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4   Electronic Supplementary Information (ESI)

5   **Enhanced Fenton-catalytic efficiency by highly accessible active sites on dandelion-like**

6   **copper-aluminum-silica nanospheres for water purification**

7   *Lai Lyu[ab], Lili Zhang[a], Chun Hu*[,ab], and Min Yang[ab]*

8   [a] Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-

9   Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.

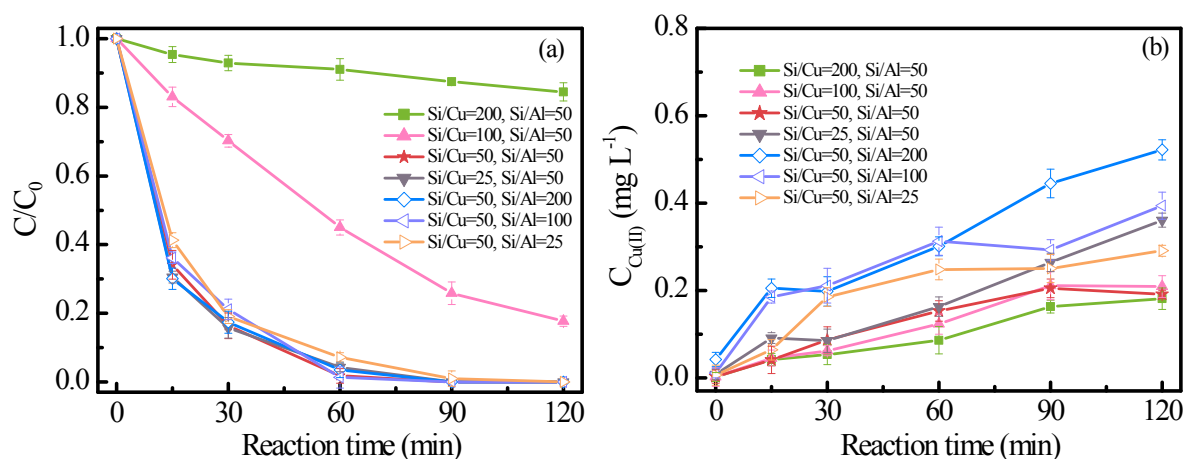10   [b] University of Chinese Academy of Sciences, Beijing 100049, China.

11   * Corresponding author. Tel.: +86 10 62849628; fax: +86 10 62923541

12   E-mail address: huchun@rcees.ac.cn (C. Hu)

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19   The Journal: **Journal of Materials Chemistry A**

20   Pages: 15, Figures: 10, Tables: 2

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Fig. S1. Effect of the Si/Cu and Si/Al mole ratios of DCAS Ns on BPA degradation with H$_2$O$_2$: a) BPA degradation curves and b) concentrations of the released Cu in the corresponding suspensions. Reaction conditions: initial pH 7, initial BPA concentration 23 mg L^{-1}, initial H$_2$O$_2$ concentration 10 mM and catalyst concentration 1.0 g L^{-1}.
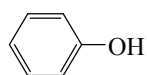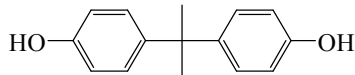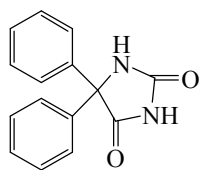
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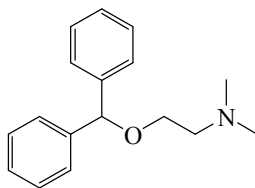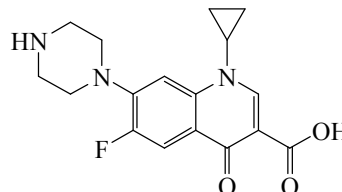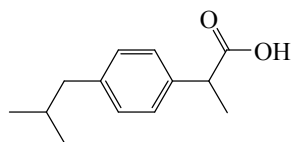phenol   bisphenol A

phenytoin   diphenhydramine   ciprofloxacin
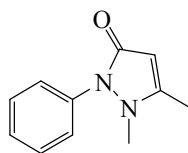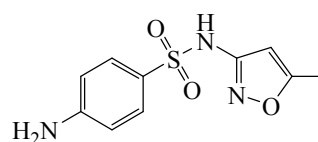
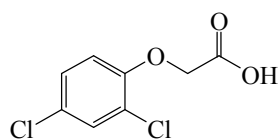ibuprofen   antipyrine   sulfamethoxazole
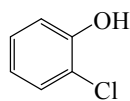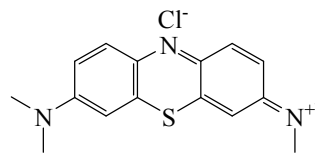
2,4-dichlorophenoxyacetic acid   2-chlorophenol   methylene blue

Fig. S2. Structures of phenol, bisphenol A, phenytoin, diphenhydramine, ciprofloxacin, ibuprofen, antipyrine, sulfamethoxazole, 2,4-dichlorophenoxyacetic acid, 2-chlorophenol and methylene blue.

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65 **Optimal Reaction Conditions.** Because the catalyst concentration and H_2O_2 dosage can

66 influence the Fenton reaction, the optimal reaction conditions were determined prior to the

67 main experiments. As shown in Fig. S3a, the reaction rate increased with an increasing

68 amount of DCAS Ns from 0.2 to 1.0 g L^{-1} and then slightly decreased. The enhancement in

69 the removal rate may be due to the increasing amount of active sites for the formation of •OH,

70 and the slight decrease in the BPA removal may be due to the agglomeration of particles and

71 scavenging of •OH by excess Cu^+.[1] Therefore, 1.0 g L^{-1} of catalyst was the optimum dosage

72 and used in all of the experiments unless otherwise specified. As shown in Fig. S3b, the

73 degradation rate increased as the H_2O_2 dosage increased from 0 to 15 mM because H_2O_2 is the

74 precursor in the reaction with Cu^+ to generate •OH. However, at a higher dosage (20 mM), the

75 degradation rate decreased, which is most likely due to the scavenging effect of •OH and

76 inhibition of copper corrosion by H_2O_2.[2] Based on the activity and economy, 10 mM H_2O_2

77 was selected and used in all of the experiments unless otherwise specified.

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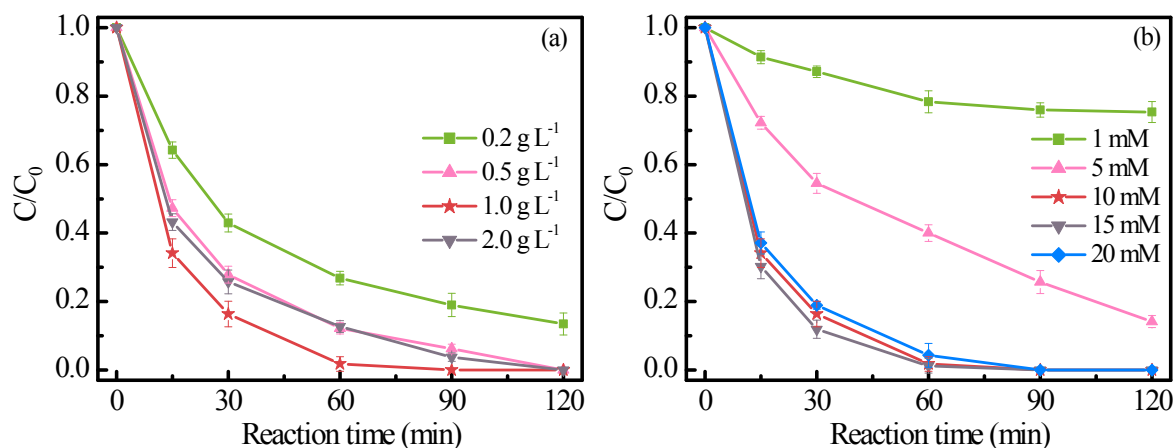
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81 **Fig. S3.** Effect of a) catalyst concentration and b) H_2O_2 concentration on BPA degradation in

82 the DCAS Ns suspension. Reaction conditions: initial pH 7, initial BPA concentration 23 mg

83 L^{-1}, initial H_2O_2 concentration 10 mM for a) and catalyst concentration 1.0 g L^{-1} for b).

84 **GC-MS Analysis.** GC-MS analysis was carried out on an Agilent 6890GC/5973MSD with a

85 DB-5 MScapillary column. The GC oven temperature program was as follows: 60 °C held for

86 2 min followed by linear temperature gradient of 6 °C min^{-1} to 280°C, which was held for 5

87 min. The samples for GC-MS analysis were prepared using the following procedure. The

88 suspension at a reaction time of 15 min was filtered, and the solid particles and the solution

89 were collected and evaporated using a freeze-drying method. Then, the residue was dissolved

90 in 2 mL of dichloromethane. After the solvent was dehydrated by anhydrous sodium sulfate,

91 trimethylsilylation was carried out at 60 °C for 30 min using 0.2 mL of BSTFA (N,O-

92 bis(trimethylsilyl)trifluoroacetamide). The precipitate was separated by centrifugation prior to

93 chromatographic analysis.

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95 **ESR measurements**: ESR spectra were recorded on a Bruker A300-10/12 ESR spectrometer

96 using BMPO as a spin trap agent at room temperature. The samples for ESR measurement

97 were prepared using the following procedure. 1g L^{-1} catalyst was added to a 0.1 mM BPA

98 aqueous solution. The suspension was stirred at room temperature for approximately 30 min

99 to establish adsorption/desorption equilibrium between the pollutant and the catalyst. Then, 10

100 mM H_2O_2 was added to the above suspension under continuous stirring. 25 mL of the

101 suspension were collected at the adsorption/desorption equilibrium point as well as at 15 min

102 after adding H_2O_2 followed by filtration. The solid particles were collected and dried at 45 °C

103 to form the powder samples. 0.01 g of the prepared powder sample was added to 1 mL of

104 water. Then, 100 μL of the above suspension, 10 μL of BMPO (250 mM) and 10 μL of H_2O_2

105 (30%, w/w) were mixed and held for 5 min for measurement.
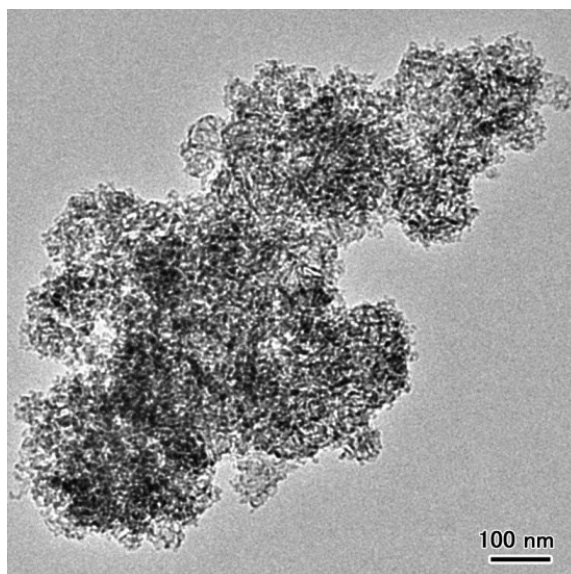
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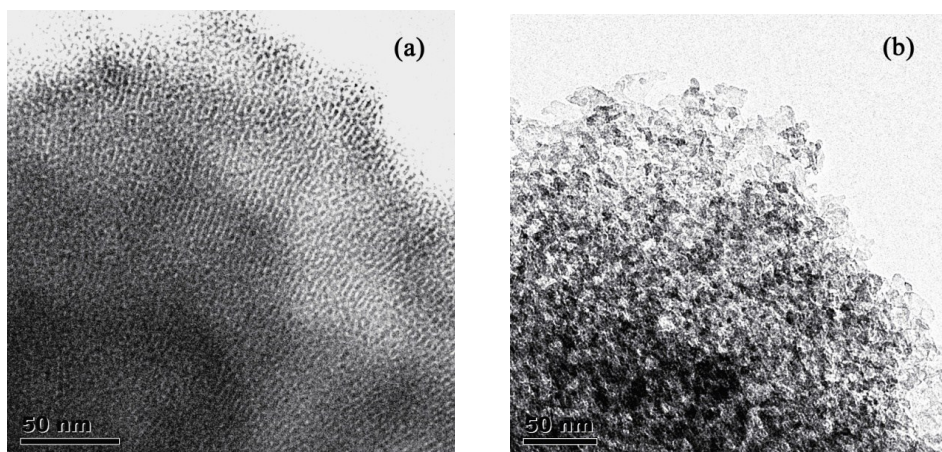**Fig. S4.** HRTEM image of DCAS Ns with Si/Cu=50 and Si/Al=25.

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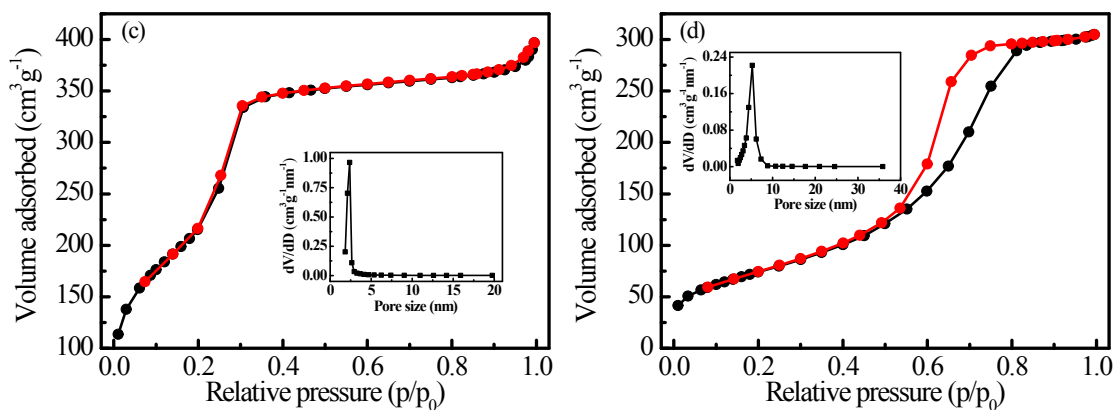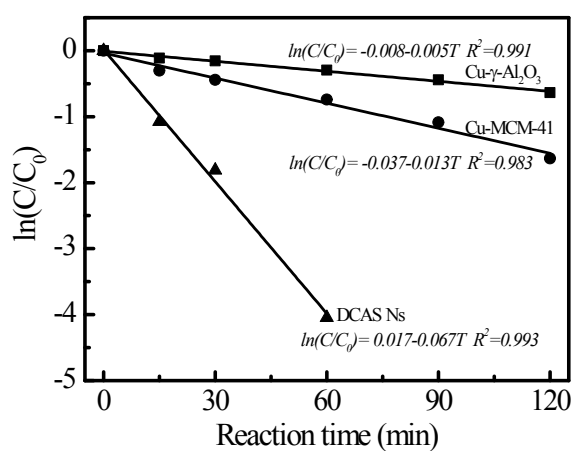122

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Fig. S5. HRTEM images of a) Cu-MCM-41 and b) Cu-γ-Al$_2$O$_3$; N$_2$ adsorption-desorption isotherms for c) Cu-MCM-41 and d) Cu-γ-Al$_2$O$_3$. Inset shows the corresponding BJH pore size distribution.
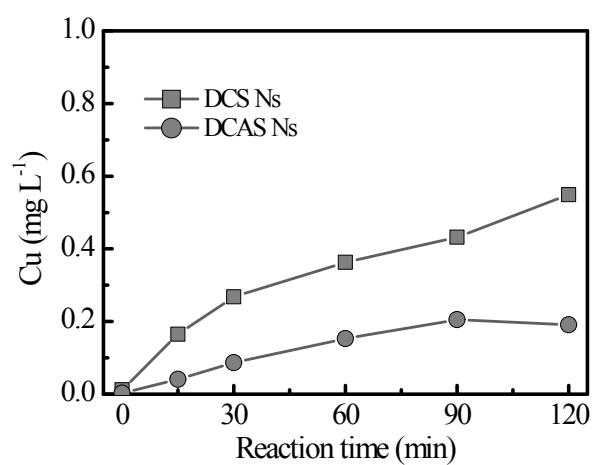
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The kinetic curves plot showing:
- $ln(C/C_0) = -0.008-0.005T$ $R^2=0.991$ Cu-γ-Al$_2$O$_3$
- Cu-MCM-41, $ln(C/C_0) = -0.037-0.013T$ $R^2=0.983$
- DCAS Ns, $ln(C/C_0) = 0.017-0.067T$ $R^2=0.993$

Y-axis: $ln(C/C_0)$, X-axis: Reaction time (min)

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Fig. S6. The kinetic curves of BPA degradation in various suspensions. Reaction conditions: initial pH 7, initial BPA concentration 23 mg L^{-1}, initial H$_2$O$_2$ concentration 10 mM and catalyst concentration 1.0 g L^{-1}.

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Fig. S7. The concentration curves of the residual Cu in the solutions of DCS Ns and DCAS Ns during the Fenton process.

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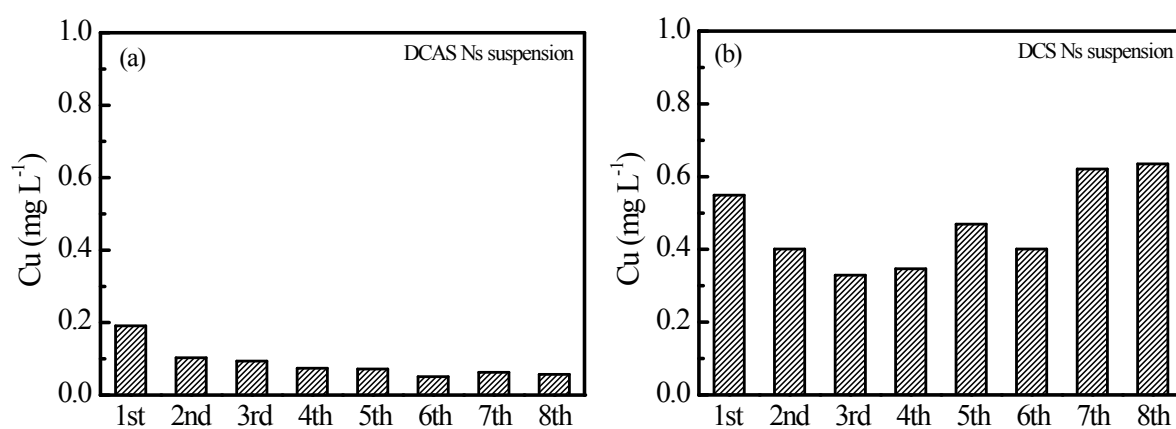
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190 **Fig. S8**. The concentrations of the residual Cu in the solutions of a) DCAS Ns and b) DCS Ns

191 after each Fenton reaction cycle.
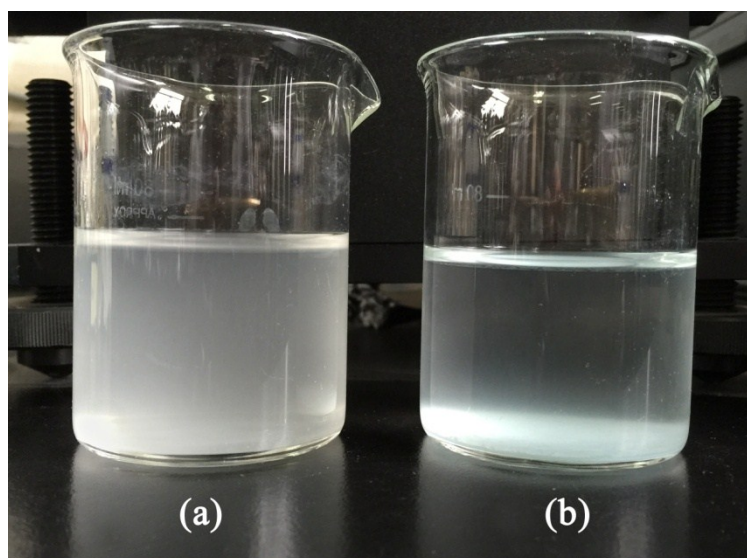
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210 **Fig. S9.** Reaction solutions of a) DCAS Ns and b) Cu-γ-Al$_2$O$_3$ without any agitation.

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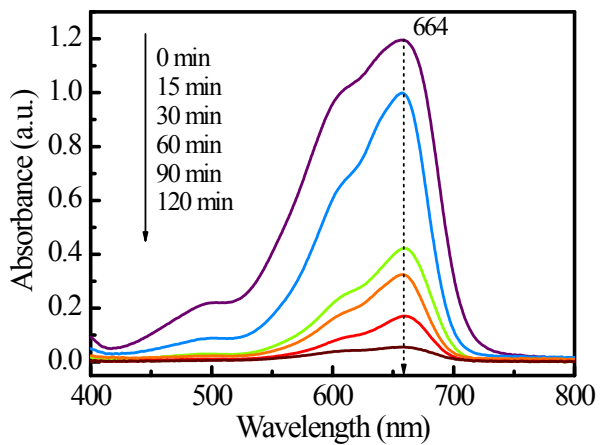
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229 **Fig. S10.** UV-Vis DRS spectral changes of methylene blue on the surface of DCAS Ns

230 recorded for DCAS Ns as a function of reaction time.

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239 **Calculation of the Utilization Efficiency of H_2O_2.** The complete mineralization of one mole

240 of BPA will theoretically consume 36 moles of H_2O_2 (eqs. S1).

241 $$C_{15}H_{16}O_2+36H_2O_2\rightarrow15CO_2+44H_2O \quad (S1)$$
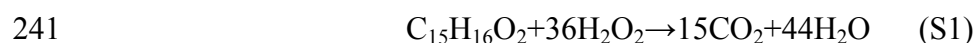
242 The utilization efficiency of H_2O_2 (η) is defined as the ratio of the stoichiometric H_2O_2

243 consumption ($[\Delta H_2O_2]_S$) for the mineralization of pollutants to the actual H_2O_2 consumption

244 ($[\Delta H_2O_2]_A$) in the Fenton-like reaction[2] and is expressed in eq. S2:

245 $$\eta= [\Delta H_2O_2]_S / [\Delta H_2O_2]_A \quad (S2)$$

246 By measuring the TOC change in the pollutant solutions, the amounts of the mineralized

247 contaminants were obtained, and the value of $[\Delta H_2O_2]_S$ was calculated. The actual H_2O_2

248 consumption ($[\Delta H_2O_2]_A$) at different reaction times was measured using the DPD method.

249 The detailed data for $[\Delta H_2O_2]_A$ and $[\Delta H_2O_2]_S$ are presented in Table S1.

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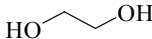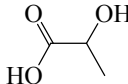
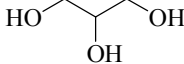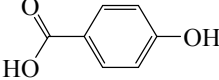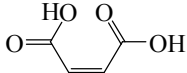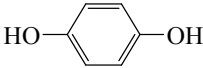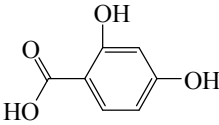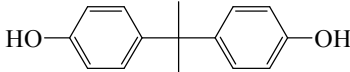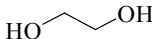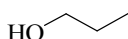251 **Table S1.** Actual H_2O_2 consumption ($[\Delta H_2O_2]_A$) and stoichiometric H_2O_2 consumption

252 ($[\Delta H_2O_2]_S$) for mineralizing BPA during the Fenton reaction.

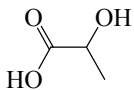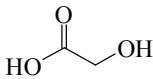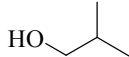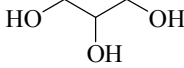| Reaction time/min	BPA (23 mg L^{-1})	
	$[\Delta H_2O_2]_A$/mM	$[\Delta H_2O_2]_S$/mM
0	0	0
15	0.65	0.60
30	1.27	1.12
60	1.79	1.55
90	2.29	1.84
120	2.96	2.19
180	3.59	2.47

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255 **Table S2.** Main products during the Fenton catalytic degradation of BPA in the DCAS Ns

256 suspension at 15 min, as detected by GC-MS.

Retention time/min	Product	Molecular structure
	Main products on the surface of DCAS Ns	
6.61	ethylene glycol	
8.33	lactic acid	
13.47	glycerine	
13.84	4-isopropylphenol	
14.17	4-hydroxybenzoic acid	
15.40	maleic acid	
16.25	hydroquinone	
17.78	2,4-dihydroxybenzoic acid	
17.93	4-hydroxyacetophenone	
33.76	bisphenol A	
	Main products in the aqueous solution	
6.58	ethylene glycol	
7.62	propyl alcohol	

8.31	lactic acid	
8.52	isopropanol	
8.71	glycolic acid	
11.20	isobutanol	
13.47	glycerine	
33.76	bisphenol A	

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References

259 1. L. J. Xu, J. L. Wang, *Environ. Sci. Technol.*, 2012, **46**, 10145−10153.

260 2. W. Luo, L. H. Zhu, N. Wang, H. Q. Tang, M. J. Cao, Y. B. She, *Environ. Sci. Technol.*,

261 2010, **44**, 1786−1791.