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# **Supplementary Information**

# Insight of bicarbonate involved efficient heterogeneous Fenton-like degradation of

sulfamethoxazole over CuFeO2 based composite under alkaline conditions

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Fig. S9 The degradation of NPA in SC@CuFeO<sub>2</sub>/(H<sub>2</sub>O<sub>2</sub>+NaHCO<sub>3</sub>) catalytic system (Conditions:

 $[NPA] = 10 \ \mu m; [SC@CuFeO_2] = 0.3 \ g/L; [H_2O_2] = 50 \ mM; [NaHCO_3] = 15 \ mM).$ 

**Fig. S10** Effect of different temperature on degradation of SMX: (a) and (d); Corresponding pseudofirst-order kinetic rate plot of SMX degradation: (b) and (e); Calculation of activation energy by the plot of lnk against 1/T for a range of temperatures: (c) and (f).

**Fig. S11** (a) GC/MS spectrum analysis after SC@CuFeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>+NaHCO<sub>3</sub> catalytic reaction; (b) Ion chromatograph for inorganic ions analysis after SC@CuFeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>+NaHCO<sub>3</sub> catalytic reaction; (c) Ion chromatograph for standard inorganic ions analysis.

Fig. S12 GC-MS/MS spectrum analysis after SC@CuFeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>+NaHCO<sub>3</sub> catalytic reaction.

Fig. S13 (a) Stability of SC@CuFeO<sub>2</sub> in the multicycle degradation of SMX in the presence of

 $H_2O_2 + NaHCO_3$ ; XRD (b) and SEM images (c) after catalytic reaction.

**Fig.S14** Toxicity tests during SMX degradation process in SC@CuFeO<sub>2</sub>/(NaHCO<sub>3</sub>+H<sub>2</sub>O<sub>2</sub>) catalytic system.

Table S1. Summary of various ways to remove SMX in the presence of HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>.

Table S2 Accurate mass measurements of by-products of SMX during its catalytic process.

### Text S1

**Electrochemical characterization.** The electrochemical tests were conducted with a CHI660C electrochemical work station (Chenhua, China) and a three-electrode cell containing a glassy carbon electrode as the working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. Na<sub>2</sub>SO<sub>4</sub> solution (0.1 M, 50 mL) was used as the working solution and replaced after each test. Specifically, the glassy carbon electrode was polished with 0.30 and 0.05  $\mu$ m alumina slurry sequentially and was left dried at ambient temperature. Then 4 mg CuFeO<sub>2</sub> and SC@CuFeO<sub>2</sub> were well disperse into a mixture of 0.8 mL water and 0.2 mL isopropanol containing 30  $\mu$ L Nafion solutions. Then, 5  $\mu$ L of the suspension was cast on the surface of the glassy carbon electrode and allowed to dry in air. And the tafel plot were recorded in a potential range from -1 to 1 V. While the impedance resistance spectra were collected at a frequency from100 kHz to 0.1 Hz under the open circuit potential.

#### Text S2

**Determination of the concentration of hydroxyl radicals.** The principle of hydroxyl radical determination is using the reaction between benzoic acid (BA) and hydroxyl radical to generate p-hydroxybenzoic acid (p-HBA), then the concentration of hydroxyl radical can be calculated through Eq. (1). The p-HBA concentration was measured by HPLC (Ultimate 3000) using C18 column at the wavelength of 255 nm. The mobile phases were mixture of phosphate solution (pH=2.6) and acetonitrile (35% *vs* 35%) with the injection volume of 20  $\mu$ L and flow rate of 0.8 mL/min. And the corresponding curve of p-HBA concentration and peak area can be shown in Fig. S2.

Cummulative  $[^{\bullet}OH]$  produced =  $[p - HBA] \times 5.87$  (1)

#### Text S3

**GC-MS-MS analysis.** The GC-MS-MS analysis was carried out using a temperature ramp of 80 °C for 1.0 min and 10 °C min<sup>-1</sup> up to 280 °C for 6 min. The helium (carrier gas) flow rate was 1.0 mL min<sup>-1</sup> and the time of each analysis was 27 min. Before each analysis, the HLB cartridge was conditioned with methanol (5.0 mL) and deionized water (5.0 mL). After that, a volume of 10 mL was removed from the wastewater reservoir and then percolated through the HLB cartridge followed by drying with N<sub>2</sub> for 20 min. Finally, the aliquot of each extract was diluted to 1 mL with acetone and eluted through the TG-5 MS cartridge then separately in different portions for injection.

### Text S4

**EPR tests**. EPR experiments were performed on a JES-FA200 EPR spectrometer: temperature 298 K; microwave frequency 9.146 GHz; microwave power 3 mW and modulation amplitude 0.5 mT. The generated 'OH and  $O_2^{-}$  in two different catalytic systems (SC@CuFeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>+NaHCO<sub>3</sub> and SC@CuFeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>) were identified using DMPO (20 mM) as spin-trapping agent. And methanol was used as reaction solution for  $O_2^{-}$  detection test, because of its disproportionation in water. While  $^{1}O_2$  was identified using TEMP as spin-trapping agent with its concentration of 2.7 g/L. Catalyst reactions were scaled down to1 mL and filtered using 0.45 µm filter before tests. Then, a quartz capillary tube was used to suck up the mixed DMPO or TEMP solution to detect spin-trapping adducts in the EPR spectrometer.

#### Text S5

**Toxicity test methods.** The toxicity of SMX degradation byproducts had been studied by evaluating the growth inhibition efficiency of Vibrio fischeri. And the Vibrio fischeri were bought form Yangtze Delta Region Institute of Tsinghua University, Zhejiang. Samples withdrawn at different time were added to the Vibrio fischeri growth medium with the same initial concentration. After reaction for 5 min at 15°C, the toxicity was expressed as the light inhibition ratio and calculated as Eq. 2. I<sub>ct</sub> is the luminescence intensity of control sample, and I<sub>t</sub> is the luminescence intensity of the sample at different reaction time.

Light inbibition%
$$(H_t) = \frac{I_{ct} - I_t}{I_{ct}} \times 100\%$$
 (2)

#### Text S6

**Relative contributions of ROS.** TBA is used to quench 'OH, p-BQ can be used to quench both 'OH and  $O_2^{\bullet}$ , while NaN<sub>3</sub> can be employed to quench 'OH and  ${}^1O_2$ . The relative contributions of 'OH,  $O_2^{\bullet}$  and  ${}^1O_2$  at different reaction time were calculated based on the differences in the amount of SMX degradation in the quenching tests. There are four sets of SMX concentrations, including: (1) the concentration in solution without adding quenching agents at reaction time t ( $C_t$ ), reflecting the amount of residual SMX and SMX degradation may be derived from all mechanisms;

(2) the concentration in solution after adding TBA at reaction time t  $\begin{pmatrix} C^{TBA} \\ t \end{pmatrix}$ , reflecting the amount of residual SMX when only 'OH has been quenched;

(3) the concentration in solution after adding TBA+p-BQ at reaction time t  $\binom{C^{TBA+p-BQ}}{t}$ , reflecting the amount of residual SMX when both 'OH and O<sub>2</sub>'- have been quenched;

(4) the concentration in solution after adding TBA+p-BQ+NaN<sub>3</sub> at reaction time t (  $C^{TBA+p-BQ+NaN3}_{t}$ ), reflecting the amount of residual SMX when •OH, O<sub>2</sub>• and <sup>1</sup>O<sub>2</sub> have been quenched.

 $C_t^{TBA}$  - Ct

Therefore, the contribution of 'OH was calculated based on ( $1 - Ct \times 100\%$ ), the

$$C^{TBA+p-BQ}_{t} - C^{TBA}_{t}$$

contribution of  $O_2^{\bullet}$  was calculated based on (  $l - Ct \times 100\%$ ), while the contribution of

$$C_{1}^{TBA + p - BQ + NaN3} - C_{t}^{MeOH}$$
  
1O<sub>2</sub> was calculated based on ( $1 - Ct \times 100\%$ ).



**Fig. S1** HPLC spectra of 10 mg/L SMX stock solution and the linear relationship between SMX concentration and the corresponding peak area.



**Fig. S2** The HPLC spectra of p-HBA raw solution and the linear relation diagram between different concentrations of p-HBA and corresponding peak area.



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Fig. S4 XPS spectra of SC@CuFeO<sub>2</sub> before and after reaction: (a) Fe 2p; (b)Cu 2p; (c) S 2p.



Fig. S5 The Tafel plots (a) and EIS analyses (b) of CuFeO<sub>2</sub> and SC@CuFeO<sub>2</sub>.



Fig. S6 The change of reaction pH in different catalytic system.



Fig. S7 Concentration of the leaching ions during different catalytic systems.



Fig. S8 Effect of different concentration of TBA on the degradation of SMX: (a)SC@CuFeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> catalytic system and (b) SC@CuFeO<sub>2</sub>/(H<sub>2</sub>O<sub>2</sub> + NaHCO<sub>3</sub>) catalytic system.



**Fig. S9** The degradation of NPA in SC@CuFeO<sub>2</sub>/(H<sub>2</sub>O<sub>2</sub>+NaHCO<sub>3</sub>) catalytic system (Conditions: [NPA]= 10 μm; [SC@CuFeO<sub>2</sub>]=0.3 g/L; [H<sub>2</sub>O<sub>2</sub>]= 50 mM; [NaHCO<sub>3</sub>]=15 mM).



**Fig. S10** Effect of different temperature on degradation of SMX: (a) and (d); Corresponding pseudofirst-order kinetic rate plot of SMX degradation: (b) and (e); Calculation of activation energy by the plot of lnk against 1/T for a range of temperatures: (c) and (f).



Fig. S11 (a) GC/MS spectrum after SC@CuFeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>+NaHCO<sub>3</sub> catalytic reaction; (b) Ion chromatograph for inorganic ions analysis after SC@CuFeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>+NaHCO<sub>3</sub> catalytic reaction; (c) Ion chromatograph for standard inorganic ions analysis.



Fig. S12 GC-MS/MS spectrum analysis after SC@CuFeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>+NaHCO<sub>3</sub> catalytic reaction.



Fig. S13 (a) Stability of SC@CuFeO<sub>2</sub> in the multicycle degradation of SMX in the presence of  $H_2O_2 + NaHCO_3$ ; XRD (b) and SEM images (c) after catalytic reaction.



Reaction time (min)

Fig. S14 Toxicity tests during SMX degradation process in  $SC@CuFeO_2/(NaHCO_3+H_2O_2)$  catalytic system.

Catalysts	Operation conditions	Degradation/ Reaction rate	Reasons for promoting or inhibiting its catalytic activity	Reference
Fe /TiO <sub>2</sub> +UV +HCO <sub>3</sub> -	[Cat]=1 g/L, [SMX] <sub>0</sub> =234 ug/L, UV:100Wxenon, [HCO <sub>3</sub> -]= 2 g/L;	0.15 vs 0.03 min <sup>-1</sup> (Blank)	CO <sub>3</sub> → have longer lifetime and more chances to diffuse away from the catalyst surface and react with SMX in the interfacial region	Tsiampalis at.al [1]
LaFeO <sub>3</sub> +H <sub>2</sub> O <sub>2</sub> +CO <sub>3</sub> <sup>2-</sup>	[LaFeO <sub>3</sub> ]=1.4 g/L, [SMX] <sub>0</sub> =3 mg/L, [H <sub>2</sub> O <sub>2</sub> ]=100μM, [CO <sub>3</sub> <sup>2-</sup> ]=1 mg/L;	0.002 <i>vs</i> 0.029 min <sup>-1</sup> (Blank)	The significant retardation caused by CO <sub>3</sub> <sup>2-</sup> may be due to their quencher for •OH radicals	Nie at.al [2]
TiO <sub>2</sub> +UV + HCO <sub>3</sub> -	[Cat]=0.3 mM, [SMX] <sub>0</sub> =200 µg/L, UV: 0.5 mW/cm <sup>2</sup> , [HCO <sub>3</sub> <sup>-</sup> ]=2 mM;	0.322 <i>vs</i> 0.544 min <sup>-1</sup> (Blank)	The inhibition of HCO <sub>3</sub> <sup>-</sup> on photocatalytic oxidation of SMX can be explained with the quenching of h <sup>+</sup> and <b>·</b> OH	Yuan at.al [3]
Co + PAA + HCO <sub>3</sub> -	[Co]=0.8 μM, [SMX] <sub>0</sub> =10 μM, [PAA]=100μM, [HCO <sub>3</sub> <sup>-</sup> ]=2 mM;	50% vs 90% (Blank)	The inhibitory effect of HCO <sub>3</sub> <sup>-</sup> in Co/PAA process would be because of the formation of unreactive Co <sup>2+</sup> - HCO <sub>3</sub> <sup>-</sup> complexes.	Wang at.al [4]
UV+ PS + HCO <sub>3</sub> -	UV: 240 W, [SMX] <sub>0</sub> =0.1mM, [PS] <sub>0</sub> =2 mM; [HCO <sub>3</sub> ·]=0.047g/L;	0.404 vs 0.735 min <sup>-1</sup> (Blank)	① OH, HCO <sub>3</sub> and CO <sub>3</sub> with lower redox potentials under alkaline conditions; ② the coexistence of OH and SO <sub>4</sub> would lead to mutual quenching.	Zhang at.al [5]
ionizing radiation(IR) +HCO3 <sup>-</sup>	IR: 0.8 kGy, [SMX] <sub>0</sub> =20 mg/L, [HCO <sub>3</sub> <sup>-</sup> ]=10 mM;	74.5% vs 91.7% (Blank)	$HCO_3$ can combine with 'OH, 'H, which scavenge 'OH and lead to a decline of 'OH concentration in the solution.	Zhuan at.al [6]
$PMS + CO_3^{2-}$	[SMX] <sub>0</sub> =10 mg/L, [PMS] <sub>0</sub> =1 mM; [CO <sub>3</sub> <sup>2-</sup> ]=20 mM;	TOC: 20% vs 2% (Blank)	The carbonate in the solution may decrease the reaction activation energy between PMS and SMX, then enhanced SMX degradation.	Sun at.al [7]
SC/CuFeO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> +HCO <sub>3</sub> -	[SC/CuFeO <sub>2</sub> ]=0.3g/L, [SMX] <sub>0</sub> =10 mg/L, [H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub> =50 mM; [HCO <sub>3</sub> <sup>-</sup> ]=20 mM;	0.037 <i>vs</i> 0.023 min <sup>-1</sup> (Blank)	•OH, $O_2$ , $O_2$ and $CO_3$ were involved in the catalytic reaction and this promoted its excellent catalytic performance.	This study

Table S1.	Summary	of various	ways to r	emove SMX	in the presence	of HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>2-</sup> .

Туре –	Mass (m/z)		Elemental formula	Proposed structure	
	Theoretical	Experimental	Elemental formula	rioposed structure	
TP1	269.0464	269.0456	$C_{10}H_{11}N_{3}O_{4}S$		
TP2	269.0464	269.0405	$C_{10}H_{11}N_3O_4S$		
TP3	93.0573	93.0523	C <sub>6</sub> H <sub>7</sub> N	NH2	
TP4	162.0093	162.0126	$C_4H_6N_2O_3S$		
TP5	299.0206	299.0302	$C_{10}H_9N_3O_6S$	O2N O	
TP6	345.0387	345.0403	$C_{12}H_{13}N_2O_8S^-$		
TP7	157.0192	157.0246	C <sub>6</sub> H <sub>7</sub> NO <sub>2</sub> S	нул-бон	
TP8	98.0474	98.0523	C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O	H <sub>2</sub> N CH <sub>3</sub>	
TP9	107.0365	107.0323	C <sub>6</sub> H <sub>5</sub> NO	NO	
<b>TP10</b>	148.0188	148.0135	$C_5H_8O_3S$	но он	
TP11	72.0569	72.0574	C <sub>4</sub> H <sub>8</sub> O	но	
<b>TP12</b>	87.0678	87.0633	C <sub>4</sub> H <sub>9</sub> NO	HO H <sub>2</sub> N CH <sub>3</sub>	

**Table S2.** Accurate mass measurements of by-products of SMX during its catalytic process.

## **Reference:**

- 1. A. Tsiampalis, Z. Frontistis, V. Binas, G. Kiriakidis and D. Mantzavinos, Degradation of sulfamethoxazole using iron-doped titania and simulated solar radiation, *Catalysts*, 2019, **9**, 612.
- Y. Nie, L. Zhang, Y. Y. Li and C. Hu, Enhanced Fenton-like degradation of refractory organic compounds by surface complex formation of LaFeO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, *J. Hazard. Mater.*, 2015, **294**, 195-200.
- R. Yuan, Y. Zhu, B. Zhou and J. Hu, Photocatalytic oxidation of sulfamethoxazole in the presence of TiO<sub>2</sub>: Effect of matrix in aqueous solution on decomposition mechanisms, *Chem. Eng. J.*, 2019, **359**, 1527-1536.
- Z. Wang, J. Wang, B. Xiong, F. Bai, S. Wang, Y. Wan, L. Zhang, P. Xie and M. R. Wiesner, Application of Cobalt/Peracetic Acid to Degrade Sulfamethoxazole at Neutral Condition: Efficiency and Mechanisms, *Environ. Sci. Technol.*, 2020, 54, 464-475.
- Y. Zhang, L. Li, Z. Pan, Y. Zhu, Y. Shao, Y. Wang and K. Yu, Degradation of sulfamethoxazole by UV/persulfate in different water samples: Influential factors, transformation products and toxicity, *Chem. Eng. J.*, 2020, **379**, 122354.
- R. Zhuan and J. Wang, Degradation of sulfamethoxazole by ionizing radiation: Kinetics and implications of additives, *Sci. Total Environ.*, 2019, 668, 67-73.
- Y. Sun, H. Xie, C. Zhou, Y. Wu, M. Pu and J. Niu, The role of carbonate in sulfamethoxazole degradation by peroxymonosulfate without catalyst and the generation of carbonate racial, *J. Hazard. Mater.*, 2020, **398**, 122827.