Supporting information

Rietveld analysis

The average coherent crystalline domain and the lattice parameters have been evaluated by means of Rietveld refinement of XRD patterns. It is worth to mention that the organic coating produced a background proportional to the amount of the residual TEG in each sample; in particular sample Co_0-Ni_{100} showed a very high background at low angle, thus its pattern has been analyzed only above $2\theta = 27°$. While this limitation poorly affects the estimation of the lattice parameter, which is extrapolated by the angular position of the residual 5 peaks, it interferes with the estimation of the peaks broadening, inducing a large error in the evaluated particles size. This explains the low value of 3.7(1) nm estimated by XRD compared to the 4.3(1) estimated from TEM images analysis.

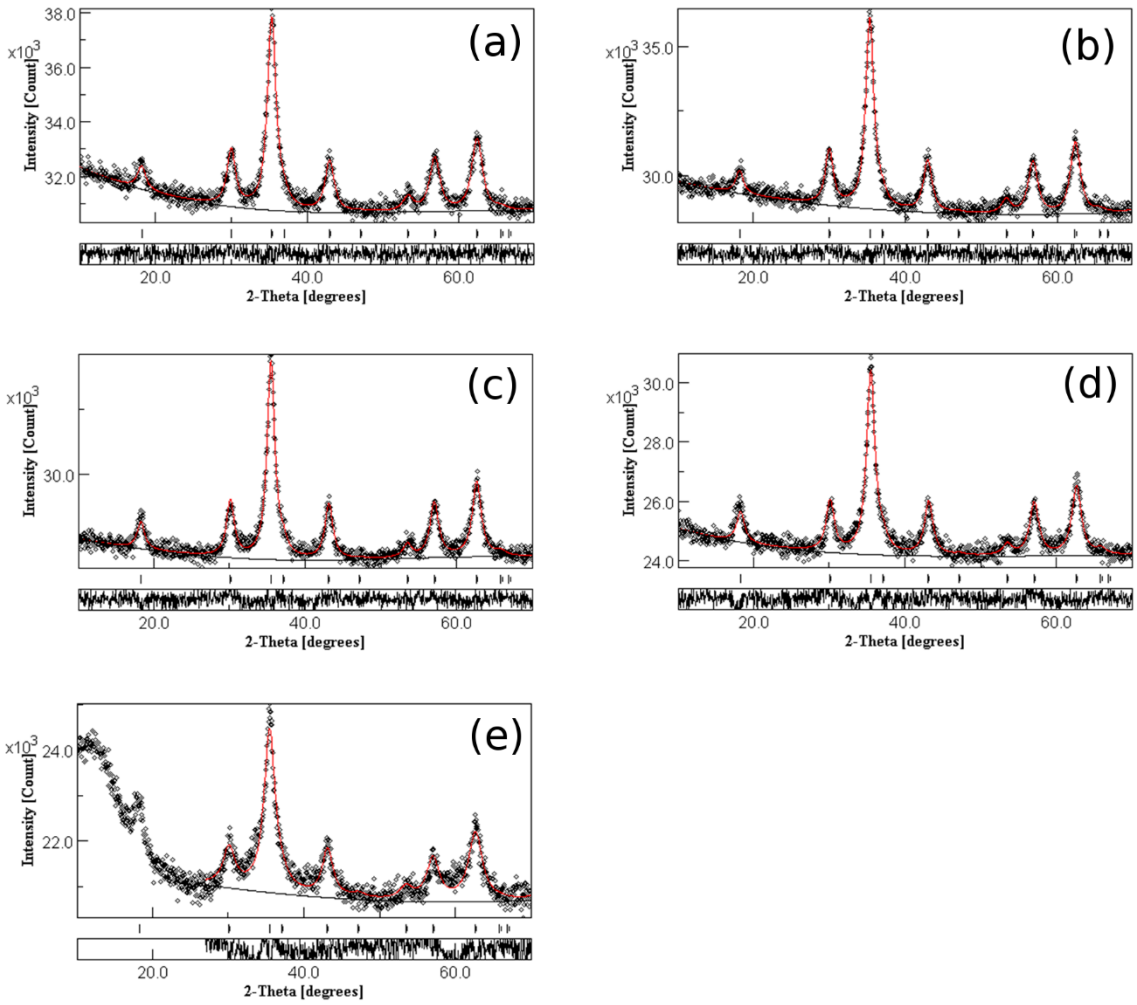

Figure S1. The XRD patterns and the respective fits from Rietveld refinement are reported for sample Co_{100}-Ni_0 (a), Co_{75}-Ni_{25} (b), Co_{50}-Ni_{50} (c), Co_{25}-Ni_{75} (d) and Co_0-Ni_{100}. The experimental data are represented as open circles, the background as a black line and the fit as a red line.

Activation volume determination

For sample Co_0-Ni_{100}, the one with the largest difference between XRD and TEM diameter, the magnetic viscosity S was measured in the range of H_{rev} between 0.2 T and 1.2 T, around its coercivity value (≈ 0.50 T). For this study the sample was brought at 5 K and saturated with a field of 5 T; then a reverse negative field (H_{rev}) was applied and the time dependence of magnetization was measured (**figure S1a**). M versus t was investigated and the logarithmic decay of the magnetization was found according to:

$$M(t) = M_0 - S\ln(t) \qquad (1)$$

where S is the magnetic viscosity[1]. By fitting the data with equation (1) (**inset figure S1a**), S was estimated at different values of the reverse field (**figure S1b**). By combining the maximum value of magnetic viscosity (S_{max}) with the irreversible susceptibility (χ_{irr}), calculated at the same field from DCD curve, an estimation of fluctuation field (H_f) was obtained:

$$H_f = \frac{S_{max}}{\chi_{irr}} \qquad (2)$$

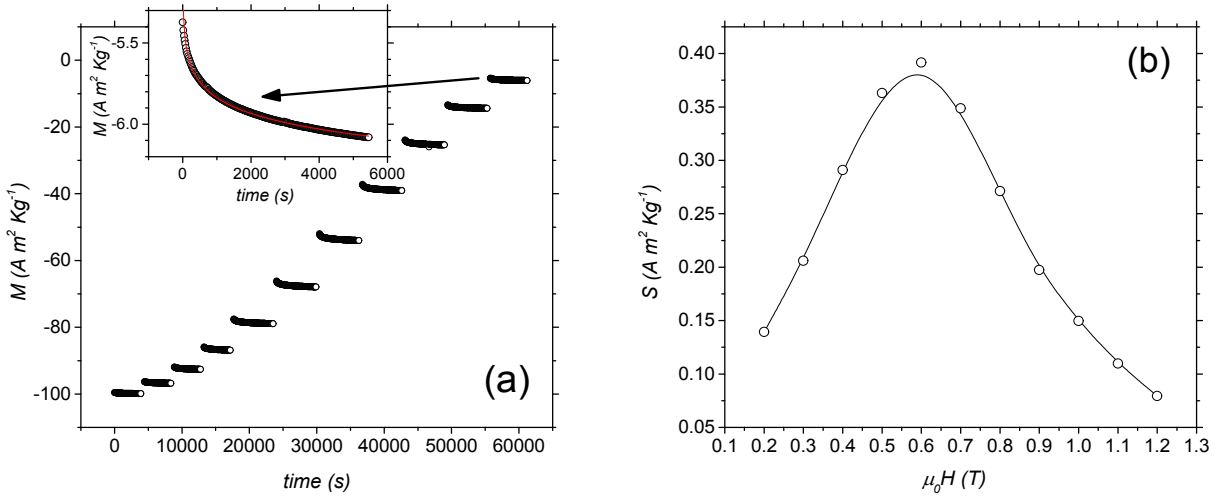

Figure S2. The time dependence of the magnetization reversal is reported in panel (a), with different field applied. For the 1.2 T field the experimental data (black circles) are reported both with the best fit (red line) using equation (1). The magnetic viscosity measured at each field is reported in panel (b).

Then the fluctuation field can be used to estimate the activation volume ($V_{act.}$)[1–3], which can be defined as the smallest volume of material that coherently reverses in a single event[3]:

$$V_{act} = \frac{k_b T}{M_{SH_f}} \qquad (3)$$

where k_B is the Boltzmann constant.

Assuming a system of spherical particles, the obtained V_{act} corresponds to a mean *magnetic grain diameter* of 4.7(5) nm, in perfect agreement with TEM measurement of 4.6(1) nm. It suggests that the larger diameter estimated by XRD can be due to a large amount of polyol coating: the background produced by the organic phase can induce to underestimate the peak broadening and thus to overestimate mean particles size.

Surface magnetic frustration and interparticle interactions in Co_0-Ni_{100}

To verify the role of surface effect on reduced remanent magnetization of Co0_Ni100 sample , an hysteresis loop at 5K was recorded after cooling the sample in an applied field of 3T (figure S3a). Any shift of the hysteresis loops is observed in FC conditions, allowing to rule out the presence of high anisotropic surface shell.

Also a detailed investigation of interparticle interactions has been carried oud by means of remanent magnetization measurements by IRM and DCD protocols. The initial state for an IRM measurement is a totally demagnetized sample cooled in zero magnetic field. In the present case, an external field was applied for 10 s; then, it was switched off and the remanence was measured (MIRM). The process was repeated, increasing the field up to saturation. In a DCD measurement, the initial state is the magnetically saturated one. An external field of −5 T was applied for 10 s; then, a small external field in the direction opposite to magnetization was applied and, after 10 s, it was switched off and the remanent magnetization (MDCD) was measured. This was repeated while increasing the field up to +5T[4].

For a system with uniaxial anisotropy and without interparticles interactions, the same energy barrier is calculated from IRM and DCD curves, as in Wohlfarth relation [5]:

$$M_{DCD}(H) = 1 - 2M_{IRM} \qquad (1)$$

Kelly et al. rewrote this expression as [6]:

$$\Delta M = M_{DCD}(H) - 1 + 2M_{IRM} \qquad (1)$$

Negative deviations in ΔM are usually taken as indicative of the presence of interactions that stabilize the demagnetized state (i.e., dipole-dipole interactions). Positive values are attributed to interactions promoting the magnetized state (i.e., exchange interactions).

Figure S3b shows only a relative small negative peak, suggesting the prevalence of small dipolar interactions.

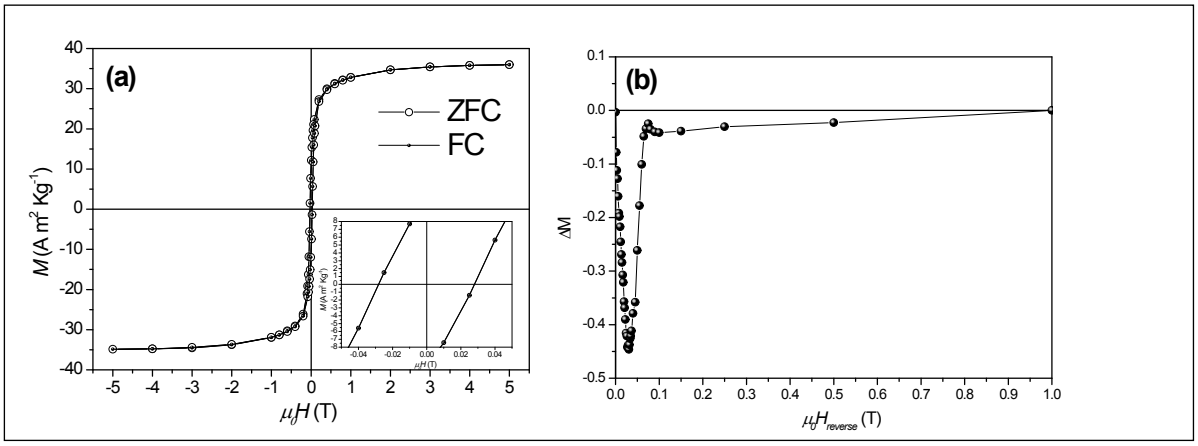

Figure S3: (a) Hysteresis loops recorded at 5 K in ZFC condition (big empty cycles) and cooling the samples under an applied field of 3T (small full circles); Inset: detail in the field range ± 0.05 T.

(b) ΔM plot recorded at 5K

Average spin-canting angle from Mössbauer

^{57}Fe Mössbauer spectra have been recorded at 10 K under a magnetic field of 8 T applied (B_{ext}) parallel to the γ –beam. In case of a non-collinear spin structure, the direction of the measured effective nucleus field (B_{eff}) differs from that of the hyperfine field (B_{ext}) due to the average canting angle ϑ as graphically illustrated in **figure S4**.

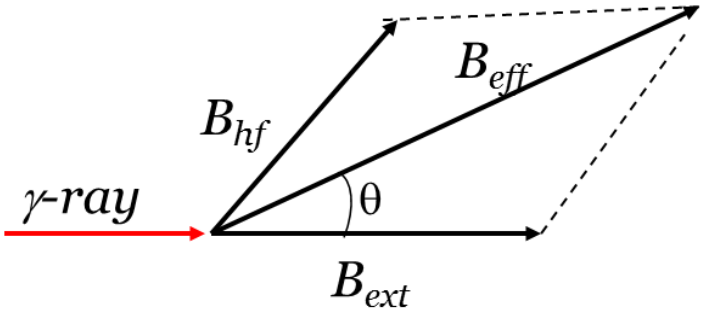

Figure S4. The setup for ^{57}Fe Mössbauer spectroscopy and the relation between the effective field (B_{eff}) and the external applied field (B_{eff}) which differ by the average canting angle θ.

The area of each peak is described by the relation:

$$3{:}2p{:}1{:}1{:}2p{:}3 \qquad (4)$$

where *p* is equal to:

$$p = \frac{2\sin^2\theta}{1+\cos^2\theta} \qquad (5)$$

By normalizing the total area to 1, the area of lines 2-5 ($A_{2,5}$) is equal to:

$$A_{2,5} = \frac{1}{2}\sin^2\theta \qquad (6)$$

From such value, the average canting angle ϑ is determined [7]:

$$\theta = arcsin\sqrt{2A_{2,5}} \qquad (7)$$

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