Supporting Information for

Manipulating the Oxygen Reduction Activity of Platinum Shells with Shape-Controlled Palladium Nanocrystal Cores

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Experiments

Synthesis of Pd Nanocrystals. In a typical synthesis of Pd nanocubes, 11 mL of an aqueous solution containing poly(vinyl pyrrolidone) (PVP, MW = 55,000, 105 mg, Aldrich), L-ascorbic acid (60 mg, Aldrich), KCl (185 mg, J. T. Baker), KBr (5 mg, Aldrich), and Na_2PdCl_4 (57 mg, Aldrich) was heated at 80 °C in air under magnetic stirring for 3 h and cooled down to room temperature. In the synthesis of Pd octahedral, PVP (105 mg, Aldrich), citric acid, (180 mg, Aldrich), and Na_2PdCl_4 (57 mg, Aldrich) were dissolved in a mixture solution containing 3 mL of ethanol and 8 mL of water. The resulting solution was heated at 80 °C in air under magnetic stirring for 3 h and cooled down to room temperature.

To load the Pd nanocrystals on the carbon powder, 80 mg of Ketjen Black was dispersed in 5 mL of deionized water and sonicated for 1 h. The carbon black suspension was then added to the 11 mL of dispersion of Pd nanocrystals and the reaction mixture was heated to 80 °C in air for 2 h. After cooling to room temperature, the precipitate was retrieved by centrifugation to give a black powder. The final product was dried in air and ready for test.

Electrochemical Evaluation and Pt Monolayer Deposition. Approximately 15 mg of the Pd/C nanocrystals was dispersed in a solvent consisting of 12 ml of water, 3 ml of isopropanol, and 60 µl of 5% Nafion (Aldrich) by ultrasonic for 10 min. 10 µl of the suspension was deposited on a pre-cleaned glassy carbon rotating disk electrode (RDE, Pine Instruments) and allowed to dry in air. The capping agents (poly(vinyl pyrrolidone), Br^- and Cl^-) on Pd surfaces can be removed using a non-destructive method at room temperature by keeping the electrode potential at the hydrogen evaluation region, for example -0.05 V for 60 s. After removing the capping agents, the catalyst was cycled between 0.08 and 0.8 V (vs. the reversible hydrogen electrode or RHE) for 5 cycles in a N_2 saturated aqueous solution of 0.1 M $HClO_4$ at 50 mV s^{-1}. The up-limit potential was set to 0.8 V to minimize the dissolution of Pd at high potentials.

The Pt shell was prepared via galvanic displacement with an underpotentially deposited (UPD) Cu monolayer prepared from a 50 mM H_2SO_4 + 50 mM $CuSO_4$ solution. The electrode, covered with a Cu monolayer was rinsed and immersed in a 1.0 mM K_2PtCl_4 (Johnson Matthey) + 50 mM H_2SO_4 (GFS Chemicals) solution for about 2 min to displace the Cu with Pt. An Ag/AgCl/KCl (3 M) leak-free electrode and Pt gauze were used as reference and counter electrodes, respectively. All potentials are quoted with respect to RHE. All of these operations were carried out under a nitrogen atmosphere. The electrochemical area and Pt loading were

measured based on the charge associated with the stripping of a UPD Cu monolayer on Pd, assuming 420, 490 and 460 μC cm^{-2} for full Cu monolayer coverage on cubes, octahedra, and conventional particles, respectively.

The oxygen reduction polarization curves were measured in an oxygen saturated 0.1 M $HClO_4$ (GFS Chemicals) solution at a scan rate of 10 mV s^{-1} at 1600 rpm. The kinetic current j_k at 0.9 V was derived by the Koutecky-Levich equation

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

where j is the measured current density, B is a constant, and ω is the rotation rate. All the Electrolytes were prepared from MilliQ UV-plus water (Millipore).

Physical Characterization. Powder X-ray diffraction patterns (XRD) were taken by a commercial diffractometer (Bruker AXS D8 Discover) using Cu Ka radiation (λ= 1.54056A˚). The particle size was calculated using the Scherrer equation.

Transmission electron microscopy (TEM) studies were done with a FEI Tecnai G2 Spirit microscope operated at 120 kV by drop casting the dispersions of nanoparticles on carbon-coated copper grids. High-resolution TEM analyses were carried out using a JEOL 3000F microscope operated at 300 kV. High-angle annular dark-field (HAADF) STEM images were acquired using an aberration corrected Hitachi HD2700C STEM.

DFT Calculations. The first-principles calculations are based on spin-polarized density functional theory (DFT) using a Generalized Gradient Approximation (GGA)[1] and projector augmented wave (PAW) method[2] as implemented in Vienna Ab-Initio Simulation Package (VASP).[3] The cut-off energy for plane wave basis set was 400 eV and Brillouin zone was sampled using a Monkhorst-Pack sampling technique[3] with 5×5×1 k-point grid for surface calculations. The Pt monolayer surfaces are modeled as pseudomorphic layers placed on top of the Pd(111) and Pd(100) surfaces with a lattice constant corresponding to the bulk substrate. Surfaces are modeled by 6-layer slabs with 2×2 surface cell separated by a 14 Å vacuum layer perpendicular to the surface. The top four layers were fully relaxed until Hellmann–Feynman forces were 0.01 eV $Å^{-1}$. The binding energy of atomic oxygen is calculated as BEo = E (O/surface) - E (surface)-1/2E (O_2). The E (O/surface) and E (surface) are total electronic energies of oxygen adsorbed on surface and surface alone. The E (O_2) is the energy of oxygen gas in its ground state. For Pd surfaces, the most stable oxygen adsorption configurations are an

fcc hollow site surrounded by three atoms on the (111) surface, and a center site surrounded by four atoms on the (100) surface, respectively. For Pd-Pt surfaces, the most stable oxygen adsorption configurations are an *fcc* hollow site surrounded by three atoms on the (111) surface, and a bridge site between two atoms on the (100) surface, respectively.

References

(1) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50,* 17953-17979.

(2) (a) Kresse, G.; Furthmuller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169-11186. (b) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758-1775.

(3) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13,* 5188-5192.
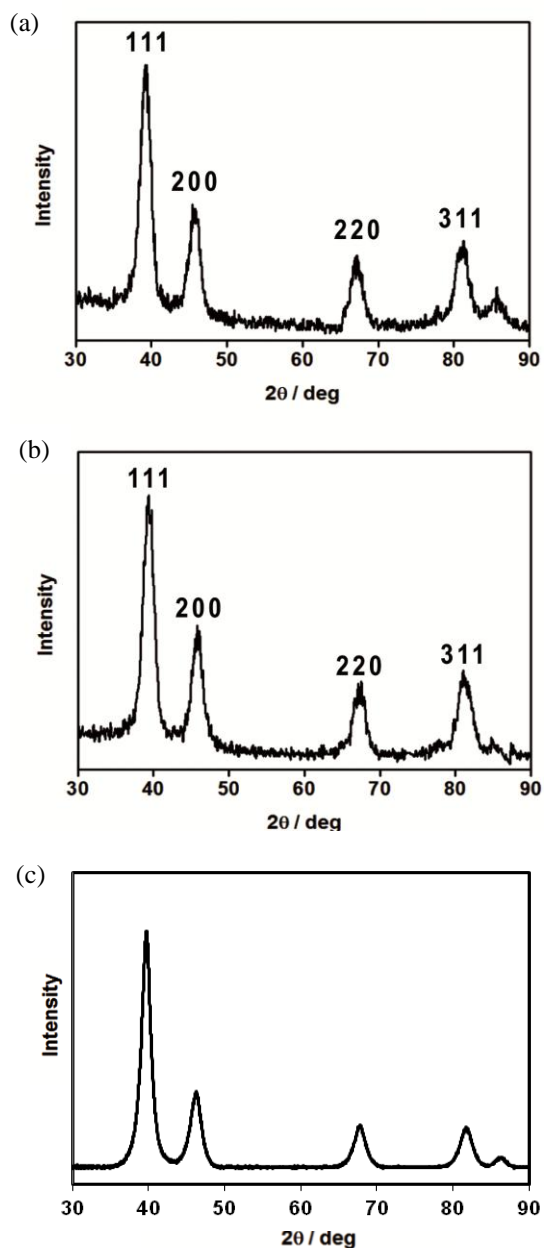
Figure S1. XRD patterns of (a) Pd/C cubes, (b) Pd/C octahedra and (c) conventional Pd/C.
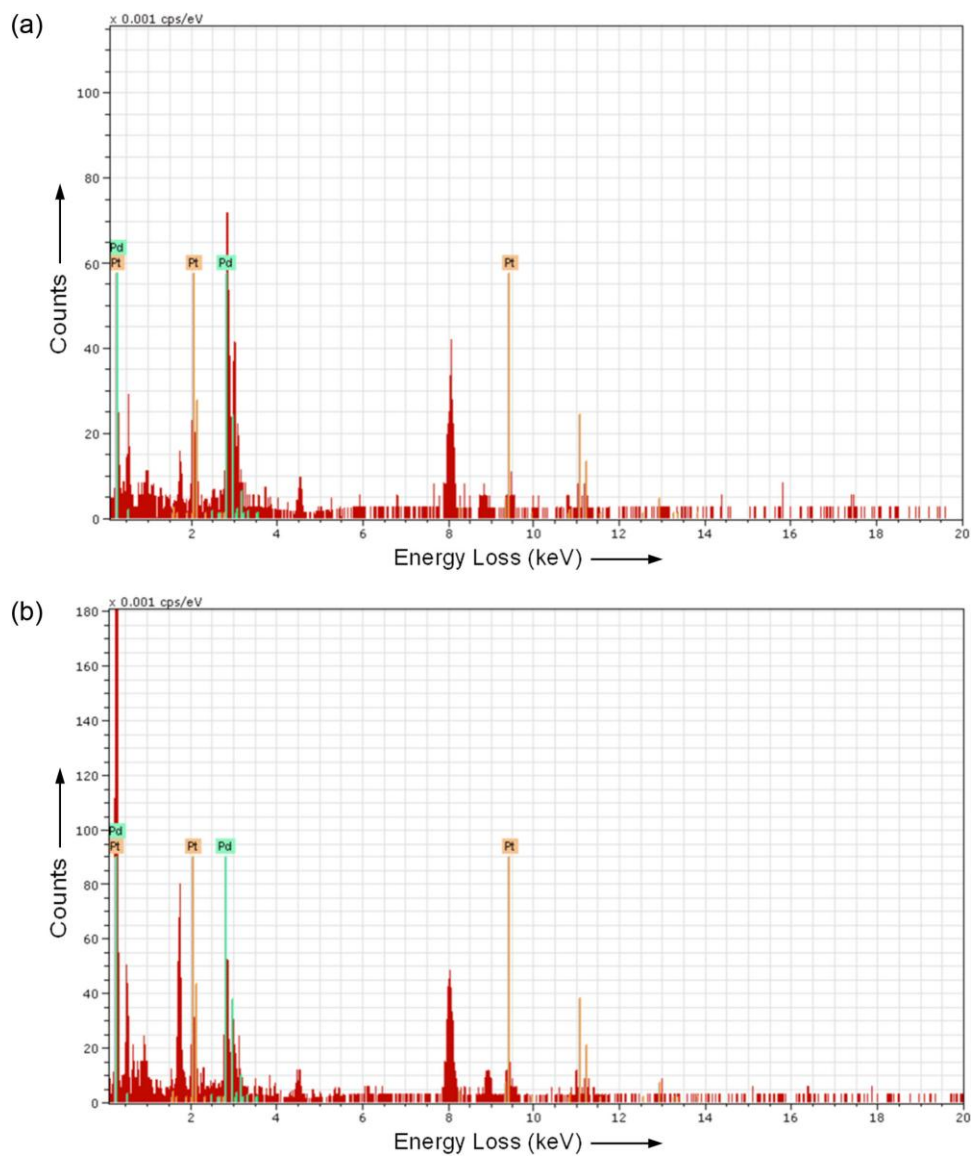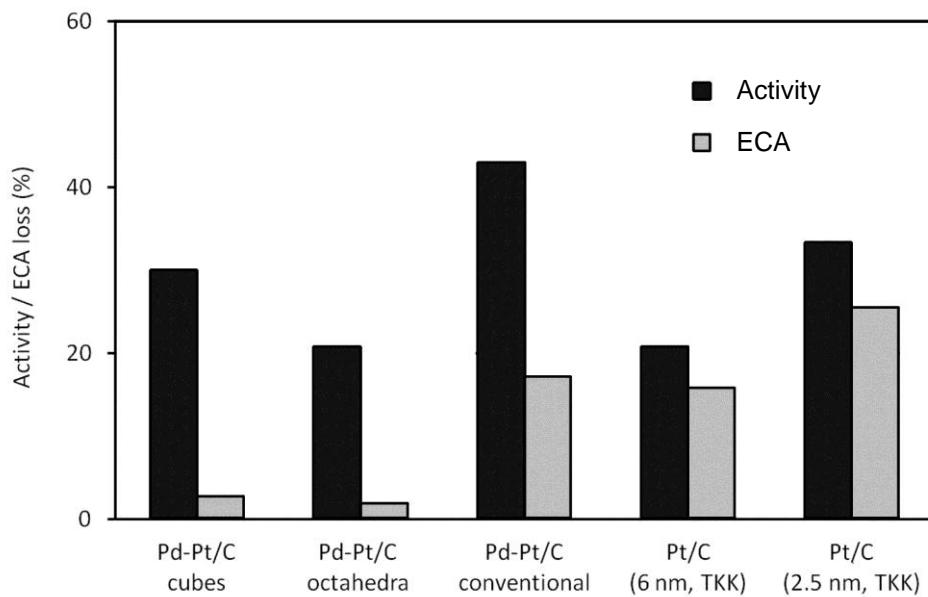
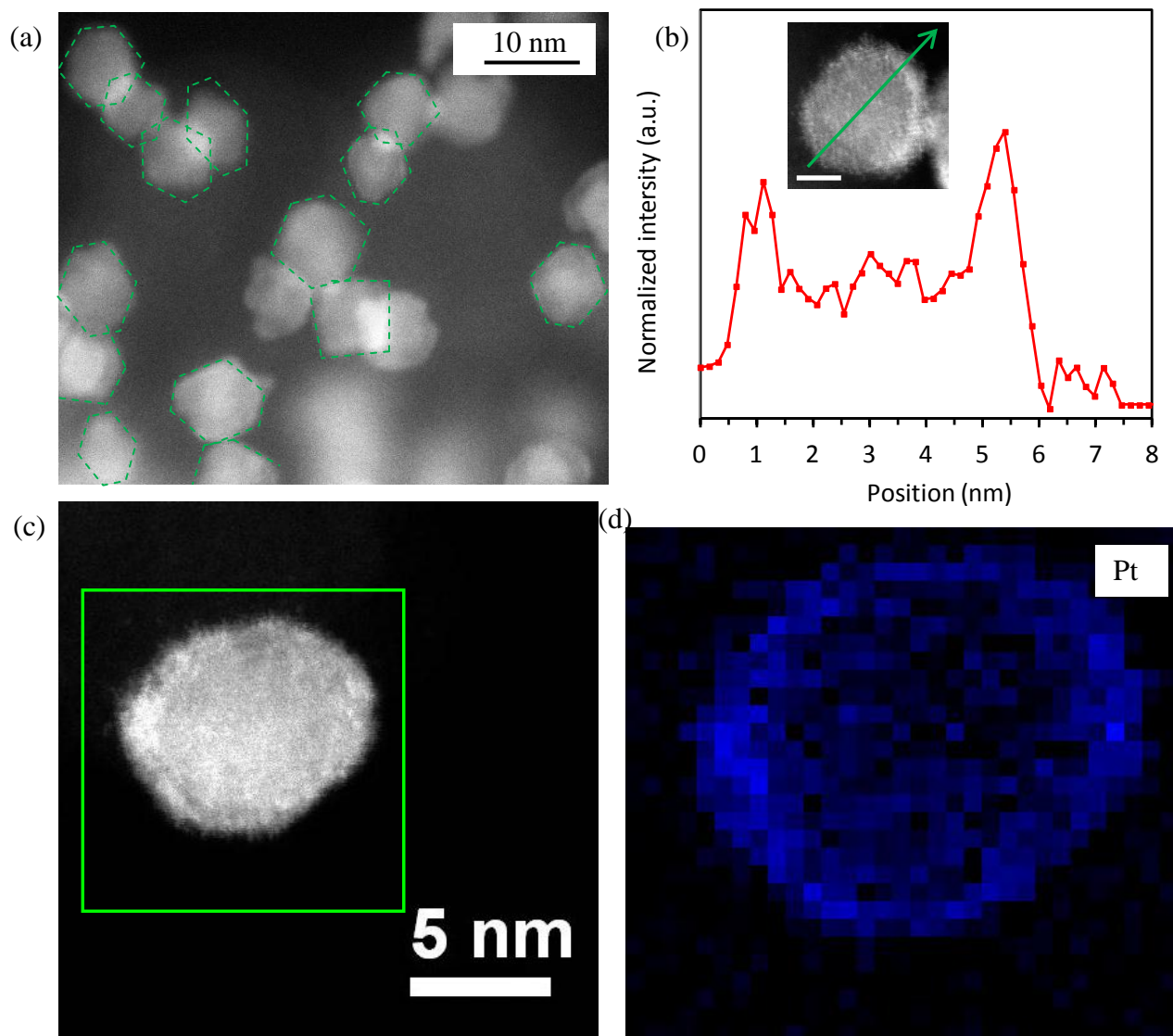**Figure S2.** EDX patterns of (a) the Pd-Pt/C cubes and (b) Pd-Pt/C octahedra.
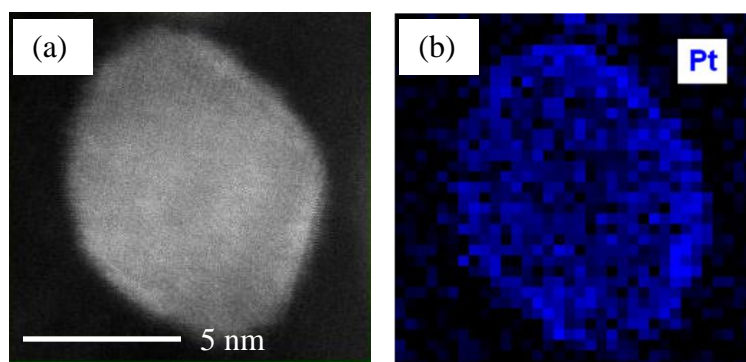
**Figure S3.** (a) STEM and (b) 2D-EELS mapping using Pt M edge of a single Pd-Pt octahedron particle.

Figure S4. Comparison of the losses in activity and ECA for Pt shells on different types of Pd cores after 5000 rounds of potential cycling, with Pt/C (6 nm and 2.5 nm) serving as the benchmark.

Figure S5. Characterization of Pd-Pt/C octahedra after 5000 potential cycles. (a) STEM images, (b) EELS line profile of Pt across a single Pd-Pt nanoparticle shown in the inset, (d) 2D-EELS mapping using Pt M edge of a single Pd-Pt octahedron particle in (c).The scale bar in the inset of (b) is 2 nm.
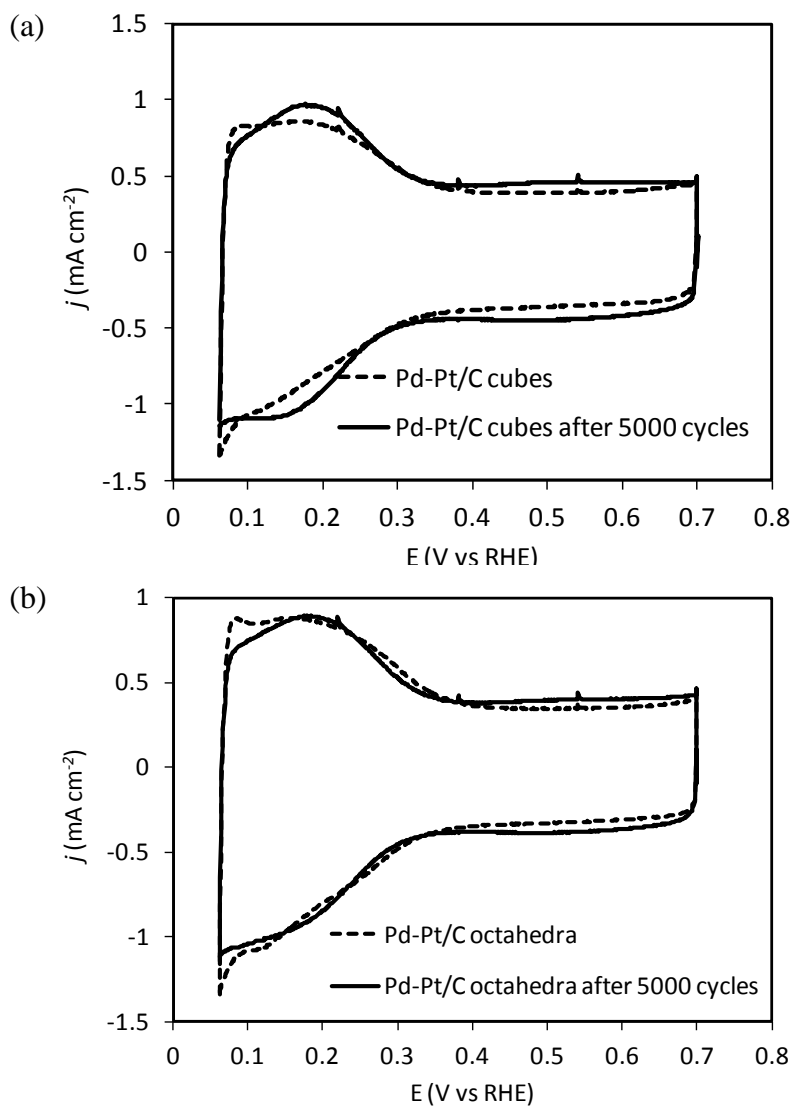
Figure S6. Voltammetry curves of Pt shells deposited on (a) Pd cubes and (b) Pd octahedra before and after potential cycling in a nitrogen-saturated 0.1 M HClO$_4$ solution. Scanning rate = 50 mV s^{-1}. The currents were normalized against the geometric area of the rotating disk electrode (0.196 cm^2).