Ultrasmall PdPtCo trimetallic nanorings with enriched low-coordinated edge sites and optimized compositions for effective oxygen reduction electrocatalysis†

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Electrocatalysts toward the oxygen reduction reaction (ORR) are the core materials for propelling the practical application of fuel cells. On the basis of extensive theoretical and experimental screening studies, platinum (Pt) has been recognized as the catalytically most effective component for the ORR.\(^1\)–\(^5\) Plenty of efforts have been devoted to the synthesis of Pt and Pt-based nanostructures with modulated compositions, surface atomic arrangements, electronic structures, lattice strains, etc. for the promotion of ORR efficiency.\(^6\)–\(^11\) However, the sluggish ORR kinetics, overly strong adsorption of oxygen intermediates (*O, *OH and *OOH),\(^12\)–\(^14\) and highly scarce and costly Pt resources jointly require further substantial improvements on the catalyst design.

In the past few years, two-dimensional (2D) ultrathin metal nanosheets (NSs) have displayed inherent superiorities for applications like heterocatalysis owing to their large specific surface area, high atomic exposure, uniform surface coordination, etc.\(^15\)–\(^18\) Based on the flat structural platform, derivatives of multimetallic NSs, including alloyed, core-shell, and other heterogeneous nanostructures, have been successively attained via a chemical synthesis and used as high-performance electrocatalysts.\(^19\)–\(^24\) For example, 3 nm-thick PdPtAg alloyed NSs showed excellent catalytic performance toward the ethanol oxidation reaction (EOR) because of their ultrathin 2D feature, improved OH\(_{\text{ads}}\) formation, and enhanced CO tolerance.\(^25\) Multimetallic Pd@PtM (M = Ni, Rh, and Ru) core-shell nanoplates exhibited superior activity and stability for the methanol oxidation reaction (MOR) owing to the combined core-shell and alloy NS structures.\(^26\) Also, 1.4 nm-thick Pd\(_{32}\)Pt\(_{48}\)Ni\(_{20}\) NSs achieved superior ORR mass activity (0.54 A mg\(^{-1}\)(Pt+Pd)) due to the ultrathin alloy feature.\(^17\) In these studies, synergies between different metal elements have been elucidated to contribute to catalysis enhancements.

Although the large top and bottom basal planes of NSs are habitually taken for granted as active sites in the heterocatalysis, the low-coordinated edge sites of some inorganic nanomaterials, including MoS\(_2\), graphene, metals, etc.,\(^27\) have been disclosed to possess extraordinary catalytic properties and arouse growing concerns. It is known that the atoms on the edges are highly unsaturated and essentially vivacious.\(^28\) For example, the edge sites of Pd NSs showed boosted CO\(_2\) electroreduction capacity for producing CO.\(^29\) The edge-enriched Pt\(_{3}\)Ni nanoframes and PtPd-based nanorings (NRs) exhibited outstanding ORR activities.\(^30\),\(^31\) Recently, we demonstrated that ultrathin 2D PdPtCu trimetallic NSs and NRs with escalating low-coordinated edge proportions from 11.74% to 45.85% can serve as top-ranked EOR electrocatalysts.\(^32\) Therefore, the edge-enriched multimetallic 2D nanostructures can serve as promising electrocatalysts by providing low-coordinated edge sites made up of multimetallic atoms in synergy with one another. This type of Pt-based nanostructures, nevertheless, is still rare for the development of ORR electrocatalysts, which evoked our passion to explore their effectiveness in promoting such an important but kinetically challenging reaction.

Here we demonstrate a facile synthesis of ultrasmall PdPtCo trimetallic annular NRs with enriched edge sites and tunable atomic ratios to serve as efficient ORR electrocatalysts in base. In the one-pot reaction, earlier
generated Pd hexagonal NSs served as self-sacrificial templates for the latter deposition of Pt and Co atoms and the simultaneous etching of central facets of hexagonal NSs to form cavities in the presence of an etchant (the Br\textsuperscript{−}/O\textsubscript{2} pairs). In terms of the average edge length, width, and thickness, the edge ratio of the PdPtCo NRs was estimated to be 2.3–4.1 times higher than those of the PdPtCo and PdPt NSs with similar dimensions but no cavities in the central area. The corresponding ORR electrocatalytic performance showed that the 2D Pd\textsubscript{55}Pt\textsubscript{18}Co\textsubscript{27} NRs, having the highest edge ratio (ca. 45%) and optimized composition, exhibited the best mass activity and specific activity, which were 21 and 15 times higher than those of the commercial Pt/C, respectively. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) analyses indicate that the alloy electronic effect and d-band center regulation of the Pd\textsubscript{55}Pt\textsubscript{18}Co\textsubscript{27} NRs, tuned by the structural and compositional parameters, can alleviate the adsorption of oxygen intermediates to their surface, therefore, accelerate the ORR kinetics. The strategy to develop effective ORR electrocatalysts combining edge-engineering and composition-modulation can be instructive for the development of other heterocatalysts.

The ultrasmall freestanding 2D trimetallic PdPtCo NRs were synthesized through a temperature-programmed one-pot approach. The mixture of metal precursors (i.e., Pd(acac)\textsubscript{2}, Pt(acac)\textsubscript{2}, and Co(acac)\textsubscript{2}) in a N,N-dimethylformamide (DMF) solution, containing W(CO)\textsubscript{6}, citrate acid, KBr, and PVP, was firstly heated at 80 °C for 3 h, and then ramped up to 150 °C and was kept for another 3 h (the details are shown in the ESI†). Transmission electron microscopy (TEM) characterization shows that the resulting products are uniform hexagonal NRs with a near 100% yield and uniform small size (Fig. 1a). We labelled this product Pd\textsubscript{55}Pt\textsubscript{18}Co\textsubscript{27} NRs according to the metal atomic ratio determined by the inductively coupled plasma mass spectrometry (ICP-MS). Further measurements show that the Pd\textsubscript{55}Pt\textsubscript{18}Co\textsubscript{27} NRs has an edge length of ca. 10.13 nm, a width of ca. 2.75 nm, and a thickness of ca. 1.96 nm (Fig. 1b and S1†). The high-resolution TEM (HRTEM) image of a single Pd\textsubscript{55}Pt\textsubscript{18}Co\textsubscript{27} NR not only clarifies the abundant inner and outer edges of the NRs, but also identifies the spacing between lattice fringes of ca. 0.23 nm (Fig. 1c), which corresponds to the \{111\} reflections of face-centered cubic (fcc) Pd.\textsuperscript{34,35} The powder X-ray diffraction (PXRD) pattern reveals a pure fcc phase with diffraction peak angles close to those of the standard Pd and Pt (Fig. 1d). The high-angle annular dark field scanning TEM (HAADF-STEM) and corresponding energy-dispersive X-ray spectroscopy (EDS) mapping demonstrate that distributions of Pd, Pt, and Co elements are homogeneous, indicating the formation of trimetallic alloys (Fig. 1e and f).

To elucidate the growth mechanism of the Pd\textsubscript{55}Pt\textsubscript{18}Co\textsubscript{27} NRs, we employed TEM and ICP-MS to characterize the synthesis intermediates sampled at different reaction times. It shows that the uniform Pd hexagonal NSs with trace Co dopants, which have a Pd/Co atomic ratio of ca. 97/3,
predominates the intermediates separated after an 80 °C, 3 h reaction (Fig. 2a). Further heating the reaction mixture to 150 °C and keeping it at this temperature for 1 h leads to the formation of PdPtCo NSs with a Pd/Pt/Co atomic ratio of ca. 80/9/11 and partly interior hole structures (Fig. 2b). Extending the reaction at 150 °C for another 2 h finally results in the yield of uniform Pd55Pt18Co27 NRs (Fig. 2c). Accordingly, we propose a stepwise growth mechanism of the trimetallic PdPtCo NRs (Fig. 2d), where Pd NSs doped with diluted Co are initially formed at 80 °C, which, then, act as templates for the latter deposition and interatomic diffusion of Pt and Co at 150 °C along with the etching of Pd until the uniform PdPtCo alloyed NRs are finally produced. The preferential etching of Pd NSs at the central area stems from the overthrow of deficient CO coordination (protection), provided by the W(CO)6, by the oxidative etching of abundant Br⁻/O₂ pairs at high temperature.21,32 This synthetic strategy is also versatile to fabricate nanorings with different multimetallic components. For example, Pd58Pt15Ni27 NRs can be gained by simply using Ni(acac)2 to replace Co(acac)2 in the synthesis (Fig. S2†).

Based on the understanding of growth mechanism, we further synthesized the Pd58Pt15Co27 and Pd74Pt26 NSs by adding a sufficient amount of W(CO)6 with the presence and absence of Co2⁺ precursors, respectively (Fig. S3†). The edge ratios of these multimetallic 2D nanostructures, defined as A_edge/(A_surface + A_edge), can be estimated from their edge lengths, thicknesses, and widths, in terms of a simple approximate model (see Note 1 in the ESI†). The resulting edge ratios of the Pd53Pt18Co27 NRs, Pd63Pt16Co21 NSs, and Pd74Pt26 NSs are 45.14%, 20.09%, and 11.08%, respectively. Other 2D trimetallic NRs like Pd57Pt10Co53 and Pd73Pt9Co5 NRs can also be generated with the same formula of generating Pd55Pt18Co27 NRs by adjusting the addition of Co2⁺ precursors. TEM images (Fig. S4†) verify their morphologies similar to those of the Pd53Pt18Co27 NRs.

To illustrate the catalytic superiority of the edge sites, we measured and compared the ORR electrocatalytic performances of the above multimetallic 2D NRs and NSs with different edge and atomic ratios (Fig. 3). These alloyed nanostructures were loaded on carbon supports (Vulcan XC-72) with 20 wt% Pd and Pt (see the ESI† for details). Before determining the ECSA, the electrochemical cleaning protocol by CV cycles was performed at a scan rate of 50 mV s⁻¹ from −0.25 to 0.85 V (vs. SCE) in N₂ saturated 0.1 M HClO₄ (Fig. S5†). CO stripping voltammetry was performed to evaluate their electrochemically active surface areas (ECASs) by normalizing the oxidation charge of the adsorbed CO monolayer with 420 μC cm⁻² (Fig. S6†). The resulting ECASs of Pd53Pt18Co27 NRs/C, Pd63Pt16Co21 NSs/C, Pd74Pt26 Co3 NSs/C, Pd63Pt16Co21 NSs/C, Pd74Pt26 Co3 NSs/C, and commercial Pt/C are 74.8, 64.2, 74.9, 65.9, 55.5, and 54.7 m² g⁻¹ Pd/Pt, respectively. The ORR polarization curves recorded in O₂-saturated 0.1 M KOH solution; (d) ORR polarization curves and (e) Tafel plots of Pd55Pt18Co27 NRs/C, Pd76Pt19Co5 NRs/C, and Pd37Pt10Co53 NRs/C recorded in the O₂-saturated 0.1 M KOH solution; (f) ORR polarization curves of Pd55Pt18Co27 NRs/C with different rotation rates: 800 (black), 1200 (red), 1600 (blue), 2000 (pink), and 2400 (green) rpm, respectively. The inset shows the linear fits of the Koutecký–Levich (K-L) equation acquired at 0.85, 0.80, and 0.60 V.

Fig. 3 ORR electrocatalytic performance tests. (a) ORR polarization curves, (b) Tafel plots, and (c) histogram of mass and specific activity at 0.9 V of the Pd53Pt18Co27 NRs/C, Pd63Pt16Co21 NSs/C, Pd74Pt26 Co3 NSs/C, and commercial Pt/C catalysts recorded in the O₂-saturated 0.1 M KOH solution; (d) ORR polarization curves and (e) Tafel plots of Pd55Pt18Co27 NRs/C, Pd63Pt16Co21 NSs/C, and Pd74Pt26 Co3 NSs/C recorded in the O₂-saturated 0.1 M KOH solution; (f) ORR polarization curves of Pd55Pt18Co27 NRs/C with different rotation rates: 800 (black), 1200 (red), 1600 (blue), 2000 (pink), and 2400 (green) rpm, respectively.

For 2D trimetallic PdPtCo NRs with different atomic ratios, the ORR performances of the above multimetallic 2D NRs and NSs were measured and compared the ORR electrocatalytic activities of them. Further ORR examinations for the 2D trimetallic PdPtCo NRs with different atomic ratios show that the ORR kinetics is faster on the Pd55Pt18Co27 NRs/C electrode (32.4 mV dec⁻¹) than on the Pd53Pt18Co27 NRs/C and Pd55Pt18Co27 NRs/C in terms of a more positive E₁/₂ (Fig. 3d) and a lower Tafel slope (Fig. 3e). These results elucidate that except the edge ratios, the atomic ratios of PdPtCo 2D NRs, which can modify the alloy electronic effect, can also exert influence on the ORR.

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kinetics, and here in this work Pd$_{55}$Pt$_{18}$Co$_{27}$ NRs have the highest ORR electrocatalytic activity.

According to the ORR polarization curves measured under different rotation rates ($\omega$) (Fig. 3f and S7–S10†), correlations between $j^{-1}$ and $\omega^{1/2}$ of Pd$_{55}$Pt$_{18}$Co$_{27}$ NRs/C, Pd$_{63}$Pt$_{16}$Co$_{21}$ NRs/C, Pd$_{63}$Pt$_{16}$Co$_{21}$, Pd$_{74}$Pt$_{26}$ NSs/C and Pd$_{74}$Pt$_{26}$ NSs/C obtained at 0.60, 0.80, and 0.85 V well fit with the Koutecký–Levich (K–L) equation.\(^{13}\) The resulting electron transfer numbers ($n$) and kinetic current densities ($j_k$) of the above electrodes are summarized in Table S1.† It can be seen that the ORR mechanism is predominant in the four-electron mixed kinetic and mass-transfer control region. The pathway in both the mass-transfer control region and the mixed kinetic and mass-transfer control region. The $j_k$ values, which are in good agreement with the $E_{1/2}$ and Tafel slopes, indicate that the Pd$_{55}$Pt$_{18}$Co$_{27}$ NRs/C electrode has the fastest ORR kinetics in comparison with the other multimetallic NSs and NRs. The long-term ORR accelerated durability tests (ADTs) demonstrate that the mass activities of high-edge-ratio NRs have obvious decrease during the repetitive cyclings (Fig. S11 and S12 and Table S2†). For example, the $j_m$ of Pd$_{55}$Pt$_{18}$Co$_{27}$ NRs/C decreases by 63% for 5000 cycles and 80% for 10000 cycles, whereas for Pd$_{63}$Pt$_{16}$Co$_{21}$ NSs/C, these values are 53% and 62%, respectively. Even so, the mass activity of Pd$_{55}$Pt$_{18}$Co$_{27}$ NRs after 10000 cycles of ADTs (0.53 A mg$^{-1}$) is still much higher than the initial activity of commercial Pt/C (0.13 A mg$^{-1}$). Then, the negative shift of the Pd 3d and Pt 4f spectra (Fig. 4a and b) and the positive shift of the Co 2p spectra (Fig. 4c) with reference to the standard values indicate that electrons can be transferred from Co to Pd and Pt, which is in line with the electronegativity order of Pt ($2.28$) > Pd ($2.20$) > Co ($1.88$). From the UPS spectra we can estimate the d-band center positions of Pd$_{55}$Pt$_{18}$Co$_{27}$ NRs, Pd$_{63}$Pt$_{16}$Co$_{21}$ NSs, Pd$_{74}$Pt$_{26}$ NSs, and Pt/C to be $−4.72$, $−4.17$, $−3.13$, and $−3.03$ eV, respectively (Fig. 4d). Unconventionally, the above electron transfer from the oxophilic Co to the Pd and Pt moieties enables the downshift of the d-band center of the whole 2D alloy nanostructure, with the Pd$_{55}$Pt$_{18}$Co$_{27}$ NRs having the lowest position. We infer that it may arise from the combining electronic and strain effects of the multimetallic alloys and the abundant edge sites of the NR. The downshift of the d-band center can effectively weaken the adsorption of oxygen intermediates,\(^{36–41}\) which facilitates the intermediate desorption from catalyst surfaces and in consequence the ORR kinetics in base. Here, the oxophilic Co component in the immediate vicinity to the active Pd, Pt sites may facilitate the desorption of oxygen intermediates.

**Conclusions**

In summary, we demonstrate the facile synthesis of ultrasmall 2D PdPtCo NRs with tunable atomic ratios and enriched edge sites through a temperature-programmed one-pot approach. The success of synthesizing such small and ultrathin trimetallic alloy NRs lies in a template directed process, where the precedingly generated Pd NSs at low temperature play the role of sacrificial templates that enable the latter deposition and diffusion of Pt and Co along with the etching of Pd at high temperature. The ORR electrocatalysis examinations show that the Pd$_{55}$Pt$_{18}$Co$_{27}$ NRs with the highest edge ratio (ca. 45.14%) and optimum composition exhibit the highest mass and specific activity, which are 21 and 15 times higher than those of the commercial Pt/C, respectively. The XPS and UPS analyses indicate that the electron transfer from Co to Pd and Pt and the downshift of the d-band center are responsible for the ORR acceleration on the Pd$_{55}$Pt$_{18}$Co$_{27}$ NRs. Our work provides a validated strategy for developing highly efficient...
ORR electrocatalysts, which may also enlighten the development of other heterocatalysts, by combining edge-engineering and composition-modulation.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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