Supporting Information:

Post Synthesis Heat Treatment of doped PtNi-alloy fuel-cell catalyst nanoparticles studied by in-situ electron microscopy

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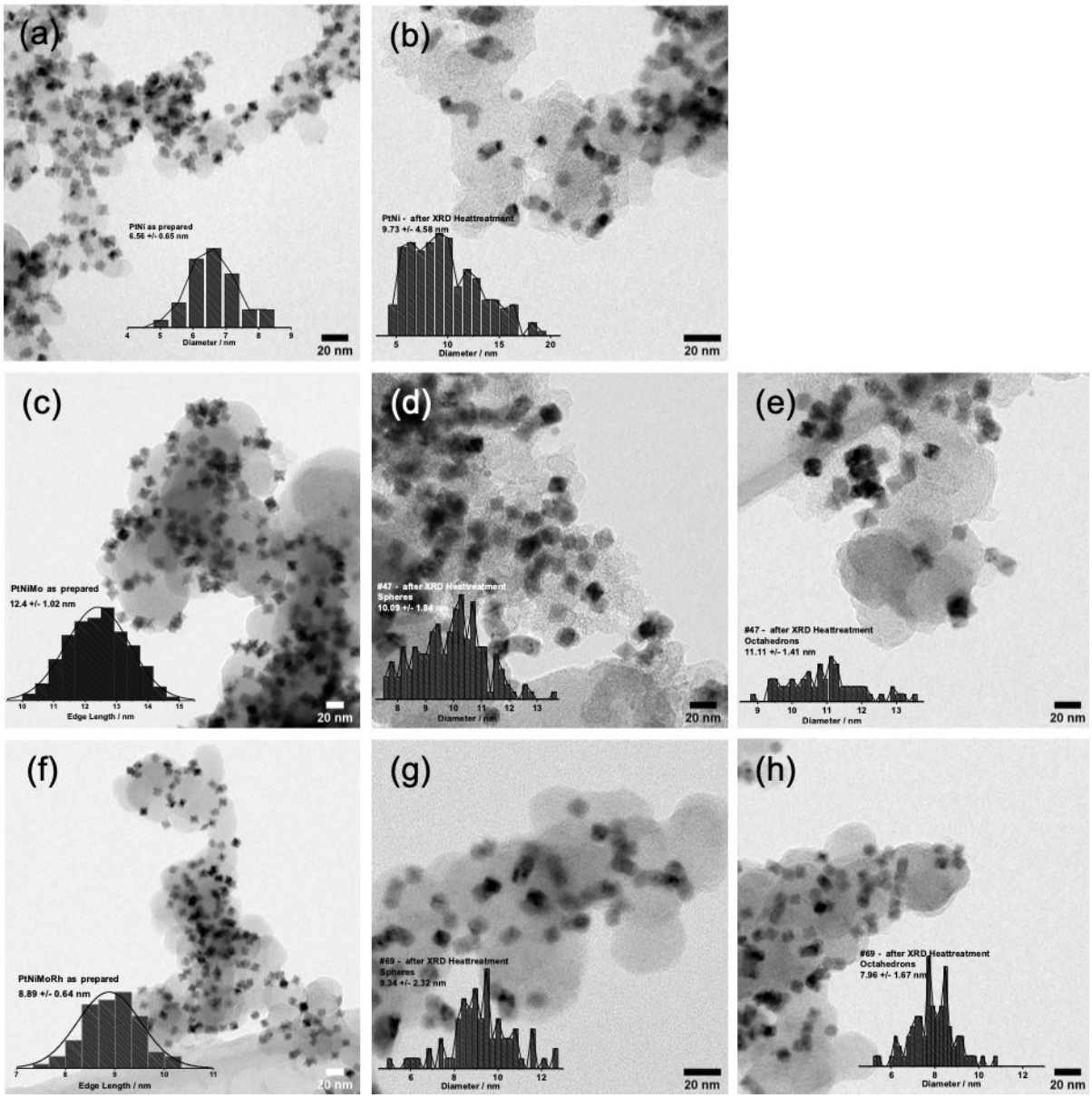

Figure S1 – Summary of the particle size distributions before and after the heat treatment. (a) and (b) show PtNi before and after heating, with average edge length of 6.6 nm ± 0.7 before and xx nm ± xx after. (c) shows before and (d) and (e) show after heat treatment for PtNiMo, with an average edge length of 12.4 nm ± 1 before and xx nm ± xx after. (f) shows before and (g) and (h) show after heat treatment for PtNiRhMo, with an average edge length of 8.9 nm ± 0.6 before and xx nm ± xx after. For PtNiMo and PtNiRhMo particle size after heat treatment are shown both based on a radius calculation using assumptions of a spherical model and edge length of the octahedral facets. PtNi did not demonstrate enough octahedrons after heating that only the spherical model has been used. For a perfect octahedron the calculated circular radius, is expected to be ~76% the size of the edge length.

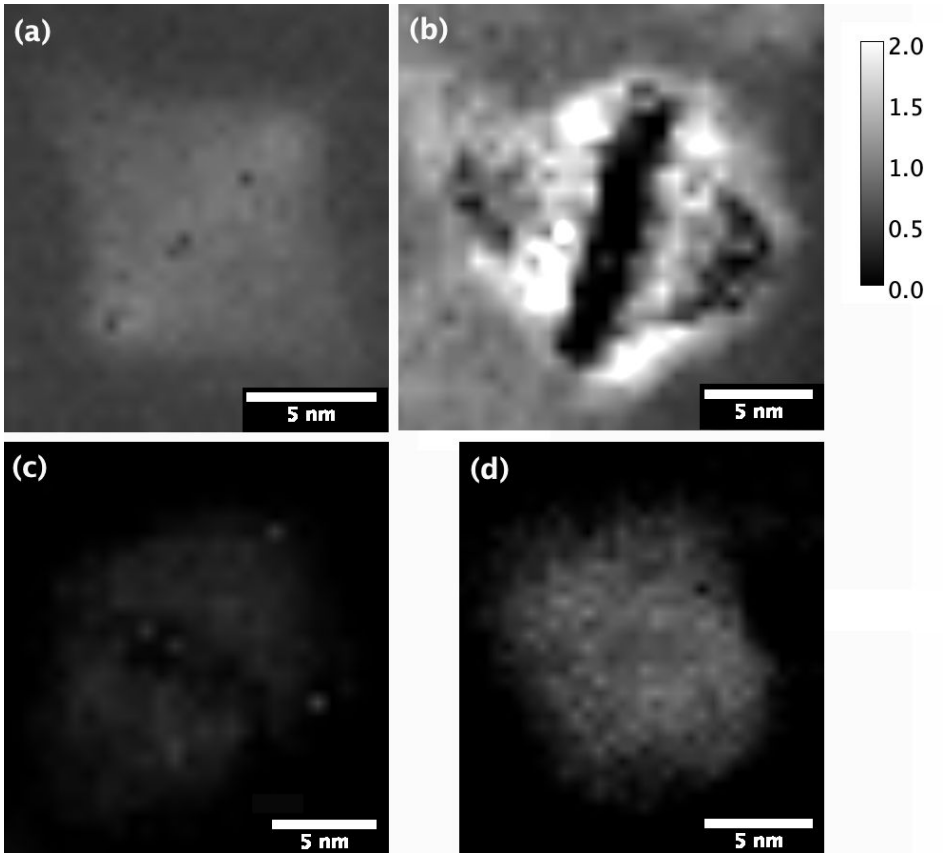

Figure S2 – Demonstration of the Mo and Rh locations after NMF decomposition with modelling fitting of the spectra. The Mo_La is shown for the PtNiMo sample before heating (a) and after heating (b). The Rh_La is shown for the PtNiMoRh sample before heating (c) and after heating (d). The intensity scale bar is in raw X-ray counts.

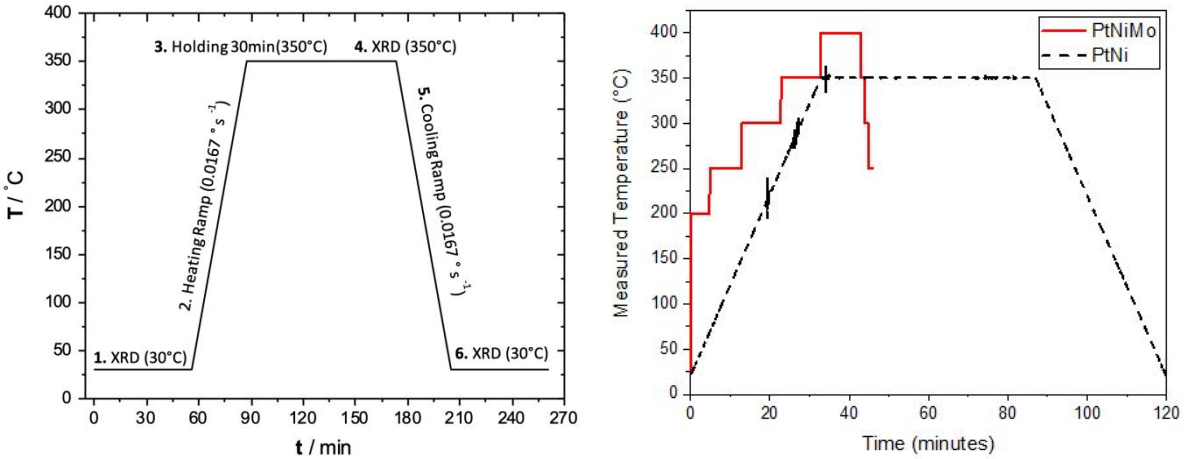

Figure S3 – Heating profile used for the in situ *XRD analysis (a) and the in-situ gas experiments (b). In the PtNi* in situ *TEM experiments the heating profile was set to match that of the* in situ *XRD.*

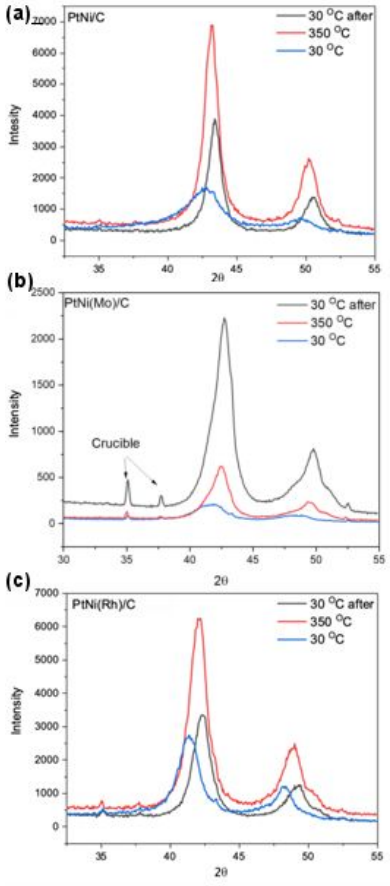

Figure S4 – In-situ XRD data showing the (111) and (200) peaks for PtNi (a), PtNiMo (b), and PtNiMoRh (c) before (30°C), during (350°C) and after (30°C after) heat treatment. The heating profile are displayed in SFig. 1, a).

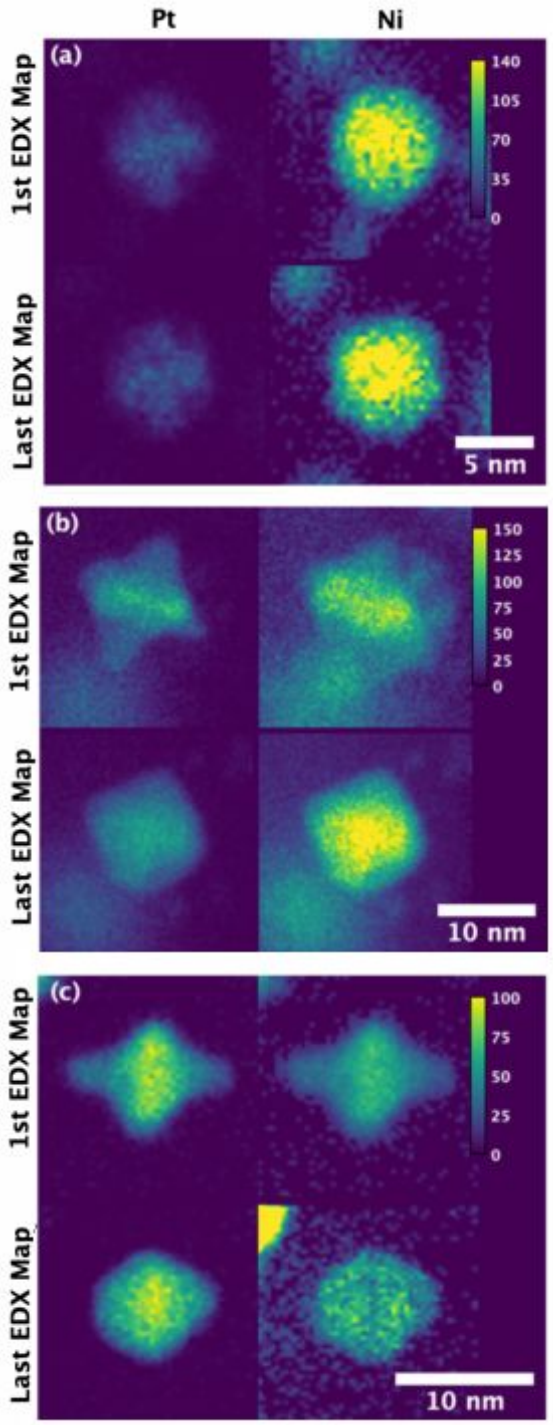

Figure S5 – Extracts from the combined in-situ heating EDX experiments, showing PtNi (a), PtNiMo (b), and PtNiMoRh (c). The first and last EDX maps in the data series are shown for each sample with the number of atom counts for Pt (left) and Ni (right) as the units of the intensity scale.

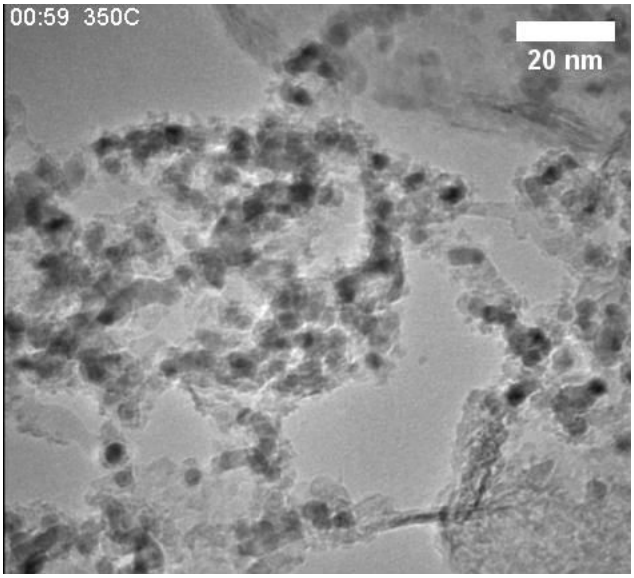

Figure S6 – An extracted figure from the PtNi in-situ heating experiment under 4% hydrogen atmosphere. The particles have completely lost their octahedral shape by the time the temperature of 350°C is reached and became mostly spherical. Time stamp is in the top left corner of the image shows that this figure was taken less than 1 minute after reaching 350°C.

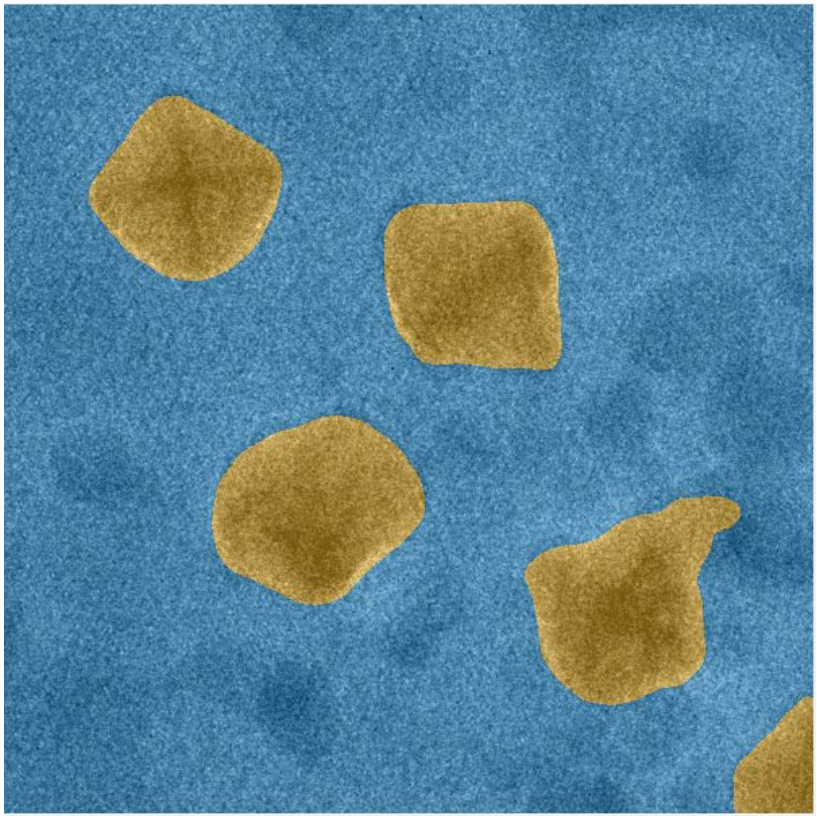

Figure S7 – Example TEM image frame during in-situ experiment under hydrogen atmosphere and binary particle segmentation map generated by a neural network.

Roundness and circularity measurements:

Roundness was calculated according to:

$$Roundness = \frac{Area \times 4}{Perimeter \times Diameter}$$

Circularity is calculated as follows:

$$Circularity = \frac{4 \times Area \times \pi}{Perimeter^2}$$

The *in-situ* X-ray diffraction (XRD) experiments were performed on a D8 advanced X-ray diffractometer equipped with a Goebel mirror, a position-sensitive LynxEye detector (PSD), and an external radiation heating chamber (MRI Physikalische Geräte GmbH, Tübingen,Germany). The heating chamber was positioned on the goniometer of the diffractometer, consisting of an AlCr foil as heater, an Al_2O_3 crucible as sample holder and a thermocouple. The Cu Ka tube was operated at a voltage of 40 kV and a current of 40 mA. The Al_2O_3 crucible was filled with 20-30mg of catalyst powder (on carbon black support) and subsequently flattened to form a smooth surface. The temperature time protocol started with an initial XRD scan at 30°C and then heated up with 0.0167 °C s^{-1} to 350°C under 4% H_2 in Ar with a flow rate of 40mLmin^{-1}. After a holding time of 30 min, XRD profiles were acquired. The XRD scanning parameters were: a 2V range from 32.5 to 55, a step size of 0.038, a holding time of 3 s per step, a fix divergence slit of 2 mm, a PSD iris anti-scattering slit of 13, and sample rotation.