

New Sustainable Utilization Approach of Livestock Manure: Conversion to Dual-Reaction-Center Fenton-like Catalyst for Water Purification

Yingtao Sun¹, Chun Hu¹, Lai Lyu^{1,2*}

¹ Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Institute of Environmental Research at Greater Bay, Guangzhou University, Guangzhou 510006, China.

² Institute of Rural Revitalization, Guangzhou University, Guangzhou 510006, China.

E-mail: **Lai Lyu**: lyulai@gzhu.edu.cn.

Supplementary Experimental Section

Chemicals and Reagents. H_2O_2 (30% w/w) was purchased from General Reagent Co., China. bisphenol A (BPA), 2-chlorophenol (2-CP), ciprofloxacin (CIP) and diphenhydramine (DP) were purchased from Aladdin Co., China. Peroxidase from horseradish (POD) was purchased from Sigma Ltd. *tert* Butyl Alcohol (TBA), *p*-benzoquinone (PBQ), furfuryl alcohol (FFA), N, N-diethyl-*p*-phenylenediamine sulfate (DPD), Cupric nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), 2,2,6,6-Tetramethyl-4-Piperidinol (TEMP) and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (37% w/w) were purchased from Adamas Reagent Co., Ltd. 5-*tert*-butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO) was purchased from Dojindo Molecular Technologies Inc., Japan. All of the other chemicals were of analytical grade. All water involved in the experiment was deionized water purified by EPED (Water Purifier Co., China).

HPLC Measurements. All of the pollutants were analyzed using a 1200 series HPLC (Agilent, U.S.A.) equipped with a UV detector and a ZORBAX Eclipse XDB- C_{18} column (4.6×150 mm, 5 μm). The mobile phase consisted of a 70/30 v/v mixture of methanol/water or 60/40 v/v mixture of acetonitrile/water at a flow rate of 1 mL min^{-1} .

HPLC-MS Analysis. High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS) analysis was conducted in auto full-scan mode (MS). A mixture of (A) water (0.25% formic acid) /(B) methanol was used as mobile phase. The column temperature was set at 40 °C. Mobile phase procedure followed a gradient elution: 20% B were kept for first 1 min, and then increase to 98% B in 10 min. The flow rate was set at 0.3 mL min^{-1} , and 10 μL of the sample was injected. Mass spectral analysis was conducted in positive mode over a mass range of 50~500 m/z . The cone voltage was 20 V and desolvation temperature was 350 °C.

3D-EEM fluorescence measurements. In general, 0.01 g of the catalyst powder was first mixed with 50 mL of the actual wastewater (35 °C) in an appropriate volume glass beaker. The suspension was stirred for approximately 15 min and then added H₂O₂ (10 mM) triggering Fenton reaction. At certain intervals, 3 mL reaction suspension was collected with a syringe and filtered with a filter (0.45 µm) for follow-up analysis.

Three-dimension excitation emission matrix (3D-EEM) fluorescence spectra of various samples were obtained on an F-7000 spectrometer (HITACHI) with a xenon excitation source, and slits were set to 5 nm for both excitation and emission. The excitation wavelengths were incremented from 200 to 450 nm in 5-nm steps; for each excitation wavelength, the emission was detected from 300 to 550 nm in 5-nm steps.

ATR-FTIR. The attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was tested with a TENSOR FTIR spectrophotometer (Bruker Scientific Inc.) with a single ATR accessory. To prepare an ATR sample, 0.2g L⁻¹ catalyst was added to a 10ppm BPA aqueous solution. The suspension was stirred at room temperature for approximately 30 min to establish adsorption/desorption equilibrium between the pollutant and the catalyst. Then the suspension was collected followed by filtration, the solid particles were collected and dried at approximately 50 °C to form the powder samples.

The FTIR spectra of these powder samples and fresh samples supported on KBr pellets at a fixed sample amount (1 wt%) were recorded on a Nicolet 8700 FTIR spectrophotometer (Thermo Fisher Scientific Inc., USA).

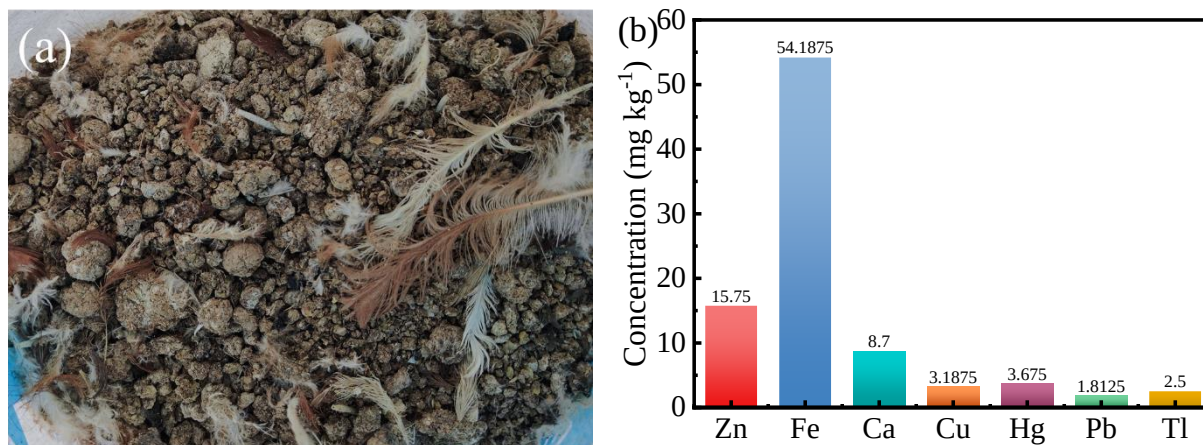
***in situ* Raman and EPR measurements.** *in situ* Raman spectra for various catalyst were tested with an HR Evolution Raman spectrophotometer (HORIBA Scientific Inc.). The catalyst was placed directly into the reaction cell and scanned from 200 to 2000 cm⁻¹ at a resolution of 1 cm⁻¹ for 60 s with 40 mW 532 nm laser light irradiation.

For the EPR spectra measurement, BMPO/TEMP-trapped EPR signals were detected in different air-saturated methanol/aqueous dispersions of the corresponding samples using a Bruker A300-10/12 EPR

spectrometer at room temperature (25°–30°). The center field is 3500 G, sweep width is 100 G, modulation frequency is 100 kHz. To detect $\cdot\text{OH}$, 0.01 g of the prepared powder sample was added to 500 μL of water. Then, 100 μL of the above suspension, 20 μL of BMPO (250 mM) and 50 μL of H_2O_2 (30%, w/w) were mixed thoroughly and then left to stand for 1 min before being drawn into a capillary for detection. To detect $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$, the steps were the same as above except that water was replaced with methanol. To detect $^1\text{O}_2$, the steps were the same as that of detecting $\cdot\text{OH}$ except that BMPO was replaced with TEMP.

Radical Quenching Experiment. Radical quenching experiment was conducted during the BPA degradation experiment. TBA, PBQ and FFA were used to quenching $\cdot\text{OH}$, $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$ and $^1\text{O}_2$ respectively. 0.01 g catalyst and 50 mL BPA solution (10.0 mg L^{-1}) containing 1mM quenching agent (TBA, PBQ and FFA) were mixed in a glass beaker and mechanically stirred for 15 min until the adsorption-desorption equilibrium had achieved. Then the Fenton-like reaction was started with the adding of 50 μL H_2O_2 (30% w/w) under continuous stirring throughout the experiment. At given time intervals, 1 mL suspensions were collected and filtered by a hydrophobic membrane (pore size 0.22 μm) immediately for detection. The concentration of BPA in the samples were measured by a high-performance liquid chromatography (HPLC, 1200 series; Agilent) with a chromatographic column (4.6 $\times$ 150 mm, 5 μm ; Agilent) and an UV-DAD (wavelength 225 nm).

Supplementary Figures and tables

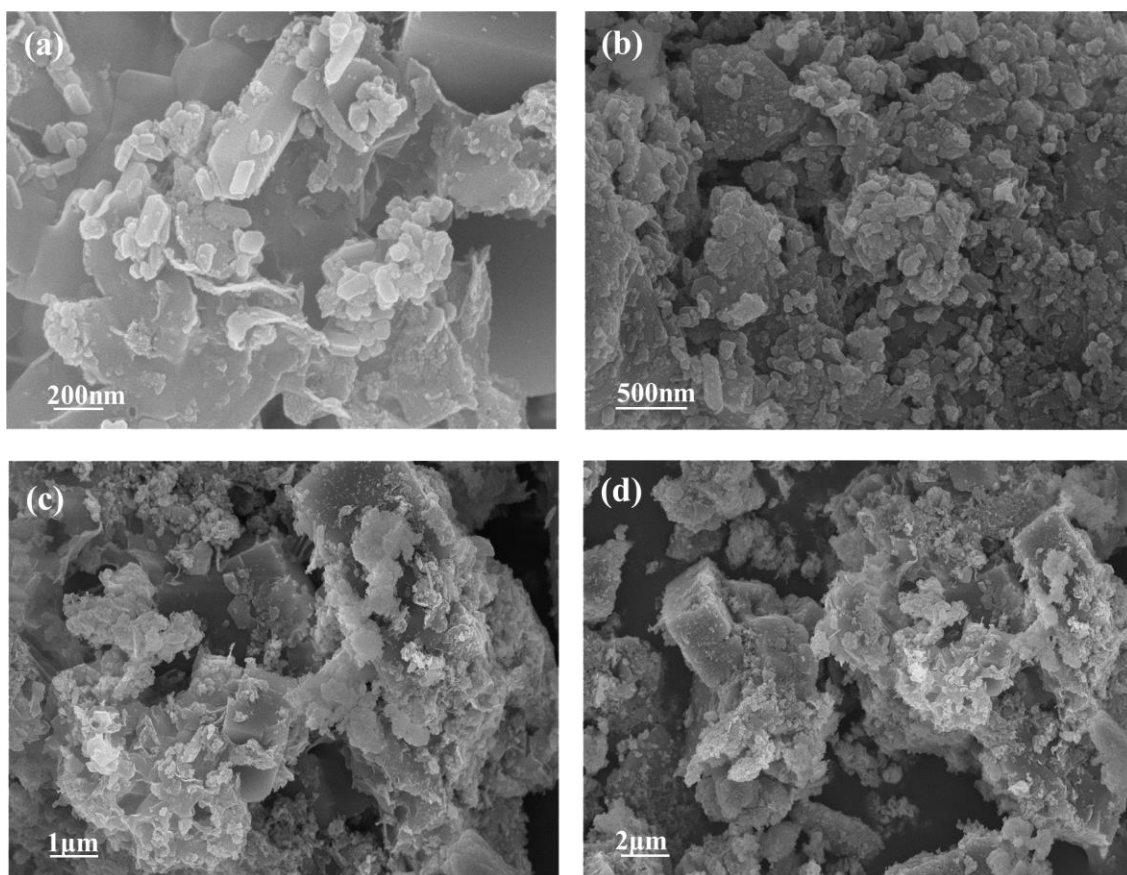


Supplementary Figure. 1. The initial parameters of chicken manure. (a) The morphology and (b) the elemental (metal elements) content of chicken manure.

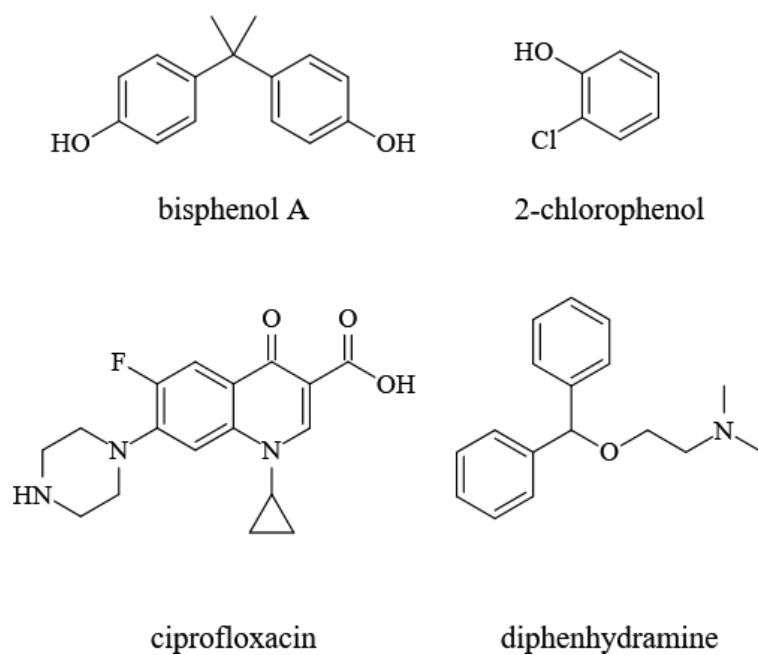
Supplementary Table 1. Chinese standard for limits of heavy metal elements in fertilizers (GB 38400-2019).

Name	Total Cd	Total Hg	Total As	Total Pb	Total Cr	Total Tl
Organic fertilizer	$\leq 3 \text{ mg kg}^{-1}$	$\leq 2 \text{ mg kg}^{-1}$	$\leq 15 \text{ mg kg}^{-1}$	$\leq 50 \text{ mg kg}^{-1}$	$\leq 150 \text{ mg kg}^{-1}$	$\leq 2.5 \text{ mg kg}^{-1}$

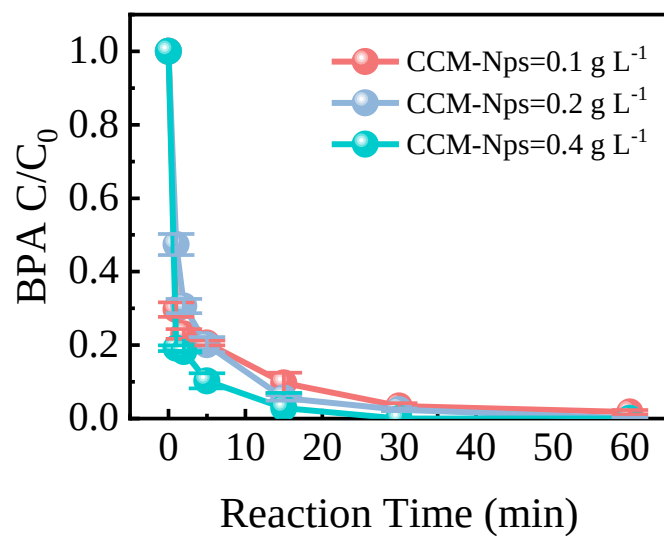
The content of heavy metals in chicken manure is higher than the standard limit based on the results of the detection (**Supplementary Figure. 1**). So, it is necessary to deal with chicken manure by new methods.



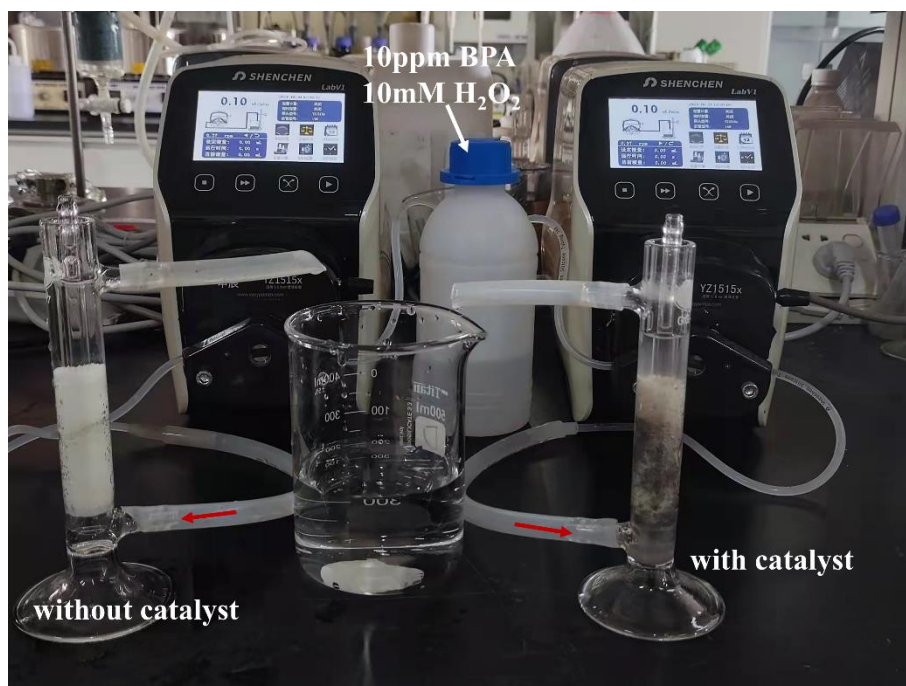
Supplementary Figure. 2. SEM images at different scales of CCM-Nps. (a) 200 nm, (b) 500 nm, (c) 1 μm and (d) 2 μm scales SEM images of CCM-Nps.



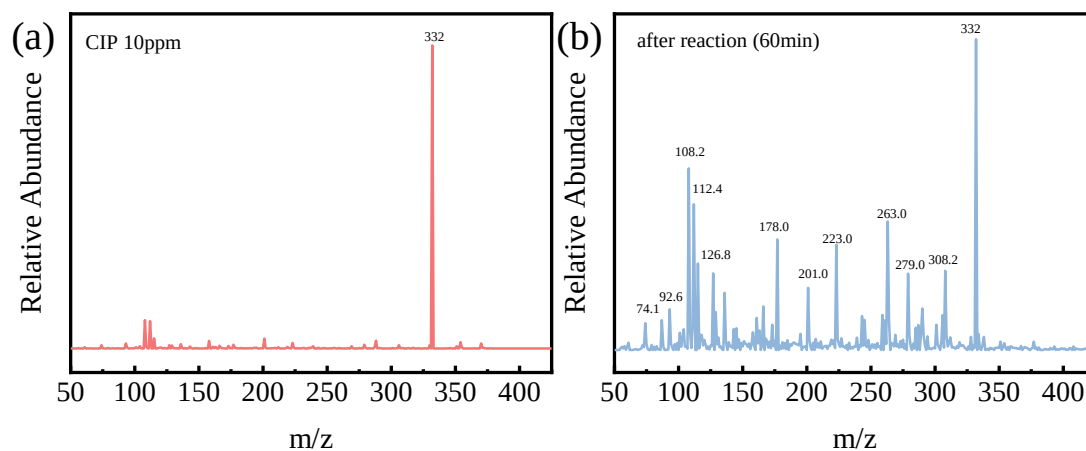
Supplementary Figure. 3. Structures of pollutant used in the activity evaluation. Including bisphenol A (BPA), 2-chlorophenol (2-CP), ciprofloxacin (CIP) and diphenhydramine (DP).



Supplementary Figure. 4. Effect of different catalyst concentrations on the reaction. Reaction conditions: [natural pH] ~ 7 , [initial pollutant] = 10 mg L⁻¹, [initial H₂O₂] = 10 mM. Two-time parallel experiments were conducted to calculate error bars.



Supplementary Figure. 5. Fixed bed reactor. Reaction conditions: [natural pH] ~ 7 , [temperature] $\sim 25\text{ }^{\circ}\text{C}$, [catalyst] = 0.5 g, [hydraulic retention time] = 50 min.



Supplementary Figure. 6. Analysis of by-products of CIP degradation in the CCM-Nps/H₂O₂ system at different times by LC-MS. (a) Characteristic peaks of the initial CIP solution. (b) Characteristic peaks of the solution after 60 min treatment by CCM-Nps/H₂O₂ system.

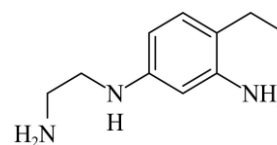
Supplementary Table 2. Constituents of actual wastewater before and after treatment.

Parameter	Raw kitchen wastewater	After treatment (30min)
pH	6.73	6.98
COD (mg L ⁻¹)	729.2	401.2
Cl ⁻ (mg L ⁻¹)	321.7	293.3
NO ₃ ⁻ (mg L ⁻¹)	134.2	147.5
SO ₄ ²⁻ (mg L ⁻¹)	90.5	99.2

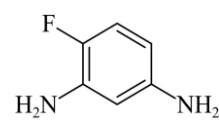
Supplementary Table 3. The main by-products detected in CCM-Nps/H₂O₂ system, which including exact mass (m/z), molecular formula and the chemical structure derived from molecular weight fragment mass spectra.

Exact mass (m/z)	Molecular formula	Chemical structure
331.9	C ₁₇ H ₁₈ FN ₃ O ₃	
308.2	C ₁₅ H ₁₈ FN ₃ O ₃	
279.0	C ₁₃ H ₁₁ FN ₂ O ₄	
263.0	C ₁₃ H ₁₁ FN ₂ O ₃	
223.0	C ₁₂ H ₁₅ FN ₂ O	
201.0	C ₈ H ₁₂ FN ₃ O ₂	

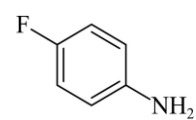
178.0

 $C_{10}H_{17}N_3$ 

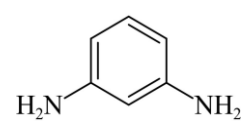
126.8

 $C_6H_7FN_2$ 

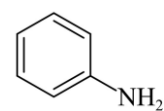
112.4

 C_6H_6FN 

108.2

 $C_6H_8N_2$ 

92.6

 C_6H_7N 

Supplementary Table 4. Comparison of catalytic performance of different Fenton-like catalysts.

Author	Time	Catalyst	Reaction conditions	Removal rate (30min)
Lai L ¹	2015	γ -Cu-Al ₂ O ₃	c(H ₂ O ₂) = 10 mM, c(BPA) ~ 20 ppm, c(Cat)= 1 g L ⁻¹	~ 65%
Lingfei L ²	2019	Cu-BN	c(H ₂ O ₂) = 5 mM, c(BPA) = 25 ppm, c(Cat)= 1 g L ⁻¹	~ 100%
Wenrui C ³	2019	RSC-CNOP	c(H ₂ O ₂) = 10 mM, c(BPA) = 10 ppm, c(Cat)= 0.2 g L ⁻¹	~ 75%
Lai L ⁴	2019	Cu-MP	c(H ₂ O ₂) = 10 mM, c(BPA) = 10 ppm, c(Cat)= 1 g L ⁻¹	~ 90%
Yumeng W ⁵	2020	d-g-C ₃ N ₄ -Fe	c(H ₂ O ₂) = 10 mM, c(BPA) = 10 ppm, c(Cat)= 1 g L ⁻¹	~ 60%
Sihui Z ⁶	2020	OV-CoZnO MPs	c(H ₂ O ₂) = 10 mM, c(BPA) = 10 ppm, c(Cat)= 1 g L ⁻¹	~ 90%
Xuejian Z ⁷	2020	mp-RSCo-SiO ₂ NSs	c(H ₂ O ₂) = 15 mM, c(BPA) = 10 ppm, c(Cat)= 1 g L ⁻¹	~ 90%
Rong-Rong D ⁸	2021	HS-CuFe ₂ O ₄ · _o	c(H ₂ O ₂) = 40 mM, c(CIP) = 10 ppm, c(Cat)= 0.5 g L ⁻¹	~100%
Yingtao S	-	CCM-Nps	c(H ₂ O ₂) = 10 mM, c(BPA) = 10 ppm, c(Cat)= 0.2 g L ⁻¹	~ 100%

Various new Fenton-like catalysts have been developed in recent years. The catalytic performance of Fenton-like catalysts has been continuously improved, the pollutant removal efficiency could reach 65%~100% within 30 min. In addition, the dosage of catalyst was kept between 0.2 g L⁻¹ and 1g L⁻¹, the amount of H₂O₂ was kept between 5 mM and 40 mM. CCM-Nps is a Fenton-like catalyst converted from CM resulting in a significantly lower synthesis cost compared to conventional catalysts. Notably, during the degradation of pollutants, the dosage of catalyst and H₂O₂ were only 0.2 g L⁻¹ and 10 mM, respectively, and the removal rate of pollutant could reach 100% within 30min.

SUPPLEMENTARY REFERENCES

1. Lyu L, *et al.* Enhanced Fenton Catalytic Efficiency of γ -Cu–Al₂O₃ by σ -Cu²⁺–Ligand Complexes from Aromatic Pollutant Degradation. *Environ. Sci. Technol.* **49**, 8639-8647 (2015).
2. Li L, *et al.* Framework Cu-doped boron nitride nanobelts with enhanced internal electric field for effective Fenton-like removal of organic pollutants. *J. Mater. Chem. A* **7**, 6946-6956 (2019).
3. Cao W, *et al.* Efficient Fenton-like Process Induced by Fortified Electron-Rich O Microcenter on the Reduction State Cu-Doped CNO Polymer. *ACS Appl. Mater. Interfaces* **11**, 16496-16505 (2019).
4. Lyu L, *et al.* Efficient Fenton-like process for organic pollutant degradation on Cu-doped mesoporous polyimide nanocomposites. *Environ. Sci. Nano* **6**, 798-808 (2019).
5. Wang Y, *et al.* Enhanced Fenton-like efficiency by the synergistic effect of oxygen vacancies and organics adsorption on Fe_xO_y-d-g-C₃N₄ with Fe–N complexation. *J. Hazard. Mater.* **408**, 124818 (2021).
6. Zhan S, *et al.* Efficient Fenton-like Process for Pollutant Removal in Electron-Rich/Poor Reaction Sites Induced by Surface Oxygen Vacancy over Cobalt–Zinc Oxides. *Environ. Sci. Technol.* **54**, 8333-8343 (2020).
7. Zhang X, *et al.* Mesoporous reduction state cobalt species-doped silica nanospheres: An efficient Fenton-like catalyst for dual-pathway degradation of organic pollutants. *J. Colloid Interface Sci.* **576**, 59-67 (2020).
8. Ding R-R, *et al.* Oxygen vacancy on hollow sphere CuFe₂O₄ as an efficient Fenton-like catalysis for organic pollutant degradation over a wide pH range. *Appl. Catal. B* **291**, 120069 (2021).