Supporting Information

Enhanced Ultrasonically-Assisted Heterogeneous Fenton Degradation of Organic Pollutants

over a New Copper Magnetite (Cu-Fe₃O₄/Cu/C) Nanohybrid Catalyst

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Figure S1. FTIR spectra of the as-synthesized MOFs.



Figure S2. (a ,b ,d, e, g, h) Different magnification SEM and (c, f, i) TEM images of (a,b,c) Fe-MOF, (d, e, f) Cu/Fe-MOF and (g,h, i) Cu-MOF.



Figure S3. SEM images of (a) Fe₃O₄/C and (b) Cu/C.



Figure S4. EDX spectra of Cu-Fe₃O₄/Cu/C along with the corresponding Element content in inset view.



Figure S5. FTIR spectrum of the as-prepared Cu-Fe₃O₄/Cu/C.



Figure S6. TOC removal rate in different (a) catalyst (b) pH systems and for US/H-Fenton degradation of RhB at 3 h of reaction time. Experimental conditions: $[Fe_3O_4/C] = [Cu/C] = [Cu-Fe_3O_4/Cu/C] = 0.1 \text{ g/L}, [H_2O_2] = 10.0 \text{ mmol/L}, [RhB] = 10.0 \text{ mg/L}, pH 3.0.$



Figure S7. (a) TGA curve of Cu-Fe₃O₄/Cu/C catalyst in the air atmosphere. (b) RhB degradation efficiency of US/H-Fenton reaction by using C and Cu-Fe₃O₄/Cu/C catalysts at pH 3.0. Experimental conditions: [C] = 0.01 g/L, $[Cu-Fe_3O_4/Cu/C] = 0.1 \text{ g/L}$, $[H_2O_2] = 10.0 \text{ mmol/L}$, [RhB] = 10.0 mg/L.



Figure S8. Effect of (a) H_2O_2 dosage, (b) Cu-Fe₃O₄/Cu/C dosage, (c) RhB concentration and (d) pH value on RhB degradation during US/H-Fenton process. Other reaction parameters were fixed at [Cu-Fe₃O₄/Cu/C] = 0.1 g/L, [H₂O₂] = 10.0 mmol/L, [RhB]= 10.0 mg/L, pH 3.0.



Figure S9. (a) SEM image and (b-e) EDS elemental mapping of the used Cu-Fe₃O₄/Cu/C.



Figure S10. HAADF-STEM images of used Cu-Fe₃O₄/Cu/C.



Figure S11. Possible degradation pathway of RhB in US/H-Fenton reaction.

Catalysts	Reaction conditions	Removal rate	Reference
α-Fe ₂ O ₃ /Graphene	pH = 2.9, [cat.] = 0.5 g/L, [H ₂ O ₂] = 6.0 mL/L, [RhB] = 10.0 mg/L, UV irradiation	~90% (60 min)	(1)
Fe ₂ O ₃	pH = 2.9, [cat.] = 0.5 g/L, [H ₂ O ₂] = 5.0 mL/L, [RhB] = 10.0 mg/L, UV irradiation	100% (30 min)	(2)
CoFe ₂ O ₄ @PPy	pH = 7.0, [cat.] = 0.2 g/L, [H ₂ O ₂] = 4.0 mL/L, [RhB] = 10.0 mg/L, UV irradiation	~100% (30 min)	(3)
Cu/C	pH = 3.9, [cat.] = 0.5 g/L, [H ₂ O ₂] = 1.0 mL/L, [RhB] = 10.0 mg/L, US (40 kHz)	~60% (70 min)	(4)
Fe ₃ O ₄	pH = 5.0, 55 °C, [cat.] = 0.5 g/L, [H ₂ O ₂] = 3.7 mL/L, [RhB] = 4.8 mg/L	~84% (60 min)	(5)
FeS ₂	pH = 3.0, [cat.] = 1.0 g/L, [H ₂ O ₂] = 0.6 mL/L, [RhB] = 19.2 mg/L	~90% (60 min)	(6)
MgFe ₂ O ₄	pH = 3.0, 45 °C, [cat.] = 1.0 g/L, $[H_2O_2] = 10.0 \text{ mL/L}, \text{ [RhB]} = 10.0 \text{ mg/L}$	~40% (60 min)	(7)
MIL-88A(Fe)	$[cat.] = 0.2 \text{ g/L}, [H_2O_2] = 2.0 \text{ mL/L},$ [RhB] = 10.0 mg/L, UV irradiation	100% (60 min)	(8)
Fe4[Fe(CN)6]3	pH = 3.5, 35 °C, [cat.] = 0.6 g/L, [H ₂ O ₂] = 1.0 mL/L, [RhB] = 25.0 mg/L, UV irradiation	97% (60 min)	(9)
ZnFe ₂ O ₄ /C	35 °C, [cat.] = 1.0 g/L, [H ₂ O ₂] = 20.0 mL/L, [RhB] = 5.0 mg/L, UV irradiation	100% (60 min)	(10)
LuFeO3	pH = 3.0, 40 °C, [cat.] = 1.0 g/L, [RhB] = 5.0 mg/L, US (40 kHz)	~60% (90 min)	(11)
FePO ₄ /N-CNTs	pH = 4.1, [cat.] = 2.0 g/L, $[H_2O_2] = 0.9$ mL/L, [RhB] = 15.0 mg/L	100% (60 min)	(12)
CuO/Fe ₂ O ₃ /kaolin	pH = 3.0, [cat.] = 30.0 g/L, voltage = 10.0 V, aeration rate = 0.8 L/min, [RhB] = 20.0 mg/L	97% (60 min)	(13)
Cu-Fe ₃ O ₄ /Cu/C	pH = 3.0, 30 °C, [cat.] = 0.1 g/L, [H ₂ O ₂] = 0.9 mL/L, [RhB] = 10.0 mg/L, US (40 kHz)	~100% (30 min)	This work

Table S1. The comparison on RhB removal rate of Cu-Fe₃O₄/Cu/C with other reported heterogeneous catalysts.

References

- Frindy, S.; Sillanpää, M. Synthesis and Application of Novel α-Fe₂O₃/Graphene for Visible-light Enhanced Photocatalytic Degradation of RhB. *Mater Design.* **2020**, 188, No. 108461.
- (2) Sun, Z. M.; Xiao, C.; Hussain, F.; Zhang, G. Synthesis of Stable and Easily Recycled Ferric Oxides Assisted by Rhodamine B for Efficient Degradation of Organic Pollutants in Heterogeneous Photo-Fenton System. J. Clean. Prod. 2018, 196, 1501–1507.
- (3) Deng, Y. M.; Zhao, X. M.; Luo, J. X.; Wang, Z.; Tang, J. N. Magnetic Recyclable CoFe₂O₄@PPy Prepared by in Situ Fenton Oxidization Polymerization with Advanced Photo-Fenton Performance. *RSC Adv.* **2020**, 10, 1858–1869.
- (4) Wang, C. Q.; Wang, H.; Cao, Y. J. Ultrasonic Improvement of Catalytic Decomposition of Rhodamine B in Simulated Wastewater by Functional Waste Printed Circuit Boards via Thermochemical Conversion, J. Clean. Prod. 2020, 253, No. 119921.
- (5) Chen, F. X.; Xie, S. L.;Huang, X. L.; Qiu, X. H. Ionothermal Synthesis of Fe₃O₄ Magnetic Nanoparticles as Efficient Heterogeneous Fenton-like Catalysts for Degradation of Organic Pollutants with H₂O₂. *J. Hazard. Mater.* **2017**, 322, 152–162.
- (6) Diao, Z. H.; Liu, J. J.; Hu, Y. X.; Kong, L. J.; Jiang, D.; Xu, X. R. Comparative Study of Rhodamine B Degradation by the Systems Pyrite/H₂O₂ and Pyrite/Persulfate: Reactivity, Stability, Products and Mechanism. *Sep. Purif. Technol.* **2017**, 184, 374–383.
- (7) Han, X.; Zhang, H. Y.; Chen, T.; Zhang, M.; Guo, M. Facile Synthesis of Metal-doped Magnesium Ferrite from Saprolite Laterite as an Effective Heterogeneous Fenton-like Catalyst. *J. Mol. Liq.* 2018, 272, 43–52.
- (8) Fu, H. F.; Song, X. X.; Wu, L.; Zhao, C.; Wang, P.; Wang, C. C. Room-temperature Preparation of MIL-88A as a Heterogeneous Photo-Fenton Catalyst for Degradation of Rhodamine B and Bisphenol a under Visible Light. *Mater. Res. Bull.* 2020, 125, No. 110806.
- (9) Wang, N.; Ma, W. J.; Du, Y. C.;Ren, Z. Q.; Han, B. H.; Zhang, L. J.; Sun, B. J.; Xu, P.; Han, X. J. Prussian Blue Microcrystals with Morphology Evolution as a High-Performance Photo-Fenton Catalyst for Degradation of Organic Pollutants. *ACS Appl. Mater. Interfaces* **2019**, 11, 1174–1184.
- (10) Wang, F. X.; Chen, Y. L.; Zhu, R. S.; Sun, J. M. Novel Synthesis of Magnetic, Porous C/ZnFe₂O₄

Photocatalyst with Enhanced Activity under Visible Light Based on the Fenton-like Reaction. *Dalton Trans.* **2017**, 46, 11306–11317.

- (11) Zhou, M.; Yang, H.; Xian, T.; Li, R. S.; Zhang, H. M.; Wang, X. X. Sonocatalytic Degradation of RhB over LuFeO₃ Particles under Ultrasonic Irradiation. *J. Hazard. Mater.* 2015, 289, 149–157.
- (12) Wei, L. M.; Zhang, Y.; Chen, S. W.; Zhu, L. P.; Liu, X. Y.; Kong, L. X.; Wang, L. J. Synthesis of Nitrogen-doped Carbon Nanotubes-FePO₄ Composite from Phosphate Residue and Its Application as Effective Fenton-like Catalyst for Dye Degradation. *J. Environ. Sci.* **2019**, 76, 188–198.
- (13) Zhang, B. G.; Hou, Y. P.; Yu, Z. B.; Liu, Y. X.; Huang, J.; Qian, L.; Xiong, J. H. Three-dimensional Electro-Fenton Degradation of Rhodamine B with Efficient Fe-Cu/Kaolin Particle Electrodes: Electrodes Optimization, Kinetics, Influencing Factors and Mechanism. *Sep. Purif. Technol.* 2019, 210, 60–68.