

Electronic Supplementary Material

Enhanced activation of persulfate using mesoporous silica spheres augmented Cu-Al bimetallic oxide particles for bisphenol A degradation

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Chemicals

The chemicals, including $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, urea ($\text{CH}_4\text{N}_2\text{O}$), tetraethoxysilane (TEOS, $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}_4$), polyvinyl pyrrolidone (PVP, $(\text{C}_6\text{H}_9\text{NO})_n$) were supplied by Sinopharm Chemical Reagent Co., Ltd. Potassium peroxydisulfate (PDS, $\text{K}_2\text{S}_2\text{O}_8$), sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH) were supplied by Tianjin BASF Chemical Co. Ltd. BPA was provided by Aladdin Industrial Corporation, China.

Characterization methods

The point of zero charge (PZC) was measured throughout the pH range from 3 to 12, according to the previous work [1].

All the electrochemical measurements were conducted at room temperature in a standard three-electrode electrochemical cell with a $\text{Hg}/\text{Hg}_2\text{Cl}_2$ (4 M KCl) reference electrode, a platinum wire counter electrode, and a catalyst-modified glassy carbon working electrode (0.196 cm^2 , Pine Research Instrumentation, USA), and the electrolyte was a mixture of 100 mM Na_2SO_4 and 100 mM PDS. Homogeneous catalyst ink was first prepared by sonication of 30 mg catalyst powder, 10 mg conductive carbon (Super P, Alfa Aesar), 0.2 mL Nafion solution (5 wt%, Sigma-Aldrich), and 2 mL absolute ethanol. Then, 5 μL of the as-prepared catalyst ink was pipetted onto the surface of the glassy carbon electrode. The catalyst layer was dried in ambient air before use. All the electrochemical data were collected on a CHI 760D electrochemical workstation (Shanghai Chenhua Instrument Co., China). Electrochemical impedance spectra (EIS) were recorded within a frequency range from 10^5 to 10^{-1} Hz using an AC voltage at a 5 mV

amplitude. Linear sweep voltammetry (LSV) was measured as the potential from -1.0~1.0 V (vs. Hg/Hg₂Cl₂) with a scanning rate of 50 mV/s. Chronoamperometries were carried out at the bias of 0.0 V (vs. Hg/Hg₂Cl₂) with 100 mM Na₂SO₄ as supporting electrolyte.

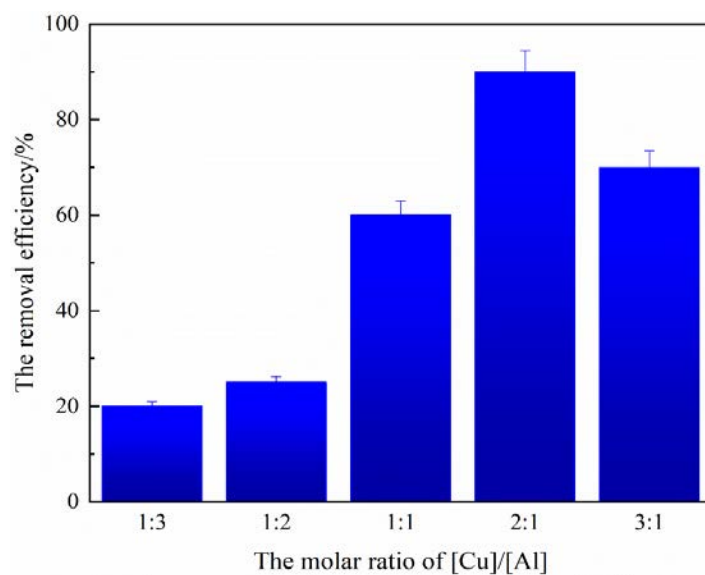


Fig. S1 The removal performances under different molar ratio of [Cu]/[Al].

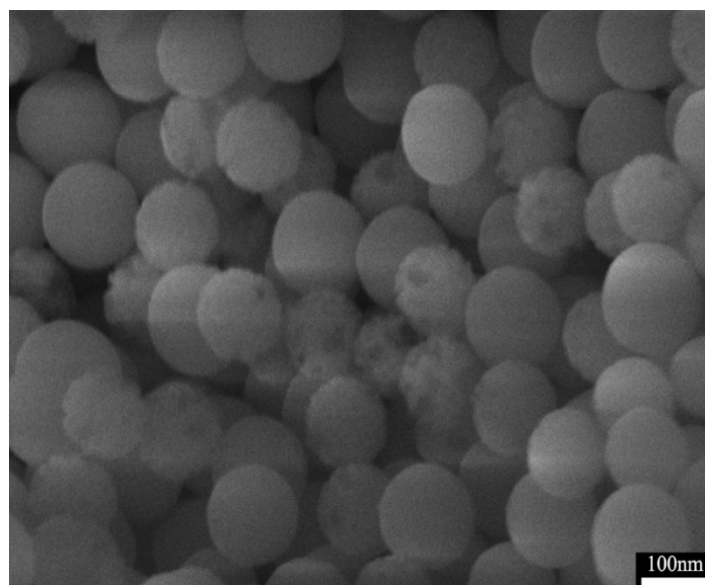


Fig. S2 Micrograph image of MSSs.

Table S1 Comparison the kinetics constant of various CuO-based Fenton-like processes.

Catalyst	pH range	Catalyst amount/g•L ⁻¹	BPA concentration	oxidizing agent	Time/min	The maximum k/min ⁻¹	Reference
Commercial CuO	7.2	0.1	5 mg/L	0.5 mM PMS	60	0.003	[2]
CuO/BC	7	0.4	0.1 mM	1 mM PDS	180	0.06	[3]
CuO/ γ -Al ₂ O ₃	4.5-6.5	2	20 ppm	2 g/L PDS	60	0.089	[4]
CuO/ <i>h</i> -BN	4-5	2	5 mg/L	0.5 g/L PDS	60	0.165	[5]
CuO/g-C ₃ N ₄	3-7	0.5	40 mg/L	13 mM PDS	30	0.19	[6]
CuO-Al ₂ O ₃	5-7	0.75	10 mg/L	12.5 mM H ₂ O ₂	90	0.027	Our previous work [7]
Cu-Al/MSSs	3-9	0.5	50 mg/L	100 mM PDS	30	0.21	This work

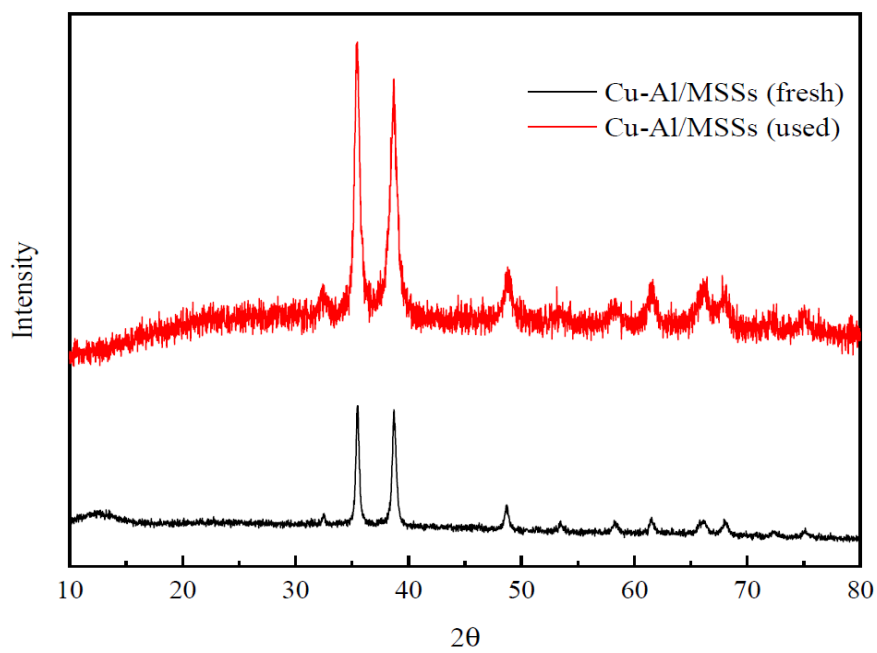


Fig. S3 XRD patterns of the fresh and fifth-used Cu-Al/MSSs.

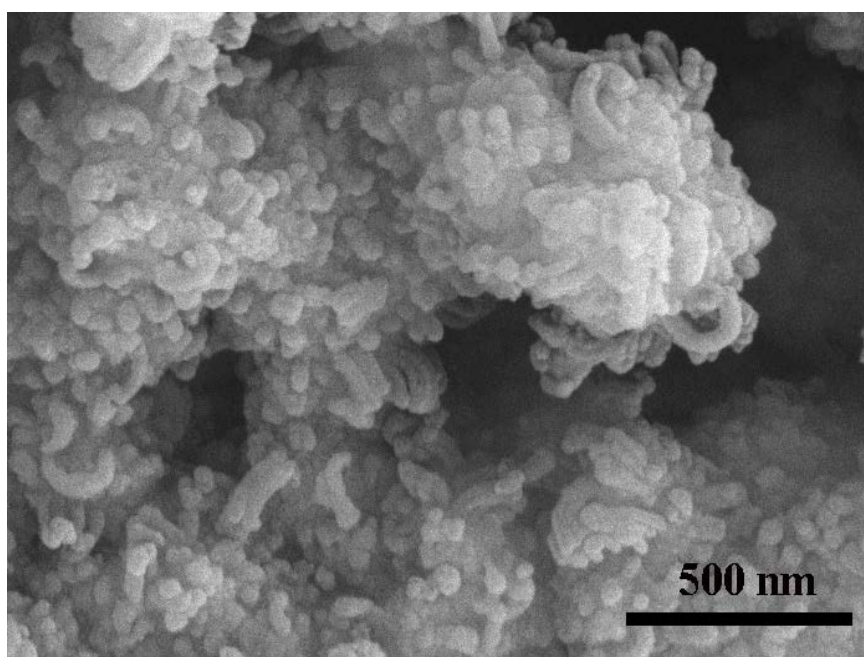


Fig. S4 Micrograph image for the fifth-used Cu-Al/MSSs.

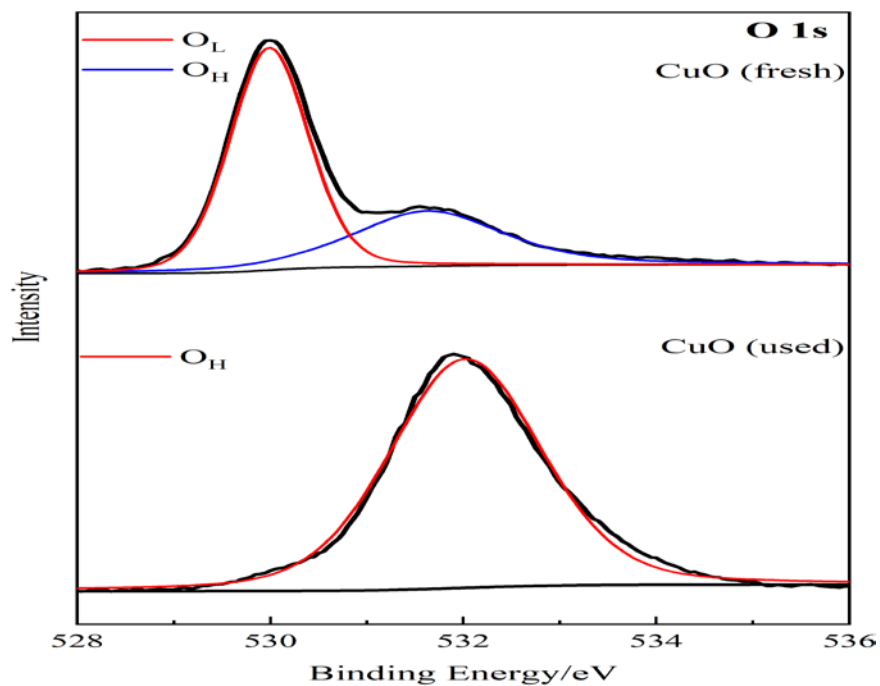


Fig. S5 O 1s for the fresh and fifth-used CuO.

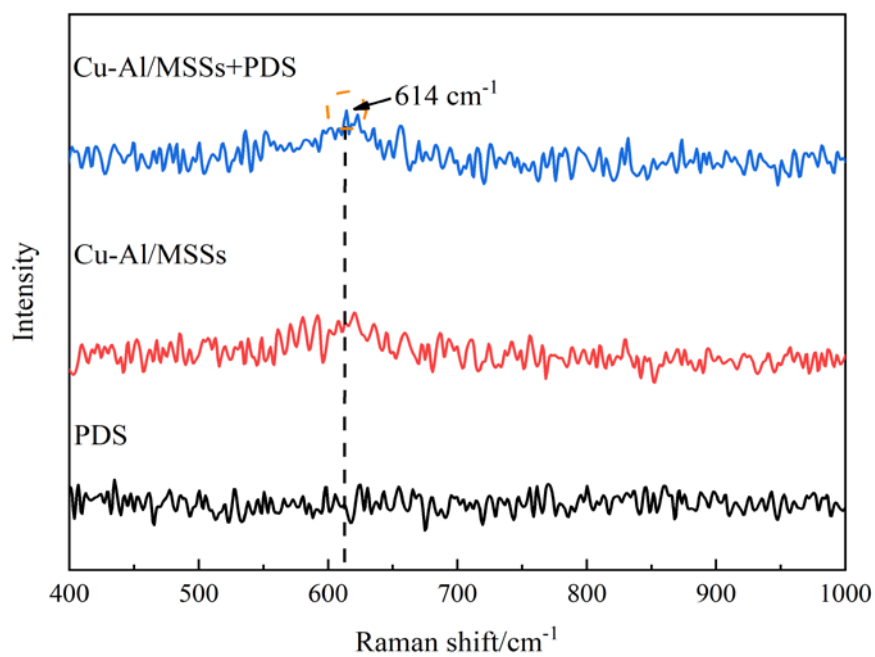


Fig. S6 Raman spectra of PDS, Cu-Al/MSSs, and Cu-Al/MSSs+PDS.

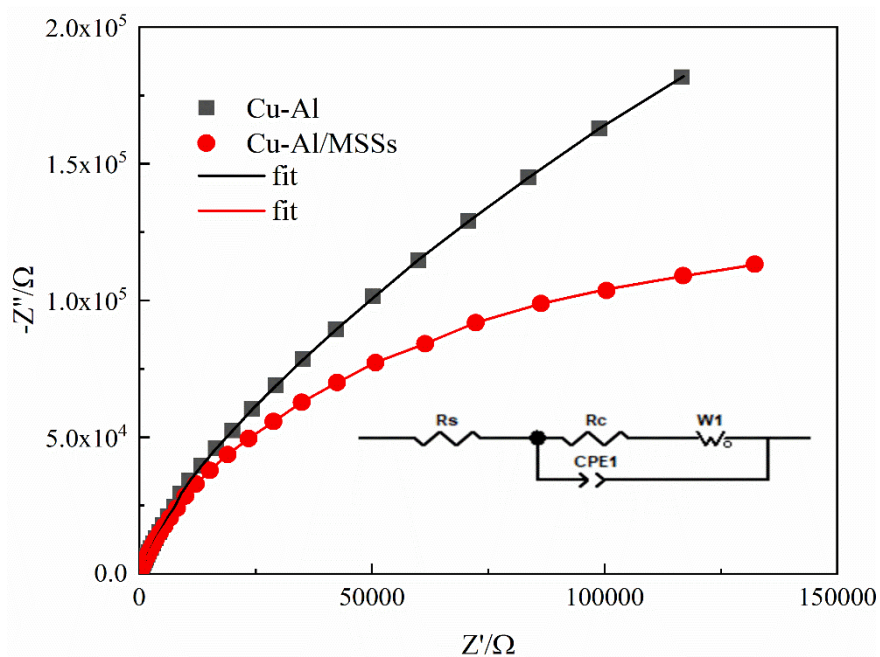


Fig. S7 EIS Nyquist plots of the Cu-Al, and Cu-Al/MSS.

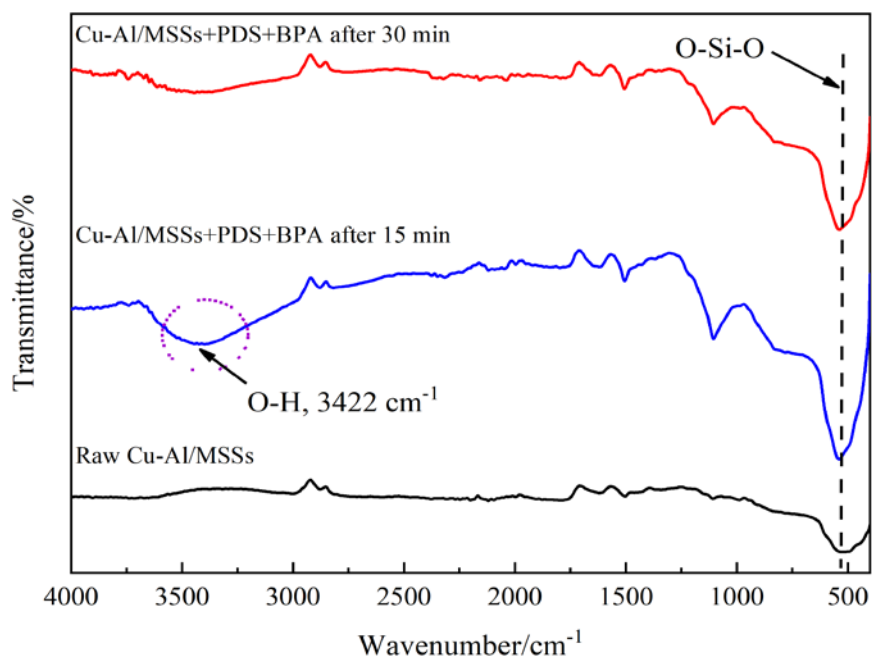


Fig. S8 FTIR spectra of Cu-Al/MSSs before and after BPA removal.

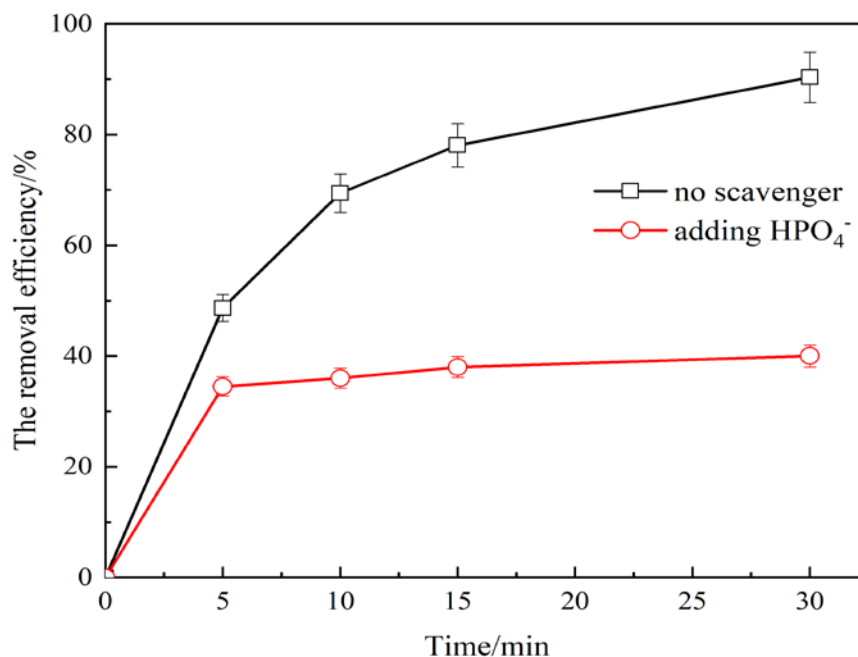


Fig. S9 The removal performance with addition of HPO₄⁻.

Reference

1. Liu Y, Tan N, Wang B, Liu Y. Stepwise adsorption-oxidation removal of oxytetracycline by Zn⁰-CNTs-Fe₃O₄ from aqueous solution. *Chemical Engineering Journal*, 2019, 375: 121963
2. Wang S X, Gao S S, Tian J Y, Wang Q, Wang T Y, Hao X J, Cui F Y. A stable and easily prepared copper oxide catalyst for degradation of organic pollutants by peroxymonosulfate activation. *Journal of Hazardous Materials*, 2020, 387: 121995
3. Luo H Y, Lin Q T, Zhang X F, Huang Z F, Fu H Y, Xiao R B, Liu S S. Determining the key factors of nonradical pathway in activation of persulfate by metal-biochar nanocomposites for bisphenol A degradation. *Chemical Engineering Journal*, 2020, 391: 123555
4. Wang J, Li B, Li Y, Fan X, Zhang F, Zhang G, Zhu Y, Peng W. Easily regenerated CuO/ γ -Al₂O₃ for persulfate-based catalytic oxidation: insights into the deactivation and regeneration mechanism. *ACS Applied Materials & Interfaces*, 2021, 13: 2630-2641
5. Oh W D, Wong Z, Chen X, Lin K Y A, Veksha A, Lisak G, Chao H, Lim T T. Enhanced activation of peroxydisulfate by CuO decorated on hexagonal boron nitride for bisphenol A removal. *Chemical Engineering Journal*, 2020, 393: 124714
6. Song H, Guan Z, Xia D, Xu H, Yang F, Li D, Li X. Copper-oxygen synergistic electronic reconstruction on g-C₃N₄ for efficient non-radical catalysis for peroxydisulfate and peroxymonosulfate. *Separation and Purification Technology*, 2021, 257: 117957

7. Sun L, Jiang H, Zhao Y X, Wan J, Li L L, Wang L Y, Zhang Y. Facile synthesis of copper-based bimetallic oxides for efficient removal of bisphenol a via Fenton-like degradation. *Separation and Purification Technology*, 2022, 205: 112529