

Supporting information

Efficient bimetallic Metal-Organic Framework Derived Magnetic Co/N-PC-800 Nanoreactor for Peroxymonosulfate Activation carbamazepine Degradation

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Materials

Cobalt nitrate hexahydrate, Zinc nitrate hexahydrate, Peroxymonosulfate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, PMS, Shanghai Aladdin Reagent Co., LTD), 4,4',4''-Nitrilotribenzoic acid (NTB, Jilin Chinese Academy of Sciences -Yanshen Technology Co., LTD), N,N-dimethylacetamide (DMA, Tianjin Fuyu Fine Chemical Co., LTD), Deionized water (H_2O , Tianjin Yongsheng Fine Chemical Co., LTD), 2-Nitroterephthalic acid, Carbamazepine (CBZ), Tert-butanol (TBA), P-benzoquinone, (P-BQ, Shanghai Maclin Biochemical Technology Co., LTD), Sodium hydroxide (NaOH, Fuchen Tianjin Reagent Co., LTD), Hydrochloric acid (HCl, Beijing Chemical Plant), Sodium chloride (NaCl, Tianjin Dingsheng Xin Chemical Co., LTD), Crystalline sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, Shenyang Reagent Factory), Sodium dihydrogen phosphate (NaH_2PO_4 , Tianjin Damao Chemical Reagent Factory), Anhydrous sodium sulfate (Na_2SO_4 , Tianjin Xintong Fine Chemical Co, LTD), Sodium bicarbonate (NaHCO_3 , Kaiyuan Chemical Reagent Factory). All reagents were used directly as supplied without further purification.

Instrumentation and Characterization

The morphologies of material were explored by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Powder X-ray diffraction (PXRD) patterns were obtained using $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation on Rigaku D-Max 2550 with a scan range of $20\text{-}80^\circ$ and scan rate of $5^\circ/\text{min}$. The elemental composition of Co/N-PC-T was analyzed by X-ray photoelectron spectroscopy (XPS) of KRATOS Analytical. The vibration characteristic of the sample was examined by Renishaw

Model 2000 confocal microscope Raman spectrometer. The magnetic properties of the sample were measured by superconducting quantum interferometer magnetometer (SQUID). UV-visible spectra were performed on UV-9000S UV-visible spectrophotometer (METASH, China). High Performance Liquid Chromatography-Mass Spectrometry (LC-MS) was used to analyze the intermediates of CBZ degradation. (Instrument model: Agilent 1260-G6125B mass spectrometry). An electron paramagnetic resonance (EPR) equipment was utilized to identify active species. (Instrument model: E500CW-EPR, Bruker ELEXSYSI)

High Performance Liquid Chromatography-Mass Spectrometry (LC-MS) was used to analyze the intermediates of CBZ degradation. (Instrument model: Agilent 1260-G6125B mass spectrometry) Mobile phase A: 0.05 % FA-Water; Mobile phase B: 0.04 % FA-ACN; Chromatographic column: ZORBAX Eclipse Plus C18 (4.60*50 mm*5 μ m). Samples were analyzed by gradient elution as follows:

Time (min)	A (%)	B (%)	Flow velocity (mL/min)
0	95	5	1
10	5	95	1
15	5	95	1

The injection volume was 30.00 μ L. The mass spectrometry scanning range was 100-320 m/z, the ion source was API-ESI, the drying gas flow rate was 10.00 L/min, the drying gas temperature was 350 $^{\circ}$ C, and the capillary voltage was 4000 V. The scanning modes were positive-negative, with collision-induced dissociation of 150, a gain of 1.00, a threshold of 150 and a step size of 0.10, at a rate of 1300 u/sec.

An electron paramagnetic resonance (EPR) equipment was utilized to identify active species. (Instrument model: E500CW-EPR, Bruker ELEXSYSI) 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as the $\text{SO}_4^{\cdot-}$ and OH^{\cdot} spin traps and 2,2,6,6-tetramethylpiperidine (TEMP) was used as the spin trap for $^1\text{O}_2$.

Instrument operating parameters: microwave frequency = 9.84 GHz, microwave power = 0.20 mW, modulation amplitude = 1 G, modulation frequency = 100 kHz, centre magnetic field = 3505 G, sweep width = 100 G.

Experimental procedure: A reaction solution comprising 20 mL of 0.05 g/L catalyst and 10 mM of spin trapping agent was agitated at room temperature for 5 minutes and a 5 mL sample was taken after that. A specified volume of PMS solution was added to the sample, yielding a mixed solution containing 0.50 mM PMS. To test the EPR, 20 μL of the combined solution was put through a 50 μL quartz capillary.

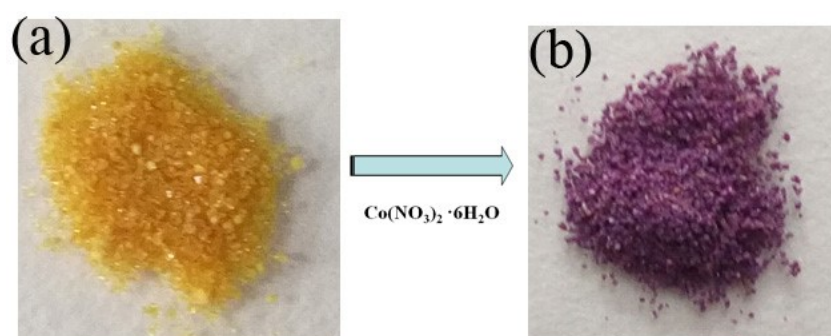


Fig. S1. Digital photos of the crystals before and after immersion

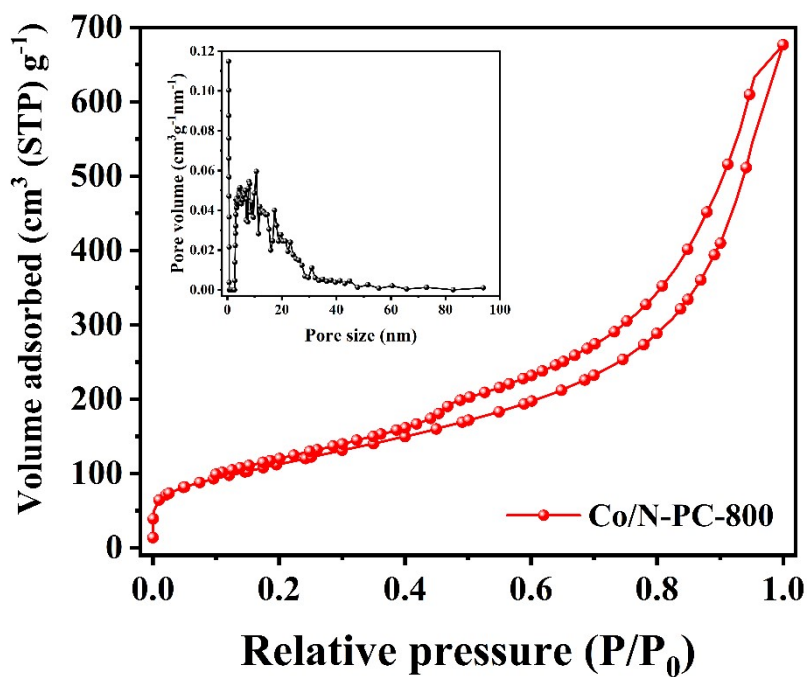


Fig. S2. N₂ adsorption-desorption isotherm of Co/N-PC-800

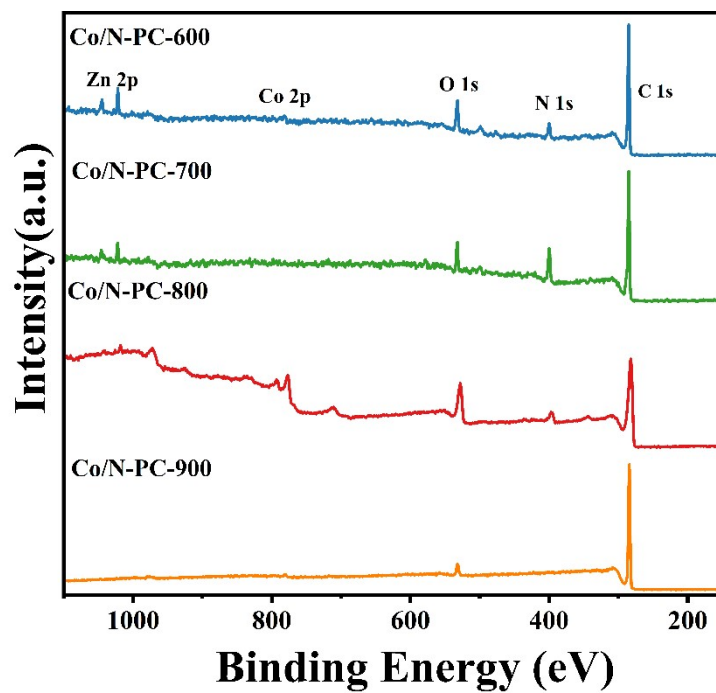


Fig. S3. XPS full spectrum of Co/N-PC-T

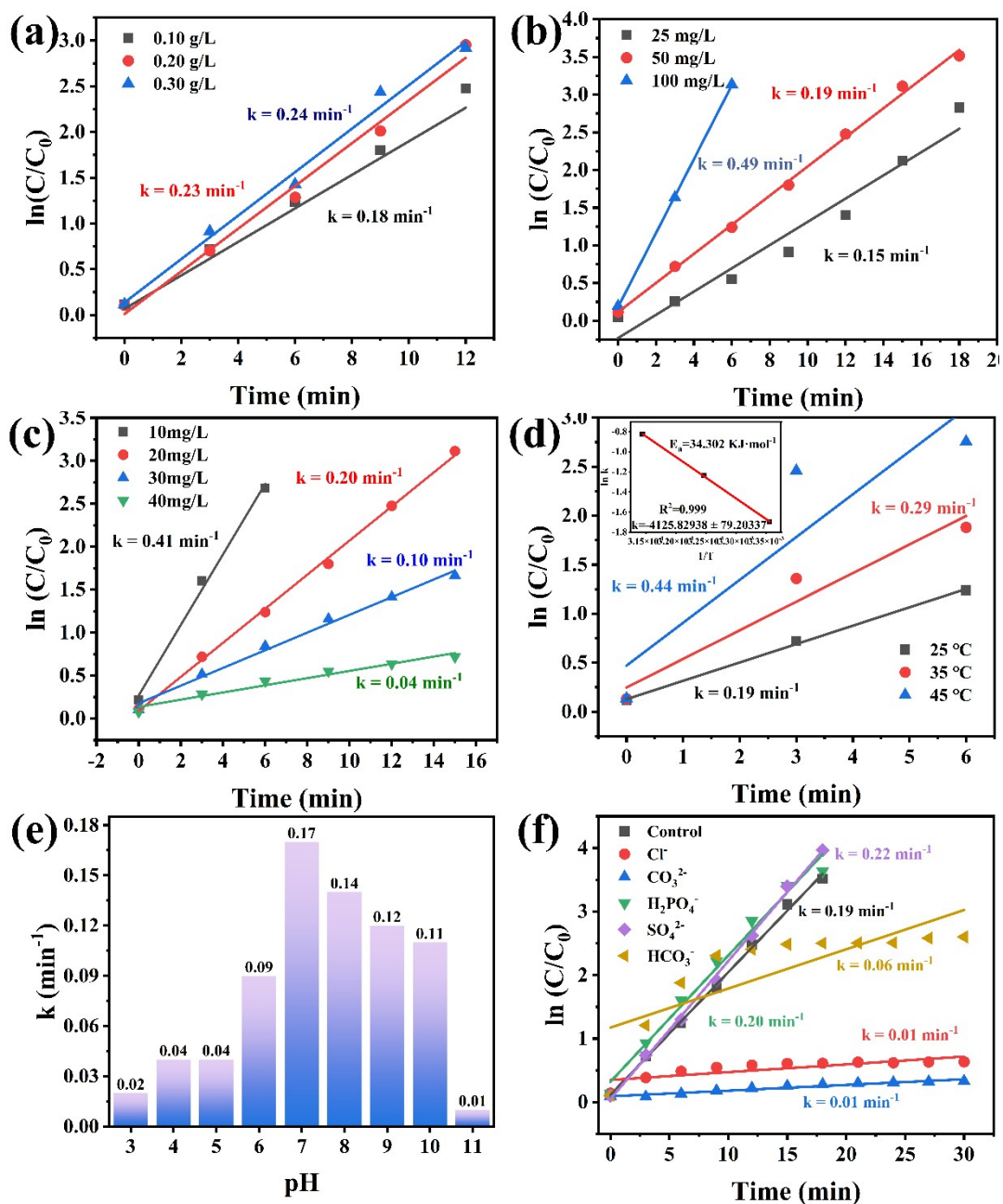


Fig. S4. Changes of the first-order kinetic rate constant of Co/N-PC-800 for CBZ degradation at varying (a) PMS dosage (b) catalyst dosage (c) CBZ concentration (d) temperature (e) initial pH and (f) common anions concentration

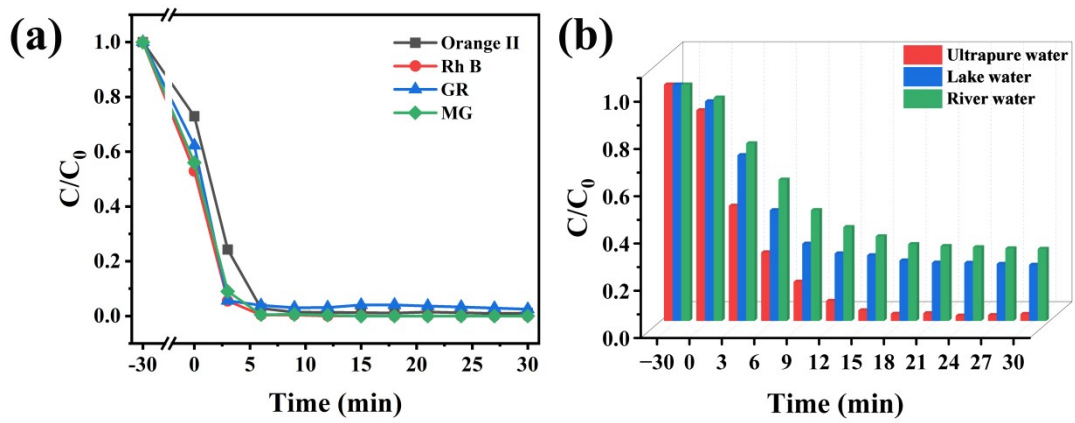


Fig. S5. (a) degradation effect of Co/N-PC-800 on dyes and (b) degradation effect of CBZ in different water systems

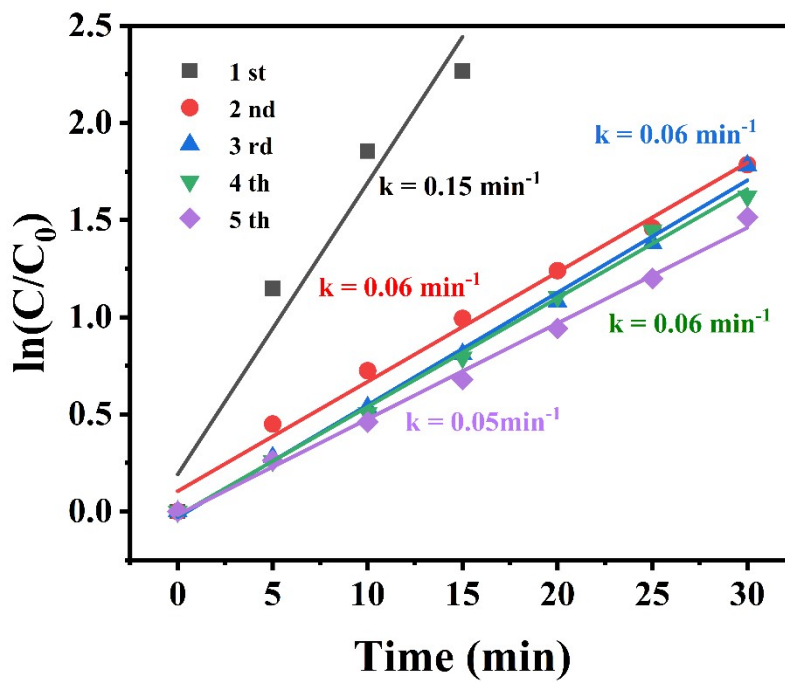


Fig. S6. Change of first-order kinetic rate constant of Co/N-PC-800 degradation of CBZ in five cycles

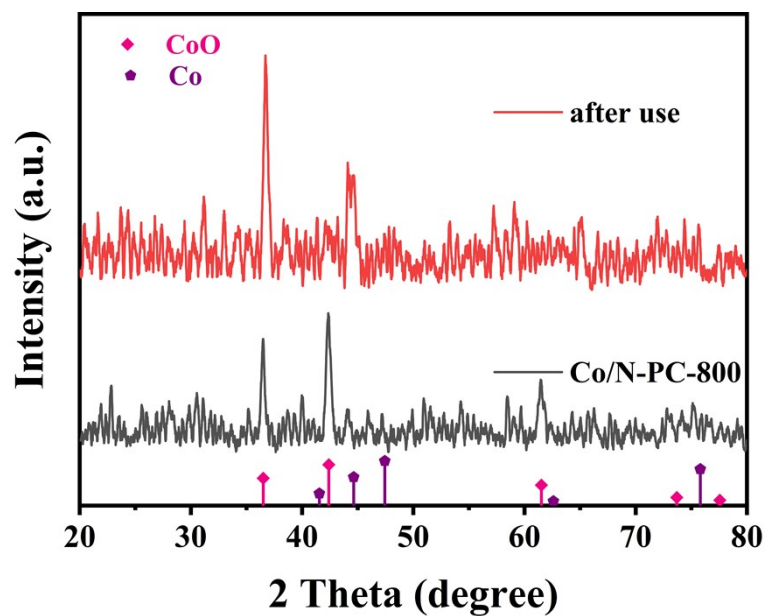


Fig. S7. XRD patten of Co/N-PC-800 before and after degradation

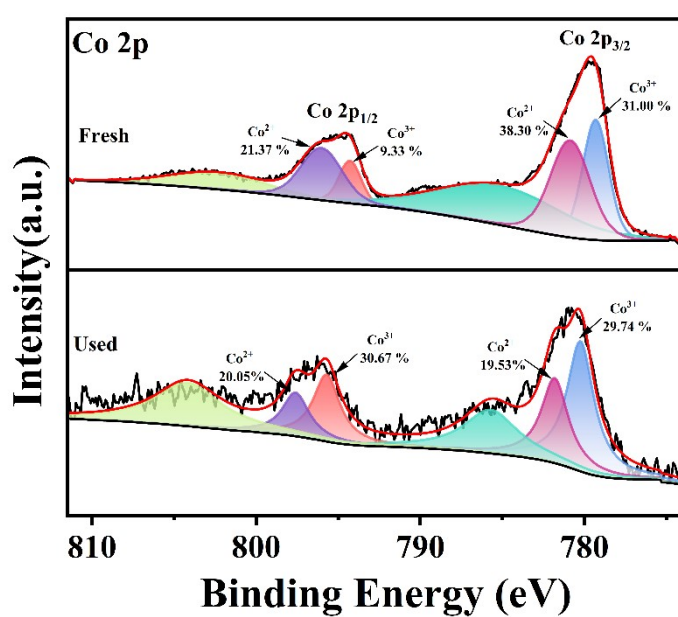
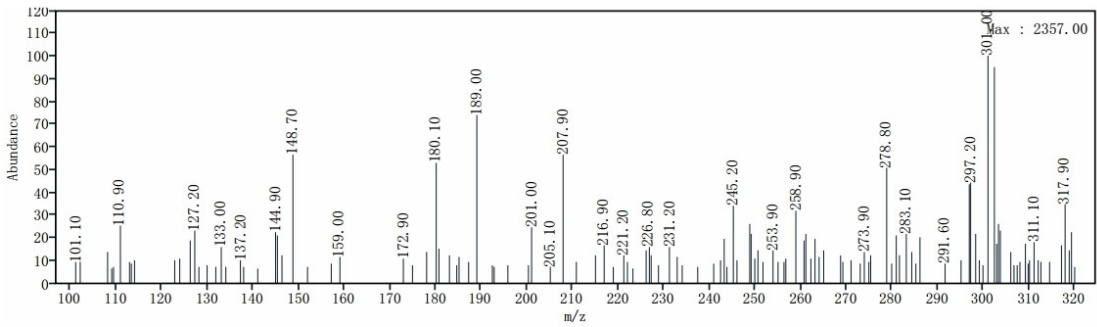
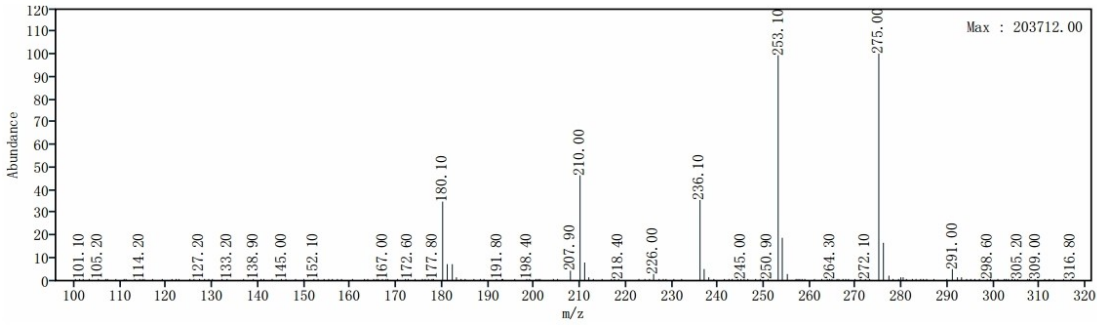
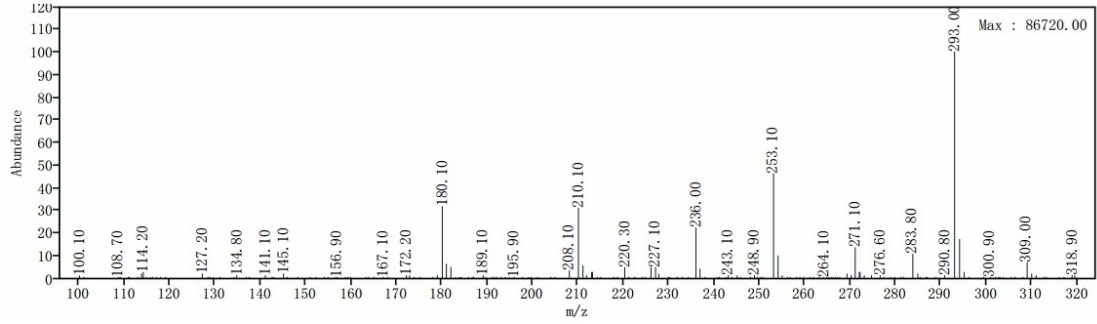
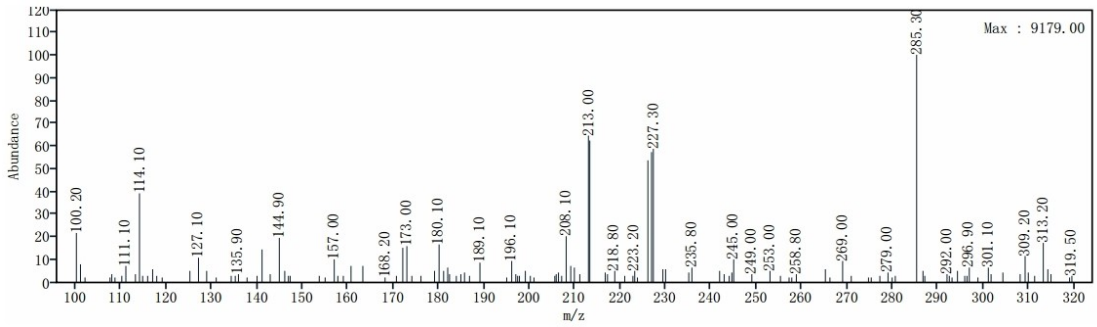
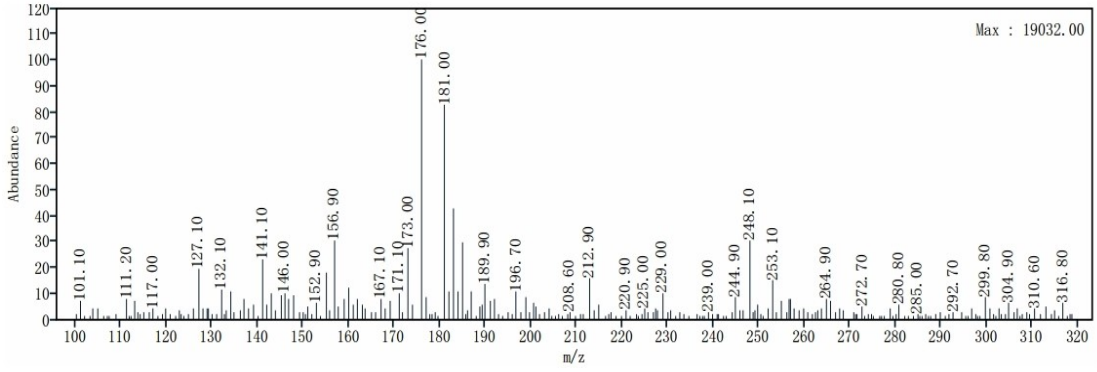
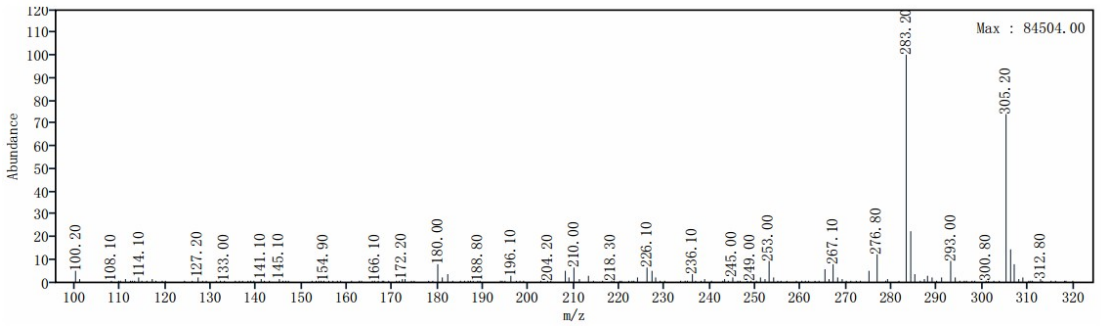
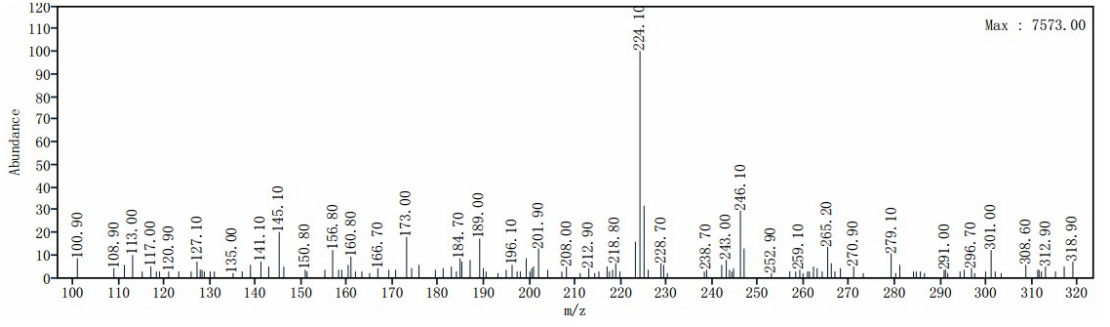
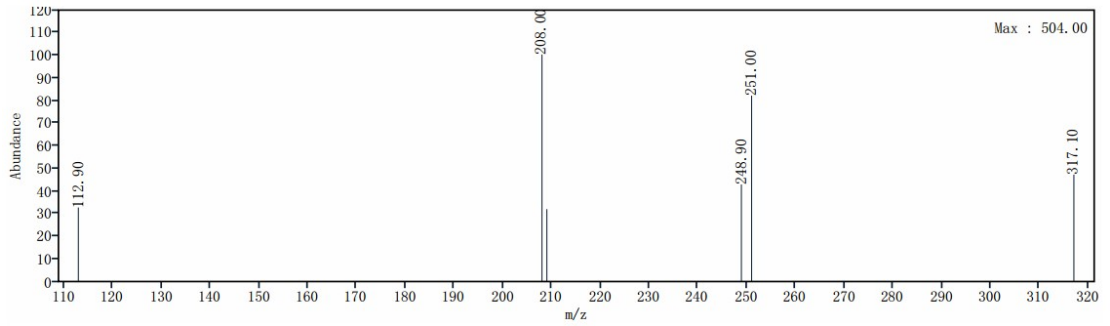
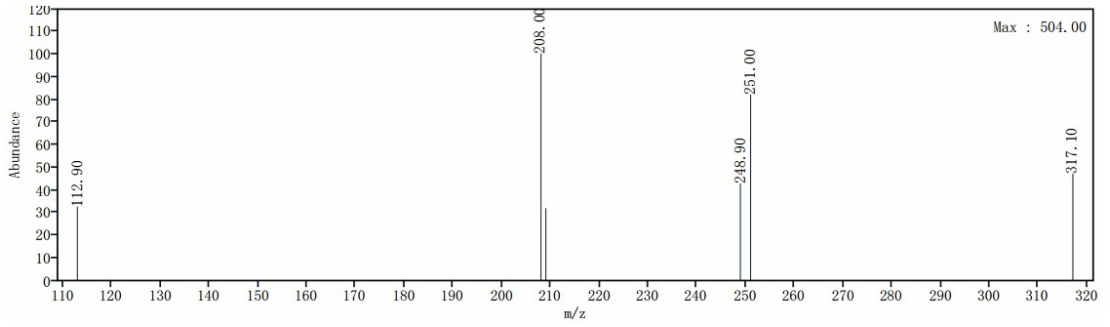
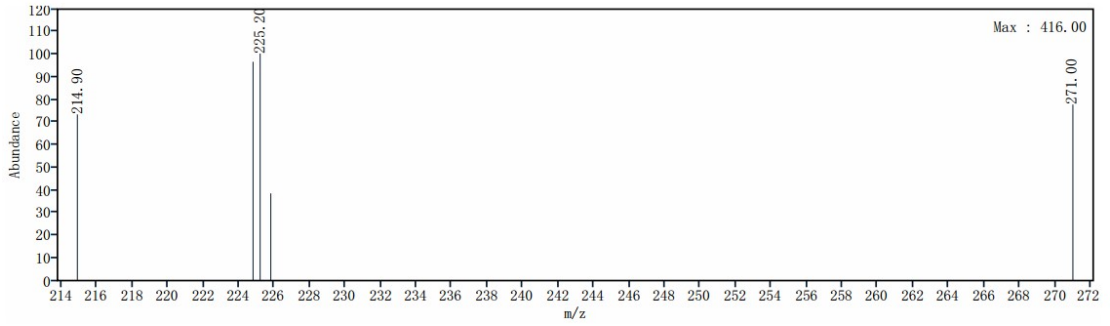


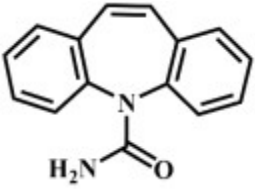
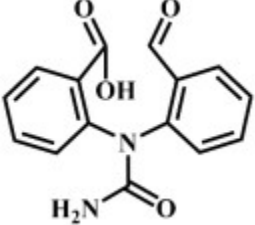
Fig. S8. XPS spectra of Co/N-PC-800 before and after use

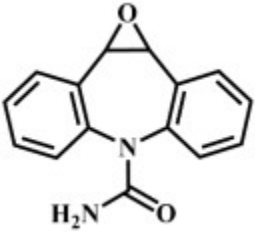
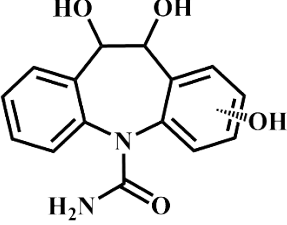
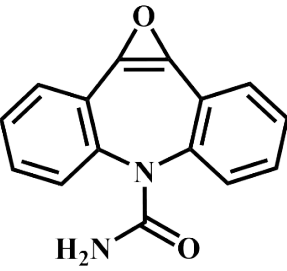
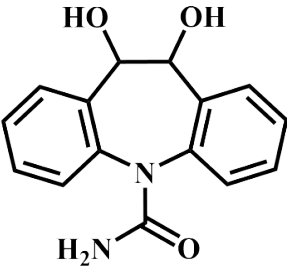
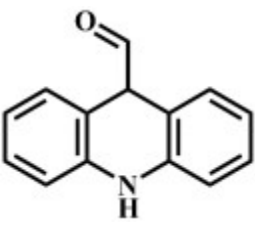
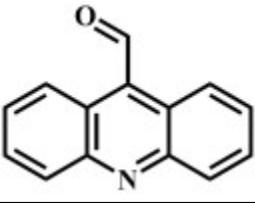
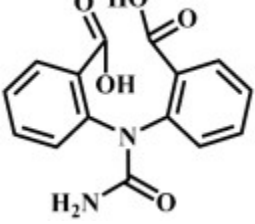




Fe ³⁺ /N-MoS ₂	10	75	100	0.696	10	90	1
Co-CCF-600	20	100	300	0.035	60	93	2
CoSBC-900	20	100	300	0.128	20	95	3
Co-RH-130	20	200	300	0.076	60	95	4
nCoFe ₂ O ₄ /O Mt	5	400	153	0.039	60	93	5
Co/N-PC-800	20	50	100	0.229	30	98	This work

Table. S3 List of main transformation products formed during the degradation process of CBZ

Product	m/z	Molecular formula	Proposed structure
CBZ	237	C ₁₅ H ₁₂ N ₂ O	
P1	285	C ₁₅ H ₁₅ N ₂ O ₄	

P2	253	$C_{15}H_{12}N_2O_2$	
P3	287	$C_{15}H_{12}N_2O_4$	
P4	251	$C_{15}H_{10}N_2O_2$	
P5	271	$C_{15}H_{12}N_2O_3$	
P6	210	$C_{14}H_{11}NO$	
P7	208	$C_{14}H_9NO$	
P8	301	$C_{15}H_{12}N_2O_5$	

P9	267	$C_{15}H_{10}N_2O_3$	
P10	224	$C_{14}H_9NO_2$	
P11	180	$C_{13}H_9N$	
P12	283	$C_{15}H_{10}N_2O_4$	
P13	196	$C_{13}H_9NO$	
P14	208	$C_{14}H_9NO$	

References

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