Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Improving the charge properties of WO_3 photoanode by a $BiFeO_3$ ferroelectric nanolayer

Mingqi Wang[a], Qingyi Zeng[a,b,*], Sheng Chang[a], Shanshan Li[a], Chun Hu[a], Zhihong Chen[a,*]

[a] *Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Guangzhou University, Guangzhou, China*

[b] *School of Resources & Environment and Safety Engineering, University of South China, Hunan 421001, China*

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[*] Corresponding authors.

E-mail addresses: qingyizeng@usc.edu.cn (Q. Zeng), chenzhihong1227@sina.com (Z. Chen)

1. Supporting Experimental

1.1 Preparation of the photoanodes

The WO_3 photoanode was prepared on fluorine-doped tin oxide (FTO) substrate using our reported method [1]. Briefly, 0.4 g $NaWO_3$ and 0.15 g ammonium oxalate were well added into the mixed solution made up with 32 mL pure water, 9 mL hydrochloric acid, 8 mL hydrogen peroxide and 30 mL alcohol. The purchased FTO-coated glass substrate (7 Ω cm^{-1}， 3 × 3 cm^2) was washed ultrasonically in acetone and deionized (DI) water for 30 min, and dried in a stream of air, sequentially. Two pieces of them were laid into the mixture, heated at 80 °C for 180 min in the water bathe and then cooled naturally. The as-prepared film was rinsed with DI water and dried down to the room temperature, then annealed at 450 ºC for 120 min to obtain the WO_3 film.

The BFO photoanode is prepared by a modified reported spin-coating method [2]. Briefly, To obtain a 0.1 M sol of precursors, bismuth nitrate and iron nitrate as raw materials were dissolved separately in 10 mL of glacial acetic acid and ethylene glycol, respectively (Bi:Fe = 1:1). Transparent bismuth nitrate sol was obtained by adding 0.1 mL of triethanolamine to the solution. A very smooth and dense surface can be also achieved by triethanolamine addition. Finally, the above solutions were mixed and stirred for 2 h. The depositions were carried out by spin-coating at 3000 rpm for 30 s. Each layer was dried at 100 °C for 10 min to remove volatile materials. The above spin-coating and drying procedures were repeated for 10 times. Finally, the thin films were calcined at 600 °C for 1 h.

The WO_3-BFO is also prepared by a spin-coating process. $Bi(NO_3)_3$ (0.85 g) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.8 g) were dissolved into ethylene glycol (4.0 g) and citric acid (1.68 g) mixed solution under 90 °C heating and stirring. The solution was spin coated onto WO_3/FTO electrodes at 2300 rpm for 60 s. Then, the BFO films were completely crystallized after annealing for 2 h at 450 °C in air, named as WO_3/BFOX, where X represent as the number of layer.

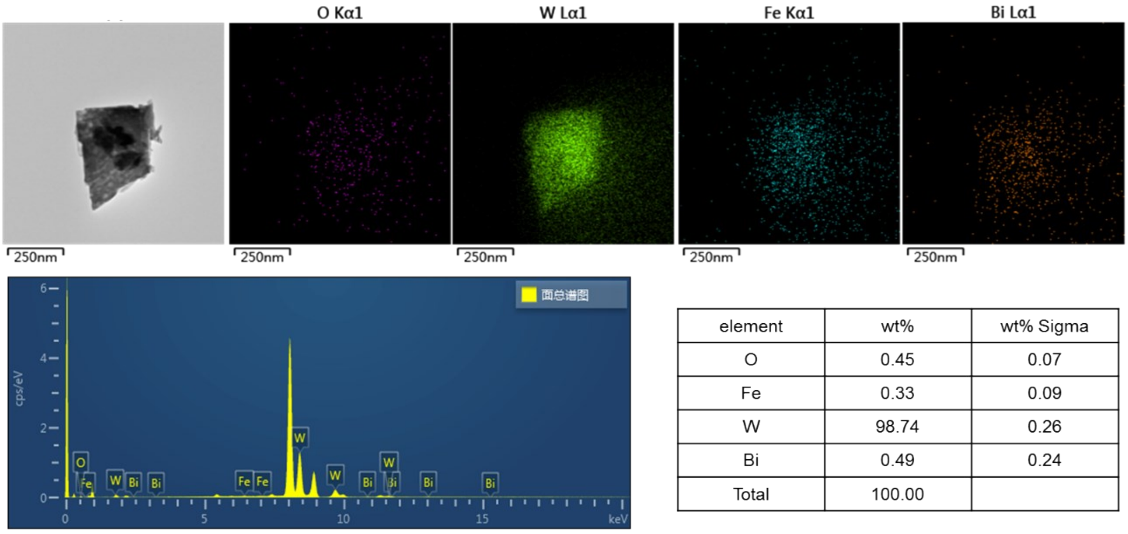
1.2. Characterization

The morphology and microstructure of the samples were investigated via field emission scanning electron microscopy (SEM, Sirion200, Philips, Netherlands) and transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). The crystal phase of the samples was characterized via X-ray diffraction (XRD, AXS-8 Advance, Bruker, Germany). The UV−vis absorption spectra of the samples were obtained using spectrophotometry (UH4150, Hitachi, Japan). The X-ray photoelectron spectroscopy (XPS) measurements were carried out by PHI 5000 (VersaProbe, Japan). The samples were irradiated with monochromatic Al-K_α radiation (hn ¼ 1486.6 eV).

The photoelectrochemcial tests were performed in a three-electrode system with Ag/AgCl as the reference, Pt foil as the counter electrode, and the WO_3/BFO as the working electrode in an electrolyte consisting of 0.1 M Na_2SO_4 solution, controlled by an electrochemical workstation (CHI 760E, CH Instruments, Inc., USA). A 300-W Xe lamp (Perfect Light, China) with an AM 1.5 filter was used for simulated sunlight illumination (light density: 100 mW cm^{-2}).

Intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) tests were recorded by an electrochemical workstation (Zennium pro, ZAHNER-elecktrik GmbH&Co.KG, Germany) equipped with a controlled intensity modulated photospectroscopy setup (CIMPS-2 pro, PP211, ZAHNER-elecktrik GmbH&Co.KG, Germany). The light source was a white light lamp (WLC02, ZAHNER-elecktrik GmbH&Co.KG, Germany). The applied modulated light was superimposed at a steady DC light intensity of 80 $mWcm^{-2}$ in the frequency range of 0.1–100 Hz.

2. Supporting results



element	wt%	wt% Sigma
O	0.45	0.07
Fe	0.33	0.09
W	98.74	0.26
Bi	0.49	0.24
Total	100.00	

Figure S1. EDS mappings and reports of the WO_3/BFO tested in TEM model.

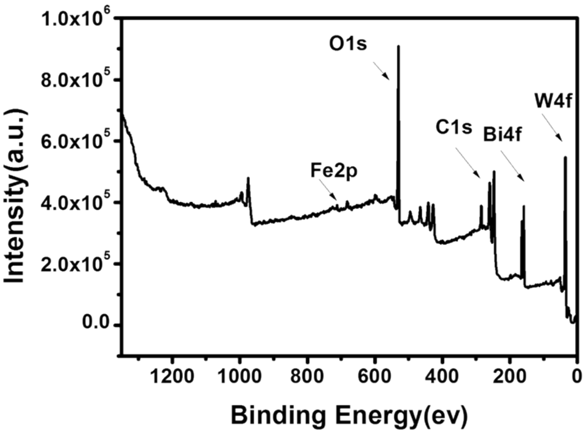


Figure S2. XPS survey of the WO_3/BFO.

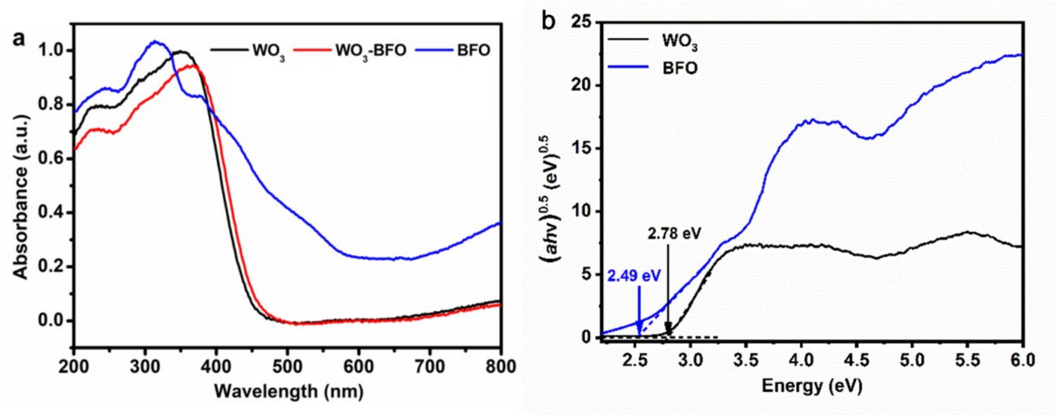


Figure S3. (a) UV-vis absorption spectra of BFO, WO_3 and WO_3/BFO films, and (b) plots of the transformed Kubelka–Munk function versus the energy of light of WO_3 and BFO.

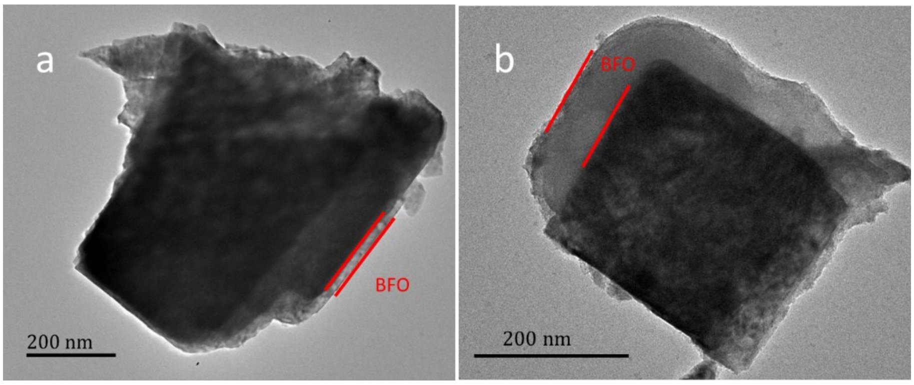


Figure S4. TEM images of (a) WO_3/BFO1 and (b) WO_3/BFO3.

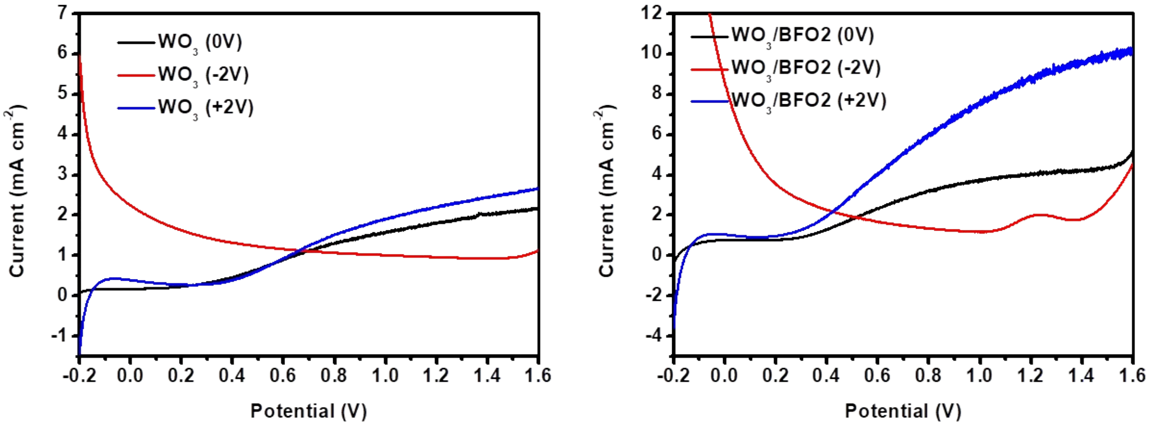


Figure S5. LSV curves (0.6 V *vs.* Ag/AgCl) of WO_3, BFO and WO_3/BFOx tested in 0.1 M Na_2SO_4 under AM 1.5 illumination after being polarized in the bias voltage of +2, -2 and 0 V, respectively.

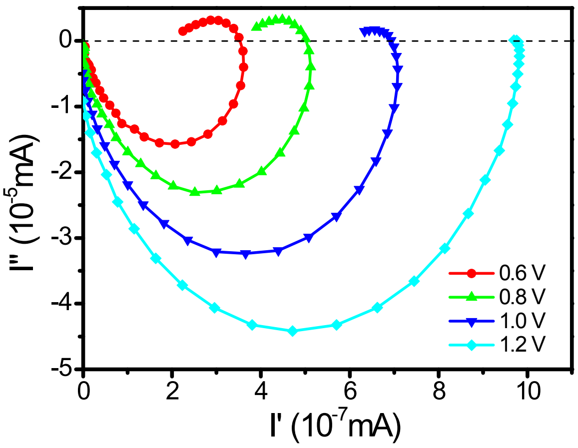


Figure S6. Nyquist plots for IMPS response of WO_3/BFO tested under various bias potential *vs* Ag/AgCl. The IMPS spectrum consists of two semicircles in lower and upper quadrants, which correspond to the relaxation time constant attenuation and the competition between charge transfer and recombination, respectively [3]. A smaller upper semicircle suggests that the charge recombination is suppressed as increase of the applied potentials. This observation is in good agreement with that the theoretical relation of water oxidation versus oxidation potential, in which more positive potential drives faster reaction rate. The rapid decrease of the upper semicircle suggests the efficient charge seperation in WO_3/BFO.

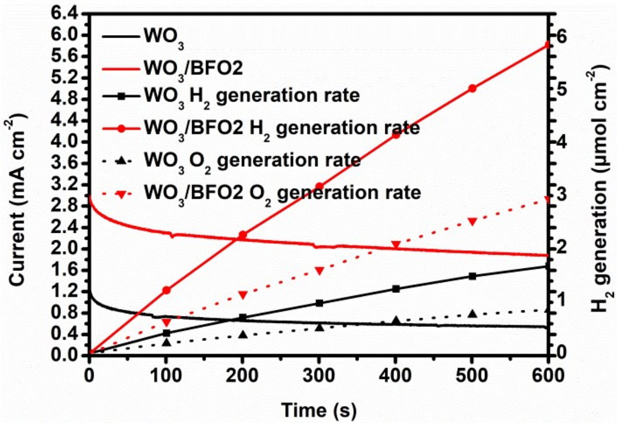


Figure S7. Chopped LSV and the H_2 and O_2 generation rate of WO_3 and WO_3/BFO2 tested in 0.1 M Na_2SO_4 under AM 1.5 illumination.

Reference

1. Q. Zeng, J. Li, J. Bai, X. Li, L. Xia and B. Zhou. Appl. Catal. B: Environ. 2017, **202**, 388-396.

2. J. Song, T. L. Kim, J. Lee, S. Y. Cho, J. Cha, S. Y. Jeong, H. An, W. S. Kim, Y. S. Jung and J. Park. Nano Res. 2018, **11**, 642-655.

3. J. Xie, C. Guo, P. Yang, X. Wang, D. Liu and C. M. Li. Nano Energy 2017, **31**, 28-36.