

**Pd@Pt Core-shell Concave Decahedra: A Class of Catalysts for the Oxygen  
Reduction Reaction with Enhanced Activity and Durability**

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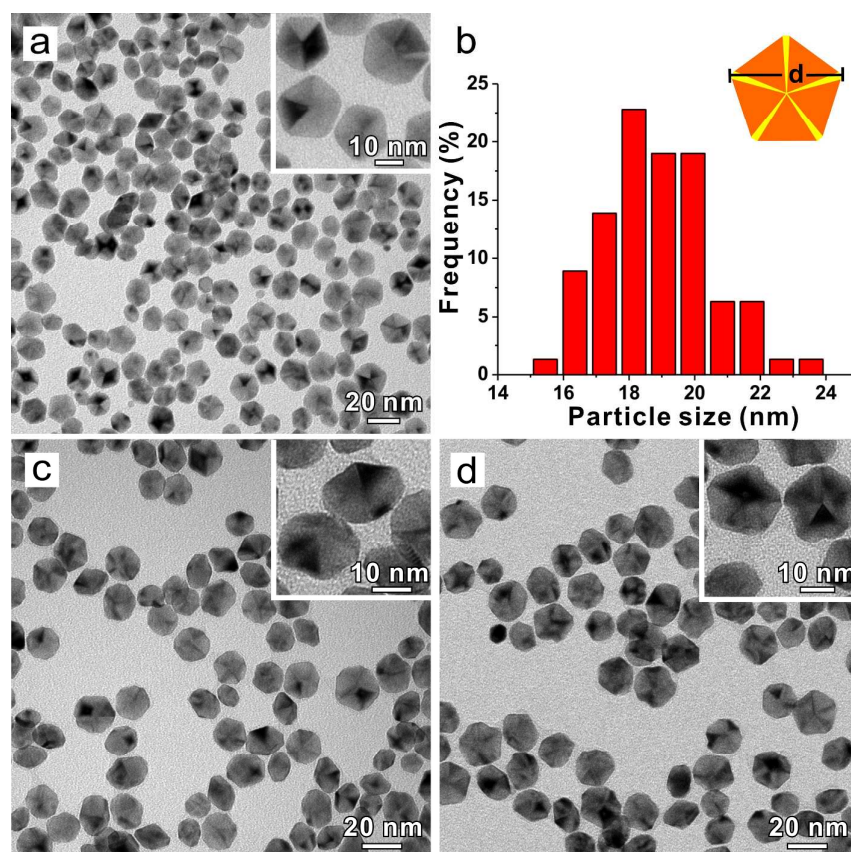
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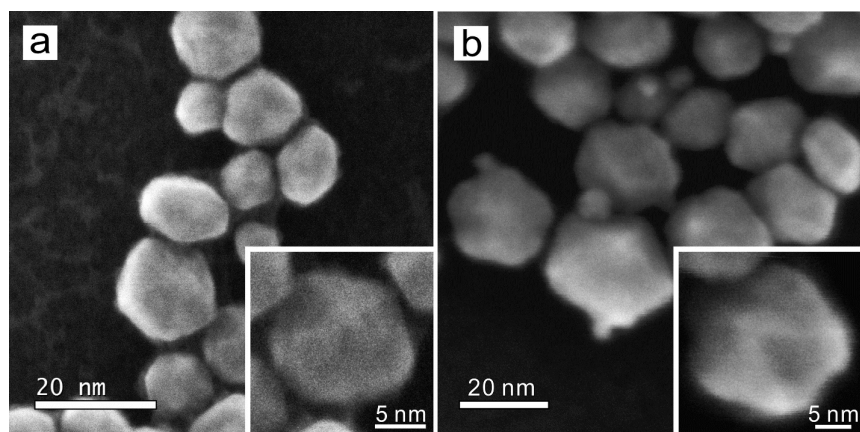
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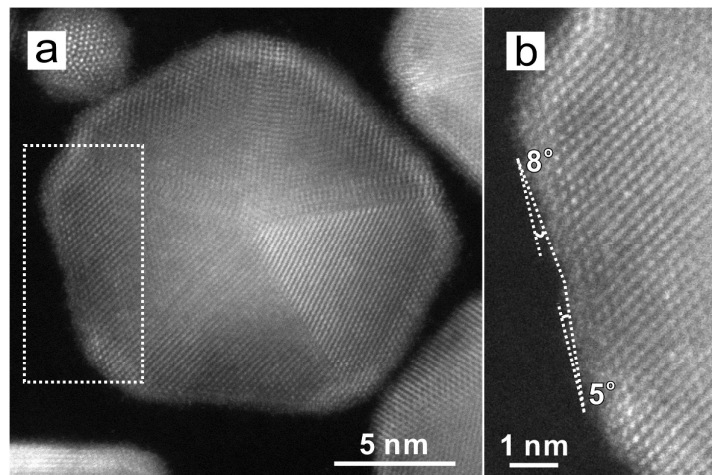
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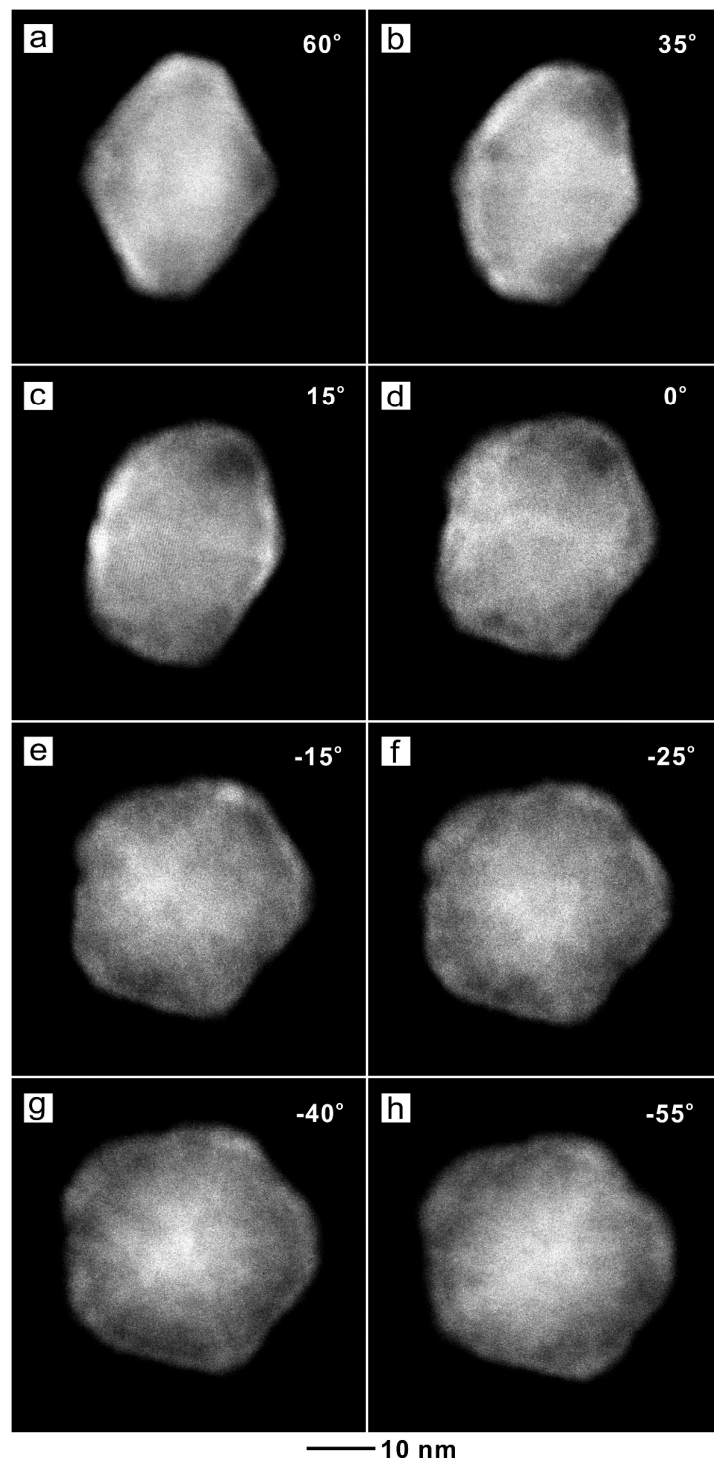
**Figure S1.** (a) TEM image and (b) size distribution of the Pd decahedral seeds. The size of a decahedron is defined in the inset of (b). (c, d) TEM images of the Pd@Pt concave decahedra with (c) 29.6 wt% Pt and (d) 47.5 wt% Pt, respectively.



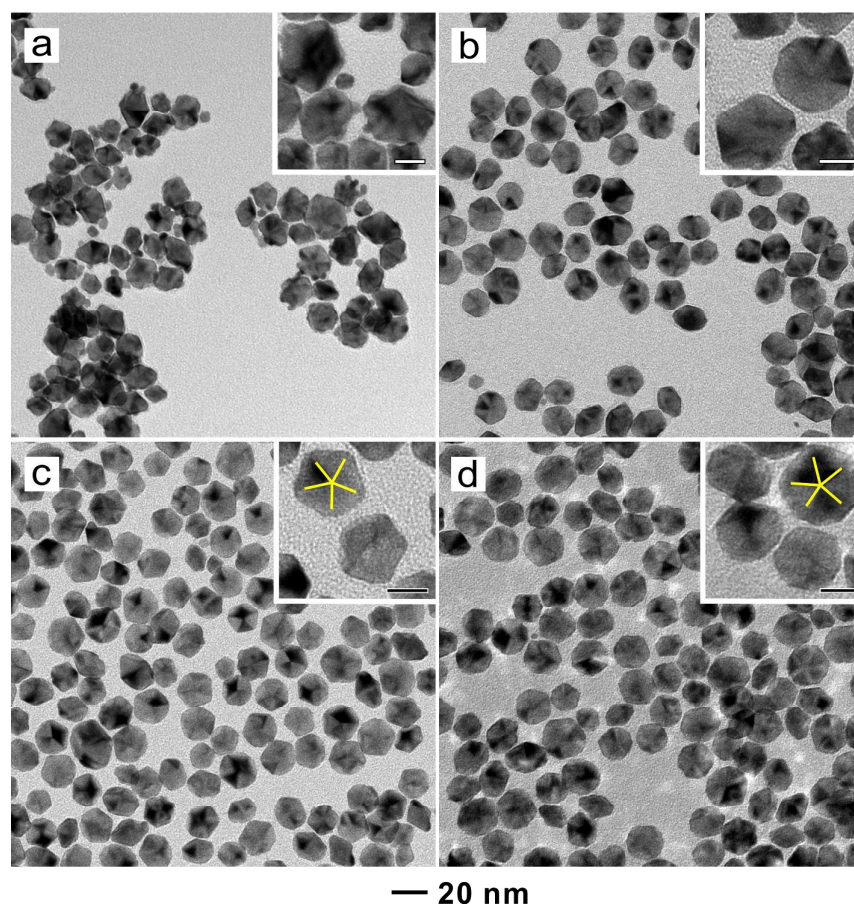
**Figure S2.** SEM images of the Pd@Pt concave decahedra with (a) 29.6 wt% Pt and (b) 47.5 wt% Pt, respectively. The higher-magnification SEM images in the insets highlight a concave structure on the surface of a particle from each sample.



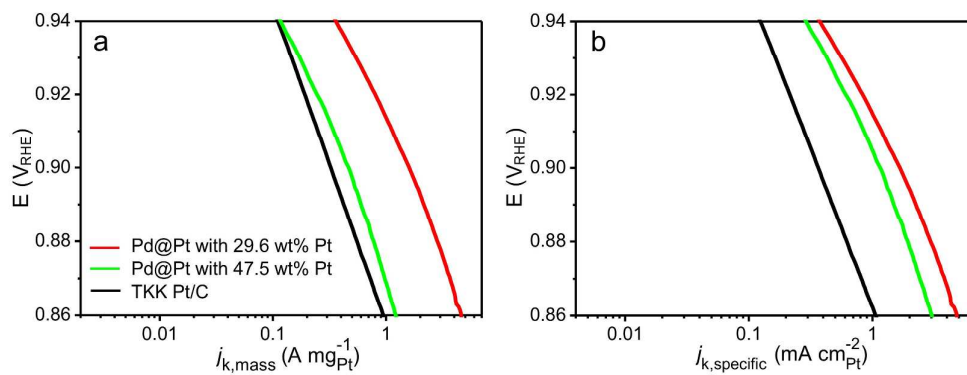
**Figure S3.** (a) Atomic-resolution HAADF-STEM image of a Pd@Pt core-shell concave decahedron with 29.6 wt% Pt viewed along its 5-fold axis (the same particle as imaged in Figure 1b). (b) Atomic-resolution HAADF-STEM image at a higher magnification, which was taken from the left side of the decahedron as marked by a box in (a). The angles between the facets on the edge and the {100} facet are  $8^\circ$  and  $5^\circ$ , which could be further used to identify the high-index facets on the edge, as summarized in Table S1. However, it is very difficult (or impossible) to identify the high-index facets on the faces as the geometry of the decahedron interferes with our ability to obtain a vertical projection of the high-index facet.



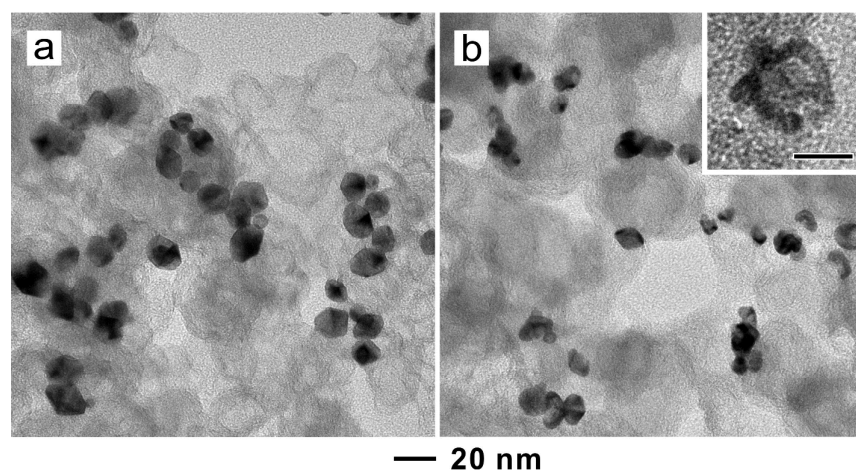
**Figure S4.** HAADF-STEM images of the Pd@Pt concave decahedra with 47.5 wt% Pt taken at different tilting angles: (a) 60, (b) 35, (c) 15, (d) 0, (e) -15, (f) -25, (g) -40, and (h) -55 degrees.



**Figure S5.** (a) TEM image of nanocrystals synthesized using the standard procedure for the concave decahedra with 47.5 wt% Pt, except for the use of a faster injection rate (4 mL/h vs. 1.5 mL/h) for the Pt precursor solution. The product contained both concave decahedra and multipods. (b) TEM image of the Pd@Pt concave decahedra with 47.5 wt% Pt, which was prepared using the standard protocol. (c, d) TEM images of nanocrystals prepared using the standard protocol for the concave decahedra with 47.5 wt% Pt, except that the reaction temperature was decreased from 200 °C to (c) 140 °C and (d) 110 °C, respectively. The scale bars in the insets are 10 nm.



**Figure S6.** (a) Mass and (b) specific activities of the catalysts presented as the kinetic current density ( $j_k$ ) normalized to the corresponding mass of Pt and ECSA, respectively.



**Figure S7.** TEM images of the carbon-supported Pd@Pt concave decahedra with 29.6 wt% Pt (a) before and (b) after 10,000 cycles of the accelerated durability test. The scale bar in the inset of (b) is 10 nm.



**Table S1.** Calculated angles between high-index  $\{hkk\}$  facets and  $\{100\}$  edge facets.

$h$	$k$	Angle with $\{100\}$
9	1	$8.93^\circ$
10	1	$8.05^\circ$
15	1	$5.39^\circ$
16	1	$5.05^\circ$
20	1	$4.04^\circ$

**Table S2.** Specific ECSAs of the Pt/C catalyst from TKK and two other catalysts based on the Pd@Pt concave decahedra.

	TKK Pt/C	Pd@Pt with 29.6 wt% Pt	Pd@Pt with 47.5 wt% Pt
Specific ECSA (m <sup>2</sup> g <sup>-1</sup> )	88.9	95.9	59.4

### Supporting Movie Legend

**Movie S1.** Video of HAADF-STEM images taken at different tilt angles for the Pd@Pt concave decahedra with 47.5 wt% Pt.