Supporting Information

Shape-selective Synthesis and Facet-dependent Enhanced Electrocatalytic Activity and Durability of Monodisperse Sub-10 nm Pt-Pd Tetrahedrons and Cubes

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Experimental Section

Synthesis

Chemicals. K_2PtCl_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), $Na_2C_2O_4$ (AR; Beijing Chemical Works, China), KBr (AR; Beijing Chemical Reagent Corp., China), KI (AR; Beijing Chemical Works, China), poly(vinylpyrrolidone) (PVP; Mw: ~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). Na_2PdCl_4 solution was prepared by mixing and dissolving 1.0 g of $PdCl_2$ and 0.66 g of NaCl with 100 mL of H_2O at room temperature under stirring overnight.

Synthesis of Pt-Pd nanotetrahedrons. In a typical synthesis, K_2PtCl_4 (0.015 mmol), Na_2PdCl_4 (0.015 mmol), $Na_2C_2O_4$ (0.75 mmol) and PVP (16.6 mg) were dissolved in 10 mL of water. Then, 0.4 mL of formaldehyde solution (40%) was added. The pH value of the solution was adjusted to about 4 by adding drops of 1 : 1 HCl solutions and 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 ℃ 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 nanocubes. In a typical synthesis, K_2PtCl_4 (0.030 mmol), Na_2PdCl_4 (0.030 mmol), KBr (3.0 mmol), KI (0.006 mmol) and PVP (100 mg) were dissolved in 10 mL of water. The pH value of the solution was adjusted to about 3 by adding drops of 1 : 1 HCl solutions and the total volume of the solution was kept at 15 mL. The homogeneous dark red solution was transferred to a 25 mL Teflon-lined stainless steel autoclave and sealed. The autoclave was then heated at 160 ℃ for 4 hours before it was cooled down to room temperature. The black nanoparticles were centrifuged with importing 45 milliliters of acetone and further washed by ethanol/cyclohexane for several times.

Instrumentation

XRD. Wide Angle X-ray diffraction (WAXRD) patterns were recorded on the dry membrane of aqueous dispersions of Pt-Pd nanotetrahedrons or nanocubes 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_α radiation (λ = 1.5406 Å).

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

XPS. X-ray Photonelectron Spectroscopy was carried out on an Axis Ultra Imaging Photoelectron Spectrometer (Kratos Analytical Ltd., UK) with a monochromatic Al Ka (1486.7 eV) X-ray source operated at 225 W with 15 kV acceleration voltage.

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. More than 200 nanoparticles of nanotetrahedrons or nanocubes were counted for the shape- and size-distribution histograms in Figure 1, Figures S1 and S2.

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.

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 nanocubes and nanotetrahedrons 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 nanocubes, nanotetrahedrons or commercial Pt/C (1 mg/mL; 20 wt% of Pt nanoparticles (< 3.5 nm) supported on activated carbons, Johnson Matthey) were transferred onto the GC electrode. After drying in air for 2 hours, the electrode was covered with 5 μL of 0.2 wt. % Nafion (Alfa Aesar) in ethanol and dried in air for another 1 hour.

Electro-oxidation of methanol. The electrolyte was fresh made 0.1 M $HClO_4$ and 1 M CH_3OH solutions diluted from 75% $HClO_4$ (AR; Beijing Chemical Reagent Corp., China) and 99.5% CH_3OH (AR; Beijing Chemical Reagent Corp., China) with Millipore ultrapure water (18.2 MΩ) and bubbled with N_2 for 30 min before electrochemical measurements. Cyclic voltammetry (CV) measurements were performed under a N_2 flow at room temperature at a sweep rate of 50 mV/s. The electrochemically active surface area (ECSA) of each sample was estimated by CV measurements carried out in fresh 0.1 M $HClO_4$ solutions with a sweep rate of 50 mV/s. Before each measurement, several hundreds of sweeps were cycled until stable CV curves (the variations of J_f values for each sample were less than 0.02 mA/cm^2 in 200 cycles) were obtained. About 800 – 1000 cycles were needed for Pt-Pd nanocubes and nanotetrahedrons while about 400 cycles were needed for the commercial Pt/C catalyst.

Supplementary Data

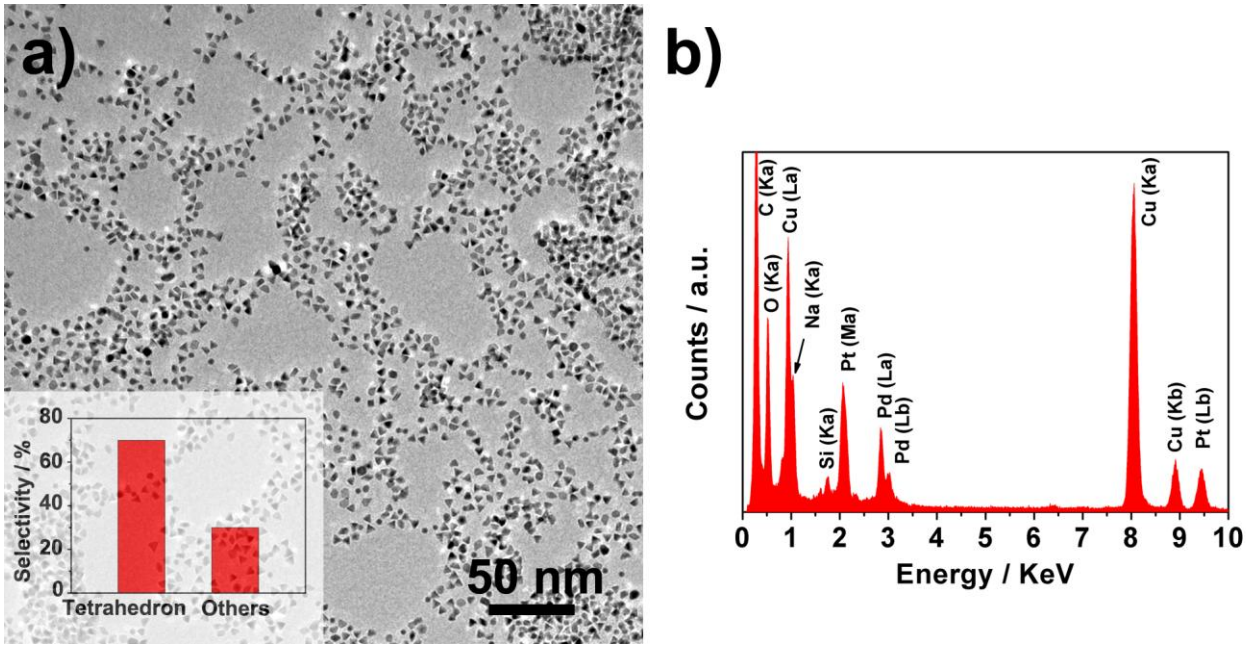

Figure S1. TEM image (a) and EDS spectrum (b) of the as-prepared Pt-Pd nanotetrahedrons. Inset in panel a is the shape selectivity histogram of the as-prepared nanotetrahedrons.

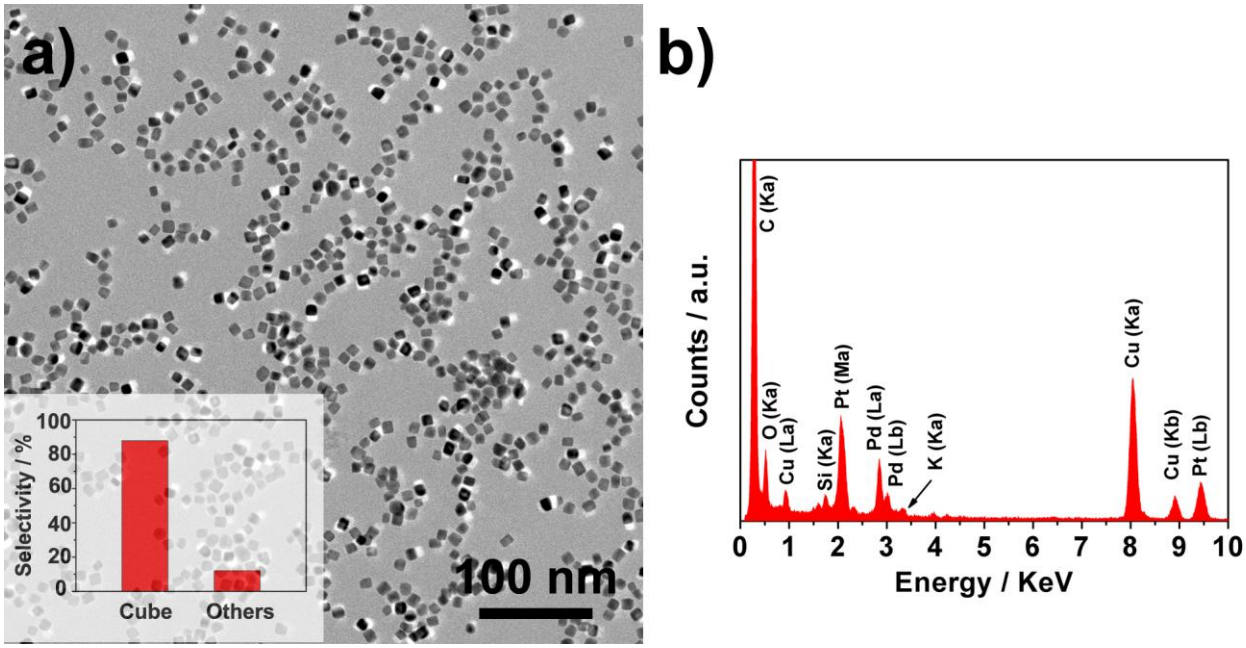

Figure S2. TEM image (a) and EDS spectrum of the-as prepared Pt-Pd nanocubes. Inset in panel a is the shape selectivity histogram of the as-prepared nanocubes.

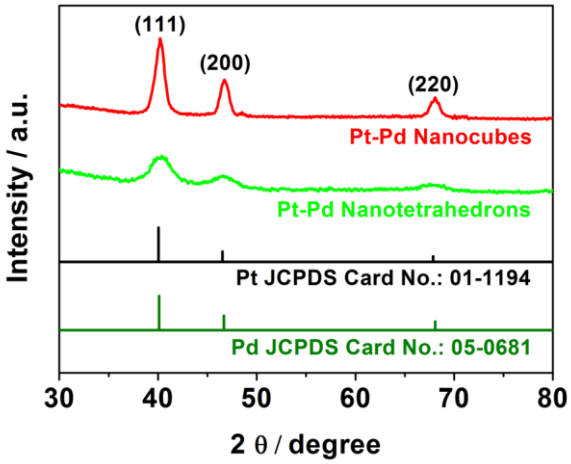

Figure S3. XRD patterns of the as-prepared Pt-Pd nanocubes and nanotetrahedrons, with the standard data for *fcc* Pt (JCPDS Card No.: 01-1194) and Pd (JCPDS Card No.: 05-0681) as references. The intensity ratios of the (200) peaks to the (111) peaks are 0.49 and 0.39 for Pt-Pd nanocubes and Pt-Pd nanotetrahedrons, respectively.

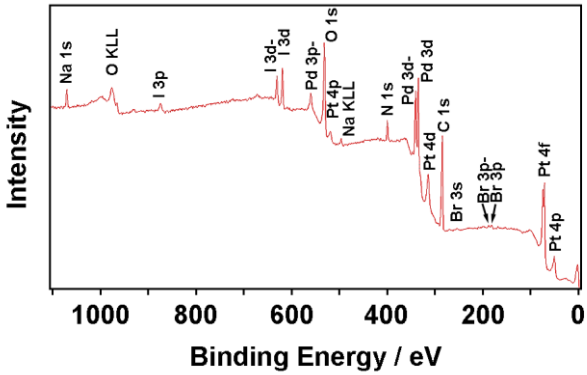

Figure S4. XPS spectra of the as-obtained Pt-Pd nanocubes, with the atomic ratio of Pt : Pd : Br : I : N = 44 : 56 : 10 : 11 : 66, indicating the quasi-homogeneous distribution of Pt/Pd elements in the as-prepared nanocrystals (compared to the ICP-AES results (Pt : Pd = 46 : 54), EDS results (Pt : Pd = 47 : 53) and HAADF-STEM-EDS line scan profiles, Figure 1) and the adsorption of some PVP molecules and tiny amount of Br and I species on the surface of Pt-Pd nanocubes (compared to the molar ratio of Pt : Pd : Br : I : N = 50 : 50 : 2500 : 5 : 750 calculated from the amount of starting chemical reagents).

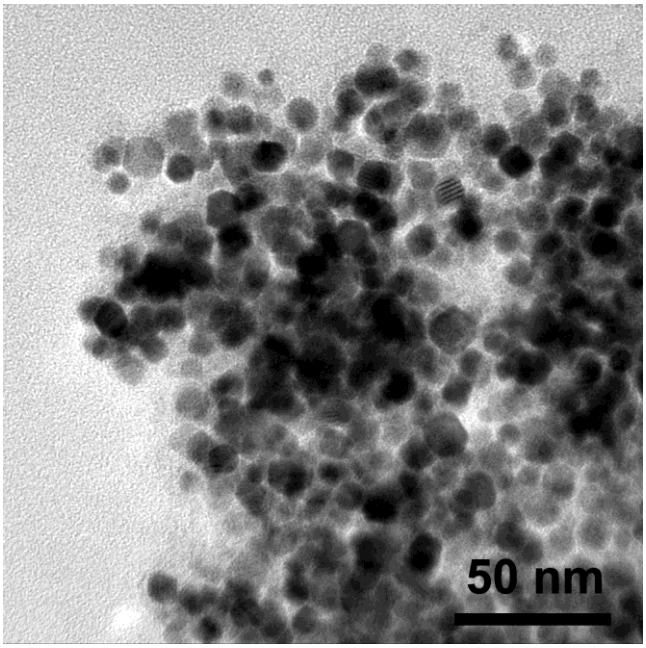

Figure S5. TEM image of the Pt-Pd nanoparticles reduced and capped by PVP (0.015 mmol of K_2PtCl_4, 0.015 mmol of Na_2PdCl_4, 16.6 mg of PVP, pH = 4, total volume: 15 mL, 180 ℃, 2 h).

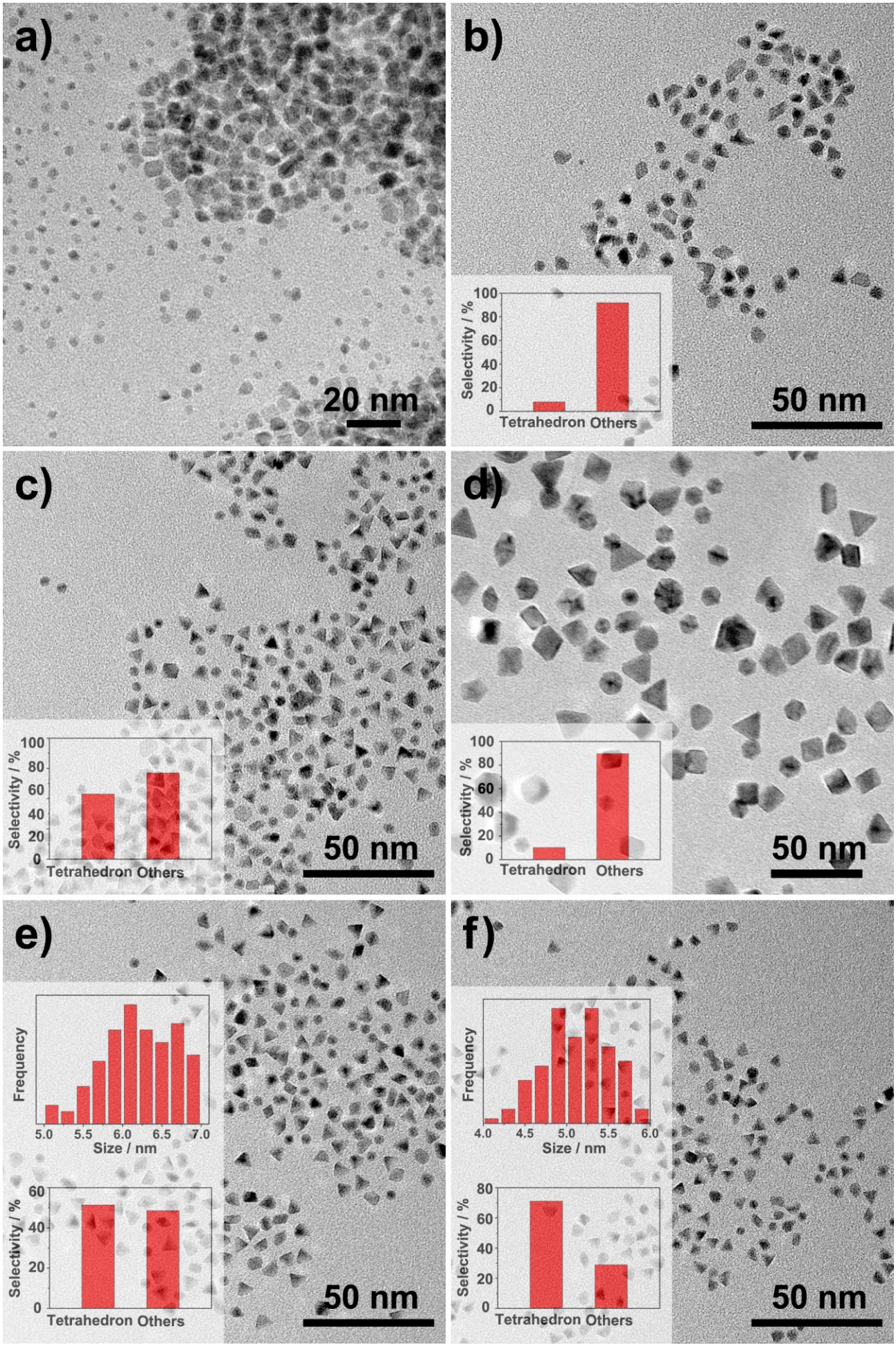

Figure S6. TEM images of the Pt-Pd nanoparticles obtained under different reaction conditions for

the highly-selective preparation of Pt-Pd nanotetrahedrons: (a) Wthout $Na_2C_2O_4$ (0.015 mmol of K_2PtCl_4, 0.015 mmol of Na_2PdCl_4, 16.6 mg of PVP, 0.4 mL of HCHO (40%), pH = 4, total volume: 15 mL, 180 ℃, 2 h); (b) With 0.375 mmol of $Na_2C_2O_4$ (0.015 mmol of K_2PtCl_4, 0.015 mmol of Na_2PdCl_4, 16.6 mg of PVP, 0.375 mmol of $Na_2C_2O_4$, 0.4 mL of HCHO (40%), pH = 4, total volume: 15 mL, 180 ℃, 2 h); (c) With 1.5 mmol of $Na_2C_2O_4$ (0.015 mmol of K_2PtCl_4, 0.015 mmol of Na_2PdCl_4, 16.6 mg of PVP, 1.5 mmol of $Na_2C_2O_4$, 0.4 mL of HCHO (40%), pH = 4, total volume: 15 mL, 180 ℃, 2 h); (d) Without HCHO (0.015 mmol of K_2PtCl_4, 0.015 mmol of Na_2PdCl_4, 16.6 mg of PVP, 0.75 mmol of $Na_2C_2O_4$, pH = 4, total volume: 15 mL; 180 ℃, 2 h); (d) With 0.2 mL of HCHO (0.015 mmol of K_2PtCl_4, 0.015 mmol of Na_2PdCl_4, 16.6 mg of PVP, 0.75 mmol of $Na_2C_2O_4$, 0.2 mL of HCHO (40%), pH = 4, total volume: 15 mL; 180 ℃, 2h); (d) With 0.8 mL of HCHO (0.015 mmol of K_2PtCl_4, 0.015 mmol of Na_2PdCl_4, 16.6 mg of PVP, 0.75 mmol of $Na_2C_2O_4$, 0.8 mL of HCHO (40%), pH = 4, total volume: 15 mL; 180 ℃, 2 h).

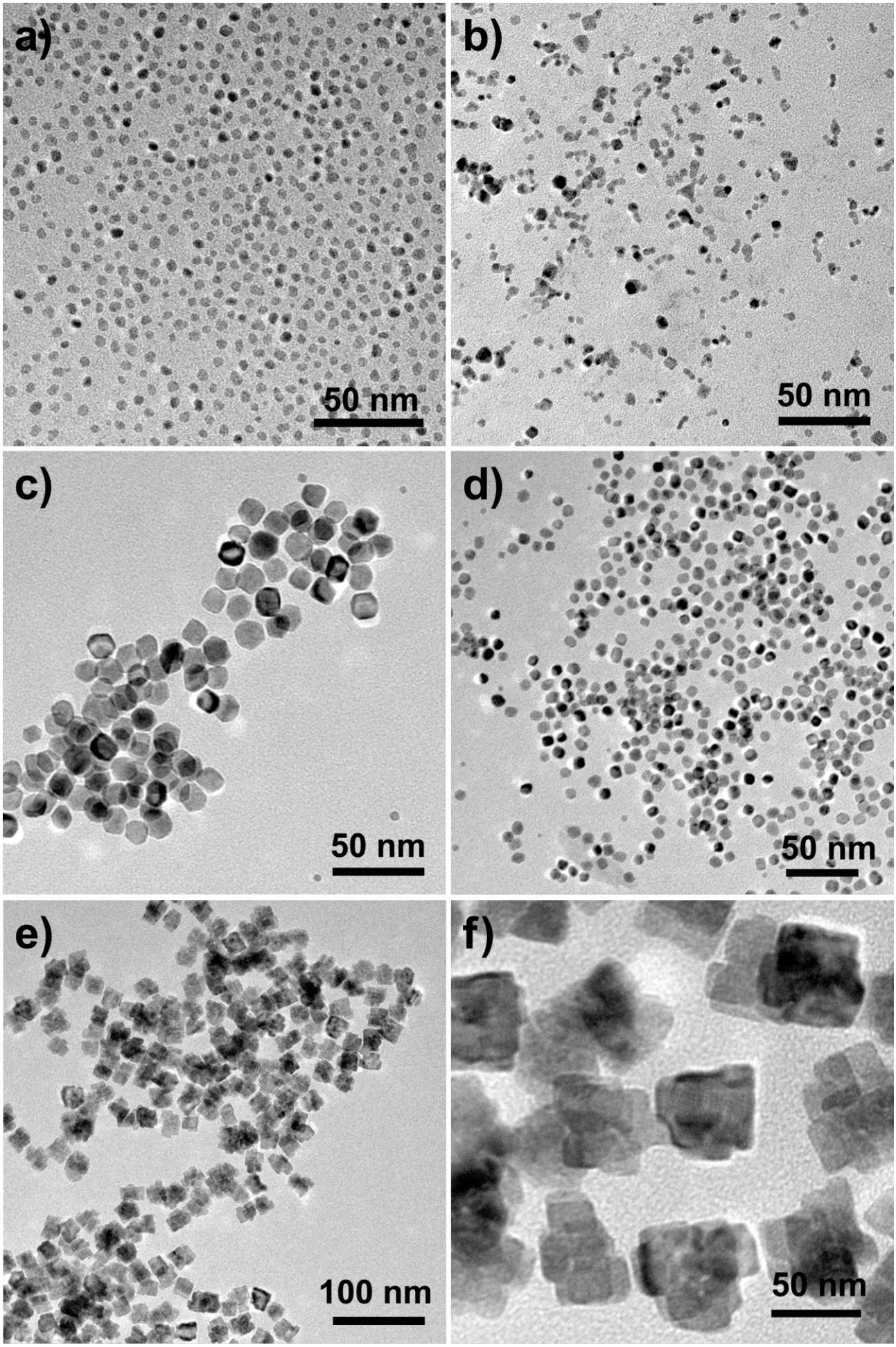

Figure S7. TEM images of the Pt-Pd nanoparticles obtained under different reaction conditions for

the highly-selective preparation of Pt-Pd nanocubes: (a) with the extra addition of 0.4 mL of HCHO (40%) (0.03 mmol of K_2PtCl_4, 0.03 mmol of Na_2PdCl_4, 3.0 mmol of KBr, 0.006 mmol of KI, 100 mg of PVP, pH = 3, total volume: 15 mL; 0.4 mL of 40% HCHO; 160 ℃, 4 h); (b) Without Br^- and I^- (0.03 mmol of K_2PtCl_4, 0.03 mmol of Na_2PdCl_4, 100 mg of PVP, pH = 3, total volume: 15 mL; 160 ℃, 4 h); (c) Without I^- (0.03 mmol of K_2PtCl_4, 0.03 mmol of Na_2PdCl_4, 3.0 mmol of KBr, 100 mg of PVP, pH = 3, total volume: 15 mL; 160 ℃, 4 h); (d) With 0.001 mmol of I^- (0.03 mmol of K_2PtCl_4, 0.03 mmol of Na_2PdCl_4, 3.0 mmol of KBr, 0.001 mmol of KI, 100 mg of PVP, pH = 3, total volume: 15 mL; 160 ℃, 4 h); and (e, f) Without Br^- and the amount of I^- was 3.0 mmol (0.03 mmol of K_2PtCl_4, 0.03 mmol of Na_2PdCl_4, 3.0 mmol of KI, 100 mg of PVP, pH = 3, total volume: 15 mL; 160 ℃, 4 h).

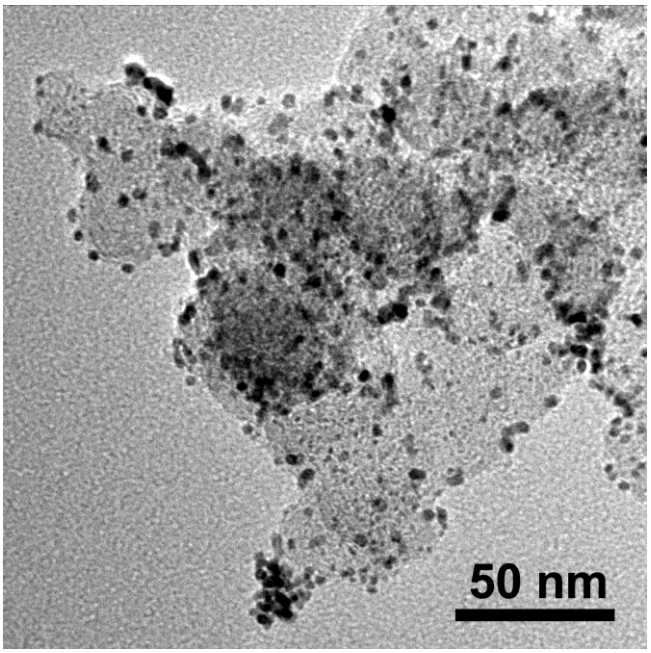

Figure S8. TEM image of the commercial Pt/C catalyst.

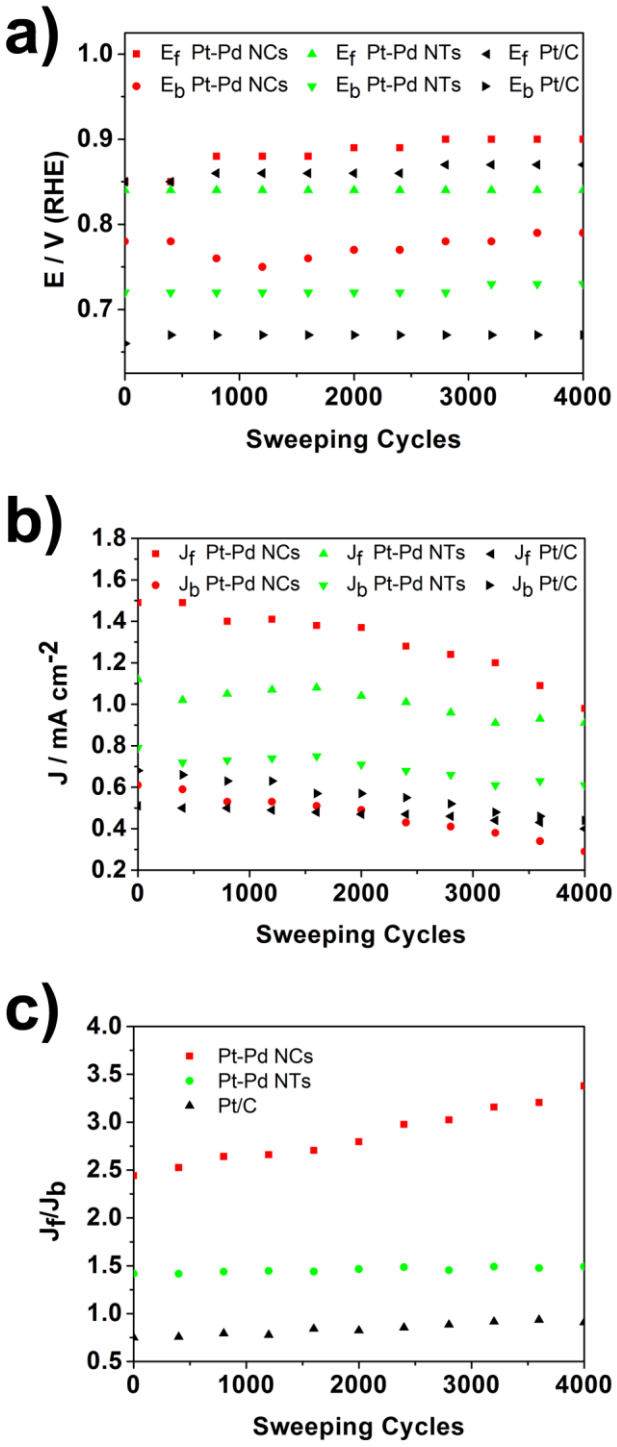

Figure S9. Methanol electro-oxidation performances of Pt-Pd nanocubes, nanotetrahedrons and commercial Pt/C catalysts during additional 4,000 cycles after stable CV curves (Figure 2a) were obtained: the variation of E_f and E_b values (a), J_f and J_b values (b) and J_f/J_b values (c) of Pt-Pd nanocubes, nanotetrahedrons and Pt/C catalysts during the additional 4,000 cycles.