

Supporting Information

Supermagnetic Mn-substituted ZnFe₂O₄ in AB-sites Hybridization for Ultra-effective catalytic degradation of azoxystrobin

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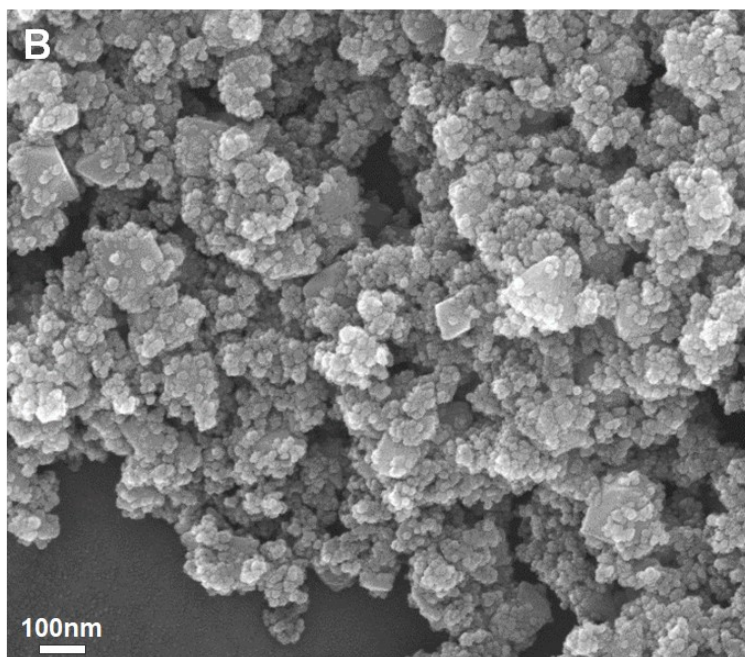
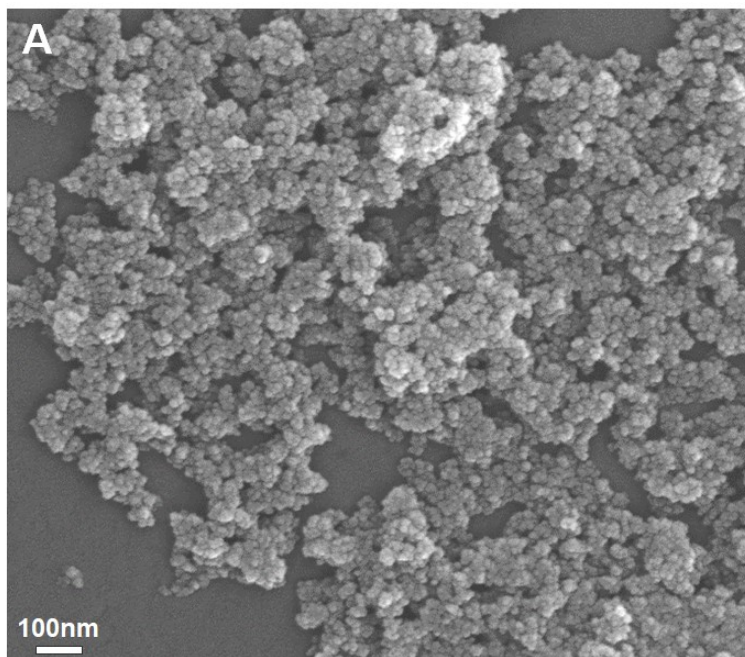


Figure S1. SEM images of the ZF and MF catalysts.

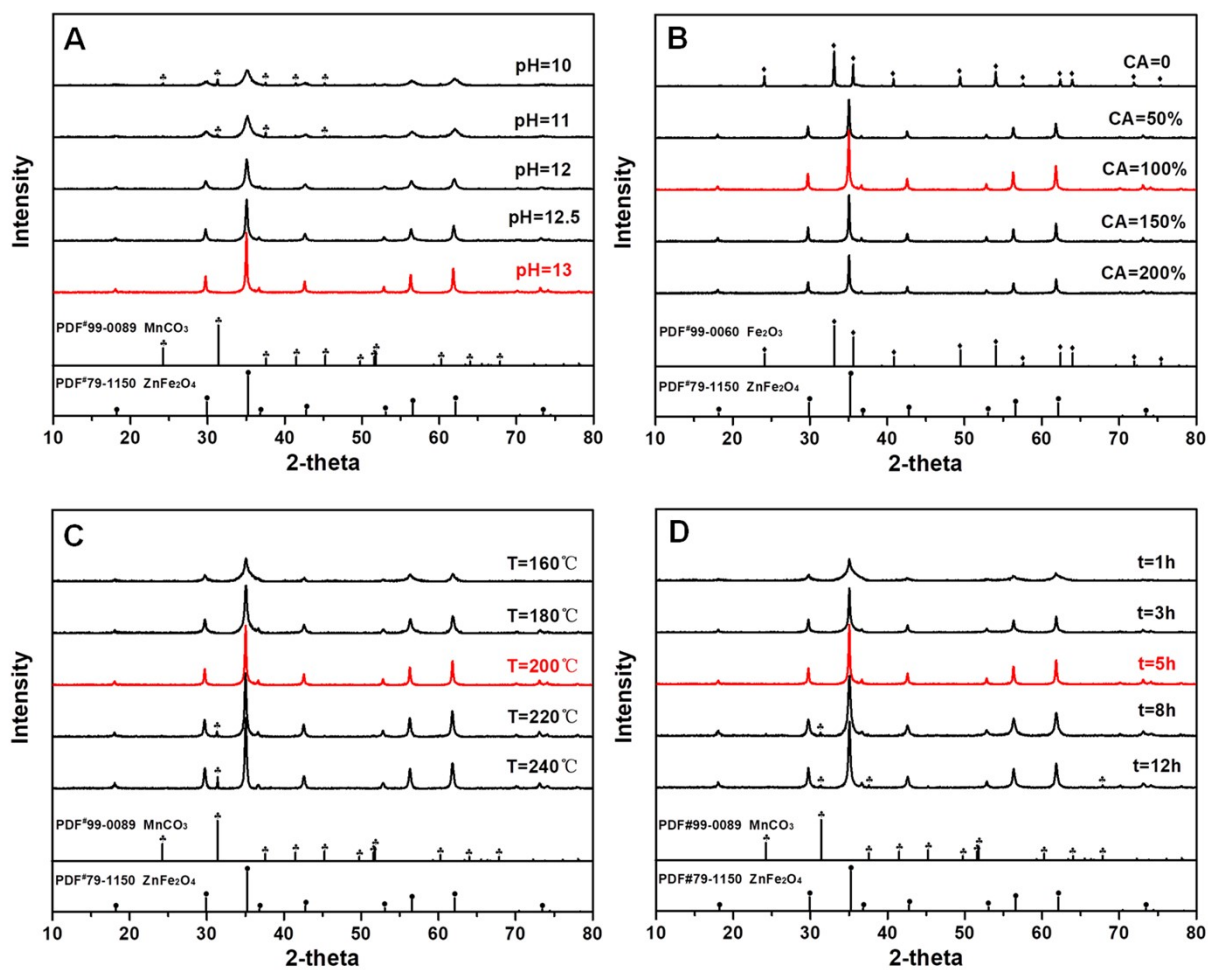


Figure S2. XRD patterns for the prepared Mn-substituted ZnFe₂O₄ samples (ZMF_{0.75}) at different pH value (A), citric acid addition (B), temperature (C) and reaction time (D) in hydrothermal reaction. Experimental conditions: (A) [CA] = 100%, T = 200 °C, t = 5 h; (B) pH = 13, T = 200 °C, t = 5 h; (C) pH = 13, [CA] = 100%, t = 5 h; (D) pH = 13, [CA] = 100%, T = 200 °C.

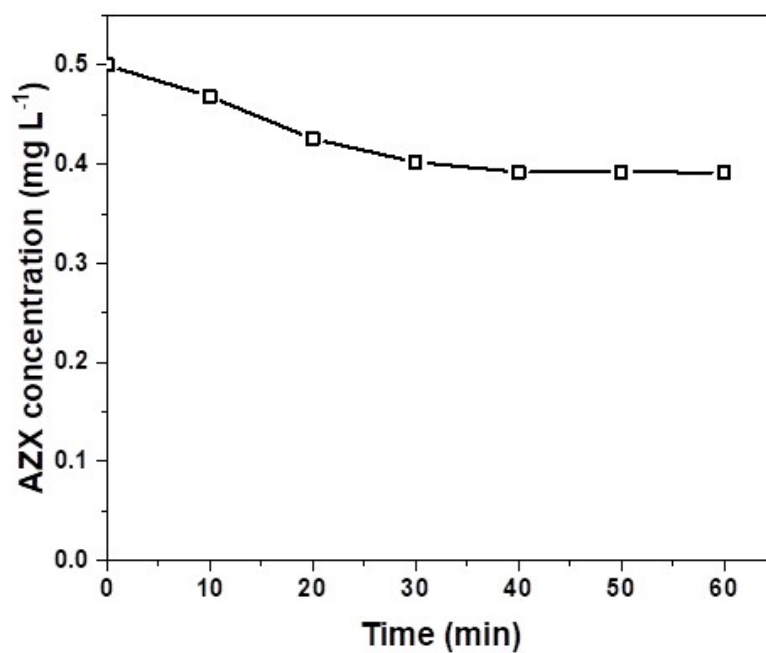


Figure S3. AZX removal efficiency by ZMF0.75 adsorption at the control experimental conditions of $[AZX] = 0.5 \text{ mg L}^{-1}$, $[ZMF_{0.75}] = 0.2 \text{ g L}^{-1}$, and $\text{pH} = 4.5 \pm 0.2$.

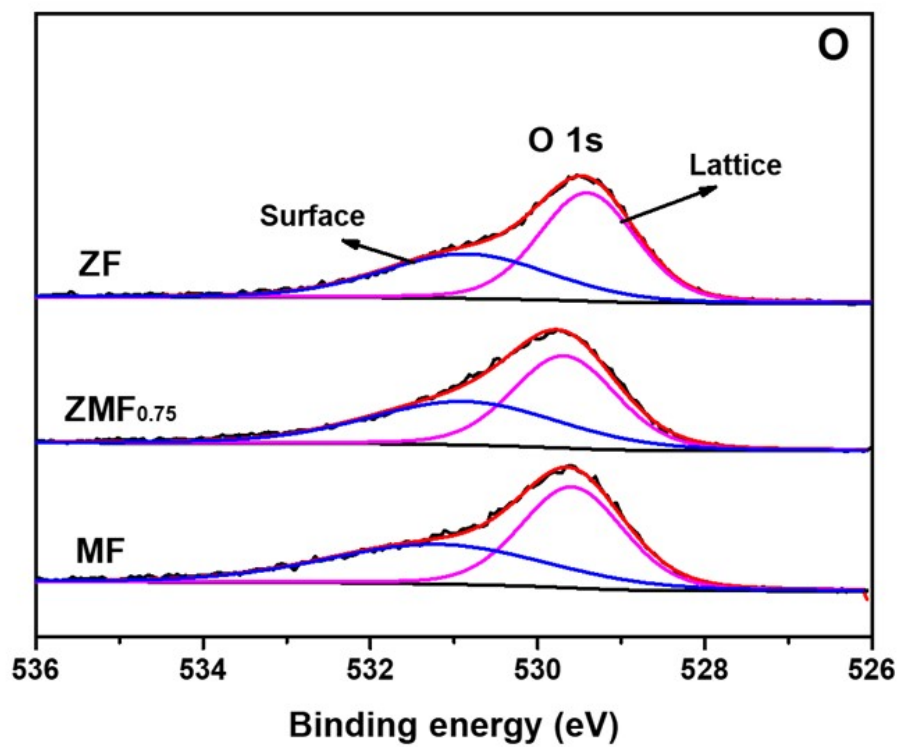


Figure S4. High resolution XPS spectra of O 1s for ZF, ZMF_{0.75} and MF, respectively.

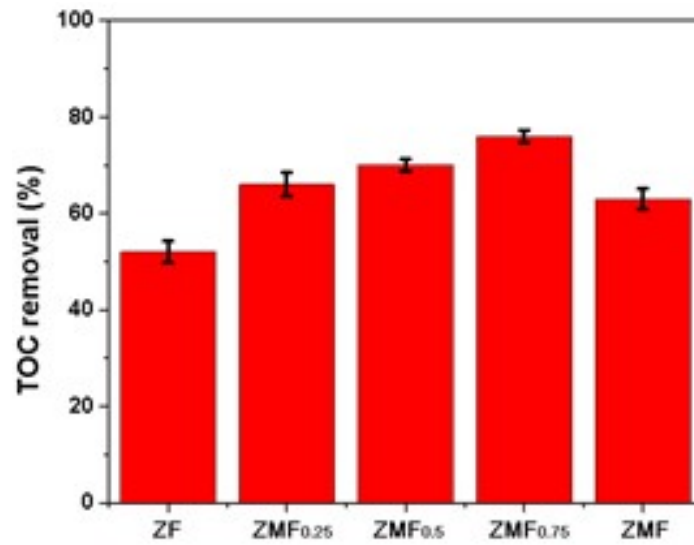


Figure S5. TOC removal based on the as-prepared catalysts in Fenton-like system at 10 hours. The experimental conditions are $[AZX] = 0.5 \text{ mg L}^{-1}$, $[\text{catalyst}] = 0.2 \text{ g L}^{-1}$, $\text{pH} = 4.5 \pm 0.2$, $[\text{H}_2\text{O}_2] = 100 \text{ mM}$.

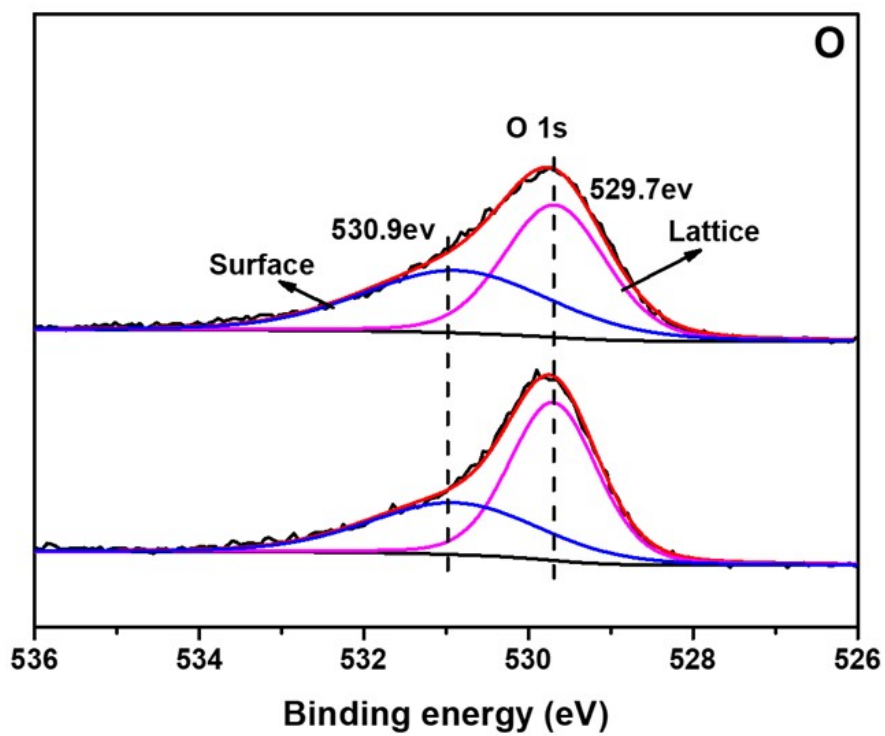


Figure S6. High resolution XPS spectra of O 1s for used ZMF_{0.75} compared with its fresh.

Table S1. Characteristics summary of the as-prepared catalysts on crystal lattice parameters and crystal size

Catalyst	Crystal structure				^a Crystallite size (nm)
	a [Å]	a [Å]	a [Å]	V [Å ³]	
ZF	8.441	8.441	8.441	602.26	9.4
ZMF _{0.25}	8.449	8.449	8.449	603.46	13.9
ZMF _{0.5}	8.467	8.467	8.467	606.94	21.2
ZMF _{0.75}	8.483	8.483	8.483	610.22	20.9
MF	8.505	8.505	8.505	614.14	19.8

^a Calculation by the Scherrer equation based on the facet (311).

Table S2. A brief of Fenton-like system driven by varied spinel ferrites for organic pollutants degradation

Catalyst	Synthesis method	Morphology/nanostructure	System conditions	Degradation rate	Radical species	Ref.
ZMF _{0.75}	Hydrothermal way	Nanocluster with nanoparticle size of 5~10 nm	[AZX] = 0.5 mg L ⁻¹ , [catalyst] = 0.2 g L ⁻¹ , [H ₂ O ₂] = 100 mM, pH = 4.5 ± 0.2	99% in 300 min	HO [•] , HO ₂ [•]	This report
Fe ₃ O ₄	Chemical coprecipitation method	Quasi-spherical particles	[4-chlorocatechol] = 1 mmol L ⁻¹ , [catalyst] = 1 g L ⁻¹ , [H ₂ O ₂] = 50 mM, pH = 6.5 ± 0.2	~99% in 180 min	HO [•] , HO ₂ [•] , O ₂ ^{-•}	1
MnFe ₂ O ₄	Sol-gel method	Near-nubby morphology	[norfloxacin] = 10 mg L ⁻¹ , [catalyst] = 0.6 g L ⁻¹ , [H ₂ O ₂] = 200 mM, pH = 6.6	90.6% in 180 min	HO [•]	2
Mn _{1.07} Fe _{1.93} O ₄	Solvothermal way	Sphere-like morphology	[methylene blue] = 400 mg L ⁻¹ , [catalyst] = 0.5 g L ⁻¹ , [H ₂ O ₂] = 1323 mM, pH at acidic	98.2% in 360 min	HO [•] , HO ₂ [•]	3

References:

- [1] J. He, X. Yang, B. Men, Z. Bi, Y. Pu, D. Wang, Heterogeneous Fenton oxidation of catechol and 4-chlorocatechol catalyzed by nano-Fe₃O₄: Role of the interface, *Chemical Engineering Journal*, 2014, 258, 433-441.
- [2] G.Wang, D. Zhao, F. Kou, Q. Ouyang, J. Chen, Z. Fang, Removal of norfloxacin by surface Fenton system (MnFe₂O₄/H₂O₂): Kinetics, mechanism and degradation pathway, *Chemical Engineering Journal*, 2018, 351, 747-755.
- [3] M., Li, Q. Gao, T. Wang, Y.S., Gong, B. Han, K.S., Xia, C.G., Zhou, Solvothermal synthesis of Mn_xFe_{3-x}O₄ nanoparticles with interesting physicochemical characteristics and good catalytic degradation activity, *Materials & Design*, 2016, 97, 341-348.