## **Supporting Information**

## Strain-induced Stranski-Krastanov growth of Pd@Pt core-shell hexapods and octapods as electrocatalysts for methanol oxidation

Yaling Xiong,<sup>a,c</sup> Yanling Ma,<sup>b</sup> Junjie Li,<sup>a</sup> Jingbo Huang,<sup>a</sup> Yucong Yan,<sup>a</sup> Hui Zhang,<sup>a,\*</sup> Jianbo Wu,<sup>b,\*</sup> and Deren Yang<sup>a,\*</sup>

<sup>a</sup>State Key Laboratory of Silicon Materials, School of Materials Science & Engineering, and Cyrus Tang Center for Sensor Materials and Applications, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China <sup>b</sup>State Key Laboratory of Metal Matrix Composites, School of Materials Science & Engineering, Shanghai Jiao Tong University, Shanghai, 200240, People's Republic of China <sup>c</sup>Hydrogen Energy R&D Department, Chemistry & Physics Center, National Institute of Clean-and-Low-Carbon Energy, Beijing, 102211, People's Republic of China

\*Correspondence to: msezhanghui@zju.edu.cn, jianbowu@sjtu.edu.cn, and mseyang@zju.edu.cn.



**Figure S1.** (a) TEM image and (b) size distribution of the Pd octahedra serving as the seeds for the synthesis of Pd@Pt hexapods.



Figure S2. (a) TEM image of the Pd@Pt hexapods at lower magnification and (b) the corresponding size distrubution.



**Figure S3.** (a, c) Fast Fourier transform (FFT) patterns of the Pd@Pt hexapods and (b, d) their corresponding HRTEM images.



**Figure S4.** Schematic illustration showing six equivalent <100> directions from six corners for an octahedral seed.



**Figure S5.** TEM images and the corresponding size distributions of the Pd@Pt hexapods obtained by varying the amount of  $H_2PtCl_6$  with Pd octahedra of 24.2 nm in size as the seeds: (a, b) 1.8, (c, d) 3.6, and (e, f) 9 mg.



**Figure S6.** (a) TEM image and (b) size distribution of the Pd octahedral seeds with average size of 18.3 nm. (c) TEM image and (d) size distribution of the Pd@Pt hexapods prepared using above-mentioned Pd octahedra as the seeds in the presence of 14 mg H<sub>2</sub>PtCl<sub>6</sub>.



**Figure S7.** (a) TEM image and (b) size distribution of the Pd octahedral seeds with average size of 33.4 nm. (c) TEM image and (d) size distribution of the Pd@Pt hexapods prepared using the above-mentioned Pd octahedra as the seeds in the presence of  $14 \text{ mg H}_2\text{PtCl}_6$ .



**Figure S8.** Change in mol % of Pt ( $\Delta$ Pt) during the reaction for the synthesis of (a) Pd@Pt hexapods and (b) Pd@Pt octapods.

**Table S1.** Average number (n) of Pt atomic layers and weight percentage (wt%) of Pt derived from the geometry analysis and ICP-AES data, and the atomic ratio of Pd/Pt determined from ICP-AES data for the samples including Pd@Pt hexapods and octapods.

samples	Reaction	atomic ratio of	wt% of Pt	wt% of Pt	n of Pt atomic
	time	Pd:Pt calculated	calculated	calculated	layers before it
	(min)	from ICP data	from ICP	from the value	switches to
			data	of n	island growth
Pd@Pt hexapods	10	1:0.09	14.2	11.4 (n=1)	
	20	1:0.15	21.6	20.8 (n=2)	
	30	1:0.29	34.7	28.7 (n=3)	4
	45	1:0.34	38.4	35.4 (n=4)	
	60	1:0.59	51.2	41.2 (n=5)	
Pd@Pt octapods	/	/	/	13.1 (n=1)	
	/	/	/	23.6 (n=2)	
	15	1:0.18	24.8	32.3 (n=3)	5
	30	1:0.46	45.7	39.5 (n=4)	
	40	1:0.51	48.3	45.6 (n=5)	
	60	1:1.75	76.2	50.7 (n=6)	



**Figure S9.** TEM images of the Pd-Pt nanocrystals that prepared using the standard producure with Pd octadra as the seeds, expect for the difference in the amount of solvent. (a) 8 mL of tetrahydronaphthalene and 2 mL of OAm, (b) 5 mL of tetrahydronaphthalene and 5 mL of OAm, (c) 2 mL of tetrahydronaphthalene and 8 mL of OAm.



**Figure S10.** (a) TEM image and (b) size distribution of the Pd cubes serving as the seeds for the synthesis of Pd@Pt octapods.



**Figure S11.** (a) TEM image at low magnification and (b) size distribution of the Pd@Pt octapods prepared by using Pd cubes of 14.6 nm in size as the seeds.



**Figure S12.** (a, c) Fast Fourier transform (FFT) patterns of the Pd@Pt octapods and (b, d) their corresponding HRTEM images.



**Figure S13.** Schematic illustration showing eight equivalent <111> directions from eight corners for an cubic seed.



50 nm

**Figure S14.** TEM images of the Pd@Pt octapods obtained by varying the amounts of  $H_2PtCl_6$  with Pd cubes of 14.6 nm in szie as the seeds: (a) 4.8, (b) 7.3, (c) 9.7, and (d) 23.2 mg. The inset in (d) shows the size distribution of the Pd@Pt octapods obtained in the presence of 23.2 mg  $H_2PtCl_6$ .



Figure S15. CV curves of the Pd@Pt hexapods (red), Pd@Pt octapods (blue), and Pt/C (black) in 0.1 M HClO<sub>4</sub> solution at a scan rate of 50 mV/s

Samples	Pd/Pt atomic ratio	ECSA $(m^2/g_{Pt})$	I <sub>f</sub> /I <sub>b</sub>
Pd@Pt hexapods	1:2.8	26.3	1.60
Pd@Pt octapods	1:4	25.8	1.28
Pt/C	/	57.8	1.26

**Table S2.** ICP-AES, ECSA, and  $I_{f}/I_{b}$  data of these three catalysts including the Pd@Pt hexapods, Pd@Pt octapods, and Pt/C.