Electronic Supplementary Information

Magnetic core-shell Fe₃O₄@Cu₂O and Fe₃O₄@Cu₂O-Cu materials as the catalysts for aerobic oxidation of benzylic alcohols assisted with TEMPO and N-methylimidazole

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Synthesis of Cu$_2$O nanoparticles:

The cubic Cu$_2$O nanocrystals were synthesized by following the reported procedure.\textsuperscript{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.\textsuperscript{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$_2$O (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%). $^1$H 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$_3$O$_4$@Cu$_2$O nanomaterial.

| Catalyst         | C(%) | O(%) | N(%) | Fe(%) | Cu(%) | Cu:Fe (mol. ratio) |
|------------------|------|------|------|-------|-------|-------------------|
| Fe$_3$O$_4$      | 7.06 | 28.44| -    | 64.51 | -     |                   |
| Fe$_3$O$_4$/L-Lys | 10.12| 29.72| 4.62 | 55.54 | -     |                   |
| Fe$_3$O$_4$@Cu$_2$O | 14.86| 21.73| 1.37 | 12.83 | 49.22 | 3.8:1             |
**Fig. S1** Calibration curve for the calculation of Cu/Cu$_2$O content in Fe$_3$O$_4$@Cu$_2$O-Cu catalysts.

**Table S2** Comparison of powder XRD strength and calculation of Cu/Cu$_2$O content in Fe$_3$O$_4$@Cu$_2$O-Cu catalysts.

| Catalyst preparation time / hrs | Intensity of Cu$_2$O (111) plane | Intensity of Cu (111) plane | Cu:Cu$_2$O |
|-------------------------------|---------------------------------|-----------------------------|------------|
| 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, \( D = \frac{K\gamma}{B \cos\theta} \).

| crystal plane | 2\(\theta \) / ° | B     | D / nm | Average Size (in nm) |
|---------------|------------------|-------|--------|----------------------|
| Cu\(_2\)O     |                  |       |        |                      |
| (111)         | 36.404           | 0.690 | 11.984 |                      |
| (200)         | 42.305           | 0.458 | 18.391 | 16.19                |
| (220)         | 61.45            | 0.502 | 18.204 |                      |

Fig. S2 Comparison of p-XRD spectra of Fe\(_3\)O\(_4@Cu\(_2\)O nanomaterial (a) fresh catalyst (b) 4\(^{th}\) recycle and (c) 7\(^{th}\) recycle.
Fig. S3 Effect of temperature on the aerobic oxidation of benzyl alcohol catalysed by Fe$_3$O$_4$@Cu$_2$O.

Fig. S4 Comparison of p-XRD spectra of fresh and reused catalysts of Fe$_3$O$_4$@Cu$_2$O-Cu-7 nanomaterial.
**Fig. S5** XPS spectra of core shell Fe$_3$O$_4$@Cu$_2$O-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$_3$O$_4$@Cu$_2$O-Cu-7 nanomaterial: Cu 2p (Top left), Cu LMM (Top right), O 1s (Bottom left) and N 1s (Bottom right); (a) fresh catalyst, (b) 3$^{th}$ recycling and (c) 7$^{th}$ recycling.

Fig. S8 Comparison of FTIR spectroscopy for Fe$_3$O$_4$@Cu$_2$O before (black) and after (red) use.
Table S4 The binding energies (eV) of XPS results of Cu, O, N in Fe₃O₄@Cu₂O nanomaterial.

|                  | Cu⁺ 2p₃/2 | Cu²⁺ 2p₃/2 | Cu²⁺Sat. | Cu⁺ 2p₁/2 | Cu²⁺ 2p₁/2 | Cu²⁺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⁺, 530.9⁺, 531.9⁺ | 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⁺, 531.0⁺, 531.7⁺ | 399.3⁺, 400.7⁺ |
| 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⁺, 531.0⁺, 531.8⁺ | 399.3⁺, 400.7⁺ |
| 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 Binding to Cu²⁺, b Binding to Cu⁺, c Surface O.

Table S5 The binding energies (eV) of XPS results of Cu, O, N in Fe₃O₄@Cu₂O-Cu7 nanomaterial.

|                  | Cu⁺ 2p₃/2 | Cu²⁺ 2p₃/2 | Cu²⁺Sat. | Cu⁺ 2p₁/2 | Cu²⁺ 2p₁/2 | Cu²⁺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⁺, 531.1⁺, 531.7⁺ | 399.2⁺, 400.6⁺ |
| 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⁺, 531.0⁺, 531.7⁺ | 399.4⁺, 400.9⁺ |
| 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 Binding to Cu²⁺, b 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.