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Enhancement of photoelectrochemical performance in ferroelectric films via the introduction of Au buffer layer

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Abstract: The inefficient separation of photogenerated carriers has become a serious problem that limits the photoelectrochemical (PEC) performance of semiconductors. Herein, a sol-gel method was used to prepare $BiFeO_3$ ferroelectric thin films with FTO and FTO/Au as substrates, respectively. The polarization electric field of the ferroelectric can more effectively separate the carriers generated in the photoelectrode. Meanwhile, the introduction of an Au buffer layer can reduce the resistance in the process of charge transfer, accelerate the carrier migration, and enhance the efficiency of the charge separation. Under light irradiation, Au/$BiFeO_3$ photoelectrode exhibited an extraordinary improvement in PEC water splitting compared with $BiFeO_3$. In addition, the ferroelectric polarization electric field causes band bending, which further accelerates the separation of electrons and holes and improves the PEC performance of the photoelectrode. This work promotes the effective application of ferroelectric films in PEC water splitting.

Key words: photoelectrochemical; $BiFeO_3$; ferroelectric films; charge separation

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SUPPORTING INFORMATION

Experimental details

Fabrication of BFO sol: The precursor solution was prepared by dissolving $Bi(NO_3)_3{\cdot}5H_2O$ (0.2 M) and $Fe(NO_3)_3{\cdot}9H_2O$ (0.2 M) in ethylene glycol methyl ether, Stir for 5 min. Citric acid monohydrate (0.4 M) was added sequentially as the chelating agent while the solution was stirred continuously for approximately 1 h. Place the prepared solution in dry air for 5 days.

Au buffer layer deposition: The Au buffer layer was fabricated on FTO substrates by DC sputtering using an Au target for 10 s (0.7 Pa Ar pressure, 20 W, room temperature).

BFO thin film deposition: BFO sol was dropped on the FTO/Au substrate and spun at 3000 rpm for 25 s in a spin coater. The spinning was repeated 7 times with baking at 200 °C for 3 min and annealing at 580 °C for 6 min between spins. Finally, we annealed in air at 580 °C for 120 min to achieve better crystallinity. For comparison, the BFO films were deposited on the FTO glass using the same procedure.

PEC measurements: The PEC performance of BFO was measured in 0.1 M Na_2SO_4 aqueous solution at PH 7, a 350 W Xe lamp and a radiometer (PM100USB, Thorlabs) were used to calibrate the light power intensity at the sample positions to simulate AM 1.5 illumination. The linear sweep voltammograms (LSVs) measurements were swept from negative to positive at a scan rate of 4 mV/s and the transient photocurrent (*I*–*t*) measures were performed at –0.4 V vs Ag/AgCl, chopper illumination interval is 5 s. The electrochemical impedance spectrum was measured with a scan rate of 5 mV/s under dark conditions.

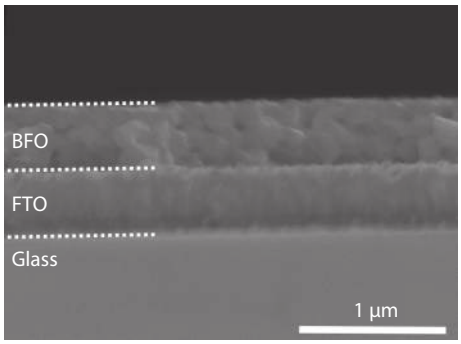

Fig. S1. SEM cross-sectional image of FTO/Au/BFO.

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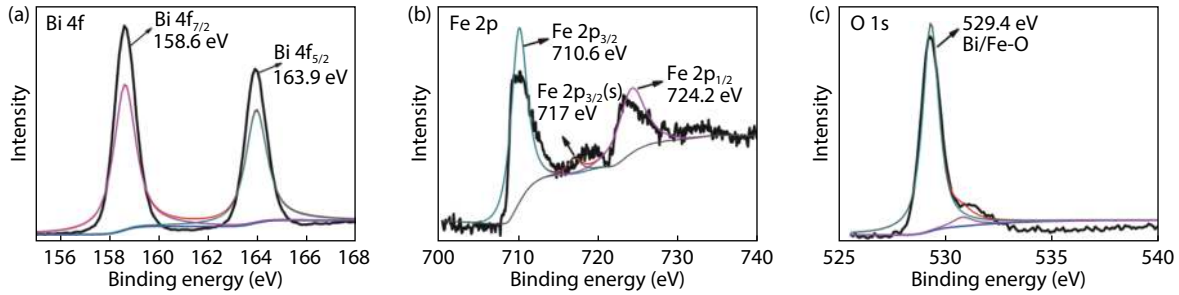

Fig. S2. XPS spectra of (a) Bi 4f, (b) Fe 2p and (c) O 1s.

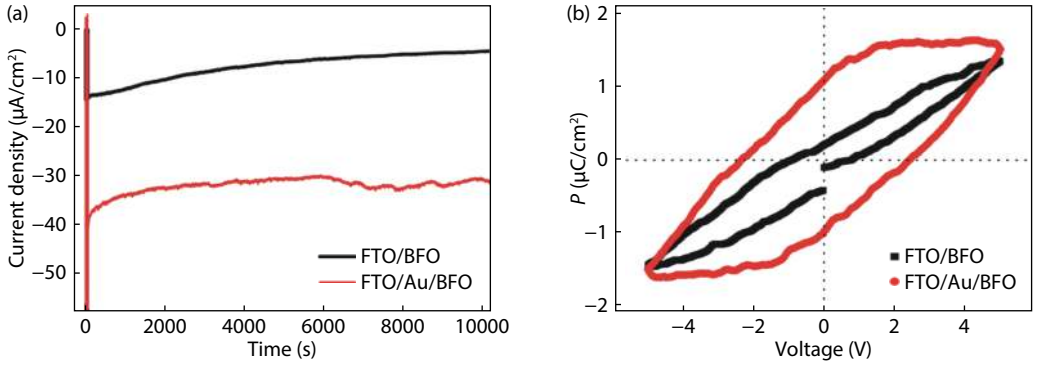

Fig. S3. (a) The stability of BFO and Au/BFO under illumination for 10000 s. (b) *P*–*E* hysteresis loop curves of BFO and Au/BFO.