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Breaking through the interfacial energy barrier limitations of the type-I heterojunctions via ferroelectric polarization engineering: A case study of $Bi_5Ti_3FeO_{15}$/BiOCl

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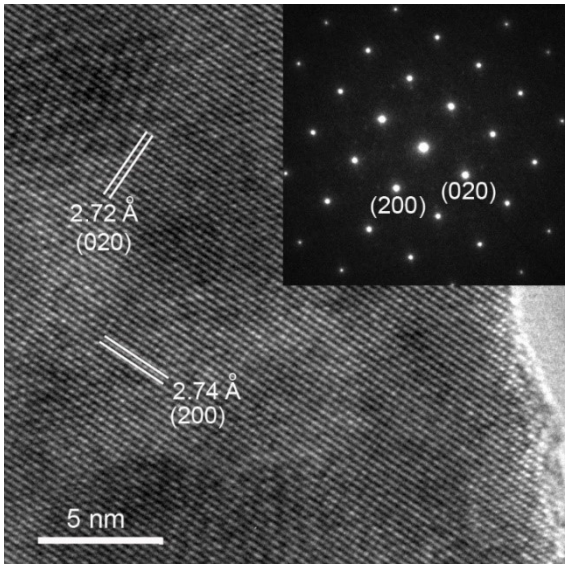

Figure S1 HRTEM image of BTF. The inset is the corresponding SAED pattern of the <001> zone axis.

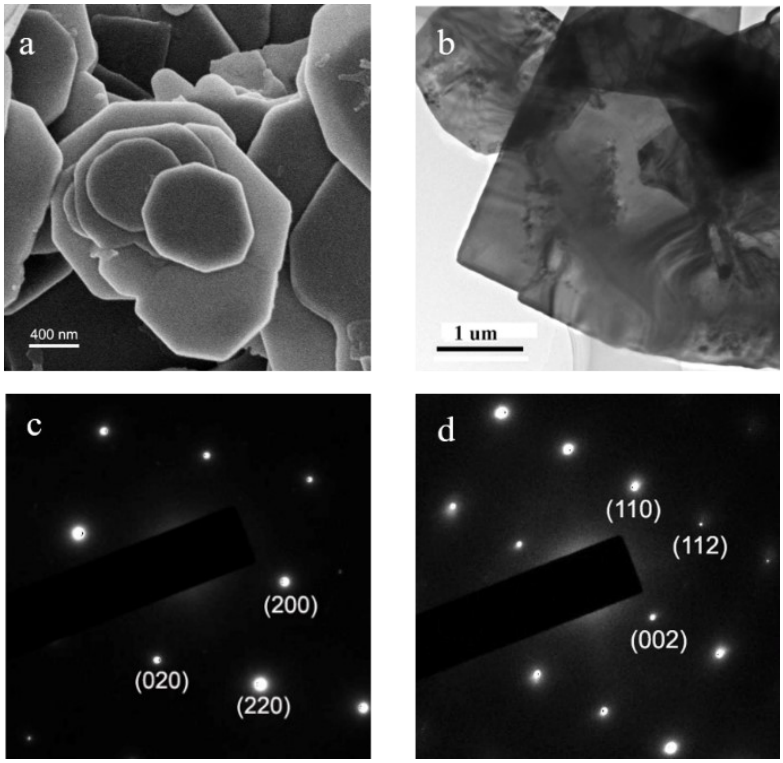

Figure S2 SEM (a), TEM (b) and SAED (c, d) images of BTF/BOC reacting for 22 h

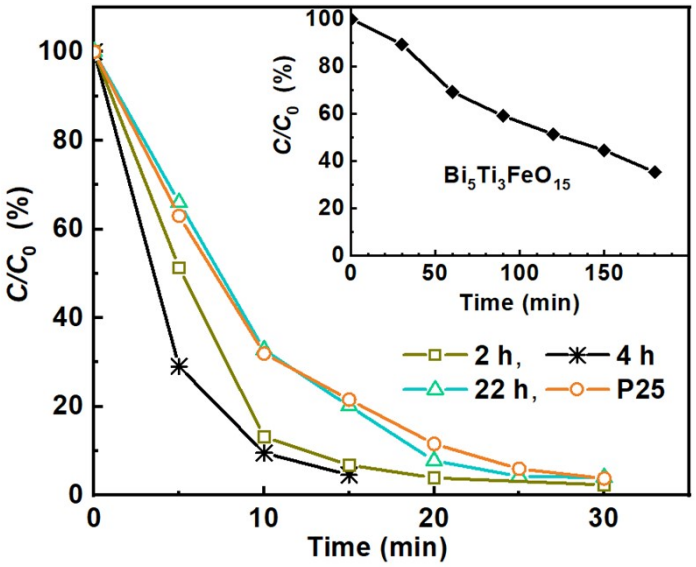

Figure S3 Degradation rate of RhB with BTF/BOC obtained by reacting in HCl solution for different time under simulated solar light irradiation

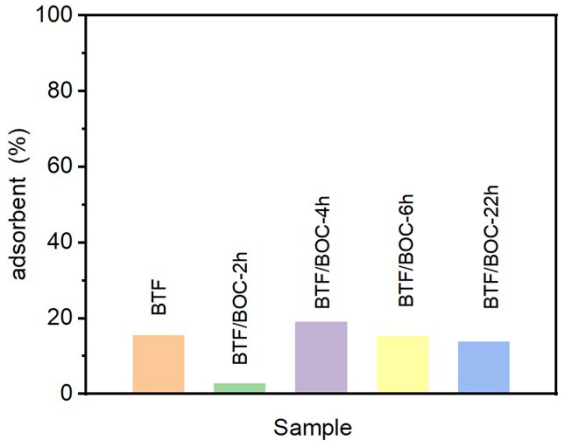

Figure S4 Adsorption capacity chart for the samples

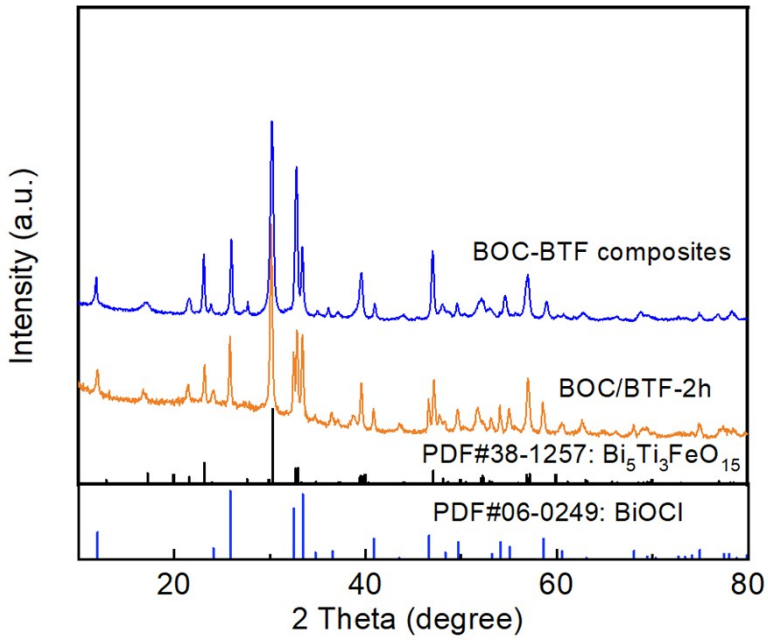

Figure S5 XRD patterns of BTF-BOC composite comparing with BTF/BOC-2h

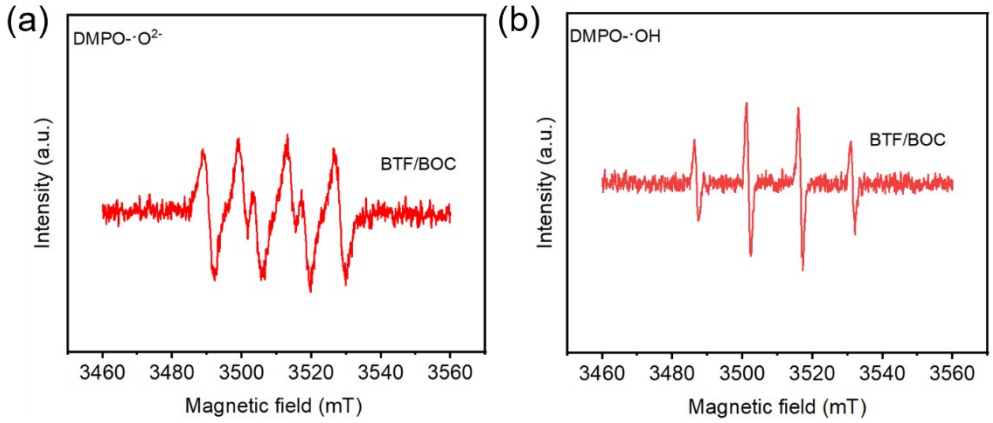

Figure S6 EPR signals of a) DMPO-$\cdot O^{2-}$ and b) DMPO-$\cdot$OH under visible light

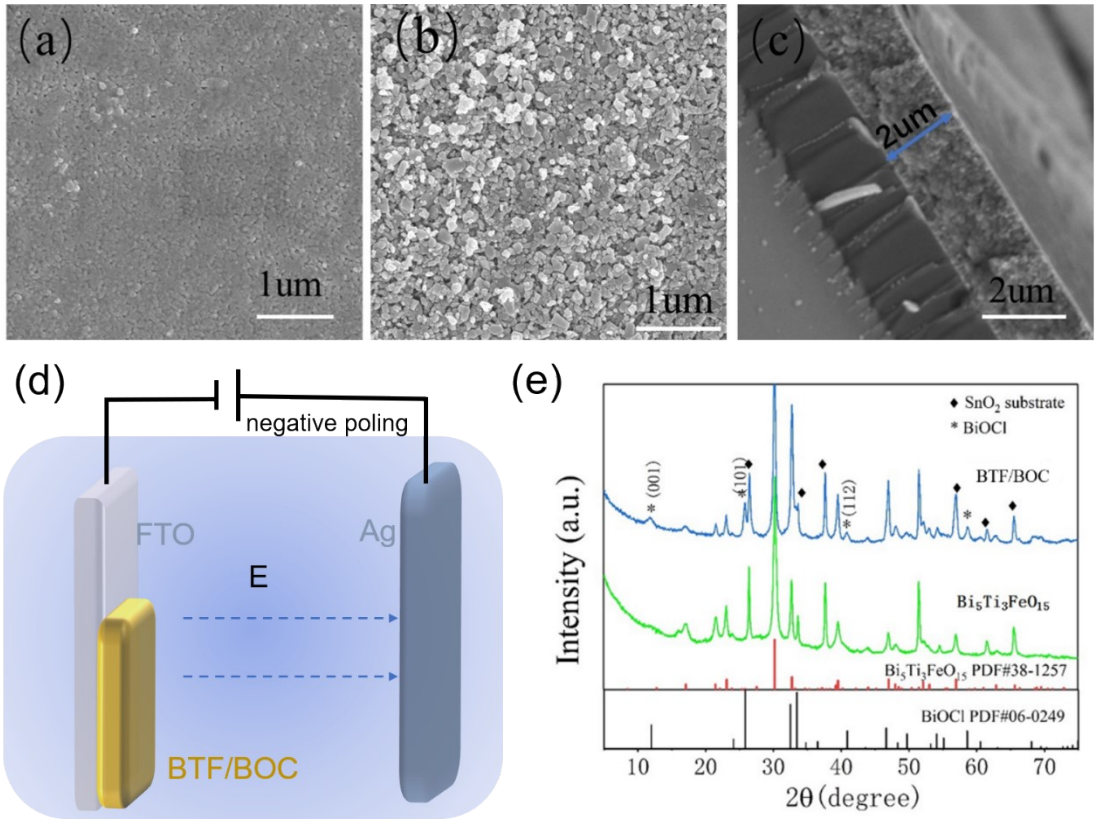

Figure S7 SEM images of (a) surface morphology and (b) cross-section view of BTF films, and (c) surface morphology of BTF/BOC films; (d) the schematic diagram of polarization; (e) XRD pattern of BTF/BOC films

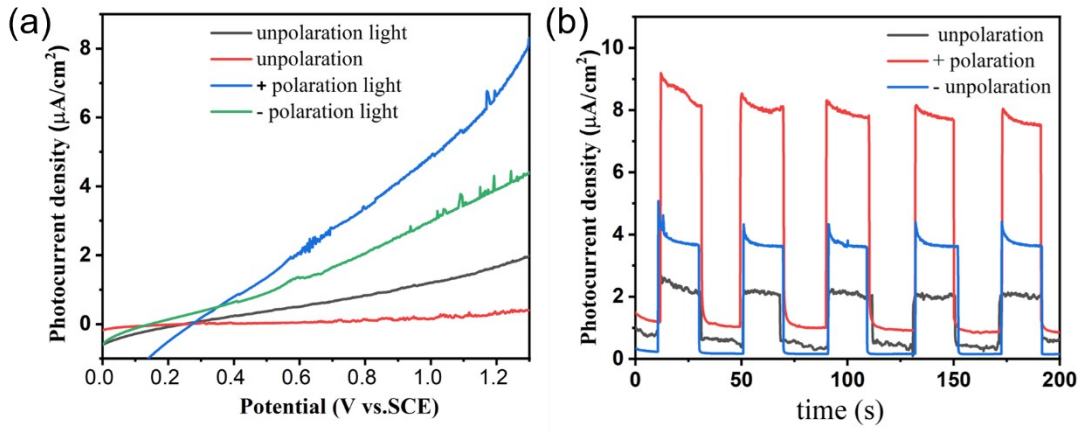

Figure S8 LSV curves (a) and photocurrent responses (b) of BTF

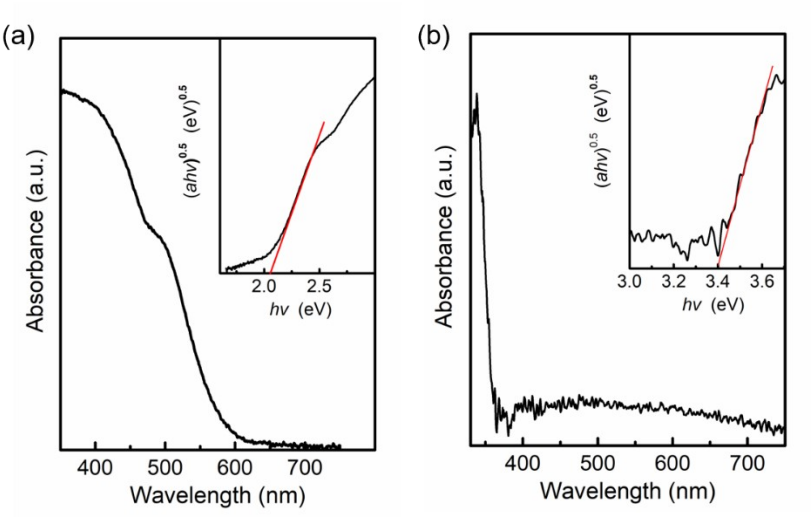

Figure S9 UV-vis absorption spectra of BTF (a) and BOC (b)

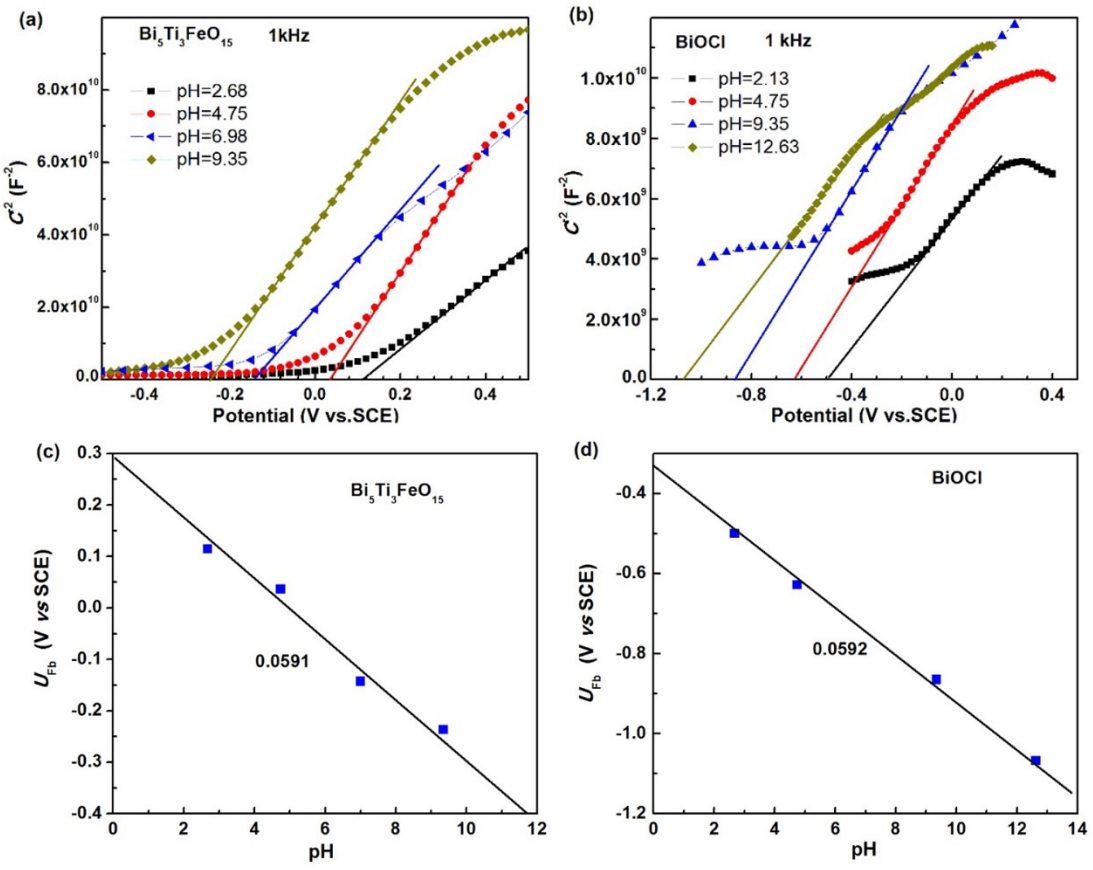

Figure S10 Mott-Schottky (M-S) plots of BTF (a) and BOC (b) in 0.5M Na_2SO_4 aqueous solution; pH dependent plot of V_{fb} for BTF (c) and BOC (d)

Methods

Preparation of BTF films and BTF/BOC films

$Bi_5Ti_3FeO_{15}$ films were prepared by a sol-gel route. The proper proportion of bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$] (5 mol% excess to compensate for the volatilization of Bi) and iron nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] were dissolved in glacial acetic acid. After dissolving, a certain quantity of acetylacetone ($CH_3COCH_2COCH_3$) was added to stabilize the solution, and was subsequently stirred for 30 min at about 65 ℃. After naturally cooling to room temperature, the certain quality of tetrabutyl titanate [$Ti(C_4H_9O)_4$] was mixed with the prepared solution. Finally, the mixed solution was stirred for about 30 min to form 0.5 M $Bi_5Ti_3FeO_{15}$ precursor. The BTF precursors were spin-coated on FTO substrates at a spinning rate of 3000 rpm for 40s. Subsequently, the wet gel films were dried at 100℃ for 20 min, pyrolyzed at 400 ℃ for 10 min, and finally annealed at 600 ℃ for 30 min to be crystallized. The steps were repeated several times to obtain about 2 μm thick BTF films. To obtain the polarized BTF films, an external electric field was mounted during the sintering. The BTF/BOC films were obtained by treating the BTF films in 1 M HCl aqueous solution for 10 min.

Characterization

The structure and morphology of the prepared samples were characterized by X-ray diffraction (XRD, Cu-Kα, X'pert Pro, PANalytical B. V., Almelo, Netherlands), scanning electron microscopy (SEM, HITACHI S-3500N, Japan) and transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-TWIN).

To build up the energy band structure of the BTF/BOC heterojunctions, UV-Vis diffusion reflectance spectra (UV-Vis DRS) of the samples were measured to determine the bandgap (E_g) of BOC and BTF nanosheets by an UV-vis spectrophotometer (HITACHI U-3310, Hitachi Co., JPN) with an integrating sphere assembly, using $BaSO_4$ as the reflectance sample. The valence band edges of the samples were measured by X-ray photoelectron spectroscopy (XPS, Al-Kα source, PHI QUANTERA-II SXM, Ulvac-PHI, INC, Japan). The flat band energies (V_{fb}) of BOC and BTF in aqueous solution *vs.* pH were electrochemically determined through Mott–Schottky measurement at 1 kHz using a three-electrode electrochemical cell by an electrochemical workstation (Zahner, China).

Tests of photocatalytic Activity

Photocatalytic activity of the obtained BTF/BOC nanosheets was evaluated by the degradation of RhB in aqueous solution at room temperature. A 300 W Xe lamp (CHF-XM300, Beijing Trusttech Technology Co., Ltd) was used as simulated solar light source with 300 nm cutoff filter. The 390 nm cutoff filter was adopted to supply visible light, and several bandpass filters (450 nm, 550 nm, 650 nm) were selected to investigate the photocatalytic response of materials to specific wavelengths. In each experiment, 0.05g prepared photocatalytic samples were dispersed into 100 ml of RhB solution (0.01mmol/L). Prior to irradiation, the suspensions were stirred for 30 min to establish the absorption/desorption equilibrium. Then the suspensions were irradiated for different periods of time under the xenon lamp. After a period, a 4 mL suspension was sampled and centrifuged to remove photocatalysts. Finally, the adsorption

spectrum of the centrifugated solution was recorded with the Hitachi U-3310 UV-vis spectrophotometer.

To determine the effect of ferroelectric polarization on the photocatalytic activity of BTF/BOC heterojunctions, photoelectrochemical (PEC) measurements of polarized and unpolarized BTF/BOC films were carried out by a three-electrode electrochemical cell with a Pt counter electrode, a saturated calomel electrode (SCE) as reference electrode and the as-fabricated films as photoanode. The electrolyte is a 0.5 M Na_2SO_4 (pH=7) aqueous solution which was bubbled with nitrogen for 30 min before measurements.