Supporting Information

Platanus hispanica-inspired Design of Co-Carbon Nanotube Frameworks through Chemical Vapor Deposition: Highly Integrated Hierarchical Electrocatalyst for Oxygen Reduction Reaction

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**Experimental section**

**Materials:** Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O), glycerol and isopropanol were purchased from Aladdin Industrial Co., (Shanghai, China). Nafion solution (5 wt %), ethanol, and potassium hydroxide (KOH) were obtained from Sinopharm Chemical Reagent Co. The other chemicals were purchased from Sigma-Aldrich. Deionized water (18.2 MX) was used throughout the experiments. All chemicals used were of analytical grade and used as received without further purification.

**Synthesis of Co-glycerate precursor:** Cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O, 0.22g) and glycerol (4.0 mL) were dissolved together in isopropanol (40 mL) under stirring for 2 h to form a transparent solution. And then the solution was transferred to a 100 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 6 h. The resulting light pink product (Co-glycerate) was harvested by several rinse-precipitation cycles with ethanol. Finally, the pink powder of Co-glycerate was dried in vacuum at 60 °C.

**Synthesis of Co-CNTFs-750, Co-CNTFs and Co-CNTFs-550:** The above obtained Co-glycerate particles were dispersed in a ceramic boat, heated to different temperature of 750, 650 and 550 °C in a CVD furnace in Ar atmosphere, respectively. Then hydrogen gas (Ar : hydrogen=5:1) was inflated into the furnace for 10 min to reduce the metallic cobalt and form porous carbon spheres. Subsequently, 350 sccm C$_2$H$_4$ was introduced for 5 min to in situ grow CNTs through porous Co-carbon spheres. Finally, the sample was rapidly cooled down to room temperature under the flow of argon. The product was noted as Co-CNTFs-750, Co-CNTFs and Co-CNTFs-550, respectively.

**Apparatus and Characterization:** Powder X-ray diffraction (XRD) patterns were obtained with a XRD-7000 (XRD, Shimadzu XRD-7000) with Cu Kα source radiation at a scanning rate of 2° min$^{-1}$ from 10 to 80°. The morphologies and microstructures were investigated by field-emission scanning electron microscopy (FESEM, JEOL-7800F), transmission electron microscope (TEM, JEM-2100), and
Energy-dispersive X-ray spectroscopy (EDX, INCA X-Max 250). The surface properties of the samples were studied by X-ray photoelectron spectroscopy (XPS, Escalab 250xi, Thermo Scientific). The Brunauer–Emmett–Teller (BET) surface area was measured by using Quadrasorb evo 2QDS-MP-30 (Quantachrome Instruments, USA). Thermogravimetric analysis was performed on Thermo Gravimetric Analyzer (TGA, Q50, USA) at a rate of 5 °C min⁻¹ under air from 30 to 700 °C.

**Electrochemical measurements:** The Co-CNTFs catalyst slurry was prepared by ultrasonically dispersing catalyst (2.0 mg) in a solution containing 1 mL of ethanol-DI water (1:1 vol) and 20 μL of 5 wt % Nafion solution. Then, 25 μL of the slurry was loaded onto a glassy carbon electrode. All electrochemical measurements were carried out on Autolab bi-potential station (CHI Instruments Inc.) by using the as-prepared electrode as working electrode, a platinum foil as counter electrode, and a Hg/HgO (1.0 M NaOH) as reference electrode. The electrolyte was 0.1 M KOH. For fuel crossover effect tests, the current response at -0.15 V Hg/HgO with an RDE rotation rate of 1600 rpm, with 5% (v/v) methanol being added into the O₂-saturated electrolyte around 100 s. Accelerated durability test (ADT) was performed between 0.2 and -0.8 V at 50 mV s⁻¹ in 0.1 M KOH solution exposed to atmosphere.

The kinetic-limiting current density (JK) for the ORR was derived from the experimental data using the Koutecky-Levich equation (Eq. 1):

\[
\frac{1}{|J|} = \frac{1}{|J_L|} + \frac{1}{|J_K|} = \frac{1}{B \sqrt{\omega}} + \frac{1}{|J_K|}
\]

\[
B = 0.2nF C_0 (D_0) ^ {2/3} \nu ^ {1/6}
\]

where J and JL are the measured current and diffusion limiting current, respectively; \(\omega\) is the rotation speed in rpm, F is the Faraday constant (96,485 C mol⁻¹), \(C_0\) is the bulk concentration of oxygen (1.2 ×10⁻⁶ mol cm⁻³), \(D_0\) is the diffusion coefficient of oxygen in 0.1 M KOH (1.9×10⁻⁵ cm² s⁻¹), and \(\nu\) is the kinetic viscosity (0.01 cm² s⁻¹). The n can be calculated from the slope of the K-L plot.
The electron transfer number (n) calculated from the RRDE measurement was based on the disk current ($J_{\text{Disk}}$) and ring current ($J_{\text{Ring}}$) via the following equation:

$$n = \frac{4J_{\text{Disk}}}{J_{\text{Disk}} + J_{\text{Ring}}/N}$$

where $N = 0.37$ is the current collection efficiency of Pt ring.
**Table. S1** The BET surface area, pore volume and average pores radius of all samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
<th>Average Pores Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial CNTs</td>
<td>112.72</td>
<td>0.256</td>
<td>1.7035</td>
</tr>
<tr>
<td>Co-PC</td>
<td>194.6</td>
<td>0.372</td>
<td>1.7065</td>
</tr>
<tr>
<td>Co-CNTFs</td>
<td>316.7</td>
<td>0.486</td>
<td>3.1476</td>
</tr>
</tbody>
</table>
**Fig. S2.** XPS spectra of Co-CNTFs.

**Fig. S3.** High-resolution XPS spectra of Co 2p
Fig. S4 LSV curves of Co-CNTFs-750, Co-CNTFs and Co-CNTFs-550 at an RDE rotation speed of 1600 rpm with a scan rate of 10 mV s\(^{-1}\) in O\(_2\)-saturated 0.1 M KOH solution.

Fig. S5. Cyclic voltammetry (CV) curves of Co-PC and Co-CNTFs on glassy carbon electrodes in O\(_2\)-saturated (solid line) or N\(_2\)-saturated (dash line) 0.1M KOH.
Fig. S6. LSV curves of Co-PC at different rotating speeds with a scan rate of 10 mV s\(^{-1}\).

Fig. S7 Rotating ring-disk electrode (RRDE) measurements of Co,N-CN. The electron transfer number was calculated to be 3.8.
Fig. S8 CV curves of Co-CNTFs in O$_2$-saturated 0.1 M KOH solution before and after ADT (2000 CV cycles between 0.2 and -0.8 V@50 mV s$^{-1}$ in KOH solution exposed to atmosphere).