Enhanced Photocatalytic Activity in Mn doped Multiferroic BiFeO₃

Supplementary Information

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Experimental

Synthesis of BiFeO₃ and Mn doped BiFeO₃ nanoparticles

All the chemicals were analytical grades and used without any further purification. These includes Bi(NO₃)₃•5H₂O (99%, Sinopharm Chemical), Fe(NO₃)₃•9H₂O (98.5%, Sinopharm Chemical), MnCl₂•(99.99% Tianjin Bodi), ethylene glycol, tartaric acid, isopropanol, absolute methanol, and nitric acid (99.5%, Sinopharm Chemical).

The BiFeO₃ (BFO) and Mn doped BFO were prepared using sol-gel method which has already reported and adopted without any modification ¹. In this method, first we dissolved the Bi(NO₃)₃•5H₂O and Fe(NO₃)₃•9H₂O in 100 mL of tartaric acid solution in ethylene glycol and kept on stirring for 48 h at 80 °C. The solution under continuous stirring while maintaining the temperature at 80 °C turned into a yellowish green powder. This powder was ground to obtain a fine powder and calcined at 500 °C for 1 hour. The sample was washed several times with distilled water, dried at 80 °C for 6 hours. The Mn doped samples were prepared using the same method where Mn content varied from 0.025 to 0.1%. The Mn doped samples were named according to Mn content in the sample such as samples with Mn molar percentage of 0.025%, 0.050%, 0.075% and 0.1% are designated as BFO-1, BFO-2, BFO-3 and BFO-4, respectively.

Material Characterizations

X-rays diffraction (XRD) analysis graphs for all the samples were obtained using a Bruker D2 PHASER powder diffractometer (Cu K α radiation) at the scan rate of 5° min⁻¹ in the 2 θ range of 20-80° under operating voltage of 30 kV and current of 10 mA. UV-Visible diffuse reflectance spectra (DRS) for all the samples were recorded using JASCO V-550 spectrophotometer equipped with an integrating sphere where BaSO₄ was used as the reference for the baseline calibration. The Mott–Schottky (MS) experiments were conducted using a three-electrode system. A slurry of the sample (BFO and BFO-2) was prepared by mixing the powder sample in isopropanol and deposited on fluorine doped tin oxide (FTO) substrate using Doctor blade's method. The prepared electrodes of the samples worked as the working electrodes while Pt as a counter electrode, and saturated mercury electrode (SCE) as a reference electrode. The electrolyte used for this experiment was 0.1 M Na₂SO₄ aqueous solution with a pH of 7 adjusted by mixing NaOH. The frequency and amplitude of AC potential were kept 1 kHz and 0.01 V, respectively. The applied potential was normalized to neutral hydrogen electrode (NHE) based on the equation $E_{(NHE)} = E_{(SCE)} + 0.241 V$.

The morphology, particle size, and distribution were examined using high resolution transmission electron microscopy (HR-TEM) with the instrument model Japan JEOL JEM-F200 operated at 200 kV voltage while the export image resolution was 4096 X 4096 equipped with EDX accessory. The powder sample was dispersed in ethanol solution and treated ultrasonically for several minutes. Then took a few drops of dispersed liquid drop by drop and added them to the copper net, after drying the sample was studied thoroughly.

X-ray photoelectron spectroscopy (XPS) experiment was carried out by X-ray photoelectron spectrometer (SHIMADZU AXIS UltraDLD). Among them, the true vacancy of the analysis chamber is 2 E-09 Torr, the excitation source was Alfa ray with the excitation energy of hv = 1486.6 eV, the working voltage is 12 kV, and the filament current was 11 mA. The full Passing-Energy spectrum was 160 eV while the narrow spectrum was 40 eV and the step size was 0.05 eV, the residence time was 200-300 ms, and the charge correction was carried out with C1s = 284.60 eV binding energy as energy standard. The photoluminescence spectra (PL) were obtained using Edinburgh FLS980 high-performance research-grade spectrometers. The PL spectra was obtained at room temperature by depositing the powder sample on FTO using Doctor's blade method. The

excitation wavelength used for this experiment was 420 nm and PL spectra was measured in the range of 450 - 800 nm.

Surface Photovoltaics (SPV) Measurements

The SPV measurements were carried out on Omni- λ 300. Samples for SPV were prepared by pressing the powder of BFO and BFO-2 to obtain a very smooth and thin pellet of 0.5 cm diameter. The scanned area was nearly 2 μ m in length while applying the 380 nm excitation wavelength in the range of 300-1000 nm wavelength.

PFM and Ferroelectric P-E Hysteresis Loops Analysis

The phase-amplitude hysteresis loop study was carried out using pellets. The pellets were prepared by pressing the sample and annealing at 600 °C for 15 minutes. Each pellet was 6 mm in diameter and 0.6 mm thick while Ag paste was deposited on both sides of the pellet to collect current. The piezoelectric response of the sample was measured by the Bruker Dimension Icon. The tip was SCM-PIT-V2 platinum-coated conductive tip, with a k of ~ 0.5 N/m. The polarization-electric (P-E) hysteresis loop and *I-V* measurements were carried out on probe station equipped with a multiferroic tester (Radiant tech.) and a multi-Source Meter (Keithley 2450).

Photocatalytic Activity Performance Test

A 300 W xenon lamp with a filtration mirror equipped with an optical filter (Hoya, L-42; $1 \ge 420 \text{ nm}$) to cut off the ultraviolet light is used as the visible light source. The distance between the lamp and the solution was kept 20 cm. All the experiments are performed in a dark box. In a general PC experiment, 20 mg catalyst is dispersed in a 50 mL RhB aqueous solution in a 100 mL glass beaker at neutral pH conditions. A flow of cooling water was used to keep the reaction suspension at 16 °C. Prior to light irradiation, the suspension (4 mg/L concentrated solution of RhB was used) was continuously stirred by a magnetic stirrer for 45 min to reach the adsorption–

desorption equilibrium. 3 mL aliquots are periodically taken out from the suspension at the interval of 10 min during the evaluation process. The UV-Vis spectrophotometer (JASCO V-550) was used to record the changes of absorption values at the respected wavelengths maxima in aqueous solutions. The photodegradation efficiency (PDE) is calculated via the formula PDE = $(C_0 - C_t/C_0) \times 100\%$, where C_0 is the concentration of initial pollutant solution and C_t is the concentration of pollutant solution measured at various irradiation time at corresponding wavelengths. In a typical recycle test, the catalyst was separated from wastewater solution under UV light irradiation using centrifuge and washed thoroughly with deionized water and dried at room temperature.

2.5 Active Species Trapping Experiment

The trapping active species experiments conducted using disodium were Ethylenediaminetetraac-etate (EDTA-2Na), Isopropanol (IPA), and Benzoquinone (BQ) as scavengers. These scavengers are specifically to trap the holes (h^+) , hydroxyl radicals ('OH), and super oxide radicals ('O₂-) respectively. In a typical experiment, 5 mg powder samples were added into 100 mL solution of RhB with addition of 1 mM amount of the scavenger content. Similar to PC activity test, first suspension was sonicated for 10 minutes and then stirred for 120 minutes in dark to obtain the adsorption-desorption equilibrium. And suspension was collected after every 5 minutes intervals and concentration of RhB was measured by UV-Vis. Absorption.



Figure S1. HR-TEM images at different resolutions; (a-c) Pure BFO (d-f) BFO-2.



Figure S2. (a) EDX analysis graph indicating the presence of Bi, Fe, and O in pure BFO (b) EDX analysis graph indicating the presence of Bi, Fe, O, and Mn in pure BFO-2.



Figure S3. EDX mapping for pure BFO shows the homogeneous distribution of Bi, Fe, and O in pure BFO.



Figure S4. (a) Mott - Schottky plots of BFO and BFO-2 (b) The calculated energy band diagram of BFO and BFO-2 showing VB and CB position.

TRPL Studies

The PL decay kinetics curves were fitted to triple exponential functions:

$$I(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3)$$
(1)

where, *t* is time, B_1 , B_2 , and B_3 are the pre-exponential factors corresponding to the exponential decays with lifetimes of τ_1 , τ_2 , and τ_3 , respectively. The average lifetime of photogenerated charge carriers is calculated using the Equation (4):

Average
$$\tau = \sum_{i=1}^{3} R_i \cdot \tau_i$$
 (2)

 R_i is the relative ratio factor which is calculated by:

$$R_{i} = B_{i/(i=1}^{3} B_{i})$$
(3)

Table S1. Table showing the average lifetime of photogenerated charges over BFO and BFO-2 calculated after analysis from TRPL.

Sample	λ_{Em}	$\tau_{l(ns)}$	$ au_{2(ns)}$	$ au_{3(ns)}$	B_1	B_2	B 3	A	χ^2	$ au_{average}$
										(ns)
BFO	380	0.8071	4.8313	41.3544	3609.4536	479.4901	51.3241	0.8234	0.8651	13.8
BFO-2	380	0.7200	5.1140	49.0498	3005.5264	346.3502	108.2284	0.6888	0.8503	29.2

PFM Phase Analysis

In PFM, phase and amplitude are two major components which gives complementary information about the piezoelectric and ferroelectric nature of the material. One of the major components of PFM is amplitude which shows the piezoelectric deformation when electric field is applied on the sample through tip. Magnitude gives semi-quantitative information about the piezoelectric nature where larger magnitude indicates higher piezoelectric coefficient. It has also two components; (1) vertical component measures the out-of-plan piezo response originating from

polarization along the polar axis and give information about piezoelectric d_{33} coefficient, (2) while lateral PFM amplitude measures the in-plane piezoresponse which is related to transverse piezoelectric d_{31} , d_{32} coefficients. In other words, amplitude is the magnitude of in-plane and out of plane piezo responses originating because of applied electric field. There are some other amplitudes which could be measured such as across channel oscillation or longitudinal displacement but vertical and lateral provide detailed and highly informative nanoscale piezoelectric contrast in PFM systems. The other major component of PFM is Phase which gives information about the orientation of polarization in the sample. Phase is further divided into two components: (1) vertical phase which shows out of plane or 180° domains where polarization direction can be flipped upward vs downward, (b) lateral phase where domains are non-180° and their directions can be flipped within the plan. These different directions of domain give the phase contrast which could be observed during phase mapping of PFM.



Figure S5. Lateral phase PFM mapping images of BFO: (a) amplitude (b) phase. Lateral phase PFM mapping images of BFO-2: (c) amplitude (d) phase (scale bar 400 nm)



Figure S6. Absorbance plots with respect to time of RhB under visible illumination; (a) pure BFO (b) BFO-1 (c) BFO-2 (d) BFO-3 (E) BFO-4. (Conditions: 4 mg/L RhB solution 50 mL, Visible light irradiation \ge 420 nm).