Au/graphene oxide/carbon nanotube flexible catalyst film: synthesis, characterization and its application for catalytic reduction of 4-nitrophenol

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1. Materials

All chemicals were used as received without further purification: graphite powder (200 mesh) (Alfa Aesar, Johnson Matthey Company); HAuCl₄·4H₂O (Sinopharm Chemical Reagent Beijing Co., Ltd); 1-methyl-2-pyrrolidone (C₅H₉NO) (Aladdin Industrial Corporation); KMnO₄, H₂O₂, Ethanol, methylene chloride (CH₂Cl₂), Acetone, acetic ether, tetrahydrofuran, toluene, N,N-Dimethylformamide (DMF) (Beijing chemical works).
2. The TEM images of G/C-Au-1, G/C-Au-3, G-Au, C-Au

Figure S1. TEM images of G/C-Au-1 (a), G/C-Au-3 (b), G-Au (c), C-Au (d).
3. The size distribution of Au nanoparticles decorated on the surface of carbon materials.

Figure S2. Particle size distributions of G/C-Au-1 (a), G/C-Au-2 (b), G/C-Au-3 (c), G-Au (d), C-Au (e) from the TEM images in Fig. S1, and EDX pattern of G/C-Au-2 (f).
4. Images of before and after the Au catalyst 4-NP reduction reaction

Figure S3. XPS spectra of G/C-Au-1 (a), G/C-Au-3 (c), G-Au (e), C-Au (g); high-resolution XPS spectra of Au 4f of G/C-Au-1 (b), G/C-Au-3 (d), G-Au (f), C-Au (h).
4. Images of before and after the Au catalyst 4-NP reduction reaction

Figure S4. Images of the Au catalysts catalyze the 4-NP reduction in water before (a) and after (b) the reactions.
5. Images of before and after the G/C-Au-2 catalytic film catalyst 4-NP reduction reaction

Figure S5. (a) The 4-NP and NaBH$_4$ water solution, (b) after addition of the G/C-Au-2 catalytic film, (c) the recycle reaction of the G/C-Au-2 catalytic film, (d) the G/C-Au-2 catalytic film before reaction, (e) the G/C-Au-2 catalytic film before reaction.
6. The TEM images of the reused G/C-Au-2 catalyst

Figure S6. TEM image of G/C-Au-2 catalyst after 10 cycles
Table S1. Au nanoparticle size (nm)\textsuperscript{a}, Au loading on support (wt.%)\textsuperscript{b}, Apparent reaction rates $k_{app}$ values, reaction time, TOF values for the Au catalysts for 4-NP reduction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>G-Au</th>
<th>C-Au</th>
<th>G/C-Au-1</th>
<th>G/C-Au-2</th>
<th>G/C-Au-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au size (nm)</td>
<td>4.1</td>
<td>4.9</td>
<td>2.5</td>
<td>2.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Au loading (wt.%)</td>
<td>19.6</td>
<td>24.0</td>
<td>11.1</td>
<td>9.8</td>
<td>9.4</td>
</tr>
<tr>
<td>$k_{app}$ (min\textsuperscript{-1})</td>
<td>0.16</td>
<td>0.12</td>
<td>0.34</td>
<td>0.75</td>
<td>0.22</td>
</tr>
<tr>
<td>Reaction time (min)</td>
<td>15</td>
<td>18</td>
<td>13</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>TOF values (h\textsuperscript{-1})</td>
<td>402</td>
<td>274</td>
<td>819</td>
<td>3015</td>
<td>1571</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Average size obtained from the size distribution histogram.

\textsuperscript{b} Calculated by TGA.