Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information:

Shape Controlled Iron Oxide Nanoparticles: Inducing Branching and Controlling Particle Crystallinity

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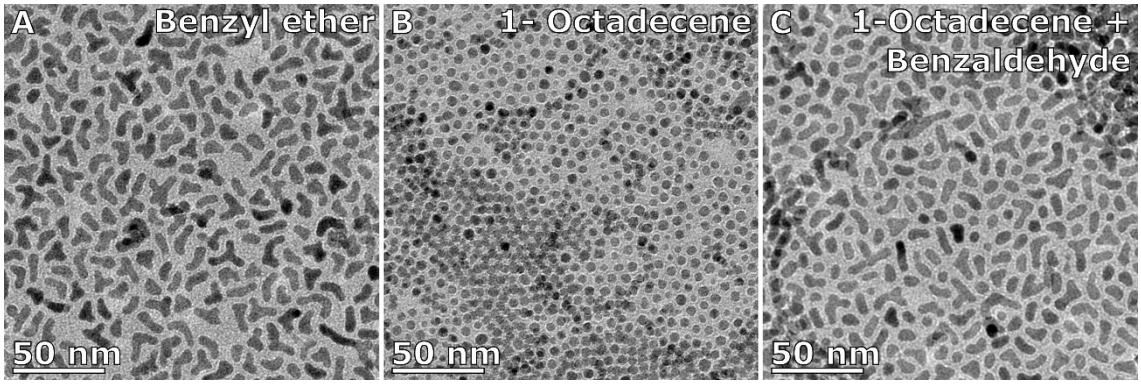

Fig. S1 TEM images of nanoparticles obtained with various solvents, A) benzyl ether B) 1-octadecene and C) mixture of 1-octadecene and benzaldehyde.

Table S1 Average size and shapes of nanoparticles formed with increasing OAm eq.

OAm	Shape	Average Size / nm	Branch Width / nm
40 eq	Spheres	6 ± 1	
25 eq	Branched	13 ± 3	5.3 ± 0.7
23 eq	Branched	12 ± 2	5.5 ± 0.7
21 eq	Branched	14 ± 3	5.6 ± 0.8
19 eq	Branched	14 ± 4	6 ± 1
17 eq	Multiply Branched	21 ± 4	6.6 ± 0.9
15 eq	Multiply Branched	17 ± 3	7 ± 1
13 eq	Multiply Branched	29 ± 4	14 ± 3
10 eq	Anisotropic/Elongated	17 ± 2	12 ± 2
5 eq	Octahedra/Cuboctahedra	16 ± 2	
0 eq			

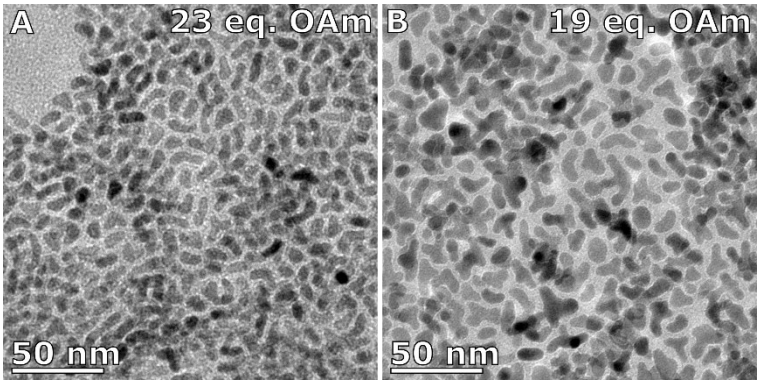

Fig. S2 TEM images of nanoparticle formed with **A)** 23 eq OAm and **B)** 19 eq OAm.

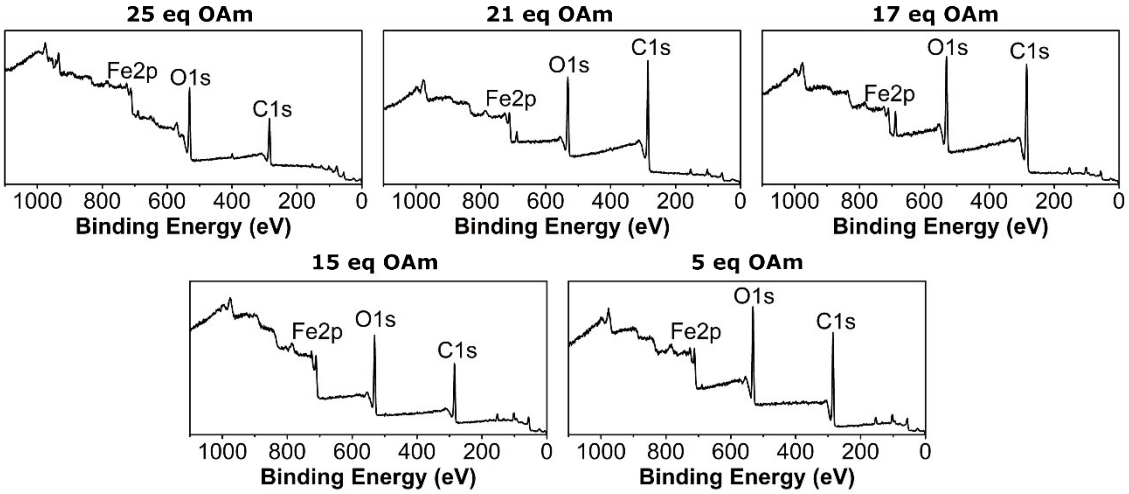

Fig. S3 XPS survey spectra of IONP synthesized with of 25 eq OAm, 21 eq OAm, 17 eq OAm, 15 eq OAm and 5 eq OAm and with purging nitrogen. The Fe2p, O1s and C1s peaks are noted, and there are additional peaks from O2s at ~22 eV and OKVV 950-1000 eV, and Fe3p ~52 eV, Fe3s ~93 eV and Fe_{LMM} at 764-904 eV. There are also peaks that come from the background and sample preparation, such as Si2p at 99-103.5 eV, Si2s at ~153 eV, as well as P2p at ~130 eV and P2s at 190 eV, Na_{KLL} at 497 eV and in some samples F1s at 684-689 eV.

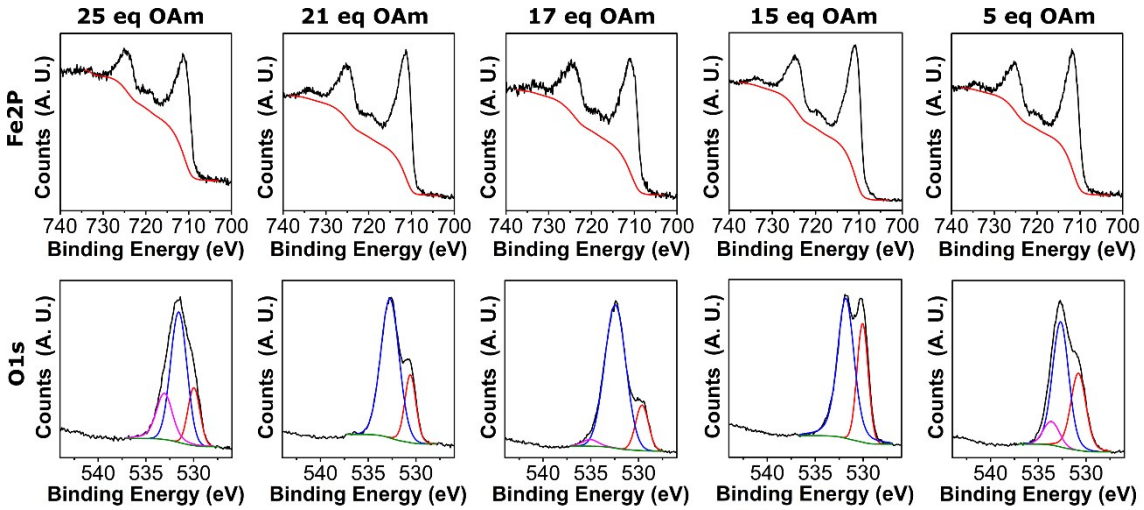

Fig. S4 XPS Fe2p and O1s spectra of IONP synthesized with of 25 eq OAm, 21 eq OAm, 17 eq OAm, 15 eq OAm and 5 eq OAm and with purging nitrogen.

Table S2 XPS peak positions of fits from the O1s and C1s regions, as well as the $Fe2p_{3/2}$ peak maximum position of 25 eq OAm, 21 eq OAm, 17 eq OAm, 15 eq OAm and 5 eq OAm synthesized with purging nitrogen.

Peak	25 eq	21 eq	17 eq	15 eq	5 eq	Assignment
O1s (O_{met})	530.2	530.5	530.2	530.5	530.2	O1s O-metal
O1s	531.8, 533.3	532.6	533.0 535.7	532.2	532.1, 533.0	O1s organic (C-O, C=O, C-OH)
$Fe2p_{3/2}$	711.2	711.2	711.4	711.3	711.0	$Fe^{3+/2+}$
$Fe:O_{met}$	0.64	0.68	0.72	0.63	0.46	Fe to metallic O Ratio

Table S3 Fitting parameters for the O1s section for the particles made with 25 eq OAm, 21 eq OAm, 17 eq OAm, 15 eq OAm and 5 eq OAm synthesized with purging nitrogen. The binding energies were referenced against the position of the main component of the C1s peak set to 284.8 eV. The O1s component can be assigned with 529-531.2 eV for O-metal, and the O1s organic component with 532.5-533.5 eV for C-O, 531.5-532.0 eV for C=O, and ~535 eV for O-F_x.

Sample	Peak	Peak BE (eV)	FWHM (eV)	Area (CPS. eV)
25 eq OAm	O1s O_{met}	530.2	1.49	8012.94
	O1s organic	531.8	2.01	24390.44
	O1s organic	533.3	1.98	9363.09
21 eq OAm	O1s O_{met}	530.5	1.37	10335.52
	O1s organic	532.6	2.26	34505.69
17 eq OAm	O1s O_{met}	530.2	1.59	6504.64
	O1s organic	533.0	2.59	33374.20
	O1s organic	535.7	1.92	1259.34
15 eq OAm	O1s O_{met}	530.5	1.37	15427.55
	O1s organic	532.2	2.06	29491.59
5 eq OAm	O1s O_{met}	530.2	1.87	12677.88
	O1s organic	532.1	1.99	21729.14
	O1s organic	533.0	1.97	3908.00

Table S4 Positive pressure nitrogen environment for various OAm eq.

Oam	Average Size / nm	Shape
23 eq	7 ± 1	Spherical
17 eq	8 ± 2	Spherical
15 eq	10 ± 3	Spherical / Cubes
13 eq	24 ± 5	Spherical
10 eq	14 ± 2	Cuboctahedra
5 eq	6.6 ± 0.8	Spherical

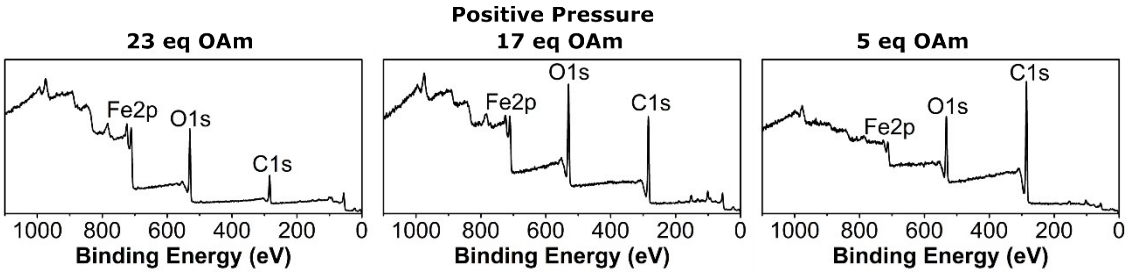

Fig. S5 XPS survey spectra of IONP synthesized with 23 eq OAm, 17 eq OAm and 5 eq OAm without purging nitrogen. The Fe2p, O1s and C1s peaks are noted, and there are additional peaks from O2s at ~22 eV and OKVV 950-1000 eV, and Fe3p ~52 eV, Fe3s ~93 eV and Fe_{LMM} at 764-904 eV. There are also peaks that come from the background and sample preparation, such as Si2p at 99-103.5 eV, Si2s at ~153 eV, as well as P2p at ~130 eV and P2s at 190 eV, Na_{KLL} at 497 eV and in some samples F1s at 684-689 eV.

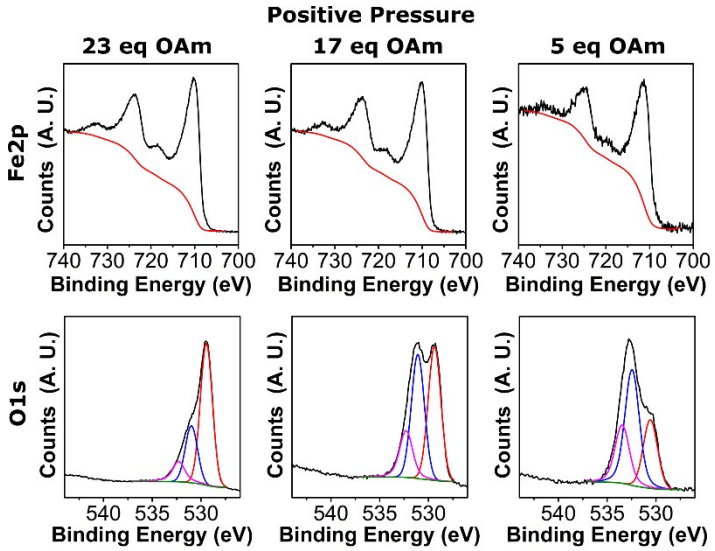

Fig. S6 XPS Fe2p and O1s spectra of IONP synthesized with 23 eq OAm, 17 eq OAm and 5 eq OAm without purging nitrogen.

Table S5 XPS peak positions of fits from the O1s and C1s regions, as well as the $Fe2p_{3/2}$ peak maximum position of 23 eq OAm, 17 eq OAm and 5 eq OAm synthesized without purging nitrogen.

Peak	23 eq	17 eq	5 eq	Assignment
O1s (O_{met})	530.1	530.2	530.4	O1s O-metal
O1s	531.6, 532.9	531.8, 532.9	532.3, 533.3	O1s organic (C-O, C=O, C-OH)
$Fe2p_{3/2}$	710.8	710.1	711.1	$Fe^{3+/2+}$
$Fe:O_{met}$	0.70	0.62	0.50	Fe to metallic O Ratio

Table S6 Fitting parameters for the O1s section for the particles made with 23 eq OAm, 17 eq OAm and 5 eq OAm synthesized without purging nitrogen. The binding energies were referenced against the position of the main component of the C1s peak set to 284.8 eV. The O1s component can be assigned with 529-531.2 eV for O-metal, and the O1s organic component with 532.5-533.5 eV for C-O, 531.5-532.0 eV for C=O, and ~535 eV for O-F_x.

Sample	Peak	Peak BE (eV)	FWHM (eV)	Area (CPS. eV)
23 eq OAm	O1s O_{met}	530.1	1.45	37477.10
	O1s organic	531.6	1.48	15357.43
	O1s organic	532.9	1.5	6993.35
17 eq OAm	O1s O_{met}	530.2	1.48	18190.07
	O1s organic	531.8	1.75	17142.27
	O1s organic	532.9	1.75	7117.52
5 eq OAm	O1s O_{met}	530.4	1.72	7289.38
	O1s organic	532.3	1.73	13165.50
	O1s organic	533.3	1.73	6853.05

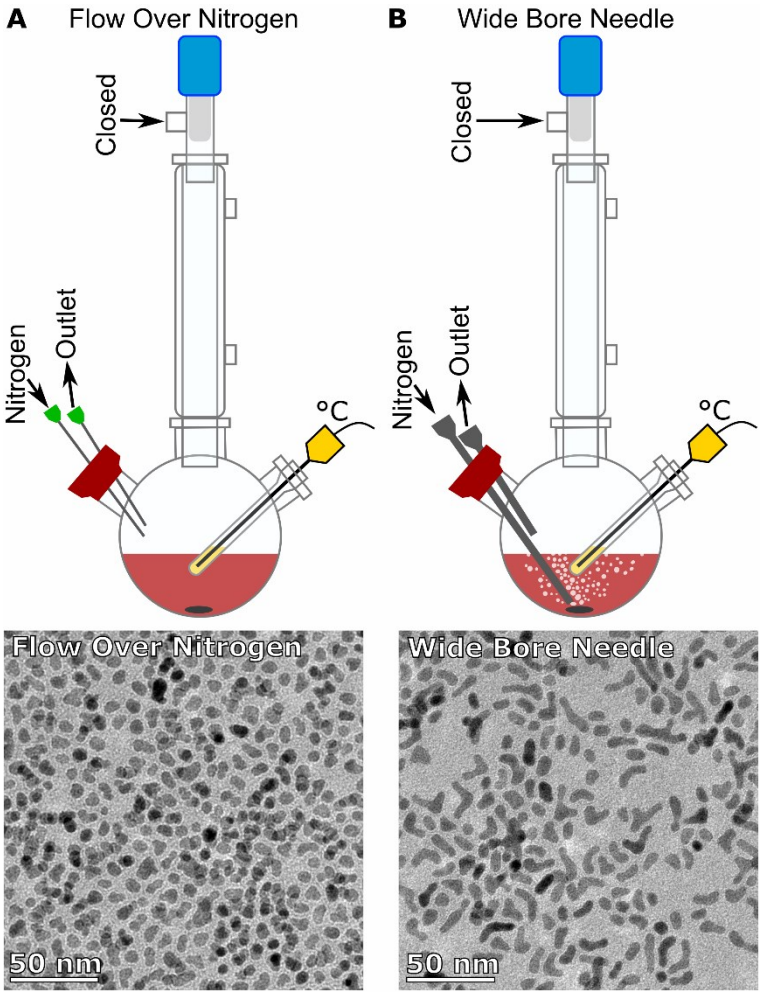

Fig. S7 Effect of varying nitrogen flow during the reaction with 23 eq OAm and 4.5 eq HDD. A) A schematic of the set up with a needle with nitrogen flowing on the surface of the reaction solution, and the TEM image of the particles below it. B) A schematic of the set up with a wider bore entry and exit needle with increased nitrogen bubbling in the reaction mixture, and the TEM image of the particles below it.

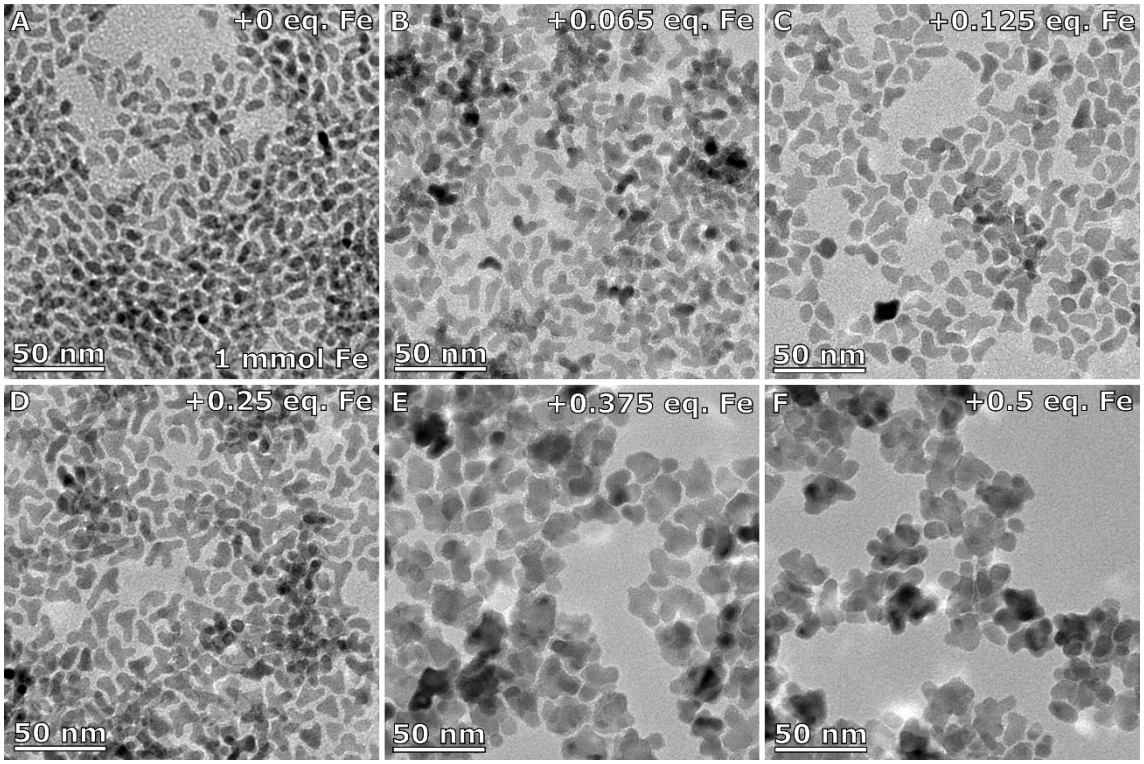

Fig. S8 The effect of increasing the amount of iron (III) acetylacetonate in solution in a reaction mixture with standard reaction configuration (purging nitrogen, 23 eq OAm and 4.5 eq HDD). With A) the standard recipe (purging nitrogen, 23 eq OAm and 4.5 eq HDD), B) +0.065 eq Fe, C) +0.125 eq Fe, D) +0.25 eq Fe E) +0.375 eq Fe, and F) +0.5 eq Fe.

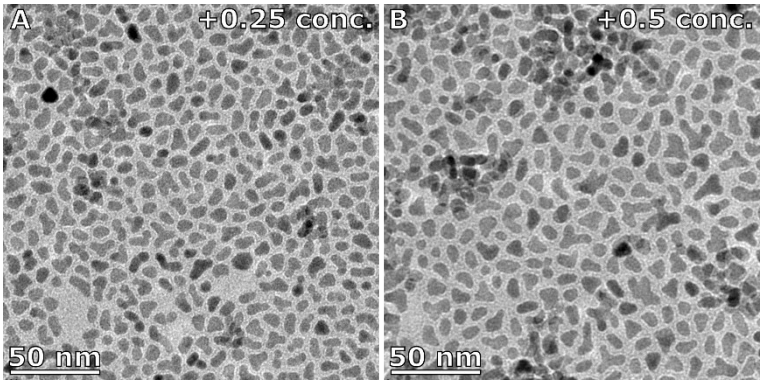

Fig.S9 Increasing concentrations of metal precursors and surfactants by A) 25% and B) 50% from the set up with purging nitrogen, 23 eq OAm and 4.5 eq HDD. This resulted in similar branching with no significant shape anisotropy.

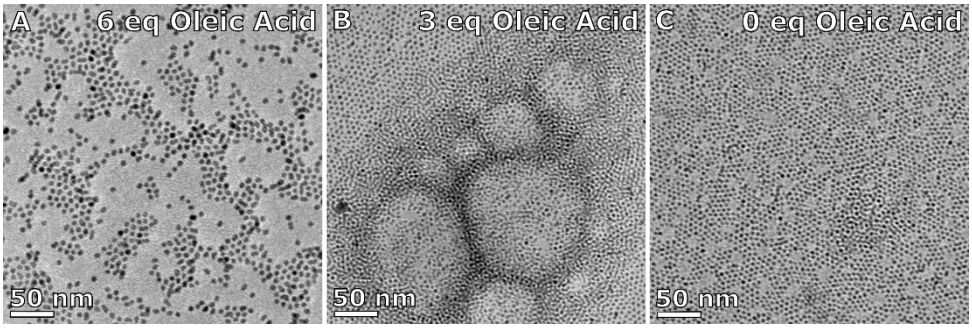

Fig. S10 Reducing the oleic acid equivalence from the standard of 9 eq to A) 6 eq, B) 3 eq and C) 0 eq in a reaction system with purging nitrogen, 23 eq OAm and 4.5 eq HDD.

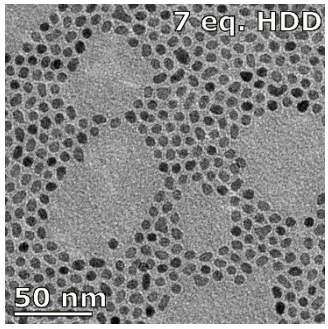

Fig. S11 Nanoparticles formed with 7 eq HDD, 23 eq OAm and purging nitrogen.

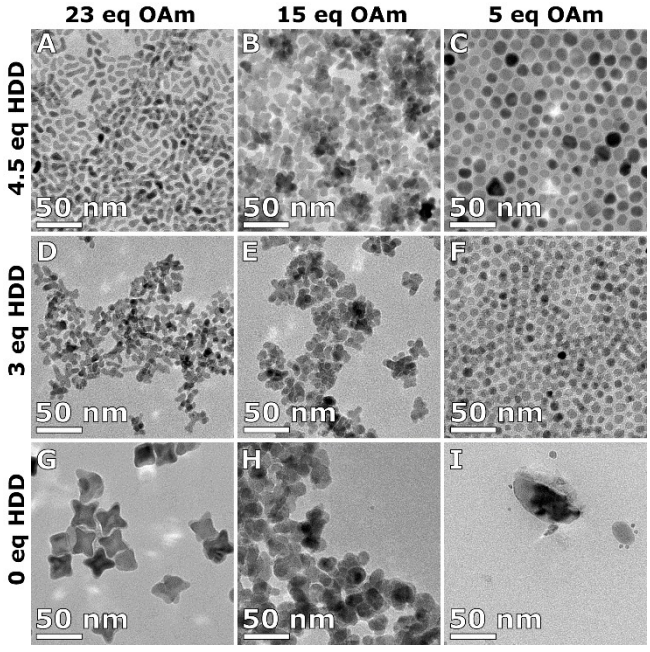

Fig. 12 TEM images of IONPs made varying the HDD and OAm and with a constant nitrogen purge using 4.5, 3 and 0 eq HDD with 23, 15 and 5 eq OAm.

Table S7 Average size and shapes of nanoparticles formed with varying the equivalents of HDD and OAm to the metal precursor.

OAm	HDD	Shape	Average Size / nm	Branch Width / nm
23 eq	**7 eq**	Elongated	7 ± 1	5.6 ± 0.5
23 eq	**4.5 eq**	Branched	12 ± 2	5.5 ± 0.7
23 eq	**3 eq**	Branched	18 ± 4	5.3 ± 0.9
23 eq	**0 eq**	Octapod	33 ± 4	
15 eq	**4.5 eq**	Multiply Branched	17 ± 3	7 ± 1
15 eq	**3 eq**	Multiply Branched	24 ± 6	7 ± 1
15 eq	**0 eq**	Aggregated	23 ± 9	13 ± 4
5 eq	**4.5 eq**	Octahedra	16 ± 2	
5 eq	**3 eq**	Spheres	8 ± 2	
5 eq	**0 eq**			

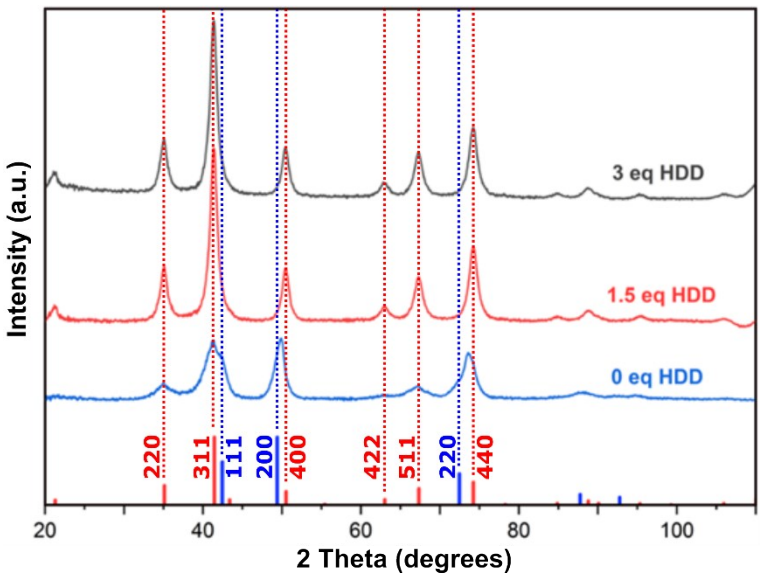

Fig. S13 XRD patterns of IONPs made with 3 eq HDD, 1.5 eq HDD and 0 eq HDD of the series all conducted at 23 eq of OAm compared to the references of iron oxide, Fe_3O_4, (PDF: 01-075-0033) and Wüstite (PDF: 01-073-2144) as the red and blue bars and hkl values respectively which are matched to the blue and red dotted lines as guides.

Table S8 Hyperthermia results reported in terms of SAR and ILP of the branched (25 eq OAm), and multiply branched (17 eq OAm and 15 eq OAm) nanoparticles made with constant nitrogen purge and spherical nanoparticles (10 eq OAm) made under positive pressure (PP). Experiments were conducted with a field value of 24.5 kA/m.

Shape	SAR [W/g] at 303 kHz	ILP [nHm²/kg] at 303 kHz	SAR [W/g] at 488 kHz	ILP [nHm²/kg] at 488 kHz
Branched (25 eq OAm)	11	0.06	37	0.13
Multiply Branched (17 eq OAm)	28	0.16	50	0.11
Multiply Branched (15 eq OAm)	260	1.42	457	1.55

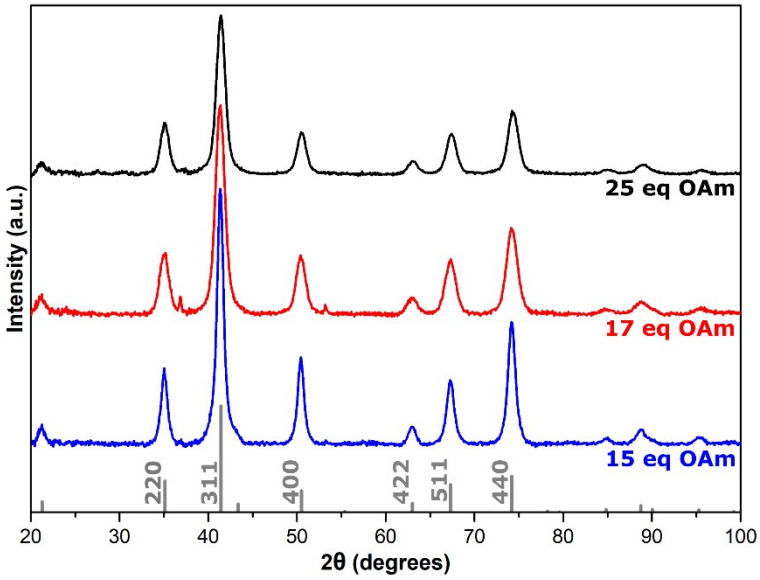

Fig. S14 XRD patterns of the branched nanoparticles (25 eq OAm) and the two multiply branched nanoparticles (17 eq OAm and 15 eq OAm). The grey bars at the bottom are referenced to iron oxide, Fe_3O_4, with the hkl values in grey (PDF: 01-075-0033).

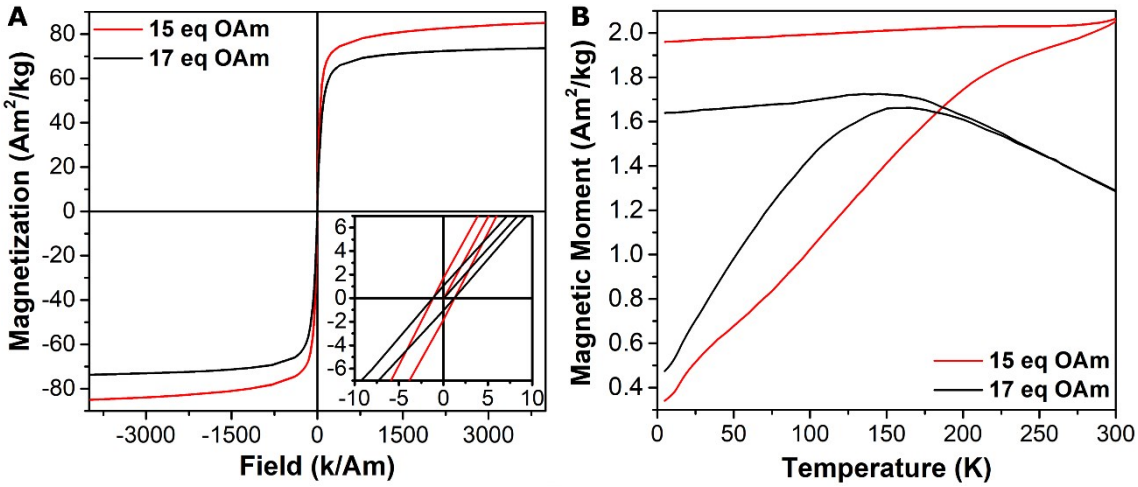

Fig. S15 A) Magnetization curves at 300 K for the multiply branched nanoparticles (15 eq OAm and 17 eq OAm) made with constant nitrogen purge, with the inset of the hysteresis behavior. B) Zero-field cooled, field cooled curves for the multiply branched nanoparticles (15 eq OAm and 17 eq OAm).

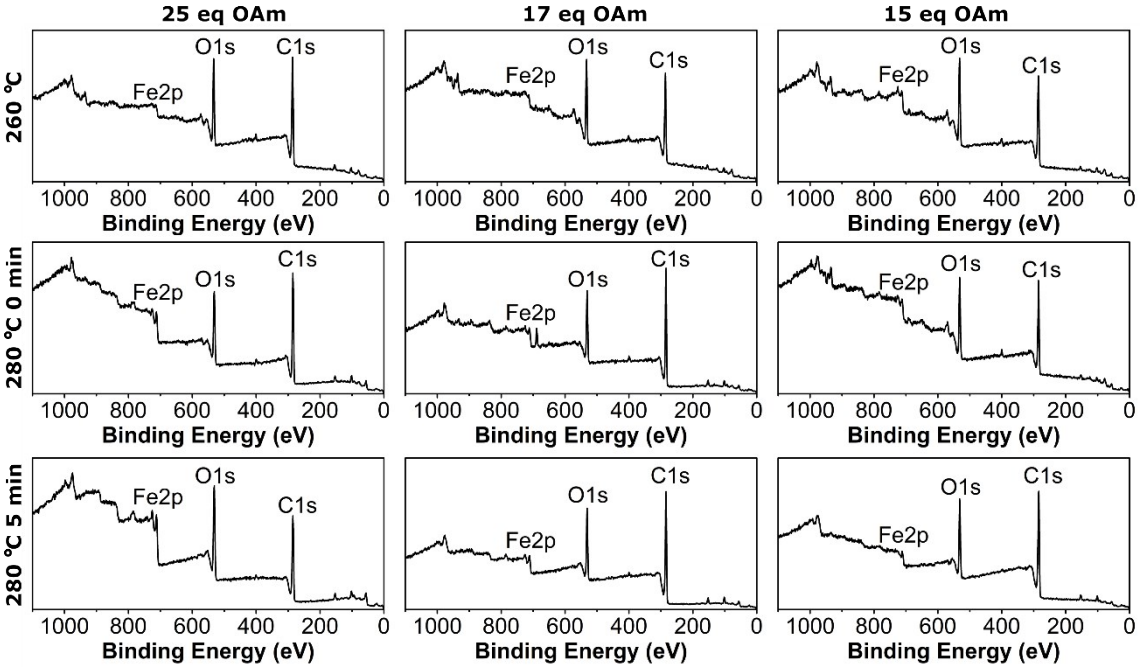

Fig. S16 XPS survey spectra of IONP synthesized with 25 eq OAm, 17 eq OAm, and 15 eq OAm sampled at 260 °C, 280 °C 0 min and 5 min after reaching 280 °C. The Fe2p, O1s and C1s peaks are noted, and there are additional peaks from O2s at ~22 eV and O_{KVV} 950-1000 eV, and Fe3p ~52 eV, Fe3s ~93 eV and Fe_{LMM} at 764-904 eV. There are also peaks that come from the background and sample preparation, such as Si2p at 99-103.5 eV, Si2s at ~153 eV, as well as P2p at ~130 eV and P2s at 190 eV, Na_{KLL} at 497 eV and in some samples F1s at 684-689 eV.

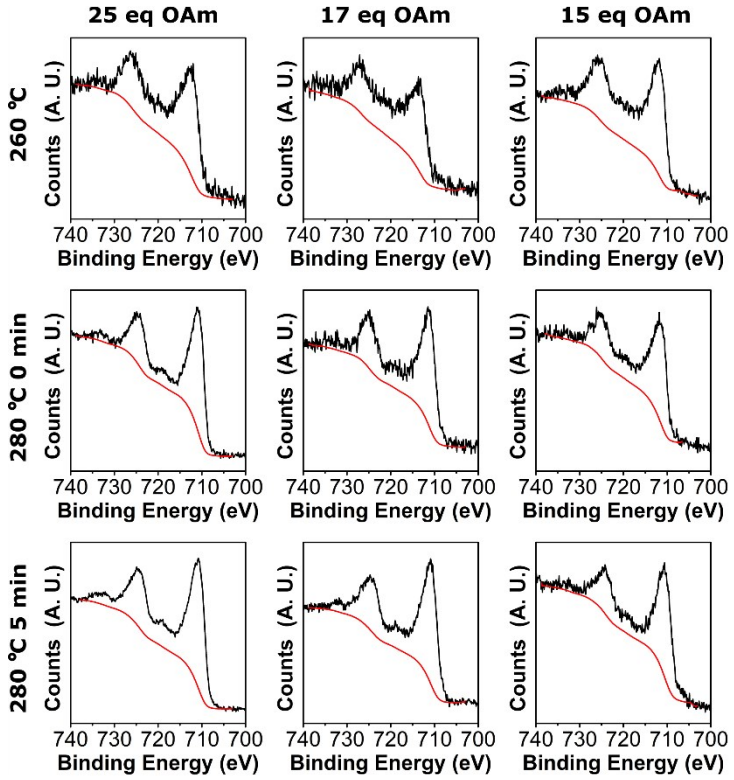

Fig. S17 XPS Fe2p spectra of IONP synthesized with 25 eq OAm, 17 eq OAm, and 15 eq OAm sampled at 260 °C, 280 °C 0 min and 5 min after reaching 280 °C.

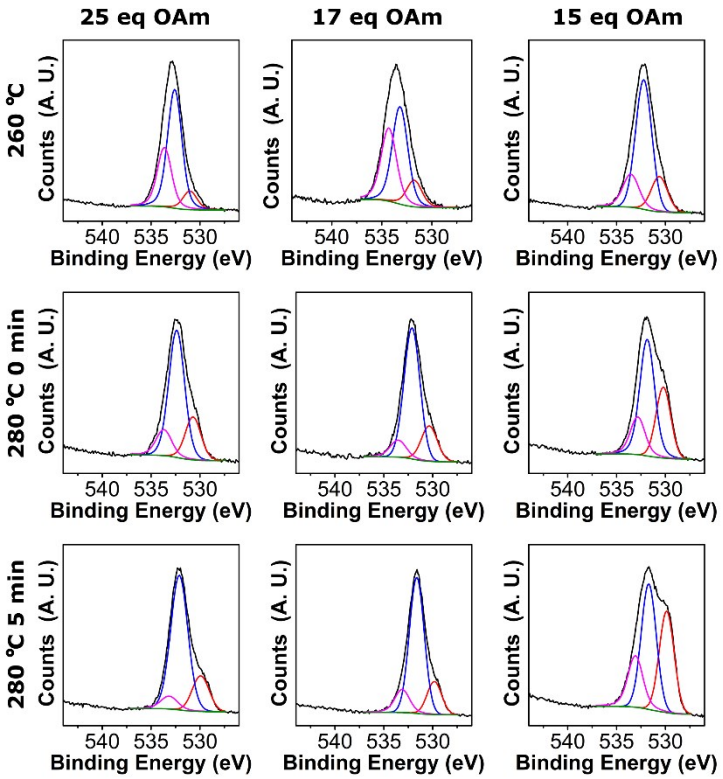

Fig. S18 XPS O1s spectra of IONP synthesized with 25 eq OAm, 17 eq OAm, and 15 eq OAm sampled at 260 °C, 280 °C 0 min and 5 min after reaching 280 °C.

Table S9 XPS peak positions of fits from the O1s and C1s regions, as well as the $Fe2p_{3/2}$ peak maximum position of IONP synthesized with 25 eq OAm, 17 eq OAm, and 15 eq OAm sampled at 260 °C, 280 °C 0 min and 5 min after reaching 280 °C. The O1s component can be assigned with 529-531.2 eV for O-Metal, and the O1s organic component with 532.5-533.5 eV for C-O, 531.5-532.0 eV for C=O, and ~535 eV for O-F_x.

OAm	Peaks	260 °C	280 °C 0 min	280 °C 5min	Assignment
15eq	O1s (O_{met})	530.3	530.3	530.5	O1s O-metal
	O1s	531.9, 533.2	532.0, 533.3	532.8, 534.0	O1s organic (C-O, C=O, C-OH)
	$Fe2p_{3/2}$	711.6	711.1	711.2	$Fe^{3+/2+}$
	$Fe:O_{met}$	0.75	0.51	0.35	Fe to metallic O Ratio
17eq	O1s (O_{met})	530.3	530.2	530.2	O1s O-metal
	O1s	531.7, 532.8	531.9, 533.3	532.0, 533.5	O1s organic (C-O, C=O, C-OH)
	$Fe2p_{3/2}$	712.0	711.1	711.3	$Fe^{3+/2+}$
	$Fe:O_{met}$	0.76	0.62	0.70	Fe to metallic O Ratio
25eq	O1s (O_{met})	530.2	530.2	530.1	O1s O-metal
	O1s	531.8 532.8	531.9 532.8	531.9 533.3	O1s organic (C-O, C=O, C-OH)
	$Fe2p_{3/2}$	711.6	710.8	711.0	$Fe^{3+/2+}$
	$Fe:O_{met}$	0.72	0.49	0.64	Fe to metallic O Ratio

Table S10 Fitting parameters for the O1s section for the particles made at 15 eq OAm at 260 °C, 280 °C at 0 min and 280 °C at 5 min. The binding energies were referenced against the position of the main component of the C1s peak set to 284.8 eV. The O1s component can be assigned with 529-531.2 eV for O-Metal, and the O1s organic component with 532.5-533.5 eV for C-O, 531.5-532.0 eV for C=O, and ~535 eV for O-F_x.

Sample	Peak	Peak BE (eV)	FWHM (eV)	Area (CPS. eV)
15 eq Oam 260 °C	O1s O_{met}	530.3	1.89	5366.11
	O1s organic	531.9	1.89	19317.37
	O1s organic	533.2	1.89	5467.2
15 eq Oam 280 °C 0 min	O1s O_{met}	530.3	1.89	4538.82
	O1s organic	532.0	1.89	13487.7
	O1s organic	533.3	1.89	2962.4
15 eq Oam 280 °C 5 min	O1s O_{met}	530.5	2.02	6691.79
	O1s organic	532.8	2.05	26033.73
	O1s organic	534.0	2.05	2692.16

Table S11 Fitting parameters for the O1s section for the particles made at 17 eq OAm at 260 °C, 280 °C at 0 min and 280 °C at 5 min. The O1s component can be assigned with 529-531.2 eV for O-Metal, and the O1s organic component with 532.5-533.5 eV for C-O, 531.5-532.0 eV for C=O, and ~535 eV for O-F_x.

Sample	Peak	Peak BE (eV)	FWHM (eV)	Area (CPS. eV)
17 eq Oam 260 °C	O1s O_{met}	530.3	1.83	2161.19
	O1s organic	531.7	1.83	7686.37
	O1s organic	532.8	1.83	6067.82
17 eq Oam 280 °C 0 min	O1s O_{met}	530.2	1.75	3031.17
	O1s organic	532.0	1.78	11061
	O1s organic	533.5	1.78	1604.47
17 eq Oam 280 °C 5 min	O1s O_{met}	530.2	1.75	4995.11
	O1s organic	532.0	1.78	20923.78
	O1s organic	533.5	1.78	3915.94

Table S12 Fitting parameters for the O1s section for the particles made at 25 eq OAm at 260 °C, 280 °C at 0 min and 280 °C at 5 min. The O1s component can be assigned with 529-531.2 eV for O-Metal, and the O1s organic component with 532.5-533.5 eV for C-O, 531.5-532.0 eV for C=O, and ~535 eV for O-F_x.

Sample	Peak	Peak BE (eV)	FWHM (eV)	Area (CPS. eV)
25 eq Oam 260 °C	O1s O_{met}	530.2	1.71	3282.21
	O1s organic	531.8	1.71	20348.76
	O1s organic	532.8	1.71	10560.83
25 eq Oam 280 °C 0 min	O1s O_{met}	530.1	1.78	8914.01
	O1s organic	531.9	1.79	15391.37
	O1s organic	533.3	1.79	5226.06
25 eq Oam 280 °C 5 min	O1s O_{met}	530.1	1.79	14059.18
	O1s organic	531.9	1.81	17657.87
	O1s organic	533.3	1.82	7972.58

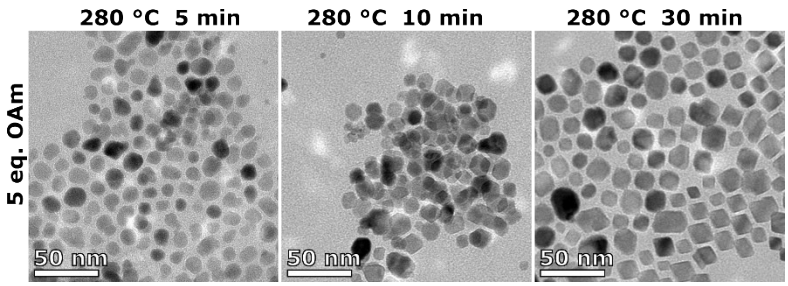

Fig. S19 TEM images of the nanoparticles in aliquots taken from the synthesis of the octahedra (5 eq OAm) at 5 min, 10 min and 30 min at 280 °C.