Size and shape effects of Pd@Pt core-shell nanoparticles: Unique role of surface contraction and local structural flexibility

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Computational Method

The size and shape effects of Pd core- 1 monolayer Pt shell (Pd@Pt) NPs on the stability and activity were studied using DFT and a particle model in nanometer size, where no geometry constrains are applied. Pd@Pt NPs with different sizes and shape of tetrahedron (TH) and sphere-like truncated octahedron (SP) were considered (Figure 1a), which have been reported as practical electrocatalysts for oxygen reduction reaction (ORR) at the cathode in PEM fuel cell.[1] The Pt monolayer on Pd(111) surface [Pt/Pd(111)] was also included to simulate the bulk-like big particles. Pt/Pd(111) was modeled by a four-layer slab with Pt in the top layer and Pd in the bottom three layers. The calculated lattice constant is 3.955 Å for Pd and 3.984 Å for Pt, resulting in 0.7% of lattice mismatch. A 2×2 array was included in each layer and a vacuum of 12 Å between the slabs. The $5 \times 5 \times 1$ k-points using the Monkhorst–Pack scheme[2] was used. All calculations were performed by using DFT as implemented in the Vienna ab-initio simulation package (VASP).[3] The spin-restricted GGA-PW91 functional,[4] a plane-wave basis set with an energy cutoff of 400 eV, and the projector augmented wave (PAW) method[5] were adopted. The NP was placed inside the cubic supercell whose size is large enough that the separation between NP and its image in three direction is >15Å.

The stability of a Pd@Pt NP was expressed with respect to that of Pt/Pd(111) as $E_s = E_s$ (Pd@Pt) – E_s (Pt/Pd) = [E(Pd@Pt) – $m_{Pd@Pt}$E(Pd) – $n_{Pd@Pt}$E(Pt)] / $A_{Pd@Pt}$ – [E(Pt/Pd) – $m_{Pt/Pd}$ E(Pd) – $n_{Pt/Pd}$E(Pt)] / $A_{Pt/Pd}$ where "E" represents total energy of a Pd@Pt NP or a Pt/Pd(111) surface including m Pd atoms and n Pt atoms, a free Pd atom and a free Pt atom. "A" is the surface area, which was calculated based on the optimized geometry and as the summation over all facets of a NP.

Atomic O was used as a probing adsorbate for activity towards the ORR.[6] To calculate binding energy (BE) of atomic O [BE-O = E(O/Pd@Pt) – E(H_2O) + E(H_2) – E(Pd@Pt)], we chose 3-fold

hollow site (i.e., the most stable adsorption site) on (111) terrace, which was found to contribute the most to the ORR activities.[1a, 7] For comparison, the adsorption of O on all NPs was considered at the hollow site which is near the centroid of the terrace and nearly equidistance away from the edge. No constraints were imposed for both the adsorbate and Pd@Pt NP during the optimization in order to explicitly capture the subtle size- and shape-effect. For Pt/Pd(111), the top two layers were allowed to relax with oxygen, while the bottom two layers were fixed at the lattice position. The 2×2 unit cell corresponds to a O coverage of 0.25 monolayer. This is a low coverage. It has been found that increasing the size of unit cell from 2×2 to 2×3 only leads to the variation in BE-O on Pt(111) of only 0.02 eV.[8] We note that the calculated BE-O from a 2×2 Pt/Pd(111) slab can be different from that of a bulk-like particle. However, the difference seems to be much smaller than that between our interested NPs and the surface.

The surface strain (S_{Pt}) was calculated as $S_{Pt} = (a_{Pt\text{-}Pt:Pd@Pt} - a_{Pt\text{-}Pt:Pt/Pd})/a_{Pt\text{-}Pt:Pt/Pd}$, where $a_{Pt\text{-}Pt}$ is the average Pt-Pt bond length on the (111) terrace of a Pd@Pt NP or a Pt/Pd(111) surface. S_{Pt} was expressed in % and with respect to that of Pt/Pd(111) slab. The negative value as shown in Figure 2b corresponds to a surface contraction or compressive surface strain compared to the Pt/Pd(111) surface. The variation in S_{Pt} before and after oxygen adsorption was also included to demonstrate the O-driven structural distortion on the (111) terrace, $\Delta S_{Pt} = S_{Pt}(O/Pd@Pt) - S_{Pt}(Pd@Pt)$ for the NPs and $\Delta S_{Pt} = S_{Pt}(O/Pt/Pd) - S_{Pt}(Pt/Pd)$ for the extended surface. The positive value shown in Figure 3b represents the case, where the contraction on the bare surface is released in some degree due to the oxygen adsorption. The Pt protrusion perpendicular to (111) terrace before and after O adsorption was also calculated as $S_{Pt\text{-}Pd} = (a_{Pt\text{-}Pd:Pd@Pt} - a_{Pt\text{-}Pd:Pt/Pd})/a_{Pt\text{-}Pd:Pt/Pd}$. $a_{Pt\text{-}Pd}$ is the average bond length between the Pt atoms on the (111) terrace and the interacted Pd atoms in underneath. $S_{Pt\text{-}Pd}$ was expressed in %. The variation in $S_{Pt\text{-}Pd}$ before and after oxygen adsorption was also included to demonstrate the O-driven structural distortion perpendicular to the (111) terrace, $\Delta S_{Pt\text{-}Pd} = S_{Pt\text{-}Pd}(O/Pd@Pt) - S_{Pt\text{-}Pd}(Pd@Pt)$ for the NPs and $\Delta S_{Pt\text{-}Pd} = S_{Pt\text{-}Pd}(O/Pt/Pd) - S_{Pt\text{-}Pd}(Pt/Pd)$ for the extended surface. For all the systems studied here, we barely observe any O-driven Pt protrusions for the Pt atoms, which do not interact directly with O. Therefore, only the three O-bound Pt atoms were considered for the calculation of $S_{Pt\text{-}Pd}$, rather than including all Pt atoms on the whole (111) terrace as the case of S_{Pt}.

Results

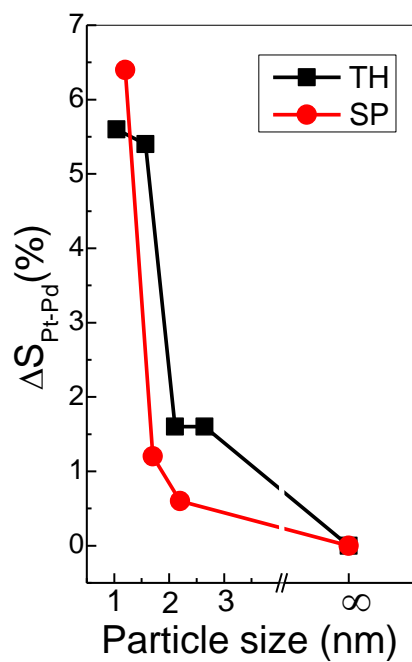**Figure S1.** Relative variation with respect to Pt/Pd(111) in Pt protrusion (ΔS_{Pt-Pd}) perpendicular to (111) terrace before and after O adsorption as a function of particle size. Pt/Pd(111) labeled as ''∞'' to describe the big bulk-like particles.

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