Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Supplementary Materials

Mechanistic Insights into MnO_x-Cocatalyzed Piezophotocatalytic Dye Degradation over S-Scheme $MnO_x/BiFeO_3$ Heterojunctions

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1. *Preparation of $MnO_x/BiFeO_3$ catalyst*

The chemicals required for the preparation of $MnO_x/BiFeO_3$, including ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), potassium hydroxide (KOH), concentrated nitric acid (HNO_3), manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$), and methanol (CH_3OH), were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd.

$BiFeO_3$ nanosheets were prepared via a hydrothermal method with the following procedure: First, 2.027 g of $FeCl_3 \cdot 6H_2O$ and 3.638 g of $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in 30 mL of dilute nitric acid solution (prepared with a volume ratio of deionized water to concentrated nitric acid of 4:1). Meanwhile, 10.0 g of KOH was dissolved in 25 mL of deionized water and stirred thoroughly until completely dissolved. Subsequently, the KOH solution was slowly added dropwise to the above metal nitrate solution under magnetic stirring and allowed to react for 1 hour to ensure thorough mixing. The resulting mixture was then moved into a stainless-steel autoclave lined with polytetrafluoroethylene and heated at 200 °C for 12 hours. After that, the product was collected by centrifugation, washed sequentially with deionized water and ethanol, and finally dried to obtain $BiFeO_3$ powder.

2. Piezocatalytic and piezo-photocatalytic reaction

The piezoelectric catalytic activity of $MnO_x/BiFeO_3$ catalysts was evaluated by measuring the degradation rate of RhB dye under ultrasonic vibration. Typically, 100 mL of RhB aqueous solution (5 ppm) was prepared, and 3 mL of the solution was collected as sample 0. Then 0.1 g prepared catalyst was dispersed into the solution under magnetic stirring. After continuous stirring for 1 h, an adsorption-desorption equilibrium between the piezocatalyst and RhB solution has been established. 3 mL solution was then collected as sample 1. After that, the piezocatalytic reaction was carried out with a digital ultrasonic generator (JIEMENG JP-020, 40 kHz, 60 W) as the mechanical press source. The temperature of the reactor was maintained between 20-30°C by replacing the cooling water. During the reaction, 3 mL of the solution was collected at every 15 min interval. The collected samples were then centrifuged to remove piezocatalysts. The supernatant was analyzed via a UV-vis spectrophotometer (Beijing Purkinje, TU-1950) to determine the RhB content based on its strongest absorbance at 554 nm.

The examination experiment process of reactive species was similar to the photodegradation experiment. A quantity of scavengers (KI, benzoquinone, and isopropyl alcohol) was introduced into the RhB solution prior to addition of the catalyst. The concentration of scavengers was controlled to be 1 mmol/L according to the previous studies. The recycling experiment was conducted four times. After each reaction, the catalyst was collected by centrifugation, washed three times with deionized water, and then dried in an oven at 60 °C for reuse.

The procedure for the photocatalytic reaction is the same as for the piezocatalytic reaction, except that the reaction is carried out under light. A 300 W Xe lamp was used as the light sources. The distance between the reactor and the Xe lamp is about 10 cm. In piezo-photocatalytic reactions, light irradiation and ultrasonic vibrations act simultaneously on the reaction solution. Most of the catalytic tests were conducted three times to ensure reliability.

Total organic carbon (TOC) of the reaction solution was monitored by a TOC analyzer in water (Vario TOC select, Germany). The TOC removal efficiency is obtained by comparing the change of TOC in the solution before and after the photocatalytic reaction.

3. Characterizations of piezocatalysts

X-ray fluorescence (XRF) spectrometer (SHIMADZU EDX-GP) was used to analyze the Mn element in $MnO_x/BiFeO_3$ catalyst. X-ray diffraction (XRD) analysis was performed on a D8 Advance (BRUKER AXS GMBH, Germany) X-ray diffractometer using Cu Kα radiation (40 kV/40 mA). The Raman spectra of the catalysts were recorded on a RM1000 spectrometer (Renishaw) via an excitation source of an Ar ion laser (514.5 nm). UV-visible diffuse reflection spectroscopy (DRS) was actualized on a UV-visible spectrophotometer (Agilent Cary5000) and the reference sample was $BaSO_4$. Scanning electron microscopy (SEM) was carried out on a Field emission scanning electron microscope (Hitachi S-4800) with the accelerating voltage of 5 kV. Transmission electron microscopy (TEM) was employed on a JEM-2010F transmission electron microscope via the accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) spectra of the catalysts were obtained via using a Thermo Scientific ESCALAB 250Xi Microprobe instrument using Al-Kα as a ray source. The C 1s signal was adjusted in the location of 284.6 eV. Ultraviolet photoelectron spectroscopy (UPS) analysis was conducted using a He resonance lamp (He I line, 21.22 eV) on the same instrument. A CHI 660E electrochemical workstation with a standard three-electrode cell was employed to perform the piezoelectric current responses, linear sweep voltammetry (LSV), and the electrochemical impedance spectroscopy (EIS). The test was operated at room temperature. The piezocatalyst, Ag/AgCl (saturated KCl), and a Pt wire were used as the working electrode, the reference electrode, and the counter electrode, respectively. The coated area of the catalyst on the ITO glass was 1.0×1.0 cm and Na_2SO_4 (0.5 M) aqueous solution was used as the electrolyte. In order to increase the adhesion of catalyst on the ITO substrate, carbon conductive adhesive was used during the preparation of working electrode. The size of carbon conductive adhesive is 1.0 cm × 1.0 cm, while the catalyst sample is coated on the carbon conductive adhesive. Surface photovoltage (SPV) analysis was conducted on a steady-state surface photovoltage spectrometer (PL-SPV/IPCE1000, PerfectLight Technology).

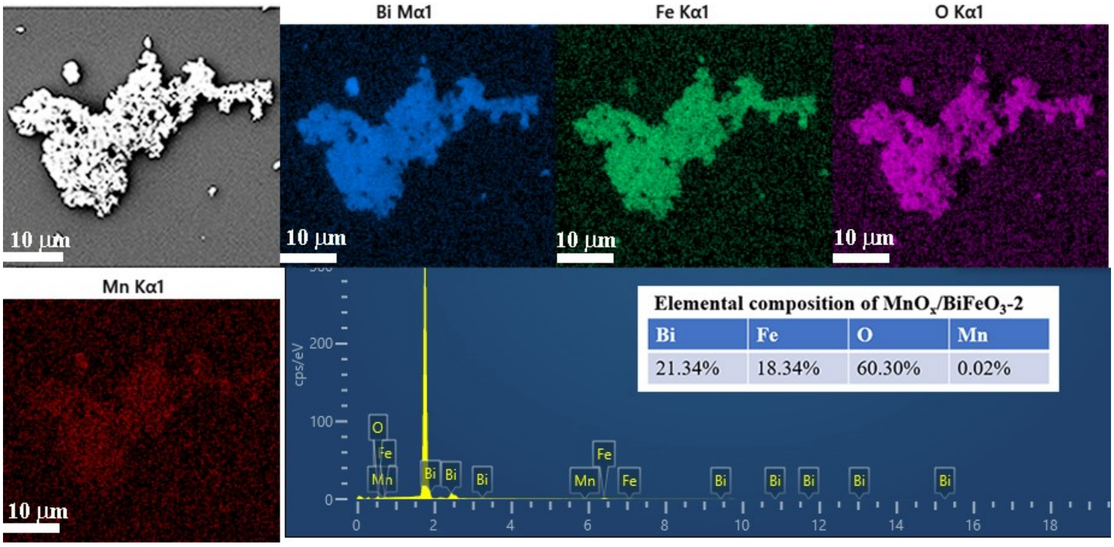
The local piezoelectric response of $BiFeO_3$ and $MnO_x/BiFeO_3$ was characterized using piezoresponse force microscopy (PFM, Cypher, Asylum Research). The probe used in PFM measurements was the SCM-PIT-V2 probe made of 0.01–0.025 Ω·cm Antimony (n) doped Si material. The probe tip was coated with conducting Pt-Ir coating. The amplitude and frequency of applied AC voltage were ±40 V and ~350 kHz. Before testing, the catalyst powder had to be prepared as a thin film on a conductive silicon wafer. The preparation process is as follows: Ten milligrams of catalyst powder are weighed into a centrifuge tube. Then, 425 μL of anhydrous ethanol and 75 μL of naphthol are added. The mixture is sonicated to ensure thorough mixing. After sonication, the solution is allowed to stand until it separates into layers. Next, 5 μL of the supernatant are pipetted onto a pre-prepared conductive silicon wafer and allowed to air dry in a fume hood.

The ESR spectra were recorded at room temperature using a Bruker model ESR JES-FA200 spectrometer. The sample for ESR measurement was prepared by adding 5 μL 5,5′-dimethyl-1-pirroline-N-oxide (DMPO) to a 50 μL of 1 g/L catalyst aqueous solution or toluene solution to detect ·OH and $\cdot O_2^-$ radicals, respectively. The photocatalysts were irradiated with the aforementioned visible light for 5 min. The ESR measurement was performed immediately after the illumination. The hole detection experiment was implemented by the similar process. Only DMPO was replaced by 2,2,6,6-tetramethylpiperidine N-oxide (TEMPO).

4. Computational Details

The finite element method (FEM) was performed by the module of the piezoelectric device in COMSOL Multiphysics software based on steady-state research. To better match the practical situation, the simulated size for the $BiFeO_3$ nanosheet was set to be 800×500×80 nm^3 and a semi-elliptic model with a major axis of 30 nm and a minor axis of 20 nm was modeled for MnO_x nanoparticles according to SEM and TEM results. The material parameters required for the simulation were obtained from the literature [Chemosphere, 335 (2023) 139084, Solid State Commun., 218 (2015) 10-13]. The compressive stress of 100 MPa was applied in the direction perpendicular to the $BiFeO_3$ nanosheet.

All the density functional theory (DFT) calculations were performed with the Vienna ab initio simulation package (VASP) code [J. Comput. Chem. 29 (2008) 2044-2078, Phys. Rev. B, 50 (1994) 17953-17979.]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was utilized. The model of amorphous MnO_x was built based on MnO_2 (100) with oxygen vacancy [ACS Appl. Mater. Interf. 15 (2023) 14228-14239]. The vacuum thickness was set to 15 Å along the z direction under boundary conditions, to avoid interlayer interaction and allow relaxation of all atoms. The plane wave cut-off energy was set to 520 eV. Van der Waals (vdW) interaction was described using Grimme's semi-empirical dispersion-corrected DFT-D3 method. The k-point density was 4×2×1 in the Brillouin zone, and the self-consistent-field convergence tolerances for the atomic positions were 0.02 eV $Å^{-1}$ for the force and 10^{-5} eV for the energy.



Elemental composition of $MnO_x/BiFeO_3$-2

Bi	Fe	O	Mn
21.34%	18.34%	60.30%	0.02%

Figure S1 SEM image of the $MnO_x/BiFeO_3$-2 sample, accompanied by EDS elemental mapping and corresponding elemental composition.

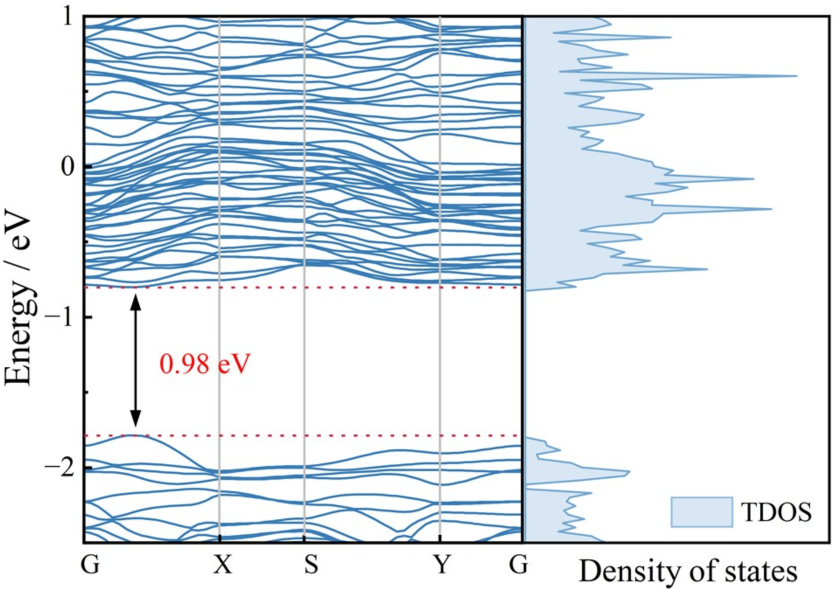


Figure S2 Electronic band structures and total density states (TDOS) of MnO_x

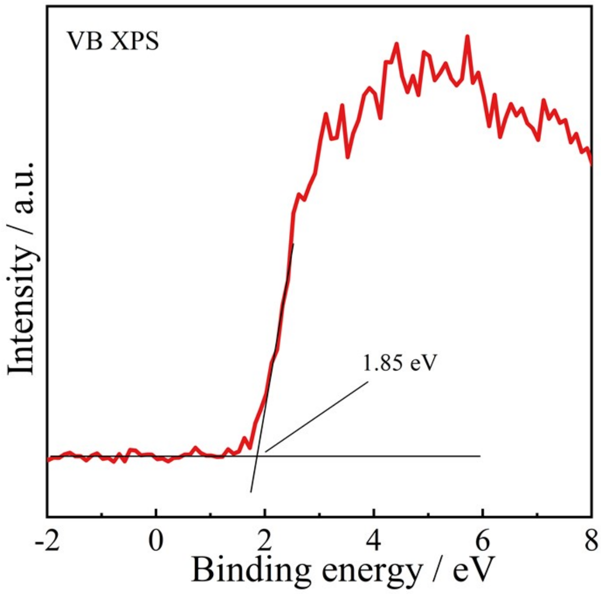


Figure S3 VB XPS spectra of $BiFeO_3$

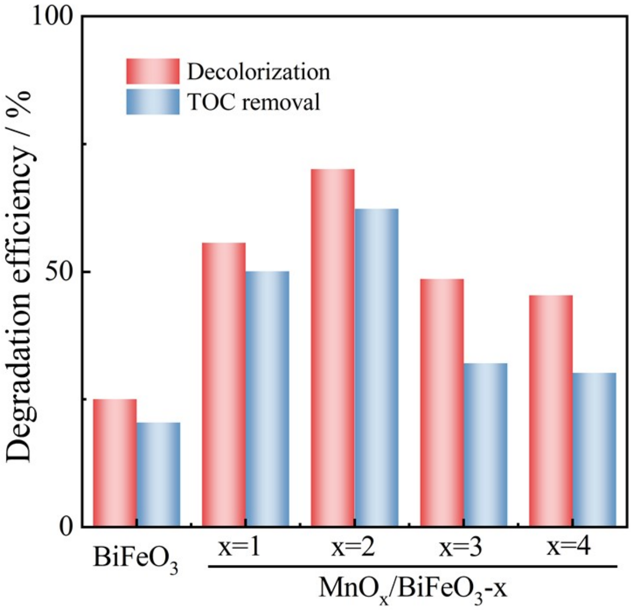


Figure S4 Decolorization and TOC removal efficiencies of pure $BiFeO_3$ and $MnO_x/BiFeO_3$ composites during the photocatalytic degradation of RhB.

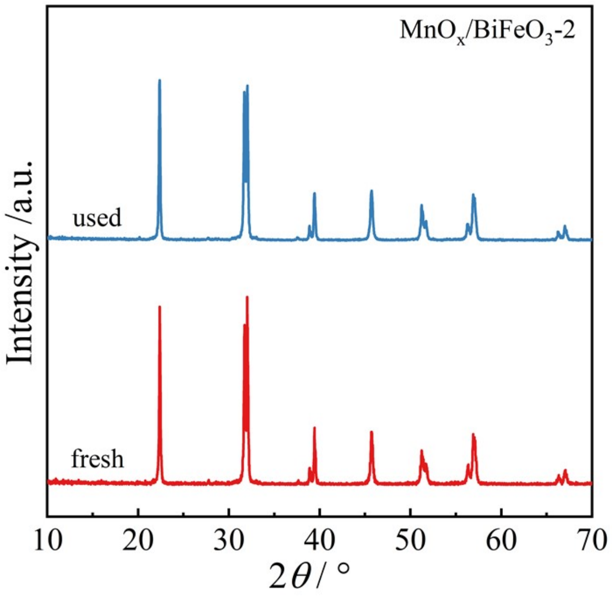


Figure S5 XRD patterns of MnOx/BiFeO$_3$-2 before and after reaction

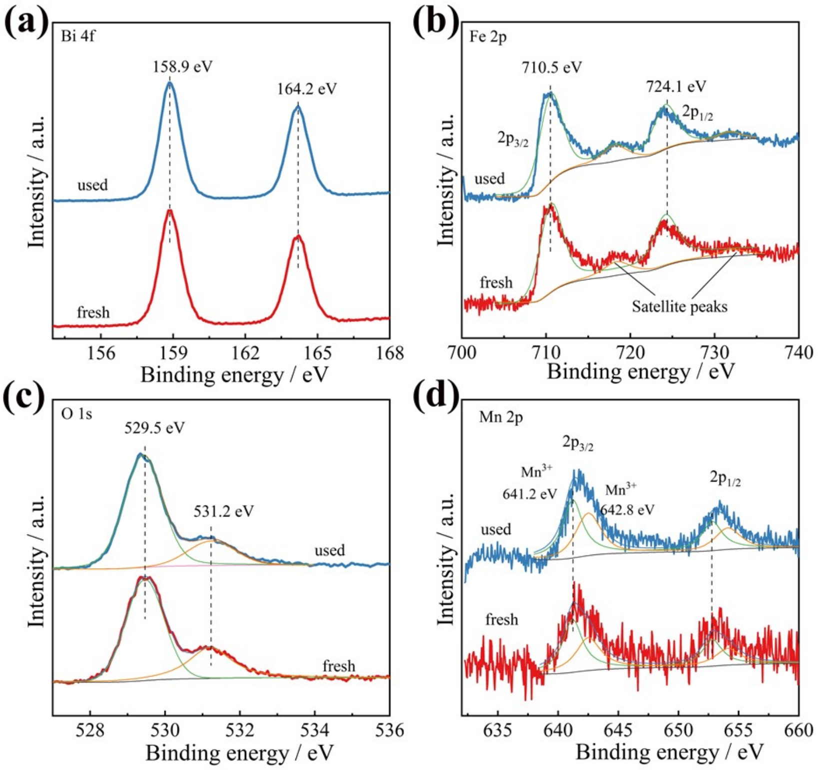


Figure S6 XPS spectra of MnOx/BiFeO$_3$-2 before and after reaction: (a) Bi4f; (b) Fe 2p; (c) O 1s; (d) Mn 2p

Table S1 Element content of various $MnO_x/BiFeO_3$ catalysts by XRF.

Catalysts	Element content /%			#Mn content
	Bi	Fe	Mn	
$BiFeO_3$	69.41	30.59	-	-
$MnO_x/BiFeO_3$-1	69.11	30.89	-	-
$MnO_x/BiFeO_3$-2	68.89	31.02	-	-
$MnO_x/BiFeO_3$-3	69.01	30.56	0.43	0.6%
$MnO_x/BiFeO_3$-4	69.41	30.01	0.58	0.8%

#: Calculated by Mn/Bi

Table S2 Comparison of catalytic degradation performance between varied piezocatalysts and $MnO_x/BiFeO_3$ sample.

Catalysts	Dye	Content	k_{app} / h^{-1}	Degradation efficiency	Vibration	Ref.
$BiFeO_3/TiO_2$	MV	10 ppm	0.26	40%(90min)	40 kHz/300W	[1]
*$BiFeO_3/TiO_2$	MV	10 ppm	1.44	88%(90min)	40 kHz/300W	[1]
β-$Bi_2O_3/BiFeO_3$	TC	10 ppm	0.34	41.4%(90min)	40 kHz/180W	[2]
*β-$Bi_2O_3/BiFeO_3$	TC	10 ppm	1.71	92.8%(90min)	40 kHz/180W	[2]
MOF-BFO	RhB	5 ppm	/	74%(80min)	40 kHz/80W	[3]
$Bi_{0.9}Gd_{0.07}La_{0.03}FeO_3$	MB	20ppm	/	37%(90min)	40 kHz/120W	[4]
*$Bi_{0.9}Gd_{0.07}La_{0.03}FeO_3$	MB	20ppm	/	95%(90min)	40 kHz/120W	[4]
$Bi_2ZnB_2O_7$ -PVDF	MB	5 ppm	0.29	30%(90min)	40 kHz/150W	[5]
$CoO_x/Bi_4Ti_3O_{12}$	MO	5 ppm	1.09	76.0 %(90min)	40 kHz/120W	[6]
I^{5+} doped Bi_2MoO_6	MB	10 ppm	1.14	77.3%(80min)	40 kHz/150W	[7]
V^{5+} doped Bi_2MoO_6	MB	10 ppm	1.17	78.6%(80min)	40 kHz/150W	[7]
Ag_2O/Bi_2WO_6	CIP	10 ppm	0.88	73.5%(60min)	40	[8]

					kHz/200W	
Au/$BiVO_4$	4-CP	13 ppm	/	83%(90min)	40 kHz/120W	[9]
	Cr (VI)	10 ppm	/	79%(90min)		
$V_2O_5/BiVO_4$	MB	5 ppm	/	40%(90min)	40 kHz/70W	[10]
$MnO_x/BiFeO_3$	RhB	5 ppm	0.78	70.0%(90min)	40 kHz/60W	This work
*$MnO_x/BiFeO_3$	RhB	5 ppm	1.4	90.5%(90min)	40 kHz/60W	

*piezo-photocatalytic performance

References:

[1] Y.L. Liu, J.M. Wu, Synergistically catalytic activities of $BiFeO_3/TiO_2$ core-shell nanocomposites for degradation of organic dye molecule through piezophototronic effect, Nano Energy 56 (2019) 74-81.

[2] X.F. Sun, T. Xian, R.S. Li, H. Yang, Heterojunction interface field and piezoelectric polarization field cooperatively facilitating photocarrier separation in heterojunction piezo-photocatalysts: Experimental and theoretical characterization, Colloids Surf. A: Physicochem. Eng. Asp. 677 (2023) 132430.

[3] J.J. Ning, Z.H. Kang, N. Qin, M.S. Chen, J. Wu, D.H. Bao, Boosting piezocatalytic performance of perovskite $BiFeO_3$ with controlled oxygen vacancies, J. Alloys Compd. 978 (2024) 173370.

[4] A.D. Mani, J. Li, Z. Wang, J. Zhou, H. Xiang, J. Zhao, L. Deng, H. Yang, L. Yao, Coupling of piezocatalysis and photocatalysis for efficient degradation of methylene blue by $Bi_{0.9}Gd_{0.07}La_{0.03}FeO_3$ nanotubes, J. Adv. Ceram. 11 (2022) 1069-1081.

[5] C. Porwal, S. Verma, A. Gaur, V.S. Chauhan, R. Vaish, $Bi_2ZnB_2O_7$-PVDF electrospun composite membrane for waste water treatment utilizing photo-piezocatalysis, Mater. Sci. Eng. B 298 (2023) 116842.

[6] K. Wang, Z. Guan, X. Liang, S. Song, P. Lu, C. Zhao, L. Yue, Z. Zeng, Y. Wu, Y. He, Remarkably enhanced catalytic performance in $CoO_x/Bi_4Ti_3O_{12}$ heterostructures for methyl orange degradation via piezocatalysis and piezo-photocatalysis, Ultrason. Sonochem. 100 (2023) 106616.

[7] T. Chen, Z. Zhu, F. Chen, C. Hu, H. Huang, Low-valence B-site cation substitution triggering polarization and oxygen vacancy enhancement for elevating piezocatalytic activity on Bi_2MoO_6, Appl. Surf. Sci. 616 (2023) 156467.

[8] B. Liu, L.Y. Sun, Y.X. Chen, S.X. Su, X.F. Wang, X. Wang, A novel Ag_2O/Bi_2WO_6 composite with enhanced piezocatalytic performance for ciprofloxacin removal, Inorg. Chem. Commun. 159 (2024) 111832.

[9] Y. Wei, Y.W. Zhang, W. Geng, H.R. Su, M.C. Long, Efficient bifunctional piezocatalysis of $Au/BiVO_4$ for simultaneous removal of 4-chlorophenol and Cr (VI) in water, Appl. Catal. B: Environ. 259 (2019)118084.

[10] G. Singh, M. Kumar, R. Vaish, Promising multicatalytic and adsorption capabilities in $V_2O_5/BiVO_4$ composite pellets for water-cleaning application, Surfaces Interf. 23 (2021) 100924.