ULTRA-LIGHT SOL-GEL DERIVED MAGNETIC NANOSTRUCTURED MATERIALS

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Abstract. Monolithic ultra-porous and ultra-light magnetic nanocomposites can be obtained by impregnating the pores of silica matrices formed by sol-gel processing, with anhydrous metal salts precursors, followed by the supercritical drying at high pressure. The crystalline phases identified by X-ray diffraction consist of metallic Ni, iron oxide spinel and Ni-ferrite, respectively.

Key words: sol-gel, nanocomposites, superparamagnetic behaviour.

1. INTRODUCTION

Magnetic particles with sizes in the nanometer scale are now of interest because of their many technological applications and unique magnetic properties which differ considerably from those of bulk materials.

Below a critical size, magnetic particles become single domain in contrast with the usual multidomain structure of the bulk magnetic materials exhibiting unique phenomena such as superparamagnetism [1] and quantum tunneling of the magnetization [2]. Magnetic nanoparticle systems exhibiting superparamagnetic behavior, display little or no remanence and coercivity while keeping a very high saturation magnetization. They have potential application in biomedicine [3-4], magnetic drug delivery and cell-sorting systems [5-6] or in magnetic refrigeration technology [7].

The confinement of nanoparticles can be achieved by using a porous matrix prepared by sol-gel process as a host. The porous amorphous matrices, within which nanostructures are developed, play an active role in determining their physical properties in addition to providing a means of particle dispersion [8]. Another important characteristic of the matrix is to act as protection of metallic

nanoparticles against air-oxidation; such is the case of metallic nickel by encapsulating them in inert matrices as graphite [9], fullerene [10] or in oxide-type matrices like zeolites [11], alumina [12-13][238], titanium dioxide [14] or silica ones [15].

Magnetic nanoparticles of Ni-ferrite have been produced in a variety of matrix materials like polystyrene [16], or silica [17], for instance.

Usually, the metal cationic species are embedded inside the pores of the silica polymeric matrix, either by *in situ* sol-gel synthesis [18] or by impregnation of mesoporous silica gels [19], in both cases using as precursors and/or desired metal salts. The resulted silica gels obtained by sol-gel hydrolysis-condensation reactions are highly porous. To preserve the high porosity, supercritical evacuation of the solvent contained in the pores is employed, in order to avoid the collapsing of gel pores. The resulted materials, named *aerogels,* are characterized by low density, very high surface area, low refractive index and low sound velocity [20]. It was reported that after supercritical drying, the resulted aerogels contain ionic or amorphous species [21], and usually to obtain the targeted metallic or oxide phases, a subsequent controlled thermal treatment often at high temperatures (500-1000°C) was required [22].

Despite the growing interest in magnetic nanoparticles, by literature survey, relatively few studies concerning aerogel nanocomposites magnetic behaviour [21, 23-30] were found. Iron oxide nanoparticles systems particularly present interesting properties with applications in several fields [31-35].

Recently, we have reported a study regarding the synthesis and characterization of iron oxide/silica aerogels with superparamagnetic behaviour [36]. The acid catalyzed sol-gel process synthesis, and impregnation followed by supercritical drying in ethanol was used in this case.

In the present study, wet silica gels were prepared in a two step acid-base catalyzed sol-gel process, using hydrochloric acid and ammonia, respectively. Subsequently, the silica gels were impregnated with two anhydrous metal (Fe(II), Ni(II)) salts, followed by supercritical drying process. The magnetic nanocomposites were directly obtained after the supercritical drying.

2. EXPERIMENTAL

Silica wet gels were prepared by hydrolysis and condensation of tetraethoxysilane (TEOS) (Aldrich 98%) using two step acid-base catalyzed sol-gel process (hydrochloric acid and ammonia as catalysts, respectively). In the first step, prepolymerized tetraethoxysilane was obtained by the reaction of TEOS in the presence of a sub-stoichiometric amount of water and acid catalyst (HCl 1 M)

ethanol solution. After one month at -25°C a viscous fluid was obtained. In the second step (basic medium) a 0.05 M NH_3 aqueous solution was added to the acid sol. After 48 h the gelation of the matrix samples, denoted TE1AB, occurred. Subsequently, the liquid contained in the pores of the silica gels was exchanged with ethanol. Two samples were obtained by the impregnation of silica gels using supersaturated alcoholic solutions of anhydrous Ni(II) acetylacetonate (Aldrich 95%) or anhydrous Fe(II) acetylacetonate (Aldrich 99.95%). A third type of sample was obtained by simultaneous impregnation of silica gels with both Ni(II) and Fe(II) alcoholic solutions. The impregnated gels samples are referred TE1ABNi (nickel containing gels), TE1ABFe (iron containing gels) and TE1ABNiFe (iron and nickel containing gels). Supercritical drying of the impregnated gels was realised in ethanol supercritical conditions, at 260 °C and a maximum pressure of 131 bars. After three hours, at the end of the supercritical treatment, the pressure in the autoclave was carefully relieved at nearly constant temperature. The obtained aerogels were left to slowly cool down to ambient temperature. No further thermal treatment was carried out. The resulted aerogels preserved the same monolithic shape as the wet gels, but they displayed a slightly diminished volume.

The as-synthesized samples were characterized by X-ray diffraction (XRD) with a D5000 Siemens X-ray powder diffractometer using CuK_α incident radiation (λ = 1.5406 Å). Diffraction patterns were recorded from 10° to 80° with a step size of 0.1° and a scanning rate of 15 s per step. Transmission electron microscopy (TEM) observations were performed using a Philips CM 30 microscope operating at 300 keV. For the microscopy analyses the samples were crushed, ultrasonically dispersed in ethanol and subsequently deposited onto a copper grid. Nitrogen adsorption data were taken at 77 K using an ASAP 2000 surface area analyzer (Micromeritics Instrument Corp.) after heating the samples at 180 °C under vacuum for 24 h to remove the adsorbed species. Surface area determinations were carried out following the BET (Brunauer-Emmett-Teller) method. Hysteresis loops were measured at room temperature by means of a vibrating sample magnetometer (VSM) with a maximum applied field of 1 T.

3. RESULTS AND DISCUSSION

The aerogel slabs obtained by impregnation method are lightweight monoliths with grey-black color (TE1ABNi sample), brownish-black color (TE1ABFe sample) and black color (TE1ABNiFe sample), respectively. The bulk density of the aerogel was determined by measuring the weight and the volume of the sample, being characterized by very low densities and high surface areas with comparable values (Table 1).

Table 1

Summary of aerogel textural characterization

Sample	Bulk density [g/cm³]	Surface area BET [m²/g]	Dparticles (TEM) (nm)
TE1AB (SiO$_2$)	0.05	957	-
TE1ABNi (Ni-SiO$_2$)	0.06	857	14 ± 2
TE1ABFe (Fe$_2$O$_3$/Fe$_3$O$_4$-SiO$_2$)	0.06	817	8 ± 1
TE1ABNiFe (NiFe$_2$O$_4$-SiO$_2$)	0.06	-	10 ± 4

In the case of silica aerogel matrix (Fig. 1a) and Ni aerogel nanocomposite sample (Fig. 1b), the both obtained N$_2$ adsorption/desorption isotherms can be associated to Type IV [37], indicating that the porous structure (Fig. 1c and Fig. 1d) is mainly situated in the mesoporous range.
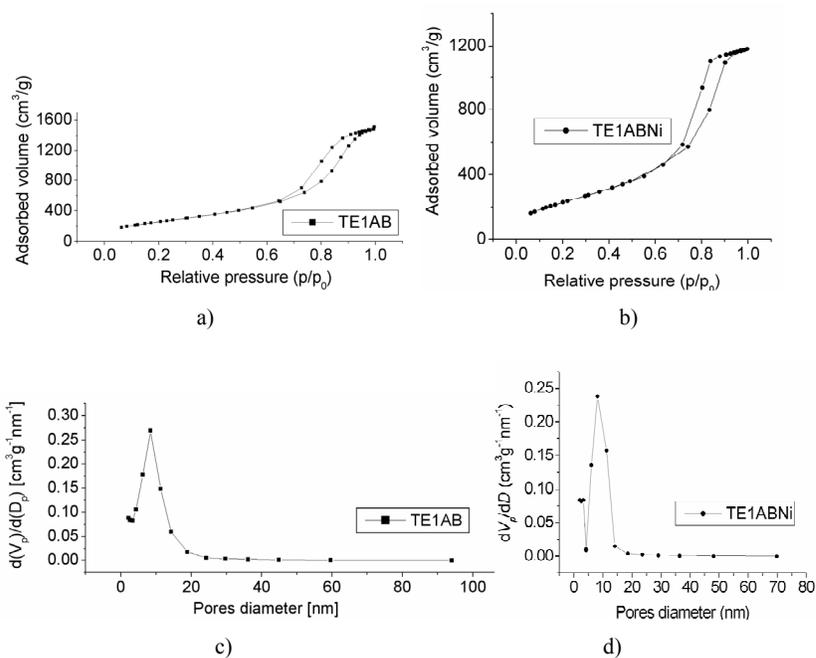

Fig. 1 – Nitrogen adsorption-desorption isotherms and pore size distribution.

X-ray powder diffraction patterns of the samples were recorded in order to identify the crystalline phase formed in the nanocomposites. At small 2θ angles, the baseline presents a broad maximum around 22-24°, which corresponds to an amorphous signal of the silica matrix. In the case of TE1ABNi XRD pattern,

(Fig. 2a), the four observed peaks corresponding to Miller indices (111), (200), (220) and (311) was assigned metallic nickel face-centered cubic type (Fm3m space group) (JCPDS 4-850) [38]. No nickel oxide signals appeared in the XRD pattern. The main diffraction lines observed in TE1ABFe X-ray diffraction pattern, (Fig. 3a) are attributable, without any doubt, to a cubic iron oxide spinel phase. But, at this point, one cannot make any accurate distinction between maghemite or magnetite phases. Further investigations, as Mössbauer spectroscopy and electron diffraction (data not shown), have proved that the identified iron oxide spinel phase is γ-Fe_2O_3. The XRD experimental pattern of the TE1ABNiFe nanocompozite aerogel sample derived from silica gel impregnated with both Fe and Ni precursors (Fig. 4a) shows that beside spinel nickel ferrite lines also metallic nickel diffraction features are present. In transmission electron microscopy (TEM images) (Figs. 2b, 3b and 4b, respectively) well defined spherical particles, which are relatively homogeneously dispersed in the silica matrix, were observed. The particles average diameter values of the synthesized aerogel samples are also given in Table 1.
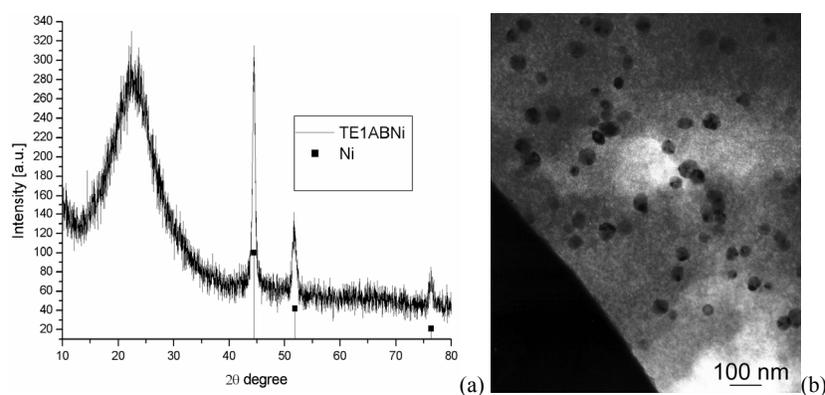

(a)   (b)

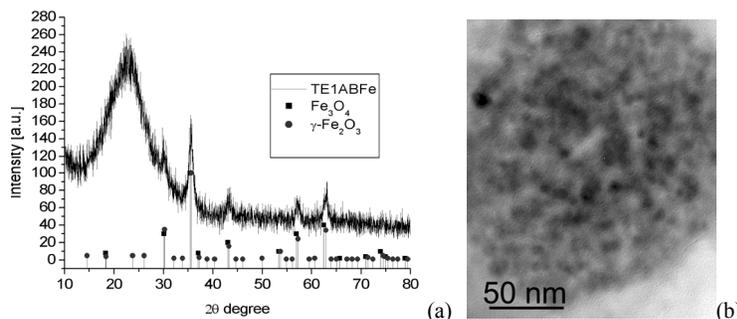Fig. 2 – X-ray diffraction (a) and TEM photograph (b) of the TE1ABNi aerogel.

(a)   (b)

Fig. 3 – X-ray diffraction (a) and TEM photograph (b) of the TE1ABFe aerogel.

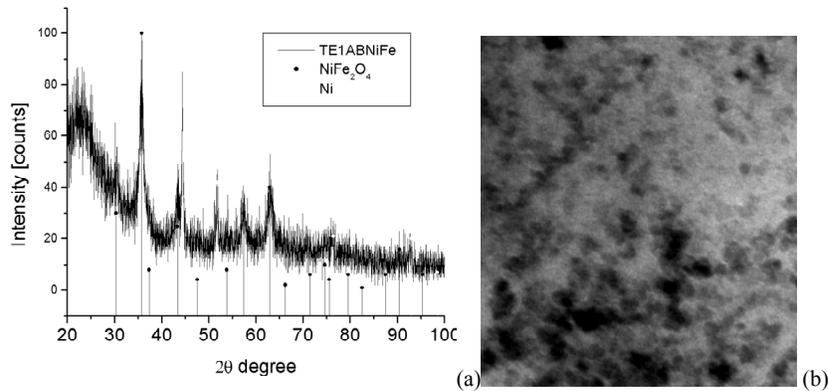(a)   (b)

Fig. 4 – X-ray diffraction (a) and TEM photograph (b) of the TE1ABFe aerogel.

In Figs. 5, 6 and 7 respectively, the ambient temperature magnetization curves of the TE1ABNi, TE1ABFe and TE1ABNiFe aerogel nanocomposite samples, are shown.

The VSM measurements, at room temperature, indicate that the TE1ABNi aerogel nanocomposite sample exhibits ferromagnetic behavior with characteristic parameters as saturation magnetization (M_s) of 2.84 emu/g and coercivity (H_c) of 100 Oe. Taking into account that the nanocomposite sample contains 6 wt. % Ni, the calculated value of the saturation magnetization of Ni was 47.3 emu/g, that is nearby the reported bulk saturation magnetization of Ni (55.4 emu/g) [39]. This value is also comparable with another evaluated value for a nickel nanoparticles system having similar nanoparticles dimensional range [40].
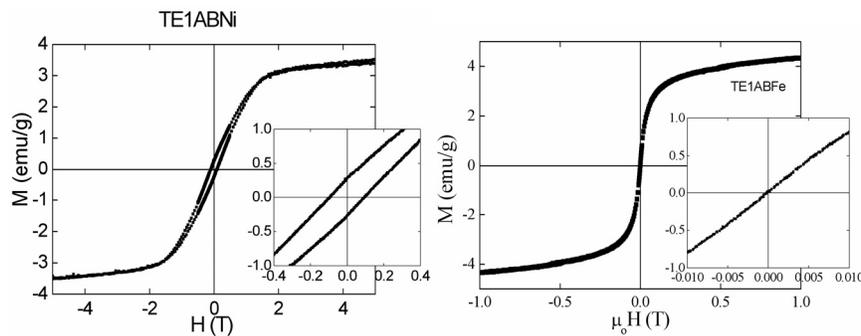

Fig. 5 – VSM magnetization curve of TE1ABNi aerogel.

The TE1ABFe sample magnetic measurement resulted in a saturation magnetization value of 3.8 emu/g and zero coercivity that confirms a superparamagnetic behavior at room temperature of the obtained nanocomposite.

The calculated saturation magnetization corresponding to γ-Fe_2O_3 concentration in the nanocomposite sample has a value of 44.3 emu/g (which is higher than those reported for maghemite nanoparticles systems of similar sizes, prepared by different other routes) [31, 41].

As shown in Fig. 6, TE1ABNiFe aerogel nanocomposite sample displays mainly superparamagnetic behavior at room temperature with a very low coercivity value (25 Oe).
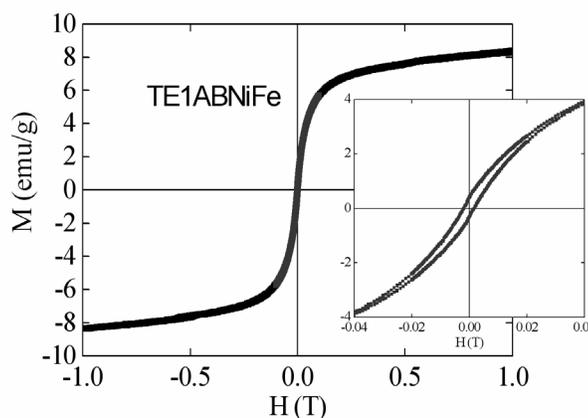

Fig. 6 – VSM magnetization curve of TE1ABNiFe aerogel.

4. CONCLUSIONS

A two step acid-base catalysed sol-gel processing resulted in formation of monolithic silica gels. After impregnation with metallic (Ni^{2+}, Fe^{2+}) ethanol solution and evacuation of solvent in supercritical conditions, monolithic aerogel nanocomposites were directly obtained. No further post-annealing treatments were required to obtain crystalline phases. These phases are: face-centered cubic metallic nickel (in Ni/silica aerogel nanocomposite sample), cubic γ-Fe_2O_3 (in Fe/silica aerogel nanocomposite sample), as well as cubic spinel nickel ferrite along metallic nickel (in (Ni,Fe)/silica aerogel nanocomposite sample).

Metallic oxide/silica aerogel nanocomposite samples (either maghemite or nickel ferrite) presented superparamagnetic behaviour at room temperature, with zero coercive field (in the case of γ-Fe_2O_3) and very low coercivity (25 Oe in the case of nickel ferrite).

Ni/silica aerogel nanocompozite sample (6 wt. % Ni) exhibited room temperature ferromagnetic magnetic properties. The obtained value of the

saturation magnetization, 47.3 emu/g, is comparable with both reported values of nickel bulk and nickel nanoparticle similar systems.

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