Supplementary Materials

S1 Quenching experiments

According to literatures [S1-S3], tertiary butyl alcohol (TBA) acts on •OH with the reaction rate constant of $k_{\mathrm{TBA,\,\bullet OH}} = 5.9 \times 10^8$ $\mathrm{M^{-1}{\cdot}s^{-1}}$, while methyl alcohol (MA) serves as a typical quencher for solution •OH or Cl• with the reaction rate constants of $k_{\mathrm{MA,\,\bullet OH}} = 9.7 \times 10^8$ $\mathrm{M^{-1}{\cdot}s^{-1}}$, $k_{\mathrm{MA,\,Cl\bullet}} = 1.0 \times 10^9$ $\mathrm{M^{-1}{\cdot}s^{-1}}$, respectively. Dimethyl sulfoxide (DMSO) could highly react with •OH ($k_{\mathrm{DMSO,\,\bullet OH}} = (5.8{-}7.0) \times 10^9$ $\mathrm{M^{-1}{\cdot}s^{-1}}$) to form the methyl radical ($\bullet CH_3$). DMSO can used to identify oxygen atom transfer reactions, such as reaction with $Fe^{IV}O^{2+}$ to form $DMSO_2$. DMSO could be an excellent masking agent for aqueous chlorine (e.g., Cl_2 or ClO^-). NaN_3 can be used to quench ClO_2 because of the reaction of ClO_2 with N_3^- with rapid back electron transfer. NaN_3 can react with Cl• or $Cl_2\bullet^-$ with the reaction rate constants of $k_{\mathrm{NaN3,\,Cl\bullet}} = 5.2 \times 10^9$ $\mathrm{M^{-1}{\cdot}s^{-1}}$, $k_{\mathrm{NaN3,\,Cl2\bullet-}} = 1.2 \times 10^9$ $\mathrm{M^{-1}{\cdot}s^{-1}}$, respectively.

[S1] J. Lee, U.V. Gunten, J. H. Kim, Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks, Environ. Sci. Technol. 54 (2020) 3064−3081.

[S2] Y. Lei, Y.F. Yu, X. Lei, X. Liang, S.S. Cheng, G.F. Ouyang, X. Yang, Assessing the Use of Probes and Quenchers for Understanding the Reactive Species in Advanced Oxidation Processes. Environ. Sci. Technol. 2023, 57, 5433−5444.

[S3] X.N. Hu, M.S. Zhu, Were Persulfate-Based Advanced Oxidation Processes Really Understood? Basic Concepts, Cognitive Biases, and Experimental Details, Environ. Sci. Technol. 2024, https://doi.org/10.1021/acs.est.3c10898.

S2 Establishment of reaction kinetics

(1) For HAC system:

$$\mathrm{ClO_2^- + H^+ \overset{k_\mathrm{d}/k_{-\mathrm{d}}}{\Longleftrightarrow} HClO_2} \tag{Rd}$$

$$\mathrm{HOFe^{III} + HClO_2 \overset{k_1}{\rightarrow} Fe^{III}ClO_2 + H_2O} \tag{R1}$$

$$\mathrm{HOFe^{II} + HClO_2 \overset{k_2}{\rightarrow} (O)Fe^{IV} + ClO^-} \tag{R2}$$

$$\mathrm{Fe^{III}ClO_2 \overset{k_3}{\rightarrow} (O)Fe^{IV} + [ClO]} \tag{R3}$$

$$\mathrm{Fe^{III}ClO_2 \overset{k_4}{\rightarrow} (O)Fe^{V+\cdot} + ClO^-} \tag{R4}$$

$$\mathrm{(O)Fe^{V+\cdot} + ClO_2^- \overset{k_5}{\rightarrow} (O)Fe^{IV} + ClO_2} \tag{R5}$$

$$\mathrm{(O)Fe^{IV} + HClO_2 \overset{k_6}{\rightarrow} HOFe^{III} + ClO_2} \tag{R6}$$

If without pollutants:

$$K = \frac{k_\mathrm{d}}{k_{-\mathrm{d}}} = \frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{[\mathrm{HClO_2}]}$$

$$\frac{\mathrm{d[ClO_2]}}{\mathrm{d}t} = \frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}(k_6[\mathrm{(O)Fe^{IV}}] + k_5[\mathrm{(O)Fe^{V+\cdot}}])$$

$$\frac{\mathrm{d[(O)Fe^{IV}]}}{\mathrm{d}t} = \frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}(k_2[\mathrm{HOFe^{II}}] + k_5[\mathrm{(O)Fe^{V+\cdot}}] - k_6[\mathrm{(O)Fe^{IV}}]) + k_3[\mathrm{Fe^{III}ClO_2}]$$

$$\frac{\mathrm{d[(O)Fe^{V+\cdot}]}}{\mathrm{d}t} = k_4[\mathrm{Fe^{III}ClO_2}] - \frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}k_5[\mathrm{(O)Fe^{V+\cdot}}]$$

$$\frac{\mathrm{d[Fe^{III}ClO_2]}}{\mathrm{d}t} = k_1[\mathrm{HOFe^{III}}][\mathrm{HClO_2}] - k_4[\mathrm{Fe^{III}ClO_2}] - k_3[\mathrm{Fe^{III}ClO_2}]$$

Given that these reactions reach a steady state, so $\mathrm{Fe^{III}ClO_2}$ and HVI concentration does not change with time, that is

$$\frac{\mathrm{d[HVI{=}O]}}{\mathrm{d}t} = 0,\ \frac{\mathrm{d[Fe^{III}ClO_2]}}{\mathrm{d}t} = 0$$

$$[\mathrm{Fe^{III}ClO_2}] = \frac{k_1[\mathrm{HOFe^{III}}][\mathrm{HClO_2}]}{k_4+k_3} = \frac{K_\mathrm{i}}{K}[\mathrm{ClO_2^-}][\mathrm{H^+}][\mathrm{HOFe^{III}}]$$

$$[\mathrm{(O)Fe^{V+\cdot}}] = \frac{K_\mathrm{i}k_4}{k_5}[\mathrm{HOFe^{III}}]$$

$$[\mathrm{(O)Fe^{IV}}] = \frac{k_2}{k_6}[\mathrm{HOFe^{II}}] + \frac{k_1}{k_6}[\mathrm{HOFe^{III}}] \approx \frac{k_1}{k_6}[\mathrm{HOFe^{III}}]$$

$$\frac{\mathrm{d[ClO_2]}}{\mathrm{d}t} = \frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}(k_2[\mathrm{HOFe^{II}}] + k_1[\mathrm{HOFe^{III}}] + k_4[\mathrm{HOFe^{III}}]) = \frac{k_1+k_4}{K}[\mathrm{HOFe^{III}}][\mathrm{ClO_2^-}][\mathrm{H^+}]$$

Where $\frac{k_1}{k_4+k_3} = K_\mathrm{i}$, $[\mathrm{HOFe^{III}}] \gg [\mathrm{HOFe^{II}}]$

Herein, the HO-Fe^{III} can be seen as the catalyst, so

$$\frac{\mathrm{d}[\mathrm{HOFe^{III}}]}{\mathrm{d}t} = 0$$

$$[\mathrm{HOFe^{III}}] = \frac{k_6}{k_1}[(\mathrm{O})\mathrm{Fe^{IV}}]$$

If with pollutants:

$$(\mathrm{O})\mathrm{Fe^{IV}} + \mathrm{genV} \xrightarrow{k_\mathrm{i}} \mathrm{P_1} \tag{Ri}$$

$$(\mathrm{O})\mathrm{Fe^{V+\cdot}} + \mathrm{genV} \xrightarrow{k_\mathrm{ii}} \mathrm{P_2} \tag{Rii}$$

$$\mathrm{ClO_2} + \mathrm{genV} \xrightarrow{k_\mathrm{iii}} \mathrm{P_3} \tag{Riii}$$

Therefore:

$$\frac{\mathrm{d}[\mathrm{genV}]}{\mathrm{d}t} = -[\mathrm{genV}](k_\mathrm{i}[(\mathrm{O})\mathrm{Fe^{IV}}] + k_\mathrm{ii}[(\mathrm{O})\mathrm{Fe^{V+\cdot}}] + k_\mathrm{iii}[\mathrm{ClO_2}])$$

$$k_\mathrm{obs} = k_\mathrm{i}[(\mathrm{O})\mathrm{Fe^{IV}}] + k_\mathrm{ii}[(\mathrm{O})\mathrm{Fe^{V+\cdot}}] + k_\mathrm{iii}[\mathrm{ClO_2}]$$

$$[\mathrm{ClO_2}] = \frac{k_1+k_4}{Kk_\mathrm{iii}[\mathrm{genV}]}[\mathrm{HOFe^{III}}][\mathrm{ClO_2^-}][\mathrm{H^+}]$$

$$[\mathrm{ClO_2}] = z\frac{[\mathrm{HOFe^{III}}][\mathrm{ClO_2^-}][\mathrm{H^+}]}{1-\eta}$$

$$[(\mathrm{O})\mathrm{Fe^{IV}}] = \frac{\frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}\left(k_2[\mathrm{HOFe^{II}}]+k_5[(\mathrm{O})\mathrm{Fe^{V+\cdot}}]\right)+k_3[\mathrm{Fe^{III}ClO_2}]}{\frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}k_6+k_\mathrm{i}(1-\eta)[\mathrm{genV}]_0} \approx \frac{\frac{K_\mathrm{i}}{K}[\mathrm{ClO_2^-}][\mathrm{H^+}][\mathrm{HOFe^{III}}]}{\frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}k_6+k_\mathrm{i}(1-\eta)[\mathrm{genV}]_0}$$

$$\frac{1}{[(\mathrm{O})\mathrm{Fe^{IV}}]} = \frac{\frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}k_6+k_\mathrm{i}(1-\eta)[\mathrm{genV}]_0}{\frac{K_\mathrm{i}}{K}[\mathrm{ClO_2^-}][\mathrm{H^+}][\mathrm{HOFe^{III}}]} = \frac{Kk_6}{K_i[\mathrm{HOFe^{III}}]} + \frac{Kk_\mathrm{i}(1-\eta)[\mathrm{genV}]_0}{K_\mathrm{i}[\mathrm{ClO_2^-}][\mathrm{H^+}][\mathrm{HOFe^{III}}]} = \frac{x_1}{[\mathrm{HOFe^{III}}]} + \frac{x_2(1-\eta)}{[\mathrm{ClO_2^-}][\mathrm{H^+}][\mathrm{HOFe^{III}}]}$$

$$[(\mathrm{O})\mathrm{Fe^{V+\cdot}}] = \frac{k_4\frac{K_\mathrm{i}}{K}[\mathrm{ClO_2^-}][\mathrm{H^+}][\mathrm{HOFe^{III}}]}{\frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}k_5+k_\mathrm{ii}(1-\eta)[\mathrm{genV}]_0}$$

$$\frac{1}{[(\mathrm{O})\mathrm{Fe^{V+\cdot}}]} = \frac{\frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}k_5+k_\mathrm{ii}(1-\eta)[\mathrm{genV}]_0}{k_4\frac{K_i}{K}[\mathrm{ClO_2^-}][\mathrm{H^+}][\mathrm{HOFe^{III}}]} = \frac{k_5}{k_4K_\mathrm{i}[\mathrm{HOFe^{III}}]} + \frac{Kk_\mathrm{ii}(1-\eta)[\mathrm{genV}]_0}{k_4K_\mathrm{i}[\mathrm{ClO_2^-}][\mathrm{H^+}][\mathrm{HOFe^{III}}]} = \frac{y_1}{[\mathrm{HOFe^{III}}]} + \frac{y_2(1-\eta)}{[\mathrm{ClO_2^-}][\mathrm{H^+}][\mathrm{HOFe^{III}}]}$$

where $[\mathrm{genV}] = (1-\eta)[\mathrm{genV}]_0$

(2) For HUC system:

$$\mathrm{ClO_2^-} + \mathrm{H^+} \overset{k_\mathrm{d}/k_{-\mathrm{d}}}{\Longleftrightarrow} \mathrm{HClO_2} \tag{Rd}$$

$$\mathrm{HClO_2} + \mathrm{US} \xrightarrow{k_\mathrm{U}} \mathrm{ClO_2}\cdot + \mathrm{H}\cdot \tag{R7}$$

If without pollutants:

$$K = \frac{k_\mathrm{d}}{k_{-\mathrm{d}}} = \frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{[\mathrm{HClO_2}]}$$

$$\frac{\mathrm{d}[\mathrm{ClO_2}]}{\mathrm{d}t} = \frac{k_\mathrm{U}[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}$$

If with pollutants:

$$\mathrm{ClO_2} + \mathrm{genV} \xrightarrow{k_\mathrm{iii}} \mathrm{P_3} \tag{Riii}$$

Therefore:

$$\frac{\mathrm{d}[\mathrm{genV}]}{\mathrm{d}t} = -k_\mathrm{iii}[\mathrm{genV}][\mathrm{ClO_2}]$$

$$k_\mathrm{obs} = k_\mathrm{iii}[\mathrm{ClO_2}]$$

(3) For HUAC system:

$$\frac{\mathrm{d}[\mathrm{ClO_2}]}{\mathrm{d}t} = \frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{K}[(k_1 + k_4)[\mathrm{HOFe^{III}}] + k_\mathrm{U}]$$

$$[\mathrm{ClO_2}] = \frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{Kk_\mathrm{iii}[\mathrm{genV}]}[(k_1 + k_4)[\mathrm{HOFe^{III}}] + k_\mathrm{U}]$$

$$[\mathrm{ClO_2}] = w\frac{[\mathrm{ClO_2^-}][\mathrm{H^+}]}{1-\eta}[(k_1 + k_4)[\mathrm{HOFe^{III}}] + k_\mathrm{U}]$$

$$r_\mathrm{HUAC} = \varphi_1 r_\mathrm{HUC} + \varphi_2 r_\mathrm{HAC} = [\mathrm{ClO_2^-}][\mathrm{H^+}](\omega_1 + \omega_2[\mathrm{HOFe^{III}}])$$

Table S1 The coupling effect of system.

Name	Values
$S_{\mathrm{U+A}}$	27.23
S_{A}	20.35
S_{A}' (U→A effect)	1.47
S_{U}	18.58
S_{U}' (A→U effect)	1.34

$$S_i = \frac{r_{\mathrm{app}\,j}}{r_{\mathrm{app}\,j-i}}$$

Table S2 The spectrum list of PMSO during GC/MS detection.

m/z	Intensity	Relative
50.22	3.96509E6	18.76
51.11	1.28649E7	60.88
53.13	2.64345E6	12.51
63.1	1.59944E6	7.57
65.12	4.36282E6	20.64
69.06	1.73398E6	8.21
74.1	2.03991E6	9.65
75.1	1.29512E6	6.13
77.12	1.39032E7	65.79
78.15	2.13469E6	10.1
81.11	1.70779E6	8.08
91.14	1.96125E6	9.28
94.13	4.5428E6	21.5
97.09	1.63177E7	77.21
109.1	1.43947E6	6.81
124.12	1.33939E6	6.34
125.09	2.11331E7	100
126.12	1.55568E6	7.36
140.11	1.73347E7	82.03
141.13	1.4168E6	6.7

Table S3 The spectrum list of $PMSO_2$ during GC/MS detection

m/z	Intensity	Relative
50.21	2.22253E6	8.01
51.11	8.37741E6	30.21
52.14	470859.3	1.7
63.1	671879.6	2.42
65.12	2.80328E6	10.11
66.14	428952	1.55
74.11	1.0722E6	3.87
75.14	638031.1	2.3
76.12	611561.3	2.21
77.13	2.77347E7	100
78.14	2.01236E6	7.26
84.05	491404.7	1.77
91.15	435482.1	1.57
93.14	1.51527E6	5.46
94.13	9.52138E6	34.33
95.14	643784.3	2.32
97.1	580499.9	2.09
141.07	5.34416E6	19.27
142.1	425077.4	1.53
156.1	4.34979E6	15.68

Table S4 The possible reactions in the system.

R#	Reaction	Second-order rate constant
Rd	$ClO_2^- + H^+ \leftrightarrow HClO_2$	$K = k_d/k_{-d}$
R1	$HOFe^{III} + HClO_2 \rightarrow Fe^{III}ClO_2 + H_2O$	k_1
R2	$HOFe^{II} + HClO_2 \rightarrow (O)Fe^{IV} + ClO^-$	k_2
R3	$Fe^{III}ClO_2 \rightarrow (O)Fe^{IV} + [ClO]$	k_3
R4	$Fe^{III}ClO_2 \rightarrow (O)Fe^{V+\cdot} + ClO^-$	k_4
R5	$(O)Fe^{V+\cdot} + ClO_2^- \rightarrow (O)Fe^{IV} + ClO_2$	k_5
R6	$(O)Fe^{IV} + HClO_2 \rightarrow HOFe^{III} + ClO_2$	k_6
R7	$HClO_2 + US \rightarrow ClO_2\cdot + H\cdot$	k_U
Ri	$(O)Fe^{IV} + genV \rightarrow P_1$	k_i
Rii	$(O)Fe^{V+\cdot} + genV \rightarrow P_2$	k_{ii}
Riii	$ClO_2 + genV \rightarrow P_3$	k_{iii}

Table S5 The comparison between k and r_{app} values under different $\mathrm{H^+}$ roles

$c(\mathrm{H^+})$ (mmol/L)	$1/c(\mathrm{H^+})$ ($(\mathrm{mmol/L})^{-1}$)	k-2^{nd}/R^2-adj		r_{app}
0.12	8.33	0.0027	0.99932	0.282
0.16	6.25	0.00628	0.99947	0.466
0.20	5.00	0.01555	0.99670	0.596
0.28	3.57	0.02438	0.99921	0.708
0.36	3.44	0.03487	0.99993	0.761

Table S6 Economic comparison of different AOPs for treatment of wastewater.

Different AOPs	Pollutant	*EE/O* (kWh/m^3)	Conditions	Refs.
US/Fe$_b$HCs/COI	genV	4.92	ibid. Fig. 2	Present study
VL/COI	BZF	886.2	Simulated solar light 300 W xenon arclamp, COI 0.1 mM, BZF 5 μM	[S1]
US/Fe^0_f/PS	AG	12.4	AG 50 μM, Fe^0_f 0.214 mM, PS 1.45 mM, I$_{US}$ 30 W/L	[S2]
HC@O$_3$	OA	58.7	OA 1.11 mM, pH 3, HC power 192 W, O$_3$ power 85 W	[S3]
HC@PS@O$_3$	OA	32.1		
HC@PS	OA	41.5		
US/Fe^0/PS	SMT	131.4	SMT 5 mg/L, pH 7, PS 1 mM, Fe^0 0.1 mM, US 60 W	[S4]
US/pre-Fe^0/PS		41.8		
US/Fe^0/PS	SD	185.7	20 mg L^{-1} SD, US 60 W/L, Fe^0 1 mM, PS 2 mM, pH 7	[S5]
US	MCHM	463.2	US 1206 W/L, $_{trans}$MCHM 1.3 μM	[S6]
US/Oxone	SMT	1500	UV power 600 W, SMT 50 mg/L, Oxone 0.6 g/L	[S7]

VL/Nd/Tm-BiVO$_4$/COI	NOR	431.1	VL: 300 W xenon lamp, COI 1.0 mM, Nd/Tm-BiVO$_4$ 30 mg/L	[S8]

a. HC: hydrodynamic cavitation, VL: visible light; Fe^0_f: foamed iron, pre-Fe^0: premagnetized Fe^0.

b. PS: persulfate

c. OA: oxalic acid, SMT: sulfamethazine, $_{trans}$MCHM: trans-4-methylcyclohexanemethanol, NOR: norfloxacin.

[S1] Yang T, Zhu M Y, An L Q, Zeng G, Fan C Q, Li J, Jiang J, Ma J (2023). Photolysis of chlorite by solar light: An overlooked mitigation pathway for chlorite and micropollutants. Water Research, 233: 119809

[S2] Xu Q H, Li Z P, You H, Li H Y, Yu Y B (2021) Foamed-Fe^0 via phase interface polishing by ultrasound to activate persulfate for treating triphenylmethane derivative. Journal of Environmental Chemical Engineering, 9: 105274.

[S3] Choi J, Cui M, Lee Y, Ma J, Kim J, Son Y, Khim J (2019). Hybrid reactor based on hydrodynamic cavitation, ozonation, and persulfate oxidation for oxalic acid decomposition during rare-earth extraction processes. Ultrasonics Sonochemistry, 52: 326–335.

[S4] Pan Y W, Zhang Y, Zhou M H, Cai J J, Tian Y S (2019). Enhanced removal of antibiotics from secondary wastewater effluents by novel UV/pre-magnetized Fe^0/H_2O_2 process. Water Research, 153: 144–159.

[S5] Zhou T, Zou X L, Mao J, Wu X H (2016). Decomposition of sulfadiazine in a sonochemical Fe-catalyzed persulfate system: Parameters optimizing and interferences of wastewater matrix. Applied Catalysis B: Environmental, 185: 31–41.

[S6] Cui D, Mebel A M, Arroyo-Mora L E, Holness H, Furton K G, O'Shea K (2017). Kinetic, product, and computational studies of the ultrasonic induced degradation of 4-methylcyclohexanemethanol (MCHM). Water Research, 126: 164–171.

[S7] Yin R L, Guo W Q, Wang H Z, Du J S, Zhou X J, Wu Q L, Zheng H S, Chang J S, Ren N Q (2018). Enhanced peroxymonosulfate activation for sulfamethazine degradation by ultrasound irradiation: performances and mechanisms. Chemical Engineering Journal, 335: 145−153.

[S8] Su R D, Huang L, Li N, Li L, Jin B, Zhou W Z, Gao B Y, Yue Q Y, Li Q (2021). Chlorine dioxide radicals triggered by chlorite under visible-light irradiation for enhanced degradation and detoxification of norfloxacin antibiotic: Radical mechanism and toxicity evaluation. Chemical Engineering Journal, 414: 128768

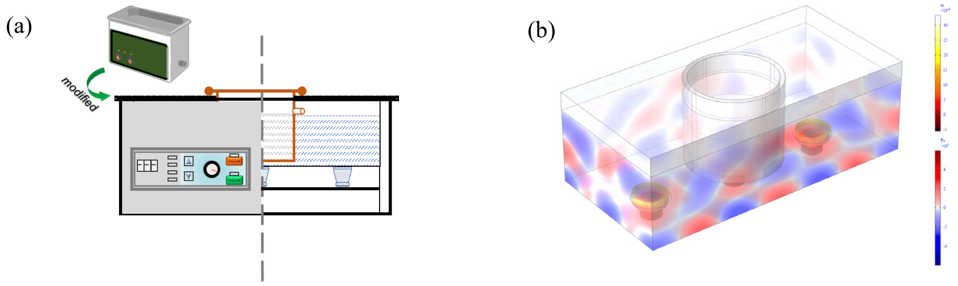

Fig. S1 (a) Schematic of the experimental reactor (bath type), and (b) 3D simulation of US field in the system.

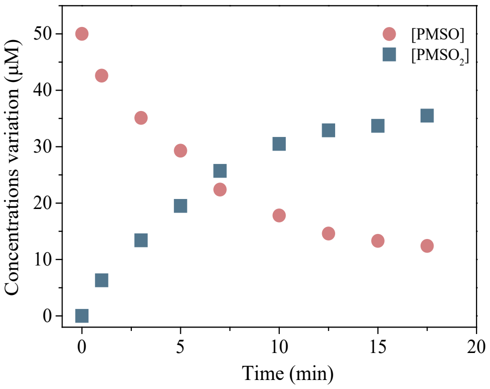

Fig. S2 PMSO and PMSO$_2$ concentrations changes in the US/Fe$_b$HCs/COI system.

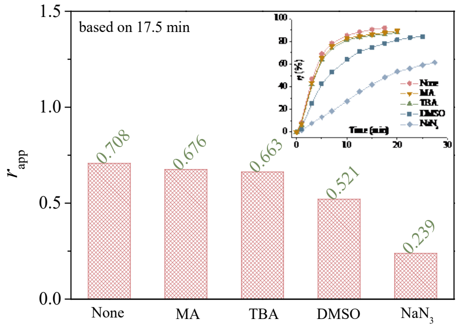

Fig. S3 Quenching experiments in the US/Fe_bHCs/COI system. [MA] = [TBA] = 0.1 M, [DMSO] = [NaN_3] = 1 mM.

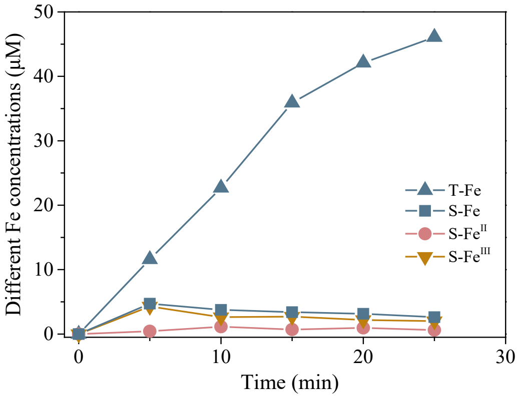

Fig. S4 Variation of various Fe concentrations in the US/Fe$_b$HCs/COI system.

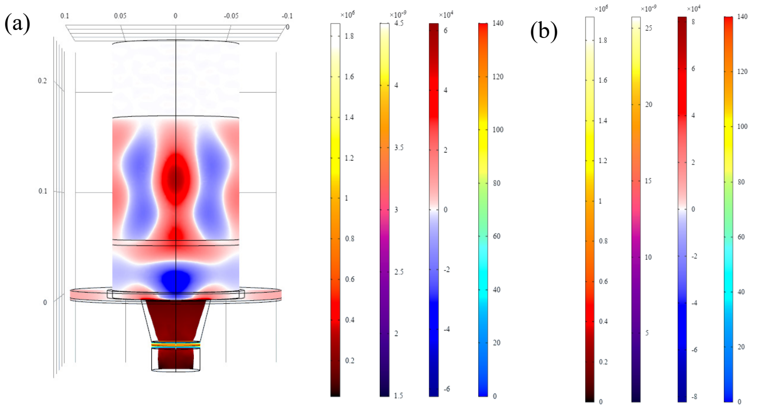

Fig. S5 (a) Simulations of acoustic-structure coupling in catalyzed device without catalytic particles, (b) The intensity regions of the simulation, here, Fig. S5b corresponding to Fig. 8d.