Preparation of Highly Anisotropic Cobalt Ferrite/Silica Microellipsoids Using an External Magnetic Field

Sébastien Abramson,*† Vincent Dupuis, ‡ Sophie Neveu, ‡ Patricia Beaunier, ‡ and David Montero§

†Laboratoire de Physicochimie des Electrolytes, et Nanosystèmes Interfaciaux, PHENIX (UMR 8234 UPMC-CNRS), ‡Laboratoire de Réactivité de Surface, LRS (UMR 7197 UPMC-CNRS), and §Institut des Matériaux de Paris Centre, IMPC (FR 2482), Université Pierre et Marie Curie, 4, place Jussieu, 75 252 Paris Cedex 05, France

Supporting Information

**ABSTRACT:** Magnetic cobalt ferrite/silica microparticles having both an original morphology and an anisotropic nanostructure are synthesized through the use of an external magnetic field and nanoparticles characterized by a high magnetic anisotropy. The association of these two factors implies that the ESE (emulsion and solvent evaporation) sol–gel method employed here allows the preparation of silica microellipsoids containing magnetic nanoparticles aggregated in large chains. It is clearly shown that without this combination, microspheres characterized by an isotropic distribution of the magnetic nanoparticles are obtained. While the chaining of the cobalt ferrite nanoparticles inside the silica matrix is related to the increase of their magnetic dipolar interactions, the ellipsoidal shape of the microparticles may be explained by the elongation of the sol droplets in the direction of the external magnetic field during the synthesis. Because of their highly anisotropic structure, these microparticles exhibit permanent magnetic moments, which are responsible, at a larger scale, for the existence of strong magnetic dipolar interactions. Therefore, when they are dispersed in water, the microellipsoids self-assemble into large and irregular chains. These interactions can be reinforced by the use of external magnetic field, allowing the preparation of very large permanent chains. This research illustrates how nanostructured particles exhibiting complex architectures can be elaborated through simple, fast, and low-cost methods, such as the use of external fields in combination with soft chemistry.

Colloidal particles have long been an important subject of investigation for many researchers in various fields, due to their applications in various industrial domains, and to their interest for the understanding of several physicochemical concepts. The first efforts were focused on the synthesis and study of monodisperse colloids of various sizes (from nanometer to micrometer), generally having some spherical shapes and composed of a single phase. ¹⁻⁴ Now, the challenge is to obtain particles with original shapes and complex structures that can show unexpected physicochemical properties, opening new fields of applications for these materials. ⁵⁻⁷ This is well-illustrated in the case of the magnetic nanocomposite particles. These materials are generally composed of magnetic nanoparticles such as cobalt, nickel, iron, ferrite, maghemite, or magnetite encapsulated in an inorganic, organic, or hybrid matrix. ⁸⁻¹² They combine the magnetic properties provided by the nanoparticles with additional characteristics such as a high chemical, biological, or thermal stability, optical transparency, high porosity, or capacity of adsorption or encapsulation. Consequently, they have been widely studied as catalysts, adsorbents for water treatment or for analysis of biomolecules, MRI contrast or magnetic hyperthermia agents, drug delivery matrices, biological or environmental sensors, and magneto-optical devices. ⁸⁻¹³ Frequently, these materials are characterized by a spherical shape with a mean diameter varying from few nanometers to several micrometers, and by an isotropic dispersion of the magnetic nanoparticles in the nonmagnetic matrix. ⁸⁻¹² However, there has been an increasing interest in the preparation of magnetic nanocomposite particles with more complex shapes and/or nanostructures. ⁸,¹⁰,¹²,¹³ In particular, these complex architectures lead to enhanced or different magnetic properties in comparison to their reference counterpart. For example, it has been recently shown that polyhedron-shaped magnetic nanocomposite particles having specific surface facets exhibited ferromagnetic properties, although they were composed of an antiferromagnetic material. ¹⁴ Among the various strategies used for the preparation of these unusual architectures, an elegant method consists of using an external magnetic field capable of increasing the dipolar interactions between the magnetic nanoparticles, to induce their self-assembly into chain-like structures. This has been exploited by several authors to prepare highly anisotropic nanocomposite particles such as wires, ¹⁵⁻¹⁸ rigid chains, ¹⁹⁻²³ fibers, ²⁴,²⁵ rods, ²⁶,²⁷ flagella-like particles, ²⁸ or opaline beads, ²⁹,³⁰ and at larger scale, anisotropic films, ³¹,³² or monoliths. ³³,³⁴ In some recent works, a slightly different procedure was also developed, where the anisotropy of

Received: April 22, 2014
Revised: July 10, 2014
Published: July 16, 2014
magnetic nanocomposite particles\textsuperscript{35} or films\textsuperscript{36} was induced through the external force resulting from the magnetic field gradient. These oriented structures often have an impact on the magnetic, optical, and colloidal properties of these materials, which consequently exhibit fascinating features, such as the possibility, when an external magnetic field is applied, to diffract the visible light,\textsuperscript{29,30} to self-organize into zigzag chains,\textsuperscript{25} to possibility, when an external magnetic field is applied, to swing around their center of gravity.\textsuperscript{23,26,35} or to "swing" in a liquid medium.\textsuperscript{28}

Here, we report the synthesis and characterization of magnetic silica nanocomposite particles having both a micro-sized ellipsoidal shape and a highly anisotropic internal structure. These microellipsoids are constituted by magnetic nanoparticles anisotropically self-assembled in a silica matrix. Because of this unique structure, they present some strong individual magnetic moments, which allow them, when suspended in water, to self-assemble into chains at a larger scale, even in the absence of an external magnetic field.

To prepare these materials, we used a strategy that can be summed into two key points. First, inorganic magnetic nanoparticles characterized by strong magnetic anisotropy energy have been used as starting materials. Anisotropy energy is an important parameter in magnetic materials.\textsuperscript{37} For an isolated nanoparticle having a single ferro- or ferrimagnetic domain, the anisotropy energy barrier, $E_a$, can be obtained by the following equation (in the absence of applied magnetic field):

\[ E_a = KV \]

where $K$ is the magnetic anisotropy constant, and $V$ is the volume of the nanoparticle.

The constant $K$ generally depends on the crystalline anisotropy, the shape, and the surface of the nanoparticle. “Hard” ferro- or ferrimagnetic phases such as cobalt ferrite (CoFe$_2$O$_4$), iron (Fe), or platinum–iron (FePt) are characterized by a high value of $K$, to the contrary of “soft” ferrimagnetic phases such as magnetite (Fe$_3$O$_4$) or maghemite ($\gamma$-Fe$_2$O$_3$). Moreover, because eq 1 shows that $E_a$ depends on $V$, larger nanoparticles are generally characterized by a higher value of $E_a$. At ambient temperature, the magnetic moment ($\mu$) of a hard nanoparticle (i.e., having a high value of $E_a$) is blocked along the easy axis of the nanoparticle, because the value of the thermal energy $kT$ is not sufficient to allow fast thermal fluctuations of $\mu$ (Neel motion). This leads to the existence of strong magnetic dipolar interactions between the nanoparticles, even in the absence of an external magnetic field, which are able in some case to induce their directional self-assembly.\textsuperscript{38–41}

The second key point of this work consists of using an external magnetic field ($H$) during the synthesis, to create a directional orientation of the nanoparticles, which tend to align their easy axis parallel to the direction of $H$. This will result first in a strong increase of the dipolar interactions between the magnetic nanoparticles inside the silica microparticles. Moreover, each microparticle will be characterized by a strong permanent magnetic moment (\(\mu_T\)), resulting from the addition of the blocked and oriented individual magnetic moments of the encapsulated magnetic nanoparticles (see Figure 1a).

While the previous works on the magnetic field-induced self-assembly of nanoparticles have been limited to the preparation of highly elongated structures constituted by one or several chains of permanently linked nanoparticles,\textsuperscript{4,19} or to the encapsulation of these chains in continuous polymeric matrices such as large spherical beads (more than 20 $\mu$m in size),\textsuperscript{29,30} films,\textsuperscript{31,32} or monoliths,\textsuperscript{33,34} herein the chained nanoparticles are encapsulated for the first time in small silica microellipsoids (less than 10 $\mu$m in size). In addition, a more complex effect of the magnetic field is evidenced here. Thus, we report a multiscale effect of the magnetic field, because its use, in combination with hard magnetic nanoparticles, allows a control of the anisotropy of the microparticles on three levels, that is, their internal structure at the nanometer scale, their shape at the micrometer scale, and their aggregation properties at larger scale.

\section*{RESULTS AND DISCUSSION}

\textbf{Preparation and Characterization of the Microellipsoids.} To prepare the magnetic nanocomposite microellipsoids, it was necessary to use an acidic dispersion of
magnetic cobalt ferrite (CoFe$_2$O$_4$) nanoparticles as starting material. These nanoparticles were synthesized by the coprecipitation of Co$^{2+}$ and Fe$^{3+}$ ions followed by a hydrothermal treatment, according to a previously published method. This procedure allows the preparation of nanoparticles characterized by a relatively large mean diameter ($d_0 = 13.2$ nm) with a polydispersity index of $\sigma = 0.4$. The TEM image and the resulting size distributions of the CoFe$_2$O$_4$ precursor are given in Figure 2. These nanoparticles were chosen because of their high value of $E_a$. Indeed, CoFe$_2$O$_4$ is a crystalline phase with a relatively high anisotropy constant ($K \approx 200$ kJ m$^{-3}$). Using eq 1, a theoretical value for $E_a$ was calculated, corresponding to $58 kT$ ($T = 298$ K, and $k$ is the Boltzmann constant), which means that these nanoparticles have a blocked magnetic moment at ambient temperature (Figure 1a,b). More details about the characteristics of the CoFe$_2$O$_4$ nanoparticles can be found in the Supporting Information (Figure S1).

The magnetic microellipsoids (also called H-CoFe$_2$O$_4$/SiO$_2$ sample) were prepared via a modified ESE (emulsion solvent evaporation) procedure described in our previous publication. In brief, a magnetic sol was first prepared using an acidic dispersion of the CoFe$_2$O$_4$ nanoparticles and a silica precursor (TEOS) previously hydrolyzed in an acidic solution. This sol was added to a vegetable oil containing a small amount of Arlacel P135, a hydrophobic surfactant. The obtained water-in-oil emulsion was evaporated under vacuum, to decrease the gel time of the silica in the sol droplets. Hence, the emulsion was mechanically stirred all night, in the presence of a permanent magnetic field of 1500 Oe, obtained by the use of two cuboid ferrite magnets in parallel. A photograph of the experimental setup can be found in the Supporting Information (Figure S2). Finally, the emulsion was broken by addition of acetone, and the particles were thoroughly washed with acetone before being dried at 70 °C. For comparison, three reference samples were prepared by the same method. The first sample was prepared using the same batch of CoFe$_2$O$_4$ nanoparticles in the absence of the external magnetic field (CoFe$_2$O$_4$/SiO$_2$ sample). The two other samples were prepared using a dispersion of $\gamma$-Fe$_2$O$_3$ magnetic nanoparticles having a low value of $E_a$ ($K = 35$ kJ m$^{-3}$, $d_0 = 7.4$ nm, and $E_a \approx 2kT$ at $T = 298$ K, see Figure 2 for their TEM image and size distributions), respectively, in the absence and in the presence of the external magnetic field ($\gamma$-Fe$_2$O$_3$/SiO$_2$ and H-$\gamma$-Fe$_2$O$_3$/SiO$_2$ samples). The $\gamma$-Fe$_2$O$_3$ nanoparticles are thus characterized by a fast Neel motion of their magnetic moment at ambient temperature (Figure 1, inset (c)). The
Figure 3. TEM images of the microparticles. (a1)–(a3) H-CoFe₂O₄/SiO₂ microellipsoids at low (a1), high (a2), and medium magnifications (a3). (b) CoFe₂O₄/SiO₂ reference sample, medium magnification. (c) γ-Fe₂O₃/SiO₂ reference sample, medium magnification. (d) H-γ-Fe₂O₃/SiO₂ reference sample, medium magnification.

Figure 4. SEM images of the microparticles. (a) H-CoFe₂O₄/SiO₂ microellipsoids. (b) CoFe₂O₄/SiO₂ reference sample. (c) γ-Fe₂O₃/SiO₂ sample. (d) H-γ-Fe₂O₃/SiO₂ reference sample.
observe the coexistence of large chains where the CoFe2O4 longitudinal and lateral magnetic dipolar interactions between the nanoparticles and orients them in the direction of the external magnetic field.38 In the CoFe2O4/SiO2 sample, the slight and nondirectional aggregation of the nanoparticles may be explained by the presence of moderate magnetic dipolar interactions between the nanoparticles existing at zero field. In the γ-Fe2O3/SiO2 and H-γ-Fe2O3/SiO2 samples, no aggregation occurs, even in the presence of the external magnetic field, because the magnetic dipolar interactions between the γ-Fe2O3 nanoparticles are considerably weakened by their lower energy anisotropy.

The ellipsoidal morphology of the H-CoFe2O4/SiO2 particles was confirmed by SEM (Figure 4a). The microellipsoids are polydisperse, and by counting the size of 500 particles on the SEM images, we determined that they have a mean Ferret diameter of 2.2 μm (standard deviation = 1.9 μm), with a mean aspect ratio of 1.3 (standard deviation = 0.1). The ellipsoidal shape is typical of the H-CoFe2O4/SiO2 sample because it was not observed on the three blank samples where a more usual spherical shape was obtained (Figure 4b–d).

The magnetic properties of the samples were analyzed by SQUID magnetometry. Figure 5a shows the magnetization–demagnetization curves obtained for the H-CoFe2O4/SiO2 and CoFe2O4/SiO2 samples. The resulting magnetic parameters of the samples are given in Table 1. The two curves are characteristic of composite materials containing ferrimagnetic nanoparticles with a blocked magnetic moment.45 In both cases, strong magnetic susceptibility and saturation magnetization (\(m_s\)) are observed simultaneously with the presence of a relatively important hysteresis at low field intensity (see the inset in Figure 5a). On the contrary, because of the unblocked magnetic moment of the γ-Fe2O3 nanoparticles, the magnetization–demagnetization curves of the two γ-Fe2O3-based samples are typical of a superparamagnetic behavior with no hysteresis (see Figure S5 in the Supporting Information for the curves). The values of \(m_s\) allowed us to determine the mass theoretical structures of the synthesized samples are presented in Figure 1.

Figure 5. (a) Magnetization–demagnetization curves of the H-CoFe2O4/SiO2 microellipsoids (black dots) and CoFe2O4/SiO2 reference sample (green dots). Inset: Magnification of the low-field part of the curves. (b) ZFC/FC curves (magnetization versus temperature) of the H-CoFe2O4/SiO2 microellipsoids (●, ZFC curve; ○, FC curve) and CoFe2O4/SiO2 sample (green ●, ZFC curve; green ○, FC curve). All of the values of magnetization are normalized to 1 g of CoFe2O4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(m_s) (emu g(^{-1}))(^a)</th>
<th>(w_{NP}) (％ w/w)(^b)</th>
<th>(M_s) (emu g(^{-1}))(^c)</th>
<th>(M_R) (emu g(^{-1}))(^c)</th>
<th>(H_C) (Oe)</th>
<th>(T_B) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-CoFe2O4/SiO2</td>
<td>20.9</td>
<td>33.7</td>
<td>11.1</td>
<td>14.5</td>
<td>150</td>
<td>&gt;400</td>
</tr>
<tr>
<td>CoFe2O4/SiO2</td>
<td>21.3</td>
<td>34.3</td>
<td>0</td>
<td>12.4</td>
<td>190</td>
<td>&gt;400</td>
</tr>
<tr>
<td>γ-Fe2O3/SiO2</td>
<td>18.1</td>
<td>33.5</td>
<td>0</td>
<td>1.2</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>H-γ-Fe2O3/SiO2</td>
<td>18.3</td>
<td>33.9</td>
<td>0</td>
<td>1.2</td>
<td>10</td>
<td>85</td>
</tr>
</tbody>
</table>

\(^a\)The saturation magnetization \(m_s\) is given in emu/g of composite sample. \(^b\)The weight fractions in magnetic nanoparticles, \(w_{NP}\), were obtained by \(w_{NP} = m_s / M_s\), where \(M_s\) is the saturation magnetization of the magnetic nanoparticles. \(^c\)\(M_s\) and \(M_R\) are given in emu/g of magnetic nanoparticles (normalized values).
fractions in magnetic nanoparticles, \( w_{NP} \). A high value of \( w_{NP} \) was obtained in all of the samples \( (w_{NP} = 33.7\% \) for the H-CoFe2O4/SiO2 microellipsoids). No major effect of the external magnetic field was observed on the magnetization-demagnetization curves of the CoFe2O4-based samples, because the coercitive fields \( (H_c) \) and the remanent magnetizations \( (M_r) \) were almost the same \( (\text{see Table 1}) \). This was first surprising for us: larger values for \( H_c \) and \( M_r \) would have been expected for the sample synthesized under field, because the external magnetic field strongly increased the structural anisotropy of these materials. However, the disordered packing of the particles in the powdered form may cancel the effect of their intrinsic anisotropy. Nevertheless, the structural difference between the two CoFe2O4-based samples was confirmed by some of the magnetic measurements. First, the initial magnetization, \( M_0 \), which was taken before the application of the magnetic field during the measurements, is non-negligible for the H-CoFe2O4/SiO2 sample, to the contrary of the reference samples \( (\text{see Table 1}) \). The existence of \( M_0 \) is thus related to the applied magnetic field during the synthesis of this sample. Furthermore, the two samples can be distinguished by the profile of their ZFC and FC curves, which represent their magnetization versus temperature at low magnetic field \( (H = 50 \text{ Oe}) \), after cooling them in the absence and in the presence of the field, respectively \( (\text{see Figure 5b}) \). The blocking temperature \( T_b \), corresponds to the maximum of magnetization in the ZFC curve. When this temperature is reached, the time needed for alignment by Neel rotation of the magnetic moments of the nanoparticles in the direction of the applied magnetic field is becoming shorter than the time used to measure the magnetization of the nanoparticles. Above this temperature, the magnetization decreases because the thermal fluctuations of the magnetic moment increase, and the ZFC and FC curves generally overlap. Here, for the two CoFe2O4-based samples, \( T_b \) is too high to be determined \( (T_b > 400 \text{ K}) \). However, for the H-CoFe2O4/SiO2 sample, the smaller value of the magnetization at 400 K in the ZFC and FC curves may indicate a larger value of \( T_b \). This can be interpreted using eq 2, which derives from the well-known Neel–Brown equation.37,46

\[
25kT_b = KV + E_{dd}
\]

Equation 2 shows that \( T_b \) depends on \( KV \), the magnetic anisotropy energy, and on \( E_{dd} \) the energy resulting from the magnetic dipolar interactions between the magnetic nanoparticles. \( KV \) is related to the nature of the magnetic nanoparticles, and the high value of \( T_b \) in the two CoFe2O4-based samples is therefore explained by the large value of \( KV \). This was confirmed by the ZFC-FC measurements on the \( \gamma \)-Fe2O3 based samples where a value of \( T_b \) of only 85K was found, due to their smaller value of \( KV \) \( (\text{see Table 1 and Figure S5 in the Supporting Information, for the ZFC-FC curves}) \). Nevertheless, the value of \( KV \) being identical in the two CoFe2O4-based samples, the probable larger value of \( T_b \) in the H-CoFe2O4/SiO2 sample can only be explained by its larger value of \( E_{dd} \). The larger strength of the magnetic dipolar interactions in this sample is in agreement with the larger aggregation state of the CoFe2O4 nanoparticles, which are organized in large chains in the silica matrix. It is however important to note that the magnetic dipolar interactions cannot be totally neglected for the CoFe2O4/SiO2 sample synthesized at zero field. Indeed, additional ZFC-FC measurements were performed on a sample obtained by dispersing the CoFe2O4 nanoparticles in a silica gel, at a dilution sufficiently high \( (w_{NP} = 0.7\%) \) to neglect the magnetic dipolar interactions. In that case, a value of \( T_b \) of 390 K was obtained, which is smaller than that for the CoFe2O4/SiO2 sample \( (\text{see Figure S6 in the Supporting Information for the ZFC-FC curve}) \).

**Formation Mechanism of the Microellipsoids.** The application of an external magnetic field during the synthesis of the H-CoFe2O4/SiO2 sample results in two structural features:
(i) an internal structure characterized by the chaining of the magnetic nanoparticles; and (ii) an ellipsoidal morphology. As was already mentioned, the field-induced chaining of the magnetic nanoparticles has been well described by many authors, and has been explained by the intensification of the dipolar interactions between the nanoparticles in the presence of the magnetic field. On the contrary, it was more difficult to understand how the shape of the microparticles is influenced by the magnetic field. To clarify this point, the following additional experiences were performed. First, an isolated and large water-in-oil droplet (more than 50 μm in size) containing the CoFe2O4 nanoparticles and the silica precursor was observed using optical microscopy. When a magnetic field was applied, the droplet was elongated in the direction of the magnetic field, thus acquiring an ellipsoidal shape (Figure 6a,b). Because the experience was performed before gelation of silica, when the magnetic field was cut, the droplet returned to its spherical shape, indicating the reversibility of the elongation phenomenon. In a second experience, the water-in-oil emulsion resulting in CoFe2O4/SiO2 samples was submitted to the same magnetic field. In that case, the droplets were also elongated along the direction of the magnetic field. However, the observation was limited because of the small size of the droplets, and because of their alignment in the direction of the field. The chaining of the droplets is due to the existence of induced magnetic moments, resulting in the appearance of magnetic dipolar interactions between the droplets (Figure 6c). When the CoFe2O4 nanoparticles were replaced by the γ-Fe2O3 nanoparticles, the ellipsoidal shape was still detected for a large and isolated water-in-oil droplet, although its aspect ratio was less pronounced (Figure 6e,f). However, the only behavior observed in the emulsion resulting in γ-Fe2O3/SiO2 samples was the alignment of the droplets in the direction of the magnetic field (Figure 6g).

The elongation of droplets under applied magnetic field has already been mentioned in several systems, such as in concentrated aqueous droplets of magnetic nanoparticles resulting from demixed ferrofluids.47−49 It has been attributed to the effect of the magnetic surface forces appearing along the normal. These forces are stronger on the poles of the magnetized droplets, which therefore tend to be elongated along the external magnetic field.49 It has been shown that elongation of the magnetic droplets depends on the competition between their magnetic energy and their interfacial energy.47,48 It has been demonstrated that the magnetic energy is related to the magnetization of the droplet, which increases with the saturation magnetization of the nanoparticles and with their magnetic dipolar interactions. Therefore, for the same concentration of nanoparticles and for the same external magnetic field, the magnetic energy is stronger for the CoFe2O4/SiO2 droplets than for the γ-Fe2O3/SiO2 droplets. When the magnetic energy is not sufficient to overcome the interfacial energy, the droplets remain in spherical shape, as it is observed in the γ-Fe2O3/SiO2 emulsion. On the contrary, the ellipsoidal shape of the CoFe2O4/SiO2 droplets is favored by their larger magnetic energy.

Finally, we found that the elongation of the CoFe2O4/SiO2 aqueous droplets became irreversible after one night under magnetic field, because the ellipsoidal shape of the droplets was maintained in the absence of applied magnetic field (Figure 6d). We believe that the ellipsoidal shape of the CoFe2O4/SiO2 sol droplets is “frozen” by the silica gelation after a few hours. The irreversibility of the elongation of the droplets may also be favored by the strong chaining of the CoFe2O4 nanoparticles inside the droplets along the direction of the main axis of the ellipsoid.

**Colloidal Behavior of the Microellipsoids.** The colloidal behavior of the H-CoFe2O4/SiO2 microellipsoids was determined by following the evolution of their aqueous dispersion.
Fe2O3/SiO2 dispersions. The microellipsoids were found to be aggregated during 1 min. (a3) SEM image of the dried dispersion. (b1–b3) γ-Fe2O3/SiO2 microspheres. (b1) Optical micrograph at t = 1 s. (b2) Optical micrograph at t = 1 min. (b3) SEM image of the dried dispersion. The scale bar is 30 μm. The arrows correspond to the direction of the applied field.

The limited aggregation observed in the CoFe2O4/SiO2 dispersion may be explained in terms of dipolar magnetic interactions existing between the microparticles. The magnetic dipolar interaction between two particles is attractive and maximum when their magnetic moments (μγ) are in head-to-tail configuration. The energy of the magnetic dipolar interaction between two aligned particles having the same value of μγ, Edd, is thus expressed by eq 3.38

\[ E_{dd} = \frac{\mu_0 g T^2}{(2\pi d^3)} \]

where \( \mu_0 \) is the magnetic permeability of vacuum, and \( d \) is the distance between the two particles.

Equation 3 shows that the larger is the value of \( \mu_0 \gamma \), the stronger are the dipolar magnetic interactions. Because of the fast Neel motion of the magnetic moments of the γ-Fe2O3 nanoparticles, the γ-Fe2O3/SiO2 particles have no net moment (\( \mu_0 = 0 \)) and do not present any magnetic dipolar interactions in the absence of external magnetic field. The limited aggregation observed in the CoFe2O4/SiO2 dispersion may be due to the existence of small permanent magnetic moments resulting from the addition of the blocked individual magnetic moments of the CoFe2O4 nanoparticles. For the H-CoFe2O4/SiO2 microellipsoids, the value of \( \mu_0 \gamma \) could be considerably increased by the anisotropic distribution of the CoFe2O4 nanoparticles resulting in a large extent of the aggregation. Therefore, the CoFe2O4-based samples can be considered as colloidal micromagnets, the presence of the magnetic field during their synthesis reinforcing this feature.

The second set of experiments was carried out immediately after submitting the colloidal dispersions to a magnetic field during 1 min (Figure 8). It is well-known that magnetic dipolar interactions are increased by the presence of an external magnetic field.38 Therefore, we observed a chaining of the particles in the direction of the external magnetic field, whatever the sample. However, the chains formed for the γ-Fe2O3/SiO2 sample were small, and when the magnetic field was stopped, the microspheres were immediately redispersed (Figure 8b1–b3). On the contrary, very large permanent chains (about 1 mm in length and 10 μm in width) were formed for the microellipsoids (Figure 8a1–a3). Interestingly, these colloidal chains were isolated on a surface by simple settlement and evaporation of the water, which allowed their observation by SEM (Figure 8a3). The preparation of permanent chains is possible after inducing the magnetic moments of the CoFe2O4 nanoparticles. For the H-CoFe2O4/γ-Fe2O3/SiO2 samples. After inducing the dispersion of the particles or from a very fast aggregation in water immediately after the ultrasonic treatment, although TEM and SEM microscopies showed that the particles are not aggregated. Furthermore, we observed a rapid growth of the length and width of these chains (Figure 7a2,a3). A more accurate observation revealed that the lateral and longitudinal growth of the chains results from short-range directional attractive forces between the aggregates (see the complete movie in the Supporting Information). The γ-Fe2O3/SiO2 microspheres exhibited a completely different behavior, because they remained perfectly dispersed during the entire period of observation (Figure 7b1–b3). It should also be noted that the directional aggregation of the particles was observed with a lesser extent for the CoFe2O4/SiO2 dispersion (see the movies in the Supporting Information). These differences can be explained in terms of dipolar magnetic interactions existing between the microparticles. The magnetic dipolar interaction between two particles is attractive and maximum when their magnetic moments (μγ) are in head-to-tail configuration. The energy of the magnetic dipolar interaction between two aligned particles having the same value of μγ, Edd, is thus expressed by eq 3.38
still a challenge in colloidal chemistry, although several authors already claimed their preparation.15–25,39–41 Here, permanent fibrous chains are spontaneously formed in water, and their strength and size can be increased by reinforcing the magnetic dipolar interactions with an external magnetic field applied during 1 min.

**CONCLUSION**

In summary, we have demonstrated that magnetic silica colloids having both an original morphology and an anisotropic organization at the nanoscopic level can be prepared through the synergistic effect of nanoparticles possessing a high magnetic anisotropy, and external magnetic field during the synthesis. While the conventional ESE method usually leads to magnetic silica microspheres with an isotropic distribution of the magnetic nanoparticles,13,41 we have obtained here magnetic silica microellipsoids containing magnetic nanoparticles aggregated in large chains. At larger scale, these particles exhibit in consequence some strong permanent magnetic moments that are responsible for the existence of magnetic dipolar interactions. Therefore, when they are dispersed in water, the microellipsoids self-assemble into large and irregular chains. These interactions can be reinforced by the use of external magnetic field, allowing the preparation of very large permanent chains. A more systematic study is now underway for a better understanding of the influence of the different parameters (concentration and size of the magnetic nanoparticles, strength of the magnetic field, etc.) on the structure and magnetic properties of these materials. Furthermore, the monodispersity of these particles remains to be improved. This may be reached through a better control of the shearing conditions in the emulsion preparation, or by operating in a microfluidics device. This research illustrates how nanocomposite particles exhibiting complex architectures can be elaborated through simple, fast, and low-cost methods, such as the use of external fields in combination with soft chemistry. Thanks to their unusual properties and the simplicity of their preparation, new fields of application in biomedicine, environment, or optoelectronics might be opened for these materials. Recent studies on the use of nanocomposite particles prepared through the assistance of a magnetic field as biophysical models,17 adsorbents for water treatment,22 microstirrers,23 viscosity sensors,27 magnetic inks,30 or as template for the preparation of bulk materials with anisotropic mechanical strength32,34 are good examples of the potential of this work.

**EXPERIMENTAL SECTION**

**Synthesis.** The magnetic CoFe$_2$O$_4$ nanoparticles were synthesized according to a previously reported method.52 Briefly, stoichiometric aqueous mixtures of cobalt(II) nitrate ($\text{Co(NO}_3\text{)}_2$) and iron(III) nitrate ($\text{Fe(NO}_3\text{)}_3$) were prepared with a total concentration of $10^{-1}$ mol L$^{-1}$. Sodium hydroxide (NaOH, 10 mol L$^{-1}$) was added to increase the pH to 13 under vigorous stirring. The mixture was stirred for 1 h at room temperature and then transferred to the Teflon vessel of an autoclave. The autoclave was then introduced to an oven at 200 °C. The oven was heated during an incubation time of 120 h. The precipitate obtained after the temperature of the suspension naturally fell to 25 °C was isolated, and then dispersed in an aqueous solution of hydrochloric acid. The γ-Fe$_2$O$_3$ nanoparticles used in this study were synthesized according to a procedure described elsewhere.31,32 Magnetite (Fe$_3$O$_4$) nanoparticles were first prepared by Massart’s method.34 Next, the Fe$_3$O$_4$ nanoparticles were oxidized to γ-Fe$_2$O$_3$ and dispersed in acidic medium by adding HNO$_3$ and Fe(NO$_3$)$_3$.52

The H-COFe$_2$O$_4$/SiO$_2$ microellipsoids were prepared via a modified ESE (emulsion solvent evaporation) sol–gel method,43 which has already been published.44 First, 1 mL of a precursor solution was prepared by adding 0.2 mL of a 0.15 mol L$^{-1}$ HNO$_3$ aqueous solution to 0.8 mL of tetraethoxysilane (TEOS). This mixture was vigorously stirred for 45 min. During this period, TEOS was hydrolyzed up to an adequate level to obtain a monophasic solution. Next, 2 mL of a magnetic sol with an equivalent concentration of iron [Fe] = 0.8 mol L$^{-1}$ was formed by adding the precursor solution to 1 mL of an aqueous dispersion of CoFe$_2$O$_4$ nanoparticles. The magnetic sol was stirred during 5 min before being added dropwise to 18 mL of an organic phase composed of a vegetable oil (usually commercial rapeseed oil) containing 0.1% (w/w) of the emulsifier Arlacel P135. The water-in-oil emulsion thus formed was stirred during 30 min and then transferred into a Buchner flask connected to a water aspirator. The ethanol formed by hydrolysis of TEOS was thus evaporated from the dispersed phase during 35 min under reduced pressure (35 mmHg), at a temperature fixed at 35 °C by way of a water bath around the flask. Next, the system was brought back to atmospheric pressure, and the flask containing the emulsion was placed in the center of the area between two cuboid ferrite magnets in parallel and was mechanically stirred for one night. It was checked that for this geometry, the magnetic field was constant ($H = 1500$ Oe) in the area containing the flask. The emulsion was finally broken by addition of a large amount of acetone. The mixture was stirred during 5 min, and the particles were recovered with a magnet. They were washed several times with acetone and water, and dried in an oven at 70 °C for 4 h. The same procedure was used for the preparation of the CoFe$_2$O$_4$/SiO$_2$, γ-Fe$_2$O$_3$/SiO$_2$ and H-Fe$_2$O$_3$/SiO$_2$ reference samples, except that γ-Fe$_2$O$_3$ nanoparticles was used instead of CoFe$_2$O$_4$ nanoparticles, and/or that the emulsion was not placed between the two cuboid ferrite magnets.

**Characterization Methods.** Transmission electron microscopy (TEM) was made on micromotected samples using a JEM JEOL 100 CX microscope operating at 100 kV. In this aim, the particles were crushed in a mortar, embedded in a resin (AGAR 100) polymerized at 70 °C during 2 days, cut in 70 nm thin sections using a LEICA ULTRACUT UCT microtome apparatus, and deposited on a copper grid. The samples were also observed by scanning electron microscopy (SEM) on a SEM-FEG Hitachi SU-70 apparatus. The images were taken in secondary electron mode with an accelerating voltage of 5 kV, Prior to analysis, the materials were coated with a thin layer of gold by sputter deposition. The size distribution of the particles and their mean aspect ratio were determined from SEM pictures analyzed using the ImageJ software. Magnetic characterizations of the samples were made on a SQUID magnetometer (Quantum Design MPMS-5S apparatus). The magnetization–demagnetization curves were taken at 300 K on a given weight of dry material encapsulated in a cell, by measuring the magnetization of the samples for a magnetic field $H$ varying from −50 000 to +50 000 Oe. For the ZFC-FC measurements, the same cells containing the samples were used. The zero field cooled (ZFC) magnetization versus temperature measurements were carried out by cooling the CoFe$_2$O$_4$ composite samples and the γ-Fe$_2$O$_3$ composite samples, respectively, from 300 to 150 K and from 300 to 20 K. A field of 50 Oe then was applied and the magnetizations measured while the CoFe$_2$O$_4$ and the γ-Fe$_2$O$_3$ composite samples were heated respectively from 150 to 400 K and from 20 to 245 K. The field cooled (FC) measurements were performed in the same manner with the difference that the field was applied before cooling. All of the measured magnetizations ($m$, in emu per g of sample) were normalized to 1 g of magnetic material ($M$, in emu per g of magnetic nanoparticles) by dividing $m$ by the weight fraction of magnetic nanoparticles, w$_{\text{NP}}$. The values of w$_{\text{NP}}$ were obtained by w$_{\text{NP}} = m/M$, where $m$ and $M$ are the values of magnetization saturations corresponding, respectively, to the composite samples and to the dry pure magnetic nanoparticles. The values of $M$ were determined using the magnetization–demagnetization curves of the pure nanoparticles in powdered form ($M = 62$ and 54 emu g$^{-1}$ of magnetic nanoparticles for CoFe$_2$O$_4$ and γ-Fe$_2$O$_3$, respectively).
The formation of the microellipsoids was studied using an optical microscope (Zeiss) equipped with an objective lens (×40 magnification). Isolated magnetic droplets dispersed in the organic phase (vegetable oil +0.1% of Arlacel P135) were prepared directly on the microscope slides by adding small drops of magnetic sol to the organic phase. The emulsion preparations and the isolated droplets were observed at zero field, and under a magnetic field obtained with a Nd–B–Fe magnet (H = 250 Oe). The colloidal behavior of the aqueous dispersions of the particles was examined using the following procedure. The dry particles (m = 0.01 g) were first dispersed in 1 mL of an aqueous ammonia solution at pH = 9. At this value of pH, the silica surface of the particles is negatively charged, and their dispersion in water is favored by their electrostatic repulsion. Hence, the dispersion was sonicated during 10 min using an ultrasound bath, and was then submitted to settlement during 1 min to eliminate the remaining large aggregates. Finally, a drop of the dispersion was immediately deposited between two microscope slides separated by a spacer, and was observed with the optical microscope (×40 magnification). For a series of experiences, a Nd–B–Fe magnet was applied during 1 min in the proximity of the slides containing the dispersion just before the observation. For the observation of the dried dispersions by SEM microscopy, a drop of the dispersion was deposited on a SEM mount, which was let between two Nd–B–Fe cubic magnets in parallel during 1 min (H = 1500 Oe). The dispersion was then dried during the night at ambient temperature in the absence of magnetic field.

ASSOCIATED CONTENT

Supporting Information

Optical microscopy movies, characterization of the magnetic nanoparticles, photograph of the experimental setup, additional TEM images, elemental mapping by SEM-EDS, and additional magnetic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

E-mail: sebastien.abramson@upmc.fr

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Aude Michel, Delphine Talbot, and Anh-Tu Ngo for their technical support, and the internship students Daniel Sittler and Malik Tebbakh. SEM microscopy and EDS analysis in the IMPC (FR 2482) was supported by the C’Nano projects of the Region Ile-de-France.

REFERENCES

(26) Fresnais, J.; Berret, J.-F.; Frka-Petese, B.; Sandre, O.; Perzynski, R. Electrostatic Co-Assembly of Iron Oxide Nanoparticles and


