Supporting Information for

Effect of solvothermal synthesis parameters on crystallite size and atomic structure of cobalt iron oxide nanoparticles

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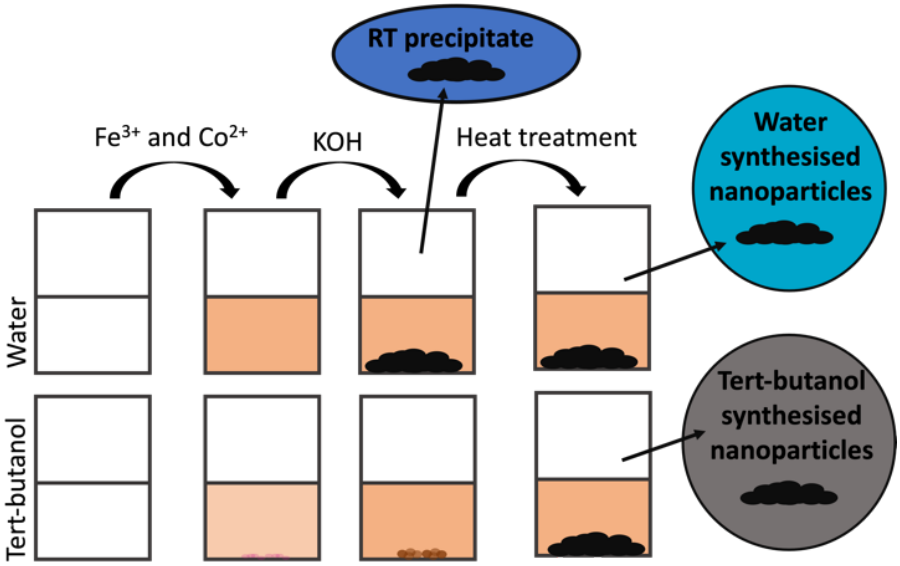

Figure S1 Synthesis approach for the three samples investigated. The room temperature precipitate was collected before heat treatment in the synthesis approach with water.

PDF real space refinements

The refinement were performed using the PDFgui software[1] and Fe_3O_4 in space group $Fd\bar{3}m$. For the water-synthesized nanoparticles a two-phase model with 2x Fe_3O_4 was used to describe the whole r-range.

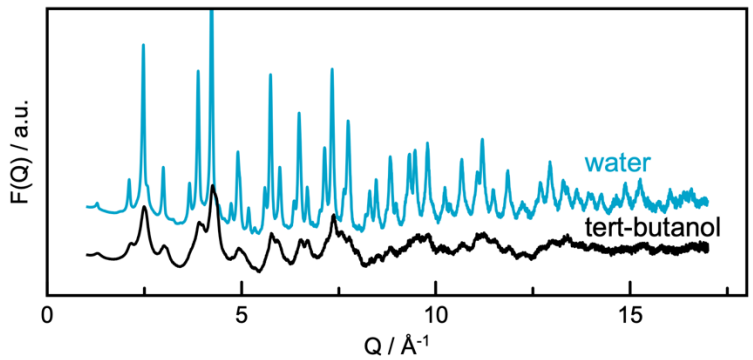

Figure S2 F(Q) for the two samples. Data collected at an Empyrean diffractometer with Ag Kα radiation (λ = 0.56 Å)

Table S1 Refined parameters for PDFs collected at an Empyrean diffractometer with Ag Kα radiation (λ = 0.56 Å)

	water (single-phase)	water (two-phase)	tert-butanol (single-phase)	tert-butanol (two-phase)	tert-butanol (two-phase)
Fe_3O_4 in $Fd\bar{3}m$					
Scale Factor	0.61 (0.013)	0.56 (0.014)	0.75 (0.038)	0.73 (0.039)	0.71 (0.040)
Scale Factor (Bulk)		0.080 (0.0071)		0.03 (0.012)	0.04 (0.010)
Fit range (Å)	1.7 Å – 100	1.7 Å – 100	1.7 Å – 30	1.7 Å – 30	1.7 Å – 30
Number of refined parameters	7	8	7	8	9
R_w	0.19	0.17	0.27	0.26	0.24
Q_{damp} (Å^{-1})	0.011	0.011	0.011	0.011	0.011
Q_{broad} (Å^{-1})	0.004	0.004	0.004	0.004	0.004
Q_{max} (Å^{-1})	17	17	17	17	17
U_{iso} (Å^2) Fe/Co	0.012 (0.00032)	0.012 (0.00032)	0.022 (0.0016)	0.021 (0.0016)	0.020 (0.0015)
U_{iso} (Å^2) O	0.029 (0.0018)	0.030 (0.0018)	0.027 (0.0045)	0.026 (0.0039)	0.026 (0.0039)
O pos	-0.75 (0.00085)	-0.75 (0.00084)	-0.75 (0.0012)	-0.75 (0.00076)	-0.75 (0.00085)
Lattice par., *a* (Å)	8.40 (0.00072)	8.40 (0.00068)	8.30 (0.0075)	8.31 (0.0072)	8.28 (0.0097)
Lattice par., *a* (Å) (bulk					8.36 (0.016)
δ_2 (Å^2)	3.52 (0.32)	3.50 (0.32)	3.40 (0.37)	3.41 (0.3)	3.36 (0.33)
Sp-diameter (Å)	85.7 (1.6)	66.0 (2.0)	23.1 (0.86)	20.4 (1.1)	20.0 (0.98)

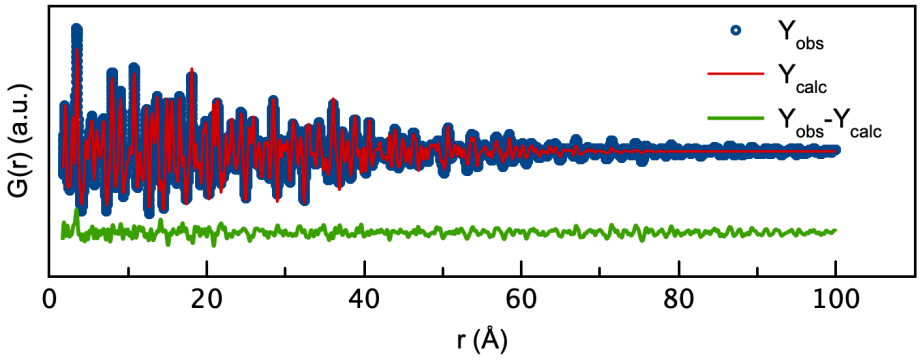

Figure S3 Refinement for the data collected for the water-synthesized nanoparticles, using a single phase, Fe_3O_4 in space group $Fd\bar{3}m$.

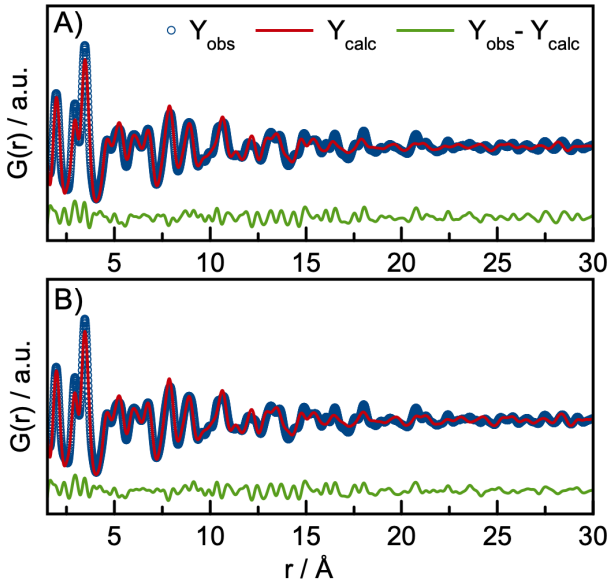

Figure S4 Two-phase refinement of data collected for the tert-butanol synthesized nanoparticles. A) Two spinel structural models where only the scale factors are refined individually for the two phases. B) Two spinel structural models where lattice parameters and scale factors are refined individually.

Table S2 PDF refined parameters for data collected at the I15-1 beamline at the Diamond synchrotron

	water	**tert-butanol**
Fe_3O_4 in $Fd\bar{3}m$		
Scale Factor	0.25 (0.022)	0.39 (0.031)
Scale Factor (Bulk)	0.10 (0.019)	
Fit range (Å)	1.7 Å – 60	1.7 Å – 30
Number of refined parameters	8	7
R_w	0.12	0.32
Q_{damp} (Å^{-1})	0.034	0.034
Q_{broad} (Å^{-1})	0.01	0.01
Q_{max} (Å^{-1})	27	27
U_{iso} (Å^2) Fe/Co	0.0075 (0.00043)	0.013 (0.0017)
U_{iso} (Å^2) O	0.020 (0.0026)	0.022 (0.0053)
O pos	-0.74 (0.0013)	-0.74 (0.00074)
Lattice par., *a* (Å)	8.40 (0.0016)	8.30 (0.011)
δ_2 (Å^2)	3.03 (0.56)	3.44 (0.27)
Sp-diameter (Å)	43.2 (6.0)	20.9 (1.4)

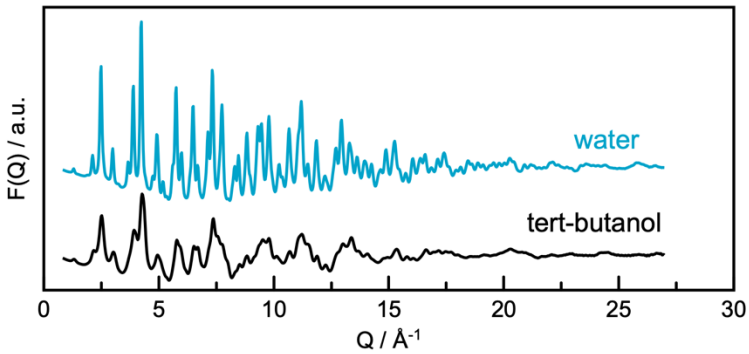

Figure S5 F(Q) for the two samples. Data collected at I15-1 beamline at the Diamond synchrotron

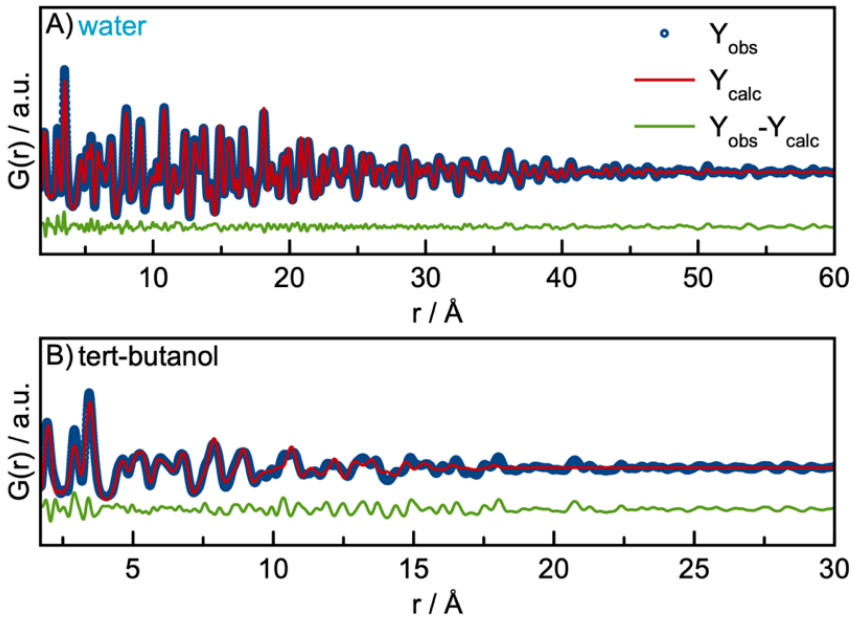

Figure S6 PDFs using Fe_3O_4 in $Fd\bar{3}m$ as the structural starting model. Data collected at the I15-1 beamline at Diamond synchrotron. The refined parameters are shown in Table S3.

Q-space Rietveld refinement

Fe_3O_4 in space group $Fd\bar{3}m$ with origin in (0,0,0) was used as the structural starting model.

Table S3 Rietveld refined parameter for the XRD collected an Empyrean diffractometer with Ag Kα radiation (λ = 0.56 Å)

	water	**tert-butanol**
Fe_3O_4 in $Fd\bar{3}m$		
Scale factor	0.212 E-06 (0.38E-08)	0.485 E-06 (0.27E-08)
Y	0.3433 (0.0075)	1.297 (0.0074)
Lattice par., *a* (Å)	8.38 (0.0015)	8.23 (0.0018)
O(x,y,z) (Å)	0.25704 (0.0011)	0.26153 (0.0074)
B_{iso}(Å^2) (Td)	0.53682 (0.11)	1.62735 (0.053)
B_{iso}(Å^2) (Oh)	0.69540 (0.097)	1.16066 (0.046)
R_{wp} (%)	15.0	11.7
Bragg R-factor	5.72	4.54

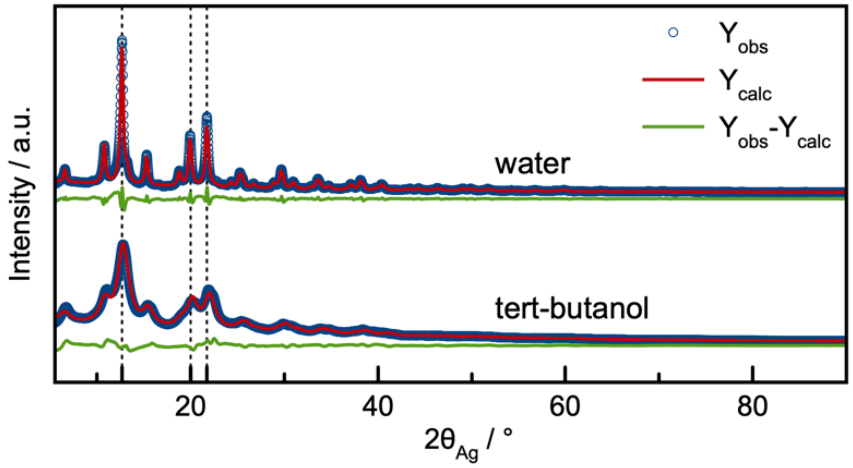

Figure S7 Rietveld refinement of the two samples using the Fe_3O_4 in space group $Fd\bar{3}m$ as the structural starting model

Elemental analysis with EDX

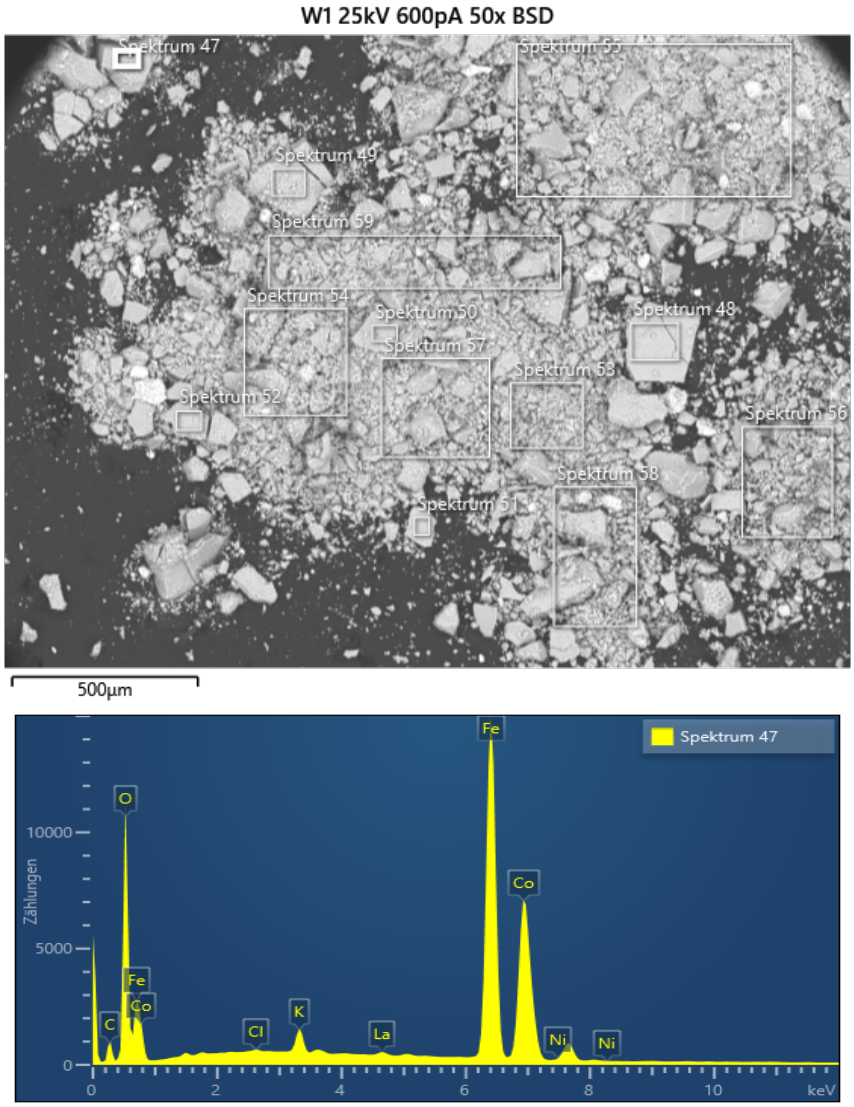

Figure S8 EDX analysis from nanoparticles synthesized with water.

Table S4 EDX analysis from nanoparticles synthesized with water. The composition and standard deviation were determined by averaging over 13 spectra taken across the sample.

Results	O	Cl	K	Fe	Co	Ni	La
Max	48.98	0.23	1.29	39.50	20.12	0.50	2.45
Min	37.13	0.02	0.92	33.15	16.39	0.17	0.00
Average	***40.32***	***0.09***	***1.08***	***38.07***	***19.03***	***0.28***	***1.12***
SD	2.91	0.05	0.14	1.59	0.92	0.10	0.94

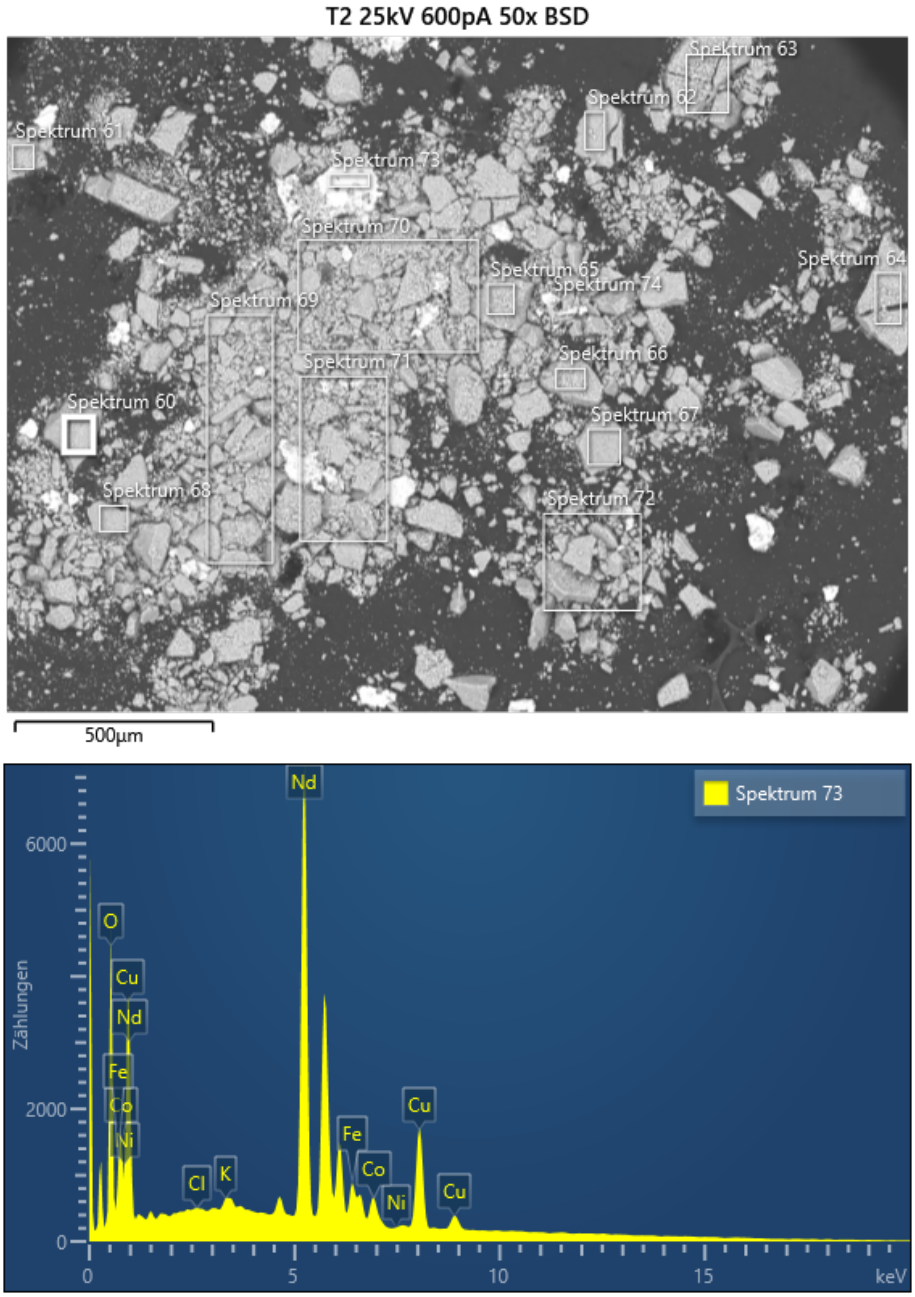

Figure S9 EDX analysis from nanoparticles synthesized with tert-butanol.

Table S5 EDX analysis from nanoparticles synthesized with tert-butanol. The composition and standard deviation were determined by averaging over 13 spectra taken across the sample.

Results	O	Cl	K	Fe	Co	Ni
Max	55.39	0.18	4.82	40.64	20.88	0.35
Min	36.57	0.00	3.73	26.84	13.85	0.04
Average	***43.46***	***0.08***	***4.19***	***34.86***	***17.19***	***0.22***
SD	5.10	0.05	0.31	3.62	1.64	0.10

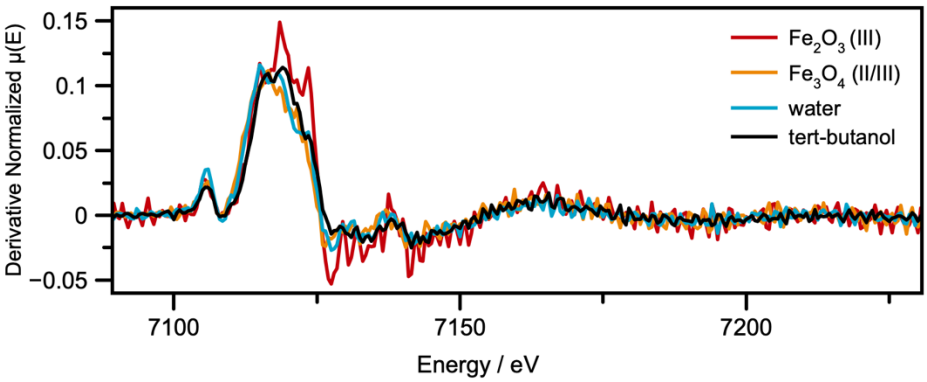

Figure S10 Derivative of the Fe *K*-edge XAS spectra for the water and tert-butanol synthesized nanoparticles with references γ-Fe_2O_3 (maghemite) and Fe_3O_4 (magnetite) reference spectra.

TEM

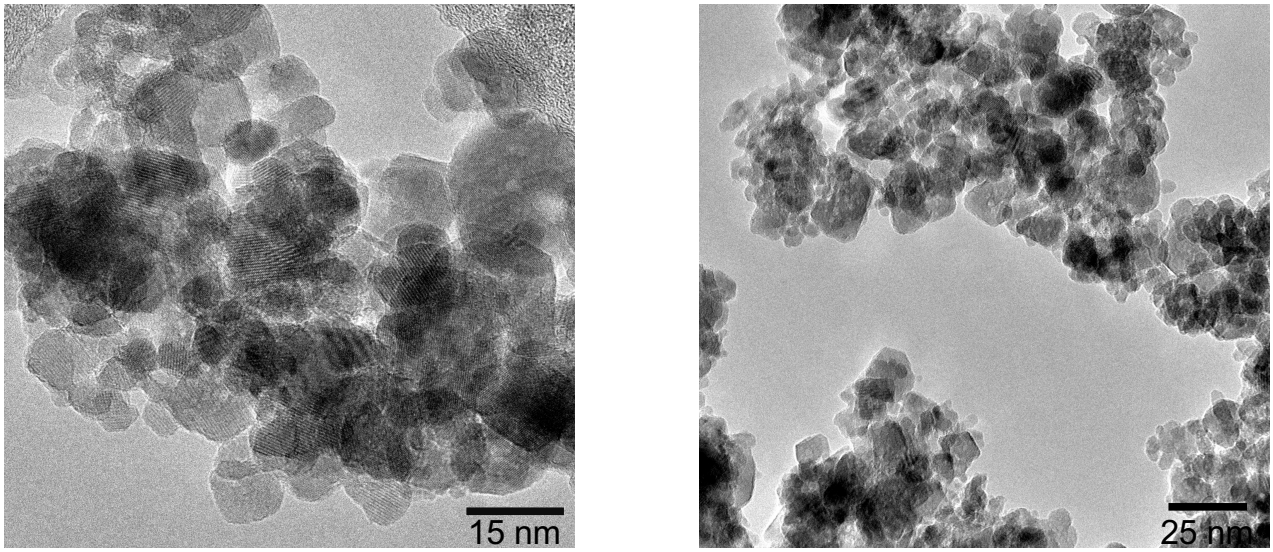

Figure S11 TEM micrographs for the water-synthesized nanoparticles

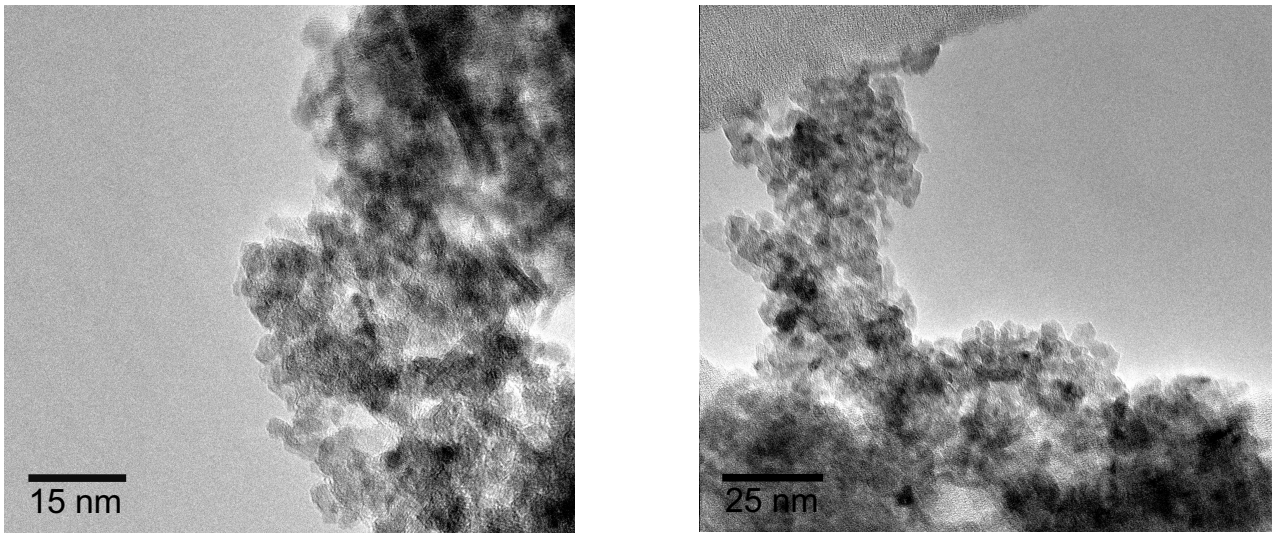

Figure S12 TEM micrographs for the tert-butanol synthesized nanoparticles

SAXS

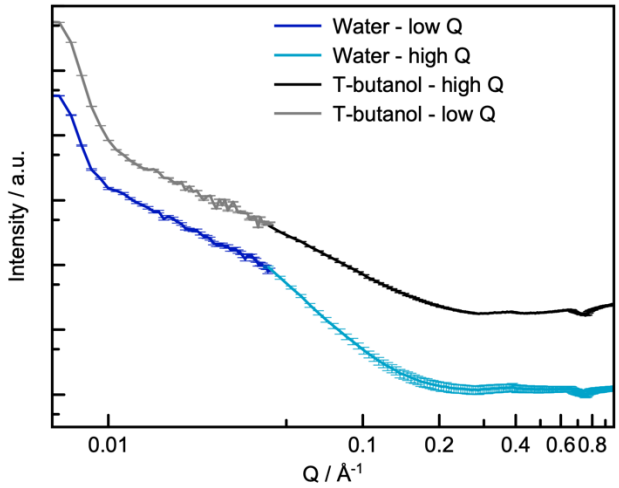

Figure S13 SAXS patterns of the water and tert-butanol synthesized nanoparticles.

Table S6 Refined parameters from SAXS refinement shown in Figure 4.

	water	**tert-butanol**
Fitting range (Å^{-1})	0.01 – 0.3	0.01 – 0.3
Dimension, a, Q^{-a}	4	4
Iqscale	0.0052 (0.062)	0.0017 (0.027)
Powerscale	$1.4 \cdot 10^{-8}$ ($3.9 \cdot 10^{-7}$)	$8.8 \cdot 10^{-8}$ ($3.4 \cdot 10^{-7}$)
background	0.0013 (0.034)	0.020 (0.029)
Mean Radius (nm)	7.7 (2.3)	4.1 (0.36)
Polydispersity	0.33 (0.0041)	0.36 (0.00053)

Neutron total scattering

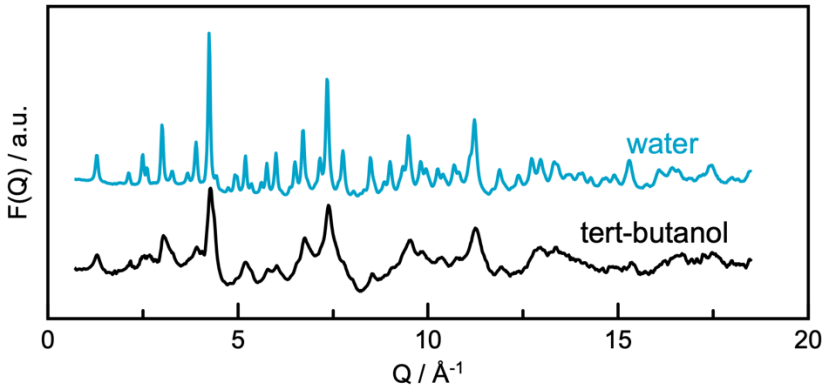

Figure S14 F(Q) for the two samples. Data collected at the Nomad beamline.

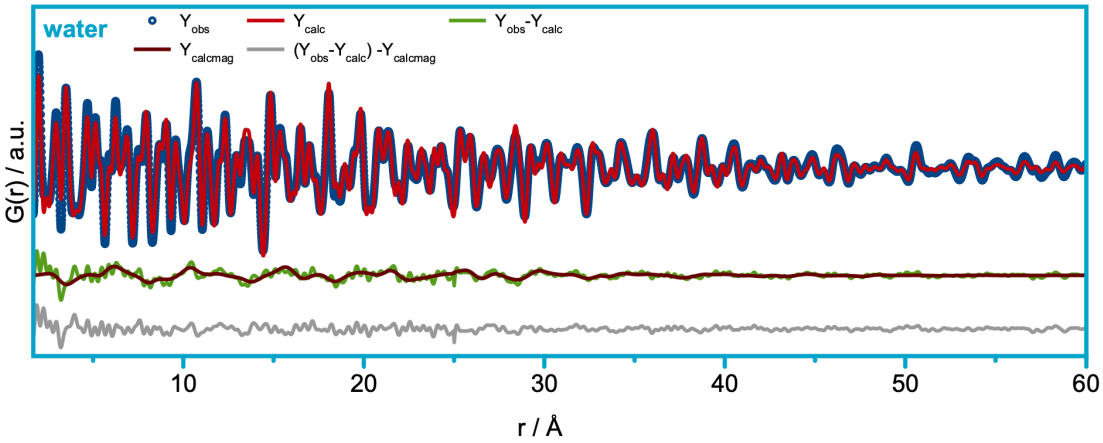

Figure S15 Neutron PDF (nPDF) and refinements using the $CoFe_2O_4$ spinel structure in space-group $Fd\bar{3}m$ for the water-synthesized nanoparticles. Here the magnetic PDF is furthermore refined as the difference curve using a collinear model.

Table S7 Refined parameters from nPDF refinements presented in Figure 5.

	water	**tert-butanol**
$CoFe_2O_4$ in $Fd\bar{3}m$		
Scale Factor	0.024 (0.013)	0.049 (0.03)
Fit range (Å)	1.5 Å – 60	1.5 Å – 30
Number of refined parameters	8	8
R_w	0.21	0.38
Q_{damp} (Å^{-1})	0.018	0.018
Q_{broad} (Å^{-1})	0.019	0.019
Q_{max} (Å^{-1})	18.5	18.5
U_{iso} (Å^2) Fe/Co	0.006 (0.0085)	0.0067 (0.014)
U_{iso} (Å^2) O	0.009 (0.016)	0.016 (0.031)
O pos	-0.74 (0.0079)	-0.74 (0.01)
Lattice par., *a* (Å)	8.38 (0.020)	8.31 (0.072)
δ_2 (Å^2)	3.30 (6.0)	3.30 (3.7)
Sp-diameter (Å)	84.4 (61)	22.3 (11)
Fe_{Td} occ	0.57 (0.63)	0.46 (0.62)

Table S8 Refined parameters for the mPDF refinement for the water-synthesized nanoparticles

	Water	Tert-butanol
Rw	0.698	0.920
Sp-diameter (Å)	63.5 (3.1)	20.6 (1.4)
Ordered moment averaged over all sites (μ_B)	3.83 (13)	3.6 (3)
Ratio of octahedral moment to tetrahedral moment	0.74 (4)	0.50 (6)

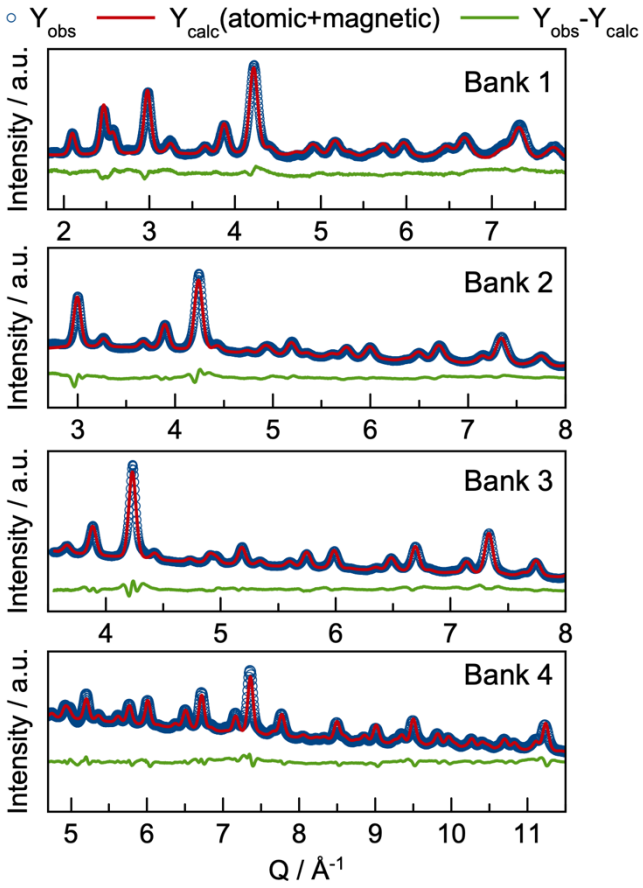

Figure S16 Rietveld refinements of the neutron scattering data collected for the water-synthesized nanoparticles.

Table S9 Refined parameters from Rietveld refinement of neutron scattering data for the water-synthesized nanoparticles.

	water
$CoFe_2O_4$ in $Fd\bar{3}m$	
Crystal structure:	
Lattice par., *a* (Å)	8.38 (0.00040)
Oxygen position	0.257 (0.00022)
B_{iso} Co/Fe (8a)	0.600 (0.071)
B_{iso} Co/Fe (16d)	0.600 (0.071)
B_{iso} O	0.500
Fe_{Td} occ	0.37 (0.013)
Co_{Td} occ	0.63 (0.013)
Fe_{Oh} occ	0.63 (0.013)
Co_{Oh} occ	1.38 (0.013)
Magnetic structure:	
Easy-axis	<100>
μ_{tet} (μ_B)	-3.46 (0.24)
μ_{oct} (μ_B)	3.44 (0.19)
Fit quality	**Bank 1/2/3/4**
R_{Bragg} (%)	7.27/7.71/8.61/11.8
R_F (%)	9.36/6.44/8.78/9.75
$R_{magnetic}$ (%)	3.68/6.70/15.7/10.9

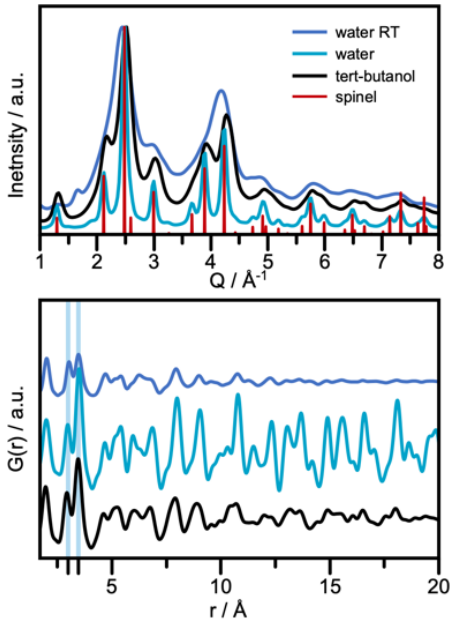

Figure S17 Comparison of the X-ray scattering data collected for the nanoparticles formed under different synthesis conditions. Solvothermal synthesis using water and tert-butanol. And synthesis collecting the precipitate in water at room temperature.

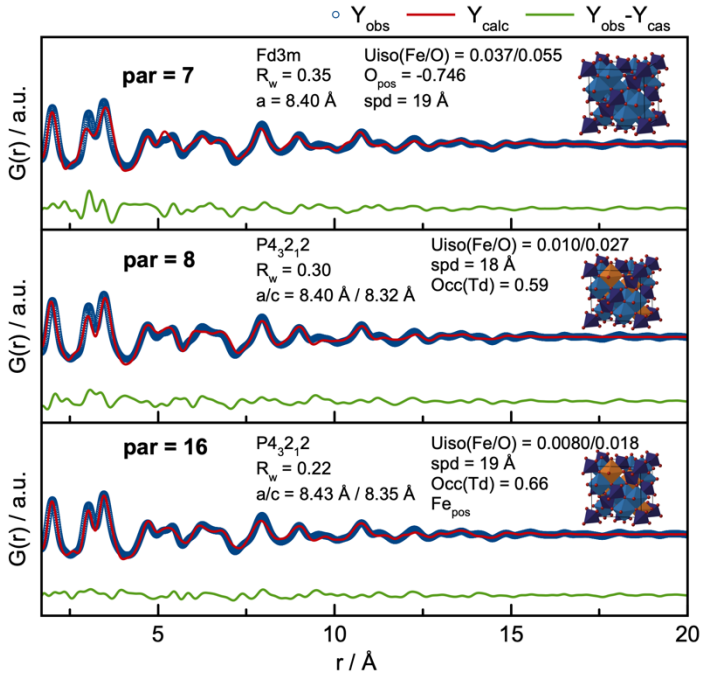

Figure S18 PDFs collected for the nanoparticles formed during co-precipitation. Refinement with two different spinel structures in space group $Fd\bar{3}m$ and $P4_32_12$ respectively.

Table S10 Refined parameters from PDF refinements of the water room temperature sample presented in Figure 6 and S17.

	Fe_3O_4 in $Fd\bar{3}m$	Fe_3O_4 in $P4_32_12$	Fe_3O_4 in $P4_32_12$
Scale Factor (Bulk)	0.47 (0.049)	0.53 (0.058)	0.53 (0.057)
Fit range	1.7 Å – 20 Å	1.7 Å – 20 Å	1.7 Å – 20 Å
Number of refined parameters	7	8	16
R_w	0.35	0.30	0.23
Q_{damp} (Å^{-1})	0.044	0.044	0.044
Q_{broad} (Å^{-1})	0.01	0.01	0.01
Q_{max} (Å^{-1})	20	20	20
U_{iso} (Å^2) Fe/Co	0.037 (0.0054)	0.009 (0.0022)	0.007 (0.0031)
U_{iso} (Å^2) O	0.005 (0.003)	0.027 (0.0088)	0.022 (0.0089)
O pos	-0.75 (0.00092)		
Fe pos			0.23 (0.0063)
			0.52 (0.0068)
			0.14 (0.0087)
			0.13 (0.0065)
			0.86 (0.0059)
			0.62 (0.0073)
			0.27 (0.0053)
			0.64 (0.0012)
Lattice par., *a* (Å)	8.41 (0.019)	8.44 (0.067)	8.43 (0.051)
Lattice par., *c* (Å)		8.32 (0.14)	8.35 (0.11)
δ_2 (Å^2)	3.53 (0.43)	3.04 (0.41)	3.45 (0.77)
Sp-diameter (Å)	19.5 (1.7)	18.0 (1.6)	18.6 (1.6)
Occ(Td)		0.59 (0.059)	0.66 (0.075)

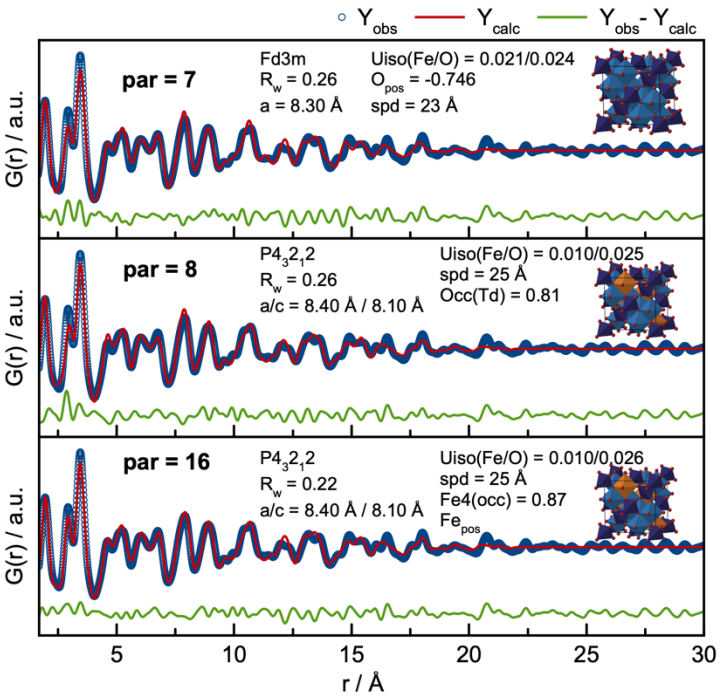

Figure S19 Refinement of the PDF from the tert-butanol-synthesized nanoparticles with two different spinel structures in space group $Fd\bar{3}m$ and $P4_32_12$ respectively.

Table S11 Refined parameters from PDF refinements of tert-butanol-synthesized nanoparticles presented in Figure S18.

	Fe_3O_4 in $Fd\bar{3}m$	Fe_3O_4 in $P4_32_12$	Fe_3O_4 in $P4_32_12$
Scale Factor (Bulk)	0.75 (0.038)	0.79 (0.044)	0.81 (0.047)
Fit range (Å)	1.7 Å – 30	1.7 Å – 30	1.7 Å – 30
Number of refined parameters	7	8	16
R_w	0.27	0.26	0.22
Q_{damp} ($Å^{-1}$)	0.011	0.011	0.011
Q_{broad} ($Å^{-1}$)	0.004	0.004	0.004
Q_{max} ($Å^{-1}$)	17	17	17
U_{iso} ($Å^2$) Fe/Co	0.022 (0.0016)	0.010 (0.0013)	0.010 (0.0019)
U_{iso} ($Å^2$) O	0.027 (0.0045)	0.027 (0.005)	0.026 (0.0052)
O pos	-0.75 (0.0012)		
			0.25 (0.0063)
			0.51 (0.0042)
			0.14 (0.0051)
			0.14 (0.0037)
			0.87 (0.0045)
			0.63 (0.0038)
			0.26 (0.0037)
			0.62 (0.012)
Lattice par., *a* (Å)	8.30 (0.0075)	8.39 (0.013)	8.39 (0.015)
Lattice par., *c* (Å)		8.10 (0.025)	8.10 (0.028)
δ_2 ($Å^2$)	3.40 (0.37)	3.05 (0.26)	3.32 (0.4)
Sp-diameter (Å)	23.1 (0.86)	25.3 (1.2)	24.8 (1.1)
Occ(Td)		0.81 (0.045)	0.87 (0.055)

References

1. C. Farrow, P. Juhas, J. Liu, D. Bryndin, E. Božin, J. Bloch, T. Proffen and S. Billinge, *Journal of Physics: Condensed Matter*, 2007, **19**, 335219.