Supplementary Information for the manuscript:

The influence of composition and porosity on the magnetic properties of FeCo-SiO$_2$ nanocomposite aerogels

Alberto Casu[a], Maria Francesca Casula[a], Anna Corrias[a], Andrea Falqui[a] *, Danilo Loche[a], Sergio Marras[a] and Claudio Sangregorio[b]

[a]Dipartimento di Scienze Chimiche and INSTM, Università di Cagliari, Cittadella Universitaria, Monserrato, 09042 (CA) – ITALY
[b]Dipartimento di Chimica and INSTM, Università di Firenze, Via della Lastruccia, 3, Sesto Fiorentino,50019 (FI) – ITALY

Representative bright field TEM images of the porous nanocomposites are reported in Figure SI-1. These images show the very porous texture of the silica matrix made out of meso- and macropores. The FeCo nanocrystals appear as darker spots with respect to the silica matrix, and due to the smaller size and lower concentration are barely detectable in the F1C1-3 and F1C1-5 samples (images a and b), whereas they are clearly evident in the F1C1-8 and F1C1-10 samples (images c and d). All TEM observations indicate that the nanocrystals are evenly distributed within the silica matrix and that no magnetic agglomerates are observed. Indeed, TEM observations point out that the FeCo nanocrystals are well embedded in the matrix even at higher loading, thanks to the textural features of the host matrix and to the co-gelation preparation procedure. As discussed in the manuscript, the average distance between the nanocrystals decreases as a function of the alloy loading in the nanocomposite. The silica matrix plays therefore a significant role not only in affecting the growth of the alloy but also in mediating the interactions among magnetic nanocrystals.
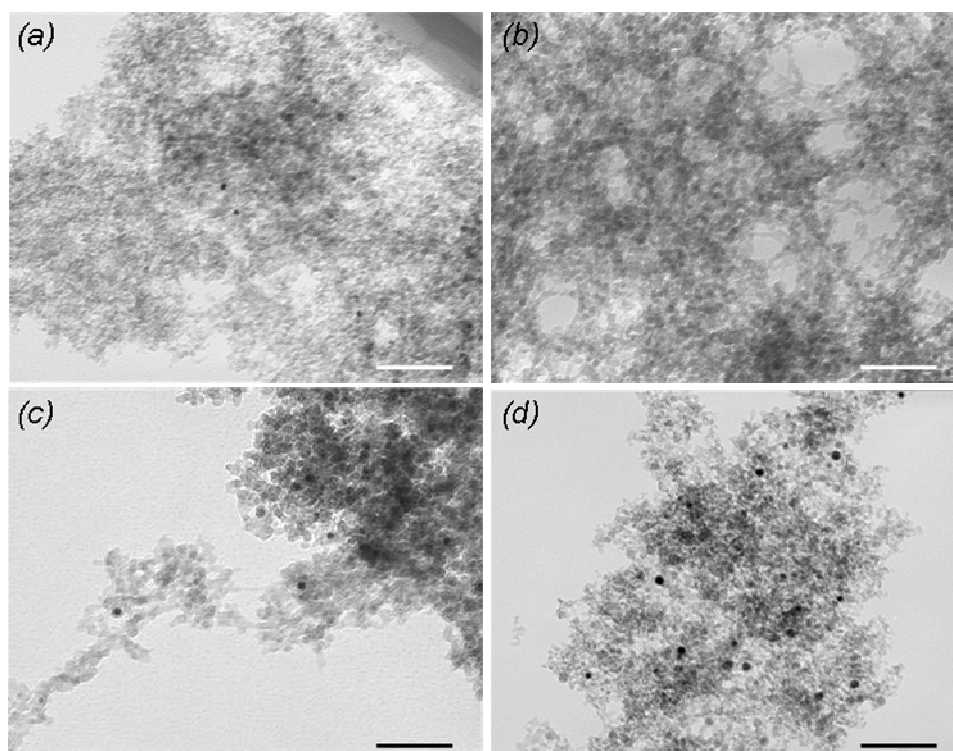

Figure SI-1 TEM bright field images of the F1C1-3 (a), F1C1-5 (b), F1C1-8 (c), and F1C1-10 (d) nanocomposite samples. Scale bar is 100 nm.

Isothermal magnetization versus applied field curves were collected for the two samples (F1C1-3 and F1C1-8) that were in a

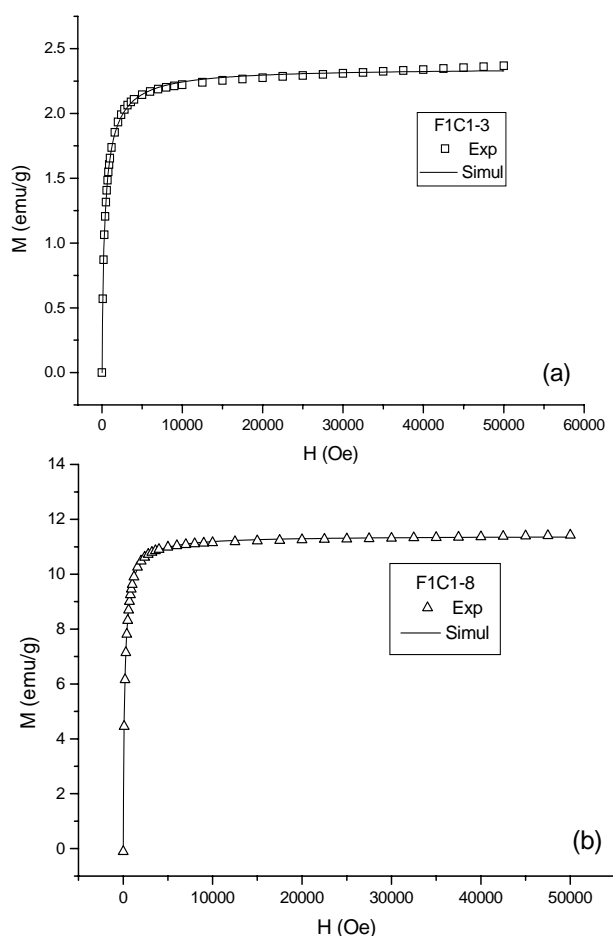complete superparamagnetic state at the maximum exploitable temperature (T=325 K) and they are shown in Figure SI-2.

Figure SI-2. Isothermal magnetization versus applied field curves at 325 K for (a) F1C1-3 and (b) F1C1-8 samples. The points correspond to experimental data, the line to the simulated curve obtained by using equation (2).

The isothermal magnetization were simulated using a simple paramagnetic model based on the only assumption that all the particles are in the superparamagnetic state at the given temperature, being this the case for the F1C1-3 and F1C1-8 samples at T=325 K. To apply this model, the size distribution of the particles must be considered, in order to take into account the occurrence of nanoparticles with different diameters. In many similar systems the particle size distribution is well described by a log-normal probability law:[1-4]

$$p(D) = \frac{1}{D\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln^2 D/D_0}{\sigma^2} \right) \right] \quad (1)$$

where D is the diameter of the particles, D_0 is the average value of D and σ^2 the standard deviation. The maximum of the probability density occurs for $D_{mp}=D_0\exp(-\sigma^2)$. The simulations were then carried out by considering the particles to have a spherical shape, as observed by TEM.

As reported in ref. [3], in a completely superparamagnetic state the sample magnetization is given by:

$$M(H,T) = x * M_S \frac{\int V(D)L\left[\frac{M_S V(D)H}{k_B T} \right] p(D)dD}{\int V(D)p(D)dD} \quad (2)$$

where x is the volume fraction of metallic phase in the sample, M_s the volumic saturation magnetization and

$$L(y) = \coth y - \frac{1}{y} \qquad (3)$$

the Langevin Function.[5] This approach assumes that the saturation magnetization does not depend on the particle size. In our case the integration limits were chosen equal to 0 and 25 nm respectively, the upper limit being large enough to include all the alloy nanoparticles in the superparamagnetic state.

By applying equation (2), it was found a $D_{mp} = 4.2$ nm for the F1C1-3 sample and a $D_{mp} = 5.8$ nm for the F1C1-8 sample. These results are in agreement with the trend observed by TEM and XRD indicating that the observed trend in the T_{max} values cannot be ascribed to the nanoparticle mean size evolution, but a different effect has to be taken into account.

References

1. J. C. Bacri, R. Parzynski, D. Salin, V. Cabuil, R. Massart, *J. Magn. Magn. Mater.*, 1986, **62**, 36.
2. J. C. Bacri, R. Parzynski, D. Salin, *J. Magn. Magn. Mater.*, 1988, **71**, 246.
3. O. Jarjayes, P. H. Fries, G. Bidan, *J. Magn. Magn. Mater.*, 1994, **137**, 205.
4. K. O'Grady, A. Bradbury, *J. Magn. Magn. Mater.*, 1983, **39**, 669.
5. A. H. Morrish, *The Physical Principles of Magnetism*, Wiley, New York, 1965.