Supporting Information

Efficient Electrocatalytic O₂ Reduction at Copper Complexes Grafted on Polyvinylimidazole Coated Carbon Nanotubes

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Catalysts preparation

Methods

Reagents. All reagents were purchased commercially and used without further purification unless otherwise noted. Multi-walled carbon nanotubes (MWCNTs, length approximately 50 µm, OD 8–15 nm, ID 3–5 nm) were purchased from Chengdu Organic Chemical Co. Ltd, Chinese Academy of Sciences. High purity water (≥ 18.25 MΩ·cm) was used for preparation of the buffers and aqueous solutions. The compounds 5-NO₂-phenanthroline [S1] and polyvinylimidazole (PVI) [S2] were prepared according to the reported literature.

Apparatus. The morphology of the catalyst composite was examined using TEM (JEOL JEM-2011) operating at 100 kV. The TEM samples were prepared by drying a droplet of sample suspension on a Cu-grid with a carbon film. XPS data were collected on a Thermo Escalab 250 XPS instrument with a monochromatic Al Kα X-ray source (hv =1486.6 eV). All binding energies were referenced to the C1s peak (284.6 eV) arising from adventitious carbon.
Catalyst preparation

Treatment of MWCNTs: Commercially available MWCNTs (300 mg) were added to 300 mL of conc. HNO₃ (65%). The mixture was then treated in an ultrasonic bath for 30 min to form a uniform dispersion, followed by refluxing at 80 °C with vigorous stirring for 20 h. The resultant mixture was diluted with deionized water (500 mL) under sonication. The deionized water was changed several times until the solution reached a neutral pH. Finally, the purified MWCNTs were dried under vacuum overnight at 60 °C. The acid treated MWCNTs was named as CNTs and used for the follow up preparations.

Preparation of PVI@CNTs (4): The acid-treated MWCNTs (50 mg) suspended in ultrapure water (50 mL) were subjected to ultra-sonication for 1 h. The suspension solution was then filtrated through a filter paper by vacuum filtration. The CNTs deposited on the filter paper were dried under vacuum, and followed by immersion them in a PVI methanol solution (10 mg/mL) for 1 h. The composite obtained was then dried under vacuum overnight.

Synthesis of CuphenNO₂-PVI@CNTs (2): The as prepared PVI@CNTs (20 mg) was dispersed in ethanol and water (V_{EtOH}: V_{H₂O} = 1:1, 10 mL), CuCl₂·2H₂O (2.0 mg, 0.012 mmol) and 5-nitro-1,10-phenanthroline (6.0 mg, 0.024 mmol) were then added. The mixture was treated in an ultrasonic bath for several minutes to form a uniform dispersion. The resultant solution was stirred at 50 °C for 1 h followed by further 15 h at room temperature. After centrifugation, the sediments were collected and washed three times with ethanol and water, and dried under vacuum overnight.

Synthesis of PVI-CuphenNO₂-PVI@CNTs (1): The prepared CuphenNO₂-PVI@CNTs was immersed in a PVI methanol solution (10 mg/mL) for 30 min at room temperature. The obtained composite was then dried under vacuum overnight.

Preparation of Cu(phenNO₂)+CNTs (3): The physisorbed catalyst composite Cu(phenNO₂)+CNTs (3) was prepared similar to (2) by replacing the PVI@CNTs with CNTs.
Electrochemical measurements

A catalyst ink was prepared as follows: The catalyst (5.0 mg) was mixed in a glass vial with a 5 wt% Nafion dispersion (Aldrich, 25 μL) and isopropanol (225 μL), and this solution was sonicated in a bath sonicator for 1 h. The catalyst ink (10 μL) was then applied to the surface of a glassy carbon disk (0.196 cm²), and the solvent was evaporated at room temperature under air to produce a uniform film with a catalyst loading of 1.0 mg cm⁻². The Pt loading for the reference Pt/C catalyst was 60 μg Pt cm⁻².

An RRDE (Pine Instruments) with a 5.0-mm diameter glassy carbon disk and Pt ring (geometric area 0.110 cm⁻²) was used to evaluate the catalyst performance on a CHI Instrument Model 760D potentiostat (CH Instrument Company, USA) in a standard three-electrode cell with a graphite rod (diameter: 4.0 mm) as the counter electrode. An Hg/HgO electrode was used as the reference electrode, and 0.1 M KOH was used as the electrolyte. Prior to the electrochemical measurements, the GC disk and Pt ring electrodes were successively polished using 0.5 and 0.3 μm alumina slurries to afford a mirror finish. The electrodes were then rinsed and sonicated in double distilled water, followed by drying under vacuum.

All cyclic voltammetry (CV) and RRDE tests were performed at room temperature with a scan rate of 10 mV s⁻¹. The electrolyte was bubbled with O₂ for 30 min prior to each experiment, and O₂ purging was maintained over the electrolyte during the analyses. Prior to each test, the electrode was pre-treated by repeated cycling of the potential between 0.0 and 1.2 V vs. RHE at a sweep rate of 100 mV s⁻¹ to remove any surface contamination. A 30 s potential hold at the open cell potential also preceded each polarization experiment. The ring potential was set at 1.3 V vs. RHE, and the ring collection efficiency (N) in the RRDE experiments was 0.16 as determined using a 10 mM solution of K₃[Fe(CN)₆] in 0.1 M KCl.

RRDE measurements: The H₂O₂ yield and electron transfer number (n) were calculated from the RRDE data using the following equation:

\[
\text{H}_2\text{O}_2\% = \frac{2 \times I_r}{(N \times I_d) + I_r} \times 100
\]

\[
n = 4 \times \frac{I_d}{I_d + I_r/N}
\]

where \(I_r\) is the ring current, \(I_d\) is the disk current, and \(N\) is the collection efficiency.
**RHE calibration**: RHE calibration was performed in high purity (99.999%) \( \text{H}_2 \)-saturated electrolyte with a Pt wire as the working electrode. The potential at which the current crossed zero was taken as the thermodynamic potential for the hydrogen electrode reactions.

### Table S1 XPS elemental analysis of PVI-Cu(phen\(^{\text{NO2}}\))-PVI@CNTs (1) and Cu(phen\(^{\text{NO2}}\))-PVI@CNTs (2)

<table>
<thead>
<tr>
<th></th>
<th>Cu(phen(^{\text{NO2}}))-PVI@CNTs (2) (Atom%)</th>
<th>PVI-Cu(phen(^{\text{NO2}}))-PVI@CNTs (1) (Atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>84.19</td>
<td>80.31</td>
</tr>
<tr>
<td>N</td>
<td>3.17</td>
<td>8.20</td>
</tr>
<tr>
<td>O</td>
<td>12.12</td>
<td>10.96</td>
</tr>
<tr>
<td>Cu</td>
<td>0.52</td>
<td>0.54</td>
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</tbody>
</table>
Figure S1 (A) TEM image of the catalyst composite Cuphen$^{\text{NO}_2}$-PVI@CNTs (2). (B) XP survey spectrum of catalyst composite (2). High-resolution XPS N1s (C) and Cu2P (D) scan of the catalyst composite (2).
Figure S2 CVs and LSV of the catalysts (1)–(4) at different rotation rates in Ar and O₂-saturated 0.1 M KOH solutions; peroxide yields and electron-transfer number of the catalysts (1)–(4) at 1600 rpm in O₂-saturated 0.1 M KOH solution. Scan rate, 10 mV s⁻¹; loading, 1.0 mg cm⁻². (A–C) for catalyst PVI-CuphenNO₂-PVI@CNTs (1); (D–F) for catalyst CuphenNO₂-PVI@CNTs (2); (G–I) for catalyst PVI@CNTs (3); (J–L) for catalyst PVI@CNTs (4).
Table S2 XPS elemental analysis of PVI-Cu(phen\textsuperscript{NO2})-PVI@CNTs (1) and Cu(phen\textsuperscript{NO2})-PVI@CNTs (2) before and after stability test (containing Nafion that was introduced from the catalyst ink preparation)

<table>
<thead>
<tr>
<th></th>
<th>Cu(phen\textsuperscript{NO2})-PVI@CNTs (2)</th>
<th>PVI-Cu(phen\textsuperscript{NO2})-PVI@CNTs (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before (Atom%)</td>
<td>after (Atom%)</td>
</tr>
<tr>
<td>C</td>
<td>69.73</td>
<td>71.71</td>
</tr>
<tr>
<td>N</td>
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<tr>
<td>O</td>
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<td>6.00</td>
</tr>
<tr>
<td>Cu</td>
<td>0.36</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Figure S3 High-resolution XPS N1s (A) and Cu2P (B) scan of the catalyst composite (1) after stability test. High-resolution XPS N1s (C) and Cu2P (D) scan of the catalyst composite (2) after stability test.
Figure S4 HRTEM images of the catalyst composite (1) before (A) and after (B) stability test. HRTEM images of the catalyst composite (2) before (C) and after (D) stability test.
Figure S5 (A) Linear scanning voltammograms, (B) Peroxide yields and (C) Electron transfer numbers calculated for PVI-Cu(phen\textsuperscript{N\textsubscript{2}})-PVI@CNTs (1) (black line), PVI-Cu(phen\textsuperscript{N\textsubscript{2}})-PVI@rGO (red line), and PVI-Cu(phen\textsuperscript{N\textsubscript{2}})-PVI@TiO\textsubscript{2} (blue line) in O\textsubscript{2}-saturated 0.1 M KOH. (D) Linear scanning voltammograms, (E) Peroxide yields and (F) Electron transfer numbers calculated for Cu(phen\textsuperscript{N\textsubscript{2}})-PVI@CNTs (2) (black line), Cu(phen\textsuperscript{N\textsubscript{2}})-PVI@rGO (red line), and Cu(phen\textsuperscript{N\textsubscript{2}})-PVI@TiO\textsubscript{2} (blue line) in O\textsubscript{2}-saturated 0.1 M KOH. Electrode rotation speed: 1600 rpm; scan rate: 10 mV s\textsuperscript{-1}; loading: 1.0 mg cm\textsuperscript{-2}.

References: