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Structural Evolution of Sub-10 nm Octahedral Platinum-Nickel Bimetallic Nanocrystals

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Abstract

Octahedral Pt alloy nanocrystals (NCs) have shown excellent activities as electrocatalysts toward oxygen reduction reaction (ORR). As the activity and stability of NCs are highly dependent on their structure and the elemental distribution, it is of great importance to understand the formation mechanism of octahedral NCs and to rationally synthesize shape-controlled alloy catalysts with optimized ORR activity and stability. However, the factors controlling the structural and compositional evolution during the synthesis have not been well understood yet. Here, we systematically investigated the structure and

composition evolution pathway of Pt-Ni octahedra synthesized with the assistance of $\text{W}(\text{CO})_6$ and revealed a unique core-shell structure consisting of a Pt core and a Pt-Ni alloy shell. Below 140 °C, sphere-like pure Pt NCs with the diameter of 3-4 nm firstly nucleated, followed by the isotropic growth of Pt-Ni alloy on the seeds at temperatures between 170 and 230 °C forming Pt@Pt-Ni core-shell octahedra with {111} facets. Owing to its unique structure, the Pt@Pt-Ni octahedra show an unparalleled stability during potential cycling, i.e., no activity drop after 10000 cycles between 0.6 and 1.0 V. This work proposes the Pt@Pt-Ni octahedra as a high profile electrocatalyst for ORR and reveals the structural and composition evolution pathways of Pt-based bimetallic NCs.

Keywords: Pt-Ni octahedra; structural evolution; core-shell; oxygen reduction reaction; durability

TOC

Oxygen reduction reaction (ORR) is the cathodic reaction for several important electrochemical systems such as fuel cells, metal-air batteries, corrosion, etc.¹⁻⁸ Pt nanocatalyst is believed as one of the best catalysts for ORR. However, its high price and the ever-increasing consumption from the industry largely impeded large-scale commercialization of fuel cells. To reduce the cost and boost the performance, significant progress has been made to optimize the multicomponent Pt-based electrocatalysts with desired size, composition and shape.^{1,4,8} Pt alloying with transition metals (Pt-M) has shown higher ORR activity and stability than pure Pt due to the optimized oxygen binding energy.⁹⁻¹³ Particularly, their activities are highly dependent on the surface facets and it was found that octahedral Pt alloy nanocrystals (NCs) enriched with {111} facets showed much higher ORR activity than conventional ones.^{1, 4, 11, 14-23}

There are two general approaches to synthesize octahedral bimetallic Pt-M NCs depending on whether CO-containing chemicals are used.^{14-16, 21-24} Taking Pt-Ni as an example, in the synthesis protocol without involving CO-containing chemicals, Pt(acac)₂ and Ni(acac)₂ (acac = acetylacetonate) mixed with appropriate solvents in a sealed autoclave were usually heated to a temperature between 120 and 200 °C.^{16, 22-23} The synthesized sub-10 nm octahedral Pt-Ni NCs showed an unusual composition distribution with Pt-rich frames and Ni-rich {111} facets.²⁴ Similar formation process was observed in the synthesis of PtNi₃ rhombic dodecahedron, consisting of a Pt-rich frame with a Ni-rich interior phase.²⁵ In the other synthesis approach including CO-containing chemicals, the mixture of Pt(acac)₂ and Ni(acac)₂, in the presence of CO or W(CO)₆ via a degassing process was heated to 200-230 °C.^{15, 21} Although the importance of W(CO)₆ and CO in controlling the morphology of Pt-Ni octahedra has been recognized by many reports,^{14-15, 21} the structural and composition evolution pathways in this protocol have not been systematically investigated. Especially, the exact role of W(CO)₆ in the morphology control of Pt-bimetallic NCs has not been demonstrated directly.

In this work, for the first time, we systematically investigated the structure and composition evolution pathways of Pt-Ni octahedra synthesized with the assistance of $\text{W}(\text{CO})_6$ using various techniques, and established the correlation between ORR activities and their structures and compositions. A unique growth pathway for Pt bimetallic alloy NCs was discovered in this study. Small sphere-like Pt seeds initially formed at relatively low temperatures followed by the isotropic growth of Pt-Ni alloy on the seeds, resulting in an octahedral morphology. No phase segregation between Pt and Ni was observed during the growth of Pt-Ni layers, which is distinct from previous studies by Gan *et al.*²⁴ and Niu *et al.*²⁵ in their solvothermal synthesis without involving CO-containing species. The core-shell structure and uniform distribution of Pt and Ni atoms in the {111} shells are responsible for the excellent stability of Pt-Ni octahedra during potential cycling.

Pt-Ni octahedra were prepared by following the previous report.¹⁵ The mixture of $\text{Pt}(\text{acac})_2$, $\text{Ni}(\text{acac})_2$, oleylamine (OAm) and oleic acid (OAc) in benzyl ether was first purged with Ar and then $\text{W}(\text{CO})_6$ was added at 130 °C as the shape control agent. (see Supporting Information for details). In order to monitor the structural evolution with temperature, the intermediate samples at different temperatures (140, 160, 170, 180, 190, 210, and 230 °C) were taken out from the reactor and immediately cooled with toluene in an iced bath, and were then characterized by transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

Figure 1. Low-magnification TEM images of as-obtained Pt-Ni nanocrystals at (a) 140 °C (3.0 ± 1.0 nm), (b) 160 °C (4.5 ± 1.0 nm), (c) 170 °C (5.4 ± 0.3 nm), (d) 180 °C (5.7 ± 0.3 nm), (e) 190 °C (7.9 ± 0.5 nm), (f) 210 °C (9.0 ± 0.5 nm), and (g) 230 °C (9.5 ± 0.5 nm). HRTEM images of individual nanocrystal at (h) 140 °C, (i) 160 °C, (j) 180 °C, (k) 210 °C, and (l) 230 °C. (m) A structural and composition evolution model for Pt-Ni octahedron. (i) Pure Pt sphere seeds with the diameter of 3-4 nm are formed at 140 °C, (ii) then truncated octahedra with trace amount of Ni are formed at 160 °C with an average diameter of 4.5 nm, (iii) then 5.4 nm octahedra at 170 °C, and (iv) finally sub-10 nm

octahedral Pt-Ni consisting of a Pt core and Pt-Ni shell are formed at 230 °C. Pt atoms in the core: green; Pt atoms in the shell: blue; Ni atoms in the shell: grey.

Figure 1 shows the TEM images of Pt-Ni NCs obtained at various temperatures from 140-230 °C. Before $W(CO)_6$ was added, i.e., when temperature was lower than 130 °C, no particle was formed. Sphere-like NCs were observed at 140 °C (Figure 1a). Most of Pt NCs have a spherical shape with a diameter of 3.0 ± 1.0 nm, unlike a branched structure observed in the study of Gan *et al.*²⁴ The lattice fringe of an individual NC in Figure 1h is ~ 2.28 Å, corresponding to that of the interplanar distance of (111) planes of pure Pt. This is also confirmed by the STEM-EELS line scan in Figure S1 where no Ni component was found. This result indicates that $Pt(acac)_2$ was reduced first to form pure Pt seeds. The formation of pure Pt seeds at a relatively low temperature can be ascribed to the higher standard redox potential of Pt^{2+}/Pt than that of Ni^{2+}/Ni , leading to the earlier reduction of Pt ions.

When temperature was further increased to 160 °C (Figure 1b), some sphere-like Pt seeds transformed into a truncated octahedral shape with an average diameter of 4.5 ± 1.0 nm. The truncated octahedral shape can be clearly seen in Figure 1i. The interplanar distance of truncated octahedra decreased to 2.26 Å, implying that Ni atoms can be reduced together with Pt at elevated temperature. When the temperature reached 170 °C, nearly all NCs had an octahedral shape with an average edge length of 5.4 ± 0.3 nm (Figure 1c). This result suggests that 170 °C is the transition point where truncated octahedra grow to octahedra.

As temperature further increases, Pt-Ni octahedra continued to grow. The average edge lengths are 5.7 ± 0.3 (Figure 1d), 7.9 ± 0.5 (Figure 1e), 9.0 ± 0.5 (Figure 1f), and 9.5 ± 0.5 nm (Figure 1g) at 180, 190, 210, and 230 °C, respectively. The interplanar distances of Pt-Ni octahedra at 180, 210, and 230 °C are 2.25 (Figure 1j), 2.23 (Figure

1k), and 2.23 Å (Figure 1l), respectively, which are typical values for the d-spacing of {111} planes of Pt-Ni alloy.¹⁵ The number of atoms reduced at different temperature intervals can be estimated based on the size of the NCs and the atomic density of Pt-Ni (~74.7 atoms nm⁻³) with a Pt to Ni molar ratio of 1:1. Figure S2 clearly shows that most Pt and Ni ions were reduced between 180 and 210 °C.

To gain insight into the elemental distribution of Pt-Ni NCs, the samples at 180 and 230 °C were characterized using aberration-corrected high-resolution STEM imaging and STEM-EELS. The HAADF-STEM images in Figure 2a-c clearly demonstrate the well-controlled octahedral morphology of Pt-Ni NCs at 180 °C. Figure 2d and e show the EELS-elemental mappings of Pt and Ni, respectively, for a single NC shown in Figure 2c. The well-resolved Ni signal in Figure 2e implies that Ni reduction occurs at temperature below 180 °C. The Ni signal is much weaker in the center than other parts of the octahedron. In contrast, the Pt signal is stronger in the center (Figure 2d). The mappings of Pt and Ni suggest that the Pt-Ni octahedron consists of a Pt-rich and Ni-poor core, and a Pt-Ni shell with uniform distribution of Pt and Ni. The existence of the Pt-rich core is consistent with the formation of the pure Pt seeds at lower temperatures.

The HAADF-STEM images of the sample taken at 230 °C in Figure 3a-c, and f also demonstrate the well-controlled octahedral shape. EELS-elemental mappings for a single Pt-Ni octahedron shown in Figure 3c along the <100> zone axis show clear Pt enrichment in the center compared to the shell (Figure 3d), while the Ni content in the center is much lower than other areas (Figure 3e). The elemental mapping results on another particle along the <110> zone axis also show the same conclusion (Figure 3f-h). In the synthesis of Pt-Ni octahedra without involving CO-containing chemicals, Gan *et al.*²⁴ found that a Pt-rich hexapod structure was formed firstly via a kinetically controlled process, followed by the deposition of a Ni-rich phase in the concave {111} facets via a thermodynamically controlled step. In our work, hexapod Pt frame was not observed.

Instead, a core-shell like structure consisting of a pure Pt core and Pt-Ni alloy shell was formed.

Figure 2. (a) ADF-STEM image of Pt-Ni octahedra at 180 °C. (b) Atomic resolution HAADF-STEM image from a single Pt-Ni octahedron along the $\langle 110 \rangle$ zone axis. (c) ADF-STEM image and (d, e) EELS element maps of a single Pt-Ni octahedron present the distribution of Pt (red) and Ni (green).

Figure 3. (a) ADF-STEM image of Pt-Ni octahedra at 230 °C. (b) Atomic resolution HAADF-STEM image from a single Pt-Ni octahedron. ADF-STEM images and STEM-EELS element maps of Pt and Ni from a single Pt-Ni octahedron recorded along the (c-e) $\langle 100 \rangle$ zone axis and (f-h) $\langle 110 \rangle$ zone axis.

The structure and composition of Pt-Ni NCs were examined by ICP-MS, XPS, and XRD. Table S1 lists the compositions of samples at different temperatures derived from ICP-MS and XPS results. The contents of Ni in samples at temperatures below 170 °C

are too small to have an accurate calculation. A general trend observed in Table S1 is that the Pt to Ni ratio decreases as temperature increases, regardless of the measurement methods. This trend is consistent with the assumption that pure Pt seeds form first, which leads to higher Pt to Ni ratios at lower temperatures. Furthermore, the Pt-Ni layers deposited at a higher temperature should have a lower Pt to Ni ratio since Ni atoms could be easily reduced at high temperatures. The XRD patterns in Figure S3 also support this argument. At 160 °C, the positions of XRD peaks are very close to those of pure Pt, consistent with other characterization results. With increasing reaction temperature, the peaks gradually shift to higher 2θ angles, suggesting that more Ni atoms exist in NCs. The other observation in Table S1 is that the Pt to Ni ratios estimated from the ICP-MS are always larger than that from XPS at the same temperature. This discrepancy is due to a short maximum sampling depth (1 to 5 nm) of the X-ray beam in XPS. It is possible that some of the Pt atoms in the core were not sampled resulting in a smaller Pt to Ni ratio than that obtained by ICP-MS.

Our X-ray fluorescence (XRF) result reveals the existence of a small amount of W (~2.4 atom%) in the Pt-Ni sample at 230 °C (Figure S4a). When the reactor was not sealed well, the percentage of W in the product increased to 18.0% (Figure S4b), implying that the amount of W residues increases with a higher oxygen level in the reaction solution. The W 4f doublet with the binding energies of 35.4 and 37.6 eV in Figure S5 can be assigned to W^{6+} species. To understand the oxidation state change of W at different temperatures, an experiment without adding Pt and Ni precursors was conducted. The solution was colorless until the temperature reached at 210 °C, at which it changed to dark blue due to the formation $WO_{2.9}$.²⁶⁻²⁷ The color further changed to yellow at 230 °C due to the formation of $WO_{3.0}$.²⁸⁻²⁹ These results imply that W formed via the decomposition of $W(CO)_6$ can be oxidized to W oxides by trace of O_2 in the reaction solution at 210 °C and higher.

To understand the role of W and CO in reducing Pt and Ni precursors, the experiment using CO instead of W(CO)_6 was conducted. As shown in Figure S6, the color of the reaction changed from yellow (140 °C) to brown (160 °C) and black (180 °C) with increasing temperature when W(CO)_6 was applied. When CO was used, the solution color changed in the same sequence but at a much slower rate from 140 to 180 °C. This result suggests that W may play a key role in promoting the reduction of Pt(acac)_2 and Ni(acac)_2 . Based on the above observations, the possible role of W(CO)_6 can be proposed as below. W(CO)_6 firstly decomposes to generate metallic W, which reduces Pt(acac)_2 and Ni(acac)_2 and forms W^{x+} ions. In the presence of trace of oxygen, W^{x+} ions are oxidized to $\text{WO}_{2.9}$ and then to $\text{WO}_{3.0}$. Our results provide a direct evidence confirming the hypothesis that W could accelerate the reduction of Pt and Ni ions proposed by Zhang *et al.*²¹ and Niu *et al.*³⁰

In order to examine the location of W in the product, EELS-elemental mappings for multiple particles formed at 230 °C were conducted and shown in Figure S7. Besides octahedral Pt-Ni particles, irregular WO_x nanoparticles were also found. To clarify whether W doping in the Pt-Ni particles occurred during the synthesis, EELS-elemental scan for a Pt-Ni octahedron was conducted and shown in Figure S8. It is clear that W atoms mainly located in the shell (surface or near the surface) of the Pt@PtNi core-shell particle. In the Pt core, the W content was negligible. This result confirms the incorporation of W in the product during the W(CO)_6 -assisted synthesis of Pt-Ni octahedra. And W incorporation mainly occurs together with the formation of the Pt-Ni shell.

Based on above experimental results and discussions, a general pathway of Pt-Ni octahedra formation is proposed and shown in Figure 1m. At temperatures below 140 °C, Pt(acac)_2 were reduced with the assistance of W forming ~3 nm sphere-like pure Pt seeds, which began to transform into truncated octahedra at ~160 °C. At higher temperatures, Pt and Ni ions were co-reduced. With the assistance of CO generated from the

decomposition of $\text{W}(\text{CO})_6$, Pt and Ni atoms might mainly deposit on (100) surfaces resulting in an octahedral shape. The morphology transformation to octahedron was nearly completed at 170 °C. Most of the Pt and Ni ions, however, were reduced between 180 and 210 °C with the edge length increasing from 5.7 to 9.0 nm. In this step, Pt and Ni atoms were deposited uniformly on the surface following an epitaxial growth mechanism, resulting in a core-shell structure consisting of a Pt-rich core and a uniform Pt-Ni shell. This mechanism is also in good agreement with our previous work on the deposition of an ultrathin (~1 nm in thickness) Pt-Ni shell on Pd NCs in a two-pot synthesis.³¹ It is worth noting that $\text{W}(\text{CO})_6$ not only provides CO to control the morphology of Pt-Ni, but also generates W^0 to facilitate the reduction of Pt and Ni ions. The exact role of $\text{W}(\text{CO})_6$ in controlling the morphology requires more detailed study.

We further correlate the structure and composition with ORR activity of samples formed at different temperatures. For Pt-Ni NCs formed at 170 °C and lower temperatures, the surfactants (OAm/OAc) could not be removed easily. Figure S9 compares the XPS spectra of N 1s of representative samples at 170, 180, and 230 °C. A strong N 1s signal (~398 eV) could be seen in the 170 °C sample, indicating the existence of residual surfactants on the surface. In contrast, it was negligible in other two samples. The high coverage of surfactants on the surface for the sample formed at 170 °C is also reflected in the cyclic voltammogram (CV, Figure S10). The CVs of samples at 180 and 230 °C show typical features of Pt alloys,³² while the faradic currents associated with H adsorption/desorption and oxide formation/reduction for the sample at 170 °C are much smaller due to surface contaminations. At low temperature, the surface is mainly composed of Pt atoms. With increasing temperature, the Ni percentage gradually increases on the surface of NCs, resulting in a lower coverage of surfactants. Based on this finding, we conclude that the interaction between surfactants and surface of Pt-Ni

NCs may be dependent on the surface composition: a stronger interaction is expected to exist on a surface with a higher Pt to Ni ratio.

The oxygen reduction polarization curves of Pt-Ni/C samples at 170, 180, 190, 210 and 230 °C in oxygen-saturated 0.1 M HClO₄ solutions are shown in Figure 4a. For comparison, the curve for a commercial Pt/C (TKK, 46%) is also included. It is clear that the ORR activity of the sample at 170 °C is very low due to surface contamination. The polarization curves of other samples are parallel to that of Pt/C in the mixed and kinetic controlled regions, and have a very similar limiting current density suggesting negligible surface contamination. It is worth noting that Pt loadings on rotating disk electrodes (RDEs) varies for different samples. Kinetic currents are normalized to the Pt mass on the RDE and real surface area derived from CO stripping, and are compared in Figure 4b and c, respectively. The Pt mass activities at 0.9 V (vs RHE) of Pt-Ni/C samples at 180, 190, 210, and 230 °C are 0.64, 1.58, 1.75, and 2.00 A mg⁻¹, respectively (Table S2). These values are also much higher than that of Pt/C (0.20 A mg⁻¹). Even though the average particle size increases with increasing temperature resulting in a lower Pt utilization, the Pt mass activity increases as a function of temperature. This trend is mainly caused by the optimization of Pt to Ni ratio during the synthesis resulting in higher specific activities. Figure 4c and Table S2 clearly show that the specific activity also increases with temperature due to larger particle sizes and optimized Pt to Ni ratios.

Figure 4. (a) The positive-going ORR polarization curves of Pt-Ni/C samples at 170, 180, 190, 210, and 230 °C, and a commercial Pt/C (TKK) in an O₂-saturated 0.1 M HClO₄ solution with a scanning rate of 10 mV s⁻¹ and the rotation speed of 1600 rpm. Pt loadings on the RDE are 5.00, 6.80, 1.48, 1.86, 2.94, and 5.00 µg for Pt-Ni/C samples at 170, 180, 190, 210, and 230 °C and Pt/C, respectively. The Tafel plots of (b) mass activity and (c) specific activity derived from (a).

Potential cycling was conducted in order to gain more insights into the structure of Pt-Ni octahedra. A triangle cycling protocol was adapted by cycling the Pt_{2.4}Ni/C formed at 230 °C between 0.60 and 1.0 V with a scanning rate of 50 mV s⁻¹ in an O₂-saturated 0.1 M HClO₄ solution. The CVs and oxygen reduction polarization curves before and after 5000 and 10000 cycles are compared in Figure 5a and 5b, respectively. The as-synthesized sample showed a couple of small current peaks in the region of 0.35 and 0.7 V, possibly associated with Ni-OH species. These currents disappeared after cycling implying that Ni atoms in the surface were removed. There is no noticeable change in ORR polarization curves with only a couple of mV shift in the half-wave potential before and after potential cycling in Figure 5b. The distributions of Pt and Ni, however, change significantly. As shown in Figure 5c, the octahedral shape was maintained after 10000 cycles. The Ni atoms were removed from the surface and sublayers of Pt-Ni octahedra, resulting in an octahedral nanostructure consisting of a Pt-rich shell, a Pt-Ni alloy interlayer and a Pt-rich core (Figure 5f). The excellent stability of Pt-Ni octahedra under the current testing condition can be ascribed to the formation of a thick (1-1.5 nm) and stable Pt layer.^{33,34} This structure and composition evolution pathways found in this study are also drastically different from that observed by Gan *et al.*²⁴ In their case, a pure Pt nanopod was formed during potential cycling due to dissolution of Ni in the Ni-rich facets. Based on these results, we conclude that the structural and composition evolution

mechanisms in both formation and degradation processes of Pt-bimetallic octahedra are highly dependent on the synthesis methods.

Figure 5. (a) CVs in a N_2 -saturated 0.1 M HClO_4 solution and (b) ORR polarization curves in an O_2 -saturated 0.1 M HClO_4 solution of octahedral $\text{Pt}_{2.4}\text{Ni}/\text{C}$ synthesized at 230 °C before (red line), and after 5000 (blue line) and 10000 (black line) cycles. The Pt loading is $10.2 \mu\text{g cm}^{-2}$. (c) ADF-STEM image of a single Pt-Ni octahedron after 10000 potential cycles. (d-f) The corresponding STEM-EELS element maps: Pt (d, red) and Ni (e, green) and their mixture (f).

In conclusion, a systematic study on formation pathways of Pt-Ni octahedra in a synthesis protocol involving $\text{W}(\text{CO})_6$ was conducted. Intermediate Pt-Ni NCs obtained at various temperatures were characterized by HRTEM, EELS, XRD, XPS and RDE. Our results revealed a unique structural and composition evolution pathway of Pt-Ni octahedra. Pure spherical Pt seeds with the diameter of 3-4 nm were formed at 140 °C and gradually changed to a truncated octahedron at 160 °C. The morphology transformation to octahedron was nearly completed at 170 °C. Most of Pt and Ni atoms were reduced between 180 and 210 °C. This step involved the epitaxial growth of Pt-Ni layers, resulting in a core-shell structure consisting of a Pt-rich core and a uniform Pt-Ni shell. Moreover, our results also provide a direct evidence confirming that $\text{W}(\text{CO})_6$ not only provides CO to control the morphology of Pt-Ni, but also generates W^0 to accelerate the reduction of Pt and Ni ions. The unique core-shell structure and uniform distribution of Pt and Ni in the {111} shell is responsible for the high ORR activity and stability. Our results also imply that it is possible to replace the Pt core with other cheaper materials under this unique structural and composition evolution mechanism. These insights will provide a guideline to rational synthesis of shape-controlled bimetallic electrocatalysts with desired electrocatalytic activity and stability. Further studies on the structural and composition changes of bimetallic NCs under different electrochemical and thermal tests are highly recommended.

ASSOCIATED CONTENT

Supporting Information

Experimental details, atom numbers and color variation figures of Pt-Ni samples, ADF-STEM images and elemental mappings, XRD of Pt-Ni samples, XRF spectra, XPS

spectra of W and N, and CVs, ORR activities of Pt-Ni/C samples,. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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