

## High magnetization FeCo nanoparticles for magnetorheological fluids with enhanced response

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### Supplementary Material

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## S1. Magnetic characterization of magnetic NPs and fabricated MR fluid

In the first part of the supplementary material, the magnetic characterization of different magnetic fillers (commercial carbonyl iron particles, CIP, Fe nanoparticles synthesized by electric explosion of wire, Fe-EEW, and FeCo NPs synthesized by the chemical reduction method) and fabricated magnetorheological fluid are detailed (FeCo MR fluid).

On the one hand, the room temperature hysteresis loops for each magnetic fillers are shown in Figure S1.1, S1.2 and S1.3 respectively. For CIP microparticles, the saturation magnetization value at room temperature is about  $177 \text{ Am}^2/\text{kg}$ , a 7% lower than the Fe-EEW fabricated nanoparticles showing a room temperature magnetization value of  $190 \text{ Am}^2/\text{kg}$ .<sup>1</sup> For bulk iron, the saturation magnetization value at room temperature is about  $221.9 \text{ Am}^2/\text{kg}$ .<sup>2</sup> Thus, micro- and nanosized particles of Fe always have an oxide layer that reduces the bulk magnetization value. This is the reason why our fabricated FeCo nanoparticles are important, in the sense that they show a room temperature saturation magnetization value of  $212 \pm 2 \text{ Am}^2/\text{kg}$ , higher than the Fe-EEW nanoparticles one as it can be observed in Figure S1.4. Regarding to the coercive field, the value for Fe-EEW nanoparticles is about  $12 \text{ kA/m}$  and the value for FeCo nanoparticles is about  $7.1 \pm 0.1 \text{ kA/m}$ .

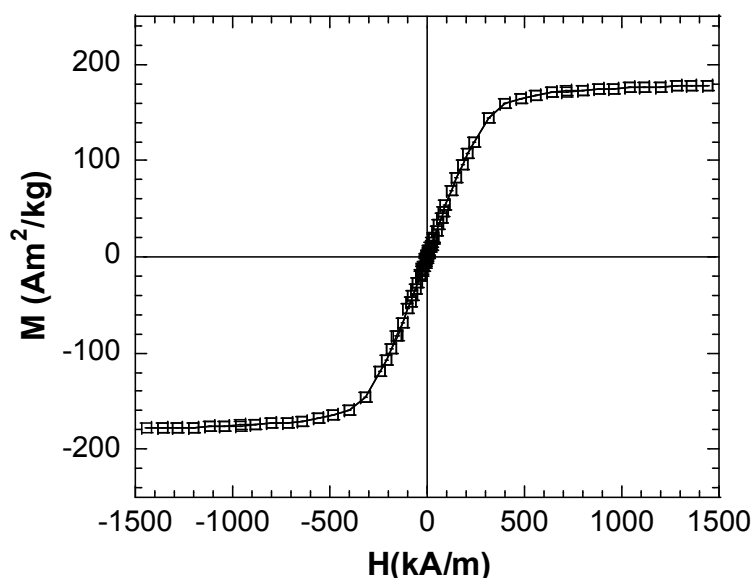


Figure S1.1. Room temperature hysteresis loop of the commercial carbonyl iron particles (CIP) provided by BASF, Germany.

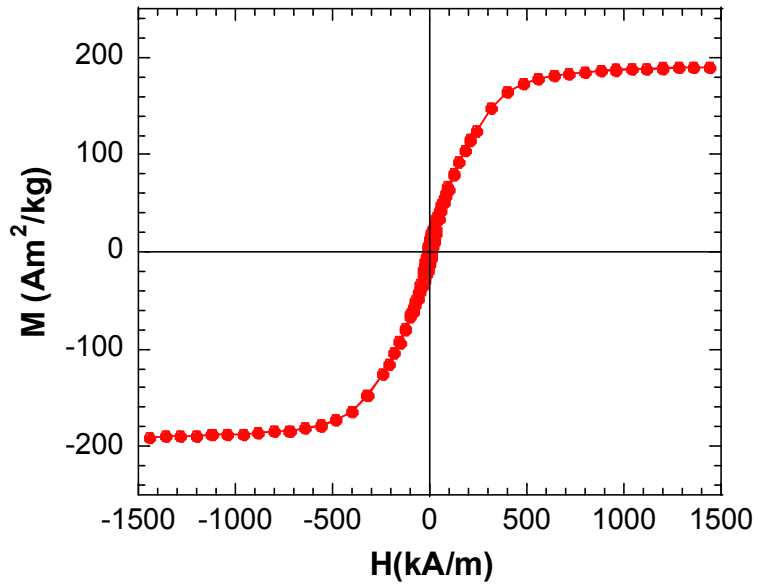


Figure S1.2. Room temperature hysteresis loop of the raw powder of Fe nanoparticles synthesized by electric explosion of wire (Fe-EEW).

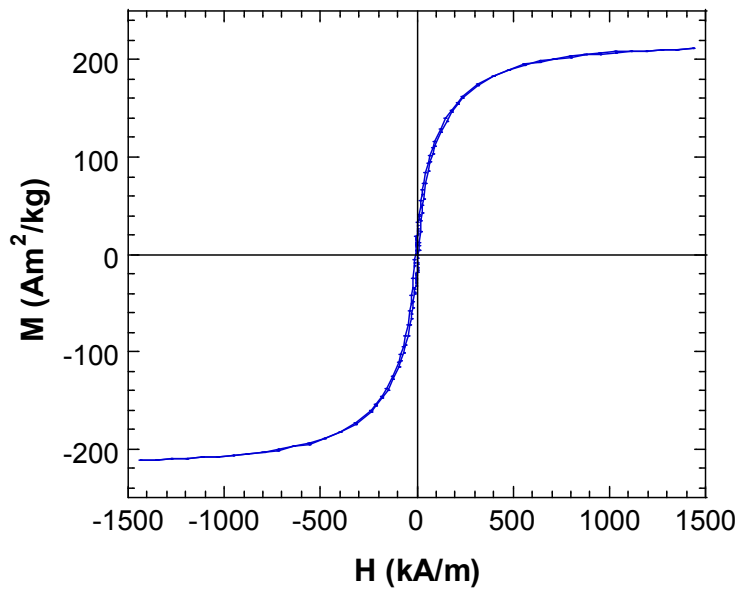


Figure S1.3. Room temperature hysteresis loop of the raw powder of FeCo NPs synthesized by the chemical reduction method.

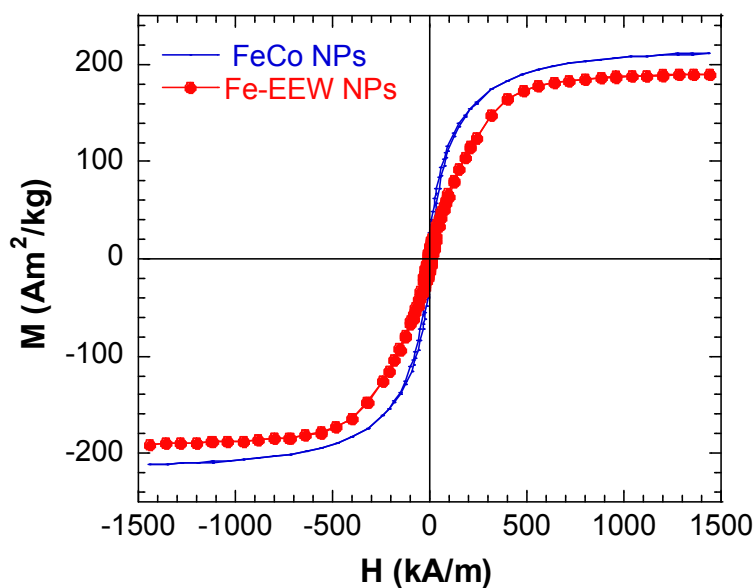


Figure S1.4. Room temperature hysteresis loops of the raw powder of FeCo NPs and Fe-EEW NPs: FeCo NPs show higher (approximately by 12%) saturation magnetization than Fe-EEW NPs.

All the observed magnetic properties of our  $\text{Fe}_{47}\text{Co}_{53}$  nanoparticles (that is, coercivity field value about  $7.1 \pm 0.1 \text{ kA/m} \sim 90 \text{ Oe}$ , and remanence to magnetic saturation ratio  $M_r/M_s = 0,086$ ) point towards the behaviour of a (magnetically) soft multidomain particle (MD) system. In our case, this multidomain particle system is mainly the one formed by the nanoparticles agglomerates, without forgetting the contribution arisen from individual nanoparticles ranging from 30 to 50 nm size, as determined by TEM observation.

Besides, ZFC-FC (zero field cooled - field cooled) magnetic measurement was performed for FeCo NPs (see Figure S1.5). This curve does not show the expected trend when a significant contribution from very small particles exists. Instead, the measured curves indicate that the particles are quite thermally stable without blocking (or superparamagnetic behaviour). Also, the slight decrease in the FC (field cooling) magnetization agrees with the characteristic curve obtained for an agglomeration of particles showing a strong dipolar-dipolar magnetic interaction (see, for example, Zhang et al.).<sup>3</sup>

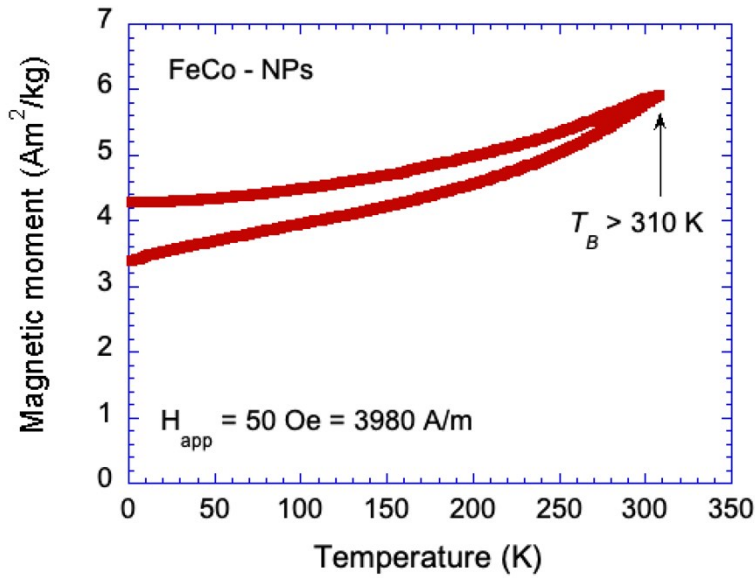


Figure S1.5: ZFC-FC (zero field cooled - field cooled) performed magnetic measurement for the FeCo NPs used in this work, measured at  $H_{app} = 50 \text{ Oe} = 3980 \text{ A/m}$

Looking to our ZFC-FC measurement, any possible blocking temperature  $T_B$  should be above 310 K (quite probably much higher than this value) and it can be related to the particle  $V$  volume through the well-known expression  $25k_B T_B = KV$ . Thus, this volume determination needs of a good (and realistic) anisotropy constant value,  $K$ . For bcc  $\alpha$ -Fe (with  $K = 40\text{-}50 \text{ kJ/m}^3$ ), the critical size for single domain particles is about 20 nm above which there will be domain walls in the particles (they will be multidomain particles, MD).<sup>4</sup>

In which concerns the expected size of one magnetic single domain (SD) for the FeCo nanoparticles, a previous work by X. Liu et al.<sup>5</sup>, used quite realistic values of the magnetocrystalline anisotropy and the stiffness constant for its calculation. For the  $\text{Fe}_{65}\text{Co}_{35}$  alloy a correlation length of the exchange magnetic interaction of about 30 nm was estimated. This length can be assumed to be the size of one magnetic single domain (SD).

Further micromagnetic modelling work concerning the threshold size corresponding to the transition from SD to MD state of a cubic Fe crystal was performed by Muxworthy et al.<sup>6</sup> In this work there is a deep revision of previous results related with the SD to MD state transition. Muxworthy et al. established this size in the range 17 to 27 nm, in good agreement with previous reported simulations and some experimental results.<sup>6</sup>

Bearing all this in, to our understanding in our case only the smallest nanoparticles are in the limit to be single-domain ones (and these are not the majority of all observed sizes), and over this size and also their agglomerates will behave as a magnetic multidomain particle system.

On the other hand, we have measured the room temperature hysteresis loop of the fabricated MR fluid (see Figure S1.6). Figure S1.7 shows a detail the measured curves for both hysteresis loops (for our raw FeCo nanoparticles, and when immersed in the fluid), at the low applied H field value region and normalized to the saturation magnetization value of FeCo NPs. From these curves, we can observe a steeper slope of the curve corresponding to the FeCo NPs immersed in the fluid as well as a lower coercive field. These observations suggest a satisfactory dispersion of the initially aggregated FeCo NPs when the magnetorheological fluid has been fabricated.

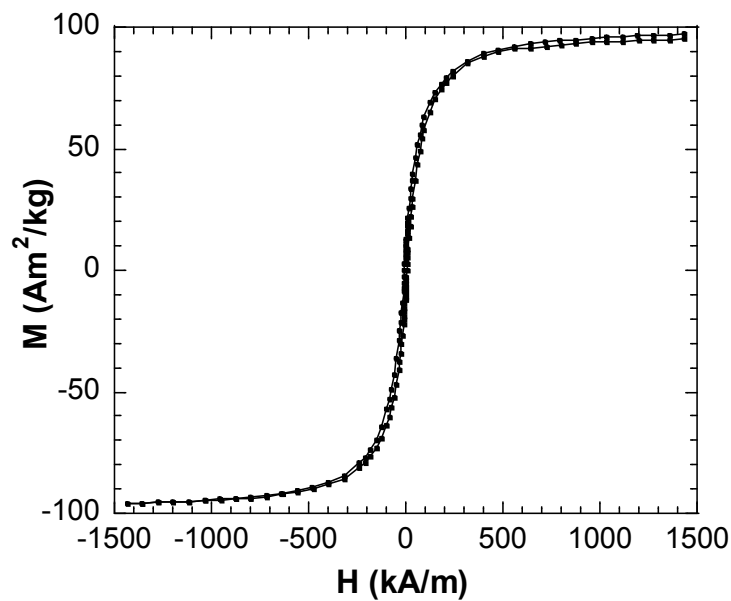


Figure S1.6. Room temperature hysteresis loops of the fabricated magnetorheological fluid containing  $\text{Fe}_{47}\text{Co}_{53}$  nanoparticles (FeCo-MR).

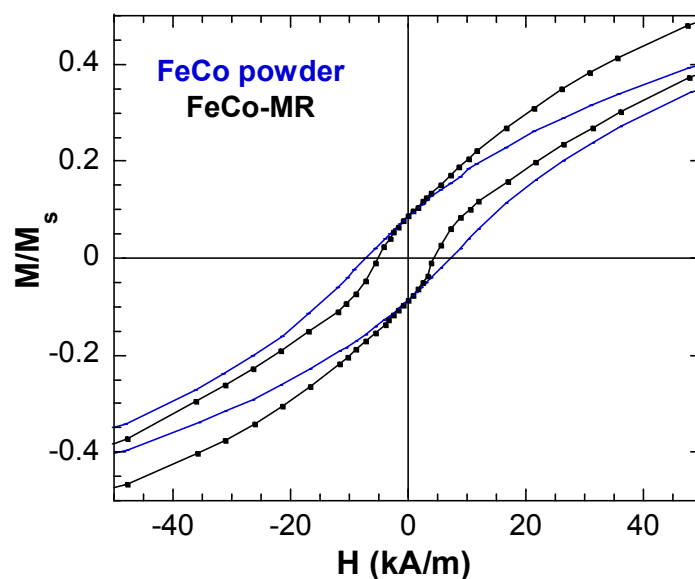


Figure S1.7. Low applied H field value region measured room temperature hysteresis loops detail for both the raw Fe<sub>47</sub>Co<sub>53</sub> nanoparticles powder and the fabricated MR fluid by using those nanoparticles.

To estimate the interaction parameter  $\lambda$ , which compares the magnetostatic energy of the dipole-dipole interaction, it is necessary to know the magnetic permeability of the magnetic fillers as well as the magnetic permeability of the carrier liquid. FeCo alloy has high permeability<sup>7</sup> compared to the carrier liquid and for that, the parameter  $\beta$  is close to 1.

$$\lambda = \frac{\pi\mu_0\mu_{cr}\beta^2 a^3 H_0^2}{2k_B T} \left(\frac{a}{a+s}\right)^3 \quad (1)$$

$$\beta = \frac{\mu_p - \mu_{cr}}{\mu_p + 2\mu_{cr}} \quad (2)$$

We have also estimated the magnetic susceptibility of MR fluid containing FeCo NPs. The obtained value is about 0.595 and therefore the magnetic relative permeability of our fabricated MR fluid is about 1.595.

## S2. Magnetorheological characterization of the fluids

In the second part of the supplementary material, we have detailed some aspects about the magnetorheological characterization. Specifically, in Figure S2.1 we show two comparative figures with the results obtained for a commercial magnetorheological fluid and the results for our fabricated MR fluid based on high magnetization FeCo nanoparticles. From previous experience of some of the authors of our manuscript, when there is wall slip behaviour between the plate and the sample the obtained measurements show inconsistent jumps with abrupt decreases in shear stress as the shear rate increases. As we can observe in Figure S2.1 (a), commercial magnetorheological fluid shows wall slip jumps, just upon reaching the yield stress indicating there is wall slip phenomenon while our fabricated MR fluid containing FeCo nanoparticles shows the typical trend of a conventional MRF (see Figure S2.1 (b)).

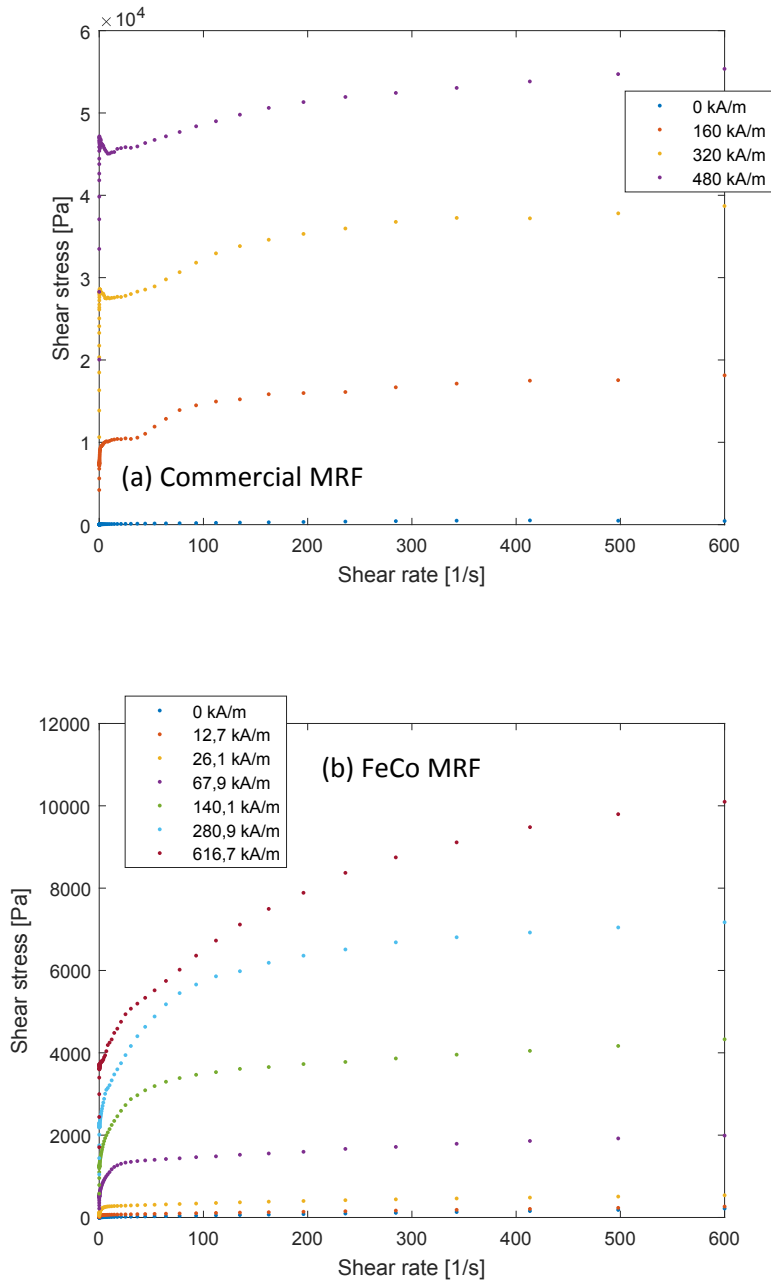


Figure S2.1. Rheological curves as function of the applied magnetic field: (a) for a commercial MR fluid and (b) for the new FeCo-MR fluid studied. For the commercial MR fluid, it can be observed inconsistent jumps with abrupt decreases in shear stress as the shear rate increases indicating a possible wall slip phenomenon.

In order to get a MR fluid containing high magnetization FeCo nanoparticles with high reversibility and a good stability after demagnetization process, different amount of oleic acid was employed for the MRF fabrication, specifically, 1.4 %wt., 2.8 %wt. and 5.3% wt. In Figure S2.2, the yield stress as function of magnetic field applied after demagnetization process for FeCo MR fluids with different amounts of oleic acid are shown. As it can be observed, the best behaviour was found for a fluid containing a 5.3 %wt. of oleic acid, mainly because the measured yield stress at 616.7 kA/m keeps



almost constant, a fact that do not happen for the FeCo MR fluids containing lower amount of oleic acid.

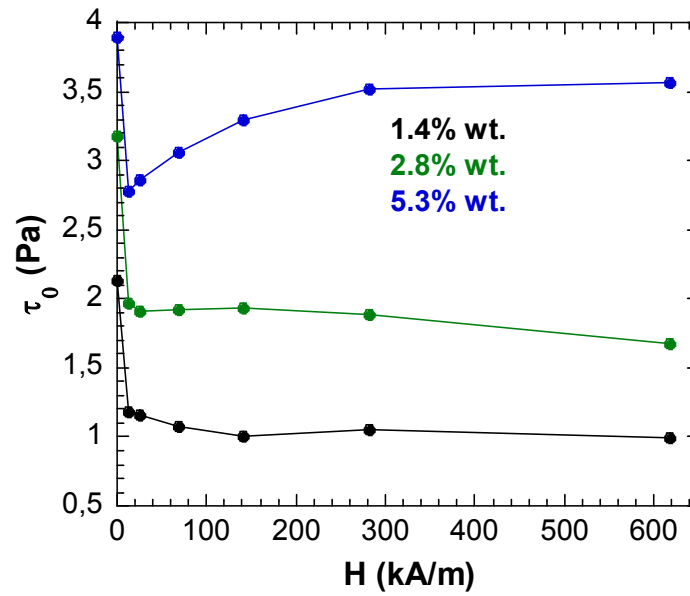


Figure S2.2. Yield stress as function of the applied magnetic field after demagnetization process for FeCo-MR fluid with different amounts of oleic acid: 1.4 %wt., 2.8 %wt. and 5.3% wt.

## References

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