

Electronic Supplementary Information

Fabrication of multiphase MoSe₂ modified BiOCl nanosheets for efficient piezo-photoelectric hydrogen evolution and antibiotics degradation

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1. EXPERIMENTAL SECTION

1.1 Materials

Sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 99%), selenium powder (Se, 99%), sodium borohydride (NaBH_4 , 99%), bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99%), dioctadecyl dimethyl ammonium chloride (DODAC, 99%), Diclofenac sodium (DCF) and lactic acid were obtained from Sinopharm Chemical Reagent Co.

1.2 Synthesis of 1T/2H MoSe_2

The NaBH_4 (0.304 g) and Se (0.316 g) were dissolved in 75 mL water, and then 0.484 g Na_2MoO_4 was added and stirred for 20 min to form a homogeneous liquid. The above solution was moved to a 100 mL hydrothermal synthesis reactor and heated to 220 °C for 20 h. After being cooled to room temperature, the black precipitate was gathered and washed several times with deionized water and ethanol. Dried overnight in a vacuum drying oven to acquire the final product.

1.3 Synthesis of 2H MoSe_2

The above obtained 1T/2H MoSe_2 catalyst was put into a tube furnace, nitrogen was passed and heated to 600 °C at a heating rate of 5 °C min^{-1} for 2 h to obtain the product.

1.4 Synthesis of BiOCl

First, a quantity of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 3 mL of concentrated nitric acid were dispersed in 40 mL of deionized water under intense stirring to obtain a clear solution. Then the above $\text{Bi}(\text{NO}_3)_3$ solution was added to the already dissolved dioctadecyl dimethyl ammonium chloride (DODAC) solution, where the mass ratio of

DODAC to $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was 0.5. Subsequently, the suspension was stirred at room temperature for 8 h. Then, the suspension was collected by centrifugation, rinsed several times with deionized water and ethanol, and dried in vacuum at 60 °C to obtain the product.

1.5 Synthesis of 1T/2H MoSe₂/BiOCl and 2H MoSe₂/BiOCl

Different doses (3, 5, 10 mg) of 1T/2H MoSe₂ and 1 g BiOCl were mixed and dispersed into anhydrous ethanol to form a homogeneous 1T/2H MS/BOC suspension under the action of ultrasound and stirring, respectively, and different mass percentages of 1T/2H MS/BOC nanosheets (0.3%, 0.5%, 1.0%) were obtained after overnight in a vacuum drying oven. The 0.5% 2H MS/BOC was prepared by weighing 5 mg 2H MoSe₂ and 1 g BiOCl nanosheets by the similar method.

1.6 Characterization

The crystalline structure of the catalyst was examined by X-ray diffraction (XRD) technique (Japan/D/MAX2500). The morphology and element distribution of samples were determined by a scanning electron microscope (SEM, SUPRA55). Microstructures were employing using transmission electron microscope and high-resolution transmission electron microscope (TEM, JEM-2100, Japan). The chemical elements and phase composition of the synthesized catalysts were analyzed by X-ray Photoelectron Spectroscopy (XPS, PHI-5000 VPIII). Electron spin resonance (EPR) spectrum were acquired by Bruker EMX PLUS EPR spectrometer.

1.7 Photoelectrochemical Measurements

Photoelectrochemical measurements were performed using an electrochemical analyzer (DH7000, China) and a Xe lamp (220V, 35W). And H₂SO₄ solution (0.5 mol/ L) was employed as electrolyte. Saturated calomel electrode (SCE) and graphite rod were utilized as the counter and reference electrodes, respectively. The working electrodes were prepared as follows: 5 mg of sample was added to a mixture of 0.5 mL of ethanol and water (1:3), and 20 μ L of Nafion solution (Dupont, 5 wt%) was added to the above suspension. Next, 5 μ L ink was dropped onto the surface of a polished glassy carbon electrode (GCE) and dried to form a working electrode. The linear sweep voltammetry (LSV) curves were obtained from -1 to -0.4 V at the rate of 5 mV·s⁻¹. The electrochemical double layer capacitance (C_{dl}) was measured by cyclic voltammetry (CV). Electrochemical impedance spectroscopy (EIS) was measured at the open-circuit potential with a fixed frequency range of 10⁻² to 10⁵ Hz.

1.8 Piezo-photodegradation DCF

Firstly, 20 mg piezo-photocatalyst was added to DCF solution (10 mg/L, 60 mL) and stirred in the dark for half an hour to reach adsorption-desorption equilibrium. Then the xenon lamp (220 V, 35 W) and ultrasonic washing device (240 W, 40 kHz) were opened for the catalytic reaction. An aliquot of 1 mL aliquots was drawn every 10 min and then filtered through a 0.22 μ m membrane for the next analysis.

1.9 HPLC Analysis Method

The model of the chromatographic column was SB-C18, and the wavelength of the UV detector was set to 276 nm. Methanol and 0.5% acetic acid (80/20, V/V) were selected as the mobile phases with a flow rate of 1.0 mL·min⁻¹ and an injection

volume of 20 μL . The intermediate products/by-products of DCF piezoelectric degradation were determined by ZORBAX Eclipse Plus C18 column and Dual AJS ESI particle source liquid chromatography mass spectrometry (Agilent 6230B). At 25 $^{\circ}\text{C}$, the injection volume was 10 μL , and the eluent was methanol (A) and water (B). The gradient of the eluent was 0-1 min at 10% A and 90% B, increasing to 90% A and 10% B over 5 min and held for 20 min.

1.10 DFT Calculation Method.

The Gaussian 09W software was utilized to select the DFT, B3LYP theoretical approach to study the material. The 6-31G+(d, p) basis set was selected for O, N, C, Cl geometry optimization and single-point energy calculation (6-31G+), and the Fukui function in Multiwfn software was used to predict the site of free radical attack on DCF molecules.

1.11 Piezo-photocatalytic H₂ Evolution.

The piezo-photocatalytic H₂ generation was carried out in a sealed quartz reactor (50 mL). In a typical reaction, 2 mg sample was scattered by ultrasonic in 20 mL aqueous solution containing 2 mL methanol as sacrificial agents. Before the reaction, the vessel was passed with nitrogen (N₂) for 30 min. During the catalytic reaction, the temperature of the reaction liquid was kept at around 30 $^{\circ}\text{C}$ by circulating water bath. A gas chromatography (A91 Plus, Ar₂ as carrier gas) was chosen to analyze the generated hydrogen.

2. Figures

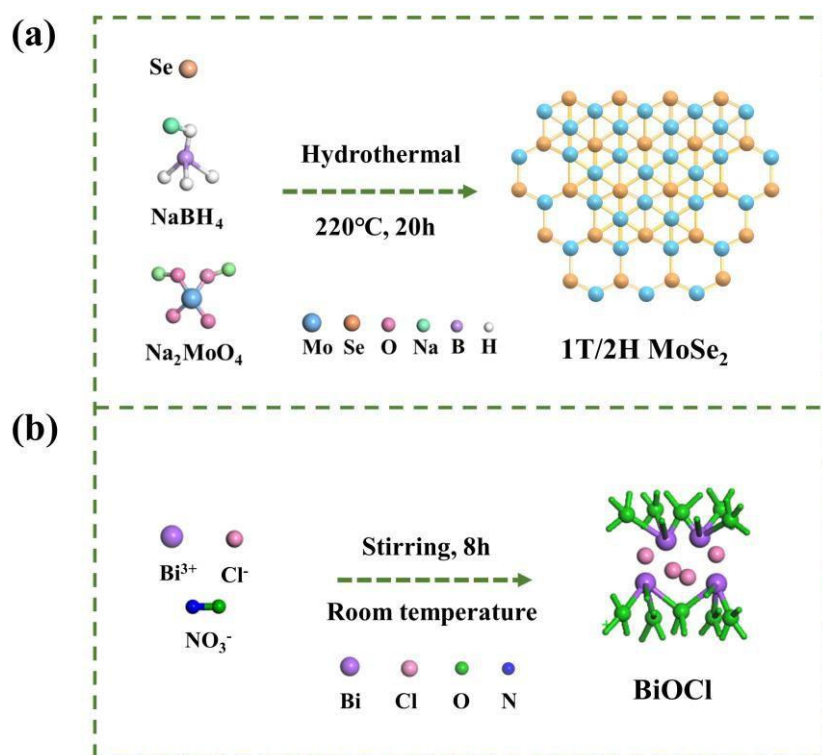


Fig. S1 Schematic drawings illustrating the fabrication process of (a) 1T/2H MoSe₂ and (b) BiOCl nanosheets.

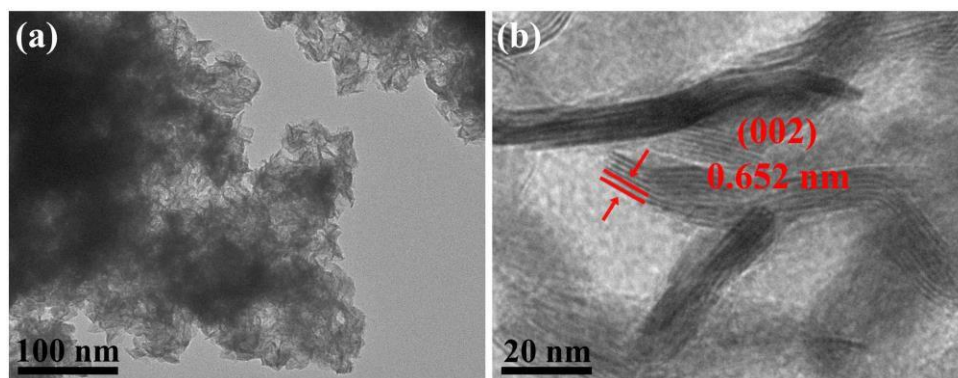


Fig. S2 (a) TEM and (b) HRTEM images of 2H MoSe₂.

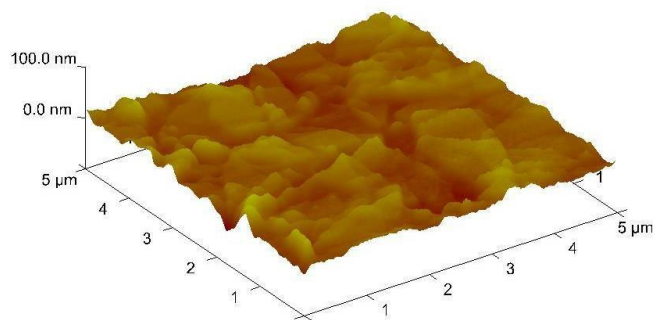


Fig. S3 The 3D AFM image of 0.5% 1T/2H MS/BOC.

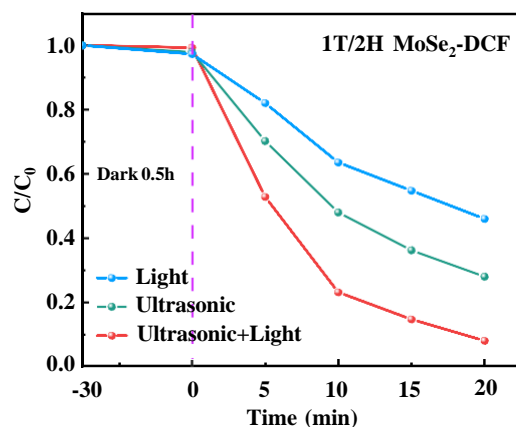


Fig. S4 DCF degradation performance curves under different conditions of 1T/2H MoSe₂.

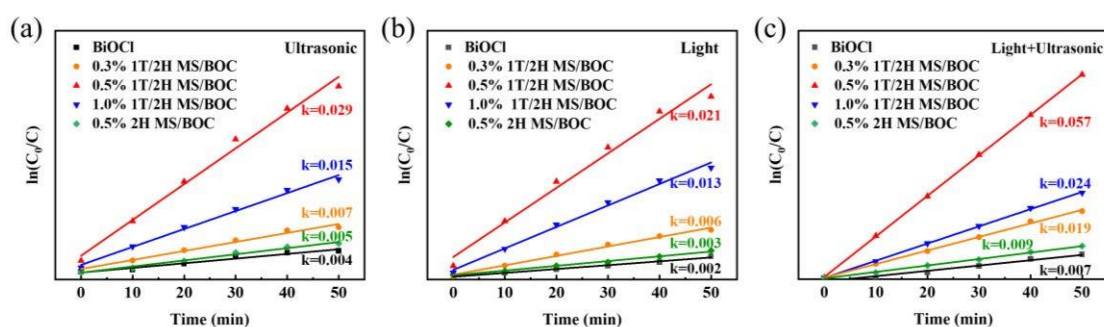


Fig. S5 Reaction kinetics of pure BiOCl, 0.5% 2H MS/BOC and different loading ratios of 1T/2H MS/BOC under (a) ultrasonic conditions, (b) light conditions, (c) ultrasonic and light.

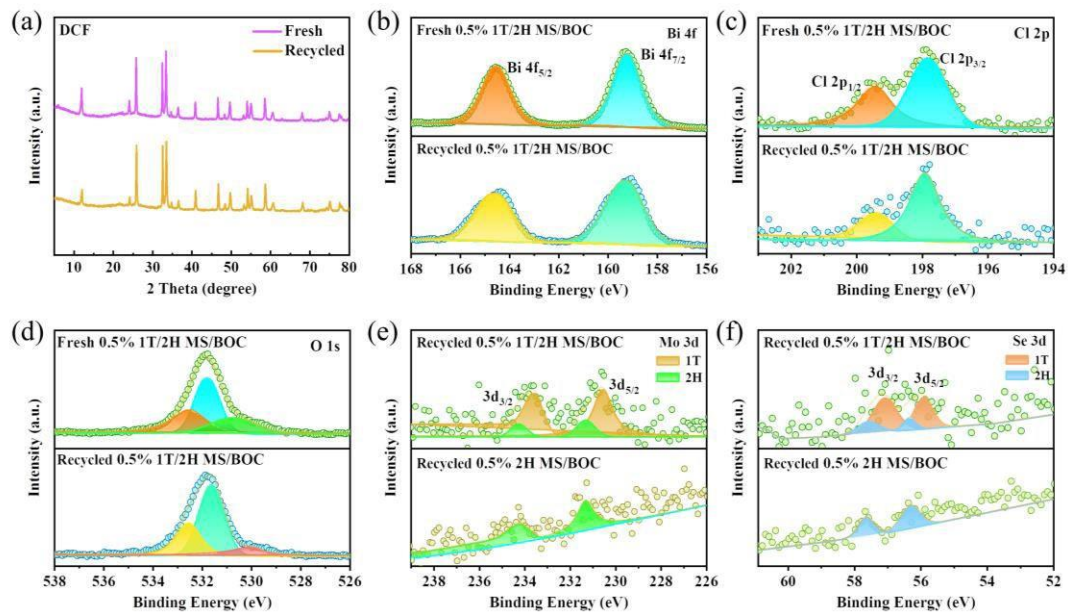


Fig. S6 (a) XRD comparison before and after reaction of DCF degradation. XPS spectra of fresh and recycled 0.5% 1T/2H MS/BOC composite: (b) Bi 4f, (c) Cl 2p, (d) O 1s. (e) Mo 3d XPS spectra and (f) Se 3d XPS spectra after the DCF degradation reaction.

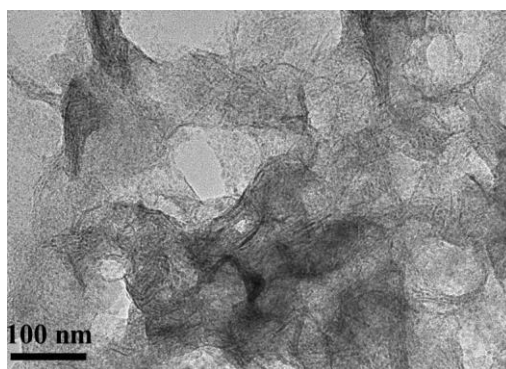


Fig. S7 TEM after degradation of DCF by 0.5% 1T/2H MS/BOC.

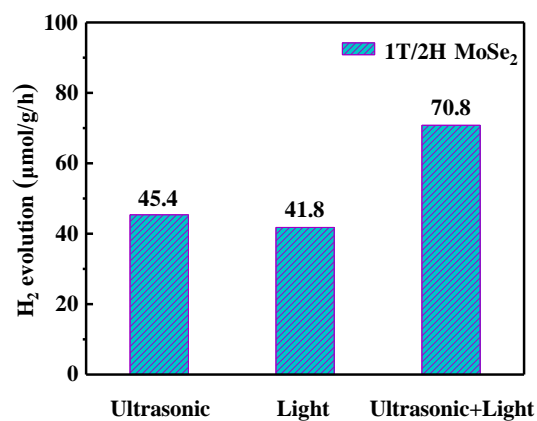


Fig. S8 H₂ evolution rate plots under different conditions of 1T/2H MoSe₂.

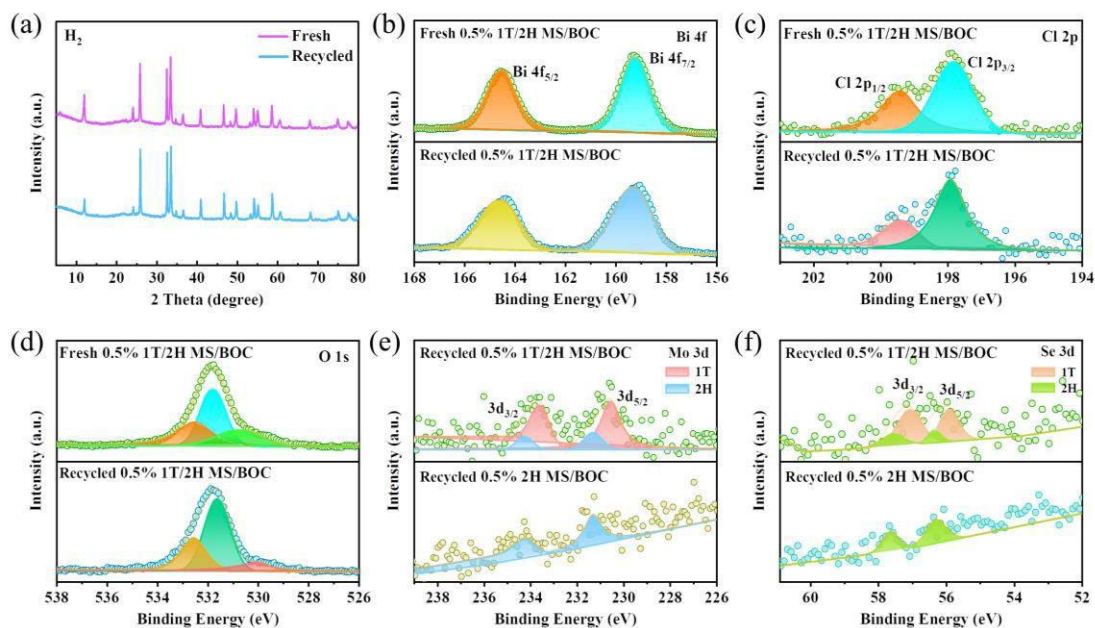


Fig. S9 (a) XRD comparison before and after reaction of H₂ evolution. XPS spectra of fresh and recycled 0.5% 1T/2H MS/BOC composite: (b) Bi 4f, (c) Cl 2p, (d) O 1s. (e) Mo 3d XPS spectra and (f) Se 3d XPS spectra after the H₂ evolution reaction.

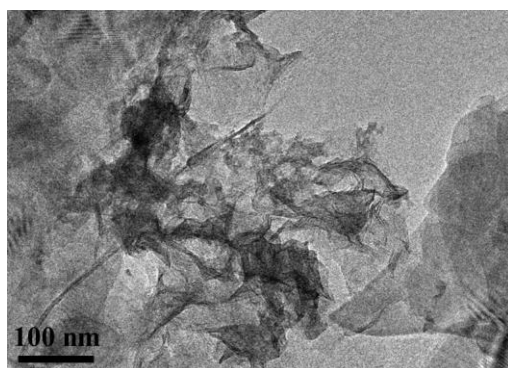


Fig. S10 TEM after H₂ evolution by 0.5% 1T/2H MS/BOC.

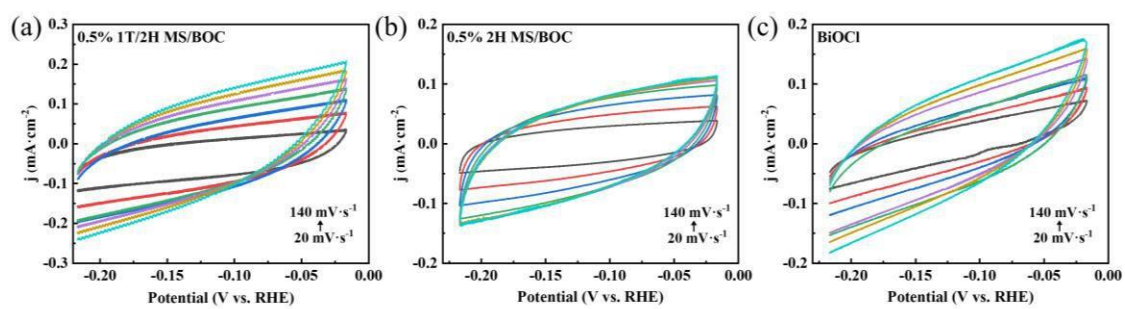


Fig. S11 CV tests of as-synthesized (a) 0.5% 1T/2H MS/BOC, (b) 0.5% 2H MS/BOC and (c) BiOCl samples at varied scan rates.

3. Table

Table S1 Comparison of piezo-photocatalytic performances for dye degradation and H₂ evolution of catalyst reported previously and in this work.

Catalyst	Pollutant	Concentration and volumetric of pollutant (mg/L, mL)	Catalyst dosage (mg)	Degradation efficiency and time (% , min)	H ₂ evolution rate (μmol/g/h)	Ref.
TB450	DCF	10, 60	15	99, 90	/	S1
SFB-15	DCF	10, 50	15	98, 90	/	S2
40-BOC/CBO	DCF	50, 40	20	90, 60	/	S3
rGO-CBS (15%)	DCF	10, 50	30	85, 60	/	S4
BiOBr	RhB	10, 50	50	99, 120	/	S5
0.15 BiOI/ZnO NRs	BPA	10, 50	10	95, 120	/	S6
5MoSe ₂ /AgBr	TC	20, 100	50	81, 90	/	S7
B/BB/B@B-10-0.3	CTC	50, 100	50	95, 90	/	S8
BiOCl(110)-PbS	/	/	/	/	16.0	S9
BU-BiOCl/Pt	/	/	/	/	79.2	S10
Pt/ZnRh ₂ O ₄ /Ag/Bi ₄ V ₂ O ₁₁	/	/	/	/	0.21	S11
0.5% 1T/2H MS/BOC	DCF	10, 60	20	94, 50	122.5	This work

Reference

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