

Promoted Peroxymonosulfate Activation by Electron Transport Channel Construction for Rapid Cu(II)/Cu(I) Redox Couple Circulation

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Text S1 Catalysts characterization

The morphologies of prepared catalysts were observed on Field emission scanning electron microscopy (FESEM, Nova NanoSEM 450) equipped with an energy dispersive X-ray system and high resolution transmission electron microscopy (HRTEM, FEI, TF20/2100F). N₂ adsorption-desorption isotherms and pore size distribution were obtained using an Autosorb-iQ analyzer (QuantaChrome, USA). Structure information of materials were researched on D-8 Advance X-ray diffractometer (XRD, Bruker-AXS, Germany) with a 40-kV voltage and a 40-mA current. Related functional groups was measured by Bruker Tensor37 (Bruker-AXS, Germany) of fourier transfer infrared (FTIR) instrument. The functional groups and related oxidation states on the catalysts surface were investigated on X-ray photoelectron spectroscopy (XPS, ThermoFisher ESCALAB 250Xi, USA). The XPS calibration was based on whether the obtained binding energy of C 1s for each sample compared to its standard binding energy at 284.6 eV is within ± 0.5 eV. The redox behavior of Cu-O-CN was measured by H₂-TPR tests, reduced by 5% H₂/Ar gas mixture from 100 to 800 °C at a heating rate of 10 °C/min. Solid electron spin resonance (ESR) was conducted for related structural defective information.

Text S2 Analytical methods

The concentrations of contaminants in the filtered solution were determined by ultraperformance liquid chromatography (UPLC, with detective limit of 50 $\mu\text{g}\cdot\text{L}^{-1}$) coupled with an UV-vis

photodiode array detector and an ACQUITY UPC² BEH C18 column: 100 × 3.0 mm, 1.7- μ m particle size. The ultrapure water and acetonitrile were used as mobile phases for BPA detection with the ratio of 38: 62 in the wavelength of 227 nm at a flow rate of 0.25 mL·min⁻¹. The injection volume was 10 μ L. The column temperature was maintained at 40°C.

The total organic carbon (TOC) was measured by a Shimadzu TOC-VCPH Analyzer. The leached Cu ions in the reaction system were detected on a Agilent 720 (Agilent, USA) ICP-OES.

Text S3 Electrochemical measurements

Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements of the Cu-O-CN reaction system were operated in 1 M Na₂SO₄ solution in the presence of 0.2 mM PMS, using three-electrode electrochemical cell equipped with a catalyst coating glass carbon as working electrode and a graphite carbon rod as counter electrode.

Text S4 Reactive oxygen species measurements

Electron spin resonance (ESR) spectra measurements were performed to directly detect the reactive oxygen species (ROS) in Cu-O-CN/PMS reaction system using 5, 5-Dimethyl-1-pyrrolidine-N-oxide (DMPO) and 4-Amino-2,2,6,6-tetramethylpiperidine (TEMP) as spin-trapping agents. In a typical procedure, 1 mg of the prepared powder was added to 1 mL of the ultrapure water. Then, 100 μ L of the above suspension, 10 μ L of DMPO or TEMP and 3 μ L of

PMS (100 mM) were consecutively mixed and held for 5 min. After that, the ESR spectra were recorded on a Miniscope MS-5000 ESR spectrometer at room temperature. The detailed parameters of ESR instrument are as follows. Magnetic field: 332-342 mT, Sweep time: 60 s, Modulation: 0.05 mT, Modulation frequency: 100 kHz, Microwave power: 10 mW.

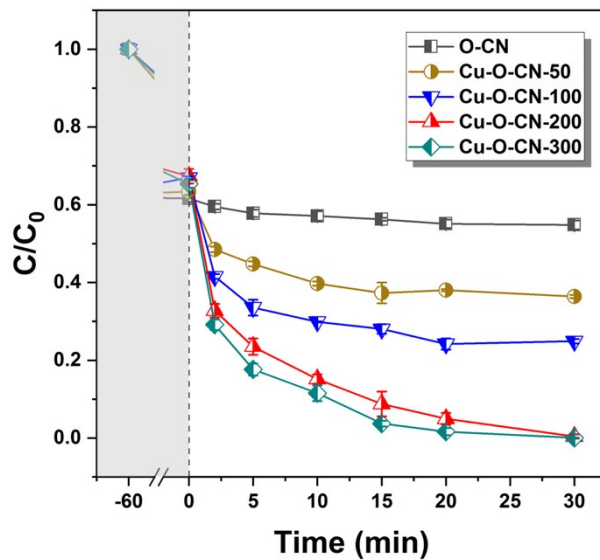


Figure S1. Catalytic performance of Cu-O-CN with different Cu content. Condition: $[BPA]_0=10$ mg/L, $[PMS]=0.2$ mmol/L, $[catalyst]=0.1$ g/L, $pH_0=6.0-6.5$.

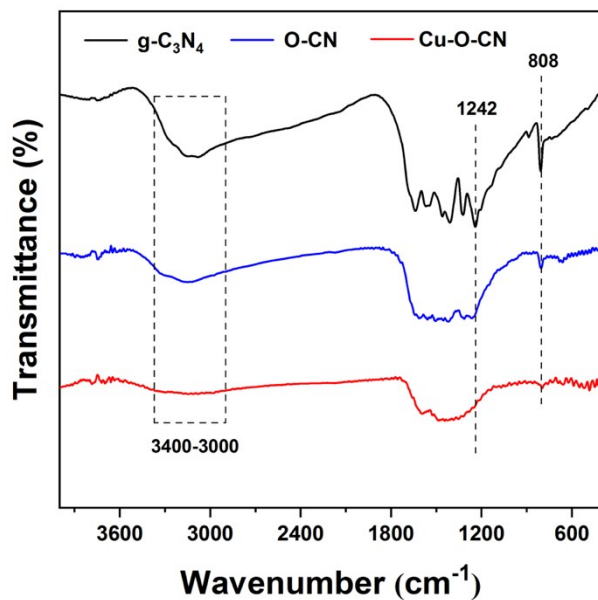


Figure S2. FTIR spectra of $g-C_3N_4$, O-CN and Cu-O-CN.

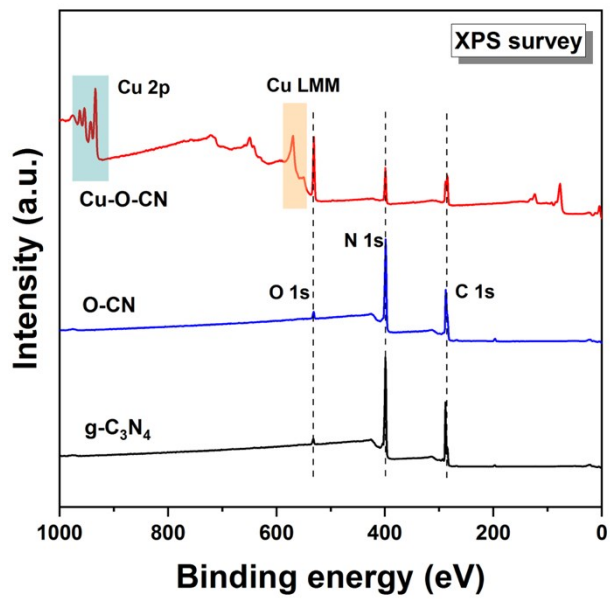


Figure S3. Comparative XPS surveys of g-C₃N₄, O-CN and Cu-O-CN.

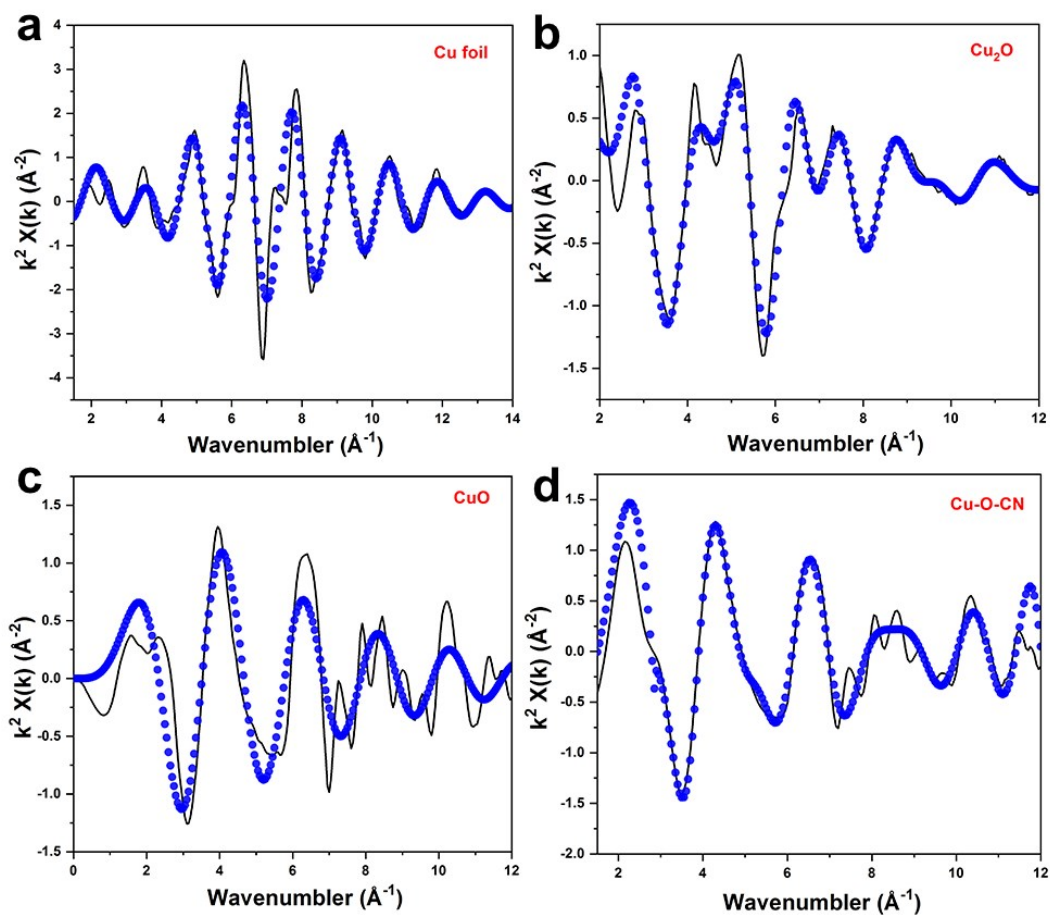


Figure S4. The zoomed fitting spectra of Cu-O-CN in K space in contrast to Cu foil, Cu₂O, and CuO.

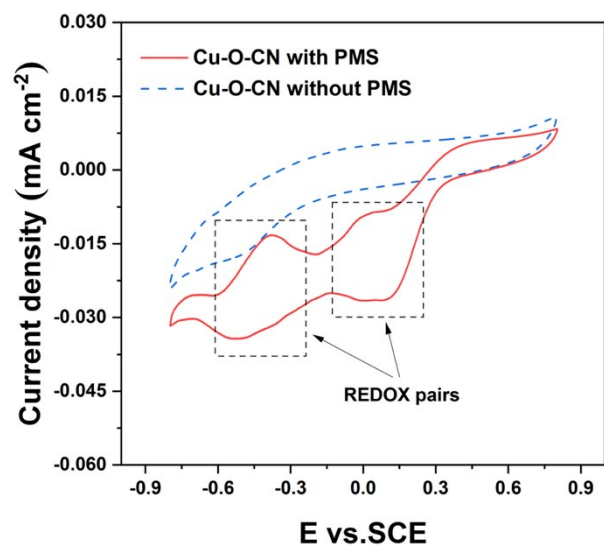


Figure S5. Cyclic voltammogram (CV) of Cu-O-CN with and without PMS addition.

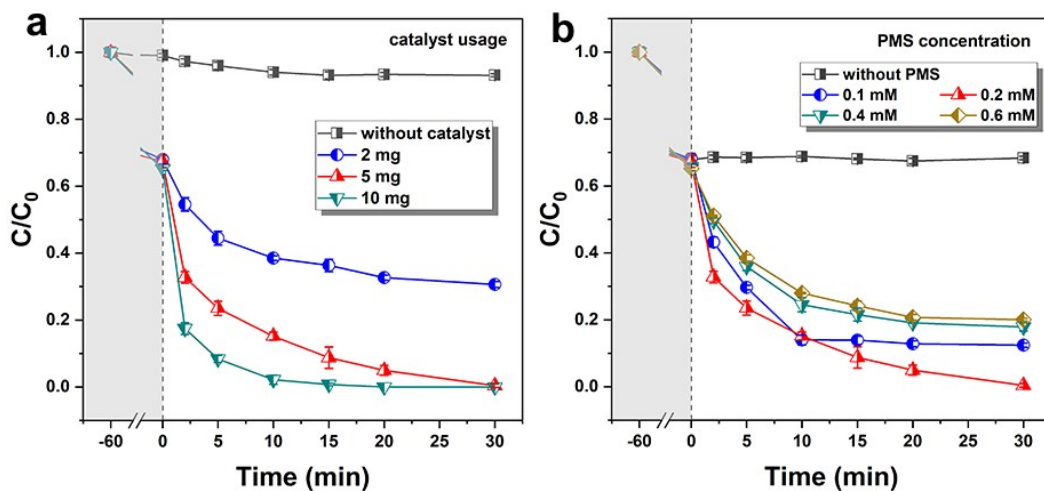


Figure S6. Effects of (a) catalyst usage and (b) PMS concentration for BPA degradation in Cu-O-CN/PMS reaction system. Condition: $[BPA]_0=10$ mg/L, $pH_0=6.0-6.5$.

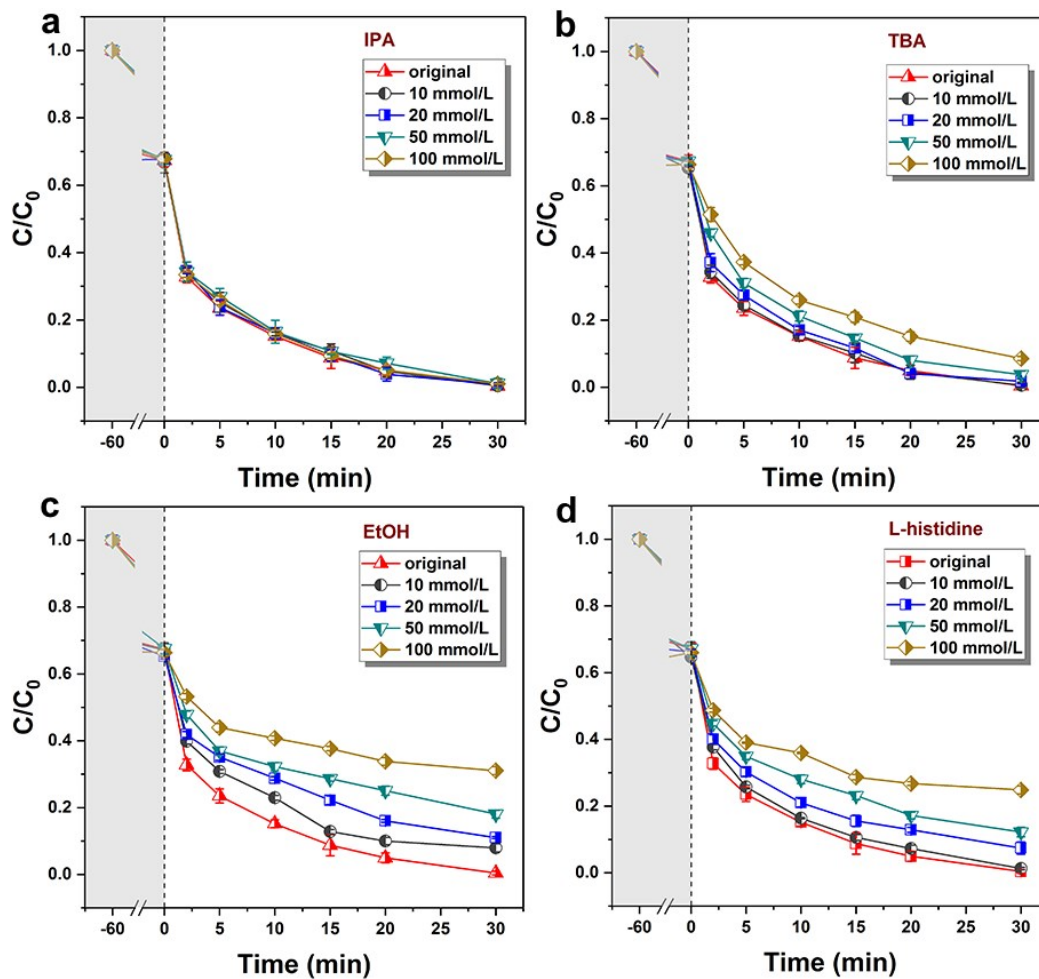


Figure S7. Quenching tests of (a) IPA, (b) TBA, (c) EtOH and (d) L-histidine with various concentrations (0, 10, 20, 50 and 100 mmol/L). Condition: $[BPA]_0=10$ mg/L, $[PMS]=0.2$ mmol/L, $[catalyst]=0.1$ g/L, $pH_0=6.0-6.5$.

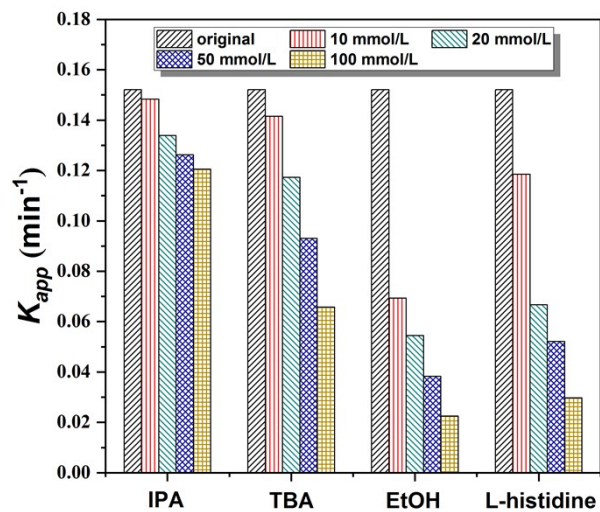


Figure S8. Calculated reaction rate constants (K_{app}) with various scavengers concentrations.

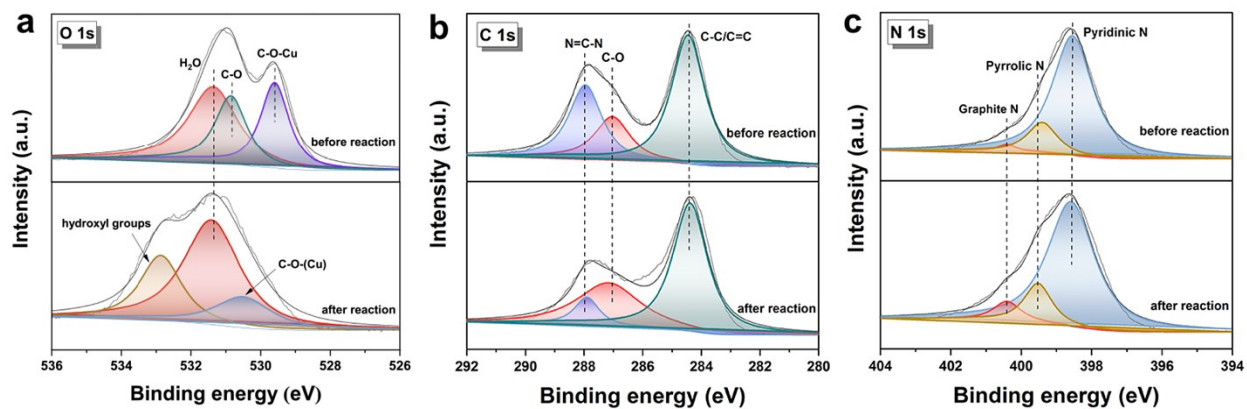


Figure S9. Comparative individual XPS spectra of (a) O 1s, (b) C 1s and (c) N 1s in Cu-O-CN sample before and after reaction.

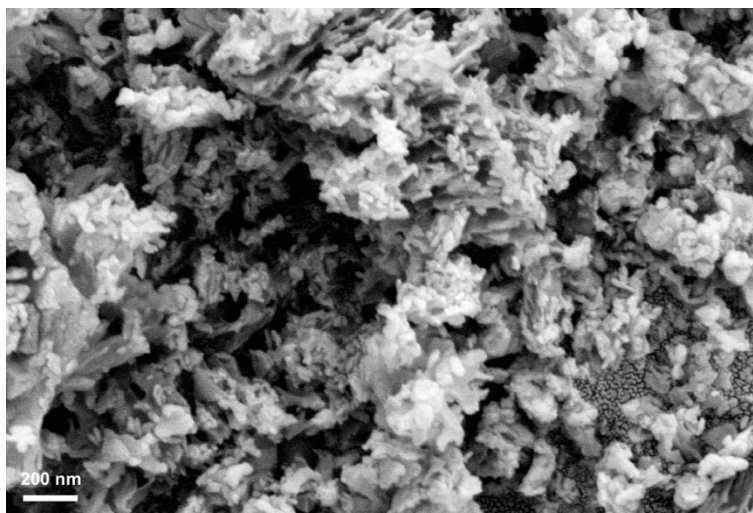


Figure S10. SEM image of Cu-O-CN after reaction.

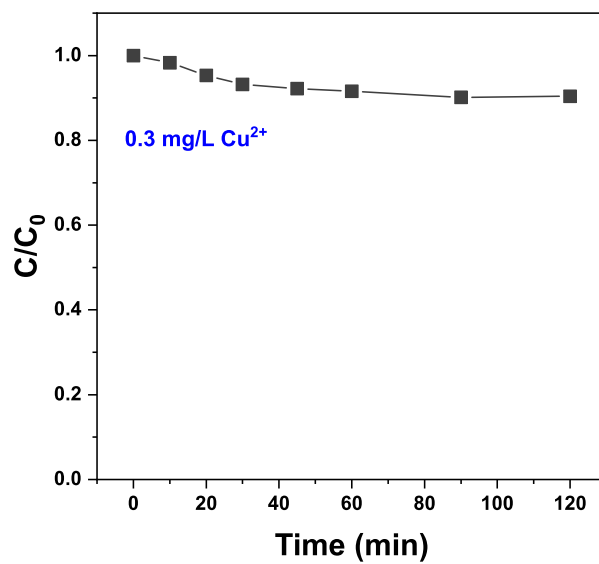


Figure S11. The effect of homogeneous catalysis for BPA degradation by PMS activation.

Conditions: $[BPA]_0=10$ mg/L, $[PMS] = 0.2$ mmol/L, $[Cu^{2+}]=0.3$ mg/L.

Table S1. ICP-OES results after each cycle experiment in Cu-O-CN/PMS reaction system.

Cycle number	Leaching Cu ions (mg/L)
1	0.25
2	0.17
3	0.10
4	0.14
5	0.05