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Gram-Scale-Synthesized Pd₂Co-Supported Pt Monolayer Electrocatalysts for Oxygen Reduction Reaction

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Gram-scale synthesis of Pt_{ML} electrocatalysts with a well-defined core–shell structure has been carried out using method involving galvanic displacement of an underpotential deposition Cu layer. The Pt shell thickness can be controlled by stepwise deposition. The Pt@Pd₂Co/C nanoparticles were characterized by X-ray powder diffraction, aberration-corrected scanning transmission electron microscopy, high-resolution energy-loss spectrometry, and in situ X-ray absorption spectroscopy. A complete Pt shell of 0.6 nm on a Pd₂Co core has been confirmed. The Pt@Pd₂Co/C core–shell electrocatalysts showed a very high activity for the oxygen reduction reaction; the Pt mass and specific activity were 0.72 A mg_{Pt}^{−1} and 0.5 mA cm^{−2}, respectively (3.5 and 2.5 times higher than the corresponding values for commercial Pt catalysts), at 0.9 V in 0.1 M HClO₄ at room temperature. In an accelerated potential cycling test, a loss in active surface area and a decrease in catalytic activity for gram-scale-synthesized Pt_{ML} catalysts were also determined.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are considered a potentially clean power source for automotive and residential applications.¹ However, the promise of their widespread application is seriously hindered by the high content of Pt in the cathode catalysts and the slow kinetics of oxygen reduction reaction (ORR) on Pt catalysts.^{2–4} New catalysts are needed that reduce considerably the Pt content while affording the possibility of enhanced catalytic activity.

Recently, we found that a Pt monolayer (Pt_{ML}) supported on a Pd(111) surface shows higher oxygen reduction kinetics than Pt(111)⁵ and that the effectiveness of the Pt_{ML} catalytic activity can be further improved by fine-tuning the Pt_{ML}–support interaction.⁶ It is generally accepted that changes in the electronic properties of Pt overlayers, particularly shifts of the weighted d-band center resulting from the cumulative contributions of lattice strain and ligand effects, are likely to account for this phenomenon.^{7–9} Studies on model systems helped in achieving a fundamental understanding of the metal–metal interactions that affect the catalytic processes on bimetallic systems, which is essential in designing new catalysts. By applying the knowledge gained from model systems to nanomaterials, we were able to develop a high-efficiency and low-cost novel Pt_{ML} ORR catalyst.^{7,10–14}

The Pt_{ML} placed on Pd and Pd alloy nanoparticles with core–shell structures shows about four or five times higher Pt mass activity than the state-of-the-art Pt catalysts,^{10–14} demonstrating the potential of Pt_{ML} approach for resolving the problem of high Pt content and low efficiency in conventional Pt electrocatalysts. By stepwise deposition of Pt monolayers on Pd and Pd₃Co cores, Wang et al.¹³ showed that the ORR activities vary with Pt shell thickness, core material, and

nanoparticle size. Lattice contractions induced by nanosize effects and lattice mismatch between Pt and the core material reduce the oxygen binding strength, which enhances the ORR activity because the ORR rate is desorption limited on Pt.¹³ This trend also indicates the importance of controlling the Pt shell thickness and uniformity.

A core–shell structure with a well-defined Pt shell can be synthesized using galvanic displacement of an underpotential deposition (upd) Cu layer, which was successfully demonstrated from a rotating disk electrode (RDE) synthesis.^{7,10–14} A method for producing a large quantity effectively is currently being pursued. Synthesis methods based on chemical reactions to produce Pt/Pd core–shell nanoparticles have generally yielded shell thicknesses of 1–2 nm.^{15–17} However, achieving thinner complete shells is difficult. In comparison, a method involving galvanic displacement of an underpotential deposition (upd) Cu layer is environmentally friendly and economical because the Cu solution can be easily recycled and organic surfactant is not used.^{7,10–13} The synthesized catalysts are free of any surface contamination, which is highly favored for fuel cell applications. More importantly, the Pt shell thickness can be controlled through stepwise deposition, which is critical in engineering core–shell nanoparticles with high catalytic activity and cost efficiency.

In this study, we synthesized electrocatalysts comprising a Pt shell on a Pd₂Co/C core in a gram batch in a home-designed glass cell using galvanic displacement of a Cu upd layer.¹⁸ Our previous RDE studies found that Pd–Co alloy is an excellent core material for making Pt_{ML} ORR catalysts.^{11–13,19,20} We report here the structural characterization of the core–shell Pt@Pd₂Co/C catalysts using powder X-ray diffraction (XRD), aberration-corrected scanning transmission electron microscopy (STEM), high-resolution electron energy-loss spectrometry (EELS), and in situ X-ray absorption spectroscopy (XAS). The ORR activity and stability of gram-scale-synthesized core–shell electrocatalysts were determined and tested on an RDE in 0.1

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M HClO₄ solution, and comparison to the same characteristics of electrocatalysts synthesized on an RDE is also discussed.

2. Experimental Methods

2.1. Sample Preparation. A Pt/C sample (46.4 wt %) from Tanaka Kikinzoku (TKK) International Inc. was used as the Pt reference. Two samples of Pt shell on 20% Pd₂Co/Ketjen EC 300J alloy core (Johnson-Matthey) were prepared. One was prepared in a small quantity (denoted thereafter as RDE Pt@Pd₂Co/C), namely, 10 μ g of Pd₂Co/C nanoparticles on a 5-mm-diameter rotating disk electrode (Pine Instruments), which served as a baseline for Pt usage and ORR activity for the catalysts from gram-scale synthesis. The gram-scale-synthesized sample (denoted thereafter as GSS Pt@Pd₂Co/C) was produced in a 300-mg batch in a home-designed glass cell, in which a piece of titanium sheet covered with RuO₂ and two platinized Pt flags were used as the working and counter electrodes. Details of the method and synthesis procedure can be found elsewhere.^{10,18} We studied Cu upd on a Pd₂Co(111) electrode and found that the Cu upd behavior and also the upd charge were very similar to that observed on a Pd(111) surface.¹⁹ Given that the Co atoms on a PtCo alloy crystal immediately dissolved after the surface was exposed to an acidic environment,²¹ it is likely that a similar Co dissolution occurs from a Pd₂Co alloy surface. This would generate a pure Pd shell on Pd₂Co catalyst, upon which a full Cu upd layer can be formed. A two-monolayer Pt shell was achieved by stepwise deposition. The metal contents in the GSS sample (9.4% Pt, 11.4% Pd, and 2.7% Co) were determined by assay elemental analysis using inductively coupled plasma (ICP) emission spectroscopy, whereas the Pt content in the RDE sample was derived from the Cu upd charge.

2.2. Electrochemical Measurements. Preparing a thin film of catalysts on a rotating disk electrode (5-mm diameter, Pine Instruments) involved dispersing a certain amount of catalyst in water (1 mg of catalyst dispersed into 1 mL of water here) and sonicating for ca. 10 min to make a uniform suspension.^{10,22} Then, 10 μ L of this suspension was placed on a glassy carbon disk and dried in the air. The electrode was covered with 5 μ L of a 4 μ g/10 μ L Nafion solution (diluted with water from 5% Nafion solution by Aldrich) and dried again before the ORR measurements.

K₂PtCl₄ (Premion, 99.99%) and CuSO₄ (anhydrous, reagent grade) were purchased from Alfa-Aesar, and all solutions were made with Milli-Q water (Millipore, Bedford, MA). All potentials were measured with a Ag/AgCl (3 M Cl⁻) electrode (Bio), but reported with respect to reversible hydrogen electrode (RHE). All electrochemical and ORR activity measurements were performed in oxygen-saturated 0.1 M HClO₄ (Optima, Fisher) solution at room temperature. The electrochemical surface area (ECSA) was calculated using the charges determined from an integrated H adsorption peak assuming of 210 μ C/cmPt².

2.3. X-ray Diffraction Measurements. Powder X-ray diffraction (XRD) patterns were obtained with a commercial diffraction meter (Phillips 3100) using Cu K α radiation (1.54056 Å). Samples for analysis were made by spreading catalyst slurries on glass slides and drying them in air. Diffraction patterns were collected from 20° to 80° at a scanning rate of 0.6° min⁻¹, with a step size of 0.02°.

2.4. X-ray Absorption Spectroscopy Measurements. In situ X-ray absorption spectroscopy (XAS) and extended X-ray absorption fine structure (EXAFS) measurements were carried out at the X19A and X-18B beamlines in National Synchrotron Light Source at Brookhaven National Laboratory (BNL). A

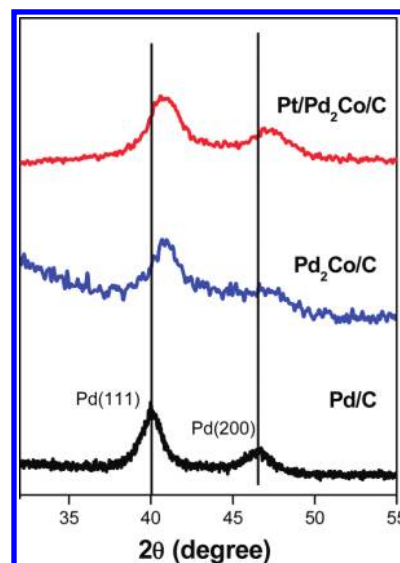


Figure 1. XRD diffraction patterns of Pd/C, Pd₂Co/C, and Pt@Pd₂Co/C nanoparticles.

proton-exchange membrane (Nafion 117, DuPont Chemical Co.) covering Pt@Pd₂Co/C core-shell catalysts loaded on a carbon film (Grafoil, Union Carbide Corp.) and a platinum foil were used as the working and counter electrodes, respectively. The electrochemical cell was described in detail elsewhere.^{18,23,24} In situ XAS data were acquired in transmission mode at the Pt L₃ edge (11564 eV), the Pd K edge (24350 eV), and the Co K edge (7709 eV) in 1 M HClO₄ solution at different potentials at room temperature in air. The X-ray energies were calibrated prior to each measurement for the Pt L₃, Pd K, and Co K edges using the corresponding bulk metal foils. The data were processed by ATHENA software.²⁵

2.5. Scanning Transmission Electron Microscopy Measurements. Atomically resolved scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) experiments were performed using the Hitachi aberration-corrected scanning transmission electron microscope (HD-2700C) at the Center for Functional Nanomaterials at BNL. The microscope was equipped with a cold-field emission source and a high-resolution Gatan Enfina energy-loss spectrometer. Under normal operating conditions, a probe size of 0.1 nm with a 0.4 eV energy resolution is routinely achieved.

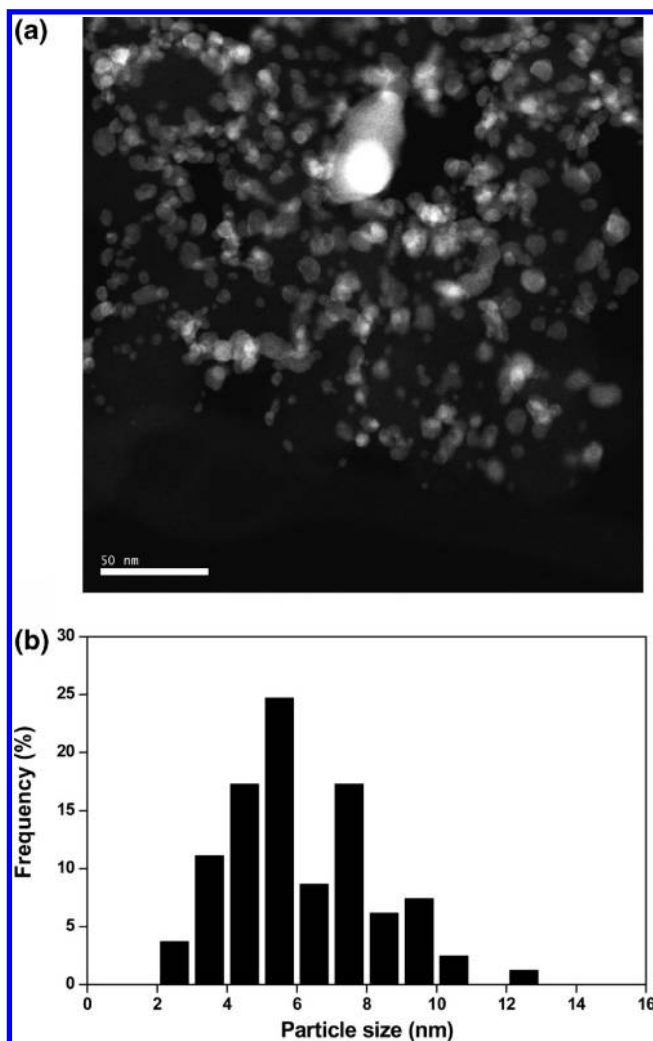
3. Results and Discussion

Figure 1 shows the XRD results for Pd₂Co/C, Pt@Pd₂Co/C, and Pd/C (reference) samples. The Pd₂Co/C sample shows characteristic diffraction patterns for the face-centered-cubic (fcc) structure of Pd and a shifting of its diffraction lines to higher 2 θ positions compared to those from Pd/C, indicating alloy formation. The Pd₂Co/C sample has a smaller lattice parameter (3.824 Å) than the Pd/C sample (3.881 Å), and this evidences the incorporation of Co atoms into the Pd lattice. Although the diffractions peaks for the Pt@Pd₂Co/C sample remained essentially at the same 2 θ positions as found for Pd₂Co/C, the diffraction peaks were broadened and became asymmetrical, suggesting that a Pt overlayer formed on top of Pd₂Co nanoparticles.¹¹ The average particle sizes of Pd₂Co/C and Pt@Pd₂Co/C, estimated from XRD using Scherrer's equation, were 3.6 and 5.1 nm (see Table 1), respectively, in good agreement with the STEM results.

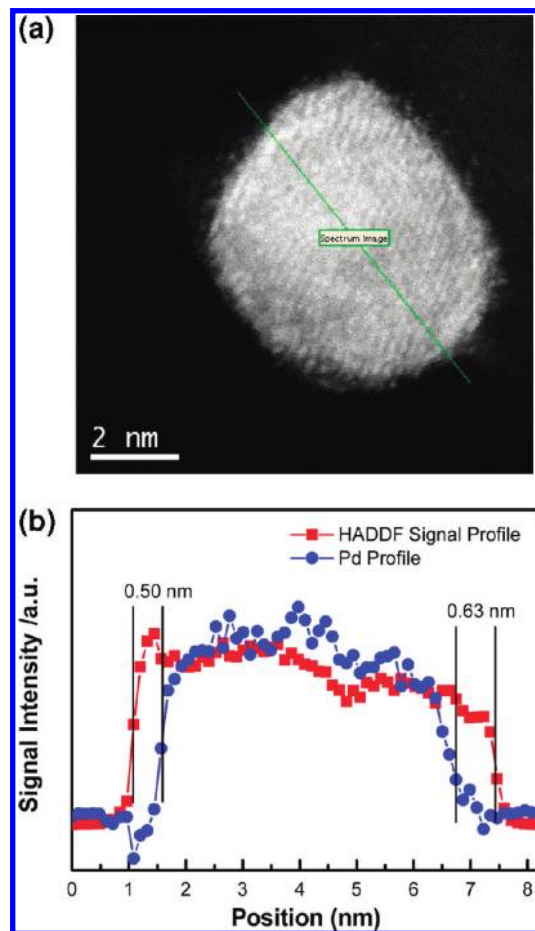
An STEM image of GSS Pt@Pd₂Co/C sample, taken in high-angle annular dark field (HAADF) detection mode (collection

TABLE 1: Average Particle Size, Electrochemical Surface Area (ECSA), Pt Mass, and Specific Activity of Pt@Pd₂Co/C and Pt/C Catalysts for the ORR

sample	particle size (XRD) (nm)	ECSA (m ² /g _{Pt})	mass activity j_k (0.9 V) (A mg _{Pt} ⁻¹)	specific activity j_k (0.9 V) (mA cm ⁻²)
Pt/C	3.1	85	0.2	0.23
Pt@Pd ₂ Co/C ^a	n/a	179	1.02	0.57
Pt@Pd ₂ Co/C ^b	5.1	129	0.7	0.54

^a RDE synthesis. ^b Gram-scale synthesis.**Figure 2.** (a) HAADF-STEM image of as-made Pt@Pd₂Co/C nanoparticles from gram-scale synthesis, along with (b) statistical results from the analysis of many different regions of nanoparticles. The histogram of particle size distributions indicates an average particle size of 5.4 ± 3.5 nm. A scale bar of 50 nm is included in image a.

angles of 64–341 mrad), is shown in Figure 2. The histogram of the particle size distribution indicates an average particle size of 5.4 nm with a somewhat broad size distribution. Coupling element-sensitive EELS with HAADF images offers further information on the thickness and uniformity of the Pt shell. Numerous individual particles of different sizes were imaged, and their Pt shell thicknesses were analyzed simultaneously by element-sensitive EELS spectroscopy. Both signals from the Pd $M_{4,5}$ and Co $L_{2,3}$ edges were detected by EELS mapping, but the data from the Co $L_{2,3}$ edge were very weak and could not be used to determine the distribution of Co in the nanoparticles. We measured the background-subtracted EELS signal intensity for the Pd $M_{4,5}$ peak between 357 and 412 eV and the HAADF

**Figure 3.** (a) Representative HAADF-STEM image of an as-made Pt@Pd₂Co/C nanoparticle from gram-scale synthesis. (b) Comparison of the corresponding HAADF (red) and Pd EELS (blue) intensity profiles in a line scan indicated in image a. HAADF and Pd EELS profiles were aligned with reference to the signal in a vacuum.

intensity in line scans to determine the sizes and shapes of the Pd core and the entire particle. Figure 3a shows a representative STEM image of a particle (~ 6.5 nm) with a line indicating where the line scan was conducted across the particle. A comparison of the HAADF and Pd EELS intensity profiles enables the direct extraction of the contribution of the Pt layers to the particle. As shown in Figure 3b, the differences of the two profiles are from 0.50 to 0.63 nm, measured at the half value of intensity, corresponding to an approximately two-monolayer Pt shell on the Pd₂Co alloy core. Measurements of many particles found some particles with inhomogeneous Pt shells (not shown). Although Pd₂Co/C nanoparticles with inhomogeneous Pt shells are present in a small proportion, these nanoparticles could be largely responsible for the activity loss observed in a stability test by potential cycling, as discussed later.

The core–shell structure of a Pt shell on a Pd₂Co/C core was further confirmed by in situ XAS studies. In situ XAS measurements of the GSS Pt@Pd₂Co/C sample in 1 M HClO₄ at room temperature at different potentials in air were carried out, and the corresponding Pt L_3 , Pd K , and Co K edges were recorded. Figure 4a shows the normalized Pt L_3 edge from Pt@Pd₂Co/C nanoparticles at four potentials. The white line intensity of the Pt L_3 edge did not show any noticeable change until the applied potential was positive of 0.90 V and exhibited a significant increase at 1.12 V with respect to that at 0.42 V. The increase of the white line intensity is due to Pt–O(H)

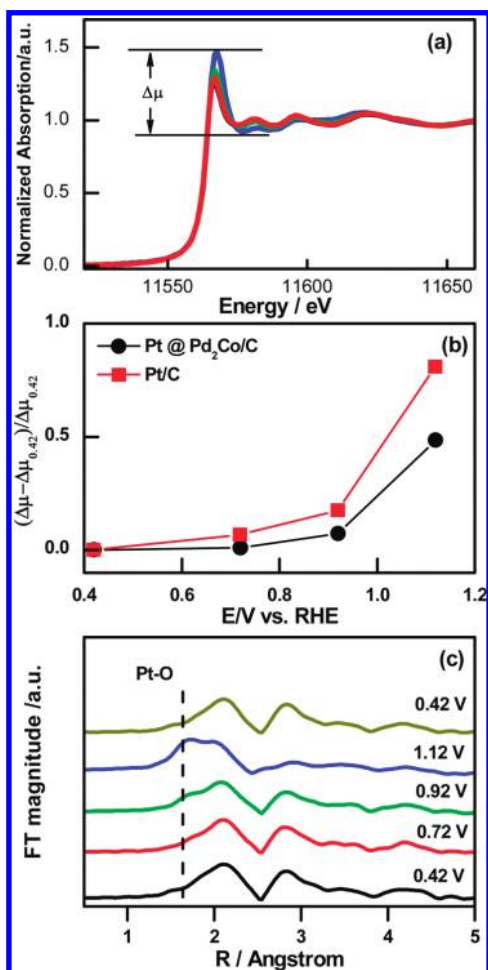


Figure 4. (a) In situ XANES signals from Pt L₃ edge for GSS Pt@Pd₂Co/C nanoparticles obtained in 1 M HClO₄ in air at four different potentials. (b) Comparison of the change of the adsorption peak as a function of potential for Pt@Pd₂Co/C and Pt/C. (c) Forward Fourier transform of EXAFS spectra (*k*³-weighted). The peak marked by a dotted line is assigned to Pt–O(H) coordination.

formation, causing a depletion of Pt d-band electrons.^{10,24} Figure 4b shows the relative changes of the Pt L₃ peak $[\Delta(\mu_E - \mu_{0.42})/\Delta\mu_{0.42}]$ as a function of potential for Pt@Pd₂Co/C and Pt/C nanoparticles as well, presenting clear evidence of suppressed oxidation of the Pt shell in comparison with pure Pt nanoparticles. In the Fourier transform of the EXAFS spectra (Figure 4c), a peak at low *R* value (<0.20 nm) clearly appeared at 0.92 V, increased significantly at 1.12 V, and disappeared as the potential was stepped back to 0.42 V. This peak appearing at low *R* value is due to oxygenate formation and reduction on the Pt surface at different potentials,^{24,26} and its intensity change with potential is consistent with the chemical information derived from cyclic voltammetry (inset in Figure 7 below). A decrease in the number of Pt–Pt and/or Pt–Pd interactions due to oxygenate adsorption is also evidenced from the peak intensity change at high *R* value (~0.28 nm): this peak decreased in intensity with increasing potential, almost disappeared at 1.12 V, and recovered again at 0.42 V. You et al.²⁷ reported that the movement of Pt atoms from their original sites [i.e., Pt and O(H) place exchange] on the Pt(111) surface occurred at 1.05 V in HClO₄ solution and that the number of Pt–Pt interactions on the surface hence decreased. Mukerjee et al.²⁴ also reported a similar decreasing of Pt–Pt interactions due to surface oxygenate formation on Pt alloy catalysts at high potentials.

Figures 5 and 6 show in situ XAS and Fourier transform spectra of EXAFS data for the K edges of Pd and Co,

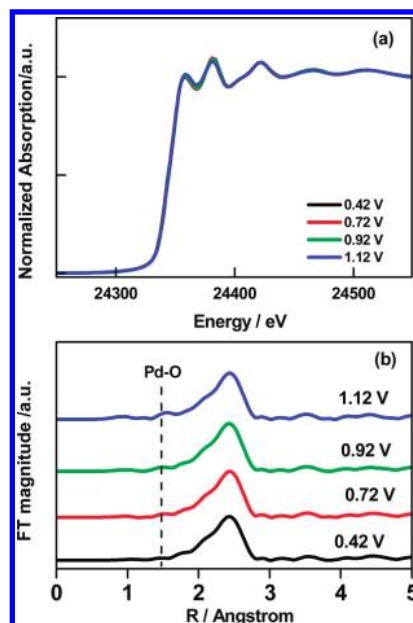


Figure 5. (a) In situ XANES and (b) forward Fourier transform of EXAFS spectra (*k*³-weighted) of Pd K edge for GSS Pt@Pd₂Co/C nanoparticles obtained in 1 M HClO₄ in air at four different potentials.

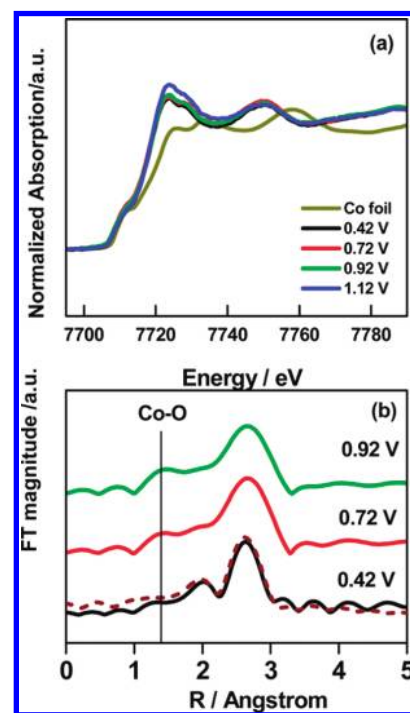


Figure 6. (a) In situ XANES and (b) forward Fourier transform of EXAFS spectra (*k*³-weighted) of Co K edge for GSS Pt@Pd₂Co/C electrocatalysts obtained in 1 M HClO₄ in air at different potentials. The XANES spectrum from Co foil is shown as a reference. A fitting including Co–O and Co–Pd interactions for Fourier transform of EXAFS spectra obtained at 0.42 V is also shown in b.

respectively, from the GSS Pt@Pd₂Co/C sample obtained under the same conditions as for the Pt L₃ edge. The white line intensity of the Pd K edge (Figure 5a) shows barely any changes with increasing potential, suggesting that the Pd atoms in the Pd₂Co core material retain the same metallic form and that no appreciable amount of oxygenate species adsorb on the Pd sites in the potential range of 0.42–0.92 V. A slight increase in the white line intensity of the Pd K edge and a small but visible bump at low *R* value (<0.20 nm) in the corresponding Fourier

transform spectra (Figure 5b) suggest a Pd–O(H) interaction forming at 1.12 V where Pt and O(H) place exchange can occur on a Pt(111) surface.^{27,28} These results indicate that the Pt layers deposited on Pd₂Co nanoparticles completely block palladium oxide formation in acidic environments to very high potentials (>0.92 V) where Pt–O(H) already forms, further confirming the formation of a complete Pt shell on a Pd₂Co alloy core.

We observed a different potential dependence for the Co K edge (Figure 6a) compared to the Pd K edge. The white line intensity of the Co K edge increased slightly as the potential increased from 0.42 to 1.12 V. Comparing with metallic Co foil, however, the Co in Pt@Pd₂Co nanoparticles had a higher white line intensity and a slightly smaller pre-edge peak, suggesting that some of the Co atoms in the nanoparticles might not be in metallic form even at 0.42 V. A fitting (dash line in Figure 5b) including the Co–O and Pd–Co contributions shows good agreement with the Fourier transform spectra obtained at 0.42 V, confirming the existence of Co–O species [indicated in the *R*-space spectra at low *R* values (<0.2 nm)]. The Co–O peak seemingly increased in intensity with increasing potential. Because the signal contributions of dissolved Co ions might overlap with those of Co–O species from the sample, the electrolyte was replaced after each potential stepping measurement from 0.42 to 1.12 V, but both peaks at low and high *R* values showed marginal changes before and after electrolyte replacement. This result suggests that the signal observed at low *R* value comes from the sample rather than the solution phase. The nanoparticles after in situ XAS measurements were collected and washed with large amounts of water and then sent for ICP measurements. ICP analysis showed that the amount of Co remaining (1.7 wt %) after in situ XAS measurements was lower than the amount in the as-made sample (2.7 wt % Co), indicating that Co dissolution occurred during in situ XAS measurements. It is quite difficult to provide a clear structural model locating cobalt oxide species in our core–shell nanoparticles from the present study. However, a segregation of subsurface Co or Ni atoms to the surface occurs in Pt–Co (Ni) systems in oxygen-rich environments.^{29,30} Mukerjee et al.²⁴ also reported the formation of cobalt oxide on a Pt/Co alloy from an in situ XAS study. In our Pt@Pd₂Co/C core–shell nanoparticles, even though the Co atoms are initially protected by a Pt shell, Co segregation to the nanoparticle surface as a result of O adsorption might occur, which would lead to the slow formation of cobalt oxide on the surface and its subsequent dissolution in acidic environments. Nevertheless, from the combined in situ XAS and ICP measurements, we concluded that there are still considerable amounts of Co atoms in the Pt@Pd₂Co/C nanoparticles being protected by a Pt shell, which could play a vital role in tuning the electronic properties of Pd and, hence, the electronic and chemical properties of the Pt shell.^{11–13,19}

The ORR activity of the GSS Pt@Pd₂Co/C catalysts was tested on an RDE in a regular electrochemical cell. Figure 7 shows a set of polarization curves for the ORR on the GSS sample in oxygen-saturated 0.1 M HClO₄ at room temperature at different rotation speeds. The inset in Figure 7 shows the Koutecky–Levich plots. The polarization curves have two characteristic regions: a well-defined limiting-current region (0.2–0.8 V) and a mixed diffusion–kinetic control region (0.8–1.05 V). The linearity and parallelism of the Koutecky–Levich plots (inset in Figure 7) suggest first-order kinetics with respect to molecular oxygen.³¹ Polarization curves for the ORR on the RDE and GSS Pt@Pd₂Co/C samples as well as on Pt/C (reference) at 1600 rpm at room temperature are compared in

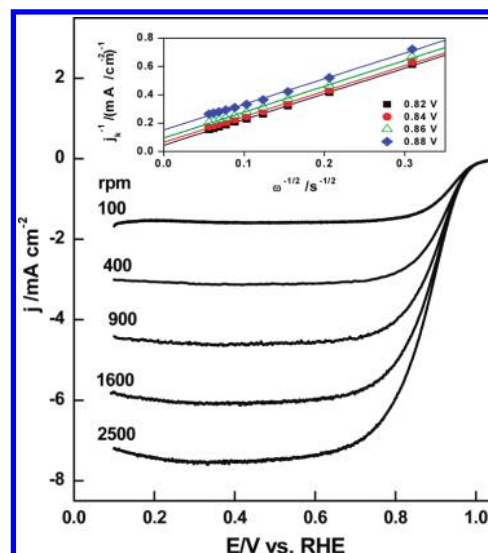


Figure 7. Polarization curves in positive-going scans for the ORR on GSS Pt@Pd₂Co/C electrocatalysts in oxygen-saturated 0.1 M HClO₄ at room temperature at different rotating speeds; the scan rate was 10 mV s⁻¹. The inset shows the Levich–Koutecky plot at various potentials.

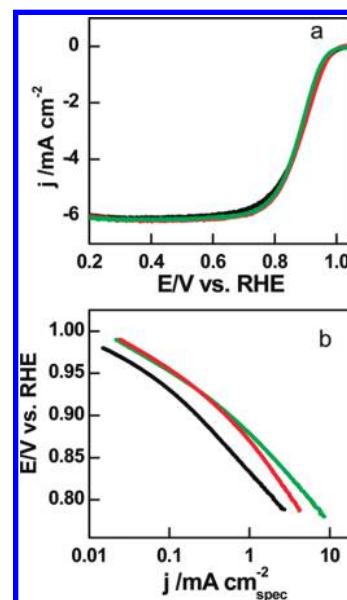


Figure 8. (a) Comparison for the ORR on the RDE- (green) and GSS- (red) synthesized Pt@Pd₂Co/C electrocatalysts, and also on Pt/C (black) at 1600 rpm. (b) Tafel plot for the comparison of ORR specific activities of the corresponding three catalysts. All measurements were made in oxygen-saturated 0.1 M HClO₄ at room temperature at a scan rate of 10 mV s⁻¹. The Pt loading was 4, 7, and 21.6 μg cm_{GCE}⁻² for the RDE and GSS samples and the Pt/C (reference) catalyst, respectively.

Figure 8a. Diffusion-current-corrected Tafel plots for these three samples are shown in Figure 8b, wherein the kinetic currents normalized to specific surface areas were obtained from the Koutecky–Levich plots.^{3,31} In the high-current-density region, the RDE sample showed a slightly higher Tafel slope than the GSS sample. At 0.9 V, the mass and specific activities for the GSS Pt@Pd₂Co/C sample were 0.72 A/mg_{Pt} and 0.5 mA cm⁻², respectively, exhibiting 3.5- and 2.5-fold enhancements compared to the same values for commercially available TKK Pt/C (0.2 A/mg_{Pt} and 0.23 mA cm⁻²). Our XAS study (Figure 4b) clearly shows a suppression of O or OH formation on Pt@Pd₂Co/C that could be mainly attributed to Pt electronic structure modification by the nanosize- and lattice-mismatch-

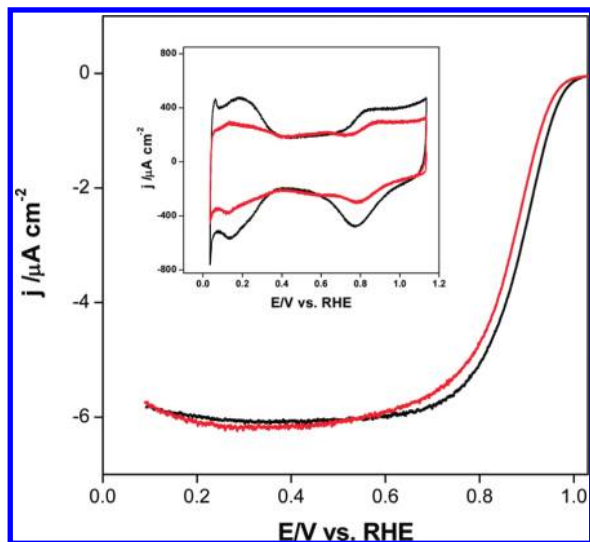


Figure 9. Polarization curves for the ORR on GSS Pt@Pd₂Co/C electrocatalysts at 1600 rpm in oxygen-saturated 0.1 M HClO₄ at room temperature before (black) and after (red) 6500 cycles; the scan rate was 10 mV s⁻¹. The inset shows the corresponding cyclic voltammetry in argon-saturated 0.1 M HClO₄; the scan rate was 50 mV s⁻¹. Stability testing measurements were performed using the square-wave function method between 0.65 and 1.15 V (10 s at each potential) on an RDE electrode in 0.1 M HClO₄ in air at room temperature.

induced strain, which, in turn, weakens the Pt–O(H) interaction and decreases the O(H) coverage on the Pt surface.^{6,13,19,32} This electronic structure modification of Pt by the Pd₂Co substrate is likely responsible for the enhanced ORR activity with respect to Pt/C.^{6,13,19,32} This result is in line with our previous observations for Pt monolayer electrocatalysts deposited on metal or metal oxide substrates.^{7,10,11,13,33,34} The Pt mass and specific activity of the GSS Pt@Pd₂Co/C sample are approaching those of the RDE sample (1.02 A/mg_{Pt} and 0.61 mA cm⁻²) (Table 1). This reproduction of ORR activity on GSS sample (Figure 8a) might suggest a successful translation of the important structural and electronic properties of the RDE-synthesized core–shell catalysts to the gram-scale material. It also demonstrates the advantages of applying the galvanic displacement of a Cu up layer to the large-scale synthesis of catalysts with well-defined core–shell structures and tunable shell thicknesses below 1 nm.

The long-term stability of an electrocatalyst is a critical requirement for its application in fuel cells. Herein, the stability of the GSS Pt@Pd₂Co/C catalysts was tested between 0.70 and 1.15 V (10 s at each potential) on an RDE using the potential square-wave cycling method in air at room temperature. The positive potential window in this stability test was set to 1.15 V, which is higher than the U.S. Department of Energy protocol requirement for fuel cell catalysts test,³⁵ which is intended for studying catalyst degradation under accelerated conditions on a short time scale. Figure 9 shows polarization curves for the ORR on the GSS Pt@Pd₂Co/C sample before and after 6500 potential cycles in 0.1 M HClO₄. The inset in Figure 9 shows the corresponding cyclic voltammetry (CV) measured in argon-saturated 0.1 M HClO₄ solution. A decrease in H adsorption and desorption charges was observed after the potential cycling test compared with those before cycling. The catalyst lost ~50% of its electrochemical surface area, and its half-wave potential (*E*_{1/2}) shifted negatively by ~22 mV following the potential cycling test.

Figure 10 shows a representative STEM image together with a histogram of the particle size distribution for the GSS sample

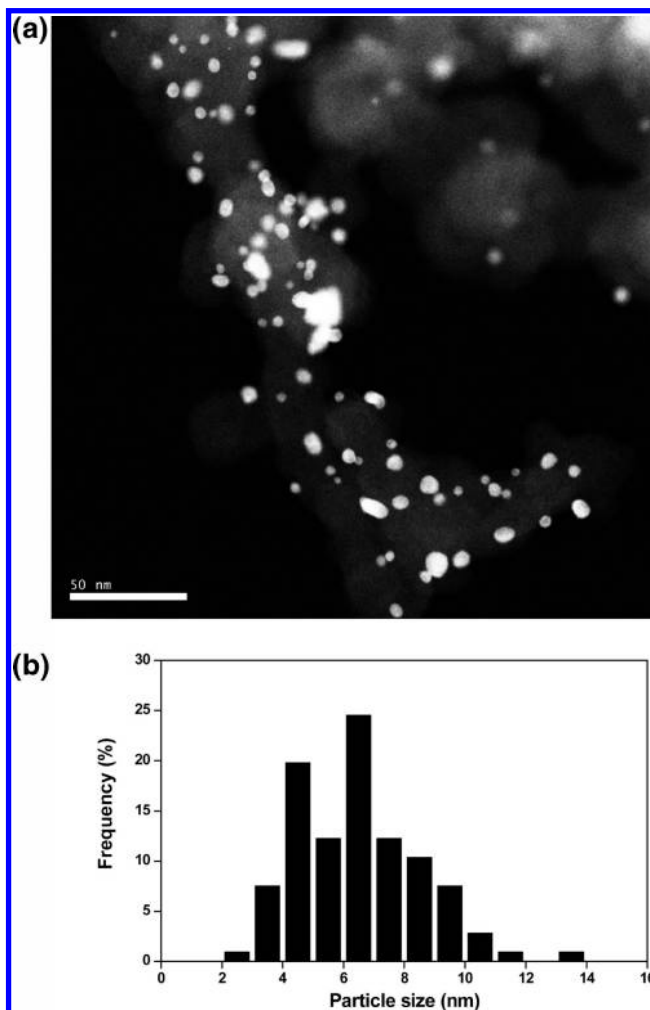


Figure 10. (a) HAADF-STEM image of GSS Pt@Pd₂Co/C nanoparticles after potential cycling test, along with (b) statistical results from the analysis of many different regions of nanoparticles. The histogram of particle size distributions indicates an average particle size of 6.5 ± 4.5 nm. A scale bar of 50 nm is included in image a.

after potential cycling test. According to a statistical evaluation of the nanoparticles in several investigated locations, the particle size increased slightly after the potential cycling test, from 5.4 nm (before cycling) to 6.5 nm (after cycling), whereas the size distributions in the two cases were almost the same (85% of the particles were in the 3.5–8.5-nm range). Numerous individual particles were also imaged, and their Pt shell thicknesses were analyzed simultaneously by EELS. A representative particle image is shown in Figure 11a, and the Pt shell thickness was derived from a comparison of the HAADF and Pd EELS intensity profiles (Figure 11b). Along the line scanned across the particle, the Pt shell thickness was around 0.5 nm at one side and 1.2 nm at the other side. Similar observations were found on other individual particles: the Pt shell seemingly grew significantly at part of catalyst surface during the potential cycling test. As mentioned above, a small portion of particles with inhomogeneous Pt shell could be less stable under the accelerated potential cycling test, because Pd atoms are unlikely to survive above 0.95 V in an acidic environment and, therefore, could be partly responsible for the loss of active surface area and change in Pt shell morphology. Segregation of Co atoms to the nanoparticle surface in an O₂-rich environment and subsequent dissolution in acid could also occur in the dynamic oxidizing and reducing conditions applied during electrochemical treatment.^{29,30,36} Dissolution of Co atoms might also cause

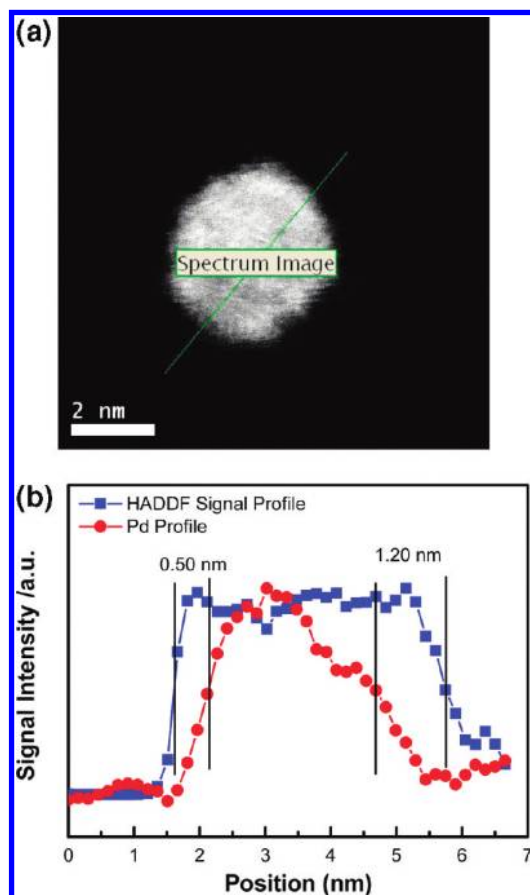


Figure 11. (a) Representative HAADF-STEM of a Pt@Pd₂Co/C nanoparticle from gram-scale synthesis after potential cycling test. (b) Comparison of the corresponding HAADF (red) and Pd EELS (blue) intensity profiles in a line scan indicated in a. HAADF and Pd EELS profiles were aligned with reference to the signal in a vacuum.

a change in the structure and composition of the nanoparticles,^{29,30} which could lead to the migration and reprecipitation of Pt to nearby particles. It is also worth mentioning that the amount of particles in several TEM-investigated locations seemed to decrease after the potential cycling test compared to that before cycling, suggesting that particles might detach from the carbon support during the stability test as a result of carbon corrosion at very high potentials (1.15 V vs RHE in our study).³⁷ This conclusion from statistical evaluation of a few locations on TEM samples needs to be further verified by other techniques, although it could be one of the reasons for the loss of active surface area, as demonstrated in a recent report by Mayrhofer et al.³⁸ As a consequence of the loss of active surface area and change in Pt shell morphology, the catalytic activity of the catalysts for the ORR decreased.

4. Summary

We have shown that a gram-scale synthesis of Pt_{ML} electrocatalysts with a well-defined core-shell structure and very high catalytic activity for the ORR can be produced using galvanic displacement of a Cu upd layer and that the Pt shell thickness can be controlled by stepwise deposition. The homogeneous and complete nature of the Pt shells on the Pd₂Co/C core nanoparticles was confirmed through combined STEM-EELS measurements, and protection of the Pd atoms in the core by the Pt shell was evidenced through in situ XAS measurements. The gram-scale-synthesized catalysts reproduced the Pt mass activity and specific activity for the ORR observed on an RDE-

synthesized sample and represented about a 3-fold enhancement over that of the state-of-the-art commercial Pt catalysts, suggesting a successful translation of the important structural and electronic properties of model catalysts to the gram-scale-synthesized materials. The galvanic displacement of a Cu upd layer demonstrated through gram-scale synthesis of Pt (shell)-Pd₂Co (core) catalysts seems very promising in scaled-up synthesis of property-tunable and highly active, cost-effective nanoparticles with a core-shell structure suitable for specific catalytic reaction requirements.

A loss of electrochemical surface area and a decrease in ORR catalytic activity for the GSS sample were determined in an accelerated stability test by potential cycling to 1.15 V. The mechanisms of Pt loss are likely due to Pd and Co dissolution and redeposition of Pt on nearby nanoparticle surfaces, and particles detaching from the carbon support could also be largely responsible for the decrease in active surface area. Our results suggest that a two-layer Pt shell is seemingly unable to completely block Co segregation to the nanoparticle surface in an O₂-rich environment and to prevent its dissolution in an acidic environment. As a consequence of the loss in active surface area and the change in Pt shell morphology, the catalytic activity decreases as well. These results provide guidelines for work aimed at further increasing the catalyst's stability while keeping its activity high.

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