

## Electronic Supplementary Information (ESI)

# Improved photocathodic performance in Pt catalyzed ferroelectric BiFeO<sub>3</sub> films sandwiched by a porous carbon layer

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### Experimental details:

#### Fabrication of BFO films:

The BiFeO<sub>3</sub> (BFO) film was deposited by a sputtering method (1.2 Pa, O<sub>2</sub>:Ar =8:32, 100 W, 600 °C deposition temperature, sputtering for 1 hour) on the indium tin oxide (ITO) coated glass substrate. For PEC measurements, all the ITO glass substrates were cut into 1.6×1.2 cm<sup>2</sup>.

#### Carbon layer deposition:

The BFO thin films on ITO glass were burned with a cigarette lighter to form a carbon layer due to the carbonization of the n-butane, as demonstrated in the following picture. To prevent local overheating, the substrate was kept moving for 30 s. The distance between BFO film and the top of lighter fire was controlled at about 3 cm. The size of the lighter fire is shown in following picture. Afterwards, the BFO film was allowed to cool down at ambient conditions and washed with deionized (DI) water to remove residuals.



**Pt nanoparticles deposition:**

The Pt nanoparticles on ITO/BFO/carbon electrode surface were fabricated by photoreduction. The 1 mM  $\text{H}_2\text{PtCl}_6$  (Sigma-Aldrich, reagent grade) solution was placed onto the sample surface through dropping. The solvent of  $\text{H}_2\text{PtCl}_6$  solution is anhydrous ethanol. The anhydrous ethanol made solution evenly cover on the sample surface. Then the samples were irradiated with a 300 W Hg lamp for 20 minutes. The amount of Pt nanoparticles presented on the electrode surface can be controlled by the amount of  $\text{H}_2\text{PtCl}_6$  solution.

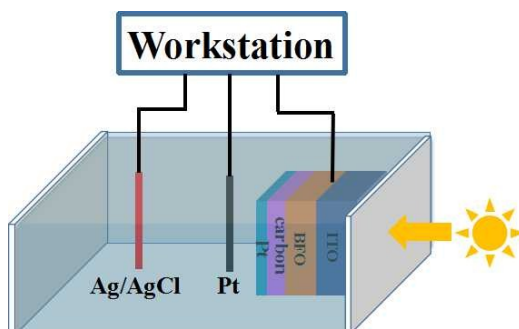
**Sample characterizations:**

The crystal structures of the BFO films were evaluated by measuring x-ray diffraction (XRD) spectra with Ni filtered  $\text{CuK}\alpha$  radiation. The surface morphologies and cross-section images were observed with a Hitachi SU8010 field-emission scanning electron microscope (SEM). The Pt was analyzed with an X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo). The element of carbon layer was confirmed by confocal microscope Raman spectrometer (HR800, HORIBA Jobin Yvon company). The UV-vis absorption spectra of ITO/BFO and ITO/BFO/carbon were recorded with a Lambda 750 UV-VIS-NIR spectrophotometer. The UV-vis diffused reflection spectra of ITO/BFO were also recorded with a Lambda 750 UV-VIS-NIR spectrophotometer.

To measure the ferroelectric properties of BFO films, about 40 nm thick Pt top electrodes with diameters of 0.28 mm were sputtered onto the BFO surface. Then, the hysteresis loops of ITO/BFO/Pt capacitor was examined using a radiant precision ferroelectric analyzer.

All measurement of electrode samples were conducted by an electrochemical workstation (CHI660D) with a  $100\text{mW}/\text{cm}^2$  Xe lamp as light source and  $0.1\text{M}$   $\text{Na}_2\text{SO}_4$  solution (PH=7) as electrolyte. The light passes through the ITO/BFO/carbon/Pt photoelectrode from the ITO glass side. During the measurement, the as-prepared sample serves as working electrode, a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The following figure is the

schematic illustrations for PEC testing of the ITO/BFO/carbon/Pt photoelectrode.



All the potentials in this work are converted using the reversible hydrogen electrode (RHE) as the reference electrode, according to the following equation:

$$E_{(RHE)} = E + E_{(Ag/AgCl)} + 0.059 \times PH$$

where  $E_{(Ag/AgCl)} = 0.197 \text{ V}$ .

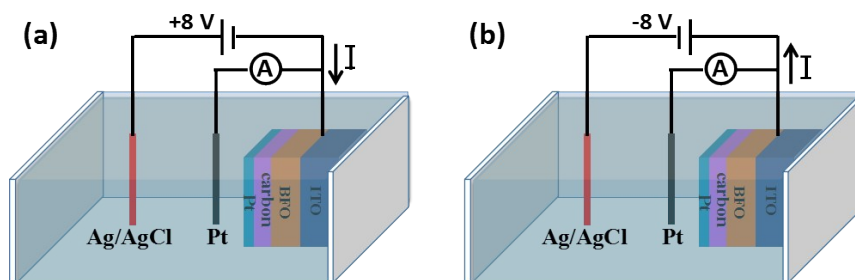
The IPCE measurement was measured under a  $100 \text{ mW/cm}^2$  Xe lamp illumination in  $0.1 \text{ M Na}_2\text{SO}_4$  solution. The IPCE value was calculated using the following equation:

$$IPCE = \frac{1240 \times I}{\lambda \times J_{light}} \times 100\%$$

where  $I$  is the photocurrent density ( $\text{mA/cm}^2$ ),  $J_{light}$  is the power density of the incident illumination ( $\text{mW/cm}^2$ ) and  $\lambda$  is the incident light wavelength (nm).

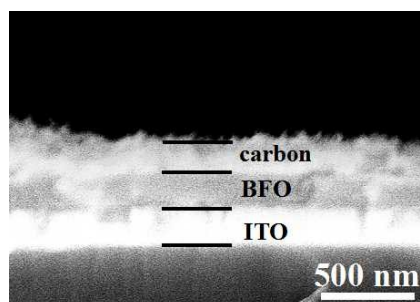
### Poling the BFO films:

The poling of BFO films were carried out using an electrochemical workstation (CHI660D) in  $0.1 \text{ M Na}_2\text{SO}_4$  electrolyte. A pulsed potential of  $+8 \text{ V}$  or  $-8 \text{ V}$  with an alternating  $0.2 \text{ s}$  on time and  $0.2 \text{ s}$  off time was applied between ITO and the Ag/AgCl reference electrode to pole the BFO films. One period of poling consists of 10 pulses. The following figure is the schematic illustrations for poling the BFO films positively (a) and negatively (b).

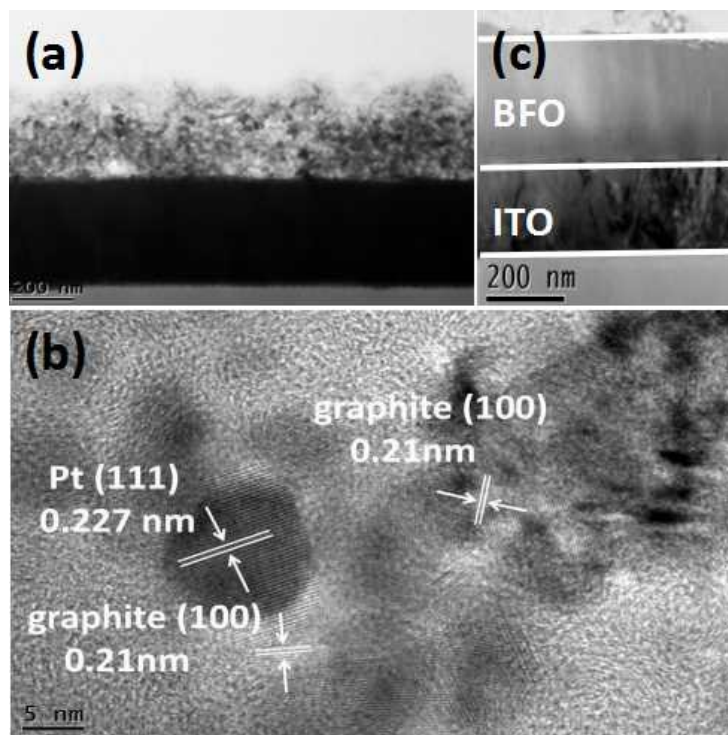


**The measurement of hydrogen evolution:**

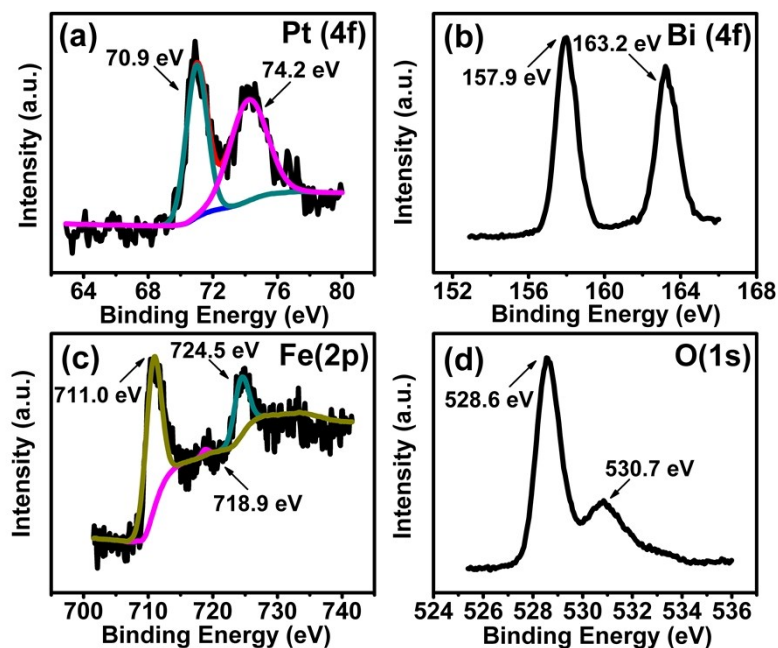
The hydrogen evolution during PEC water splitting was conducted in an air-tight photo-reactor which was made of quartz glass. The electrode samples and the Pt counter electrode were placed in different tubular chambers, which decrease the mixing of hydrogen generated on the electrode samples and oxygen on the Pt counter electrode. The measurements were conducted in a solution containing 0.1 M  $\text{Na}_2\text{SO}_4$  under  $100 \text{ mW/cm}^2$  Xe lamp illumination at 0.6 V vs. RHE. The amount of hydrogen was determined by a gas chromatography equipped with TCD (Tianmei, GC 7890T).



**Fig. S1** The cross-sectional SEM of the ITO/BFO/carbon, showing the thicknesses of BFO and carbon layer.



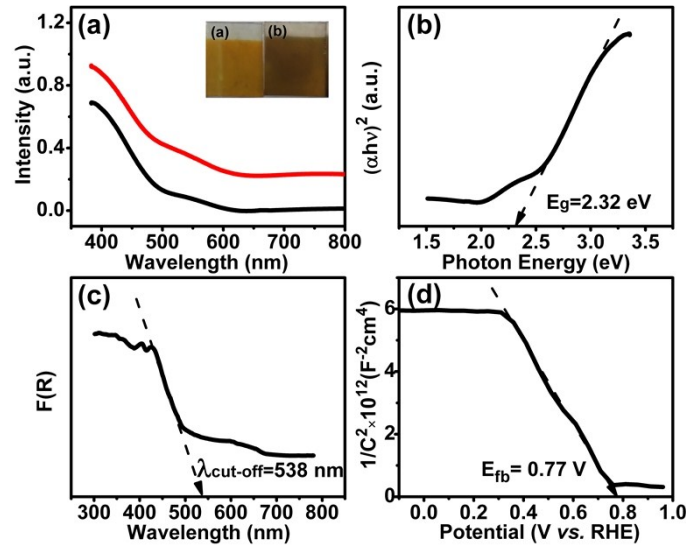
**Fig. S2** (a) TEM picture of ITO/BFO/carbon/Pt. (b) The enlarged HRTEM picture of the carbon and Pt nanostructures above the black ITO/BFO part in (a). (c) HRTEM picture for ITO and BFO.



**Fig. S3** XPS spectra of Pt 4f (a) , Bi 4f (b), Fe 2p (c), O 1s (d) on ITO/BFO/carbon/Pt .

The XPS spectra of the Bi 4f orbital shows two distinct peaks. The peaks at 157.9 eV and 163.2 eV are related to Bi 4f<sub>7/2</sub> and Bi 4f<sub>5/2</sub> orbitals, respectively. Both these peaks and their positions are characteristic of the presence of bismuth in the +3 oxidation state.<sup>1</sup> The Fe 2p orbital (shown in Fig. S3c) is split with the Fe 2p<sub>1/2</sub> peak at

724.5 eV and Fe 2p<sub>3/2</sub> peak at 711 eV, revealing the predominant presence of iron in the +3 oxidation state. The Fe<sup>3+</sup> satellite peak observed at 718.9 eV is 7.9 eV above the 2p<sub>3/2</sub> peak, which indicates the presence of pure Fe<sup>3+</sup> in the BFO sample.<sup>2</sup> The XPS spectra of the O 1s is shown in Fig.S3d. The two asymmetric peaks at 528.6 eV and 530.7 eV correspond to oxygen-metal bonds and surface adsorbed oxygen, respectively.<sup>3</sup>

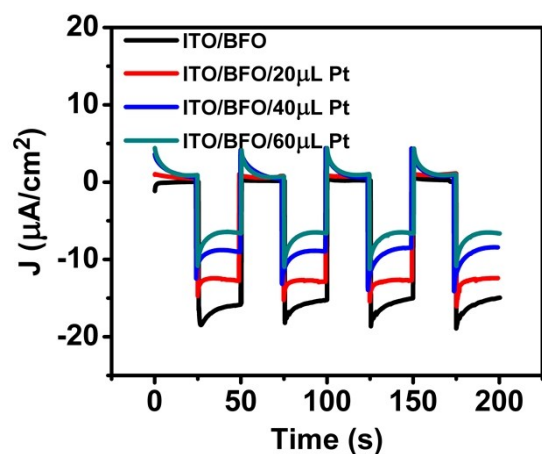


**Fig. S4** (a) UV-vis absorbance spectra of ITO/BFO (black) and ITO/BFO/carbon (red). Inset: the actual pictures of ITO/BFO (left) and ITO/BFO/carbon (right). (b) Optical band gap of the BFO film. (c) The UV-vis diffused reflection spectra of BFO film. (d) Mott-Schottky plot for the BFO film.

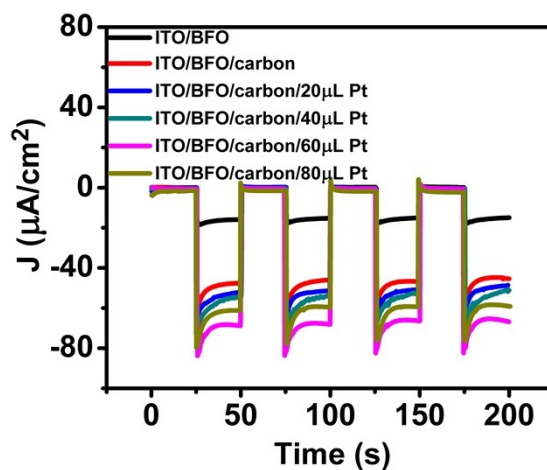
The energy band gap ( $E_g$ ) of a semiconductor could be inferred from its UV-vis spectra using the following equation:

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

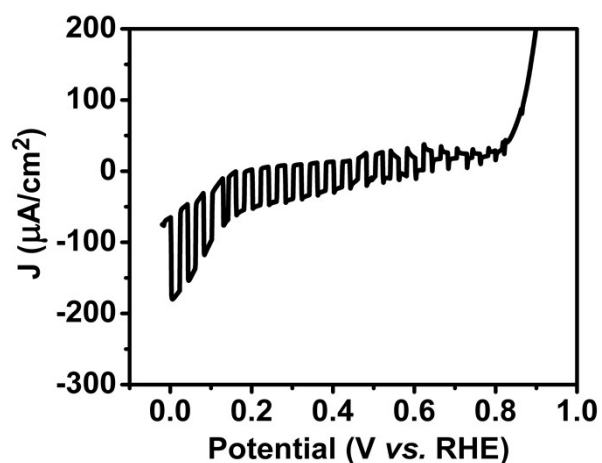
where  $\alpha$  corresponds to the absorption coefficient,  $h\nu$  is the photon energy,  $A$  is a proportionality constant related to the material, and  $n$  represents the index which depends on the electronic transition of the semiconductor (for direct band-gap semiconductors,  $n = 2$ ).<sup>4</sup> The  $E_g$  is obtained by extrapolating the linear portion of  $(\alpha h\nu)^2$  to zero, and the value is determined to be 2.32 eV for the current BFO film. In addition, the energy band gap can also be obtained from the UV-vis diffused reflection spectra in Fig. S4c, where the absorption edge is 538 nm, corresponding to a band gap of  $\sim 2.3$  eV.



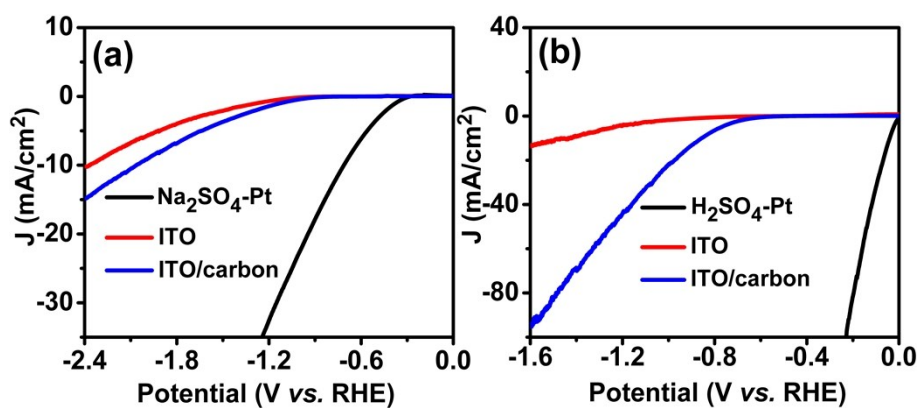
**Fig. S5** Photocurrent-time (J-T) curves at 0.6 V vs. RHE of ITO/BFO/Pt loaded with different amount of Pt.



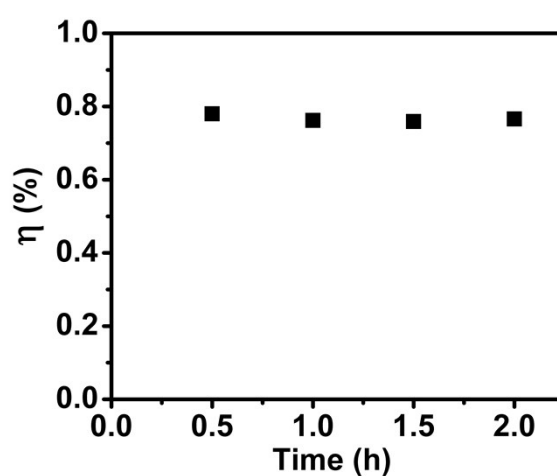
**Fig. S6** J-T curves at 0.6 V vs. RHE of ITO/BFO/carbon/Pt loaded with different amount of Pt.



**Fig. S7** J-V curve of ITO/BFO/carbon/Pt after negatively poling the BFO films. The  $J_0$  and  $V_{op}$  are about 100  $\mu\text{A}/\text{cm}^2$  and 0.8 V vs. RHE, respectively.



**Fig. S8** The electrocatalytic activity of the carbon layer deposited directly on ITO in the 0.1M Na<sub>2</sub>SO<sub>4</sub> (a) or 0.5M H<sub>2</sub>SO<sub>4</sub> (b) solution.



**Fig. S9** Faradic efficiency ( $\eta$ ) for the H<sub>2</sub> production within the 2 h continuous PEC reaction.

## Notes and references

- 1 V. S. Dharmadhikari, S. Sainkar, S. Badrinarayan and A. Goswami, *J. Electron Spectrosc. Relat. Phenom.*, 1982, **25**, 181.
- 2 T. Yamashita and P. Hayes, *Appl. Surf. Sci.*, 2008, **254**, 2441.
- 3 S. J. A. Moniz, C. S. Blackman, P. Southern, P. M. Weaver, J. W. Tang and C. J. Carmalt, *Nanoscale*, 2015, **7**, 16343.
- 4 J. Tauc, R. Grigorovici and A. Vancu, *Phys. Status Solidi B*, 1966, **15**, 627.