Electronic Supplementary Information

Non-nitrogen Doped and Non-metal Oxygen Reduction
Electrocatalysts based on Carbon Nanotubes: Mechanism and Origin of ORR Activity

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Double Layer Normalization

All of the data from the electrochemical measurements are normalized to the electrochemical surface area (ECSA) derived from the double layer (dl) capacitance of our sample taken under saturated Ar conditions by assuming the typical dl capacitance of carbon materials as 25 μF cm$^{-2}$. This allows for the comparison of actual electrochemical-effective surface area. The ORR polarization curves were obtained by subtracting the Ar and O$_2$ current responses and also normalized to the double layer taken from CV in saturated Ar conditions.

TPD Quantitative Characterization

The quantity of CO and CO$_2$ gas evolved from temperature programmed desorption (TPD) measurements done by calibrating the sensitivity of the mass spectrometer detector using an H-implanted Si substrate. The amount of oxygen functionalities was also determined quantitatively from data supplied by TPD characterization as shown in Table S1.

Table S1. CO and CO$_2$ desorption quantization from TPD characterization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO (mol/g)</th>
<th>CO$_2$ (mol/g)</th>
<th>Total oxygen desorbed (wt%)</th>
<th>Total oxygen desorbed (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionalized MWNTs (precursor) (PMWNT)</td>
<td>1.8×10$^{-3}$</td>
<td>9.0×10$^{-4}$</td>
<td>5.76</td>
<td>4.38</td>
</tr>
<tr>
<td>DMWNT-HNO$_3$</td>
<td>4.1×10$^{-3}$</td>
<td>1.8×10$^{-3}$</td>
<td>12.32</td>
<td>9.53</td>
</tr>
<tr>
<td>DMWNT-H$_2$SO$_4$</td>
<td>3.4×10$^{-3}$</td>
<td>4.7×10$^{-4}$</td>
<td>6.94</td>
<td>5.30</td>
</tr>
</tbody>
</table>

Table S2. $I_D/I_G$ characterization for different MWNTs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMWNT</td>
<td>1.14</td>
</tr>
<tr>
<td>DMWNT-HNO$_3$</td>
<td>1.56</td>
</tr>
<tr>
<td>DMWNT-H$_2$SO$_4$</td>
<td>1.43</td>
</tr>
<tr>
<td>DMWNT-H$_2$SO$_4$-Ar900</td>
<td>1.46</td>
</tr>
</tbody>
</table>
Supplementary Figures

Figure S1. Digital photograph of typical as-prepared buckypaper
Figure S2. Digital photographs of the working electrode setup
Figure S3. TEM micrographs of typical as-prepared (a) functionalized precursor to chemical drilling (PMWNT), (b) DMWNT-HNO₃, and (c) DMWNT-H₂SO₄ showing the effects of the chemically drilled holes and defects on the MWNTs. The TEM images were obtained using FE-TEM (JEOL, JEM-2010F) operated at 200 kV.
Figure S4. XPS survey scan for DMWNT-HNO$_3$ and DMWNT-H$_2$SO$_4$. X-ray photoelectron spectroscopy (XPS) measurements were carried out using Perkin-Elmer XPS model 5500MT, with a monochromatized Al Kα X-ray source.

Figure S5. (a) XPS C1s spectrum and (c) XPS O1s spectrum of the corresponding samples.
Figure S6. Raman spectra for DMWNT-H$_2$SO$_4$ before (black) and after annealing in Ar at 900 °C DMWNT-H$_2$SO$_4$-Ar900 (red). Raman spectra were taken under ambient condition using an NRS-3100 Series (JASCO) with and Ar-ion laser beam at an excitation wavelength of 532 nm.
Figure S7. ORR polarization curve showing as-prepared (red) DMWNT-H$_2$SO$_4$, (black) DMWNT-HNO$_3$, and (blue) DMWNT-HNO$_3$ after annealing at 300°C in Ar taken in 0.1 M HClO$_4$ with scan rate of 1 mV/s. The inset shows a reduced current density and potential window.
Figure S8. Temperature programmed desorption (TPD) (a) CO₂ and (b) CO spectra of (black) as-prepared DMWNT-HNO₃ and (red) DMWNT-HNO₃ following annealing in Ar at 900°C showing the effects of oxygen recombination.

Figure S9. (a) CO₂ (b) CO, TPD spectra showing “as prepared” DMWNT-H₂SO₄ (blue). The flat dotted line shows the measurement taken directly afterwards. The sample was then exposed to air and subsequently characterized with TPD again, labeled as “after O-recombination” (green) showing the partial recombination of oxygen functional groups.
Figure S10. Electron spin resonance (ESR) spectra for (a) as-prepared precursor containing functionalized MWNTs (PMWNT) and (b) PMWNT following annealing in Ar at 900°C.
Figure S11. XPS spectra containing Co 2p and N 1s regions of the (black) precursor functionalized MWNTs and (red) DMWNT-H$_2$SO$_4$ following annealing in Ar at 900°C.
Figure S12. Cyclic voltammetry (CV) curves of buckypaper fabricated from Pristine MWNT-Ar900 (red) and DMWNT-H₂SO₄-Ar900 (blue). CV was taken in 0.1 M HClO₄ with scan rate of 1 mV/s in Ar (solid) and O₂ (dotted).
Figure S13. Cyclic voltammetry (CV) showing DMWNT-H₂SO₄-Ar900 (DMWNT-H₂SO₄ annealed at 900°C in Ar) initial (fresh catalyst), after 8000 cycles (for durability test) and re-annealing (after proceeding durability test) at 900°C under Ar atmosphere. CV was taken in 0.1 M HClO₄ with scan rate of 1 mV/s. Meanwhile, durability test was conducted by cycling under O₂ with a scan rate of 50 mV/s, voltage window [0.2 - 0.6] V vs. Ag/AgCl.
Figure S14. $\text{N}_2$ adsorption-desorption isotherm of (a) DMWNT-H$_2$SO$_4$-Ar900, (b) BJH plot for corresponding samples-confirming their microporosity characteristics, equipped with t-plot analysis for DMWNT-H$_2$SO$_4$ (c) as-prepared and (d) after annealing under Ar at 900 °C.
Figure S15. Digital photograph taken from microscope (Keyence VHX-2000) of typical (a) clean RDE electrode (diameter: 5 mm) (b) RDE drop-casted with sample DMWNT-H$_2$SO$_4$ that was heat treated in Ar at 900°C, followed with ink preparation and drop-casting on glassy carbon (GC) electrode (c) close up of DMWNT-H$_2$SO$_4$ prepared RDE electrode of the red rectangle (d) 3D topology of close up area showing the uneven catalyst coating and (e) RDE drop-casted with an alternative technique, instead of removing O-functionalities by Ar treatment, DMWNT-H$_2$SO$_4$ ink (containing functionalities) directly drop casted on a detachable GC. The drop-casted GC disk then annealed under Ar atmosphere at 900°C. For these microscope photographs, the ink procedures is as follows: 4 mg carbon sample (Ar treated or not), 0.8 mL water, 0.2 mL ethanol and 10 μL of 5 wt% Nafion, followed by vigorous sonication for at least 30 minutes. The multicolored tint is caused by Nafion.
Figure S16. a) ORR polarization and b) Koutecky-Levich plots showing the electron number at different potentials of DMWNT-H₂SO₄-Ar900. ORR polarization was derived by linear scan voltammetry (LSV) sweep in Ar and O₂ atmosphere at a scan speed of 5 mV/s, under various rotating speed 300-1800 rpm (interval 300 rpm)
References


