Supporting Information

Core/Shell Face-Centered Tetragonal FePd/Pd Nanoparticles as an Efficient Non-Pt Catalyst for the Oxygen Reduction Reaction

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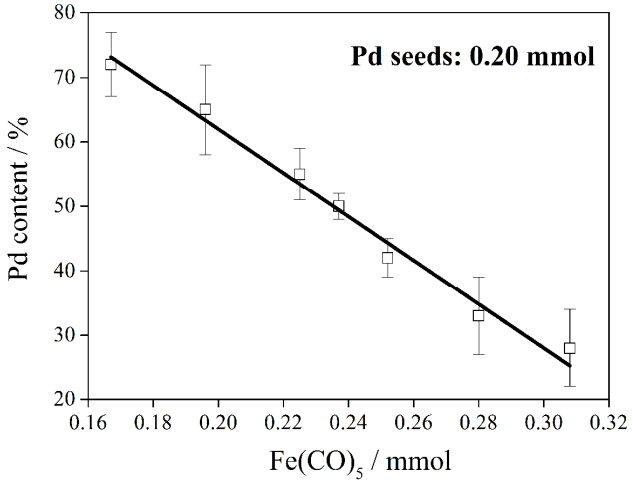

Figure S1. Relationship between the amount of $Fe(CO)_5$ added and the Pd content obtained within Pd/Fe_3O_4 NPs under a constant Pd loading of 0.20 mmol.

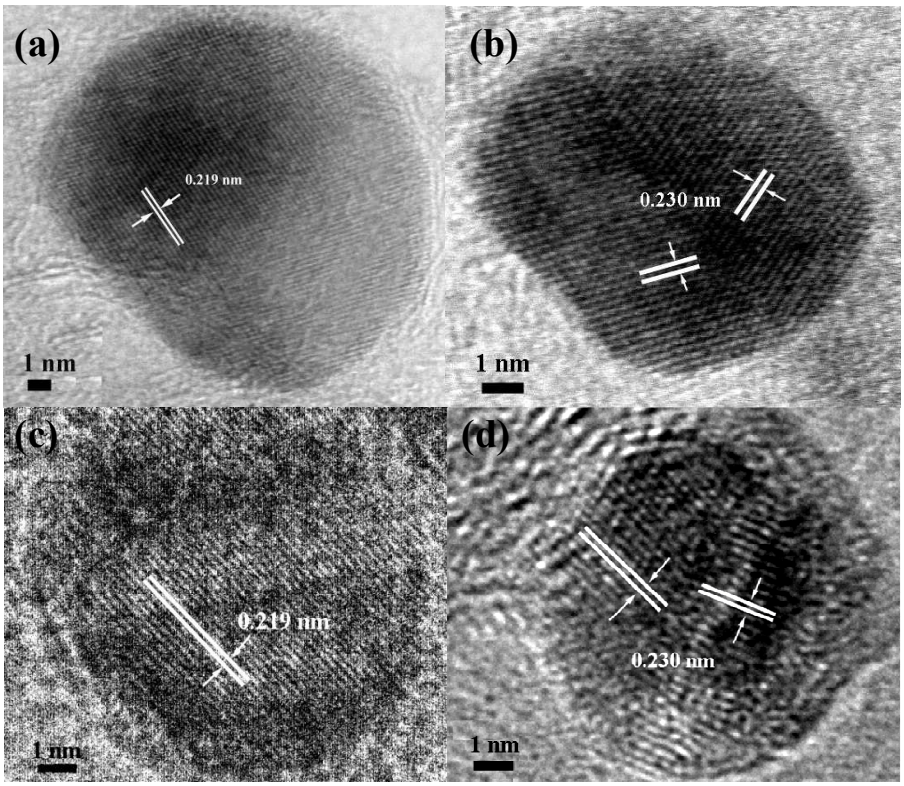

Figure S2. HRTEM images of the C-*fct*-FePd (a, c) and C-*fcc*-FePd (b, d) NPs before (a, b) and after (c, d) the cycling in O_2-saturated $HClO_4$ solution.

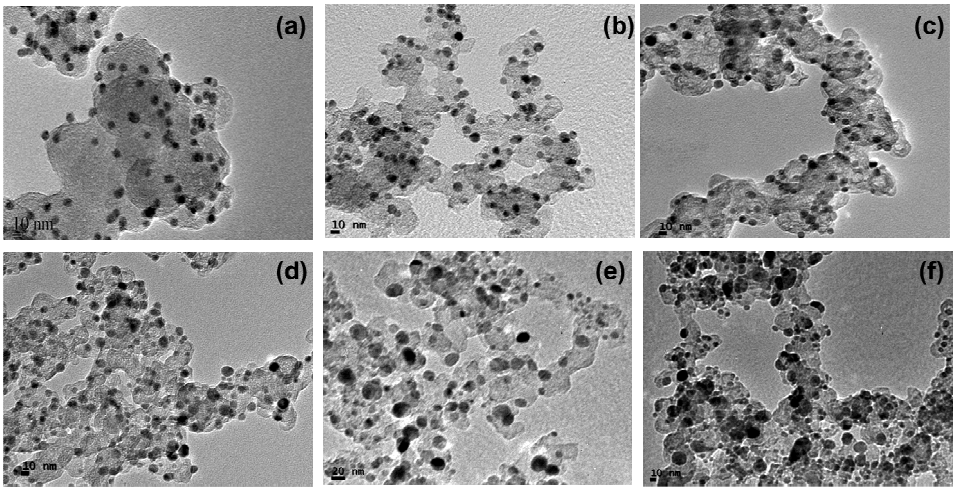

Figure S3. TEM images of the C-$Fe_{46}Pd_{54}$ NPs after annealed at 400 ^{o}C for 1 h (a), and 600 ^{o}C for 1 h (b), 2 h (c), 3 h (d), 4 h (e) and 5 h (f).

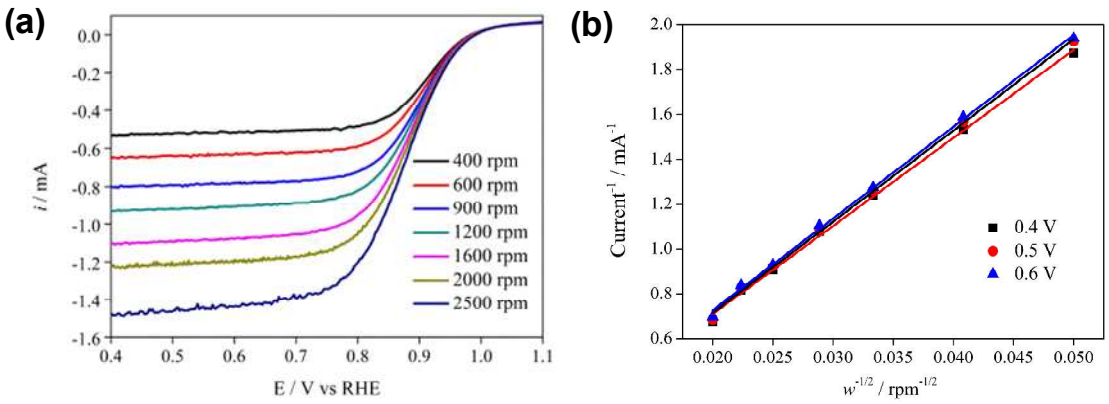

Figure S4. ORR polarization curves (a) for C-*fct*-FePd-1.0 kOe at different rotation rates and corresponding K-L plots (b).

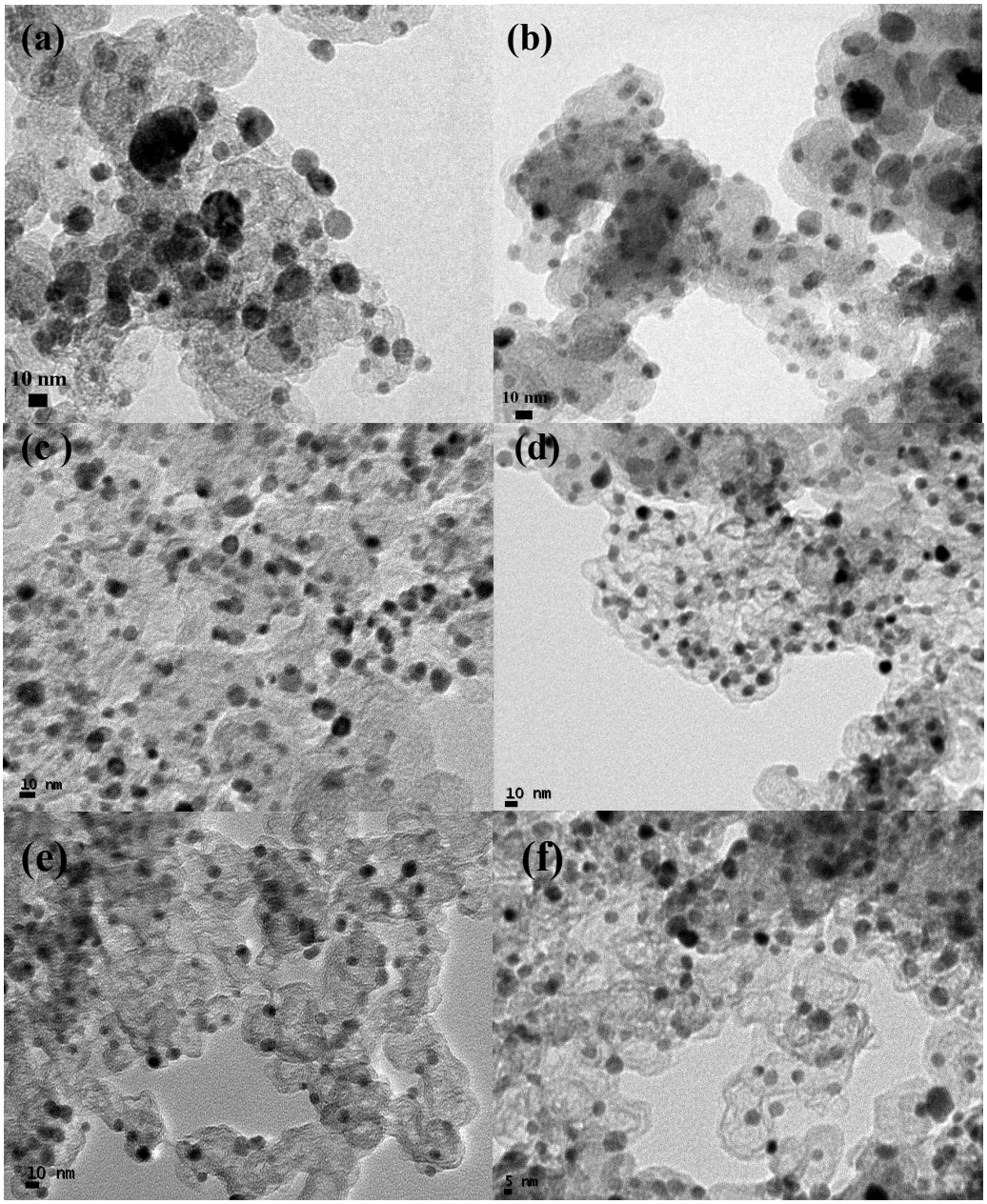

Figure S5. TEM images of the C-*fcc*-FePd (a), C-*fct*-FePd-0.6 kOe (b), C-*fct*-FePd-1.0 kOe (c), C-*fct*-FePd/Pd-0.27 (d), C-*fct*-FePd/Pd-0.65 NPs (e) and C-*fct*-FePd/Pd-0.81 (f) after 3000 potential cycling in 0.1 M O_2-saturated $HClO_4$ solution. The core/shell NPs have the H_c ~1 kOe.

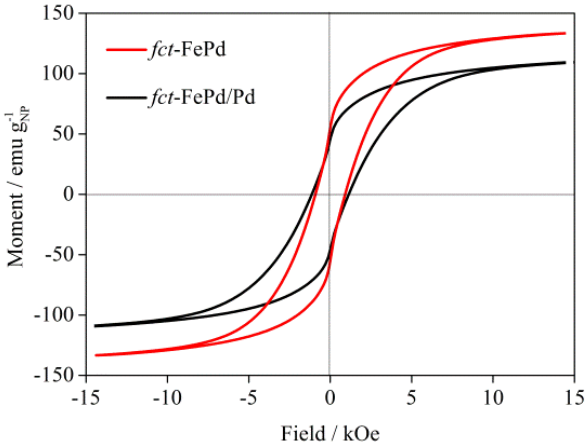

Figure S6. Hysteresis loops of the *fct*-FePd-1.0 kOe and corresponding core/shell *fct*-FePd/Pd.

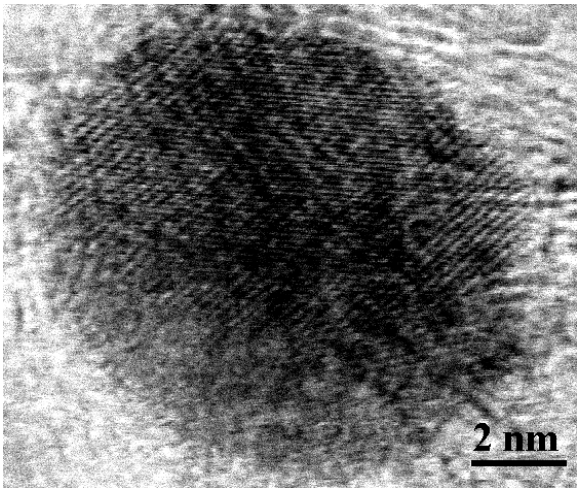

Figure S7. HRTEM image of a single *fct*-FePd/Pd NP after the acetic acid treatment at 50 °C before 400 °C annealing.

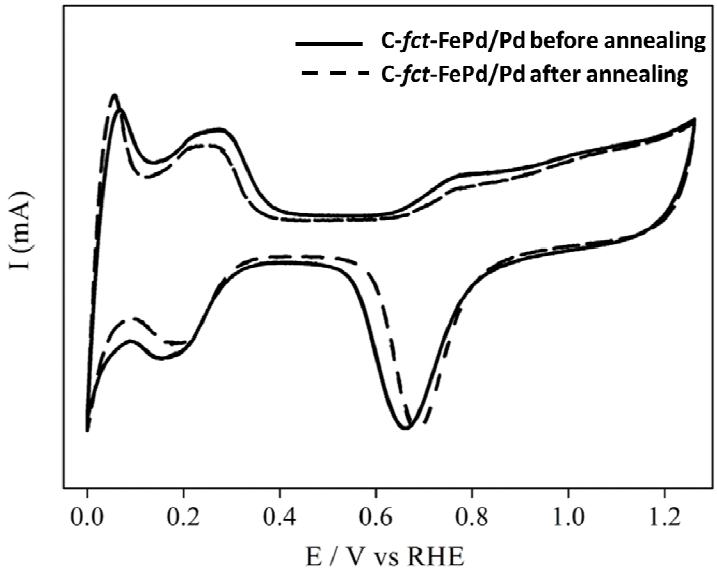

Figure S8. CVs of the C-*fct*-FePd/Pd-0.65 before and after 400 °C annealing in N_2-saturated 0.1 M $HClO_4$ solution.

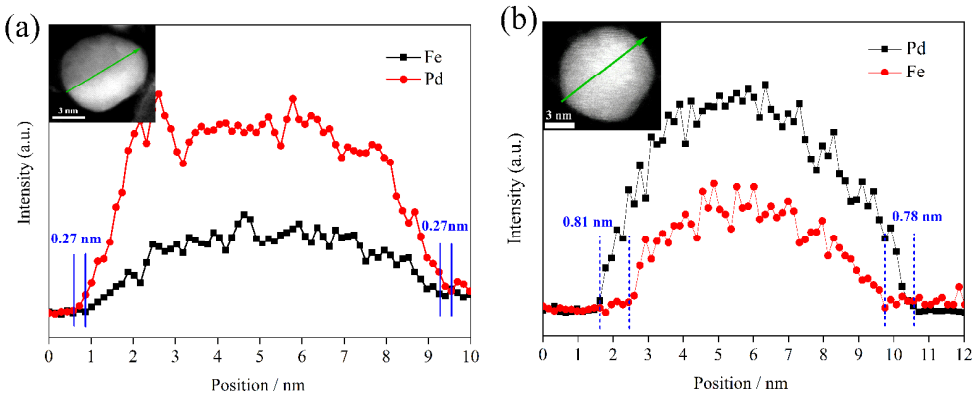

Figure S9. STEM-EELS line scan crossing one *fct*-FePd/Pd NP obtained after 25 °C (a) and 70 °C (b) acetic acid treatment overnight, indicating the formation of 0.27 nm and 0.81 nm Pd shell, respectively. The inset shows the NP scanned.

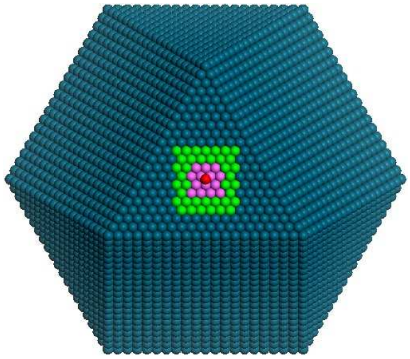

Figure S10. Atomic configuration of a cuboctahedral NP for QM−MM calculation, viewing along the <111> direction. The entire system is partitioned into a QM region (red, pink, and green spheres) and a MM region (blue spheres). The red sphere represents the adsorbed O atom.

Table S1. Specific activities for the catalysts measured at 0.90 V in O_2-saturated $HClO_4$ solution

Catalyst	Electrochemical area / cm^2 mg^{-1}Pd	Specific activity at 0.90 V/ mA cm^{-2}
C-*fcc*-FePd	679	0.051
C-*fct*-FePd-0.3 kOe	605	0.058
C-*fct*-FePd-0.6 kOe	593	0.119
C-*fct*-FePd-1.0 kOe	595	0.168
C-*fct*-FePd-1.0 kOe-0.27 nm	563	0.163
C-*fct*-FePd-1.0 kOe-0.65 nm	583	0.164
C-*fct*-FePd-1.0 kOe-0.81 nm	559	0.103

Table S2. $E_{1/2}$ decay of C-*fcc*- and C-*fct*-FePd with different coecivities after 3000 cycling in O_2-saturated 0.1 M $HClO_4$ solution

Coercivity / kOe	0.086 (*fcc*-FePd)	0.3	0.6	1.0	C-Pt
$E_{1/2}$ decay / mV	~42	~40	~32	~26	~15