A Study on the Synthesis of $Ni_{50}Co_{50}$ Alloy Nanostructures with Tuned Morphology through Metal-organic Chemical Routes

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Electronic Supplementary Information (ESI)

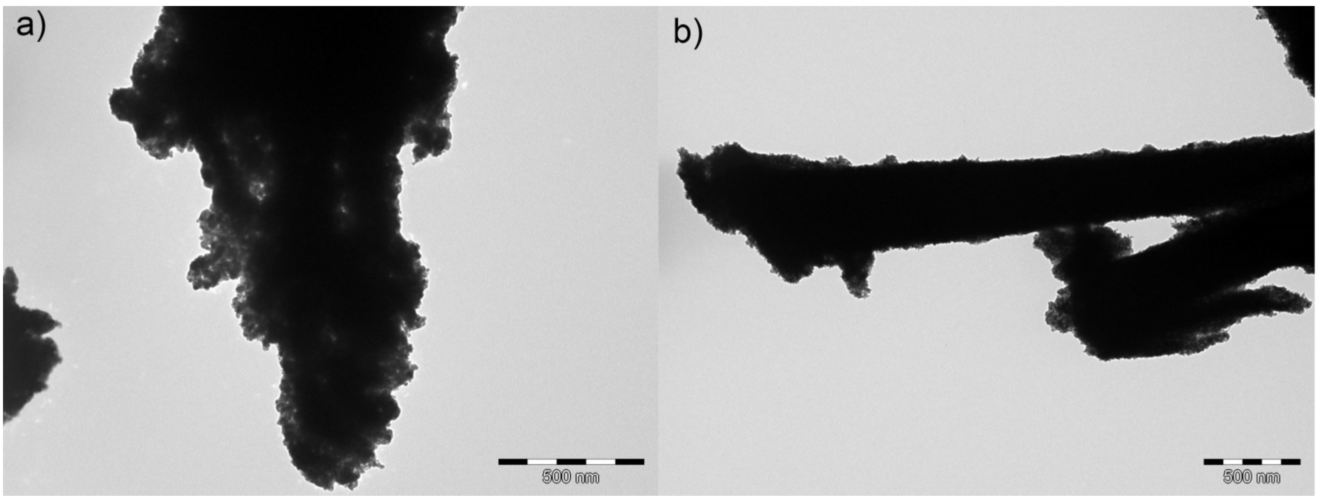


Fig. S-1 TEM images for samples S1 (a) and S2 (b)

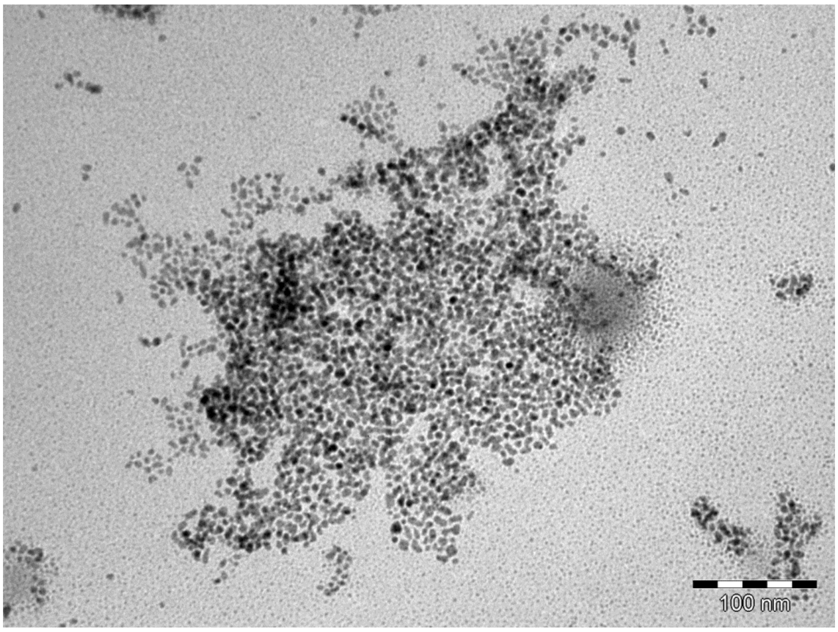


Fig. S-2 TEM image for the sample S4

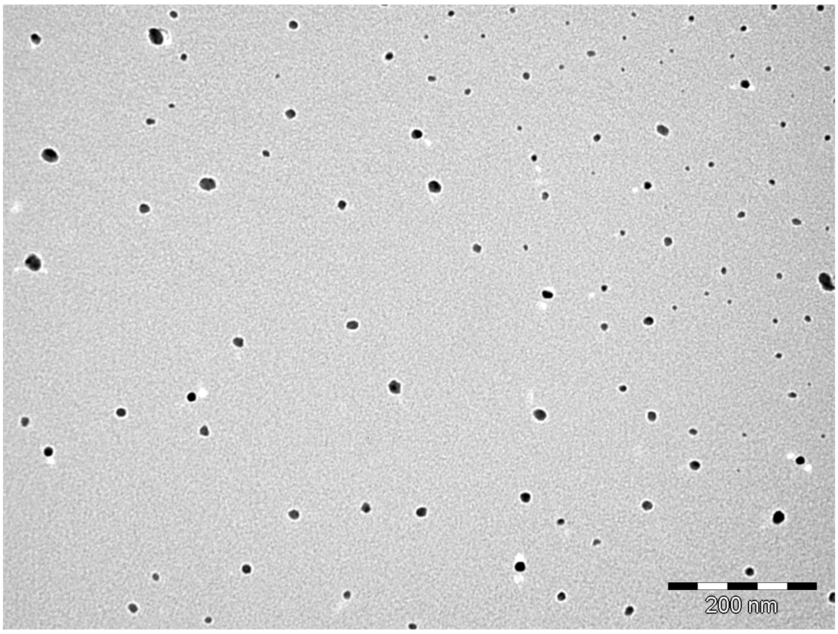


Fig. S-3 TEM image for sample S5

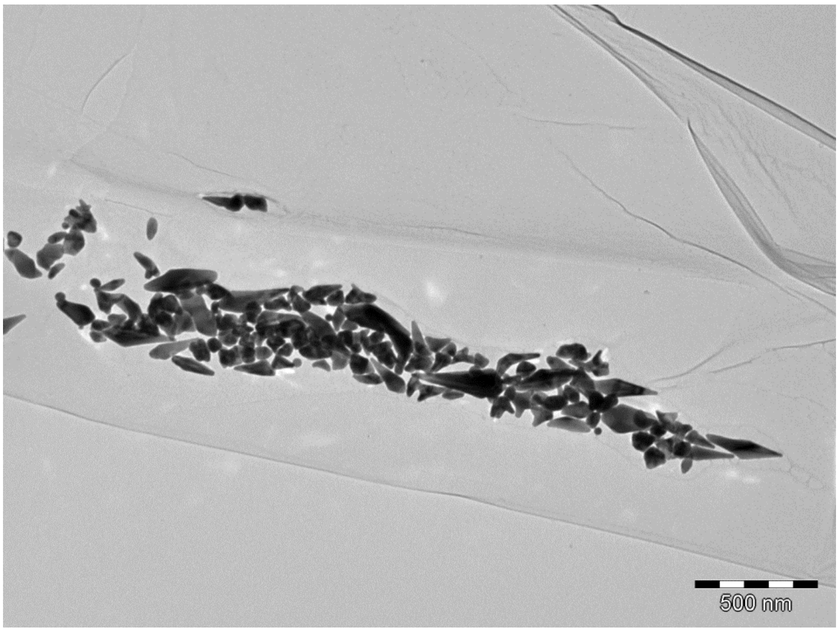


Fig. S-4 TEM image for sample S6

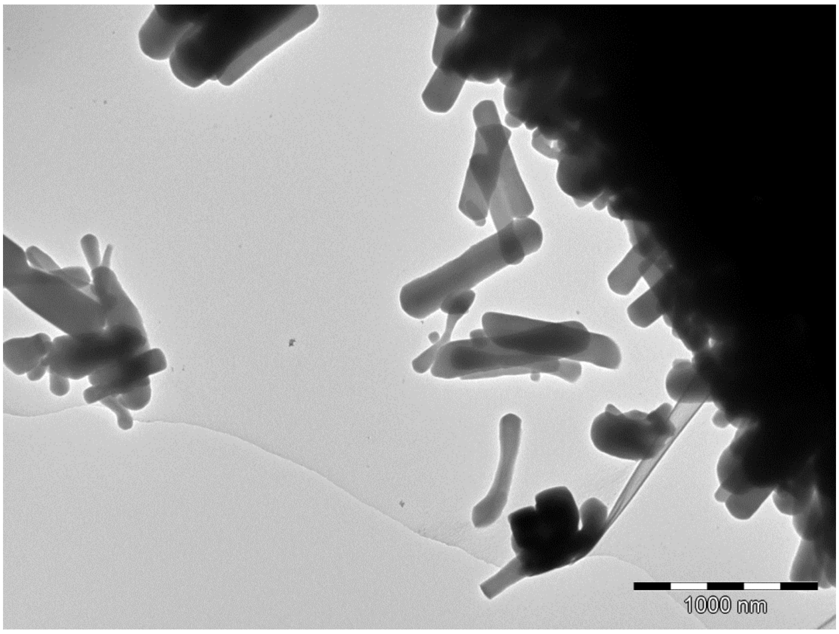


Fig. S-5 TEM image for sample S7

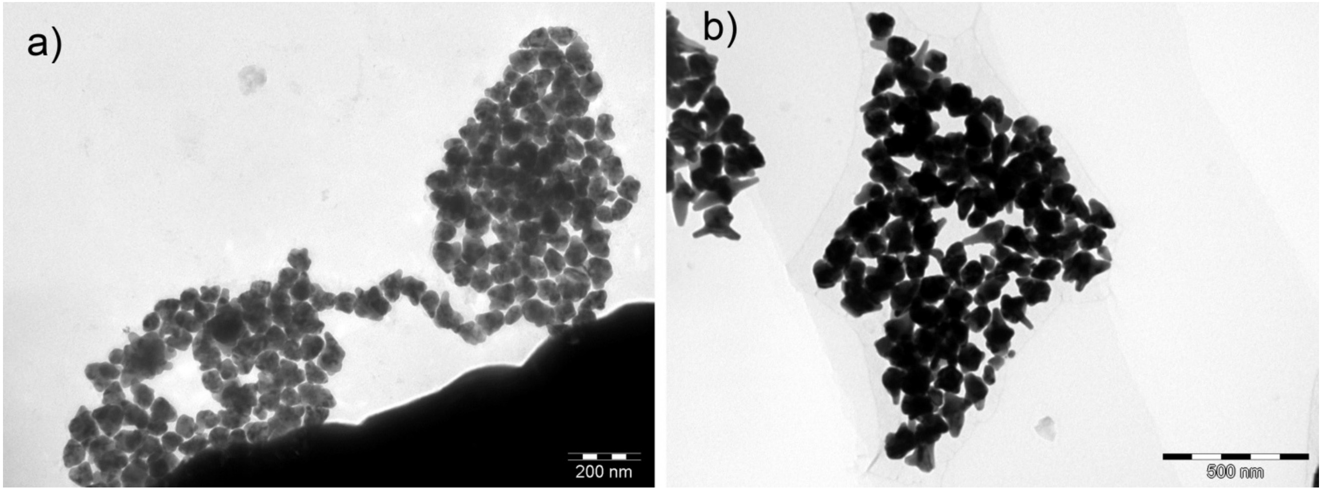


Fig. S-6 TEM images for samples S11 (image a) and S10 (image b)

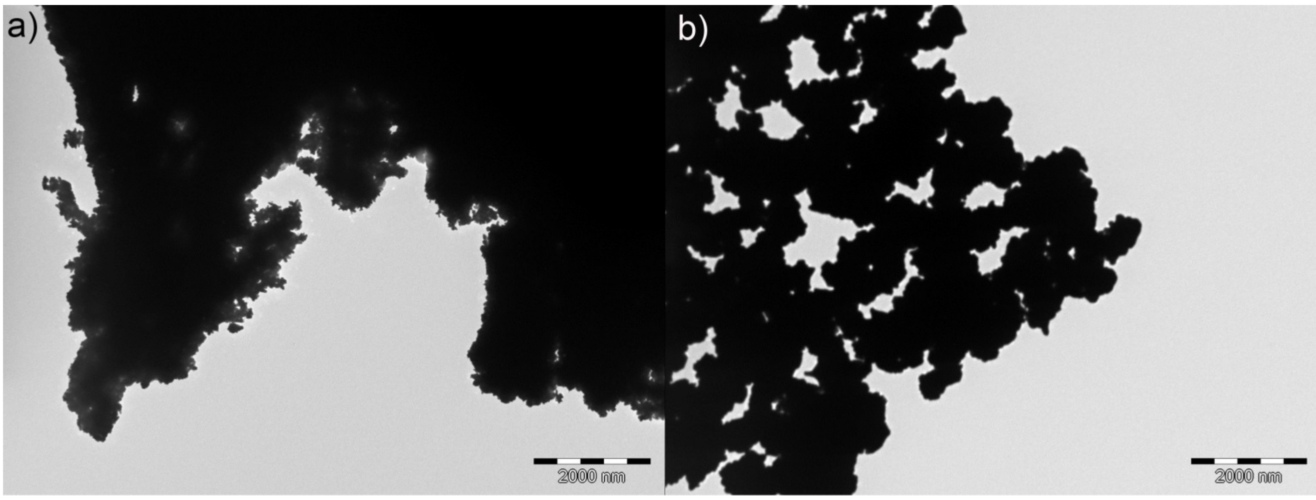


Fig. S-7 TEM images for samples S12 (a) and S13 (b)

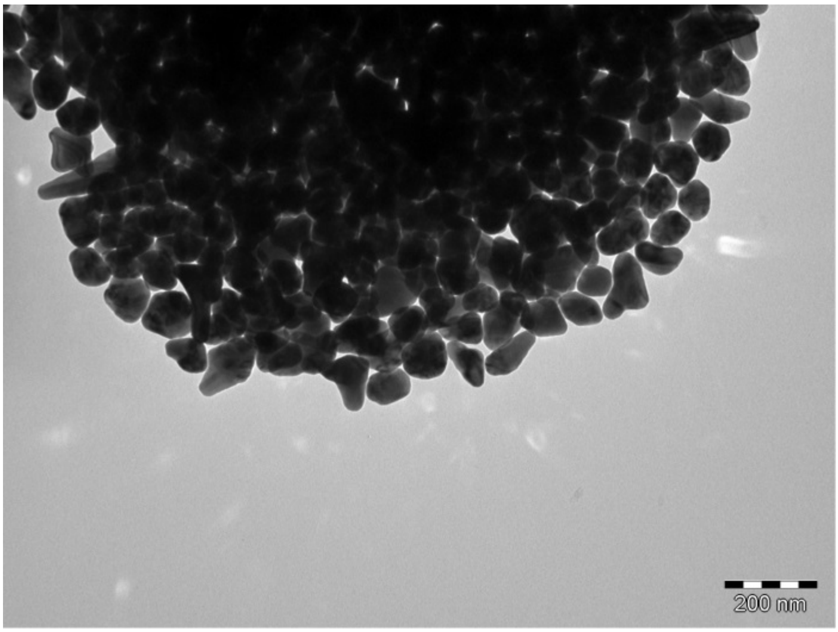


Fig. S-8 TEM image for sample S15

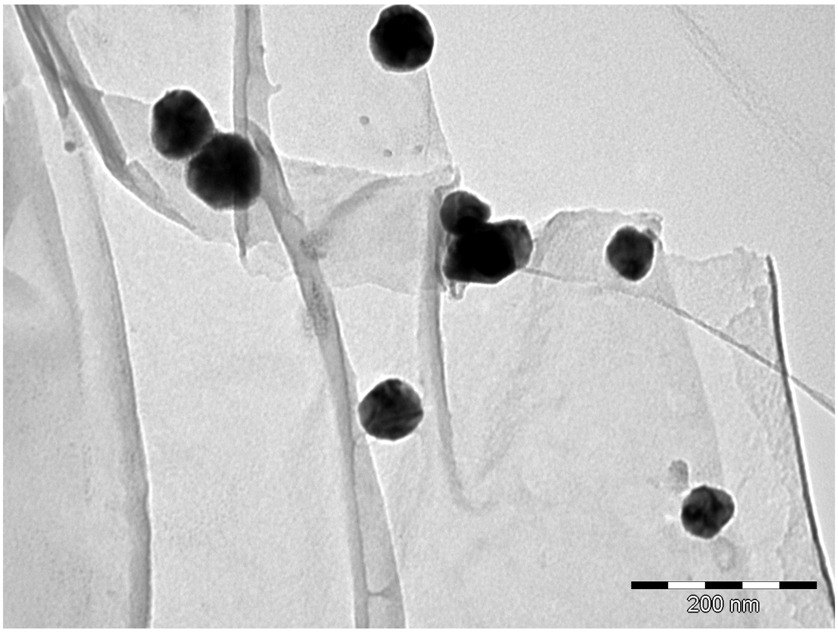


Fig. S-9 TEM image for sample S17

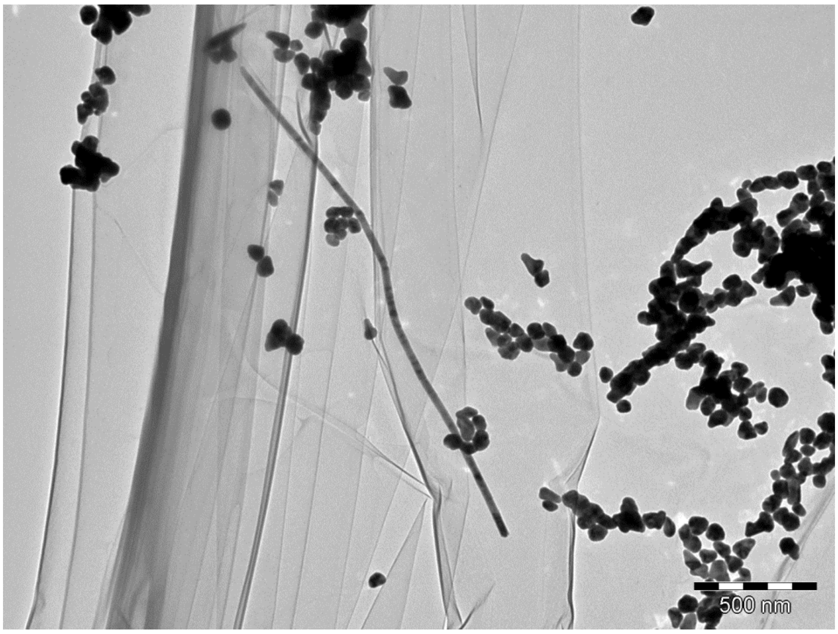


Fig. S-10 TEM images for sample S18

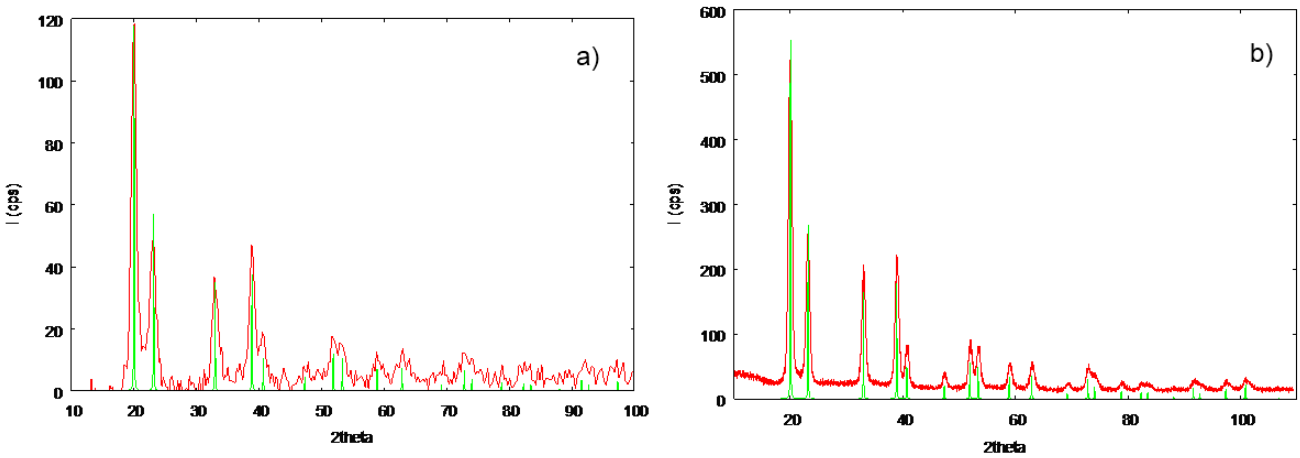
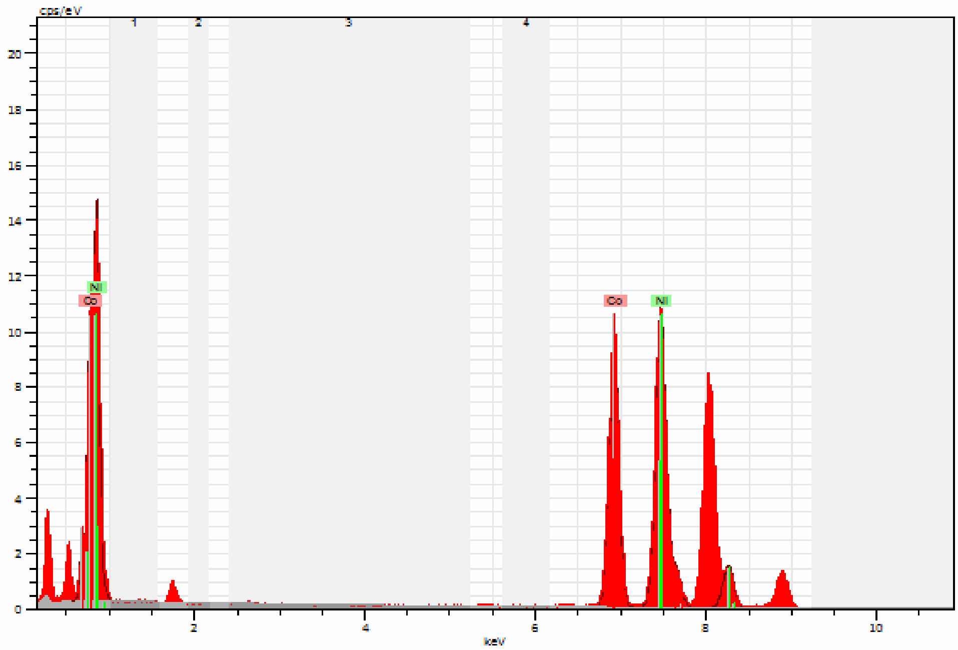


Fig. S-11 WAXS measurement for samples S19 (a) and S18 (b). The red curves are the sample spectra and the green lines denote the 'bulk' reference peaks of NiCo.



Element	Series	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
cobalt	K-series	46.83	46.73	1.0
nickel	K-series	53.17	53.27	1.1
	Total:	100.00	100.00	

Fig. S-12 HRTEM/STEM-EDS analysis for sample S10.

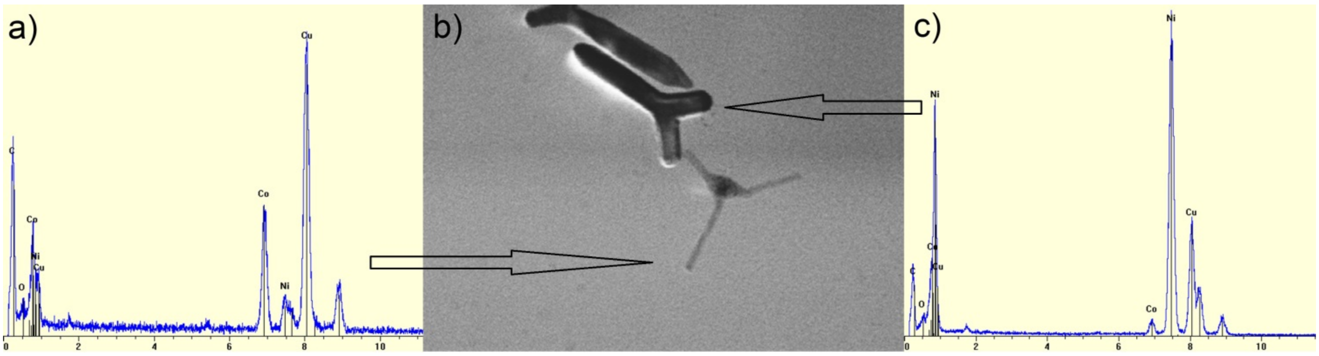


Fig. S-13 HRTEM image for sample S20 (b). Figures a) and c) are EDS spectra which correspond to the 'thin' tripod and larger anisotropic structures respectively.

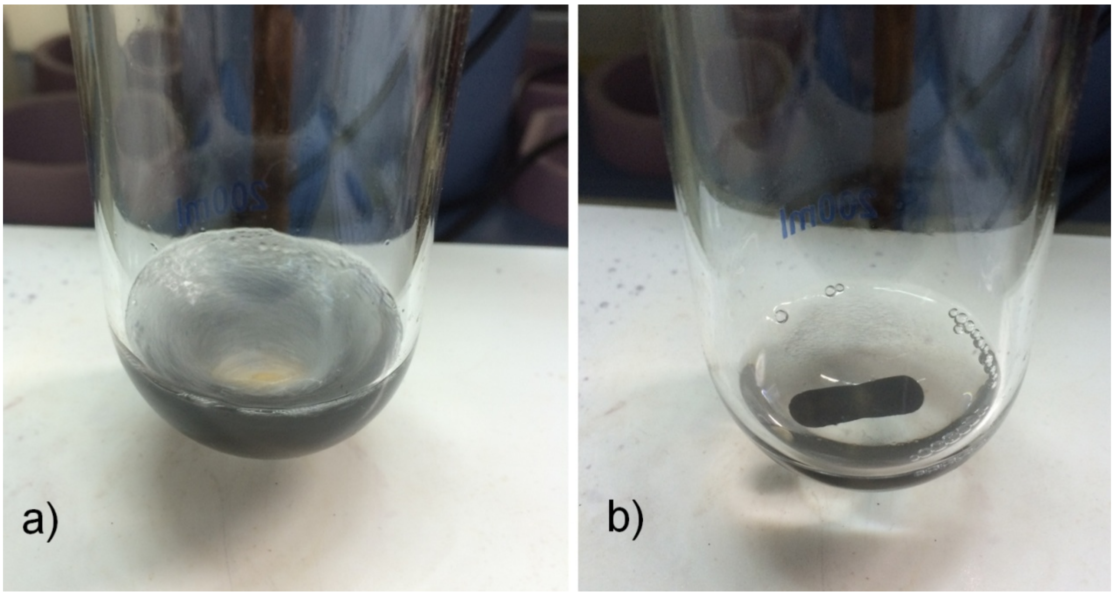


Fig. S-14 Stirring conditions, applied during synthesis provide a grey-black color, indicating a 'colloidal' character for the nanoparticle solution (a); As soon as the reaction is finished, stirring is stopped also and the magnetic (metallic) nanomaterial is collected onto the stirring magnet, leaving excess surfactants diluted into the transparent solution of the supernatant liquid (b). Aftewards, removal of the supernatant with a canula and further washing cycles with pentane and THF facilitate the isolation of a product with high metallic content.

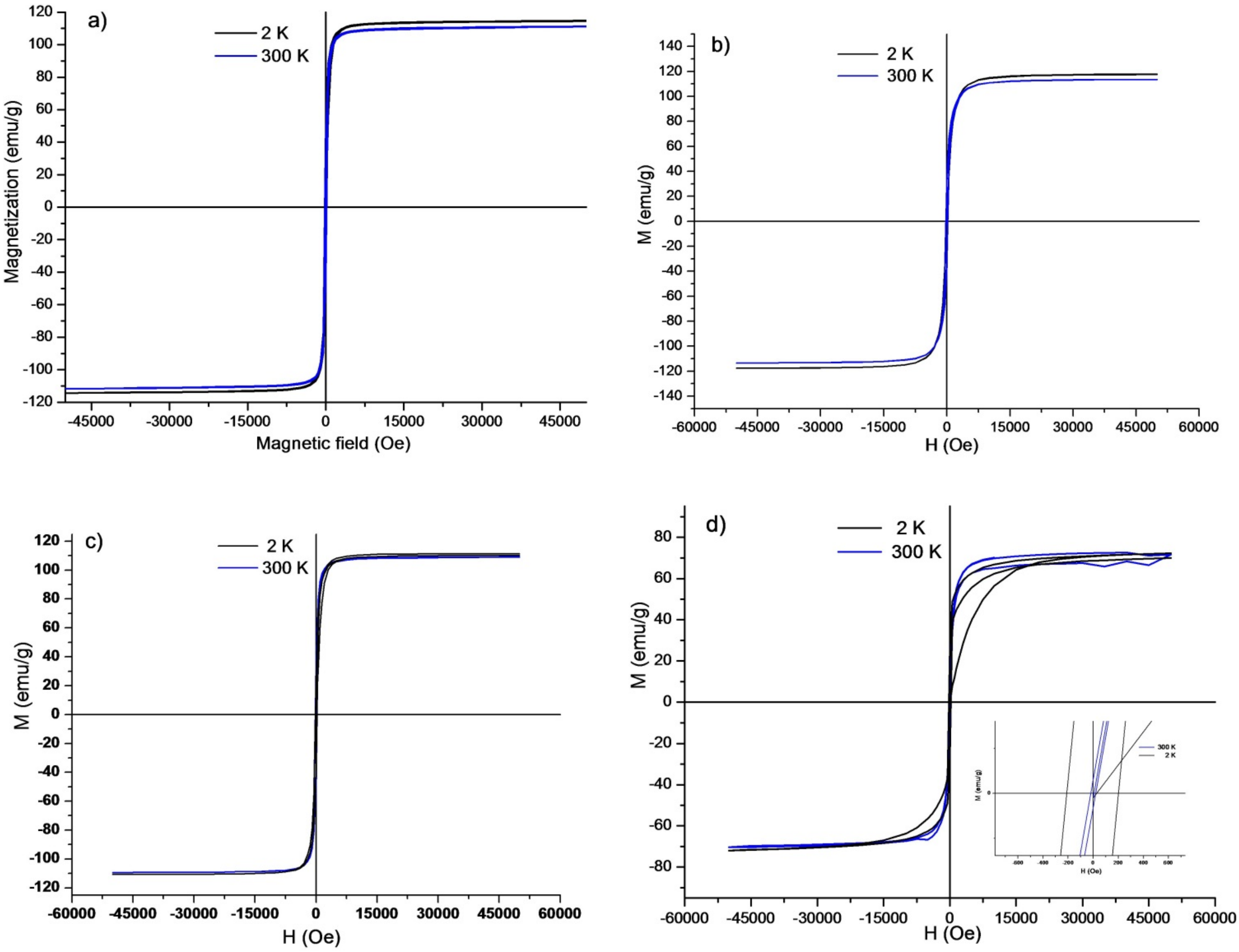


Fig. S-15 M-H plots for samples S19, S18, S15 and S3, @ 2K and 300 K by SQuID magnetometer [(a), (b), (c) and (d) respectively).

Estimation of the population of surface atoms of nanoparticles covered by stabilizer

If ‘d’ is the diameter of an atom, and ‘R’ is the radius of the nanoparticle, then for a particle of a size of 10 nm and spherical shape, we have R = 5. The surface atoms form a spherical shell in the outer part of the nanoparticle with a thickness ‘d’. The particle’s total radius is R and its inner radius is (R-d). Thus the volume of the shell is :

$V_{shell} = (4/3)\pi R^3 – (4/3)\pi(R-d)^3 = (4/3)\pi[R^3 – (R-d)^3]$

The whole volume of the sphere (nanoparticle) is:

$V_{nanoparticle} = (4/3)\pi R^3$

To find the percentage of surface atoms, it’s enough to find the ratio of the shell’s volume to the nanoparticle’s total volume:

$V_{shell} / V_{nanoparticle} = (4/3)\pi(R^3 – (R-d)^3 / [(4/3)\pi R^3] = [R^3 – (R-d)^3] / R^3$

For a particle of a size of 10 nm, R = 5. As the cell parameters of the $Ni_{50}Co_{50}$ fcc alloy are similar to those of the Ni fcc lattice, we may assume that d ~ 0.248 nm.

That gives a result of a ratio ~ 14% of surface atoms for the case of 10 nm NiCo nanoparticles.

Then, using an average organic (surfactant) mass percentage of 100 – 92 = 8% (after washing) and also taking into account the molecular weight of NiCo (118 g) and an average molecular weight of the surfactants (~ 275 g), we calculate that approximately every 4 equivalents of NiCo surface atoms, there is 1 eq. of surfactants. This value may indicate a low coverage by surfactants, but we should also consider that such alkyl chain surfactants have long molecules, that extend to a length of ~ 2 nm. Similarly, for a particle of ~ 50 nm size, we may find that the surfactant coverage will be quite higher, as in that case the percentage of surface atoms would be limited at around ~ 6,5%. That is, because, for an average surfactant mass percentage of 8% compared to the total sample mass, the surface atoms of the NP will have a lower population ratio at the samples of ~ 50 nm, compared to the ~10 nm-sized nanoparticles.