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Structural dependence of oxygen reduction reaction on palladium nanocrystals[†]

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We have synthesized sub-10 nm Pd cubic and octahedral nanocrystals and then evaluated their activities towards oxygen reduction reaction (ORR). The ORR activity of Pd nanocubes was one order of magnitude higher than that of Pd octahedra, and comparable to that of the state-of-the-art Pt catalysts.

The slow kinetics of oxygen reduction reaction (ORR) is one of the main obstacles hindering the commercialization of low-temperature fuel cells.^{1,2} Platinum is by far the most effective electrocatalyst for ORR, but it is an extremely rare and expensive element. One way to address this problem is to increase the ORR activity of a Pt catalyst by optimizing the shape of constituent nanoparticles and thus maximizing the expression of facets most reactive towards ORR reaction.³⁻⁶ In a non- or weakly-adsorbed electrolyte (such as HClO₄) solution, it has been established that the ORR activity on lowindex Pt surfaces increases in the order of Pt(100) < Pt(111) \approx Pt(110).⁵ Another approach is to develop new catalysts based on other noble metals. Palladium is a possible candidate but the ORR activity of conventional Pd nanoparticles is at least five times lower than that of their Pt counterparts, preventing their direct use in fuel cells.^{9,10} It is not clear if facet engineering will be able to drastically enhance the activity of Pd nanocrystals and thus lead to the development of Pd-based catalysts for ORR. A recent study by Kondo et al. demonstrated that the ORR activity on Pd single crystals followed a trend opposite to that of Pt, *i.e.*, $Pd(110) < Pd(111) \ll$ Pd(100), suggesting that the Pd(100) surface offers the most active sites for ORR.⁷ However, Xiao et al. proposed that the Pd(110) is more active than other sites based on their theoretical calculations.⁸ Here we report a systematic study on the ORR activities of shape-controlled Pd nanocrystals, including cubes and octahedra. Our results show that the ORR activity of Pd nanocubes enclosed by {100} facets were one order of magnitude higher than that of Pd octahedra enriched with

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 $\{111\}$ facets, and comparable to that of the state-of-the-art Pt nanocatalysts.

The Pd nanocubes were synthesized in an aqueous solution by reducing Na₂PdCl₄ with L-ascorbic acid in the presence of Cl⁻ and Br⁻ ions as the capping agents to promote the formation of {100} facets, as reported previously.¹¹ Fig. 1A shows a transmission electron microscopy (TEM) image, revealing that the sample contained 80% cubes with an edge length of approximately 6 nm and 20% nanobars with an aspect ratio of 1:2. The powder X-ray diffraction (XRD) pattern (Fig. S1A in ESI⁺) of the Pd cubes confirms that they had a face-centered cubic (*fcc*) structure (*Fm3m*, a = 3.958 Å, JCPDS Card No. 87-0641). The dimensions of the Pd cubes calculated using the Scherrer formula was 6.4 nm, which was in agreement with the TEM data. The high-resolution TEM (HRTEM) image of a single Pd cube (Fig. 1B) clearly shows continuous fringes with a period of 1.97 Å, which is consistent with the {200} lattice spacing of fcc Pd. The corresponding FT pattern (Fig. 1B, inset) shows a square symmetry for the spots, indicating that the Pd cube was a piece of single crystal bound by {100} facets.



Fig. 1 (A) TEM and (B) HRTEM images of Pd cubes synthesized by heating an aqueous solution containing Na_2PdCl_4 , L-ascorbic acid, KCl, KBr, and PVP at 80 °C for 3 h. (C) TEM and (D) HRTEM images of Pd octahedra synthesized by heating a water–ethanol mixture containing Na_2PdCl_4 , citric acid, and PVP at 80 °C for 3 h.

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Saint Louis, MO 63130, USA. E-mail: xia@biomed.wustl.edu † Electronic supplementary information (ESI) available: Experimental procedures, TEM images and XRD patterns of Pd cubes and octahedra. TEM images of carbon-supported Pd nanocrystals, and additional voltammetry curves. See DOI: 10.1039/clcc11004g

The Pd octahedra were prepared by heating a water-ethanol mixture containing PVP, citric acid, and Na2PdCl4 at 80 °C for 3 h. As shown in Fig. 1C, the product mainly contained Pd nanocrystals in an octahedral shape (>90%) with an edge length of 5–6 nm, which matched well with the size (5.8 nm) obtained from the XRD data (Fig. S1B in ESI⁺). Both the HRTEM image and corresponding FT pattern of a single Pd octahedron recorded along the [011] zone axis reveal that the Pd octahedron was also a single crystal enclosed by {111} facets (Fig. 1D). The fringes with lattice spacing of 1.97 and 2.28 Å can be indexed as {200} and {111} of Pd, respectively. In our synthesis, the water-ethanol mixture was critical to the formation of sub-10 nm Pd octahedra. When the synthesis was conducted in an ethanol solution instead of a water-ethanol mixture with other experimental parameters being kept the same as in Fig. 1C, the product mainly contained polyhedral nanocrystals with size of nearly 15 nm (Fig. S2A in ESI[†]). On the other hand, small particles with sizes of less than 5 nm were observed when the synthesis was conducted in an aqueous solution without ethanol (Fig. S2B in ESI[†]). We believe that ethanol could accelerate the reduction rate of Pd ions, thus increase the sizes of Pd nanoparticles. However, a complete understanding of the role of ethanol in this synthesis may require further studies through not only experiments but also simulations.

Fig. S3 shows typical TEM images of the carbon-supported Pd cubes and octahedra, respectively, suggesting that all the Pd nanocrystals were uniformly dispersed on the carbon particles. Fig. 2 shows cyclic voltammetry curves for the Pd nanocrystals in 0.1 M HClO₄ solution. Since the surfaces of the as-synthesized Pd nanocrystals were covered by capping agents such as Br-, Cl-, and PVP, no clear hydrogen adsorption features were observed (dashed lines). The capping agents could be completely removed by a non-destructive proprietary method at room temperature. For Pd cubes, a well-defined hydrogen adsorption peak was observed at 0.16 V after the removal of capping agents. On the other hand, a broader hydrogen adsorption peak appeared at 0.21 V for Pd octahedra. The higher hydrogen adsorption potential implies that the adsorption energy of hydrogen on Pd octahedra is stronger than that on Pd cubes. The CVs of Pd nanocrystals



Fig. 2 Voltammetry curves of carbon-supported Pd nanocrystals before and after removal of capping agents in a nitrogen-saturated 0.1 M HClO₄ solution. Scanning rate = 50 mV s⁻¹. The currents were normalized to the geometric area of the rotating disk electrode (0.196 cm²).

were also compared with those from the conventional (cubo-octahedral) Pd nanoparticles (Pd/C, BASF). To minimize the particle size effect, the as-received Pd/C powder was heat treated at 500 °C in Ar for 2 h to achieve an average particle size of 7.1 nm (denoted as Pd/C-HT). The Pd/C-HT sample only showed a broad hydrogen adsorption peak at 0.22 V, mainly from the contribution of (111) sites (Fig. S4 in ESI†). The dominance of (111) signal can be explained by the fact that ~70% of the surface atoms on a 7.1 nm cubo-octahedral nanoparticle are at (111) sites (Fig. S5 in ESI†).

The ORR activities of the Pd nanocrystals were measured with a thin film-rotating disk electrode (TF-RDE). The results are compared to Pd/C-HT in Fig. 3A. The oxygen polarization curve of Pd/C cubes shifts to much more positive potentials compared to those of octahedra and Pd/C-HT. This indicates that the Pd/C cubes were much more active for oxygen reduction. The intrinsic/specific ORR activities of Pd atoms



Fig. 3 (A) Anodic polarization curves for the ORR on Pd cubes and octahedra supported on carbon black in 0.1 M HClO₄. The data of regular Pd/C (BASF) annealed at 500 °C for 2 h (Pd/C-HT) is also included for comparison. Sweep rate = 10 mV s⁻¹; rotating speed = 1600 rpm; and room temperature. The currents were normalized to the geometric area of the rotating disk electrode. The electrochemically active areas of Pd/C cubes, Pd/C octahedra, and Pd/C-HT were 1.27, 1.4, and 0.98 cm², respectively. Inset: Comparison of specific activities for Pd/C cubes, Pd/C octahedra, Pd/C-HT, Pt/C, and Pt/C-HT at 0.9 V. (B) Anodic polarization curves in 0.1 M HClO₄ and coverage of OH of Pd/C cubes, Pd/C octahedra, and Pd/C-HT after subtracting the double layer current density. The currents were normalized to the electrochemical active area. The coverage of OH was calculated by integrating the charge associate with OH_{ad} formation and normalized to half of the charge of Cu UPD.

in different samples were obtained by normalizing the kinetic currents at 0.9 V to the electrochemically active areas (ECAs) and compared in the inset of Fig. 3A. To avoid the interference of hydrogen absorption in calculating the hydrogen adsorption charge, the ECAs of Pd were obtained by integrating the stripping charge of a Cu monolaver underpotentially deposited on Pd, assuming 420, 490, and 460 μ C cm⁻² for full Cu monolayer coverage on cubes, octahedra, and cubo-octahedra, respectively (Fig. S6 in ESI[†]).^{12,13} The specific activities of Pd/C cubes, Pd/C octahedra, and Pd/C-HT were 0.31, 0.033 and 0.055 mA cm⁻², respectively. The activity enhancement of Pd cubes was about 10 and 6 times over Pd/C octahedra and Pd/C-HT, respectively. The Pd/C cubes were even more active than the state-of-the-art Pt/C catalysts (TKK, 46.6 wt%) with an average particle size of 2.8 nm, and comparable to Pt/C-HT with a similar size range for the particles (TKK, 50 wt%, 7 nm). Our results demonstrate that Pd(100) sites are much more active than Pd(111) at the nanoscale, consistent with the extended surface study.7

The ORR kinetics is controlled by the amount of available active sites on the catalyst's surface and the interaction between the surface and oxygen-containing species (e.g., O₂, O, OH, and OOH).^{14,15} The chemisorbed OH (OH_{ad}) acts as a poison species in the potential range where oxygen reduction is under combined kinetic-diffusion control, since it blocks the surface sites for O₂ adsorption.^{1,14} The anodic branches of the voltammetry curves (0.65-0.9 V) for Pd/C cubes, Pd/C octahedra and Pd/C-HT after subtracting the double laver currents are compared in Fig. 3B. The onset potential of OH_{ad} formation for both Pd octahedra and Pd/C-HT was ~ 0.7 V, which is more than 50 mV lower than that on Pd cubes (>0.75 V). The coverage of OH_{ad} (θ_{OH}) on the Pd surface was calculated and also compared in Fig. 3B. It's clear that the OH_{ad} coverage on Pd cubes was much lower than other surfaces in the potential range > 0.7 V. Thus, the higher ORR activity on Pd cubes can be attributed to its lower OH_{ad} coverage and consequently more available reaction sites.

In summary, we thoroughly studied the structure dependence of ORR activity for shape-controlled Pd nanocrystals with a particle size ~ 6 nm. The Pd cubes enclosed by {100} facets were one order of magnitude more active than Pd octahedra enclosed by {111} facets towards ORR. Our results demonstrated that the ORR activity was strongly dependent on the atomic structure on the surface of a Pd nanocatalyst with the {100} facets being much more active than the {111} facets. The activity of Pd cubes was even comparable to that of the state-of-the-art Pt electrocatalysts. With a much lower price for Pd (\$654.1/Oz.) as compared to Pt (\$1796.9/Oz.), the cost of fuel cells could be considerably lowered by switching from Pt- to Pd-based catalysts.⁹ We believe that our results are also important to guide the design of more active catalysts for fuel cells and other applications. Further work on the catalytic activity of Pd cubes will address the question of their fuel cell performance and long-term stability.

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