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 burnt in muffle furnace at 500°C to obtained 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 CuSO₄·5H₂O solution was added to the filtered and stirred for 10 minute. 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-Kα X-ray source (λ = 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 AlKalpha 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% H₂O₂ 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 NaSO₄ and
concentrated via rotary evaporation. The CuO catalyst could be used consecutively for five times for the oxidation of 4-nitrobenzyldehyde (1st recycle 95%, 2nd recycle 94% and 3rd recycle 92%, 4th recycle 91% and 5th 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 $^1$H NMR, $^{13}$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:

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

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

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

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

ii) 3-Nitrobenzoic acid:

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

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

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

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

iii) 2-chloro benzoic acid:

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

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

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

GCMS (M/Z %): 156 (M^+, 100)

iv) 4-chloro-3-nitrobenzoic acid:
IR (KBr, cm\(^{-1}\)) v: 3527, 3460, 3085, 2954, 2885, 2839, 2661, 2529, 1957, 1828, 1694, 1630, 1602, 1542, 1426, 1357, 1254, 1121, 1050, 936, 912, 855, 811, 780, 769, 747, 728, 698, 662, 606, 529, 481.

\(^{1}\)HNMR (CDCl\(_3\), 300MHz) δ: 8.48 (s, 1H), 8.21 (dd, 1H), 7.79 (dd, 1H)

\(^{13}\)C NMR (DMSO-d\(_6\), 75 MHz) δ: 157.0, 139.9, 125.4, 123.8, 122.9, 122.2, 117.9.

GCMS (M/Z %): 201 (M\(^+\), 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\(^{-1}\)) v: 3084, 2885, 2816, 2661, 2523, 1709, 1614, 1546, 1466, 1411, 1352, 1300, 1272, 1184, 1066, 923, 747, 720, 633, 544.

\(^{1}\)HNMR (CDCl\(_3\), 300MHz) δ: 8.71(s, 2H)

\(^{13}\)C NMR (CDCl\(_3\), 75 MHz) δ: 156.2, 142.3, 125.0, 121.0, 116.0.

GCMS (M/Z %): 246 (M\(^+\), 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 catalyst
Table S1: Comparison of the CuO catalyst for the oxidation of 4-nitrobenzylaldehyde with earlier reported catalyst.

<table>
<thead>
<tr>
<th>SL No</th>
<th>Catalyst</th>
<th>Oxidising agent</th>
<th>Temperature</th>
<th>Solvent</th>
<th>Time (hr)</th>
<th>Yield (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[CH₃(n-C₈H₁₇)₃N]HSO₄</td>
<td>30% H₂O₂</td>
<td>90°C</td>
<td>Toluene</td>
<td>5</td>
<td>88</td>
<td>[1]</td>
</tr>
<tr>
<td>2</td>
<td>Pd/C</td>
<td>O₂(air)</td>
<td>Room temperature</td>
<td>Water: Methanol (2:1)</td>
<td>8</td>
<td>86</td>
<td>[2]</td>
</tr>
<tr>
<td>3</td>
<td>3,5-Bis(perfluoroctyl) benzeneselinic acid</td>
<td>30% H₂O₂</td>
<td>Room temperature</td>
<td>Dichloroethane</td>
<td>4</td>
<td>78</td>
<td>[3]</td>
</tr>
<tr>
<td>4</td>
<td>(NH₄)₂(Fe)(SO₄-6H₂O)</td>
<td>70% t-BuOOH</td>
<td>80°C</td>
<td>DMSO</td>
<td>6.6</td>
<td>90</td>
<td>[4]</td>
</tr>
<tr>
<td>5</td>
<td>CuO</td>
<td>30% H₂O₂</td>
<td>60°C</td>
<td>Acetonitrile</td>
<td>1</td>
<td>95</td>
<td>Present work</td>
</tr>
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References