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# Cobalt-Doped Pd@Pt Core—Shell Nanoparticles: A Correlative Study of Electronic Structure and Catalytic Activity in ORR

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the synthesized catalyst with X-ray absorption fine structure at the Pt L3-edge and cobalt K-edges, together with performance tests, has revealed information about the effect of the dopants on the catalytic activity of catalysts. The results of the local and electronic structures of the catalysts are correlated with electrocatalytic activity to optimize performance. Cobalt has been found to be simultaneously efficient in enhancing catalytic activity, increasing long-term durability, and reducing the platinum content in the catalysts.

# 1. INTRODUCTION

Depletion of petroleum-based energy resources and the serious impact of climate change have made fuel cell technologies a reliable alternative to current power sources.<sup>1,2</sup> Among all fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) have been acknowledged as a clean and sustainable technology for energy conversion in portable and transportation applications. However, the necessity of using platinum-based catalysts, high overpotential, and the sluggish kinetics of oxygen reduction reaction (ORR), as a cathodic reaction in PEM fuel cells, pose a significant obstacle to their large-scale commercialization.<sup>3</sup>

cobalt to further boost their durability and activity. Characterizing

To overcome these challenges, the surface active area, specific activity, and durability of the catalysts must be enhanced, while minimizing the use of platinum. This can be achieved by optimizing the binding energy of oxygenated species using different strategies. Until now, the primary strategy has been tuning the Pt d-band center of the catalysts by alloying it with other 3d transition metals such as Ni, Co, or Fe.<sup>4–6</sup> Alloyed NPs with their modified surface properties and reactivity through the strain effect, by altering platinum lattice parameter, and ligand effects, by the interaction of platinum with other transition metals, have been shown to be a promising inexpensive candidate for the ORR reaction. Specifically, the PtCo catalyst has exhibited high activity in both half-cell and single-cell

tests.<sup>7–10</sup> Another efficient strategy is to reduce the platinum loading and enhance its overall activity by coating a thin layer of platinum on a less expensive core.<sup>11-13</sup> Although the core-shell structure will have the exact same surface active area as the same size pure platinum nanoparticle, its mass activity can be elevated due to lower platinum usage. Recently, palladium has been widely used as a substrate for platinum deposition in core-shell catalysts due to their close lattice match, and both theoretical and experimental studies have shown that the activity can be enhanced as a result of electronic coupling between Pd and Pt. Another strategy for obtaining a decent ORR performance in platinum would be hindering its shape to some specific facets and optimizing the surface structure through shape-controlled synthesis, as ORR is a structure-sensitive reaction.<sup>14,15</sup> The specific activity of Pd@Pt core@shell catalyst has shown to increase in the order of (100) < (110) < (111).<sup>16–18</sup> In all cases, the Pt d-band center will be downshifted, resulting in reduced

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Scheme 1. Snapshot of the Whole Particle, Illustrating the Synthesis Procedure of Pd@Pt-Co Nanoparticles, which can be Divided into Three Main Steps



oxygen binding energy on platinum.<sup>19–21</sup> Stamenkovic et al. have demonstrated that the d-band center has an optimum value, and the highest specific activity follows a volcano plot in relation to oxygen binding energy.<sup>22,23</sup> Despite the sole incorporation of all these techniques in previous studies and reports showcasing the successful synthesis of Pt-based catalysts with remarkable activity toward ORR, practical use is still confined due to their low durability in the corrosive operating conditions of ORR. The low durability is mainly attributed to the thermodynamically unstable structures, which are necessary for highly active catalysts, but result in rapid performance losses.

To overcome these difficulties, it is essential to control the surface and near surface structure; the nature and position of each atom can substantially influence the catalytic performance and durability. Recent studies have explored the possibility of adding transition-metal dopants to the near surface region for a chance to introduce a class of active and stable Pt-based catalyst. For example, Beermann et al. found that adding Rh as a dopant in Pt-Ni NPs increased stability and improved the persistence of the catalyst morphology in durability tests.<sup>24</sup> In another study, Choi and colleagues reported that Au dopants were effective in reducing Pt dissolution under dynamic potential cycling, and nickel dopants significantly boosted the durability of Pd@Pt NPs in ORR conditions.<sup>25,26</sup> Positive outcomes were also observed for the use of transition metals, such as Mo, Co, Cr, Mn, and Fe in Pt<sub>3</sub>Ni NPs, which helped to acquire a stable octahedral shape even after durability tests of more than 16,000 potential cycles. Additionally, molybdenum and copper have shown to be effective dopants in Pt-Ni NPs, demonstrating outstanding performance and stability in ORR reaction.<sup>27</sup>

Although previous studies have introduced Pt-based catalysts with enhanced activity and stability, the specific role of the dopant element is still elusive. In order to overcome this challenge and maximize the usage, activity, and durability of platinum, this work combines the benefits of all of these strategies to synthesize a shape-controlled cobalt-doped Pd@Pt catalyst. The focus is on Pd@Pt core@shell NPs due to their unique structure, which modifies the structural and electronic properties of Pt, resulting in significant mass activity and durability toward ORR.<sup>28,29</sup> Cobalt is also chosen as the dopant because of its substantial role in increasing the durability of Ptbased catalysts.<sup>30–33</sup> Octahedral Pd@Pt is also reviewed and confirmed to have the highest ORR performance among all other facets.<sup>16,18</sup> To the best of our knowledge, this is the first time that cobalt has been used as a metal dopant in a Pd@Pt core—shell structure to enhance both the activity and durability. By combining synthetic efforts, electrochemical measurements and ex-situ and in situ synchrotron-based X-ray absorption spectroscopy (XAS), the study demonstrates that the cobaltdoped Pd@Pt NP is an effective and state-of-the-art electrocatalyst for ORR, due to its simultaneous remarkable electrocatalytic activity and superior stability with respect to undoped NPs and commercial Pt/C catalysts. This implication can be extended to practical fuel cell applications.

# 2. EXPERIMENTAL SECTION

2.1. Synthesis of Pd@Pt and Co-Doped Pd@Pt Octahedral Nanoparticles. In this study, a previous explained colloidal chemistry method was used to synthesize Pd nanoparticles with tunable size and shape, as the properties of NPs depend highly on these factors.<sup>34</sup> To prepare the core–shell catalysts, the first step is to synthesize Pd seeds with a cubic morphology. The synthesis process involves placing 8.0 mL of aqueous solution containing: Poly(vinylpyrrolidone) (PVP, 105 mg, acting as a stabilizer), ascorbic acid (AA, 60 mg), and potassium bromide (KBr, 600 mg, acting as a capping agent) in a 20 mL vial and preheating it for 10 min at a temperature of 80  $^{\circ}$ C. Then, 3.0 mL of aqueous solution containing Na<sub>2</sub>PdCl<sub>4</sub> (57 mg) was injected to the solution, and the reaction was proceeded for another 3 h at the same temperature.<sup>35</sup> The products were collected by centrifugation, washed at least 3 times with a mixture of ethanol and water to eliminate PVP, and finally dispersed in water. Scanning electron microscopy (SEM) figure of cubic Pd NPs is shown in Figure S1A.

In the next step, Pd octahedral NPs are synthesized using Pd NCs as seeds. Heating the following solution: poly-(vinylpyrrolidone) (105 mg), formaldehyde (0.1 mL), pure water (8 mL), and cubic seeds (0.3 mL) at a temperature of 60 °C for 5 min and adding 2.9 mL of aqueous solution containing  $Na_2PdCl_4$  (29 mg) will result in octahedral Pd NPs after 3 h of



**Figure 1.** (A,B) Bright-field TEM images of octahedral Pd@Pt-Co core-shell nanocrystals. (C) Typical low-resolution STEM image of octahedral cobalt-doped Pd-Pt nanocrystals on carbon black. (D) HAADF-STEM image of a single Pd@Pt-Co nanoparticle. (E) STEM-EDX elemental mapping images of Pd, Pt, and Co, along with the merged image. (F) Elemental line-scanning profiles along the direction marked by a white line in panel "D".

reaction proceeding. The resulting product was washed with a mixture of water and ethanol at least three times before being dispersed in EG.<sup>36</sup> SEM images of both the as-synthesized cubic and octahedral palladium NPs are shown in Figure S1.

Then, Pd seeds were utilized as the starting material to synthesize octahedral Pd@Pt core-shell nanoparticles. To

achieve a uniform and smooth platinum shell that covers the palladium core, a water-based system was used.<sup>37</sup> The water-based approach offers several advantages over other conventional methods, such as a higher yield of the final product and a significantly shorter reaction time.<sup>38</sup> To deposit four layers of Pt, a mixture of 35 mg of PVP, 60 mg of citric acid, and 10 mL of

octahedral Pd (obtained from the first step) was preheated for 10 min at a temperature of 95 °C. After heating the solution, 3 mL of K<sub>2</sub>PtCl<sub>4</sub> (1.4 mg mL<sup>-1</sup>) was added in one pot to the mixture, and the reaction was allowed to proceed under magnetic stirring for an entire day. The samples were collected by centrifugation and were further doped with Co to investigate its impact on ORR kinetics. The doping process involved dispersing the core–shell nanoparticles and cobalt(II) acetylacetonate [Co-(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>, 99%], as the dopant precursor, in DMF, and heating the solution for 48 h at 170 °C.<sup>39</sup> Scheme 1 shows a schematic of the synthesis procedure. The final doped nanoparticles were then centrifuged, washed, and loaded onto carbon black (Vulcan XC-72) to investigate their electrochemical behavior. The metal loading (Pd + Pt) on carbon black

mass spectrometry (ICP-MS). 2.2. Characterization of the Nanoparticles. These nanoparticles were characterized using several techniques such as ICP-MS, X-ray diffraction (XRD), XAS, X-ray photoemission spectroscopy (XPS), transmission electron microscopy (TEM), SEM, and high-resolution transmission electron microscopy (HRTEM) to provide valuable information about their crystallinity, local and electronic structure, morphology, and composition. The fundamental information obtained from these analyses about the morphology, structure, and electronic properties of these nanoparticles will be correlated to their catalytic activity for ORR.

was determined to be 20% using inductively coupled plasma

2.3. Electrochemical Measurements. The activity and durability of the electrocatalysts were assessed in a threeelectrode cell. To serve as the working electrode, a glassy carbon rotating-disk electrode from Pine Instruments was employed, while a Pt mesh and a reversible hydrogen electrode (RHE) were used as the counter and reference electrodes, respectively.<sup>40</sup> To study the kinetics of ORR, a working electrode was prepared by loading 20  $\mu$ L of catalyst ink (containing 3 mg of Pd@Pt/C, 1 mL of deionized water, 1 mL of 2-propanol, and 20  $\mu$ L of Nafion) onto a glassy carbon rotating disk electrode. In the first step, the nanoparticles were cycled in the potential range of 0.05–1.1  $V_{RHE}$  in N<sub>2</sub> saturated 0.1 M HClO<sub>4</sub> until constant cyclic voltammetry (CV) was obtained and the surface of the catalyst was completely cleaned and stabilized.<sup>41</sup> The hydrogen adsorption/desorption charge on the platinum surface in the H<sub>UPD</sub> region was then integrated, and using the electrochemically active surface area (ECSA) formula presented in eq 1 and assuming 210  $\mu$ C/cm<sup>2</sup> as the charge related to the full hydrogen coverage of Pt, the electrochemical surface active area of these samples was calculated.<sup>42</sup>

$$ECSA_{Pt} (m^{2}g_{Pt}^{-1}) = \left[\frac{Q_{H-adsorption}(C)}{210 \,\mu C \, cm_{Pt}^{-2}L_{Pt}(mg_{Pt} \, cm^{-2})A_{g}(cm^{2})}\right] \times 10^{5}$$
(1)

· 2 1.

In this formula,  $L_{\rm Pt}$  is the platinum loading on RDE,  $A_{\rm g}$  is the geometric surface area of the RDE, which is 0.196 cm<sup>2</sup> in this study, and  $Q_{\rm (H-adsorption)}$  corresponds to the hydrogen adsorption charge.

The ORR polarization curves of nanoparticles were measured in oxygen-saturated 0.1 M HClO<sub>4</sub> electrolyte with a potential scan rate of 10 mV s<sup>-1</sup> and a rotation rate of 1600 rpm. Due to existence of mixed diffusion and activation processes on the rotating disk electrode, the Koutecky–Levich equation (eq 2) was used to determine the kinetic current and compare ORR activity of the samples.<sup>4</sup>

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}}$$
(2)

where *j* is the measured current density,  $\omega$  is the rotation speed, and *B* is the Levich slope given by

$$B = 0.62nFD^{2/3}\nu^{-1/6}C_0 \tag{3}$$

## 3. RESULTS AND DISCUSSION

The overall schematic of the synthesized catalyst and the required steps in the process are illustrated in Scheme 1. Highangle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) was used to characterize and study a single Pd@Pt core-shell nanoparticle. As shown in Figure S2A, the particles have a regular shape with sharp edges, indicating high morphological uniformity and purity. The octahedral shape is intact after the synthesis steps, including the loading of a four-layer thin shell of Pt or Pt-Co, as seen in both parts of Figures S2 and 1. Detailed lattice measurements (Figure 1B) of the particles indicate that the dominant exposing facets are  $\{111\}$  facets with  $\{100\}$  facets on the rounded corners. STEM energy-dispersive X-ray (STEM-EDX) elemental mapping is also presented in Figure S2B-E, which confirms the existence of Pd in the core and its coverage by a dense and smooth shell of Pt. TEM images show a brighter shell compared with the core, which is caused by the difference in the atomic number of platinum and palladium. The successful doping of Co onto the Pt shell of Pd@Pt nanoparticles is also confirmed by the cobalt signal in STEM energy-dispersive X-ray (STEM-EDX) elemental mapping of Figure 1. Elemental line scanning profiles in Figures 1 and S2 illustrate the distribution of Pt, Co, and Pd in a single nanoparticle of cobalt-doped Pd@Pt.

Elemental mapping and line scanning, as presented in Figure 1, confirmed the existence of platinum and cobalt only in the shell and the palladium core within this dense shell. The existence of a platinum shell, with a thickness of 0.8 nm (equivalent to four atomic layers of Pt) on Pd core, was confirmed by sharp peaks at the sides of the elemental linescanning profiles. The overall composition of a single NP was measured by EDX (91.3/7.0/1.7), which was consistent with the bulk composition measured from ICP-MS (90.7/8.2/1.1), indicating a uniform composition for all NPs. However, the surface compositions differed, with 15.5% Co, indicating that Co was mainly sitting on the surface of NPs. The lattice spacings presented in Figure 1B reveal that the incorporation of cobalt, with its smaller radius, into the platinum structure has caused a shrinkage of the lattice of platinum compared to pure Pt. Specifically, two lattice spacings of 2.24 and 1.93 Å were observed for (111) and (200) planes, respectively, which are slightly smaller than the values for pure Pt [2.26 and 1.96 Å for (111) and (200) planes, respectively]. HRTEM images of both doped and undoped Pd@Pt nanoparticles are presented in Figure S3, which show that the carbon-supported nanoparticles consist of a core-shell structure with platinum serving as the shell that covers the palladium core. The cobalt-doped Pd@Pt nanoparticles were loaded onto carbon black for further electrochemical characterizations, as shown in Figure S4. The nanoparticles, which have an average edge length of  $54.5 \pm 3.7$ nm, were uniformly distributed on the support. The side and top

views of the Co-doped Pd@Pt nanoparticles, as shown in Figure S4 further confirm the formation of an octahedral shape.

The crystal structure of the Pd@Pt-Co/C powder was analyzed by using XRD to obtain lattice structure information, and the results are shown in Figure S5. The XRD patterns of the core-shell nanoparticles before and after doping revealed that all peaks can be assigned to the face-centered cubic (f.c.c) structure of Pt and Pd, corresponding to the (111), (200), and (220) planes.<sup>43</sup> The diffraction peaks of both samples were shifted to higher  $2\theta$  angles compared to pure platinum, indicating a decreased lattice constant of the Pd@Pt coreshell NP both before and after doping with Co. This positive shift compared to Pt is attributed to the smaller radius of both Pd and Co compared to platinum and is supported by Vegard's law calculations.<sup>44,45</sup> The calculated relative microstrain ( $\varepsilon$ ) also confirms the existence of structural modifications in the doped sample compared to that in undoped and pure platinum. Bragg's law was used to calculate the *d*-spacing and lattice parameter of the two samples,<sup>46</sup> and the obtained quantitative parameters are shown in Table 1. All of these factors together confirm the

Тa	ıble	e 1.	Summary	of XRD	Results	Regarding	(111)	) Facets
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catalyst	lattice parameter (Å)	d-spacing (Å)	relative $\varepsilon_{ m microstrain}$ compared to Pt/C (%)
Pt	3.922	2.26	
Pd@Pt	3.897	2.25	0.63
Pd@Pt-Co	3.879	2.24	1.08

contraction in the platinum structure due to the influence of Pd and Co. The XPS was employed to investigate the chemical states of the surface species, as shown in Figure S6. The binding energies of all spectra were referenced to the C 1s core level at 284.5 eV. Pt 4f spectra demonstrated that the Pt remained in the same state before and after Co doping. However, the Pd 3d peaks exhibited more asymmetry, suggesting a slight charge transfer from Pd to the oxygen species induced by the Co doping (Co is easily oxidized on the surface).

As shown in Figure 2A and Table 2, a core-shell catalyst exhibits slightly higher ECSA compared to the commercial Pt/C catalyst due to the higher efficiency in platinum usage and having more active sites.<sup>47</sup> Moreover, the Pd@Pt nanoparticles before and after doping show almost identical active surface areas due to their identical facet, size, and structure.<sup>48</sup> The obtained CV results show that the cobalt-doped NP has a slight positive shift of 10 mV for the onset potential of the oxide reduction peak, indicating a weakened binding strength of oxygen-containing species on Pt sites caused by the cobalt dopant. Furthermore, Figure 2B presents the ORR polarization curves of core-shell and commercial platinum nanoparticles. The calculated kinetic currents were normalized by the platinum loading and ECSA to determine the mass and surface specific activity. Figure 2C,D shows that Pd@Pt-Co exhibits enhanced mass and specific activity compared to the undoped Pd@Pt and the commercial Pt/C. The mass activity of the ORR on Pd@Pt-Co nanoparticles is 1.1 (A mg<sub>Pt</sub><sup>-1</sup>), which is approximately 11 and 2.3 times higher than commercial platinum and the undoped Pd@ Pt at 0.9  $V_{RHE}$ . Additionally, the half-wave potential, which is an indicator of competency in lowering ORR overpotential and can be measured from the mix-controlled region of ORR polarization curves at 1600 rpm, was 0.863 versus RHE for Pd@Pt-Co, 14 mV higher compared to the undoped sample (0.849 V),

and 43 mV higher compared to Pt/C (0.820 V). All of the calculated data are shown in Table 2.

To investigate the kinetics of ORR on core-shell nanoparticles, polarization curves were obtained at different rotation rates.<sup>49</sup> The Koutecky-Levich (K-L) plots, as presented in Figure S7, show various ORR curves acquired at different rotation speeds. The linear relationship between  $j^{-1}$  and  $\omega^{-0.5}$ confirms the existence of first-order kinetics on these Pt-based nanoparticles and endorses the possibility of using K–L equation (eq 2) for calculations.  $^{50}$  In RDE, reactant species are supplied to the electrode surface through convection, and increasing the electrode rotation speed can enhance the supplied reactant species and increase the monitored current. The K-L equation (eqs 2 and 3) is used to determine the proportionality of the current and rotation speed, where *j* represents the measured current density, n is the number of electrons involved in the reaction, F is Faraday's constant (96,485 C/mol), D is the diffusion coefficient of  $O_2$  in the 0.1 M HClO<sub>4</sub> electrolyte,  $C_0$  is the oxygen concentration in 0.1 M HClO<sub>4</sub> solution, and  $\nu$  is the kinematic viscosity of the solution. The fitted lines in Figure S7D were plotted at different electrode potentials, and each line had a specific slope. As mentioned in eq 2, the slope of the fitted lines can be used to obtain the B value, which can be used to determine the number of participating electrons in the ORR. The average number of transferred electrons was calculated to be 3.73 and 3.91 for Pd@Pt and cobalt-doped Pd@Pt, respectively. This result indicates that the cobalt dopant in the nanoparticles promotes the desired four-electron pathway.<sup>51,52</sup>

The ADT was also carried out to evaluate the stability of the electrocatalysts. A total of 20,000 cycles were scanned between 0.6 and 1.0  $V_{RHE}$  at a scan rate of 100 mV s<sup>-1</sup> for each sample, and the ECSAs, specific, and mass activities were determined after ADT. As presented in Figure 2E,F, the stability of Pd@Pt has greatly improved after the introduction of cobalt. According to Table 2, Pd@Pt lost 19% of its initial mass activity after ADT, which is much higher than the cobalt-doped sample that largely retained its activity and only dropped by 2% after 20k cycles. The substantial stability of cobalt-doped nanoparticles is mainly attributed to the beneficial role of cobalt in enhancing mass activity while simultaneously preserving the shape and composition of the octahedral nanoparticles.<sup>30,53</sup> By comparing these new synthesized NPs with other reported data in the literature for bimetallic nanoparticles, it is clear that the cobalt dopant has significantly improved the durability of the Pd@Pt core-shell catalyst (Table S1).

In this study, X-ray absorption fine structure (XAFS) has been employed to correlate the catalytic activity and electronic structure of the nanoparticles. Ex-situ and in situ XAFS measurements at the Pt, Pd, and Co edges are used to characterize the structure and behavior of the Pd@Pt-M (M = transition-metal dopant) system. XAFS monitors the absorption coefficient using tunable X-ray from a synchrotron light source and can probe the local and electronic structures of the absorbing atom, providing information on the oxidation state, coordination number, and local symmetry of the atom of interest (Pt, dopant element, and Pd) before and after doping, compared to commercial Pt/C.<sup>24,54-56</sup> The Pt  $L_{3,2}$  edge can also be investigated to track the unoccupied densities of states of 5d electrons, which essentially determines the catalytic activity.<sup>57</sup> In the Pt L<sub>3</sub>-edge X-ray absorption near-edge spectra (XANES) spectra, the white line (a strong peak just above the absorption threshold  $E_0$  intensity is directly associated with the dipole



**Figure 2.** (A) CVs and (B) ORR polarization curves for the Pt/C, Pd@Pt/C, and cobalt-doped Pd@Pt/C catalysts. The current densities (j) were normalized against the geometric area of RDE (0.196 cm<sup>2</sup>). (C) Mass activities and (D) specific activities, given as kinetic current densities ( $j_k$ ) normalized against the mass of Pt and the ECSA of the catalyst, respectively (the inset shows the specific activity of the catalysts at 0.9 V<sub>RHE</sub>.). (E,F) Linear sweep voltammetry of Pd@Pt–Co (E) and Pd@Pt (F) catalysts before and after 20,000 cycles between 0.6–1.0 V<sub>RHE</sub> in an O<sub>2</sub> saturated 0.1 M HClO<sub>4</sub> electrolyte [the insets show the mass activity (at 0.9 V<sub>RHE</sub>) of the catalysts before and after the accelerated durability test (ADTs)].

transition from the Pt  $2p_{3/2}$  orbital to the unoccupied 5d orbitals, reflecting the degree of Pt oxidation.<sup>58</sup>

All XAS measurements were conducted under the fluorescence mode at a beamline 44A of the Taiwan Photon Source (TPS). The XAS data was processed using the software package ATHENA.<sup>59</sup> Spectra were measured at room temperature for the  $L_3$  edge of Pt and K edge of Pd and Co and the energy of all spectra was calibrated according to the absorption edge of the standard metal foil. Figure 3 depicts the normalized XANES of cobalt-doped Pd@Pt catalyst, while spectra of Pd@Pt, Pt/C, and platinum foil (reference sample) are also provided for the matter of comparison. As indicated by the inset picture in Figure 3A, cobalt-doped Pd@Pt showed a slightly lower white line peak intensity at the Pt  $L_3$ -edge than that of Pd@Pt, which indicates electron transfer from Co to Pt.<sup>27</sup> It is well known that electron transfer from other metals to platinum can fill its d-orbital and

Table 2. Electrochemical Performance of Cobalt-Doped Pd@ Pt Nanoparticles Compared to Pd@Pt and Commercial Pt/C

catalyst	$\mathop{ECSA}\limits_{\left(m^2g_{Pt}^{-1}\right)}$	$\begin{array}{c} \text{SA at 0.9 } \text{V}_{\text{RHE}} \\ \text{(mA cm}_{\text{Pt}}^{-2}) \end{array}$	$\begin{array}{c} \text{MA at 0.9} \\ \text{V}_{\text{RHE}} \\ \text{(A mg_{\text{Pt}}^{-1})} \end{array}$	mass activity loss after ADT
Pt/C	69	0.43	0.09	
Pd@Pt	73	1.49	0.48	19%
Pd@Pt-Co	74	2.28	1.10	2%

tune the electronic structure, consequently downshifting the dband center of platinum, which results in higher catalytic activity due to the influence of electronic structure on the binding of surface-poisoning species. The improved stability of Pd@Pt– Co catalysts during the voltage-cycling process can be attributed to the reduced intensity of the white line compared to undoped nanoparticles (NPs). This observation has been extensively discussed in studies conducted by Lim et al.<sup>39</sup> and Beermann et al.<sup>24</sup> These studies suggest that the presence of transition-metal dopants induces compressive strain, leading to a less oxophilic surface. Consequently, the vacancy formation energy ( $\Delta E_{vac}$ ) of Pt atoms increases, reducing the likelihood of oxidation and dissolution into Pt<sup>2+</sup> ions, which are major contributors to the instability of Pt-based ORR catalysts.<sup>60–62</sup> By incorporating cobalt dopants, adjacent Pt sites are stabilized, promoting the stability of the octahedral shape enriched with (111) facets and inhibiting acidic dissolution.<sup>7,27,57,63</sup> Overall, numerous studies have consistently demonstrated the effectiveness of transitionmetal dopants in enhancing the stability of Pt-based catalysts.<sup>24,25,27,39,64</sup> In addition, as discussed previously, XANES can also be used to review the oxidation state of platinum in each sample. To do so, the inflection points of the two catalysts are compared to platinum foil, and it is clear that both doped and undoped samples have identical inflection points compared to the reference sample, endorsing the metallic status of platinum atoms in these NPs. It is also worth mentioning that Co in the Pd@Pt–Co catalyst is oxidized, as seen from the energy space (Figure 3C) as well as the R-space (Figure 3D) of Co K-edge.

Another imperative parameter in defining the catalytic activity of catalysts is the geometrical structure of nanoparticles, which can be determined using extended XAFS (EXAFS).<sup>65</sup> The EXAFS can be used to reveal the local structural ordering and bonding distance around the target atom in the Pd@Pt NPs before and after doping. The changes in the bond length and the interaction between Pt, dopant, and Pd atoms can affect the dband structure of Pt and can be effective in optimizing the adsorption energy of intermediate oxygen species on Pt.<sup>23</sup> Fitting the presented EXAFS data in Figure 3B, Fourier-



**Figure 3.** X-ray absorption studies of Pd@Pt and cobalt-doped Pd@Pt catalysts compared to commercial Pt/C and Pt foil. (A) Normalized XANES spectra at Pt  $L_3$ -edge and (B)  $k^2$ -weighted Fourier transform spectra from EXAFS. The inset in (A) shows the enlarged spectra at Pt  $L_3$ -edge white line. (C) Co K-edge XANES of Co foil and Pd@Pt-Co. (D) R-space at Co K-edge of Co foil and Pd@Pt-Co.

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**Figure 4.** (A,B) Pt L<sub>3</sub>-edge XANES and R-space of Co-doped Pd@Pt collected under in situ/operando conditions, respectively. (C,D) Pt L<sub>3</sub>-edge XANES and R-space of Pt/C collected under in situ/operando conditions, respectively. (E) Potential-dependent changes in platinum L<sub>3</sub>-edge white line peaks  $[\Delta \mu = \mu(E) - \mu(0.54 \text{ V})]$ . (F) Pd K-edge XANES and R-space of Co-doped Pd@Pt collected under in situ/operando conditions.

transformed EXAFS shows that Co has slightly reduced the Pt– Pt bonding distance in the doped sample compared to undoped core@shell NPs and this has assisted to weaken the oxygenated species bond on Pt and further enhance its ORR activity.<sup>54</sup> This compressive strain is also observed by the XRD pattern in Figure S5 and is reasonable based on the radius of the cobalt atom. The platinum lattice contraction can be beneficial in terms of d-band center downshift and can diminish surface poisoning species and weaken hydroxyl adsorption energy. This lattice contraction by a doping element has been also observed by other studies such as the use of Mo, Ga, and Rh in Pt–Ni NPs, which all have shown a lattice compression.<sup>24,39,57</sup>

To reveal the role of surface cobalt dopant in the enhanced activity and stability of doped NPs in ORR under reactive conditions, operando XAS was carried out (Figure 4). Operando XAS is an essential step in the characterization of NPs and in confirming the results obtained from ex-situ methods when reviewing the evolution of NPs during potential cycling. The operando XAS was performed in the Quick EXAFS mode using a custom-built electrochemical cell, setup shown in Figure S9, in which 0.1 M HClO<sub>4</sub> electrolyte was saturated with N<sub>2</sub> or O<sub>2</sub> at room temperature. The electrochemical cell consisted of a Agl AgCl reference electrode, platinum wire as the counter electrode, and catalyst ink sprayed on carbon paper as the working electrode. All spectra were obtained 30 min after setting the potential to a static value to reach a pseudosteady state, along the anodic sweep of CV. The first spectrum was taken at open circuit potential (OCV), and then the working electrode was kept at potentials ascending from 0.54 to 1.5 V vs RHE. After obtaining spectra for each fixed potential, the electrode was fully cycled again to clean the surface of electrodes from any accumulated oxo species and obtain stabilized voltammograms.

By examination of XAS spectra shown in Figure 4, it was initially determined that the intensities of the white line at the Pt L<sub>3</sub>-edge exhibit an increase as the potential is raised. This increment can be attributed to the electron withdrawal caused by the presence of adsorbed oxygen species. The augmentation of the white line becomes particularly significant at potentials exceeding 1.1 V vs RHE. At these higher potentials, the formation of surface oxides becomes apparent, as supported by the appearance of a Pt-O contribution in the Fourier transformed EXAFS spectra. This Pt-O contribution is evident at low r values (<2 Å), along with an increase in the width of the white line in XANES spectra.<sup>66-68</sup> Upon analyzing FT-EXAFS spectra, it is evident that the overall structure of the catalysts undergoes minimal changes at potentials below 1.1 V. This observation is supported by the slight growth of the Pt-O scattering peak around 1.7 with increasing potentials. The presence of oxides holds crucial importance in the context of catalyst degradation, as the oxidation of the catalyst has been linked to the dissolution of Pt and ripening of Pt nanoparticles.<sup>69</sup> It was also found that operando XANES of palladium remains unchanged at different potentials ranging from 0.54 to 1.5 V, signifying that palladium is completely covered and protected from oxidation by the platinum shell and is not directly exposed to the electrochemical environment (Figure 4F).

To reveal the role of cobalt in facilitating ORR in Pd@Pt–Co, the surface sensitive  $\Delta\mu$ -XANES was used in this study, which can identify the key ORR intermediates on the surface of platinum and can be used to estimate the coverage of O and H adsorbates, demonstrated by  $\Delta\mu$  amplitude, as a function of the applied potential.<sup>43,70–72</sup>  $\Delta\mu$  is shown in Figure 4E and is obtained by subtracting the normalized Pt L<sub>3</sub> edge XANES collected at 0.54 V (located at the double layer region and relatively free of O and H adsorbates) from the collected XANES at elevated potentials;  $\Delta \mu$  can remove the contribution from the unaffected bulk and can highlight the small changes happening on the surface of catalysts due to adsorption and can be used to correlate the changes in Pt-O bond strength and poisonous \*OH coverage with compressive strain in the platinum shell of NPs and ORR activity.<sup>71,73</sup> It is clear that the white line intensities of XAS spectra at different potentials vary by increasing potentials. As shown in Figure 4E,  $\Delta \mu$  for Pt/C is increased monotonically by increasing potential, caused by the charge transfer from platinum to oxygenated adsorbents on its surface, whereas Pd@Pt-Co shows a different trend in oxygen adsorbents coverage. Both Pt/C and Pd@Pt-Co show an increase in  $\Delta \mu$  when the potential was increased from 0.54 to 0.7 V, mainly caused by the coverage of \*OH on both NPs. As discussed by Ge et al., \*OH adsorption initiate in potentials higher than 0.6 V, and coverage increases with enhanced potentials.<sup>74</sup> Despite the further increase of  $\Delta \mu$  in Pt/C at 0.9 V, Pd@Pt–Co shows a decrease in  $\Delta \mu$ , illustrating the suppressed coverage of oxygenated adsorbents on this NP at 0.9 V. This confirms that highly active Pt sites on cobalt-doped NPs bind oxygen more weakly compared to commercial Pt/C, which results in decreased \*OH coverage on Pt. This is mainly caused by the higher occupancy of Pt valence bonds and the shorter Pt-Pt bonding distance, which can weaken the Pt-O binding energy and is likely the main reason behind the superior activity of Pd@Pt-Co in ORR. It is crucial to desorb \*OH and other oxygenated species from the active sites of platinum during ORR to ensure that the surface of platinum is available for  $O_2$ reactants.<sup>75</sup> However, it is also necessary to consider that Pt-O cannot be overly weakened, as ORR will again be limited by the dissociation of adsorbed  $O_2$ .<sup>71,73</sup>

With further increases in potential,  $\Delta \mu$  increases in both samples, although Pd@Pt-Co exhibits a smaller increase than that of Pt/C. This provides evidence for the advantageous role of cobalt doping in reducing oxygen coverage on the surface of the catalyst at high potentials. It is known that platinum is oxidized at potentials above 1.0 V, starting mainly with the dehydration of \*OH, leaving O on the surface of the nanoparticle and eventually generating Pt-O. A further increase in potential leads to surface oxidation of platinum, with oxygen entering the platinum layers and forming higher orders of platinum oxides, such as PtO<sub>2</sub> or Pt<sub>3</sub>O<sub>4</sub>. It is clear that Pd@Pt-Co exhibits a lower level of oxidation in its platinum shell compared with Pt/C at elevated potentials. Therefore, the superior ORR activity and stability of cobalt-doped Pd@Pt can be attributed to the interaction between cobalt dopants and Pt, which weakens the adsorption of oxygen species intermediates on Pt active sites after the reaction.<sup>23</sup> Additionally, the geometric and electronic interaction between Pd and the platinum shell has further contributed to enhancing the activity of these core-shell nanoparticles by shortening the Pt-Pt bonding distance through strain effects.<sup>76</sup> The incorporation of cobalt into the platinum shell of NPs is believed to suppress its oxidation, resulting in significantly reduced dissolution from the NP and tremendous stability compared to those of undoped NPs, commercial Pt/C, and even other core@shell NPs.

EXAFS fitting of Pt  $L_3$  edge spectra was also conducted on the in situ series of Pt@Pd–Co sample.<sup>59</sup> Only first-shell single scattering paths (Pt–O, Pt–Pt, Pt–Pd, and Pt–Co) were considered to semiquantitatively understand the changes in the coordination environment of Pt under different potentials (Figure S10). For the Pt L<sub>3</sub>-edge, the fitted k- and R-ranges were set to be 2.7–15 and 1.3–3.4 Å, respectively. For the Co K-edge,

the fitted k- and R-ranges were set to be 3.0-9.0 and 1.0-3.0 Å, respectively. The fitting parameters, including the amplitude damping term  $S_0^2$ , the coordination number of each species N, the interatomic distance *R*, the energy correction  $\Delta E_0$ , and the thermal vibration/displacement term  $\sigma^2$ , were used to fit the well-established EXAFS equation.<sup>77</sup> The amplitude term  $S_0^{-2}$  was set to an empirical value of 0.84. To ensure more reliable comparisons, the thermal displacement term  $\sigma^2$  of the Pt-Pt path was fixed at 0.0065  $Å^2$ . The fitted results are summarized in Table S2. It should be noted that the uncertainties in these fitting sets tend to be greater than those of normal ex-situ samples due to the applied potential and changing structure. The quantitative results obtained from this study support the other characterizations conducted. It is evident that the cobalt dopant is oxidized on the surface, with coordination of around 8 Co-O and 4 Co-Pt/Pd bonds. The FT-EXAFS fitting results provide further insights into the intricate changes occurring in the coordination environment of platinum (Pt) under different potentials. A notable observation is the competitive relationship between the bond lengths of Pt-O and Pt-Co. When a potential of 1.1 V is applied, Pt shows signs of oxidation, accompanied by noticeable changes in its chemical structure. At higher potentials of 1.3 and 1.5 V, the dissolution of Pt becomes evident. During this process, several trends emerge. The number of Pt–Pt bonds  $(N_{Pt}-P_{t})$  decreases, while the number of Pt–Pd bonds  $(N_{Pt}-_{Pd})$  increases, primarily due to the reduction in surface Pt content. Notably, the robustness of Co became apparent as the number of Pt–Co bonds  $(N_{Pt}-_{Co})$  increased, suggesting its resilience amidst the dissolution of Pt. Additionally, the bond lengths of Pt-Pt, Pt-Pd, and Pt-Co exhibit a tendency to increase during the Pt dissolution and oxidation process. These findings provide valuable insights into the structural changes and interactions occurring within the coreshell catalyst system under varying potentials.

## 4. CONCLUSIONS

In summary, our study presents the synthesis of an advanced ORR catalyst based on Pd@Pt-Co octahedra, which effectively combines three different strategies involving the utilization of transition metal, shape control, and core-shell formation. The remarkable stability of cobalt-doped Pd@Pt NPs, with only 2% loss of initial activity after 20k cycles of stability tests, confirms the efficiency of cobalt in simultaneously enhancing catalytic activity and stabilizing the octahedral shape of Pd@Pt NPs by diminishing Pt dissolution. Our EXAFS results suggest that the shorter Pt-Pt distance in Pd@Pt-Co NPs weakens the Pt-O bond and enhances ORR activity. XRD patterns have also shown lattice contraction in platinum due to cobalt doping, which can enhance oxygen species adsorption on the platinum surface. Additionally, the lower white line intensity of Pd@Pt-Co XANES confirms electron transfer from Co to Pt, which can further improve the catalytic activity of the NPs. Overall, the cobalt-doped Pd@Pt NPs presented in this study show promising potential as highly efficient and stable ORR catalysts for fuel cell applications.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c04274.

SEM, HAADF STEM, and HR-TEM images of NPs; EDX spectra; XRD pattern and XPS results of NPs; K-L

plots and CVs of methanol oxidation; schematic illustration of in situ/operando XAS; and Pd K-edge XANES and R-space of NPs and electrochemical performance comparison table (PDF)

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## Notes

The authors declare no competing financial interest.

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