

## Supporting Information

### Origin of the switchable photocurrent direction in BiFeO<sub>3</sub> thin films

Yaqiong Wang, Matyas Daboczi, Man Zhang, Joe Briscoe, Ji-Seon Kim, Haixue Yan\*,

Steve Dunn\*

#### 1. Supplementary Figures

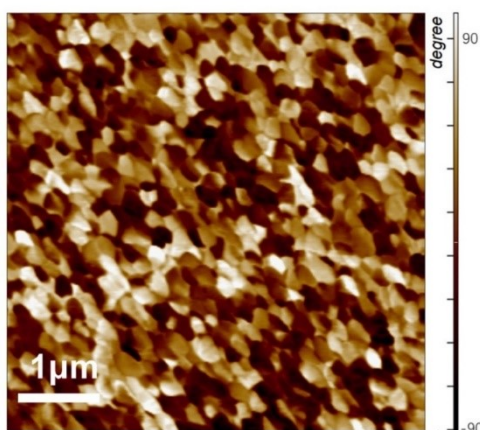


Figure S1. Phase image of BiFeO<sub>3</sub> thin film. The BiFeO<sub>3</sub> film is polycrystalline with different domains randomly oriented with no preferred polarization direction.

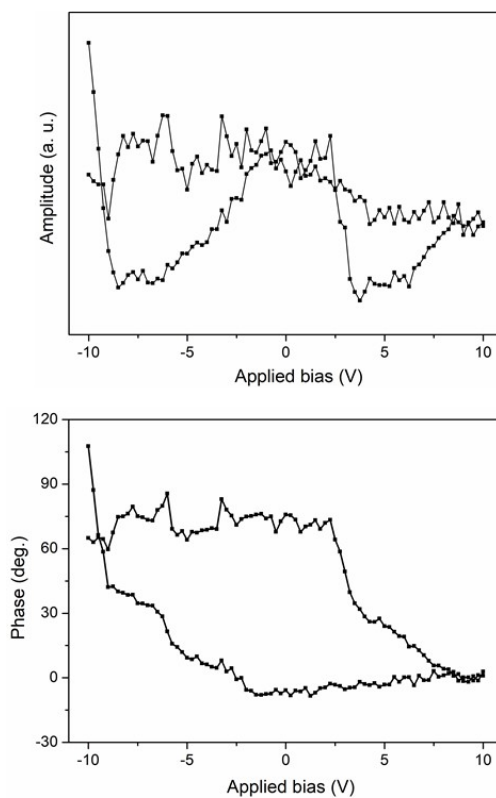


Figure S2. Local PFM hysteresis loops of the BiFeO<sub>3</sub> film: amplitude signal (top); phase signal (bottom).

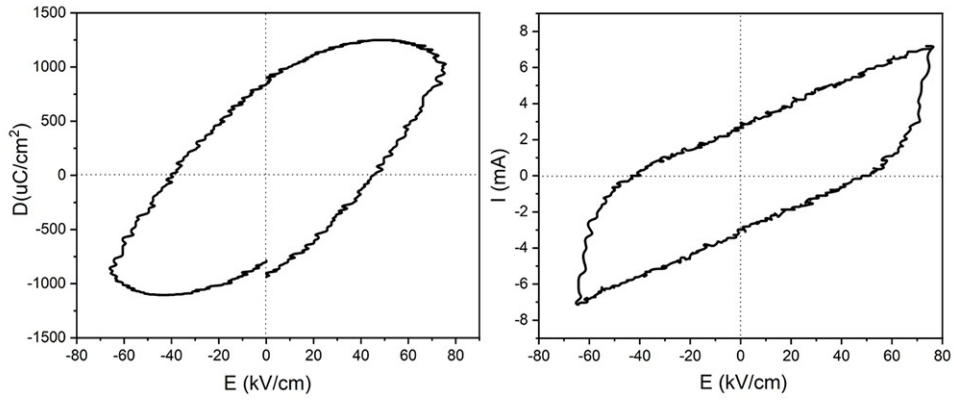


Figure S3. D-E (left) and I-E loops (right) of the as-prepared BiFeO<sub>3</sub> film.

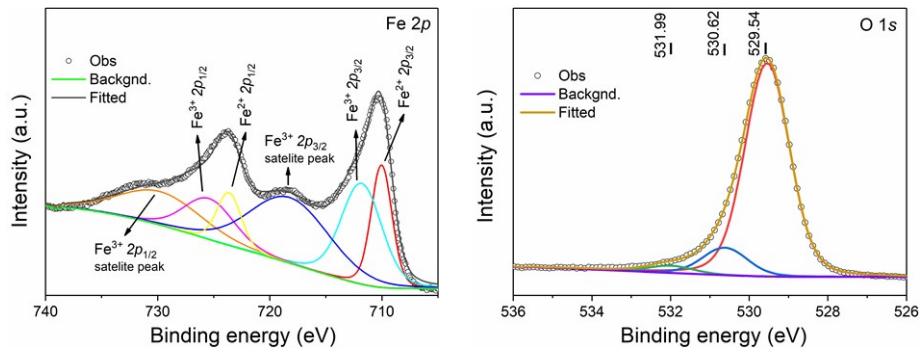


Figure S4. Fe 2p and O 1s XPS spectra of the BiFeO<sub>3</sub> films (air annealed)

Table S1. Fitted parameters for XPS spectra (Fe 2p and O 1s) of BiFeO<sub>3</sub> thin films

Sample	Fe <sup>2+</sup>		Fe <sup>3+</sup>		O <sub>L</sub>	O <sub>V</sub>
	2p <sub>3/2</sub>	2p <sub>1/2</sub>	2p <sub>3/2</sub>	2p <sub>1/2</sub>		
B.E. (eV)	709.98	723.58	711.76	725.36	529.34	530.82
Area (%)	17.45	8.72	22.76	11.38	96.14	3.86

Note: O<sub>L</sub> represents lattice oxygen, O<sub>V</sub> represents oxygen associated with vacancies

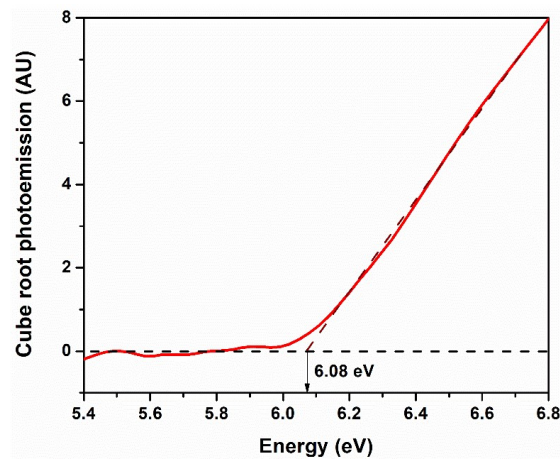


Figure S5. UV-APS data of BiFeO<sub>3</sub>, showing valence band maximum of - 6.08 eV.

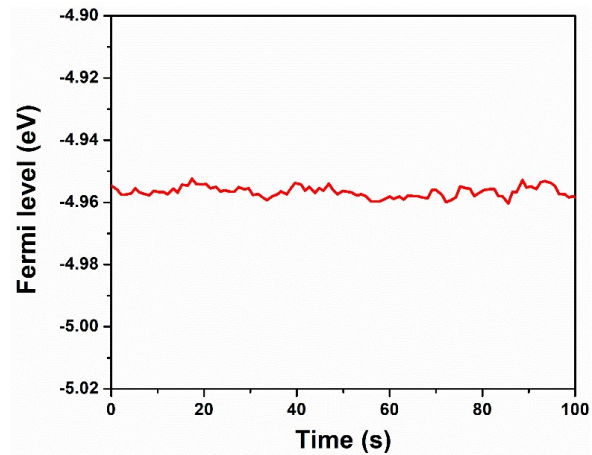


Figure S6. Fermi energy level of BiFeO<sub>3</sub> measured by Kelvin probe at - 4.96 eV, showing a stable value over 100 s measured.

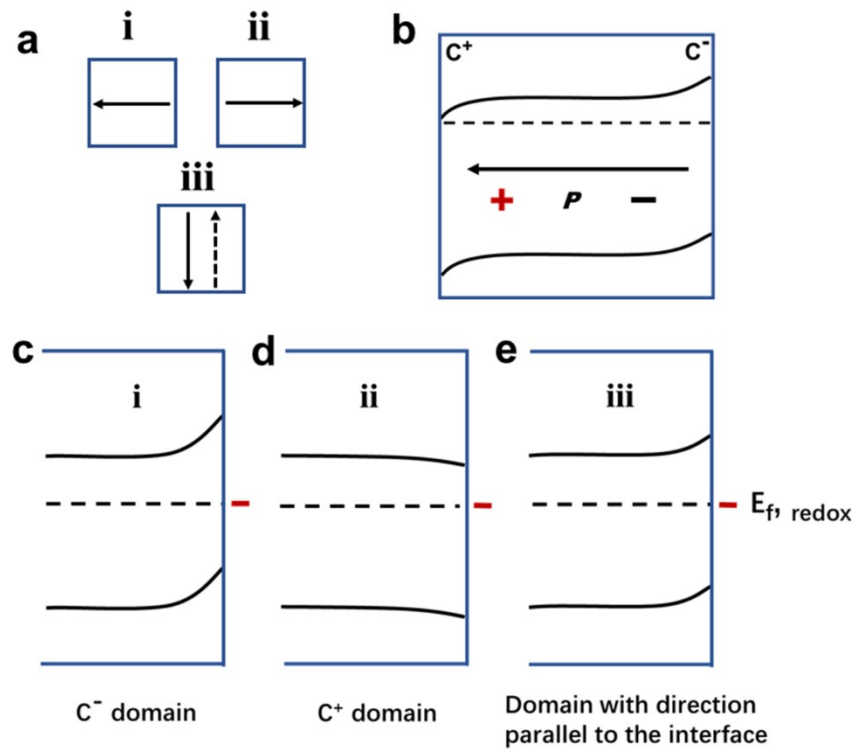


Figure S7. Schematic of (a) Domains at the surface of the film, with different dipole directions. i, ii, iii represent domains with dipole directions pointing against, to or parallel the film surface, respectively. (b) Dipole and the associated band bending within one domain.  $P$  is the dipole or the spontaneous polarization vector. The dipole produces positive charges on the surface following the  $P$  direction ( $C^+$  domain) and negative charges on the surface against the dipole direction ( $C^-$  domain). Free electrons accumulate on the  $C^+$  surface and lead to downward band bending while holes accumulate on the  $C^-$  surface and lead to upward band bending. (c) When in contact with the electrolyte, the upward band bending of  $C^-$  domain will increase. (d) the downward band bending of  $C^+$  domain will be reduced. (e) domain with polarization direction parallel to the

interface will have upward band bending as a general semiconductor.

## 2. Supplementary Methods

BiFeO<sub>3</sub> thin films were deposited on fluorine doped tin oxide coated float glass (FTO, Tec 15 Pilkington) by chemical solution deposition.<sup>1</sup> The FTO glass was cut to a size of 1 cm\*1.5 cm and cleaned by sonication in acetone. The precursor solution was prepared by dissolving 0.73 g bismuth nitrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, ≥ 98%, Sigma-Aldrich, UK) and 0.61 g iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, ≥ 98%, Sigma-Aldrich, UK) in 4 ml 2-methoxyethanol (C<sub>3</sub>H<sub>8</sub>O<sub>2</sub>, 2-MOE, 99.8%, SigmaAldrich, UK) and 2 ml acetic anhydride (C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>, ≥ 99%, Sigma-Aldrich, UK). The solution was spin-coated onto FTO substrate at 3000 rpm for 30 s, followed by drying at 90 °C for 1 min and pyrolysed at 350 °C for 5 min on a hotplate. The deposition procedure was repeated 5 times with a film thickness of ~150 nm achieved. The samples were then transferred to a tube furnace and held at 450 °C for 30 min and then heated up to 650 °C with a ramp rate of 5 °C/min and held for 1 h. The annealing procedure was conducted under ambient atmosphere.

X-ray diffraction (XRD) patterns of the films were obtained by a Panalytical Xpert Pro diffractometer using Cu Ka radiation. The surface morphology of the films was observed using a scanning electron microscope (SEM, FEI Inspect F). X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Fisher Nexsa X-ray photoelectron spectrometer. Peaks were calibrated to the C1s peak at 284.8 eV. Spectra of three points located in different area of the BiFeO<sub>3</sub> film were collected for XPS.

The ferroelectric property was characterized by piezoelectric force microscopy (PFM) using a commercial scanning probe microscopy (NT-MDT Nova). Conductive Pt coated silicon cantilevers (HQ:NSC35/Pt, MikroMasch, US) were used for PFM measurement. PFM was performed at 55 kHz with ac voltage of 2 V amplitude. For electrical measurements, Au electrodes are deposited on the BiFeO<sub>3</sub> film surface with shadow masks by using magnetron sputtering. The optical absorption of the BiFeO<sub>3</sub>

films was measured using a Perkin Elmer Lambda 950 UV-Vis spectrophotometer. The band gap ( $E_g$ ) of the BiFeO<sub>3</sub> film was calculated using the following equation:<sup>2</sup>

$$(ahv)^n = A(hv - E_g) \quad (1)$$

where  $a$  is the absorbance coefficient,  $hv$  is the light energy and  $A$  is a constant.  $n$  is 0.5 and 2 for indirect bandgap and direct bandgap materials, respectively. The energy levels of BiFeO<sub>3</sub> were measured using an APS04 system (KP Technology). The work function of the sample was calculated by measuring the contact potential difference between a gold-alloy tip and the grounded sample. The work function of the tip was measured on the same day using a silver reference. Ambient photoemission spectroscopy was performed by illuminating the sample with UV light within the excitation energy range of 4.0-7.0 eV. Data of one point was collected. The cube root of the photoemission signal was fitted linearly and extrapolated to zero in order to obtain the valance band maximum of the semiconductor sample.

The PEC measurements were conducted using a three-electrode cell with a potentiostat (Gamry Potentiostat Interface 1000). A Ag/AgCl electrode and a glassy carbon rod were used as reference and counter electrode, respectively. The three-electrode cell was home-made, which consists of two parts: a metal plate to attach the sample and a Teflon chamber for the electrolyte solution. The BiFeO<sub>3</sub> sample was attached onto the metal plate with the film side facing upside. A small hole (0.125 cm<sup>2</sup>) was designed on the metal plate to let the light in, which is the actual working area of the sample. The same-sized hole was designed on the chamber as well for the electrolyte to touch the sample. A rubber O-ring was placed into the chamber hole to prevent electrolyte leakage. The metal plate was fixed to the chamber by two screws. The cell was clamped to a retort stand and placed with the metal side facing the solar simulator. All PEC measurements were conducted under back illumination in this study. The electrolyte was 0.2 M Na<sub>2</sub>SO<sub>4</sub> or 0.2 M Na<sub>2</sub>SO<sub>4</sub> with 0.5 M H<sub>2</sub>O<sub>2</sub> in deionized water. The Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> solutions were used within a few hours of their preparation. A solar simulator

(Sciencetech, Class: ABA) with an AM 1.5 filter was used for illumination of the measurements.

The reported potentials were converted to the normal hydrogen electrode (NHE) scale using the Nernst equation:

$$E_{\text{NHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl}}^0 \quad (2)$$

where  $E_{\text{Ag/AgCl}}^0$  (3.0 M KCl) = 0.209 V at 25 °C.

- 1 Q. Zhang, N. Valanoor, O. Standard, *J. Appl. Phys.* 2014, **116**, 066810.
- 2 J. Tauc, R. Grigorovici, A. Vancu, *physica status solidi (b)* 1966, **15**, 627.