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Immobilization of magnetic iron oxide nanoparticles on laponite discs – an easy way to biocompatible ferrofluids and ferrogels

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Abstract

Magnetic nanocomposites containing iron oxide (maghemite) nanoparticles, well embedded in a synthetic clay matrix (laponite) were prepared by a new one step chemical route and characterized by TEM, XRD, magnetization measurements, Mössbauer spectroscopy, DLS, and MRI measurements. The synthetic procedure leads to non-stoichiometric $\gamma\text{-Fe}_2\text{O}_3$ with a controllable content in the nanocomposite. Magnetic nanoparticles incorporated in the diamagnetic clay matrix exhibit a mean diameter of 13 nm, superparamagnetic behavior with a high saturation magnetization achievable at low applied magnetic fields. In-field Mössbauer spectra and ZFC/FC magnetization curves reveal a perfect ferrimagnetic ordering within nanoparticles with negligible spin frustration and interparticle interactions due to the complete coating of maghemite surfaces by the nanocrystalline laponite matrix. Magnetic iron oxide nanoparticles embedded in laponite matrix exhibit strong T_2 weighted MRI contrast. The maghemite/laponite composite particles have 200 nm hydrodynamic diameter and form very stable hydrosols and/or hydrogels depending on their concentration in water.

Keywords

$\gamma\text{-Fe}_2\text{O}_3$; nanoparticles; ferrofluids; hydrogels; laponite; nanocomposites; magnetic resonance imaging (MRI)

1. Introduction

Over the last decades, there has been a growing interest in the synthesis of nanophase magnetic composite materials because of their potential applications in many scientific and technological areas. Among magnetic materials, iron oxides are of particular interest due to their unique magnetic properties, chemical stability and biocompatibility. Magnetic iron oxide nanoparticles based on Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ have been used in information storage [1], catalysis [2], environmental protection [3,4] and in the most rapidly developing area of biomedical

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applications such as magnetic drug delivery, cell separation, magnetic hyperthermia, DNA detection, and magnetic resonance imaging (MRI) [5–9].

At the same time, the gels constitute a very important class of materials due to their applications in templated materials synthesis [10], drug delivery [11], separations [12], and biomimetics [13]. Particularly, magnetic gels and/or ferrogels have become an interesting subject of study among scientific research community due to their promising applications in the high-power actuators and biomedicine [14–19]. The most widely used approach for the preparation of a ferrogel involves the addition of a ferrofluid in a polymer matrix followed by a cross linking reaction [20,21].

Natural swelling clay minerals, especially montmorillonites, are used in various industrial products and processes as rheology modifiers and stability controllers; for instance, they are used most extensively in drilling fluids and muds [22]. In many research works on the macroscopic properties of swelling clays, laponite, a plate-like synthetic hectorite-type clay, is used as a model system, mainly because of its high purity, optical transparency and excellent stability of its dispersions. When hydrated in aqueous media, Laponite dispersions display various phase transitions, from the formation of isotropic free flowing suspensions, to thixotropic gel-like structures (isotropic or nematic phases) and phase-separated flocs, depending upon the volume fraction of the solid and the presence of other ionic species. [23–25]. From the phase diagram, the critical laponite concentration is about 3 wt. % [26,27]. Laponite nanodisks is extensively studied from the viewpoint of the formation of clay/polymer hydrogels [28] and clay/polymer composites [29–34], immobilization of biomolecules such as DNA or proteins for biosensing applications [35–39], and designing of optical materials through the interactions with dye molecules [40–42].

Here, we report on the immobilization of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles on laponite nanodisks and subsequent formation of maghemite/laponite composite nanomaterials which form very stable aqueous colloidal solutions or hydrogels depending on the composite material concentration. In addition, they are biocompatible and reveal high saturation magnetization because of the ability to load the laponite disks with high magnetic contents. It is worth to mention that the immobilization of the magnetic particles leads to a significant suppression of the magnetic interparticle interactions. The synthesis of the magnetic hybrid was carried out by a one step precipitation method using ferrous chloride as an iron precursor. The synthesized composite materials were studied by a series of complimentary techniques in order to elucidate the structure and composition of the final material as well as to reveal its magnetic properties.

2. Experimental section

2.1. Preparation of $\gamma\text{-Fe}_2\text{O}_3$ /laponite nanocomposites

Magnetic iron oxide nanoparticles/laponite nanodisks composite materials were synthesized by a precipitation method based on the slow oxidation of $\text{Fe}(\text{OH})_2$ by atmospheric oxygen in alkaline environment. The used synthetic clay of Laponite RD type (kindly provided from Rockwood, Clay additives GmbH), consists of colloidal disks, with a diameter of 30 ± 5 nm and a thickness of about 1 nm. In the typical synthetic procedure, 500 mg of laponite nanodisks were dispersed in 50 ml degassed by N_2 distilled H_2O at 60°C under gently magnetic stirring. Next, 2 and/or 4 mmol of hydrated FeCl_2 , dissolved in 20 ml H_2O , was added under N_2 bubbling. Through the different content of ferrous chloride, we were able to control the final content of magnetic nanoparticles in the nanocomposites. After 15 min, the drop wise addition of 10 ml 1 M NH_3 solution produced a deep green reaction mixture suggesting the formation of $\text{Fe}(\text{OH})_2$ gel. At this point, the reaction mixture was cooled at room temperature and the N_2 gas was removed allowing the formation of maghemite phase through slow oxidation of Fe^{2+} cations by atmospheric oxygen. The reaction mixture was stirred for 1 h and the cooled

solid was separated by centrifugation at 14000 rpm. The solution was then washed twice with 50 ml of the distilled water and the final precipitate was left to dry in air spreading it on a glass plate. Maghemite formation takes place after the initial formation of green ferrous hydroxides (and oxohydroxides) through solution reconstructive transformation, dehydration, and condensation reactions [43,44].

A simplified path can be possibly described as follows:

2.2. Characterization of prepared $\gamma\text{-Fe}_2\text{O}_3$ /laponite nanocomposites

TEM micrographs were obtained using a JEM2010 microscope operated at 200 kV with a point-to-point resolution of 1.9 Å. Before measurements, the samples were dispersed in ethanol and the suspension was treated in ultrasound for 10 minutes. A drop of very dilute suspension was placed on a carbon-coated grid and allowed to dry by evaporation at ambient temperature.

The X-ray powder diffraction (XRD) experiments were performed with a PANalytical X'Pert PRO instrument (CoK α radiation) equipped with an X'Celerator detector. Samples were spread on a zero-background Si slides and step-scanned in the 2θ range of 10–100° in steps of 0.017° for 720 s per step. Electrophoretic measurements based on laser Doppler velocimetry and dynamic light scattering (DLS) were performed with a Malvern Instruments Nano ZetaSizer equipped with a 4 mW He-Ne laser, operating at a wavelength of 633 nm and having an avalanche photodiode as a detector. In DLS, scattered light is detected at an angle of 173° (backscattering), while in electrophoretic measurements it is detected at a forward angle of 17°. The hydrodynamic diameter then represents the intensity-weighted average particle size obtained with the cumulants analysis method.

Zero-field Mössbauer spectra were recorded at 300 K in a constant acceleration mode with a 50 mCi $^{57}\text{Co}(\text{Rh})$ source. The values of the isomer shift are reported with respect to $\alpha\text{-Fe}$. In-field Mössbauer measurements were performed in a constant acceleration mode when the sample was placed in a cryomagnetic system (Oxford Instruments) at a temperature of 5 K and exposed to an external magnetic field of 5 T, applied parallel to the direction of γ -rays.

A superconducting quantum interference device (SQUID, MPMS XL-7, Quantum Design) has been used for the magnetic measurements. The hysteresis loops were collected at a temperature of 2 and 300 K in external magnetic fields from – 7 T to + 7 T. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves were recorded on warming in the temperature range from 5 to 300 K and in an external magnetic field of 1000 Oe after cooling in a zero magnetic field and a field of 1000 Oe, respectively.

2.3. Measurement of Transverse relaxation time (T_2) and MRI contrast

For MRI experiments, samples at given concentrations were suspended in water and placed in 20 mL tubes. To assess MRI properties and the MRI contrast enhancing effect of the samples, transverse relaxation time T_2 were measured at different concentrations using a MRI scanner at magnetic field strength of 3T. A multi-echo fast spin echo sequence was used to collect a series of data points simultaneously at different echo times (TEs of 6 – 180 ms with 6 ms increment). T_2 relaxation time of the sample was calculated by fitting the decay curve on a pixel-by-pixel basis using the simplified non-linear mono-exponential algorithm of $M(\text{TE}) = M_0 * \exp(-\text{TE}/T_2)$, where $M(\text{TE})$ is the signal intensity observed at a given echo time, M_0 is the signal intensity at the initial magnetization without decay time. Relaxivities r_2 , can be

obtained from the slopes of the plot from the concentration vs. relaxation rate, R_2 which is the reciprocal relaxation time (e.g., $R_2 = 1/T_2$), at a given concentration unit.

3. Results and Discussion

3.1. TEM and XRD results

Figure 1 shows TEM images of the γ -Fe₂O₃/laponite nanocomposite systems that differ in the loading percentage of the magnetic iron oxide material. This controlled loading was achieved by the suitably chosen content of FeCl₂ precursor in the synthetic procedure. In Samples 1 and 2, the iron oxide content is 23.5 and 50.2 wt. % respectively, as checked by XRF. From Figure 1, it is obvious that both studied samples consist of the magnetic nanoparticles that are well embedded in the laponite matrix without the presence of free assemblies of magnetic nanoparticles. The magnetic nanoparticles have predominantly globular shape and their size distributions are governed by an appropriate log-normal distribution function as discussed later (see Section 3.3 and Fig. 6). In both cases, the mean diameter of the magnetic nanoparticles, derived from the particular log-normal curves, is ≈ 13 nm.

XRD patterns of the studied γ -Fe₂O₃/laponite nanocomposites are shown in Figure 2. The spinel type structure is evidenced by the peak positions (indicated with the filled box in Figure 2) and their relative intensities are in a good agreement with those found in the JCPDS card (No. 19-0629) for maghemite. The average particle size, calculated from the Scherrer equation, is about 14 nm for both systems, which is in good agreement with the average value derived from TEM images. However, the XRD pattern itself is inadequate to identify whether the nanoparticles correspond to maghemite or magnetite, because these oxides are isostructural and the peak positions corresponding to maghemite and magnetite generally overlaps. In most cases, their distinction is possible by Mössbauer spectroscopy applied in a wide range of temperatures and external magnetic fields (see Section 3.2). The unassigned peaks in XRD patterns are related to laponite whose relative intensities decrease as the loading of the magnetic phase increases (see Figure 2).

3.2. Mössbauer spectroscopy results

In order to deeply investigate the structural and magnetic properties of the prepared nanocomposite systems, zero-field and in-field Mössbauer spectroscopy has been employed. The recorded zero-field and in-field Mössbauer spectra for the two studied samples are depicted in Figure 3 and Figure 4, respectively. The results of the fitting procedure, including hyperfine parameters for each spectral component, are summarized in Tables 1 and 2.

For both investigated samples, the zero-field Mössbauer spectra, recorded at room temperature, reveal a complex profile, characterized by a coexistence of one doublet component and two sextet components. The simultaneous appearance of doublet and sextets reflects a distribution of particle size, meaning that some portion of nanoparticles (i.e. the nanoparticles with the smallest size in their assembly) are superparamagnetic whereas the rest remains in a blocked magnetic state at room temperature with respect to the time window of the used experimental technique (for Mössbauer spectroscopy, the characteristic time of the measurement is 10^{-8} s). Since the relative spectral areas of the doublets are the same in the spectra of both samples, this indirectly indicates that both studied samples exhibit nearly the same particle size distribution. Based on the derived values of the isomer shift of the doublets (i.e. $\delta_{\text{Doublet}} = 0.33$ mm/s for Sample 1 and $\delta_{\text{Doublet}} = 0.34$ mm/s for Sample 2, see Table 1), only iron atoms in a Fe³⁺ state are present in the fraction of the smallest particles and contribute to their observed superparamagnetic behavior. As far as the sextets are concerned, a distribution of the magnetic hyperfine field has been used when analyzing one sextet component. This comes from the fact that nanoparticles possess a high surface-to-volume ratio and that the binding to synthetic

laponite further segregates a certain portion of the surface-to-middle atoms of the nanoparticle that exhibit significantly different surroundings with respect to those typical of atoms in the nanoparticle core. For this reason it is impossible to distinguish between the two crystallographic sites (i.e. tetrahedral and octahedral sites) in the assumed maghemite structure due to increased linewidths of the sextet spectral lines in comparison to those observed for well-crystallized bulk maghemite and/or individual nanoparticles significantly unhampered by the finite-size and surface effects. Therefore, for both investigated systems, the deconvolution of the room-temperature zero-field Mössbauer spectra leads to two sextets (denoted as Sextet 1 and Sextet 2 in Figure 3 and Table 1) that differ in the values of the isomer shift and magnetic hyperfine field. In the framework of our accepted model that nanoparticle surface atoms experience different hyperfine interactions, Sextet 1 can be assigned to magnetically-active ions in the core of the nanoparticle, occupying both tetrahedral and octahedral crystallographic positions, whereas Sextet 2 corresponds to the nanoparticle surface atoms, lying in the surface layers of a definite thickness, which are characterized with reduced crystal symmetry, coordination, oxygen deficiency and weakened chemical and superexchange bonds induced by the surface effects and binding of synthetic laponite. This manifests itself mainly in a distribution of the magnetic hyperfine field that completely describes the behaviour of the surface atomic magnetic moments. Here, the expression “surface atoms” is not restricted only to the ultimate surface layers as in a nanoparticle system, since the boundary between surface and core of the nanoparticle is not sharp; there is no step change observed in any physical or chemical properties since they change continuously from the surface to the core. In our approach, the term “surface atoms” thus corresponds to all atomic layers that are close to the surface of the nanoparticle and significantly feel the effect of surface and binding to laponite matrix (assigned thus as “surface-to-middle” iron atoms in Table 1). Owing to the weakened superexchange bonds and binding of diamagnetic laponite, the magnetic moments of the surface atoms may therefore thermally fluctuate more easily than those of the core atoms at room temperature. The whole magnetic moment (i.e. the “superspin”) of each magnetic nanoparticle can thus fluctuate around its easy axis of magnetization, producing collective magnetic excitations [45]. In the Mössbauer spectrum, this phenomenon is manifested by the inward bending of outermost and middle lines towards the centre of the spectrum and by the reduction of the values of the magnetic hyperfine field. Since a similar profile is observed for both studied samples, we can conclude that the magnetic regime of the nanoparticles, which are in a blocked state at room temperature, is significantly influenced by the collective magnetic excitations.

As it has been already noted, Sextet 1 involves a contribution from the particle core magnetically-active atoms that are located in the tetrahedral and octahedral positions of the spinel maghemite structure. This assignment is based on the derived value of the isomer shift ($\delta_{\text{Sextet1}} = 0.31$ mm/s for both samples) which is typical for Fe^{3+} ions in a high-spin state and close to that usually observed for bulk maghemite [46]. However, for Sextet 2, a higher value of the isomer shift ($\delta_{\text{Sextet2}} = 0.43$ mm/s for both samples) is observed. This offers an explanation that at the surfaces of the nanoparticles, a lower valence state of iron is present that breaks the ideal chemical stoichiometry of maghemite particles. It thus turns out that the surface layers of the particles involve Fe^{2+} ions that partly fill the vacant positions. Based on the result of the Mössbauer analysis, the magnetic particles are non-stoichiometric maghemite from the chemical viewpoint. Apart from this, the cubic structure of maghemite is further supported by almost zero values of the quadrupole splitting for both sextets. As it has been already pointed out, the presence of the magnetic collective excitations causes, together with the finite sizes of the particles, a reduction in the values of the magnetic hyperfine field in comparison to those reported for bulk maghemite (≈ 50 T at room temperature) [46]. Note that for Sample 2, the spectral area of Sextet 1 gets bigger at the expense of the spectral area of Sextet 2. This is probably connected with a higher amount of iron oxide nanoparticles present

in the laponite matrix that weakens its diamagnetic influence in the system (the diamagnetic shell probably gets thinner in Sample 2).

To find how the prepared nanocomposite systems respond to an external magnetic field, in-field Mössbauer spectroscopy has been utilized. Both studied samples have been exposed to a homogeneous external magnetic field of 5 T, oriented parallel to the direction of the propagation of γ -rays. Despite the different weight content of magnetic oxide nanoparticles in Sample 1 and 2, the in-field Mössbauer spectra of both systems, recorded at a temperature of 5 K, look pretty much the same (see Figure 4), and their mathematical deconvolution results in three distinguishable spectral sextet components (denoted as Sextet 3, Sextet 4 and Sextet 5, see Table 2). The analysis of the Mössbauer hyperfine parameters of the individual sextet reveals that Sextet 3 corresponds to the iron atoms occupying the tetrahedral crystallographic positions of an ideal maghemite structure (with isomer shift, quadrupole splitting and effective magnetic hyperfine field values being equal to those typically found in other purely maghemite systems) while Sextet 4 and Sextet 5 are related to the iron atoms located in the octahedral sites of maghemite crystal structure. If one adds the relative spectral areas of Sextet 4 and Sextet 5 and divide the obtained number with the relative spectral area of Sextet 3, we will arrive at a value of ≈ 1.70 which is very close to 1.67, the ratio reported for stoichiometric maghemite. The necessity of fitting the octahedral crystallographic positions with two sextets originates from the fact that a certain amount of Fe^{2+} ions are present in the sites which should be vacant. Thus, based on the values of the isomer shift of Sextet 4 and Sextet 5, we can distinguish iron atoms that have a trivalent valence state ($\delta_{\text{Sextet5}} = 0.48$ mm/s for Sample 1 and $\delta_{\text{Sextet5}} = 0.47$ mm/s for Sample 2) and their surroundings are not affected by the presence of Fe^{2+} ions (in other words, Fe^{2+} ions are too far from the probed Fe^{3+} ions), and iron atoms (with $\delta_{\text{Sextet4}} = 0.60$ mm/s for Sample 1 and $\delta_{\text{Sextet4}} = 0.58$ mm/s for Sample 2) that are both Fe^{2+} and Fe^{3+} and Fe^{3+} surroundings thus sense the presence of neighboring Fe^{2+} ions. The existence of Fe^{3+} and Fe^{2+} ions, close to each other, may also induce an electron hopping process between Fe^{3+} and Fe^{2+} ions that is frequently observed in non-stoichiometric maghemite at these low temperatures. The sites, taking place in the electron hopping phenomenon, then possess an effective valence state that is between 2+ and 3+ with corresponding value of the isomer shift between that for pure Fe^{2+} and Fe^{3+} at a given temperature. Note that for both samples, the overall spectral profile misses the 2nd and the 5th lines since their intensities are almost zero. This implies that at this temperature of the measurement, the atomic magnetic moments within each nanoparticle are perfectly aligned (parallel and/or antiparallel) with respect to the direction of the applied magnetic field as observed for ideal ferromagnetic and/or ferrimagnetic materials in the used experimental geometry of the in-field Mössbauer measurement. Thus, the magnetic nanoparticles do not exhibit a spin canting phenomenon that is connected with some sort of magnetic disorder, taking place both at the surface of the nanoparticle and within the whole particle volume due to structural defects. The magnetization is homogeneous and uniform within each magnetic nanoparticle which indicates a perfect ferrimagnetic ordering of its atomic magnetic moments in the applied magnetic fields. If some spin canting is present, it must be very weak and might be observed at much lower applied magnetic fields.

To conclude the results of zero-field and in-field Mössbauer spectroscopy, the studied nanocomposite systems consist of non-stoichiometric maghemite nanoparticles which exhibit a perfect ferrimagnetic ordering. In addition, no other iron oxide phase (i.e. hematite, magnetite, etc.) has been detected in the Mössbauer spectra, which means that the synthesis conditions secure the formation of a single magnetic phase.

3.3. Magnetization measurement results

While ^{57}Fe Mössbauer spectroscopy gives information on local magnetic properties of the probed iron atoms, data from magnetization measurements report on the global magnetic

properties of the investigated samples. The results of magnetization measurements for both studied systems are depicted in Figure 5 and the main hysteresis parameters, derived from the particular hysteresis loops, are summarized in Table 3.

In order to study the magnetic dynamics of an assembly of magnetic nanoparticles in Sample 1 and 2, the ZFC and FC magnetization curves have been measured. From Figure 5, it is obvious that the profile of the ZFC and FC magnetization curves is very similar for both samples. Three general features are observed: (i) the ZFC and FC magnetization curves begin to diverge from each other at a certain temperature, assigned as the temperature of irreversibility T_{irr} (determined as a temperature at which the separation of the FC magnetization curve is 1 % from the ZFC magnetization curve); (ii) the ZFC magnetization curve exhibits maximum at a certain temperature, assigned as the blocking temperature T_{B} ; (iii) the FC magnetization curve still increases as the temperature falls lower than the corresponding blocking temperature. The appearance of the maximum in the ZFC magnetization curve suggests that the assembly of magnetic nanoparticles passes from the blocked state to the superparamagnetic regime as the temperature rises. Since the both systems exhibit a size distribution, the blocking temperature is related to the superparamagnetic transition of the nanoparticles with the most probable size in their assembly whereas the temperature of irreversibility corresponds to the superparamagnetic transition of the largest nanoparticles in the assembly. In other words, the difference between the values of T_{irr} and T_{B} is thus a quantitative measure of the size range of the magnetically-active nanoparticles present in the system. When comparing the derived values of T_{irr} and T_{B} for both samples ($T_{\text{irr}} = 128$ K and $T_{\text{B}} = 36$ K for Sample 1, $T_{\text{irr}} = 145$ K and $T_{\text{B}} = 38$ K for Sample 2), it follows that both studied systems possess comparable size distribution with nearly the same average particle size. In addition, the monotonous increase of the FC magnetization curves for the temperatures below the particular blocking temperature confirms that the magnetic interparticle interaction are significantly suppressed in both samples with different iron oxides contents. It is experimentally well documented [47] that if some interparticle interactions exist in the nanoparticle system, they frequently manifest themselves by the change of the FC profile below the corresponding blocking temperature which becomes nearly constant as the strength of the interparticle interactions increases.

The static magnetic properties of the studied system have been monitored by measuring the hysteresis loops at 2 and 300 K. At 2 K, field-dependent magnetization curves exhibit hysteresis (see Figure 5), meaning that the nanocomposite system is in a magnetic blocked state. The values of coercivity for both samples ($H_{\text{C}} = 201$ Oe for Sample 1 and $H_{\text{C}} = 195$ Oe for Sample 2) corresponds well to the values reported for maghemite nanosystems, where their coercivity is predominantly driven by the magnetocrystalline anisotropy (other contributions to the overall anisotropy are negligible). The observed values of the saturation magnetization are ≈ 18.3 emu/g for Sample 1 and 38.6 emu/g for Sample 2, which, taking into account the weight content of iron oxide nanoparticles in the samples and diamagnetic response of laponite matrix, amount to ≈ 77 emu/g that is smaller than the value reported for bulk maghemite (≈ 80 emu/g). [48] This reduction of the saturation magnetization is often observed in nanoparticle systems and is merely a consequence of the size reduction of the magnetic material. When the temperature increases, individual magnetic nanoparticles enter the superparamagnetic state, independently on each other, at temperatures, corresponding to their size. At 300 K, all magnetic nanoparticles behave in a superparamagnetic manner from the viewpoint of the magnetization measurements since no hysteresis is observed in the particular room temperature hysteresis loops (see Figure 5). Note that both systems reach saturation at relatively low applied magnetic field (≈ 1.5 T, see Figure 5). This indicates that within each magnetic nanoparticle, the atomic magnetic moments are ideally magnetically ordered, cooperating thus uniformly through the whole volume of the nanoparticle. In addition, the low-temperature hysteresis loops are pretty symmetrical which implies that exchange bias phenomenon is missing in our investigated samples. It is known that exchange bias is connected with an existence of interface between

differently magnetically ordered phases [49]. Since the presence of magnetic interparticle interactions of the exchange type causes the magnetic disorder of the surface layer (having thus a spin-glass-like behaviour), it results in asymmetrical hysteresis loops. Thus, the overall magnetic behaviour of our nanocomposite systems is not affected by the exchange interparticle interactions which are effectively and almost completely suppressed by the laponite matrix.

In order to further check, whether the interparticle interactions are present and how significantly influence the overall magnetic behavior of an assembly of magnetic nanoparticles, we have used the well-known Chantrell model to evaluate the “magnetic size” of the nanoparticles [50]. The Chantrell model is based on the behavior of the magnetization of an assembly of magnetic nanoparticles in the superparamagnetic state at low and high applied magnetic fields, assuming that the magnetization of every magnetic particle, participating on the overall magnetic response, can be well described by the Langevin curve. To use this model, some assumptions have to be fulfilled. The particle size distribution has to be lognormal, nanoparticles should be roughly spherical and should not magnetically interact via dipolar and/or exchange interparticle interactions. The measured profile of the particle size distribution from TEM (green bars in Figure 6) has been tested statistically to confirm its lognormal character. To do so, the statistical χ^2 -test has been applied, leading to the statistical agreement better than 99 % between the experimental data and the theoretical curve. The fit of the TEM experimental data is represented by the blue curve in Figure 6. From the analysis, it follows that the mean particle size is about 13.2 nm with the standard lognormal deviation of about 0.4. After the confirmation of the lognormal particle size distribution, the Chantrell model has been used to evaluate the mean “magnetic size”, D_{MAG} , of the nanoparticles, leading to $D_{\text{MAG}} \approx 12.5$ nm with the standard lognormal deviation of about 0.3. The distribution of the magnetic size of the featured nanoparticles is depicted by the red curve in Figure 6. From the comparison of these two curves, it is obvious that, to some extent, the magnetic size distribution corresponds to the size distribution obtained from TEM. On the basis of these results, one can thus conclude that the magnetic interparticle interactions are significantly suppressed in the Sample 2 due to diamagnetic laponite, which covers efficiently and completely the surface of maghemite nanoparticles.

3.4. Solubility and gel formation

The as-prepared iron oxide/laponite nanocomposites form, in concentrations up to 30 mg/l, colloidal solutions in water producing hydrosols that are very stable for months without signs of precipitation and exhibit ferrofluidic behavior under an external magnetic field, Figure 7a. When the concentration of the composite nanoparticles increases above the critical value of 30 mg/l, the hydrogel formation takes place, showing high resistance to external magnetic fields.

The discotic shape of the basic structural units of laponite is evident by the footprint of its hydrodynamic diameter distribution diagram, observed by DLS measurements (see Figure 8). Laponite particles respond as having two different diffusion coefficients, one corresponding to smaller and another to larger particles. This pattern is interpreted on the basis of the nanodiscs orientation in relation to the vector of velocity. Those particles moving with their large fore-front against the solvent display small diffusion rates, while those (or when) particles moving with their thin edges against the solvent exhibit higher diffusion rates (i.e. a smaller apparent hydrodynamic diameter).

These basic characteristics are retained in the magnetically modified laponite, manifested by the tail of the distribution towards smaller particle sizes (see Figure 8a). Nevertheless, they are significantly suppressed as expected because of the lower aspect ratio of the laponite discs after the growth of the magnetic particles. The hydrodynamic diameter of the magnetically modified laponite has increased by a factor of about two (200 nm), compared to that of the starting

material (~80 nm). The observed increase could be possibly attributed to the growth of the magnetic nanocrystallites on the laponite surfaces and, furthermore, due to the possibility of some of these particles to act as bridging species between two or more laponite platelets. It is noted that the measurements were performed in distilled water in ~0.001M NaCl (pH=6, conductivity = 60 $\mu\text{S cm}^{-1}$).

Turning to the zeta-potential measurements, the negative value of – 54 mV (see Figure 8b) testifies the very good stability of the colloid (generally, ζ_p values of $\geq |30|$ mV denote adequate electrostatic repulsion to provide colloidal stability) [51]. The excellent stability is also macroscopically manifested since no evidence of aggregation and sedimentation was observed for several months.

3.5 Reduction of transverse relaxation time T_2

Magnetic iron oxide nanoparticles embedded in laponite matrix exhibit strong T_2 weighted MRI contrast. The transverse relaxivity r_2 of the Sample 2 is 64 $\text{S}^{-1} \text{mM}^{-1}$ which is almost two folds higher than that of mono-dispersed iron oxide nanoparticles with core size of 13 nm, i.e., 21 $\text{S}^{-1} \text{mM}^{-1}$. Such stronger T_2 shortening effect, typically from stronger magnetic susceptibility, leads to spin dephasing and substantial MRI signal drop which generated a “darkening” contrast as seen in T_2 weighted MR images. The improved the relaxivity of Sample 2 over mono-dispersed iron oxide nanoparticles may be attributed to the reduced interparticle interactions with diamagnetic laponite and increased paramagnetic property.

4. Conclusions

- i. Maghemite/laponite composite nanoparticles have been synthesized by a one step chemical method providing several important advantages, including the controllable content of magnetic particles, their perfect embedding in the diamagnetic matrix and superparamagnetic behavior with a high saturation magnetization. Moreover, the particles show a narrow size distribution and almost completely suppressed interparticle interactions.
- ii. At concentrations of up to 30 mg/l, the composite particles are very stable in water as documented by a high zeta-potential value of ferrofluid (– 54 mV). At higher concentrations, the system loses the ferrofluidic properties and a magnetic ferrogel with a pronounced resistance to the external magnetic fields can be produced.
- iii. Magnetic iron oxide nanoparticles embedded in laponite matrix exhibit strong T_2 weighted MRI contrast which is almost two folds higher than that of mono-dispersed iron oxide nanoparticles with core size of 13 nm.
- iv. Taking into account the above-mentioned advantageous properties of maghemite/laponite nanocomposites, they seem to be the promising materials in various practical fields, including ferrofluid technologies, biomedical applications (MRI) or as magnetic sorbents.

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Figure 1. TEM images of Sample 1 and Sample 2. The inset demonstrates the crystal planes of the nanocrystalline laponite matrix covering the magnetic nanoparticles.

Figure 2.
Powder XRD patterns of Sample 1 and Sample 2 magnetic nanocomposites.

Figure 3.
Zero-field room temperature Mössbauer spectra of Sample 1 and Sample 2 with individual spectral components.

Figure 4.
In-field low-temperature Mössbauer spectra of Sample 1 and Sample 2, measured at a temperature of 5 K and in an external magnetic field of 5 T.

Figure 5. ZFC and FC magnetization curves of Sample 1 and Sample 2 (left) and hysteresis loops (right) for both samples measured at a temperature of 2 and 300 K.

Figure 6. Particle size distribution of Sample 2 (50.2 wt. % iron oxide loading), derived from TEM image and measurement of the superparamagnetic hysteresis loop.

Figure 7. Optical photos of **(a)** ferrofluid, under an external magnetic field, (concentration of maghemite/laponite particles is about 15 mg/ml) and **(b)** ferrogel (concentration of maghemite/laponite particles is about 35 mg/ml).

Figure 8.

(a) Intensity weighted particle size distribution of ~ 0.02 % w/v Sample 2 and laponite suspension as obtained from DLS measurements, (b) zeta-potential distribution diagram obtained from Sample 2.

Figure 9.

(A) Transverse relaxation rate R_2 (or $1/T_2$) of Sample 2 and mono-dispersed iron oxide nanoparticle (IONP) at different Fe concentrations were measured at a magnetic field strength of 3 T using a multi-echo spin echo method. (B) T_2 weighted fast spin echo images showed Fe concentration dependent reduction of MRI signals, which is typically observed as the MRI contrast effect of magnetic iron oxide nanoparticles

Mössbauer hyperfine parameters derived from the room temperature zero-field Mössbauer spectra of Samples 1 and 2, where δ is the isomer shift, ΔE_Q is the quadrupole splitting, B_{hf} is the magnetic hyperfine field, Γ is the linewidth and RA is the relative spectral area of the individual spectral components.

Table 1

Sample	Component	$\delta \pm 0.01$ (mm/s)	$\Delta E_Q \pm 0.01$ (mm/s)	$B_{\text{hf}} \pm 0.3$ (T)	$\Gamma \pm 0.01$ (mm/s)	RA ± 1 (%)	Assignment
1	Doublet	0.33	0.71	-----	0.58	5	Superparamagnetic Fe ³⁺ ions
	Sextet 1	0.31	0.01	46.9	0.64	22	Core blocked Fe ³⁺ ions
	Sextet 2	0.43	0.00	44.2*	0.65	73	Surface-to-middle blocked Fe ³⁺ and Fe ²⁺ ions
2	Doublet	0.34	0.70	-----	0.57	5	Superparamagnetic Fe ³⁺ ions
	Sextet 1	0.31	-0.01	47.4	0.62	37	Core blocked Fe ³⁺ ions
	Sextet 2	0.43	-0.01	44.5*	0.63	58	Surface-to-middle blocked Fe ³⁺ and Fe ²⁺ ions

* Since the second sextet spectral component (i.e. Sextet 2) has been fitted with a distribution of the magnetic hyperfine fields, the value of B_{hf} corresponds to the most probable value derived from the particular profile of the B_{hf} -distribution (not shown).

Mössbauer hyperfine parameters derived from the in-field Mössbauer spectra of Sample 1 and 2, measured at 5 K and in an external magnetic field of 5 T, where δ is the isomer shift, ΔE_Q is the quadrupole splitting, B_{eff} is the effective magnetic hyperfine field, Γ is the linewidth and RA is the relative spectral area of the individual spectral components.

Table 2

Sample	Component	$\delta \pm 0.01$ (mm/s)	$\Delta E_Q \pm 0.01$ (mm/s)	$B_{\text{eff}} \pm 0.3$ (T)	$\Gamma \pm 0.01$ (mm/s)	RA ± 1 (%)	Assignment
1	Sextet 3	0.33	0.00	54.6	0.71	38	Tetrahedral Fe ³⁺
	Sextet 4	0.60	0.01	49.3	0.69	39	Octahedral Fe ²⁺ – Fe ³⁺
	Sextet 5	0.48	0.00	45.9	0.72	23	Octahedral Fe ³⁺
2	Sextet 3	0.34	0.00	55.0	0.70	37	Tetrahedral Fe ³⁺
	Sextet 4	0.58	– 0.02	49.9	0.68	40	Octahedral Fe ²⁺ – Fe ³⁺
	Sextet 5	0.47	0.00	47.3	0.72	23	Octahedral Fe ³⁺

Table 3

Parameters of the hysteresis loops of Sample 1 and 2, measured at a temperature of 2 and 300 K, where M_{S+} represents the saturation magnetization at + 7 T, M_{S-} denotes the saturation magnetization at - 7 T, H_{C+} stands for the positive coercivity, H_{C-} is the negative coercivity, M_{R+} represents the positive remanent magnetization and M_{R-} stands for the negative remanent magnetization. Here, the M_{S+} , M_{S-} , M_{R+} and M_{R-} values are normalized to the weight of maghemite and laponite mixture.

Sample	T (K)	M_{S+} (7 T) (emu/g)	M_{S-} (7 T) (emu/g)	H_{C+} (Oe)	H_{C-} (Oe)	M_{R+} (emu/g)	M_{R-} (emu/g)
1	2	18.31	-18.31	201	-201	5.95	-5.95
	300	13.92	-13.92				
2	2	38.63	-38.63	195	-195	12.15	-12.15
	300	32.21	-32.21				