Synthesis and characterization of core–shell structure silica-coated Fe_{29.5}Ni_{70.5} nanoparticles

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Abstract

In view of potential applications of magnetic particles in biomedicine and electromagnetic devices, we made use of the classical Stöber method—base-catalyzed hydrolysis and condensation of tetraethoxysilane (TEOS)—to encapsulate FeNi nanoparticles within a silica shell. An original stirring system under high power ultrasound made it possible to disperse the otherwise agglomerated particles. Sonication guaranteed particles remained dispersed during the Stöber synthesis and also improved the efficiency of the method. The coated particles are characterized by electron microscopy (TEM) and spectroscopy (EDX) showing a core–shell structure with a uniform layer of silica. Silica coating does not affect the core magnetic properties. Indeed, all samples are ferromagnetic at 77 K and room temperature and the Curie point remains unchanged. Only the coercive force shows an unexpected non-monotonic dependence on silica layer thickness.

1. Introduction

Magnetic-metal nanoparticles encapsulated in a dielectric inorganic material are considered to have practical applications in electromagnetic devices, biology and fundamental studies to improve the local physical investigation of magnetic nanostructures. In the core–shell structure, the core size-dependent magnetic susceptibility at room temperature, combined with the chemical stability of the silica coatings, suggests that the resulting nanocomposite may be a good candidate for biomedical applications, such as magnetic separation, drug targeting, image contrast in magnetic resonance imaging and hyperthermia therapy [1–3]. Magnetic fluids dedicated for clinical applications are typically colloidal suspensions of iron, magnetite, iron–nickel and cobalt nanoparticles coated with biocompatible surfactants [4]. Actually, there are two fundamental criteria to prevent the catalysis of damaging reactions within cells: the reduction of the toxicity of the vector conveying the solution due to its oxidative alteration and its chemical time stability. Accordingly, the silica coating of magnetic nanoparticles is one of several promising tools to ensure this specific biocompatibility and leads to low toxicity material.

Magnetic–dielectric nanocomposites have also attracted sustained interest over one century owing to their unusual combined magnetic and electric properties. In fact, due to their metallic nature, eddy currents limit application of magnetic nanoparticles at high frequency. The coating by an insulating shell on the surface of soft magnetic nanoparticle cores such as FeNi confines to the material a high permeability independent of the frequency, even in the gigahertz range [5, 6]. Such materials are typically suited for applications in telecommunications [7]. On the other hand, the ability to control magnetic interactions is an important
consequence of the coating of magnetic particles, which has been explored in detail by several authors for particles in solution [8] and close-packed thin films [9]. Coating thickness controls both insulation of nanoparticles and interparticle distance and, therefore, the interparticle interactions [10, 11]. This provided substantially reliable results to study magnetic nanostructure of nanoparticles using electron holography [12].

Several synthetic routes for producing magnetic nanoparticles have been explored during the last decade including chemical vapour condensation (CPVD), powder pyrolysis and sonochemical synthesis [13–15]. However, nanoparticles synthesized by these methods frequently display a relatively poor crystallinity or polydispersity in their shape and/or size, which affects their magnetic properties. The evaporation–cryo-condensation process has been developed to overcome some of these problems. In the present work, cryogenic melting has been used to produce Fe29.5Ni70.5 nanoparticles and consequently to guarantee more crystallinity and a better stability in the elemental chemical composition. Additionally, several approaches, such as the sol–gel process [16], co-precipitation [17–19], metal–dielectric co-sputtering deposition [20] or metal ion deposition, have been used to prepare magnetic-insulator nanocomposites. Our present approach is to start from metallic nanoparticles and to coat them with an inorganic-dielectric polymer in order to control the morphology of the shell. In this paper, a modified Stöber approach has been used to encapsulate in silica the as-prepared metallic FeNi particles. In fact, we have introduced high-power sonochemistry not only in the dispersion step, but also during the synthesis to improve the effectiveness of the classical Stöber method [21, 22].

2. Experimental details

2.1. Synthesis of Fe29.5Ni70.5 nanoparticles

FeNi nanoparticles with well-defined morphology and homogeneous chemical composition were synthesized using the cryogenic melting technique. This method consists in sliding down a feeding bar of metal (Fe29.5Ni70.5) into a radio frequency (RF) reactor. A drop of molten metal forms at the edge and falls onto the inductors where it is levitated to complete the transformation into nanocrystalline powder. In order to have sufficient vapour pressure, the metal must be heated to several hundred degrees above its melting temperature (over 2000 °C for Fe and Ni). The size of particle depends critically on the metal vapour pressure. The gas produced from the cryogenic liquid carries the particles into a canvas filter. Technical details are reported in [23, 24]. The as-obtained iron–nickel nanopowders are composed of spherical particles with an average diameter of about 50 nm [25]. From electron energy loss spectroscopy (EELS) the chemical composition is homogeneous from one particle to another as well as inside the nanoparticles. The fraction of iron, x = 0.295, is of particular interest since large amounts can be produced with no deviation in chemical composition [25]. Because metallic nanoparticles are pyrophoric in air, they are collected in hexane where an oxide layer of approximately 2 nm forms, making possible their manipulation without risk. The magnetization of as-prepared iron–nickel particles (75 A m kg−1) is 20% lower compared to the bulk alloy magnetization, which confirms the non-magnetic nature of the oxide layer observed from electron microscopy and analysed using XPS (x-ray photoemission spectroscopy). Essentially nickel hydroxides Ni(OH)2 and Ni(OH)3, iron oxide Fe2O3 and FeO were detected [25].

2.2. Synthesis of silica-coated Fe29.5Ni70.5 nanoparticles

The silica shell onto FeNi core was synthesized according to the Stöber method [26] (sol–gel reaction) without any silane coupling agent (like 3-aminopropyltrimethoxysilane which is sometimes used for noble metal nanoparticles’ silica coating [27]).

Ethanol (95–96% synthesis grade) and ammonia solution (28% analytical grade) were purchased from SDS/CARLO ERBA, tetraethylorthosilicate (TEOS) ≥98% (GC) from FLUKA. All reagents were used as received without further purification.

Ultrasonic dispersion was carried out with a Bandelin 200 W (variable from 10 to 100%) ultrasonic processor (Sonopuls HD 2200) fitted out with a horn of 13 mm × 3 mm. All experiments were made in a glass flask equipped with a cooling jacket to keep the mixture temperature constant.

Typically, 80 mg of raw Fe29.5Ni70.5 nanoparticles were first sonicated in 50 ml of ethanol during 90 min under a controlled ultrasonic power of 3 W cm−3. Then, various volumes of TEOS and ammonia 28% (NH4OH) were successively introduced into the suspension and the mixture was again sonicated for 90 min under a power of 0.5 W cm−3 to complete the sol–gel reaction (figure 1). Finally the suspensions are centrifuged at 3000 rpm for 10 min, the solvent is discarded and the FeNi nanoparticles are ultrasonically dispersed in 50 ml of ethanol. This purification process (centrifugation/dispersion under sonication) was repeated three times. The particles were then transferred into ethanol to avoid any further growth or chemical modification of the silica layer. Subsequently, an amount of the coated nanoparticles was dried under reduced pressure and moderate temperature
to remove the remaining solvent and to prepare samples for the physical characterization. Four samples with different reagent concentrations have been produced (see table 1).

The oxide shell covering FeNi nanoparticles is expected to enhance the SiO₂ shell binding. Indeed, the oxides are mainly formed of nickel hydroxides, Ni(OOH) and Ni(OH)₂, which present an isoelectric point (pH point of zero charge) in the range of 11–12 [28]. Our sol–gel reaction is carried out in ammonia as catalyst (pH = 8); consequently the oxide shell is charged positively and thus facilitates its grafting with the silicate complexes carrying a negative charge after the nucleophilic substitution.

### 2.3. Characterization and techniques

Thermal degradation analyses were made with a Perkin-Elmer Pyris 6-TGA instrument using standard ceramic crucibles and sample mass of 1–29 mg. The samples were heated at a rate of 10 °C min⁻¹ from room temperature to 1000 °C in an air flow of 10 ml min⁻¹ or an argon flow of 80 ml min⁻¹. The analyser was coupled to a permanent magnet producing a gradient field in the crucible to measure the Curie temperature (Tₘ). Our sol–gel reaction is carried out in ammonia as catalyst (pH = 8); consequently the oxide shell is charged positively and thus facilitates its grafting with the silicate complexes carrying a negative charge after the nucleophilic substitution.

### Table 1. Summary of the FeNi@SiO₂ synthesis, presenting the various volumes of reagents used. The silica-layer thickness was estimated using HRTEM analysis (tTEM) and magnetic investigation (tMAG).

| Sample | TEOS (μl) | NH₄OH (ml) | tTEM (nm) | tMAG (nm) |
|--------|-----------|------------|-----------|-----------|
| Sample 1 | 0         | 0          | 0         | 0         |
| Sample 2 | 50        | 0.35       | 3         | 4         |
| Sample 3 | 100       | 0.7        | 8         | 9         |
| Sample 4 | 200       | 1.4        | 15        | 17        |
| Sample 5 | 500       | 3.5        | 33        | 24        |

* Maximum error for TEM analysis.

3. Results and discussion

Fourier transform infrared (FTIR) spectroscopy was used to identify the functional groups present on the surface of FeNi@SiO₂ nanoparticles. Comparison of uncoated and silica-coated particles’ FTIR spectra (figure 2) shows a pronounced change detected in the 1300–700 cm⁻¹ region, which clearly indicates the presence of the silica coating. The peaks at 970 and 1070 cm⁻¹ correspond to the characteristic Si–O–Si bond, typically attributed to the Si–O⁻ symmetric stretching and Si–O–Si asymmetric stretching, respectively, in agreement with [29]. Analysis of bonding configurations from FTIR data suggests also the existence of Si–O–C and/or Si–O–Si= functions (bands under 1000 cm⁻¹). Nevertheless, the spectra are obviously dominated by the Si–O–Si bond vibrations, for all coated samples. The presence of this type of strained bond is clear evidence of the mechanical stress in the silica sheath, which in turn may strain the FeNi nanoparticles.

The chemical composition was examined using energy-dispersive x-ray (EDX) spectroscopy, which shows a Fe₂₉.₃Ni₇₀.₇ core coated by silica shell (figure 3). The copper lines in this figure are due to the copper grid used as TEM sample holder. An atomic ratio of Si/O = 1/0.6 was obtained on the core–shell structure, indicating that the off-stoichiometric silica shell is silicon-rich in nature. The structural evolution study suggests that the silica layer grows without affecting the integrity of the FeNi core. Indeed, the spectra do not reveal other elements except those present initially in the FeNi core, the oxide layer, the silica shell and the copper grid.

Figure 4(b) illustrates the statistical size distribution of the as-prepared FeNi nanoparticles deduced from local TEM investigations of an assembly of particles shown in figure 4(a). The study was done by manual counting of about 180 particles and we obtained typically a lognormal distribution commonly observed for particles prepared by gas condensation.
Figure 3. In the lower inset is the EDX spectrum of Fe$_{29.5}$Ni$_{70.5}$ core-free nanoparticles. In the upper inset is the EDX spectrum of silica portion of FeNi@SiO$_2$ nanoparticles when the beam was focused on silica edges.

Figure 4. Representative transmission electron micrographs of (a) an assembly of as-prepared Fe$_{29.5}$Ni$_{70.5}$ nanoparticles and (c) an assembly of silica-coated FeNi particles corresponding to sample 4. (b) Statistical particle size histogram deduced from TEM image (a). The dots correspond to a lognormal distribution calculated from the experimental data.

techniques [30]. The mean particle size is around 50 nm and the standard deviation is about 25 nm. Interestingly, more than 35% of the particles are of sizes between 40 and 55 nm. Figure 5(c) exhibits a TEM picture of a group of silica-coated FeNi nanoparticles corresponding to sample 4. The uniformity of the silica layer is confirmed and the covering is homogeneously present on the surface of the majority of nanoparticles.

Figure 5 shows TEM pictures of FeNi@SiO$_2$ particles synthesized using various TEOS volumes. Observation of figure 5 images (a)–(d) clearly shows the shell thickness dependence on TEOS concentration (see also table 1). Additionally energy filtered in scanning TEM mode, which one can see as an illustration in the inset (f) of figure 5, comes to support the elementary chemical nature of the silica layer surrounding the nanoparticles. In fact, the image exhibits a chemical cartography obtained from EELS and undeniably shows the formation of silica uniformly on the FeNi core.

The properties of oxidation resistance of the FeNi@SiO$_2$ composite were tested by TGA. Figure 6 shows the typical curves of thermal analysis of metallic materials [31]. Correspondingly, the weight increment of the coated particles (sample 5) caused by FeNi oxidation decreased from 28% to 5% relative to that of the uncoated FeNi particles (sample 1). It is clear that a thicker shell of silica can protect the nickel–iron from oxidation more efficiently. For instance the oxidation of the FeNi core of FeNi@SiO$_2$ composites (sample 4) proceeds at $\sim$430 $^\circ$C, which is 250 $^\circ$C higher than for as-prepared FeNi nanoparticles. The weight loss, observed for coated samples starting from RT, is attributed to the surface dehydration of the silica monolayer and the loss of other organic compounds which are volatile in this range of temperature [32].

For many applications of core–shell particles, such as electromagnetic devices, it is of essential importance to control precisely the thickness of the shell. In the system under
Figure 5. ((a)–(d)) Example of local transmission electron analysis of the silica-coated FeNi nanoparticles corresponding, respectively, to samples 1, 2, 4 and 5. (e) HRTEM pattern for the FeNi@SiO$_2$ (sample 4) which shows the presence of a 15 nm thick silica layer lying at the particle surface. (f) Typical EFTEM analysis using metallic silicon as the silica source (Si K-edge), which displays the chemical cartography showing a silica-rich shell (sample 4).

Figure 6. Thermal gravimetric curves (TGA) of FeNi@SiO$_2$ nanocomposites (samples 1–5) under air flow. Thermal nanopowder alteration obviously depends on the amount of silica in the sample.

Figure 7. Plot of silica-layer thickness as a function of various volume of precursor TEOS, estimated from HRTEM analysis ($t_{TEM}$) and magnetic characterization ($t_{MAG}$) (see also table 1).

consideration, the simplest approach to vary shell thickness is to use different amounts of TEOS. Consequently, we investigate the effect of adding various amounts of TEOS in a single step. Figure 5(e), which features a typical high resolution image (HRTEM) for sample 4, reveals a core–shell structure with a uniform amorphous silica coating (thickness 15 nm). For comparison, the thickness of the silica shell is deduced from magnetic characterization. In fact, the volume of SiO$_2$ can be estimated using

$$V_{SiO_2} = \frac{m_{SiO_2}}{\rho_{SiO_2}} = \frac{m_{Coated}}{\rho_{SiO_2}} (1 - \frac{M_{s(\text{Coated})}}{M_{s(\text{Free})}})$$

where $V$ and $m$ are for volume and weight, respectively, $\rho_{SiO_2}$ is the silica density estimated experimentally (2270 kg m$^{-3}$) and $M_s$ (A m$^2$ kg$^{-1}$) is the specific magnetic moment at saturation; ‘coated’ indicates the coated sample, and ‘free’ corresponds to the raw FeNi powder.

Assuming that the nanoparticles are monodisperse and 50 nm in diameter, the theoretical thickness $t_{MAG}$ required to increase the radius $R$ of the seed particle to a final radius $R + t_{MAG}$ is given by [33]

$$t_{MAG} = R \left( \sqrt{\frac{V_{SiO_2} \rho_{FeNi}}{m_{FeNi}} + 1} - 1 \right)$$

where $m_{FeNi} = m_{Coated} - m_{SiO_2}$ is the weight of the effective magnetic component in the nanocomposite. The bulk Fe$_{29.5}$Ni$_{70.5}$ density was used (8450 kg m$^{-3}$ [34]).

Figure 7 shows the dependence of the thickness of the silica shell, deduced from TEM analysis and magnetic measurements, on TEOS volume. Interestingly, the two data are consistent with a quantitative silica formation on the nanoparticles for thin silica layer up to 20 nm. Above this limit $t_{MAG}$ presents a discrepancy compared to $t_{TEM}$ for a thicker silica layer (beyond 20 nm). This could be explained by the presence of free silica nanoparticles synthesized when a large amount of TEOS is added. After centrifugation, the calculated volumic amount of silica coating the nanoparticles is underrated and therefore, the deduced silica-shell thickness is erroneous.
Figure 8. Thermal gravimetric curves (TGA) of FeNi@SiO$_2$ nanocomposites (samples 1–5) under argon flow. See table 2 for Curie temperatures assessed from curves.

4. Magnetic properties

The TGA recordings under constant magnetic field are presented in figure 8. Due to the neutral atmosphere (argon flow), oxidation was inhibited. Up to 600 °C we observe a weak weight drop due to a chemical desorption from the silica shell for coated particles as reported in [32]. Comparable weight loss is observed for uncoated sample 1 due to the desorption of organic chains adsorbed in the oxidized FeNi surface during the passivation step of the nanoparticles. The TGA traces show a characteristic feature for all samples, which reveals a typical ferromagnetic-to-paramagnetic transition at the Curie temperature ($T_c$). Noticeably, the nanocomposites (samples 2–5) exhibit a broader transition. Obviously, this makes difficult the extraction of $T_c$, which roughly maintains a stable value of 605 °C (±5 °C) for all samples in agreement with the literature [35].

Table 2. Magnetic properties for uncoated FeNi (sample 1) and silica-coated FeNi (samples 2–5) nanoparticles. $M_s$ is the specific saturation magnetization, $M_r$ is the remanent magnetization, $T_c$ is the Curie temperature and $H_c$ is the coercive field.

| Sample   | $M_s$ (A m$^2$ kg$^{-1}$) | $M_r/M_s$ | $H_c$ (kA m$^{-1}$) | $T_c$ (°C) |
|----------|---------------------------|-----------|---------------------|-------------|
| 77 (K)   | 300 (K)                   | 300 (K)   | 300 (K)             | 77 (K)      |
| Sample 1 | 80 (K)                    | 0.32 (K)  | 33.9 (K)            | 598 (°C)    |
| Sample 2 | 72 (K)                    | 0.30 (K)  | 28.2 (K)            | 608 (°C)    |
| Sample 3 | 58 (K)                    | 0.26 (K)  | 28.8 (K)            | 607 (°C)    |
| Sample 4 | 40 (K)                    | 0.27 (K)  | 33.8 (K)            | 607 (°C)    |
| Sample 5 | 32 (K)                    | 0.28 (K)  | 34.3 (K)            | 607 (°C)    |

A comparative measurement of hysteresis loops at 300 K (RT) and 77 K was performed for both uncoated and silica-coated nanoparticles using VSM as mentioned previously. Magnetization curves are reported in figure 9 and the main quantities are listed in table 2 (specific saturation magnetization, remanent magnetization and coercivity at 77 K and RT). All curves at RT saturate approximately at the same applied field than those measured at 77 K. For the same operating temperature, loops for coated samples appear to have a component whose magnetization continues to increase with increasing field up to 200 kA m$^{-1}$, whereas the raw FeNi powder saturates much faster than the nanocomposites. In fact, the interparticle interactions are modulated by the thickness of the coating layer, which isolates the particles. As a result the nanocomposite hardens magnetically and its saturation becomes difficult [8, 20, 36]. For all samples there is only a slight deviation regarding the saturation magnetization between 77 K and RT because RT/$T_c$ ≈ 0.3. Furthermore, the coating quality is examined in saturation magnetization versus silica-layer thickness plots as an inset in figure 9 (right side). It is clearly seen that the specific magnetization decreases with increasing thickness of the silica shell. Accordingly the diamagnetic contribution of silica leads to a lower saturation magnetization than the core-free FeNi particles (table 2).

Figure 9. Magnetic quasi-static hysteresis loops for samples with various silica shells (samples 1–5). On the left, magnetization curves recorded at 300 K. The inset on the lower right corner illustrates the changes in the $M_s$ as a function of the silica-shell thickness. On the right the $M$–$H$ curves recorded at 77 K. The inset on the lower right corner illustrates the changes in the coercive field as a function of the silica-shell thickness.
The inset, left side of figure 9, illustrates the coercive field versus the thickness of the silica shell at 77 K and RT. Noticeably, the temperature dependence of coercivity indicates a slight increase for all samples when temperature decreases which is consistent with an increase of anisotropy, regardless of its origin. On the one hand, for randomly oriented nanoparticles with cubic anisotropy, the coercive field should be \( H_c \approx 0.64 K_I / J_I [37] \). If we consider the bulk Fe\(_{30}\)Ni\(_{30}\) magnetocrystalline anisotropy \( K_I \approx 700 \text{ J m}^{-3} [38] \) and the measured saturation magnetization \( J_s = 0.8 \text{ T} \), we find \( H_c \approx 560 \text{ A m}^{-1} \), which is in disagreement with the experimental coercivity. On the other hand, the morphology and size effect are believed to be the reason of high coercivity observed for all samples (22 kA m\(^{-1} \) \(< H_c \approx 32 \text{ kA m}^{-1}\), see table 2). According to the pioneering work of Néel [39], for soft magnetic nanoparticles a dissymmetry of some atomic layers is sufficient in order to make the contribution of demagnetizing field become dominant and to lead to an enhancement of the coercivity. The shape anisotropy effect is due to the asphericity of the nanoparticles below a critical size. The coercive field in an elongated single-domain particle is given by \( H_c = 2 K_I / J_s [40] \), where \( K_s = (N_b - N_a) J_s \) is the shape anisotropy. \( N_b \) and \( N_a \) represent the demagnetizing coefficients along the two axes of an ellipsoid of revolution [41]. For an asphericity \( 0.86 < \gamma < 1.14 \), \( N_a = \frac{1}{4} (\gamma - 2\gamma^2) \) and since \( N_a + 2N_b = 1 \) we find \( K_s = (\gamma - 1)J_s / 5\mu_0 \). Consequently, we deduce

\[
H_c = \frac{2(\gamma - 1)J_s}{5\mu_0}.
\]

If we assume a coercive field \( H_c = 33 \text{ kA m}^{-1} \), we find an asphericity of 13%. The result is consistent with TEM observations (figure 5(b)) where \( 0.80 < \gamma < 1.2 \) was found for spheroidal particles. In addition, the twins formed from sintered particles after collisions in the calefaction layer during the synthesis behave as elongated particles and yield to very high values of the asphericity \( \gamma \). Nevertheless, the presence of these particles is limited compared to almost spherical grains as illustrated in figure 4. The coercive field dependence on silica layer thickness shows a non-monotonic evolution. For a thin silica layer a sensitive drop in coercivity is observed followed by an increase before recovering the initial value. This is probably due to a competition between dipole–dipole interaction and magneto-elastic anisotropy. In the one hand, dipolar interactions are reduced as the distance between magnetic cores is increasing. On the other hand, it has been shown by FTIR the existence of stress in the silica shell. As the thickness of the shell increases, the stress experienced at the surface of FeNi nanoparticles is enhanced, yielding an increasing magneto-elastic anisotropy. These two contributions are balanced for a thickness of ~15 nm. Classically, for ultrafine nanoparticles (~10 nm or less) dispersed in non-magnetic material, anhysteretic loops are expected because of the superparamagnetic behaviour of the nanoparticles, as already reported [42, 43]. For the FeNi nanoparticles described in this paper, the shape anisotropy dominates the magnetocrystalline anisotropy \( (K_s = 20 \text{ kJ m}^{-3} \gg K_I) \) so the critical size for which the superparamagnetism is observed at room temperature is given by

\[
D_{\text{sp}} \approx \sqrt{\frac{150k_B T}{\pi K_s}} \approx 27 \text{ nm}
\]

compared with \( \sqrt{\frac{256k_B T}{\pi K_s}} \approx 72 \text{ nm} [44] \), where \( T \) is the measuring temperature and \( k_B \) is the Boltzmann constant. Considering the mean size of the nanoparticles (50 nm), this is in line with the hysteresis observed for all samples (figure 9). Because part of the particles is smaller than 27 nm and because some are nearly spheroidal \( (\gamma < 0.05) \) a superparamagnetic contribution is not excluded. Nevertheless, the superparamagnetism is blocked by the dipole–dipole interactions, which make the nanoparticles magnetically coupled and thus to behave like ferromagnetic particles [45]. Figure 4 shows the smallest FeNi particles, which tend to be arranged in chains, a signature of magnetostatic interactions. Another interesting feature is the remarkable stability of the squareness ratio regardless of temperature and coating (see table 2). The \( M_r / M_s \) ratio is noticeably lower than 0.5 predicted for single-domain particles according to Néel and Sizer [46, 47]. On the other hand, the particle size analysis (figure 4) shows that most of the nanoparticles are intermediate in size between the upper bound to single-domain behaviour and the lower critical size of multi-domain structure. Actually, we intend an incoherent mode of magnetization. Indeed, the low squareness value is typical of vortex-like magnetic structure composed of an out-of-plane uniformly magnetized core surrounded by a crown of curling spins [12]. Alternatively to a coherent rotation, the magnetization process consists initially into an irreversible switch of the vortex core followed by a screw-like rotation of the external curling spins [48].

5. Conclusions and perspectives

The preparation of silica-coated FeNi particles was successfully achieved by a combination of two original synthetic procedures, a cryogenic evaporation of master alloy Fe\(_{29.5}\)Ni\(_{30.5}\) to obtain nanoparticles with well-defined size and composition, and subsequently a modified classical Stöber method which permits us to encapsulate the latter within a silica shell. The coating can be accomplished through a direct, simple, one-step procedure. FTIR, EDX and EELS analysis are consistent with the presence of silica in the nanocomposites synthesized. Consequently, the silica-shell thickness could be conveniently controlled through the TEOS volume added to the colloidal FeNi solution. Our study allowed us to correlate the silica-shell thickness with the evolution of the magnetic properties of the final nanocomposite. The magnetic investigations demonstrate the possibility of making property-tunable magnetic nanoparticles ready for surface engineering in particular with bioactive molecules or for electromagnetic device applications aiming to enhance frequency limits. These aspects will undoubtedly require further longer-term ageing studies. In particular, the chemical stability must be ensured before any in vivo applications are intended. Electronic holography experiments are in course to confirm the expected vortex structure of the FeNi nanoparticles.
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