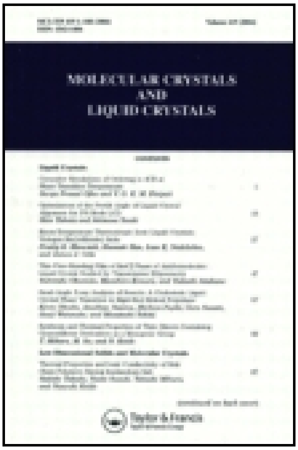

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Nanophase Magnetic Materials: Synthesis and Properties

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Nanophase Magnetic Materials: Synthesis and Properties

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Self-assembly preparative techniques in confined media that lead to magnetic materials with nanometer dimensions are described. Synthesis of nanoparticles using the restricted environments offered by surfactant systems such as water-in-oil microemulsions (reverse micelles) provide excellent control over particle size, inter-particle spacing, and particle shape. These environments have been used in the synthesis of γ-Fe_2O_3, Fe_3O_4, $MnFe_2O_4$, $CoFe_2O_4$, Fe and Fe/Au with particle sizes ranging from 10–20 nm. The controlled environment of the reverse micelle also allows sequential synthesis, which can produce a core-shell type structure (e.g., iron nanoparticles with gold coatings). Lyotropic liquid crystal media also offer template effects for the synthesis of non-spherical magnetic nanostructures. The structures, theory and modeling concepts and novel physical properties of these materials are discussed with emphasis given to the differences between course and fine grained magnetic materials.

Keywords: Nanoparticles; nanophase; superparamagnetism; ferrites; self-assembly

INTRODUCTION

The demand for smaller particles for use in high density storage media is one of the fundamental motivations for the fabrication of ultra-small nanoscale magnetic materials. As particle sizes incorporated into devices become

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smaller and smaller, the dimensionality of the particle approaches that of a molecule. There is currently a great deal of interest in novel synthetic routes that lead to the fabrication of particles that have supra-molecular dimensions.

In general, synthetic methods for the fabrication of magnetic materials with nanometer scale dimensions can be classified into two categories: one from molecular precusors (gas condensation, chemical precipitation, aerosol reactions, biological templating, and other self assembly processes), the other from processing of bulk precursors (such as mechanical attrition). Self assembly from molecular precusors is preferred in order to gain the most control over a variety of microscopic aspects of the condensed ensemble.

A variety of chemical methods, such as precipitation, reduction, pyrolysis, aerogel/xerogel processes, and hydrothermal reaction can be used to synthesize nanostructued materials.[2] For example, amorphous alloy nanoparticles of Fe or Co with B can be prepared by reduction of the iron or cobalt ion in aqueous solution by use of $NaBH_4$.[3] Nanoparticles of amorphous iron carbide can be prepared by thermal decomposition of $Fe(CO)_5$ in organic solvents containing appropriate surfactant.[3] The average particle size depends on the type of surfactant used. The nanoparticles of □-Fe, Fe_3C, and Fe_7C_3 can be produced by carbon dioxide laser pyrolysis of vapor mixture of $Fe(CO)_5$-C_2H_4.[4] Nanoparticles (<35 nm) of □-Fe_4N and □-Fe_3N can be prepared by vapor phase pyrolysis of $Fe(CO)_5$-NH_3 with a carbon dioxide laser in Ar and N_2 atmosphere.[5] Manganese zinc ferrite nanoparticles can be synthesized via a hydrothermal reaction.[6] The pH value of the starting mixture has a decisive influence on the composition of the product, whereas the heating temperature and time determine the size of the particles.

Water-in-oil micromulsions, also called reversed micelles have been used to synthesize a variety of nanoparticles of silver halides, superconductors and magnetic materials.[7] Reversed micelles are nanodroplets of water sustained in an organic phase by a surfactant that can hold and dissolve inorganic salts. The inorganic salts are then converted to an insoluble inorganic nanoparticle after chemical reaction and removal of water. For example, superparamagnetic Fe_3O_4 particles (5-20nm) were prepared by the reaction of $FeCl_2/FeCl_3/NaOH$ within the droplets of water of bis(2-ethylhexyl)sulfosuccinate sodium salt in isooctane solvent.[8]

In a recent synthesis of cobalt ferrite nanoparticles using the reversed micelles method,[11] the size of cobalt ferrite particles from 2 to 5 nm was controlled by the reactant concentration in oil-in-water micelles. Using this method it was possible to obtain the particles either suspended in the solvent to form a ferrofluid or in dry powder. When particles were isolated in a fluid, the interactions between particles were small. The reduced susceptibility increased progressively with the size of the particles and did not reach a plateau. With dry powder made of nanosized particles, the magnetic size was higher. The reduced susceptibility strongly increased with increasing the particle size to reach a plateau for an average size equal to 3 nm. This was explained by the increase in the attractive interactions between particles. By heating the powder, the reduced remanence, M_r/M_s, and the coercivity, H_c, increased with the increase in annealing temperature. This was attributed to the increase in the particle size and to the release of the adsorbed surfactant on the particles. The largest size of particles could be obtained either by annealing of the smallest one or from direct synthesis at room temperature.[9]

Another recent example[8] was the synthesis of the superparamagnetic microspheres of ferrite-polymer composite by incorporating nanometer-sized iron oxide crystals into micron-sized phenolic polymer particles. The synthesis of ferrite particles was conducted in the microenvironment of inverse microemulsions (reversed micelles) and in novel surfactant-based organogels, where interconnecting water channels provided the microenvironment for oxide formation. The microenvironment was used either to restrict oxide growth to the nanometer scale, or to direct growth in specific directions. Subsequently, enzymatic polymerization of p-ethylphenol was conducted in these media to encapsulate the ferrite particles while preserving particle arrangement. The polymer precipitated in spherical morphologies and during precipitation ferrite nanocrystals were incorporated, and uniformly distributed in the polymer matrix.

Functionalized reverse micelles were used to prepare Cu and Co nanoparticles differing by their size and shape by reduction of the surfactant metal complexes with N_2H_4. Fe-Cu alloy (30 at.% Fe) and composite (70 at.% Fe) particles were also prepared. A correlation was shown between the structure of the mesophase in the surfactant system with the size and shape of the formation of pure Cu particles. A functionalized surfactant was used to prepare Co nanoparticles where the size decreased with water content as a consequence of the formation of an oxide shell which prevented the particle growth. Nano-powders of Fe-Cu alloys were formed; magnetization curves before and after annealing were measured revealing a strong correlation with composition which is due to internal structural changes.[10]

By matrix-mediated or confined synthesis it is meant that a rigid structure is provided to act as a host or a matrix for the confined growth of the nanoscale magnetic particles. Several such host materials have been explored including those based on carbon fullerenes and nanotubes, organic resins, zeolite and mesoporous solids, and protein cages. The host or matrix not only provides spatially localized sites for nucleation but also imposes an upper limit on the size of the nanoparticles. As a result, this method will produce the nanoparticles with uniform dimensions.

The approach that we have used in synthesis of nanophase materials is to employ the spatially and geometrically restricted, self-assembling media of reverse micelles and microstructured gel phases. Our earlier studies on ferrite synthesis in these systems have shown particle growth restricted to the nanometer range with a narrow size distribution.[11] These preparations employed reverse micelles formed with a twin-tailed anionic surfactant *bis*-(2-ethylhexyl) sodium sulfosuccinate (AOT) or cetyltrimethyl-ammonium bromide (CTAB). Ferrite nanoparticles exhibit classical superparamagnetic behavior and the colloidal dimensions allow the particles to be suspended in solution, thereby creating a ferro-fluid. We have extended this reaction scheme to include sequential reaction conditions to prepare a core/shell nanostructured material.

Another interesting application of nanophase particles is in the formation of intelligent gels that can respond to external stimuli.[12] The composition of such gels is a polymer network swollen in a solvent. To the external stimuli such as temperature, Ph, electric field, light, and magnetic field, the viscosity or the volume of the gel can change.[13] Such sensitive responses to the stimuli present potential novel applications in sensors, controlled delivery systems, separators, and artificial muscles.[14]

In this report, the preparation and characterization of nanometer sized magnetic particles, composite core-shell particles, and particle-gel assemblies are presented.

EXPERIMENTAL

Materials

All chemicals used during the course of this work were of analytical grade. These were used as received from a commercial source (Aldrich Chemical). The surfactant AOT had a variable moisture content when purchased and was therefore dried at 70°C for several hours to remove this moisture to a w_0 ($[H_2O]/[AOT]$) below 0.4.

Synthesis

Ferrite Particles. By using dioctyl sulfosuccinate (AOT) and isooctane, reverse micelles can be made with a water pool of a specific size controlled by the water/surfactant ratio. This combination of oil phase, surfactant, and aqueous solutions allows a very narrow distribution of sizes from 5 nm up to 40 nm micelles. At the extreme size limits of 5 nm and 40 nm, the size distribution increases due to problems in micelle stability and crystallization. This system has been used extensively as the reaction environment for the growth of nanophase ferrites.

The synthesis of the ferrite Fe_3O_4 is prepared using an injection technique. Two separate micelle solutions are prepared with the desired size using 0.65M AOT in isooctane solution and aqueous solutions of 0.92M $FeSO_4$ as a metal containing solution, and aqueous NH_4OH. For example if 10 nm particles are to be made, 10 ml of $FeSO_4$(aq) are mixed with 90 ml of AOT. Any suspended impurities of the micelles are removed by centrifuging at 3500 rpm for 15 minutes. The clear micelle solutions are mixed together with constant stirring (low speed) using a magnetic stir plate. As the solutions are mixed, the solution turns green, and then a few minutes later will turn reddish in color. Over the course of 2 hours the ferrite crystallizes inside the aqueous pools. Mixed ferrites can be formed in the same fashion as that of Fe_3O_4. The metal containing micelle solution is prepared using 1:2 molar ratio of 1M $FeSO_4$ and 1M MSO_4, where M= Mn or Co.

The ferrite is removed from the reaction mixture by a magnetic separation technique. The reaction solution is transferred to a separatory funnel placed in a magnetic field. The mixture is washed several times with large excesses of a 50:50 methanol/water solution. The ferrite particles are retained in the separatory funnel by the magnetic field as the surfactant and other by-products are washed away.

This same technique can be used to synthesize γ-Fe_2O_3. The only change to the synthesis from that of Fe_3O_4 is a third micelle solution of 30% hydrogen peroxide. After the Fe^{2+} micelle solution has been mixed with the NH_4OH solution, the third solution of H_2O_2 is added. This helps to facilitate the complete oxidation of Fe^{2+} to Fe^{3+}. The ferrites are collected in the same fashion as described above.

This synthetic technique is very versatile and also offers an opportunity for oxidation/reduction chemistry as well as sequential synthetic procedures that lead to the fabrication of core-shell structures.

Iron coated gold nanoparticles. Metallic iron nanoparticles are synthesized in reverse micelles of cetyltrimethyl-ammonium bromide (CTAB).[15] Iron(II) is incorporated into the water pools of a reverse micellar solution formed by using CTAB as the surfactant, butanol as a cosurfactant, and octane as the oil phase. Hydrazine is injected into the solution reducing Fe(II) to Fe(0). The metallic iron particles grow to fill the centers of the micelle and minimal aggregation of iron centers occurs since the organic portions of the micelle keep particles separate. After complete reaction, chloroauric acid is added to the iron/CTAB mixture. Addition of the chloroauric acid solution increases the size of the reverse micelle and the Au(III) is reduced to Au(0) via excess hydrazine. Since gold and iron grow with complementary crystal structures, the metallic gold can form an epitaxial coating on the outer surface of the iron particles. The gold shells on the iron particles provide the functionality required to form organized arrays. Thin films of the gold coated particles are made by self-assembly reactions between the gold surface of the particle and (3-Mercaptopropyl)trimethoxysilane functionalized substrates.

Ferrite Chlorophenol Gel. A portion of the dry reversed micelle is dissolved in CCl_4 to prepare a 0.3 M AOT solution in CCl_4. An equal volume of 0.3 M p-chlorophenol in CCl_4 is then added and the solution thoroughly mixed. A transparent reddish-brown gel formed immediately. Other gels with different concentrations of the AOT and p-chlorophenol, or with different volume ratio of AOT:p-chlorophenol, are prepared with the same procedure.

Magnetic Experiments

Magnetic experiments were carried out using a Quantum Design MPMS-5S SQUID magnetometer. Calibration and measurement techniques are described elsewhere.[16] The DC susceptibility experiments were preformed from 2K through 300K at a field of 1000guass. Two different procedures were used for the dc magnetic susceptibility experiments: (1) zero field cooling, where the sample was slowly cooled in zero field to a temperature of

1.7 K, at which point the measuring field of 1.0 kG was switched on and the magnetization was then measured as a function of temperature; (2) field cooling, where the field of 1.0 kG was turned on at a temperature well above the superparamagnetic blocking temperature before the sample was cooled to 1.7 K. Standard magnetization versus applied magnetic field hysteresis loops were recorded at temperatures both below and above the blocking temperature by completing one cycle of 5T to –5T at temperatures of 2K and 300K.

Electron Microscopy

TEM images were performed on a Zeiss 100 microscope. For the measurements on the gels, a thin layer of the gel was deposited on a TEM grid coated carbon membrane. It was then heated to 200°C at a rate of 5°C/min, and subsequently to 260°C at a rate of 2°C/min. Heating removed the organic solvent and surfactant, and left the particles on the TEM grid. A Phillips-Norelco X-Ray diffractometer with a graphite monochromator and PMT detector was used to obtain XRD plots.

RESULTS AND DISCUSSION

Nanoparticles of Fe_3O_4, MnO, and Fe_3O_4/MnO composites with approximately 10nm dimensions were prepared and isolated as powders. DC magnetic susceptibility experiments were preformed on these particles. Figure 1 illustrates the DC magnetic susceptibility of the $MnFe_2O_4$ nano-particles. The materials display superparamagnetic behavior with a blocking temperature of about 40K. Temperature dependent dc magnetic susceptibility data for the samples were obtained by two different methods, field cooled (FC) and zero field cooled (ZFC). At high temperature, FC and ZFC magnetization data exhibit the same trend and are coincident. However, they diverge significantly at low temperature. The ZFC curve data show a dramatic

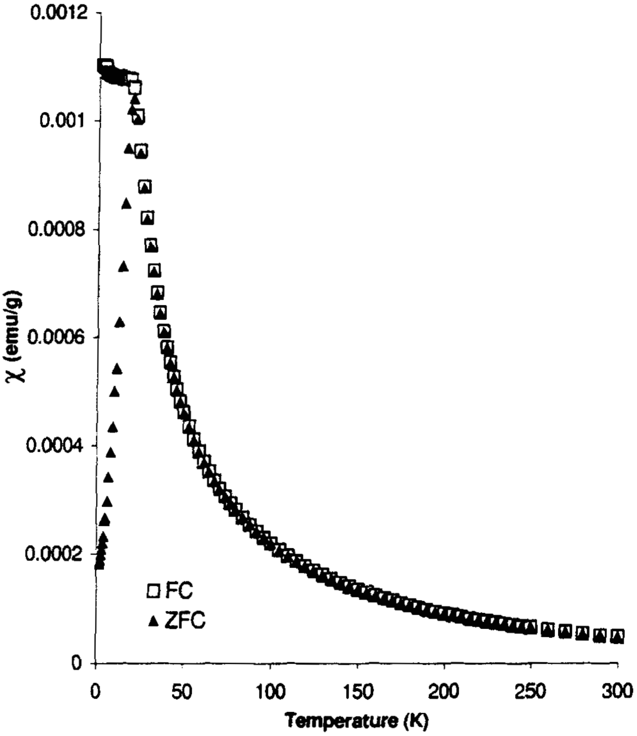

Figure 1. Magnetic susceptibility of 10 nm particles of $MnFe_2O_4$ measured as a function of temperature.

decrease in magnetization, while the FC data reach a plateau. The ZFC data also show a sharp maximum in the magnetization when plotted as a function of temperature. This maximum is a characteristic of superparamagnetic and spin glass materials.[17] It occurs at about 40K for each of the ferrite-containing particles studied here. This blocking temperature is further verified with TRM and IRM experiments.

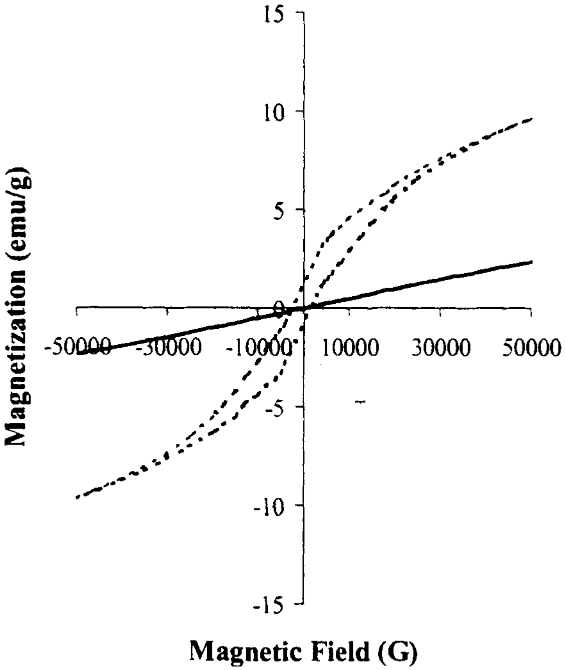

Figure 2. Magnetic Hysteresis 10 nm particles of MnFe$_2$O$_4$ measured above (T = 300K) and below (T = 2K) the superparamagnetic blocking.

Field dependent hysteresis loops were measured at temperatures both below and above the blocking temperature. Figure 2 shows the hysteresis curves at 2K and 100 K. The magnetization versus field data at 100 K illustrate the data to be perfectly superimposable within experimental error as the field is cycled between ±50 kG, with zero coercivity. This lack of coercive hysteresis is characteristic of superparamagnetic particles or single-domain particles of very small dimensions. As the temperature is significantly lowered, the sample starts to display some hysteresis. The presence of hysteresis at temperatures below the blocking temperature, together with the absence of hysteresis at temperatures above the blocking temperature, confirms the superparamagnetic behavior of these materials.

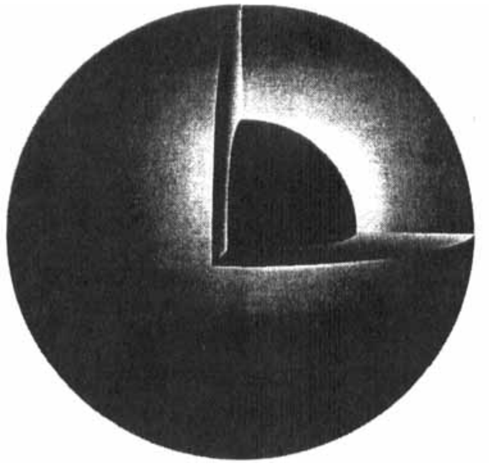

Figure 3: Schematic of a core shell particle, for example Fe core and Au shell.

The controlled environment of the reverse micelle also allows sequential synthesis which can produce a core-shell type structure. Figure 3 illustrates a schematic representation of iron nanoparticles with gold coatings. The gold coated iron nanoparticles were separated on a magnet and washed with solutions of chloroform and methanol. Since CTAB is soluble in this solvent system, it and any other non-magnetic by-products are washed away from the gold coated iron particles. An X-Ray diffraction pattern was obtained on a powder sample of gold coated iron and is presented in Figure 4. From the position of the peaks, it is clear that only gold and iron exist in the sample and the 2.5nm thick gold coating effectively prevents any oxidation of the metallic iron core.

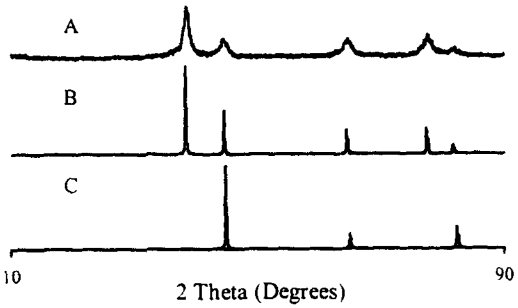

Figure 4. XRD pattern of (A) gold coated iron nanoparticles; (B) Au metal; (C) Fe metal.

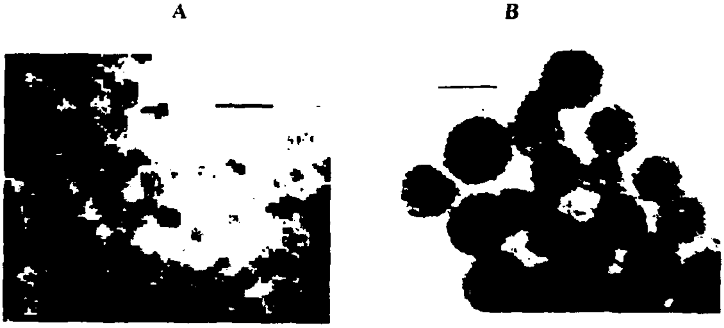

Figure 5. TEM images of (A) 15 nm Au/Fe nanoparticles (bar = 50nm); (B) 4x4 array of self-assembled 15 nm Au/Fe nanoparticles on a thiolated SiO TEM grid (bar = 15nm).

TEM images, shown in Figure 5, illustrate the dramatic differences between samples prepared in two different ways. The image presented in Figure 5A was obtained by placing a drop of a methanol suspension of 15nm gold coated iron particles onto a formvar coated TEM grid and allowing the solvent to evaporate. Aggregation of the particles due to the attraction of the magnetic cores is prevalent as expected. Figure 5B shows the patterning of 15 nm gold coated iron particles onto a thiol functionalized SiO TEM grid. No agglomeration is noticed in this sample and areas are organized into small arrays.

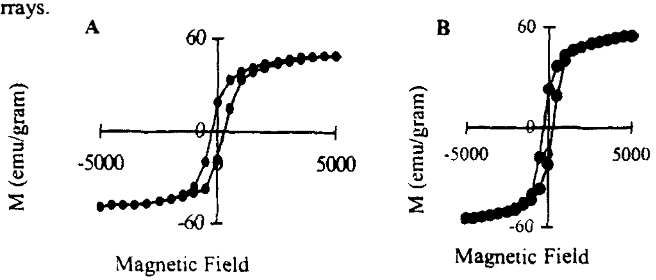

Figure 6. Magnetization as a function of field for (A) 15 nm iron and (B) 15 nm gold coated iron nanoparticles measured at a temperature of 2K.

Magnetic measurements performed on powdered samples of gold coated iron nanoparticles illustrate that the gold has a minimal effect on the magnetic properties when compared to that of pure iron. The blocking temperature is 8 K and the coercivity is 275 G in both cases. As shown in Figure 6, the only difference in the properties for the iron and gold coated iron lies in the remanent magnetization. The smaller moment of 18emu/gram for the gold coated iron is due to the additional non-magnetic mass of gold as compared with 22emu/gram for pure 15 nm iron. From the Scherrer equation, the magnetic grain size is estimated as 12nm. This is in excellent agreement with a total particle size of approximately 15nm as the gold coating is expected to be about 2.5nm thick

Ferrite Chlorophenol Organogel

The ferrite chlorophenol organogel was prepared as described in the experimental section. It was found that the magnetic behavior of the ferrite gel matches that of ferrites in reversed micelles. This reveals that the ferrite particles do not aggregate in the gel media. The result is consistent with the TEM observation. For the studies of the ferrite chlorophenol gel formation, two series of gel samples were prepared: 1) 0.3 M AOT/CCl_4 mixed with 0.3 M chlorophenol/CCl_4 with different volume ratios; 2) various concentrations of AOT/CCl_4 (0.2 to 0.6 M) mixed with the same concentration of chlorophenol/CCl_4 and volume ratio.

The ferrite particles incorporated into the gel are coated with surfactant AOT. Figure 7 is the TEM image of the particles in the gel media. They are scattered and distributed throughout the gel. The size of the particles ranges from 10 to 15 nm. They are spherical in shape. The size and the shape of the particles are controlled by the template effect provided by the reverse micelles during the synthesis of the particles. The concentration of the ferrite nanoparticles in the gel depends on the concentration of AOT, the hardness of the gel, and the size of the particles. From the NMR characterizations, we can assume that most of the AOT and chlorophenol molecules are located close to

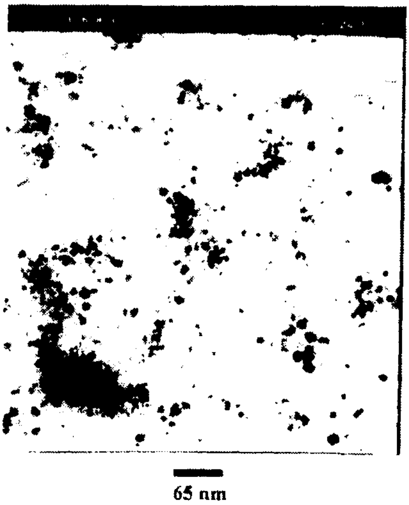

Figure 7. TEM image of the particles in the gel media.

the particles. Since the AOT and chlorophenol molecules are the two components assembling into the gel network, we propose that more gel strands extend around the surface of the ferrite particles. In other words, the ferrite particles are surrounded by gel strands.

CONCLUSION

Nanosized materials can be prepared in reverse micelles with a narrow size distribution. The reverse micelle synthetic technique allows a sequential preparation procedure that leads to a core shell structure in the resulting particle. The core shell synthetic procedure is most successful when there is a close match in lattice parameters of the two components as with the ferrite/MnO system.

TEM images of self-assembled gold coated nanoparticles on thiolated TEM grids show dramatic differences when compared to images of non self-assembled particles. The magnetic results demonstrate that the gold coating on the iron particles has a negligible effect on the magnetic properties and should not dramatically change the properties of the assembled particles. Work involving gold coated cobalt and cobalt platinum alloy particles is currently being investigated.

Nanosize ferrite particles can be incorporated into a chlorophenol organogel to yield a magnetic organogel. The particles can be suspended in the gel media, and serve as an agent of magnetic properties. The magnetic properties of the gel are dependent on that of the incorporated ferrite particles. The introduction of the ferrite particles causes more gel strands to form around the particles. This system can be considered as a precursor example for a magnetic sensitive gel. It gives us a hint that a magnetic sensitive gel might be generated by adjusting the components in the system and applying proper stimuli.

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