Size-controlled PtNi3 nanoparticles between 3 and 10 nm are successfully synthesized by tailoring nucleus composition during organic solution reduction. The PtNi3 nanoparticles exhibit an unusual “volcano-shaped” size effect on the oxygen reduction reaction (ORR) activity and stability, largely due to their size-dependent Ni dissolution during ORR electrocatalysis. The results provide important guidelines for further improvement of active and stable cathode catalysts for proton-exchange-membrane fuel cells.
Size-Controlled Synthesis of Sub-10 nm PtNi₃ Alloy Nanoparticles and their Unusual Volcano-Shaped Size Effect on ORR Electrocatalysis

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Dealloyed Pt bimetallic core–shell catalysts derived from low-Pt bimetallic alloy nanoparticles (e.g., PtNi₃) have recently shown unprecedented activity and stability on the cathodic oxygen reduction reaction (ORR) under realistic fuel cell conditions and become today's catalyst of choice for commercialization of automobile fuel cells. A critical step toward this breakthrough is to control their particle size below a critical value (~10 nm) to suppress nanoporosity formation and hence reduce significant base metal (e.g., Ni) leaching under the corrosive ORR condition. Fine size control of the sub-10 nm PtNi₃ nanoparticles and understanding their size dependent ORR electrocatalysis are crucial to further improve their ORR activity and stability yet still remain unexplored. A robust synthetic approach is presented here for size-controlled PtNi₃ nanoparticles between 3 and 10 nm while keeping a constant particle composition and their size-selected growth mechanism is studied comprehensively. This enables us to address their size-dependent ORR activities and stabilities for the first time. Contrary to the previously established monotonic increase of ORR specific activity and stability with increasing particle size on Pt and Pt-rich bimetallic nanoparticles, the Pt-poor PtNi₃ nanoparticles exhibit an unusual “volcano-shaped” size dependence, showing the highest ORR activity and stability at the particle sizes between 6 and 8 nm due to their highest Ni retention during long-term catalyst aging. The results of this study provide important practical guidelines for the size selection of the low Pt bimetallic ORR electrocatalysts with further improved durably high activity.

1. Introduction

Rational design of highly active and durable Pt bimetallic nanoparticulate electrocatalysts for oxygen reduction reaction (ORR) is crucial for the commercialization of proton-exchange-membrane fuel cells (PEMFCs). Although exceptional electrocatalytic ORR activities have been achieved through different catalyst designs using Pt bimetallic nanostructures,[1–8] demonstration of their practical viability particularly both high initial Pt-normalized mass activity and high long-term stability in realistic PEMFCs still remains limited.[9] Guided by the atomistic insights into the structural and surface compositional evolution during ORR electrocatalysis,[10,11] we recently developed a new generation of dealloyed PtNi₃ core–shell electrocatalysts that surpassed the U.S. Department of
Energy commercialization targets of 2017 for activity and stability, showing a high initial mass activity (>0.6 A mg\textsubscript{Pt}\textsuperscript{−1}) and high durability after 30,000 potential cycles (activity drop <50%) under realistic PEMFC conditions\textsuperscript{[12]} One key factor toward this achievement was to control the particle size below a critical value (e.g., 10 nm) to form nonporous core–shell NPs. These NPs were unique in that they were able to retain large fractions of their initial base metal in the lattice-contracted alloy core thereby exerting sustained compressive surface lattice strain and ORR activity\textsuperscript{[5,13,14]} Despite these progresses, a critical question concerning how particle size affect the activity and stability of nonporous sub-10 nm PtNi\textsubscript{3} NPs still remains unaddressed. An answer to this question would have great bearing on further improvement of active and stable PEMFC cathode catalysts.

In fact, while size-dependent oxygen reduction electrocatalysis of Pt\textsuperscript{[15–17]} and Pt-rich\textsuperscript{[18,19]} bimetallic NPs has been extensively studied and the formation conditions of porous structures have been unraveled\textsuperscript{[11,20–22]} the size-dependence on the ORR electrocatalysis for the nonporous low-Pt bimetallic NPs has still remained elusive. This is largely because that size-selected synthesis of sub-10 nm low-Pt bimetallic NPs still remained unachieved, despite significant progresses in size-controlled syntheses of Pt-rich bimetallic NPs during past years. For instance, Shevchenkov et al\textsuperscript{[23,24]} prepared size-selected Pt\textsubscript{x}Co NPs from 2 to 9 nm in diameter; however, in an effort to adjust the particle composition by changing the molar ratios between Pt- and Co-precursors, these NPs showed a constant Pt-rich Pt\textsubscript{x}Co stoichiometry. Later, Ahrenstorff et al. reported tunable compositions of Pt\textsubscript{1−x}Ni\textsubscript{x} NPs\textsuperscript{[25,26]} yet increasing particle size led to increased Ni content (and vice versa), indicating a coupling effect between the size and the composition. Choi et al. reported octahedral Pt-Ni NPs with tunable sizes whereas their compositions were mainly Pt-rich\textsuperscript{[19]} Recently, Snyder et al. prepared size-selected PtNi\textsubscript{3} NPs ranging from 8 to 20 nm\textsuperscript{[22]} most of which showed the formation of nanoporous particles above a critical size of ~12 nm and the size controlled preparation of nonporous sub-10 nm PtNi\textsubscript{3} NPs was still missing.

In this study, we report a facile strategy for fine size control of monodispersed sub-10 nm PtNi\textsubscript{3} NPs between 3 and 10 nm and disclose a novel size-selected growth mechanism by using transmission electron microscopy (TEM). This allowed us, for the first time, to address the size-dependent ORR activities and stabilities of the sub-10 nm low-Pt bimetallic nanoparticles. To gain atomic insights into their size dependence, we followed their atomic structural and compositional evolutions during ORR electrocatalysis by using TEM, aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). Unlike previously established monotonic size-dependence on the activity and stability of Pt-rich NPs, the Ni-rich PtNi\textsubscript{3} NPs demonstrate an unusual “volcano-shaped” size effect on the ORR electrocatalysis, showing the highest specific activity and stability at the initial sizes between 6 and 8 nm due to the highest retention of Ni under the corrosive ORR conditions. Our results provide an answer as to how to further improve the activity and durability of the new generation dealloyed PtNi\textsubscript{3} core–shell fuel cell catalysts.

2. Results and Discussion

The PtNi\textsubscript{3} bimetallic NPs studied here were prepared by solvothermal reduction of Pt(acac)\textsubscript{2} and Ni(acetate)\textsubscript{2} in dioctyl ether solvent in the presence of oleylamine and oleic acid, which mainly acted as capping agents, and 1,2-tetradecanediol (TDD), which acted as the reducing agent. To control their particle size while at a constant PtNi\textsubscript{3} composition, either tailoring the concentration of the oleylamine/oleic-acid or changing the reaction temperature exclusively failed. Instead, we found that tuning the amount of the reducing agent TDD alone was a facile and robust way to achieve this goal. Figure 1A–E shows the TEM images of the PtNi\textsubscript{3} NPs with increasing particle size prepared by employing increasing amounts of TDD from 0 to 75 mg under otherwise constant conditions. All these NPs showed a perfectly constant PtNi\textsubscript{3} composition (see energy dispersive X-ray spectroscopy (EDX) results indicated in Figure 1). Interestingly, the PtNi\textsubscript{3} NPs could be formed even in absence of TDD, showing the smallest particle size of 3.2 nm (Figure 1A). This result was likely due to a reducing power offered by oleylamine\textsuperscript{[27]} which can act as not only a capping agent but also a mild reducing agent. Thus, the reducing agent pair composed of oleylamine and TDD appears to be a facile tool for fine-tuning the particle size. High-resolution TEM (HRTEM) images in the inset of Figure 1D and Figure S1 (Supporting Information) indicate that the PtNi\textsubscript{3} NPs show a dominant single crystal face-centered cubic (fcc) cuboctahedral structure, while few exhibit a multiple-twinned decahedral shape (Figure S1, Supporting Information). The [111] interplane distance (around 2.16 Å) in between that of pure Pt (2.26 Å) and Ni (2.03 Å) suggests a high extent of alloying of Pt and Ni, though some invisible amorphous surface Ni oxide may also exist. The obtained size-selected PtNi\textsubscript{3} NPs can be further uniformly dispersed onto high surface area carbon supports (XC-72) for electrocatalytic applications, as exemplified in Figure 1F.

The size-controlling protocol can be also extended to Pt\textsubscript{1−x}Ni\textsubscript{x−y} NPs with other compositions. For instance, by changing the initial molar ratios of the Pt and Ni precursors to 1:1, PtNi NPs with the size of 3.5, 4.1, and 5.0 nm can be prepared by adding 12.5, 25 and 50 mg TDD (Figure 1G–I), respectively. Nevertheless, further increasing the amount of TDD led to irregular shaped particles with Pt-richer composition. Thus, the present method appears to be a robust way to fine-tuning the particle size of Pt\textsubscript{1−x}Ni\textsubscript{x−y} NPs at various constant compositions, while the tunable size range could be different for different compositions.

To gain insights into the role of TDD on the size-controlled synthesis, we studied the growth mechanism of the 3.2 nm PtNi\textsubscript{3} NPs (prepared without TDD) and the 7.8 nm PtNi\textsubscript{3} NPs (prepared with 50 mg TDD) by tracking their size and compositional evolutions across different reaction time (1, 5, 10, and 60 min). We uncover that the amount of TDD substantially controls the chemical composition of the nuclei particles initially formed after 1 min reaction. Without TDD, the initial nuclei show a particle size around 2 nm and a very Ni-richer composition (Figure 2A), while those nuclei formed in presence of 50 mg TDD exhibit a larger size of
around 3 nm and much Pt-richer composition (Figure 2B). To explain this discrepancy we hypothesize that the nuclei composition is associated with a different reduction rate ratio of Pt to Ni at the early nucleation stage. The Pt bimetallic NP nucleation was initiated by the reduction of Pt that subsequently induced a coreduction of Pt and Ni driven by the negative heat of alloying of PtNi; this is supported by the fact that Ni itself cannot be reduced under these conditions,[14,22,25,28] Thus, in the absence of TDD, both Pt(acac)2 and Ni(acetate)2 were obviously reduced more slowly by the mild reducing agent oleylamine, favoring Ni-richer nuclei; in contrast, adding or increasing the concentration of the strong reducing agent TDD significantly accelerated the reduction of Pt, leading to Pt-richer nuclei.

Surprisingly, once Pt-richer nuclei formed, they underwent much faster growth, with their size (Figure 2C, red circle) and Ni content (Figure 2D, red circle) increasing greatly to 7.8 nm and PtNi3, respectively (more TEM images shown in Figure S2, Supporting Information). The formed NPs featured a Pt-rich core and Ni-rich shell, as evidenced by the elemental mapping (Figure 2E) acquired using STEM-EELS. In contrast, the growth of the Ni-richer nuclei remained limited, with their size and Ni-content increased moderately to 3.2 nm PtNi3 (Figure 2C and D, green cubic).

Following earlier reports, the kinetics and thermodynamics of NP nucleation and growth can be generally described by the LaMer mechanism[29] or the Finke’s model.[22,30] The former mechanism postulates a fast, homogeneous “burst nucleation” at some critical supersaturation of the monomer, followed by a slow diffusion-controlled growth, whereas the latter mechanism proposes a slower continuous nucleation followed by an autocatalytic growth that is rate-limited by the incorporation of monomers onto the NP surface. According to the LaMer mechanism, increasing the concentration of the reducing agent results in a faster reduction of metal precursors and a high concentration of metal monomers, thus leading to a fast nucleation and smaller particles; this is, however, contrary to our results. We argue that the size-controlled synthesis of PtNi1−x NPs appears to follow the Finke’s model as schemed in Figure 2F. The Pt-richer nuclei formed under a higher concentration of TDD held more surface Pt sites for a fast, catalytic reduction of Pt(acac)2 and Ni(acetate)2 and subsequent NP growth.[31]

As a result, metal precursors were consumed quickly and
continuous multiple nucleation was suppressed, leading to larger particles. In addition, Pt-richer nuclei also suffered from less adsorbed oleic acid that was proved to tightly binds on Ni site,[25] also favoring a faster growth. In contrast, the Ni-richer nuclei formed under a low concentration of TDD grew slowly due to less surface Pt sites for catalytic reduction of metal precursors and more tightly adsorbed oleic acid on Ni sites. This in turn favored a sustained high concentration of monomers and thereby a continuous nucleation and slow growth, leading to small particle sizes. We therefore conclude that the concentration of the reducing agent TDD becomes a robust tool for fine-tuning the nuclei particle composition, which further substantially determinates the final NP size.

The successful fine size control of the sub-10 nm the PtNi$_3$ NPs then allows us to comprehensively explore their size dependence on the ORR electrocatalytic activity and stability. To form catalytically active core–shell structures, all PtNi$_3$ catalysts were activated by potential cycling between 0.06 V and 1.0 V/RHE, during which near surface Ni atoms were selectively dissolved and Pt-rich shells formed (electrochemical dealloying).[10] Expectedly, the electrochemical surface area (ECSA) of the activated PtNi$_3$ NPs, either evaluated from hydrogen under potential deposition (H$_{upd}$, Figure 3A) or measured by CO stripping method (Figure S6, Supporting Information), increased with decreasing particle size. The

Figure 3 presents the electrochemical measurement of ORR electrocatalysis on the annealed size-selected PtNi$_3$ NPs. To form catalytically active core–shell structures, all PtNi$_3$ NPs were activated by potential cycling between 0.06 V and 1.0 V/RHE, during which near surface Ni atoms were selective dissolved and Pt-rich shells formed (electrochemical dealloying).[10] Expectedly, the electrochemical surface area (ECSA) of the activated PtNi$_3$ NPs, either evaluated from hydrogen under potential deposition (H$_{upd}$, Figure 3A) or measured by CO stripping method (Figure S6, Supporting Information), increased with decreasing particle size. The
ORR polarization curves (Figure 3B) indicate that all activated PtNi₃ catalysts exhibit significant activity improvement relative to the state-of-the-art commercial TKK Pt/C catalyst. Figures 3C,D compare quantitatively the Pt-mass normalized activities (Figure 3C) and specific activities (Figure 3D) of the activated (diamond) and aged (cubic) PtNi₃ catalysts as a function of the initial particle sizes. As we will show later, all the PtNi₃ nanoparticles would undergo dynamic size shrinkage due to continuous Ni-leaching under ORR electrocatalysis; nevertheless, the actual particle size still shows a linearly increase with increasing initial particle sizes. Therefore, we choose to use the particle sizes of the as-prepared PtNi₃ nanoparticles (namely the initial particle sizes), which we can experimentally control, to describe their size-dependence on the ORR activities and stabilities. Figure 3C shows that, after electrochemical activation (diamond), the “3.2 nm PtNi₃” catalyst exhibits the highest mass activity (0.93 mA/mg Pt at 0.9 V/RHE), six times that of the commercial TKK Pt/C catalyst. This is the highest Pt-mass activity reported so far in nonshaped Pt bimetallic nanoparticle catalysts (e.g., Pt-Cu,[2,5] Pt-Co,[2,34] Pt-Fe,[35] etc.). Increasing the particle size led to decreased Pt-mass activity due to decreased surface area. The Pt-ECSA normalized specific activities after activation (Figure 3D, diamond), which represent the intrinsic surface reactivity, first increase as initial size increases from 3.2 to 6.7 nm and then decrease as the initial size further increases to 9.6 nm. This trend is radically different from previously reported size dependence of pure Pt and Pt-rich catalysts, which invariably showed a monotonic increase of specific activity with increasing particle size (see the gray dash line in Figure 3D as a guideline for pure Pt NP catalyst).[15–18]

We further examined the size-dependent catalytic stability of the PtNi₃ catalysts after 10,000 cycles of electrode potential cycling between 0.6–1.0 V (Figure 3C,D, cubic). The changes in the ORR polarization curves and the ECSA are shown in Figures S7 and S8 (Supporting Information). All aged catalysts exhibit evident mass activity drop (Figure 3C, cubic). For PtNi₃ NPs below 7.8 nm, the smaller the initial particle size, the more significant the activity drop, leading to a nearly constant retained Pt-mass activity irrespective of the particle size between 3.2 and 7.8 nm. Unexpectedly, larger PtNi₃ NPs (9.6 nm and above) also underwent a higher extent of activity degradation, contrary to previously held insight that larger Pt NPs are more stable. As a consequence, the “7.8 nm PtNi₃” catalyst appears to be most stable (32% drop). Inspection of the specific activities (Figure 3D, cubic) suggests that the aged “7.8 nm PtNi₃” also holds the highest specific activity among the nonporous PtNi₃ catalysts between 3 and 10 nm, accounting for its highest stability in the Pt-mass activity.

To understand the unusual “Volcano-shaped” size dependence on the activity and stability of PtNi₃ catalysts, we examined the morphological and compositional evolution of the activated and aged catalyst NPs (Figure 4A–F; more TEM images are shown in Figures S9 and S10, Supporting Information). The activated PtNi₃ catalysts underwent apparent size shrinking due to significant Ni-leaching (Figure 4E), whereas the aged catalysts show no obvious change in particle sizes, suggesting the absence of significant
Ostwald ripening. Importantly, the retained Ni content in the activated and aged PtNi$_3$ NPs (Figure 4F) also shows a “Volcano-shaped” dependence on the initial particle size. After activation (Figure 4F, red diamond), the Ni content appears to slowly increase with the size increasing to 9.6 nm, and finally decreases in the 25 nm NPs. Once subjected to electrochemical aging (Figure 4F, green cubic), both smaller particles (6.7 nm and below) and larger particles (9.6 nm and above) suffered from obvious further Ni leaching, whereas the “7.8 nm PtNi$_3$” catalyst shows the minimum Ni loss with the highest retained Ni content (from 37 at% to 32 at%), consistent with its highest catalyst stability.

We rationalized the unique size-dependency on the retained Ni content as a consequence of several counterbalancing effects. First, geometrically, the larger the particles, the smaller ratio of surface atoms, and thus the more Ni retained at the solid particle core after surface leaching. Second, according to the Gibbs–Thomson effect,$^{[36]}$ the electrochemical dissolution potential at which NPs of diameter $d$ start dissolving is always more negative than that of bulk materials; it decreases with $1/d$, thus the dissolving tendency of (near) surface Ni atoms would increase as the particle size decreases. In consequence, this leads to lower retained Ni contents for smaller PtNi$_3$ NPs. Third, following earlier reports,$^{[10,11,20,22]}$ the extent of Ni leaching also sensitively depends on the particle size due to kinetically controlled surface atomic dealing processes involving the dissolution of Ni competing with the diffusion of Pt. The surface diffusion rate of residual Pt atoms cannot compete with the Ni leaching rate of Ni at larger particles, leading to a higher extent of Ni dissolution, thicker skeleton Pt shells with low average coordination, and even nanoporosity.$^{[11,21]}$ In this context, larger PtNi$_3$ particles demonstrate even worse Ni retention, an effect akin to the previously reported anti-Gibbs–Thomson effect.$^{[37]}$ This is corroborated by the STEM and EELS spectrum imaging (Figure 4G,H): the aged “7.8 nm PtNi$_3$” NPs exhibit a solid core–shell structure with a large amount of Ni survived at the core and a thin Pt shell of around 1 nm, whereas the 25 nm NPs featured a nanoporous structure with minimum retained Ni (see more TEM images in Figure S10, Supporting Information), consistent with our previous findings.$^{[10,11]}$ Taken together, the highest retained Ni content at a medium particle size of 7.8 nm appears to be a compromise among the geometric effect, the thermodynamic Gibbs–Thomson effect and the kinetic anti Gibbs–Thomson effect.

The size-dependent Ni dissolution—revealed for the first time in this study—provides important insights into the “Volcano-shaped” size-dependency on the activity and stability of the PtNi$_3$ catalysts. Previously established size effect of Pt or Pt-rich NPs on the surface-specific ORR activity was
generally accounted by the size-dependent surface coordination: larger NPs hold less low-coordinated surface Pt atoms, favoring higher ORR activity and stability.[16,17] For the Ni-rich PtNi₃ bimetallic catalysts, our results suggest that the size-dependent Ni dissolution plays an additional, perhaps more critical role compared with the surface-coordination effect in determining the size-dependent ORR specific activities and stability. A higher retained Ni content at the core favors a sustained higher surface compressive strain and higher ORR activities[5,13] which nicely accounts for the highest ORR specific activity and stability on the PtNi₃ NPs with the initial sizes between 6.7 and 7.8 nm. Our study therefore highlights the significant difference on the size dependence between Pt-rich and low-Pt bimetallic nanocatalysts. We are aware that the highest specific activity after initial activation occurred at the “6.7 nm PtNi₃” instead of the “9.7 nm PtNi₃” as one should expect from the both larger size and higher retained Ni content of the latter. This may arise from a lower average surface coordination in associated with a higher surface roughness on the “9.7 nm PtNi₃” due to its slower Pt surface diffusion during Ni leaching.

3. Conclusion

We developed a robust approach to finely control the particle size of sub-10 nm PtNi₃ bimetallic NPs at a constant particle composition by simply tailoring the concentration of the reducing agent during organic solvothermal reduction. We further revealed an unusual ‘Volcano-shaped’ dependency of the ORR activity and stability on the initial particle size of the low-Pt bimetallic (PtNi₃) catalysts, contrary to the monotonic increase of specific activity with increasing size as widely established in pure Pt and Pt-rich NPs. The PtNi₃ NPs with initial particle sizes between 6 and 8 nm showed the most durably high activity due to their highest retained Ni contents under the acidic ORR condition. Our results highlight the complexity of the size-related structural and compositional behaviors of low Pt bimetallic catalysts under the corrosive electrocatalytic condition. We are confident these new findings will provide new insights and spark fresh impetus into the science of size effect of bimetallic NPs in electrocatalysis, particularly the dealloyed PtNi₃ catalysts that held the record activity and stability in realistic fuel cells so far,[8,12] to harvest all advantages of this new generation fuel cell electrocatalyst.

4. Experimental Section

Nanoparticle Synthesis: In a typical synthesis of the 7.8 nm PtNi₃ nanoparticles (NPs), 0.3 mmol of Ni(acetate)₃, 0.4 mmol of 1,2-tetradecanediol (TDD), 0.6 mL of oleic acid, and 0.6 mL of oleylamine were added into 40 mL of dioclytether in a three-neck flask. The solution was then heated to 80 °C in magnetic heating mantle and maintained at this temperature for 0.5 h under nitrogen flow to remove trace water. The temperature was then increased to 200 °C in 15 min, and then 0.1 mmol platinum acetylacetone (Pt(acac)₂) dissolved in 0.7 mL dichlorobenzene was added to the reaction flask via syringe. The reaction solution was held at 200 °C for 1 h and then cooled down to room temperature. The nanoparticles were precipitated, washed by ethanol and mixed with XC-72 carbon black support at a nominal Pt loading of 15 wt.%,[31]

By adding different amount of TDD (0, 12.5, 25, 50, and 75 mg) while keeping other conditions constant, PtNi₃ NPs with different sizes (3.2, 5.3, 6.7, 7.8, and 9.6 nm, respectively) were obtained. Similarly, size-selected PtNi NPs with an average size of 3.5, 4.1, and 5.0 nm can be prepared by adding 0.1 mmol Pt(acac)₂, 0.1 mmol of Ni(acetate)₃ and different amount of TDD (12.5, 25, and 50 mg TDD), respectively.

Electrochemical Measurement: Electrochemical experiments were performed in a three-compartment glass cell with a rotating disk electrode (RDE, 5 mm in diameter of glassy carbon, Pine Instrument) and a potentiostat (Biologic) at room temperature. A Pt-mesh and a Hg/Hg₂SO₄ electrode (in saturated K₂SO₄) were used as counter electrode and reference electrode, respectively. All potentials reported in this paper were normalized with respect to the reversible hydrogen electrode (RHE). To prepare the working electrode, 8.00 mg of carbon supported PtₙNiₙ₋₁ catalyst was suspended in 3.98 mL of ultrapure water (Millipore, 18 MΩ), 1.00 mL of isopropanol, and 20 µL of 5 wt% Nafton solution with sonication for 15 min to form a uniform ink. Ten microliters of the ink was pipetted onto prepolished and cleaned RDE electrode and dried at 60 °C for 20 min in air, resulting in a uniform catalyst thin film with around 12 µg Pt cm⁻². All working electrodes were prepared using freshly prepared catalyst inks and tested immediately.

Microscopic and Spectroscopic Characterization: TEM, HRTEM, and energy dispersive X-ray spectroscopy (EDX) measurements were performed in a FEI Tecnai G2 20 S-TWIN electron microscope (200 kV) equipped with a LaB₆ cathode and a field-emission transmission electron microscope FEI Tecnai 30 operated at 300 kV. High-resolution STEM and EELS experiments were performed in a FEI TITAN 80–300 electron microscope (300 kV) equipped with a probe corrector (CEOS) and a high-angle annular dark field (HAADF) detector. “Z-Contrast” conditions were achieved using a probe semiangle of 25 mrad and an inner collection angle of the detector of 70 mrad. EELS elemental mapping were recorded with a Gatan image filter Tridiem 866ERS system.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank the Zentraleinrichtung für Elektronenmikroskopie (Zelmi) at Technical University Berlin for its support of TEM and EDX measurements. This work was supported by U.S. DOE EERE award DE-EE0000458 via subcontract through General Motors and Deutsche Forschungsgemeinschaft (DFG) grants STR 596/4-1 (“Pt stability”), STR 596/5-1 (“Shaped Pt bimetallics”), and HE 7192/1-1. HRTEM and nanoparticle growth mechanism

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studies were partly supported by National Science Foundation of China (Grant No. 21573123) and Basic Research Projects of Shenzhen (Grant No. JCYJ20140902110354242) in China.


Received: January 4, 2016
Revised: February 19, 2016
Published online: