

# **Built-in Electric Field for Photocatalytic Overall Water Splitting**

## **through a TiO<sub>2</sub>/BiOBr P-N Heterojunction**

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### **Supporting Information**

### **Experimental Section:**

Chemicals: amorphous titanium dioxide (P25), sodium hydroxide (NaOH), hydrochloric acid (HCl), bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), mannitol, potassium bromide (KBr), and anhydrous ethanol (EtOH) were obtained from Sinopharm Chemical Reagent Co. Ltd., China. All the chemicals were used without further purification. Deionized water was used in the whole experimental process.

### **Characterizations:**

X-ray diffraction (XRD) patterns of the samples were recorded by a D8 Advance system equipped with Cu-K $\alpha$  radiation, operating at 40 kV and 40 Ma, at a scan rate of 5° minute<sup>-1</sup>. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy with an energy dispersive X-ray (STEM-EDX) experiments were performed on a JED-2300T transmission electron microscope with a field emission gun operated at 200 kV. Raman spectroscopic analysis was performed by using a micro-Raman system (Horiba) with an Ar ion laser 488 nm, and a probing laser 50 W cm<sup>-2</sup> was guided during the illumination. X-ray photoelectron spectroscopy (XPS) examination was employed to identify the chemical states of the surface compositions in a Thermo Kalpha system equipped with monochromatic Al K $\alpha$  X-rays.

The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were scanned using a spectrometer (CARY 300/PE lambda 750S) with BaSO<sub>4</sub> as the reference sample. Fourier transform infrared (FT-IR) spectra were conducted using a Thermoelectric Nikol Is5 type spectrometer, and the KBr was served as a reference sample. Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption measurements were determined by Quadrasorb SI surface area and pore size analyzer. The room-temperature photoluminescence (PL) spectra were measured

on a fluorescence spectrometer (JY HORIBA FluoroLog-3) equipped with a Xe lamp (300 W) as excitation source at the wavelength of 320 nm. Zeta potential was measured by Zeta potential analyzer (Zetasizer nano). The atomic force microscopy (AFM) and surface potential were obtained by Bruker Dimension Edge system with Kelvin Probe. The surface photovoltage measurements (SPV) were measured by an instrument assembled with a photovoltaic cell (CEL-SPS1000).

#### **Photoelectrochemical measurements:**

1.0 mg as-prepared sample was dispersed in 1 mL ethanol, and then it was uniformly spin-dropped onto a 1 cm×1 cm FTO glass substrate by a spin coater (VTC-50A, China).

Subsequently, the glass was heated at 60 °C in a vacuum oven for 10 hours.

The electrochemical impedance spectra (EIS) and transient photocurrent-time curves were measured on an electrochemical workstation (PGSTAT128N, Metrohm AG) and carried out in a three-electrode system with a working electrode at a frequency of 1kHz, Ag/AgCl (saturated KCl) as reference electrode, and Pt foil as the counter electrode. 0.1 M K<sub>2</sub>SO<sub>4</sub> was used as the electrolyte solution. A 300 W Xe lamp (China Education AU-light Company Limited, Beijing) was used as the light source, and the intensity was 100 mW cm<sup>-2</sup>.

#### **Photocatalytic reaction:**

Photocatalytic overall water splitting reactions were carried out in a side-irradiation vessel connected to a glass gas-circulation system. It was performed in CEL-PAEM-D6 online system (China Education AU-light Company Limited, Beijing) under different light irradiation, respectively. A 300 W Xe lamp (CEL-HXF100) was used as incident light source to trigger the photocatalytic reaction, and the intensity was 100 mW cm<sup>-2</sup>. In a typical photocatalytic overall water splitting reaction, 50 mg of the prepared samples was dispersed in of deionized water (50

mL) under constant magnetic stirring and top-irradiation. After the completely removing air from the reaction slurry by evacuation, the reaction system was irradiated for one hour. During irradiation, the collected gas was analyzed by A GC-7920 gas chromatograph equipped with a thermal conductivity detector and a 5 Å molecular sieve column, and N<sub>2</sub> as carrier gas. The pressure of the system was nearly to the vacuum environment, the starting relative vacuum degree was -0.1 MPa and its absolute vacuum degree  $< 4 \times 10^{-4}$  MPa.

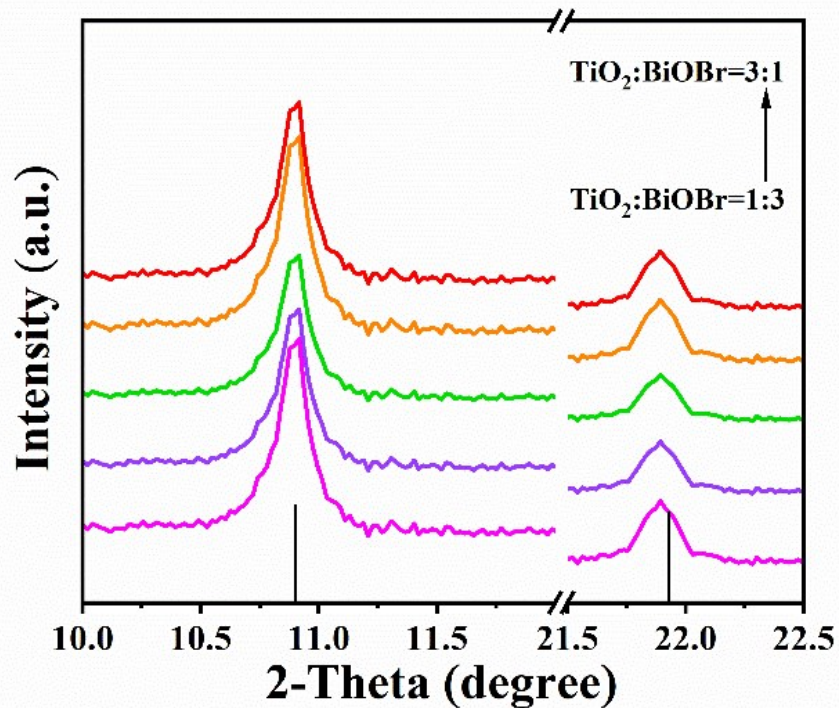


Fig. S1 XRD patterns of the as-obtained samples with different ratios of  $\text{TiO}_2$  to  $\text{BiOBr}$  through selective amplification.

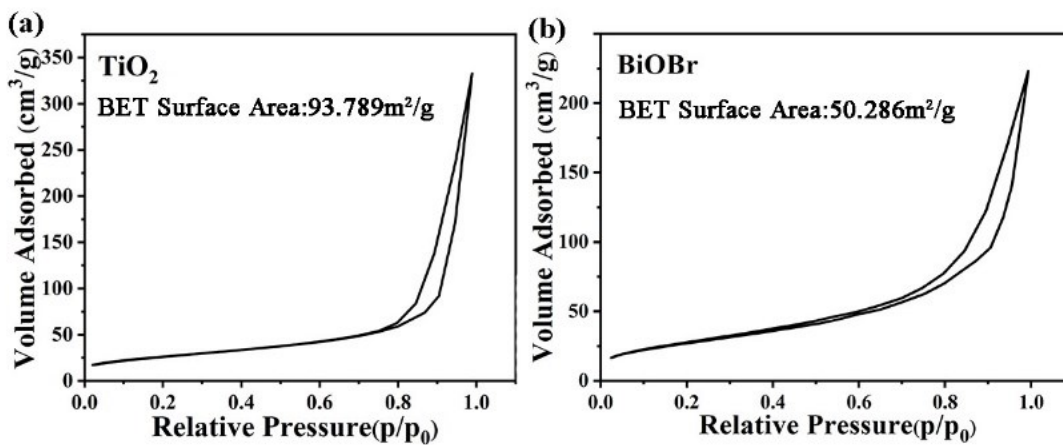
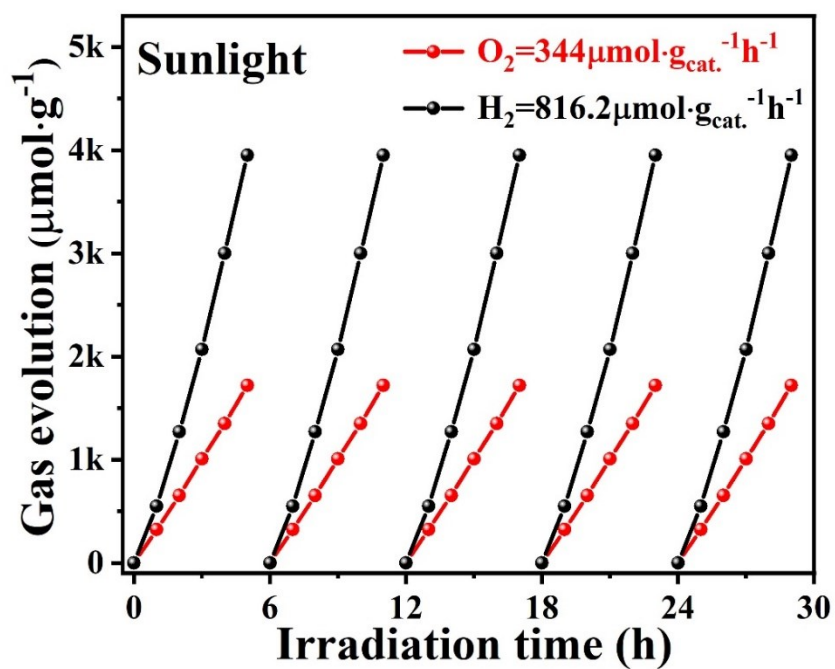
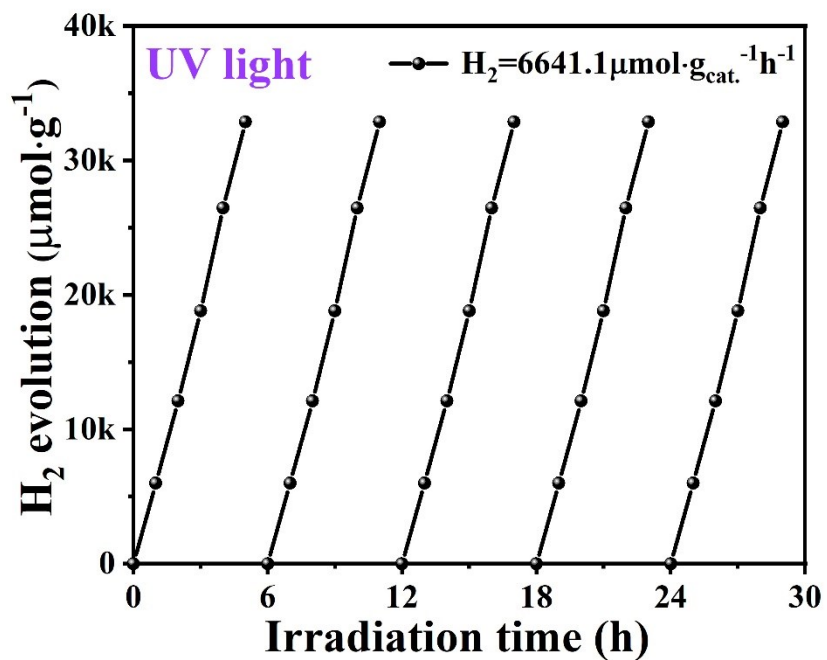


Fig. S2 Nitrogen adsorption-desorption isotherms of (a)  $\text{TiO}_2$  and (b)  $\text{BiOBr}$ .



**Fig. S3** Simulated sunlight driven photocatalytic water splitting for  $\text{H}_2$  and  $\text{O}_2$  evolution of  $\text{TiO}_2/\text{BiOBr}$  (3:1).



**Fig. S4** UV light driven photocatalytic water splitting with  $\text{H}_2\text{PtCl}_2$  for  $\text{H}_2$  evolution of  $\text{TiO}_2/\text{BiOBr}$  (3:1).

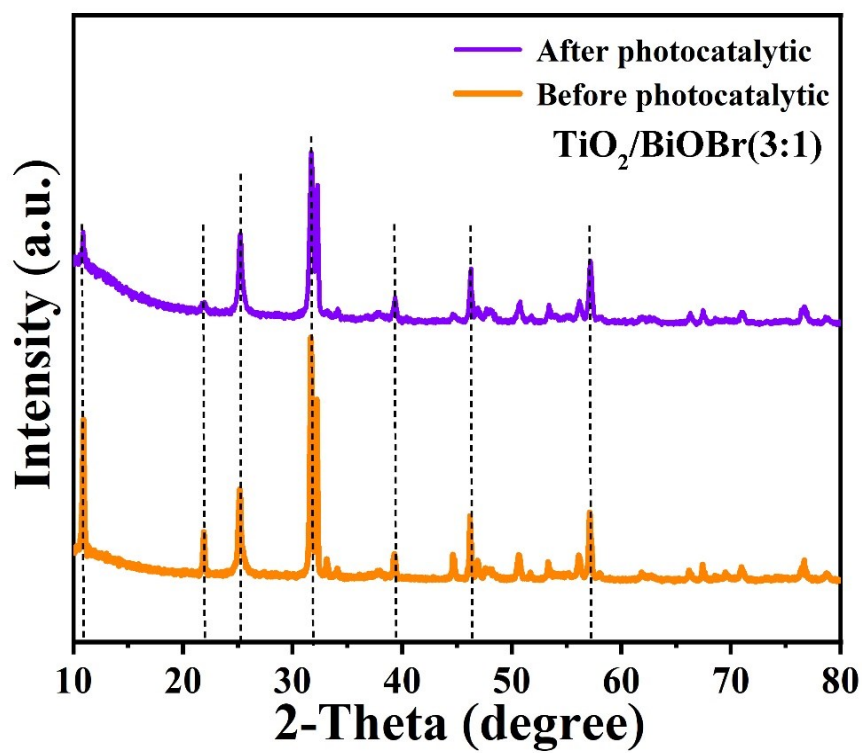


Fig. S5 XRD patterns of  $\text{TiO}_2/\text{BiOBr}$  (3:1) before and after photocatalysis.

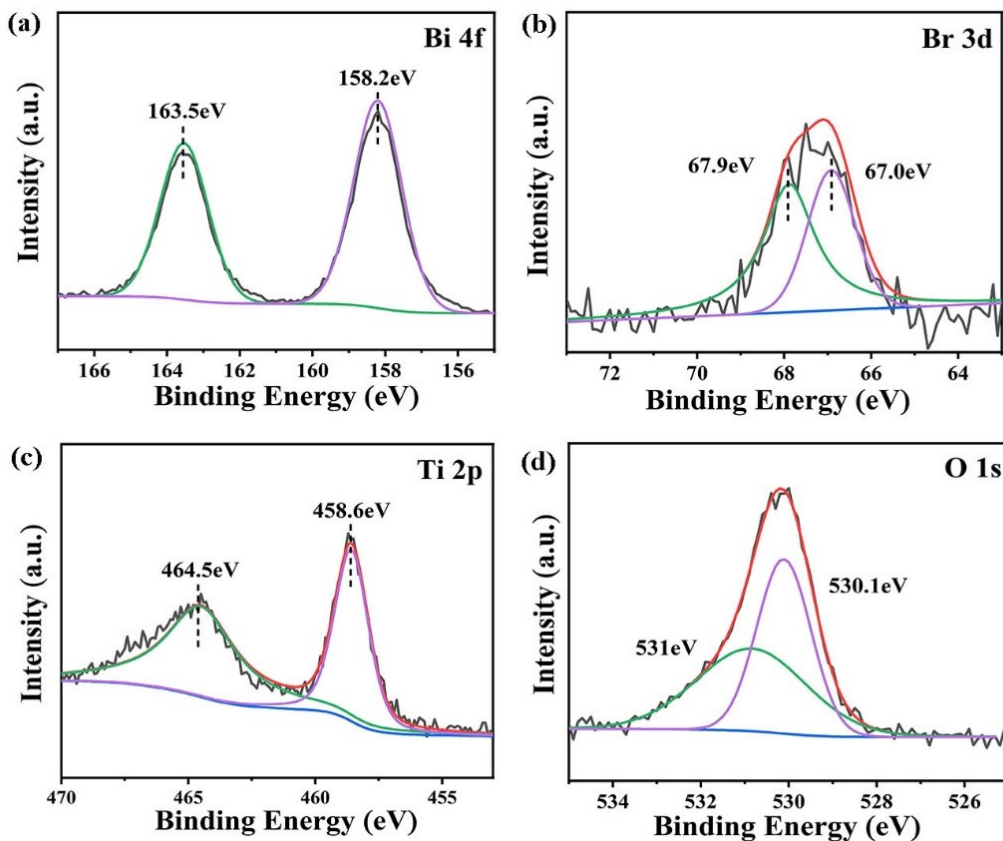


Fig. S6 XPS spectra of  $\text{TiO}_2/\text{BiOBr}$  (3:1) after photocatalysis.

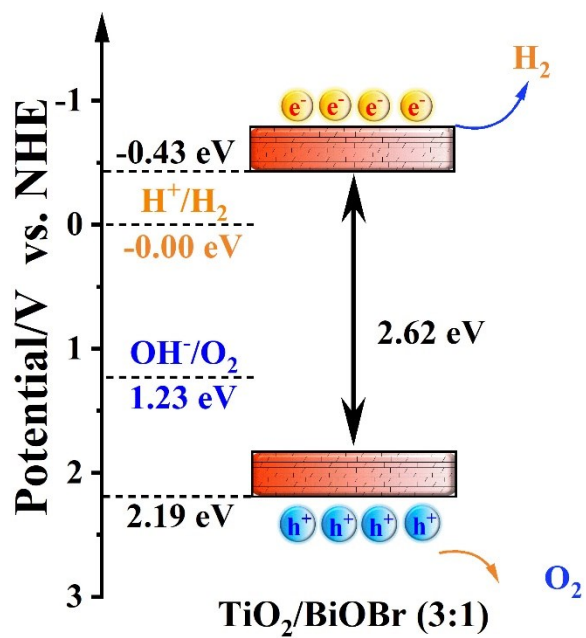
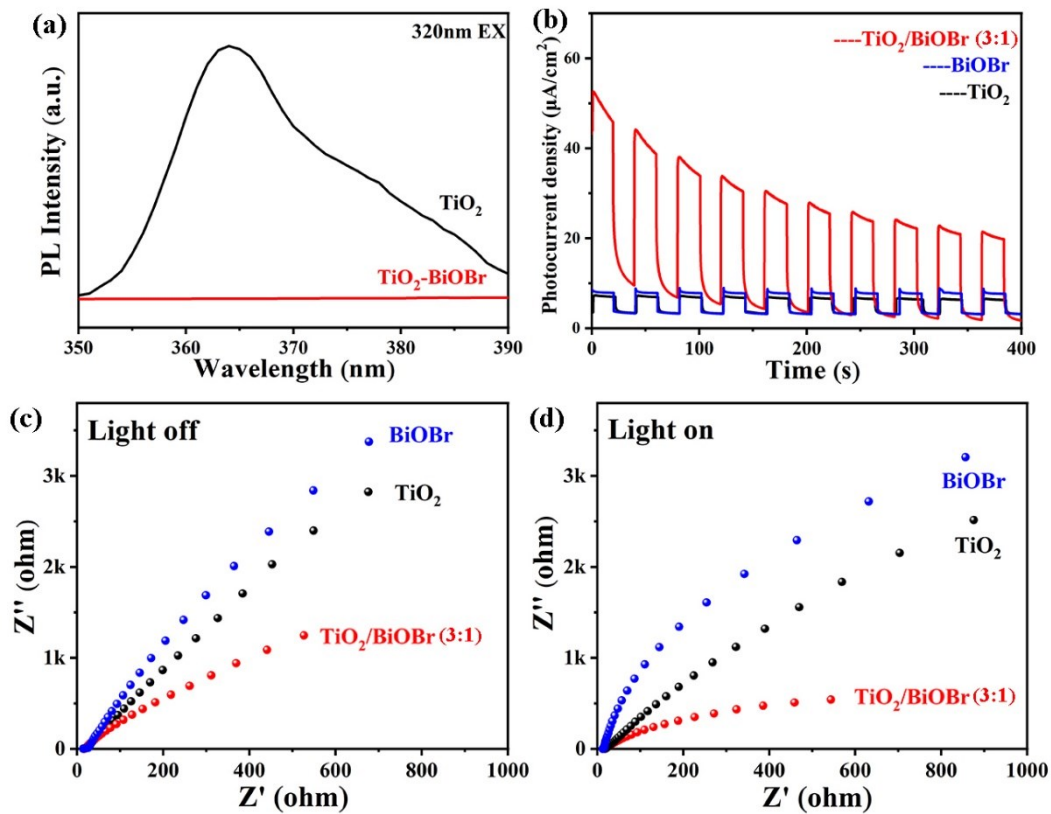
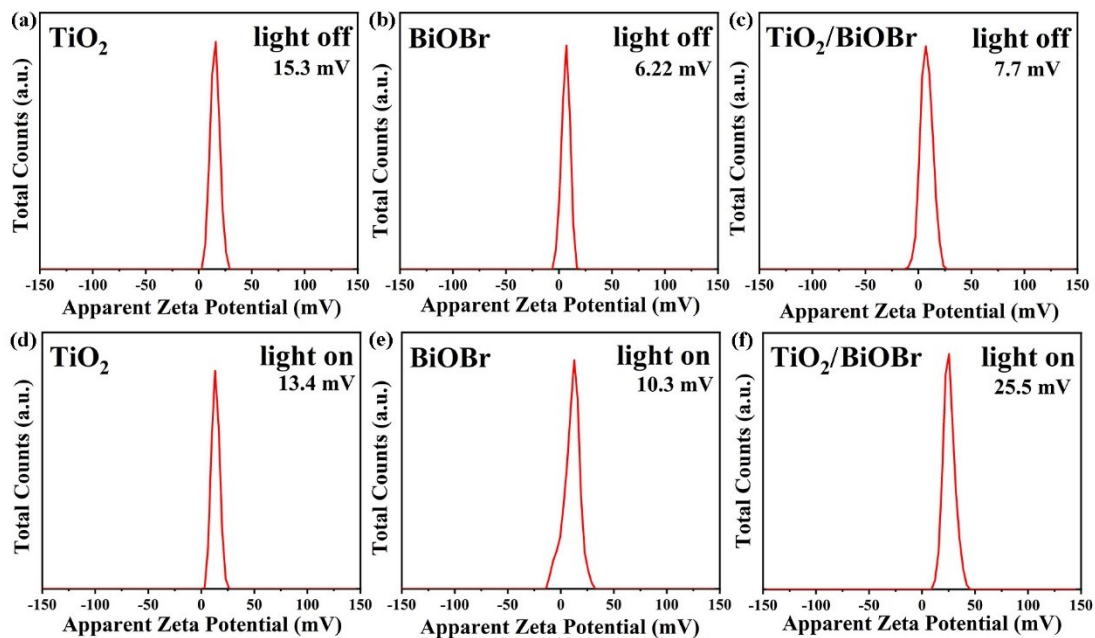


Fig. S7 The band structure diagram of  $\text{TiO}_2/\text{BiOBr}$  (3:1).





**Fig. S8** (a) and (b) PL spectra excited by 320 nm and the transient photocurrent-time curves of the TiO<sub>2</sub> and TiO<sub>2</sub>/BiOBr (3:1) samples. (c) and (d) electrochemical impedance spectra under light on/off.



**Fig. S9** Zeta potential of (a) TiO<sub>2</sub>, (b) BiOBr and (c) TiO<sub>2</sub>/BiOBr (3:1) of on and off state.