Supporting Information

Palladium–Cobalt Nanotube Arrays Supported on Carbon Fiber Cloth as High-Performance Flexible Electrocatalysts for Ethanol Oxidation**

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Experimental Section

**Synthesize of PdCo NTAs/CFC:** All the chemical reagents were analytical grade (AR) and were used without any additional purification. Electrodeposition was carried out in a simple two-electrode cell by galvanostatic electrolysis, and the graphite electrode was used as a counter electrode (spectral grade, 1.8 cm²) and the carbon fiber cloth (CFC) (Phychemi Company, Hong Kong) was utilized as a working electrode (0.5 cm × 2 cm). The details are given in the following:

(i) ZnO nanorod arrays (NRAs) were electrodeposited on CFC in the solution of 1 mM Zn(NO₃)₂ + 5 mM NH₄NO₃ at a current density of 0.4 mA cm⁻² for 1.5 h at 70 °C.

(ii) ZnO@PdCo core-shell NRAs/CFC are synthesized by electrodeposition of PdCo on the surface of ZnO NRAs in solution of 0.9 mM PdCl₂+1.0 mM Co(SO₄)₂+0.005 mM sodium citrate (pH is controlled to 4 using NaOH). The ZnO@Pd core-shell NRAs/CFC were also fabricated in solution of 0.9 mM PdCl₂ + 0.005 mM sodium citrate by the same route.

(iii) The fabricated ZnO@PdCo NRAs/CFC and ZnO@Pd NRAs/CFC were then immersed in 2 mM H₂SO₄ solution for 5 h to remove ZnO NRAs. Then PdCo nanotube arrays (NTAs)/CFC and Pd NTAs/CFC were fabricated.

**Structural characterization:** The morphologies of samples were characterized by field emission scanning electron microscopy (FE-SEM, JSM-6330F) and transmission electron microscopy (TEM, JEM-2010HR). Chemical-state analysis was determined by X-Ray photoelectron spectroscopy (XPS) using an ESCAKAB 250 X-Ray photoelectron spectrometer, all peaks corrected by C 1s line at 284.6 eV as standard, and curve fitting and background subtraction were accomplished. Chemical component analysis was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using TJA IRIS(HR) spectrometer.
**Electrochemical characterization:** The electrochemical tests were conducted in the three-electrode cell. All the electrochemical measurements were carried out using an electrochemical workstation (CHI 760). A Pt foil served as the counter electrode. A saturated calomel electrode (SCE) electrode was used as the reference electrode. The potential values used in this study were changed to $E$(RHE) from $E$(SCE) according to the formula $E$(RHE)=$E$(SCE)+0.2412+0.05916×pH. The PdCo NTAs/CFC, Pd NTAs/CFC and commercial Pd/C catalysts were used as working electrodes, respectively. The commercial Pd/C catalysts (Johnson Matthey, 20% Pd/C, Vulcan XC-72, Pd nanoparticle size 4 nm) were utilized in this study. The Pd loadings of PdCo NTAs/CFC, Pd NTAs/CFC, and commercial Pd/C were 23.4, 20.2, and 28 $\mu$g/cm$^2$, respectively. Before the electrochemical measurements, the surfaces of electrocatalysts were covered by 8 $\mu$L Nafion (5 wt%) solution. To study the electrocatalytic activity and stability, the cyclic voltammetry (CV) was tested from 0.27 V to 1.27 V vs RHE at 50 mV/s and the chronoamperometry measurements were carried out at 0.77 V in the solution of 1.0 M KOH+1.0 M C$_2$H$_5$OH. Prior to all experiments, the electrolyte solution was purged with high purity N$_2$ gas for 10 min. All electrochemical measurements were carried out at 25°C.
Figure S1. Typical SEM image of carbon fibers in the CFC (inset is the optical image of CFC).
Figure S2. SEM images of ZnO NRAs/CFC with different magnifications: (a) low-magnification; (b) high-magnification.
Figure S3. SEM images of ZnO@PdCo NRAs/CFC with different magnifications: (a) low-magnification; (b) high-magnification.
Figure S4. Optical images of the flexible PdCo NTAs/CFC at (a) normal, (b) bending, and (c) twisting states.

Figure S5. XRD pattern of PdCo NTAs/CFC.
**Figure S6.** SEM images of Pd NTAs/CFC with different magnifications: (a) low-magnification; (b) high-magnification.
Table S1. The mass activity comparison of various catalysts at a certain potential (vs RHE).

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>0.60 V</th>
<th>0.65 V</th>
<th>0.70 V</th>
<th>0.75 V</th>
<th>0.80 V</th>
<th>0.85 V</th>
<th>0.90 V</th>
<th>0.95 V</th>
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<tbody>
<tr>
<td>PdCo NTAs/CFC (mA/mg)</td>
<td>207</td>
<td>336</td>
<td>509</td>
<td>704</td>
<td>924</td>
<td>1141</td>
<td>1391</td>
<td>1491</td>
</tr>
<tr>
<td>Pd NTAs/CFC (mA/mg)</td>
<td>223</td>
<td>359</td>
<td>543</td>
<td>721</td>
<td>887</td>
<td>662</td>
<td>274</td>
<td>125</td>
</tr>
<tr>
<td>Commercial Pd/C (mA/mg)</td>
<td>188</td>
<td>250</td>
<td>308</td>
<td>360</td>
<td>387</td>
<td>345</td>
<td>274</td>
<td>186</td>
</tr>
</tbody>
</table>

Figure S7. CVs of PdCo NTAs/CFC, Pd NTAs/CFC, and commercial Pd/C in 1.0 M KOH+1.0 M C₂H₅OH at 50 mV/s (the current densities all are normalized to the ECSAs of catalysts).
Figure S8. The comparisons of mass peak current densities and ECSA peak current densities of PdCo NTAs/CFC, Pd NTAs/CFC, and commercial Pd/C in 1.0 M KOH+1.0 M C₂H₅OH at 50 mV/s.

Figure S9. CVs of PdCo NTAs/CFC in solution of 1.0 M KOH+1.0 M C₂H₅OH at 50 mV/s (the current densities all are normalized to the mass of Pd).
Table S2. The summary of mass peak current densities at different Pd/Co ratios.

<table>
<thead>
<tr>
<th>Pd/Co atom ratio</th>
<th>Mass current density (mA mg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17</td>
<td>1283.57</td>
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<tr>
<td>0.23</td>
<td>1562.10</td>
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<tr>
<td>0.68</td>
<td>1432.14</td>
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<tr>
<td>2.50</td>
<td>1311.43</td>
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<tr>
<td>4.04</td>
<td>892.60</td>
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</tbody>
</table>

Figure S10. CO stripping voltammograms on the Pd NTAs/CFC performed in solution of 1.0 M KOH at 50 mV/s.
Figure S11. CO stripping voltammograms on the commercial Pd/C performed in solution of 1.0 M KOH at 50 mV/s.