Electronic Supplementary Material (ESI) for Chemical Communications.

# Supporting information

# Monoclinic dibismuth tetraoxide (m-$Bi_2O_4$) for piezocatalysis: new use for neglected material

Fengling Liu[a], Haoxuan Chen[a], Chenmin Xu[b, *], Linlin Wang[a], Pengxiang Qiu[a, *], Shuo Gao[a], Jiawei Zhu[a], Shuai Zhang[a], Zhaobing Guo[a, *]

[a] Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (CIC-AEET), School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, China.

[b] School of Environment, Nanjing Normal University, Nanjing 210023, China.

## Materials and methods

**Catalysts preparation.** Monoclinic-$Bi_2O_4$ was hydrothermally prepared using $NaBiO_3{\cdot}2H_2O$. Briefly, 1.12 g of $NaBiO_3{\cdot}2H_2O$ powder (Aladdin, Shanghai) was dispersed in 40 mL ultrapure water. Then the mixture was transferred into a Teflon-lined stainless autoclave and was heated at 433 K for 12 h. After the hydrothermal reaction, the sample was washed with ultrapure water and ethanol several times. The material was obtained after drying at 328 K for 12 h. The traditionally used piezoelectric materials, $BaTiO_3$ (Aladdin, Shanghai) and BiOCl (Macklin, Shanghai), were chosen as reference catalysts to evaluate the piezocatalytic activity under ultrasound vibration.

**Characterization.** The powder X-ray diffraction (XRD) pattern of m-$Bi_2O_4$ was collected with Cu Kα radiation on a powder X-ray diffractometer (Shimadzu XRD-6100). The morphology and microstructure of m-$Bi_2O_4$ was recorded by a scanning electron microscope (SEM, Hitachi S4800) and a transmission electron microscope (TEM, FEI Tecnai G2). X-ray photoelectron spectroscopy (XPS) and valence band X-ray photoelectron spectroscopy (VBXPS) were used to analyze the surface electronic states and valence band of the catalysts (Thermo-VG Scientific ESCALAB 250Xi). The electron paramagnetic resonance (EPR) spectrum was taken on Bruker A320. The specific surface areas of m-$Bi_2O_4$, $BaTiO_3$, and BiOCl determined by the Brunauer-Emmett-Teller (BET) equation were obtained using nitrogen adsorption-desorption experiments on a gas adsorption analyzer (Quantachrome, IQ-AG-MP) at 77K. The piezoelectric property of m-$Bi_2O_4$ was characterized on a piezoresponse force microscope (PFM, Bruker Dimension Icon). The bandgaps of the tested materials were calculated by Kubelka–Munk function based on UV–vis diffuse reflectance spectra (ThermoFisher Cary 5000). The Mott-Schottky plots were tested on an electrochemical workstation (CHI660E) with a common three-electrode system, where Ag/AgCl and a Pt sheet were used as reference electrode and counter electrode, respectively. The working electrode was prepared on an ITO glass. Briefly, 7 mg of m-$Bi_2O_4$ and 40 μL of nafion solution were dispersed in 5 mL of ethanol by sonication for 30 min. The suspension was dropped onto the ITO glass with an area of around 1 cm × 1 cm. The potential ranged from -0.8 V to 0.5 V with the frequency at 1000 Hz. The measurement was operated in 0.5 M $Na_2SO_4$ solution.

**Piezocatalytic degradation experiments.** An antibiotic pharmaceutical, SM was selected as an organic pollutant to evaluate the piezocatalytic activities of m-$Bi_2O_4$. Typically, 60 mg of m-$Bi_2O_4$ powder and 50 mL of SM solution (10 mg/L) were placed into a 100 mL beaker. After adsorption-desorption equilibrium for an hour in the dark, the beaker was placed in an ultrasonic cleaner (40 kHz, 300 W). To avoid the influence of temperature and light on degradation, the reactor was kept in the dark at a temperature of 299.5 K±1.5 K. When the water temperature began rising, some ice was added into the ultrasonic cleaner. 1 mL of suspended solution was sampled at different time intervals and separated by filtration with a nylon fiber filter (0.22 μm). The concentration of SM was analyzed on a high-performance liquid chromatography (HPLC, Waters e2695) with a wavelength of 270 nm (Waters 2998 PDA Detector). Control experiments without catalyst was carried out to explore the contributions of ultrasound degradation. In order to assess the universal applicability of piezocatalytic degradation toward aqueous organic pollutants, some other common organic pollutants such as methyl orange (MO, 10 mg/L) and bisphenol A (BPA, 10 mg/L) were also included in the work. Additionally, the factors such as ultrasonic power and frequncey that influence the catalytic degradation efficiency were also included.

## Figures

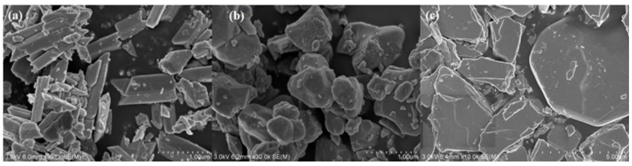

Fig. S1 SEM images of (a) m-$Bi_2O_4$, (b) $BaTiO_3$, and (c) BiOCl.

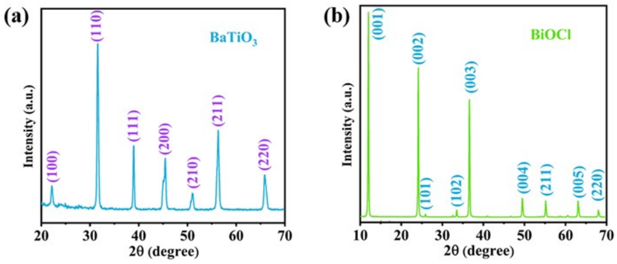

Fig. S2 XRD patterns of (a) $BaTiO_3$ and (b) BiOCl.

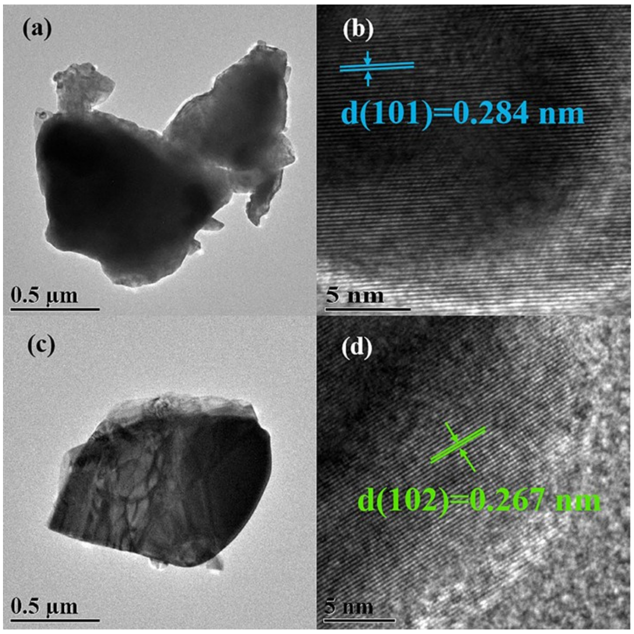

Fig. S3 TEM images of (a, b) $BaTiO_3$ and (c, d) BiOCl.

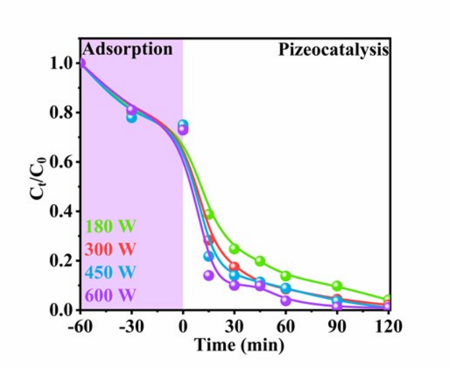

Fig. S4 Piezocatalytic degradation of SM by m-$Bi_2O_4$ under ultrasound with different powers.

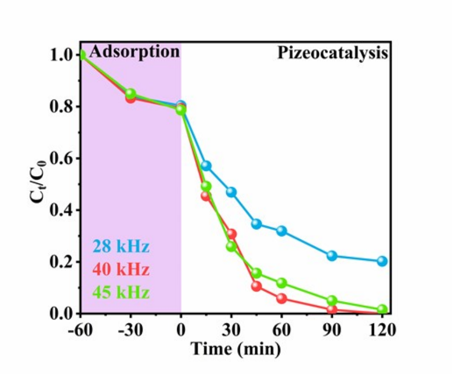

Fig. S5 Piezocatalytic degradation of SM by m-$Bi_2O_4$ under ultrasound with different frequencies.

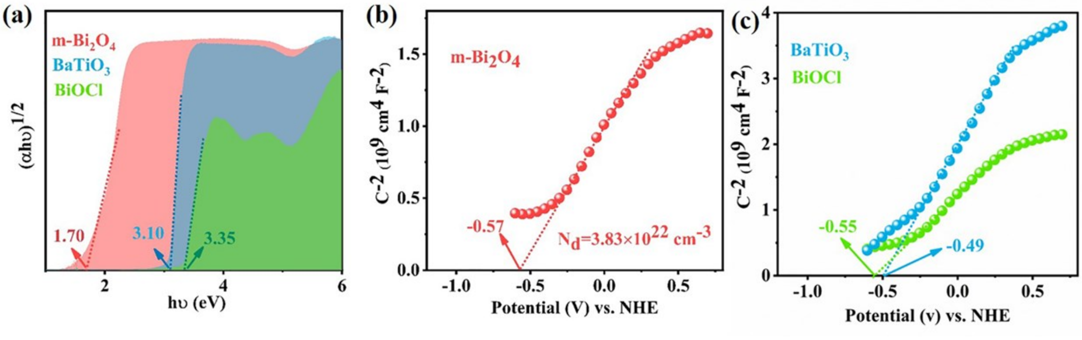

Fig. S6 The Kubelka-Munk curves (a) and Mott-Schottky plots of m-$Bi_2O_4$ (b), $BaTiO_3$ and BiOCl (c).

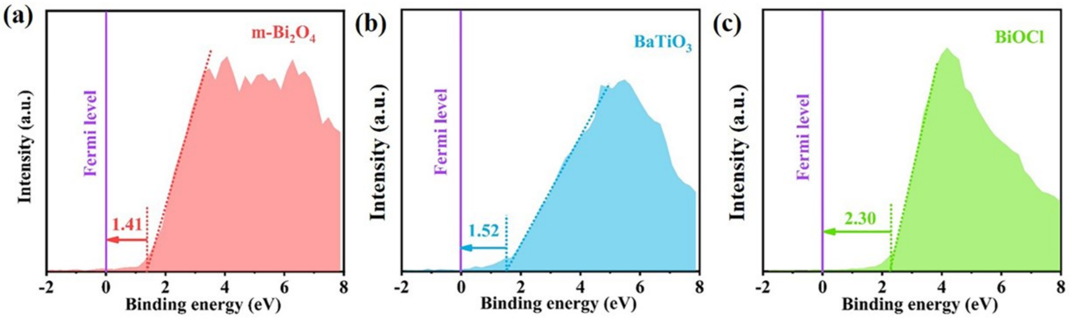

Fig. S7 VBXPS spectrums of (a) m-$Bi_2O_4$, (b) $BaTiO_3$, and (c) BiOCl.

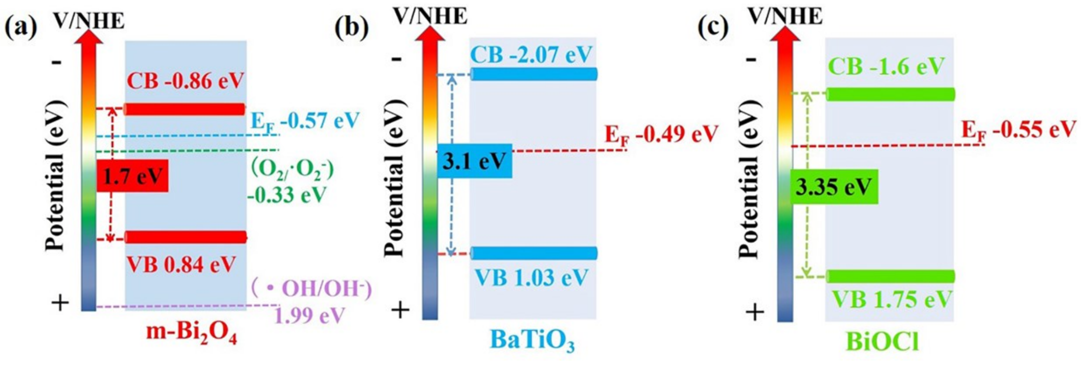

Fig. S8 The band illustration of (a) m-$Bi_2O_4$, (b) $BaTiO_3$, and (c) BiOCl.

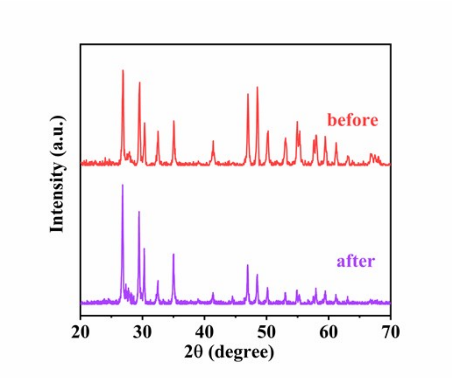

Fig. S9 The XRD spectrums of m-$Bi_2O_4$ before and after SM degradation experiment.

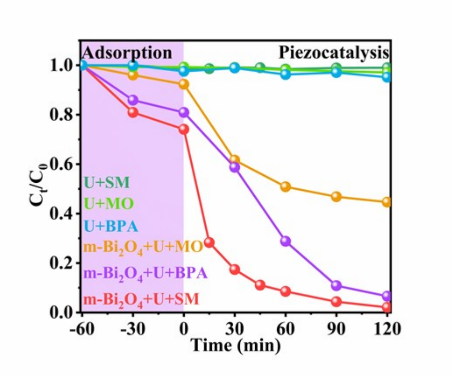

Fig. S10 Piezocatalytic degradation of SM, MO, and BPA by m-$Bi_2O_4$. U in the legends means ultrasonic.

## Equations

$$\frac{1}{C^2} = \frac{2}{e\varepsilon\varepsilon_0 A^2 N_d}\left(E - E_{fb} - \frac{kT}{e}\right) \tag{s1}$$

$$N_d = \frac{2}{e\varepsilon\varepsilon_0 A^2 m} \tag{s2}$$

Eq. (S1) and Eq. (S2) the carrier density ($N_d$). Where C is interface capacitance; A is electrode area; ε is the dielectric constant of catalyst, assigned as 15.85. $\varepsilon_0$ is vacuum permittivity; k is the Boltzmann constant; e is electron charge; E is the potential versus the normal hydrogen electrode; $E_{fb}$ is the flat band potential; m is the slope of the straight part.

$$O_2 + e^- \rightarrow \cdot O_2^- \tag{s3}$$

$$H^+ + \cdot O_2^- \rightarrow \cdot OOH \tag{s4}$$

$$2 \cdot OOH \rightarrow H_2O_2 + {}^1O_2 \tag{s5}$$

$$H_2O_2 + e^- \rightarrow \cdot OH \tag{s6}$$