Supporting information

First application of Core-Shell Ag@Ni magnetic nanocatalyst for transfer hydrogenation reactions of aromatic nitro and carbonyl compounds

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General methods and experimental procedures

Experimental Techniques

All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 percoated plates were used, respectively. The spots were visualized using UV light. X-ray diffraction (XRD) patterns of the as-synthesized nanoparticles were recorded using a PANalytical X’pert PRO x-ray diffractometer with Cu-Kα radiation. Transmission electron microscopy (TEM) was performed on a TECNAI F-30 transmission electron microscope operating at 300 kV. Energy dispersive x-ray spectroscopy (EDS) analyses in both spot and line-scan mode were used to identify the chemical components of single nanoparticles. The TEM samples were prepared by dropping the particle suspensions in toluene onto a copper grid coated with carbon film before drying at room temperature under ambient conditions. Proton NMR spectra were recorded on a Bruker, 300, 5 mm probe at 300 MHz. 1H shifts are reported relative to internal TMS.

Preparation of Ag–Ni core–shell nanoparticles

Ag–Ni core–shell nanoparticles were prepared via the thermal decomposition of nickel(acetylacetonate)(Ni(acac)₂ 96%, Acros) and AgNO₃ (99.8%, SCRC) in oleylamine (80–90%, Acros) using a one-pot seed-growth method. In a typical synthesis, a mixture of 6 ml of oleylamine, 0.1 mmol of triphenylphosphine (TPP; CP grade, SCRC), 0.4 mmol of Ni(acac)₂ and 0.1 mmol of AgNO₃ was decanted into a three necked flask and kept under a flow of high-purity argon gas at room temperature for 20 min. After that the mixture was heated to 80 °C and kept at this temperature for 15 min with strong magnetic stirring. The resulting solution was then slowly heated up to a temperature of 190 °C (the reaction temperature may range from 180 to 230 °C) directly and aged for 40 min. After cooling down to room temperature naturally, excess acetone was added to the black solution to give a black precipitate which was isolated via centrifugation. The precipitate was then washed fully with a mixture of hexane and acetone, and dried in a vacuum.
General method for the reduction of nitroarenes and carbonyl compounds

The nitroarene 1 or the carbonyl compound 3 (1 mmol), isopropyl alcohol (3 mL), KOH (1.5 mmol) and Ag@Ni (50 mg), were stirred at 80 °C for an appropriate time. After completion of the reaction (monitored by TLC), the catalyst was separated magnetically. The resultant product extracted with ethyl acetate and repeatedly washed with water (5 to 7 times) to remove KOH. Then the organic solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel using n-hexane and ethyl acetate as eluent.

Proton Interpretation of synthesized compound

Aniline (2a): Obtained in 95% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.14 (t, $J = 7.6$ Hz, 2H), 6.74 (t, 1H, $J = 7.2$ Hz), 6.66 (d, 2H, $J = 7.5$ Hz), 3.53 (br s, 2H).

2-Methoxy aniline (2b): Obtained in 91% yield; $^1$H NMR (300 MHz, DMSO) δ: 6.78 (d, 1H, $J = 7.8$Hz), 6.69-6.61 (m, 2H), 6.54-6.48 (m, 1H), 4.65 (br s, 2H), 3.73 (s, 3H).

2-Chloro aniline (2c): Obtained in 86 % yield; $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.22 (d, 1H, $J = 8.1$Hz), 7.04 (t, 1H, $J = 7.6$ Hz), 6.70-6.62 (m, 2H), 3.99 (br s, 2H).

4-Bromo aniline (2d): Obtained in 94% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.23 (d, 2H, $J = 8.7$ Hz), 6.55 (d, 2H, $J = 8.7$ Hz), 3.65 (br s, 2H).

3-Bromo aniline (2 e): Obtained in 93% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.01-6.96 (t, 1H, $J_\perp = 7.6$ Hz), 6.86-6.80 (t, 2H, $J = 8.5$ Hz), 6.57 (d, 1H, $J_\perp = 7.8$ Hz), 3.67 (br s, 2H).

4-Fluro aniline (2f): Obtained in 89% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ: 6.87-6.81 (m, 2H), 6.62-6.57 (m, 2H), 3.54 (br s, 2H).

2, 5-dichloro aniline (2g): Obtained in 88% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.13-7-10 (m, 1H), 6.71 (d, 1H, $J = 1.5$ Hz), 6.65-6.62 (m, 1H), 4.09 (br s, 2H).

3-Methyl aniline (2h): Obtained in 93% yield; $^1$H NMR (300 MHz, DMSO) δ: 6.87 (t, 1H, $J = 7.5$Hz), 6.37 (s, 1H), 6.32-6.29 (m, 1H), 4.90 (s, 2H), 2.13 (s, 3H).

4-hydroxy aniline (2i): Obtained in 90% yield; $^1$H NMR (300 MHz, DMSO) δ: 8.31 (br, s, 1H), 6.49-6.40 (q, 4H), 4.35 (br s, 2H).

1-Amino naphthalene (2j): Obtained in 85% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.81-7.78 (m, 2H), 7.45-7.43 (m, 2H), 7.32-7.22 (m, 2H), 6.77-6.75 (dd, 1H, $J = 6.6$ and 1.8 Hz), 4.12 (s, 2H).

Ortho-phenylenediammine (2k): Obtained in 93% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ: 6.72 (m, 4H), 3.36 (br s, 4H).

3-Nitro aniline (2l) : Obtained in 94% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.59-7.56 (dd, 1H, $J = 8.1$ and $1.2$ Hz), 7.49 (s, 1H), 7.30-7.26 (m, 1H), 6.96-6.93 (dd, 1H, $J = 7.8$ and $1.5$ Hz), 4.00 (br s, 2H).
4-Amino benzonitrile (2m): Obtained in 91% yield; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.41 (d, 1H, $J = 7.6$ Hz), 6.66 (d, 1H, $J = 7.5$ Hz), 4.22 (br s, 1H).

4-Ethyl 4-amino benzoate (2n): Obtained in 93% yield; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.87 (d, 2H, $J = 8.7$ Hz), 6.64 (d, 2H, $J = 8.7$ Hz), 4.34-4.27 (q, 2H, $J = 7.0$ Hz), 4.08 (br s, 2H), 1.38 (t, 3H, $J = 7.0$ Hz).

4-Amino acetophenone (2o): Obtained in 94% yield; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.81 (d, 2H, $J = 7.8$ Hz), 6.65 (d, 2H, $J = 7.8$ Hz), 4.19 (s, 2H), 2.50 (s, 3H).

1-Phenylethanol (4a): Obtained in % yield; $^1$H NMR (300 MHz, DMSO) $\delta$: 7.33-7.27 (m, 4H), 7.22-7.18 (m, 1H), 5.16 (br s, 1H), 4.74-4.72 (m, 1H), 1.33 (d, 3H, $J = 6.0$ Hz).

1-(4-Chlorophenyl) ethanol (4b): Obtained in % yield; $^1$H NMR (300 MHz, DMSO) $\delta$: 7.35 (s, 4H), 5.22 (s, 1H), 4.75-4.68 (m, 1H), 1.31 (d, 3H, $J = 6.3$ Hz).

1-(4-Bromophenyl) ethanol (4c): Obtained in 91% yield; $^1$H NMR (300 MHz, DMSO) $\delta$: 7.50 (d, 2H, $J = 8.1$ Hz), 7.31 (d, 2H, $J = 7.8$ Hz), 5.23 (br, 1H, -OH), 4.72-4.68 (m, 1H), 1.31 (d, 3H, $J = 6.3$ Hz).

Cyclohexanol (4d): Obtained in 90% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 4.45 (d, 1H, $J = 2.7$ Hz), 3.39 (br, 1H), 1.74-1.63 (m, 4H), 1.48-1.45 (m, 1H), 1.25-1.07 (m, 5H).

Optimization of reaction conditions with 4-hydroxy nitrobenzene

First we performed reaction without catalyst and base, and after 12 hours no corresponding product was observed (Table 1, entry 1). Either KOH or nanocatalyst is also not enough to perform hydrogen transfer reaction as well (Table 1, entries 2 and 3). Depending on the amount of Ag@Ni core shell NPs yield increased from 35 to 90% (Table 1, entries 4 to 6). Indeed, increasing the quantity of catalyst from 10 mg to 50 mg lead to an increase in the yield of reaction. The reduction reactions were also carried out in NaOH, but the results were less satisfactory (Table 1, entry 7).
Table 1. Optimization of reaction conditions for the reduction of 4-hydroxy nitrobenzene.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base</th>
<th>Time (h)</th>
<th>Isolated yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>------</td>
<td>------</td>
<td>12</td>
<td>NR\textsuperscript{b}</td>
</tr>
<tr>
<td>2</td>
<td>------</td>
<td>KOH</td>
<td>12</td>
<td>NR\textsuperscript{b}</td>
</tr>
<tr>
<td>3</td>
<td>Ag@Ni core shell NPs</td>
<td>------</td>
<td>12</td>
<td>NR\textsuperscript{b}</td>
</tr>
<tr>
<td>4</td>
<td>Ag@Ni core shell NPs</td>
<td>KOH</td>
<td>2</td>
<td>35\textsuperscript{c}</td>
</tr>
<tr>
<td>5</td>
<td>Ag@Ni core shell NPs</td>
<td>KOH</td>
<td>2</td>
<td>65\textsuperscript{d}</td>
</tr>
<tr>
<td>6</td>
<td>Ag@Ni core shell NPs</td>
<td>KOH</td>
<td>2</td>
<td>90\textsuperscript{e}</td>
</tr>
<tr>
<td>7</td>
<td>Ag@Ni core shell NPs</td>
<td>NaOH</td>
<td>2</td>
<td>78</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: Nitrocompound (1 mmol), Base (1.5 mmol), Temp. 80 °C, IPA (3 mL), catalyst = 50 mg  
\textsuperscript{b} NR= No reaction  
\textsuperscript{c} 10 mg catalyst used  
\textsuperscript{d} 30 mg catalyst used  
\textsuperscript{e} 50 mg catalyst used

TEM and Histogram of Ag@Ni core-shell nanocatalysts

Transmission emission micrograph and histogram are depicted in Figure 1. These NPs have a very narrow size distribution with a standard deviation of 1.14 nm.

![TEM and Histogram](image)

Figure 1: TEM at 100 nm (Right) and particle size distribution of core-shell nano catalysts (left).
Table 2. Comparison of reduction of nitrobenzene with existing protocol

<table>
<thead>
<tr>
<th>Entries</th>
<th>Reaction conditions</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>γ-Fe$_2$O$_3$, KOH, IPA</td>
<td>6</td>
<td>80$^1$</td>
</tr>
<tr>
<td>2</td>
<td>Mesoporous COHMA, KOH, IPA</td>
<td>2</td>
<td>91$^2$</td>
</tr>
<tr>
<td>3</td>
<td>NanoMgO-ZrO$_2$</td>
<td>2</td>
<td>94$^3$</td>
</tr>
<tr>
<td>4</td>
<td>Ni-MCM41, KOH, IPA</td>
<td>4</td>
<td>93$^4$</td>
</tr>
<tr>
<td>5</td>
<td>Pd-DNA nanohybrids, H$_2$ balloon,</td>
<td>4</td>
<td>95$^5$</td>
</tr>
<tr>
<td>6</td>
<td>Fe$_3$O$_4$-Ni, glycerol, KOH</td>
<td>3</td>
<td>94$^6$</td>
</tr>
<tr>
<td>7</td>
<td>Core-shell Ag@Ni, KOH, IPA (present work)</td>
<td>2</td>
<td>96</td>
</tr>
</tbody>
</table>

a) IPA- Isopropyl alcohol,

From above table, it is clear that present protocol is superior to existing protocol, in terms of yield of aniline. Pd-DNA nanohybrids catalyst found to be comparable to present protocol, but the main drawback of this protocol is that use of expensive Pd metal.
Proton NMR Spectra of compounds

Proton NMR spectra of aniline (2a)

Proton NMR of 2-methoxy aniline (2b)
Proton NMR of 2-chloro aniline (2c)

Proton NMR of 4-bromo aniline (2d)
Proton NMR of 3-bromo aniline (2e)

Proton NMR of 4-fluro aniline (2f)
Proton NMR of 2, 5-dichloro aniline (2g)

Proton NMR of 3-methyl aniline (2h)
Proton NMR of 4-hydroxy aniline (2i)

Proton NMR of naphthyl amine (2j)
Proton NMR of ortho-phenylene diamine (2k)

Proton NMR of 3-nitro aniline (2l)
Proton NMR 4-amino benzonitrile (2m)

Proton NMR of 4-ethyl ester aniline (2n)
Proton NMR of 4-amino acetophenone (2o)

Proton NMR of 1-phenyl ethanol (4a)
Proton NMR of 1-(4-Chlorophenyl)ethanol (4b)

Proton NMR of 1-(4-Bromophenyl)ethanol (4c)
Proton NMR of Cyclohexanol (4d)
References


