Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Monitoring the formation of PtNi nanoalloy supported on hollow graphitic spheres by *in-situ* pair distribution function analysis

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1. Experimental Setup at ESRF

Fig. S1 Experimental setup at the ID22 beamline at ESRF: (1) Perkin-Elmer XRD 1611CP3 flat panel detector, (2) movable hot air blower, (3) beam path, (4) sample holder.

2. Temperature Program

Stepwise heating of PtNi precursor was performed from 25 to 800 °C with a heating rate of 5 °C/min and data were collected at each selected temperature, i.e., 25-250-300-400-450-500-550-600-650-700-750-800 °C for 45 min. Data during stepwise cooling were collected for 45 min at each selected temperature as well, i.e., 750-700-650-600-550-500-450-400 °C as shown in Fig. S2.

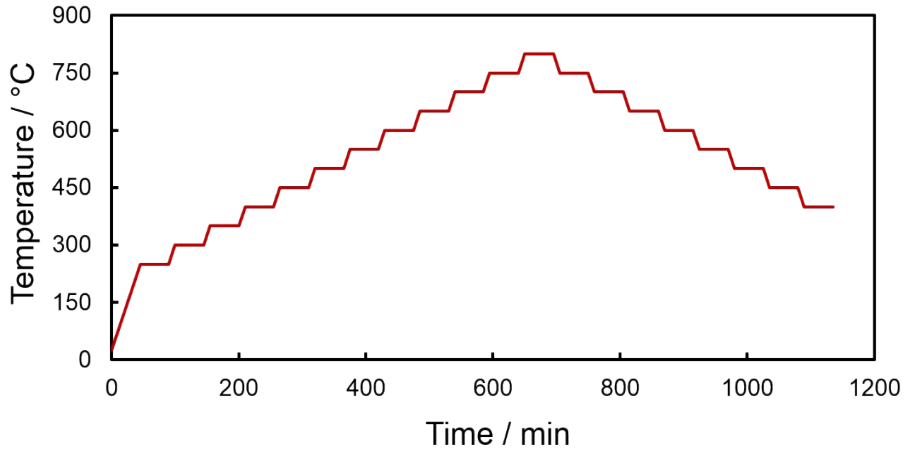

Fig. S2 Temperature program used for studying the formation of PtNi precursor.

3. Experimental setup at DLS

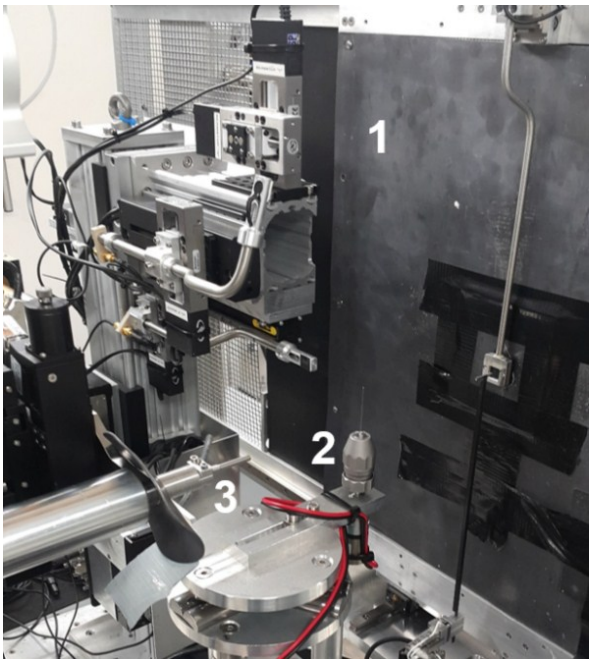

Fig. S3 Experimental setup at the I15 beamline at DLS: (1) two-dimensional flat panel Perkin-Elmer 1621 EN flat panel detector, (2) sample holder, (3) X-ray beam.

4. *In-situ* formation of PtNi nanoalloy-Heating

4.1. Rietveld Analysis

For the background a polynomial background function (Chebyshev) was applied. Pearson VII function was applied for the peak profile. Instrumental reflection broadening was determined by refining LaB_6 (NIST-standard) data for the measurements performed at ESRF. The unit cell parameters and the scale factors were refined, while the atomic site occupancies, fractional coordinates and the atomic displacement parameters were fixed. Fig. S4 shows the Rietveld plots of the data recorded at 700 and 750 °C, while the results are provided in Table S1.

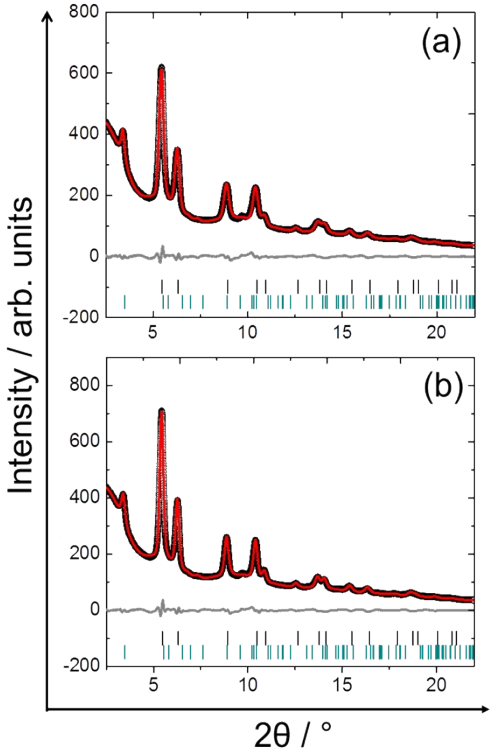

Fig. S4 Rietveld analyses of *in-situ* HR-XRPD data: (a) 700 °C, (b) 750 °C. The black curve represents the experimental data, while the red and the grey curves represent the calculated data and the difference, respectively. Tick marks: (black) disordered PtNi, (green) carbon.

Table S1: Results obtained from the Rietveld analyses of *in-situ* HR-XRPD data recorded at 700 and 750 °C.

Parameters		**Temperature / °C**	
		700	**750**
Unit cell parameter of the disordered PtNi / Å	Before fitting	$a = b = c = 3.7499$ (1)*	
	After fitting	3.7735 (3)	3.7758 (2)
Fit residual (R_{wp}) / %		2.4	2.2

*Room temperature crystal structure data were obtained from ICSD-105317.

4.2. PDF Analysis

Calculated Partial PDFs-Heating:

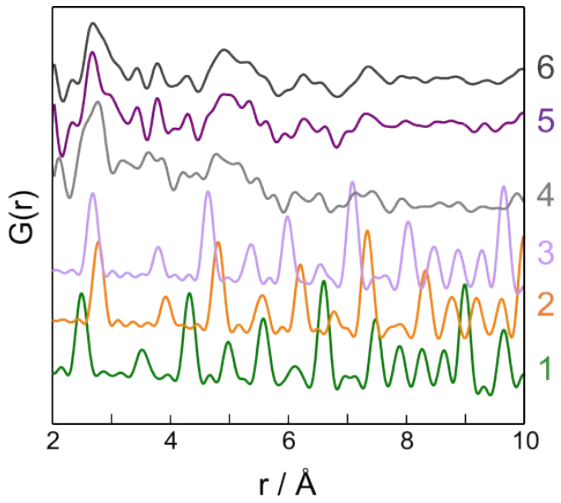

Fig. S5 Calculated partial PDFs in comparison to the experimental *in-situ* PDF data: (1) Ni-Ni, (2) Pt-Pt, (3) disordered PtNi; experimental data recorded at (4) 25 °C, (5) 250 °C, (6) 300 °C.

Table S2: Experimental interatomic distances at 800 °C compared to the theoretical distances of the disordered model. All theoretical interatomic distances belong to PtNi-PtNi pairs. Only some of the distances are listed for briefness.

Theoretical / Å		**Experimental / Å**
@ 25 °C[a]	**@ 800 °C[b]**	**@ 800 °C**
2.65	2.68	2.67
3.75	3.78	3.77
4.59	4.63	4.63
5.30	5.35	5.33

[a] The room temperature interatomic distances were calculated with the Diamond program using the room temperature crystal structure data from ICSD-105317.

[b] The theoretical interatomic distances at 800 °C were calculated with the Diamond program using the unit cell parameters obtained after PDF fitting.

***In-situ* PDF Fitting:**

Contributions from the quartz glass capillary and HGS support were subtracted from the experimental PDF data. The instrument dependent parameters, i.e., Q_{damp} and Q_{broad} were obtained by fitting PDF data of LaB_6 (NIST-standard) measured at ESRF, as 0.007 and 0.004 $Å^{-1}$, respectively. Both parameters were fixed during PDF fitting in the PDFgui. Fitted parameters include unit cell parameters, isotropic displacement parameters (U_{iso}), scale factor, and delta-1 parameter for the correlated atomic motion effect that sharpens the first PDF peak. Particle diameter in the PDFgui (spdiameter parameter) was fixed to 57 Å during PDF fitting in the r-range of 2-20 Å, as the spdiameter parameter was found to be nearly 57

Å by fitting the data in the r-range of 2-60 Å (not shown here). In addition, it is known from the HAADF-STEM analysis results that the average particle diameter is around 50-60 Å.

5. *In-situ* formation of PtNi nanoalloy-Cooling

5.1. Rietveld Analysis

For Rietveld analysis of *in-situ* XRPD data collected during cooling, the same strategy was followed as for heating (Section 4.1).

Table S3: Results obtained from the Rietveld analyses of *in-situ* HR-XRPD data recorded at 400 °C during cooling.

Model		Parameters after fitting	
		Unit cell parameters	Fit residual (R_{wp}) / %
Ordered[1]		a = 2.6726 (4), c = 3.733 (1)	7.8
Partially ordered	Ordered	$a = b$ = 2.7068 (3), c = 3.6225 (7)	1.7
	Disordered[2]	$a = b = c$ = 3.7616 (2)	

[1] Room temperature crystal structure data were obtained from ICSD-646297.

[2] Room temperature crystal structure data were obtained from ICSD-105317.

5.2. PDF Analysis

Calculated partial PDFs-Cooling:

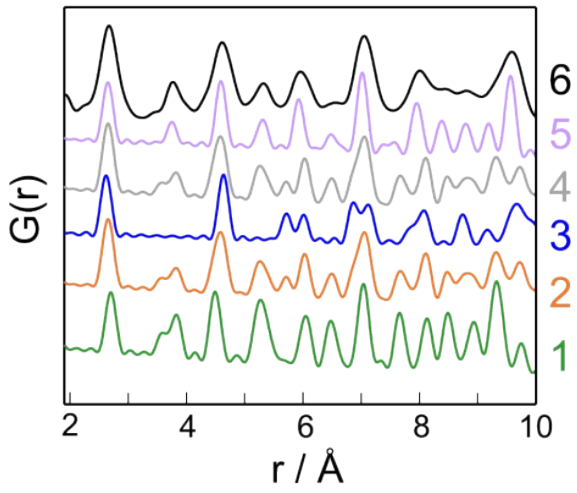

Fig. S6 Calculated partial PDFs in comparison to the experimental *in-situ* PDF data collected at 400 °C during cooling: calculated partial PDFs of the ordered PtNi model are (1) Ni-Ni, (2) Pt-Pt, (3) Pt-Ni and (4) total PDF of ordered PtNi, (5) total PDF of disordered PtNi, (6) 400 °C (experimental).

***In-situ* PDF Fitting-Cooling:**

The instrument dependent parameters for the ESRF data are given in Section 4.2. *In-situ* cooling PDF data were fitted by following the same strategy used for *in-situ* PDF data collected during heating (Section 4.2).

Table S4: Experimental interatomic distances at 400 °C during cooling compared to the theoretical interatomic distances. The theoretical distances of disordered PtNi alloy belong to PtNi-PtNi pairs. Only some of the distances are listed for briefness.

Theoretical distances / Å						**Experimental distances / Å**
Ordered PtNi				**Disordered PtNi**		
@ 25 °C[a]		**@ 400 °C[b]**		**@ 25 °C[c]**	**@ 400 °C[b]**	**@ 400 °C**
2.62 (Ni-Pt)	4.49 (Ni-Ni), (Pt, Pt)	2.66	4.59	2.65	2.66	2.67
2.70 (Ni-Ni), (Pt, Pt)	4.63 (Ni-Pt)	2.68	4.63	3.75	3.77	3.77
3.59 (Ni-Ni), (Pt, Pt)	5.24 (Ni-Ni), (Pt, Pt)	3.72	5.31	4.59	4.62	4.61
3.82 (Ni-Ni), (Pt, Pt)	5.40 (Ni-Ni), (Pt, Pt)	3.79	5.37	5.30	5.33	5.32

[a] The room temperature interatomic distances were calculated with the Diamond program using the room temperature crystal structure data obtained from ICSD-646297.

[b] The theoretical distances at 400 °C were calculated with the Diamond program using the unit cell parameters obtained after PDF fitting.

[c] The room temperature interatomic distances were calculated with the Diamond program using the room temperature crystal structure data obtained from ICSD-105317.

Table S5: Comparison of the results from the PDF fits in the *r* range of 2-20 Å using two different models for the data collected at 400 °C during cooling.

Parameters	**Parameters after fitting**	
	Disordered model	**Partially ordered model**
Unit cell parameters / Å	$a = b = c = 3.772$ (1)	Ordered $a = b = 2.704$ (1), $c = 3.672$ (2) Disordered $a = b = c = 3.769$ (2)
U_{iso} / Å^2	0.018 (1)	Ordered Pt = 0.010 (2), Ni = 0.011 (7) Disordered 0.018 (1)
Fit residual (R_w) / %	19	17

6. *Ex-situ* PDF Fitting

Table S6: Experimental interatomic distances of the *ex-situ* synthesised sample in comparison to the theoretical distances of the disordered model which were calculated with the Diamond program using the room temperature crystal structure data obtained from ICSD-105317. The theoretical distances belong to PtNi-PtNi pairs.

Theoretical / Å		**Experimental / Å**	
2.65	5.93	2.68	5.96
3.75	6.49	3.76	6.49
4.59	7.02	4.62	7.04
5.30	7.50	5.31	7.97

For the analysis of *ex-situ* PDF data, the instrument dependent parameters, i.e., Q_{damp} and Q_{broad} were obtained by fitting the PDF data of CeO_2 (NIST-standard) measured at DLS, as 0.01 and 0.07 $Å^{-1}$, respectively. Both parameters were fixed during the data fitting in the PDFgui. Fitted parameters include unit cell parameters, isotropic displacement parameters (U_{iso}), scale factor and delta-2 parameter for the correlated atomic motion effect that sharpens the first peak in PDF. Particle diameter was found to be 65.9 Å by long range order PDF fit (not shown here) and fixed during fitting the PDF range of 2-20 Å.

Table S7: Results obtained from PDF fit of *ex-situ* data collected for the *ex-situ* synthesised sample.

Parameters	**Parameters after refinement**
	Disordered model
Unit cell parameters / Å	$a = b = c =$ 3.7649 (1)
U_{iso} / $Å^2$	0.009 (1)
Fit residual (R_w) / %	19