Convenient preparation methods for magnetic colloids

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Abstract

We present convenient laboratory-scale preparation methods for maghemite grafted with fatty acids as well as maghemite–silica core–shell colloids. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ferrofluids with a wide variety of magnetic materials and solvents are currently available. Oleic acid stabilized magnetite in an organic solvent, by now a classical system, is still widely used. Basically, two methods are known to graft magnetite with oleic acid: long-term grinding of bulk magnetite in the presence of pure surfactant and grafting of surfactants onto chemically precipitated magnetite in an alkaline aqueous solution. The latter method, described by Khalafalla and Reimers [1], is still frequently used to synthesize organophilic magnetite. Here we present a new and convenient laboratory-scale preparation method for this type of fatty acid stabilized ferrofluid. Unlike Khalafalla’s method, heating is not required and the grafting step takes only a few minutes to complete.

A second type of colloid we investigated are the silica spheres with iron oxide cores [2,3]. They are prepared by hydrolyzing tetraethoxysilane (TES) which subsequently polymerizes as silica on the surface of the magnetite particles. Since this reaction is carried out in an alkaline ethanol/water mixture, the point of zero charge (PZC) of magnetite must be lowered before these particles can be dispersed in the reaction mixture. Originally, the PZC was lowered by precipitating a very thin silica layer from a metastable sodium silicate solution [2]. However, the PZC can also be lowered by adsorption of citric acid. This makes the tricky precipitation step obsolete, but still allows further silica growth using TES.

2. Experiments

2.1. Preparation of maghemite

Magnetite was precipitated by dissolving 2.08 g FeCl$_2$ anh. and 5.22 g FeCl$_3$ anh. in 380 ml
per liter. The X-ray di
disorder, coded FF, contained 5.6 g of solid material
demineralized water. The resulting black disper-
reddish yellow sediment was dispersed by adding
sedimentation and washing with 2 M HNO
it at its boiling temperature for 1 h [4]. After
60 ml 0.35 M Fe(NO
oxidation to maghemite was completed by adding
sediment and the mixture was stirred for 5 min. The
40 ml 2 M HNO
net, the supernatant was removed by decantation.
A typical experiment was conducted as follows.
The PZC of FF was lowered by adding a 0.01 M
citric acid solution [4] to 45 ml FF until floccula-
tion was visible. The precipitate was redispersed by
increasing the pH to 7 with tetramethylammonium
hydroxide. Of the resulting dispersion 1 ml was
added to a mixture of 75 ml ethanol, 20 ml water
and 5 ml 25% NH3. While stirring, 0.1 ml TES was
added, and after a day an additional amount of
0.2 ml TES was added. TEM micrographs show
particles similar to those in earlier work [2,3]. The
average particle radius is 39.0 ± 8.1 nm. This
radius is corrected for the shrinkage of approxim-
ately 5% of these particles in the electron micro-
scope. Most of the silica particles contain clusters of
magnetic particles; these clusters were also present
demineralized water and adding 20 ml of 25% NH3
to this solution while stirring vigorously [4]. After
sedimenting the precipitate with a permanent mag-
etic particles with other fatty acids, such
as dodecanoic acid. Since fatty acids with saturated
chains are solid at room temperature, the extrac-
tion must be performed above the melting temper-
ature of the fatty acid (usually around 50°C).
Repeated experiments showed that the amount of
water has no noticeable effect on the final product;
it merely facilitates stirring. Excessive washing with
ethanol did not decrease the stability of the final
product. The amount of oleic acid does not play
a role as long as it is large; at least 13 ml oleic acid
per gram maghemite was needed to extract and
stabilize all particles.

3. Grafting maghemite with oleic acid

A typical experiment was conducted as follows.
2 ml FF was diluted by adding 50 ml demineralized
water. The sol was flocculated by adding a few
drops of 25% NH3, and sedimented using a perma-

4. Silica deposition from a TES solution

The PZC of FF was lowered by adding a 0.01 M
citric acid solution [4] to 45 ml FF until floccula-
tion was visible. The precipitate was redispersed by
increasing the pH to 7 with tetramethylammonium
hydroxide. Of the resulting dispersion 1 ml was
added to a mixture of 75 ml ethanol, 20 ml water
and 5 ml 25% NH3. While stirring, 0.1 ml TES was
added, and after a day an additional amount of
0.2 ml TES was added. TEM micrographs show
particles similar to those in earlier work [2,3]. The
average particle radius is 39.0 ± 8.1 nm. This
radius is corrected for the shrinkage of approxim-
ately 5% of these particles in the electron micro-
scope. Most of the silica particles contain clusters of
in the magnetic silica spheres prepared before [2]. An estimate of the number of magnetic particles per silica sphere was made using

\[
C = \frac{V_{\text{Fe}_3\text{O}_4,\text{total}}/\langle V_{\text{Fe}_3\text{O}_4,\text{grain}} \rangle}{V_{\text{m-SiO}_2,\text{total}}/\langle V_{\text{m-SiO}_2,\text{grain}} \rangle} = \frac{V_{\text{Fe}_3\text{O}_4,\text{total}}}{kV_{\text{TES}} + V_{\text{Fe}_3\text{O}_4,\text{total}}} \left( \frac{\langle d_{\text{m-SiO}_2}^3 \rangle}{\langle d_{\text{Fe}_3\text{O}_4}^3 \rangle} \right). \tag{1}
\]

where \(d\) and \(V\) indicate diameter and volume, respectively, and \(k \equiv V_{\text{SiO}_2}^{\text{mol}}/V_{\text{TES}}^{\text{mol}} = 0.1422\). The lower density of TES-hydrolyzed silica is taken into account in the calculation of \(k\). \(V_{\text{Fe}_3\text{O}_4}\) was calculated from the total mass of \(\gamma\)-Fe₂O₃ and its density. The subscript ‘m-SiO₂’ denotes a magnetic silica particle. Taking \(\langle d^3 \rangle \approx \langle d \rangle^3(1 + 3\sigma^2)\), an average cluster size of 13 is found. This is roughly twice as large as the estimated cluster size in Ref. [2]. Clusters of this size are also thought to be present in other ferrofluids [10].

How silica is linked to the surface of magnetic particles is not resolved, but it is probably anchored on spots where no citric acid is adsorbed. Since gold particles stabilized with citric acid are ‘vitreophobic’ [11], attachment of silica to citric acid itself seems unlikely.

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**References**