Supporting information

Gram-scale Synthesis of Single-atom Metal-N-CNT Catalysts for Highly Efficient CO₂ Electroreduction

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1. Experimental section

Chemicals
Nickel (II) acetate tetrahydrate, manganese (II) acetate tetrahydrate, iron (II) acetate, platinum (II) chloride, ruthenium (III) chloride, zinc (II) acetate dihydrate and carbon nanotube (multi-walled) were purchased from Sigma-Aldrich Pty Ltd. Cobalt (II) acetate tetrahydrate and dimethyl sulfoxide were purchased from Ajax Finechem Pty Ltd. Copper (II) acetate monohydrate and 1,10-Phenanthroline monohydrate were purchased from BDH Chemicals. Ethanol was purchased from Chem-Supply Pty. Ltd. All reagents and solvents were of analytical grade and used as received without additional purification. The CO$_2$ and Ar feed gases were purchased from air liquide in Australia.

Preparation of Ni-N-CNT
In a typical experiment of preparing 1.5 % Ni-N-CNT (1.5 wt%), multiwalled carbon nanotube (76.44 mg) was dispersed in ethanol (4 mL) with ultrasonication for 2 h to get a uniform suspension solution. At the same time, 1, 10-phenonathroline monohydrate (14.85 mg) and nickel acetate tetrahydrate (6.20 mg) (molar ratio of 3:1 for 1,10-phenanthroline: Ni) were dissolved in ethanol (2 mL) under stirring at room temperature. This solution was then added into the carbon nanotube suspension to get a mixed solution. After which, the mixed solution was heated at 60 °C for 4 h in oil-bath with stirring and then at 80 °C for 2 h to evaporate ethanol, yielding a black solid. After cooling down to room temperature, the black solid was lightly ground using a mortar and pestle, then transferred into a ceramic crucible and put in a tube furnace. The black solid was heated at 350 °C for 2 h and then 1000 °C for 2 h at a ramping rate of 5 °C/min under Ar flow, the final product was obtained and denoted as 1.5 % Ni-N-CNT. Using similar methods, x % Ni-N-CNT (x=1, 2, 2.5, 3, 3.5) was prepared.

Large-scale synthesis of Ni-N-CNT
Large-scale synthesis of Ni-N-CNT was carried out using the same procedures as for 1.5 % Ni-N-CNT but with different mass of the reactants: multiwalled carbon nanotube (1528.8 mg), 1, 10-phenonathroline monohydrate (297 mg), nickel acetate tetrahydrate (124 mg). The obtained final product Ni-N-CNT with 1.5 wt% Ni loading was 1535.2 mg with high yield of 78.74 % (the yield was calculated as the ratio of the mass of final product Ni-N-CNT to the total mass of multiwalled carbon nanotube, 1, 10-phenonathroline monohydrate, and nickel acetate tetrahydrate), which confirmed the mass-production of Ni-N-CNT.

Preparation of CNT-N, CNT-Ni, and CNT
CNT-N and CNT-Ni were prepared using same steps for 1.5 % Ni-N-CNT but
without introducing nickel acetate tetrhydrate and 1, 10-phenonathroline monohydrate. CNT was heated at 350 °C for 2 h and then 1000 °C for 2 h at a ramping rate of 5 °C/min under Ar flow.

**Preparation of 1.5 % Mn-N-CNT, 1.5 % Fe-N-CNT, 1.5 % Co-N-CNT and 1.5 % Zn-N-CNT**

Different metal salts (manganese (II) acetate tetrhydrate, iron (II) acetate, cobalt (II) acetate tetrhydrate and zinc (II) acetate dihydrate) and 1,10-phenanthroline monohydrate were used. Keep the molar ratio of 1,10-phenanthroline: metal be 3:1. Preparation procedures were the same as that for 1.5% Ni-N-CNT.

**Preparation of 1.5 % Cu-N-CNT, 1.5 % Ru-N-CNT and 1.5 % Pt-N-CNT**

Metal precursors copper (II) acetate monohydrate, ruthenium (III) chloride and platinum (II) chloride, and nitrogen precursor 1,10-phenanthroline monohydrate were employed to prepare these catalysts. Synthetic steps were same as that for 1.5% Ni-N-CNT, except that DMSO rather than ethanol was used. Because of higher boiling point of DMSO, the solvent was evaporated at 190 °C.

**Catalyst characterizations**

The details of structure and morphology of the fabricated materials were investigated X-ray diffractometer (Rigaku MiniFlex), X-ray photoelectron spectroscopy (Thermo Scientific ESCALAB 250Xi), ICP-OES and scanning electron microscope (SEM, JSM-7001F, and QUANTA 450). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and Energy-dispersive X-ray spectroscopy (EDS) were obtained from JEOL JEM-ARM200F.

**Electrochemical measurements**

A three-electrode sealed H-type cell was employed for all electrochemical tests. Catalysts (5 mg) were introduced in a solution of H₂O (150 μL), ethanol (50 μL), and 5 wt% Nafion solution (50 μL). After sonication for 2 h, a uniform catalyst ink was obtained. Then, the ink was dropped onto a polished glassy carbon and dried in air, giving a working electrode with catalyst loading of 0.5-1 mg cm⁻². The reference and counter electrodes were a saturated calomel electrode (SCE) electrode and a Pt wire. All LSV and potentiostatic data were collected in 0.5 M KHCO₃ and corrected with 90 % IR compensation. All potentials were calculated using the Nernst equation:

\[ E_{\text{RHE}} = E_{\text{SCE}} + 0.0591 \times \text{pH} + 0.241 \text{ V (25 °C)} \]

The products and Faradic efficiency of CO₂ electroreduction were measured by chronoamperometry at fixed potentials. The gaseous products were quantified by a gas chromatograph with a flame ionization detector (FID) for CO and CH₄ and a
thermal conductivity detector for H₂ quantification. The carrier gas was ultrapure Ar (99.999%). The CO₂ flow rate was 20 sccm controlled by a Cole-Parmer mass flow meter.

The faradaic efficiencies were calculated as the following:

$$FE_{CO} = \frac{0.1315 \times V_{CO2} \times \left(\frac{0.015039 A_{CO}}{1000000}\right)}{I_{total}} \times 100\%$$

$$FE_{H2} = \frac{0.1315 \times V_{CO2} \times \left(\frac{10.87417 A_{H2} - 36.35039}{1000000}\right)}{I_{total}} \times 100\%$$

V_{CO2}: flow rate (sccm)
A_{CO}: integral area of CO peak tested by GC
A_{H2}: integral area of H₂ peak tested by GC
I_{total}: total current (A)

**Electrochemical active surface areas (ECSA) measurements**

The ECSA is proportional to double-layer capacitance (C_{dl}) values. C_{dl} was determined in H-type cell by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammetry (CV). The CV ranged from -0.5 to -0.6 V vs SCE. The scan rates were 10, 20, 40, 60, 80 and 100 mV/s. C_{dl} was estimated by plotting the anodic and cathodic current density difference at -0.55 V vs SCE against the scan rates.

ECSA was calculated based on the definition:

ECSA = C_{dl}/C_s

Where C_{dl} corresponds to the slope of the double-layer charging current vs the scan rate plot, and the value of C_s we used is 40 μF cm⁻².
2. Supplemental Figures

Fig. S1 SEM images of (a) CNT, (b) CNT–N, (c) CNT-Ni, (d) Pt-N-CNT, (e) Cu-N-CNT, (f) Zn-N-CNT, (g) Ru-N-CNT, (h) Mn-N-CNT, (i) Fe-N-CNT, (j) Co-N-CNT.
Fig. S2 ICP data for 1.5% Ni-N-CNT and CNT.
Fig. S3 X-ray diffraction patterns of (a) 1.5% Ni-N-CNT and reference catalysts, (b) different metal single atom catalyst, and (c) 1.5 % Ni-N-CNT after acid washing with 3M HCl at room temperature for 8h.
**Fig. S4** X-ray spectroscopy of (a) Ni 2p XPS spectrum of CNT, (b) N 1s XPS spectrum, (c) C 1s XPS spectrum, (d) Fe 2p XPS spectrum and (e) Al 2p XPS spectrum of 1.5% Ni-N-CNT and CNT.
Fig. S5 (a) Ni K-edge XANES spectra of Ni foil, NiPc, and 1.5% Ni-N-CNT. (b) Fourier transformation of the EXAFS spectra at R space.
Fig. S6 Synthetic route for preparing Ni-N-CNT at large-scale.
Fig. S7 Schematic of CO₂ electrolysis in H-cell.
Fig. S8 (a) LSV, (b) FE$_{\text{CO}_2}$, and (c) CO partial current density of 1.5 % Ni-N-CNT and 1.5 % Ni-N-CNT after acid washing with 3M HCl at room temperature for 8h.
Fig. S9 CVs of (a) 1.5% Ni-N-CNT, (b) bare CNT, (c) CNT, (d) CNT N, and (e) CNT Ni with various scan rates (10-100 mV/s) in the region of 0.067 to 0.167 V vs. RHE. (f) Charging current density differences plotted against scan rates for these samples.
Fig. S10 CVs of (a) 1.5% Co-N-CNT, (b) 1.5% Cu-N-CNT, (c) 1.5% Fe-N-CNT, (d) 1.5% Mn-N-CNT, (e) 1.5% Pt-N-CNT, (f) 1.5% Ru-N-CNT, and (g) 1.5% Zn-N-CNT with various scan rates (10-100 mV/s) in the region of 0.067 to 0.167 V vs. RHE. (h) Charging current density differences plotted against scan rates for these samples.
### 3. Table

**Table S1** Comparison of different catalysts for the CO₂RR performance towards CO

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrolyte</th>
<th>Cell</th>
<th>$E/V$ vs. RHE</th>
<th>FE/$%$</th>
<th>$J$/mA cm$^{-2}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-N-CNT</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.8</td>
<td>94</td>
<td>28</td>
<td>This work</td>
</tr>
<tr>
<td>Ni-N-C</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.9</td>
<td>71.9</td>
<td>10.48</td>
<td>1</td>
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<tr>
<td>Ni-N-CNT</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.7</td>
<td>91.3</td>
<td>23.5</td>
<td>2</td>
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<tr>
<td>Ni-N-MEGO</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.7</td>
<td>92.1</td>
<td>26.8</td>
<td>3</td>
</tr>
<tr>
<td>Ni-N-Graphene</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.68</td>
<td>92</td>
<td>10.2</td>
<td>4</td>
</tr>
<tr>
<td>Ni-N-Gr</td>
<td>0.1 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.8</td>
<td>90</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Ni-NG</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.62</td>
<td>95</td>
<td>~11</td>
<td>6</td>
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<tr>
<td>A-Ni-NSG</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.8</td>
<td>~90</td>
<td>22.5 mA cm$^{-2}$ @ -0.72 V</td>
<td>7</td>
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<tr>
<td>A-Ni-NG</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.8</td>
<td>~90</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>NC-CNTs</td>
<td>0.1 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.8</td>
<td>~90</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>Ni-CNT-CONH</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.65</td>
<td>98</td>
<td>18.6</td>
<td>9</td>
</tr>
<tr>
<td>Ni-CNT-PP</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.65</td>
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<td>13.4</td>
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<tr>
<td>Ni-N-RGO</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.8</td>
<td>97</td>
<td>5 mA cm$^{-2}$ @ -0.71 V</td>
<td>10</td>
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<tr>
<td>Ni-N-C</td>
<td>0.1 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.78</td>
<td>85</td>
<td>-</td>
<td>11</td>
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<tr>
<td>NiSA-NGA</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.8</td>
<td>90.2</td>
<td>-</td>
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<tr>
<td>NiN-GS</td>
<td>0.1 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.8</td>
<td>93</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>SANi-GO</td>
<td>0.5 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.63</td>
<td>96.5</td>
<td>8.3</td>
<td>14</td>
</tr>
<tr>
<td>Ni/NC</td>
<td>0.1 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.9</td>
<td>96.5</td>
<td>12.6 mA cm$^{-2}$ @ -1.2 V</td>
<td>15</td>
</tr>
<tr>
<td>Ni/NC</td>
<td>0.1 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.8</td>
<td>92.3</td>
<td>4</td>
<td>16</td>
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<td>H-cell</td>
<td>-0.65</td>
<td>95.2</td>
<td>&gt;15</td>
<td>17</td>
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<tr>
<td>NiIMP/NC$_{923}$</td>
<td>0.1 M KHCO$_3$</td>
<td>H-cell</td>
<td>-0.6</td>
<td>82</td>
<td>-</td>
<td>18</td>
</tr>
</tbody>
</table>
4. References