

Electronic supplementary information

In-situ imprinted cavities fabrication into BiOBr@porphyrin composites for selective and efficient degradation of trace norfloxacin

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S1.1. Characterization

The morphologies of the obtained materials were studied using a Gemini SEM 500 field emission scanning electron microscope (SEM) (Carle Zeiss Management Co., Ltd., Germany) with silicon wafer as the substrate and a JEM-2100 transmission electron microscope (TEM) (JEOL Co., Japan) with copper grid as the substrate. The Zeta potential was obtained by a nano particle size and zeta potential analyzer (Malvern Zetasizer Nano ZSE, UK). The water contact angle (WCA) was determined by an optical contact angle and interface tension meter (KRUSS DSA100, Germany). The X-ray diffraction (XRD) patterns were recorded on an XRD-6100 X-ray diffractometer (Shimadzu Co., Japan) with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) data were collected using a X-ray photoelectron spectroscope (Thermo Scientific ESCALAB Xi+, America). The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. The fitting results of XPS curves were analyzed with Avantage software. Nitrogen adsorption was performed on a Micromeritics ASAP-2020 analyzer (Shimadzu, Japan) at 77 K. Each sample (100 mg) was degassed at 473 K for 3 h before an adsorption measurement. The average pore diameters of the samples were estimated by the Barrett-Joyner Halenda method. UV-vis diffuse reflectance spectra and UV-vis transmittance spectra were recorded on a PE Lambda950 UV-vis-NIR spectrophotometer (Cel Network Co., China). The free radicals were analyzed via an electron paramagnetic resonance spectrometer (EPR, Bruker-A300, Germany). The capturing agent for active species ($\cdot\text{O}_2^-$ and $\cdot\text{OH}$) was 5,5-dimethyl-1-pyrroline N-oxide (DMPO), and the capturing agent for holes was 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO). The electrochemical impedance spectroscopy was performed on a CH Instruments electrochemical workstation (CHI660E, America). Photoluminescence (PL) spectra and time-resolved fluorescence decay (TRPL) spectra were measured using Edinburgh FLS9 fluorescence spectrometer (Edinburgh, UK) with an excitation wavelength of 322 nm. The intermediate products in the degradation process were determined by LCMS-2020 (Shimadzu, Japan) using the same mobile phase. The scanning range of the MS was 50-350 m/z in the positive ion mode. The total organic carbon test (TOC) was measured using a Shimadzu TOC analysis system (TOC-LCPH, Japan).

S1.2 Analysis of adsorption data

To obtain rate control mechanisms in surface adsorption processes, Eq. (S1) was adopted to calculate the adsorption amounts (Q , mg g $^{-1}$) of BiOBr@TAPP-MIP or BiOBr@TAPP-NIP for NOR. Pseudo-first order and pseudo-second order kinetic models were used for the description of the kinetic data, in accordance with Eqs. (S2) and (S3), respectively.

$$Q = (C_0 - C_e)V/W \quad (\text{S1})$$

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (\text{S2})$$

$$t/Q_t = 1/k_2Q_e^2 + t/Q_e = 1/v_0 + t/Q_e \quad (S3)$$

Where, C_0 and C_e (mg g^{-1}) are NOR original and equilibrium contents, respectively. V (mL) is the volume of NOR solution, and W (mg) stands for the mass of the materials. Q_t (mg g^{-1}) and Q_e (mg g^{-1}) refer to the adsorption capacity at time (t , min) and equilibrium adsorption capacity, respectively. k_1 (min^{-1}) indicates the equilibrium rate constants of the pseudo-first order equation. v_0 ($\text{mg g}^{-1} \text{min}^{-1}$) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are respectively the original adsorption rate and the equilibrium rate constant of the pseudo-second order equation.

S1.3 Analysis of photocatalytic degradation

The degradation rate (η) of NOR and degradation kinetics were assessed as the following Eq. (S4) and Eq. (S5), respectively.

$$\eta = (C_0 - C)/C_0 \quad (S4)$$

$$\ln C_1/C = kt \quad (S5)$$

where, C_0 is the initial concentration of NOR solution ($\mu\text{g mL}^{-1}$) and C_1 is the concentration of NOR solution ($\mu\text{g mL}^{-1}$) at the beginning of degradation. C represents the concentration of NOR solution ($\mu\text{g mL}^{-1}$) at a certain time. k denotes the rate constant (min^{-1}). Regression coefficient (R^2) was employed to evaluate the fitness of first-order kinetics to the experimental data.

S1.4 Analysis of selectivity

The adsorption imprinting factor (IF_Q) and adsorption selectivity coefficient (SC_Q) were ruled by Eqs. (S6) and (S7) respectively to assess the adsorption selectivity of BiOBr@TAPP-MIP.

$$IF_Q = Q_{\text{MIP}} / Q_{\text{NIP}} \quad (S6)$$

$$SC_Q = IF_{Q_t} / IF_{Q_c} \quad (S7)$$

Where Q_{MIP} ($\mu\text{mol g}^{-1}$) and Q_{NIP} ($\mu\text{mol g}^{-1}$) denote as respective adsorption amounts to template molecules or competitors of BiOBr@TAPP-MIP and BiOBr@TAPP-NIP. IF_{Q_t} is the adsorption imprinting factors for template molecules NOR, while IF_{Q_c} represents those of its competitor LVX.

Similarly, the photodegradation imprinting factor (IF_η) and selectivity coefficient (SC_η) were ruled by Eqs. (S8) and (S9) respectively to assess the photodegradation selectivity of BiOBr@TAPP-MIP.

$$IF_\eta = \eta_{\text{MIP}} / \eta_{\text{NIP}} \quad (S8)$$

$$SC_\eta = IF_{\eta_t} / IF_{\eta_c} \quad (S9)$$

Where η_{MIP} and η_{NIP} denote as respective photodegradation rate to template molecules or competitors of BiOBr@TAPP-MIP and BiOBr@TAPP-NIP. IF_{η_t} is the photodegradation imprinting factors for template molecules NOR, while IF_{η_c} represents those of its competitor LVX.

S1.5 Analysis of turnover frequency values (TOF)

The turnover frequency (TOF) was calculated by using the following Eq. (S10) to normalize the data relevant to the photodegradation performance.

$$\text{TOF (\%)} = m_{\text{R-NOR}} / (m_i \times t) \quad (\text{S10})$$

where $m_{\text{R-NOR}}$ (mg) and m_i (mg) represent the removal amount of NOR and the used amount of photocatalyst, respectively. t represents the time of removal process.

S1.6 Analysis of band structure

The band-gap energy E_g was calculated by the Kubelka-Munk equation (Eq. (S11)).

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (\text{S11})$$

where α , h , ν , E_g , and A represent the absorption coefficient, Planck constant, light frequency, and a constant.

n values of BiOBr and TAPP are 4 and 2, respectively.

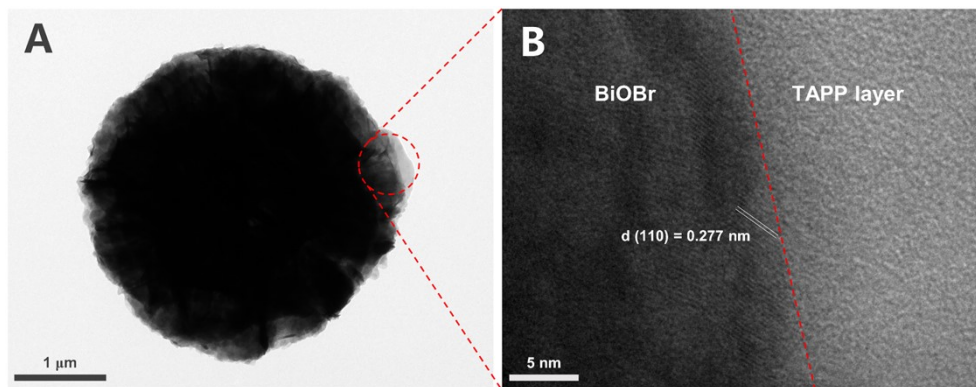


Fig. S1 TEM (A) and HRTEM (B) images of BiOBr@TAPP-MIP.

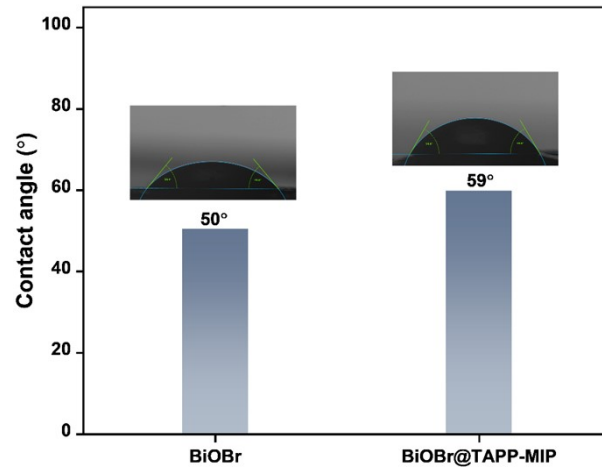


Fig. S2 Water contact angle of BiOBr and BiOBr@TAPP-MIP.

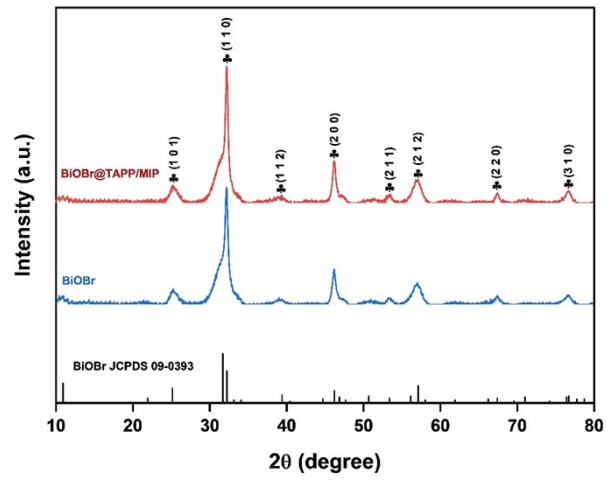


Fig. S3 XRD patterns of BiOBr (blue line) and BiOBr@TAPP-MIP (red line).

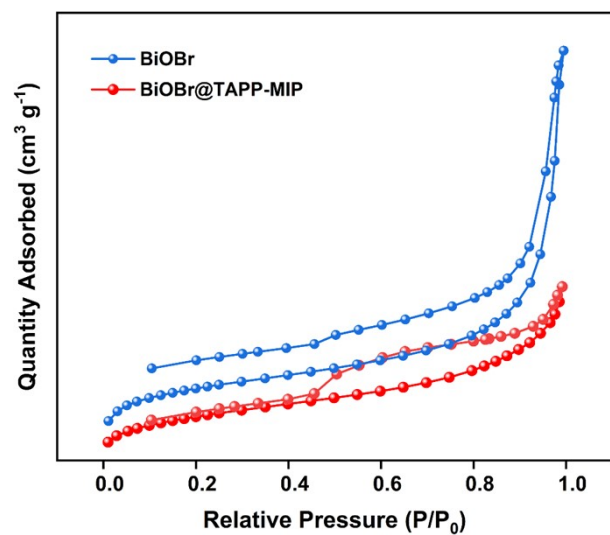


Fig. S4 N₂ adsorption-desorption isotherms of BiOBr (blue line) and BiOBr@TAPP-MIP (red line).

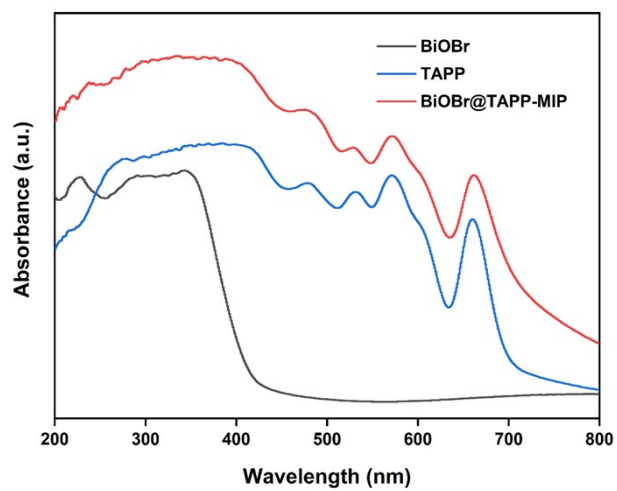


Fig. S5 UV-vis DRS of as-prepared materials.

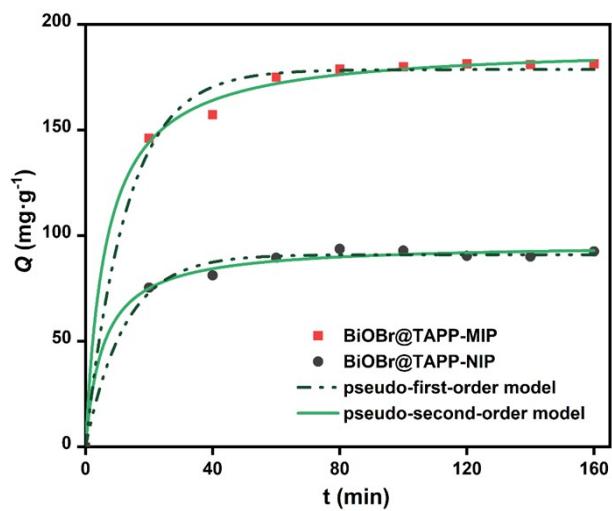


Fig. S6 Adsorption kinetic curves and kinetic models of BiOBr@TAPP-MIP and BiOBr@TAPP-NIP.

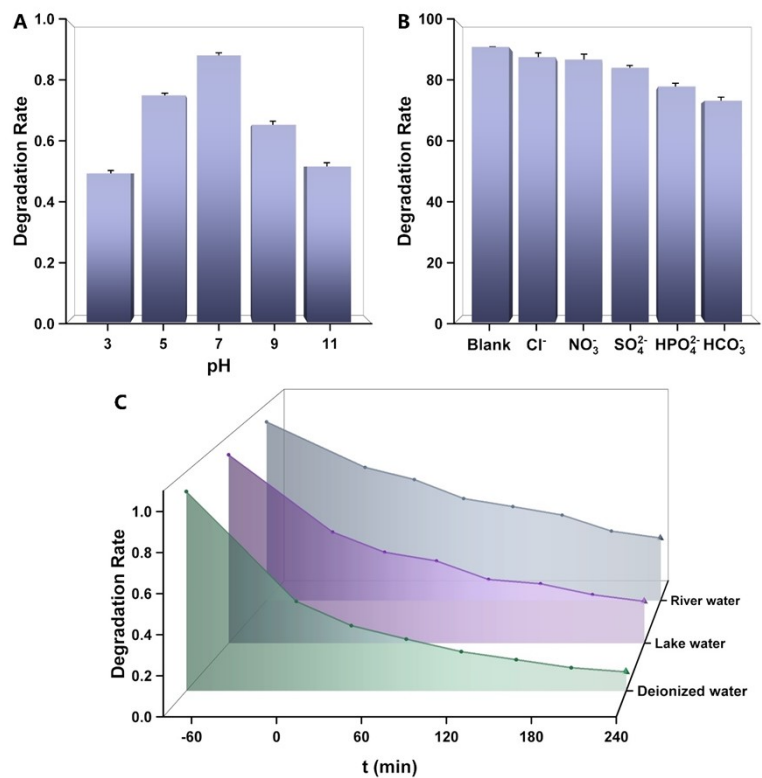


Fig. S7 Effect of environmental factors of pH (A), ions (B), and water media (C) on photodegradation.

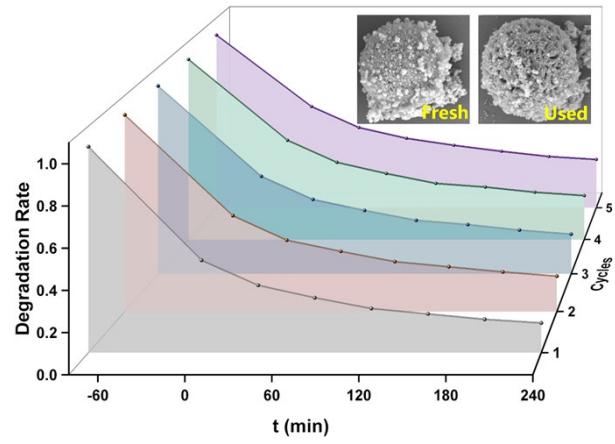


Fig. S8 Recycling test and SEM images (insert) of fresh and used BiOBr@TAPP-MIP.

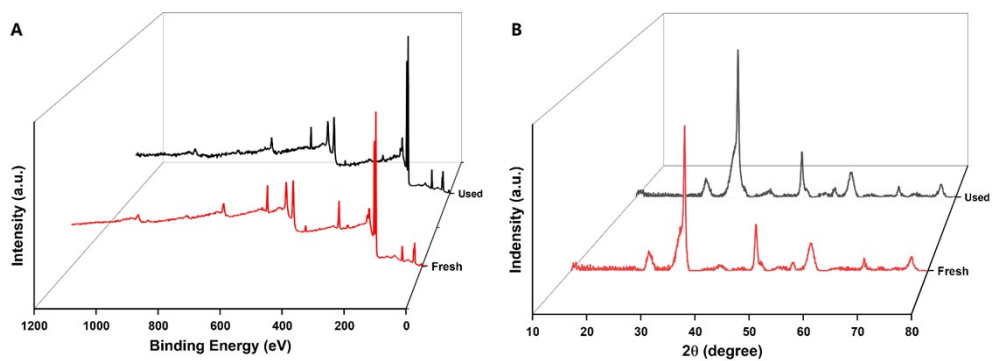


Fig. S9 XPS spectra (A) and XRD patterns (B) of fresh and used BiOBr@TAPP-MIP.

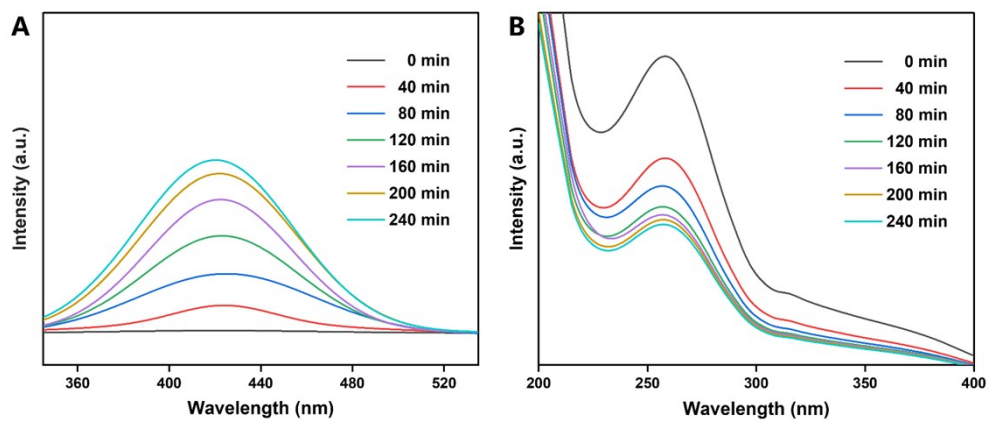


Fig. S10. Time-dependent intensity change of TA (A) and NBT (B) degradation over BiOBr@TAPP-MIP.

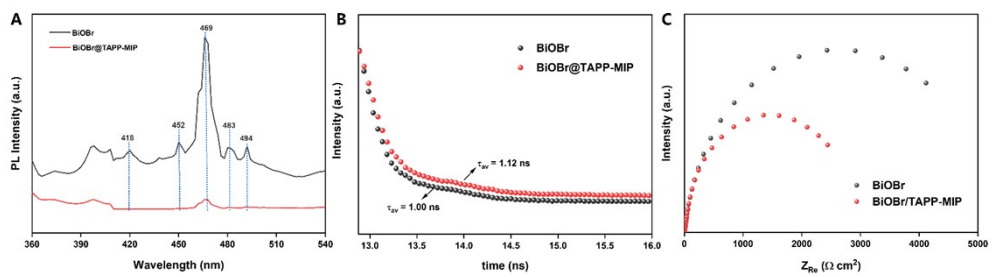


Fig. S11. The PL spectra (A), time-resolved fluorescence decay spectra (B), and EIS Nyquist plots (C) of the obtained materials.

Table S1 Some parameters for real water samples.

| Water quality parameters | Lake Samples | River Sample |
|---|--------------|--------------|
| pH | 8.34 | 8.49 |
| Electrical Conductivity ($\mu\text{S cm}^{-1}$) | 490.76 | 829.30 |
| Total nitrogen (mg L^{-1}) | 2.87 | 7.52 |
| total phosphorus (mg L^{-1}) | 0.12 | 0.27 |
| dissolved carbon (mg L^{-1}) | 1.35 | 4.48 |

Table S2 Surface areas, pore volumes, and pore sizes of the obtained materials

| Parameter | BiOBr | BiOBr@TAPP-MIP |
|--|---------|----------------|
| BET surface area (m ² g ⁻¹) | 16.42 | 112.9 |
| Pore size (nm) | 15.38 | 7.069 |
| Pore volume (cm ³ g ⁻¹) | 0.06313 | 0.1772 |

Table S3 Equations and parameters for the pseudo-first-order and pseudo-second-order kinetic models

| Model | Equations parameters | BiOBr@TAPP-MIP | BiOBr@TAPP-NIP |
|---------------------|---|--|--|
| | Equation | $\ln (178.6 - Q_t) = \ln 178.6 - 0.07693t$ | $\ln (105.2 - Q_t) = \ln 105.2 - 0.05123t$ |
| pseudo-first-order | $Q_{e,f}^a$ (mg g^{-1}) | 178.6 | 90.98 |
| | k_1 (min^{-1}) | 0.07693 | 0.08081 |
| | R^2 | 0.990 | 0.991 |
| | Equation | $t / Q_t = 0.005255t + 0.03365$ | $t / Q_t = 0.008503t + 0.1101$ |
| pseudo-second-order | $Q_{e,s}^b$ (mg g^{-1}) | 190.3 | 96.23 |
| | k_2 ($10^{-3}, \text{g mg}^{-1} \text{min}^{-1}$) | 0.8207 | 1.840 |
| | v_0 ($\text{mg g}^{-1} \text{min}^{-1}$) | 29.72 | 17.04 |
| | R^2 | 0.996 | 0.987 |

Table S4 Adsorption selectivity parameters of BiOBr@TAPP-MIP and BiOBr@TAPP-NIP.

| Analytes | Q_{MIP} (mg g ⁻¹) | Q_{NIP} (mg g ⁻¹) | IF_Q | SC_Q |
|----------|---------------------------------|---------------------------------|--------|--------|
| NOR | 181.1 | 92.5 | 1.96 | - |
| LVX | 45.8 | 41.2 | 1.11 | 1.77 |

Table S5 Photodegradation selectivity parameters of BiOBr@TAPP-MIP and BiOBr@TAPP-NIP.

| Analytes | η_{MIP} (%) | η_{NIP} (%) | IF_η | SC_η |
|----------|-------------------------|-------------------------|------------------|------------------|
| NOR | 90.2 | 66.4 | 1.35 | - |
| LVX | 78.3 | 62.7 | 1.25 | 1.08 |