

A Novel Two-Step Silica-Coating Process for Engineering Magnetic Nanocomposites

Qingxia Liu,[†] Zhenghe Xu,^{*,‡} J. A. Finch,[§] and R. Egerton^{||}

Research and Technology Center, USG Corporation, 700 North Highway 15, Libertyville, Illinois, Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, T6G 2G6, Department of Mining and Metallurgical Engineering, McGill University, Montreal, Quebec, H3A 2B2, and Department of Physics, University of Alberta, Edmonton, Alberta, Canada, T6G 2J1

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A novel two-step silica-coating process, sol-gel followed by dense liquid coatings, is described. The maghemite surfaces coated with silica, using the two-step process, are characterized by X-ray photoelectron spectroscopy, electrokinetics, leaching test, and magnetization measurement. Compared with the single-step sol-gel or dense-liquid-coating process, the two-step process produces magnetic nanocomposites of the highest protection against acid attack at the lowest level of silica coatings with maximized magnetization.

Introduction

Magnetic nanocomposites have applications ranging from ferrofluids¹ to separation science and technology.^{2–4} In clinical applications,⁵ for example, magnetic nanocomposites are used to induce hyperthermia under an external alternating magnetic field of desired frequencies. The challenge for these applications is to engineer magnetic nanocomposites of great stability against coagulation and full protection of iron oxide substrate particles from leaching in an acidic environment, with maximized magnetization only in an external magnetic field. To meet these requirements, nanosize magnetic particles with a thin layer of silica film, which are often superparamagnetic, need to be engineered.⁶

In view of the technological importance of producing magnetic nanocomposites, a few methods have been reported on silica-magnetite/maghemite nanocomposites. Nanosize maghemite particles have been synthesized in situ in a nanodimensional cavity of horse spleen ferritin and organic polymer matrixes.⁷ Recently, a porous silica network formed by the sol-gel process was

used as a template to obtain magnetic particles of controlled sizes.⁸ Although these methods produced nanoscale magnets in various matrixes, the overall magnetic strength is often rather limited. This limited strength presents a major hurdle to their various applications, especially in magnetic carrier technology. Ultrathin silica films coated on nanosize magnetic particles are in special interest due to their high stability against aggregation and acid leaching with minimal reduction of magnetization. The silica surfaces are amenable for further functionalization by silanization, using silane coupling agents to produce functional magnetic nanocomposites. This approach remains, therefore, a principal method in engineering magnetic nanocomposites. Two conventional methods suitable for silica coatings on finely dispersed particles are sol-gel and dense-liquid processes.

Sol-Gel Process. The sol-gel process is a commonly used method for coating fine particles. The coating is performed in an organic solvent and the process is based on the hydrolysis of the precursors, such as tetraethoxy silane (TEOS), in the presence of water and a catalyst, and subsequent condensation of hydrolyzed TEOS on surface metal hydroxyls. With controlled hydrolysis of TEOS, an M-O-Si chemical linkage is established between surface metallic atoms (M) and TEOS, followed by lateral polymerization, and finally formation of a three-dimensional network via siloxane bond formation (Si-O-Si) with increasing TEOS concentration and degree of hydrolysis. The sol-gel process is particularly useful for preparing thin inorganic films of tailored porosity, refractive index, and compositional homogeneity, and has been used to prepare magnetic nanocomposites.⁹ However, it is well known that silica coatings by the sol-gel process are

* Author to whom correspondence should be sent.

[†] USG Corp.

[‡] Department of Chemical and Materials Engineering.

[§] Department of Mining and Metallurgical Engineering.

^{||} Department of Physics.

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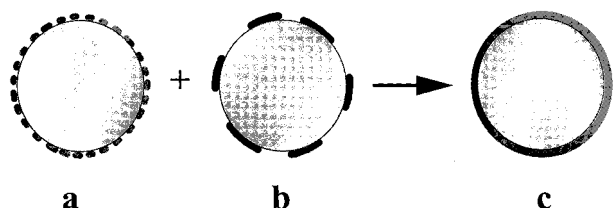


Figure 1. Schematics of silica-coated magnetic nanocomposites by (a) sol-gel, (b) dense-liquid, and (c) two-step (i.e., a followed by b) processes.

porous, as schematically shown in Figure 1a. To protect the substrate particles from dissolving in acidic solutions, a thick layer of coatings is required, which reduces the magnetizability significantly and hinders the technological applications of magnetic nanocomposites.

Dense-Liquid Process. This method was first introduced by Iler in 1959 to coat titania with a silica layer from supersaturated silica solutions.¹⁰ Now, the dense-liquid process is widely used to form silica films on surfaces of carbon, steel, alumina, and polymer resins to promote adhesion, to minimize photodegradation, and/or to prevent materials oxidation/corrosion. By controlling the supersaturation level of monosilicic acid (constant reactant addition), silica layers were formed on titania surface through heterogeneous followed by homogeneous coatings. It has been recognized that surface coating using the dense-liquid process is a complex physicochemical process. At least three competitive processes are present simultaneously: (i) heterogeneous coatings (on a substrate of different chemical compositions; e.g., SiO_2 on $\gamma\text{-Fe}_2\text{O}_3$); (ii) homogeneous coatings (on a substrate of the same chemical compositions; e.g., SiO_2 on SiO_2); and (iii) homogeneous nucleation (e.g., formation of SiO_2 nuclei) followed by homogeneous coatings. In general, the lowest supersaturation level is required for homogeneous coatings, followed by heterogeneous coatings, and finally homogeneous nucleation, which requires an excess energy, as predicted by the Kelvin equation, to account for extremely high curvatures of nuclei.^{11,12} In general, homogeneous nucleation can be avoided by careful control of (silica) supersaturation level just above the critical concentration of heterogeneous coatings (on maghemite). The homogeneous surface coating often presents a challenge to uniform surface coatings. It is evident that, as soon as the substrate is coated with silica even at the submonolayer level, the growth of the coated area (a process similar to homogeneous coating) prevails because it requires a lower supersaturation level. As a result, a nonuniform, patchwise (island) coating, as schematically shown in Figure 1b, is often obtained. With the dense-liquid-coating process, it is therefore unavoidable to expose substrate cores to the environment and poison the system by the released species, unless a thick coating layer is applied.

Two-Step Coating. It is clear that neither the sol-gel nor the dense-liquid process could meet the requirement of making magnetic nanocomposites of certain technological applications. To coat magnetic particles

with a thin protective silica layer and minimize reduction of saturation magnetization, a novel two-step coating process (the sol-gel followed by the dense liquid coating) has been developed in our laboratory. This approach is based on the idea that the sol-gel process can coat a surface uniformly, although the film is often porous, as shown in Figure 1a. In the second step, using the dense-liquid process, the residual ethoxy groups in nano- or microsize pores of the silica film prepared using the sol-gel process are further hydrolyzed, and the pores are anticipated to be closed by and filled with silica under low supersaturation conditions. It is clear that the two-step silica-coating process integrates the advantages of uniform coatings by the sol-gel process and a low supersaturation level required for homogeneous coating by the dense-liquid process. As a result, a uniform thin silica layer, as shown in Figure 1c, can be coated on maghemite to protect the particles, with minimal reduction in saturation magnetization (a key feature of magnetic carrier technology), and to provide a surface for further functionalization. The proof-of-concept is the focus of this communication. It is important to note that the objective of the two-step coating is not to coat more silica on the particles but rather to protect the substrate particles with the thinnest silica coatings possible to maximize the magnetic property of the coated particles.

Experimental Section

Chemicals. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$, 99+%) from Alpha Chemicals was dried in a vacuum oven at 120 °C for 24 h prior to the coating experiments. The average particle size was found by transmission electron microscope (TEM) to be ca. 30 nm, and the specific surface area was measured to be 44 m^2/g using the BET method with nitrogen as the carry gas. Tetraethoxy silane (TEOS) distilled in quartz from Petrarch and reagent grade ammonium hydroxides from Caledon were used in the sol-gel process. Absolute ethanol, distilled in-house, was used as the solvent. A 27% SiO_2 by weight in 14% sodium hydroxide solution (Aldrich) was used in dense liquid silica coatings. Millipore water was used whenever needed.

Sol-Gel Coatings. In a typical experiment, 0.9 g of maghemite was mixed with 40 mL of absolute ethanol by ultrasonification for 30 min, followed by the addition of 14 mL of TEOS solution (0.2 mL of TEOS in 13.8 mL of absolute ethanol). A 6-mL ammonium hydroxide solution (30%) was added in a dropwise manner into the suspension as a catalyst, and coating was allowed for 5 h to ensure the maximum hydrolysis of TEOS and the formation of the monosilicic acid necessary for condensation. The particles treated as such were separated from solution by a hand-magnet, rinsed with ethanol, dried in a vacuum oven at 110 °C, and stored in a desiccator for further characterization.

Dense Liquid Coatings. Precisely weighed maghemite particles were mixed with 90 mL of water in a 500-mL three-necked flask by vigorous mechanical agitation. The pH of the suspension was raised to 9.5 ± 0.1 by adding 0.1 N NaOH, and the suspension was heated to 90 ± 3 °C. A 0.1 M aqueous silica solution (10 mL) was added to the flask, concurrently with 0.1 M H_2SO_4 , within a period of 1 h, while maintaining the solution pH at 9.5 ± 0.2 (note: The addition of a strong alkaline silica solution would increase suspension pH to undersaturation condition if acid were not added during this stage). The reaction continued for 1 h, after which the suspension was cooled to the room temperature. The coated particles were separated from solution with the hand-magnet, rinsed with Millipore water three times, dried in the vacuum oven, and stored in the desiccator.

Two-Step Coatings. Similar procedures, as in the aforementioned sol-gel process, were used for the first-step silica

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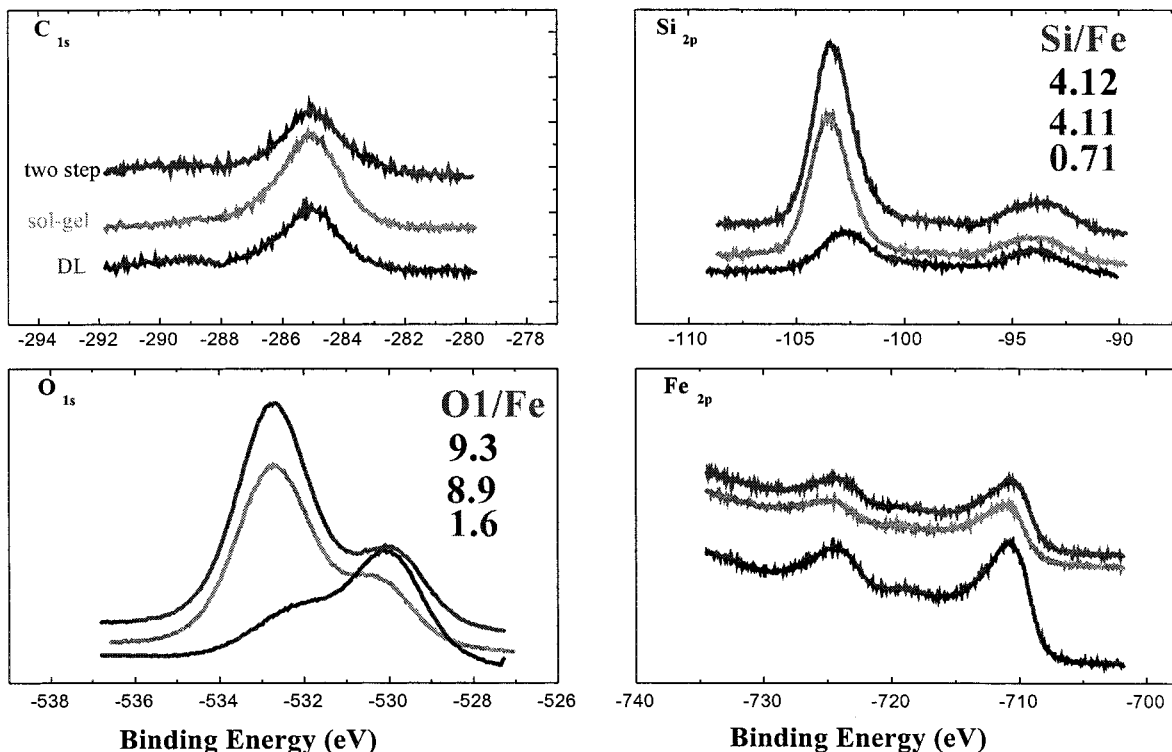


Figure 2. Narrow-scan X-ray photoelectron spectra of magnetic nanocomposites prepared with various silica-coating processes.

coating. The coated particles were further processed using the dense-liquid process just described. The total silica level in these two steps (6 and 5%, respectively) was kept the same as that used in the single-step coating processes (11%) to compare the coating performance.

X-ray Photoelectron Spectroscopy (XPS) Analysis. XPS spectra were obtained on an ESCALAB Mark-II instrument with a MgK α anode ($h\nu = 1253.6$ eV) at a takeoff angle normal to the sample. The source X-ray was not filtered and the instrument was calibrated against the C_{1s} band (284.8 eV). The spectra were recorded using a band-pass energy of 20 eV, corresponding to an energy resolution of 1.2 eV. The powder samples, pressed against a copper adhesive tape, were maintained under a background pressure of 1×10^{-9} Torr for ~ 1 h in the sample chamber before spectral acquisition. The spectra presented here were corrected for background charging by determining the C_{1s} (284.8 eV) signal both at the outset and at the end of a series of narrow scans for each sample. No significant charging was detected. Band-fitting and spectral deconvolution were performed using the commercial program Surf-Soft.

Zeta Potential. The zeta potential of maghemite particles, with and without silica coatings, was measured in 5 mM KCl background electrolyte solutions using a Lazer-zee meter (Model 501, Pen Kem, Bedford Hills, NY). About 5-mg particles were conditioned for 10 min in 100 mL of a test solution at a given pH, which was adjusted by addition of NaOH or HCl stock solutions. The suspension was then taken for zeta potential measurement. The results presented in this communication are the average of three independent measurements with a typical variation of ± 2 mV. It should be noted that the marginal increase in particle size by silica coating has negligible effect on the changes of measured zeta potentials.

Leaching Test. To examine the coverage and property of coated silica films, 20-mg coated maghemite particles were mixed with 25 mL of 0.01 N HCl acid solutions for 20 h. The suspension was then centrifuged using a Sorvall RC-5B refrigerated superspeed centrifuge (Du Pont Instruments) at 12 000 rpm for 30 min. The supernatant was collected and analyzed for iron concentration by atomic absorption spectroscopy (Perkin-Elmer 310, Perkin-Elmer, Norwalk, CT).

Transmission Electron Microscope (TEM). To examine the uniformity and to determine the thickness of silica coatings, a JEOL-2010 transmission electron microscope was used to obtain TEM micrographs. A fine drop of nanoparticle suspension at 10 ppm solid concentration was produced at the tip of a microsyringe and placed on a holey carbon TEM grid supported on self-locking tweezers. After evaporation of the water under ambient conditions, the specimen was transferred into TEM sample chamber and micrographs were taken at 200 000 \times magnification (200 kV) in the conventional TEM mode.

Results and Discussion

Using the approach described by Bergna et al.,¹³ it is calculated that 5.5% SiO₂ by weight is required for an atomic monolayer coverage of 40 nm particles by silica. To ensure the full protection of substrate particles with a minimum reduction in magnetizability of magnetic nanocomposites, a total silica level of 11 wt % of the total solids was used in all of the coating experiments, except as otherwise stated. The narrow scan XPS spectra of magnetic nanocomposites prepared with three different processes are shown in Figure 2. Compared with the spectra of uncoated particles,¹⁴ the presence of a silicon band at 103.4 eV and an additional oxygen band at 532.8 eV on the spectra of coated particles confirms silica coating on maghemite. A penetration depth of ca. 10 nm in XPS technique allows detection of iron in the underlying substrate, which provides a means to conduct semiquantitative surface analysis. Area ratios of silicon-to-iron bands (Si/Fe, normalized by corresponding atomic sensitivities) of 0.7, 4.1, and

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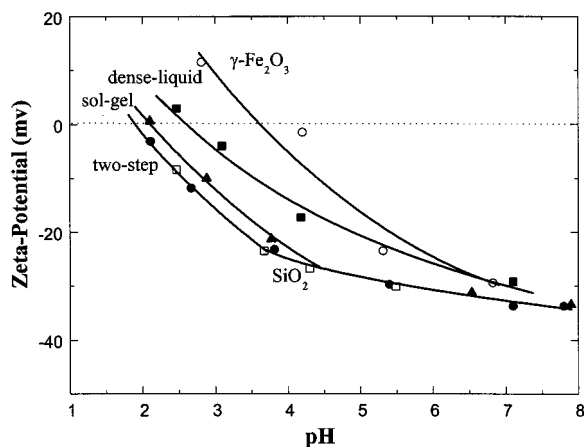


Figure 3. Zeta potentials of magnetic nanocomposites compared with single-phase silica and maghemite.

4.1 for the particles coated using the dense liquid, sol-gel, and two-step processes, respectively, were obtained. It is evident that the amounts of silica coated on maghemite by the sol-gel and two-step processes are comparable and higher than that by the dense-liquid process, as indicated by a higher Si/Fe mole ratio. The formation of siloxane bonds was confirmed for all the coatings by diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS).¹⁵ In contrast to the dense liquid or two-step coating process, unhydrolyzed ethoxy was detected for particles coated using the sol-gel process alone. The presence of Si-OEt terminal groups is partially responsible for the porous nature of the coated films that is often observed with the sol-gel process.

To further study the surface properties of the magnetic nanocomposite particles, the electrokinetics of the particles was measured, and the results are presented as zeta potentials in Figure 3. For comparison, the zeta potentials of maghemite and fused silica powder (Cab-O-Sil, Tuscola, IL) are also included in this figure. As shown, the isoelectric point (IEP) of pH 3 for maghemite coated using the dense-liquid process is significantly lower than that for uncoated particles (pH_{IEP} 4.5). However, this value is higher than the IEP of fused silica (pH_{IEP} 2.1), suggesting that silica was coated on maghemite, but only partially (probably in the form of islands) by the dense-liquid process, as illustrated schematically in Figure 1b. When the sol-gel process was used, an IEP of pH 2.4 was obtained, showing an improved coating compared with the dense-liquid process. This value, however, remains slightly higher than the IEP of fused silica, indicating that the surface coating is either incomplete or porous, as confirmed later by leaching tests (Table 1). When the two-step process was used, an identical electrokinetic behavior between the coated particles and fused silica was observed over the pH range studied, indicating the same surface properties between the two and confirming a full coverage of particles with silica. It is important to note that silica-like electrokinetics of silica coated maghemite with the two-step process ensures its dispersion, as required in many of its technological applications.

Table 1. Stability as Measured by the Amount of Iron Leached Out in Acid (pH 2.5) and Saturation Magnetization (M_s) of Magnetic Nanocomposites Prepared by Dense-Liquid, Sol-Gel, and Two-Step Coatings on Maghemite at 11% SiO₂

coating method ^a	Fe in 0.01 N HCl (mg/g)	M_s (emu/g)
dense-liquid	2.8	48.2
sol-gel	1.1	43.2
two-step	nil	42.5

^a Uncoated maghemite exhibited an M_s value of 52 emu/g, with 60.3 mg of Fe per gram of particles being leached out under the same conditions.

To further examine the state of silica film on maghemite, leaching tests were conducted, and the results are summarized in Table 1. Also shown in this table is the saturation magnetization of coated particles measured using a vibrating sample magnetometer developed in-house and, calibrated with a piece of single-crystal nickel before each measurement. It is evident that the amount of iron leached out became undetectable for the particles coated with the two-step process. In contrast, 1.1 or 2.8 mg of iron per gram of particles was detected in leachate of maghemite coated with silica by either the sol-gel or dense-liquid process.

The saturation magnetization, on the other hand, is comparable for the particles coated by the sol-gel or two-step process (43.2 emu/g), and lower than that for the particles coated by the dense-liquid process (48.5 emu/g). A higher reduction in saturation magnetization represents a higher level of silica coating. From the added mass of silica film at 11%, as used in coating process, a reduction of saturation magnetization to 46.3 emu/g is anticipated if a zero magnetization is assumed for silica. This value appears higher than that experimentally determined, and the difference may be accounted for by considering a diamagnetic nature of silica whose magnetic dipole moment opposes the magnetization field. The observed trend in the reduction of saturation magnetization is consistent with that derived from the quantitative XPS analysis, showing a higher surface silicon-to-iron mole ratio for particles coated by the sol-gel process or the two-step process compared with that for particles coated by the dense-liquid process. Our experimental results further illustrate that the property of coated films on a surface is determined not only by the amount of silica coated, but also by the method of coatings. Considering that the amount of silica coated on maghemite surface by the sol-gel and two-step processes is virtually the same (i.e., the two methods are equally effective in terms of putting silica on maghemite), it is readily seen that the film structure plays an important role in protecting the matrix component of magnetic nanocomposites. It is evident that the two-step silica-coating process is successful in making silica-protected magnetic nanocomposites at the lowest silica coating levels. It should be noted that the silica-coated particles remained superparamagnetic. The saturation magnetization was reduced, however, with increasing the level of silica coatings. For example, the saturation magnetization was reduced from 52 to 30 emu/g when the substrate particles were coated at 50% SiO₂ by weight using the sol-gel process, although the substrate particles coated at this silica level were protected, judged by an unde-

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tectable amount of iron in leachate. With such a low saturation magnetization level, the application of the magnetic nanocomposites in separation science and magnetic fluids becomes increasingly limited.¹⁶ For the dense-liquid process, maghemite coated at the silica level as high as 27 wt % remained iron leachable (e.g., 1.5 mg Fe per gram of particles was detected), with a saturation magnetization of 35 emu/g. Apparently, the formation of a uniform silica coating on maghemite by the dense-liquid process is energetically unfavorable. In the two-step coating process, only a minimal silica supersaturation level is maintained. As a result, silica homogeneous nucleation and sintering between magnetic particles can be minimized to ensure magnetic nanocomposites of uniform coatings. The TEM micrographs (Figure 4) show that silica-coated particles retained their original shape, with minimal aggregation (sintering) among the particles being observed. Compared with uncoated maghemite particles (Figure 4, top), a uniform thin layer (ca. 5 nm) of silica (light shades) is seen around core maghemite particles (dark spots) coated by the two-step coating method. The thin silica film formed on maghemite in two-step coating process ensures the stability of magnetic nanocomposites against aggregation and iron releasing, which may otherwise contaminate the system in applications. In the absence of an external magnetic field, an isotropic ferrofluids dispersion can be readily obtained from silica-coated maghemite due to electrostatic repulsion and strong hydration forces between silica-like surfaces. The dispersion can be switched to an anisotropic structure in an external magnetic field. Also, the silica surface on maghemite provides an easy route for surface functionalization by well-known silanization–condensation reactions. Such particles with strong and superparamagnetic magnetization have important applications in immunodiagnostic assays, biological cell separations, use as the host of catalysts and carrier for drug delivery, and detoxification of industrial effluents and municipal water.

Summary and Conclusions

We have demonstrated a novel two-step silica-coating process for engineering magnetic nanocomposites. By integrating the principal advantages of uniform coating and the nonporous nature of the films with the sol–gel and dense-liquid coating processes, magnetic nanocomposites, prepared by our two-step process, exhibited the highest saturation magnetization at the lowest level of silica coating, with an identical electrokinetic character of a natural silica surface. At the same level of 11% silica coating, the two-step coating produced particles completely protected by silica layers against acid leach-

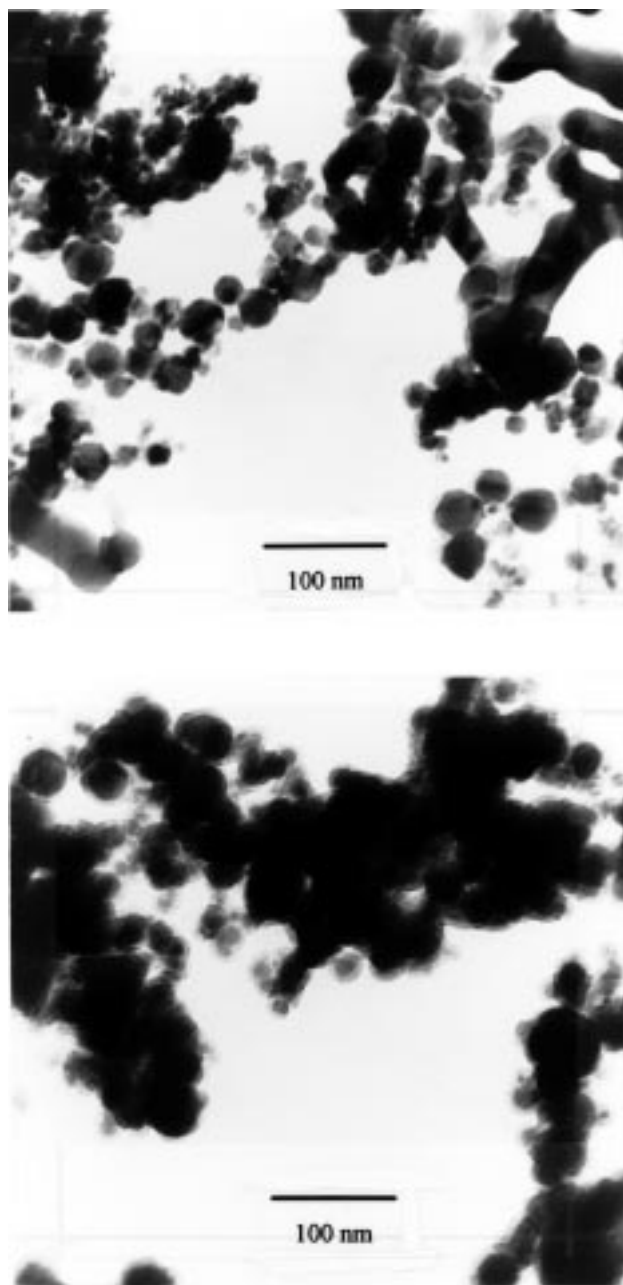


Figure 4. TEM micrograph of maghemite without (top) and with (bottom) silica coatings using the two-step silica-coating process.

ing. Such magnetic nanocomposites are well suited for stable ferrofluids and magnetic carrier applications.

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