Supporting Information

Nitrogen-rich cobalt metal-organic framework as heterogeneous catalyst to degrade organic dye pollutants in water via peroxymonosulfate activation

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S1. Materials and Methods

All chemical reagents for synthesis were purchased commercially and were used directly without further purification. Powder X-ray diffraction (PXRD) data were obtained on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 3°$ up to $50°$ with $0.02°$ increment. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250Xi electron spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). The UV-vis absorption spectra were carried out using Jasco V-770 spectrometer (JAPAN) spectrophotometer. The metal ion content in the solution is tested by Inductively coupled plasma (ICP) mass spectrometer (NexION 350X, United States). Total organic carbon was analyzed with a TOC analyzer (Shimadzu TOC-L-CPH). Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker A300 spectrometer.

S2. Synthesis of Co$_3$-btca

Co$_3$-btca was synthesized according to the reported procedure with modification[1]. A mixture of Co(NO$_3$)$_2$·6H$_2$O (58 mg, 0.2 mmol) and H$_2$btca (benzotriazole-5-carboxylic acid, 20 mg, 0.12 mmol) was dissolved in N,N-dimethylacetamide (DMA) and H$_2$O (6 mL, 1:1, V/V) solution. The final mixture solution was sealed in a 10 mL Teflon-lined stainless autoclave and heated at 130 °C for 72 hours. After the reaction, the autoclave was then cooled slowly down to the room temperature. The precipitates were washed by deionized water for three times and purple crystal Co-MOF **Co$_3$-btca** was collected.

S3. Heterogeneous MV and RhB degradation by Co$_3$-btca/PMS

In this study, model pollutants RhB (Rhodamine B) and MV (Methyl Violet) are chosen to evaluate the catalytic performance of **Co$_3$-btca** for PMS activation. The oxidation degradation experiments contain 100 mL of dye (RhB or MV) solution with the concentration of 20 mg/L, catalyst **Co$_3$-btca** (10 mg) and PMS (1.0 mM) in 250 mL reactor. The experiments were carried out at 20 °C under ambient atmospheric condition. Before addition of PMS, the solution including **Co$_3$-btca** catalyst and dye solution was magnetically stirred for 10 min to establish adsorption-desorption equilibrium. And then we added PMS to the system. After desired intervals, 1.0 mL

of the degraded solution was taken with adding 1.0 mL of 6 mM $Na_2S_2O_3$ aqueous solution to quench the reaction and filtered with a 0.22 -μm filter to separate the supernatant liquid from catalyst for analysis. The RhB and MV dye concentrations were analyzed by using the UV-visible spectrophotometer at their maximum absorbance wavelengths of 554 nm and 584 nm. The influence factors of dye concentration, catalyst loading, PMS concentration, and temperature were carried out to assess the performance of dye degradation. To test the recyclability of **Co₃-btca** catalyst, after degradation each experiment, the **Co₃-btca** was collected by centrifugation, washed with water and ethanol many times and dried at 70 °C for 12 h. Then the same catalyst was used for the next run catalytic degradation experiment.

A general pseudo-first-order reaction was used to estimate the degradation reaction rate as shown below:

$$\ln(C/C_0) = -kt$$

where C_0 and C are the initial concentration and the concentration at various time, respectively, k is the first order reaction kinetic constant of MV and RhB removal (min^{-1}).
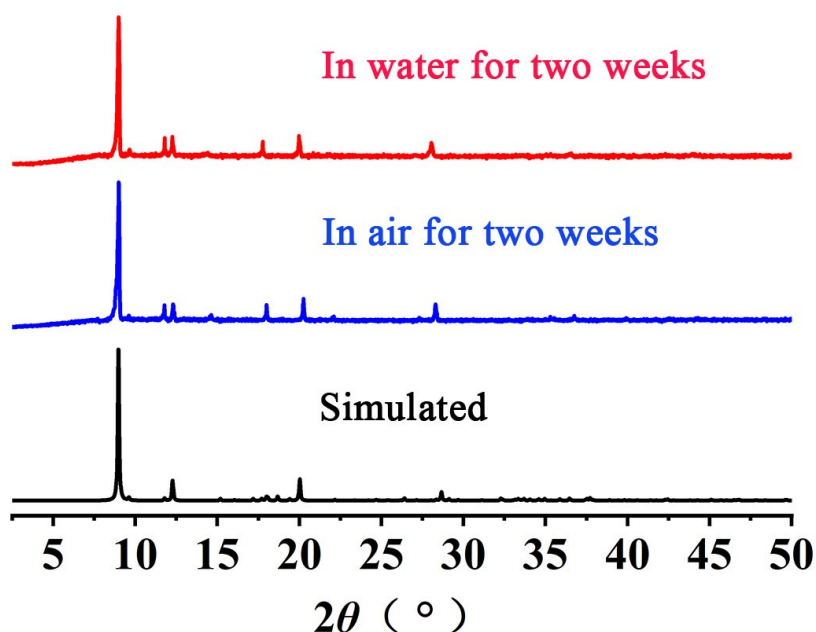

Fig. S1 The PXRD patterns of the **Co₃-btca**. Black: simulated, blue: exposed in air for two weeks, and red: exposed in water for two weeks, respectively.

Table S1 Comparison of different Co-containing catalysts towards pollutants for PMS activation.

Catalyst	pollutant	PMS dose	Catalyst dose (g/L)	Degradation efficiency	Ref.
HCo_3O_4/C	BPA, 87.6 μm	325.3 μM	0.1	97%, 4 min	2
$CoMn_2O_4$	SA, 10 mg/L	0.1 g/L	0.05	100%, 30 min	3
$Fe_3Co_7@C$-650	BPA, 20 mg/L	0.2 g/L	0.1	98%, 30 min	4
Co-MOF	MO, 20 mg/L	1.0 mM	0.1	98.56%, 4.5 min	5
ZIF-67/PAN	AY, 500 mg/L	0.5 g/L	0.233	95.1%, 10 min	6
ZIF-67	RhB, 50 mg/L	0.15 g/L	0.01	80%, 60 min	7
CuCo-MOF-74	MB, 0.2 mM	2.0 mM	0.05	100%, 30 min	8
MCNC	RhB, 10 mg/L	0.05 g/L	0.01	90%, 10 min	9
$NiCo_4$-LDH	CIP, 50 mg/L	1.25 g/L	0.25	95%, 10 min	10
10%-AZCN	LVFX, 10 mg/L	2.0 mM	1.0	87.3%, 60 min	11
JLNU-500	RhB, 50 mg/L	1.0 mM	0.1	99.8%, 6 min	12
Co_3-btca	MV, 20 mg/L	1.0 mM	0.1	99.78%, 9 min	this work
Co_3-btca	RhB, 20 mg/L	1.0 mM	0.1	99.58%, 15 min	this work

BPA, bisphenol A, SA, sulfanilamide, AY, acid yellow, MO, methyl orange, MB, methylene blue, CIP, ciprofloxacin, LVFX, levofloxacin, MV, Methyl Violet, RhB, rhodamine B.
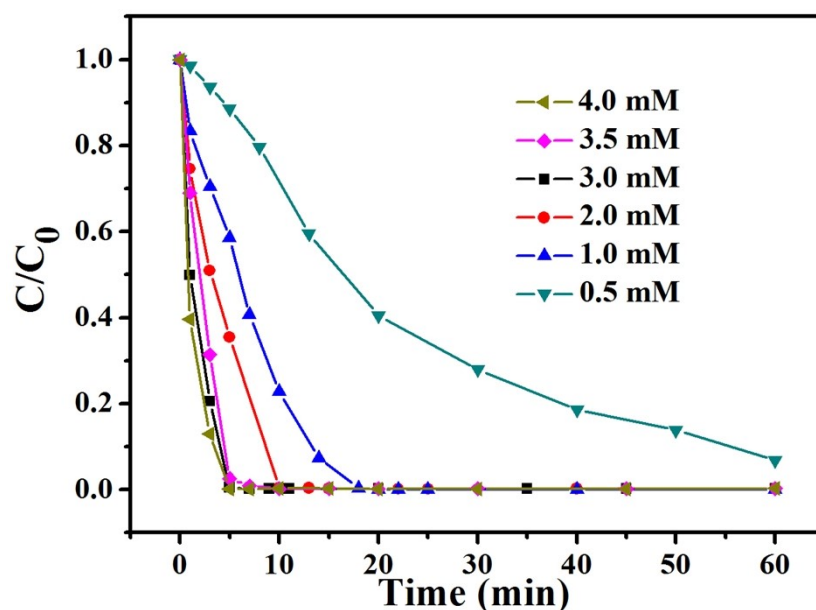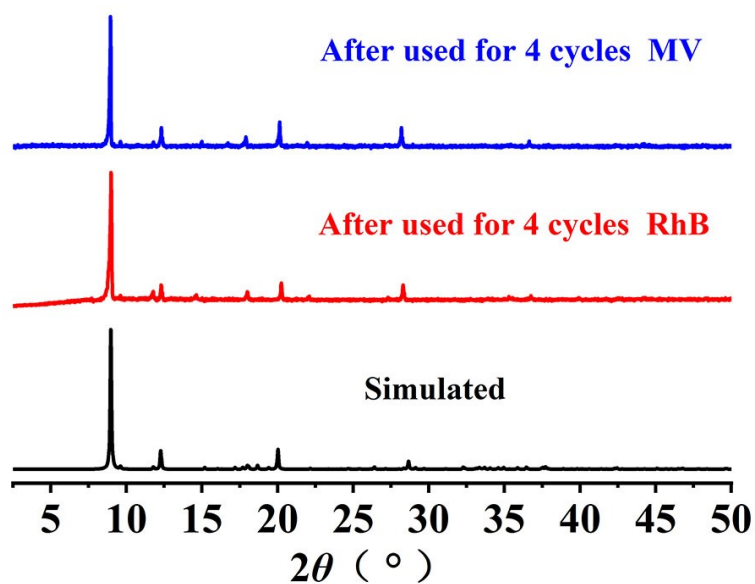

Fig. S2 Effect of PMS concentration on the degradation of RhB. Experiment

condition: [RhB] = 20 mg L^{-1}, [Co$_3$-btca] = 10 mg, [PMS] = 1.0 mM, T = 20 ℃.
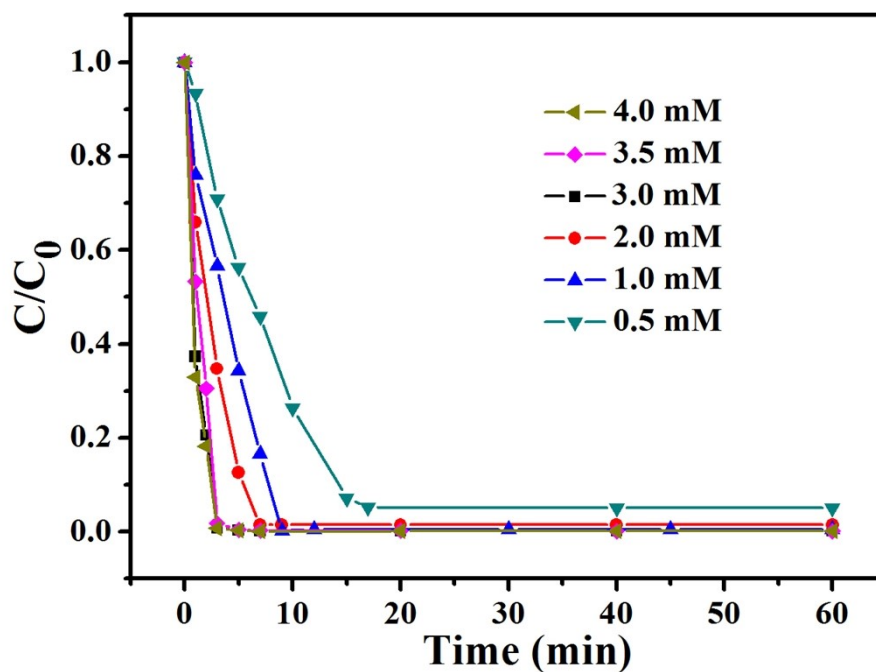
Fig. S3 Effect of PMS concentration on the degradation of MV. Experiment condition:

[MV] = 20 mg L^{-1}, [Co$_3$-btca] = 10 mg, [PMS] = 1.0 mM, T = 20 ℃.

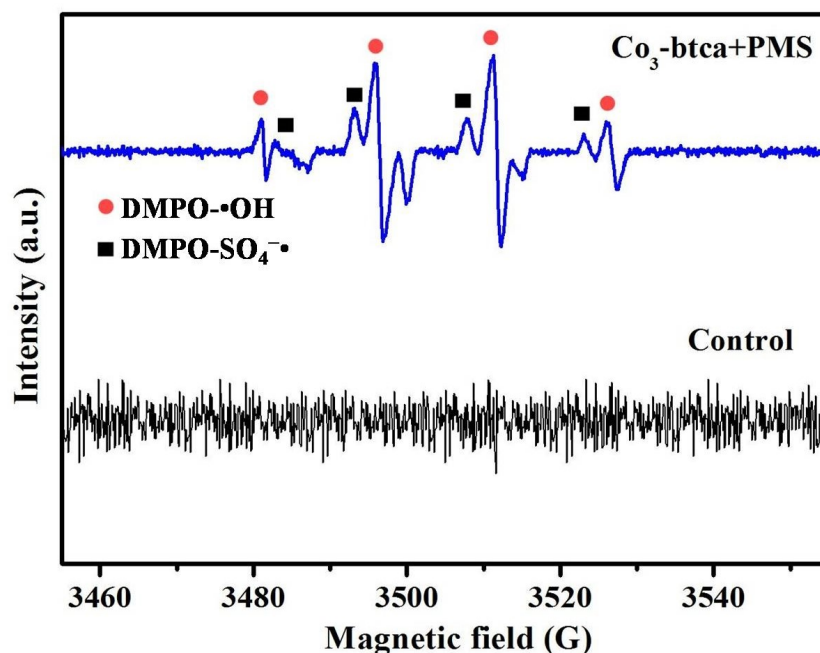**Fig. S4** The PXRD patterns of **Co$_3$-btca** after used for 4 cycles.

Fig. S5 EPR spectra obtained using DMPO as spin-trapping agent.

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