Surface Segregation of Fe in Pt–Fe Alloy Nanoparticles: Its Precedence and Effect on the Ordered-Phase Evolution during Thermal Annealing

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Coupling electron microscopy techniques with in situ heating ability allows us to study phase transformations on the single-nanoparticle level. We exploit this setup to study disorder-to-order transformation of Pt–Fe alloy nanoparticles, a material that is of great interest to fuel-cell electrocatalysis and ultra-high density information storage. In contrast to earlier reports, we show that Fe (instead of Pt) segregates towards the particle surface during annealing and forms a Fe-rich FeO$_2$ outer shell over the alloy core. By combining both ex situ and in situ approaches to probe the interplay between ordering and surface-segregation phenomena, we illustrate that the surface segregation of Fe precedes the ordering process and affects the ordered phase evolution dramatically. We show that the ordering initiates preferentially at the pre-existent Fe-rich shell than the particle core. While the material-specific findings from this study open interesting perspectives towards a controlled phase evolution of Pt–Fe nanolloys, the characterization methodologies described are general and should prove useful to probing a wide-range of nanomaterials.

Fuel-cell research has witnessed tremendous progress in the recent past, forging a technology that in addition to holding pivotal scientific relevance, also enjoys a great industrial appreciation.\cite{1–5} Catalysts design for the oxygen reduction reaction (ORR) in a proton-exchange membrane fuel cell (PEMFC), in particular, is an area that has received momentous thrust as an effect. The principal findings of this research effort provide much expansive insight into the fundamental understanding of nanoscale materials.\cite{6–13} Although platinum (Pt) is known to exhibit exceptional activity towards the sluggish ORR kinetics, it still remains an economically nonviable option for large-scale implementation of PEMFC, owing to its depleting natural sources and exceedingly high costs.\cite{10, 14–16} Currently, there exists a clear agreement in the literature that nanoscale alloying of Pt with 3d transition metals (Pt–M alloys; M = Fe, Co, Ni, Cu), in addition to reducing the mass loading of Pt, also enhances catalytic activity towards the ORR.\cite{5, 16–24} Various bimetallic\cite{18, 25} and ternary alloy\cite{26–29} systems have been investigated till date and the findings constantly suggest that ordered nanolloys exhibit an extended catalytic durability over their disordered counterparts.\cite{8, 12, 22, 30–32}

Pt–Fe system, in particular, has gathered a lot of interest in recent years not only on the account of its enhanced ORR electrocatalysis,\cite{8, 12, 20, 22, 28, 31–34} but also because of its magnetic properties that are deployable in ultra-high density information storage.\cite{10, 37–42} The PtFe$_2$ (L1$_0$) ordered phase exhibits a very high uniaxial magnetocrystalline anisotropy along the c direction of the crystal structure. The Pt$_2$Fe$_3$ (L1$_1$) phase delivers an enhanced ORR activity from the compressively strained Pt overlayers that encapsulate ordered alloy cores. Therefore, the chemical synthesis of Pt–Fe alloy nanoparticles in these ordered phases has been extensively studied in the past years. For example, novel alloy structures such as intermetallic Pt–Fe/Pt core shells,\cite{8} Pt–Fe–Cu ternary alloy nanoparticles,\cite{12} mono-disperse Ni/FePt core shells,\cite{36} and face-centered tetragonal (fct) FePt nanoparticles\cite{38} have been explored with reported ORR specific activities of 0.55 mA cm$^{-2}$, 0.75 mA cm$^{-2}$, 1.95 mA cm$^{-2}$, and 3.16 mA cm$^{-2}$, respectively. Unfortunately, the wet-chemical synthesis yields disordered nanoparticles in the face-centered cubic (fcc) A1 phase. Hence, the thermal annealing procedure (typically at 800 °C, 1 h) is generally performed to transform disordered A1 phase into L1$_0$ or L1$_1$ phases. It is widely reported that the thermal annealing also promotes a preferential surface segregation of Pt in addition...
to the ordering process.\textsuperscript{[21, 33, 34, 43–48]} The preference of Pt over Fe is ascribed to the larger atomic radius and low surface energies of Pt atoms as compared to Fe. On the contrary, we report herein on the surface segregation of Fe. Using atomic-resolution imaging under scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS), we show that the annealed Pt–Fe nanoparticles bear an Fe-rich shell over the alloy core. We find that the thermal annealing can result in unique structures including (i) Pt–Fe alloy (core)–Pt-rich (inner shell)–Fe-rich (outer shell), (ii) Pt-rich alloy (core)–Fe-rich (shell), and (iii) Pt-Fe-L\textsubscript{1}\textsubscript{3} (core)–Fe-rich (shell), based on the core alloy composition. To get a better insight into the surface segregation of Fe and its order of occurrence with respect to atomic ordering, we also investigated the phase transformation of a single nanoparticle in situ, over the course of annealing. Our findings reveal that the surface segregation of Fe precedes the ordered transformation. Finally, we also illustrate a dramatic effect that the pre-existent Fe-rich shell can have on the atomic-ordering process.

Results and Discussion

Pt–Fe alloy nanoparticles were synthesized by impregnating Pt/C precursors with appropriate amounts of Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O salt (see Experimental Section for details). Subsequent annealing at 800°C (1 h, 8% H\textsubscript{2}/Ar atmosphere) resulted in structures shown in Figure 1. The images in Figure 1a1 and 1b1 are atomic-resolution STEM high-angle annular dark-field images (STEM–HAADF, see Experimental Section for details) of the particles characterized. In Figure 1a1, the particle core architecture (viewed along [110] zone axis) exhibits alternating bright and dark intensities. STEM–HAADF is an atomic-number (Z) contrast technique with image intensities roughly proportional to Z\textsuperscript{3/2}. Hence, the alternating bright and dark intensities observed in Figure 1a1 correspond to atomic columns of Pt and Fe, respectively. Thus, the images confirm that the particle transformed into an ordered alloy core architecture upon annealing. The particle in Figure 1b1, however, is off a zone axis highlighting this alternating intensity and, therefore, the ordering is not obvious.

Further, the elemental distribution of Pt and Fe within these nanoparticles was examined using STEM–EELS compositional mapping (see Experimental Section for details) as shown in Figure 1a2–a4 and Figure 1b3–b5. Figure 1a2, a3 reveal the projected Fe and Pt distribution within the particle shown in Figure 1a1. The Pt-versus-Fe composite map (Figure 1a4) indicates that the particle core is composed of Pt–Fe alloy. It is also visible from a detailed inspection of Figure 1a4 that the core is surrounded by two shells, 1) surface-segregated Fe-rich outer shell and 2) Pt-rich inner shell. For better clarity, an EELS line profile (Figure 1a5) was taken along the white arrow indicated in Figure 1a4. From the Fe L\textsubscript{2,3} edge (green) and Pt M\textsubscript{4,5} edge (red) profiles between 1.0 and 2.05 nm in Figure 1a5, the Fe-rich outer shell (≈0.7 nm thick) and Pt-rich inner shells (≈0.2 nm thick) are clearly evidenced. Additional confirmation can also be found in the EELS spectra (ranging from 600 eV to 2500 eV) provided in Figure 1a6; the spectrum in blue and green corresponds to a region in the particle core (dotted blue box in Figure 1a4) and Fe-rich shell (dotted green box in Figure 1a4), respectively. In the blue spectrum (core region), both Fe L\textsubscript{2,3} edge (at 708 eV) and Pt M\textsubscript{4,5} edge (at 2206 eV) can be identified, confirming the Pt–Fe alloy core structure. However, in the green spectrum (outer shell region), only the Fe L-edge can be identified with no evidence of Pt. Notably, the surface-segregating Fe atoms in the nanoparticles could interact with the annealing atmosphere (reducing H\textsubscript{2}/Ar atmosphere), and even traces of O\textsubscript{2} (ppm level) present in the reducing H\textsubscript{2}/Ar mixture can cause oxidation.\textsuperscript{[49]} This can be confirmed by analyzing the EELS spectrum (of the shell region) ranging between 450 eV and 900 eV, in which the O–K edge can be identified, as shown in Figure 1a7. From Figure 1a6 and 1a7, it can therefore be confirmed that the outer shell is Fe-rich (FeO).

The micrographs in Figure 1b3 and b4 reveal the projected Fe and Pt distribution within the particle described in Figure 1b1. The Pt-versus-Fe composite map (Figure 1b5) indicates that the Pt-rich alloy core is surrounded by a surface-segregated Fe-rich shell (≈0.35 nm thick). Unlike the particle shown in Figure 1a4, there is no evidence of Pt segregation in this particle. For a better visibility of surface-segregated Fe-rich shell, a small region (dotted red lines) in the STEM–HAADF image (Figure 1b1) was bandpass-filtered to generate the picture in Figure 1b2. This filtering is solely used to improve the visibility of the weaker intensities adjacent to the strongly scattering Pt atoms so that the dynamic range of the images allows visualizing the existing structure. The segregated Fe-rich shell (region outside the yellow line) surrounding the Pt-rich alloy core is clearly visible in the band-pass filtered image (Figure 1b2).

From the results presented in Figure 1, it is clear that nanoparticles emerged with a surface-segregated Fe-rich shell upon thermal annealing (see Supporting Information, Figure S1, for additional statistics). However, this finding is in apparent contradiction to earlier reports that suggested a surface segregation of Pt.\textsuperscript{[33, 34, 43–48]} In general, the segregation phenomenon of bimetallic systems is based on the surface energies and atomic radii of two metals, with the element having a larger atomic radius and a lower surface energy segregating towards the free surface.\textsuperscript{[50]} However, kinetics can certainly play a dominant role over thermodynamics in nanoscale phase transformations. It appears that the segregation of Fe atoms is kinetically more favored over Pt to result in the formation of core (alloy)–shell (Fe-rich) structures described in Figure 1. Irrespective of the element segregating towards the surface, these studies clearly indicate that the thermal annealing procedure results in both ordering and surface-segregation events that can influence the other. Therefore, it is crucial to investigate their relative orders of occurrence. In the following, we illustrate that surface segregation of Fe precedes the ordering process, using both ex situ and in situ methods. The ex situ methodology involved comparing the nanoparticle structures annealed at 800°C (Figure 1) with those annealed before the disorder-to-order phase-transition temperature (≈500°C). However, the ex situ analysis is vastly limited by the interferences derived from comparing nonidentical particles in the ensemble. There-
Figure 1. Atomic-resolution imaging and spectroscopy of Pt–Fe nanoparticles annealed at 800 °C (1 h). a, b) STEM–HAADF and STEM–EELS compositional maps of two different particles from the heat-treated sample. a1, b1) STEM–HAADF images. Parallel lines in a1 indicate alternating bright (pink) and dark (blue) intensities. The particle core in this region is close to [110] orientation. a2, b3) 2D EELS map of Fe (green). a3, b4) 2D EELS map of Pt (red). a4, b5) The composite Fe-versus-Pt maps. a5) EELS line profiles of Fe L-edge (green) and Pt M-edge (red) taken along the white arrow highlighted in a4. a6) EELS spectra (in the range 600 eV–2500 eV) integrated over a selected region at the core (dotted blue box) and the shell (dotted green box) in a4. a7) EELS spectra (in the range 450 eV–900 eV) integrated over the dotted green box region in a4. b2) Bandpass-filtered image of the region (marked in red) selected from b1.
fore, an in situ annealing experiment (up to 800 °C) was also performed by tracking the same nanoparticle over the course of heat treatment.

The results describing the ex situ method are discussed as follows. The STEM–HAADF images and STEM–EELS chemical maps shown in Figure 2 correspond to particles annealed at 300 °C (1 h), alongside detailed analysis on one individual particle (Figure 2b). The STEM–HAADF image shown in Figure 2a reveals dark patches (white arrows) within the particle core regions. The contrast in STEM–HAADF imaging is essentially sensitive to the atomic number and specimen thickness. Therefore, the observed dark patches in Figure 2a suggest compositional Fe-rich regions and/or structural inhomogeneity (voids) within the particle cores. The compositional inhomogeneity is better revealed from the STEM–EELS elemental profiles acquired at high spatial resolution. The EELS map in Figure 2b illustrates the projected Fe distribution within the particle shown in Figure 2b1. The white arrows marked in Figure 2b2 indicate the regions with depleted Fe content. The depletion in Fe over this region is compensated by an increase in Pt content, as confirmed by the corresponding Pt (red) versus Fe (green) composite map (white arrows in Figure 2b4), highlighting a compositional inhomogeneity within the particle core.

From the above findings, it is evident that the particle cores remain disordered (compositionally inhomogeneous) upon a thermal treatment at 300 °C. This is consistent with the predicted disorder-to-order phase-transition temperature (500 °C) by Delalande et al. Furthermore, a careful observation of particle surfaces in the Pt (red) versus Fe (green) composite maps for both regions (Figure 2a4 and Figure 2b4) clearly indicate that the disordered particle cores are surrounded by Fe-rich shells. Therefore, from the ex situ methodology that involved comparing the nanoparticle structures annealed at 800 °C (Figure 1) with those annealed before the disorder-to-order phase-transition temperature (<500 °C), it can be concluded that the surface segregation of Fe precedes the ordering process.

Importantly, the ex situ analyses involved comparing nonidentical particles. It can be argued that the local environments surrounding these particles were dissimilar and thereby, lead to varied segregation behaviors. These limitations can be overcome by tracking the same nanoparticle, over the course of annealing. In the following section, we illustrate this through an in situ annealing experiment. To the best of our knowledge, a simultaneous STEM–HAADF and STEM–EELS characterization on the same nanoparticle over the course of thermal treatment is unprecedented.

The in situ heating was performed inside an aberration-corrected STEM using a microelectromechanical systems (MEMS)-based heating holder (Aduro model from Protochips, see Experimental Section for details). The as-synthesized Pt–Fe nanoparticles were deposited onto the holder. Heat treatment involved an annealing procedure (under vacuum) by holding the sample at 200 °C, 400 °C, 500 °C, 600 °C, 700 °C, until 800 °C for 30 min each and finally quenching back to room temperature. At the onset, one as-synthesized particle was carefully picked from the ensemble. With the help of STEM–HAADF scans, the same nanoparticle was tracked over the course of thermal treatment. At every temperature, STEM–HAADF imaging coupled with STEM–EELS mapping was performed to obtain its structural and compositional information.

In Figure 3a and 3b, STEM–HAADF images of the as-synthesized Pt–Fe nanoparticles prior to heat treatment are shown. Similarly to Figure 2a1, the dark patches (yellow arrows) in these images confirm the disordered alloy structure. Further, to clarify that the as-synthesized particles did not already bear a Fe-rich shell, STEM–EELS elemental mapping was also performed on representative particles, and this is illustrated in the Supporting Information, Figure S2. Additionally, STEM–EDX analyses performed on randomly sampled particles (few tens in number) further confirm that the average composition of
the as-prepared particles is approximately (67 ± 5)% Pt and (33 ± 5)% Fe. The STEM–HAADF image in Figure 3c1 shows one such disordered particle (size = 9 nm) that was chosen for in situ tracking. For purposes of clarity, this large particle shall be identified as particle L in future discussions. The series of images shown in Figure 3c2–c8 illustrate particle L tracked over various stage during annealing. Note that the STEM–HAADF images and STEM–EELS spectra were acquired after 30 min at every temperature. Hence, the labeled value of 400 °C for instance, indicates that the particle was exposed to 200 °C (for 30 min) plus 400 °C (for 30 min) overall. For better clarity, a schematic representation of the temperature profile is provided in Figure S3.

In Figure 4a–d STEM–EELS compositional analyses of the particle L are shown at 400, 600, 700, and 800 °C, respectively. In addition to the typical elemental mapping (Figure 4a1, 4b1, 4c1, 4d1) as before, the line profiles of Fe L-edge (green) and Pt M-edge (red) were also extracted, along the blue (Figure 4a2, 4b2, 4c2, 4d2) and yellow (Figure 4a3, 4b3, 4c3, 4d3) scan directions.

In the Figure 4a3, the Fe (green) and Pt (red) profiles reveal the presence of both Fe-rich (green arrow) and Pt-rich (red arrow) regions within the particle. The observed compositional inhomogeneity confirms that the particle L was still disordered at 400 °C. This is consistent with the fact that the overall heat transferred to particle from a treatment at 400 °C is lower than that from a treatment at the predicted disorder-to-order phase-transition temperature, i.e., 500 °C (Supporting Information, Section 1). Furthermore, the Fe (green) profile in Figure 4a2 indicates that the particle surface is enriched in Fe (≈ 0.5 nm), as shown by the black arrows. Clearly, this must be the result of surface segregation of Fe as witnessed earlier from the ex situ approach (Figure 2). However, Fe enrichment at the surface is not seen in Figure 4a3, based on a profile from the same particle, but taken in a different section, in which Pt-rich region (black arrows) can be seen exposed to the surface. Quantification of EELS intensities in these regions revealed a Pt/Fe content (on % basis) of 100.0/0.0 (black arrow on the left) and 75.4/24.6 (black arrow on the right). Hence, it can be concluded that although not complete enough to cover the surface entirely, the surface segregation of Fe began while the particle L still remained disordered. Consistent with the ex situ results discussed earlier, the in situ findings thus demonstrate that surface segregation of Fe precedes the ordering process during thermal treatment.

Additionally, a careful examination of the particle surface at 600, 700, and 800 °C (black arrows in Figure 4b2, b3, c2, c3, d2, d3) reveals that the surface was fully covered with Fe-rich shell during later stages of annealing. As discussed below, our findings also reveal that the particle L finally existed in a PtFe-L1₀ (core)–Fe-rich (shell) alloy structure upon quenching to room temperature, following a disorder-to-order phase transition that occurred between the treatments at 400 °C and 800 °C. In Figure 5a and 5b, STEM–EELS mapping and line profiles are shown for the particle L at room temperature (upon quenching). Clearly, the particle core is surrounded by an Fe-rich shell (≈ 0.4 nm thick) as revealed by the Fe (green) profile in Figure 5b (indicated by black arrows). After accounting for Fe content in the shell region, it is noticeable from Figure 5b that the EELS intensities of Pt M-edge match very closely with those of Fe L-edge. The EELS intensities were also quantified by using the standard procedure[35] of comparing the cross-
section weighted, background subtracted, integrated signals. In Table 1 the quantified Fe and Pt contents on overall particle (58.2 % Fe, 41.8 % Pt), core (56.7 % Fe, 43.3 % Pt), and the shell (93.7 % Fe, 6.3 % Pt) regions are listed. This suggests an approximately 50:50 compositional mixture of Pt and Fe in the particle core, which therefore should exist in L1\textsubscript{0} ordered phase as dictated by the phase diagram. The corresponding STEM–HAADF image shown in Figure 3 c8 resolves the ambiguity, by revealing alternating bright and dark intensities within the particle (with (001) planes oriented parallel to electron beam) that, owing to atomic-number contrast, correspond to Pt and Fe atomic planes, respectively. The present observation that the particle L existed with an L1\textsubscript{0} ordered core alloy structure after the treatment and the earlier finding that the particle remained disordered at 400 °C suggest that the disorder-to-order phase transition in particle L occurred between the treatments at 400 and 800 °C. Notably, this inference is very well consistent with the predicted disorder-to-order phase transition (≈500 °C) by Delalande et al.\textsuperscript{10}

Finally, in Figure 5 the EELS spectra (between 450 and 800 eV), recorded over an integrated area in the shell region, for the in situ and ex situ annealed particles are shown. For the ex situ annealed particle, as discussed earlier in Figure 1a7, evidence for the Fe-rich shell as FeO\textsubscript{x} can be found by identifying O K and Fe L\textsubscript{2,3}-edges. However, for the in situ annealing experiment it is expected that the vacuum maintained inside the microscope column contained significantly low concentration of O compared to that under ex situ annealing atmosphere. Hence, the Fe-rich FeO\textsubscript{x} shell is more likely to be pure Fe shell. This can be evidenced by the absence of O K-edge in the pink spectrum shown in Figure 5c that corresponds to the in situ annealed particle. These observations therefore suggest that the surface segregation of Fe occurred even under a minimum availability of O\textsubscript{2}.

Other processes such as Ostwald ripening and coalescence were also captured during the in situ annealing experiment, and the details can be found in Figure S4. By acquiring a time series of STEM–HAADF images, we were able to capture (1) shrinking of a small particle (≈2.5 nm) through atom migration (Figure S4 (a)), and (2) an atomic cluster (≈1 nm) detaching from an intermediate-size particle to coalesce with neighboring bigger particle (Figure S4 (c)). Expectedly, these phenomena would enable a mass transport between the particles that might further lead to variations in the composition as well as particle size, over the course of thermal treatment.

So far, we have demonstrated surface segregation of Fe and its precedence over the ordering process using both ex situ and in situ approaches. We can surmise that the pre-existent Fe-rich shell can serve as a heterogeneous boundary to these single-crystal nanoparticles and, consequently, affect the order-
Elemental mapping and EELS line profiles across particle after in situ annealing process. However, these alternating bright and dark fringes correspond to atomic columns of Pt and Fe, respectively. Noticeably, the atomic ordering starts at the Fe-rich shell and propagates inwards (yellow arrows). Similar observations can also be made on the small particle also visible in Figure 6a and b, such as the Fe-rich shell covering the particle surface and the initiation of the ordering process at the Fe-rich shell (Figure 6a, the color code for the arrows and lines can be found in the figure caption). This effect must be caused by the pre-existent Fe-rich shell that provides a heterogeneous boundary to the nanoparticle. Therefore, the formation of nuclei (L1_2 or L1_1) for ordering is expectedly more favored to initiate at the Fe-rich shell than the particle core. Notably, the local elemental distribution can also play a dominant role in the formation of these ordered nuclei. For instance, in the region identified by dashed yellow box in Figure 6a, a local enrichment in Pt concentration is evidenced, as revealed by the bright intensities of the atomic columns with a lattice spacing of 0.20 nm. Hence, despite the proximity of this region to the Fe-rich shell, ordering process is not initiated.

In addition, there are also interesting crystallographic effects that can be identified in these particles. Consider the region identified by solid yellow box (1) shown in Figure 6a. Along (001), the first atomic planes pointed at with short pink arrows show bright intensity, whereas the latter ones in the particle core alternate with bright (long pink line) and dark intensities (long blue lines). Similar observations can be made for the regions identified by solid yellow boxes (2) and (3), in which the bright intensity for the terminating atomic columns/planes can only be seen as pockets and not homogeneously distributed throughout the particle. This observation suggests that the ordering process is still not complete. The dashed red box drawn in Figure 6a clearly identifies this transition, in which a progressive ordering front is evident on the left half (visible as alternating intensities), and the region onto right half shows no evidence of atomic ordering. The image in Figure 6b is a gamma-adjusted STEM–HAADF image corresponding to the image in Figure 6a and a close observation at the particle surface reveals the segregated Fe-rich shell as indicated. Noticeably, the atomic ordering starts at the Fe-rich shell and propagates inwards (yellow arrows). Similar observations can also be made on the small particle also visible in Figure 6a and b, such as the Fe-rich shell covering the particle surface and the initiation of the ordering process at the Fe-rich shell (Figure 6a, the color code for the arrows and lines can be found in the figure caption). This effect must be caused by the pre-existent Fe-rich shell that provides a heterogeneous boundary to the nanoparticle. Therefore, the formation of nuclei (L1_2 or L1_1) for ordering is expectedly more favored to initiate at the Fe-rich shell than the particle core. Notably, the local elemental distribution can also play a dominant role in the formation of these ordered nuclei. For instance, in the region identified by dashed yellow box in Figure 6a, a local enrichment in Pt concentration is evidenced, as revealed by the bright intensities of the atomic columns with a lattice spacing of 0.20 nm. Hence, despite the proximity of this region to the Fe-rich shell, ordering process is not initiated.

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Conclusions

Using atomic-resolution imaging and electron energy loss spectroscopy, we have demonstrated the surface segregation of Fe in annealed Pt–Fe alloy nanoparticles. This finding is in contrast with earlier reports that suggested a Pt surface segregation. For probing the interplay between segregation and atomic ordering, we have looked beyond traditional ex situ characterization. Both imaging and electron energy loss spectroscopy were performed on one single nanoparticle, in situ, over the course of thermal treatment. By combining both
ex situ and in situ approaches, the segregation of Fe was shown to precede the ordering process. Various unique structures resulting from a typical thermal treatment were elucidated, including particles with (i) Pt–Fe alloy (core)–Pt-rich (inner shell)–Fe-rich (outer shell), (ii) Pt-rich alloy (core)–Fe-rich (shell), and (iii) PtFe-L10 (core)–Fe-rich (shell). The effect of such pre-existent Fe-rich shell on the ordering process was also studied and our findings reveal that the ordering is more favored to initiate at the Fe-rich shell than the particle core. This study opens interesting perspectives towards rational design and controlled phase evolution of Pt–Fe nanoalloys, ultimately intended for viable applications in ORR electrocatalysis and magnetic storage devices. Finally, the characterization methodologies described in this work is not limited to Pt-alloy nanoparticles, but should prove useful to an atomic-scale probing of a broad-range of nanostructures in general.

Outlook

Herein, we reported on the surface segregation of Fe during the thermal treatment of Pt–Fe alloy nanoparticles. Routinely, a vast majority of catalyst varieties, including the annealed Pt nanoalloy systems, undergo a pretreatment before the ORR measurements with a procedure termed voltammetric dealloying (VD). The VD typically involves continuous electrochemical voltammetric sweeps between 0.05 and 1.2 V over 50–100 cycles. In addition, the charge resulting from the adsorption–desorption reaction of molecular H (Q_{ads/des}) on Pt (between 0 and 0.3 V) is found to increase upon VD, indicating an increase in the electroactive Pt surface area (ECSA). Consequently, the resulting nanoparticle surfaces are reported to exhibit a surface catalytic activity that is approximately 5 times enhanced (Pt mass basis) compared to a nondealloyed catalyst particle. Although a lot of research has been performed on correlating the observed increase in ECSA from VD with the affected modification to the nanoparticle surface-structures, the current knowledge is still vastly limited to interpreting the features in the recorded voltammograms with the aid of DFT calculations. Particularly, in the voltage range from 0.3 V to 0.7 V, a small oxidation peak is consistently observed during the first few VD cycles, and is seen to gradually diminish with the cycling number. With additional insights from DFT calculations, these oxidation peaks have been attributed to the dissolution of Fe, Cu, Co, and Ni for Pt–M (M = Fe, Cu, Co, Ni) systems, and it is believed that the VD imparts a Pt skin structure by (1) dissolving these less noble metal alloy components from the surface and (2) promoting atomic rearrangement through surface-diffusion. For the Pt–Fe system, our present findings on the surface segregation of Fe in the annealed particles corroborate with the electrochemical viewpoint, validating that the origin of oxidation peaks observed during VD must be an effect of the surface dealloying of Fe-rich shell. For disordered Pt–M alloy nanoparticles, the VD has been shown to massively remove the less noble alloy component, associated with a drastic rearrangement of Pt surface atoms and bulk atoms by surface diffusion. However, for the particles observed in this work, for which a Pt inner shell also exists underneath the Fe-rich shell, it still remains a question whether or not the VD in-

Figure 6. Atomic-resolution STEM–HAADF images of a Pt–Fe nanoparticle annealed at 600 °C (1 h). a) STEM–HAADF image of the particle viewed along [110] zone-axis. Parallel lines drawn in pink and blue indicate bright and dark intensities, respectively. Yellow arrows identify the regions where alternating bright and dark intensities can be observed. Solid yellow boxes (1, 2, 3) and enlargement of (2) identify regions with terminating atomic columns with bright intensities. The dashed red box identifies a transition region. The dashed yellow box identifies a region locally enriched in Pt. Explanations of pink and blue arrows are given in the main text. b) STEM–HAADF image generated after adjusting the gamma in (a). Green arrows indicate the Fe-rich FeO_x shell that could not be observed solely in (a). Yellow arrows indicate the ordering direction.
volves surface atomic rearrangement or serves merely as a surface-cleaning procedure. This crucial question needs to be addressed. Recently, we have performed an in situ potential cycling of disordered Pt–Fe nanoparticles inside a TEM. In the future, by coupling this setup with the EELS technique, we look forward to gaining more insights into the surface tunability of the VD procedure.

**Experimental Section**

**Nanoparticle synthesis**

20 wt% Pt/C precursor powder was first made by using a method described in the literature (briefly discussed as follows). The Pt/C precursor nanoparticles were made by depositing a specific volume of a colloidal Pt solution onto Vulcan XC-72R. The Pt colloids were synthesized by first dissolving PtCl$_4$ (0.4652 g, Alfa Aesar, 99.9% metal basis) in ethylene glycol (50 mL, EM Science) containing 0.15 m NaOH. The pH of the synthesis solution was known to define the resulting particle size of the Pt colloids. The solution was stirred for 1 h at RT, and subsequently heated under reflux at 160°C for 3 h. A dark brown colloidal Pt solution was formed in this manner, which was then allowed to cool in air and at RT for 1 h, before mixing with Vulcan XC-72R (1.077 g) in a beaker, and finally was allowed to stir for 24 h. An appropriate amount of 1 m HNO$_3$ was added to adjust the pH to 2 allowing for complete deposition of the Pt colloids onto the carbon support. After 24 h, the Pt/C powder was filtered and extensively washed with water and ethanol. A clear filtrate was obtained indicating that the Pt colloids were completely deposited onto the carbon support. The powder was then dried in an air oven at 80°C overnight, and subsequently homogenized in a glass mortar by grinding.

The as-synthesized Pt–Fe alloy nanoparticles were prepared by ultrasonically dispersing 500 mg samples of the Pt/C precursor powder (prepared with methods discussed above) in water (120 mL) in a 250 mL beaker for 1.5 h. Fe(NO$_3$)$_3$·9H$_2$O (Alfa Aesar, 99.99% Fe basis) was used as precursor salts. This precursor salt (≈ 0.2072 g) was impregnated onto 20 wt% Pt/C suspension (0.5 g). Upon dissolution of the precursor salts, the pH of the suspension was adjusted to 4 by adding a few drops of 1 m HNO$_3$ to facilitate dissolution much further. The solution was then well stirred for 30 min at RT. Subsequently, the water was evaporated at a slow rate (for 3–4 h) and under stirring at 80°C and the dried powders were then ground in a glass mortar to homogenize. These powders were then immersed in 1 m HNO$_3$ acid solution for 1 h under continuous magnetic stirring to leach out any single-phase Fe particles.

**Scanning transmission electron microscopy (STEM)**

Detailed structural characterization was performed using a FEI-Titan 80-300 cubed TEM, operated at 300 kV in scanning TEM mode (STEM). The microscope was equipped with a high-brightness Schottky electron source, aberration correctors for both probe-forming and image-forming lenses, a monochromator and a high resolution Gatan-Quantum spectrometer (Gatan Inc., Pleasanton, CA).

STEM–HAADF: Atomically resolved HAADF images were acquired in the STEM mode. At the operating conditions, a sub-angstrom resolution was achievable. Also called STEM–HAADF technique, these images are generated by collecting electrons scattered at high angles on passing through the samples, using a Fischione HAADF detector. The acquired image intensity is roughly proportional to Z$_4$, with Z is the atomic number of scattering atoms.

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**Author Contributions:** S.P and G.A.B conceived and designed the experiments. C.B synthesized the nanoparticles and carried out ex situ heat treatments. S.P, M.B, and G-Z.Z jointly performed the in situ annealing experiment. Data analysis and processing were carried out by S.P and M.B. S.P drafted the manuscript with feedback from all the authors on results and revisions of the manuscript.

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