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Electronic Supplementary Information

Magnetic core-shell Fe_3O_4@Cu_2O and Fe_3O_4@Cu_2O-Cu materials as the catalysts for aerobic oxidation of benzylic alcohols assisted with TEMPO and N-methylimidazole

Binyu Xu,[a] Samuthirarajan Senthilkumar,[b] Wei Zhong,*[b] Zhongquan Shen,[b] Chunxin Lu[b] and Xiaoming Liu*[a,b]

[a]School of Chemistry, Nanchang University, Nanchang, Jiangxi, China
[b]College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing, Zhejiang, China.
Email: weizhong@mail.zjxu.edu.cn; xiaoming.liu@mail.zjxu.edu.cn

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Synthesis of Cu_2O nanoparticles:

The cubic Cu_2O nanocrystals were synthesized by following the reported procedure.[1] About 5 mL of NaOH (2.0 mol/L) was added dropwise into 50 mL of aqueous $CuCl_2$ (0.01 mol/L) at 55 ˚C. After adequate stirring for 30 minutes, 5 mL of ascorbic acid solution (0.6 mol/L) was added dropwise into the solution. The mixed solution was adequately stirred 5 hours at 55 ˚C. The resulting precipitate was collected by centrifugation and decanting, then washed with distilled water and absolute ethanol, and finally dried in vacuum at room temperature for 12 hours. The as prepared catalyst was used for the TEMPO assisted aerobic oxidation of alcohols.

Synthesis of TEMPOH:

The synthesis of TEMPOH was following the reported procedure.[2] TEMPO (0.5 g, 3.2 mmol) was added into a round flask charged with sodium ascorbate (1.0 g, 5.3 mmol) and H_2O (9 mL). Then the suspension was stirred vigorously at room temperature until completely decolorized with the appearance of a white precipitate. The resulting suspension was extracted with diethyl ether. Afterward, the ether extracts were washed with water and brine, dried over anhydrous sodium sulfate and evaporated under reduced pressure to provide TEMPOH. (white solid, 476 mg, 94.6%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.49 (s, 6H), 1.14 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 58.5, 39.4, 16.9.

Table S1 EDX analysis of the core-shell $Fe_3O_4@Cu_2O$ nanomaterial.

Catalyst	C(%)	O(%)	N(%)	Fe(%)	Cu(%)	Cu:Fe (mol. ratio)
Fe_3O_4	7.06	28.44	-	64.51	-	
Fe_3O_4/L-Lys	10.12	29.72	4.62	55.54	-	
$Fe_3O_4@Cu_2O$	14.86	21.73	1.37	12.83	49.22	3.8:1

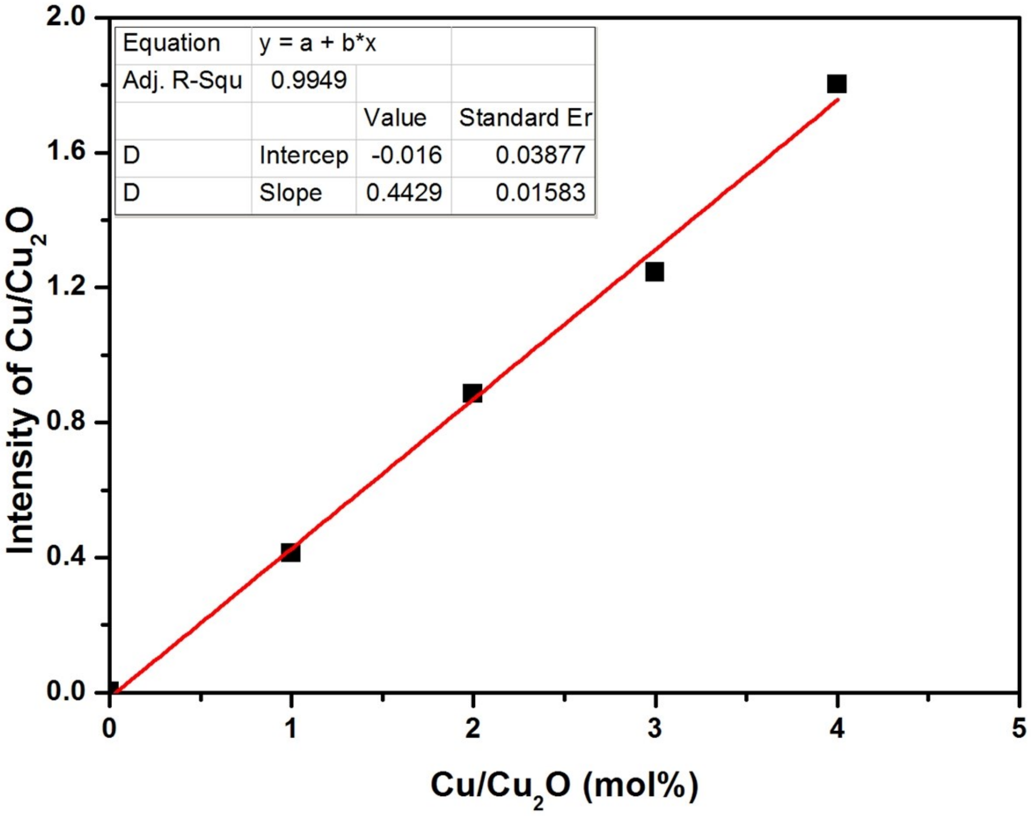

Fig. S1 Calibration curve for the calculation of Cu/Cu_2O content in Fe_3O_4@Cu_2O-Cu catalysts.

Table S2 Comparison of powder XRD strength and calculation of Cu/Cu_2O content in Fe_3O_4@Cu_2O-Cu catalysts.

Catalyst preparation time / hrs	Intensity of Cu_2O (111) plane	Intensity of Cu (111) plane	Cu:Cu_2O
4	476	30	0.18
5	410	51	0.32
7	457	197	1.01
9	1038	874	1.94
12	750	1082	3.29
24	163	2596	36.00

Table S3 Calculation of average crystal size from p-XRD analysis using Scherrer's formula.

Scherrer's equation for average crystal size, **$D = K\gamma / B \cos\theta$**.

	crystal plane	**2θ / °**	**B**	**D / nm**	**Average Size (in nm)**
Cu_2O	(111)	36.404	0.690	11.984	16.19
	(200)	42.305	0.458	18.391	
	(220)	61.45	0.502	18.204	

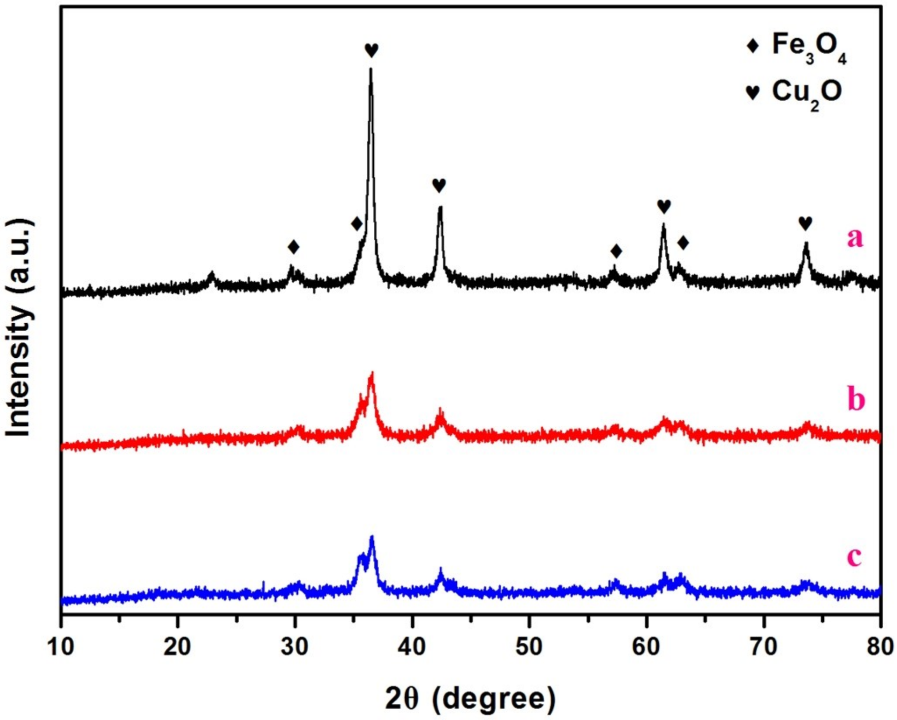

Fig. S2 Comparison of *p*-XRD spectra of Fe_3O_4@Cu_2O nanomaterial (a) fresh catalyst (b) 4th recycle and (c) 7th recycle.

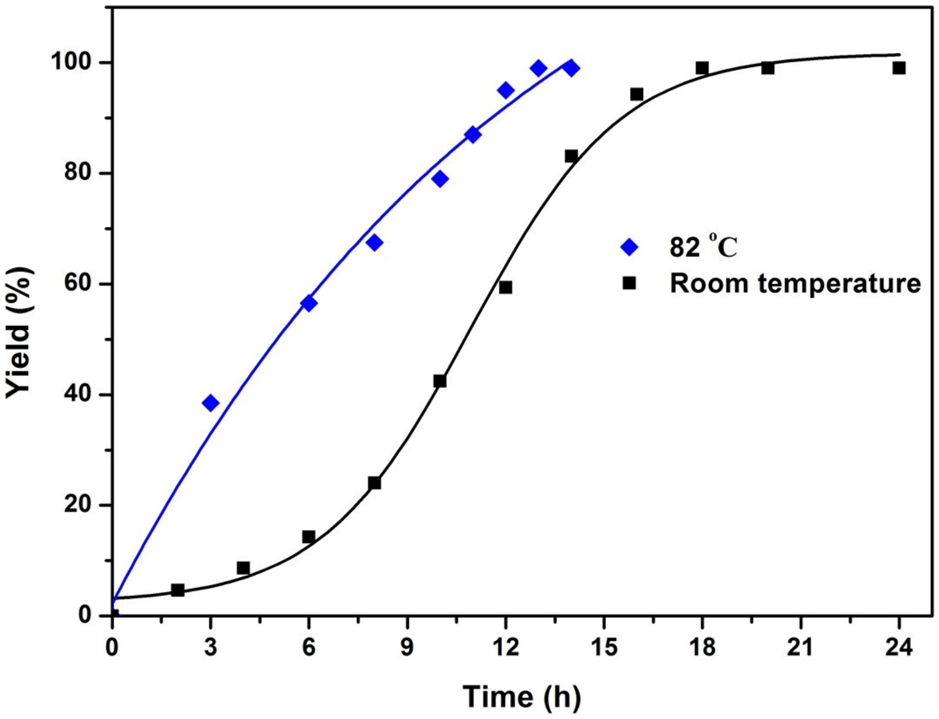

Fig. S3 Effect of temperature on the aerobic oxidation of benzyl alcohol catalysed by Fe_3O_4@Cu_2O.

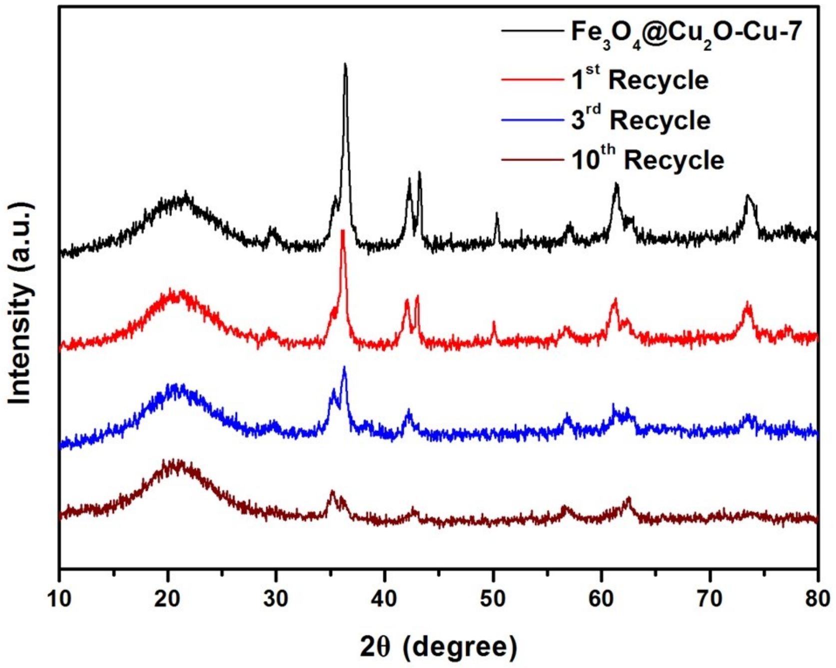

Fig. S4 Comparison of p-XRD spectra of fresh and reused catalysts of Fe_3O_4@Cu_2O-Cu-7 nanomaterial.

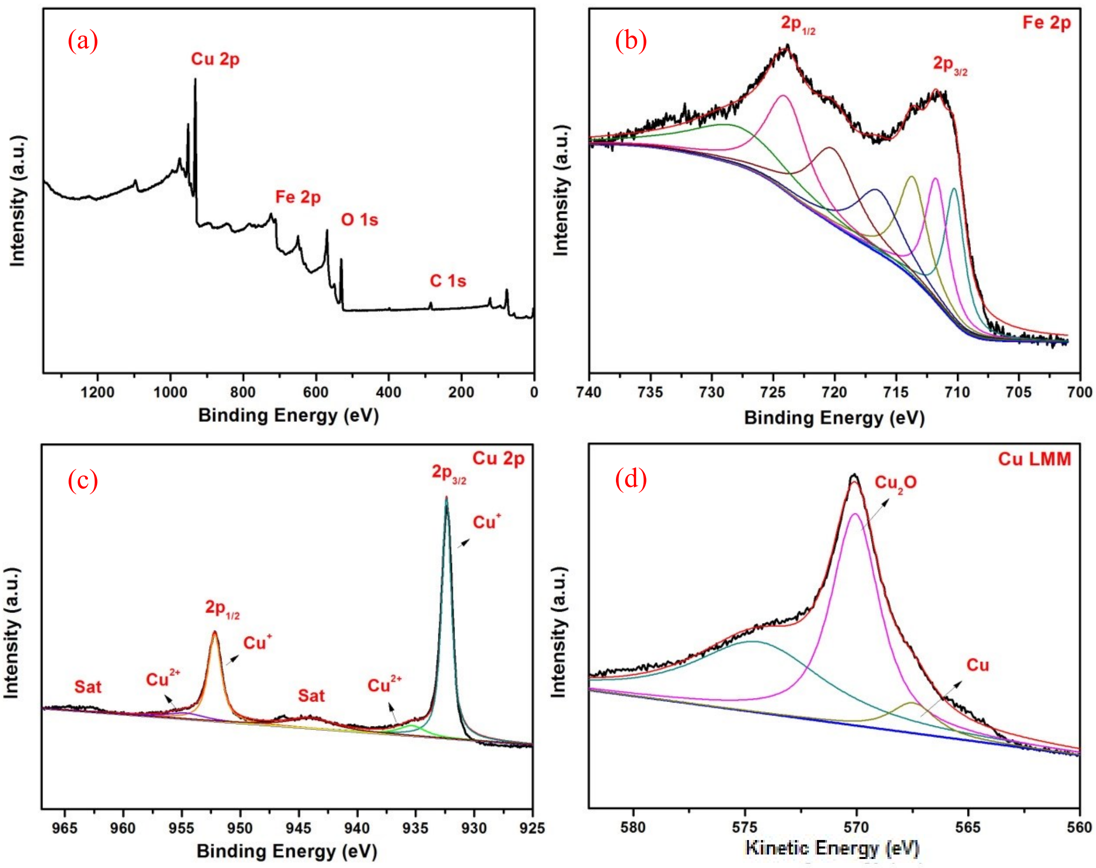

Fig. S5 XPS spectra of core shell Fe_3O_4@Cu_2O-Cu-7 nanomaterial: (a) Survey spectrum; (b Fe 2p; (c) Cu 2p; (d) Cu LMM Auger spectra.

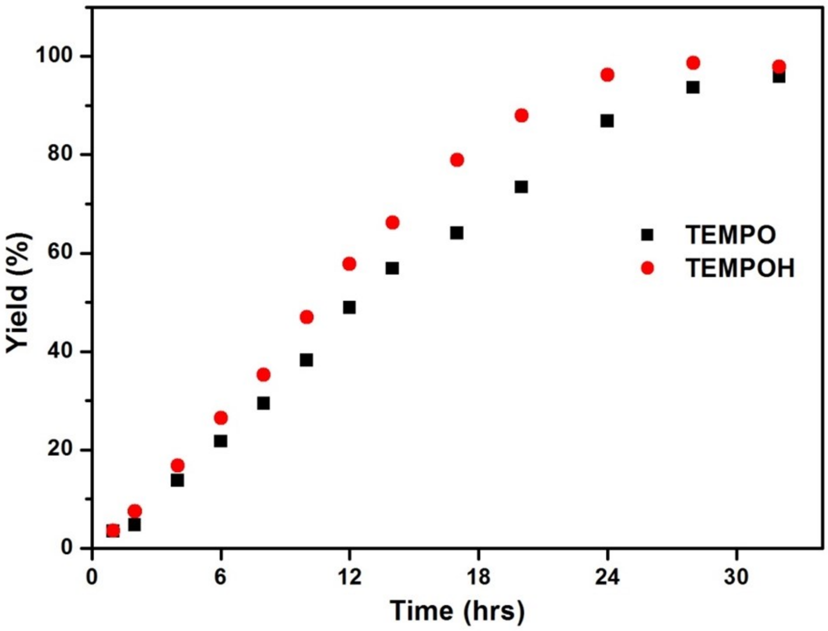

Fig. S6 Comparison for the effect of TEMPO and TEMPOH on the catalysis.

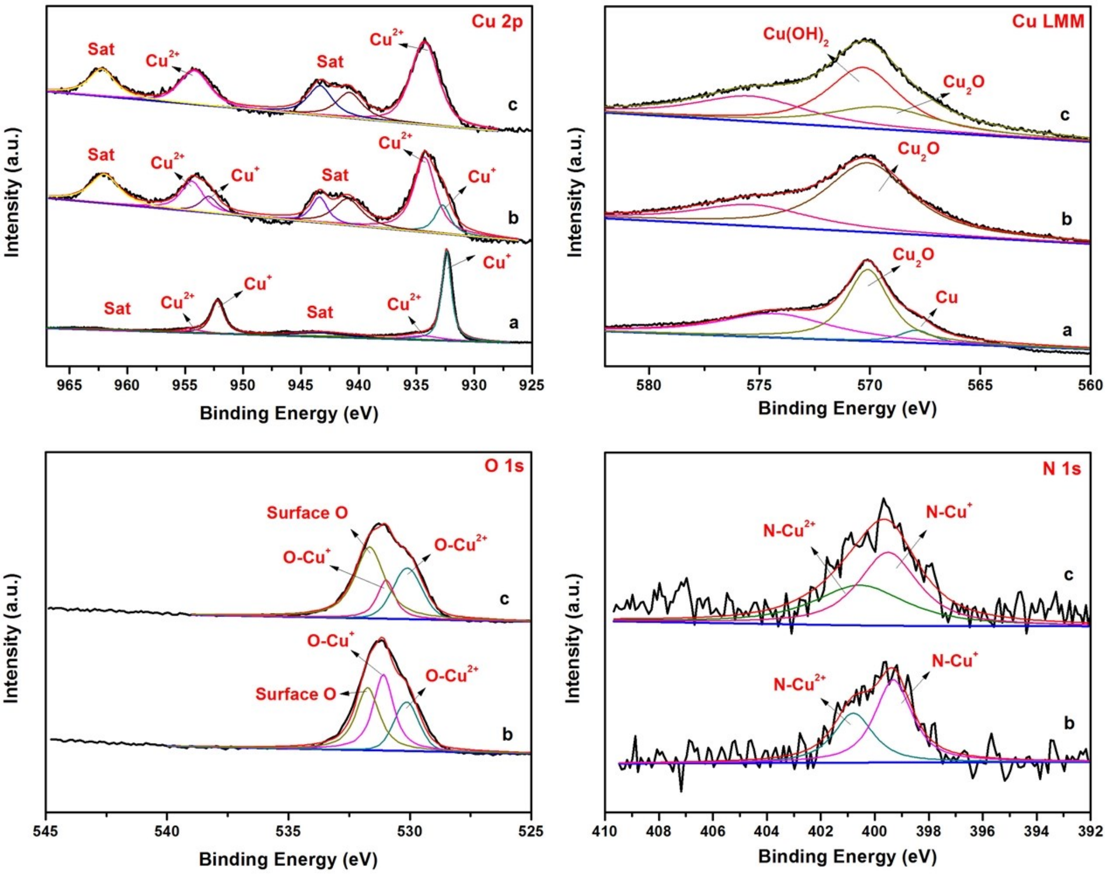

Fig. S7 Comparison of XPS spectra of fresh and recycled Fe_3O_4@Cu_2O-Cu-7 nanomaterial: Cu 2p (Top left), Cu LMM (Top right), O 1s (Bottom left) and N 1s (Bottom right); (a) fresh catalyst, (b) 3th recycling and (c) 7th recycling.

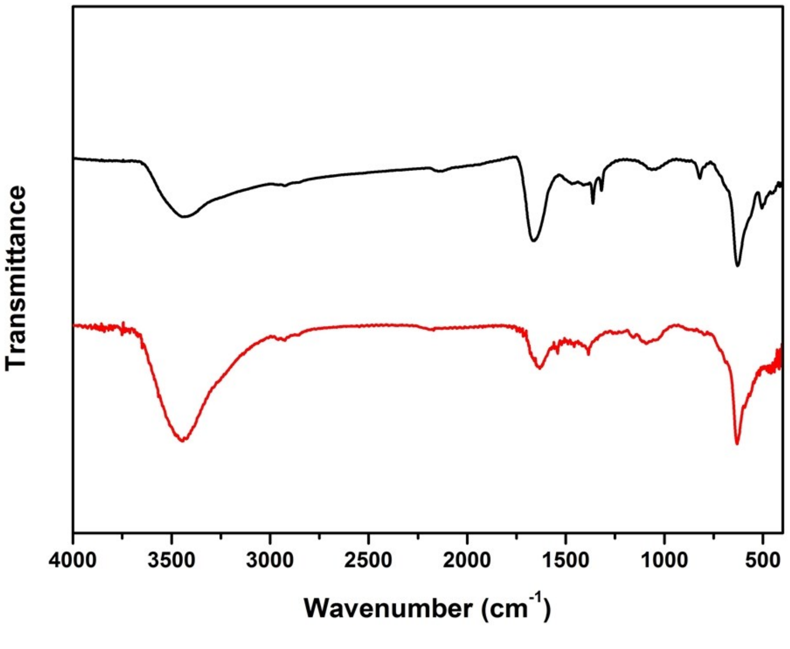

Fig. S8 Comparison of FTIR spectroscopy for Fe_3O_4@Cu_2O before (black) and after (red) use.

Table S4 The binding energies (eV) of XPS results of Cu, O, N in Fe_3O_4@Cu_2O nanomaterial.

	Cu$^+$ 2p$_{3/2}$	**Cu^{2+} 2p$_{3/2}$**	**Cu^{2+} Sat.**	**Cu$^+$ 2p$_{1/2}$**	**Cu^{2+} 2p$_{1/2}$**	**Cu^{2+} Sat.**	**Cu LMM**	**O 1s**	**N 1s**
Fresh catalyst	932.3	934.4	941.0, 943.6	952.1	954.2	962.0	570.0	530.1[a], 530.9[b], 531.9[c]	398.6
Related peak area	54850.2	39365.7	10929.5, 16092.5	25535.8	16311.4	7495.7	37999.4	27739.1, 15107.2, 15852.8	1018.1
4th recycles	932.5	934.1	941.0, 943.6	952.3	954.2	962.0	568.5, 570.0	530.1[a], 531.0[b], 531.7[c]	399.3[d], 400.7[e]
Related peak area	11906.0	78094.1	53694.9, 14298.4	6249.1	38933.9	35029.1	7526.8, 38349.3	13212.8, 33826.3, 20513.8	1810.4, 748.2
7th recycles	932.5	934.1	940.8, 943.5	952.4	954.2	961.9	568.5, 570.0	530.1[a], 531.0[b], 531.8[c]	399.3[d], 400.7[e]
Related peak area	12248.2	49413.2	29391.4, 11236.6	5909.6	23561.6	23920.4	8334.9, 20184.0	19151.3, 18067.7, 17872.2	2074.9, 1232.0

[a, e] Binding to Cu^{2+}, [b, d] Binding to Cu$^+$, [c] Surface O.

Table S5 The binding energies (eV) of XPS results of Cu, O, N in Fe_3O_4@Cu_2O-Cu-7 nanomaterial.

	Cu$^+$ 2p$_{3/2}$	**Cu^{2+} 2p$_{3/2}$**	**Cu^{2+} Sat.**	**Cu$^+$ 2p$_{1/2}$**	**Cu^{2+} 2p$_{1/2}$**	**Cu^{2+} Sat.**	**Cu LMM**	**O 1s**	**N 1s**
Fresh catalyst	932.4	934.3	940.8, 943.3	952.2	954.2	962.0	568.0, 570.1	/	/
Rel.peak area	469444.2	73972.6	57290.9, 100990.8	229259.4	30916.3	28193.7	56832.5, 246334.5	/	/
3rd recycles	932.3	934.3	940.8, 943.3	952.2	954.2	962.0	569.5	530.1[a], 531.1[b], 531.7[c]	399.2[d], 400.6[e]
Related peak area	12880.2	67982.0	26668.5, 18075.8	6663.8	30746.9	30361.0	139149.8	15214.7, 24859.0, 23333.8	1799.2, 1865.6
7th recycles	-	934.3	940.8, 943.3	-	954.2	962.2	569.5, 570.4	530.1[a], 531.0[b], 531.7[c]	399.4[d], 400.9[e]
Related peak area	-	68414.3	22116.6, 24452.7	-	29909.2	23943.7	48888.1, 107052.3	18663.5, 10791.6, 33820.5	1890.5, 941.9

[a, e] Binding to Cu^{2+}, [b, d] Binding to Cu$^+$, [c] Surface O. “-” Not detected. “/” Not tested.

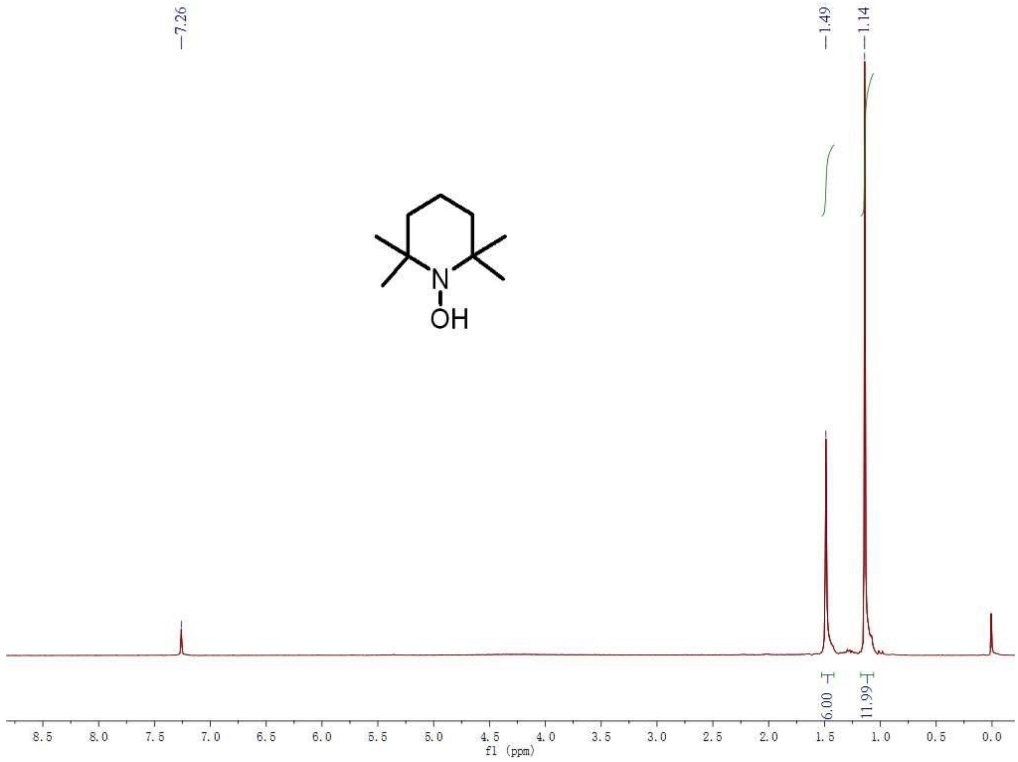

Fig. S9 ^{1}H-NMR spectrum of TEMPOH

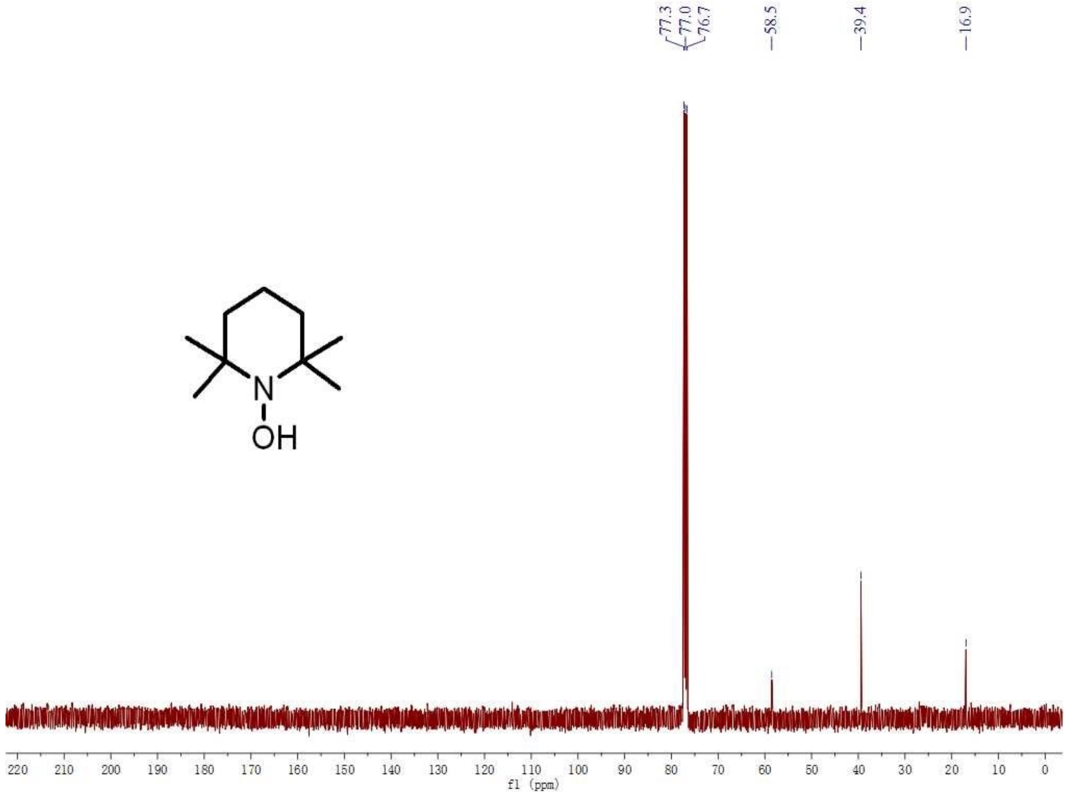

Fig. S10 ^{13}C-NMR spectrum of TEMPOH

Reference:

1. Q. Hua, K. Chen, S. Chang, H. Bao, Y. Ma, Z. Jiang and W. Huang, *RSC Advances*, 2011, **1**, 1200-1203.

2. Y. Zhu, L. Li, and Z. Shen, *Chem.Eur.J.,* 2015, **21**, 13246-13252.