Supporting Information

Electro-enhanced Mass Transfer Boosting Photocatalysis towards Ionized Organic Pollutants

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Section S1 Experimental methods

1.1 Chemicals and materials

2-methylimidazole ($C_4H_6N_2$, 98%), zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 98%), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, 98%), ethylene glycol ($C_2H_6O_2$, 98%), tetracycline hydrochloride ($C_{22}H_{24}N_2O_8 \cdot HCl$, 96%), hydrochloric acid (HCl, 25%), potassium hydroxide (KOH, 95%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Deionized water was lab-made by an ultrapure water system (YOUPU UPHC-I-90T, Chengdu, China). All reagents were used as received without further purification.

1.2 Preparation of ZIF-8-derived porous carbon

1.2.1 Preparation of the precursor (ZIF-8)

Firstly, 18 g of 2-methylimidazole was added to 500 mL of deionized water and dissolved through thorough stirring to form Solution A. Next, 12 g of zinc acetate was added to 500 mL of deionized water and dissolved through thorough stirring to form Solution B. Subsequently, solution A was thoroughly mixed with solution B and stirred for 12 h at room temperature. Finally, after several times of centrifugation, the sample was dried in a vacuum oven at 60 °C for 12 hours. The obtained product was designated as ZIF.

1.2.2 Carbonization of ZIF

An appropriate amount of ZIF material was transferred to an alumina boat and heated to 800 °C in a tube furnace under a nitrogen atmosphere and kept for 2 h at a heating rate of 5 °C min^{-1}, with a nitrogen flow rate of 50 mL min^{-1}. The resulting material was washed with 1 M HCl for 12 h, followed by extensive washing with deionized water until the solution turned neutral, and dried in a vacuum oven at 60 °C for 12 hours. The ZIF-8-derived carbon was obtained and designated as ZIF-C.

1.2.3 Activation of ZIF-C

12 g of ZIF-C was dispersed in 40 mL of deionized water, and an equal mass of KOH was added to the mixture, which was stirred for 12 hours. The well-stirred mixture was placed in an oil bath to evaporate the water. The resulting sample was transferred to a nickel-porcelain boat and heated to 800 °C in a tube furnace for 2 h under a nitrogen atmosphere at a heating rate of 5 °C min^{-1}, with a nitrogen flow rate of 50 mL min^{-1}. The product was obtained by adding 1 M HCl and stirring for 12 h, followed by washing with large amounts of deionized water until neutral and drying in a vacuum oven at 60 °C for 12 h. The final product was designated as C.

1.3 Preparation of BOB/C composites

0.017 mol of bismuth nitrate pentahydrate was added to 50 mL of ethylene glycol and dissolved by stirring for 1 h at room temperature. Subsequently, 0.0168 mol of KBr was added by stirring for 30 min at room temperature, followed by the addition of 0.5 g of porous carbon (C), with stirring for an additional hour. The resulting composites were subjected to hydrothermal treatment at 140 °C for a duration of 12 h. The composites were then filtered and rinsed three times alternately with ethanol and deionized water to eliminate surface impurities, and subsequently dried in a vacuum oven at 60 °C for 12 h to yield BiOBr/C composites, designated as BOB/C. By adjusting the amount of the carbon, BOB/C with different carbon contents can be obtained.

1.4 Characterization techniques

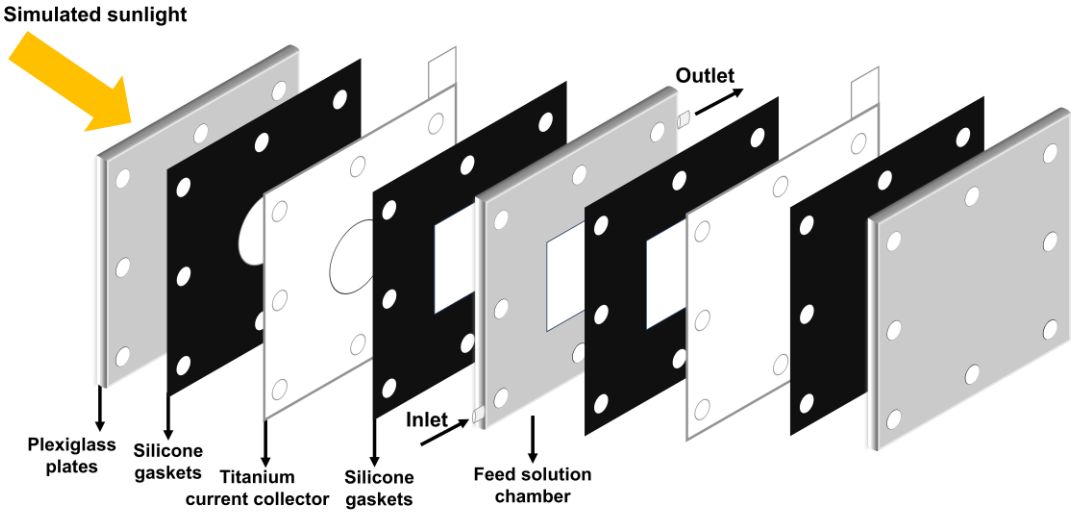
The morphology was characterized by field emission scanning electron microscopy (FE-SEM, JSM-7800F&TEAM Octane Plus, JEOL Co., Ltd.) and high-resolution transmission electron microscopy (HR-TEM, JEM-2100&X-Max80, JEOL Co., Ltd.). X-ray powder diffraction measurements (XRD) were carried out on an X-ray diffractometer (PANalytical Empyrean, Netherlands) equipped with a CuKα radiation source (λ=0.154 nm). The specific surface area was evaluated by N_2 adsorption-desorption isotherms at 77 K (ASAP-3Flex, Micromeritics, USA) employing the Brunauer-Emmett-Teller (BET) method with pore size distributions analyzed by the non-linear density functional theory (NLDFT) model. Chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha+, Thermo Fisher Scientific Inc., UK). Raman spectroscopy was performed using a Raman spectrometer (INVIA REFLEX, Renishaw, UK) equipped with a 532 nm laser. UV-Vis diffuse reflectance spectroscopy was performed using a UV-Vis-NIR spectrometer (UV-3600PLUS, Shimadzu, Japan). Three-dimensional excitation-emission matrix fluorescence spectroscopy (3D-EEM) was performed using a fluorescence spectrophotometer (F-7000, Hitachi, Japan). The setup of *in-situ* electrochemical surface-enhanced Raman spectroscopy was lab-made, and the SERS chip was provided by Shangdong Wisens Technology Co., Ltd., China.

1.5 Three-electrode measurements

Electrochemical/photochemical measurements were conducted in a three-electrode system using an electrochemical workstation (CHI 760E, Shanghai Chenhua Instrument Co., Ltd., China). The three-electrode system was consisted of a working electrode, a counter electrode (Pt foil), a reference electrode (saturated Ag/AgCl electrode), and 1 M NaCl aqueous solution as the electrolyte (1 M Na_2SO_4 for photochemical measurements). Detailed methodologies for the three-electrode measurements were reported in our previous works (Nano Energy, 2023, 117, 108914 and Journal of Advanced Ceramics, 2022, 11(7), 1069-1081).

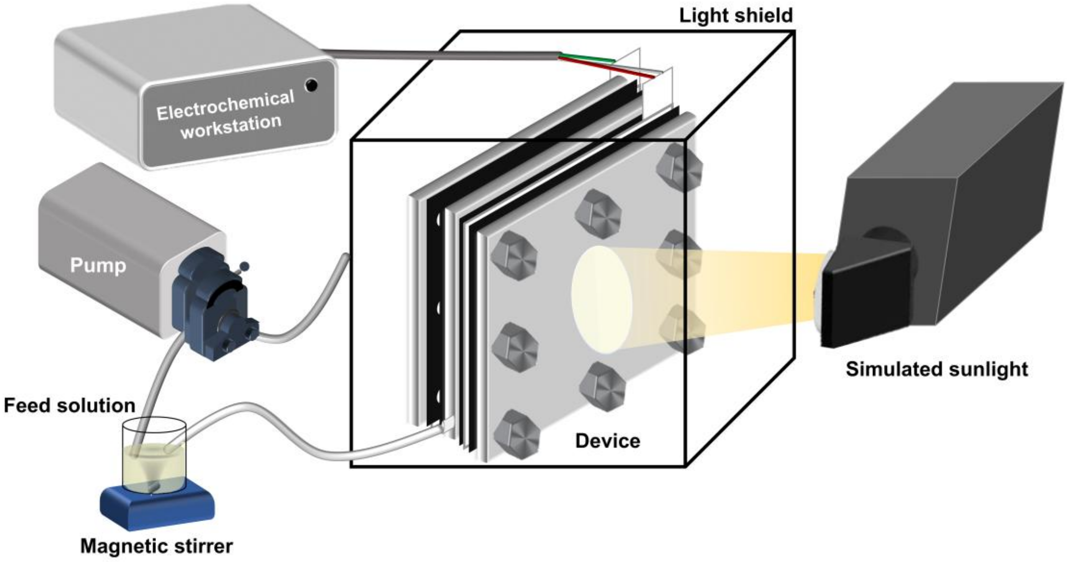
1.6 Device setup for tetracycline removal

The device for tetracycline removal consists of two plexiglass plates, two titanium current collector (the effective area is 8 cm × 8 cm), four silicone gaskets (prevent liquid leakage), and one feed solution chamber made of plexiglass. The structure is shown in the figure below. There are circular holes (the diameter is 3.2 cm) in the center of the silicone gaskets and current collector on one side to ensure light penetration. The material and mass of two electrodes are the same.



1.7 Tetracycline removal experiment

The structure of the EP system is shown in the figure below. Typically, a mixed solution (100 mL) with 100 mg L^{-1} of tetracycline hydrochloride and 10 mM NaCl was placed in a beaker as the feed solution. Before test, the experimental setup was placed in the dark, and the feed solution was circulated at a flow rate of 30 mL min^{-1} for 16 h, which allowed the system to reach its adsorption-desorption equilibrium. During operation, the device was powered by an electrochemical workstation and was irradiated by a sunlight simulator (CEL-PF300-T8E, Beijing China Education Au-light Co., Ltd.) equipped with an AM1.5 optical filter (the light intensity was 1 sun). 1 mL of solution was taken from the beaker every 1 h and the concentration of tetracycline was measured by the UV-Vis spectrophotometer (UV-2600i, Shimadzu, Japan).



1.8 Evaluation of the tetracycline removal performance

The tetracycline removal rate (TRR, mmol g^{-1} h^{-1}) was calculated as:

$$\mathrm{TRR} = \frac{(C_0 - C_\mathrm{t}) \times 0.1\ \mathrm{L}}{m \times t}$$

where C_0 and C_t are the tetracycline concentration of the feed solution (mmol L^{-1}), m and t are the mass of the active material in one electrode (g) and the operation time (h).

Section S2 Supplementary figures

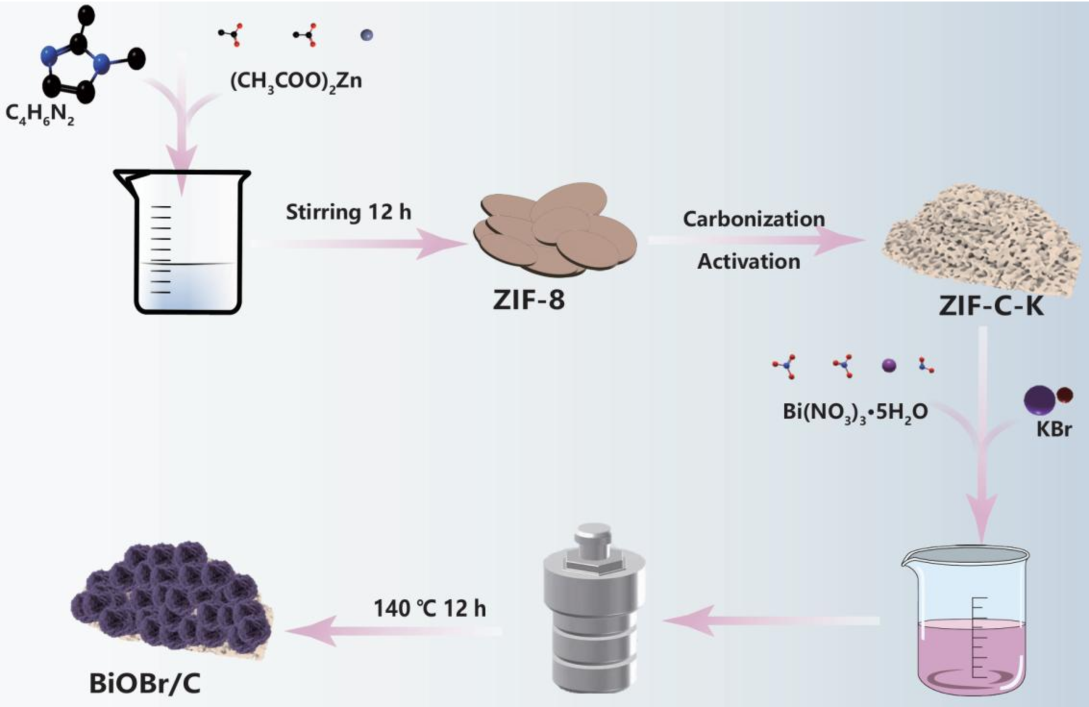


Fig. S1 Preparation procedure of BOB/C

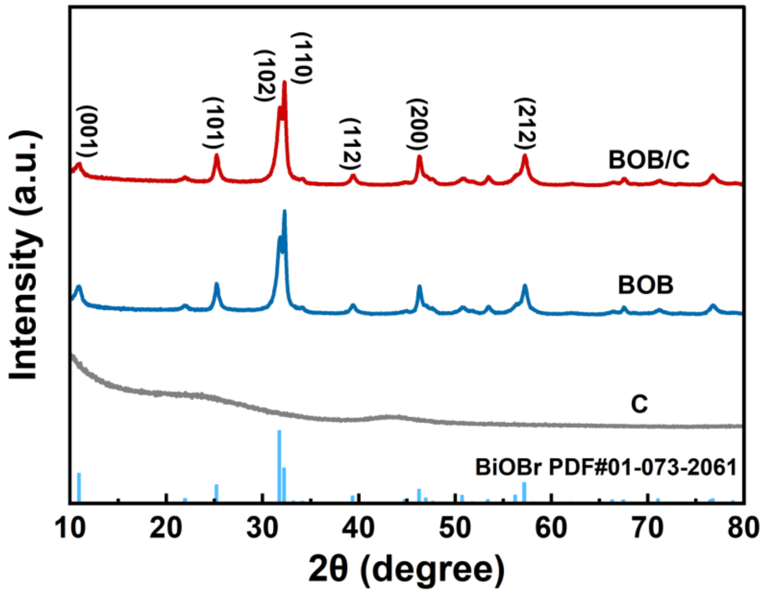


Fig. S2 XRD patterns of C, BOB, BOB/C

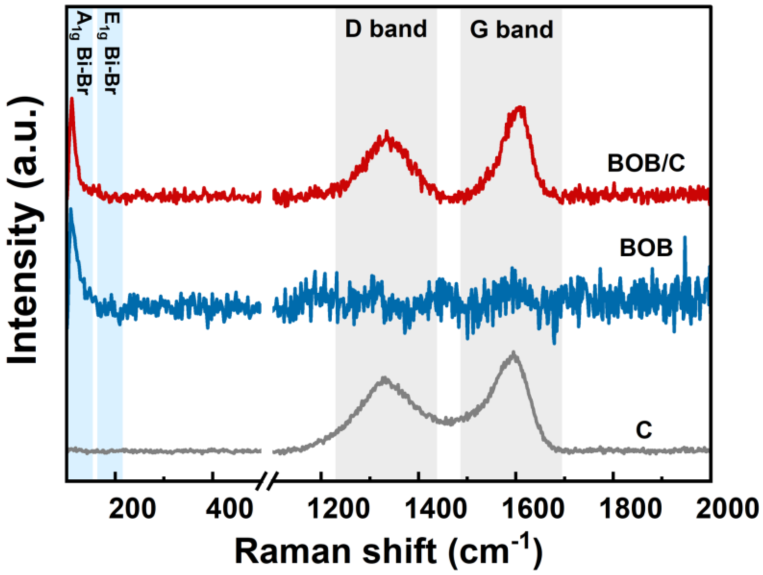


Fig. S3 Raman spectra of C, BOB, and BOB/C

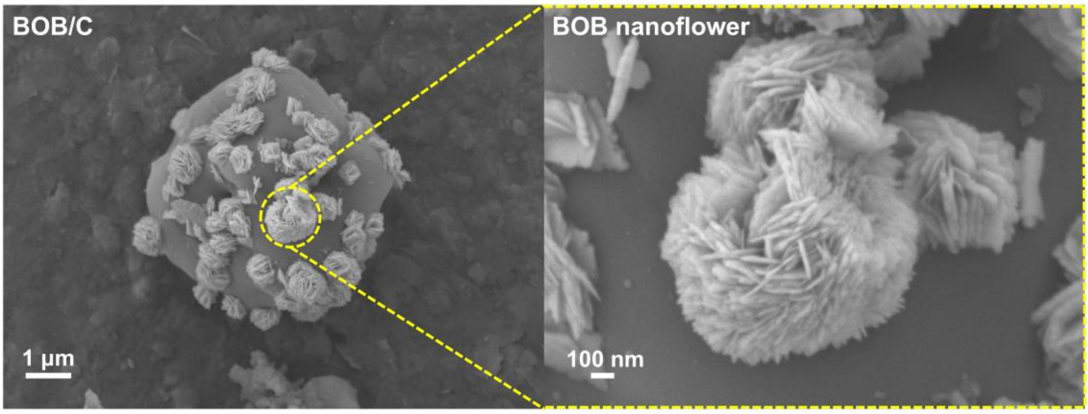


Fig. S4 SEM images of BOB/C and BOB nanoflower

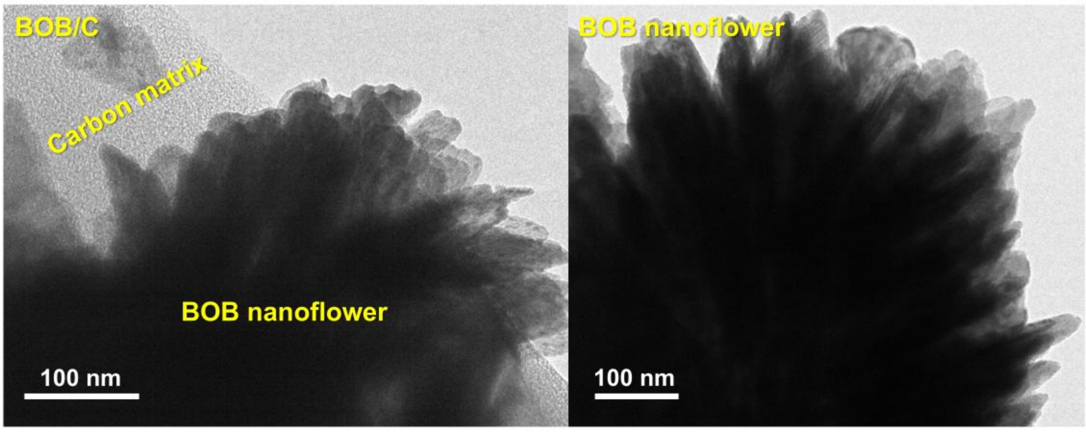


Fig. S5 TEM images of BOB/C and BOB nanoflower

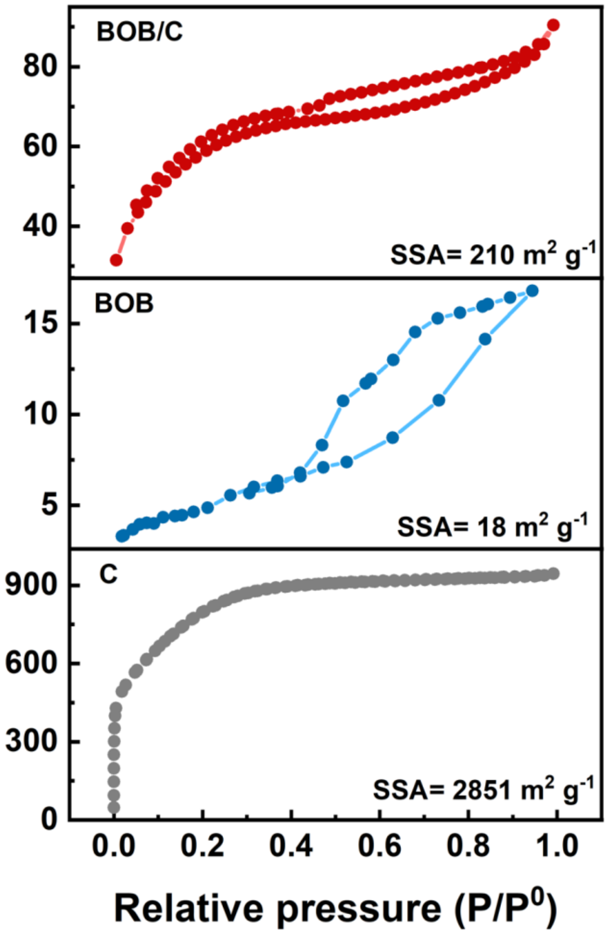


Fig. S6 N_2 adsorption-desorption isotherms of C, BOB, and BOB/C

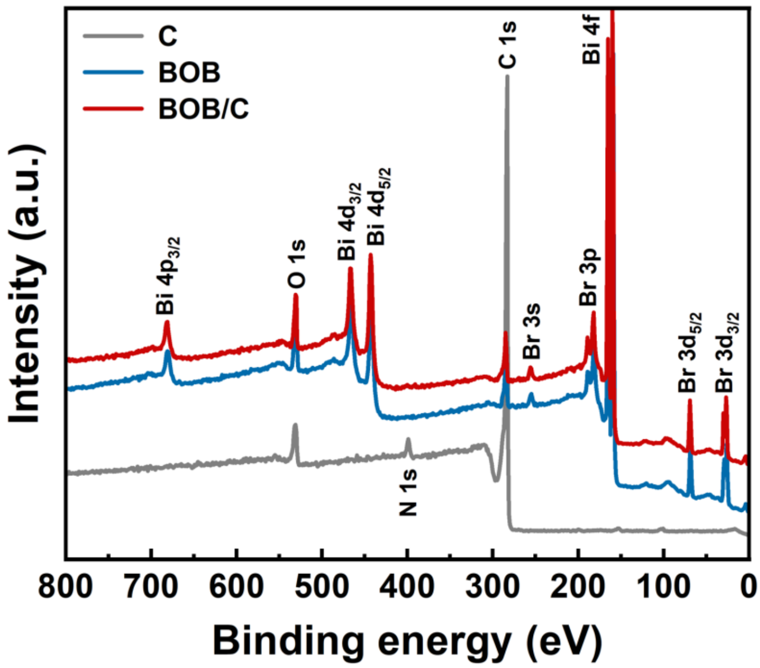


Fig. S7 XPS survey spectra of C, BOB, and BOB/C

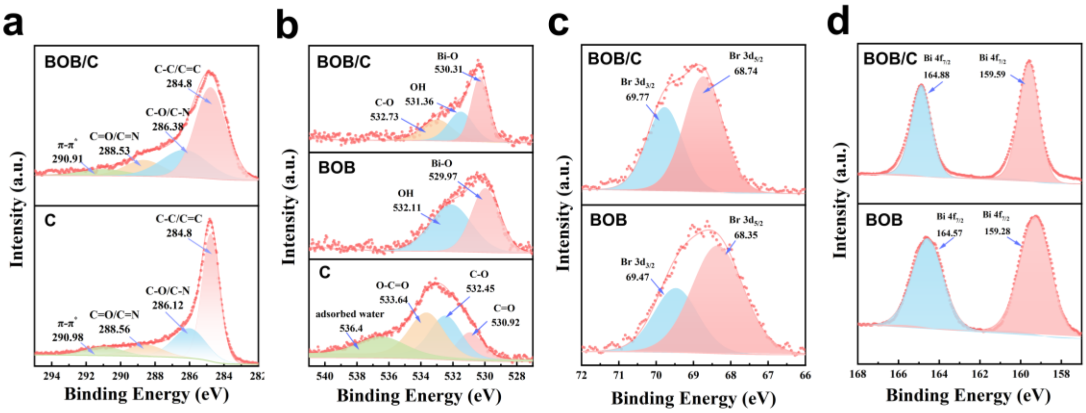


Fig. S8 Evolution of core level spectra: (a) C *1s*, (b) O *1s*, (c) Br *3d*, and (d) Bi *4f* of various samples

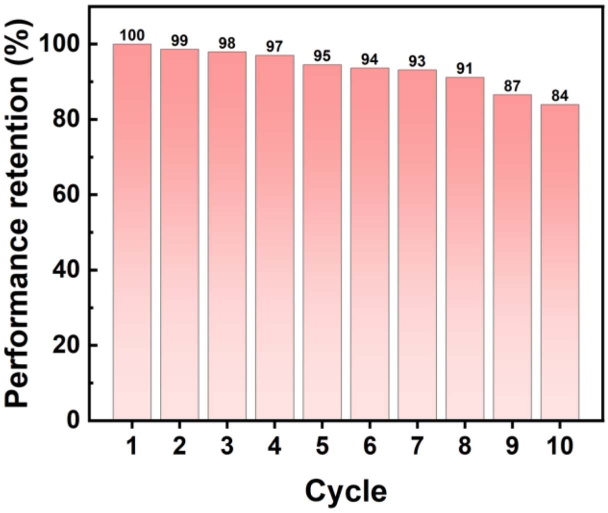


Fig. S9 Long-term stability of EP syst

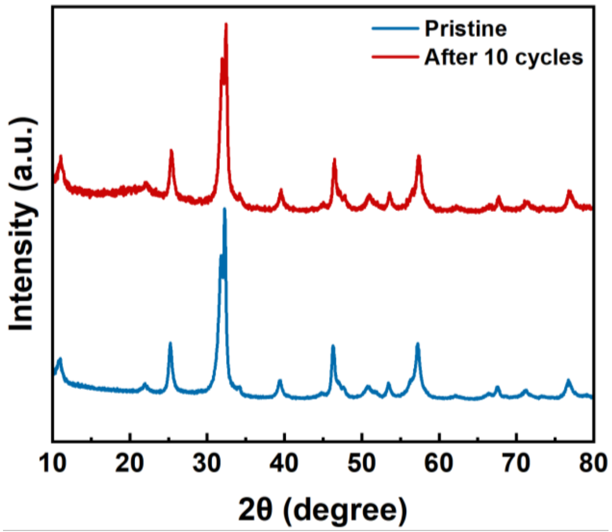


Fig. S10 XRD patterns of the electrodes before and after stability tests.

Section S3 Supplementary tables

Table S1 Properties and tetracycline removal rate of various samples

Sample name	**Carbon content (wt.%)**	**Specific capacitance (mF cm^{-2})**	**Tetracycline removal rate (mmol g^{-1} h^{-1})**
BOB	0	0.33	0.03315
BOB/C-1	5.5	2.42	0.05341
BOB/C-2	7.2	7.26	0.07139
BOB/C-3	8.9	23.42	0.08241
BOB/C-4	10.5	11.31	0.03947
BOB/C-5	12.0	10.17	0.02168
C	100	66.62	0.02803

*Note: Specific capacitances were measured by CV at the scan rate of 100 mV s^{-1}. The tetracycline removal rates were tested in the EP system. Carbon content was evaluated by measuring Bi content in the samples. Bi content was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, ICP-Avio 200, PE Instruments, USA).

Table S2 Tetracycline removal rate at various feed concentrations

Tetracycline concentration (mg L^{-1})	**Removal rate (mmol g^{-1} h^{-1})**
50	0.033
100	0.082
200	0.113
500	0.205

*Note: The tetracycline removal rates were tested in the EP system.

Table. S3 Performance comparison of our work with the literature data

System	Efficiency	Solution volume (mL)	Concentration ($mg\ L^{-1}$)	Removal rate ($mmol\ g^{-1}\ h^{-1}$)	Reference
Photocatalytic degradation	88%	30	10	0.032	Journal of Rare Earths 41 (2023) 1532e1540
Photocatalytic degradation	90%	10	100	0.040	Carbohydrate Polymers 296 (2022) 119970
Photocatalytic degradation	98.47%	50	10	0.069	Journal of Cleaner Production 451 (2024) 141983
Photocatalytic degradation	95.12%	100	20	0.063	Chemical Engineering Journal 464 (2023) 142694
Photocatalytic degradation	83.54%	50	20	0.0084	Applied Catalysis B: Environmental 330 (2023) 122621
Photocatalytic degradation	97.65%	100	10	0.035	Applied Catalysis B: Environmental 330 (2023) 122623
Photocatalytic degradation	81.61%	50	20	0.079	Chemical Engineering Journal 442 (2022) 136249
Photocatalytic degradation	78.1%	30	20	0.015	Chemical Engineering Journal 453 (2023) 139819
EP	85.4%	100	100	0.082	This work

Section S4 Supplementary discussions

4.1 Relationship between electrode spacing and tetracycline removal rate

As shown in Table S4, as the electrode spacing decreases, the tetracycline removal rate gradually increases due to reduced internal resistance and enhanced electric field intensity. However, excessively short electrode spacing can lead to a narrower flow channel, restricting the volume of solution that can pass through and consequently increasing the energy consumption of the pump.

Table S4 Relationship between electrode spacing and tetracycline removal rate

Electrode spacing (mm)	**1**	**2**	**3**
Removal rate (mmol g^{-1} h^{-1})	0.082	0.078	0.075

Test conditions: EP system, 1.2 V, 100 ppm tetracycline + 10 mM NaCl, pH=2.

4.2 Relationship between flow rate and tetracycline removal rate

As shown in Table S5, as the flow rate increases, the tetracycline removal rate gradually increases due to reduced diffusion boundary layer, which enhances mass transfer. However, excessively high flow rate would increase operating costs.

Table S5 Relationship between flow rate and tetracycline removal rate

Flow rate (mL min^{-1})	**0**	**30**	**60**
Removal rate (mmol g^{-1} h^{-1})	0.066	0.082	0.092

Test conditions: EP system, 1.2 V, 100 ppm tetracycline + 10 mM NaCl, pH=2.

4.3 Performance of the EP system in the presence of competitive ions

The tetracycline removal rate of the EP system in the presence of competitive ions (NaCl, KCl, CaCl, $MgCl_2$ with equal molar concentrations) are shown in Table S6. The results indicate that although the presence of multiple ions reduces the removal rate of tetracycline due to competitive adsorption, this combined system remains promising and competitive for treating real antibiotic wastewater.

Table S6 Tetracycline removal rates of EP system at various salt concentrations

Concentration (mM)	**10**	**50**	**100**
Removal rate (mmol g^{-1} h^{-1})	0.079	0.072	0.064

Test conditions: EP system, 1.2 V, 100 ppm tetracycline, pH=2.

Feed solution: 100 ppm of tetracycline along with NaCl, KCl, CaCl, $MgCl_2$ with equal molar concentrations.

4.4 Performance of EP system at various feed-solution pH value

The pH value of the feed solution significantly influences the speciation of the tetracycline molecule (Fig. S11a). We compared the tetracycline removal rates of various systems at different feed-solution pH values (Fig. S11b). Our results indicate that the performance of the EP system is lower than that of the R-EP system at the pH of 12, which further supports our theory: At the pH of 12, tetracycline molecules exist primarily as anions. A negatively-polarized electrode will suppress mass transfer, thus leading to a lower removal rate. However, it is important to note that even at alkaline condition, the removal rate of the EP system remains higher than that of the P and E systems, demonstrating the feasibility of this system for treating alkaline wastewater.

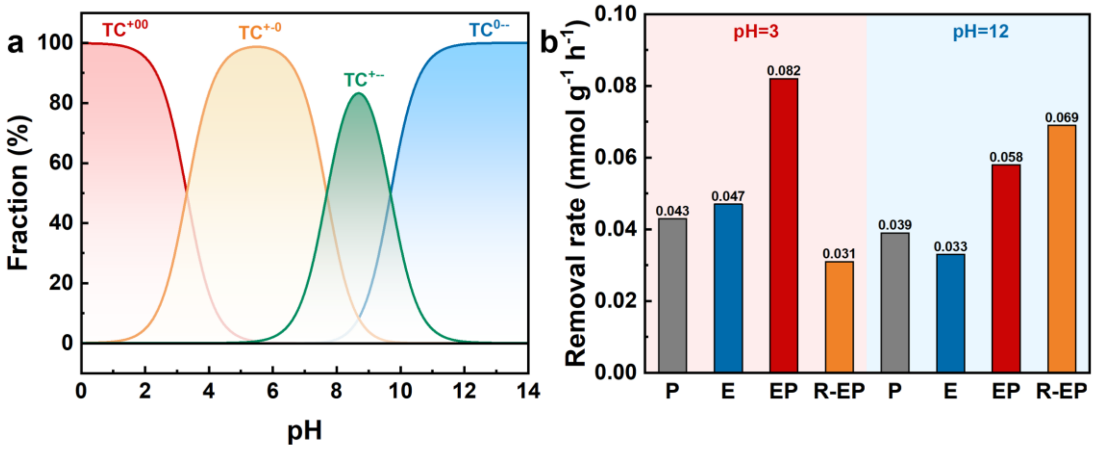


Fig. S11 (a) pH dependent speciation of tetracycline molecule; (b) Tetracycline removal rate of different systems at pH of 2 and 12. Test conditions: EP system, 1.2 V, 100 ppm tetracycline + 10 mM NaCl.