Electronic Supplementary Information (ESI)

Chemical etching of graphene supported PdPt alloy nanocubes into concave nanostructures for enhanced catalytic hydrogen production from alkaline formaldehyde aqueous solution

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Experimental

Chemicals. Natural graphite flake (~325 mesh, Alfa Aesar), K$_2$PdCl$_4$ (Aladdin, P106044), K$_2$PtCl$_4$ (Sigma-Aldrich, 520853), Na$_2$PtCl$_6$·6H$_2$O (Aladdin, S109436), poly(vinyl pyrrolidone) (PVP, M.W. ~ 8,000, Aladdin, P110608; M.W. ~ 55,000, Sigma-Aldrich, 856568) and ethylene glycol (EG, Sigma-Aldrich, 324558) were used in the synthesis. All other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used as received without further purification. The water used in all experiments was de-ionized.

Synthesis of rGO-Pd NCs. In a typical synthesis of rGO-Pd NCs, K$_2$PdCl$_4$ (19.6 mg), KBr (357 mg), PVP (M.W. ~ 8,000, 100 mg) were dissolved in 10-mL aqueous GO suspension (1 mg/mL). Then 0.6 mL of KI solution (0.01 mol/L) was added, and pH value of the solution was adjusted to about 3 by adding drops of 1-M HCl solution. Subsequently, the total volume of the suspension was diluted to 15 mL with water. The suspension was then transferred to a 20-mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 4 h. After the autoclave had cooled down to room temperature, the resultant product was separated by centrifugating and washing with acetone one, water three times and ethanol two times.

Synthesis of rGO-Pt NCs and bare Pt nanoparticles. In a typical synthesis of rGO-Pt NCs, 6 mg of graphite oxide was dispersed in 3.5 mL of EG to form a graphene oxide (GO) suspension with probe sonication (Scientz-IID, China) for 1 h. Then 20 mg of KBr and 200 mg of PVP (M.W. ~ 55,000) were dissolved in the EG suspension of GO. The suspension was transferred into a 25 mL flask and preheated at 180 °C for 10 min with magnetic stirring. Subsequently, 0.5 mL of Na$_2$PtCl$_6$·6H$_2$O solution (40 mg/mL, in EG) was injected into the flask, and the reaction was carried out at 180 °C for 20 min and was then immediately cooled with an ice-water bath. The resultant product was separated by centrifugating and washing with acetone one, water three times and ethanol two times. Bare Pt nanoparticles were synthesized by following the same procedure for rGO-Pt NCs except without use of GO.
Fig. S1 TEM images of (a) graphite oxide and (b) exfoliated graphene oxide (GO) nanosheets.
Fig. S2 Low-magnification TEM images of (a) rGO-Pd$_{50}$Pt$_{50}$ NCs, (b) rGO-Pd$_{70}$Pt$_{30}$ NCs and (c) rGO-Pd$_{90}$Pt$_{10}$ NCs.
Fig. S3 Size distribution histograms and average edge lengths (L) of the as-prepared PdPt alloy nanocubes on rGO nanosheets: (a) rGO-Pd$_{50}$Pt$_{50}$ NCs, (b) rGO-Pd$_{70}$Pt$_{30}$ NCs and (c) rGO-Pd$_{90}$Pt$_{10}$ NCs.
Fig. S4 Low-magnification TEM images of (a) rGO-Pd$_{50}$Pt$_{50}$ CNCs, (b) rGO-Pd$_{70}$Pt$_{30}$ CNCs and (c) rGO-Pd$_{90}$Pt$_{10}$ COPs.
Fig. S5 Size distribution histograms and average edge lengths (L) of the as-obtained PdPt concave nanostructures on rGO nanosheets: (a) rGO-Pd$_{50}$Pt$_{50}$ CNCs, (b) rGO-Pd$_{70}$Pt$_{30}$ CNCs and (c) rGO-Pd$_{90}$Pt$_{10}$ COPs.
Fig. S6 (a) XRD pattern and (b-d) XPS spectra of graphite oxide: (b) survey spectrum, (c) C1s and (d) O1s high-resolution spectrum.
Fig. S7 XPS survey spectrum of rGO-Pd<sub>50</sub>Pt<sub>50</sub> CNCs.
Fig. S8 Raman spectra of graphite oxide and rGO-Pd$_{50}$Pt$_{50}$ CNCs.
**Fig. S9** Schematic illustrating the synthesis of rGO-Pd NCs and rGO-Pt NCs as well as the chemical etching of them with nitric acid.
Fig. S10 (a-c) TEM and (d) HRTEM images of rGO-Pd NCs.
Fig. S11 (a-c) TEM and (d) HRTEM images of rGO-Pt NCs.
Fig. S12 XRD patterns of rGO-Pd NCs and rGO-Pt NCs.
Fig. S13 Size distribution histograms and average edge lengths (L) of the as-prepared Pd and Pt nanocubes on rGO nanosheets: (a) rGO-Pd NCs and (b) rGO-Pt NCs.
Fig. S14 TEM images of (a,b) rGO-Pd NCs and (c,d) rGO-Pt NCs after the chemical etching with HNO$_3$. 
Fig. S15 TEM images of bare Pd₅₀Pt₅₀, Pd₇₀Pt₃₀ and Pd₉₀Pt₁₀ nanocubes.
**Fig. S16** TEM images of bare Pd$_{50}$Pt$_{50}$, Pd$_{70}$Pt$_{30}$ and Pd$_{90}$Pt$_{10}$ concave nanostructures after treatment with HNO$_3$. 
Fig. S17 Time-dependent H₂ evolution over bare rGO, bare Pd₅₀Pt₅₀, Pd₇₀Pt₃₀ and Pd₉₀Pt₁₀ concave nanostructures.
Fig. S18 TEM image of bare rGO nanosheets.
Fig. S19 TEM images of rGO-Pd$_{90}$Pt$_{10}$ COPs after the catalytic cyclic process.
**Fig. S20** Time-dependent H$_2$ evolution over bare Pd$_{90}$Pt$_{10}$ concave octapods in four successive cycles.
Fig. S21 (a) TEM image of pure Pt nanoparticles and (b) average H$_2$ production rate of bare Pt nanoparticles in comparison with that of rGO-Pd$_{90}$Pt$_{10}$ COPs.
Table S1 Chemical compositions of the rGO-PdPt NCs, rGO-PdPt CNSs, rGO-Pd NCs and rGO-Pt NCs determined by ICP-MS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ratio of Pd : Pt</th>
<th>Weight ratio of metal : rGO</th>
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<tr>
<td>rGO-Pd_{50}Pt_{50} NCs</td>
<td>51.2 : 48.8</td>
<td>75.3 : 24.7</td>
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<tr>
<td>rGO-Pd_{30}Pt_{30} NCs</td>
<td>71.9 : 28.1</td>
<td>72.4 : 27.6</td>
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<tr>
<td>rGO-Pd_{10}Pt_{10} NCs</td>
<td>91.2 : 8.8</td>
<td>69.7 : 30.3</td>
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<tr>
<td>rGO-Pd_{50}Pt_{50} CNSs</td>
<td>49.2 : 50.8</td>
<td>70.7 : 29.3</td>
</tr>
<tr>
<td>rGO-Pd_{70}Pt_{30} CNSs</td>
<td>68.4 : 31.6</td>
<td>62.0 : 38.0</td>
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<tr>
<td>rGO-Pd_{90}Pt_{10} COPs</td>
<td>88.3 : 11.7</td>
<td>48.5 : 51.5</td>
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<tr>
<td>rGO-Pd NCs</td>
<td>100 : 0</td>
<td>68.1 : 31.9</td>
</tr>
<tr>
<td>rGO-Pt NCs</td>
<td>0 : 100</td>
<td>79.2 : 20.8</td>
</tr>
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