Electronic Supplementary Information (ESI)

Galvanic-like cells produced by negative charge nonuniformity of lattice oxygen on *d*-TiCuAl-SiO_2 nanospheres for enhancement of Fenton-catalytic efficiency

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Experimental

Chemicals and materials: BPA (≥99%) was obtained from Acros (Geel, Belgium). Cetylpyridinium bromide hydrate (CBH, 98%), catalase from bovine liver (2000-5000 units/mg protein), *N,N*-diethyl-*p*-phenylenediamine sulfate (DPD, 98%) and horseradish peroxidase (POD) were purchased from Sigma-Aldrich (St. Louis, United States). The reagent 5-tert-butoxycarbonyl 5-methyl-1-pyrroline N-oxide (BMPO) used as the spin trapping agent in the electron paramagnetic resonance studies (EPR), was purchased from the Bioanalytical Lab (Sarasota, FL). Cyclohexane (≥99.5%), n-pentanol (≥98.5%), tetraethyl orthosilicate (TEOS, 99%), hydrogen peroxide (H_2O_2, 30%, w/w) and all the other chemicals were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Deionized water was used throughout this study.

***Characterization*:** Extended X-ray absorption fine structure (EXAFS) spectra were recorded at the beam lines BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. Cu foil, CuO and Cu_2O were used as references. The samples were sealed between two layers of adhesive PVC tape. The Cu K-edge (8.979 keV) EXAFS spectra of the samples were collected under ambient conditions in transmission mode. The parameters for EXAFS measurements, data collection modes and error calculations were all controlled according to guidelines set by the International XAFS Society Standards and Criteria Committee. The EXAFS data were analyzed by the Athena program. EXAFS oscillations $\chi(k)$ were extracted using spline smoothing and weighted by k^3 to compensate for the diminishing amplitude in the high k range. The filtered k^3 weighted $\chi(k)$ were Fourier transformed (FT) to R space in the k range of 2 to 11 $Å^{-1}$. A nonlinear least-squares algorithm was applied to the EXAFS fitting with phase correlation in the R space between 1 and 4 Å for the Cu K-edge. The structural

parameters of the samples were obtained via curve fitting procedures using the FEFF8.4 code.[1]

Fenton-catalytic performance measurement: The total carbon (TC) and inorganic carbon (IC) were determined by a Shimadzu TOC-V_{CPH} analyzer using high-temperature combustion, and the total organic carbon (TOC) was automatically calculated by TC minus IC. The concentration of H_2O_2 was determined using a DPD method, as previously reported in literature.[2] The leaching of metallic ions during reaction were analyzed by ICP-OES on an OPTIMA 2000 (Perkin Elmer, U.S.A.). The reusability of *d*-TiCuAl-SiO_2 Ns was tested by recovering the catalyst through filtration. Typically, after one Fenton reaction, the catalyst was filtered out using a 0.22-μm Millipore filter. The remaining solid was washed with deionized water 5 times under neutral conditions. Then the solid sample was dried at 70 °C for 6 h and reused in the following cycle.

GC-MS analysis: The sample for GC-MS analysis was prepared using the following procedure. The *d*-TiCuAl-SiO_2 Ns suspension at the Fenton reaction time of 15 min was filtered. The solid particles and the solution were collected and evaporated using a freeze-drying method. Then, the residue was dissolved in 4 mL of dichloromethane. After the solvent was dehydrated by anhydrous sodium sulfate, trimethylsilylation was carried out at 60 °C for 30 min using 200 μL of BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide). The precipitate was separated by centrifugation prior to chromatographic analysis. GC-MS analysis was carried out on an Agilent 6890GC/5973MSD with a DB-5 MScapillary column. The GC oven temperature

program was as follows: 60 °C held for 2 min followed by linear temperature gradient of 6 °C min^{-1} to 280°C, which was held for 5 min.

Reactive oxygen species (ROS) detection: To detect the ROS, **electron spin resonance (ESR)** spectra measurement was performed. The BPA-adsorbed samples and the used samples after BPA disappearing were prepared by the following procedure. 0.8 g L^{-1} catalyst was added to a 0.1 mM BPA aqueous solution. The suspension was stirred at room temperature for approximately 30 min to establish adsorption/desorption equilibrium between the pollutant and the catalyst. Next, 12 mM H_2O_2 was added to the above suspension under continuous stirring, and 25 mL of the suspension was collected at the adsorption/desorption equilibrium point for all of the suspensions, as well as at 60 min after adding H_2O_2 for *d*-TiCuAl-SiO_2 Ns suspension and 180 min after adding H_2O_2 for *d*-Cu-SiO_2 Ns and *d*-CuAl-SiO_2 Ns suspensions followed by filtration. The solid particles were collected and dried at approximately 50 °C to form the powder samples. In a typical procedure, 0.01 g of the prepared powder sample was added to 1 mL of water or methanol. Then, 100 μL of the above suspension, 10 μL of BMPO (250 mM) and 10 μL of H_2O_2 (30%, w/w) were mixed and held for 5 min, and then the EPR spectra were recorded on a Bruker A300-10/12 EPR spectrometer using BMPO as a spin trap agent at room temperature.

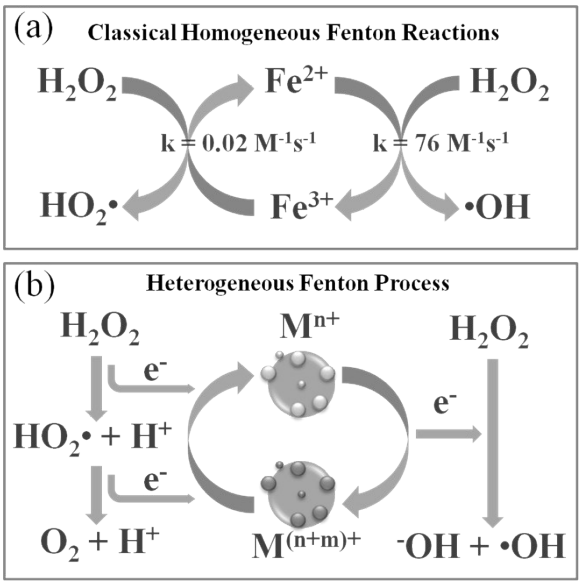
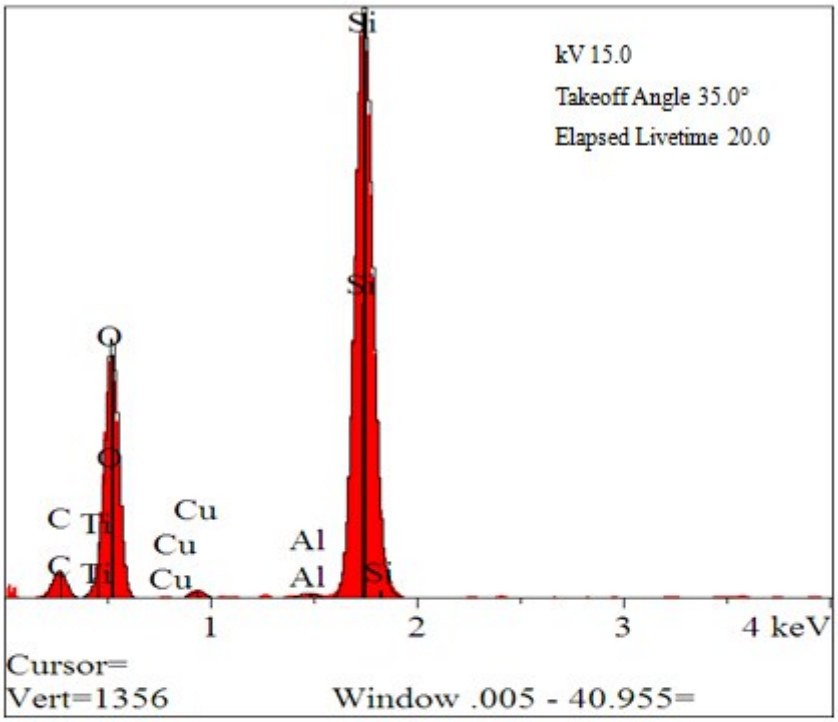


Fig. S1. Schematic diagrams for a) classical homogeneous Fenton reactions and b) heterogeneous Fenton process.



Elt.	Line	Intensity (c/s)	Atomic %	Conc	Units	Error 2-sig	MDL 3-sig	
C	Ka	26.54	23.047	14.899	wt.%	0.694	0.583	
O	Ka	244.42	49.788	42.873	wt.%	0.637	0.204	
Al	Ka	6.31	0.250	0.363	wt.%	0.057	0.121	
Si	Ka	716.08	26.216	39.629	wt.%	0.332	0.109	
Ti	Ka	4.29	0.184	0.474	wt.%	0.070	0.129	
Cu	Ka	4.28	0.515	1.762	wt.%	0.181	0.000	
			100.000	100.000	wt.%			Total

Fig. S2. The energy dispersive spectroscopy (EDS) analysis results of *d*-TiCuAl-SO_2 Ns.

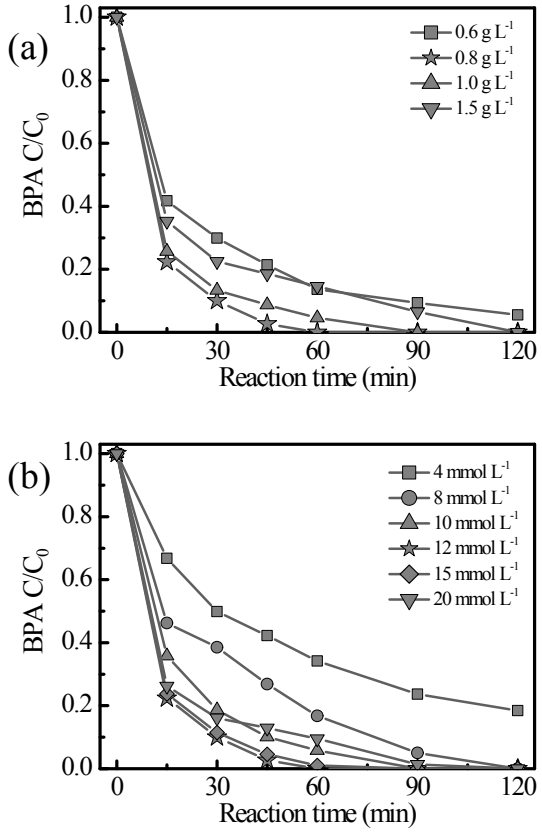


Fig. S3. Effect of (a) catalyst concentration and (b) H_2O_2 concentration on BPA degradation in the *d*-TiCuAl-SiO_2 Ns suspension. Reaction conditions: initial pH 7, initial BPA concentration 23 mg L^{-1}, initial H_2O_2 concentration 12 mM for a) and catalyst concentration 0.8 g L^{-1} for b).

Table S1 BET surface area and metal content information of various samples.

sample	BET Surface Area/m^2g^{-1}	Cu content/wt%		Al content/wt%		Ti content/wt%	
		total	surface	total	surface	total	surface
d-Cu-SiO_2 Ns	305.1	1.20	0.58	_	_	_	_
d-CuAl-SO_2 Ns	309.5	1.13	0.71	0.33	0.08	_	_
d-TiCuAl-SO_2 Ns	483.5	1.18	0.90	0.35	0	0.31	0.29

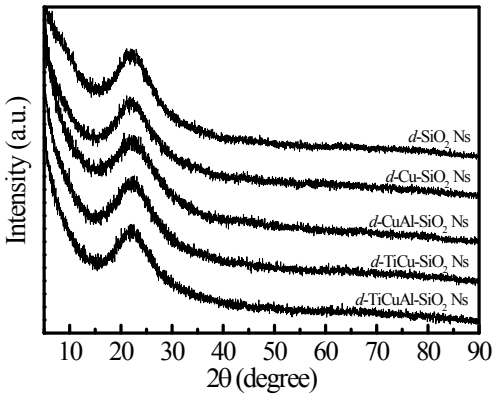


Fig. S4. XRD of the various sample.

Table S2. Comparison of the degradation of BPA by heterogeneous Fenton methods.

Entry	Catalyst	BPA Conc.	H_2O_2 dose	Conditions	Reaction time	Removal efficiency	Utilization efficiency	Ref.
1	Fe_3O_4 NPs	0.1	20	pH 5	120	19	5.2	3
2	Cu_2O MPs	0.1	20	pH 5	120	60	19.6	3
3	$CuFeO_2$ MPs	0.1	20	pH 5	120	99.2	57.8	3
4	Fe_3O_4 MNPs	~0.1	160	pH 3 ultrasonic	480	100	——	4
5	$BiFeO_3$	0.1	10	pH 5 303 K	120	20.4	——	5
6	*d*-CuTiAl-	0.1	12	ambient conditions	60	100	80.6	**This work**
7	Au/SRAC	~0.5	~16	pH 3 313 K	720	89	——	6
8	Au/Fe_2O_3	~0.5	~16	pH 3 313 K	720	10.1	——	6
9	Au-Fe_2O_3/Al_2	~0.5	~16	pH 3 313 K	720	6.6	——	6
10	*d*-CuTiAl-	0.5	20	ambient conditions	150	98.5	88.4	**This work**

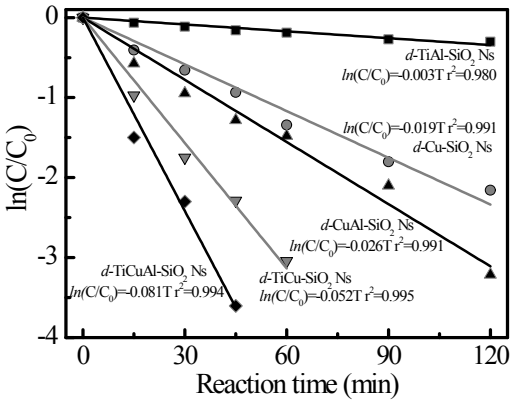


Fig. S5. Kinetic curves of BPA degradation in various suspensions (Reaction conditions: 0.1 mmol L^{-1} (23 mg L^{-1}) BPA, 12 mmol L^{-1} H_2O_2, 0.8 g L^{-1} catalyst, initial pH 7, room temperature).

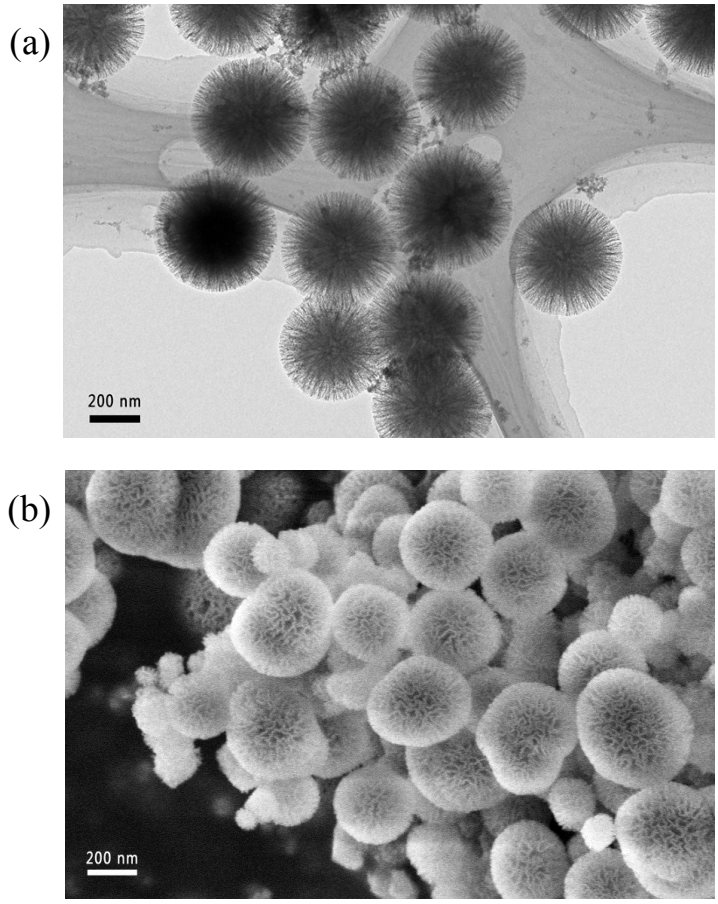


Fig. S6. (a) TEM image and (b) SEM image of *d*-TiCuAl-SiO_2 Ns after the Fenton reaction of 8 times.

Calculation of the Utilization Efficiency of H_2O_2. The complete mineralization of one mole of BPA will theoretically consume 36 moles of H_2O_2 (eqs. S1).

$$C_{15}H_{16}O_2+36H_2O_2 \rightarrow 15CO_2+44H_2O \qquad (S1)$$

The utilization efficiency of H_2O_2 (η)[7] is defined as the ratio of the stoichiometric H_2O_2 consumption ($[\Delta H_2O_2]_S$) for the mineralization of pollutants to the actual H_2O_2 consumption ($[\Delta H_2O_2]_A$) in the Fenton-like reaction and is expressed in eq. S2:

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

By measuring the TOC change in the pollutant solutions, the amounts of the mineralized contaminants were obtained, and the value of $[\Delta H_2O_2]_S$ was calculated. The actual H_2O_2 consumption ($[\Delta H_2O_2]_A$) at different reaction times was measured using the DPD method. The detailed data for $[\Delta H_2O_2]_A$ and $[\Delta H_2O_2]_S$ are presented in **Table S3**.

Table S3. Actual H_2O_2 consumption ($[\Delta H_2O_2]_A$) and stoichiometric H_2O_2 consumption ($[\Delta H_2O_2]_S$) for mineralizing BPA during the Fenton reaction.

(a) *d*-TiCuAl-SiO_2 Ns suspension

Reaction time/min	BPA (0.1 mM)	
	$[\Delta H_2O_2]_A$/mM	$[\Delta H_2O_2]_S$/mM
0	0	0
15	0.75	0.67
30	1.39	1.18
60	2.02	1.63
90	2.70	2.00
120	3.49	2.28
150	3.95	2.41
180	4.29	2.54

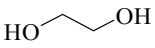
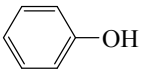
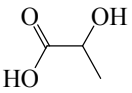
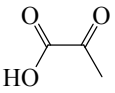
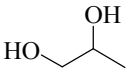
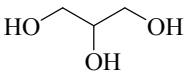
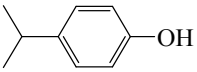
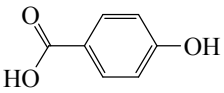
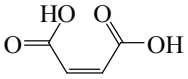
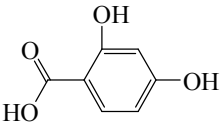
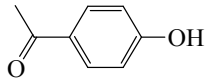
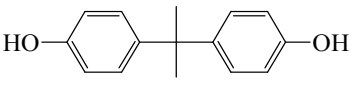
(b) *d*-CuAl-SiO_2 Ns suspension

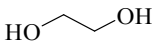
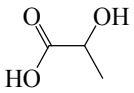
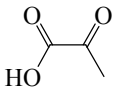
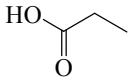
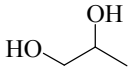
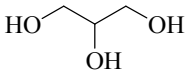
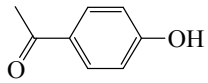
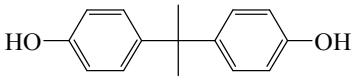
Reaction time/min	BPA (0.1 mM)	
	$[\Delta H_2O_2]_A$/mM	$[\Delta H_2O_2]_S$/mM
0	0	0
15	0.55	0.51
30	1.16	1.02
60	1.63	1.38
90	2.33	1.66
120	3.05	1.85
150	4.29	2.02
180	5.82	2.14

(c) *d*-Cu-SiO_2 Ns suspension

Reaction time/min	BPA (0.1 mM)	
	$[\Delta H_2O_2]_A$/mM	$[\Delta H_2O_2]_S$/mM
0	0	0
15	0.77	0.60
30	1.34	1.00
60	2.14	1.42
90	2.89	1.62
120	3.46	1.68
150	4.47	1.80
180	6.36	1.89

Table S4. Main products during the Fenton-catalytic degradation of BPA in the *d*-TiCuAl-SiO_2 Ns suspension at the reaction time of 15 min, as detected by GC-MS.

Retention time/min	Product	Molecular structure
Main products on the surface of the catalyst		
6.62	ethylene glycol	
8.17	phenol	
8.32	lactic acid	
8.67	pyruvic acid	
12.72	1,2-propanediol	
13.44	glycerine	
13.81	4-isopropylphenol	
14.15	4-hydroxybenzoic acid	
15.37	maleic acid	
16.63	hydroquinone	
17.76	2,4-dihydroxybenzoic acid	
18.13	4-hydroxyacetophenone	
31.00	bisphenol A	

Main products in the aqueous solution		
6.62	ethylene glycol	
8.32	lactic acid	
8.66	pyruvic acid	
11.18	propanoic acid	
12.72	1,2-propanediol	
13.45	glycerine	
18.14	4-hydroxyacetophenone	
31.01	bisphenol A	

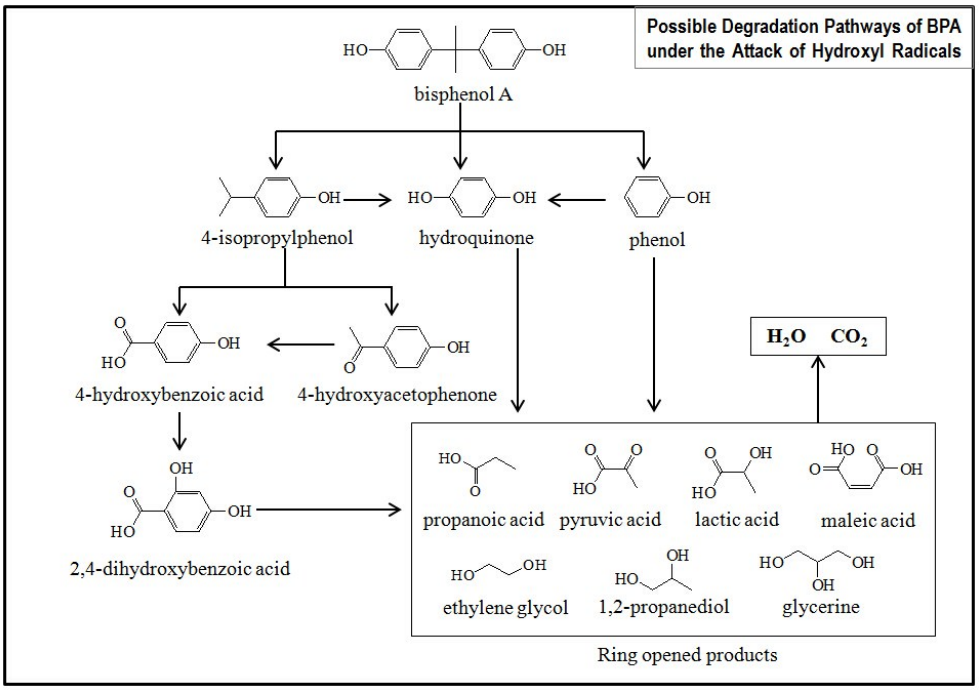


Fig. S7. Possible degradation pathways of BPA under the attack of hydroxyl radicals in the *d*-TiCuAl-SiO_2 Ns suspension with H_2O_2.

References

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