

# Supporting Information

## Synthesis of Pd-Pt Bimetallic Nanocrystals with a Concave Structure through a Bromide-Induced Galvanic Replacement Reaction

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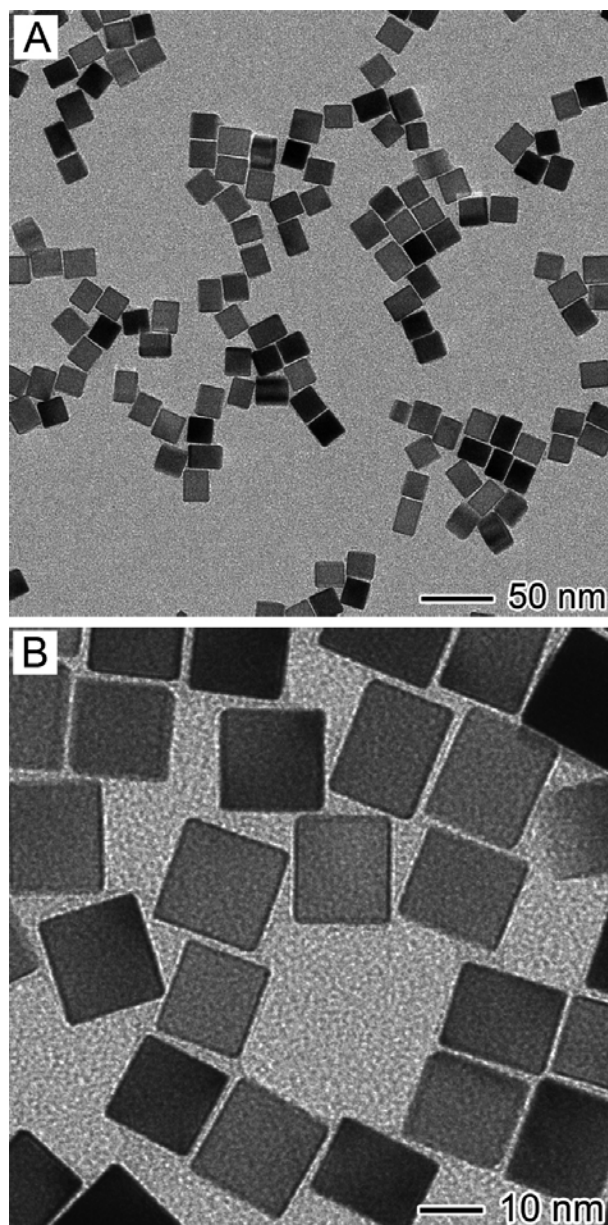
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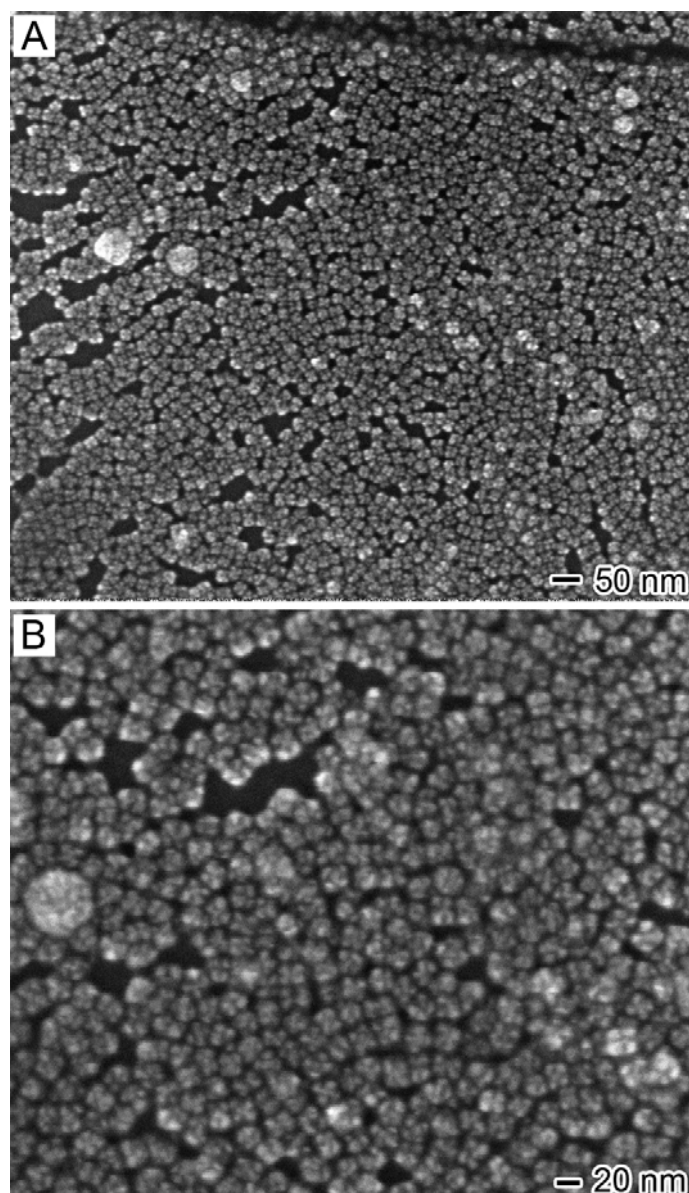
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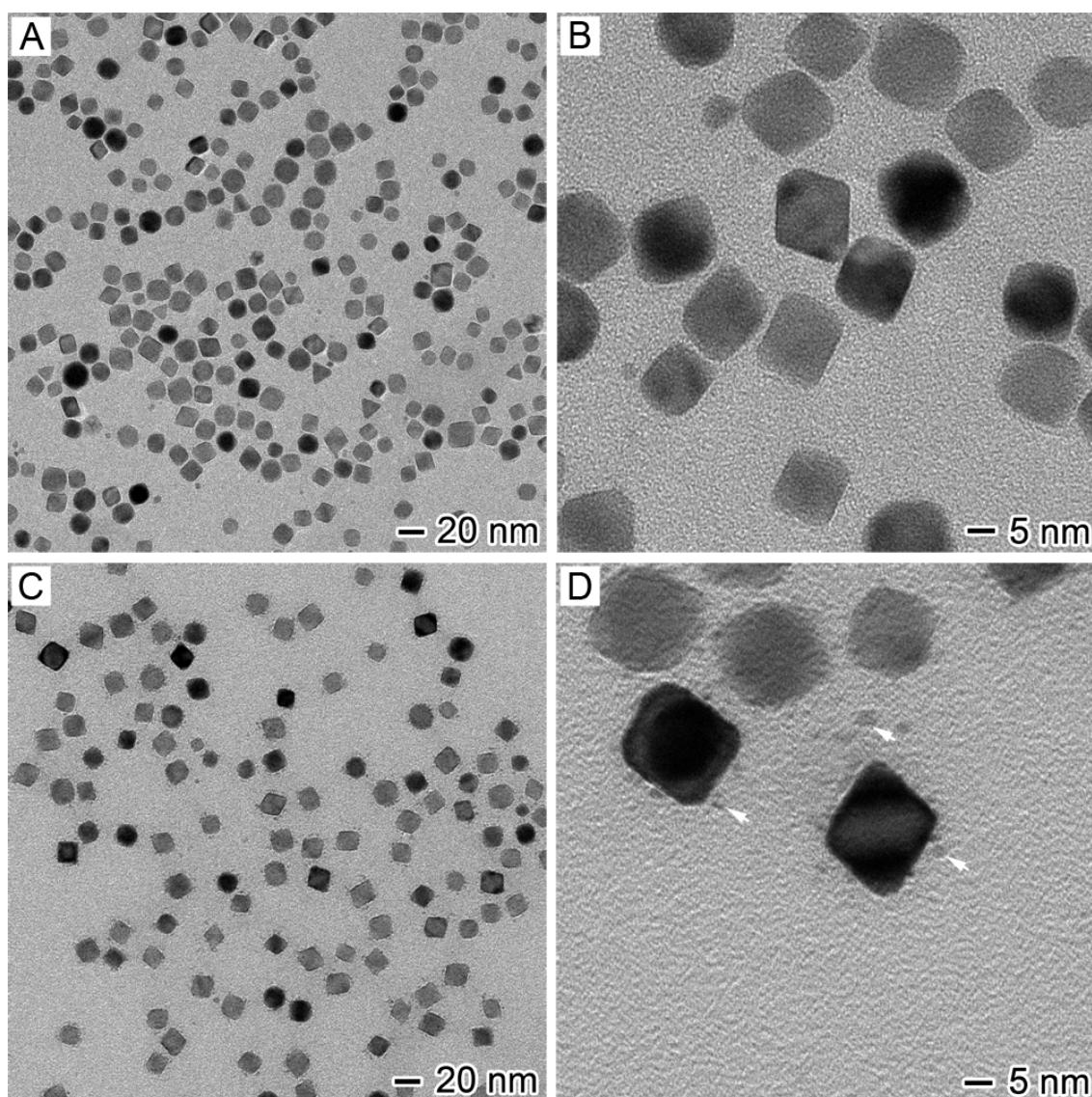
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**Figure S1.** TEM images of Pd nanocubes with an average edge length of 18 nm. Some of them may show a slightly elongated morphology, but their surfaces should still be enclosed by {100} facets, similar to those of nanocubes.

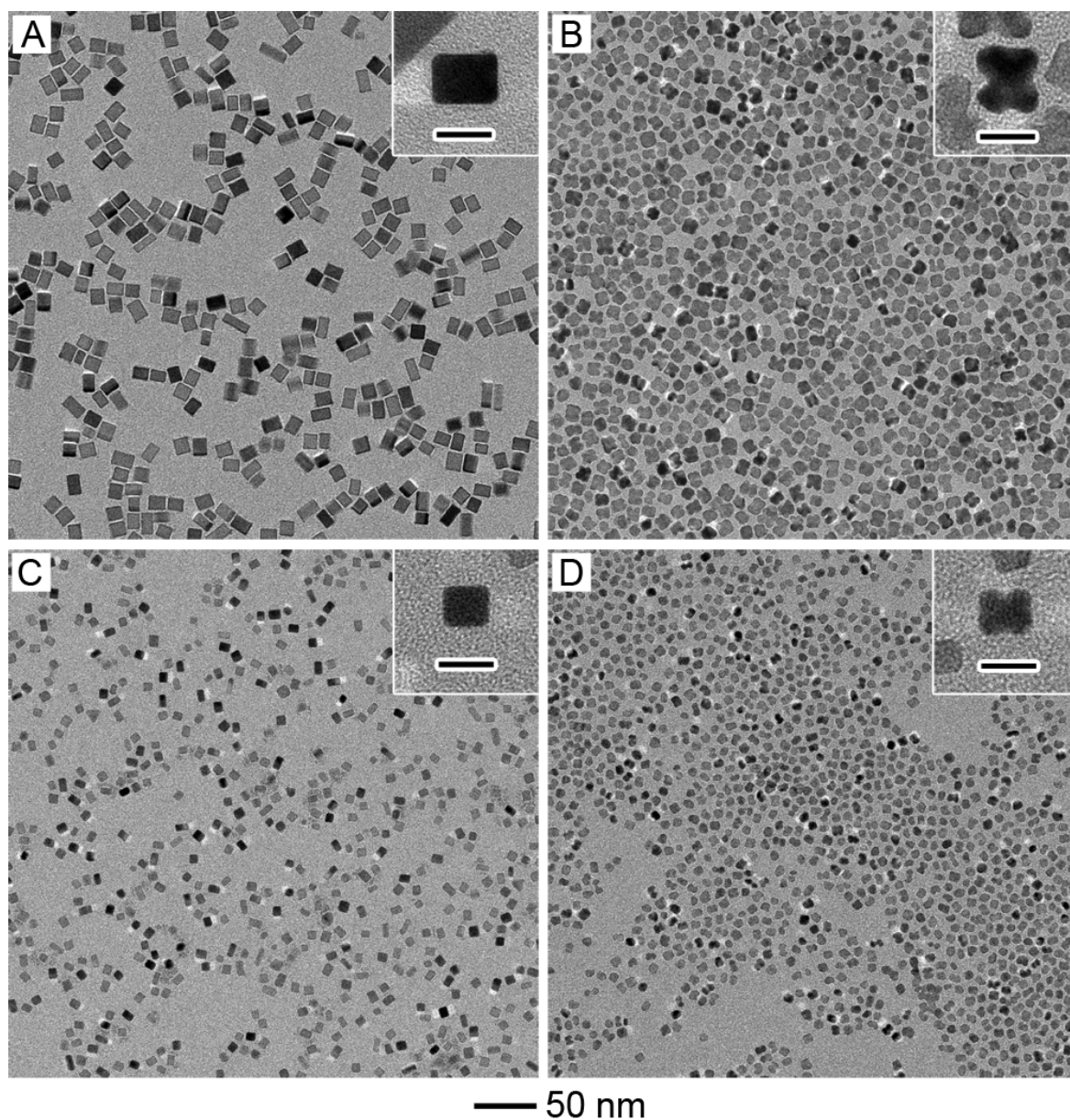


**Figure S2.** SEM images of Pd-Pt concave nanocubes prepared via galvanic replacement by reacting the 18-nm Pd nanocubes with 7.0 mg of  $\text{H}_2\text{PtCl}_6$  in an aqueous solution at 90 °C for 12 h.

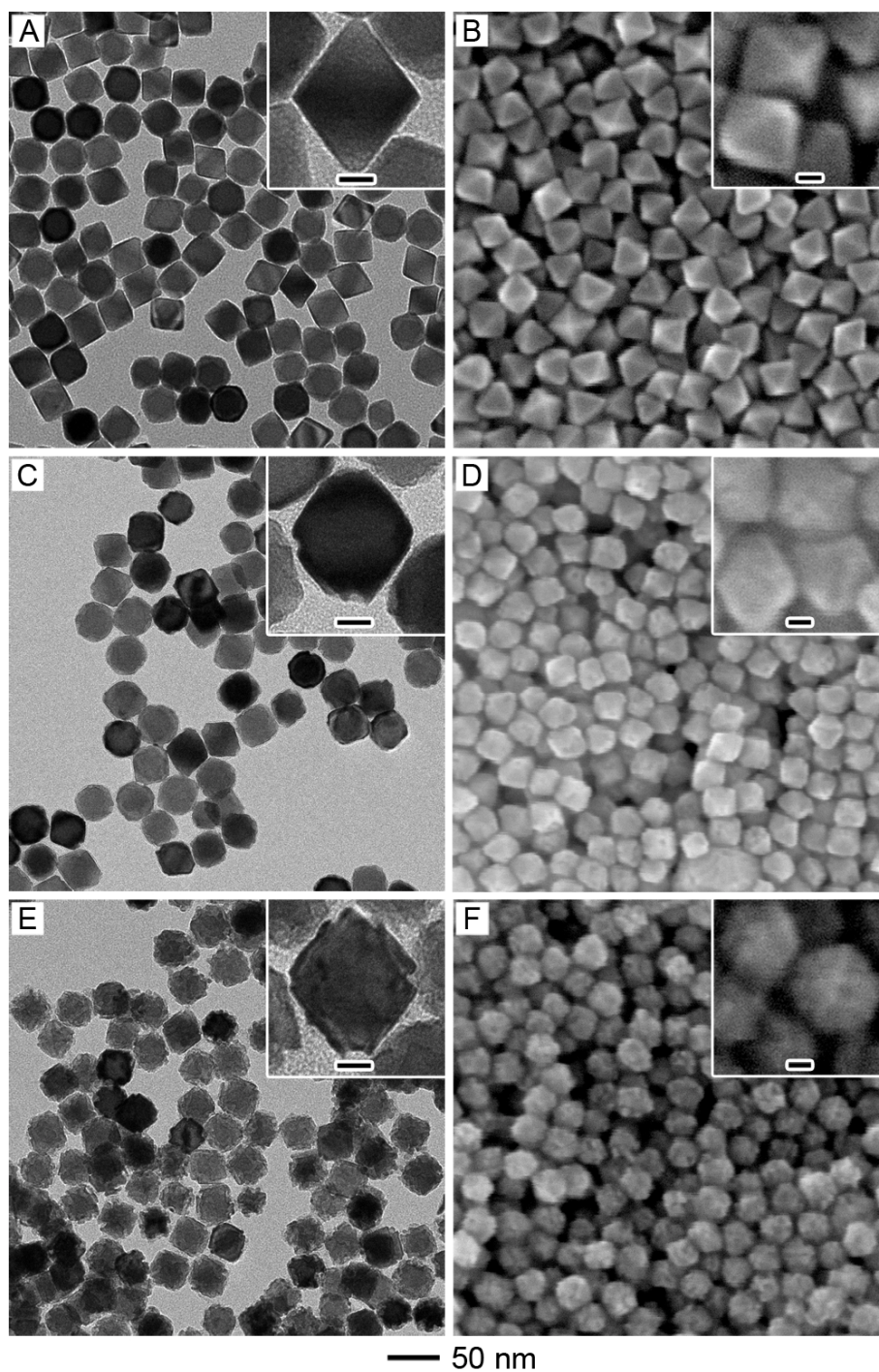


**Figure S3.** (A, B) TEM images of Pd octahedrons with an edge length of 16 nm. (C, D) TEM images of Pd-Pt nanocrystals obtained by reacting the Pd octahedrons with 7.0 mg of  $\text{H}_2\text{PtCl}_6$  at 90 °C for 12 h in the absence of KBr.



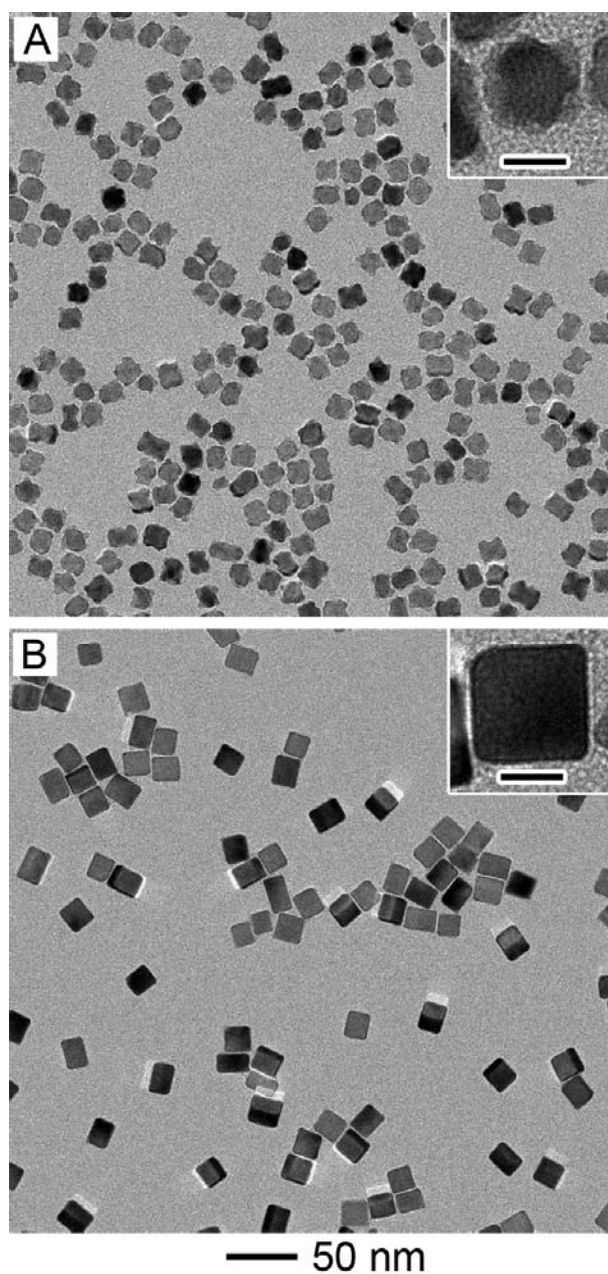


**Figure S4.** TEM images of (A, C) Pd nanocubes of 10 and 6 nm, respectively, in size and (B, D) their corresponding Pd-Pt concave nanocubes synthesized using the standard procedure. The insets show TEM image of individual nanocrystals at a higher magnification. The scale bars in the insets are 10 nm.

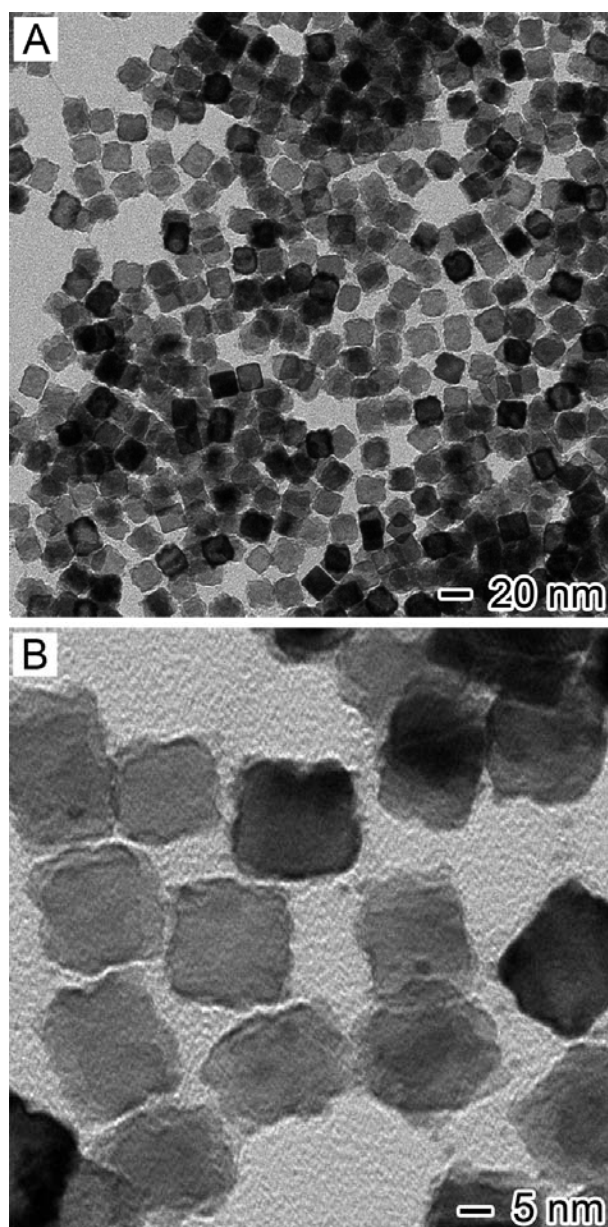


**Figure S5.** (A) TEM and (B) SEM images of Pd octahedrons with an average edge length of 33 nm. (C, E) TEM and (D, F) SEM images of Pd-Pt concave octahedrons prepared via galvanic replacement at 90 °C for 12 h, with 1.4 and 3.5 mg H<sub>2</sub>PtCl<sub>6</sub> added, respectively. The insets show TEM and SEM images of individual nanocrystals at a higher magnification, respectively. The scale bars in the insets are 10 nm.





**Figure S6.** (A) TEM image of Pd-Pt nanocrystals synthesized using the standard procedure, except the replacement of 300 mg KBr with 188 mg KCl. (B) TEM image of Pd nanocrystals obtained using the standard procedure, except the replacement of 3.5 mg  $\text{H}_2\text{PtCl}_6$  with 3.8 mg KCl. The insets show TEM image of individual nanocrystals at a higher magnification. The scale bars in the insets are 10 nm.



**Figure S7.** TEM image of Pd-Pt nanocrystals obtained using the standard procedure, except the replacement of  $\text{H}_2\text{PtCl}_6$  with 7.0 mg  $\text{K}_2\text{PtCl}_4$ .

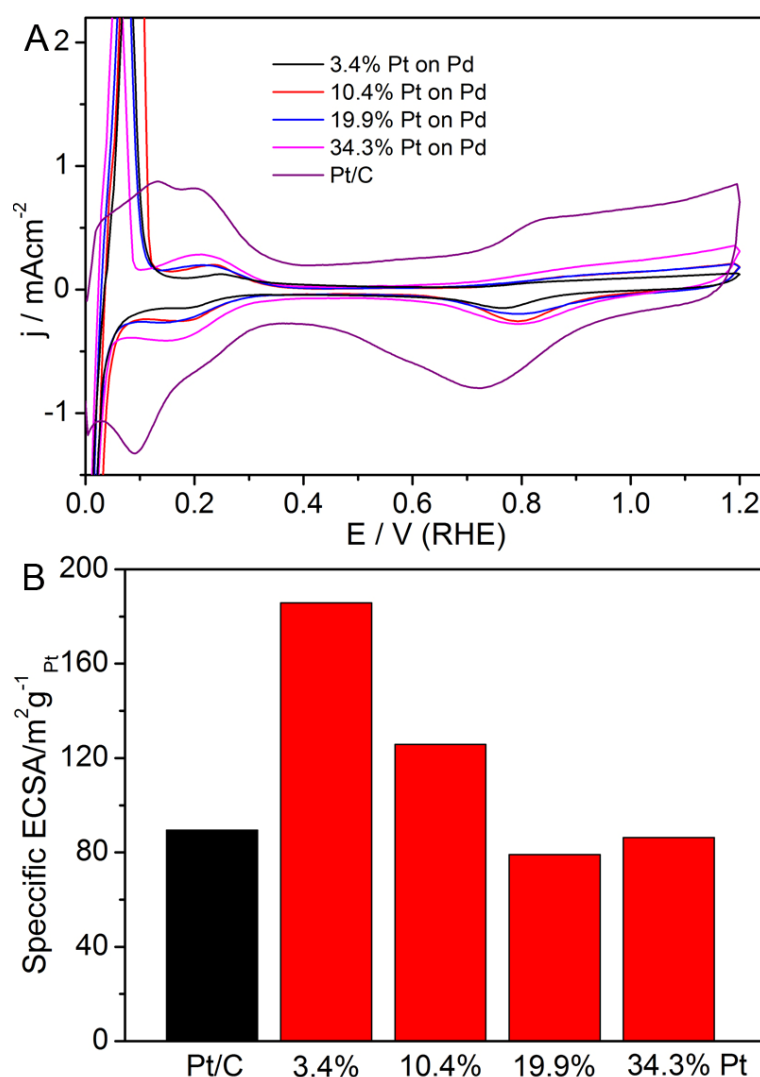


**Table S1.** ICP-MS data of the samples obtained using the standard procedure, except the replacement of  $\text{H}_2\text{PtCl}_6$  by KCl to maintain the same molar concentration of  $\text{Cl}^-$ .

Etching sample	$\text{Pd}^{2+}$ (in solution, $\mu\text{g/mL}$ )
Sample 1 (1.5 mg)	9.6
Sample 2 (3.1 mg)	8.6
Sample 3 (3.8 mg)	9.4
Sample 4 (7.6 mg)	8.5

**Table S2.** ICP-MS data of Pd-Pt concave nanocubes obtained using the standard procedure except different amounts of  $\text{H}_2\text{PtCl}_6$ , and their corresponding supernatants after centrifugation once.

Galvanic sample	$\text{Pd}^{2+}$ (in the supernatant solution, $\mu\text{g/mL}$ )	Pt (in the concave nanocubes, $\mu\text{g/mL}$ )	$\text{Pd}^{2+}/\text{Pt}$ molar ratio
Sample 5 (1.4 mg )	15.4	14.9	1.9
Sample 6 (2.8 mg)	33.7	26.1	2.4
Sample 7 (3.5 mg)	40.5	31.4	2.4
Sample 8 (7.0 mg)	93.7	53.5	3.2



**Figure S8.** (A) CV curves of the Pd-Pt concave nanocubes with Pt weight percentage of 3.4, 10.4, 19.9, and 34.4, and the commercial Pt/C recorded at room temperature in N<sub>2</sub>-purged 0.1 M aqueous HClO<sub>4</sub> solutions with a sweep rate of 50 mV/s. For the Pd-Pt concave nanocubes and Pt/C catalysts, the total loading of metals on the RDE was 15.3  $\mu\text{g}/\text{cm}^2$ . The current densities were normalized relative to the geometric area of RDE (0.196 cm<sup>2</sup>). (B) Specific ECSA based on the mass of Pt for these five catalysts. For the four Pd-Pt concave nanocubes with different percentages of Pt, the ECSA was calculated in the H<sub>upd</sub> adsorption region from 0.1 to 0.4 V. While, the ECSA of the Pt/C catalyst was calculated in the standard region from 0.02 to 0.4 V.