Magnetic hydrophobic nanocomposites: Silica aerogel/maghemite


1. Introduction

Nanocomposite materials, such as porous matrices hosting other specimens, combine the properties of their components. The guest may be an optically or a photochemically active molecule, an antibody, a nanoparticle, a magnetic nanoparticle (MN), etc. In this way these materials are multifunctional and attractive for chemical, biochemical and magnetic applications [1]. Silica aerogels are derived by sol–gel process followed by hypercritical drying. These materials exhibit an accessible internal porous structure, both in meso and micro size scales that make them good matrix hosts for holding both molecules and particles. Their high specific area (700–1000 m²/g) and their extremely low density (0.003–0.4 g/cm³) make them excellent thermal and electric insulators, they also bear an important degree of transparency to visible light [1]. These outstanding properties make them suitable for a large number of applications, which range from thermal and acoustical insulation to chemical sensors [2] and more are foreseen using them as hosts for magnetic materials, such as semitransparent light magnets or materials for magneto-optical devices.

On the other hand, single domain MN with uniaxial anisotropy axis behave as magnets and are of great interest for investigations of nanomagnetism phenomena and their applications. It is often desirable to incorporate magnetic oxides within an inorganic matrix in which the nanoparticles are stabilized and spatially distributed, avoiding agglomeration. The synthesis procedure may be used to control the growth and distribution of magnetic particles, which subsequently affect their final magnetic properties. Magnetic oxides have been incorporated into sol–gel-derived SiO₂ aerogels and xerogels [4,5]. These aerogels are hydrophilic. The sol–gel procedure involves the hydrolysis of Si-OCH₂CH₃ to Si-OH and subsequent condensation reaction between Si-OH and Si-OR groups forming Si–O–Si linkage groups. In the resulting matrix some of the hydroxyl and alkoxyl groups remain unreacted. Hydroxyl groups interact attractively with water. Therefore, the network collapses when it gets wet, even from ambient moisture [6], which makes them deteriorate with time limiting long term uses.

Here we produce MHA that may have applications when dealing with magnetic fluids. From the three methods known to produce hydrophobic silica aerogels, all based in the replacement of the hydroxyl surface group [3], we have chosen the one using an organosilane as SiO₂ co-precursor, particularly MTMS. This selection was based on a previous determination of the properties of two step SiO₂ aerogels synthesized with various co-precursors [6].

2. Experimental

The nanocomposite gels were prepared by one step sol–gel method following the synthetic path described in [4] modified to achieve hydrophobicity. A solution of Fe(NO₃)₃·9H₂O in methanol
(MeOH), was added to TEOS (Si(OCH2CH3)4), MTMS (Si(OCH3)3CH3) and water. The mixture jellified under simultaneous hydrolysis and condensation reactions within 4–6 days. Molar ratios MTMS/TEOS = 0.5, MeOH/TEOS = 2.3 and H2O/TEOS = 1.8 were kept fixed in all of the syntheses.

MTMS was added to achieve the hydrophobic property. MeOH was used as a solvent instead of EtOH for two reasons: gelation times are shorter, and hydrophobicity and other physical properties are better, because the smaller chain alkyl groups (–CH3) present in methanol solvents minimizes the steric hindrance during hydrolysis [6].

Gels were dried under hypercritical conditions of 110 bar and 330 °C. The samples studied here have nominal Fe/Si mass ratios $r_{Fe}$=0, 0.0825, 0.207 and 0.33 and are labeled as J1, J2, J3 and J4, respectively. X-J4 is similar to J4 but atmospherically dried (xerogel). Hydrophobicity property was checked loading and unloading the MHA with organic liquids, and observing the contact surface between water drops and MHA with an optical microscope.

Magnetic phase identification was performed with Möbbauer Effect (ME). Size and structural features were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). TEM images were obtained with a Jeol JEM-3010 microscope at 300 kV (1.7 Å-resolution).

Porous matrix structure was studied by SAXS, which is known to be useful to determine the backbone pore structure in porous materials [7]. Measurements were performed at the D11A-SAXS/LNLS beamline ($\lambda = 1.7556 \text{ Å}, q = 4\pi \sin(\theta)/\lambda = 0.01–0.2 \text{ Å}^{-1}$). Differential cross-section $I (\text{cm}^{-1})$, that arises from elastic X-ray scattering, was obtained after background subtraction and normalization using constant scattering from water.

The magnetic measurements were carried out in a Quantum Design superconducting quantum interference device (SQUID, a RN3M [8] facility) in the range 3–350 K.

### 3. Results and discussion

ME spectra and XRD of the three MHA are quite similar. Each ME spectra consists of a broad doublet. Best fits were obtained using a Voigtian line shape (Gaussian distribution of Lorentzian lines). The mean values of the fitted hyperfine parameters (splitting $a = 0.91(3) \text{ mm/s}$ and isomer shift $\delta_{Fe} = 0.36(2) \text{ mm/s}$) are consistent with those reported for superparamagnetic $\gamma$-Fe2O3 [9] but different from those of super paramagnetic magnetite [10]. HR-TEM images show the presence of spherically like nanoparticles. In Fig. 1 crystalline planes are seen in a 10 nm size particle proving that the magnetic particles are well formed and crystalline. XRD patterns display a broad reflection ($\{220\}$ at 5.5°) line at 20 = 23° originated from the amorphous silica matrix. No reflection lines from Fe oxide phase were recorded suggesting that particle size must be much smaller than that obtained when this synthetic procedure is performed without MTMS. Results are consistent with the presence of a single magnetic phase $\gamma$-Fe2O3, and with previous and more extended phase identification in hydrophilic aerogels [5,12].

SAXS data (Fig. 2) generally give information on three main features of the aerogel structure: the mean size of the clusters ($\zeta$), which are connected to form the network, the mean size of the primary particles ($a$), which stick together to build the cluster and the fractal dimension $D_f$, which expresses the clusters compactness. We choose the Beaucage unified function [11] to fit the data because only one crossover $q_c$, related to the inverse of $\zeta$, appears in our data range. $q_c$ crossover is lost due to very small primary particles. Using this function with $G_c=B_c=0$, the gyration radius $R_g$ and $R_{sub}$ are related to $\zeta$ and $a$ through ($\zeta, a$) = (5/2)$^{1/2}$ ($R_g, R_{sub}$). Usually $R_{sub} = R_g$ and $p = D_f$ (1 $\leq p < 3$) for a typical mass fractal, and $p = D_c - 6$ (3 $\leq p < 4$) for surface fractals [7]. Our data is consistent with a mass fractal structure built from primary particles smaller than 1.6 nm radius. Results from best fits are summarized in Table 1.

SSA of 698 m2/g, 690 m2/g and 311 m2/g and mean pore diameter $\phi$ of 5 nm, 9 nm and 2 nm were measured by BET on J4, J0 and X-J4. $\phi$ values are quite low indicating a large amount of microporosity besides mesoporosity, in agreement with SAXS $D_f$ values, indicating large degree of compactness.

Magnetization temperature dependence, under zero-field cooling (ZFC) and field-cooling (FC) conditions, for an applied dc-field of 50 Oe, is shown in Fig. 3. $M_{ZFC}(T)$ curves show maxima at $T_m$=41, 40 and 33 K for J2, J3 and J4, respectively, reflecting the transition from the blocked state to the superparamagnetic equilibrium one. Thermo remnant magnetization TRM was recorded for J3, and $M_{RC} - M_{ZFC} \approx M_{TRM}$ condition essentially holds, as it is expected for a non interacting assembly of magnetic moments.
The close coincidence of the ZFC peak and the onset of the irreversibility ($T_i$) between the ZFC and FC magnetization curves allow us to exclude a large extent of particle aggregation or large size distributions for J4 ($\Delta T = T_i - T_m = 6$ K), which is consistent with the TEM characterization (see Fig. 1). For J2 and J3, $\Delta T$ values are equal to 39 and 35 K.

For these DC magnetization measurements the observation time is $\tau_{\text{obs}} = 10^2$ s, then the Néel-Brown model leads to $K_{\text{eff}} V = 27.6 K \tau_{\text{obs}}$, where $K_{\text{eff}}$ is the effective anisotropy constant. Assuming $K_{\text{eff}} \approx 10^5$ J/m$^3$, deduced from a previous ac dynamic study of $\gamma$-Fe$_2$O$_3$ hosted in hydrophilic aerogels [12], MN diameters $d_{\text{MN}} \approx 7$, 7 and 6 nm are derived for J2, J3 and J4.

$M$ vs. $H$ measurements at 300 K are reported in Fig. 4. They show superparamagnetic (SPM) behavior for all the specimens. To model these curves a convolution between a Langevin function and a superparamagnetic (SPM) behavior for all the specimens. To model these curves a convolution between a Langevin function and a superparamagnetic (SPM) behavior for all the specimens.

At 5 K, well below $T_{\text{irr}}$ a hysteretic behavior is observed and the magnetization measured up to 7 T, never reaches saturation. $\chi_p$ values listed in Table 1 are consistent with the hysteresis loop recorded at 5 K. Ferromagnetism is a cooperative phenomenon, which exists only in sufficiently multi-atomic clusters. The minimum size down to which a particle remains with noticeable magnetization was estimated in [13]. For $d < 2$ nm, within a core-shell magnetic structure model, almost all atoms lay in the particle surface shell.

### 4. Conclusions

Hydrophobic magnetic aerogels were produced. The nanoparticles were held inside aerogels, showing a backbone structure consistent with a mass fractal built of primary particles of radii $\sim 1$ nm.

The system behaves as a collection of non interacting $\gamma$-Fe$_2$O$_3$ particles of 6–7 nm with ferrimagnetic or weak ferromagnetic ordered cores and magnetically non-ordered shells. They exhibit blocked to superparamagnetic regimes low transition temperatures, small magnetic moments, significant low temperature coercivities and no magnetic saturation under external magnetic fields of up to 7 T. This behavior may be related to the presence of very small particles, less than 2 nm in diameter for which no magnetic order is expected, of non magnetically ordered surface spins in larger particles, and to the reduction of the Fe average magnetic moment inside the magnetically ordered cores.

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### References