Electronic Supporting Information

for

Enhancing Degradation of Ciprofloxacin in Water using Oxone activated by Urchin-like Cubic and Hollow-structured Cobalt@N-doped Carbon prepared via Etching-Engineering: A Comparative Study with Mechanistic and Eco-toxic Assessments

Text S1: Experimental details

1.1 Materials

Chemical reagents used in this study were purchased from commercial suppliers and employed as received without additional purifications. 2-methylimidazole (2-MeIm) ($C_4H_6N_2$) (99%) was obtained from Acros Organics (Belgium). Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) (>98%) was purchased from Showa Chemicals (Japan). Oxone®, monopersulfate compound ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), cetyltrimethylammonium bromide (CTAB) (>98%), gallic acid ($C7H6O5$) (>98%), methyl alcohol (99.9%), ethyl alcohol (>99.8%), tert-butanol (>99.5%), sodium azide (NaN_3) (99.5%) were purchased from Sigma-Aldrich (USA).

1.2 Material preparation and characterizations

Hollow-engineered nanostructured cobalt embedded nitrogen-doped carbon (H-Co@NC) was prepared as illustrated in Fig. 1. First, Co-ZIF was constructed based on reported studies with some minor modifications [29]. Specifically, 1 mmol cobalt nitrate hexahydrate and 0.01 mmol CTAB were dissolved in a beaker containing 10 mL DI water, which was subsequently added dropwise into another beaker containing 0.7 M of 2-MIM. The mixture was then vigorously stirred at room temperature for 1 h. Eventually, the precipitation was collected by centrifugation, washed several times by DI water/ethyl alcohol, and dried in an oven overnight to obtain Co-ZIF.

Next, the as-prepared Co-ZIF was derived into H-Co@NC via partial etching and carbonization processes. Typically, a small amount of Co-ZIF was taken into a solution containing gallic acid, and the mixture was then stirred intensely for 10 min to complete the partial etching process. The remaining product was assembled via centrifugation, rinsed by ethyl alcohol before

drying in an electric oven at 65°C for 24 h. Finally, this as-obtained product was carbonized in N_2 atmosphere at 600°C for 4 h to acquire hollow-engineered nanostructured cobalt embedded nitrogen-doped carbon (H-Co@NC).

For characterizations, the surface morphology of catalysts was characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM) (JEOL JSM-7800 F and JEM-1400, Japan). The elemental composition of H-Co@NC was also determined by energy dispersive X-ray (EDX) (Oxford Instruments, UK). The X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (Bruker, USA). Surface chemical states of elements in H-Co@NC were verified by X-ray photoelectron spectroscopy (XPS) (ULVAC-PHI, PHI 5000, Japan). Besides, Raman spectra were obtained from a Raman spectrometer (TII Nanofinder 30, Japan). Moreover, BET surface area of H-Co@NC was determined using N_2 sorption isotherms by a volumetric analyzer (Anton Paar Autosorb IQ, Austria). As H-Co@NC contains Co^0, possessing strong magnetism, its magnetic property was examined by a magnetometer (Quantum Design, USA). Furthermore, the surface charges of H-Co@NC were further determined using a zetasizer (Nano-ZS, Malvern Instruments Ltd, UK).

1.3 CIP degradation using H-Co@NC-activated Oxone

CIP degradation using H-Co@NC coupled Oxone was investigated by batch-type experiments. Specifically, a certain amount of H-Co@NC (i.e., 100 mg/L) was initially added into CIP solution with the initial concentration (C_0) of CIP was 5 mg/L for 45 min to examine the adsorption capability of H-C@NC to CIP. Then, 100 mg/L of Oxone was instantly added into the solution to launch the degradation experiment. At different reaction time t (min), an aliquot (i.e., 3 mL) was

taken out and passed through a filter to split off H-Co@NC from CIP solution. The concentration of CIP at t min (C_t) remained in the filtrate was subsequently measured by high-performance liquid chromatography (HPLC) and UV-vis spectroscopy at 277 nm. The effects of different experimental parameters including catalyst dosage, Oxone dosage, temperatures, initial pH values, types of water, co-existing components and inhibitors on CIP degradation using H-Co@NC coupled Oxone were thoroughly examined.

To shed a light on the advantageous of hollow-engineered structure of H-Co@NC, non-hollow-engineered structure cobalt embedded in nanostructured nitrogen-doped carbon (denoted as S-Co@NC) and commercial cobalt oxide (com-Co_3O_4) were also employed as reference catalysts for activating Oxone to degrade CIP in comparison with H-Co@NC+Oxone system. Moreover, as ROS might be generated during the activation and involved in CIP degradation, these species were necessarily determined by electron paramagnetic resonance (EPR) using 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) as radical spin-trapping agents to reveal the mechanism of CIP degradation. Besides, the intermediates derived from CIP degradation were also determined using a mass spectrometer (Thermo Finnigan Corporation, LCQ ion-trap mass spectrometer, USA). The recyclability of H-Co@NC for multiple CIP degradation cycles was also performed by re-assembling and re-employing the used H-Co@NC.

1.4 DFT calculation

Active sites on the C4mim molecule and intermediates can be realized through Fukui function using DFT calculation which was performed with Gaussian 16 software: method = B3LYP and basis set = 6-31+g(d,p).

Definition of Fukui function and Fukui indexes (f^-, f^0, f^+)

Fukui function: $f(r) = \left[\dfrac{\partial \rho(r)}{\partial N} \right]_v$

Where; $\rho(r)$ is the electron density at a point γ in space; N is the electron number in the system; v is the external potential.

Fukui function (f) in reaction:

Nucleophilic attack: $f^+(r) = \rho_{N+1}(r) - \rho_N(r) \approx \rho^{LUMO}(r)$

Electrophilic attack: $f^-(r) = \rho_N(r) - \rho_{N-1}(r) \approx \rho^{HOMO}(r)$

Radical attack: $f^0(r) = \dfrac{f^+(r) + f^-(r)}{2} = \dfrac{\rho_{N+1}(r) - \rho_{N-1}(r)}{2} \approx \dfrac{\rho^{HOMO}(r) + \rho^{LUMO}(r)}{2}$

Table S1. A comparison of activation energy (E_a) between H-Co@NC

Catalyst	E_a (kJ/mol)	Reference
H-Co@NC	48.2	This work
Fe^0/Fe_3C	52.49	[1]
Co-Fe/SiO$_2$	51.6	[2]
ZCFO	29.9	[3]

Table S2. Detected by-products of CIP degradation by H-Co@CN+Oxone

	Structure	Name	m/z
CIP		*Ciprofloxacin*	332
P1.		*1-cyclopropyl-6-fluoro-2-hydroxy-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid*	348
P2.		*(E)-1-cyclopropyl-2,5-dihydroxy-4-oxo-6-(2-(piperazin-1-yl)ethylidene)-1,4,5,6-tetrahydropyridine-3-carboxylic acid*	325
P3.		*(E)-1-cyclopropyl-3,6-dihydroxy-2-(2-(piperazin-1-yl)ethylidene)-2,3-dihydropyridin-4(1H)-one*	310
P4.		*2-hydroxy-3-(methylamino)-5-(piperazin-1-yl)pentanoic acid*	232
P5.		*2-(2-aminoethyl)-1-cyclopropyl-3,6-dihydroxy-2,3-dihydropyridin-4(1H)-one*	212
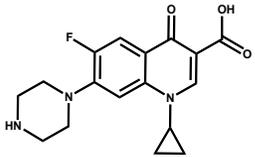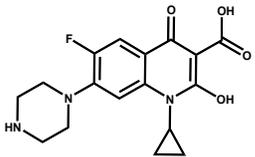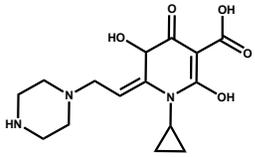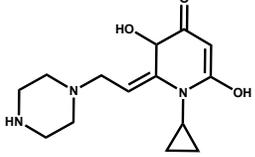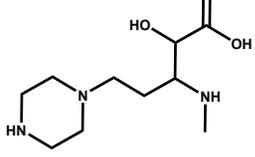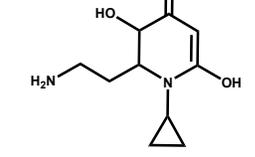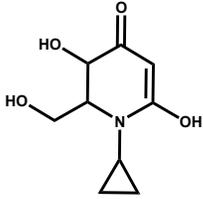
P6.		*1-cyclopropyl-3,6-dihydroxy-2-(hydroxymethyl)-2,3-dihydropyridin-4(1H)-one*	199
P7.		*N1-ethylethane-1,2-diamine*	88
P8.		*6-(2-aminoethyl)-1,4,5,6-tetrahydropyridine-2,4,5-triol*	174
P9.		*1,4,5,6-tetrahydropyridine-2,4,5-triol*	132
P10.		*3,5-diaminopentane-1,1,2-triol*	150
P11.		*2-((dihydroxymethyl)amino)butane-1,4-diol*	150
P12.		*butane-1,2,4-triol*	106
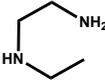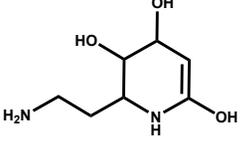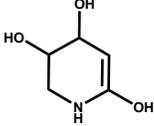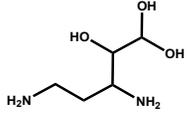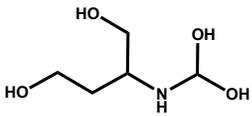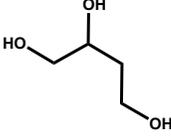
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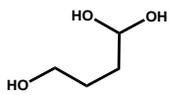
P13.		*butane-1,1,4-triol*	106

Table S3. Toxicity classification according to the Globally Harmonized System of Classification and Labelling of Chemicals

Toxicity range (mg/L)	Classification
LC_{50} [a]/EC_{50} [b]/ChV [c] ≤ 1	Very toxic
$1 < LC_{50}/EC_{50}/ChV \leq 10$	Toxic
$10 < LC_{50}/EC_{50}/ChV \leq 100$	Harmful
$LC_{50}/EC_{50}/ChV > 100$	Not harmful

[a] LC_{50}, Half lethal concentration; [b] EC_{50}, Half effective concentration; [c] ChV, Chronic toxicity value
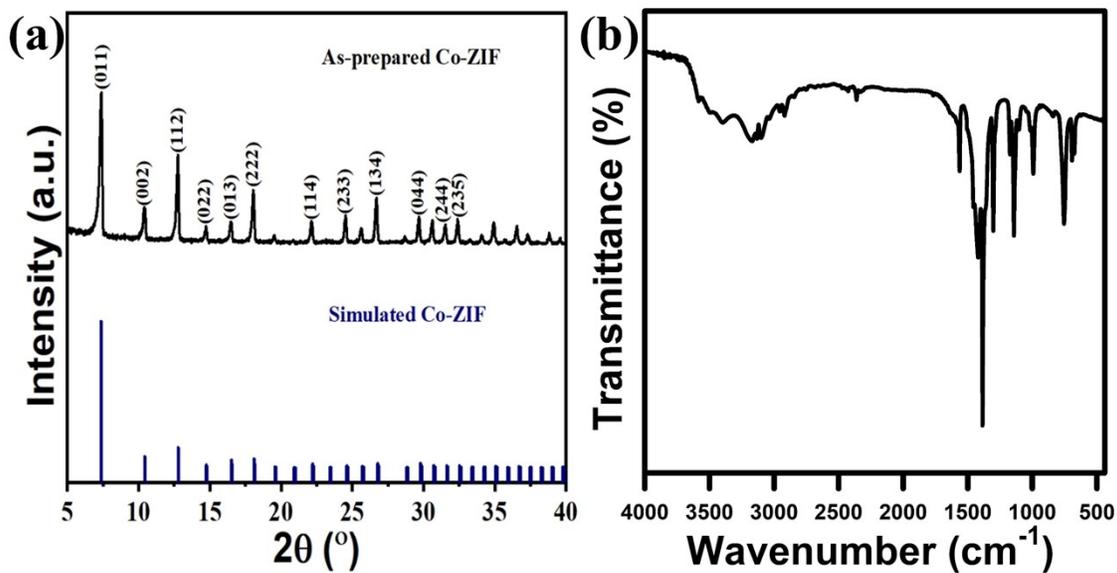
Fig. S1. (a) XRD patterns of the as-prepared and stimulated Co-ZIF, and (b) FTIR profile of Co-ZIF.
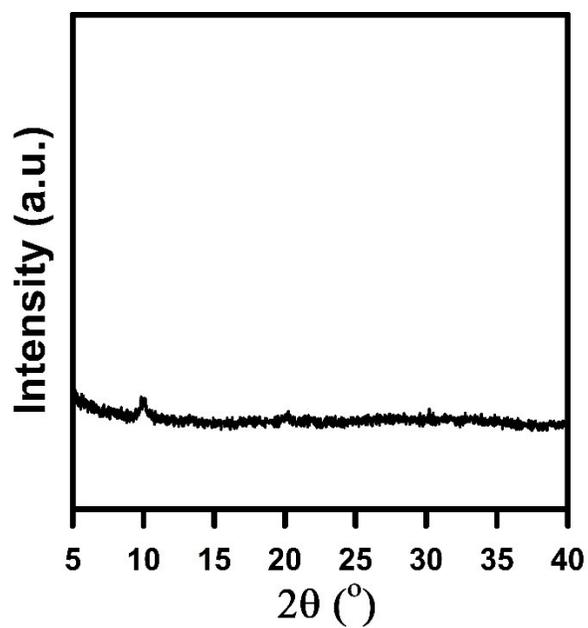
Fig. S2. XRD profile of the resultant product after partial etching step with gallic acid.
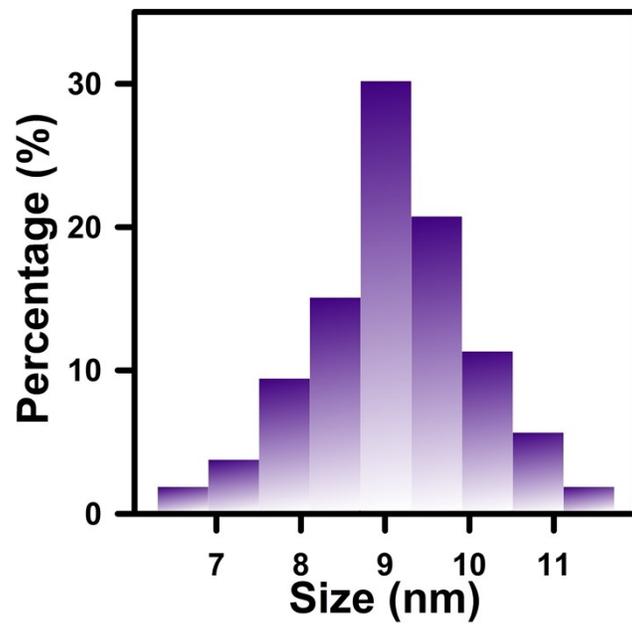
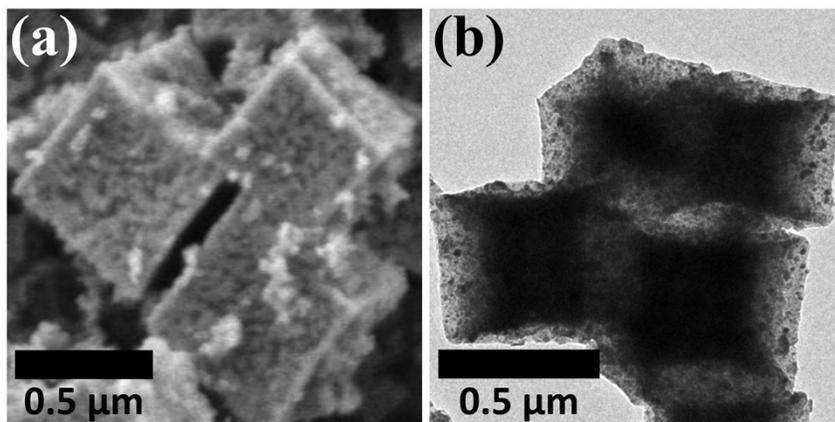Fig. S3. Particle size distribution of H-Co@NC.

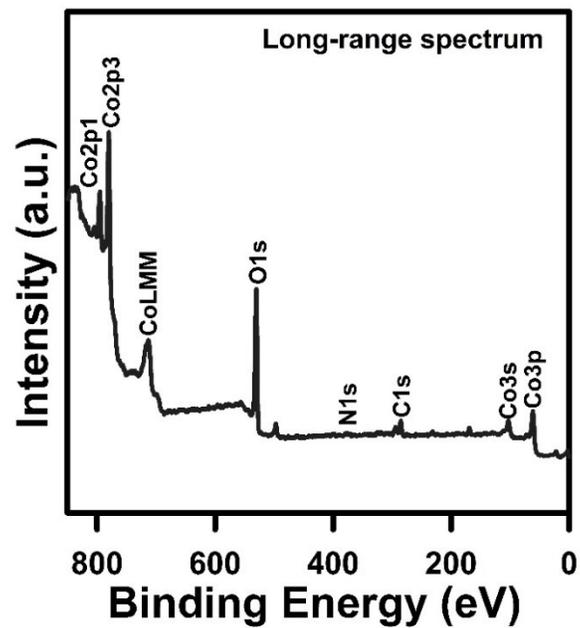Fig. S4. (a) SEM and (b) TEM images of S-Co@NC.
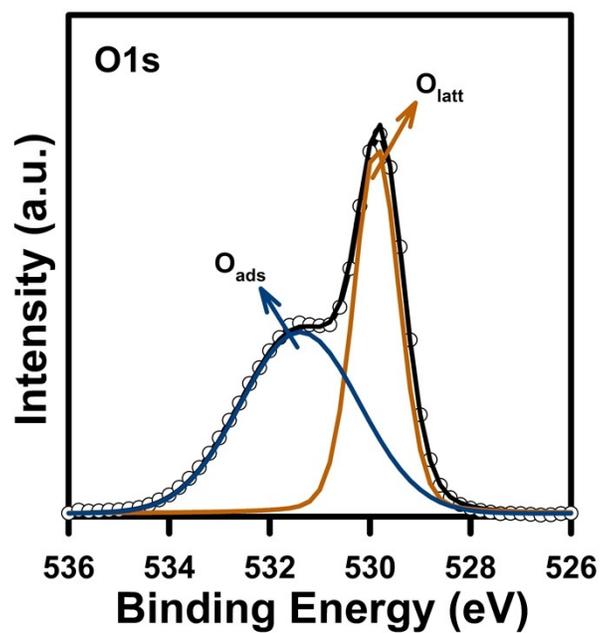
Fig. S5. Long-range survey spectrum of H-Co@NC.
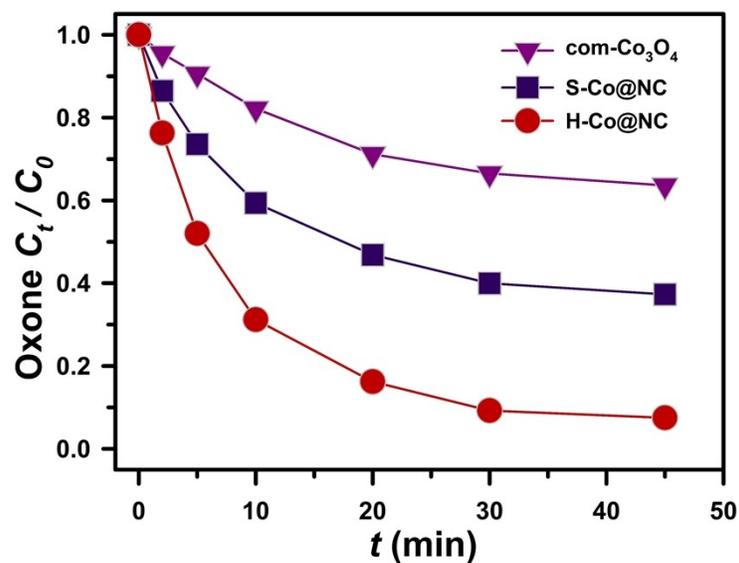

Fig. S6. O 1s of H-Co@NC.

Fig. S7. Oxone decomposition using com-Co$_3$O$_4$, S-Co@NC, and H-Co@NC.
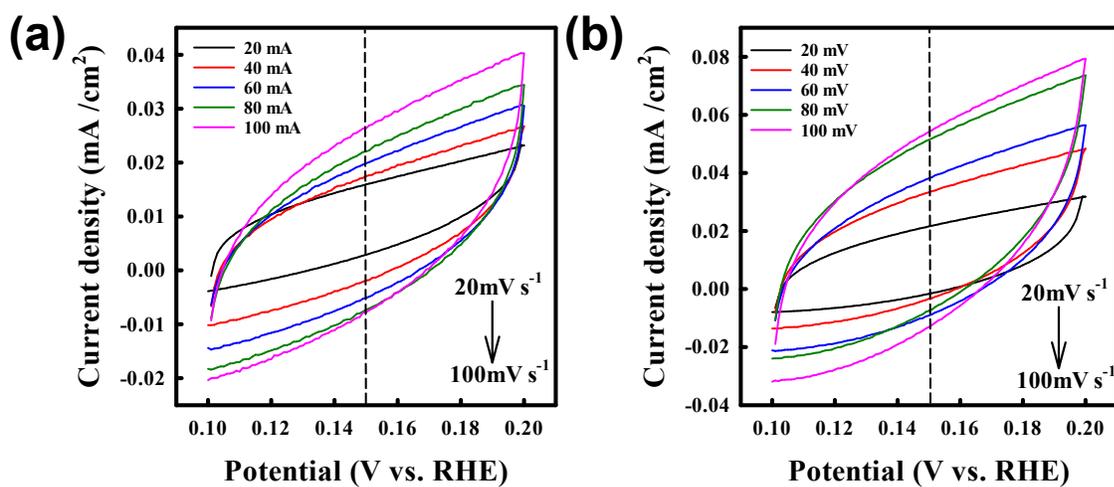

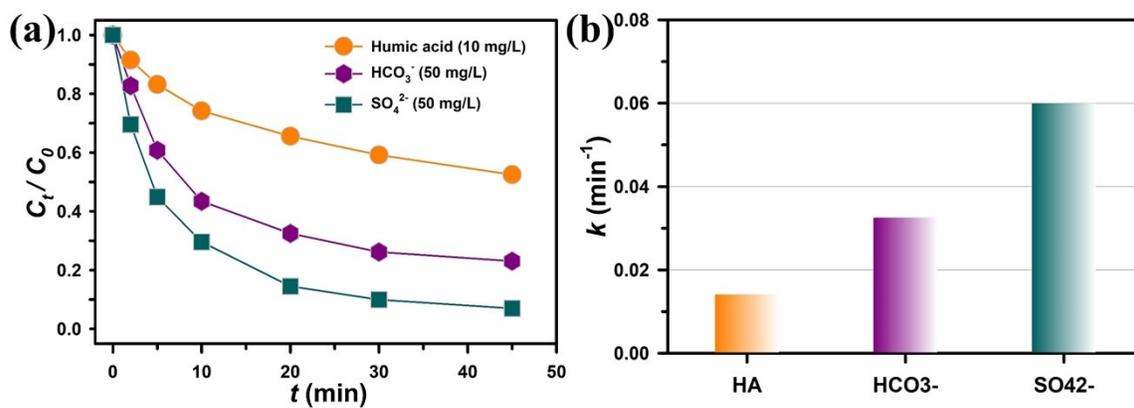Fig. S8. CV curves of (a) S-Co@NC and (b) H-Co@NC at different scan rates.

Fig. S9. (a) effects of other co-existing anions (i.e., HCO_3^-, SO_4^{2-}) and humic acid (HA) on the degradation of CIP using H-Co@NC+Oxone. (Experimental conditions: catalyst = 100 mg/L, Oxone = 100 mg/L, T = 30oC, initial CIP conc. = 5 mg/L, initial pH = 7).
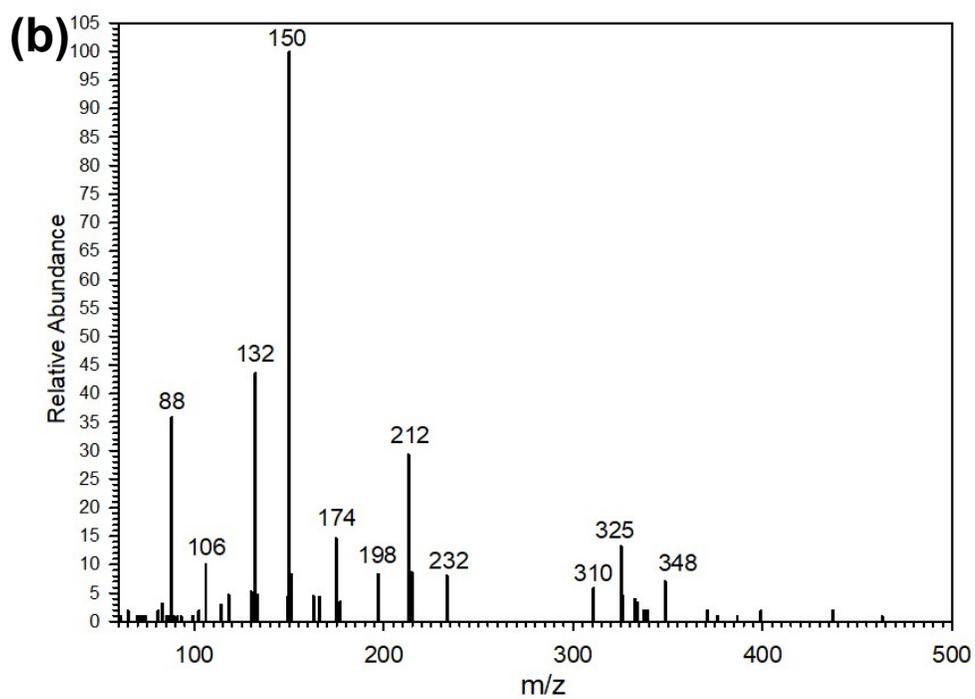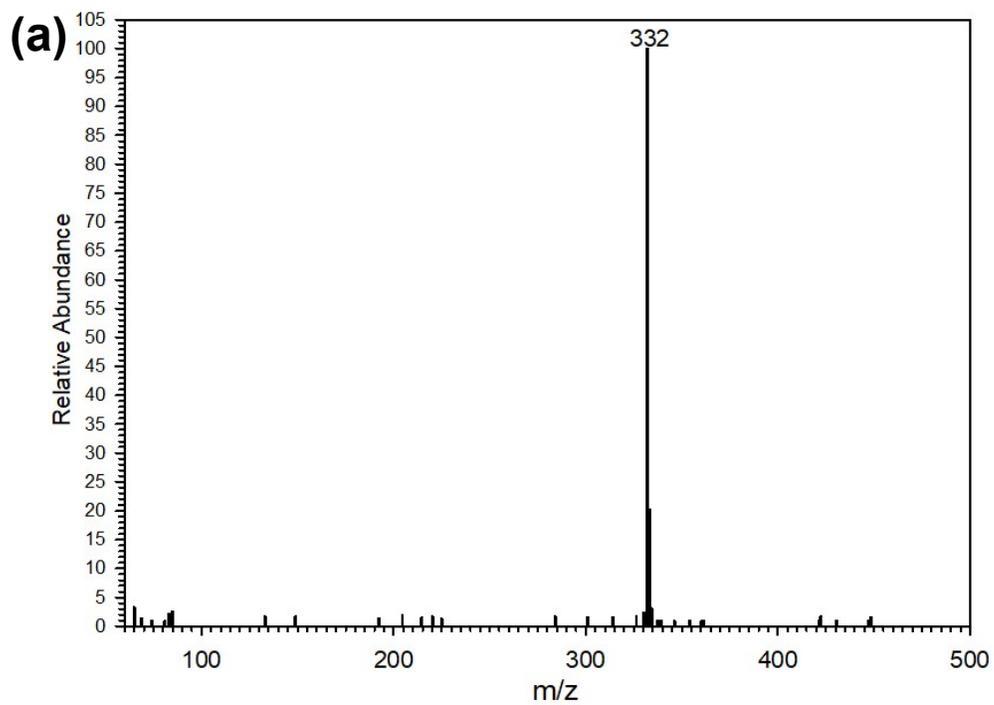
Fig. S10. ESI mass spectra of (a) CIP and (b) intermediates of CIP degradation.

Reference

[1] S. Zhu, W. Wang, Y. Xu, Z. Zhu, Z. Liu, F. Cui, Iron sludge-derived magnetic Fe0/Fe$_3$C catalyst for oxidation of ciprofloxacin via peroxymonosulfate activation, Chemical Engineering Journal, 365 (2019) 99-110.

[2] S. Zhu, Y. Xu, Z. Zhu, Z. Liu, W. Wang, Activation of peroxymonosulfate by magnetic Co-Fe/SiO$_2$ layered catalyst derived from iron sludge for ciprofloxacin degradation, Chemical Engineering Journal, 384 (2020) 123298.

[3] R. Yu, J. Zhao, Z. Zhao, F. Cui, Copper substituted zinc ferrite with abundant oxygen vacancies for enhanced ciprofloxacin degradation via peroxymonosulfate activation, Journal of Hazardous Materials, 390 (2020) 121998.