Electronic Supplementary Information (ESI)

for

Efficient Fenton-like Process for Organic Pollutant Degradation on Cu-doped Mesoporous Polyimide Nanocomposites

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Supplementary Experiment and Calculation Section

Chemicals and reagents

Horseradish peroxidase (POD, 99%) and ciprofloxacin (CIP) were purchased from TCI (Shanghai) Development Co., Ltd. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, >98%), *N,N*-diethyl-*p*-phenylenediamine sulfate (DPD, 99%), rhodamine B (RhB, 96%), bisphenol A (BPA, >98%), acid orange 7 (AO7, 99%), 2-chlorophenol (2-CP, 99%), ethylenediamine (EDA, 99%) and pyromellitic dianhydride (PMDA, >98%) were purchased from Adamas Reagent Co., Ltd. (Switzerland). N,N-Dimethylformamide (DMF, ≥99.8%), Copper(II) chloride dihydrate ($CuCl_2$•$2H_2O$, ≥99%) and glucose (AR) were obtained from Shanghai Titan Scientific Co., Ltd (Shanghai, China). Hydrogen peroxide (H_2O_2, 30%, w/w) and all the other chemicals were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Deionized water was used throughout this study.

Procedures and analysis

The concentrations of BPA, 2-CP and CIP were measured by a high-performance liquid chromatography (HPLC, 1260 Infinity II; Agilent) with an auto-sampler, a Poroshell 120 EC-C18 column (4.6 × 100 mm, 2.7 μm) and a UV detector. The mobile phase was a mixture of methanol/water and was operated at a flow-rate of 1.0 mL min^{-1}. The concentrations of RhB and AO7 were measured by a Hitachi Model UH4150 spectrophotometer. The total organic carbon (TOC) was determined by a TOC-L CPH CN200 analyzer (Shimadzu), using high-temperature combustion. The H_2O_2 concentration was determined using the reported DPD method.[1] The amount of metallic ions released from the catalysts during the reaction were measured using inductively coupled plasma mass spectrometry (ICP-MS) on a NexION 300

(PerkinElmer, U.S.A.). DMPO-trapped EPR signals were detected in different air-saturated methanol/aqueous dispersions of the corresponding samples. The EPR spectra were recorded on a Bruker A300-10/12 EPR spectrometer at room temperature. Typically, 0.01 g of the prepared powdered sample was added to 1 mL of water (for detecting $^{\bullet}OH$) or methanol (for detecting $O_2^{\bullet-}$). Then, 100 μL of the above suspension, 10 μL of H_2O_2 (30%, w/w, if needed) and 20 μL of DMPO were mixed and held for 1 min. The solution was then drawn into the capillary to carry out EPR detection.

Computational methods of density functional theory (DFT): The optimization of geometry and wave function was performed using the B3LYP functional and 6-31G(d) basis set with the Gaussian 09 package. The valence-electron density was analyzed with the Multiwfn package. The dangling bonds were terminated with H atoms to obtain a neutral cluster. Due to the size and edge effects, the properties estimated with the finite-size model may vary from those of the real system to some extent. However, the results obtained with the current model would be qualitatively reliable in predicting the local chemical properties.

Calculation of the utilization efficiency of H_2O_2. The complete mineralization of one mole of RhB will theoretically consume 73 moles of H_2O_2 (Eqs. S1).

$$C_{28}H_{31}ClN_2O_3+73H_2O_2 \rightarrow 28CO_2+87H_2O+HCl+2HNO_3 \quad (S1)$$

The utilization efficiency of H_2O_2 (η) is defined as the ratio of the stoichiometric consumption of H_2O_2 ($[\Delta H_2O_2]_S$) for the mineralization of pollutants to the actual consumption of H_2O_2 ($[\Delta H_2O_2]_A$) in the Fenton-like reaction[2] and is expressed in Eq. S2:

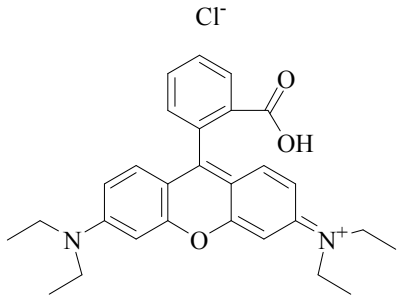
$\eta = [\Delta H_2O_2]_S / [\Delta H_2O_2]_A$ (S2)

By measuring the TOC change in the pollutant solutions, the amounts of the mineralized contaminants were obtained, and the value of $[\Delta H_2O_2]_S$ was calculated. The actual consumption of H_2O_2 ($[\Delta H_2O_2]_A$) at different reaction times was measured using the DPD method.[1] The detailed data for $[\Delta H_2O_2]_A$ and $[\Delta H_2O_2]_S$ are presented in the following Table.

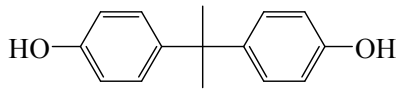
Table. Actual consumption of H_2O_2 ($[\Delta H_2O_2]_A$) and stoichiometric consumption of H_2O_2 ($[\Delta H_2O_2]_S$) for mineralizing RhB during the Fenton-like reaction.

Reaction time/min	RhB (10 mg L^{-1})	
	$[\Delta H_2O_2]_A$/mM	$[\Delta H_2O_2]_S$/mM
0	0	0
30	0.459	0.385
60	0.816	0.669
90	1.071	0.795
120	1.531	0.924

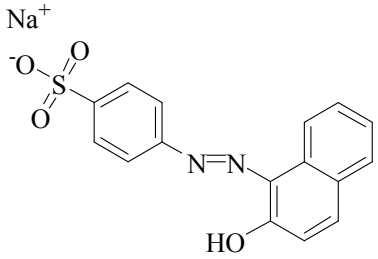
rhodamine B



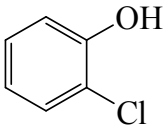
bisphenol A



acid orange 7



2-chlorophenol



ciprofloxacin

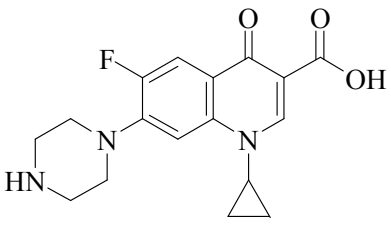


Figure S1. Structures of rhodamine B (RhB), bisphenol A (BPA), acid orange 7 (AO7), 2-chlorophenol (2-CP) and ciprofloxacin (CIP).

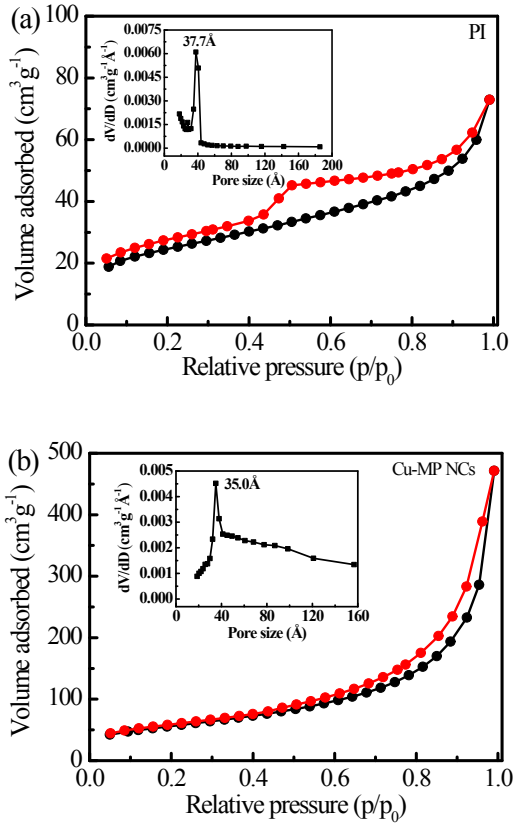


Figure S2. N_2 adsorption-desorption isotherms and BJH pore size distribution (inset) of (a) PI and (b) Cu-MP NCs.

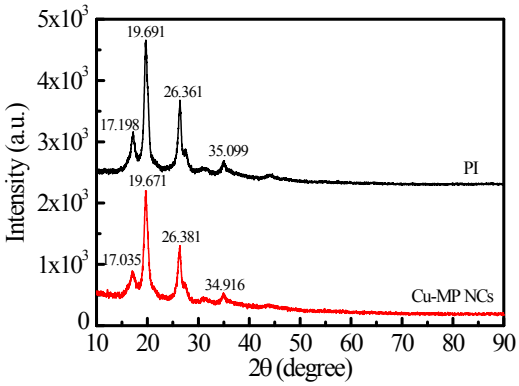


Figure S3. XRD patterns of PI and Cu-MP NCs.

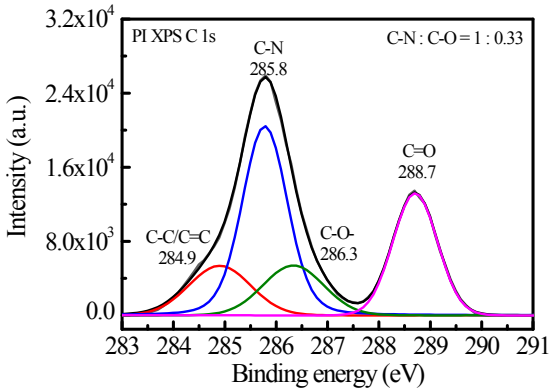


Figure S4. C 1s XPS spectrum of PI.

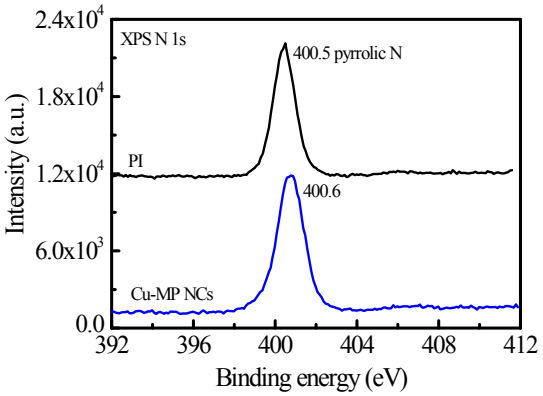


Figure S5. N 1s XPS spectra of PI and Cu-MP NCs.

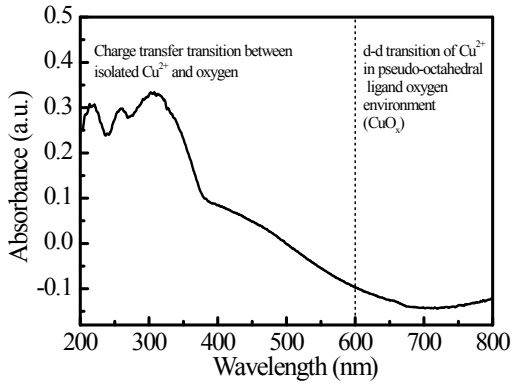


Figure S6. UV-Vis DRS spectrum of Cu-MP NCs.

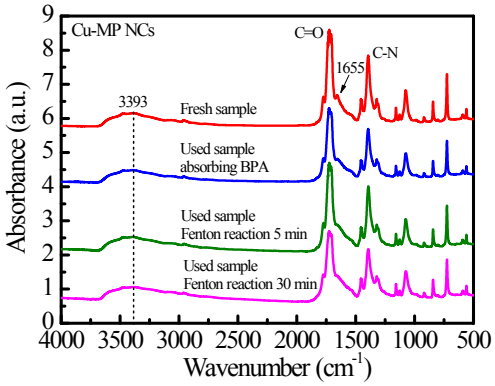


Figure S7. FTIR spectra of the Cu-MP NCs samples after absorbing BPA and after Fenton-like reaction with BPA.

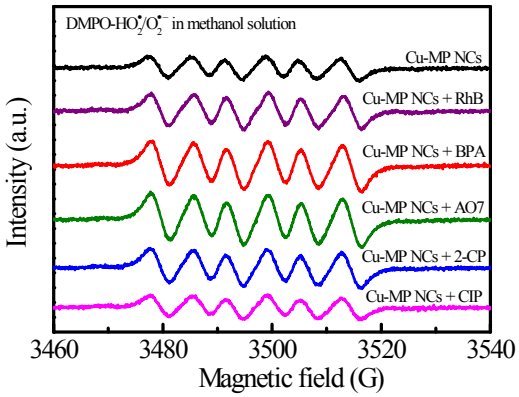


Figure S8. DMPO spin-trapping EPR spectra for $HO_2^{\bullet}/O_2^{\bullet-}$ in Cu-MP NCs aqueous suspensions before/after adding different pollutants (without H_2O_2).

References

1. H. Bader, V. Sturzenegger and J. Hoigne, Photometric-method for the determination of low concentrations of hydrogen-peroxide by the peroxidase catalyzed oxidation of N,N-Diethyl-P-Phenylenediamine (DPD), *Water Res.*, 1988, **22**, 1109-1115.
2. W. Luo, L. H. Zhu, N. Wang, H. Q. Tang, M. J. Cao and Y. B. She, Efficient removal of organic pollutants with magnetic nanoscaled $BiFeO_3$ as a reusable heterogeneous Fenton-like catalyst, *Environ. Sci. Technol.*, 2010, **44**, 1786-1791.