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Supporting Information

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Palladium Concave Nanocubes with High-Index Facets and Their Enhanced Catalytic Properties**

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Supporting Information

Experimental section

Synthesis of Pd nanocubes: The Pd nanocubes were synthesized using a recently published procedure. In a typical synthesis, 8.0 ml of an aqueous solution containing 105 mg PVP (Mw ≈ 55,000), 60 mg AA, and different amounts of KBr and KCl in a 20-ml vial was heated for 10 min at 80 ^{o}C under magnetic stirring. Subsequently, 3.0 ml of an aqueous solution of Na_2PdCl_4 (57 mg) was added with a pipette. After that, the reaction was allowed to continue at 80 ^{o}C for 3 h. The size of Pd nanocubes was controlled by varying the amounts of KBr and KCl: for example, with the use of 600 mg KBr, 300 mg KBr, or 5 mg KBr and 185 mg KCl, the Pd nanocubes had an edge length of 18, 10, or 6 nm. The product was collected by centrifugation, washed three times with water to remove excess PVP, and dispersed in 11 mL water to make a seed solution with a concentration of 1.8 mg/ml for elemental Pd.

Synthesis of Pd concave nanocubes: In a standard procedure, 7.7 ml of an aqueous solution containing 105 mg PVP (Mw ≈ 55,000), 60 mg AA and 300 mg KBr, and 0.3 ml of the Pd seeds were mixed in a glass vial. The mixture was heated to 60 ^{o}C in air under magnetic stirring. Meanwhile, 3.0 ml of an aqueous solution of Na_2PdCl_4 (14.5 mg) was added to the mixture by pipette under magnetic stirring. The synthesis was allowed to proceed at 60 ^{o}C for 3 h. Finally, the solution was centrifuged and washed three times with water to remove excess PVP before characterization. The morphology of Pd nanocrystals was controlled by manipulating the concentrations of reagents, including Na_2PdCl_4, KBr, and AA. Palladium concave nanocubes with different sizes were synthesized by controlling the size of Pd nanocubes serving as the seeds.

Suzuki coupling reaction: The coupling between phenylboronic acid and iodobenzene was performed according to a previous report. In a typical reaction, iodobenzene (0.034 ml, 0.3 mmol) was added into 4 ml of ethanol containing phenylboronic acid (0.073 g, 0.6 mmol), K_2CO_3 (0.138 g, 1 mmol), and 100 μl of the Pd catalyst (100 μg/ml). The mixture was placed in an oil bath at 85 ℃ under magnetic stirring for 20 min. The product was extracted with CH_2Cl_2, and then separated by gas chromatography (GC) and analyzed by mass spectrometry

(MS).

Electrochemical measurements: The electrochemical measurements were performed at room temperature using a glassy carbon rotating disk electrode (RDE, Pine Research Instrumentation, United States) connected to a PARSTAT 283 potentialstat (Princeton Applied Research, United States). A hydrogen electrode (Gaskatel, Germany) was used as the reference. The counter electrode was a Pt mesh (1 x 1 cm^2) connected to a Pt wire. To prepare the working electrode, 15 μl of an aqueous suspension of the catalyst was transferred to the RDE with a geometric area of 0.196 cm^2. Upon drying under air for 2 h, the electrode was covered with 15 μl of Nafion dispersed in water (0.05%). Underpotential deposition of Cu was performed in a solution containing 0.05 M H_2SO_4 and 0.05 M $CuSO_4$ at a sweep rate of 5 mV/s. Electro-oxidation of formic acid measurements were conducted in a solution containing 0.1 M $HClO_4$ and 2 M HCOOH using the RDE at a sweep rate of 50 mV/s and at room temperature.

Instrumentation: TEM images were captured using a FEI Tecnai G2 Spirit microscope operated at 120 kV by drop casting the dispersions of particles on carbon-coated Cu grids, followed by drying under ambient conditions. High-resolution TEM analyses were conducted with a JEOL 2100F microscope operated at 200 kV. The concentrations of the catalysts were determined using an inductively-coupled plasma mass spectrometer (ICP-MS, PerkinElmer Elan DRC II ICP-MS). The GC-MS analysis was performed on Agilent 5975 series MSD.

Calculation of the total number of Pd atoms contained in a Pd nanocube enclosed by {100} or {730} facets, and the total number of Pd atoms on the surface

(1) Conventional nanocubes enclosed by {100} facets

(a) Number of Pd atoms contained in a nanocube

The edge length of a Pd nanocube is 37 nm. Its volume is $(37\ nm)^3 = 5.06 \times 10^4\ nm^3$. Pd has a face-centered-cubic structure with a lattice constant of 0.389 nm. The volume of a unit cell is $(0.389\ nm)^3 = 0.059\ nm^3$. Each unit cell contains four Pd atoms. As such, the total number of Pd atoms in a single Pd nanocube is $(5.06 \times 10^4\ nm^3) / (0.059\ nm^3) \times 4 = 3.44 \times 10^6$.

(b) Number of Pd atoms on the surface of a nanocube

A Pd nanocube is enclosed by 6 {100} facets. The total surface area is $(37\ nm)^2 \times 6 = 8.21 \times 10^3\ nm^2$. Each two-dimensional unit cell on the {100} facets contains two Pd atoms, and the area of this unit cell is $(0.39\ nm)^2 = 0.15\ nm^2$. The total number of Pd atoms on the surface of a single nanocube is $(8.21 \times 10^3\ nm^2) / (0.15\ nm^2) \times 2 = 1.09 \times 10^5$.

(c) Total number of Pd atoms on the surface of nanocubes used in the catalytic reaction

The total number of Pd atoms in the catalyst is $(100 \times 10^{-6}\ g) / (106.42\ g/mol) \times (6.02 \times 10^{23}\ mol^{-1}) = 5.66 \times 10^{17}$. The number of Pd nanocubes involved in the catalytic reaction is $(5.66 \times 10^{17}) / (3.44 \times 10^6) = 1.64 \times 10^{11}$. The total number of Pd atoms on the surface of Pd nanocubes used in the catalytic reaction is $(1.09 \times 10^5) \times (1.64 \times 10^{11}) = 1.79 \times 10^{16}$.

(2) Concave nanocubes enclosed by {730} facets

(a) Volume of a single concave nanocube

The Pd concave nanocube with an average size of 37 nm can be considered as a cube with a truncated square pyramid excavated at the center of each side face. The volume of a cube with an edge length of 37 nm is $(37\ nm)^3 = 5.06 \times 10^4\ nm^3$. The volume of a square pyramid is $1/3 \times (37\ nm)^2 \times (37/2 \times 3/7\ nm) = 3.62 \times 10^3\ nm^3$. As such, the volume of a concave nanocube is $(5.06 \times 10^4\ nm^3) – [6 \times (3.62 \times 10^3\ nm^3)] = 2.89 \times 10^4\ nm^3$.

(b) Number of Pd atoms in a concave nanocube

The number of Pd atoms contained in a single Pd concave nanocube is $(2.89 \times 10^4\ nm^3) / (0.0589\ nm^3) \times 4 = 1.96 \times 10^6$

(c) Number of Pd atoms on the surface of a concave nanocube

The atomic density of {730} planes is 3/7 of that of {100} planes. Considering a cube of 37 nm in edge length, the total surface area of the cube is $(37\ nm)^2 \times 6 = 8.21 \times 10^3\ nm^2$. The total number of Pd atoms on the {730} facets of a single concave nanocube is $(8.21 \times 10^3$

nm^2) / (0.151 nm^2) $\times 2 \times 3/7 = 4.67 \times 10^4$.

(d) Total number of Pd atoms on the surface of concave nanocubes in the catalytic reaction

The total number of Pd atoms in the catalytic reaction is 5.657×10^{17}. The number of Pd concave nanocubes in the catalytic reaction is $(5.66 \times 10^{17}) / (1.96 \times 10^6) = 2.89 \times 10^{11}$. As such, the total number of Pd atoms on the surface of concave nanocubes in the catalytic reaction is $(4.67 \times 10^4) \times (2.89 \times 10^{11}) = 1.35 \times 10^{16}$.

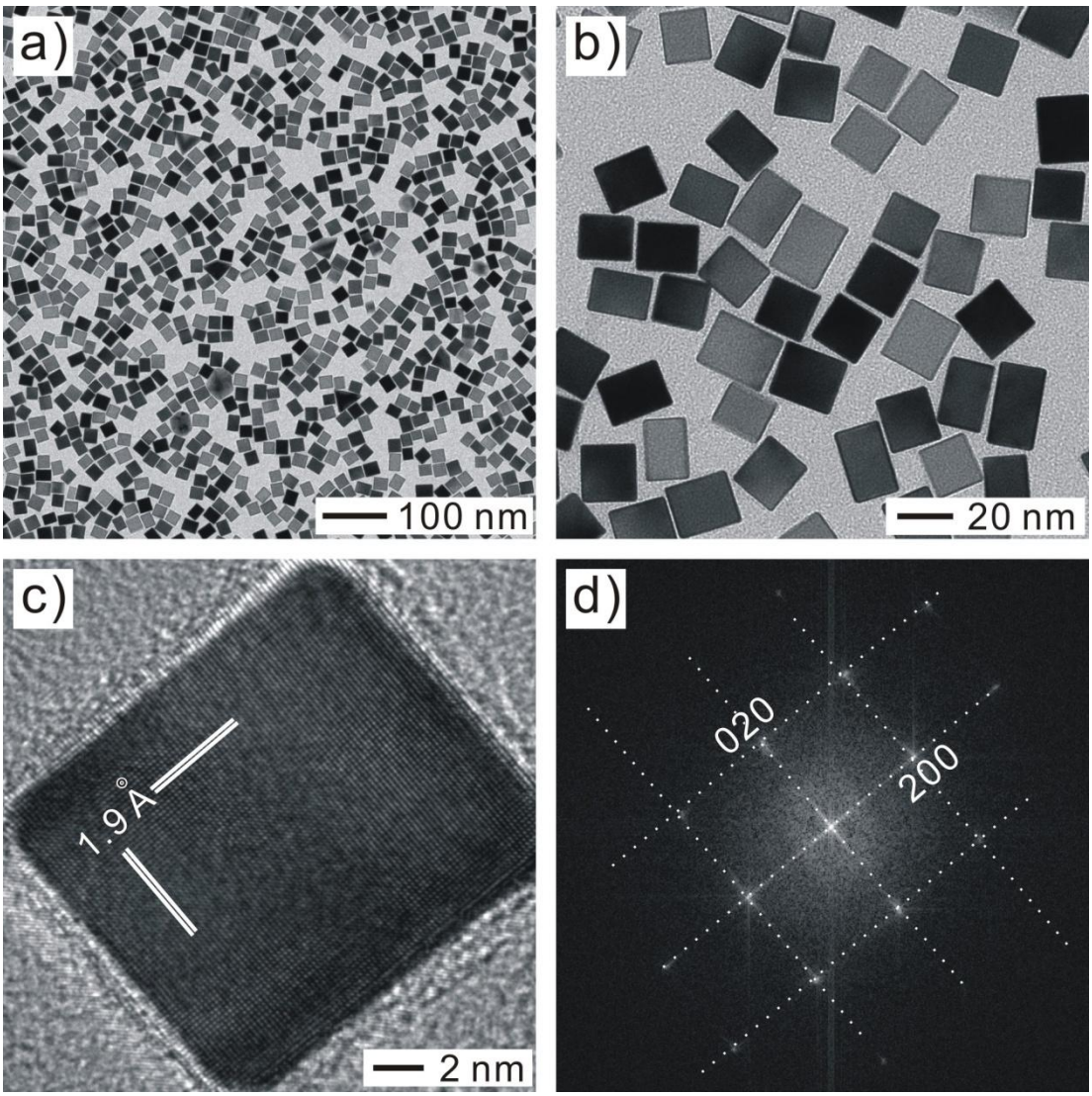


Figure S1. (a, b) TEM and (c) HRTEM images of Pd nanocubes synthesized by reducing Na_2PdCl_4 with ascorbic acid in the presence of KBr as a capping agent. (d) FT pattern of an individual nanocube shown in (c) recorded along the <001> zone axis.

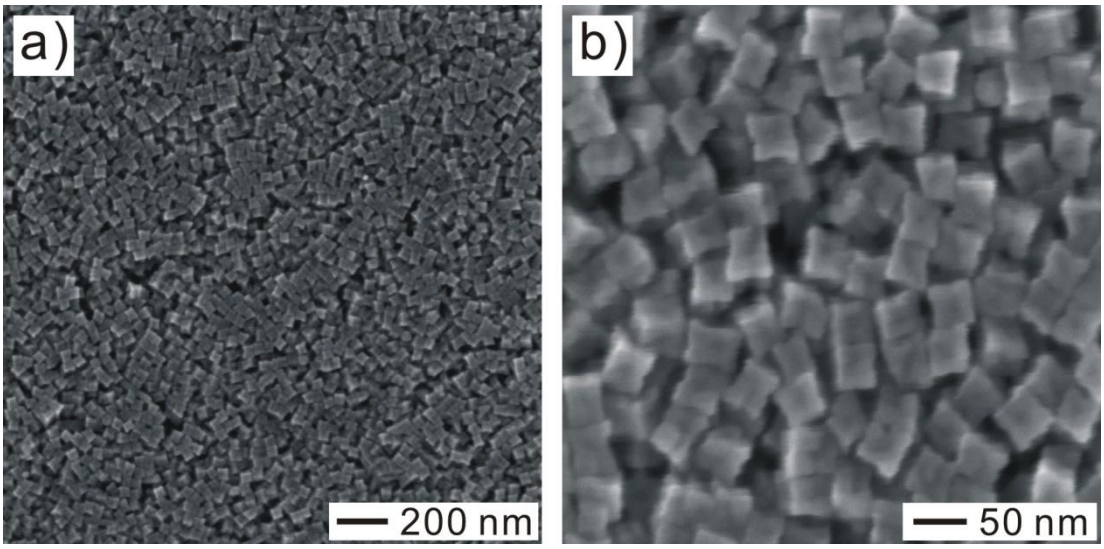
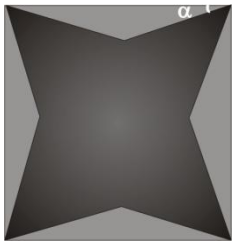


Figure S2. Additional SEM images of the Pd concave nanocubes at (a) lower and (b) higher magnifications, respectively, relative to the image shown in Figure 1a.

Table S1. Projection angles and geometrical parameters of concave nanocubes bounded by different types of high-index facets.

Projection direction	Geometrical model of the polyhedron	Equation for the projection angle	Calculated projection angle	
			(*hkl*)	α
[001]		α = arctan(*k*/*h*)	(410)	14.0 º
			(720)	15.9 º
			(310)	18.4 º
			(830)	20.6 º
			(520)	21.8 º
			(730)	23.2 º

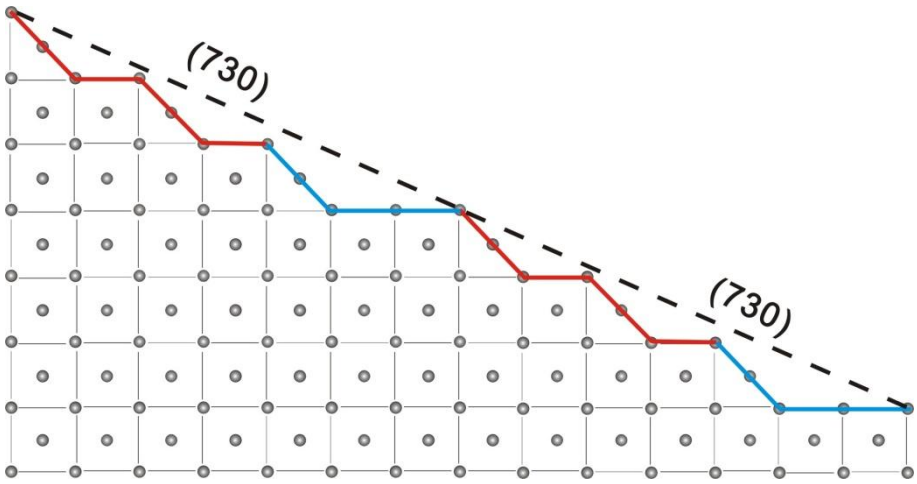


Figure S3. An atomic model of the {730} plane projected along the <001> axis. The red and blue colors represented {420} and {310} facets, respectively

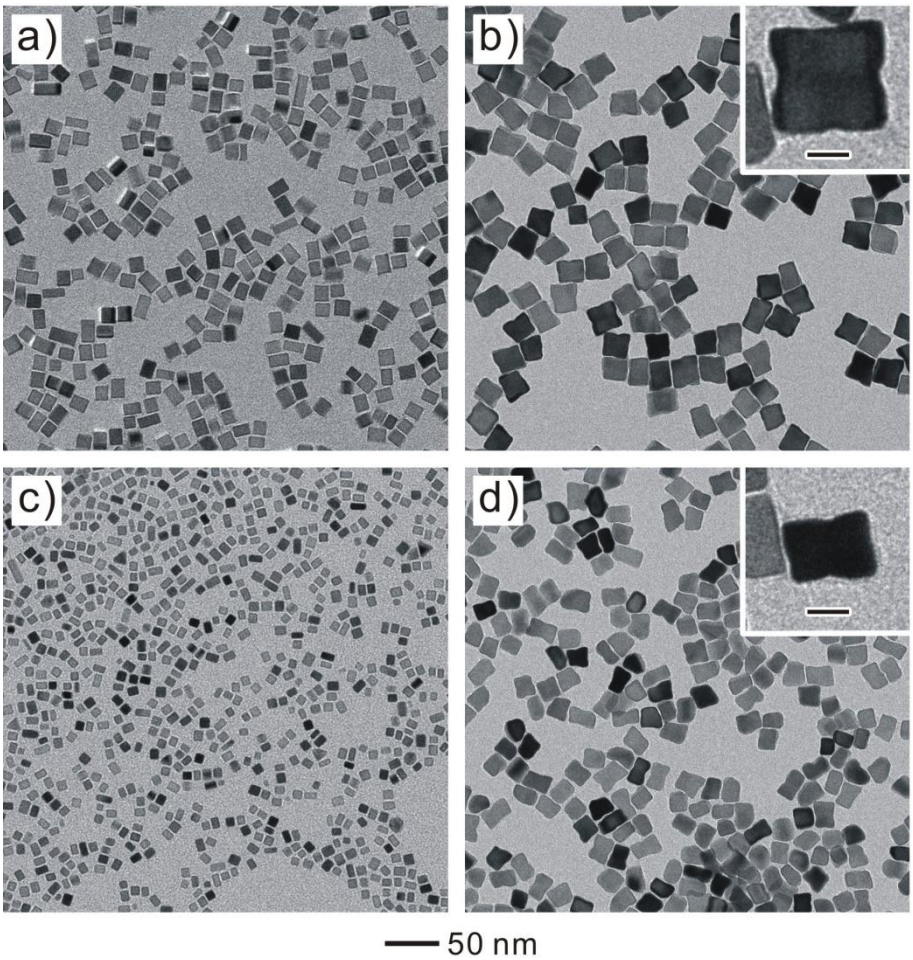


Figure S4. TEM images of (a, c) Pd nanocubes of 10 nm and 6 nm, respectively, in edge length and (b, d) their corresponding Pd concave nanocubes synthesized using the standard procedure. The scale bars in the insets are 10 nm.

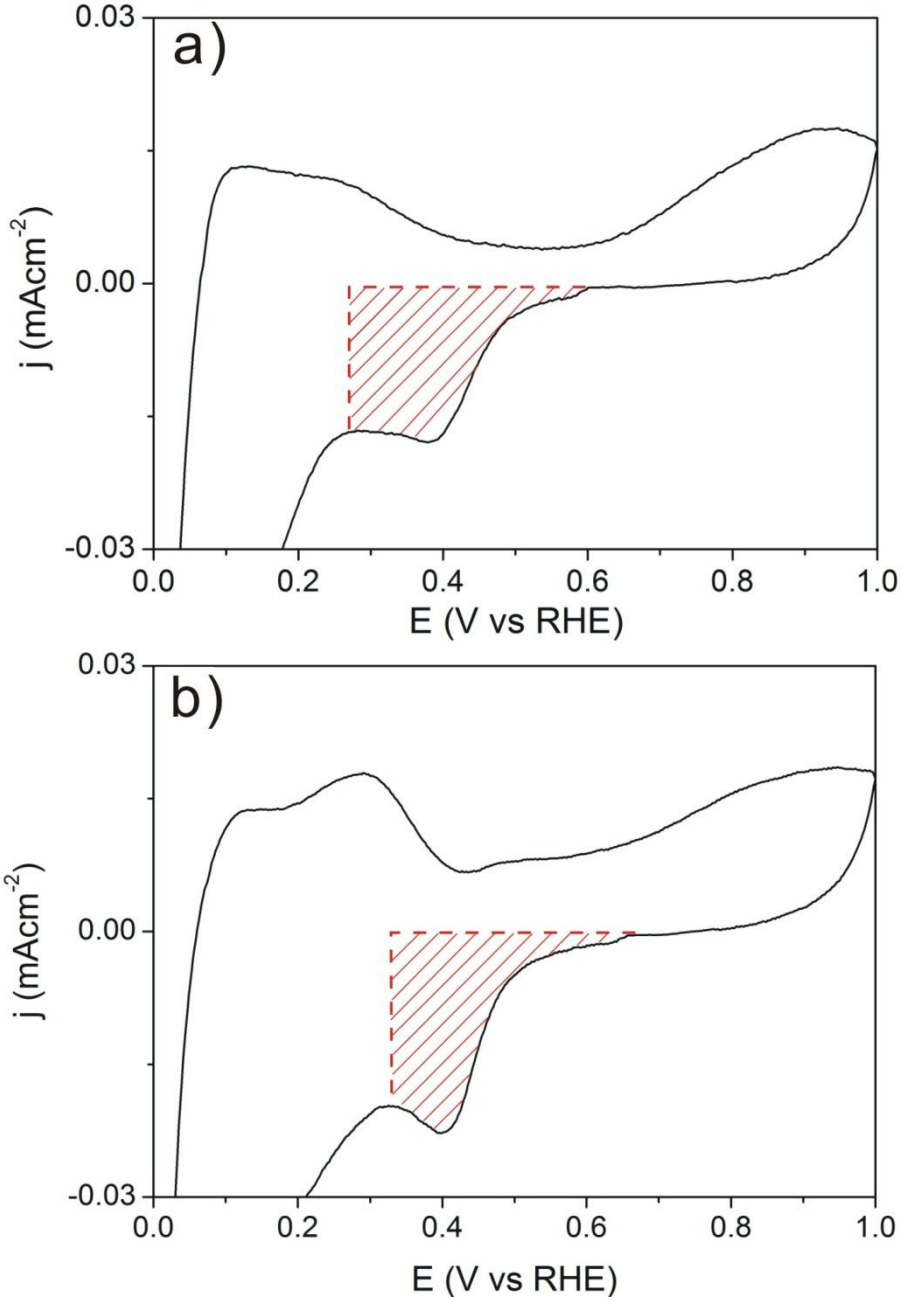


Figure S5. Cyclic voltammograms (CV) of Cu monolayer underpotentially deposited on (a) Pd nanocubes and (b) Pd concave nanocubes in a solution containing 0.05 M H_2SO_4 and 0.05 M $CuSO_4$ at a sweeping rate of 5 mV/s. The region hatched with red lines in each curve corresponds to the ECSA of that catalyst.

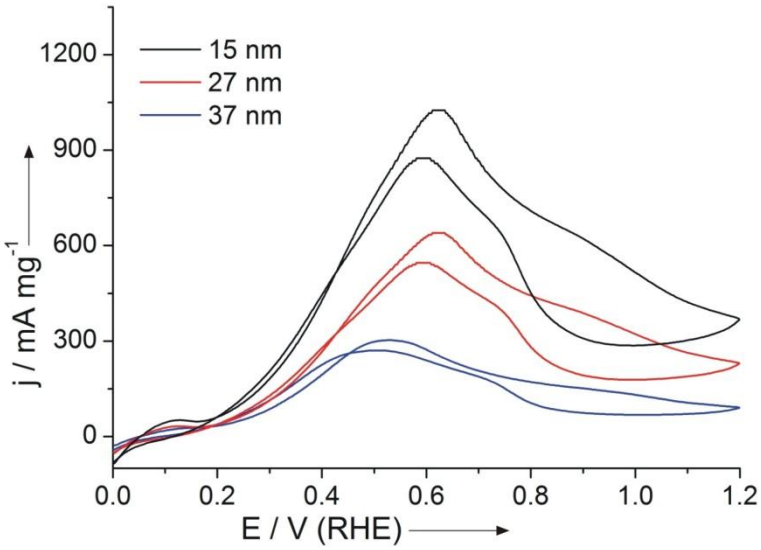


Figure S6. Cyclic voltammograms (CVs) of the Pd concave nanocubes with different sizes, which were recorded at room temperature in a solution containing 2 M HCOOH and 0.1 M $HClO_4$ at a sweep rate of 50 mV/s. The current density was normalized against the loading amount of Pd. For all the Pd catalysts, the loading on a RDE was 76.5 μg/cm^2.

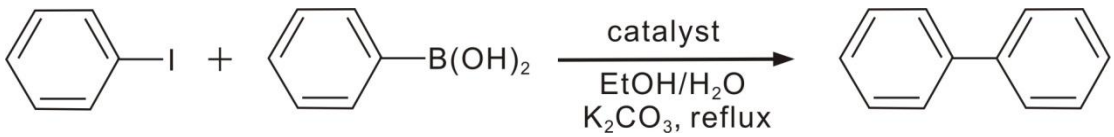


Figure S7. The Suzuki coupling reaction between iodobenzene and phenylboronic acid used in the present work to evaluate the catalytic activity of Pd nanocubes and concave nanocubes.

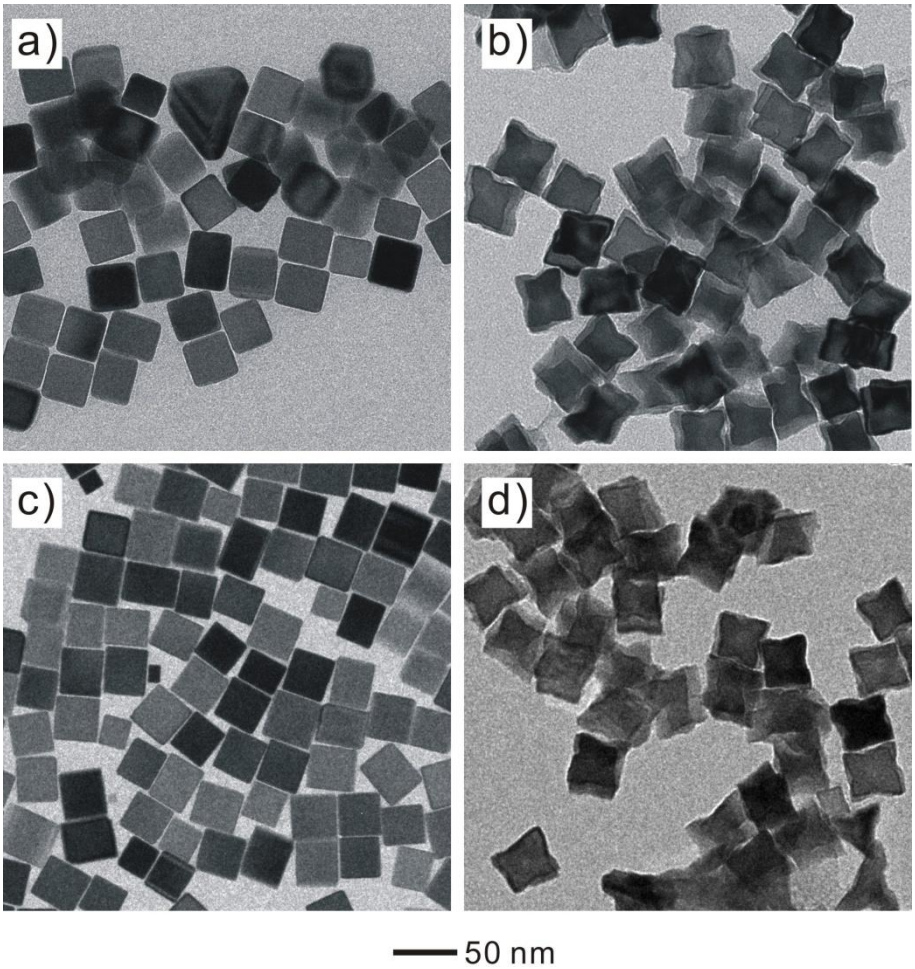


Figure S8. TEM images of (a, c) the cubes and (b, d) concave cubes of Pd after formic acid oxidation and Suzuki coupling reaction respectively. Their shapes were essentially kept during the reaction.