Supporting Information

Textile supported silver nanoparticles as highly efficient and recyclable heterogeneous catalyst for nitroaromatics reduction at room temperature

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1 General Procedures and Methods

Proton nuclear magnetic resonance (1H NMR) and carbon NMR (13C NMR) spectra were recorded in CD$_3$OD and CDCl$_3$ unless otherwise stated. 1H (400 MHz) and 13C (101 MHz) with complete proton decoupling were performed on a 400 MHz Bruker Ultra Shield NMR spectrometer. Chemical shifts were reported as δ in units of parts per million (ppm) downfield from tetramethylsilane (δ 0.00), using the residual solvent signal as an internal standard: CD$_3$OD (1H NMR, δ 3.31; 13C NMR, δ 49.0), CDCl$_3$ (1H NMR, δ 7.26 singlet; 13C NMR, δ 77.0 triplet). Multiplicities were given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), and br (broad). Coupling constants (J) were recorded in hertz (Hz). The number of proton atoms (n) for a given resonance was indicated by nH. MS was reported in units of mass to charge ratio (m/z). Mass samples were dissolved in MeCN (AR grade). X-Ray Photoelectron Spectroscopy (XPS) was performed on a PerkinElmer, PHI1600 spectrometer. Inductively Coupled Plasma (ICP) was carried out on a Shimadzu ICPE-9800 Series system.

All commercial reagents were purchased from Sigma- Aldrich, Fluka, Alfa Aesar, Merck, TCI, or Acros and were of the highest purity grade available. They were used without further purification unless specified. Reaction solvents were AR grade THF and deionized water.

2 Representative procedure for textile supported nanosilver catalyst preparation

Commercially available white cotton textile was washed with deionized water and dried in oven at 60 °C. Silver nitrate (0.7 g) and (3-Aminopropyl) triethoxysilane (APTES) (10ml) were dissolved in deionized water (1L). The dried cotton textile (30g) was bathed in the solution at 60 °C for 10 min. The textile was then washed thoroughly with deionized water and soaked for 10 min in a sodium borohydride (5 mM) solution at room temperature. A yellow color was formed on the textile due to the formation of silver nanoparticles on its surface. The textile was ready to use after rinsing with deionized water to remove any excess reactants and un-bonded silver nanoparticles. It was then dried at room temperature in drying cabinet.
3 Reaction optimizations

Table S1 Optimization of TsNS catalyzed 4-nitrophenol reduction.

| Entry | Solvent A | Solvent B | X  | Time (hours) | Yield (%) |
|-------|-----------|-----------|----|--------------|-----------|
| 1 b   | 2 ml DCM  |           | 1  | 12           | trace     |
| 2 b   | 2 ml MeCN |           | 1  | 12           | ~8%       |
| 3 b   | 2 ml THF  |           | 1  | 12           | ~10%      |
| 4     | 1 ml THF  | 1 ml H₂O  | 1  | 3            | 73%       |
| 5     | 1 ml THF  | 1 ml H₂O  | 0.5| 3            | 46%       |
| 6     | 1 ml THF  | 1 ml H₂O  | 2  | 3            | 75%       |
| 7 b   | 1.5 ml THF| 0.5 ml H₂O| 1  | 3            | 50%       |
| 8 c   | 0.5       | 1.5       | 1  | 3            | 26%       |
Nitrophenol, catalyst and NaBH₄ were mixed in solvent and stirred at room temperature. *isolated yield. ²NaBH₄ is not completely dissolved. ³ nitrophenol is not completely dissolved. Entry 4 is the best condition.

4 Representative procedure for nanotextile catalyzed nitroaromatic reduction

To a 25ml rbf was added a magnetic stirring bar, 2 cm² nanosilver textile catalyst, 0.2 mmol nitro compound and 1mmol NaBH₄, following this, 1ml THF and 1ml deionized water were added. The mixture was stirred at room temperature (25°C, 100°C for certain substrate) until substrate was completely consume as indicated by TLC monitoring. Then the catalyst was taken out and washed thoroughly with deionized water, which was combined with the reaction mixture. Extract with Ether for three times and the organic layers were combined and dried with Na₂SO₄, concentrated and purified by flash chromatography.

5 NMR and Mass data for products

All compounds were purified by flashing silica chromatography with hexane and ethyl acetate (EA) mixture as eluent.

Compound 1: 4-aminophenol

¹H NMR (400 MHz, MeOD) δ 6.62 (td, J = 9.0, 6.4 Hz, 4H). ¹³C NMR (101 MHz, MeOD) δ 151.32, 140.22, 118.54, 116.74. LRMS (ESI) m/z 110.0 (M + H⁺). Eluent: Hexane/ EA = 5/1.

Compound 2: 2-methyl-1H-indol-5-amine

¹H NMR (400 MHz, MeOD) δ 7.05 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 2.0 Hz, 1H), 6.57 (dd, J = 8.4, 2.1 Hz, 1H), 5.92 (s, 1H), 2.35 (s, 3H). ¹³C NMR (101 MHz, MeOD) δ 139.20, 137.04, 133.32, 131.34, 112.81, 111.55, 107.03, 99.49, 13.49. LRMS (ESI) m/z 147.2 (M + H⁺). Eluent: Hexane/ EA = 1/1.

Compound 3: indolin-5-amine

¹H NMR (400 MHz, CDCl₃) δ 6.61 – 6.56 (m, 1H), 6.52 (d, J = 8.1 Hz, 1H), 6.42 (dd, J = 8.1, 2.3 Hz, 1H), 5.49 (t, J = 8.3 Hz, 2H), 3.16 (br, 3H), 2.95 (t, J = 8.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 144.11, 139.15, 131.27, 114.27, 113.15, 110.76, 47.57, 30.47. LRMS (ESI) m/z 135.0 (M + H⁺). Eluent: Hexane/ EA = 1/1.

Compound 4: aniline

¹H NMR (400 MHz, MeOD) δ 7.24 – 7.14 (m, 2H), 7.00 – 6.93 (m, 2H), 6.85 (tt, J = 7.5, 1.1 Hz, 1H). ¹³C NMR (101 MHz, MeOD) δ 152.69, 129.61, 121.97, 115.14. LRMS (ESI) m/z 93.9 (M + H⁺). Eluent: Hexane/ EA = 10/1.

Compound 5: 2-(2-aminophenyl) ethanol
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.07 (t, \(J = 8.2\) Hz, 2H), 6.85 – 6.61 (m, 2H), 3.90 (t, \(J = 6.1\) Hz, 2H), 2.96 (br, 3H), 2.80 (t, \(J = 6.1\) Hz, 2H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 144.81, 130.60, 127.69, 124.40, 119.37, 116.39, 63.32, 34.75. LRMS (ESI) m/z 138.1 (M + H\(^+\)). Eluent: Hexane/ EA = 1/1.

Compound 6: 3-aminophenol

\(^1\)H NMR (400 MHz, MeOD) \(\delta\) 7.70 (ddd, \(J = 8.2, 2.2, 0.9\) Hz, 1H), 7.62 (t, \(J = 2.3\) Hz, 1H), 7.42 (t, \(J = 8.2\) Hz, 1H), 7.18 (ddd, \(J = 8.2, 2.4, 0.9\) Hz, 1H). \(^1\)C NMR (101 MHz, MeOD) \(\delta\) 159.81, 150.65, 131.26, 122.92, 115.09, 110.87. LRMS (ESI) m/z 110.0 (M + H\(^+\)). Eluent: Hexane/ EA = 3/1.

Compound 7: 1-aminonaphthalen-2-ol

\(^1\)H NMR (400 MHz, MeOD) \(\delta\) 7.86 (dd, \(J = 8.5, 0.7\) Hz, 1H), 7.68 (d, \(J = 8.2\) Hz, 1H), 7.36 (ddd, \(J = 8.4, 6.8, 1.3\) Hz, 1H), 7.23 (ddd, \(J = 8.8, 5.5, 2.1\) Hz, 2H), 7.08 (d, \(J = 8.7\) Hz, 1H). \(^1\)C NMR (101 MHz, MeOD) \(\delta\) 141.79, 130.50, 129.16, 128.04, 126.61, 125.79, 123.68, 121.58, 120.14, 118.31. LRMS (ESI) m/z 182.3 (M + Na\(^+\)). Eluent: Hexane/ EA = 1/1.

Compound 8: 3-chloroaniline

\(^1\)H NMR (400 MHz, MeOD) \(\delta\) 7.14 (t, \(J = 8.0\) Hz, 1H), 6.96 (t, \(J = 2.1\) Hz, 1H), 6.84 – 6.77 (m, 2H). \(^1\)C NMR (101 MHz, MeOD) \(\delta\) 154.53, 135.54, 130.83, 121.12, 114.46, 112.90. LRMS (ESI) m/z 127.9 (M + H\(^+\)). Eluent: Hexane/ EA = 10/1.

Compound 9: 4-methoxybenzene-1,2-diamine

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.63 (d, \(J = 8.4\) Hz, 1H), 6.31 (d, \(J = 2.7\) Hz, 1H), 6.25 (dd, \(J = 8.3, 2.7\) Hz, 1H), 3.72 (s, 3H), 3.29 (s, 4H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 154.60, 137.09, 127.36, 118.34, 104.10, 102.96, 55.54. LRMS (ESI) m/z 139.0 (M + H\(^+\)). Eluent: Hexane/ EA = 3/1.
6 NMR Spectra

Compound 1

HO
| NH₂

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Bruker

Current Data Parameters
D: 2H2O
P: 1.90 ppm
FOUR 2100 MHz
WAX 39.5°
INVA
11.06°
H 9.96
ACQ 1021.17
ZOOM 5 nm TRACS 21

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Bruker

Current Data Parameters
D: 2H2O
P: 1.90 ppm
FOUR 2100 MHz
WAX 39.5°
INVA
11.06°
H 9.96
ACQ 1021.17
ZOOM 5 nm TRACS 21

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Bruker

Current Data Parameters
D: 2H2O
P: 1.90 ppm
FOUR 2100 MHz
WAX 39.5°
INVA
11.06°
H 9.96
ACQ 1021.17
ZOOM 5 nm TRACS 21

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Compound 2

\[ \text{NH}_2 \]

**1H NMR**

- **Resonance at 7.80 ppm**
- **Resonance at 7.39 ppm**
- **Resonance at 7.15 ppm**
- **Resonance at 6.79 ppm**

**13C NMR**

- **Resonance at 103.6 ppm**
- **Resonance at 35.7 ppm**
- **Resonance at 15.8 ppm**
Compound 3

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{N} \\
\text{H} \\
\end{array}
\]
Compound 4

\[
\text{NH}_2
\]
Compound 5

\[
\begin{align*}
\text{NH}_2 \\
\text{Ph} & - \\
\text{OH}
\end{align*}
\]
Compound 6

\[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{OH} \\
\end{array}
\]
Compound 7

\[
\text{NH}_2\quad \text{OH}
\]
Compound 9

\[
\begin{align*}
&\text{NH}_2 \\
&\text{NH}_2 \\
&\text{O}
\end{align*}
\]