Supporting Information for

Structural Dependence of Oxygen Reduction Reaction on Palladium Nanocrystals

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Experimental Section

Synthesis of Pd Nanocubes. 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.

Synthesis of Pd octahedra. 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.

Preparation of carbon-supported Pd nanocrystals. 80 mg of carbon black was dispersed in 5 mL of deionized water and sonicated for 1 h. The carbon black solution 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 blak powder.

Electrochemical measurements. Approximately 15 mg of the Pd nanoparticles supported on carbon powder were dispersed in a solvent consisting of with 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 the pre-cleaned glassy carbon substrate (RDE, Pine Instruments) and allowed to dry. After PVP removing procedure, Pd/C was cycled between 0.08 and 0.8 V (vs RHE) for 5 cycles in a N_2 saturated 0.1 M $HClO_4$ at 50 mV $s^{-1.}$ The up-limit potential was set to 0.8 V to minimize the Pd dissolution at high potential. The electrode was then transferred to an electrochemical cell containing an O_2 saturated 0.1 M $HClO_4$ for oxygen reduction activity measurements. The kinetic currents were calculated based on eq. 1:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \tag{1}$$

where j and j_d are the measured current and limited current, respectively.

The electrochemical area was measured based on the charge associated with the stripping of a Cu monolayer underpotentially deposited (UPD) on Pd assuming 420, 490 and 460 µC cm^{-2} for full Cu monolayer coverage on cubes, octahedra, and cubo-octahedra, respectively. The 50 mM H_2SO_4 + 50 mM $CuSO_4$ solution was used to perform Cu underpotential deposition. CV and ORR polarization curves were obtained with an EG&G Princeton 273 potentiostat.

Characterization. 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 performed using a JEOL 2100F microscope operated at 200 kV accelerating voltage. Powder XRD patterns were obtained with a Rigaku D-MAX/A diffractometer at 35 kV and 35 mA.
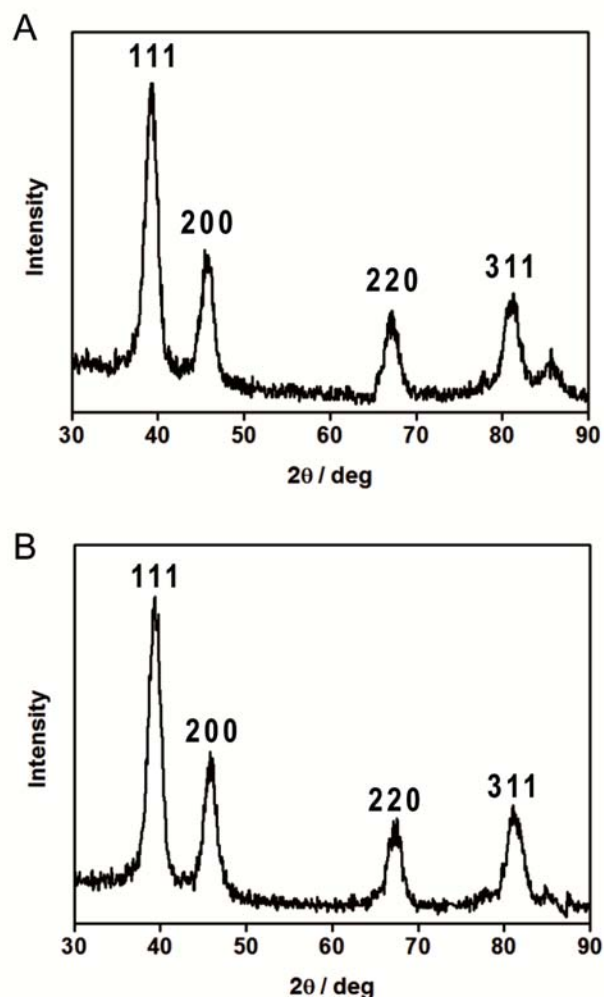
Fig. S1. XRD patterns of (A) Pd cubes, (B) Pd octahedra. The XRD peaks of Pd nanocrystals were well matched with JCPDS file no. 87-0641.
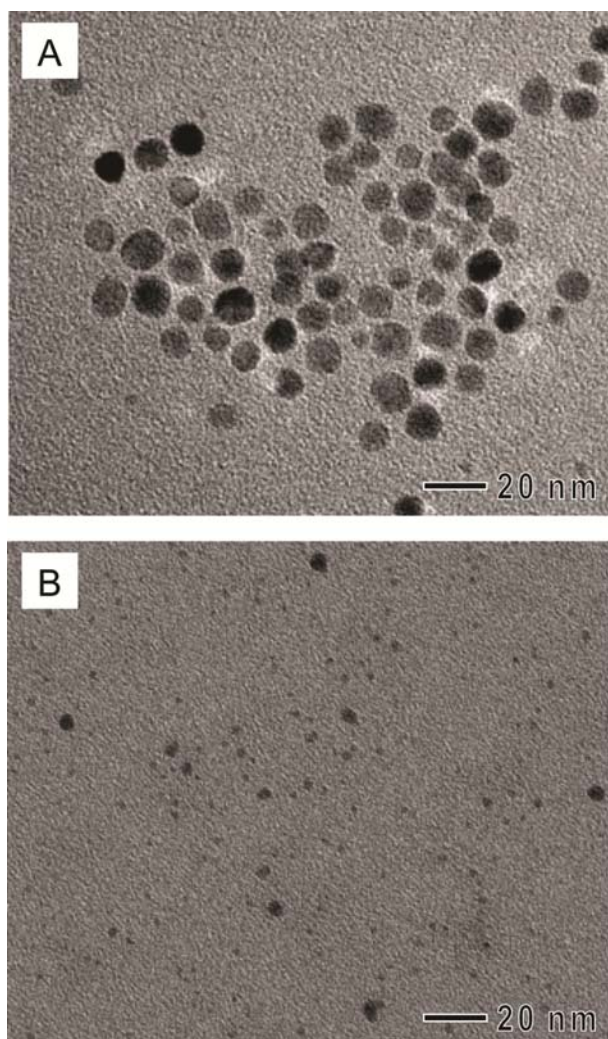
Fig. S2. (A) TEM image of the sample prepared under the same condition as those in Figure 1c except that the synthesis was conducted in only ethanol instead of water−ethanol mixture. (B) TEM image of the sample prepared under the same condition as those in Figure 1c except that the synthesis was conducted in only water without ethanol.
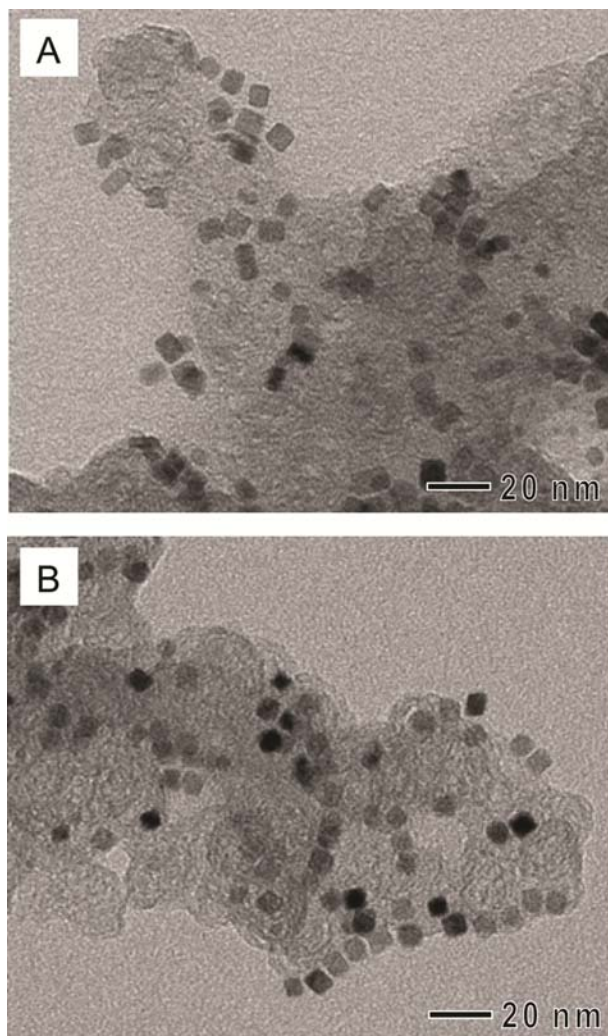
Fig. S3. TEM images of (A) Pd cubes and (B) Pd octahedra dispersed on carbon support.
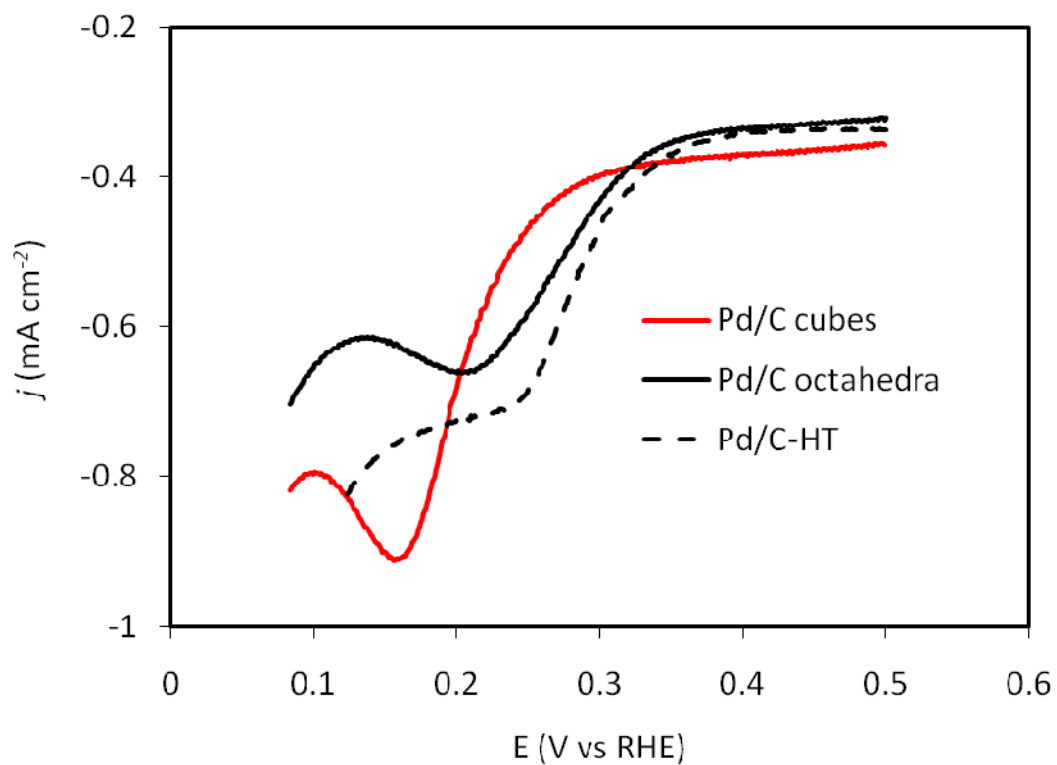
Fig. S4. Voltammetry curves (only showing the hydrogen adsorption region) of carbon supported Pd samples in a nitrogen saturated 0.1 M $HClO_4$ solution. Scanning rate = 50 mV s^{-1}. The currents were normalized to the geometric area of the rotating disk electrode (0.196 cm^2).
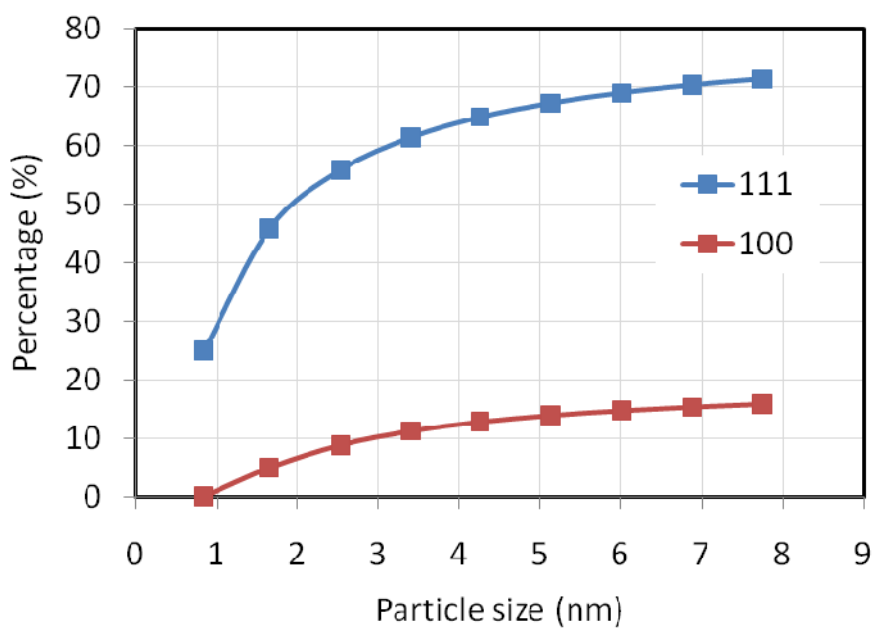
Fig. S5. Surface atom distribution at (111) and (100) sites for a model cubo-octahedral nanoparticle as a function of particle size.
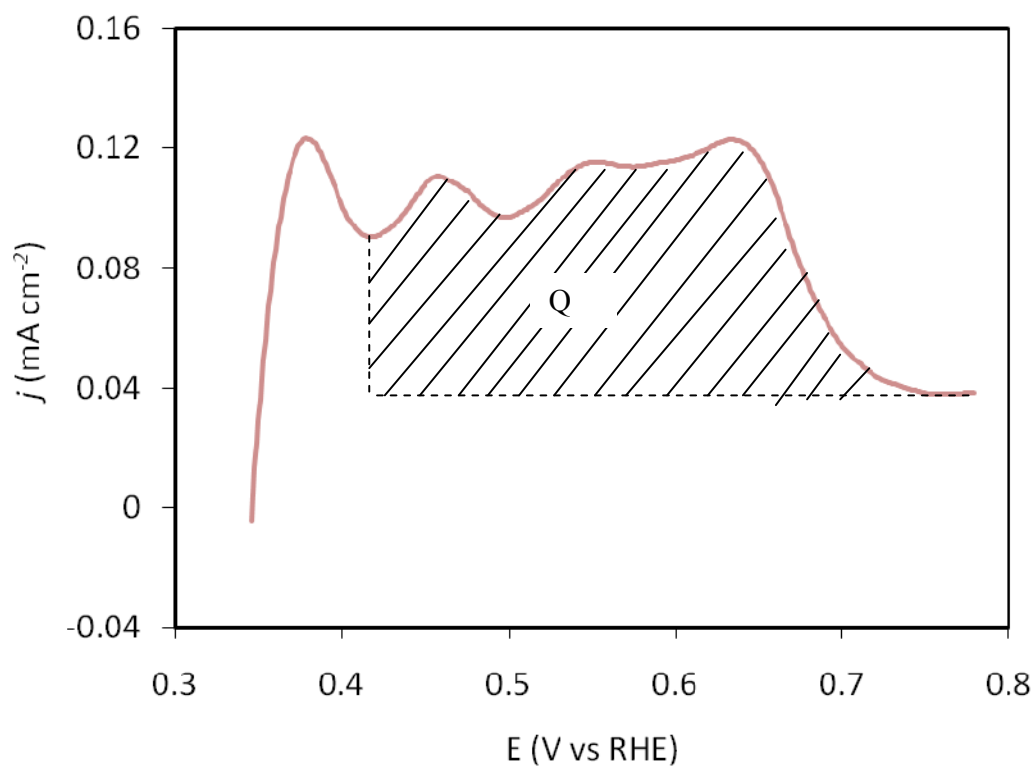
Fig. S6. Cu stripping curve (red line) for an underpotentially deposited Cu monolayer on regular Pd/C. Scanning rate = 5 mV s^{-1} in 0.05 M H$_2$SO$_4$ + 0.05 M CuSO$_4$ solution. The electrochemical area of Pd was calculated based on the Cu stripping charge (Q) assuming 460 μC cm^{-2} for full Cu monolayer coverage.