

Hard-soft core shell architecture formation from cubic cobalt ferrite nanoparticles

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Table S1. Synthesis condition for the samples.

Sample	n Oleate (mmol) ^a	Seeds (mg)	1-pentanol (mL)	Ethanol (mL)	Toluene (mL)	Distilled water (mL)	Temperature (°C)	Reaction time
Co	2.75	-	10	-	10	5	220	10
Co@Mn	1	20 (Co)	10	-	10	5	220	10

^aReferred to M^{II} - Fe^{III} oleates.

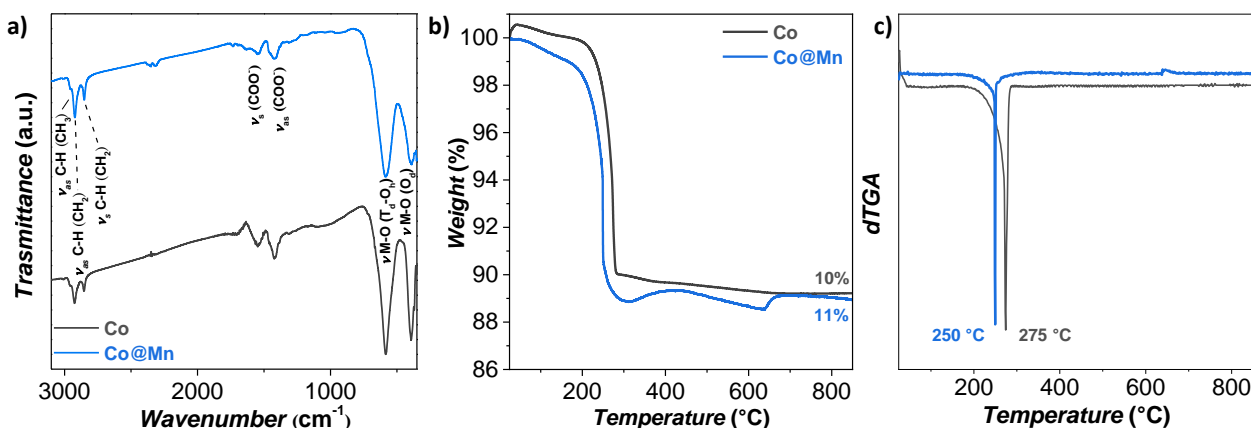


Figure S1. FTIR spectra (a), TGA curves (b) and corresponding derivatives (c) of the Co and Co@Mn samples.

FTIR spectra show the main vibrational modes related to the oleate molecule, *i.e.*, the COO^- vibrational modes ($\nu_{as} COO^-$, $\nu_s COO^-$ at 1550 and 1420 cm^{-1} , respectively) and the ones related to the hydrocarbon chain ($\nu C=C$, $\nu_{as} C-H(CH_3)$, $\nu_{as} C-H(CH_2)$, $\nu_s C-H(CH_2)$, $\nu_s C-H(CH_3)$, at 3007, 2956, 2924, and 2853 cm^{-1} , respectively). The bands at about 584 cm^{-1} and 394 cm^{-1} are due to the Me-O stretching mode of both the tetrahedral and octahedral sites, or the only octahedral sites of the spinel structure, respectively.^{1,2}

TGA curves display a weight loss from about 200 $^{\circ}C$ till 300 $^{\circ}C$, correspondent to the oleate decomposition.^{5,6} The percentage, similar for the two samples, corresponds to a monolayer of capping molecule on the nanoparticles' surface.

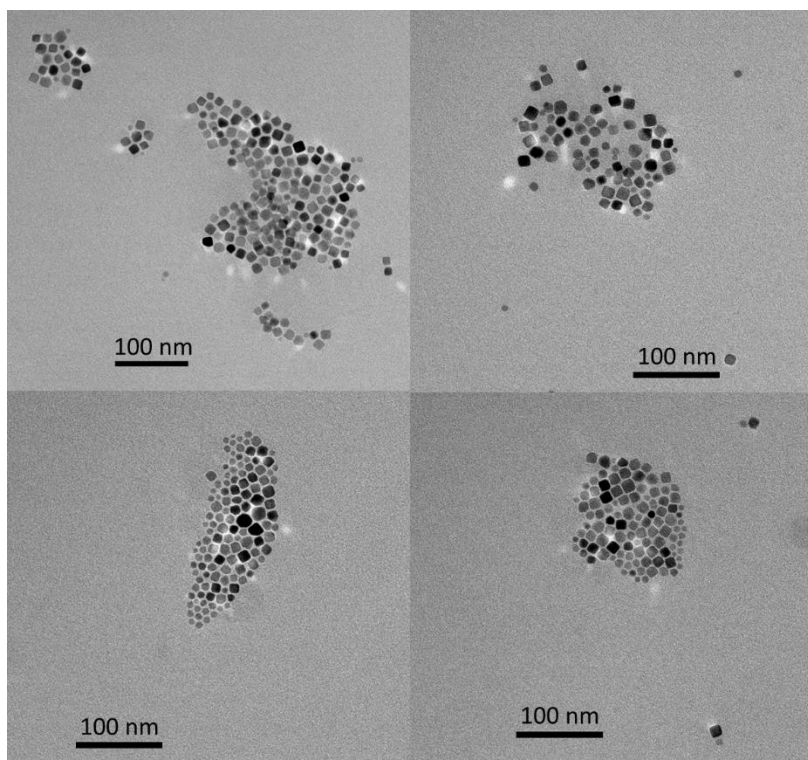


Figure S2. TEM micrographs of the Co sample.

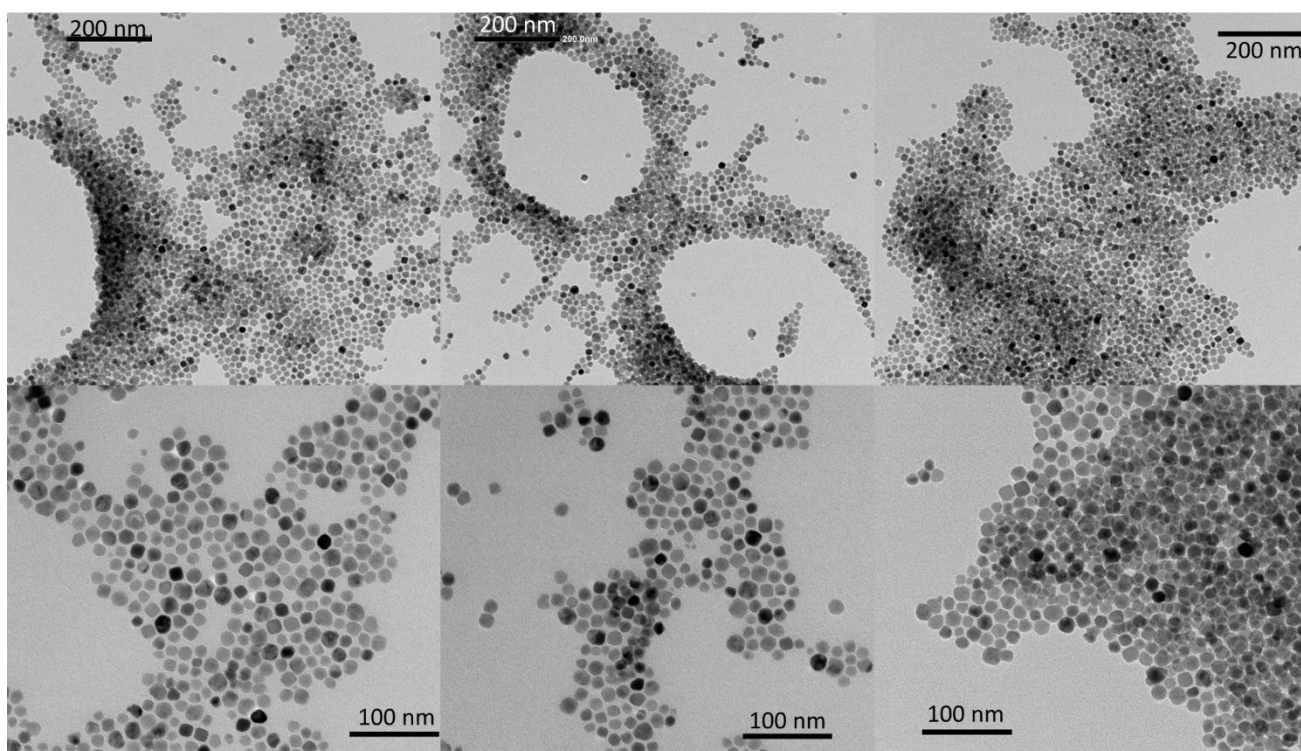


Figure S3. TEM micrographs of the Co@Mn sample.

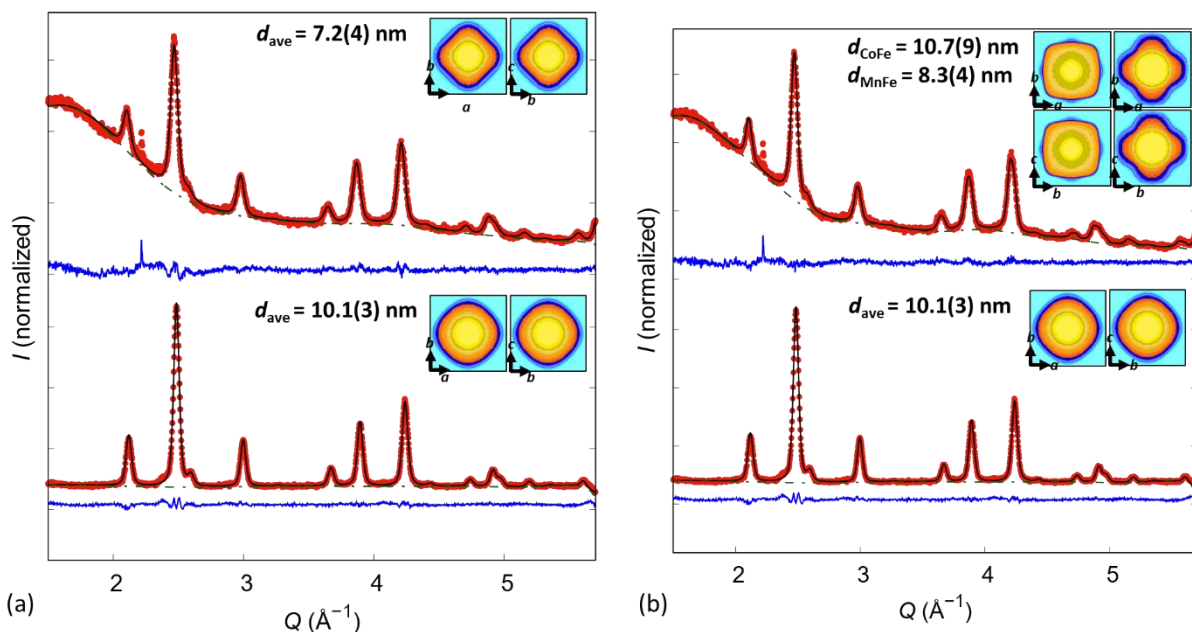


Figure S4. Rietveld refinement by FullProf software of the XRD patterns of Co (pattern at the bottom) and Co@Mn (pattern in the upper part) samples by using (a) one spinel ferrite phase (CoFe_2O_4) for both samples and (b) two spinel ferrite phases (CoFe_2O_4 , MnFe_2O_4).

Table S2. Refined structural parameters obtained by Rietveld refinement of the XRD patterns of Co and Co@Mn samples by using one spinel ferrite phase (CoFe_2O_4) for both samples.

parameter	MA15105	MA15146
	CoFe_2O_4	CoFe_2O_4
a (Å)	8.3914(2)	8.4493(5)
u (x, y, z)	0.2558(1)	0.2563(2)
profile function	Thompson–Cox–Hastings pseudo-Voigt	
BOV (\AA^2)	1.30(2)	0.07(3)
G (0.01°)	0.217(2)	0.361(6)
Zero (0.01°)	0.065(1)	0.195(3)
Spherical harmonics	Laue class – m3m	
K_{00}	5.85(7)	8.8(2)
K_{41}	-0.71(8)	-1.9(1)
K_{61}	-0.04(1)	0.4(1)
K_{62}	0.00	0.00
K_{81}	-0.01(1)	0.00
Background	Chebyshev polynomial	
n	11	17
R_B (%)	2.80	3.18
R_f (%)	2.57	2.16
R_p (%)	3.61	2.76

$R_{\text{exp}} (\%)$	3.22	1.98
χ^2	1.26	1.94

Table S3. Refined structural parameters obtained by Rietveld refinement of the XRD patterns of Co and Co@Mn samples by using two spinel ferrite phases (CoFe_2O_4 , MnFe_2O_4) for the Co@Mn sample.

parameter	MA15105	MA15146	
	CoFe ₂ O ₄	CoFe ₂ O ₄	MnFe ₂ O ₄
a (Å)	8.3914(2)	8.4030(9)	8.4684(7)
<i>u</i> (<i>x</i> , <i>y</i> , <i>z</i>)	0.2558(1)	0.2561(6)	0.2566(4)
profile function	Thompson–Cox–Hastings pseudo-Voigt		
BOV (Å²)	1.30(2)	-	-
G (0.01°)	0.217(2)	0.318(8)	0.080(5)
Zero (0.01°)	0.065(1)	0.145(3)	
Spherical harmonics	Laue class – m3m		
K ₀₀	5.85(7)	3.4(4)	11.0(2)
K ₄₁	-0.71(8)	-1.8(3)	1.0(2)
K ₆₁	-0.04(1)	0.4(2)	-0.3(1)
K ₆₂	0.00	0.00	0.00
K ₈₁	-0.01(1)	0.7(1)	-1.0(1)
Background	Chebyshev polynomial		
n	11	22	
R _B (%)	2.80	2.99	2.53
R _f (%)	2.57	2.53	2.14
R _p (%)	3.61	2.25	
R _{exp} (%)	3.22	1.98	
χ²	1.26	1.29	

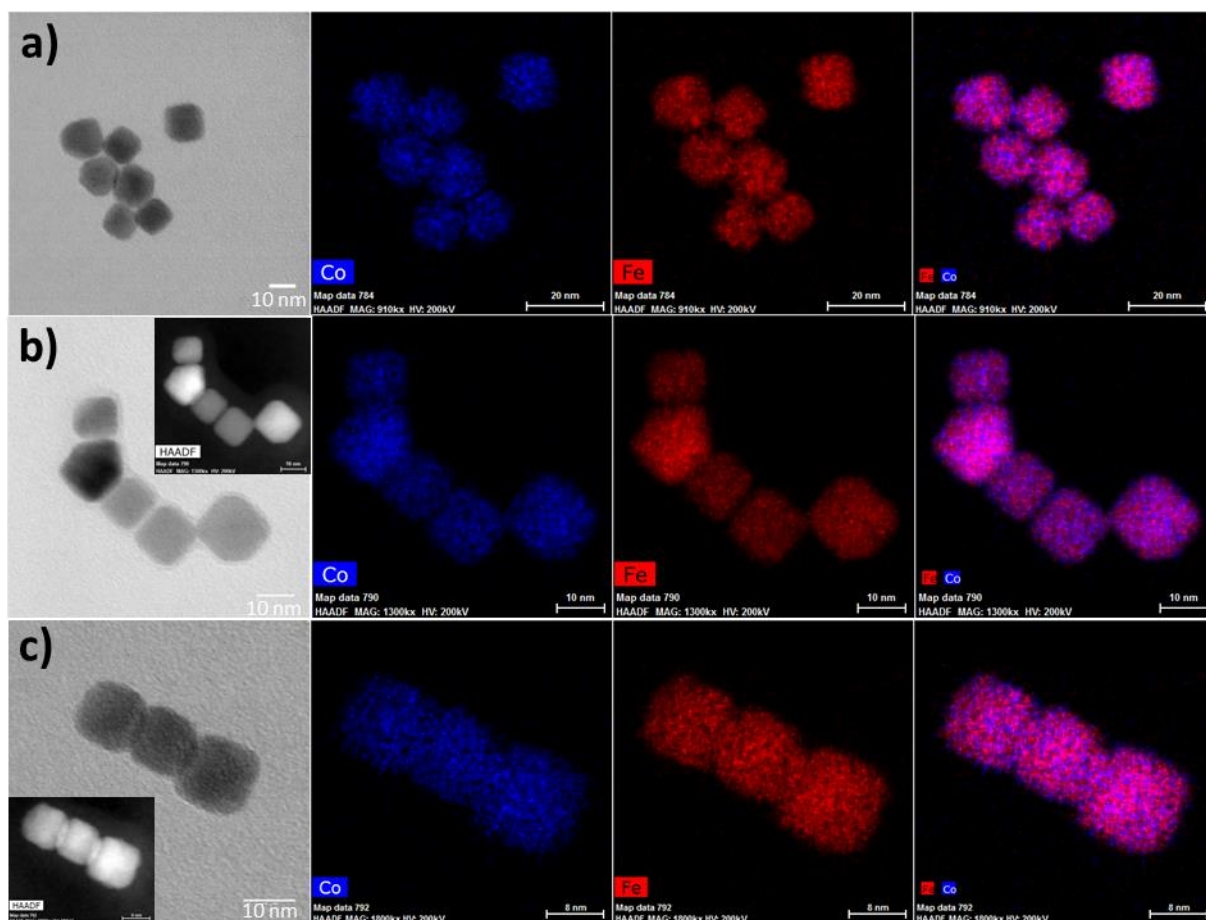


Figure S5. STEM-EDX chemical mapping (a,b,c) for the sample Co.

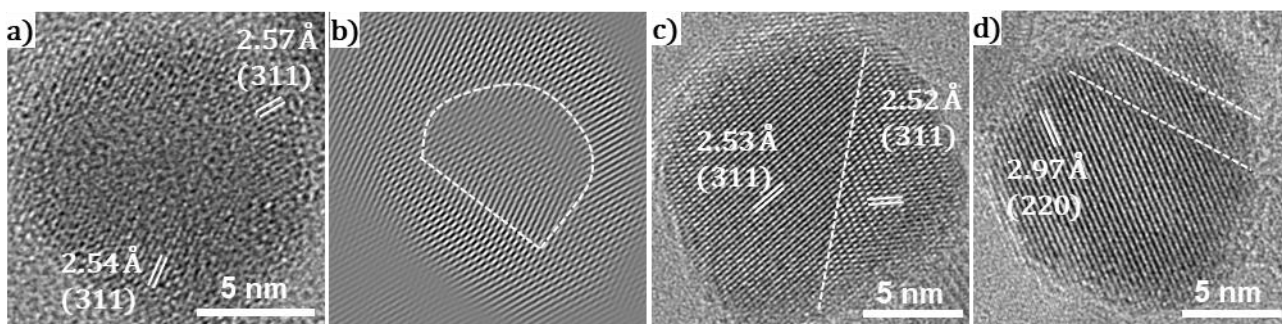


Figure S6. HRTEM images (a, c, d) of the sample Co@Mn revealing structural defects; b) represents the masked inverted FFT image of a).

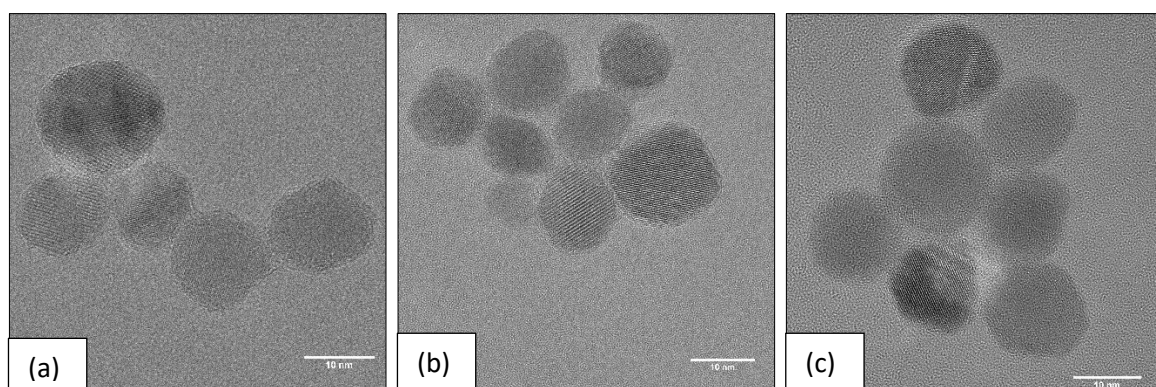


Figure S7. HRTEM micrographs (a, b, c) of the sample Co@Mn revealing structural defects.