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

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Abstract

We report the synthesis of core/shell face-centered tetragonal (fct)-FePd/Pd nanoparticles (NPs) via reductive annealing of core/shell Pd/Fe3O4 NPs followed by temperature-controlled Fe etching in acetic acid. Among three different kinds of core/shell FePd/Pd NPs studied (FePd core at ~8 nm and Pd shell at 0.27, 0.65, or 0.81 nm), the fct-FePd/Pd-0.65 NPs are the most efficient catalyst for the oxygen reduction reaction (ORR) in 0.1 M HClO4 with Pt-like activity and durability. This enhanced ORR catalysis arises from the desired Pt lattice compression in the 0.65 nm Pd shell induced by the fct-FePd core. Our study offers a general approach to enhance Pd catalysis in acid for ORR.

Keywords: FePd · face-centered tetragonal structure · core/shell nanoparticles · electrocatalysis · oxygen reduction reaction

Nanostructured palladium (Pd), especially Pd nanoparticles (NPs), has been a popular choice of catalysts for many chemical reactions.1,2 Pd NPs have also been explored as a promising non-Pt catalyst for electrochemical oxidation of formic acid with high CO tolerance3–5 and for electrochemical reduction of oxygen6–8 with activity in acid superior to carbon-based9,10 and metal/metal oxide catalysts.11,12 Recent studies indicate that, like Pt, Pd can alloy with a first-row transition metal M (M = Cu, Ni, Co, Fe, etc.), and Pd catalytic properties for both fuel oxidation13 and oxygen reduction reaction (ORR)14–16 can be improved. Especially, when a thin layer of Pd is coated around MPd NP, the Pd–O binding strength is optimized to the level where the Pd catalysis for ORR may become comparable to Pt.17,18 Despite the progress made in developing Pd as an alternative catalyst for electrochemical reactions, the Pd-based catalysts demonstrated thus far have poorer durability than Pt in acid.16,19–21 and consequently, they are much inferior to Pt in catalyzing ORR.

One new strategy to stabilize the alloy catalyst in the corrosive electrochemical reaction environment, such as in ORR, is to have the alloy adopt an intermetallic structure.22 Take FePt NPs for example, once prepared, these NPs often have a face-centered cubic (fcc)-type solid solution structure, which is unstable (subject to fast Fe leaching) in acid, making it difficult to assess Fe effect on FePt catalysis for ORR in 0.1 M HClO4. However, when the Fe/Pt atomic ratio is near 50/50, the fcc-FePt can be converted to an intermetallic face-centered tetragonal (fct) structure.23 Such an fct-structure is formed due to the strong 3d–5d interaction between Fe and Pt along the crystallographic c-direction. In this structure, Fe is greatly stabilized, and fct-FePt NPs have shown much enhanced chemical stability against acid etching and therefore much enhanced ORR catalysis.24 The enhanced catalytic efficiency arises from the core/shell fct-FePt/Pt structure in which the Pt lattice in the thin Pt shell (<1 nm) is more compressed than that in the common surface Pt shell from the pure Pt NPs.25 Once the fct-ordering is further

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enhanced catalysis for ORR in 0.1 M HClO4 with Pt-like acid corrosion. Here we demonstrate our studies on coated with a thin layer of Fe3O4, and the core/shell of core/shell fct-FePd/Pd NPs. First, the Pd NPs are synthesized oleylamine (OAm)-capped Pd NPs by (diameter: 8.5 nm) and room-temperature coercivity of 1.0 kOe are the magnetic fct-FePd/Pd NPs with 0.65 nm thick Pd shell ordering and on the thickness of the Pd shell. Ferro-NPs is dependent both on the degree of the Fe/Pd is controlled by annealing time at 600°C.

RESULTS AND DISCUSSION

We then deposited the Pd/Fe3O4 NPs on Ketjen carbon (C) and annealed them at temperatures up to 600 °C in Ar + 4% H2. In this high-temperature reductive annealing condition, Fe3O4 was reduced to Fe, leaving behind defects in the Fe lattice which facilitated Fe–Pd interdiffusion and the formation of fct-FePd NPs, similar to the synthesis of fct-FePd NPs. The annealing temperature of 600 °C and Fe/Pd ratio of 46/54 were found to be optimal for the formation of fct-FePd phase. Too much Fe or Pd in the Pd/Fe3O4 structure or annealing at temperatures lower than 600 °C led to the formation of fcc-FePd NPs. Figures 2b and S2 give the typical TEM and high resolution TEM (HRTEM) images of the fct-Fe46Pd54 NPs (obtained from annealing at 600 °C for 3 h) on carbon support (denoted as C-fct-FePd), which show an average size of 8.5 ± 0.5 nm and (111) lattice fringe distance of 0.219 nm. The NPs remain well-dispersed on carbon and show no sign of aggregation/sintering after the thermal treatment. Figure 2c is the 2D scanning TEM-electron energy-loss spectroscopy (STEM-EELS) elemental mapping of one representative fct-Fe46Pd54 NP. The mapping shows clearly the Fe diffusion into Pd lattice. The structure and the related magnetic property changes upon Fe–Pd diffusion were monitored by X-ray diffraction (XRD) patterns and vibrating sample magnetometer (VSM) measurements. Compared with the original 8 nm Pd NPs, the fcc-Fe46Pd54 (obtained from annealing at 400 °C for 1 h) and fct-Fe46Pd54 show obvious (111) peak shift to a larger angle (Figure 2d), confirming that the (111) lattice is compressed due to the Fe alloying with Pd. The formation of fct-FePd structure is further evidenced by the appearance of characteristic superlattice peaks (marked by black arrows). The room-temperature VSM measurements show that fcc-Fe46Pd54 NPs are superparamagnetic with their magnetic moment saturated at 169 emu·g⁻¹·FePd while the fct-Fe46Pd54 NPs are ferromagnetic (coercivity Hc = 1.0 kOe) with their moment saturated at 132 emu·g⁻¹·FePd (Figure 2e), indicating the strong Fe–Pd interaction in the fct-structure. The degree of Fe/Pd ordering in the Fe46Pd54 structure is related to Hc; the larger the Hc, the higher the ordering degree. From the annealing-dependent Hc data (Figure 2f) we can see that longer annealing time can help to increase the NP Hc and therefore to increase Fe/Pd ordering. But too long an annealing (over 3 h) can cause the FePd NPs to aggregate/sinter (Figure S3).

To test FePd structure-dependent catalysis, the C-fct-FePd annealed at 400 °C for 1 h and C-fct-FePd annealed at 600 °C for 1 h (Hc = 0.3 kOe), 2 h (Hc = 0.6 kOe) and 3 h (Hc = 1.0 kOe) were selected for catalytic studies. Figure 3a,b presents their ORR polarization curves and corresponding mass activities, which are then compared to the commercial Pd (denoted as C–Pd) and Pt catalyst (20% mass loading with 2.5–3.5 nm Pt NPs, denoted as C–Pt). All C-FePd catalysts are more active than the C–Pd one with their polarization curves positively shifted, confirming that
introduction of Fe into Pd lattice enhances the ORR activity. The C-fcc-FePd shows a half-wave potential \( E_{1/2} \) of 0.84 V and mass activities of 34.8 mA·mg\(^{-1}\) Pd at 0.90 V and 189 mA·mg\(^{-1}\) Pd at 0.85 V, while the C-fct-FePd shows the \( H_c \)-dependent increase in \( E_{1/2} \)'s (from 0.86 to 0.88 V) and mass activities (from 41.3 to 99.7 mA·mg\(^{-1}\) Pd (at 0.90 V) and 238 to 351 mA·mg\(^{-1}\) Pd (at 0.85 V). Figure S4a shows the rotation-rate-dependent ORR polarization curves of the C-fct-FePd-1.0 kOe in O\(_2\)-saturated HClO\(_4\) solution. From the slopes of the

Figure 3. (a) ORR polarization curves and (b) corresponding mass activities of the C-fcc-FePd and C-fct-FePd with different \( H_c \)'s, C—Pd, and C—Pt in 0.1 M O\(_2\)-saturated HClO\(_4\) solution. The rotating disk electrode was set at a rotation rate of 1600 rpm.
TABLE 1. Composition Change during the Durability Test of the C-fct-FePd/Pd (Hc = 1.0 kOe) with Different Pd Shell Thickness

<table>
<thead>
<tr>
<th>treatment</th>
<th>composition</th>
<th>relative standard deviation for Pd ratio</th>
<th>after 3000 cycles</th>
<th>relative standard deviation for Pd ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-fct-FePd-0.27</td>
<td>Fe\textsubscript{43}Pd\textsubscript{57}</td>
<td>0.012</td>
<td>Fe\textsubscript{42}Pd\textsubscript{58}</td>
<td>0.044</td>
</tr>
<tr>
<td>C-fct-FePd-0.65</td>
<td>Fe\textsubscript{39}Pd\textsubscript{61}</td>
<td>0.015</td>
<td>Fe\textsubscript{40}Pd\textsubscript{60}</td>
<td>0.029</td>
</tr>
<tr>
<td>C-fct-FePd-0.81</td>
<td>Fe\textsubscript{38}Pd\textsubscript{62}</td>
<td>0.013</td>
<td>Fe\textsubscript{37}Pd\textsubscript{63}</td>
<td>0.021</td>
</tr>
</tbody>
</table>

Koutecky–Levich (K-L) equation plots (Figure S4b), we estimated the number of electrons transferred for reducing one oxygen molecule in the ORR to be 3.94–4.02, indicating the ORR on this catalyst proceeds via a 4e process, similar to the case on Pt. The specific activities of these C-FePd catalysts were also found to be Hc dependent (Table S1); the superparamagnetic C-fcc-FePd has the value of 0.051 mA cm\textsuperscript{-2} at 0.90 V, while the ferromagnetic C-fct-FePd’s show the increased values from 0.058 (for the catalyst with Hc = 0.3 kOe) to 0.168 mA cm\textsuperscript{-2} (for the one with Hc = 1.0 kOe) at 0.90 V.

The durability of these catalysts was evaluated by cycling in the potential range of 0.66–1.06 V in 0.1 M O\textsubscript{2}-saturated HClO\textsubscript{4} solution, which is characterized by the decay of E\textsubscript{l/2} after 3000 cycles (Table S2). The C-fcc-FePd has the largest potential decay of ~42 mV, while the C-fct-FePd’s with the increased Hc become more and more stable with the decay reduced from ~40 to ~26 mV. These indicate that the higher degree of Fe/Pd ordering in the fct-FePd structure leads not only to larger Hc but also much enhanced ORR catalytic efficiency. The NP morphology (TEM and HRTEM) and Fe/Pd ratios (measured by ICP-AES) of the fcc-FePd, fct-FePd-0.27 (or C-fct-FePd/Pd-0.81) (Figure S9). In general, Fe/Pd ratios from 46/54 to 44/56 (or to 37/63), generating a 0.27 (or 0.81 nm) shell, denoted as C-fct-FePd/Pd-0.65 (Figure 4b). HRTEM image in Figure 4c confirms the smooth surface (without 400 °C annealing the Pd shell is defected, Figure S7). The redox properties of the C-fct-FePd/Pd-0.65 before and after 400 °C annealing were studied by cyclic voltammetry. Figure S8 gives their cyclic voltammograms (CVs), showing that the Pd oxide formation and corresponding reduction peak of the annealed C-fct-FePd/Pd-0.65 shifts to a more positive potential compared to the same core/shell NPs without 400 °C treatment. Such a shift is representative of the formation of a smooth Pd shell with less low-coordinated Pd sites after thermal annealing.

The high-angle annular dark field (HAADF)-STEM image (inset of Figure 4d) and the HAADF line scan profile of the C-fct-FePd/Pd-0.65 NP (Figure 4d) confirm the formation of the Pd shell and the intermetallic FePd core. We should also mention that in the Fe etching experiment, the Pd shell thickness was controlled by the etching temperature. For example, when treated in acetic acid at 25 °C (or 70 °C), the NPs changed their Fe/Pd ratios from 46/54 to 44/56 (or to 37/63), generating a 0.27 (or 0.81 nm) shell, denoted as C-fct-FePd/Pd-0.27 (or C-fct-FePd/Pd-0.81) (Figure S9).

Figure 5a,b compares the ORR polarization curves and corresponding mass activities at 0.90 V for the C-fct-FePd/Pd-0.65 and the commercial Pt catalyst.
Figure 4. (a) TEM of the C-fct-FePd/Pd-0.65 NPs. (b) STEM-EELS line scan crossing one fct-FePd/Pd-0.65 NP. The inset shows the NP scanned. (c) HRTEM of one fct-FePd/Pd-0.65 NP. (d) HAADF-STEM image of a representative fct-FePd/Pd-0.65 NP with the scan direction from the shell to the core, and the corresponding HAADF line profile normalized with Z contrast of metal atoms; the inset shows the NP scanned.

Figure 5. (a) ORR polarization curves and (b) the corresponding mass activities at 0.90 V for the C-fct-FePd/Pd-0.65 and C–Pt before and after durability test in O2-saturated 0.1 M HClO4. (c) ORR polarization curves and (d) the corresponding mass activities at 0.90 V for the C-fct-FePd/Pd with different shell thicknesses before and after durability test in O2-saturated 0.1 M HClO4.
FePd/Pd-0.81 and C-fct-FePd/Pd-0.65 NPs lost only durability tests were analyzed by ICP-AES. The C-fct-ratios in the C-fct-FePd/PdNPs before and after the aggregation compared to the C-fct-FePd, suggesting shows the TEM images of these C-fct-FePd/Pd catalysts for ORR with Pt-like activity and durability. tested, the C-fct-FePd/Pd-0.65 NPs are the best catalyst core. Overall, among three di we performed theoretical simulation on this system. could in >0.6 nm.36 Therefore, we focus on the surface strain to elucidate the superior ORR activity on NPs with a thickness is often negligible for core/shell NPs with a thickness >0.6 nm.36 Therefore, we focus on the surface strain to elucidate the superior ORR activity on NPs with 0.65 nm shell to those with 0.81 nm shell. To this end, we calculated oxygen adsorption energy ($E_O$), which is an excellent descriptor for ORR activity. There exists an optimal $E_O$ value under which the ORR activity of the catalyst reaches the maximum.37,38 In convenience, we set the optimal $E_O$ at 0 eV, and $\Delta E_O$ is defined relative to this optimal value. Both density functional theory (DFT) and quantum mechanics-molecular mechanics (QM-MM) calculations were performed to determine $\Delta E_O$. First, a flat Pd (111) surface is modeled under a lateral compression up to 2.5% with DFT as shown in Figure 6a. The DFT calculations reveal a linear relationship between the surface strain and $\Delta E_O$. A more compressive strain would shift $E_O$ toward the value on the Pt (111). In particular, the Pd surface with a compressive strain of ~2.1% could yield the same ORR activity as the Pt surface. We then modeled an 8 nm fct-FePd/Pd NP with 0.6 nm Pd shell thickness. The lattice mismatch between the fct-FePd core and the Pd-shell generates ~1.7% compressive strain on the NP surface; the corresponding $\Delta E_O$ value is ~0.25 eV, which is close to the value (~0.2 eV) on Pt (111). Hence the ORR activity on the fct-FePd/Pd-0.6 NP should approach that on Pt. As the shell thickness increases to 0.8 nm, the compressive surface strain is released as indicated in Figure 6b. $\Delta E_O$ becomes more negative leading to a less active ORR catalysis. Therefore, the superior ORR activity of fct-FePd/Pd-0.6 NPs stems from the desired compressive strain. Note that a thicker NP could release its stress more readily than a thinner one. Hence the strain distribution on the 0.8 nm NPs is more uniform (or less broadened) than that on the thinner one (0.6 nm), as shown in Figure 6b.

For NPs with 0.2 nm shell, the ligand effect cannot be ignored. Here we calculate $\Delta E_O$ on a monolayer Pd (0.2 nm interlayer distance), which is deposited on a flat fct-FePd surface. The $\Delta E_O$ value becomes positive (0.29 eV) and moves to the other side of the volcano plot.37 The significantly weakened Pd–O binding is due to the ligand effect. As the $\Delta E_O$ value of the 0.2 nm shell is farther away from the optimal value than that of 0.6 nm shell, the corresponding core/shell NPs with the
by adding ethanol and centrifugation. The NPs were further cooled down to room temperature, the Pd NPs were collected.

**METHODS**

**Synthesis of Pd NPs.** Pd NPs were prepared following the reported method. In a reaction flask with a continuous N2 flow to remove hexane. After 30 min, the solution was heated to 40 °C. After 30 min of heating at 40 °C, 2.5 mmol of borane morpholine complex dissolved in 4 mL of OAm was injected into the solution, leading to an instant color change from transparent yellow to black-brown. The solution was then heated to 90 °C at a rate of 3 °C/min and kept at this temperature for 1 h. Once cooled down to room temperature, the Pd NPs were collected by adding ethanol and centrifugation. The NPs were further purified with hexane/ethanol and redispersed in hexane for further use.

**Synthesis of fct-FePd NPs.** A solution of 0.20 mmol of Pd NPs in 3 mL hexane was mixed with 12 mL 1,2,3,4-tetrahydronaphthalene and 0.34 mL OAm. The solution was heated to 40 °C under a continuous N2 flow to remove hexane. After 30 min, the temperature was raised to 120 °C and under a blanket of N2 protection, a controlled amount of Fe(CO)5 was injected into the solution to initiate Fe nucleation on the Pd seeds. The solution was further heated to 180 °C at a rate of 3–4 °C/min and kept at this temperature for 30 min before cooled down to room temperature. The reaction system was then open to air, and Pd/FePd NPs were obtained and collected by adding isopropanol and centrifugation. The NPs were further purified with hexane/ethanol and stored in hexane.

**Conclusions.** Upon annealing, the C-NPs were mixed with 25 mL acetic acid and 2.5 mmol of borane morpholine complex dissolved in 4 mL of OAm under vigorous magnetic stirring. The mixture was heated to 90 °C at a rate of 3 °C/min and kept at this temperature for 1 h. Once cooled down to room temperature, the C-NPs were separated by centrifugation. The relationship between the amount of Fe(CO)5 added and the catalytic activity of the fct-FePd core/shell NPs is shown in Figure S1.

**Characterization.** TEM images were obtained from a Philips CM 20 operated at 200 kV. HRTEM images were acquired on a JEOL 2100F (200 kV). Each sample was prepared by depositing a single drop of diluted NPs dispersion on an amorphous carbon-coated copper grid. STEM analyses were carried out on FEI Titan 80–200 (200 kV) with a Cs-corrector at Zhejiang University. The EELS line-scan was obtained by a high-resolution Gatan Enfina ER with a probe size of 0.8 Å. A power law function was used for EELS background subtraction. To determine the Fe/Pd ratio, the catalyst was first digested with aqua regia (HNO3/HCl = 1/3 in volume) at 200 °C and then diluted by 2% HNO3 aqueous solution. The solution was then filtered to remove the residue carbon, and the filtrate was collected for ICP-AES measurement.

**Electrochemical Measurements.** The catalyst was suspended in a mixture of deionized water and Nafion solution. A single drop of diluted NPs dispersion on a carbon tape. The mixture was heated to 90 °C at a rate of 3 °C/min and kept at this temperature for 30 min before cooled down to room temperature. The reaction system was then open to air, and Pd/FePd NPs were obtained and collected by adding isopropanol and centrifugation. The NPs were further purified with hexane/ethanol and stored in hexane. The NPs were then sealed in a glass tube and annealed at 400 °C under a N2 flow. The annealing time varied from 1 to 5 h. The treated samples were then annealed at 400 °C for 2 h under a gentle Ar + 4% H2 flow to form a smooth Pt shell on the NP surface.

**Electrochemical Measurements.** The catalyst was suspended in a mixture of deionized water, isopropanol, and Nafton solution. Twenty microliters of the NPs dispersion were then deposited on a G2 80–200 copper grid. The TEM images were acquired from a Philips CM 20 operated at 200 kV. HRTEM images were acquired on a JEOL 2100F (200 kV). Each sample was prepared by depositing a single drop of diluted NPs dispersion on an amorphous carbon-coated copper grid. STEM analyses were carried out on FEI Titan 80–200 (200 kV) with a Cs-corrector at Zhejiang University. The EELS line-scan was obtained by a high-resolution Gatan Enfina ER with a probe size of 0.8 Å. A power law function was used for EELS background subtraction. To determine the Fe/Pd ratio, the catalyst was first digested with aqua regia (HNO3/HCl = 1/3 in volume) at 200 °C and then diluted by 2% HNO3 aqueous solution. The solution was then filtered to remove the residue carbon, and the filtrate was collected for ICP-AES measurement.

**DFT Calculation of ΔEC on Pt Surface.** The EC values were determined by placing an O atom on the fcc hollow site of (111) surface, following

$$
\Delta E = E_{Pd/Fe} - E_{Pt/Fe} - E_{Pt} - E_{2O}/2
$$

where $E_{Pd/Fe}$ and $E_{Pt/Fe}$ are total energies of the Pd shell with and without O adsorbate, respectively. $E_{Pt}$ is the total energy of a oxygen molecule. For DFT calculations of Pd surface, we used $3 \times 3$ ($\sqrt{3} \times \sqrt{3})$R30° unit cells. A four-layer slab was used for these calculations with the top two layers fully relaxed. For the slab of fct-FePd/Pt, the top first layer is pure Pd, and the remaining three layers consist of fct-FePd. The ΔEC value was calculated.

**Conclusion.** In conclusion, we have synthesized fcc-FePd and fct-FePd via reductive annealing of core/shell Pd/Fe3O4 NPs. The degree of the Fe/Pd ordering in the fct-FePd (characterized by the increase of magnetic coercivity from 0.3 to 2.55 kOe) can be controlled by the thermal annealing. The stronger ferromagnetic fct-FePd shows higher ORR activity and durability in 0.1 M HClO4 than the fcc-FePd. When etched with acetic acid at a controlled temperature (from 25 to 70 °C), the fct-FePd NPs are converted to core/shell fct-FePd/Pd NPs with the Pd shell thickness controlled to be 0.27, 0.65, or 0.81 nm. The 1.0 kOe fct-FePd/Pt NPs with 0.65 nm Pd shell are more active and durable for ORR than any other FePd NPs studied here, and they even show the Pt-like activity and durability. By examining both the strain and ligand effects, our DFT simulations suggest that the high ORR activity originates from the desired compressive strain on the 0.65 nm Pd shell induced by the fct-FePd core. Our result demonstrates a new way of tuning Pd-based NPs as a new class of non-Pt catalyst for ORR and other chemical reactions in acid media.
then calculated by shifting \( E_d \) relative to the optimal value. The DFT calculations were carried out using the VASP package\(^49\) with the projector augmented wave pseudopotentials (PAW)\(^41\) and Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA). An energy cutoff of 400 eV was used for the plane-wave basis set. The Brillouin zone was sampled on the basis of the Monkhorst–Pack scheme\(^43\) with a \( 3 \times 3 \times 1 \) k-point mesh. The force convergence criterion for atomic relaxation is 0.02 eV/Å. For systems with presence of Fe, spin-polarized calculations are performed.

**Computational Models of the Core/Shell NPs.** The fct-FePd/Pd NPs are modeled by 8 nm cuboctahedrons with eight (111) facets and six (100) facets as shown in Figure 6b. The NP consists of a fcc-Pd shell and a fct-FePd core. To study the shell thickness effects on ORR, we have considered two core/shell NPs with shell thickness of 0.6 and 0.8 nm denoted as fct-FePd/Pd-0.6 NP and fct-FePd/Pd-0.8 NP, respectively. Note that these shell thicknesses are slightly different from the experimental values. The minor differences (~0.05 nm) reflect the precision of the experimental measurements. Since the ORR activity is influenced by the lateral strain as opposed to the vertical strain, these differences are inconsequential.

**Calculation of Surface Strains on NPs.** All atoms of the core/shell NPs were fully relaxed by the embedded atom method with interatomic potentials.\(^44\) There are eight (111) facets in the cuboctahedral NP, and for each (111) facet we selected 37 O adsorbed sites (fcc hollow sites) to measure the local strain. Thus, for each NP model, 296 sites were included in the strain distribution.

**QM-MM Simulations.** As shown in Figure S10, the entire NP model is partitioned into two spatial domains: a QM region (red, pink and green spheres) treated by DFT and a MM region (blue spheres) by empirical atomistic simulations. The QM region measures 16.9 Å around the adsorbed oxygen atom on the fcc hollow site. The MM region consists of the rest of the system where the strain effect due to the core/shell lattice mismatch can be captured. The DFT calculations are carried out using the VASP package with the PAW and PBE-GGA. The calculations are performed at \( \Gamma \) point with 40 eV energy cutoff. The EAM potentials\(^45\) are used in the MM simulations, which have been rescaled to yield the same lattice constant and bulk modulus as those of DFT. The force convergence criterion for atomic relaxation is 0.03 eV/Å. The \( E_d \) value was determined by placing an O atom on the fcc hollow site at the center of the (111) facet, following

\[
E_{\text{DFT}} = \text{EQM-MM}_{\text{NP}} - \frac{\text{EQM-MM}_{\text{NP}} - E_{\text{DFT}}}{2}
\]

where EQM-MM\(_{\text{NP}}\) and EQM-MM\(_{\text{NP}}\) are total energies of the core/shell NP with and without O adsorbate, respectively, from QM-MM calculations. And the local strain value is measured at the center of the (111) facet within the interior QM region.

**Conflict of Interest:** The authors declare no competing financial interest.

**Supporting Information Available:** The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b04361.

Relationship between the amount of Fe(CO)\(_5\) and the Pd content within Pd/Fe\(_3\)O\(_4\) NPs: HRTEM images of the C-fct-FePd/Pd-0.6 and C-fct-FePd/Pd-0.8 NPs before and after thermal annealing; STEM-EELS line scan crossing one fct-FePd/Pd NP after acetic acid treatment; Atomic configuration of a cuboctahedral NP for QM-MM calculation (PDF)

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**REFERENCES AND NOTES**


