Supporting Information:

Tailoring the Magnetic Properties of $Fe_xCo_{(1-x)}$ Nanopowders prepared by Polyol Process

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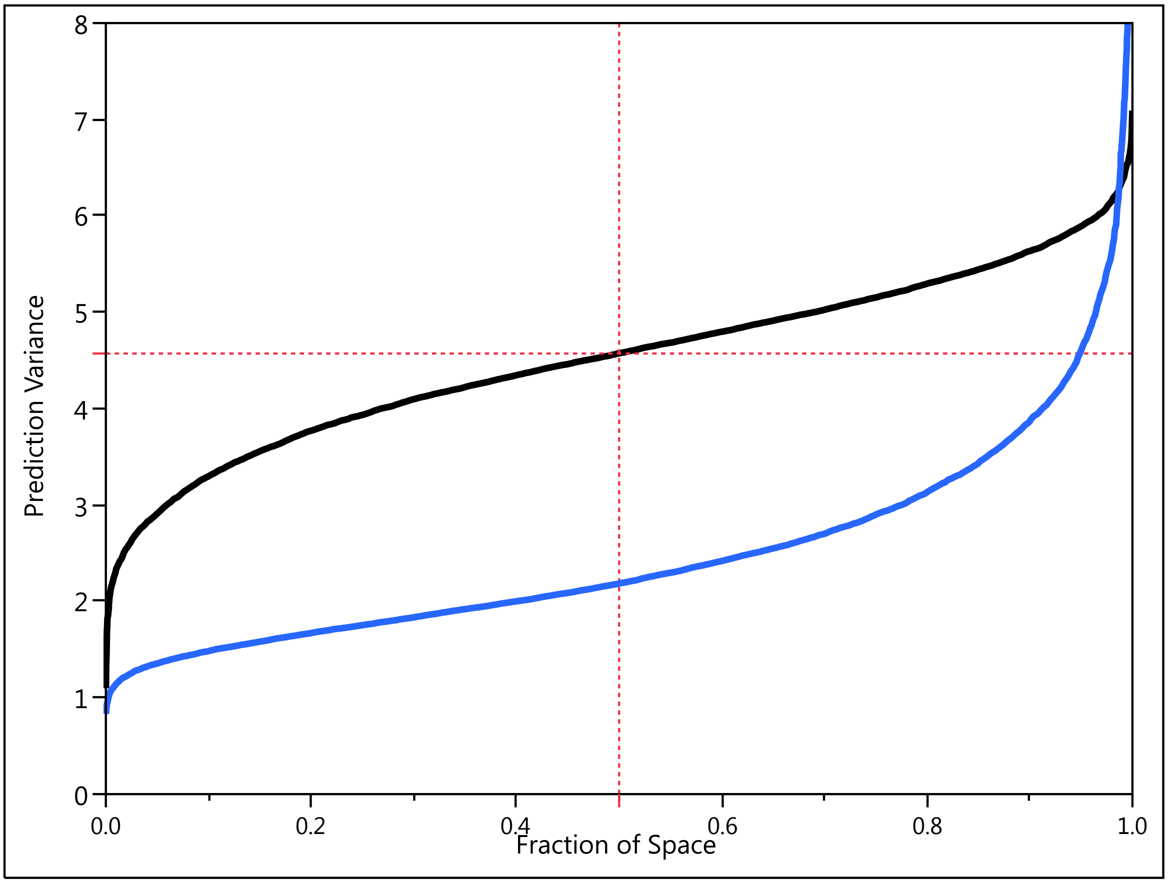

Figure S1: Overlay plot of I-optimal design prediction variance (blue, bottom) over D-optimal design (black, top) from original DOE. The I-optimal design, as used in this DoE, gives a lower prediction variance values over the entire design space (x-axis).

Table S1. Custom Design Experiment Table containing all validation experiments with all responses.

RUN ID	[OH] M	Rx time (mins)	[Ag] M	[Ag]/[Fe+Co] molar ratio	[Fe+Co] M	[OH]/[Fe+Co] molar ratio	Stir Rate (stir cycle/s)	[Fe]/[Co] molar ratio	% FeCo alloy (bcc) phase	% ferrite (cubic) phase	% Co (fcc)	% Ag (fcc) phase	% NaCl phase	morphology	Hc (kOe)	Ms (emu/g)	particle size (nm)	FeCo (110) crystallite size (nm)	atomic % of Co in Fe (EDS)	Fe/Co at. Composition (EDS)
1	1.5	32	6E-05	6E-04	0.10	15	Hi	2.5	18	77	5	0	0	spheroid	0.26	111	160	36	37	1.7
2	1.5	32	1E-05	1E-04	0.09	17	Lo	4.5	23	77	0	0	0	spheroid	0.24	92	184	23	24	3.1
3	3.0	32	6E-05	4E-04	0.15	20	Hi	2.5	58	42	0	0	0	chain	0.23	160	170	35	-	-
4	3.0	24	1E-02	1E-01	0.09	32	Med	1.7	60	0	0	40	0	cuboid	0.23	145	185	20	-	-
5	3.0	24	6E-05	4E-04	0.15	20	Med	2.1	74	16	10	0	0	chain	0.1	186	201	28	47	1.1
6	3.0	24	1E-03	2E-02	0.05	60	Med	2.6	80	0	0	20	0	chain	0.09	208	250	46	-	-
7	1.5	32	2E-04	2E-03	0.10	15	Lo	0.5	84	0	16	0	0	cuboid	0.12	181	148	45	73	0.4
8	3.0	12	0E+00	0E+00	0.09	32	Med	1.9	93	0	0	0	7	chain	0.13	166	164	42	48	1.1
9	1.5	24	2E-04	4E-03	0.05	30	Lo	2.1	96	4	0	0	0	chain	0.19	188	131	39	36	1.8
10	3.0	32	5E-05	1E-03	0.05	59	Lo	0.5	96	0	4	0	0	chain	0.25	177	117	28	72	0.4
11	3.0	16	1E-05	2E-04	0.05	60	Hi	2.1	100	0	0	0	0	chain	0.21	191	101	38	32	2.1
12	3.0	32	1E-05	2E-04	0.05	58	Hi	0.9	100	0	0	0	0	chain	0.33	169	76	32	58	0.7
13	1.5	32	1E-05	2E-04	0.05	29	Med	0.9	100	0	0	0	0	cuboid	0.31	176	76	31	58	0.7
14	3.0	32	1E-05	7E-05	0.15	20	Med	0.9	100	0	0	0	0	chain (and ellipsoid)	0.16	196	136	34	54	0.9
15	3.0	16	1E-05	2E-04	0.05	60	Lo	0.5	100	0	0	0	0	chain	0.26	170	108	28	69	0.5
16	3.0	16	1E-05	2E-04	0.05	63	Lo	1.8	100	0	0	0	0	chain	0.16	198	119	38	35	1.9
17	3.0	32	1E-05	2E-04	0.05	63	Lo	1.8	100	0	0	0	0	chain	0.18	195	125	38	41	1.5
18	3.0	16	1E-05	1E-04	0.10	30	Lo	0.5	100	0	0	0	0	cuboid	0.15	178	113	31	72	0.4
19	1.5	32	6E-05	1E-03	0.05	30	Hi	2.6	100	0	0	0	0	chain	0.14	202	108	34	36	1.7
20	3.0	24	6E-05	4E-04	0.15	20	Hi	0.9	100	0	0	0	0	chain (and ellipsoid)	0.15	195	120	34	55	0.8
21	3.0	32	2E-04	4E-03	0.05	63	Hi	1.8	100	0	0	0	0	chain	0.2	185	126	38	47	1.1
22	3.0	16	2E-04	4E-03	0.05	63	Med	1.8	100	0	0	0	0	chain	0.16	196	141	38	33	2.0
23	3.0	32	2E-04	1E-03	0.15	20	Hi	2.5	100	0	0	0	0	spheroid	0.11	199	82	35	41	1.5
24	3.0	16	2E-04	2E-03	0.10	30	Med	0.5	100	0	0	0	0	cuboid	0.12	186	141	28	69	0.4
25	3.0	32	2E-04	1E-03	0.15	19	Med	1.3	100	0	0	0	0	chain	0.23	194	92	26	52	0.9
26	1.5	16	2E-04	4E-03	0.05	30	Lo	0.5	100	0	0	0	0	cuboid	0.13	185	161	23	67	0.5
27	3.0	16	2E-04	4E-03	0.05	60	Lo	2.1	100	0	0	0	0	chain	0.13	215	176	51	35	1.9
28	1.5	24	2E-04	4E-03	0.05	30	Lo	2.1	100	0	0	0	0	chain	0.18	209	151	44	38	1.6
29	3.0	32	2E-04	4E-03	0.05	60	Lo	0.5	100	0	0	0	0	cuboid	0.15	175	149	28	70	0.4
30	3.0	32	6E-05	1E-03	0.05	63	Hi	1.8	100	0	0	0	0	chain	0.25	185	108	44	-	-
31	3.0	24	5E-05	5E-04	0.09	32	Hi	1.9	100	0	0	0	0	chain	0.23	209	135	41	40	1.5
32	3.0	24	2E-05	2E-04	0.09	32	Hi	1.7	100	0	0	0	0	chain	0.37	174	80	29	-	-
33	3.0	24	0E+00	0E+00	0.09	32	Med	1.7	100	0	0	0	0	chain	0.13	205	180	37	42	1.4
34	3.0	24	0E+00	0E+00	0.05	63	Med	1.8	100	0	0	0	0	chain	0.25	153	149	33	54	0.9
35	3.0	24	0E+00	0E+00	0.14	21	Med	1.8	100	0	0	0	0	chain	0.13	204	173	40	41	1.4
36	3.0	16	2E-04	4E-03	0.05	60	Lo	2.6	100	0	0	0	0	chain	0.26	197	135	45	29	2.4
37	3.0	16	2E-04	4E-03	0.05	60	Lo	2.1	100	0	0	0	0	chain	0.23	209	152	40	33	2.1
38	3.0	16	2E-04	4E-03	0.05	60	Lo	2.1	100	0	0	0	0	chain	0.24	200	144	37	33	2.0
39	3.0	24	2E-04	4E-03	0.05	60	Lo	0.5	100	0	0	0	0	cuboid	0.4	173	71	29	71	0.4

40	1.5	*16*	*2E-04*	*4E-03*	*0.05*	*30*	*Lo*	*0.5*	100	0	0	0	0	cuboid	0.22	183	125	27	-	-
41	3.0	*16*	*1E-06*	*2E-05*	*0.05*	*60*	*Hi*	*2.1*	100	0	0	0	0	chain	0.18	208	135	43	30	2.3
42	3.0	*32*	*1E-06*	*2E-05*	*0.05*	*58*	*Hi*	*0.9*	100	0	0	0	0	chain	0.27	192	117	32	57	0.8
43	1.5	*32*	*1E-06*	*2E-05*	*0.05*	*29*	*Hi*	*0.9*	100	0	0	0	0	chain	0.23	197	116	29	50	1.0
44	3.0	*16*	*1E-06*	*2E-05*	*0.05*	*60*	*Lo*	*0.5*	100	0	0	0	0	chain	0.27	177	97	30	52	0.9
45	3.0	*16*	*1E-06*	*2E-05*	*0.05*	*63*	*Lo*	*1.8*	100	0	0	0	0	chain	0.22	200	150	42	37	1.7
46	3.0	*24*	*1E-04*	*1E-03*	*0.09*	*33*	*Med*	*2.0*	100	0	0	0	0	chain	0.2	215	130	45	40	1.5
47	3.0	*24*	*0E+00*	*0E+00*	*0.09*	*33*	*Med*	*2.0*	100	0	0	0	0	chain	0.13	209	172	39	43	1.3
48	3.0	*24*	*0E+00*	*0E+00*	*0.09*	*33*	*Med*	*2.0*	100	0	0	0	0	chain	0.15	148	174	35	-	-
49	3.0	*24*	*0E+00*	*0E+00*	*0.09*	*33*	*Med*	*2.0*	100	0	0	0	0	chain	0.12	202	170	31	41	1.4
50	3.0	*24*	*5E-05*	*1E-03*	*0.05*	*56*	*Lo*	*0.5*	100	0	0	0	0	chain	0.23	188	114	29	72	0.4
51	3.0	*16*	*5E-05*	*1E-03*	*0.05*	*58*	*Lo*	*0.5*	100	0	0	0	0	chain	0.19	176	106	29	-	-
52	0.05	*16*	*1E-05*	*1E-04*	*0.10*	*1*	*Lo*	*1.0*	-	-	-	-	-	no product	-	-	-	-	-	-
53	0.05	*16*	*1E-05*	*9E-05*	*0.11*	*0*	*Lo*	*1.2*	-	-	-	-	-	no product	-	-	-	-	-	-
54	0.05	*24*	*1E-05*	*7E-05*	*0.15*	*0*	*Lo*	*1.1*	-	-	-	-	-	no product	-	-	-	-	-	-
55	0.05	*32*	*1E-05*	*7E-05*	*0.15*	*0*	*Lo*	*2.8*	-	-	-	-	-	no product	-	-	-	-	-	-
56	0.05	*16*	*1E-05*	*2E-04*	*0.05*	*1*	*Med*	*4.0*	-	-	-	-	-	no product	-	-	-	-	-	-
57	0.05	*24*	*1E-05*	*2E-04*	*0.05*	*1*	*Hi*	*0.7*	-	-	-	-	-	no product	-	-	-	-	-	-
58	0.05	*24*	*1E-05*	*7E-05*	*0.15*	*0*	*Hi*	*0.9*	-	-	-	-	-	no product	-	-	-	-	-	-
59	0.05	*16*	*1E-04*	*2E-03*	*0.05*	*1*	*Med*	*1.5*	-	-	-	-	-	no product	-	-	-	-	-	-
60	0.05	*24*	*1E-04*	*7E-04*	*0.15*	*0*	*Hi*	*2.0*	-	-	-	-	-	no product	-	-	-	-	-	-
61	0.05	*16*	*2E-04*	*1E-03*	*0.15*	*0*	*Lo*	*2.0*	-	-	-	-	-	no product	-	-	-	-	-	-
62	0.05	*24*	*2E-04*	*2E-03*	*0.10*	*1*	*Med*	*1.0*	-	-	-	-	-	no product	-	-	-	-	-	-
63	0.05	*16*	*2E-04*	*1E-03*	*0.15*	*0*	*Hi*	*2.0*	-	-	-	-	-	no product	-	-	-	-	-	-
64	0.05	*16*	*2E-04*	*1E-03*	*0.15*	*0*	*Hi*	*0.5*	-	-	-	-	-	no product	-	-	-	-	-	-

Equipment

The as-synthesized nanopowders were analyzed by XRD using an X'Pert Pro diffractometer (Panalytical) to identify all phases present as well as measure mean crystallite size (Scherrer) of the (110) in all $Fe_xCo_{(1-x)}$ phases. The XRD analysis used a Cu $K_{\alpha 1}$ = 1.54 Å anode, Bragg-Brentano configuration, oriented single crystal Si wafer as sample holder, 0.5 degree slit with a 1° fixed divergence slit and a 0.5 ° anti-scatter slit, 10 mm mask and a Ni filter to remove Cu K_β. Scanning electron microscopy (SEM) was performed to investigate morphology and obtain mean particle diameters using a Hitachi, SU-70 FE-SEM. Transmission electron microscopy (TEM) was used to probe microstructure by brightfield imaging and confirm phase presence by selected area electron diffraction (SAED) using a Zeiss Libra at 120 keV. Vibrating sample magnetometry (VSM) was performed to measure saturation magnetization (emu/g) and coercivity (Oe) of each as-synthesized nanopowder. Each nanopowder was massed in a polyethylene capsule and centered onto a non-magnetic (≤1 e^{-6} emu) brass sample holder and was oscillated in a sweeping field from -3 to 3 T using a Quantum Design Versalab VSM.

For high [OH]:[Metal] ratios above 30 the $Fe_xCo_{(1-x)}$ alloy formation is expected throughout the entire Fe/Co composition range. In contrast, for lower OH/Metal ratios, multi-phasic nanopowders were synthesized. Cobalt ferrite and Co (fcc) were formed at higher Fe/Co molar ratios (< 1.8) and $Fe_xCo_{(1-x)}$ alloy containing Co (fcc) at lower Fe/Co (< 1)ratios. Increasing the [OH]:[Metal] > 60 becomes problematic for vertical stirring where concentrations of [OH] ≤ 7 M were appropriate.

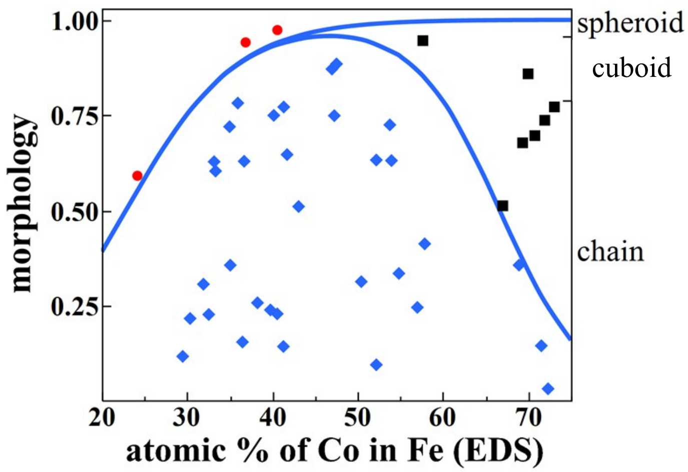

Figure S2. Logistic fit (Prob>ChiSq <0.0001) of morphology versus atomic % of Co in Fe by EDS analysis for all nanopowders synthesized.

Table S2. Correlation Probabilities and their sources for modelling % FeCo phase as a response in nanopowders synthesized using significant parameters as shown. These parameters were used to generate the RSM in Figure S3.

Source	LogWorth	PValue
[OH]/[Fe+Co]	30.012	0.00000
[OH]/[Fe+Co]*[OH]/[Fe+Co]	24.958	0.00000
[Fe]:[Co] molar ratio*Rx time (mins)	1.790	0.01622
[Fe]:[Co] molar ratio*[Fe]:[Co] molar ratio	1.549	0.02822
[Fe]:[Co] molar ratio	1.125	0.07498

Table S3. Correlation Probabilities and their sources for modelling mean crystallite size (nm) as a response in FeCo-based nanopowders synthesized using significant parameters as shown. These parameters were used to generate the RSM in Figure 8.

Source	LogWorth	PValue
[Fe]:[Co] molar ratio	4.705	0.00002
[Fe]:[Co] molar ratio*[Ag]/[Fe+Co] molar ratio	1.975	0.01060
[Fe]:[Co] molar ratio*[Fe]:[Co] molar ratio*[Fe]:[Co] molar ratio	1.176	0.06666

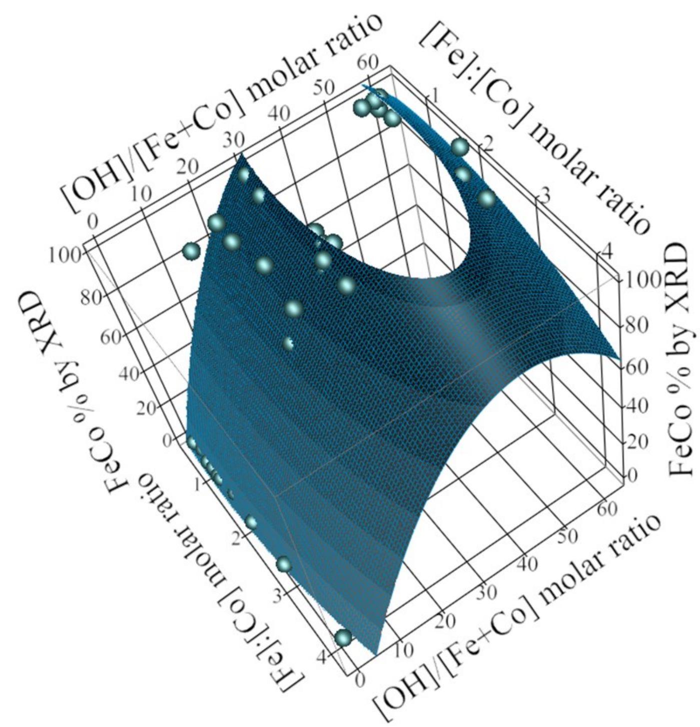

Figure S3. RSM of FeCo % of total phase by XRD by synthesis parameters of [OH]/[Fe+Co] and [Fe]/[Co] molar ratios.

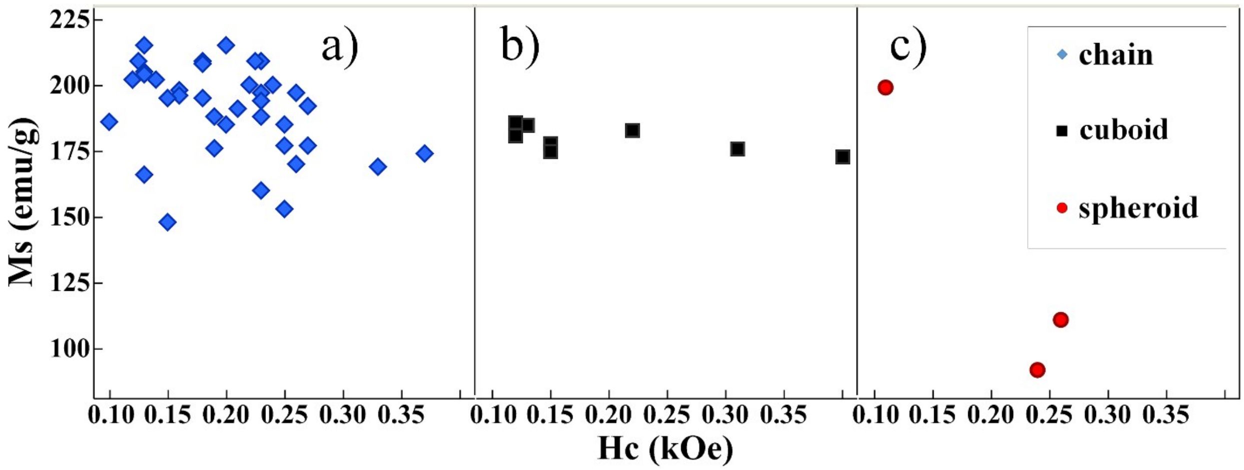

Figure S4. Plots of measured M_s (emu/g) and H_c (Oe) for each nanopowder containing either a) chain-, b) cuboid-, or c) spheroid-based morphologies.

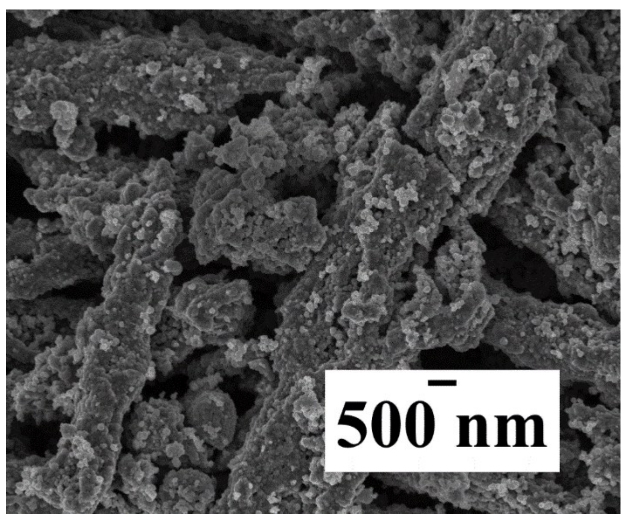

Figure S5. SEM indicating spheroids on the surface of large agglomerates. The nanopowder sample contained FeCo by XRD and possessed an M_s = 199 (emu/g). (see RUN ID 23 in TABLE S1)

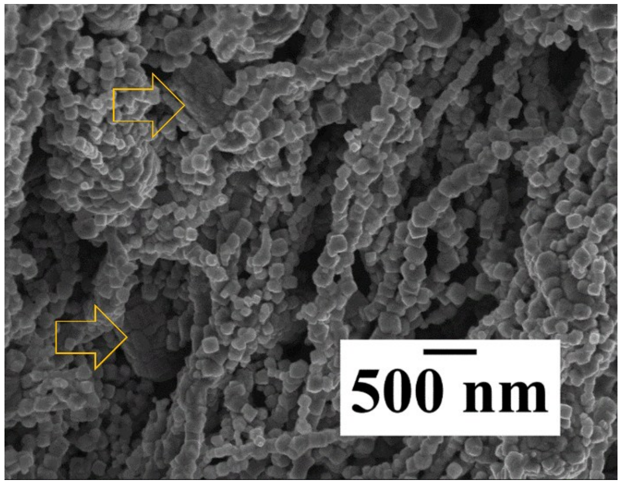

Figure S6. SEM showing mixed morphology of chain and ellipsoid (orange arrows) combinations of FeCo by XRD. (see RUN ID 14 in TABLE S1).

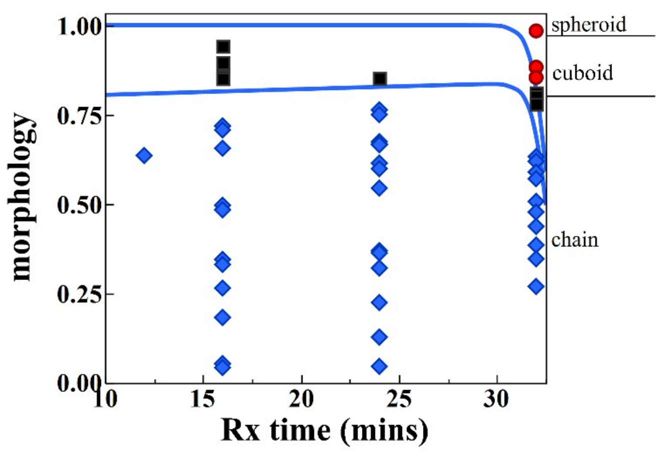

Figure S7. Logistic fit (Prob>ChiSq<0.00340) of morphology with total reaction time (mins).

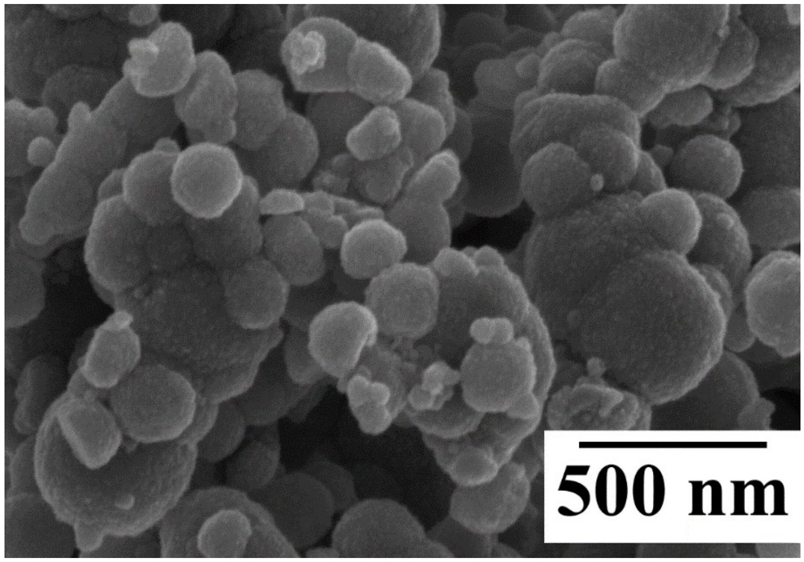

Figure S8. SEM showing ferritic spheroids synthesized using an [Fe]/[Co] molar ratio = 4.5 as a validation experiment. (see RUN ID 2 in TABLE S1)

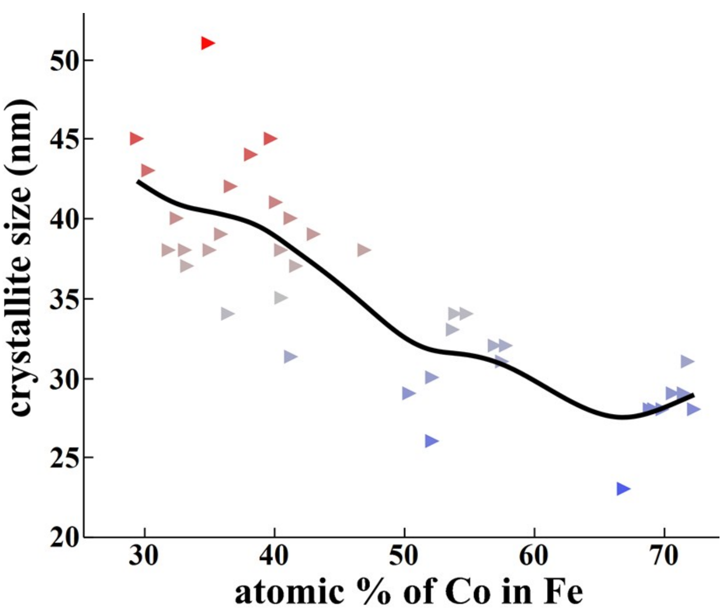

Figure S9. The mean crystallite size of the (110) in FeCo (bcc) of as-synthesized nanopowders with respect to their atomic % of Co in Fe by EDS analysis.

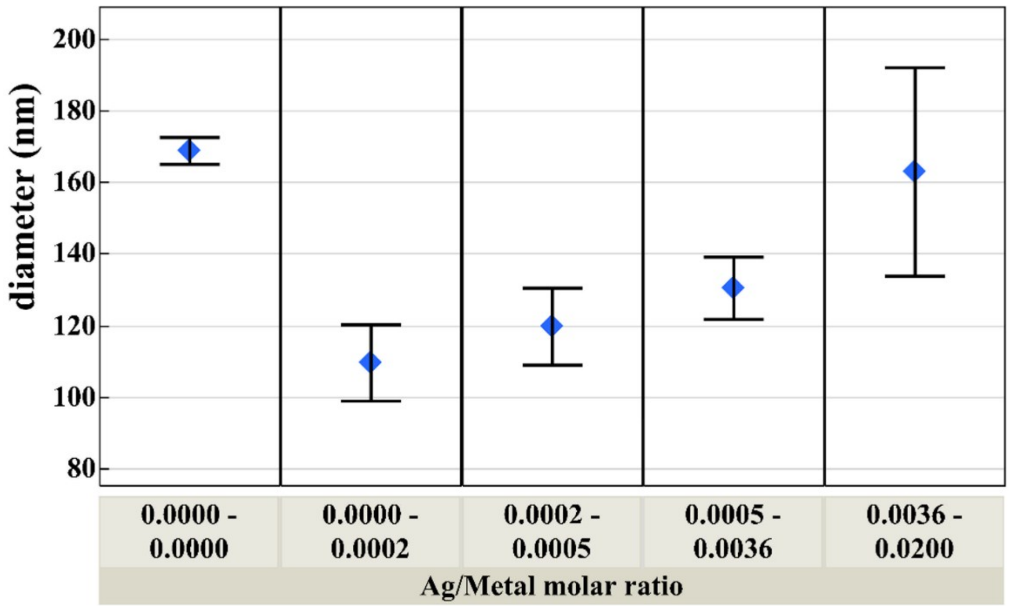

Figure S10. Mean particle diameters were measured for nanopowders synthesized by using various ranges of [Ag]/[Fe+Co] molar ratios. The lowest mean particle diameter is indicated for [Ag]/[Fe+Co] molar ratio ~1E^{-4}. Std error bars are shown.

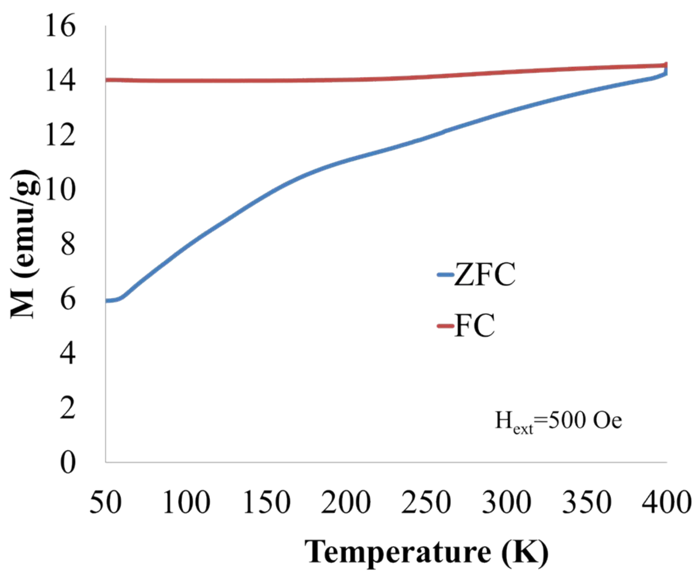

Figure S11. ZFC and FC curves acquired of a 100 % FeCo nanopowder with mean diameter ~ 71 nm (run ID 39, Table S1).