Supporting Information

Atomically dispersed Ni as the active site towards selective hydrogenation of nitroarenes

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**Fig. S1** (a) SEM image and (b) TEM image of MgO.
Fig. S2 (a) SEM image, (b) TEM image (inset: the corresponding SAED pattern), (c) HAADF-STEM image and (d) EDS mapping of Ni-N-C-600.
Fig. S3 (a) SEM image, (b) TEM image (inset: the SAED pattern of the region marked with red cycle), (c) HAADF-STEM image and (d) EDS mapping of Ni-N-C-800.
Fig. S4 (a) SEM image and (b) TEM image of Ni-NC (inset: the corresponding SAED pattern).
Fig. S5 Pore size distribution of Ni-N-C-600, Ni-N-C-700, and Ni-N-C-800.
Fig. S6 Raman spectra for Ni-N-C-600, Ni-N-C-700, Ni-N-C-800 and Ni-NC.
Fig. S7 XPS spectra of the Ni-N-C catalysts. (a) Survey spectra of different Ni-N-C, NiPc and Ni-NC, (b) N1s XPS spectra of Ni-NC, (c) N1s XPS spectra of NiPc.
Fig. S8 The corresponding EXAFS fitting curves of (a) Ni-N-C-600, (b) Ni-N-C-700 and (c) Ni-N-C-800.
Fig. S9 The GC-MS spectra of reduction reaction intermediate products.
Fig. S10 A proposed reaction mechanism for Ni-N-C-700 catalyze reduction of nitroarene
Fig. S11 The GC-MS spectra of hydrogenation of 4-nitrostyrene reaction. Reaction condition: 0.25 mmol nitrostyrene in 5 ml ethanol, 4 mg catalyst, 120 °C, 3Mpa H₂, 10 h.
**Fig. S12** Catalytic stability and selectivity of Ni-N-C-700 catalysts. Reaction condition: 0.25 mmol 4-nitrochlorobenzene in 5 ml ethanol, 4 mg catalyst, 120 °C, 3Mpa H₂, 10h up to 3th recycle and 16h for 4th and 5th recycles.
Fig. S13 (a) SEM image, (b) TEM image (inset: the corresponding SAED pattern), (c) HAADF-STEM image and (d) EDS mapping of Ni-N-C-700 after recycle test.
Fig. S14 Schematic diagram of leaching test.
For NiN$_2$C$_2$-1 and NiN$_2$C$_2$-2, the former is more stable than the later with the lower energy of 0.50 eV, therefore, in the following nitrobenzene adsorption process, we only consider the case of NiN$_2$C$_2$-1 as a substrate.

$$E_f = E_{Ni-N_x} - E_{GN_x} - E_{Ni}$$
Fig. S16 Adsorption structures of nitrobenzene on Ni-Nₓ substrates. The gray, blue, light blue, red, and white balls stand for C, N, Ni, O, and H atoms, respectively.
Fig. S17 Co-adsorption structures of nitrobenzene molecules and H\(_2\) on the other optimized Ni-N\(_3\) structures. The gray, blue, light blue, red, and white balls stand for C, N, Ni, O, and H atoms, respectively.
Table S1. EXAFS data fitting results of Ni-N-C-600, Ni-N-C-700, and Ni-N-C-800 for Ni K edge.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>$N^a$</th>
<th>$R$ (Å)$^b$</th>
<th>$\sigma^2$ (Å$^2$ 10$^{-3}$)$^c$</th>
<th>$\Delta E_0$ (eV)$^d$</th>
<th>$R$ factor (%)$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-N-C-600</td>
<td>Ni-N</td>
<td>3.7</td>
<td>1.86</td>
<td>6.9</td>
<td>-0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Ni-N-C-700</td>
<td>Ni-N</td>
<td>3.3</td>
<td>1.84</td>
<td>6.4</td>
<td>-5.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Ni-N-C-800</td>
<td>Ni-N</td>
<td>2.6</td>
<td>1.86</td>
<td>5.0</td>
<td>-9.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

[a] CN, coordination number; [b] R, bonding distance; [c] $\sigma^2$, Debye-Waller factor; [d] $\Delta E_0$, inner potential shift; [e] R factor is used to value the goodness of the fitting.
**Table S2.** Ni content of catalysts

<table>
<thead>
<tr>
<th>sample</th>
<th>Ni-N-C-600</th>
<th>Ni-N-C-700</th>
<th>Ni-N-C-800</th>
<th>Ni-NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni[^a] wt%</td>
<td>4.9</td>
<td>4.4</td>
<td>3.6</td>
<td>10.3</td>
</tr>
<tr>
<td>Ni[^b] at%</td>
<td>1.006</td>
<td>0.993</td>
<td>0.62</td>
<td>2.42</td>
</tr>
<tr>
<td>Ni[^c] wt%</td>
<td>4.5</td>
<td>4.2</td>
<td>2.9</td>
<td>9.8</td>
</tr>
</tbody>
</table>

[a] Ni content (wt) of catalysts as measured by ICP-OES. [b] Ni content of catalysts as measured by XPS. [c] It was calculated based on the contents of C, N, O and Ni.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>At%</th>
<th>pyridinic</th>
<th>Ni–N</th>
<th>pyrrolic</th>
<th>quaternary</th>
<th>oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-N-C-600</td>
<td>10.6</td>
<td>3.65</td>
<td>2.40</td>
<td>2.29</td>
<td>1.12</td>
<td>1.37</td>
</tr>
<tr>
<td>Ni-N-C-700</td>
<td>8.5</td>
<td>2.54</td>
<td>1.95</td>
<td>1.34</td>
<td>1.57</td>
<td>1.1</td>
</tr>
<tr>
<td>Ni-N-C-800</td>
<td>5.2</td>
<td>1.52</td>
<td>1.14</td>
<td>0.78</td>
<td>0.91</td>
<td>0.85</td>
</tr>
<tr>
<td>Ni-NC</td>
<td>3.5</td>
<td>0.68</td>
<td>0.65</td>
<td>0.51</td>
<td>0.96</td>
<td>0.70</td>
</tr>
</tbody>
</table>

[a] It was calculated according to the peak area of different types of N.
### Table S4. Evaluation of reaction conditions for the reduction of 4-chloronitrobenzene$^a$

![Reaction Scheme](image.png)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>NaBH$_4$</th>
<th>$T$ (h)</th>
<th>Yield$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni-N-C-600</td>
<td></td>
<td></td>
<td>73</td>
</tr>
<tr>
<td>2</td>
<td>Ni-N-C-700</td>
<td>5 equiv</td>
<td>0.25</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>Ni-N-C-800</td>
<td></td>
<td></td>
<td>46</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 0.25 mmol 4-nitrochlorobenzene in 1 ml H$_2$O, 2mg Catalyst. $^b$ isolated yield.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NaBH₄ (equiv)</th>
<th>Temp °C</th>
<th>Time (min)</th>
<th>TOF (h⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-N-C-700</td>
<td>5</td>
<td>r.t.</td>
<td>15</td>
<td>667.7</td>
<td>This work</td>
</tr>
<tr>
<td>N-G</td>
<td>100</td>
<td>r.t.</td>
<td>21</td>
<td>-</td>
<td><em>Energy Environ. Sci.</em> 2013, 6, 3260-3266,[¹]</td>
</tr>
<tr>
<td>N-CNTs</td>
<td>100</td>
<td>r.t.</td>
<td>48</td>
<td>-</td>
<td><em>Environ. Sci. Technol.</em> 2014, 48, 10191-10197,[²]</td>
</tr>
<tr>
<td>N-G</td>
<td>10</td>
<td>r.t</td>
<td>300</td>
<td>-</td>
<td><em>Green Chem.</em> 2016, 18, 4254-4262.[³]</td>
</tr>
<tr>
<td>N, P-G</td>
<td>100</td>
<td>35</td>
<td>2.5</td>
<td>-</td>
<td><em>J. Catal.</em> 2018, 359, 233-241.[⁴]</td>
</tr>
<tr>
<td>S, N-CNTs</td>
<td>32</td>
<td>r.t.</td>
<td>10</td>
<td>-</td>
<td><em>Adv. Mater.</em> 2016, 28, 10679-10683.[⁵]</td>
</tr>
<tr>
<td>AA/GO</td>
<td>750</td>
<td>r.t.</td>
<td>80</td>
<td>-</td>
<td><em>Nano Res.</em> 2015, 8, 3992-4006.[⁶]</td>
</tr>
<tr>
<td>Ni/mZSM-5</td>
<td>4</td>
<td>r.t.</td>
<td>-</td>
<td>450</td>
<td><em>RSC Adv.</em> 2015, 5, 34398-34414.[⁷]</td>
</tr>
<tr>
<td>Co@NC</td>
<td>-</td>
<td>r.t.</td>
<td>-</td>
<td>45</td>
<td><em>J. Mater. Chem. A</em> 2016, 4, 7476-7482.[⁸]</td>
</tr>
<tr>
<td>Cu&amp;Fe₅O₄-mC</td>
<td>10</td>
<td>r.t.</td>
<td>-</td>
<td>12.5</td>
<td><em>Green Chem.</em> 2014, 16, 4198-4205.[⁹]</td>
</tr>
</tbody>
</table>
### Table S6. Results of Hydrogenation of nitroarenes catalyzed by Ni-N-C-700

Catalyst, NaBH₄  
\[ \text{H₂O, r.t.} \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactant</th>
<th>Product</th>
<th>( T (h) )</th>
<th>Yield(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl-( \text{NH}_2 )</td>
<td>Cl-( \text{NH}_2 )</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Br-( \text{NO}_2 )</td>
<td>Br-( \text{NH}_2 )</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>H(_3\text{C})-( \text{NO}_2 )</td>
<td>H(_3\text{C})-( \text{NH}_2 )</td>
<td>0.25 h</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>H(_3\text{CO})-( \text{NO}_2 )</td>
<td>H(_3\text{CO})-( \text{NH}_2 )</td>
<td>96</td>
<td></td>
</tr>
</tbody>
</table>

\[a\] Reaction conditions: 0.25 mmol 4-nitrochlorobenzene in 1 ml H₂O, 2mg Catalyst. \[b\] isolated yield
Table S7. Comparison of the hydrogenation of nitroarenes activity between Ni-N-C-700 and other nonprecious catalysts in literature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reducing agent</th>
<th>Temp °C</th>
<th>P (MPa)</th>
<th>TOF (h(^{-1}))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-N-C-700</td>
<td>H(_2)</td>
<td>120</td>
<td>3</td>
<td>8.4</td>
<td>This work</td>
</tr>
<tr>
<td>Ni-N-C-600</td>
<td>H(_2)</td>
<td>120</td>
<td>3</td>
<td>6.2</td>
<td>This work</td>
</tr>
<tr>
<td>Ni-N-C-800</td>
<td>H(_2)</td>
<td>120</td>
<td>3</td>
<td>6.4</td>
<td>This work</td>
</tr>
<tr>
<td>Ni–NiFe(_2)O(_4)</td>
<td>H(_2)</td>
<td>150</td>
<td>1</td>
<td>5</td>
<td><em>Green Chem.</em> 2015, 17, 821-826.(^{[10]})</td>
</tr>
<tr>
<td>Ni/C(_{60})-Ac-B-4</td>
<td>H(_2)</td>
<td>110</td>
<td>2</td>
<td>7.8</td>
<td><em>Catal. Commun.</em> 2017, 97, 83-87.(^{[11]})</td>
</tr>
<tr>
<td>Ni/C</td>
<td>H(_2)</td>
<td>140</td>
<td>2</td>
<td>10.6</td>
<td><em>Chem. Eng. J.</em> 2015, 275, 36-44.(^{[12]})</td>
</tr>
<tr>
<td>Ni/NGr@C-800</td>
<td>H(_2)</td>
<td>110</td>
<td>5</td>
<td>2.5</td>
<td><em>Green Chem.</em> 2016, 18, 3594-3599.(^{[13]})</td>
</tr>
<tr>
<td>Ni@SiCN</td>
<td>H(_2)</td>
<td>110</td>
<td>5</td>
<td>5</td>
<td><em>ChemCatChem.</em> 2016, 8, 129-134.(^{[14]})</td>
</tr>
<tr>
<td>Ni-L/P-CNTs</td>
<td>H(_2)</td>
<td>140</td>
<td>2</td>
<td>1.5</td>
<td><em>Catal. Sci. Technol.</em> 2013, 3, 982-991.(^{[16]})</td>
</tr>
<tr>
<td>Fe(_2)O(_3)-NC</td>
<td>H(_2)</td>
<td>120</td>
<td>5</td>
<td>1.9</td>
<td><em>Science</em> 2013, 342, 1073-1076.(^{[17]})</td>
</tr>
<tr>
<td>Co(_3)O(_4)/CNT</td>
<td>H(_2)</td>
<td>110</td>
<td>3</td>
<td>6.2</td>
<td><em>Acs Catal.</em> 2015, 5, 4783-4789.(^{[18]})</td>
</tr>
<tr>
<td>Co-Co(_3)O(_4)/CN</td>
<td>H(_2)</td>
<td>110</td>
<td>5</td>
<td>16.7</td>
<td><em>Nat. Chem.</em> 2013, 5, 537-543.(^{[19]})</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Fresh</td>
<td>Recycle</td>
<td></td>
<td></td>
<td></td>
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<td>----------</td>
<td>-------</td>
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</tr>
<tr>
<td>Ni wt%</td>
<td>4.4</td>
<td>2.8</td>
<td></td>
<td></td>
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</table>
References


