Electronic Supplementary Information (ESI)

Promotion effect of surface negative electrostatic field on the photogenerated charge separation of BiVO₄ and its contribution to the enhanced PEC water oxidation

Mingzheng Xie,^{a,b} Ji Bian,^a Muhammad Humayun,^a Yang Qu,^a Yujie Feng,^b and Liqiang Jing^{*a}

^aKey Laboratory of Functional Inorganic Materials Chemistry (Heilongjiang University), Ministry of Education, School of Chemistry and Materials Science, Harbin 150080, P. R. China.

^bState Key Lab of Urban Water Resource and Environment (Harbin Institute of Technology), Harbin 150001, P. R. China.

*E-mail: jinglq@hlju.edu.cn.

Experimental Section

All of the reagents were of analytical grade and used as received without further purification. Deionized water was used throughout.

Synthesis of Materials: To prepare phosphate-modified BiVO₄ films electrode, the corresponding paste was prepared in advance as follows: in a typical experiment, Bi(NO₃)₃ 5H₂O (0.01 mol) was dissolved in HNO₃ solution (100 mL, 2 mol/L) under vigorous stirring at room temperature. Afterwards, 1 g polyethyleneglycol (PEG) was added to the reaction mixture. The mixture was kept under stirring for 15 min, and then NH₄VO₃ (0.01 mol) was added to it and continuously stirred for 30 min to obtain a yellow homogeneous solution. The pH value of the resultant solution was adjusted to approximately 7 with ammonia solution under constant stirring, along with the generation of an orange precipitate. Through centrifugation, the precipitate was obtained and washed with distilled water followed by absolute ethanol, in turn, and then dissolved in absolute ethanol (50 mL). After that, desired amount of phosphate acid (0.05 mmol/L, 0.1 mmol/L, 0.2 mmol/L and 0.3 mmol/L, respectively) was added to it and kept under stirring for 10 h, and the paste was obtained.

Phosphate-modified BiVO₄ films were prepared by the doctor blade method using conductive fluorine-doped tin oxide (FTO)-coated glasses as the substrates and scotch tape as the spacer. Following drying in air for 10 min, films were sintered at 450 °C for 30 min. After cooling to room temperature, the FTO glass covered by the film was cut into approximately 1.0 cm \times 3.0 cm pieces with a film surface area of 1.0 cm \times 1.0 cm. The working geometric surface area of film was 0.5 cm \times 0.5 cm where the remaining area was covered with epoxy resin. Meanwhile, a special film with surface area of 3.0 cm \times 5.0 cm was made through similar process and used in the measurement of zeta potential. For comparison, BiVO₄ film was prepared without adding phosphate acid. The obtained film is denoted by XP-BVO, in which P represents phosphate, BVO means BiVO₄ and X respresents the mole ratio percentage of phosphate and BiVO₄.

Characterization: The films were characterized by XRD with a Rigaku D/MAX-rA powder diffractometer (Japan), using Cu K α radiation (= 0.15418 nm), an accelerating voltage of 30 kV, and emission current of 20 mA. The UV-vis DRS of the samples were recorded with a Model Shimadzu UV2550 spectrophotometer. Scanning electron microscopy (SEM) images were taken using a Hitachi S-4800 instrument operating at 15 KV. The Fourier transform infrared spectra

(FT-IR) of the powder samples, which are scraped from the films, were collected with a Bruker Equinox 55 Spectrometer, using KBr as diluents. The zeta potential of the film samples are collected by a SurPASS electrokinetic analyzer (Anton Paar, Austria) at room temperature. The pH conditions were adjusted by using hydrochloric acid or caustic soda.

The adsorption of RhB was performed in a 50 mL beaker. The powder sample, which is scraped from the film, and RhB solution (20 mL, 20 mg/L) were added into the beaker and stirred for 1 h in dark. The RhB concentration was analyzed with a Model Shimadzu UV2550 spectrophotometer.

PEC experiments were performed in a cubic quartz cell containing a NaClO₄ solution (0.5 mol/L), of which pH could be adjusted by HCl and NaOH, using 500 W Xenon lamp to produce a visible light source with an intensity of 64 mW/cm² after using a filter to remove light below the wavelength of 420 nm (for IPCE (incident photon-to-current efficiency) measurements, a monochromator (CM110, Spectral Produts) was used to produce the light with single wavelength). The working electrode was the as-prepared film, irradiated from the FTO glass side. Platinum plate (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 the work were referred to SSE. Oxygen-free nitrogen gas was used to bubble through the electrolyte before and during the experiments. Applied potentials were controlled by a commercial computer controlled potentiostat (AUTOLAB PG STAT 101). For comparison, the current was also measured in dark condition. IPCE spectra were calculated from photocurrent and incident light intensity.

The transient surface photovoltage (TS-SPV) measurement was performed with a self-assembled device in air atmosphere at room temperature. The as-prepared film sample was fabricated to electrode as shown in the **Fig. S6** and then immersed in NaClO₄ solution (0.5 mol/L), of which pH could be adjusted by HCl and NaOH. The film samples were excited by a 355/532 nm-laser beam with 10 ns pulse width from a second harmonic Nd: YAG laser (Lab-130-10H, Newport, Co.). The laser intensity was modulated with an optical neutral filter and measured by a high energy pyroelectric sensor (PE50BF-DIF-C, Ophir Photonics Group). The TS-SPV signals were registered by a 1 GHz digital phosphor oscilloscope (DPO 4104B, Tektronix) with a preamplifier. *Evaluation of Activity* :To measure the amount of O₂ produced in the PEC water oxidation, the as-prepared films were used as working electrodes in a sealed quartz cell with 0.5 mol/L Na₂SO₄

solution of 80 mL as electrolyte, and high-purity nitrogen gas was employed to bubble through the electrolyte before the experiment. The films were illuminated from the FTO glass side, whose illuminated working area was about 0.25 cm^2 , at the constant bias of 0.6 V. During the experiment, the amount of O₂ produced was detected quantitatively with an Ocean Optics fluorescence-based oxygen sensor (NFSC 0058) by putting the needle probe into the electrolyte, near to the working electrode, and the irradiation was lasted for 10 min using 500 W Xenon lamp to produce a visible light source with an intensity of 64 mW/cm² after using a filter to remove light below the wavelength of 420 nm.

Figures



Fig. S1. XRD patterns (A), DRS spectra (B) and TEM images (C (a): BVO; C (b): 2P-BVO) of films, (The film are denoted by *X*P-BVO, in which P and BVO indicate phosphate and BiVO₄, *X* represents the mole ratio percentage of phosphate to $BiVO_4$.).



Fig. S2. FT-IR spectra of powder samples.



Fig. S3. Zeta potential of BVO and 2P-BVO films on different pH conditions.



Fig. S4. I-V curves of films in dark.



Fig. S5. IPCE data of BVO and 2P-BVO films at 0.6 V bias.



Fig. S6. Schematic of electrode structure for TS-SPV measurement in water.



Fig. S7. TS-SPV responses under the irradiation of a laser beam of 355 nm in NaClO₄ solution (0.5 mol/L).



Fig. S8. TS-SPV responses of BVO and 2P-BVO films on different pH conditions under the irradiation of a laser beam of 532 nm.



Fig. S9. I-V curves of BVO film on different pH conditions: in dark (A) and under visible light irradiation (B).



Fig. S10. I-V curves of 2P-BVO film on different pH conditions: in dark (A) and under visible light irradiation (B).