

**Electronic Supplementary Information**

**Large Au@Pd/PdO<sub>x</sub> core-porous shell nanoparticles as efficient  
ethanol oxidation electrocatalysts**

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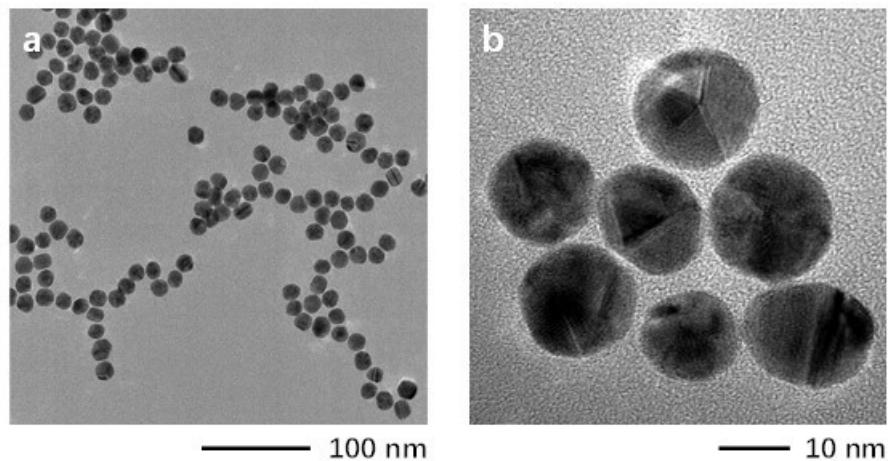
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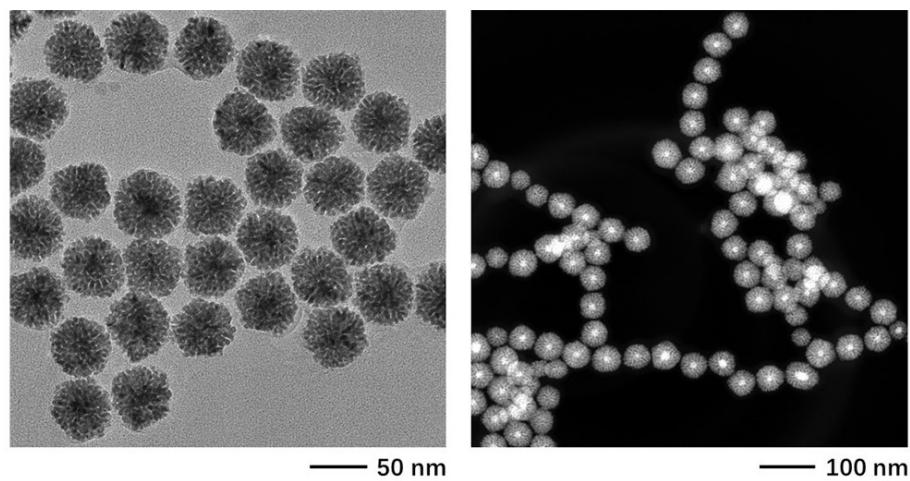
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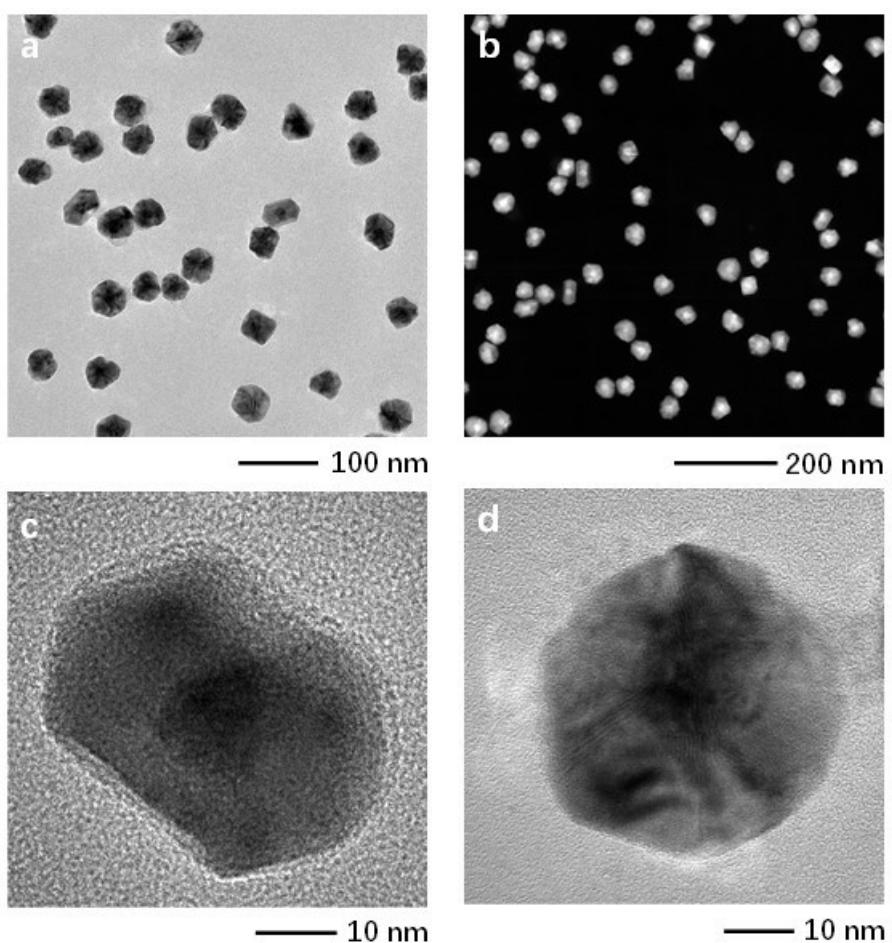
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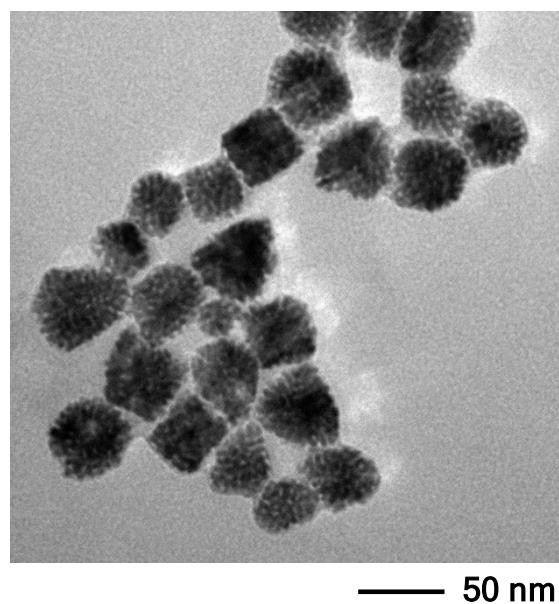
**Fig. S1.** (a) TEM and (b) HR-TEM images of Au seeds synthesized by the citrate-reduction method.



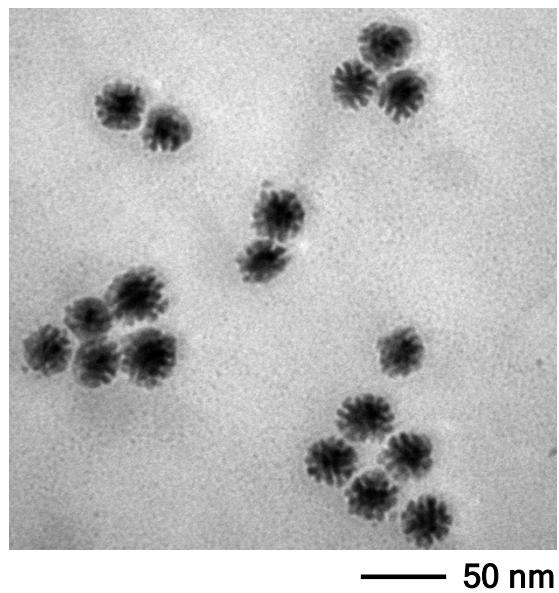
**Fig. S2.** The representative bright-field and dark-field TEM images of Au@Pd core-porous shell NPs.



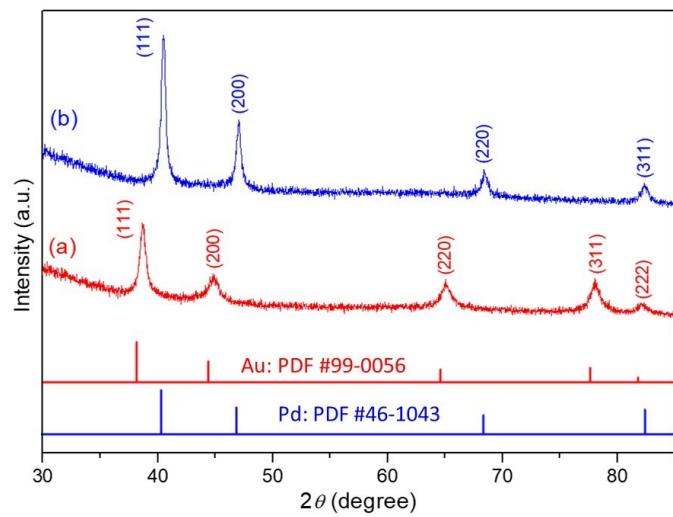
**Fig. S3.** (a) Bright-field, (b) dark-field, and (c, d) high-resolution TEM images of Au@Pd core-shell NPs synthesized in the presence of CTAB.



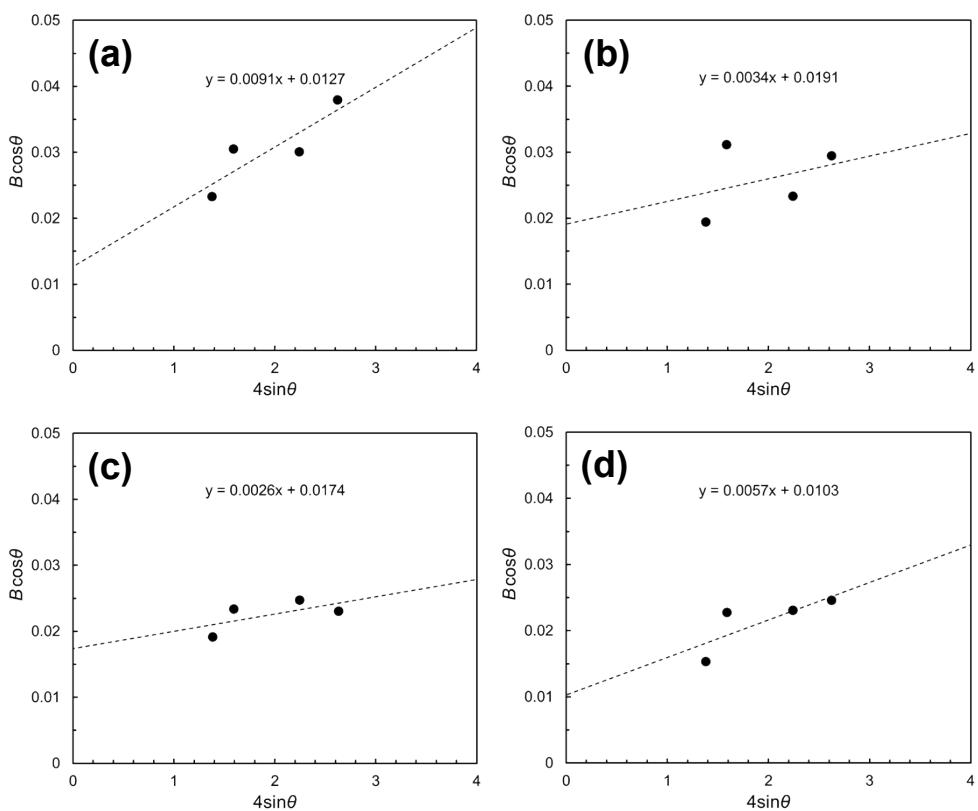
**Fig. S4.** TEM image of porous Pd NPs synthesized in the absence of Au seeds.



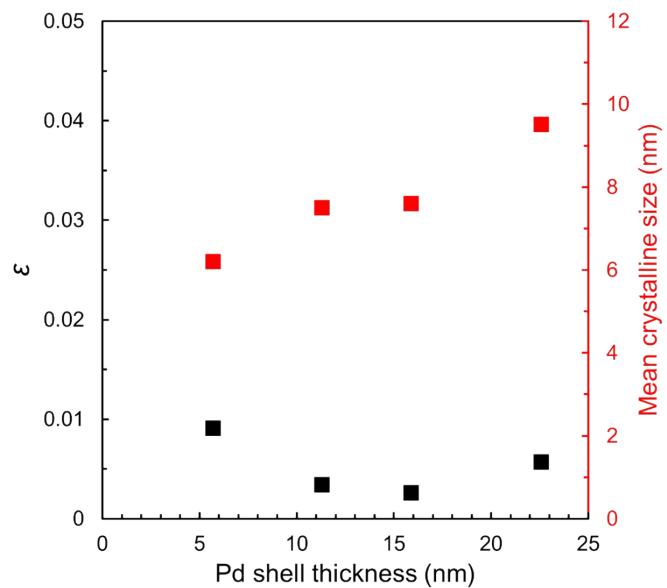
**Fig. S5.** TEM image of Au@Pd core-shell NPs synthesized using HDPC instead of using CTAC.



**Fig. S6.** XRD patterns of (a) Au seeds and (b) Pd NPs.



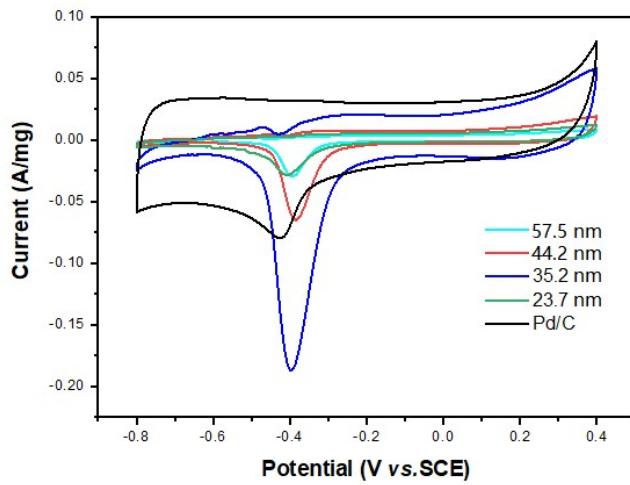
**Fig. S7.** Williamson-Hall analysis of the strain of Pd shell in Au@Pd core-porous shell NPs with different sizes: (a) 23.7 nm, (b) 35.2 nm, (c) 44.2 nm, and (d) 57.5 nm.



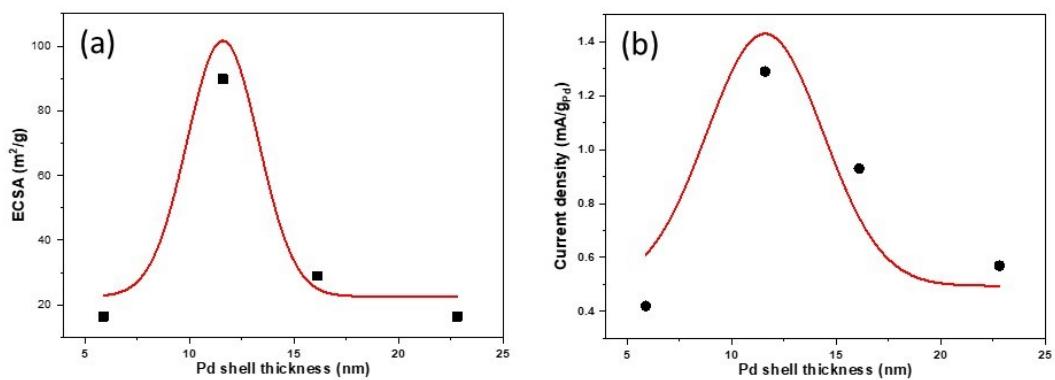
**Fig. S8.** The relation of Pd shell thickness in Au@Pd core-porous shell NPs with strain ( $\epsilon$ ) and mean crystalline size of Pd calculated by the Scherrer formula using the (111) peak of Pd.

**Table S1.** Peak parameters obtained by deconvolution of Pd 3d peaks.

		23.7 nm	35.2 nm	44.2 nm	57.5 nm
Pd shell thickness (nm)		5.7	11.3	15.9	22.6
Pd <sup>0</sup>	3d <sub>5/2</sub> Peak position (eV)	335.0	335.2	335.2	335.2
	3d <sub>5/2</sub> FWHM (eV)	1.51	1.50	1.36	1.31
	3d <sub>3/2</sub> Peak position (eV)	340.2	340.5	340.5	340.5
	3d <sub>3/2</sub> FWHM (eV)	1.36	1.56	1.39	1.34
Spin-orbit intensity ratio					
Pd <sup>2+</sup> (PdO)	3d <sub>5/2</sub> Peak position (eV)	336.1	336.1	336.1	336.1
	3d <sub>5/2</sub> FWHM (eV)	1.64	2.5	2.5	2.5
	3d <sub>3/2</sub> Peak position (eV)	341.4	341.4	341.4	341.4
	3d <sub>3/2</sub> FWHM (eV)	1.18	2.5	2.5	2.5
Spin-orbit intensity ratio					
Pd <sup>4+</sup> (PdO <sub>2</sub> )	3d <sub>5/2</sub> Peak position (eV)	337.6	338.0	338.0	338.0
	3d <sub>5/2</sub> FWHM (eV)	1.60	1.64	1.93	1.79
	3d <sub>3/2</sub> Peak position (eV)	342.9	343.3	343.3	343.3
	3d <sub>3/2</sub> FWHM (eV)	1.61	1.68	1.82	1.81
Spin-orbit intensity ratio					



**Fig. S9.** CV curves of the Au@Pd/PdO<sub>x</sub> core-porous shell NPs with different sizes and commercial Pd/C in 1 M KOH solution.



**Fig. S10.** (a) The ECSAs and (b) current density of Au@Pd/PdO<sub>x</sub> core-porous shell NPs to ethanol electrooxidation versus the Pd shell thickness.