).

Photoelectrochemical (PEC) test:

BBVO-SSR, BBVO-Flux, and S-BBVO-Flux electrodes were prepared using the drop-casting method. 20 mg powder was dissolved in 5 mL isopropanol and sonicated for 6 h. Subsequently, the solution was uniformly dropped onto fluorine-doped tin oxide (FTO) conductive glass (1 x 2 cm²) and dried in air. 10 μL TiCl_4 anhydrous methanol solution (10 mM) was then dropped on the above electrodes and dried for five times. Finally, the electrodes were calcined in a muffle furnace in air at 773 K for 30 min for further use. All (photo)electrochemical tests were performed using a CHI660E electrochemical workstation and a three-electrode system, where saturated calomel electrode is the reference electrode, a platinum sheet is the counter electrode, and the FTO glass is the working electrode. A 0.5 M Na_2SO_4 solution was used as the electrolyte (NaOH was used to

adjust the pH to 8) and the light source was a 300 W xenon lamp ($\lambda \geq 420$ nm, $i = 20$ A, CEL-HXF300H5, Beijing Zhongjiao Jinyuan Technology Co., Ltd.).

The apparent quantum efficiency (AQE) measurement was carried out as the above mentioned condition except that a 420 nm band-pass filter was used. The following equation was employed to calculate the AQE (φ):

$$\varphi (\%) = AR / I \times 100$$

A represents the coefficient (4 for O₂ evolution reaction), R represents the gas evolution in an hour, and I represents the number of the incident photons.

Characterization:

X-ray powder diffraction (XRD) was measured using an X-ray diffractometer (D8 discover). Scanning electron microscope microscopy (SEM) was obtained on a Nova Nano SEM450 and Talos F200S. X-ray photoelectron spectroscopy (XPS) measurements were obtained on an ESCALAB 250Xi instrument. A Cary 60 UV-Visible spectrophotometer was used to measure the UV-vis diffuse reflectance spectrum (UV-vis DRS) of the samples. The photoluminescence (PL) emission spectra were measured with a spectrophotometer (FSP 920). DFT calculations were performed using Vienna Ab initio Simulation Package (VASP).¹ The Blöchl's all-electron-like projector augmented wave (PAW) method was used to treat the interaction between ion nuclei and valence electrons.² The exchange-correlation energies were calculated using the PBE-D3 generalized gradient approximation (GGA). The kinetic energy of plane wave has a truncation energy of 400 eV and the Monkhorst-Pack is used to integrate the Brillouin zone using a $6 \times 6 \times 1$ k-point grid.³ The convergence criterion of minimum energy change was 1×10^{-5} eV. The on-site Coulomb interaction

potentials were Bi 4.8 eV, V 6 eV,⁴ respectively.

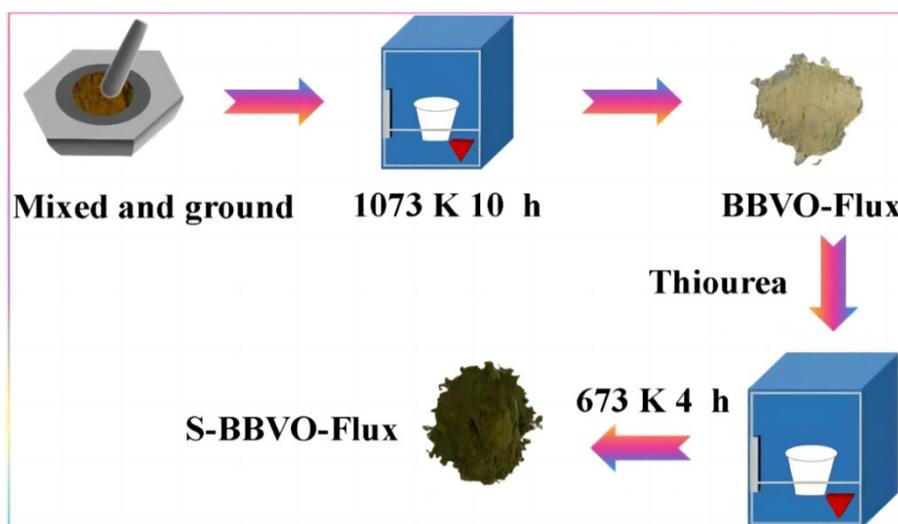


Fig. S1 Schematic illustration of synthesizing BBVO-Flux and S-BBVO-Flux.

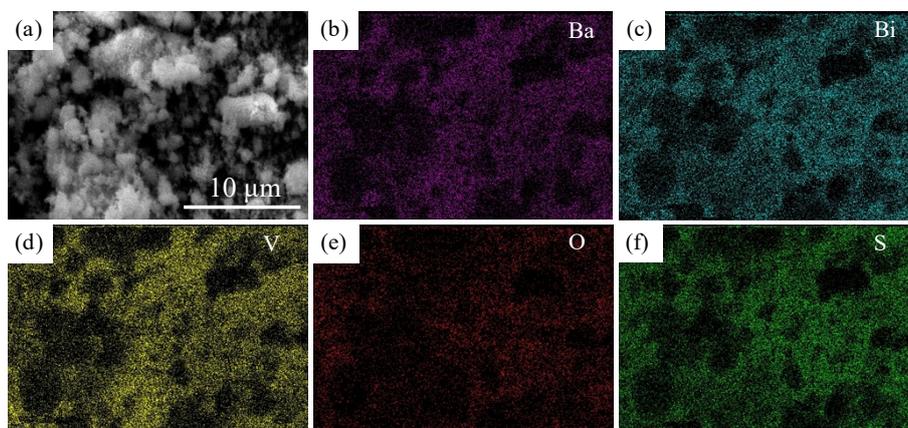


Fig. S2 (a) SEM images of S-BBVO-Flux. Elemental mapping results of the typical elements of (b) Ba, (c) Bi, (d) V, (e) O, and (f) S.

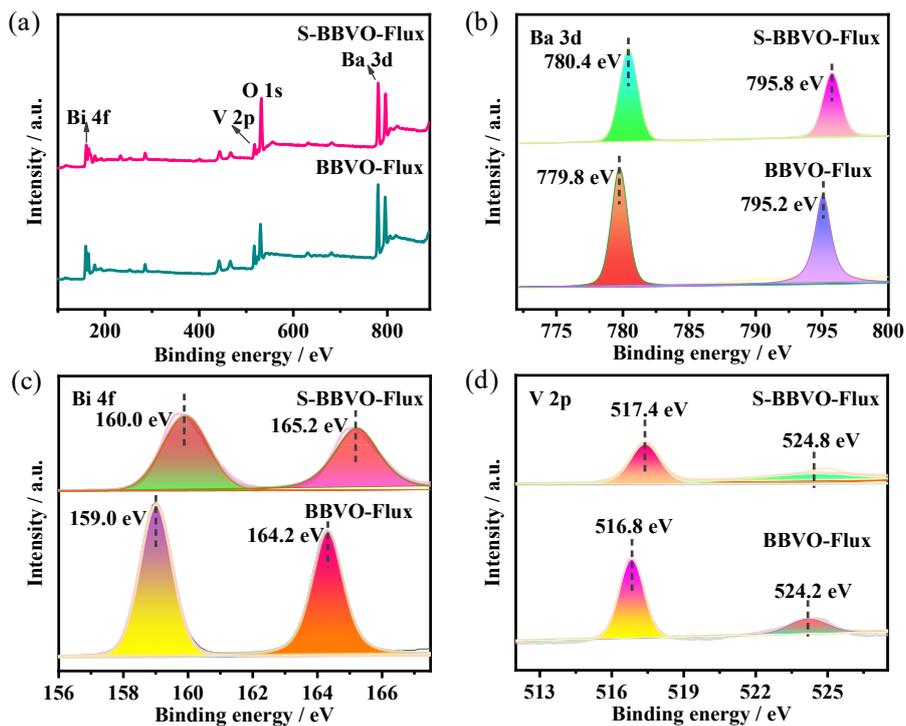


Fig. S3 (a) XPS survey, (b) Ba 3d, (c) Bi 4f, and (d) V 2p spectra of BBVO-Flux and S-BBVO-

Flux samples.

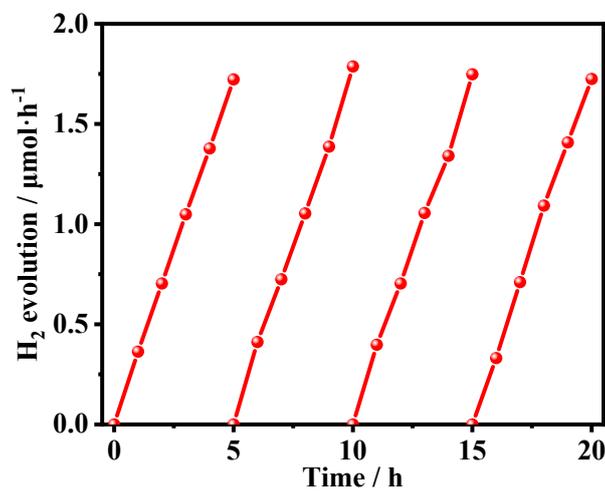


Fig. S4 Hydrogen production of BBVO-Flux proceeded for 20 h with intermittent evacuation

every 5 h.

References

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