Supporting Information

Polarization synergizes defective interface heterojunction boosting piezocatalytic hydrogen production simultaneous pollutant degradation

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Experimental section

1. Sample preparation

1.1 Chemicals: All chemicals used in this work are analytical grade and utilized without further purification.

1.2 Fabrication of BiOIO₃ (BIO): 2 mmol of Bi(NO₃)₃·5H₂O and 1mmol of I₂O₅ were dissolved in 30 mL of ultrapure water at room temperature and stirred for 0.5 hour. Then, the mixture was transferred to a 50 mL PTFE-lined vessel and placed in a hydrothermal autoclave, where it was kept at 180 °C for 12 hours. After the reaction, the product was thoroughly washed with deionized water and ethanol, and finally dried in air at 60 °C for 12 hours to obtain BiOIO₃, denoted as BIO.

1.3 Fabrication of BiOIO₃-VO (BIOVO): BiOIO₃-VO was obtained through glyoxalassisted hydrothermal method. In a typical procedure, 200 mg of the above obtained BiOIO₃ and a quantitative amount of glyoxal (10, 15, 20 uL) were added to 30 mL of ultrapure water at room temperature and stirred for 0.5 hour. Then, the mixture was transferred to a 50 mL PTFE-lined vessel and placed in a hydrothermal autoclave, where it was kept at 100 °C for 6 hours. After the reaction, the product was thoroughly washed with deionized water and ethanol, and finally dried in air at 60 °C for 12 hours to obtain BiOIO₃-VO. The BiOIO₃-VO samples synthesized using different amount of glyoxal (10, 15, 20 uL) were denoted as BIOVO-L, BIOVO, and BIOVO-H, respectively.

1.4 Fabrication of NH₂-MIL-125 (NM): NH₂-MIL-125 with exposed (111) crystal face was prepared by controlling the type and proportion of solvents using solvothermal method. Specifically, add 1.5 mmol of aminoterephthalic acid (NH₂-BDC) to a solution of 9mL of N, N-dimethylformamide (DMF), 1mL of methanol, and 0.53 mL of acetic acid, and ultrasonically stirring for 5 minutes. Subsequently, titanium source was introduced, 1 mmol of isopropyl titanate was added and stirred. Then, the mixed solution was transferred to a 50 mL PTFE-lined vessel and placed in a hydrothermal

autoclave, where it was kept at 150 °C for 48 hours. After cooling to room temperature and reaction, the product was thoroughly washed with DMF and methanol, and finally dried under vacuum at 80 °C for 24 hours to obtain NH_2 -MIL-125, denoted as NM.

1.5 Fabrication of BiOIO₃ -VO/NH₂-MIL-125 (BIOVO/NM): BiOIO₃ -VO/NH₂-MIL-125 heterojunctions were synthesized by electrostatic self-assembly method. Disperse a certain amount of NH₂-MIL-125 and BIOVO in 50 mL distilled water, and then vigorously stir at room temperature for 8 hours. Then obtain the precipitate, wash and dry it. The BiOIO₃ -VO/NH₂-MIL-125 heterojunctions with mass ratios of 1:1, 3:1, 5:1, 7:1, and 9:1 are represented as BIOVO/NM-1, BIOVO/NM-3, BIOVO/NM-5, BIOVO/NM-7, and BIOVO/NM-9, respectively.

2. Characterization

The phase composition and crystal structure of the prepared photocatalyst were characterized by Bruker D8 powder X-ray diffraction (XRD). The chemical states of all surface elements of the samples were recorded using Fourier transform infrared spectroscopy (FTIR, Thermo Fisher). The morphology and interplanar spacing of the synthesized samples were determined using S-4800 scanning electron microscopy (SEM), JEM-F200 transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). The surface chemical properties of the catalyst were detected using X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250XI). Record the UV visible diffuse reflectance spectrum (DRS) of the sample using a PerkinElmer Lambda 35 spectrophotometer. The deformation and polarization of the surface potential of the catalyst was detected using an in-situ Kelvin probe force microscope (KPFM). Measure the surface electrical properties of the material using a Zeta potential tester.

3. Test of piezocatalytic activity

Using an ultrasonic machine with a maximum output power of 300W as the mechanical stress source, piezocatalytic H_2 production synchronous degradation tests were conducted on typical organic pollutants (tetracycline hydrochloride, enoxacin, rhodamine B, methylene blue) to evaluate the piezocatalytic performance of the catalyst. Usually, solid catalyst (20 mg) is dispersed in a 50 mL solution containing organic pollutants. Under dark conditions, stir the suspension with strong magnetic stirring for 15 min. Then transfer the suspension into an offline catalytic reactor, completely remove the air with a vacuum pump, and inject high-purity argon gas as the carrier gas. Using an ultrasonic machine with a maximum output power of 300 W as the mechanical stress source for piezoelectric catalytic reaction, 1 mL of gas is extracted from the reactor every 30 min and injected into the gas chromatograph for H_2 production detection. After each sampling, replace the water in the ultrasonic machine to ensure stable water temperature. After 2 h of reaction, take 4 mL of the solution and centrifuge. Measure the absorbance of organic pollutants using a UV spectrophotometer.

4. Piezoelectric electrochemical measurements

The piezoelectric electrochemical properties of the material were measured using an electrochemical analyzer (CHI 660E, Shanghai), including transient piezoelectric current, electrochemical impedance spectroscopy, and LSV plot. Using a standard three electrode configuration, with Pt wire as the counter electrode, saturated Ag/AgCl electrode as the reference electrode, and fluorine doped tin oxide (FTO) glass coated on the sample as the counter electrode, the sample was tested with mechanical stress provided by an ultrasonic machine with a maximum power of 300 W. Choose 0.1M Na₂SO₄ as the electrolyte solution. Specifically, the preparation of the working electrode involves dispersing 10 mg of catalyst powder into a 1 mL ethanol solution containing $1g \cdot L^{-1}$ ethyl cellulose, followed by thorough dispersion using ultrasound. After dispersion, evenly drop the suspension onto FTO glass and dry overnight at room temperature. The electrochemical test was conducted at room temperature with a voltage of 0.0 V.

5. Active species trapping experiments

In order to identify the reactive species during the piezocatalytic process, sodium oxalate (Na₂C₂O₄, h⁺ quencher), silver nitrate (AgNO₃, e⁻ quencher) and isopropanol (IPA, \cdot OH quencher) were used as quenchers for active species trapping experiments. The entire piezocatalytic experiment was conducted in an argon atmosphere without the participation of O₂, so \cdot O₂⁻ was not considered.

6. Density functional theory (DFT) calculation

All the calculations were carried out in the framework of DFT with the projector augmented plane-wave method, as implemented in the Vienna ab initio simulation package (VASP). Adopting PBE exchange functional under generalized gradient approximation. The dispersion corrected DFT-D3 method was used to describe van der Waals interactions. For the BiOIO₃ model, we fabricated $2\times1\times2$ super monomers and constructed a 15 Å vacuum layer along the b-axis direction to avoid periodic interference. On this basis, the BiOIO₃ model of Ovs was constructed. We have chosen 480 eV as the cut-off energy for the plane wave expansion of the Kohn Sham wave function. Using a $2\times1\times2$ Monkhorst-Pack K-point grid for regional integration in the Brillouin zone. The convergence criteria for energy and force are set to 10^{-5} eV and 0.01 eV/Å, respectively.

For NH₂-MIL-125, we first constructed a $1\times1\times1$ monomer and performed geometric optimization. Then cut out a planar model of the {111} surface from the optimized monomer structure. Cut out the organic metal monomers from the {111} model and construct a heterojunction model together with the $2\times1\times2$ BiOIO₃ model. Place a 15 Å vacuum layer in the direction perpendicular to the surface. In the geometric optimization process, atoms of about 6 Å in the lower layer of BiOIO₃ and the NH₂-MIL-125 monomer base skeleton were fixed. The remaining atoms in the heterojunction model were allowed to relax without constraints. For geometric models containing a large number of atoms (248 and 257), gamma points are used for Brillouin zone integration, and conjugate gradient method and quasi-Newton method are used to calculate convergence. The convergence standards for energy and force are set to 10⁻⁵ eV and 0.05 eV/Å, respectively. The adsorption energies (E_{ads}) were calculated by the **Equation (S1)**:

$$E_{ads} = E_{tot} - E_{htj} - E_H$$
(S1)

where $E_{\text{tot}},\,E_{\text{htj}},\,\text{and}\,\,E_{\text{H}}$ represent the total energy of the heterojunction adsorption $H^{\scriptscriptstyle +}$

system after structural optimization, the total energy of the heterojunction matrix, and the energy of isolated H element, respectively. The Gibbs free energy change (ΔG) of hydrogen evolution processes was determined using the computational hydrogen electrode (CHE) model, as shown in **Equation (S2)**:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \tag{S2}$$

where ΔE , ΔE_{ZPE} , ΔS represent the change of energy obtained by DFT calculations, zero-point energy, and entropy, respectively, and T is the thermodynamic temperature.

Results an Discussion

1.Zeta potential



Fig. S1 Zeta potentials of NM and BIOVO.

2. SEM images



Fig. S2 SEM images of (a) NM, (b) BIO, (c-d) BIOVO and (e-f) BIOVO/NM-5.

3. The lattice distances in Fig. 1g



Fig. S3 The corresponding lattice distances of the BIOVO/NM-5 in Fig. 1g.

4. EDS elemental maps



Fig. S4 EDS elemental maps of N and O in BIOVO/NM-5.

5. FTIR spectra



Fig. S5 FTIR spectra of the NM \cdot BIO \cdot BIOVO and series BIOVO/NM-X (X = 1, 3, 5, 7, 9) heterojunctions.

6. XRD patterns



Fig. S6 XRD patterns of (a) BIO, BIOVO-L, BIOVO, BIOVO-H, (b) NM and BIOVO/NM-X (X = 1, 3, 5, 7, 9).

7. XPS high resolution spectra



Fig. S7 The XPS high resolution spectra of (a) Bi 4f, (b) N 1s and (c) Ti 2p in NM, BIO, BIOVO and BIOVO/NM-5.

8. UV–Vis DRS spectra



Fig. S8 UV–Vis DRS spectra of NM ${\scriptstyle \sim}$ BIO ${\scriptstyle \sim}$ BIOVO and BIOVO/NM-5.

9. XPS valence band spectra



Fig. S9 XPS valence band spectra of NM and BIOVO.



10. Piezocatalytic H₂ production performance in pure water and simulated seawater conditions

Fig. S10 (a) Piezocatalytic H_2 production of BIO, BIOVO-L, BIOVO and BIOVO-H in pure water. (b) Piezocatalytic H_2 production of BIOVO, NM and BIOVO/NM-X (X=1,3,5,7,9) in pure water. (c) Piezocatalytic H_2 production rates of BIOVO/NM-5 at different ultrasonic powers. (d) Simulating seawater environment, piezocatalytic H_2 production rate of BIOVO/NM-5 at different NaCl concentrations. (e) Piezocatalytic (240W) H_2 production rates of BIO/NM-5 in pure water. (f) Comparison of piezocatalytic H_2 production simultaneous degradation performance of BIO/NM-5 and BIOVO/NM-5 in MB solution.

11. Simultaneous degradation absorbance of piezocatalytic H₂ production simultaneous degradation under different pollutants



Fig. S11 (a-d) Synchronous degradation absorbance curves of H₂ production simultaneous degradation in TC, ENO, RhB and MB solutions (5ppm).





Fig. S12 (a-d) Simultaneous degradation absorbance curves of H₂ production simultaneous degradation under different concentrations of MB solution.

13. Piezocatalytic H_2 production simultaneous degradation performance under blank conditions (without catalyst)



Fig. S13 Piezocatalytic H₂ production simultaneous degradation performance under blank conditions (without catalyst).

14. XRD and SEM characterization of BIOVO/NM-5 after stability testing



Fig. S14 (a) SEM and (b) XRD of BIOVO/NM-5 after stability testing.



Fig. S15 LSV curves under ultrasound free and ultrasound conditions (300W).

16. Structural models of BiOIO₃-VO



Fig. S16 Structural models of BIOVO, (a) OV-1, (b) OV-2, (c) OV-3.

Location of OV in IO ₃	Internal energy of the system (eV)
OV-1	-468.61

-468.31

-468.80

OV-2

OV-3

 Table 1 Internal energy of BiOIO3 system at different vacancy positions.

17. Optimized crystal cell structure of NH₂-MIL-125



Fig. S17 Optimized crystal cell structure of NH₂-MIL-125, (a) Front view, (b) side view, and (c) top view.