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Supplementary Material

Construction of MIL-101(Fe)/layered bimetallic oxide heterojunction for enhanced ciprofloxacin removal

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Text S1 The cycling test

Firstly, 20 mg of catalyst was added in a CIP solution (40 ml, 20 ug/ml). After dark adsorption for 60 min, the sample solution was degraded under the light irradiation. 1.0 mL sample solution was took out at 10 min intervals and then measured using a UV-Vis spectrophotometer. After the first cycle, the remaining solution was centrifuged and separated, and the obtained precipitate was washed with ethanol and deionized water. In the second cycle, the remained catalyst was used for the following dark adsorption and light irradiation as the above first cycle experiments. Due to the sampling operation, some catalyst was lost, which will lead to the decrease of the degradation rate with the increase of the cycling times.

Text S2 UPLC-UV/MS analysis

This is a description of the analytical conditions for an Ultimate 3000 Ultra High-Performance Liquid Chromatography (UPLC) system using a Hypersil GOLD C18 column (2.1 mm inner diameter, 1.9 μm particle size, Thermo Scientific). The UPLC mobile phase consists of mobile phase A (water containing 0.1% formic acid) and mobile phase B (acetonitrile). The flow rate is 0.2 mL/min. The gradient elution program was as following: from 0 to 10.0 min, a linear gradient from 90% to 10% A; from 10 to 15 min, remained 10% A; from 15.00 to 15.01 min, a rapid increase from 10% to 90% A, and then the re-equilibration time of gradient elution was from 15.01 min to 30.0 min. The UV detection wavelength was 315 nm, and the column temperature was maintained at 30 ℃. The mass spectrometry conditions are positive ion mode, sheath gas flow rate of 3.5, auxiliary gas flow rate of 1.0, spray voltage of 3.7 kV, ion source temperature of 350 ℃, and auxiliary gas temperature of 350 ℃.

Tables

Table S1 Band structure of the three samples*

Sample	Eg (eV)	E_{CB} (eV)	E_{VB} (eV)
MIL-101(Fe)	2.56	0.19	2.96
ZnCrZr-LBMO	3.10	-0.41	2.69
MIL-101(Fe)/ZnCrZr-LBMO	1.77	-0.05	1.82

***Note:** The bandgap energy (Eg, eV) is determined by the Kubelka-Munk equation:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad \text{(S1)}$$

Where α: absorbance coefficient; h: Planck constant; ν: incident photon frequency; A: absorbance; Eg: apparent bandgap energy. By extending the linear portion of the curve until it intersects with the x-axis at $(\alpha h\nu)^2 = 0$, the apparent bandgap energy can be determined. A bandgap energy diagram transformed using the Kubelka-Munk formula was shown in Fig. 4. The bandgap values of MIL-101(Fe), ZnCrZr-LBMO, and MIL-101(Fe)/ZnCrZr-LBMO are presented in Table S1.

Figures

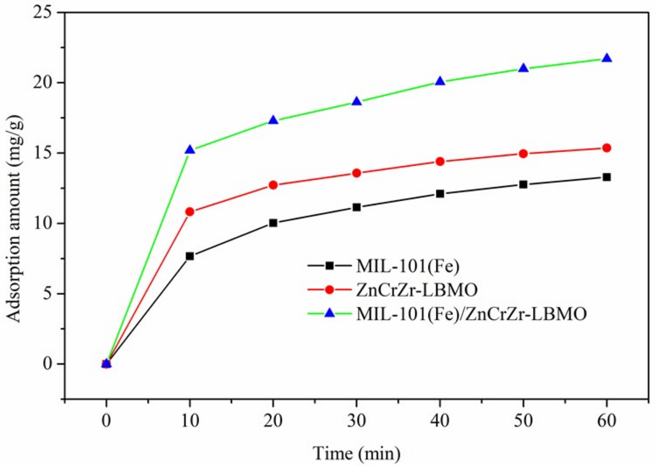

Figure S1 Dark adsorption/desorption equilibrium of CIP on MIL-101(Fe), ZnCrZr-LBMO, and MIL-101(Fe)/ZnCrZr-LBMO composites, respectively.

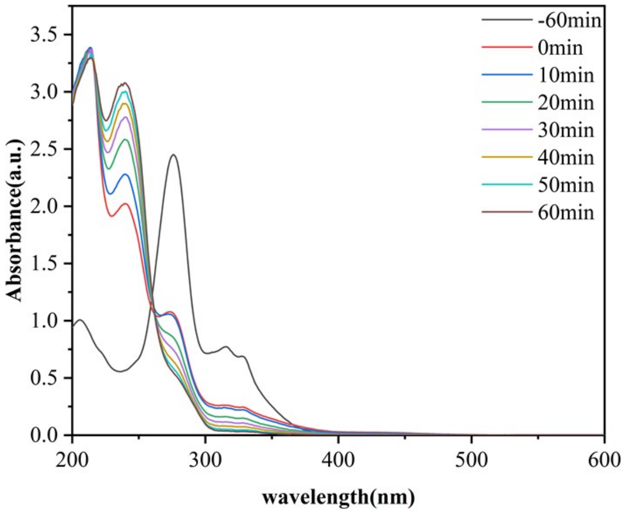

Figure S2. Absorbance spectra of ciprofloxacin solution versus time during degradation.

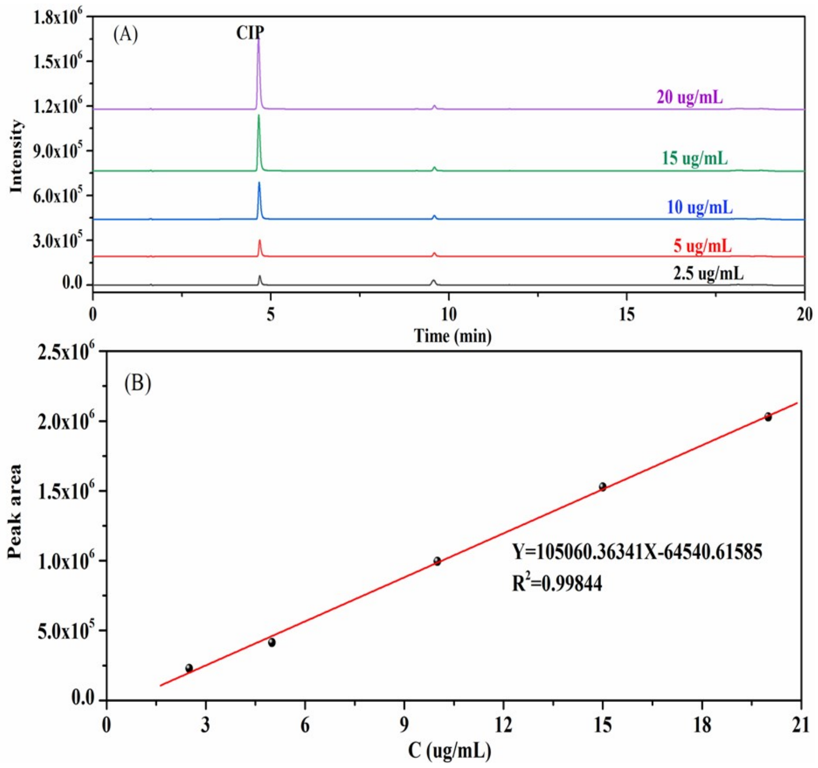

Figure S3. Typical HPLC-UV chromatograms of CIP (A) and the corresponding calibration curve (B, Y=105060.36X-64540.62), concentration range (0-20 μg/mL), and linear regression coefficient (R^2=0.9984) for CIP determination by UPLC-UV under optimal conditions.

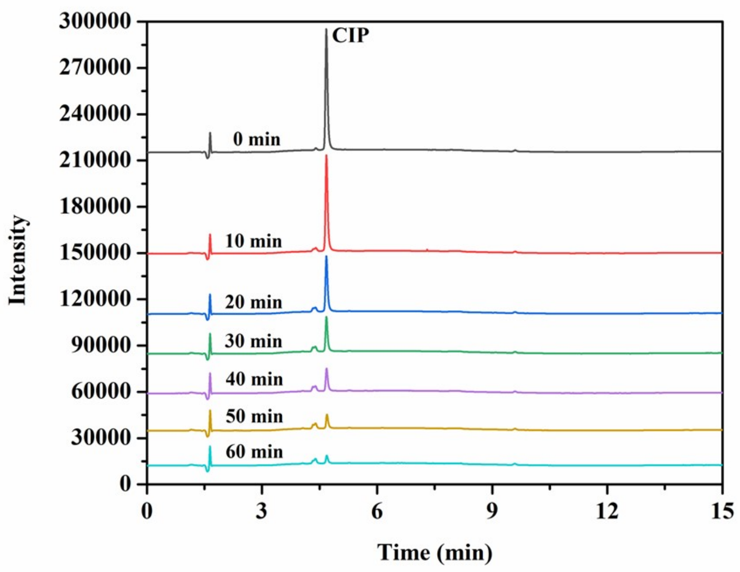

Figure S4. Typical HPLC-UV chromatograms of CIP (sample solution spiked with 20 μg/mL) without any degradation, and after degradation with different time from 0 to 60 min by using MIL-101(Fe)/ZnCrZr-LBMO composite, respectively.

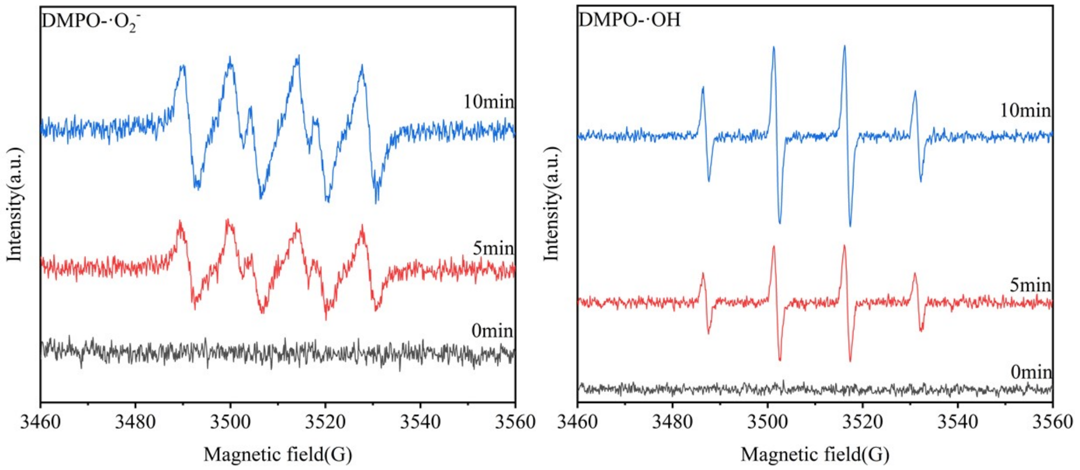

Figure S5. The ESR spectra of DMPO-·O^{2-},and DMPO-·OH.

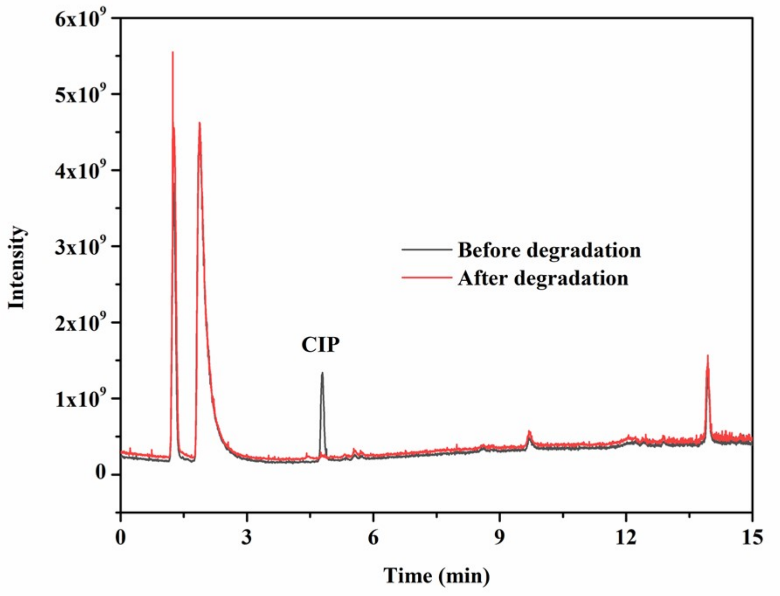

Figure S6. Typical total ion chromatograms of CIP solution before and after photocatalytic degradation on MIL-101(Fe)/ZnCrZr-LBMO composites.

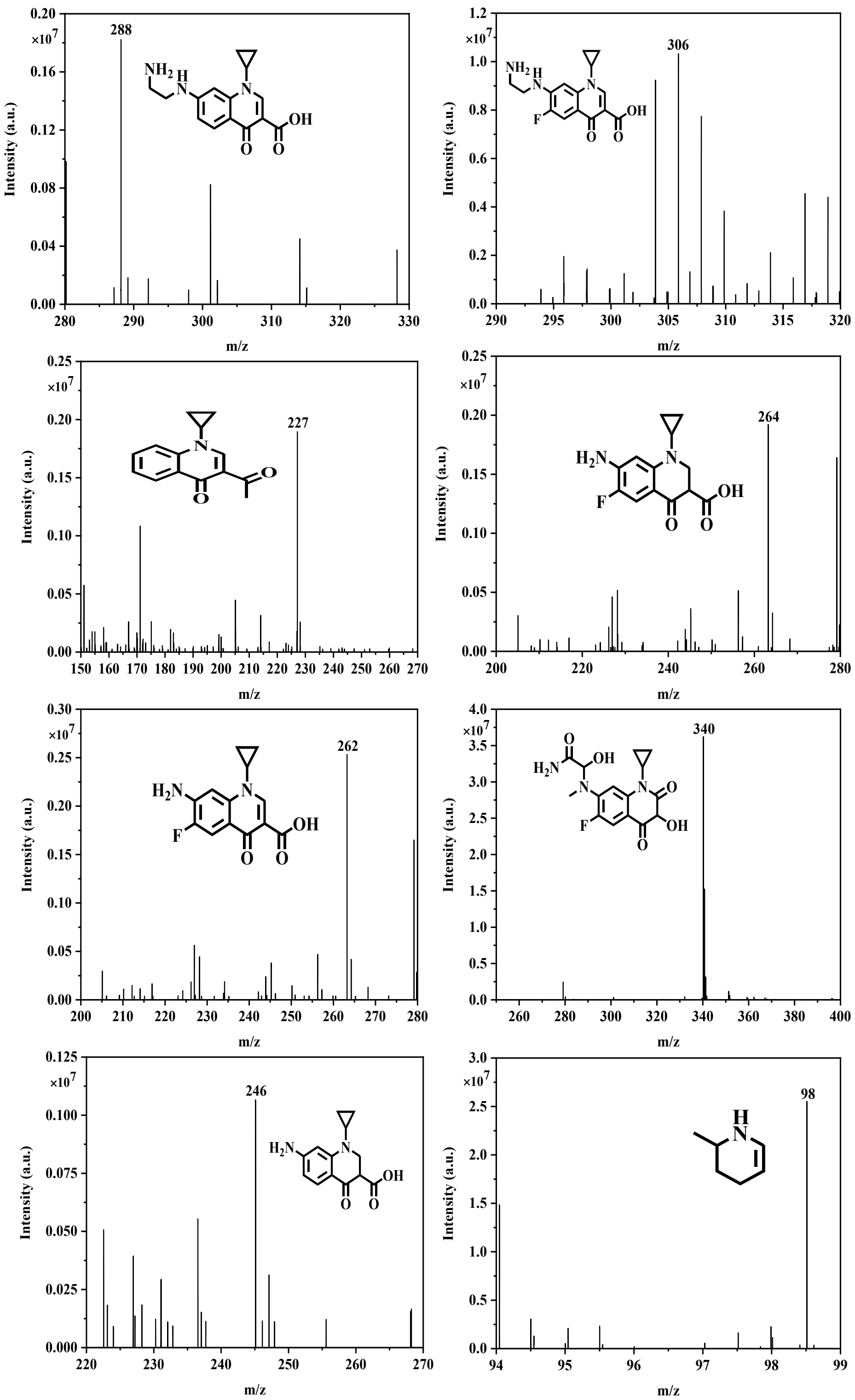

Figure S7. Typical MS of CIP photodegradation products obtained by LC-MS method

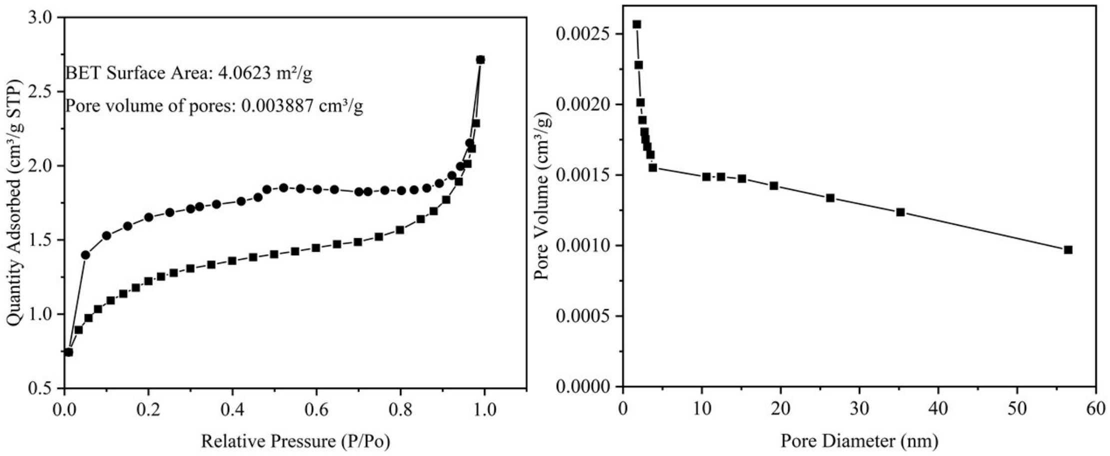

Figure S8. Nitrogen adsorption-desorption isotherms and pore size distributions curves of MIL-101(Fe)/ZnCrZr-LBMO.

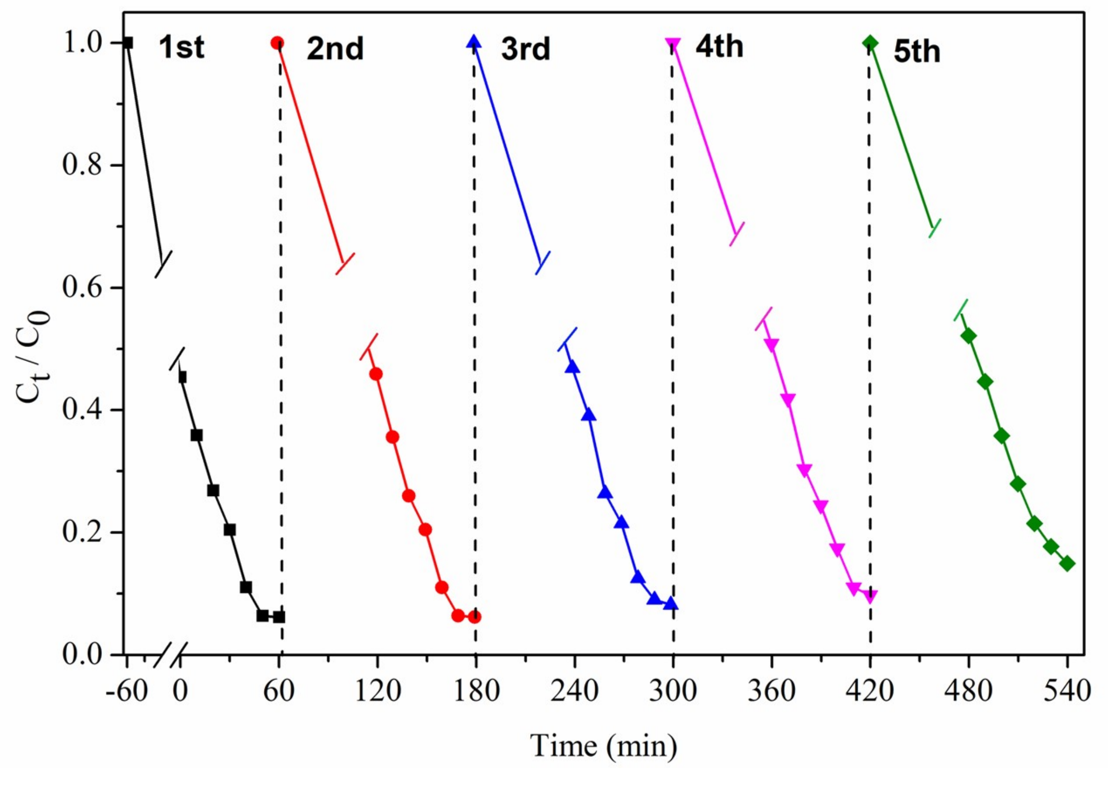

Figure S9. Photocatalytic degradation recycle experiment of CIP for five times

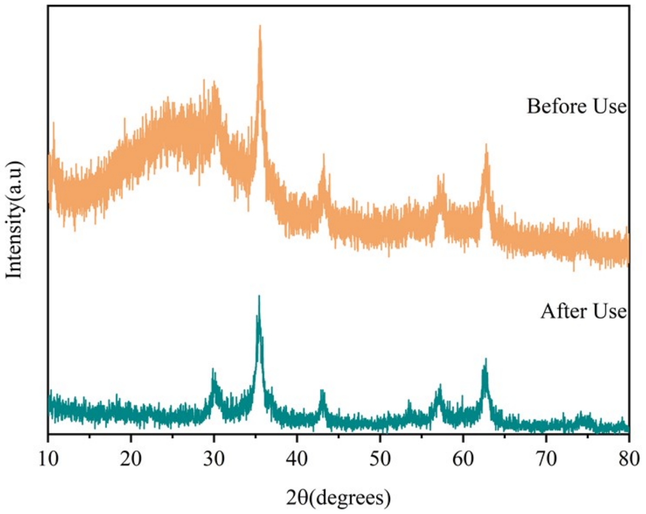

Figure S10. XRD image of the material after five cycles.

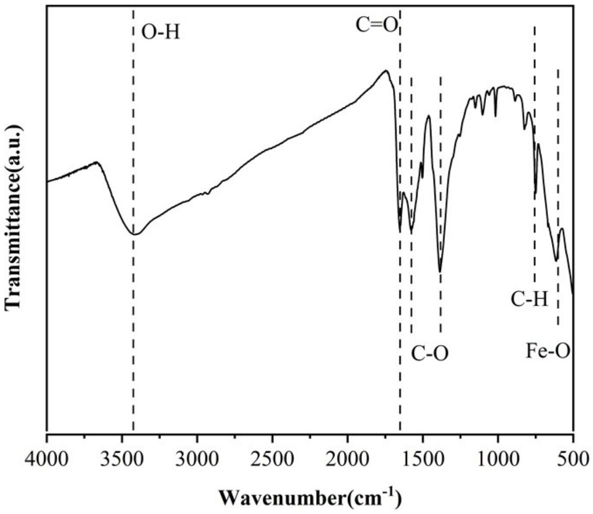

Figure S11. FTIR spectra of MIL-101(Fe)/ZnCrZr-LBMO after five cycling test.