Electronic Supplementary Material (ESI) for Environmental Science: Nano.


**Supplementary Material**

# Enhanced purification efficiency of pharmaceutical wastewater through pollutant-mediated $H_2O_2$ activation pathway over CuZnS nano-aggregated particles

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**Supplementary Experimental Section**

**Chemicals and Reagents.** $H_2O_2$ (30% w/w) was purchased from General Reagent Co., China. phenytoin (PHT), ciprofloxacin (CIP) and sulfamethoxazole (SMZ) were purchased from Aladdin Co., China. Peroxidase from horseradish (POD) was purchased from Sigma Ltd. N, N-diethyl-p-phenylenediamine sulfate (DPD), Copper chloride ($CuCl_2 \cdot 6H_2O$), Polyvinyl alcohol (PVA) Zinc acetate ($Zn(CH_3COO)_2$), Sodium sulfide ($Na_2S \cdot 9H_2O$) and 2,2,6,6-Tetramethyl-4-Piperidinol (TEMP) 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).

**Material Characterization.** The surface morphology and elemental composition information for the catalysts were detected by a field emission scanning electron microscope (FE-SEM) (JSM-6700F, JEOL Co., Japan) equipped with an energy dispersive X-ray (EDX) detector system. The X-ray powder diffraction (XRD) patterns of the catalysts were recorded on a Philips X'Pert PRO SUPER diffractometer. Surface chemical information for the samples was collected via the X-ray photoelectron spectroscopy (XPS) (VG Multilab 2000, Thermo Electron Co., America) using

monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. Solid EPR spectra were obtained using a Bruker model A300-10/12 electron paramagnetic resonance spectrometer.

**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 $min^{-1}$.

**GC-MS analysis.** The samples for GC-MS analysis were prepared using the following procedure. The suspension at a reaction time of 60 min and 120 min was filtered, and the solution was collected and evaporated using a freeze-drying method. Then, the residue was dissolved in 2 mL of dichloromethane. After the solvent was dehydrated by anhydrous sodium sulfate, trimethylsilylation was carried out at 60 °C for 30 min using 0.2 mL of BSTFA (N, O-bis (trimethylsilyl) trifluoroacetamide). The precipitate was separated by filtration before chromatographic analysis via GC-MS (Shimadzu, GCMS-QP2020NX). The GC oven temperature program was as follows: 60 °C held for 2 min followed by a linear temperature gradient of 6 °C min-1 to 280 °C, which was held for 5 min.

**Electrochemical impedance.** Electrochemical impedance was measured on an electrochemical workstation (Shanghai Chenhua Instrument Co., L TD.) equipped with standard three electrodes. The working electrode was prepared from the sample material coated on conductive glass, the reference electrode was extremely saturated calomel, a platinum electrode was used as the pair electrode, and the electrolyte was 0.1 mol/L $Na_2SO_4$ solution or 10 mg/L PHT prepared with 0.1 mol/L $Na_2SO_4$.

**3D-EEM fluorescence measurements.** In general, 0.02 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 $H_2O_2$ (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.

**EPR measurements.** 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°C–30°C). To detect $^{\bullet}OH$, 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 $HO_2^{\bullet}/O_2^{\bullet-}$, the steps were the same as above except that water was replaced with methanol. To detect $^1O_2$, the steps were the same as that of detecting $^{\bullet}OH$ except that BMPO was replaced with TEMP.

## Supplementary Figures

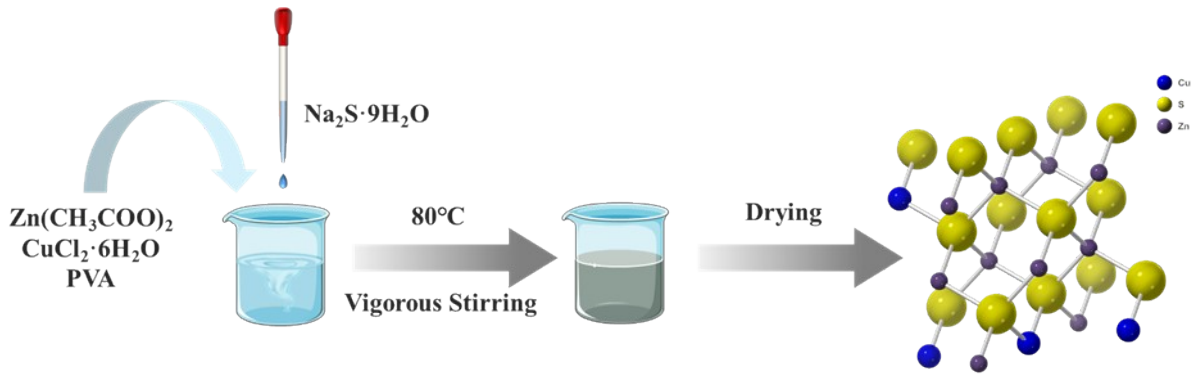



**Fig. S1.** Schematic illustration of the synthesis process of CuZnS-Naps.

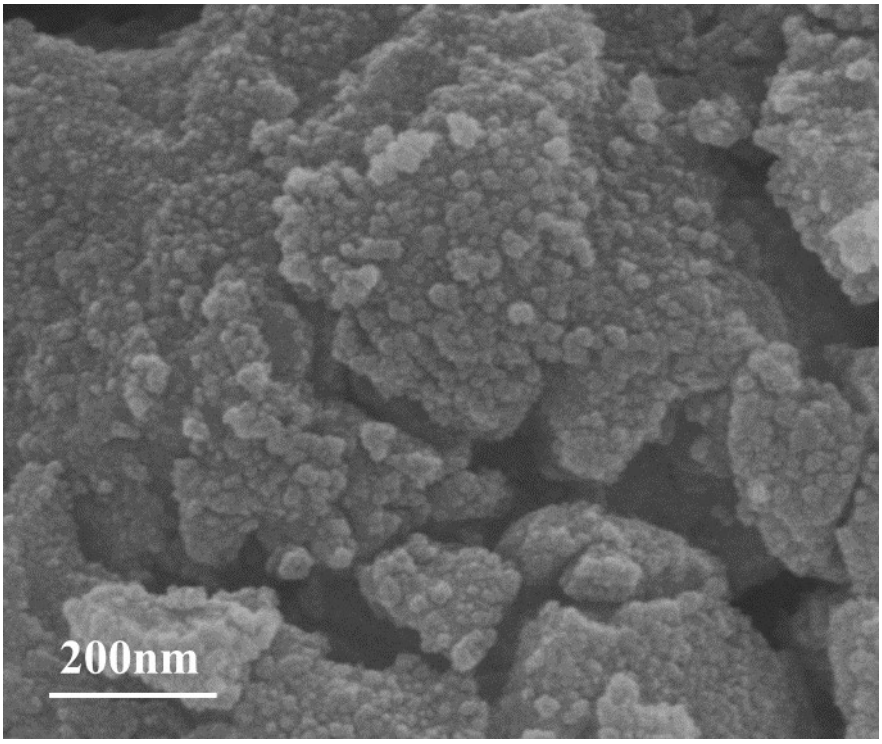



**Fig. S2.** SEM images of CuZnS-Naps.

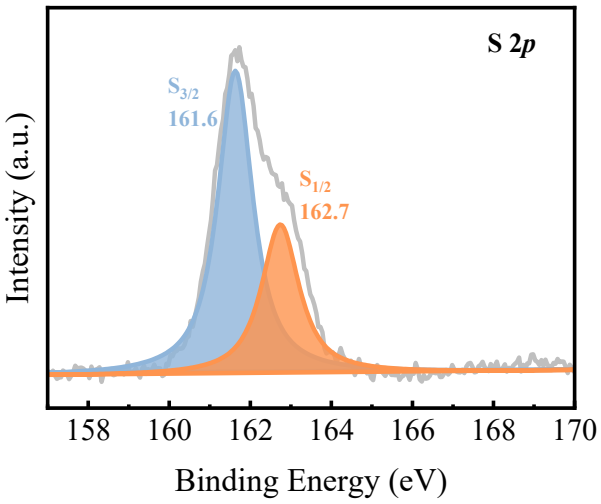



**Fig. S3.** S 2*p* XPS spectra for CuZnS-Naps and ZnS-Naps.

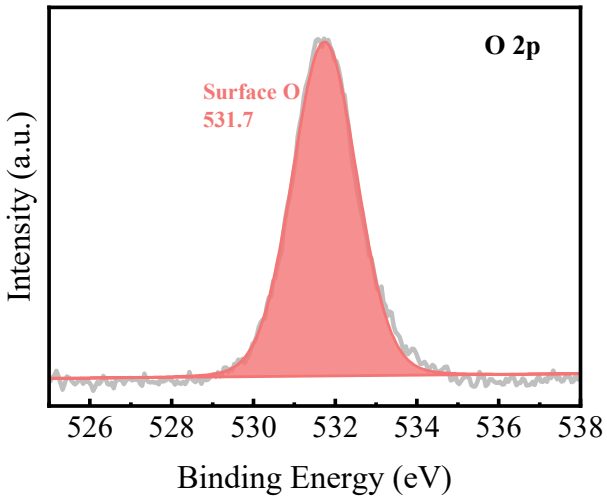
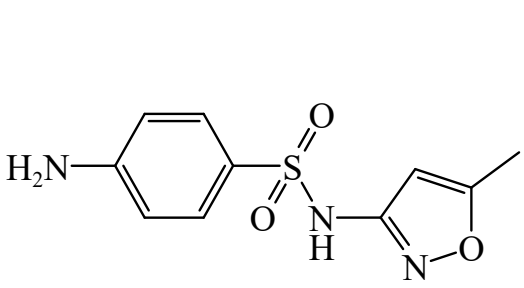
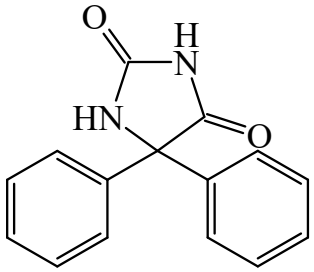


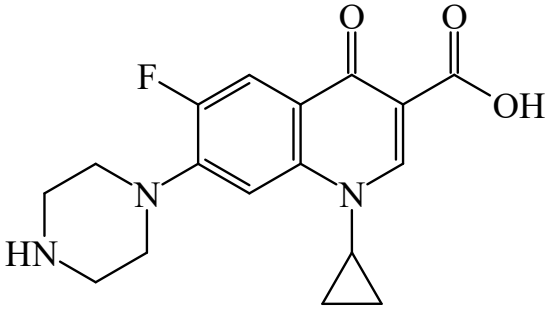

**Fig. S4.** O 2*p* XPS spectra for CuZnS-Naps.



Sulfamethoxazole



5,5-Diphenylhydantoin



Ciprofloxacin

**Fig. S5.** Structure of selected emerging organic pollutants.

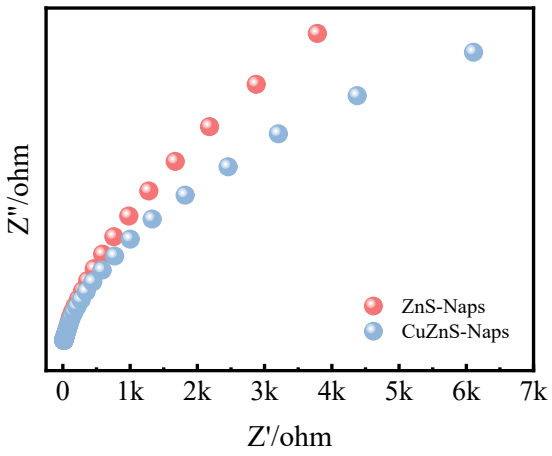
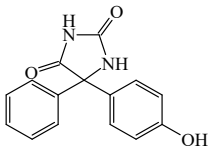
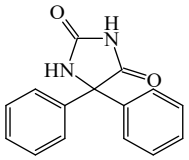
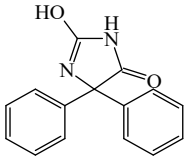
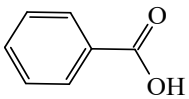
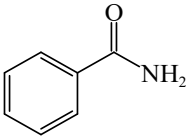
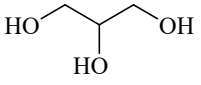



**Fig. S6.** Electrochemical impedance spectroscopy (EIS) Nyquist plots of CuZnS-Naps and ZnS-Naps.

**Table S1.** The main by-products detected in CuZnS-Naps/$H_2O_2$ system, which including retention time (min), exact mass (m/z), molecular formula and the chemical structure derived from molecular weight fragment mass spectra.

| Retention time (min) | Exact mass (m/z) | Molecular formula | Chemical structure |
|---|---|---|---|
| 36.235 | 269.3 | Hydroxyphenytoin |  |
| 33.450 | 252.29 | 5,5-Diphenylhydantoin |  |
| 34.290 | 252.29 | 5,5-Diphenylimidazolidine-2,4-dione |  |
| 13.760 | 122.13 | Benzoic acid |  |
| 18.150 | 121.15 | Benzamide |  |
| 14.415 | 92.11 | Glycerol |  |

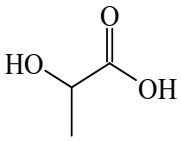
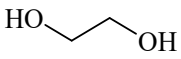
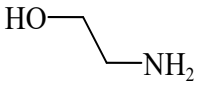
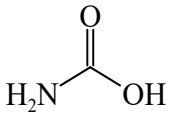
| | | | |
|---|---|---|---|
| 8.970 | 91.1 | Lactic acid |  |
| 7.075 | 62.08 | Ethylene glycol |  |
| 8.920 | 61.1 | Ethanolamine |  |
| 8.130 | 61.05 | Carbamate |  |

**Table S2.** Parameters of the actual pharmaceutical wastewater.

| Parameters | Raw wastewater | After treatment |
|---|---|---|
| pH | 7.67 | 6.98 |
| $F^-$ (mg $L^{-1}$) | - | 6.08 |
| $Cl^-$ (mg $L^{-1}$) | 132.12 | 130.46 |
| $NO_3^-$ (mg $L^{-1}$) | 14.42 | 15.85 |
| $SO_4^{2-}$ (mg $L^{-1}$) | 9.97 | 50.3 |