

Supporting Information

Influence of Reagents Addition Strategy on Fenton Oxidation of Rhodamine

B: Control of Competitive Reaction of $\bullet\text{OH}$

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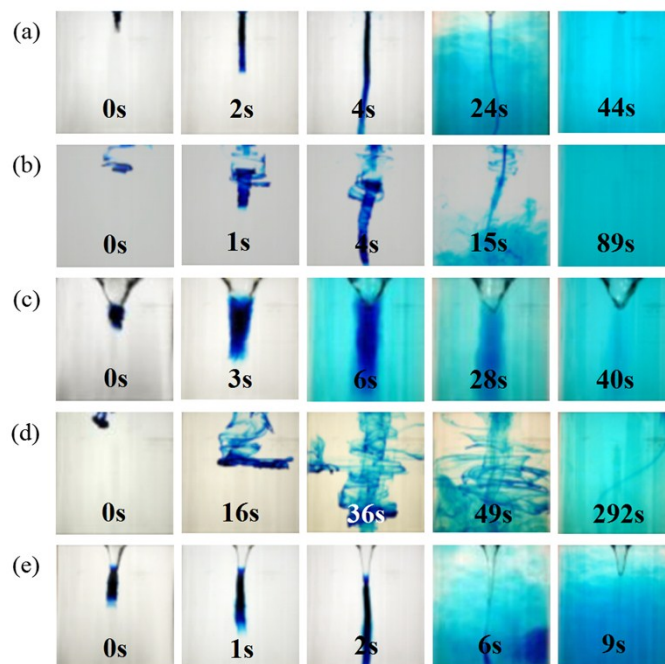
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Fig. S1 Mixing process of tracer in bulk solution by different stirrer. (a) 27mm, 500 rpm; (b) 27 mm, 100 rpm; (c) 48 mm, 500 rpm; (d) 10mm, 500 rpm; (e) 27mm, 1000 rpm.



As Fig. S1(d) shown, stirrer with length of 10 mm could not disperse tracer in a certain route, which can not strictly control the reagent diffusion process. As Fig. S1(c) shown, stirrer with length of 48 mm disperse tracer violently, also making it difficult to control the process.

1 Moreover, in this work, 48 mm stirrer with 1500 rpm couldn't work, as liquids may spill over.

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4 **Table S1** pH change in Fenton system by different addition approaches. Conditions: $[H_2O_2]=30$
5 mM; $[Fe^{2+}]=0.5$ mM; $[RhB]=0.2$ mM; initial pH 3.0; T=25°C.

Addition Approach	0 min	2.5 min	5 min	7.5 min	10 min	15 min	20 min	25 min	30 min
A1	3.08	3.09	3.09	3.08	3.07	3.06	3.05	3.06	3.07
A2	3.06	3.06	3.07	3.07	3.08	3.07	3.08	3.08	3.07
A3	3.05	3.04	3.05	3.05	3.06	3.07	3.07	3.07	3.08
A4	3.02	3.09	3.10	3.11	3.11	3.11	3.12	3.12	3.07
a1	3.00	3.02	3.05	3.06	3.07	3.06	3.06	3.05	3.06
a2	2.99	3.00	2.99	3.00	3.01	3.01	3.01	3.02	3.01
a3	3.00	2.98	2.99	3.00	3.02	3.03	3.02	3.02	3.04
B1	3.02	3.04	3.05	3.04	3.03	3.03	3.04	3.05	3.04
B2	2.96	2.96	2.97	2.98	2.97	2.99	2.98	2.99	2.98
B3	2.99	3.00	3.01	3.00	3.00	3.00	3.01	3.02	3.02
B4	3.05	3.04	3.04	3.05	3.06	3.06	3.06	3.05	3.06
b1	3.05	3.06	3.05	3.05	3.06	3.06	3.07	3.06	3.07
b2	3.00	3.01	3.00	3.00	3.02	3.04	3.02	3.02	3.02
b3	3.02	3.02	3.03	3.03	3.02	3.03	3.04	3.03	3.04
C1	3.00	3.05	3.05	3.04	3.05	3.05	3.06	3.07	3.06
c2	3.00	3.04	3.05	3.05	3.06	3.05	3.07	3.06	3.06
c3	3.02	3.04	3.05	3.05	3.06	3.06	3.05	3.06	3.06

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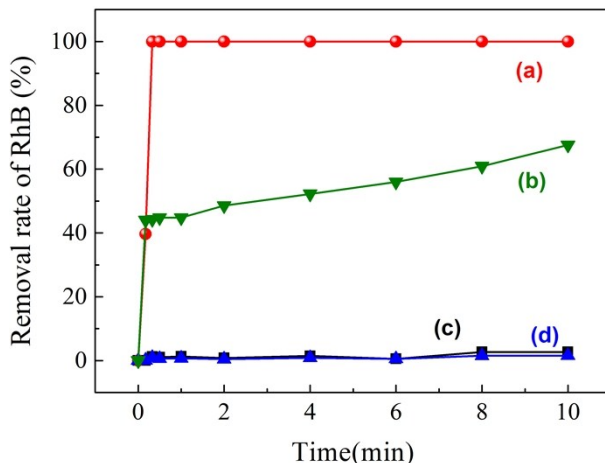
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1 **Fig. S2** Removal rate of RhB in different systems. (a) Fenton-1,4-BQ system; (b) Fenton system;
2 (c) H₂O₂ system; (d) Fenton-DMSO system. Conditions: [H₂O₂]=30 mM; [Fe²⁺]=0.5 mM;
3 [RhB]=0.2 mM; [DMSO]=60 mM; [1,4-BQ]=60 mM; initial pH 3.0; T=25°C.



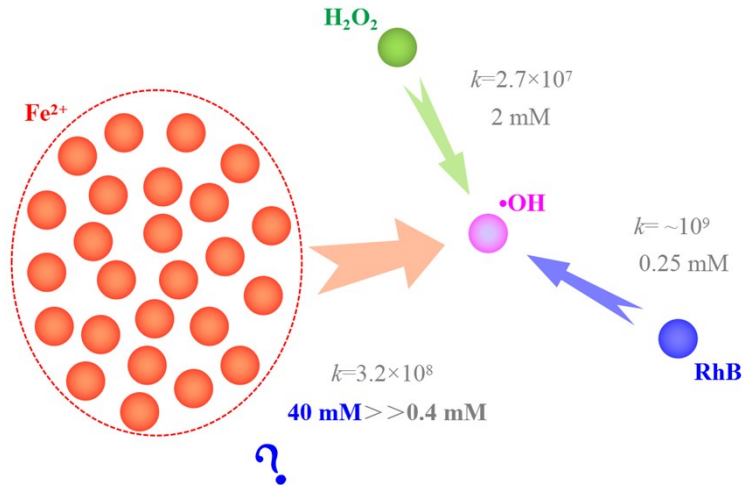
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5 DMSO was used to trap •OH^[1], 1,4-BQ was used to trap HO₂• (rate constant $k=1.0\times 10^9$ M⁻¹ s⁻
6 ¹)^[2]. As Fig. S1 shown, RhB can't be removed by H₂O₂. Once •OH was captured, RhB can't be
7 removed by Fenton-DMSO system. Results of (a) further showed that once HO₂• was captured
8 and generation of •OH was enhanced, the removal of RhB could be accelerated. The above
9 results suggested that •OH is the major species for RhB removal.

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12 **Calculation 1** The temporary localized concentration of Fe²⁺ by one drop by one drop addition of
13 20 mL Fe²⁺ solution to H₂O₂ bulk solution.



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2 Conditions: $[H_2O_2]=2$ mM; $[Fe^{2+}]=0.4$ mM; $[RhB]=0.25$ mM; initial pH 3.0; $T=25^\circ C$. The
 3 volume of bulk solution is 2000 mL, 20 mL Fe^{2+} solution was added to bulk solution one drop by
 4 one drop without stirring.

5 What should be noted is that the above conditions shows the concentration of different species
 6 only when they are uniformly dispersed in bulk solution. Once Fe^{2+} solution was added one drop
 7 by one drop, the localized Fe^{2+} concentration is absolutely not 0.4 mM. After a long time, the
 8 localized Fe^{2+} diffused to bulk solution, resulting in a Fe^{2+} concentration of 0.4 mM.

9 The concentration of Fe^{2+} in 20 mL solution is calculated as follows:

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$$C = \frac{2000mL + 20mL}{20mL} \times 0.4mM = 40.4mM$$

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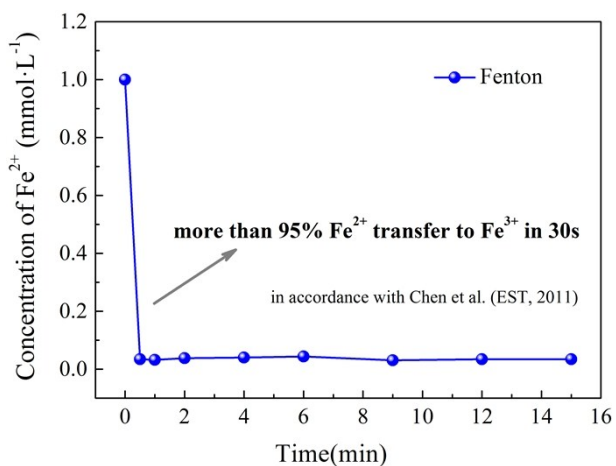
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1 **Fig. S3** Change of Fe^{2+} concentration in typical well mixed Fenton system.



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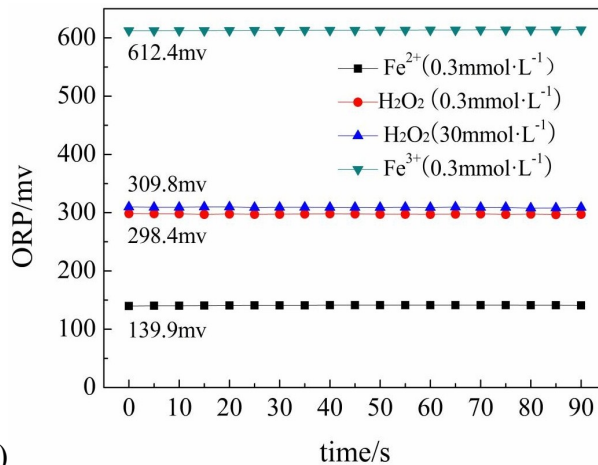
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5 **Fig. S4** (a) The oxidation-reduction potential (ORP) of different substances in Fenton system. (b)

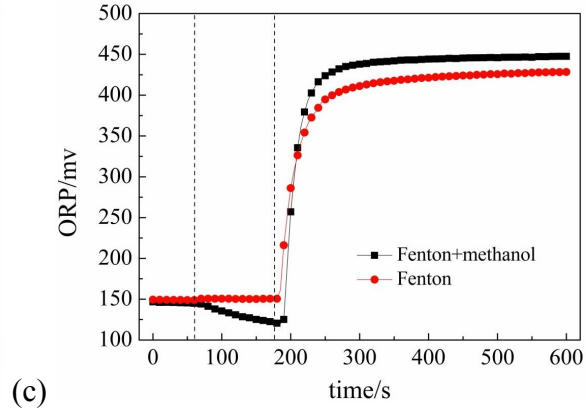
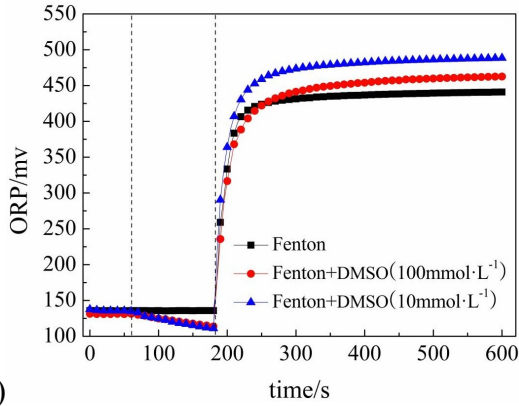
6 Influence of hydroxyl capture agent (dimethyl sulfoxide, DMSO) on solution ORP. (c) Influence

7 of hydroxyl capture agent (methyl alcohol) on solution ORP.



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(a)



1 (b)

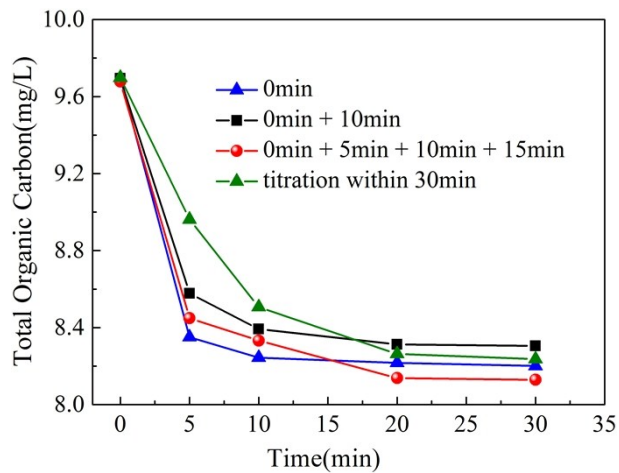
(c)

2 (a) showed that Fe^{3+} is the major substances contribute to solution ORP. (b) and (c) showed
 3 that $\bullet\text{OH}$ isn't a contributor of solution ORP. Since $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycle is one of the focus of Fenton's
 4 research, which directly determines the generation of $\bullet\text{OH}$ and hence, ORP could act as a way to
 5 show the difference between different adding approaches of Fenton's reagents.

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8 **Fig. S5** The TOC removal during the degradation of 0.25mM RhB. (Run A1, A2, A3, and A4.
 9 The liquid sample was diluted by 10 times)



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11 Once generated, $\bullet\text{OH}$ attack RhB molecules, causing color removal and mineralization.
 12 Decrease of Absorbance at 554 nm is a measure of color removal, and TOC is a measure of RhB
 13 mineralization. In this work, decolorization of 50%~98% was achieved. However, only a small
 14 proportion of RhB mineralized (lower than 16.5%). Fig. S2 suggested that $\bullet\text{OH}$ mainly

1 contributed to decolorization of RhB. During 30 min, no significant difference of TOC removal
2 was observed among A1, A2, A3, and A4.

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5 **References:**

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