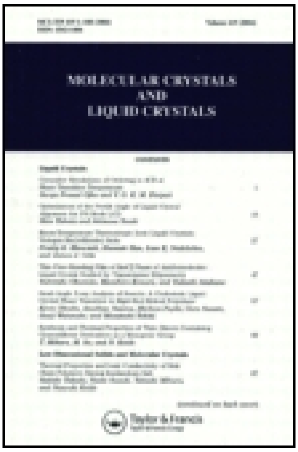

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# Synthesis and Manipulation of Nanophase Magnetic Materials

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# Synthesis and Manipulation of Nanophase Magnetic Materials

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Synthesis of various types of inorganic materials, namely metals, ternary metal oxides (ferrites), cadmium sulfide (doped with Mn) and alkaline trifluoromanganates, in their nanocrystalline state is performed in aqueous solutions. Restricting conditions for crystal growth were provided using reverse micelle water-in-oil microemulsions technique. The obtained materials have been characterized using electron microscopy TEM imaging, X-ray diffractometry and SQUID magnetometry.

Keywords: nanoparticles; reverse micelles; superparamagnetics; ferrites; ferromagnetic metals; metal sulfides; metal fluoromanganates

Chemical methods for manufacturing of nanocrystalline substances give advantage of wide variety of accessible substances with high purity, excellent possibility for size fractionation and even size and shape controlled synthesis[1-4]. Such high-quality nanoparticles can be assembled to form ordered poly-dimensional structures. In addition, chemical methods generally allow preparations in a larger scale than methods based on condensation of supersaturated vapor.

In order to obtain stable nanocrystalline substance suitable for processing, it is necessary to take control over its excessive surface energy. This is commonly achieved by using surfactant molecules that bind to the surface of nanocrystals. These molecules are usually well-known ligands from coordination chemistry modified with more or less long hydrocarbon chain. Purpose of these hydrocarbon chains is to inhibit aggregation, to protect the nanocrystals from reactive environment and to provide solubility in non-polar solvents such as hydrocarbons for purification, size selection and finally assembling into 2- or 3-D structures. Modified with reactive functional groups, these chains can act as a link between nanoparticle and biological molecules. The resulting composites may be used as diagnostic and therapeutic agents in medicine[5].

There are several solution reactions synthetic techniques. In some, the nanoparticles are stabilized with the ligand-surfactant that is introduced into the reaction system in the beginning, so that crystal growth is inhibited by complex formation[6-9]. In other systems the nanoparticles are stabilized with ionic shell[10] resembling the electric double layers known from classical colloidal chemistry. In this paper we report our results on synthesis of various classes of inorganic substances in their nanoscale state using strategy of the restricted crystal growth environment. This is basically an aqueous solution reactions technique performed in the reactors of the "nanoliter" volume. The tiny droplets of reaction solutions are encapsulated in the inversed micelles formed by surfactant molecules (or ion pairs) in non-polar liquid medium[11] (usually hydrocarbon). Micellar microemulsion medium is a dynamic system where colliding micelles coalesce, exchange their content and split. This property provides conditions for desired chemical reactions of synthesis. On the other hand, this property causes instability of colloidal solutions over time. Freshly formed nanocrystalline particles protected from further growth in micelles, have high surface energy and once micelles coalesce, particles readily aggregate. To prevent from this, in some systems the surfactant-ligand was added into micellar system shortly after the reaction of synthesis finished. Products after such treatment retain their identity as nanoscale molecular clusters in powder form and in solutions of appropriate solvents. In other systems surface passivation was achieved by coating with inert shell (Au) or by molecular or ionic agents provided from reaction environment.

Size of the particles was controlled by molar ratio of the surfactant to water, $w = [H_2O]/[CTAB]$. Syntheses of metallic nanoparticles were performed using cetyltrimethylammonium bromide (CTAB) as the surfactant and n-butanol as a co-surfactant. Syntheses of oxide and sulfide nanoparticles were performed with surfactant sodium diisooctylsulfoccinate (AOT).

All reagents, surfactants and solvents were used as received from Aldrich, Alfa Aesar and EM Scientific. The crystallite size and structure was analyzed by a Phillips-X'PERT X-ray diffractometer with a scintillation detector. Electron microscopy (TEM), EDS and SAD were preformed on a JEOL 2010. Magnetic measurements were done using a MPMS SQUID magnetometer.

## Metallic Au Nanoparticles

To prepare 6 nm particles, the micellar solutions (CTAB, $w = 6$) were prepared: 0.1M $HAuCl_4$ (aq) and 0.6M $NaBH_4$ (aq). These solutions were mixed and allowed to react for 2 hours. At the end the solution had characteristic clear red color expected for a gold colloid. For isolating the hydrocarbon-soluble material, the equivalent quantity of dodecane thiol dissolved in octane was added. After 1-2 hour of stirring at room temperature, solution was mixed with equal volume of methanol and centrifuged. The precipitated Au nanopowder was washed with methanol and redissolved in hydrocarbon solvent for size fractionation (by precipitation with ethanol) and self-assembling. Fragment of self-assembled monolayer of Au 5.7 nm nanoparticles is displayed on TEM image in Figure 1. The assembly exhibits hexagonal close packed structure.

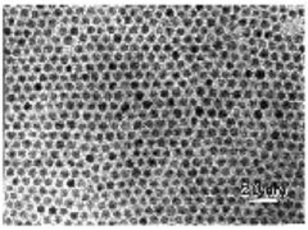

FIGURE 1 Self-assembled 5.7 nm Au nanoparticles

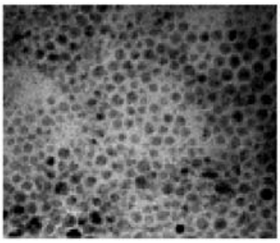

FIGURE 2 TEM image for Co nanoparticles

Metallic Fe and Co Nanoparticles

All syntheses were performed under argon using Schlenk technique. Two micellar (with CTAB, $w$ = 16) solutions were prepared: one with metal salts (0.425 mmol per 2.5g of aqueous solution) and another with reducing agent $NaBH_4$ (2.9 mmol per 2.5g of aqueous solution). Then the solutions were mixed and stirred for two hours. An excess of borohydride was used to suppress oxidation of Fe and Co by water. At the end, particles were passivated with Au by adding 0.06M aqueous

$HAuCl_4$. The magnetic particles were isolated using a magnetic field, washing with chloroform/methanol (1:1) and drying in vacuum.

The TEM image for Co nanoparticles is shown on Figure 2. The magnetization versus temperature zfc and fc curves for gold-coated cobalt nanoparticles (Figure 3) show that material was superparamagnetic above its blocking temperature 60 K. Hysteresis plot (Figure 4) obtained at 10 K showed coercivity 20 Oe.

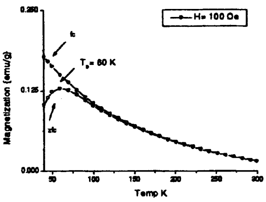

FIGURE 3 Magnetization vs. temperature for Co particles

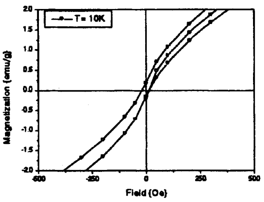

FIGURE 4 Magnetization vs. field for Co particles

## Ferrite Nanomaterials

Two portions of a stock 0.5-0.65M solution of AOT in isooctane were combined with aqueous solutions of the reactants, one containing metal salts and another one containing the precipitating agent $NH_4OH$. In typical preparation, solution A: 1 mmol of $FeSO_4 \cdot 7H_2O$ + 0.5 mmol of $MSO_4 \cdot xH_2O$ + 5.0 ml of $H_2O$ + 45 ml of 0.65 M AOT/isooctane was combined with solution B: 3.0 ml of 30% aqueous $NH_3$ + 2.0 ml of $H_2O$ + 45 ml of 0.65 M AOT/isooctane. After mixing and aging for 2 hours, the resulting solution was mixed with an equal volume of acetone or isopropanol and centrifuged. The product was washed with water and acetone and dried in air.

Plot of temperature dependence of susceptibility for nanoparticles of $MnFe_2O_4$ measured at 1000 Oe is shown in Figure 5. Material was superparamagnetic above its blocking temperature 30 K. Hysteresis curve obtained at 2 K (Figure 6) showed the coercivity value 3800 G.

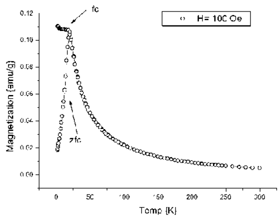

FIGURE 5 Magnetization vs. temperature for $MnFe_2O_4$ particles

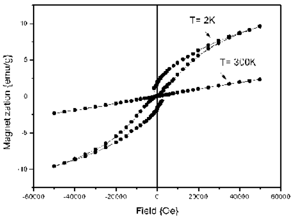

FIGURE 6 Magnetization vs. field for $MnFe_2O_4$ particles

Sodium and Potassium Trifluoromanganates(II)

The nanoparticles were synthesized by using a microemulsion system with CTAB, n-butanol and n-octane with *w* values in the range 5-20. Solutions containing a 0.1 M aqueous solution of $MnCl_2{\cdot}4H_2O$ and a 0.4 M KF or NaF were mixed, aged for few minutes to several hours and then combined with 1:1 methanol/chloroform mixture. Precipitated products were centrifuged, washed with methanol and dried at 50°C.

TEM microphotograph (Figure 7) shows the 35 nm nanocrystals of $KMnF_3$. Temperature dependence

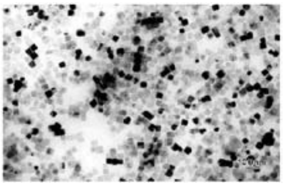

FIGURE 7 TEM image for $KMnF_3$ with average particle size 35 nm.

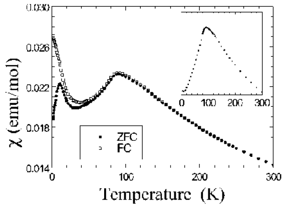

FIGURE 8 Magnetization vs. temperature for 13 nm $KMnF_3$

of magnetic susceptibility of 13 nm nanocrystals of $KMnF_3$ (Figure 8) shows antiferromagnetic behavior that is evidenced by transition at Neel point at 90K similarly to the bulk phase substance[12]. The zero-field curve exhibits also a maximum at 10K that supposingly corresponds to the blocking temperature.

## CdS Doped with Mn

Two micellar solutions (AOT, *w* = 10): $Na_2S \cdot 9H_2O$ and $Cd(OAc)_2 \cdot 2H_2O$ + $MnCl_2 \cdot 4H_2O$ were mixed so that the resulting ratio $([Cd^{2+}] + [Mn^{2+}]) / [S^{2-}] = 0.9\text{-}1.0$ was achieved. After aging for several hours at room temperature, an equivalent quantity of trioctylphosphine dissolved in isooctane was added to the clear yellow solution. After 1-2 hours, solution was mixed with equal volume of methanol, the precipitated product was centrifuged, washed with methanol and dried in air. This way we have prepared nanocrystals of $Cd_{1-x}Mn_xS$ (x = 0.02, 0.08, 0.2). For x = 0.02, TEM micrographs (Figure 9) show the particles to be spherical, with an average size of 7nm and a very narrow size distribution of about 6%. Magnetic measurements (Figure 10) confirm the existence of antiferromagnetically coupled $Mn^{2-}$-clusters with an

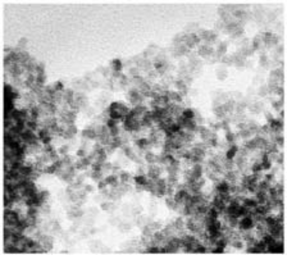

FIGURE 9 TEM image for 7 nm particles of $Cd_{0.98}Mn_{0.02}S$

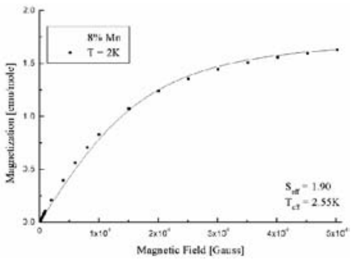

FIGURE 10 Magnetization vs. field for $Cd_{0.92}Mn_{0.08}S$

effective spin $S_{eff}$ that decreases with increasing $Mn^{2+}$ content: $S_{eff}$ = 1.90 and 1.60 for 8% and 25% Mn samples, respectively.

We have demonstrated that the reverse micelle technique can be successfully employed for synthesis of various types of nanocrystalline inorganic materials, ranging from metals to ternary metal oxides, sulfides and fluorides. This technique allowed obtaining nanopowders with narrow particle size distribution after a short purification procedure.

## Acknowledgements

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