Electronic Supplementary Information

Catalytic CO$_2$ Hydrogenation to Formic Acid over Carbon Nanotube–Graphene Supported PdNi Alloy Catalysts

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S1. Synthesis of graphene oxide

Graphene oxide was synthesized by Hummers method using graphite flake. Briefly, 2g of graphite flake was added into a mixture solution of H$_2$SO$_4$ (50 mL) and NaNO$_3$ (1 g) in a 3 neck round bottom flask (500 mL). The mixture was vigorously stirred with magnetic bar in 10 min, then put in an ice-bath (0 – 5°C) and further stirring 20 min to obtain green solution. KMnO$_4$ (6 g) was slowly added to flask under continuous stirring in ice-bath (0 – 5°C). After 20 min, ice-bath was removed and temperature increased to 35°C. The solution was further stirred at 35°C for 2 h and then 100 mL DI H$_2$O was added dropwise to the mixture. The solution temperature increased up to 98°C and kept for 30 min until no bubble appeared and dark brown solution turned to light brown solution. After that, the reaction was terminated by addition of 300 mL DI H$_2$O (40°C) and mixture of 4 mL H$_2$O$_2$ 35% solution in 40 mL DI H$_2$O. The product was filtered using mixed-cellulose ester membrane filter (pore size: 0.45μm) and washed 2 times with DI H$_2$O. The resulting mixture was then re-dispersed in 350 mL DI H$_2$O (40°C) to remove residual metal ions and acid and kept stirring for 1 h at 40°C. After the second filtering, graphite oxide was washed with liquid N$_2$ and transferred to Freeze drying in 4 days. Finally, we obtained around 3.3 g of graphite oxide after grinding (Fig. S1).

Fig. S1 (a) Photograph of GO and (b) XRD pattern of GO
1. Catalyst characterization

1.1. Energy dispersive spectrum (EDS) - High angle annular dark field (HAADF) TEM image

Fig. S2 (a) EDS spectrum and (b) HAADF TEM image of Pd$_3$Ni$_7$/CNT-GR.

1.2. Fourier transform infrared (FTIR) and Raman spectroscopy

Fig. S3 (a) FTIR spectra and (b) Raman spectra of Pd$_3$Ni$_7$/CNT-GR and GO samples
1.3. Ni 2p XPS spectra

Fig. S4 Ni 2p XPS spectra comparison of Pd$_3$Ni$_7$/CNT-GR and Ni/CNT-GR.

1.4. Pd concentration on the surface of catalysts

Fig. S5 Linear relation of intended composition of Pd and surface Pd determined by XPS.
1.5. Catalytic activity of Pd, Ni, Pd₃Ni₇ on CNT-GR

Fig. S6. Formic acid yield as a function of catalyst composition. Reaction conditions: 1 mmol (Pd+Ni) catalysts, 90ml, H₂O, P = 50 bar (H₂/CO₂ = 1), 40 °C, 15 h. No formic acid product was obtained from Ni/CNT-GR catalyst.

1.6. Recycling test of Pd₃Ni₇/CNT-GR catalyst

Fig. S7 Formic acid yield as a function of batch cycles. Reaction conditions: 1 mmol (Pd+Ni) catalysts, 90ml, H₂O, P = 50 bar (H₂/CO₂ = 1), 40 °C, 5 h. Catalyst was regenerated with H₂ treatment (130 °C, 1 h) before each run of catalytic reactions.
2. Catalytic studies

Calculation of turnover number (TON)

\[ TON = \frac{\text{Mole of Formic acid (mmol)}}{\text{Mole of Pd active sites (mmol)}} \]

Calculation of turnover frequency (TOF = TON s\(^{-1}\))

\[ \text{TOF (s}^{-1}\text{)} = \frac{\text{Mole of Formic acid (mmol)}}{\text{Mole of Pd active sites (mmol)} \times \text{Reaction time (s)}} \]

HPLC analysis of liquid product

![HPLC analysis of liquid product](image)

**Fig. S8** HPLC analysis of Formic acid (desirable product) and Acetic acid (minor product) after CO\(_2\) hydrogenation reaction.
Table S1. Textural properties of materials.

<table>
<thead>
<tr>
<th></th>
<th>Pd₃Ni₇/CNT-GR</th>
<th>CNT-GR</th>
<th>CNT</th>
<th>GR</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m²/g)</td>
<td>266</td>
<td>288</td>
<td>224</td>
<td>33.0</td>
</tr>
<tr>
<td>External Surface Area\textsuperscript{a} (m²/g)</td>
<td>213</td>
<td>231</td>
<td>160</td>
<td>30.7</td>
</tr>
<tr>
<td>Micropore Area\textsuperscript{a} (m²/g)</td>
<td>52.6</td>
<td>56.9</td>
<td>62.4</td>
<td>2.33</td>
</tr>
<tr>
<td>Mesopore Volume\textsuperscript{b} (m³/g)</td>
<td>0.777</td>
<td>0.677</td>
<td>0.636</td>
<td>0.0935</td>
</tr>
<tr>
<td>Micropore Volume\textsuperscript{c} (cm³/g)</td>
<td>0.0187</td>
<td>0.0202</td>
<td>0.0249</td>
<td>N.A.\textsuperscript{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculated by t-method
\textsuperscript{b} BJH adsorption pore volume
\textsuperscript{c} Not available because of too low adsorption amount.
Table S2. Comparison of catalytic performance of pure formic acid formation from CO₂.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>P (H₂/CO₂)</th>
<th>Time (h)</th>
<th>FA (M)</th>
<th>TON / TOF (s⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru aqua complex</td>
<td>20 ml water (pH = 2.5 – 5.5)</td>
<td>40</td>
<td>55 / 25</td>
<td>70</td>
<td>0.035 – 0.055</td>
<td>35 – 55 / 1.4 × 10⁻⁴</td>
<td>Chem. Commun., 2004, 2714–2715</td>
</tr>
<tr>
<td>Ir aqua complex</td>
<td>20 ml water (pH = 3)</td>
<td>40</td>
<td>55 / 25</td>
<td>0.5</td>
<td>0.012</td>
<td>12 / 6.7 × 10⁻³</td>
<td>Dalton Trans., 2006, 4657–4663</td>
</tr>
<tr>
<td>Rh aqua complex</td>
<td>5 ml water (HCOONa 0.5 M)</td>
<td>50</td>
<td>50 / 50</td>
<td>20</td>
<td>0.13</td>
<td>0.3 / 4.5 × 10⁻⁶</td>
<td>Catal. Commun. 2011, 14, 74–76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 ml water</td>
<td>50 / 50</td>
<td>120</td>
<td>0.11</td>
<td>0.08 / 1.8 × 10⁻⁷</td>
<td>Nat. Commun. 2014, 5:4017, 2014</td>
</tr>
<tr>
<td>Ru complex</td>
<td></td>
<td>50</td>
<td>50 / 50</td>
<td>120</td>
<td>1.31</td>
<td>0.95 / 2.2 × 10⁻⁴</td>
<td>This work</td>
</tr>
<tr>
<td>Pd₃Ni₇/CNT-GR</td>
<td>45 ml water</td>
<td>40</td>
<td>25 / 25</td>
<td>15</td>
<td>0.036</td>
<td>5.4 / 10⁻⁴</td>
<td>This work</td>
</tr>
</tbody>
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