

## Supporting information

### Bio-derived CuO nanocatalyst for oxidation of aldehyde: a greener approach

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## **Materials and Methods**

### **Synthesis of CuO nanoparticles:**

In this method, the peel of *Musa balbisiana* was dried then burnt in muffle furnace at 500°C to obtain ash of the peel. To the 1 g of ash of the peel, 20 ml of distilled water was added and filtered. 5 ml 1M CuSO<sub>4</sub>·5H<sub>2</sub>O solution was added to the filtered and stirred for 10 minutes. Light blue precipitate was obtained. After filtration, the precipitate was heated for 2 h at 500°C temperature for the formation of powder CuO nanoparticles. It is the first report of eco-friendly bio-derived synthesis of CuO nanoparticles by using peel of *Musa balbisiana*.

### **Characterization**

Scanning electron microscopy (SEM) characterization was performed on JEOL JSM - 6360 at 15 kV. X-ray diffraction (XRD) measurement were carried out by Rigaku X-ray diffractometer (Model: ULTIMA IV, Rigaku, Japan) with Cu-K $\alpha$  X-ray source ( $\lambda = 1.54056$  Å) at voltage 40 kV. The X-ray photoelectron spectroscopy (XPS) analysis was done on instrument ESCA-3000 (VG Scientific, UK). The source used is AlK $\alpha$  having energy 1486.6 eV. The high resolution transmission electron microscopy (HRTEM) images were recorded by a JEOL Model 2100 EX, Japan operated at voltage of 200 kV.

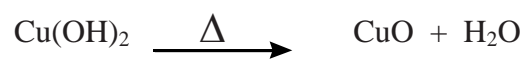
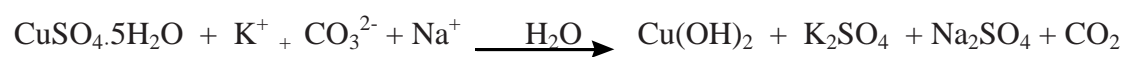
### **Optimization of reaction**

The oxidation reaction was first optimized by using different solvent like acetonitrile, ethanol, DMSO etc under the same reaction condition of temperature (60°C) and pressure (1 atm) and amount of CuO (2 mol%) catalyst.

### **Catalytic oxidation of aldehydes**

To 5 ml of acetonitrile added 10 mmol aldehyde and 10 equiv. 30% H<sub>2</sub>O<sub>2</sub> and then refluxed for about 1 h at temperature 60°C in presence of 2 mol % CuO nanoparticles. The progress of the reaction was monitored by thin layer chromatography (TLC). The reaction mixture was extracted with ethyl acetate. The combined organic layer was dried with NaSO<sub>4</sub> and

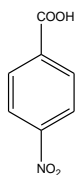
concentrated via rotary evaporation. The CuO catalyst could be used consecutively for five times for the oxidation of 4-nitrobenzaldehyde (1st recycle 95%, 2nd recycle 94% and 3<sup>rd</sup> recycle 92%, 4<sup>th</sup> recycle 91% and 5<sup>th</sup> recycle 90% 4-nitrobenzoic acid was obtained). The product was purified by column chromatography by using hexane/ethyl acetate as solvent system in different concentration to obtain the pure compound. If the solubility of crude product is poor in organic solvent, the residue was purified by pre-loaded silica-gel column chromatography with appropriate methanol/chloroform eluent system. The structure of the compounds was further confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, GC-MS analysis.



Scheme 1: Plausible mechanism in synthesis of CuO nanoparticles by using peel of *Musa balbisiana*

## Scheme 2. Spectroscopic analysis of isolated compounds

i) 4-nitro benzoic acid:



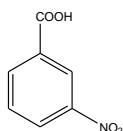
IR (KBr,  $\text{cm}^{-1}$ ) v: 3078, 2921, 2851, 1708, 1646, 1600, 1522, 1522, 1462, 2427, 1348, 1302, 1267, 1120, 1107, 877, 789, 716

$^1\text{H}$ NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 8.24 (d, 2H), 8.29(d, 2H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 175.7, 136.3, 131.1, 123.5.

GCMS (M/Z %): 167 ( $\text{M}^+$ , 100), 137 (20), 120 (42), 108 (24), 81(14), 65(56).

ii) 3-Nitrobenzoic acid:



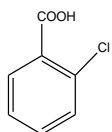
IR (KBr,  $\text{cm}^{-1}$ ) v: 3087, 2994, 2873, 2810, 2667, 2540, 1994, 1848, 1691, 1616, 1530, 1482, 1449, 1416, 1354, 1326, 1291, 1151, 1084, 926, 824, 810, 777, 722, 702, 662, 650, 567, 528.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 9.65(s, 1H), 8.96(s, 1H), 8.48(d, 1H), 8.45(d, 1H), 7.73(t, 1H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 170.1, 148.4, 135.8, 130.9, 129.9, 128.4, 125.3.

GCMS (M/Z %): 167 ( $\text{M}^+$ , 100), 150 (6), 121 (14), 104 (4).

iii) 2-chloro benzoic acid:



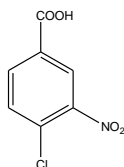
IR (KBr,  $\text{cm}^{-1}$ ) v: 3500, 3104, 3034, 2960, 2856, 2649, 2517, 1934, 1714, 1630, 1589, 1521, 1475, 1384, 1353, 1267, 1141, 1118, 1046, 895, 851, 803, 736, 539.

$^1\text{H}$ NMR ( $\text{CDCl}_3$ , 300MHz)  $\delta$ : 8.37(d, 1H), 8.23(m, 1H), 8.20(m, 1H), 8.18(d, 1H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 168.9, 150, 135.9, 133.9, 133.1, 126.4, 121.5.

GCMS (M/Z %): 156 ( $\text{M}^+$ , 100)

iv) 4-chloro-3-nitrobenzoic acid:



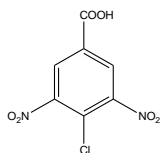
IR (KBr, cm<sup>-1</sup>) v: 3527, 3460, 3085, 2954, 2885, 2839, 2661, 2529, 1957, 1828, 1694, 1630, 1602, 1542, 1426, 1357, 1319, 1254, 1121, 1050, 936, 912, 855, 811, 780, 769, 747, 728, 698, 662, 606, 529, 481.

<sup>1</sup>HNMR (CDCl<sub>3</sub>, 300MHz) δ: 8.48 (s, 1H), 8.21 (dd, 1H), 7.79 (dd, 1H)

<sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75 MHz) δ: 157.0, 139.9, 125.4, 123.8, 122.9, 122.2, 117.9.

GCMS (M/Z %): 201 (M<sup>+</sup>, 40), 203 (M+2, 8), 171 (18), 115(28), 99(100), 69(54), 55(58).

v) 4-Chloro-3,5-dinitrobenzoic acid:



IR (KBr, cm<sup>-1</sup>) v: 3084, 2885, 2816, 2661, 2523, 1709, 1614, 1546, 1466, 1411, 1352, 1300, 1272, 1184, 1066, 923, 747, 720, 633, 544.

<sup>1</sup>HNMR (CDCl<sub>3</sub>, 300MHz) δ: 8.71(s, 2H)

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ: 156.2, 142.3, 125.0, 121.0, 116.0,

GCMS (M/Z %): 246 (M<sup>+</sup>, 100), 248 (M+2, 18).

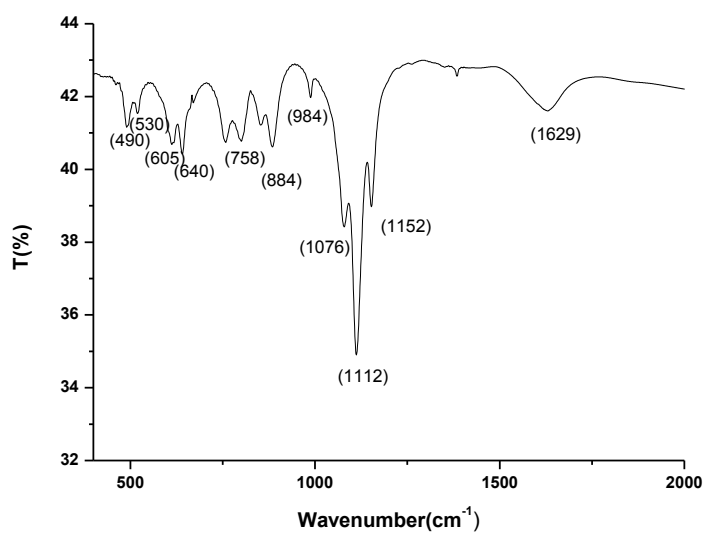


Figure S1: FT-IR spectra of CuO nanoparticles synthesised by *Musa balbisiana*

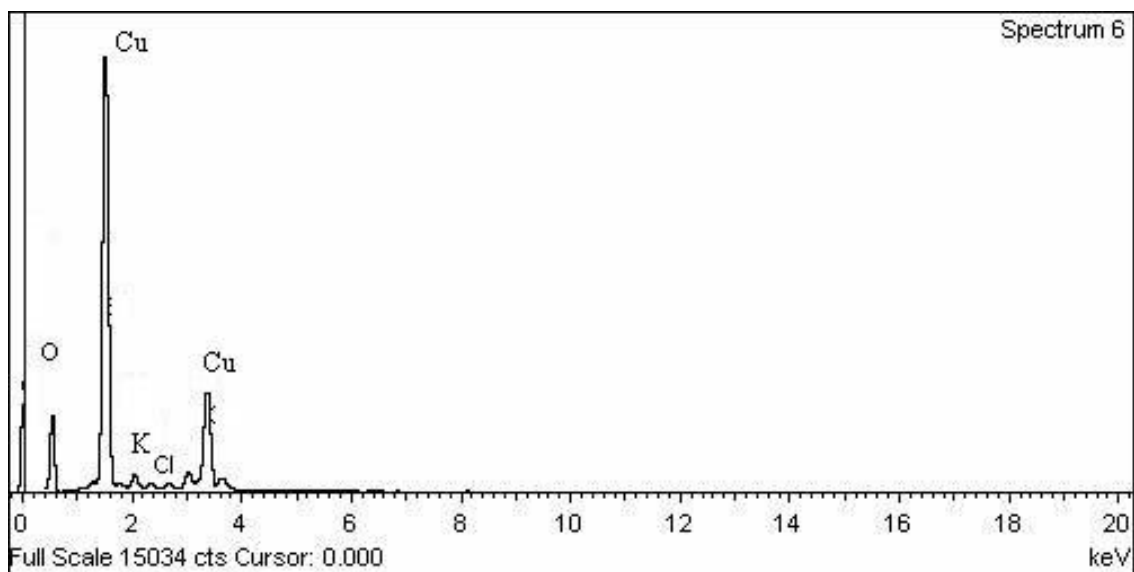


Figure S2: EDX spectra of CuO nanoparticles.

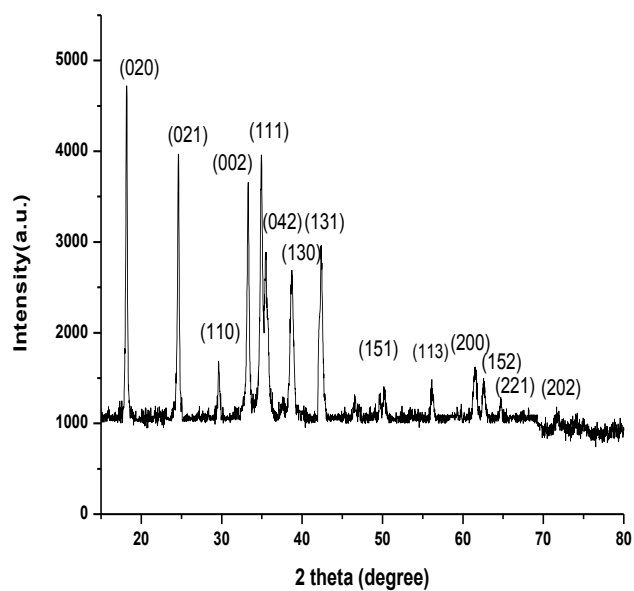


Figure S3: XRD spectrum of CuO catalyst after 5 recycle

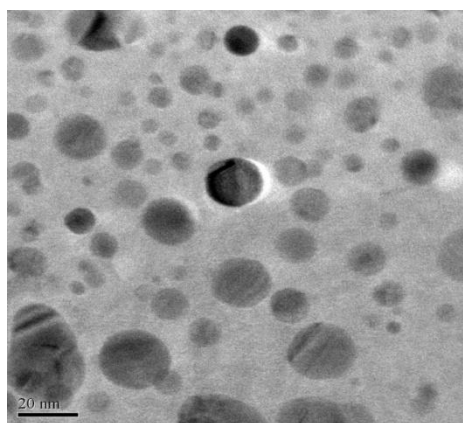


Figure S4: TEM image after 5 recycle of CuO cata



Table S1: Comparison of the CuO catalyst for the oxidation of 4-nitrobenzyldehyde with earlier reported catalyst.

SL No	Catalyst	Oxidising agent	Temperature	Solvent	Time (hr)	Yield (%)	Ref
1	[CH <sub>3</sub> ( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> N]HSO <sub>4</sub>	30% H <sub>2</sub> O <sub>2</sub>	90°C	Toluene	5	88	[1]
2	Pd/C	O <sub>2</sub> (air)	Room temperature	Water: Methanol (2:1)	8	86	[2]
3	3,5-Bis(perfluorooctyl) benzeneseleninic acid	30% H <sub>2</sub> O <sub>2</sub>	Room temperature	Dichloroethane	4	78	[3]
4	(NH <sub>4</sub> ) <sub>2</sub> (Fe)(SO <sub>4</sub> ·6H <sub>2</sub> O)	70% <i>t</i> -BuOOH	80°C	DMSO	6.6	90	[4]
5	CuO	30% H <sub>2</sub> O <sub>2</sub>	60°C	Acetonitrile	1	95	Present work

#### References

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3. G.-J.T. Brink, J.M. Vis, I.W.C.E. Arends, R.A. Sheldon, *Tetrahedron* 2002, 58, 3977-3983.
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