# Supporting Information

## Electron-deficient $Fe_3O_4$@AC-$NH_2$@Cu-MOF Nanoparticles for Enhanced Degradation of Electron-rich Benzene Derivatives via Synergistic Adsorption and Catalytic Oxidation

Qingpeng Cao[a†], Mengjia Huang[a†], Libin Qian[a], Jin Wang[a], Di Wang[a*], Xubin Zheng[a*]

[a] *Intelligent Perception Research Institute, Zhejiang Lab, Hangzhou, China*

*† Authors have contributed equally to this work.*

**Corresponding Auther at: Intelligent Perception Research Institute, Zhejiang Lab, Hangzhou, China ( Xubin Zheng and Di Wang).*
*E-mail address: zhengxb@zhejianglab.com (Xubin Zheng), diwang@zhejianglab.com (Di Wang).*

## Characterizations

All reagents and solvents were purchased from commercial sources and were used without further purification. Elemental analyses were carried out on a Perkin–Elmer 2400 automatic analyzer. FT–IR spectra data (4000–400 $cm^{-1}$) were collected by a Nicolet impact 410 FT–IR spectrometer. Scan electron microscope (SEM) images were recorded by Rili SU 8000HSD Series Hitachi New Generation Cold Field Emission SEM. The emission properties were recorded with Edinburgh FLS 920 fluorescence spectrometer equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube. An Edinburgh Xe900 450 W xenon arc lamp was used as an exciting light source. Thermal analysis was performed on a ZRY-2P thermogravimetric analysis from 30 to 700 °C with a heating rate of 10 $°C \cdot min^{-1}$ under a flow of air. Powder X-ray diffraction (PXRD) patterns were recorded in the 2θ range of 5 – 50° using Cu Kα radiation with a Shimadzu XRD-6000 X-ray diffractometer. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν = 1253.6 eV).

## Single-Crystal X-Ray Crystal Structure Determination

The X-ray diffraction data taken at room temperature for Cu-opa was collected on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0. 71073 Å). The structure of Cu-opa was solved by direct methods and refined on $F^2$ by the full-matrix least squares using the SHELXTL-97 crystallographic software. Anisotropic thermal parameters are refined to all of the non-hydrogen atoms. The hydrogen atoms were held in calculated ideal positions on carbon atoms and nitrogen atoms in ligands and that were directly included in the molecular formula on water molecules. The chemical formulas were determined by the combination of single crystal data, TGA results and elemental analysis. The CCDC 1974699 contains the crystallographic data Cu-opa of this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/ deposit. Crystal structure data and details of the data collection and the structure refinement are listed as Table S1, selected bond lengths and bond angles of Cu-opa are listed as Table S2.

**Table S1.** Crystal data and structure refinement parameters of Cu-opa

| Identification code | Cu-opa |
|---|---|
| Empirical formula | $C_{18}H_{13}CuN_2O_6$ |
| CCDC | 1974699 |
| Formula mass | 416.85 |
| Crystal system | Triclinic |
| Space group | *P* -1 |
| *a* (Å) | 8.7600(14) |
| *b* (Å) | 9.7857(15) |
| *c* (Å) | 10.6019(17) |
| *α* (˚) | 93.472(2) |
| *β* (˚) | 106.982(2) |
| *γ* (˚) | 107.340(2) |
| V (Å$^3$) | 818.8(2) |
| Z | 2 |
| $D_c$/(g cm$^{-3}$) | 1.691 |
| $\mu$ (Mo Kα)/mm$^{-1}$ | 1.375 |
| *F*(000) | 424 |
| $\theta$ range (°) | 2.58 – 25.00 |
| Limiting indices | $-10 \le h \le 10$ |
| | $-11 \le k \le 11$ |
| | $-11 \le l \le 12$ |
| Data/Restraints/Parameters | 2870 / 0 / 244 |
| GOF on $F^2$ | 1.070 |
| $R_1$[a] | 0.0307 |
| $wR_2$[b] | 0.1143 |
| $R_1$ | 0.0331 |
| $wR_2$ | 0.1178 |

[a] $R_1 = \sum||F_o| - |F_c||/ \sum|F_o|$;

[b] $wR_2 = [\sum[ w (F_o^2 - F_c^2)^2] / \sum[ w (F_o^2)^2]]^{1/2}$.

**Table S2.** Selected bond lengths (Å) and bond angles (°) for Cu-opa

| Cu-opa | | | |
|---|---|---|---|
| Cu(1)-O(6) | 1.9450(19) | Cu(1)-N(2) | 2.007(2) |
| Cu(1)-O(2) | 1.9851(16) | Cu(1)-O(5)#2 | 2.1755(17) |
| Cu(1)-O(4)#1 | 1.9912(16) | | |
| | | | |
| O(6)-Cu(1)-O(2) | 96.91(8) | O(4)#1-Cu(1)-N(2) | 87.34(7) |
| O(6)-Cu(1)-O(4)# | 188.43(7) | O(6)-Cu(1)-O(5)#2 | 96.37(8) |
| O(2)-Cu(1)-O(4)#1 | 143.00(8) | O(2)-Cu(1)-O(5)#2 | 102.93(8) |
| O(6)-Cu(1)-N(2) | 174.58(7) | O(4)#1-Cu(1)-O(5)#2 | 112.85(7) |
| O(2)-Cu(1)-N(2) | 84.47(8) | N(2)-Cu(1)-O(5)#2 | 88.41(8) |

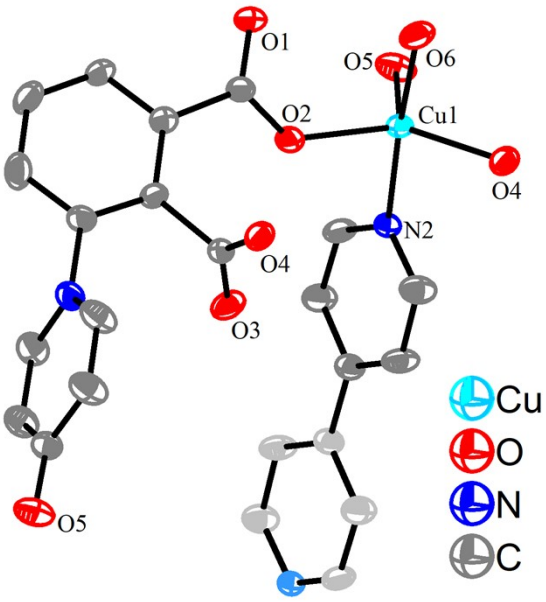


**Fig. S1** The structural unit of Cu-opa with labeling scheme and 50% thermal ellipsoids (hydrogen atoms are omitted for clarity)

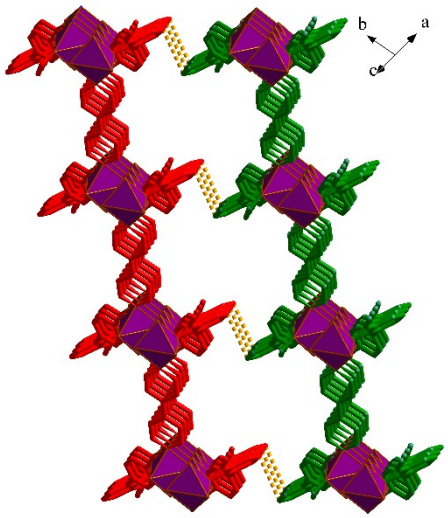


**Fig. S2** The π···π stacking ($d_{\pi\cdots\pi}$ = 3.6971 Å) to form 3D framework of compound Cu-opa.

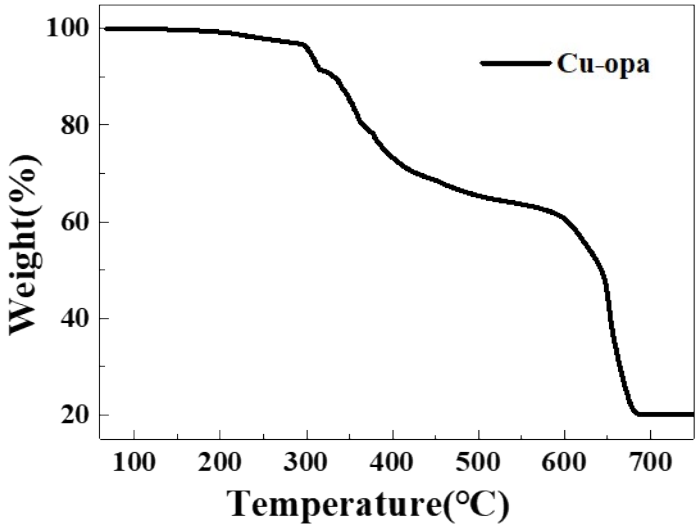


**Fig. S3** Thermal gravimetric curves of Cu-opa

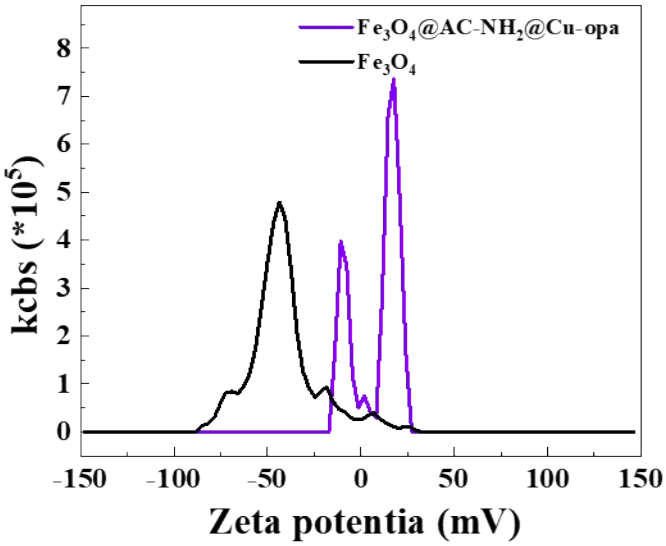


**Fig. S4** Zeta potential analysis for $Fe_3O_4$ and $Fe_3O_4$@AC-$NH_2$@Cu-opa.

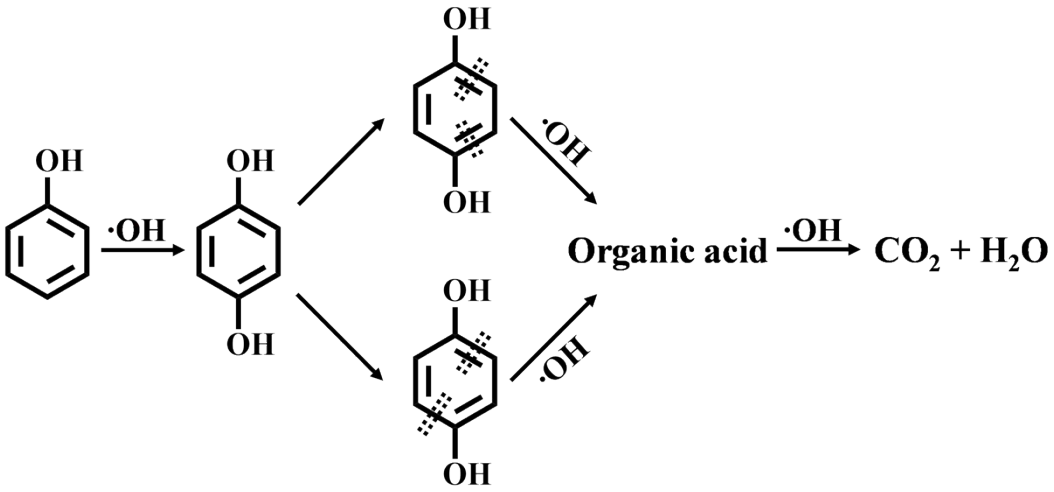


**Fig. S5** Possible pathway for phenol mineralization.

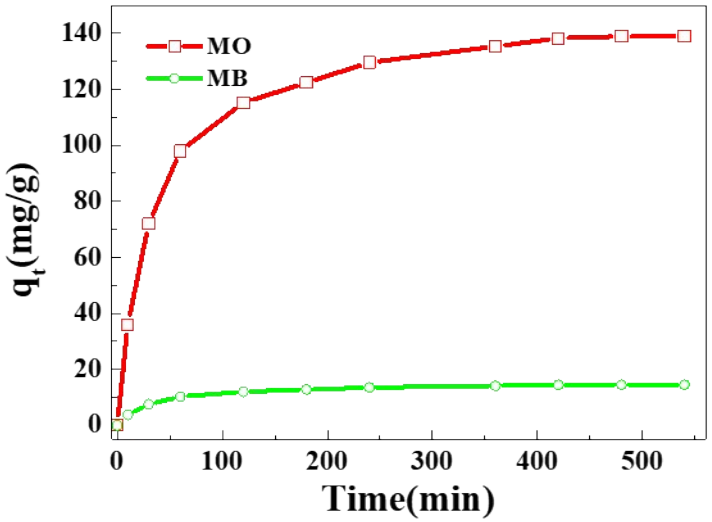


**Fig. S6**. Kinetic study of **Cu-opa** toward MO and MB.

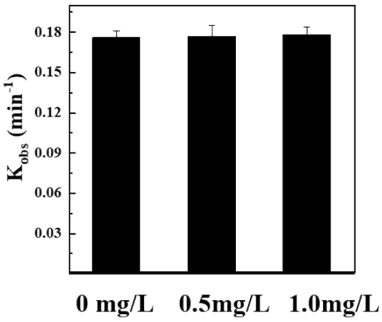


**Fig. S7.** The impact of leaching Fe on phenol degradation.

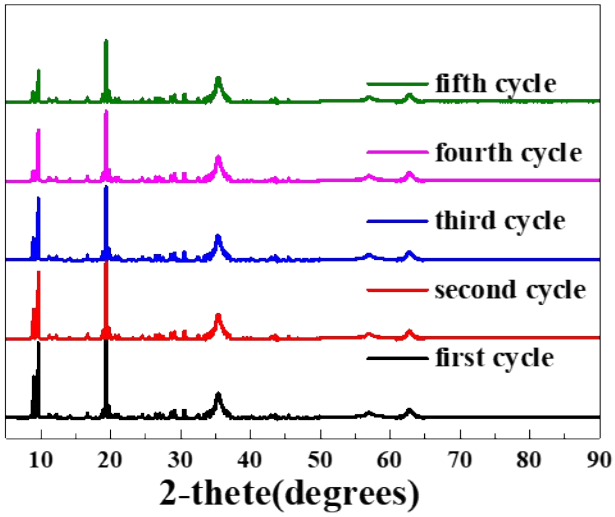


**Fig. S8** PXRD patterns of fresh $Fe_3O_4$@AC-$NH_2$@Cu-opa after five cycle.

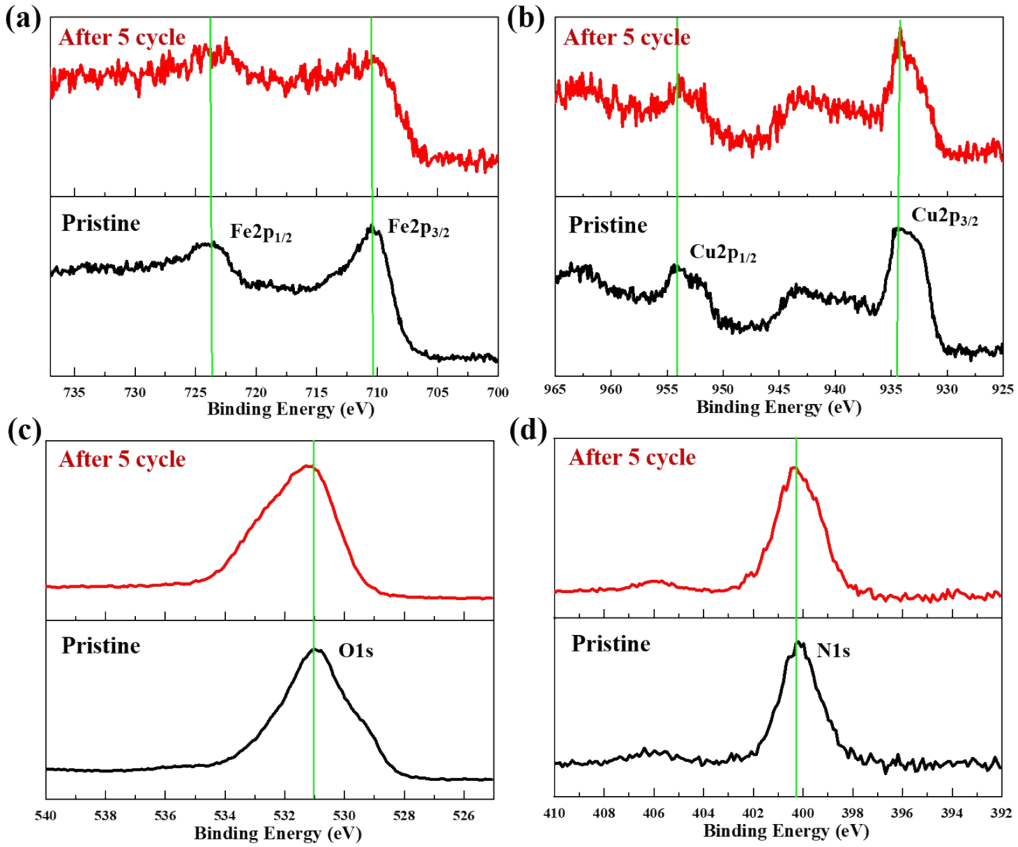


**Fig. S9** (a) XPS Fe 2p spectra after recycle; (b) XPS Cu 2p spectra after recycle; (c) XPS O 1s spectra after recycle; (d) XPS N 1s spectra after recycle.

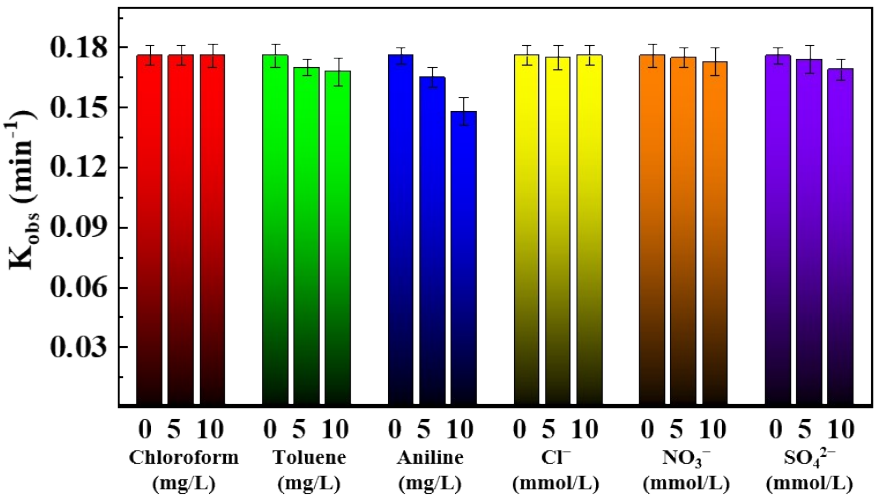


**Fig. S10** The impact of organics and anions in terms of the catalytic degradation of phenol by $Fe_3O_4$@AC-$NH_2$@Cu-opa.

**Table S3.** The summary of relevant article.

| Catalyst | Process | Operating Conditions | Wastewater source | Removal (%) | Reference |
|---|---|---|---|---|---|
| Co-SAM-SCS | Catalytic | Catalyst loading = 0.7 g/L; SMZ concentration = 50 mg/L; $H_2O_2$ dosage = 4%; Temperature = 25 °C | River water | 95% (180min) | Water Research, 2018,138:7-18 |
| 20%ZnO–AgBr/SBA-15 | Catalytic | Catalyst dosage 0.4 g/L, Phenol red concentration of 20 mg/L, pH = 5 | Hong River; Hoan Kiem Lake; West Lake | 94.7%, 69.6%, 89.8% (150min) | RSC Adv., 2023,13, 12402-12410 |
| magnetic CFA | Catalytic | Catalyst dose: 2 g/L, T: 20 °C, initial pH: 5.0, $[H_2O_2]_0$: 22 mM | Tap water | 90% (60min) | Chemical Engineering Journal, 2019, 369: 470–479 |
| δ-FeOOH/γ-$Al_2O_3$ | Catalytic | Conditions: 10 g δ-FeOOH/γ-$Al_2O_3$, 40 mM $H_2O_2$, 100 mL real industrial wastewater, pH = 4, t = 25 °C, pump speed 50 rpm. | Industrial wastewater | 50.8% (240min) | Journal of Environmental Chemical Engineering, 2021,9(6):106796 |
| Cu–NiO | Catalytic | Catalyst (50 mg) | Leather industries real effluents | 86.15% (150 min) | Materials Chemistry and Physics,2020,242:122520 |
| tyrosinase-MNPs | Catalytic | Catalyst dosage 15mg, Phenol concentration of 250 mg/L, pH = 7.0 | Well water | 90% (60min) 100% (240min) | 3 Biotech, 2018, 8: 419 |
| NC-700 | Catalytic and adsorption | [MB]0 = 50 mg/L, catalyst = 0.3 g/L, PMS = 0.4 g/L and temperature = 25 °C | Ultrapure water | 100% (10min) | Science of the Total Environment, 2019, 680: 51–60 |
| $Fe_3O_4$@GO@MIL-100(Fe) | Catalytic and adsorption | $Fe_3O_4$@GO@ MIL-100(Fe): 0.2 g/L, $H_2O_2$: 3 mmol/L, 2,4-DCP: 50 mg/L, pH = 3.0; Vis 500 W | Ultrapure water | 100% (20min) | Journal of Hazardous Materials, 2019, 371: 677–686 |
| $Fe_3O_4$@AC-$NH_2$@Cu-opa | Catalytic and adsorption | ([$Fe_3O_4$@AC-$NH_2$@Cu-opa] = 0.5 g/L, $[H_2O_2]$ = 40 mmol/L, [phenol] = 100 mg/L, pH = 4 | Tap water; Ultrapure water | 97.2% (60min) 99.4% (～30min) | This work |