Supporting Information for

Multiply twinned Pt–Pd nanoicosahedrons as highly active electrocatalyst for methanol oxidation

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Experimental Section

Synthesis

**Chemicals.** K$_2$PtCl$_4$ (AR; Shenyang Research Institute of Nonferrous Metal, China), PdCl$_2$ (AR; Shenyang Research Institute of Nonferrous Metal, China), NaCl (AR; Beijing Chemical Works, China), Na$_2$C$_2$O$_4$ (AR; Beijing Chemical Works, China), poly(vinylpyrrolidone) (PVP; $M_w$: ~29,000; Sigma-Aldrich) and formaldehyde solution (40%; AR; Beijing Yili Fine Chemical Reagent Corp., China) were used as received. The water used in all experiments was ultrapure (Millipore, 18.2 MΩ).

**Synthesis of Pt–Pd nanoicosahedrons (NIs).** In a typical synthesis, K$_2$PtCl$_4$ (0.015 mmol), Na$_2$PdCl$_4$ (0.015 mmol), Na$_2$C$_2$O$_4$ (0.23 mmol) and PVP (33 mg) were dissolved in 10 mL of water. Then, 0.010 mL of formaldehyde solution (40%) and 0.24 mL of 1 M HCl solution were added. The total volume of the solution was kept at 15 mL. The homogeneous light yellow solution was transferred to a 25 mL Teflon-lined stainless steel autoclave and sealed. The autoclave was then heated at 180 °C for 2 hours before it was cooled down to room temperature. The black nanoparticles were centrifuged with importing 15 mL of acetone-ethanol mixture (1:1 in v/v) and washed with ethanol/water for several times.

**Synthesis of Pt–Pd nanotetrahedrons (NTs).** In a typical synthesis, K$_2$PtCl$_4$ (0.015 mmol), Na$_2$PdCl$_4$ (0.015 mmol), Na$_2$C$_2$O$_4$ (0.75 mmol) and PVP (17 mg) were dissolved in 10 mL of water. Then, 0.40 mL of formaldehyde solution (40%) and 0.025 mL of 1 M HCl solution were added. The total volume of the solution was kept at 15 mL. The homogeneous light yellow solution was transferred to a 25 mL Teflon-lined stainless steel autoclave and sealed. The autoclave was then heated at 180 °C for 2 hours before it was cooled down to room temperature. The black nanoparticles were centrifuged with importing 15 mL of acetone-ethanol mixture (1:1 in v/v) and washed with ethanol/water for several times.

Instrumentation

**XRD.** Wide Angle X-ray diffraction (WAXRD) patterns were recorded on the dry membrane of aqueous dispersions of Pt–Pd NIs or NTs on a glass wafer by a Rigaku D/MAX-2000 diffractometer (Japan) with a slit of 1/2 ° at a scanning rate of 4 ° min$^{-1}$ using Cu K$_\alpha$ radiation ($\lambda$ = 1.5406 Å).
TEM. Samples for transmission electron microscopy (TEM) observations were prepared by drying a drop of diluted colloid dispersion of Pt–Pd alloy nanocrystals in water on copper grids coated by amorphous carbon. Particle sizes and shapes were examined by a TEM (JEM-2100, JEOL, Japan) operated at 200 kV.

HRTEM, EDS, HAADF-STEM and HAADF-STEM-EDS line scan. High resolution TEM (HRTEM), energy dispersive X-ray spectroscopy (EDS) analysis, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and HAADF-STEM-EDS line scans were performed on a FEG-TEM (JEM-2100F, JEOL, Japan) operated at 200 kV.

ICP-AES. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was performed on a Profile Spec ICP-AES spectrometer (Leeman, USA).

Electrochemical measurements

Electrochemical measurements were carried out with a CHI 840B electrochemical analyzer (CH Instrument, TX, USA). A three-electrode cell was used with a glassy carbon (GC) electrode (6 mm in diameter) as the work electrode, a AgCl/Ag/KCl (saturated) electrode as the reference electrode and a Pt wire as the counter electrode. All potentials in this work were converted to values versus reversible hydrogen electrode (RHE) references.

Preparation of working electrode. Pt–Pd NIs and NTs were washed several times with ethanol/water to remove excess surface capping agents, collected and redispersed in water. Then, 10 μL of the aqueous dispersions of Pt–Pd NIs or NTs were transferred onto the GC electrode. After drying in air for 2 hours, the electrode was illuminated by a UV lamp (10 W, with 185 nm and 254 nm emissions) at the distance of about 5 mm for 4 hours to remove the organic capping agents before electrochemical measurements. Then the electrode was covered with 5 μL of 0.2 wt. % Nafion (Alfa Aesar) in ethanol and dried in air for another 1 hour. For Pt black or Pt/C catalysts, 10 μL of the aqueous dispersion of Pt black (Alfa Aesar, 1 mg/mL) or Pt/C (20 wt% of Pt nanoparticles (< 3.5 nm) supported on activated carbons, Johnson Matthey, 1mg/mL) was used for each measurement.

Electro-oxidation of methanol. The electrolyte was fresh made 0.1 M HClO₄ and 1 M CH₃OH solutions and bubbled with N₂ for 30 min before electrochemical measurements. Cyclic voltammetry (CV) measurements were performed under a N₂ flow at room temperature at a sweep rate of 50 mV s⁻¹. The electrochemically active surface area (ECSA) of each sample was estimated by CV measurements carried out in fresh 0.1 M HClO₄ solutions with a sweep rate of 50 mV s⁻¹ (Fig. S10).
**Supplementary Data**

![XRD patterns](image)

**Figure S1.** XRD patterns of the Pt-Pd NIs and NTs and the standard data of Pt (JCPDS Card No.: 01-1194) and Pd (JCPDS Card No.: 05-0681).

![TEM image](image)

**Figure S2.** TEM image (a) and corresponding EDS spectrum (b) of the Pt-Pd NIs.
Figure S3. TEM images on the effect of Na$_2$C$_2$O$_4$ amounts on the formation of Pt–Pd NIs. The amounts of Na$_2$C$_2$O$_4$ were (a) 0 mmol, (b) 0.30 mmol, (c) 0.75 mmol, (d) 1.5 mmol, (e) 2.3 mmol and (f) 3.0 mmol. All the other reaction conditions are the same: K$_2$PtCl$_4$ (0.015 mmol), Na$_2$PdCl$_4$ (0.015 mmol), PVP (33 mg), HCHO (40 wt% aqueous solution, 0.010 mL), HCl (1.0 M aqueous solution, 0.24 mL), 180 °C and 2 h.
Figure S4. TEM images on the effect of HCHO amounts on the formation of Pt–Pd NPs. The amounts of HCHO (40 wt% aqueous solution) were (a) 0 mL, (b) 0.005 mL, (c) 0.010 mL, (d) 0.020 mL, (e) 0.050 mL and (f) 0.10 mL. All the other reaction conditions are the same: K$_2$PtCl$_4$ (0.015 mmol), Na$_2$PdCl$_4$ (0.015 mmol), PVP (33 mg), Na$_2$C$_2$O$_4$ (2.3 mmol), HCl (1.0 M aqueous solution, 0.24 mL), 180 °C and 2 h.
Figure S5. TEM images on the effect of HCl amounts on the formation of Pt–Pd NIs. The amounts of HCl (1.0 M aqueous solution) were (a) 0 mL, (b) 0.12 mL, (c) 0.24 mL, (d) 48 mL and (e) 0.72 mL. All the other reaction conditions are the same: K$_2$PtCl$_4$ (0.015 mmol), Na$_2$PdCl$_4$ (0.015 mmol), PVP (33 mg), Na$_2$C$_2$O$_4$ (2.3 mmol), HCHO (40 wt% aqueous solution, 0.010 mL), 180 °C and 2 h.
**Figure S6.** TEM images on the effect of reaction temperature on the formation of Pt–Pd NIs. The reaction temperatures were (a) 150 °C, (b) 160 °C, (c) 170 °C, and (d) 180 °C. All the other reaction conditions are the same: K₂PtCl₄ (0.015 mmol), Na₂PdCl₄ (0.015 mmol), PVP (33 mg), Na₂C₂O₄ (2.3 mmol), HCHO (40 wt% aqueous solution, 0.010 mL), HCl (1.0 M aqueous solution, 0.24 mL) and 2 h.
**Figure S7.** TEM images on the effect of reaction time on the formation of Pt–Pd NIs. The reaction temperatures were (a) 0.5 h, (b) 1 h, (c) 2 h, and (d) 4 h. All the other reaction conditions are the same: K$_2$PtCl$_4$ (0.015 mmol), Na$_2$PdCl$_4$ (0.015 mmol), PVP (33 mg), Na$_2$C$_2$O$_4$ (2.3 mmol), HCHO (40 wt% aqueous solution, 0.010 mL), HCl (1.0 M aqueous solution, 0.24 mL) and 180 °C.
Figure S8. TEM images on the effect of Pt/Pd ratio on the formation of Pt–Pd NIs. The amounts of K$_2$PtCl$_4$ and Na$_2$PdCl$_4$ were (a) 0.030 mmol + 0 mmol, (b) 0.022 mmol + 0.0075 mmol, (c) 0.0075 mmol + 0.022 mmol, and (d) 0 mmol + 0.030 mmol. All the other reaction conditions are the same: PVP (33 mg), Na$_2$C$_2$O$_4$ (2.3 mmol), HCHO (40 wt% aqueous solution, 0.010 mL), HCl (1.0 M aqueous solution, 0.24 mL), 180 °C and 2 h.
Figure S9. TEM images of (a) the Pt–Pd NTs and (b) Pt black used in the electrochemical tests.

Figure S10. CV (scan rate: 50 mV s\(^{-1}\)) curves of Pt–Pd NIs, NTs, Pt black and Pt/C in 0.1 M HClO\(_4\).

Figure S11. CV (scan rate: 50 mV s\(^{-1}\)) curves (a) and I–t (b) curves of Pt–Pd NIs and NTs in 0.1 M HClO\(_4\) + 1 M CH\(_3\)OH. The mass activity of different catalysts was normalized in reference to the loading amount of Pt.