PdO Nanoparticles Enhancing the Catalytic Activity of Pd/Carbon Nanotubes for 4-Nitrophenol Reduction

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1. Materials

All chemicals were used as received without further purification: Palladium (II) nitrate dihydrate, Potassium tetrachloropalladate, (Sinopharm Chemical Reagent Beijing Co., Ltd). Palladium (II) acetate, Palladium dichloride, 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$], (Tokyo Chemical Co., Ltd). Ethanol, methylene chloride (CH$_2$Cl$_2$), Acetone, acetic ether, tetrahydrofuran, toluene, N,N-Dimethylformamide (DMF), (Beijing chemical works).

2. Experimental setup

Figure S1 shows the experimental setup of the gas-liquid interfacial plasma. The glow discharge plasma was generated between the top flat stainless steel (SUS) and bottom ionic liquid electrode by using a DC power source (KIKUSUI PMC500-0.1A). Argon gas was introduced and used as the plasma-forming gas. The chamber was a stainless steel with inner diameter of 70 mm and four glass windows, and the gap between electrodes is 4mm.
Figure S1. A schematic illustration of plasma system.

3. The TEM images of Pd-1, Pd-2, Pd-3, Pd-4

Figure S2. TEM images of Pd-1 (a), Pd-2 (b), Pd-3 (c), Pd-4 (d).
4. The size distribution of Pd nanoparticles decorated on the surface of OCNTs

Figure S3. Particle size distribution of Pd-1 (a), Pd-2 (b), Pd-3 (c), Pd-4 (d) from the TEM images in Fig. S2.
5. The TEM images of Pd-5

Figure S4. TEM images of Pd-5.
6. The characterization results of Pd-5.

Figure S5. XPS spectra of Pd-5 (a), (b); (c) the enlarged XPS spectra of Pd3d of Pd-5 (magenta), Pd-1 (black curve), Pd-2 (olive curve), Pd-3 (red curve) and Pd-4 (blue curve); (d) The XRD patterns of Pd-5.
7. High-resolution XPS spectra of C1s of Pd-1

Figure S6. High-resolution XPS spectra of C1s of Pd-1.
Figure S7. UV-vis spectra of 4-NP in water after the addition of NaBH₄ and successive absorption spectra of the conversion from 4-NP to 4-AP with Pd-n catalysts: Pd-1 (a), Pd-2 (b), Pd-3 (c), Pd-4 (d).
9. UV-vis spectra of Pd-5 catalysts for 4-NP reduction reaction

Figure S8. Successive absorption spectra of the conversion from 4-NP to 4-AP with PdO catalysts (a); (f) plots of ln(C/C₀) versus time for the conversion from 4-NP to 4-AP with Pd-5 catalysts.
10. Apparent rate constant of Pd-n catalysts for 4-NP reduction reaction

Figure S9. Plots of $\ln(C/C_0)$ versus time for the conversion from 4-NP to 4-AP with Pd-n catalysts.
11. The TEM images of the reused Pd-1 catalyst

![TEM image of Pd-1 catalyst after 10 cycles](image)

Figure S10. TEM image of Pd-1 catalyst after 10 cycles
Table S1. Pd nanoparticle size (nm)\textsuperscript{a} and Pd loading on OCNTs (wt.%\textsuperscript{b}).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd-1</th>
<th>Pd-2</th>
<th>Pd-3</th>
<th>Pd-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-n size (nm)</td>
<td>3.5</td>
<td>3.7</td>
<td>8.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Pd loading (wt.%)</td>
<td>9.5</td>
<td>10.0</td>
<td>5.1</td>
<td>8.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Average size obtained from the size distribution histogram.  
\textsuperscript{b} Calculated by ICP.

Table S2. Apparent reaction rates $k_{app}$ values for the Pd-n catalysts for 4-NP reduction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd-1</th>
<th>Pd-2</th>
<th>Pd-3</th>
<th>Pd-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent reaction rate (min\textsuperscript{-1})\textsuperscript{a}</td>
<td>0.60</td>
<td>0.25</td>
<td>0.15</td>
<td>0.1</td>
</tr>
<tr>
<td>Apparent reaction rate (min\textsuperscript{-1})\textsuperscript{b}</td>
<td>1.00</td>
<td>0.56</td>
<td>0.50</td>
<td>0.21</td>
</tr>
</tbody>
</table>

\textsuperscript{a} In quartz cuvette (method A).  
\textsuperscript{b} In micro-reaction vial (method B).