Electronic Supplementary Material

Piezocatalytic performance of Fe_2O_3-Bi_2MoO_6 catalyst for dye degradation

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2.1. Preparation of the catalysts

The Fe_2O_3-Bi_2MoO_6 composite catalysts were prepared by a hydrothermal method. Typically, 0.1573 g of $Na_2MoO_4 \cdot 2H_2O$ was added into the solution of 0.6306 g of $Bi(NO_3)_3 \cdot 5H_2O$ in ethylene glycol under magnetic stirring, followed by the addition of 32 mL of ethanol. Next, different volumes of 10 mg/mL $Fe(NO_3)_3 \cdot 9H_2O$ solution were introduced to the solution and stirred for 30 min. The mixture was transferred into a Teflon-lined autoclave and sustained at 160 °C for 12 h, after which the solid residue was collected by centrifugation after cooling, washed 4 times with distilled water and dried in vacuum at 60 °C. Finally, the obtained powders were put into a muffle furnace and heated to 250 °C at a heating rate of 2 °C/min for 2 h. For comparison, pure Bi_2MoO_6 catalyst was also synthesized by the same method. The as-synthesized Fe_2O_3-Bi_2MoO_6 composite catalysts with different Fe_2O_3 content were labeled as 1% Fe_2O_3-BM, 3% Fe_2O_3-BM and 5% Fe_2O_3-BM individually, and the pure Bi_2MoO_6 catalyst was tagged as BM.

2.2. Characterizations of catalysts

The crystal phase and crystallinity of the catalysts were determined by the powder X-ray diffraction (XRD, Philips PW3040/6) using Cu Kα radiation at a scanning speed of $2° \cdot min^{-1}$ in a 2θ scanning range of 5°-70°. The morphology of the catalyst was observed by a scanning electron microscopy (SEM, LEO-1530). Transmission electron microscopy (TEM, JEOL-2100F) was carried out to further investigate the microstructure of catalyst at an accelerating voltage of 200 kV. The Fourier transform infrared spectroscopy (FT-IR) analysis was performed using a

NEXUS670 infrared spectrometer in a range of 400-4000 cm^{-1}. Ultraviolet-visible diffuse reflectance spectroscopy (DRS) was utilized to analyze the light absorption properties of photocatalysts and recorded with a Nicolet Evolution 500 UV-Visible spectrometer within a scanning range of 200-700 nm. X-ray photoelectron spectroscopy (XPS, VG ESCAL AB) was employed to examine the surface composition and chemical state of the sample, and the binding energies were corrected using C1s signal located at 284.6 eV. The piezoelectric current and electrochemical impedance (EIS) measurements were conducted on an electrochemical workstation (CHI660E, China) fitted with catalyst as a working electrode, Pt as a counter electrode, Ag/AgCl as a reference eletrode, and 0.5 M Na_2SO_4 aqueous solution as the electrolyte, respectively.

2.3. Piezocatalytic experiments

The catalytic activity of Fe_2O_3-BM catalyst was evaluated for the degradation of different dyes. 10 mg of catalyst was added into 50 mL of rhodamine B (RhB), methylene blue (MB) or methyl orange (MO) solution (15 mg/L), and the suspension was initially stirred and adsorbed in the darkness for 30 min to reach the adsorption-desorption equilibrium between the catalysts and dye. Afterwards, the piezoelectric catalytic experiment was conducted in an ultrasonic cleaner (JP-020S) with a frequency of 40 kHz and power of 120 W. The temperature of the reaction system was maintained at 25 °C by frequent water inflow and outflow operation. Approximately 5 mL of the suspension was taken out and centrifuged to get rid of the solid powder after the interval of 10 min. The decomposition ratio (η) was measured

using a UV-vis spectrophotometer and calculated on the basis of Eq. (2-1):

$$\eta=(C_0-C)/C_0 \times 100\% \quad (2\text{-}1)$$

Where, C_0 and C are the initial and residual dye concentration at time 0 and t min, respectively.

2.4. Free radicals trapping experiments

The active species were determined by radicals trapping experiments under the same conditions as the piezoelectric catalytic degradation reaction, except for the additional 1 mmol of scavenger. The isopropyl alcohol (IPA), triethanolamine (TEA), benzoquinone (BQ) were used as the scavenger for ·OH, h^+ and $\cdot O_2^-$.

3.1. Possible piezoelectric catalytic mechanism

The conduction band (E_{CB}) and valence band (E_{VB}) of BM and Fe_2O_3 catalysts can be calculated by the following equations:

$$E_{VB}=X - E_C + 1/2\ E_g \quad (3\text{-}1)$$

$$E_{CB}=E_{VB} - E_g \quad (3\text{-}2)$$

Wherein, X is the absolute electronegativity of the semiconductor material, E_C is the energy of free electrons (4.50 eV), and E_g is the bandgap energy of the semiconductor material. The values of CB and VB for the BM catalyst were calculated to be 0.28 eV and 2.98 eV and that for the Fe_2O_3 catalyst were -0.72 eV and 1.28 eV, separately. The values are consistent with those reported in the literatures [1,2]. In addition, the VB potential of BM and Fe_2O_3 was further determined by X-ray photoelectron spectroscopy valence band spectroscopy (VB-XPS). According to Fig. S4, the VB values of the as-prepared BM and Fe_2O_3 catalysts are 2.97 eV and 1.30 eV, which are very close to the theoretical calculated values.

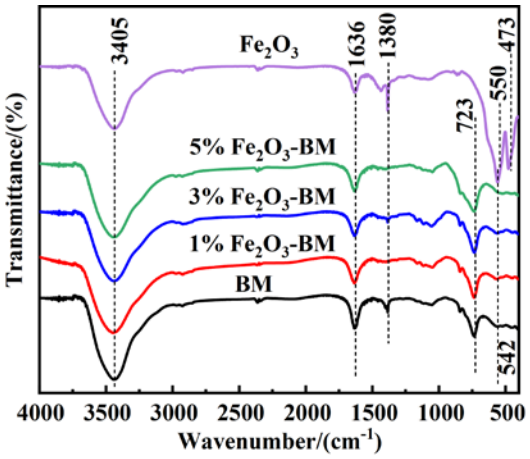


Fig. S1 FT-IR spectra of different Fe_2O_3-BM catalysts

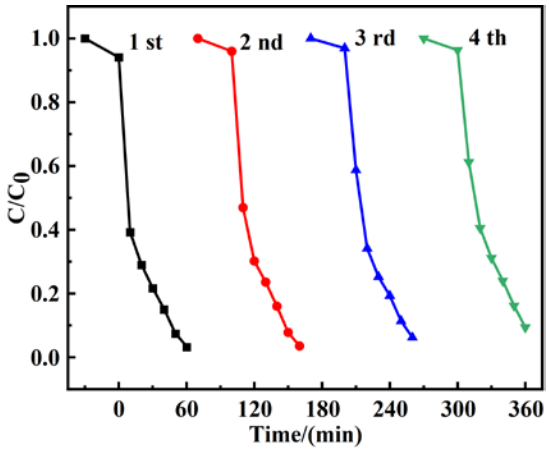
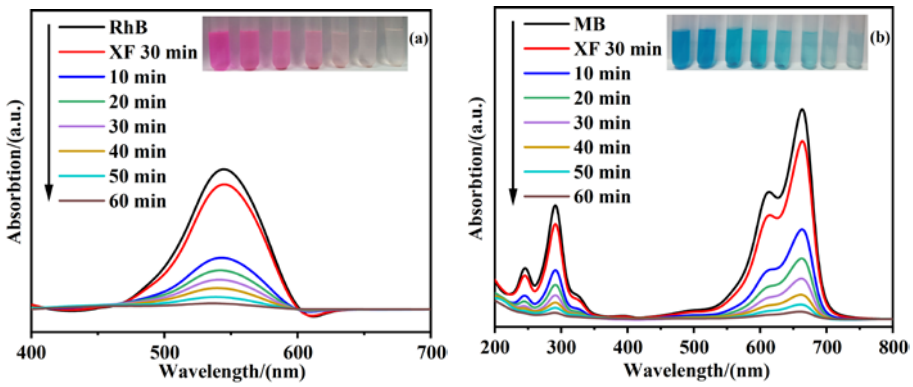


Fig. S2 Piezoelectric catalytic degradation experiment of dyes with 3% Fe_2O_3-BM catalyst



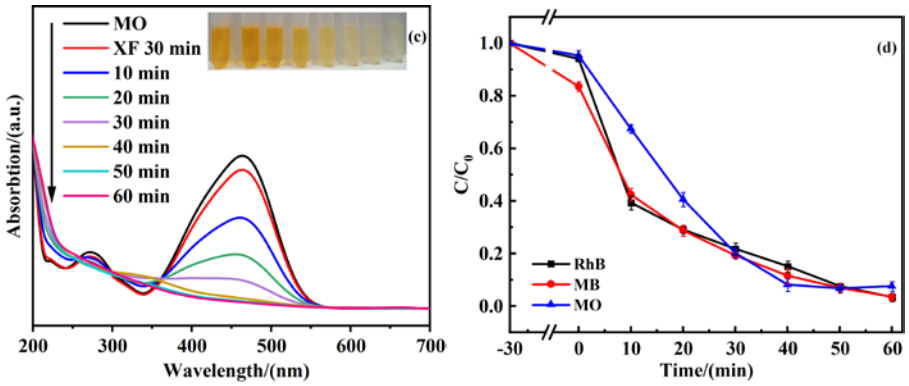


Fig. S3 UV-vis absorption spectra of (a) RhB, (b) MB, (c) MO upon piezoelectric degradation catalyzed by 3% Fe_2O_3-BM catalysts (The insets are the photographs of the organic solutions upon degradation), and (d) Time-dependent piezocatalytic activity

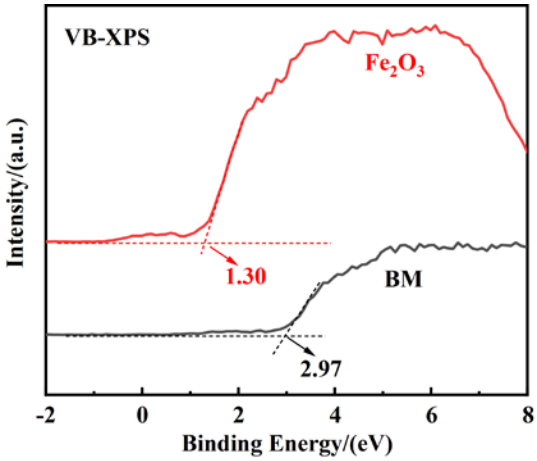


Fig. S4 VB XPS spectra of BM and Fe_2O_3 catalyst

References

[1] Li S J, Hu S W, Zhang J L, Jiang W, Liu J S. Facile synthesis of Fe_2O_3 nanoparticles anchored on Bi_2MoO_6 microflowers with improved visible light photocatalytic activity. Journal of Colloid and Interface Science, 2017, 497: 93-101

[2] Zhao J, Lu Q F, Wei M Z, Wang C Q. Synthesis of one-dimensional α-Fe_2O_3/Bi_2MoO_6 heterostructures by electrospinning process with enhanced photocatalytic activity. Journal of Alloys and Compounds, 2015, 646: 417-424