

Electronic Supplementary Information (ESI) for

Controlled Synthesis of Pd-Pt Alloy Nanohypercubes under Microwave Irradiation

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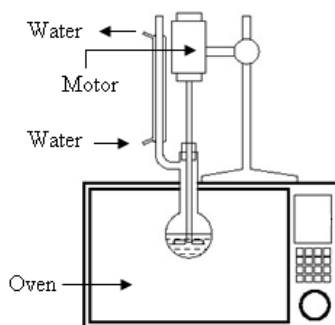
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Experimental Details

Reagents: Tetraethylene glycol (TEG) was purchased from Acros Chemicals Reagent Co., Na₂PdCl₄, H₂PtCl₆, PVP (average molecular weight, $M_w = 30000$) and KI were purchased from Sinopharm Chemical Reagent Co., Ltd.(Shanghai, China). All reagents were used as received without further purification.

Synthesis: In a typical synthesis, 50 mg of KI and 100 mg of PVP were dissolved in 8.75 mL of TEG with rigorous stirring in a 50-mL round-bottomed flask at room temperature. Then, 1 mL of 0.01 mol·L⁻¹ Na₂PdCl₄ and 0.25 mL of 0.04 mol·L⁻¹ H₂PtCl₆ solution in TEG were added. The final volume was 10mL and the molar ratio of Na₂PdCl₄/H₂PtCl₆/KI/PVP was 1/1/30/90. After stirring for 45 min, the color of the solution changed from light yellow to deep red. The resulting

transparent deep red solution was then put into a modified domestic microwave oven (Galanz, 1000W) and heated for 100 sec with 100% output of the power and the dark red colloids were obtained. After being cooled to room temperature, the resultant homogeneous colloids were precipitated by acetone, separated by centrifugation and further purified by ethanol. Under the same conditions, the same reaction process was conducted by changing irradiation time or the amount of KI, as well as using KBr or KCl in stead of KI with the same concentration. The microwave oven was modified without changing the power as follows (Scheme S1): a water-cooled condenser outside the oven's cavity was connected by a glass joint of a glass round-bottomed flask set inside. A teflon stirrer was set in the flask and was driven by a motor. The power output was adjusted by the microwave machine with a routine on-off manner and the temperature didn't have to be controlled.



Scheme S1. Schematic of microwave reactor

Characterization: Transmission electron microscopy (TEM) measurements were conducted on a FEI Tecnai G² 20 transmission electron microscopy operated at 200 kV. High-resolution TEM (HRTEM), high-angle annular dark-field scanning TEM (HAADF-STEM), and energy dispersive X-ray (EDX) analyses were performed using a JEM-2100F field emission transmission electron microscope (JEOL, Tokyo, Japan) operated at 200 kV. Diffractograms of HRTEM were obtained

by fast Fourier transformation. X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 advance X-ray diffractometer employing Cu $K\alpha$ radiation with 40 kV and 50 mA. X-ray photoelectron spectroscopy (XPS) was performed on a VG Multilab 2000 X-ray photoelectron spectrometer using Mg $K\alpha$ radiation under a vacuum of 8×10^{-7} Pa. All binding energy values were determined with reference to carbon, $C_{1s} = 284.6$ eV.

Electrochemical Measurements: Cyclic voltammetry (CV) and CO stripping experiments were conducted using a CHI660E electrochemical workstation which was interfaced for data acquisition and analysis. All experiments were carried out at room temperature (25°C). The modified working electrodes were fabricated by depositing ethanol dispersion of the Pd-Pt alloy nanohypercubes onto a glassy carbon electrode followed by natural drying. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and counter electrode, respectively. For the electro-oxidation of formic acid, CV curves were recorded at a sweep rate of 50 mV/s in 0.5 M H_2SO_4 + 0.5 M HCOOH. For the electrooxidation of methanol, the cyclic voltammograms were recorded at a sweep rate of 50 mV/s in 0.1 M $HClO_4$ + 0.1 M CH_3OH . Before cyclic voltammetry measurements, two cycles of potential sweeps between -0.25 V and 1.2 V were applied to clean the surfaces of the modified working electrodes in-situ. Both positive and negative CV scans were performed on each sample. The arrows in the CV curves indicated the scanning direction. The same electrochemical experiment was conducted for commercial Pt black.

To perform oxidative stripping experiments of CO, a CO saturating layer on Pd-Pt alloy nanohypercubes was prepared by bubbling high-purity CO (99.999%) for 15 minutes through the 0.1 M $HClO_4$ solution in which the modified electrode was immersed. The modified electrode was

then quickly transferred into a fresh 0.1 M HClO₄ solution and the CO stripping voltammetry was recorded at a sweep rate of 5 mV/s from 0 to 1.2V.

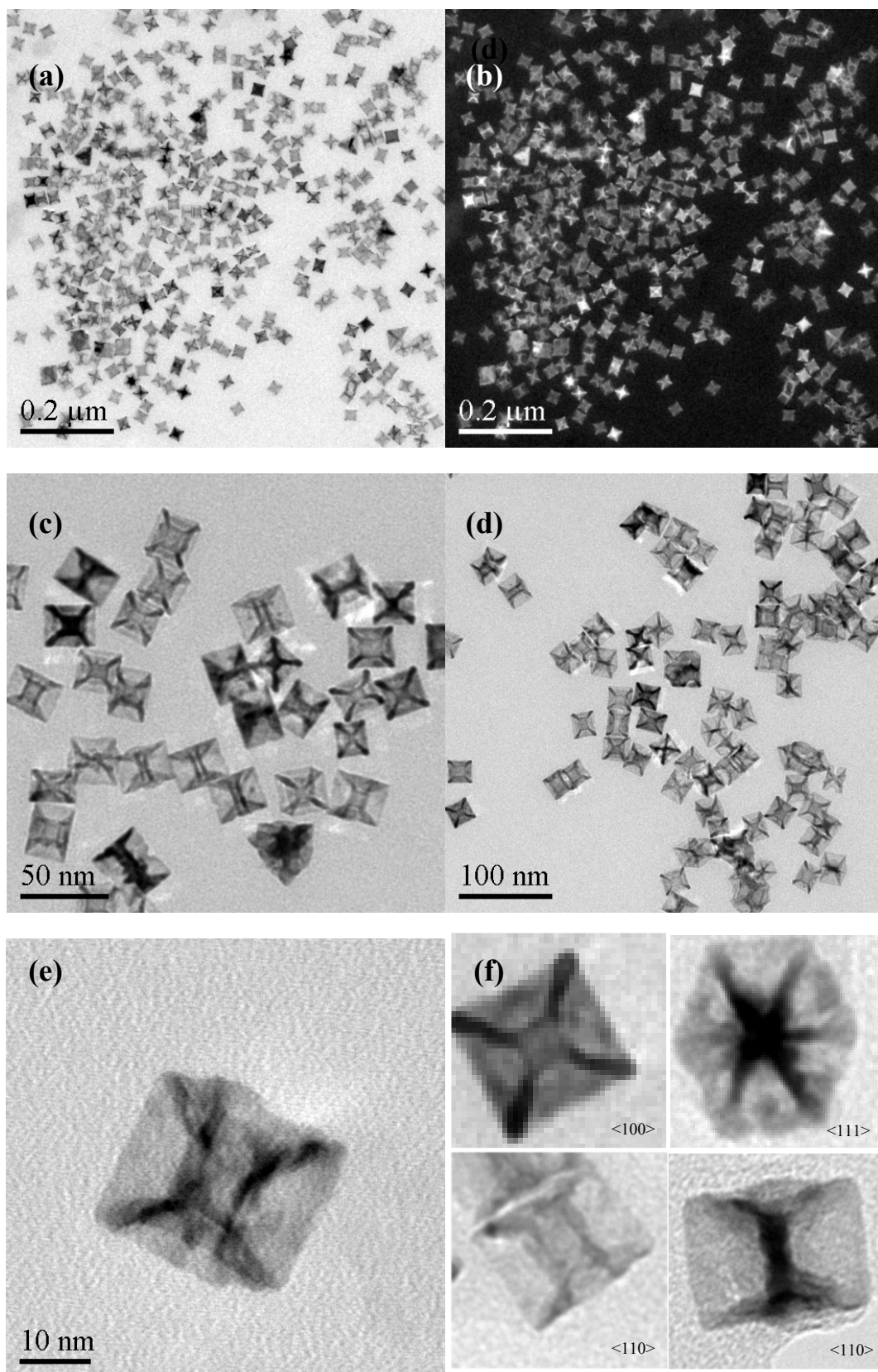


Figure S1. (a)-(e) TEM images of the as-prepared Pd-Pt alloy nanohypercubes. (f) TEM images of

individual nanohypercube projected along [100], [111], and [110] zone axes.

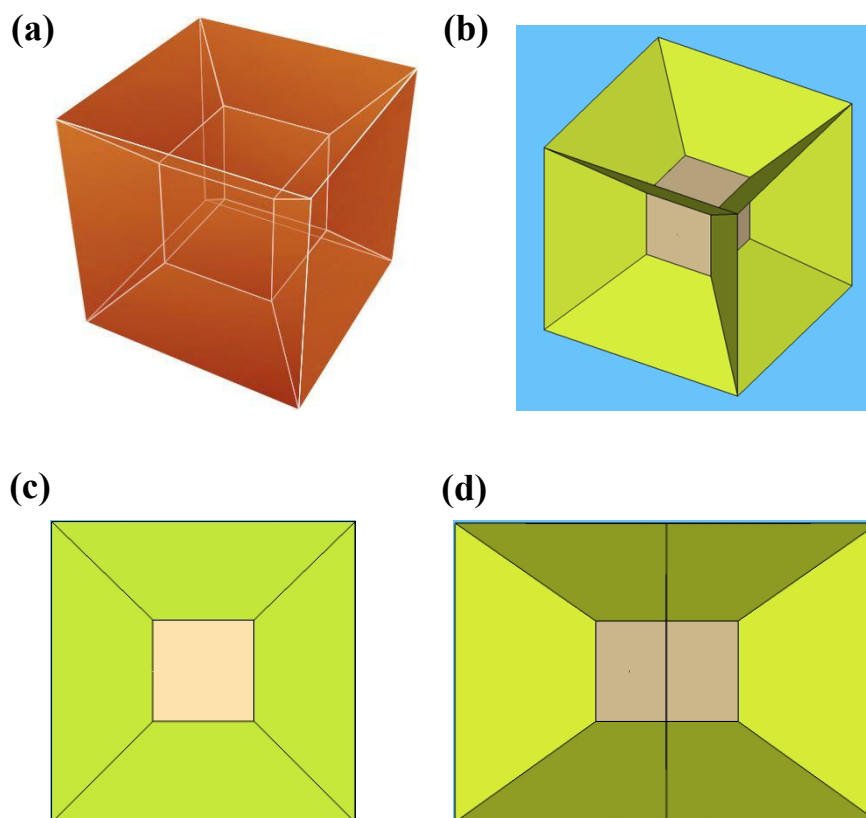


Figure S2. Enlarged pictures of the models (a,b), Schlegel diagram (c) and other projection (d) for the Pd-Pt hypercube nanostructure.

Notes: Hypercube (or tesseract) also known as 8-cell regular octachoron, is a mysterious and unimaginable geometric object. Up to now, geometric object in four-dimensional space has not obtained. The hypercube can give a projection in 2-dimensional plane so called Schlegel diagram, which reflects the relationship between vertices. Schlegel diagrams are commonly used as a means of visualizing four-dimensional polytopes. A Schlegel diagram can be constructed by a perspective projection viewed from a point outside of the polytope, above the center of a face. All vertices and edges of the polytope are projected onto a hyperplane of that face.

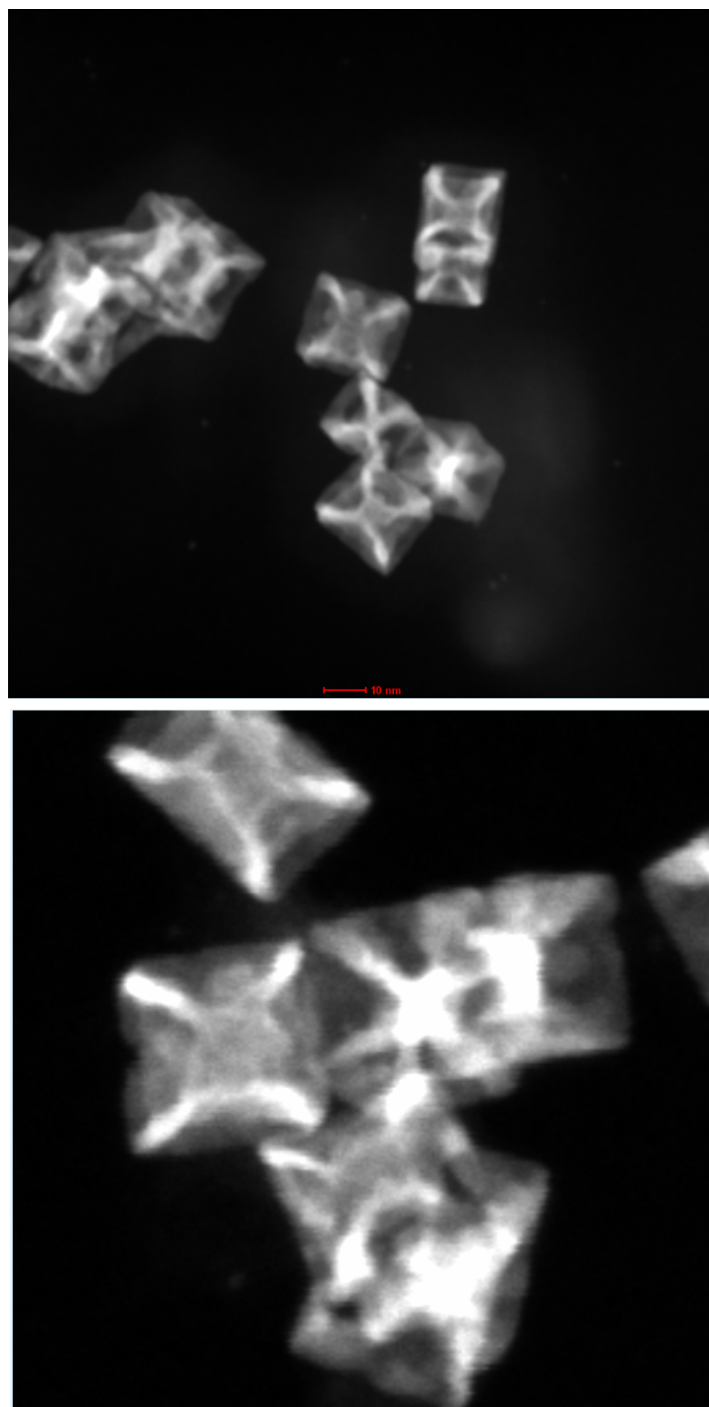


Figure S3. HAADT-STEM image of the as-prepared Pd-Pt hypercubes.

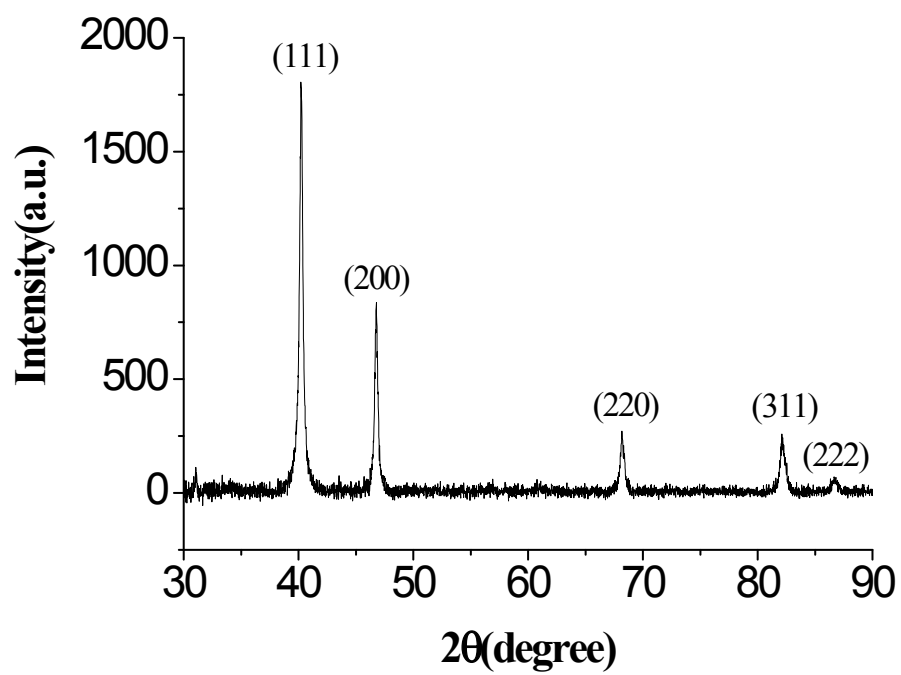


Figure S4. XRD patterns of the as-prepared Pd-Pt alloy nanohypercubes.

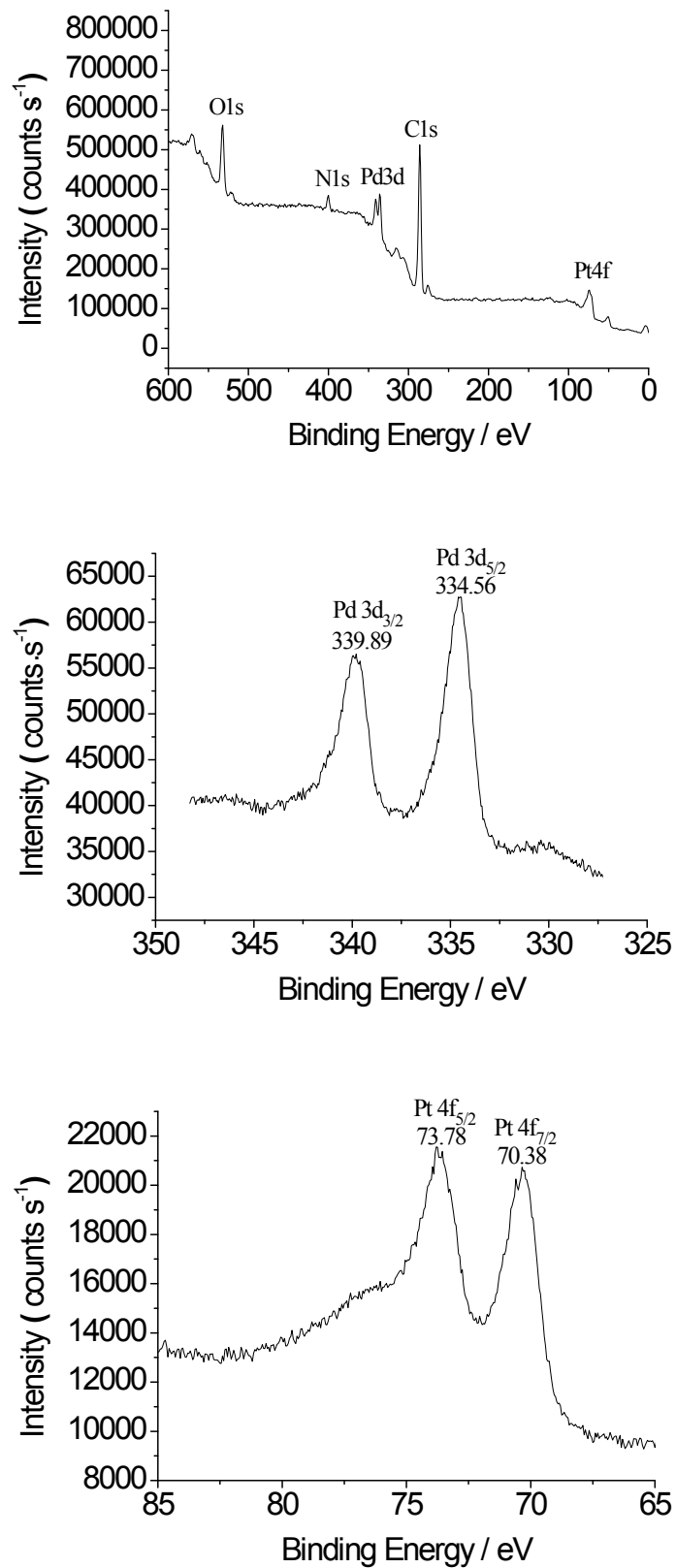


Figure S5. XPS spectrograms of the as-prepared Pd-Pt alloy nanohypercubes.

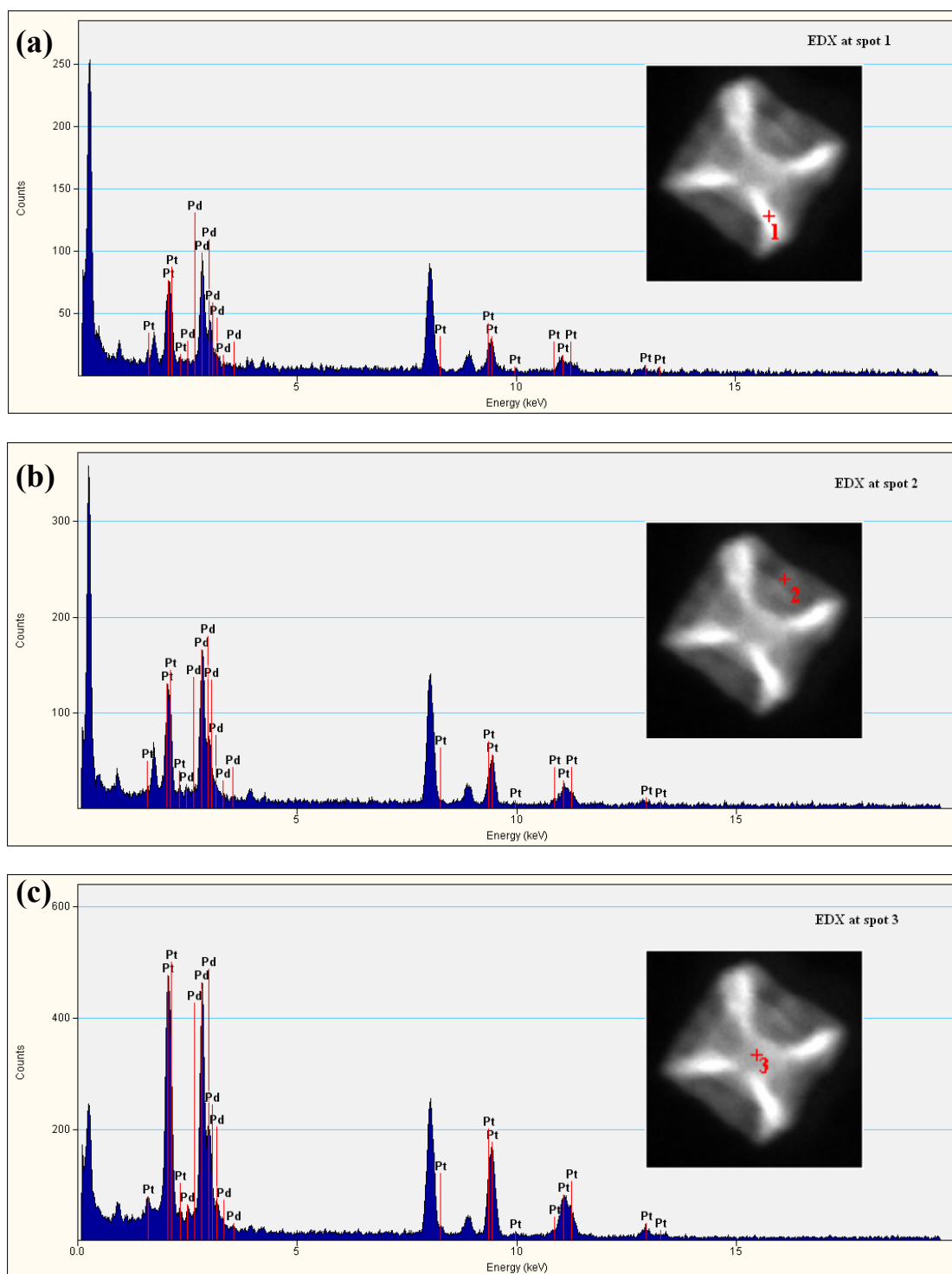


Figure S6. EDX spot analysis spectra on three selected areas of a single Pd-Pt hypercube. (a) spot 1, 72% Pd and 28% Pt; (b) spot 2, 40% Pd and 60% Pt; (c) spot 3, 65% Pd and 35% Pt, corresponding to Figure 3d in the text.

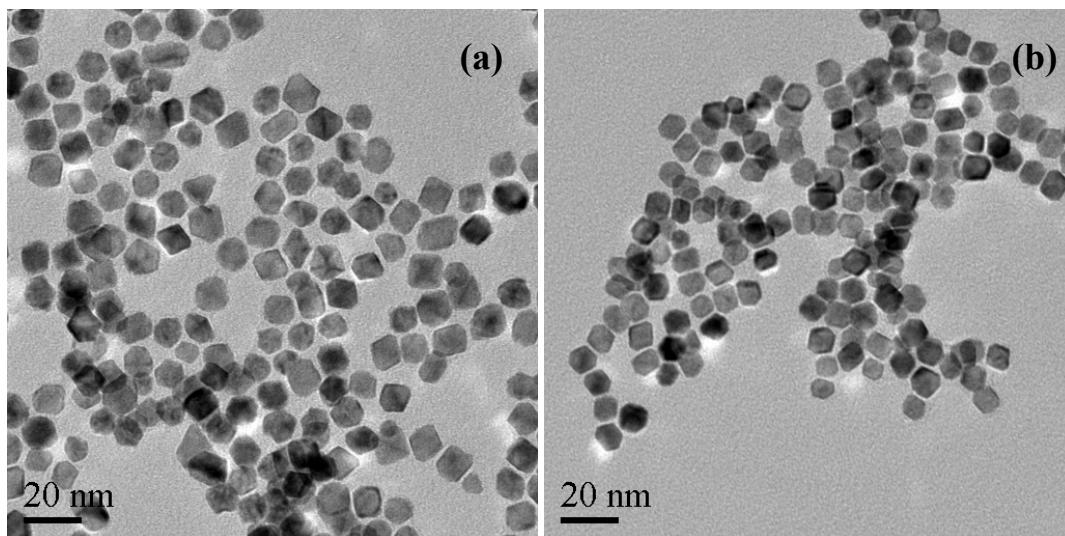


Figure S7. TEM images of nanoparticles obtained with using an equal amount of KCl (a) or KBr (b) instead of KI under the same conditions.

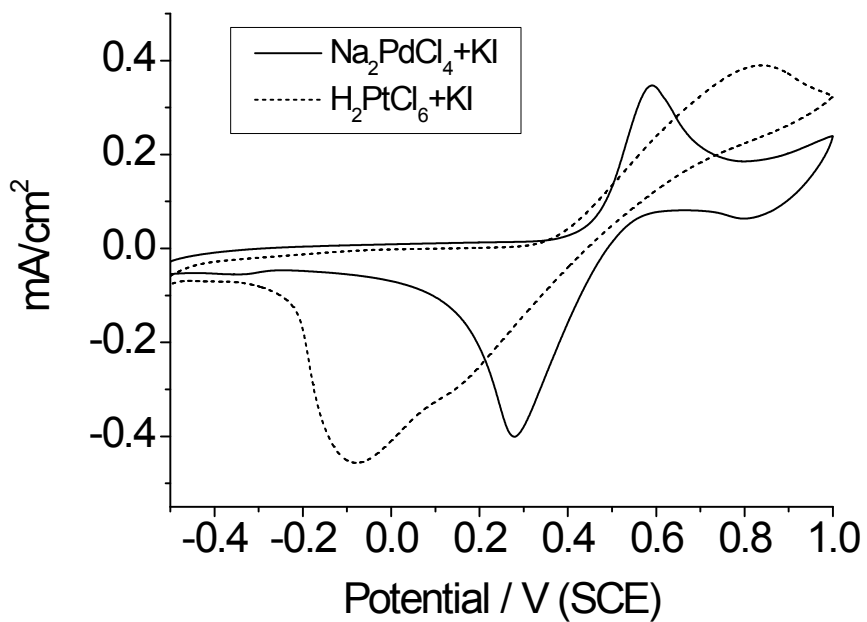
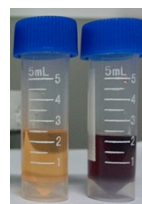
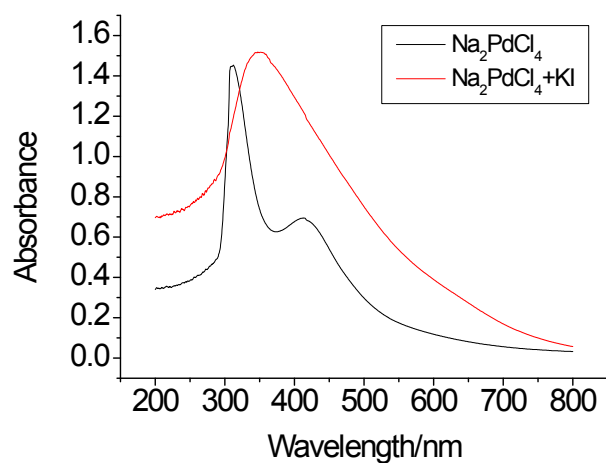
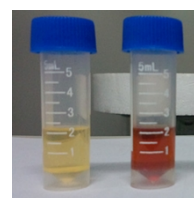
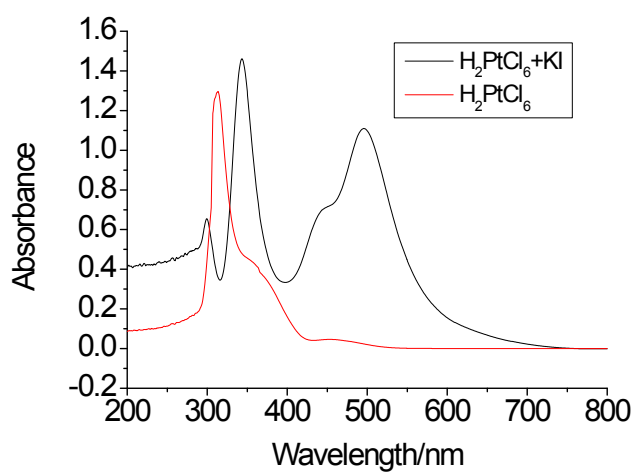


Figure S8. CV curves of 0.001 M H₂PtCl₆ and 0.001 M Na₂PdCl₄ solution in the presence of 0.03 M KI with the cyclic potential sweeping between -0.5 and 1.0 V at a sweep rate of 100 mV·s⁻¹.



Left: Na_2PdCl_4
Right: $\text{Na}_2\text{PdCl}_4+\text{KI}$



Left: H_2PtCl_6
Right: $\text{H}_2\text{PtCl}_6+\text{KI}$

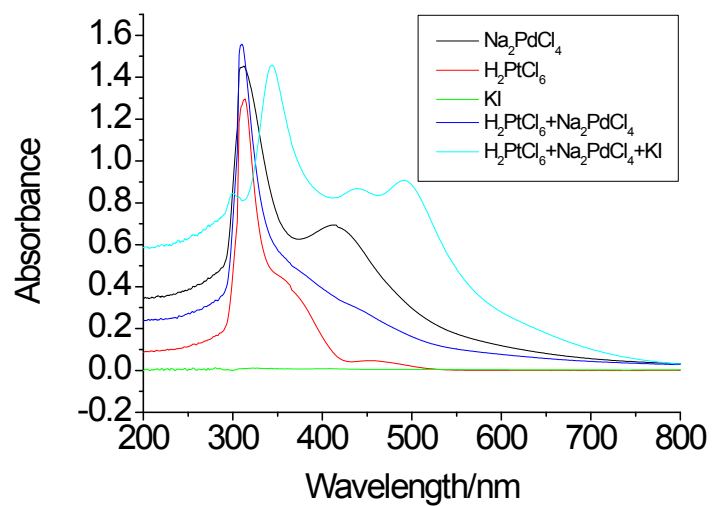


Figure S9. UV-vis absorption spectra of the precursors in water.

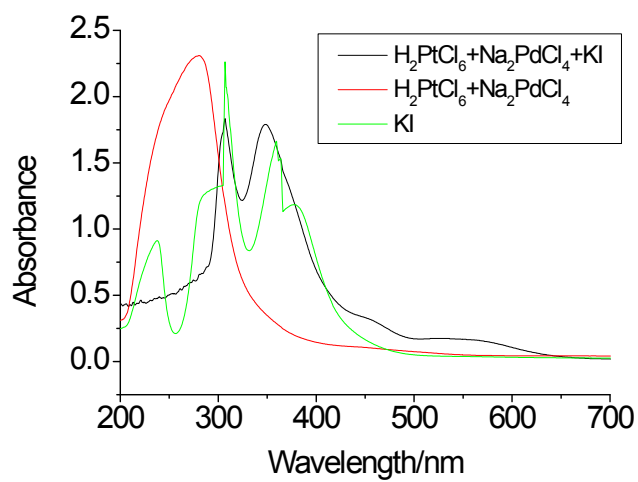
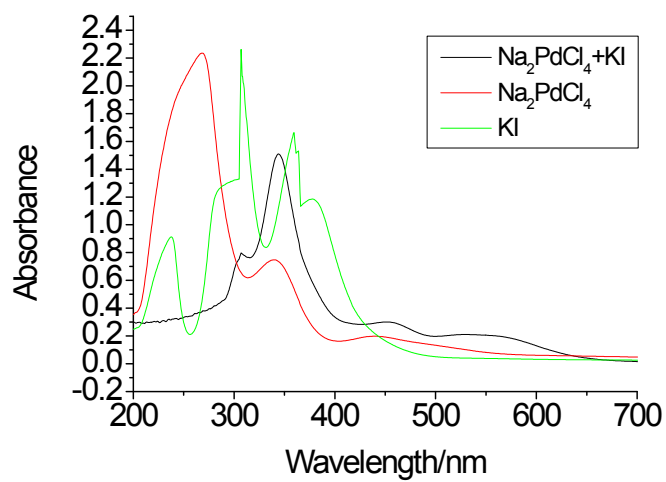
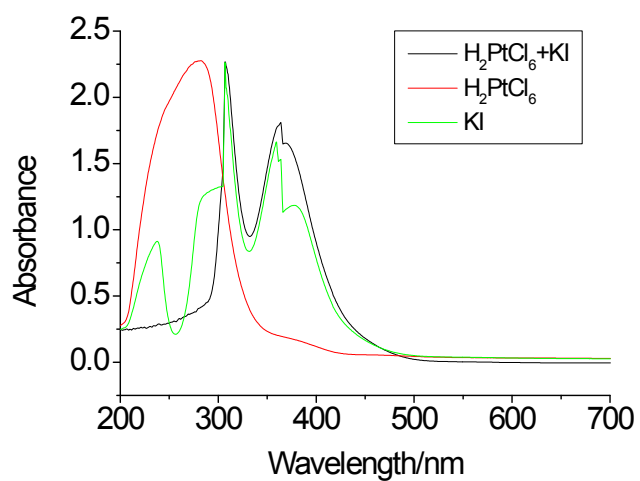


Figure S10. UV-vis absorption spectra of the precursors in TEG.

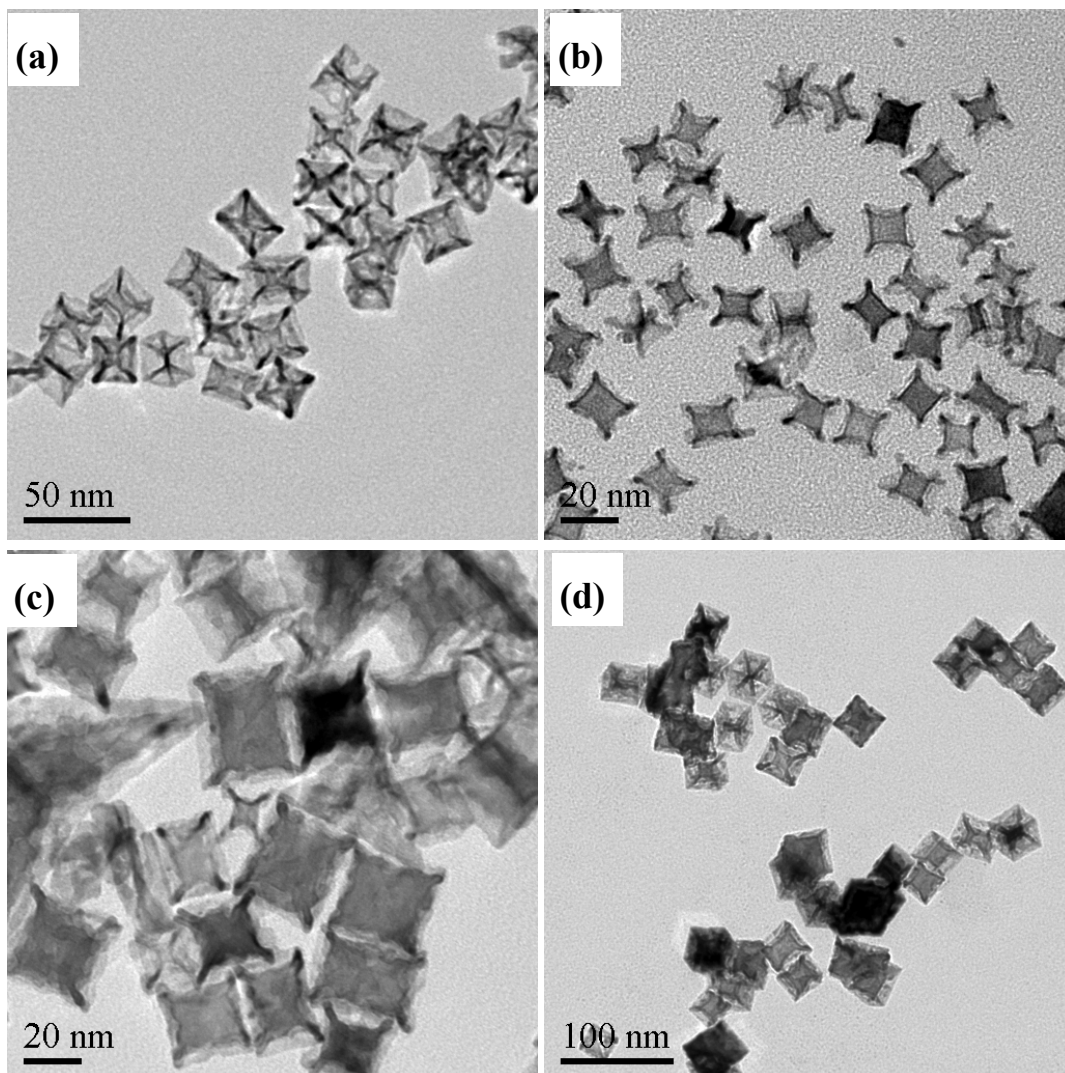


Figure S11. TEM images of nanoparticles prepared with other palladium salts as precursors. (a) $\text{Pd}(\text{acac})_2$; (b) PdCl_2 ; (c) $\text{Pd}(\text{Ac})_2$; (d) $\text{Pd}(\text{NO}_3)_2$.

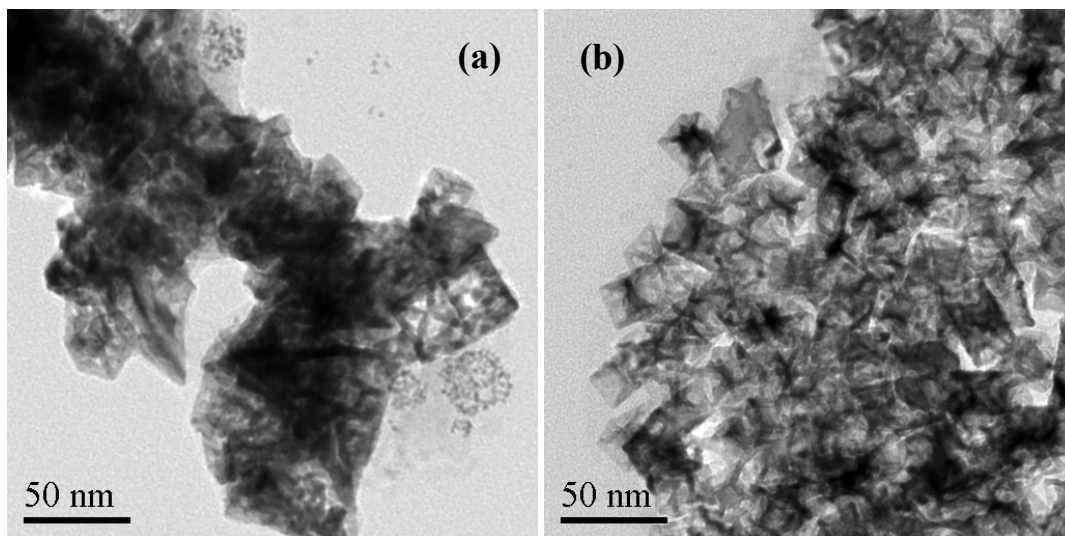


Figure S12. TEM images of nanoparticles obtained without PVP (a) or with a little amount (25 mg) of PVP (b).

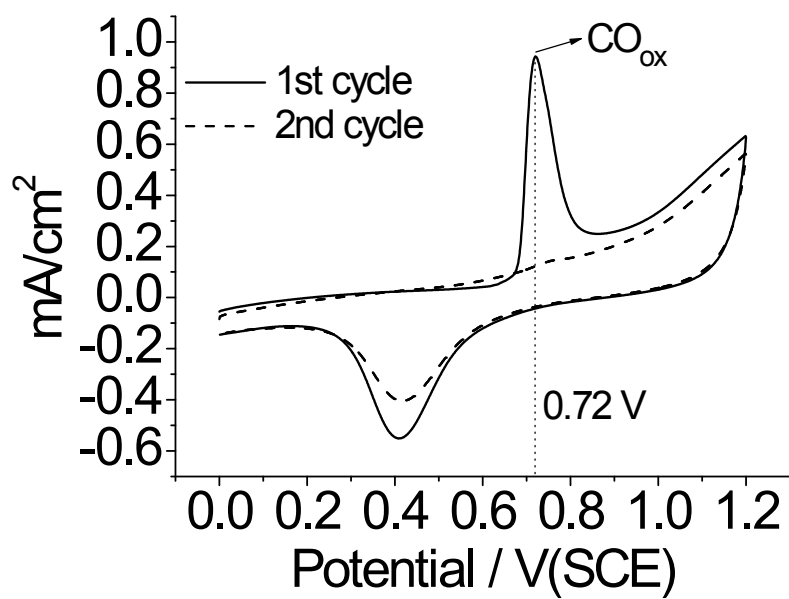


Figure S13. CO stripping voltammetry of the Pd-Pt alloy nanohypercubes in 0.1M HClO₄ solution at a scan rate of 5mV/s between 0 and 1.2 V.

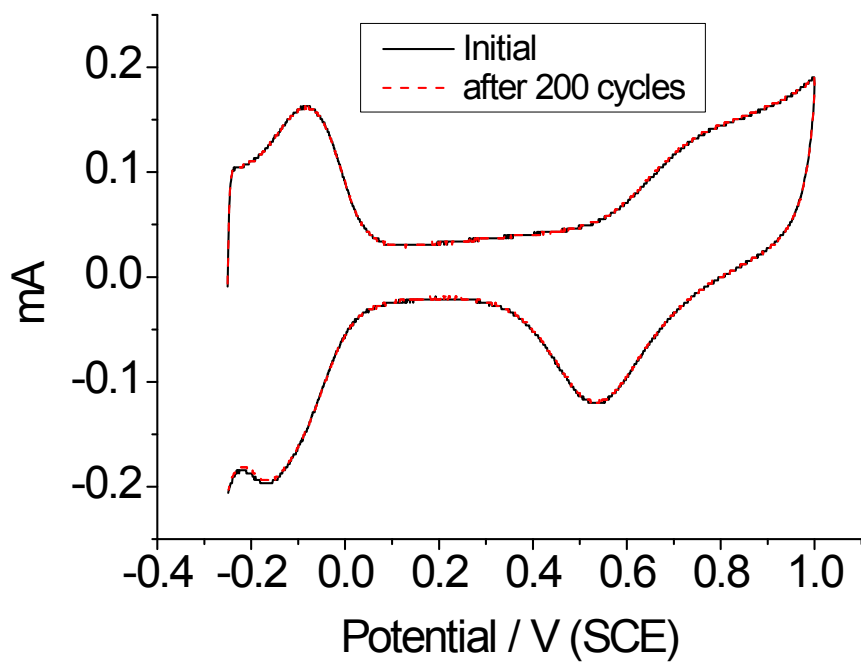


Figure S14. Electrochemical stability test for Pd-Pt alloy nanohypercubes. The CV tests were carried out in 0.5 M H₂SO₄ solutions with the cyclic potential sweeping between -0.25 and 1.0 V at a sweep rate of 250 mV/s.