Supporting Information for

Enhanced heterogeneous activation of peroxymonosulfate by Co and N codoped porous carbon for degradation of organic pollutants: the

synergism between Co and N

Guanlong Wang, ¹ Xiaowa Nie,² Xiaojing Ji,² Xie Quan, *¹ Shuo Chen,¹ Haozhi Wang,² Hongtao Yu,¹ and Xinwen Guo²

¹ Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education, China), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

² State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, P.R. China

*Corresponding author: Xie Quan E-mail: <u>quanxie@dlut.edu.cn</u> Tel: +86-411-84706140; Fax: +86-411-84706263

Text S1. The preparation of NPC, CoPC and Fe-N-PC.

Preparation of NPC. The NPC was prepared from the ZIF-8. Briefly, 10 mL $Zn(NO_3)_2 \cdot 6H_2O$ solution (74.4 g L⁻¹) was added into 90 mL imidazole derivative (2-methylimidazole) solution (137 g L⁻¹) at room temperature. The mixture, which immediately turned into a turbid liquid, was stirred with a magnetic bar for 24 h, and the milky colloidal dispersion was then centrifuged at 8000 rpm for 10 min. The deposited particles were washed with methanol three times and dried at 40 °C for 48 h to obtain ZIF-8. The carbonization process was the same as that of Co-N-PCs.

Preparation of CoPC. The CoPC was prepared from the Co doped MOF-5. Typically, $Zn(NO_3)_2 \cdot 4H_2O$ (2.34 g, 8.95 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.11 g, 1.79 mmol), and 1,4-benzenedicarboxylic acid (0.49 g, 2.98 mmol) were dissolved in 75 mL of N,N-diethylformamide. The mixture was then transformed into Teflon-lined stainless steel sealed vessel and heated at 105 °C for 20 h. After cooling down to room temperature, the basal precipitate was isolated by centrifugation and washed thoroughly with DMF. The carbonization process was the same as that of Co-N-PCs.

Preparation of Fe-N-PC. The Fe-N-PC with the Fe content of 7.78% was obtained from Fe substituted ZIF-8. Typically, $Zn(NO_3)_2 \cdot 6H_2O$ (1.12 mmol) and FeSO₄ $\cdot 7H_2O$ (0.22 mmol) were dissolved in 15 mL DMF solvent and then mixed with DMF solution of 2-methylimidazole (15 mL, 0.08 M) under stirring. The resulting mixture was stirred for another 30 min at room temperature and then transformed into teflonlined stainless steel sealed vessel and heated at 140 °C for 48 h. After cooling down to room temperature, the basal precipitate was isolated by centrifugation and washed thoroughly with DMF. The carbonization process was the same as that of Co-N-PCs.

Text S2. Chemicals, analytic methods and computational details.

Chemicals. All the chemicals, including cobaltous nitrate hexahydrate $(Co(NO_3)_2 \cdot 6H_2O, 99\%)$, Zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O, 99\%)$, potassium peroxymonosulfate (2KHSO₅·KHSO₄·K₂SO₄, PMS), *tert*-butyl alcohol (TBA), and methanol were obtained from Guangfu Fine Chemicals, Tianjin, China. 2-methylimidazole (98%) was obtained from Aladdin. They were at least of analytical

grade and were used without further purification. All the reaction solution were prepared with Millipore water (resistivity >18 M Ω ·cm, Laikie Instrument Co., Ltd., Shanghai, China).

Analytic methods. The concentrations of phenol, bisphenol A, atrazine and sulfamethoxazole solution were analyzed by a high performance liquid chromatography (HPLC, Waters) equipped with a C-18 column and a PDA detector. For phenol, the mobile phase was composed of 70% ultrapure water and 30% methanol and flowed at 1 mL min⁻¹. The concentration of bisphenol A was measured using the same mobile phase as that of phenol. For atrazine, the mobile phase was composed of 40% ultrapure water and 60% acetonitrile flowed at 1 mL min⁻¹. For sulfamethoxazole, the mobile phase was composed of 45% acetonitrile and 55% acetic acid (0.1%) and flowed at 1 mL min⁻¹. The TOC values of all the samples were measured by a total carbon analyzer (MultiNC2100, Germany).

Computational details. All the calculations were performed using Gaussian 09¹ with the hybridized B3LYP functional². The Pople basis set of $6-31G^{*3}$ was applied for C. H, O, N, S atoms while the effective core potential LANL2DZ⁴ was used for Co atom. All atoms were allowed to relax during structural optimization. The Berny method implemented in Gaussian was adopted to optimize the transition states, which were confirmed to have only a single imaginary vibrational frequency along the reaction coordinate. We constructed three different doped carbon models based on our experimental studies, including the Co, N codoped carbon, N doped carbon and Co doped carbon, denoted as Co-N-PC, NPC and CoPC, respectively. All these models were established based on the defect carbon matrix, similar as models used in literature^{5, 6}. The NPC contains four nitrogen atoms derived from the undercoordinated pyrrole carbons of the defect site. Based on this model, we placed one Co atom at the center of the four N atoms, to construct the Co-N-PC model. For the Co-PC model, we placed one Co atom at the center of the defect graphene matrix containing pyridine C atoms which is widely used in DFT studies related to Co doped carbon materials^{7, 8}.

 Table S1. The Co content (wt%) of Co-N-PC catalysts derived from MOF precursors with different Zn/Co molar ratio..

Zn/Co ratio	100	40	20	5	0
Co content	0	1.72	3.07	7.78	10.3



Fig. S1 Phenol removal by PMS in the presence of phosphate buffer solution. ([Phenol] = 20 mg L^{-1} , [catalyst] = 0.05 g L^{-1} , [PMS] = 1.6 mM, 1 mM phosphate buffer at pH = 7).



Fig. S2 The SEM images of a series Co substituted ZIF-8 with different Zn/Co molar ratio of (a) 0; (b) 5; (c) 20; (d) 40 and their corresponding porous carbons (e) CoNPC-10.3; (f) CoNPC-7.78; (g) CoNPC-3.07; (h) CoNPC-1.72.



Fig. S3 The EDS mapping results of Co-N-PC.



Fig. S4 TEM images of (a) CoNPC-1.72, (b) CoNPC-3.07, (c) CoNPC-7.78 and (d) CoNPC-10.3.

Table S2 BET surface areas, total pore volumes and micropore volumes of Co-N-PCs.

Sample	$S_{BET}/m^2g^{\text{-}1}$	$V_{total}/cm^3 \ g^{-1}$	V_{micro}/cm^3g^{-1}
CoNPC-10.3	211	0.50	0.05
CoNPC-7.78	387	0.84	0.13
CoNPC-3.07	564	1.02	0.23
CoNPC-1.72	584	1.05	0.24
NPC	998	0.99	0.45

 Table S3 Element composition of Co-N-PCs (at%).

Sample	С	Ν	0	Со
CoNPC-10.3	84.75	4.00	9.78	1.47
CoNPC-7.78	86.18	6.99	5.54	1.29
CoNPC-3.07	85.02	7.58	6.38	1.02
CoNPC-1.72	85.53	5.84	7.83	0.80
NPC	88.92	5.19	5.14	0



Fig. S5 Raman spectra of Co-N-PCs.



Fig. S6 The catalytic performance of CoNPC-7.78, FeNPC-7.78 and NPC ([phenol] = 20 mg L^{-1} , [catalyst] = 0.05 g L^{-1} , [PMS] = 1.6 mM, T = 25 °C, initial pH=7.0).



Fig. S7 The TOC removal on various Co-N-PC catalysts. ([catalyst]=0.05 g L⁻¹, [PMS]=1.7 mM, [phenol]=20 mg L⁻¹, T=25 °C, initial pH=7.0).



Fig. S8 Catalytic performances of CoNPC-7.78 and homogeneous Co^{2+} for removal of (a) phenol, (b) BPA and (c) atrazine and (d) SMX; ([catalyst] = 0.05 g L⁻¹, [PMS] = 1.6 mM, [pollutant] = 20 mg L⁻¹, T = 25 °C, initial pH = 7.0).

catalytic system	catalyst	pollutant	Removal	Kinetic constant
	(g L ⁻¹)	(µM)	efficiency	(\min^{-1})
Ferrihydrite/H ₂ O ₂	0.1	4.6	\	0.003
γ -Cu-Al ₂ O ₃ /H ₂ O ₂	1	46	100% (120 min)	0.025
CoNPC-7.78/PMS	0.05	92	100% (60 min)	0.081

Table S4 Comparison of CoNPC-7.78/PMS system with other AOPs for atrazine degradation.

Catalyst (load, g L ⁻¹)	PMS dosage (g L ⁻¹)	Pollutant (mg L ⁻¹)	Removal efficiency	Specific rate constant (L m ⁻² min ⁻¹)	Ref.
Co ²⁺ @PMAP (0.4)	1.8	Phenol (10)	100% (50 min)	3.62×10 ⁻⁴	9
α -MnO ₂ (0.4)	2.0	Phenol (25)	100% (20 min)	6.06×10 ⁻³	10
$Fe_{0.8}Co_{2.2}O_4(0.1)$	0.2	BPA (20)	95% (60 min)	7.90×10 ⁻³	11
NG-700 (0.1)	2.0	Phenol (20)	100% (30 min)	1.40×10 ⁻²	12
N-CNT (0.2)	2.0	Phenol (20)	100% (40 min)	1.99×10 ⁻³	13
SNG-0.3 (0.2)	2.0	Phenol (20)	100% (90 min)	3.18×10 ⁻³	14
$Fe_1Mn_5Co_4-N@C$ (0.1)	0.2	BPA (20)	100% (10 min)	7.27×10 ⁻²	15
CoNPC-7.78 (0.05)	0.5	Phenol (20)	100% (20 min)	1.55×10 ⁻²	This work
CoNPC-7.78 (0.05)	0.5	BPA (20)	100% (5 min)	9.82×10 ⁻²	This work

Table S5 Comparison of the reaction parameters with previously reported catalysts for PMS activation. The specific reaction rate constant was obtained through dividing the kinetic constant of pollutant degradation by the specific surface area per volume.



Fig. S9 (a) the reusability test of CoNPC-7.78/PMS system; (b) the kinetic constant of CoNPC-7.78 for phenol degradation in each recycle. ([phenol] = 20 mg L^{-1} , [catalyst] = 0.05 g L^{-1} , [PMS]

= 1.6 mM, initial pH=7.0)

Text S3. The Co leaching. The Co leaching from the Co-based catalysts is always undesirable because the toxic Co²⁺ pose potential threat to ecological environment and even human health. As shown in Fig. S10a, the Co leaching increases slightly with the reaction time and reaches approximately stable at $0.12 \text{ mg } \text{L}^{-1}$ after 60 min reaction. This value is much lower than the discharge limit of Co²⁺ in the "Standards for the surface water source for centralized drinking water" (1 mg L⁻¹). To check the contribution of dissolved Co²⁺ in catalytic process, its performance for the phenol degradation was investigated. The results shows that the reaction rate for phenol degradation by dissolved Co²⁺ is only 0.9% of that for CoNPC-7.78/PMS (Fig. S10b), meaning homogenous Co²⁺ contributes little to CoNPC-7.78/PMS catalytic system. The Co leaching of CoNPC-7.78/PMS system at different pH value was also investigated and presented in Fig. S10c. It is found the Co leaching decreases gradually from the acid to basic condition, and the highest Co leaching at pH of 3.1 is only 0.20 mg L⁻¹. Fig. S10d shows the CoNPC-7.78/PMS system could also maintain low Co leaching (less than 0.12 mg L⁻¹) in each cycle of reusability tests. The low Co leaching of in Co-N-PC/PMS system is possibly owing to the strong binding between Co and N atoms.



Fig. S10 (a) The Co leaching of CoNPC-7.78/PMS system during 60 min reaction (pH 7.6); (b) the catalytic activity of Co-N-PC and dissolved Co^{2+} in phenol degradation. (c) the Co leaching of CoNPC-7.78/PMS system at different pH condition after 60 min reaction; (d) the Co leaching of CoNPC-7.78/PMS system in each cycle after 60 min reaction ([catalyst]=0.05 g L⁻¹, [PMS]=1.6 mM, [phenol]=20 mg L⁻¹, T=25 °C, initial pH=7.0).



Fig. S11 The high resolution XPS spectra of Co 2p for Co-N-PC.



Fig. S12 Kinetic constant of phenol degradation in the present (a) TBA and (b) MeOH.

Text S4. The quantification of SO₄⁻. The generation rate of SO₄⁻⁻ was measured by the reaction of benzoic acid (BA) and SO₄⁻⁻ due to the fast reaction rate constant (1.2 $\times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$) between them. The high concentration of BA ([BA]/[PMS] =10) was chosen in order to avoid the radical quenching by unreacted PMS. A correct strategy for determining the quantitation of SO₄⁻⁻ was to eliminate 'OH contribution using a radical scavenger selective to 'OH. TBA was an appropriate radical scavenger for 'OH because its reactivity with 'OH is 3 orders of magnitude higher than that with SO₄⁻⁻ ($k_{\text{SO}^{4--},\text{TBA}}$ =4.0 $\times 10^5 \text{ M}^{-1} \cdot \text{s}^{-1}$, $k_{\cdot \text{OH},\text{TBA}}$ = 6.0 $\times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$). The reaction between sulfate radical and the reaction of BA with SO₄⁻⁻ followed the pseudo-first-order kinetics (eq. S1), and k_{BA} refers to the reaction rate of BA degradation.

$$-\frac{d[BA]}{dt} = k_{BA}[BA] \tag{S1}$$

By employing TBA to eliminate 'OH, the eq. S2 was obtained, and the v_{SO4} refers to the generation rate of SO₄.

$$v_{\mathrm{SO4}} = k_{\mathrm{SO4}}, \mathbf{BA}[\mathrm{BA}][\mathrm{SO_4}] = k_{\mathrm{BA}}[\mathrm{BA}]$$
(S2)

Then the rate constant of SO₄⁻⁻ generation ($k_{SO_4}^{--}$) was regarded as the slope of the fitting line (eq. S3).

$$v_{\mathrm{SO4}} = k_{\mathrm{SO4}} = [\mathrm{PMS}] \tag{S3}$$



Fig. S13 Concentration of BA as a function of time in different PMS catalytic systems ([catalyst]=0.05 g L⁻¹, [PMS]=0.2 mM, [BA]=2 mM, [TBA]=20 mM, T=25 °C, initial pH=7.0)



Fig. S14 The high-resolution XPS spectra of N 1s for different Co-N-PC catalysts.



Fig. S15 Relationship between the amount of CoN_x and the reaction rate for phenol degradation of Co-N-PC catalysts.



Fig. S16 The high-resolution XPS spectra of Co 2p for Co-N-PC catalysts.

Table S6 The content of Co species in Co-N-C catalysts (at%).

sample	NPC	CoNPC-1.72	CoNPC-3.07	CoNPC-7.78	CoNPC-10.3
Co ⁰	0	0.09	0.13	0.28	0.30
Co ²⁺	0	0.24	0.27	0.35	0.35
Co ³⁺	0	0.16	0.24	0.32	0.35



Fig. S17 (a) The phenol removal as a function of time and (b) the removal efficiency of phenol within 30 min for CoNPC/PMS system with or without phosphate.

Text S5. The PMS adsorption experiment.

To support the claim that the N doping mainly promotes the PMS adsorption, the PMS adsorption experiment on different CoNPCs was performed. In this experiment, 1.6 mM PMS was mixed with 0.05 g L⁻¹ catalysts in the aqueous solution, the sample was withdrawn after 5 min adsorption and the PMS concentration in it was immediately analyzed. The PMS concentration was quantified using the method based on an iodine (λ_{max} =352 nm) forming reaction between PMS and iodide¹⁶. As shown in the Fig. S18, the CoNPCs exhibit much higher PMS adsorption capacity than that of CoPC. To rule out the influence of specific surface area, the PMS adsorption capacity normalized by specific surface area was calculated. After normalization, the PMS adsorption capacity of catalysts follows the order of CoNPC-7.78 > CoNPC-3.07 > CoNPC-1.72 > CoNPC-10.3 > CoPC. According to the Table 1, the total content of active N species (Co-N_x, graphitic N, pyridinic N and pyrrolic N) follows

the same order of CoNPC-7.78 > CoNPC-3.07 > CoNPC-1.72 > CoNPC-10.3 > CoPC. Hence, the results further confirm the N doping plays a crucial role in promoting the PMS adsorption.



Fig. S18 The PMS adsorption capacity and the normalized PMS adsorption capacity of Co-N-PCs.



Fig. S19 The electrochemical impedance spectra of CoPC-7.78, CoPC-3.07 and CoPC-1.72 (electrolyte is consisted of $0.01 \text{ M Na}_2\text{SO}_4$ and 1.6 mM PMS).



Fig. S20 The charge population of Co, N codoped carbon (a), Co doped carbon (b) and N doped carbon (c).

Table S7 The adsorption energy (E_{ads}) of PMS on Co, N codoped carbon, N doped carbon and Codoped carbon.

Model	Co, N codoped carbon	N doped carbon	Co doped carbon
E _{ads} (kJ/mol)	-144.2	-189.3	-122.1



Fig. S21 Schematic illustration of PMS activation process over (a) Co, N codoped carbon, (b) Co doped carbon and (c) N doped carbon. The light blue, dark blue, grey, red, and yellow spheres represent the Co, N, C, O and S atoms respectively.

models	state	lo-o (Å)	ls-o (Å)	Q (e)
HSO ₅ -		1.45	1.66	0
	IS	1.45	1.85	
(a)	TS	3.09	1.66	-0.70
	FS	2.65	1.54	
(b)	IS	1.44	1.89	
	TS	3.20	1.72	-0.60
	FS	2.85	1.63	
(c)	IS	1.43	2.38	
	TS	1.63	2.16	-0.22
	FS	2.49	1.94	

 Table S8 The variation of bond length of O-O (lo-o), bond length of S-O (ls-o) and charge change

of PMS in different models.

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