Supporting Information

Shape Stability Of Octahedral PtNi Nanocatalysts For Electrochemical Oxygen Reduction Reaction Studied By in situ Transmission Electron Microscopy

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This Supplementary Materials includes:

- Figure S1, Figure S2 and Figure S3 – with additional in situ LMTEM micrographs, including a comparing measurement regarding the influence of the electron beam;
- Details and information for a continuous in situ LMTEM experiment;
- Figure S4, S5 and S6 – with additional in situ HAADF STEM micrographs, including EDX mappings;
1) Additional LMTEM images

Figure S1 shows the continuation to 800 °C of the LMTEM image series in Figure 2 of the main manuscript. At higher temperatures, coalescence leads to sintering of the octahedral NPs (see arrow in Figure S1 and Figure 2F of main), whereas the smaller NPs are maintained.

Figure S2 shows an additional image series recorded during the same LMTEM heating experiment.

**Figure S1:** LMTEM images as investigated during in situ heating experiment at high temperatures.

**Figure S2:** LMTEM images of different agglomerates as investigated during same in situ heating experiment.
**Influence of electron beam?**

Before and during the continuous heating TEM experiment (at 400°C) images were taken at a comparable catalyst region (Figure S3), which was not influenced by the beam during the heating steps. Herein, similar features are observed as before: at 400°C the octahedra are characterized by rounded corners, which were identified as the transformation from octahedral to cuboctahedral by HRTEM (Figure 3 main paper). Accordingly, we can conclude that all changes described in the main paper are induced as a result of thermal annealing and not by electron beam damage.

**Figure S3:** LMTEM images taken before (A+B) and during continuous heating experiment (C+D) at catalyst agglomerate, which was not investigated during in situ heating.
2) Continuous heating experiment

For a continuous heating experiment a rate-dependent heating profile was used which was paused in between for imaging for about 3 min. The following heating profile was used: 100 – 200°C (5 K/min) – images every 20°C; 200 – 500°C (2 K/min) – images every 10°C; 500 – 600°C (10 K/min) – images every 50°C.

The obtained image sequences (video files) are attached to electronic SI as supporting online files and the corresponding date are described below – check image sequences recorded at two different magnifications:

- at magnification of 71’000: See avi file named “nn7b09202_si_001.avi”
- at magnification of 97’000: See avi file named “nn7b09202_si_002.avi”

Results of „continuous“ heating experiment:

- changes occurring step by step – starting >300°C
- edges rounding off – up to 450°C – before octahedral shape is lost at ~470°C
- possible temperature range for optimal structure-stability: 350-450°C
  - 350°C: start of morphology transfer
  - 450°C: just shortly before shape „collapse“

3) Additional HAADF STEM images

The structural evolution of PtNi$_{1.5}$ octahedral NPs was also investigated by STEM under in situ heating conditions. Figure S4 shows a HAADF STEM image series of a PtNi$_{1.5}$ octahedral NP at 23, 300, and 800 °C. The NP shows clear changes of the Z-contrast: In the initial image, strong bright stripes and darker facet regions are seen, which can be associated to a Pt-rich frame and Ni-rich \{111\} facets. During heating, the strong Z-contrast differences vanish and a more homogeneous contrast is observed. This contrast distribution can be correlated to a stronger intermixing of Pt at the facets and is in accordance with our proposed model in Figure 4 of the main manuscript.
**Figure S4.** HAADF STEM image series of PtNi$_{1.5}$ octahedral NPs examined under in situ thermal heating conditions from RT (23 °C) to 800 °C (A-C). The NP in the center shows clear changes of the Z-contrast distribution.

Additionally, the elemental distribution was investigated of NPs after a heat treatment to 300 °C in the HRTEM. After being transferred to the STEM instrument an EDX mapping was recorded (Figure S5). The images clearly show a Pt surface enrichment at 300°C, which in accordance to the proposed mechanism in Figure 4.

**Figure S5.** HAADF STEM images (A+C) and corresponding EDX maps (B+D) of PtNi$_{1.5}$ octahedral NPs heated under in situ thermal conditions to 300 °C and transferred to the STEM instrument afterwards. Pt surface enrichment is indicated by arrows.
During EDX mapping beam damage effects have to be especially taken into account. The HAADF STEM images in Figure S6 demonstrate the impact of beam damage during long duration EDX maps on the particles in the as-prepared state. Accordingly, a STEM-EDX mapping of identical NPs during an *in situ* experiment is unfortunately not possible.

**Figure S6.** Impact of beam damage investigated on PtNi$_{1.5}$ octahedral NPs in as-prepared state: Long duration (10 min) EDX map (B) and HAADF STEM images taken before (A) and after (C) acquisition of the EDX map. The arrows especially indicate changes with respect to the Ni distribution.