Influence of Metal–Ligand Coordination on the Elemental Growth and Alloying Composition of Pt–Ni Octahedral Nanoparticles for Oxygen Reduction Electrocatalysis

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ABSTRACT: Understanding the role of surfactants or ligands on the growth mechanism of metal/alloy nanoparticles (NPs) is important for controlled synthesis of functional metallic NPs with tailored structures and properties. There have been a number of works showing the significant impact of surfactants/ligands on the shape-controlled synthesis of nanocrystals with well-defined surfaces. Beyond the morphological shape control, impact of the surfactants/ligands on the alloying structure of bimetallic nanocrystals, however, still remains largely unaddressed. We reveal here a significant effect of benzoic acid ligand on the elemental growth and alloying phase structure of octahedral Pt–Ni NPs, a class of highly active electrocatalyst for oxygen reduction reaction in fuel cells. Contrary to previous reports showing the critical role of benzoic acid in directing the growth of octahedral Pt–Ni NPs, we found that benzoic acid played a minor role in forming the octahedral shape; instead, it can strongly coordinate with Ni cation and significantly slows down its reduction rate, leading to a phase separation in the Pt–Ni NP products (a mixture of Pt-rich octahedral NPs and nearly pure Ni NPs). Such phase separation further resulted in a lower catalytic activity and stability. These results help us comprehensively understand the effect of metal–ligand coordination chemistry on the elemental growth mechanism and alloying phase structure of bimetallic NPs, complementing previous emphasis on the role of surfactants in purely morphological shape control.

INTRODUCTION

The elemental growth kinetics of metal alloy nanoparticles (NPs) can greatly impact their shape, composition, and thereby their physicochemical properties. To synthesize shaped NPs with specific surface structures and functionalities, it is usual to grow the NPs with the desire surfaces under the protection of a certain surfactant. For instance, there have been intense interests in the synthesis of octahedral PtNi alloy NPs enclosed by {111} facets, which represents one of the state-of-the-art highly active electrocatalyst for the cathodic oxygen reduction reaction (ORR) in fuel cells. Several methods have been successfully developed during past years, including organic phase reduction using oleylamine and oleic acid as the surfactants and solvothermal synthesis in a N,N-dimethylformamide (DMF) solvent with or without benzoic acid (BA) as the surfactant. Studying the effect of surfactants on the elemental growth kinetics is critical to guide the morphology and surface compositional control of the shaped alloy NPs. Although the effect of surfactants on the NP morphology/shape has been extensively studied and more recently quantitatively analyzed through a ligand chemistry approach, the impact of surfactants on the elemental growth kinetics and alloying phase structure of bimetallic alloy NPs has been rarely studied. This work aims to fill this knowledge gap.

Taking the DMF-solvothermal synthesis of octahedral Pt–Ni NPs as a typical example, the role of BA surfactant in forming the octahedral NPs is still in debate. Carpenter and Cui et al. showed that the octahedral Pt–Ni NPs can be prepared by the DMF-solvothermal reduction without any dedicated surfactants, making it an ideal method for synthesizing octahedral Pt–Ni NPs with clean catalytic surfaces. However, Huang reported that the use of BA was critical for the growth of Pt–Ni octahedral NPs in the DMF solvent. When BA was replaced with phenol or benzaldehyde, only small cubes or irregular particles formed. They concluded that it was the BA adsorbed on the {111} facets that promoted the formation of octahedral Pt–Ni NPs. Besides the unclarified role of the BA in controlling the octahedral shape, how BA affects the alloying structure of PtNi NPs also remains unaddressed.
Here, we reveal the effect of BA on the elemental growth kinetics and alloying phase structure of octahedral PtNi NPs during the DMF-solvothermal synthesis by using a transmission electron microscope (TEM) combined with ultraviolet (UV)/visible spectroscopy and Fourier transform infrared spectroscopy (FTIR). We show that regardless the usage of BA surfactant, PtNi octahedral NPs can be steadily synthesized by the DMF solvothermal reduction, although BA may improve the quality of the octahedral shape. However, it is also found that BA can significantly decrease the NP size and more importantly slows down the reduction kinetics of Ni precursor via forming a new Ni−(BA) complex precursor, leading to a phase separation in the final Pt−Ni NPs. Refining previously well-recognized shape-directing role,3,6 our results contribute to a deeper understanding on the metal−ligand coordination chemistry and its effect on the elemental growth mechanism and phase separation of bimetallic alloy NPs.

■ RESULTS AND DISCUSSION

We prepared Pt−Ni NPs using the DMF-solvothermal reduction at different temperatures (120−200 °C) in the presence and absence of BA. The as-prepared NPs were further supported on a high-surface-area carbon support (Vulcan XC, Cabot), and their TEM images are shown in Figure 1. In the absence of BA (Figure 1a−d, and the particle size histogram shown in Figure 1j), most of the NPs exhibit the octahedral shape except that the NPs turn to a cuboctahedral shape at the highest temperature (200 °C), which was ascribed to the selective adsorption of acac ligand on the {111} facets.12 The NP size increases with the increase of reaction temperature. The bulk compositions of the NPs were measured by inductively coupled plasma (ICP) mass spectrometry, showing that the Ni content in the NPs increases with increasing temperature (from Pt62Ni38 at 120 °C to Pt30Ni70 at 200 °C).

This is reasonable because the Pt ion has a more positive reduction potential than Ni ion, and thus the Ni precursor was reduced much slower at lower temperatures. As the temperature increases, the reduction rate of Ni precursor increases, leading to increased Ni content in the NPs.

When BA was added into the reaction solution, we obtained octahedral Pt−Ni NPs (denoted as PtNi-BA) with much smaller NP size (about 4 nm in ledge length), as shown by the TEM images in Figure 1e−h and the particle size histogram in Figure 1l. The smaller particle size also indicates a strong effect of BA in inhibiting the NP growth. In addition, we found that the Ni content of NPs formed with BA (Figure 1k) was generally lower than those prepared without BA (Figure 1i) at identical temperatures, although higher temperature again resulted in higher Ni content. This indicates that BA may slow down the reduction rate of the Ni precursor.

The effect of BA on the alloying structure of Pt−Ni NPs was further characterized by X-ray diffraction (XRD, Figure 2). In the absence of BA, all Pt−Ni NPs show the same face-centered cubic structure, whereas the diffraction peaks shifting to higher angles at higher synthesis temperatures, indicating a higher alloying content of Ni in the Pt−Ni alloy phase due to a larger contraction of lattice parameter. However, in the presence of BA, the XRD patterns of the Pt−Ni NPs prepared under higher temperatures show no obvious shift of the diffraction peaks relative to the one prepared at 120 °C, even though the Ni content also increases with increasing temperature as shown by ICP. Instead, a separate pure Ni phase, identified by the Ni(111) peak at 44.5°, starts to emerge at 140 °C and higher temperatures. We therefore conclude that BA can strongly
affect the elemental growth kinetics of the octahedral Pt−Ni NPs, leading to the separated Pt-rich NPs and nearly pure Ni NPs. The existence of a separate Ni-rich phase in the Pt−Ni NPs prepared in the presence of BA was also confirmed by high-angle annular-dark field scanning transmission electron microscopy (STEM) images (Figure S1), whereas no pure Ni NPs were found in the synthesis without BA.

We further investigated the effect of different amounts of BA (0, 0.25, 2.5, and 5 mmol) on the growth of octahedral Pt−Ni NPs at 160 °C. Figure 3a−e shows that all NPs show a similar octahedral shape but the size decreases with increasing amount of BA, indicating a strong effect of BA in inhibiting the NP growth. The XRD result (Figure 3f) further shows that with increasing amount of BA, the diffraction peaks shift to lower angles, indicating decreasing alloying degree of Pt and Ni. Again, the separate pure Ni phase identified by the Ni(111) peak at 44.5° exists on all Pt−Ni NPs synthesized with BA. Thus, our results indicate a strong effect of BA on the elemental growth of octahedral Pt−Ni NPs, thus leading to decreased alloying extent of Pt−Ni and the formation of a separate pure Ni NPs.

To gain insight into the origin of the impact of BA, we conducted UV/vis and FTIR spectroscopy of Pt(acac)2, Ni(acac)2, BA, and their mixtures in an ethanol solvent (Figure 4). Figure 4a shows that the UV/vis spectrum of a mixed solution of BA and Pt(acac)2 is simply coincided with the addition of the UV/vis spectrum of BA and the UV/vis spectrum of Pt(acac)2. Because the absorbance is proportional to the concentration of the absorbent, it indicates that BA has no interaction with Pt(acac)2. In contrast, when mixing BA and Ni(acac)2 in ethanol (Figure 4b), both the adsorption peaks of BA (λmax = 227 nm) and Ni(acac)2 (λmax = 295 nm) decreased, suggesting a possible interaction between BA and Ni(acac)2.

More information on the interaction between BA and Ni(acac)2 can be induced from the FTIR measurement (Figure 4c,d). The FTIR spectrum of the mixed solution of BA and Pt(acac)2 again can be well decomposed into the spectrum of pure Pt(acac)2 and the spectrum of BA, indicating no interaction between Pt(acac)2 and BA (Figure 4c). However, for the mixed solution of BA and Ni(acac)2 (Figure 4d), the adsorption bands associated with the −COOH group in the BA (Figure 4d, denoted by the open marks) weakened significantly, whereas the adsorption bands assigned to the benzene ring (denoted by the solid marks in Figure 4c) in the BA almost kept unchanged. This result suggests a strong coordination of Ni2+ with the carboxylic group rather than the benzene ring in BA. Indeed, two new adsorption bands at 1571 and 1382 cm−1 emerged, which were assigned to the asymmetric and stretch vibration of the −COO− group coordinated with metal cations in several carboxylates, respectively, such as zinc benzoate and sodium benzoate (see Figure S2). This indicates a likely similar coordination of benzoate group with the Ni ion. We note that Ni(acac)2 has a higher complex stability constant (10.7) than Ni benzoate (0.9), indicating that the acac ligand should be more strongly

![Figure 2. XRD analysis of Pt−Ni octahedral NPs prepared without and with BA at different temperatures.](image)

![Figure 3. (a−d) TEM images of the Pt−Ni octahedral NPs prepared with different amounts of BA at 160 °C: (a) 0, (b) 0.25, (c) 2.5, and (d) 5 mmol. (e) Particle size distributions of Pt−Ni NPs prepared with different amounts of BA at 160 °C. (f) XRD analysis of Pt−Ni octahedral NPs prepared with different amounts of BA at 160 °C.](image)
coordinated with Ni. Therefore, the BA may act as additional ligands coordinated with the Ni center (as illustrated in Figure 4e). However, because of much higher concentration (2.5 mM) of BA than Ni(acac)₂ (0.5 mM), direct replacement of acac ligand by benzoate ligand cannot be excluded. In fact, several previous works have also reported the formation of various coordination structures including a chained structure between BA, Ni²⁺ ion, and water molecule. The preferential coordination of BA with Ni²⁺ rather than Pt²⁺ can be ascribed to the existence of more empty 3d state in Ni²⁺, which allows the additional complex with BA.

Regardless its detailed structure, the newly formed Ni complex must have a stronger metal–ligand interaction compared to the original Ni(acac)₂ complex and thus would make the reduction of Ni²⁺ more difficult, which would further impact the growth kinetics of the octahedral Pt–Ni NPs. Following our previous study, during the growth of the Pt–Ni octahedral NPs, the Pt-rich phase grew first into a hexapod structure because of the higher reduction potential of Pt²⁺, whereas the Ni-rich phase deposited subsequently on the concave surface with the aid of step sites, as schemed in Figure 5a. This sequential deposition of Pt and Ni leads to the compositional segregation (Ni-rich facets and Pt-rich edges/}

Figure 4. UV/vis spectra (a,b) and FTIR spectra (c,d) of mixtures of Pt(acac)₂, Ni(acac)₂, and BA at room temperature. The assignment of each adsorption band is according to refs 17 and 18. (e) Schematic of a typical coordination of BA with Ni²⁺.

Figure 5. Schematic illustration of the elemental growth mechanism and alloying structure of Pt–Ni octahedral NPs without (a) and with (b) BA.
In the presence of BA, the reduction rate of Ni was further slowed down so that reduction/deposition of Ni may no longer catch up the reduction/deposition of Pt (Figure 5b). In this context, the preformed Pt-rich hexapods will finally grow into Pt-rich octahedral NPs. Once Pt-rich octahedral NPs complete, there will be no step sites for accommodating Ni deposition. In addition, the absorbed BA on the surface of the Pt-rich nucleus may also inhibit the successive deposition of Ni atoms. Therefore, separate pure Ni NPs have to nucleate and grow separately, whereas the preformed Pt-rich octahedral NPs showed a lower extent of alloying compared those prepared without BA, fully consistent with the XRD results.

Figure 6 further compares the ORR catalytic activities of the Pt−Ni NPs synthesized with and without BA. The electrochemically active surface area (ECSA) of the Pt−Ni NPs prepared with BA is generally larger than those prepared without BA because of the smaller particle sizes of the former (see Table 1). To compare their activities, we calculated the kinetic current at 0.9 V from the ORR polarization curves and normalized them by both the ECSA and the Pt mass. The mass activities of the PtNi-BA catalysts have no obvious advantage over the PtNi catalysts and even showed lower mass activity at 140 and 180 °C. More importantly, the specific activity of the PtNi catalysts is substantially higher than that of PtNi-BA catalysts. This is consistent with the higher Ni content and higher alloying extent in the former. Generally, a higher alloying degree means a higher Ni content in the Pt−Ni alloy phase. This would result in higher content of Ni at the subsurface region of the dealloyed Pt−Ni NPs during the ORR test, which would further lead to a higher extent of compressive strain on the Pt-rich surface and thus a higher ORR activity. Therefore, although the addition of BA reduces the size of the NPs and increases the ECSA, the phase separation caused by BA results in a decrease in the intrinsic specific activity of the PtNi octahedral NPs because of the attenuation of the Ni-induced strain and ligand effects.

We further evaluated the electrochemical durability of the PtNi and PtNi-BA catalysts by conducting the accelerated durability test between 0.6 and 1.0 V in N2-saturated 0.1 M HClO4 at a scan rate of 50 mV/s (Figure 7). After 4000 cycles, the mass activities of PtNi-140-BA, PtNi-160-BA, and PtNi-180-BA decayed by 69, 68, and 57%, respectively, whereas PtNi-140, PtNi-160, and PtNi-180 decayed by 47, 52, and 57%, respectively, whereas PtNi-140, PtNi-160, and PtNi-180 decayed by 47, 52, and 57%, respectively, whereas PtNi-140, PtNi-160, and PtNi-180 decayed by 47, 52, and 57%, respectively.
54%, respectively. This result shows that the PtNi octahedral NPs synthesized without BA are more stable than the PtNi-BA octahedral NPs with BA. This is due to the smaller NPs synthesized with BA possessed increased ratio of atoms at low-coordination sites, which are more prone to oxidation and dissolution and easier to diffuse from the vertex and edge to the center, thereby losing the octahedron morphology and showing decreased catalytic activity.

**CONCLUSIONS**

We studied the effect of BA on the morphology and structure of the Pt–Ni octahedral NPs synthesized by the DMF-solvothermal synthesis. Regardless of the presence or absence of BA, octahedral Pt–Ni NPs can be steadily synthesized in the DMF solvent, indicating a minor role of BA in selective protecting of the {111} facets. Moreover, besides the conventional effect in inhibiting the NP growth and hence decreased the particle size, we found that BA preferentially changed the reduction/deposition kinetics of Ni by forming a new complex compound with Ni²⁺, leading to slower reduction/deposition rate of Ni and thereby a phase separation (i.e., the coexistence of Pt-rich alloy NPs and pure Ni NPs) in the final product. Therefore, in the presence of BA, the Pt–Ni octahedral NPs showed not only much smaller particle size but also a low alloying extent because of the formation of a separate pure Ni NPs, which further lead to lower ORR electrocatalytic activity and stability. Our results demonstrate that the metal–ligand coordination chemistry can not only determine the morphology/shape but also the elemental reduction kinetics and alloying structure of bimetallic NPs.

**EXPERIMENTAL SECTION**

**Chemicals.** Platinum(II) acetylacetonate [Pt(acac)₂], nickel(II) acetylacetonate [Ni(acac)₂], and BA were purchased from Sigma-Aldrich. Nafion solution (5 wt %) and isopropanol were purchased from Sigma-Aldrich. All of the chemicals were used as received without further purification. The water (18 MΩ/cm) used in all experiments was purified through a Milli-Q lab system (Nihon Millipore Ltd.).

**Synthesis of Pt–Ni NPs.** In a typical synthesis of octahedral Pt–Ni NPs, 0.2 mmol Pt(acac)₂, 0.5 mmol Ni(acac)₂, and 209 mg of Vulcan XC-72 carbon support were mixed together in 50 mL of DMF, followed by 10 min vigorous stirring. The resulting homogeneous solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated from room temperature to different reaction temperatures (120, 140, 160, 180, and 200 °C) for 42 h before it was naturally cooled down to room temperature. The products were collected by centrifugation and washed with ethanol/water three times. The as-synthesized NPs were denoted as PtNi-120, PtNi-140, PtNi-160, PtNi-180, and PtNi-200. The octahedral Pt–Ni NPs with BA were synthesized following the same procedure except by adding 2.5 mmol BA to the solution before stirring. The as-synthesized NPs were denoted as PtNi-120-BA, PtNi-140-BA, PtNi-160-BA, PtNi-180-BA, and PtNi-200-BA.

**Materials Characterization.** TEM images were conducted on a FEI Tecnai G² spirit operated at an accelerating voltage of 120 kV. The real metal loading and composition of the Pt–Ni NPs was measured by ICP optical emission spectrometry (ARCOS II MV SPECTRO). XRD patterns were collected on a D8 ADVANCE-diffactometer (Bruker) equipped with a LynxEye detector and KFL Cu 2K X-ray tube. UV/vis spectroscopy was carried out on an Agilent Cary 5000 spectrometer. The FTIR spectra were measured on a Thermo Scientific Nicolet i550 spectrometer by placing a few drops of the solution on the surface of a diamond cell.

**Electrochemical Measurements.** The catalyst ink was prepared by mixing 5 mg of carbon-supported Pt–Ni catalysts in 5 mL of a mixed solution of ultrapure water, isopropanol solution, and 5 wt % Nafion, which was then ultrasonicated for 15 min. A 10 μL aliquot was added dropwise onto a 5 mm-diameter rotating disk electrode (RDE), resulting in nominal Pt loading of about 6 μg/cm². The ink was dried in an oven at 50 °C for 20 min forming a uniform thin film at the RDE surface. A Pt wire and a saturated Hg/Hg₂SO₄ were used as counter electrode and reference electrode, respectively. All electrode potentials were recorded with respect to the reversible hydrogen electrode (RHE) and iR-compensated. Before testing the oxygen reduction activities, cyclic voltammetry (CV) was conducted in N₂-saturated 0.1 M HClO₄ solution between 0.05 and 1.0 V at 100 mV/s for 20 cycles. The 20th potential cycle was recorded to evaluate the ECSA. Linear sweep voltammetry was then conducted in O₂-saturated 0.1 M HClO₄ solution from 0.05 to 1.0 V at 5 mV/s (1600 rpm). The stability test was performed between 0.6 and 1.0 V in N₂-saturated 0.1 M HClO₄ at 50 mV/s for 4000 cycles.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03366.

STEM images of the PtNi-180 and PtNi-BA-180 catalysts and standard FTIR spectra of BA and sodium benzoate (PDF)

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We thank the financial supports by Nature Science Foundation of China (NSFC) (under grant numbers 21573123 and 16221033), the Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (grant no. 2017BT01N111), Guangdong Natural Science Foundation for Distinguished Young Scholars (2016A03036035), and Basic Research Program of Shenzhen (JCYJ20160531194754308) in China. This work made use of the TEM facilities at the Electron Microscopy Laboratory, Materials and Devices Testing Center, Graduate School at Shenzhen, Tsinghua University.
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