Electronic Supporting Information

Capping agent dissolution method for the synthesis of metal nanosponges and their catalytic activity towards nitroarene reduction under mild conditions

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The kinetics of the catalytic reduction of 4-nitrophenol

The kinetics of the catalytic reduction of 4-nitrophenol with metal nanosponges were investigated and typical time dependent absorption spectra are shown in Fig. 8 (main manuscript). As the initial concentration of NaBH₄ is high as compared to 4-nitrophenol, pseudo-first order kinetics was used to compute the rate constant. Therefore, the rate equation could be expressed as

\[
\frac{dc_t}{dt} = -kc_t
\]

where, \( c \) is the concentration of 4-nitrophenol at time \( t \) and \( k \) is the rate constant of the reaction. Integrating the rate equation at boundary condition of: at \( t = 0, c_t = c_0 \) and \( t = t, c_t = c_t \), results in

\[
\ln \frac{c_t}{c_0} = -kt
\]

Considering that absorbance of 4-nitrophenol (\( \lambda = 400 \text{ nm} \)) is proportional to its concentration during the course of the reaction, concentration could be substituted by absorbance value. At time zero, \( t = 0, A_0 = c_0 \) and at \( t = t, A_t = c_t \), yields

\[
\ln \frac{A_t}{A_0} = -kt
\]

From a linear plot of \( \ln(A_t/A_0) \) vs time (\( t \)), the slope gives the apparent rate constant of the reaction (Figure S11). The rate constants were calculated from the liner plots.
Figure S1: High resolution SEM images of a) Ag, b) Au, c) Pd, d) Pt, and e) Cu nanosponges.

Figure S2. $^{11}$B-NMR spectrum of dried filtrate obtained after the hydrolysis reaction of Ag@BNH$_x$ nanocomposite. Dried filtrates were dissolved in distil water and NMR spectra was recorded.
Figure S3. $^{11}$B-NMR spectrum of dried filtrate obtained after the hydrolysis reaction of Au@BNH$_x$ nanocomposite. Dried filtrate was dissolved in distil water and NMR spectra was recorded.

Figure S4. $^{11}$B-NMR spectrum of dried filtrate obtained after the hydrolysis reaction of Pd@BNH$_x$ nanocomposite. Dried filtrate was dissolved in distil water and NMR spectra was recorded.
Figure S5. $^{11}$B-NMR spectrum of dried filtrate obtained after the hydrolysis reaction of Pt@BNH$_x$ nanocomposite. Dried filtrate was dissolved in distil water and NMR spectra was recorded.

Figure S6. $^{11}$B-NMR spectrum of dried filtrate obtained after the hydrolysis reaction of Cu@BNH$_x$ nanocomposite. Dried filtrate was dissolved in distil water and NMR spectra was recorded.
**Figure S7.** Powder X-ray diffraction stack plot of dried filtrates obtained after the hydrolysis reaction of different M@BNHₓ (M= Ag, Au, Pd, Pt, Cu) nanocomposites. The JCPDS card number for the corresponding phases are: NH₄Cl: 07-0007; (NH₄)₂B₄O₇.4H₂O: 19-0061; NH₄B₅O₈.4H₂O: 74-1233; NH₄B₅O₈.3H₂O: 12-0637.

**Figure S8.** FT-IR spectral stack plot of dried filtrates obtained after the hydrolysis reaction of M@BNHₓ (M= Ag, Au, Pd, Pt, Cu) nanocomposites.
**Figure S9:** EDS spectra of a) Ag, b) Au, c) Pd, d) Pt, and e) Cu nanosponges.

**Figure S10:** BET surface area of a) Ag, b) Au, c) Pd, d) Pt and e) Cu nanosponges; and BJH pore size distribution (from desorption branch) of f) Pd, g) Pt and h) Cu nanosponges.
Hydrolysis of Pd@BNH₅ nanocomposite at different temperature

In order to evaluate the kinetics of hydrogen evolution at a different temperature, the nanocomposite of Pd@BNH₅ was prepared at 1:10 ratio of palladium chloride to AB. In a typical synthesis of Pd@BNH₅ nanocomposite, palladium chloride (89 mg, 0.5 mmol) was added in a batch-wise manner into pre-heated (60 °C) AB (155 mg, 5 mmol) in the solid state under vigorous stirring in an inert atmosphere. After completing the addition process, the mixture was allowed to stir for 3 h at 60 °C.

a) Then the reaction mixture was cooled down to room temperature (30 °C) and 10 mL of water was added subsequently. Upon addition of water, vigorous effervescence of hydrogen gas bubbles was noted. The evolved hydrogen gas was measured using a gas burette connected to the Schlenk tube. The final volume was noted by adjusting the water levels in the gas burette and the reservoir.

b) In a different reaction, after stirring for 3 h at 60 °C, 10 mL of water was added into the reaction mixture at 60 °C and the gas evolved was measured using a gas burette connected to the Schlenk tube.

After the hydrolysis, the black precipitate formed was filtered off and washed thoroughly with water several times and finally with acetone and dried over 12 h. BET surface area was measured for both the samples.

![Figure S11. a) BET surface area co-plot of palladium nanosponges obtained after hydrolysis at 30 °C (red) and 60 °C (blue), solid square for adsorption branch and empty square for desorption branch; b) hydrogen generation from hydrolysis of Pd@BNH₅ nanocomposite.](image-url)
Figure S12. Kinetics analysis of the catalytic activities of metal nanosponges for the reduction of 4-nitrophenol by NaBH$_4$. Plot of $\ln(A_t/A_0)$ vs time; a) Ag, b) Au, c) Pd, d) Pt, and e) Cu nanosponges as catalysts.

Figure S13. a) Recyclability test for the palladium nanosponge as a catalyst for nitrobenzene reduction, b) BF-TEM image and c) HRTEM image of the palladium catalyst after 5th cycle.
Table S1. Hydrogenation of nitrobenzene by palladium nanosponge using different reducing agents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reducing agent</th>
<th>Time (min)</th>
<th>%Conv.(^a)</th>
<th>TOF (min(^{-1}))(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ammonia borane (NH(_3)·BH(_3))</td>
<td>30</td>
<td>&gt;99</td>
<td>33.3</td>
</tr>
<tr>
<td>2</td>
<td>Sodium borohydride (NaBH(_4))</td>
<td>30</td>
<td>&gt;99</td>
<td>33.3</td>
</tr>
<tr>
<td>3</td>
<td>Hydrazine (N(_2)H(_4)·H(_2)O)</td>
<td>30</td>
<td>6.9</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>Ammonium formate (HCOONH(_4))</td>
<td>30</td>
<td>3.4</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>Hydrogen (H(_2), 1 atm)</td>
<td>30</td>
<td>2.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Reaction conditions: 5 mmol of nitrobenzene, 0.005 mmol of Pd nanosponge catalyst, 15 mmol of reducing agent, at constant temperature of 30 °C in 10 mL of methanol; \(^a\)conversion to aniline was determined by GC/MS analysis using n-decane as an internal standard, \(^b\)turnover frequency = mol (aniline)/mol (Pd nanosponge)·min.

Figure S14. a) Recyclability test for the palladium nanosponge as a catalyst for nitrobenzene reduction, b) BF-TEM image, c) HRTEM image, and d) SAED pattern of the palladium catalyst after 7th cycle.
Table S2. Hydrogenation of nitrobenzene to aniline using different catalysts and reaction condition

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction conditions</th>
<th>Time</th>
<th>%Conv.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raney Nickel (85 mol%)</td>
<td>Nitrobenzene (2 mmol), NaOH (5 mmol), glycerol (3 ml) and 70 °C</td>
<td>5 h</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>Pd/C (5 mol%)</td>
<td>Nitrobenzene (5 mmol), 1,4-cyclohexadiene (30 mmol), methanol (10 ml), microwave and 120 °C</td>
<td>5 min</td>
<td>&gt;99</td>
<td>2</td>
</tr>
<tr>
<td>Au/TiO₂ (0.8 mol%)</td>
<td>Nitrobenzene (0.6 mmol), N₂H₄ (2.4 mmol), 2 mL of ethanol and 60 °C</td>
<td>6 h</td>
<td>92</td>
<td>3</td>
</tr>
<tr>
<td>10% Pd/C</td>
<td>Nitrobenzene (0.28 mmol), B₁₀H₁₄ (10 mg), methanol (5 ml), AcOH (two drops) and heat</td>
<td>1.5 h</td>
<td>90</td>
<td>4</td>
</tr>
<tr>
<td>Au-MgO (0.5 mol%)</td>
<td>Nitrobenzene (1.08 mmol), H₂O (10 mL), NaBH₄ (0.05 mol), room temperature</td>
<td>1 h</td>
<td>98</td>
<td>5</td>
</tr>
<tr>
<td>Pd-Fe₃O₄ (1 mol%)</td>
<td>0.5 mmol of nitrobenzene, 1.5 mmol of NH₃BH₃, 5 mL of methanol, room temperature</td>
<td>5 min</td>
<td>68</td>
<td>6</td>
</tr>
<tr>
<td>Pt-Fe₃O₄ (1 mol%)</td>
<td>0.5 mmol of nitrobenzene, 1.5 mmol of NH₃BH₃, 5 mL of methanol, room temperature</td>
<td>5 min</td>
<td>69</td>
<td>6</td>
</tr>
<tr>
<td>PVP-Pd NPs (0.1 mol%)</td>
<td>0.25 mmol of nitrobenzene, 1 mmol of NaBH₄, a mixture of EtOH : H₂O 1 : 6 (final volume 3.5 mL), room temperature</td>
<td>1 h</td>
<td>97</td>
<td>7</td>
</tr>
<tr>
<td>Pd NPs (6 mol%)</td>
<td>Nitrobenzene (0.5 mmol), (CH₃)₂NH·BH₃ (1.5 mmol), 3 mL of water/methanol (v/v = 2/1), room temperature</td>
<td>10 min</td>
<td>&gt;99</td>
<td>8</td>
</tr>
<tr>
<td>Pd-Pol (1.7 mol%)</td>
<td>1.0 mmol of nitrobenzene, 10 mmol of NaBH₄, 5 mL of water were stirred at room temperature under nitrogen</td>
<td>2 h</td>
<td>96</td>
<td>9</td>
</tr>
<tr>
<td>Pd/Fe₃O₄@C (40 mg)</td>
<td>Nitrobenzene (1 mmol), EtOH (6 ml), NaBH₄ (3 mmol), at 60 °C</td>
<td>1 h</td>
<td>&gt;99</td>
<td>10</td>
</tr>
<tr>
<td>Pd nanosponge (0.1 mol%)</td>
<td>5 mmol of nitrobenzene, 15 mmol of NH₃BH₃, 10 mL of methanol, room temperature</td>
<td>30 min</td>
<td>&gt;99</td>
<td>This work</td>
</tr>
</tbody>
</table>
Gas chromatogram:

Reduction of nitrobenzene without catalyst

![Gas chromatogram of reduction of nitrobenzene without catalyst](image1)

GC: Table 4 entry 1

![Gas chromatogram of Table 4 entry 1](image2)
GC: Table 4 entry 2

![Retention time graph for Table 4 entry 2 with the compound structure and relative intensity indicated.](image1)

GC: Table 4 entry 3

![Retention time graph for Table 4 entry 3 with the compound structure and relative intensity indicated.](image2)
GC: Table 4 entry 4

![Graph showing retention time against relative intensity for n-decane and another compound labeled with nitrogen atoms.]

GC: Table 4 entry 5

![Graph showing retention time against relative intensity for n-decane and another compound labeled with nitrogen atoms.]

GC: Table 4 entry 6

![GC Chromatogram](image1)

GC: Table 4 entry 7

![GC Chromatogram](image2)
GC: Table 4 entry 8

GC: Table 4 entry 9
GC: Table 4 entry 10

![Retention time vs. Relative intensity graph for n-decane](image)

GC: Table 4 entry 11

![Retention time vs. Relative intensity graph for n-decane](image)
GC: Table 4 entry 12

![GC chromatogram for Table 4 entry 12](image)

GC: Table 4 entry 13

![GC chromatogram for Table 4 entry 13](image)
GC: Table 4 entry 14

![Retention time vs. Relative intensity graph for Table 4 entry 14 with n-decane compound with CH₂ and NH₂ groups.]

GC: Table 4 entry 15

![Retention time vs. Relative intensity graph for Table 4 entry 15 with n-decane compound with NO₂ group.]

S19
GC: Table 4 entry 16

GC: Table 4 entry 17
GC: Table 4 entry 18

![Retention time graph for Table 4 entry 18]

GC: Table 4 entry 19

![Retention time graph for Table 4 entry 19]
GC: Table 4 entry 20

![Graph showing retention time and relative intensity for n-decane and a compound with the chemical structure of a phenyl ring with amino and cyano groups.]

GC: Table 4 entry 21

![Graph showing retention time and relative intensity for n-decane and a compound with the chemical structure of a phenyl ring with amino and carboxylic acid groups.]

References:


