Electronic Supplementary Information for

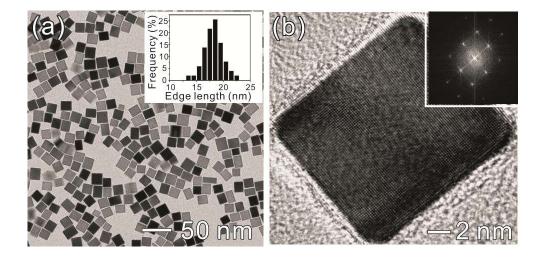
## Palladium nanocrystals enclosed by {100} and {111} facets in controlled proportions and their catalytic activities for formic acid oxidation

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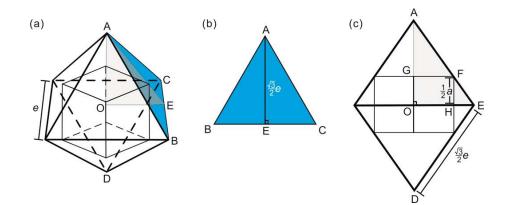
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**Fig. S1** (a) TEM and (b) the corresponding HRTEM images of the Pd cubic seeds 18 nm in edge length that served as seeds in the standard synthesis. The insets show the size distribution and FT pattern, respectively.

## Calculation of the smallest size of an octahedron grown from a cubic seed.

We proposed a simple model (Fig. S2) to calculate the smallest size of an octahedron grown from a cubic seed. In this model, *e* and *a* represent the edge length of the octahedron and the cubic seed, respectively. The blue triangle represents one of the octahedron's side faces. The apexes of the gray, right-angled triangle include one of the vertices of the octahedron (A), the center of the octahedron (O), and the middle point of one of the octahedron's edges (E). The distance between points A and O (AO) is  $(2^{1/2}/2)e$ . The distance (AG) between A and G is  $(2^{1/2}/2)e - (1/2)a$ . The distance between F and G (FG) is  $(2^{1/2}/2)a$ . The distance between E and O (EO) is (1/2)e. The relationship between *a* and *e* can be obtained using "homothetic triangle theory", (AG)/(AO) = (FG)/(EO), as e = 2.1a. Based on this model, the smallest octahedron grown from a cubic seed with an edge length of 18 nm was 38 nm in edge length.



**Fig. S2** (a) A model showing the smallest octahedron grown from a cubic seed, (b) a schematic showing one of the octahedron's side faces (the blue, equilateral triangle), and (c) the same mode projected along the <110> direction.

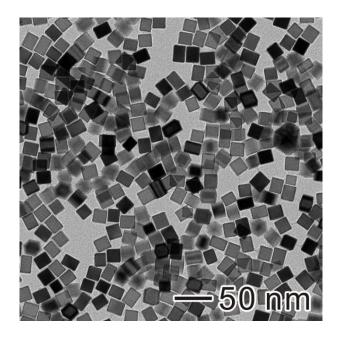


Fig. S3 TEM image of the Pd nanocrystals obtained from a standard synthesis except that no  $Na_2PdCl_4$  was added.

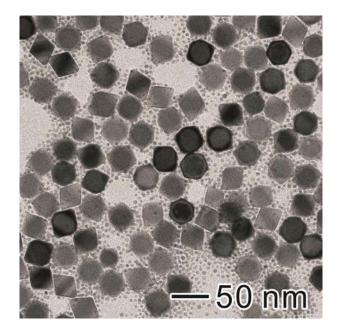
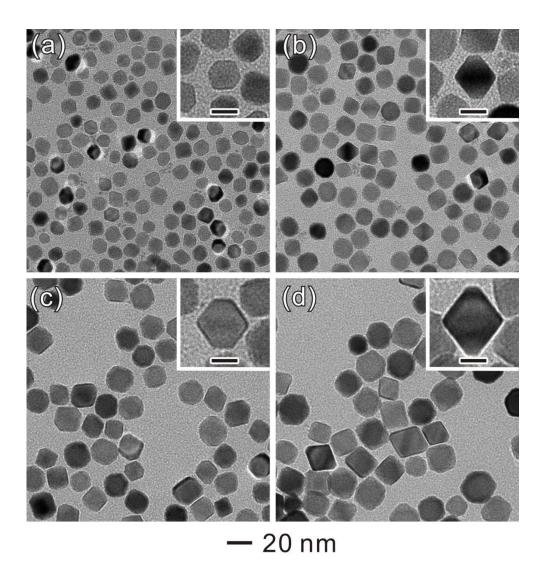
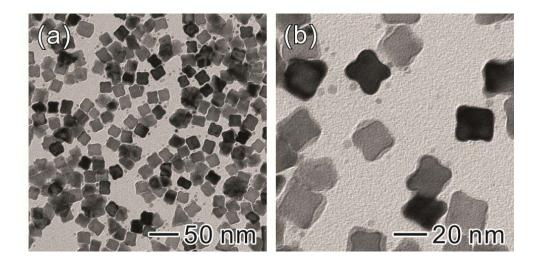


Fig. S4 TEM image of the Pd nanocrystals prepared using the standard procedure except that the amount of  $Na_2PdCl_4$  was increased to 57.0 mg. In addition to the formation of Pd octahedrons 37 nm in edge length, there were a lot of small Pd nanoparticles 3 nm in size that were formed through homogeneous nucleation.



**Fig. S5** TEM images of Pd cuboctahedrons and truncated octahedrons prepared using (a, b) 6-nm and (c, d) 10-nm Pd nanocubes as seeds. The scale bars in the insets are 10 nm.



**Fig. S6** TEM images of Pd nanocrystals prepared using the standard procedure except that formaldehyde was substituted with L-ascorbic acid as the reducing agent. In this case, growth preferentially occurred at corners and edges to generate Pd concave nanocubes.

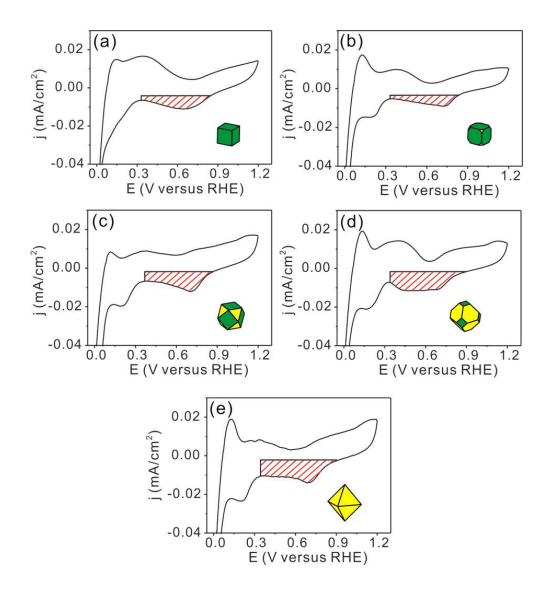


Fig. S7 Cyclic voltammograms (CV) of Cu monolayers underpotentially deposited on the different types of Pd polyhedrons in a solution contraining  $0.05 \text{ M H}_2\text{SO}_4$  and  $0.05 \text{ M CuSO}_4$  at a sweeping rate of 5 mV/s. The region hatched with red lines in each curve corresponds to the electrochemical surface area of that catalyst.

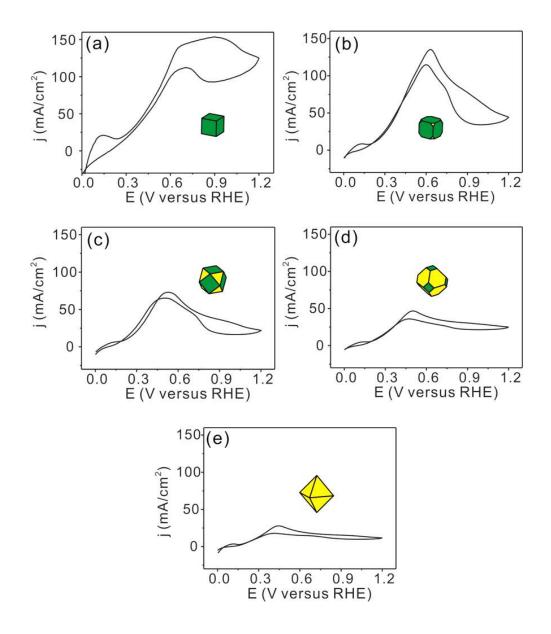
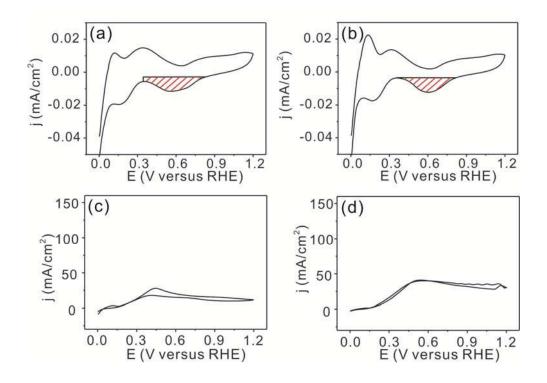


Fig. S8 Cyclic voltammograms (CV) of the different types of Pd polyhedrons recorded at room temperature in a soluition containing 2 M HCOOH and 0.1 M  $HCIO_4$  at a sweep rate of 10 mV/s. The current densities were normalized against the electrochemical surface area.



**Fig. S9** Cyclic voltammograms (CV) of Cu monolayers underpotentially deposited on Pd octahedrons with two different edge lengths: (a) 21 and (b) 14 nm, respectively. The solution contained 0.05 M H<sub>2</sub>SO<sub>4</sub> and 0.05 M CuSO<sub>4</sub> and the sweeping rate was 5 mV/s. The region hatched with red lines in each curve corresponds to the electrochemical surface area of that catalyst. (c, d) Cyclic voltammograms (CV) of the differently sized Pd polyhedrons recorded at room temperature in a solution containing 2 M HCOOH and 0.1 M HClO<sub>4</sub> at a sweep rate of 10 mV/s. The current densities were normalized against the electrochemical surface area.