

**Palladium-Platinum Core-Shell Electrocatalysts for Oxygen Reduction
Reaction Prepared with the Assistance of Citric Acid**

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Experimental

500 mg of 35% Pd/C nanoparticles (TKK) were dispersed in 50 mM H₂SO₄ in a custom reactor consisting of a graphite sheet, carbon cloth and Ag/AgCl (leak-free, BASi) as the working, counter and reference electrodes, respectively. The Pd/C nanoparticles were cycled between 0.3 and 0.6 V (vs RHE) in order to fully wet the powder and reduce Pd oxides. After pretreatment, a deaerated aqueous solution consisting of 10 mM K₂PtCl₄ and 0.2 M citric acid was added dropwise to the reactor in 15 min to deposit Pt shell on Pd nanoparticles. The mixture was stirred for another 45 min. During the deposition of Pt, 10 ml of the suspension was taken out by a syringe after 2, 5, 10, 20, 45 and 60 min reaction, respectively. The suspension was then filtered and rinsed with ultrapure water (Milli-Q® UV-plus) and dried in a vacuum oven at 60°C. The compositions of catalysts, denoted as Pd@Pt/C were measured by inductively coupled plasma – mass spectrometry (ICP-MS) measurements. The synthesis of Pd@Pt/C without citric acid followed the exact protocols except that the deposition solution only consisted of 10 mM K₂PtCl₄.

The synthesis of Pd@Pd/C on a gram batch size via the Cu-UPD-Pt-displacement reaction was described elsewhere. In brief, the potential of the working electrode (graphite sheet) was held at approximately 0.37 V to deposit an atomically thin layer of Cu (copper) on the Pd nanoparticles in a deaerated aqueous 50 mM CuSO₄ solution + 50 mM H₂SO₄ in the same reactor described above. Immediately upon completion of the Cu UPD layer, the same Pt solution used in the spontaneous deposition was added dropwise to the reactor to replace the Cu by Pt.

In situ XRD measurements in respective He and H₂ environments were performed at Beamline X18A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory in New York. A detailed experiment procedure can be found elsewhere.¹ The Mo K α ($\lambda = 0.7107 \text{ \AA}$) incident radiation was used in XRD measurements. High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and electron energy loss spectroscopy (EELS) data were collected using a Hitachi aberration-corrected scanning transmission electron microscope (HD-2700C). An electron probe diameter of 1.3 \AA with a convergence angle of 28 mrad was used. The EELS line scans were collected with a pixel time of 0.02 s using a Gatan Enfina-ER detector.

The electrochemical behaviors of Pd@Pt/C were evaluated by a thin film rotating disk

electrode (RDE) technique. The details of the preparation of the thin film electrode can be found elsewhere. The electrode with catalyst thin film was cycled between 0.02 and 1.2 V for 20 cycles in a nitrogen-saturated 0.1 M HClO₄ (GFS Chemicals) at 100 mV s⁻¹. Then a stable cyclic voltammetry (CV) curve that was used to calculate the electrochemical area (ECA) was recorded at 50 mV s⁻¹. The oxygen reduction polarization curves were measured in an oxygen-saturated 0.1 M HClO₄ solution at a scan rate of 10 mV s⁻¹ at 1600 rpm. The kinetic current j_k at 0.9 V was derived by the Koutecky-Levich equation. Long term durability of Pd@Pt/C was tested by potential cycling between 0.65 and 1.0 V (5s each) with a square-wave signal in an oxygen-saturated 0.1 M HClO₄ solution at the room temperature. The ORR polarization curves were recorded after a certain number of cycles. All the potentials were corrected to RHE in this paper.

Molecular Dynamic simulations

The interaction energy of citric acid with Pd and Pt monolayer surfaces was calculated using Material Studio (Version 6.1, Accelrys Inc, 2014) with the Discover module. The periodic canonical ensemble (NVT) with the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) forcefield was used to calculate the potential energy of the system.² This forcefield is particularly useful for this system because its parameters are derived from *ab initio* data, which can be applied to predict organic and inorganic materials in both gas-phases and condensed-phases.³ The palladium lattice ($a = b = c = 3.88 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$) was cleaved into the (111) slab surface with dimensions of $\sim 25 \times 25 \text{ \AA}$ and thickness of 15 \AA . To compare the interaction of the surface with a deposited monolayer of Pt, the top surface of the Pd surface is replaced with Pt atoms, such that they follow the (111) lattice packing system. The adsorption of citric acid was simulated using a model that consists of fifty molecules placed randomly at a distance from the surface with a further 10 \AA vacuum space, and the simulation was run for 300 ps. The interaction energy of the surface molecules with the Pd or Pt monolayer surface was calculated using $E(\text{interaction}) = E(\text{total}) - E(\text{surface}) - E(\text{molecules})$.

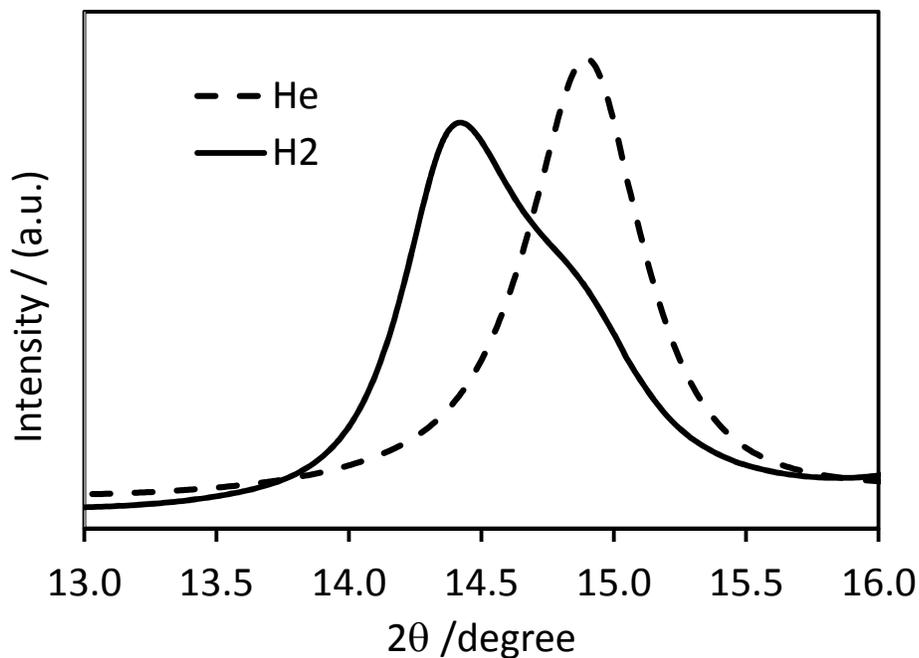


Figure S1. The XRD peak positions of (111) reflection of Pd@Pt/C synthesized without citric acid in He (dashed line) and H₂ (solid line) atmospheres. The shoulder peak at 14.8 degree in the H₂ atmosphere demonstrates the existence of large Pt clusters. The Mo K α ($\lambda = 0.7107 \text{ \AA}$) incident radiation was used in XRD measurements.

References

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