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Supplementary Material

Plasmon Bi/BiFeO₃ Heterojunctions toward Optimized Photothermal-Photocatalytic Performance

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2. Experimental

2.1 Preparation

Bismuth nitrate and iron nitrate were dissolved in ethylene glycol methyl ether in a 1:1 molar ratio, then tartaric acid with the equal molar amount of metal ions was added into the above solution under stirring to form a homogeneous solution, and then a small amount of ammonia was introduced drop by drop until the viscosity of the system rose. The resultant sample was dried in the oven at 150 °C, and subsequently calcined at 350 °C for 30 min in a muffle furnace. The collected products (BiFeO₃, BFO) and sodium borohydride were mixed with the molar ratio of 1:1 in a tube furnace under a nitrogen atmosphere at 400 °C for 60 min. After washed several times with anhydrous ethanol and deionized water, dried, and collected, Bi⁰-BiFeO₃ (denoted as BBFO) was obtained. The synthesis process of BBFO assembly is illustrated in Figure 1a.

2.2 Characterizations

The structure and phase of materials were determined using a SmartLAb SE Xray diffractometer (Rigaku, Japanese) with Cu-K as the radiation source, with a 20 range of 5 to 80°. A ESCALAB Xi+ X-ray photoelectron spectrometer (Thermo Fisher, America) with an Al-K radioactive source was used to examine the elements on the surface of the samples. On a Regulus 8220 scanning electron microscope (Hitachi, Japanese) and a JEM-2100 transmission electron microscope (JEOL, Japanese), the microscopic morphologies of the samples were examined. The UV-vis

DRS spectra were recorded in the range of 200~800 nm using a UV 2600 UV-vis spectrophotometer (Shimadzu, Japanese) using BaSO₄ as a reference standard. The photoluminescence (PL) spectra of samples were measured using a LS 55 fluorescence spectrometer (Perkin Elmer, USA), with an excitation wavelength of 350 nm.

2.3 Photocatalytic degradation of organic pollutants

Using a Xenon arc lamp (PLS-SXE300+, Beijing PerfectLight) with a cutoff filter ($\lambda > 420$ nm) and a tetracycline hydrochloride (TC) as a contaminant, the photocatalytic degradation characteristics of BFO and BBFO was investigated. 20 mg of each item was dissolved in 100 mL of TC solution with a solubility of 10 mg L⁻¹ at pH 5.2. For 20 min, the solution was stirred in the dark. The solution was filtered after a sample (5 mL) was taken every 20 min. TC residuals were detected using a UV spectrophotometer. Pure distilled water was served as a reference sample.

2.4 Photoelectrochemical properties

The photocurrent test, electrochemical impedance spectroscopy (EIS) and the Mott-Schottky plots of the samples were performed on a CHI-660E electrochemical workstation (Chenhua, China). To initiate the photoelectrochemical tests, a Xenon arc lamp (300 W, Beijing Aulight) with a cutoff filter ($\lambda > 420$ nm) was used as the light source. We started by dissolving 20 mg of material in ethanol. With an art airbrush, the dispersion was then uniformly sprayed on an FTO glass. Finally, the BFO or BBFO-coated FTO

glass was calcined at 350 °C for 2 h in a N_2 environment. The three-electrode electrochemical station included an aqueous Na_2SO_4 solution as the electrolyte, a platinum plate as the counter electrode, FTO glass as the photoanode, and Ag/AgCl as the reference electrode. To de-aerate the solution, the electrolyte was purged with N_2 gas before use.

Sample	a [Å]	b [Å]	с [Å]	Volume [Å ³]
BBFO	4.35	4.49	14.00	273.63
BFO	5.58	5.58	13.86	431.21

Table S1. Lattice parameters, lattice cell volumes for BFO and BBFO, respectively.



Fig. S1. The XPS survey spectra of BFO and BBFO, respectively.



Fig. S2. Infrared photographs of BFO (a) and BBFO (b) under irradiation at 0 s.



Fig. S3. EPR spectra of BBFO..



Figure S4. The pH during the photocatalytic process.



Figure S5. Degradation of 10 ppm TC on BBFO photocatalysts with and without photothermal activation(BBFO-CT). Controls: the degradation rate constants with BFO and

BBFO without light source.



Figure S6. XRD patterns of BBFO sample before and after photocatalytic reaction.

Abbr.	pollutant name	Chemical structure	molecular weights	Solubility
TC	tetracycline hydrochloride		480.9	50 g/L

 Table S2. The physicochemical parameters of the studied pollutant (TC)