Nanostructures synthesized by the reverse microemulsion method and their magnetic properties

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Abstract

The reverse microemulsion (ME) based synthesis is a versatile route for obtaining a variety of nanomaterials with controlled size and shape. Optimization of the various components involved in the formation of a ME is necessary to obtain the desired morphology and size. Magnetic materials have great significance in various fields like data storage, biomedical imaging, therapeutics, catalysis and sensor applications to name a few. It is seen that the magnetic properties of the nanostructures synthesized by ME methods are distinct from the structures obtained by other methods. Further, even for the nanostructures synthesized by the ME method, the magnetic properties depend upon their size and morphology. Thus, tuning the size and morphology of the nanostructures to tailor the magnetic properties is a desirable objective of several research projects. This mini-review comprehensively discusses those nanostructures synthesized by the ME method whose magnetic properties were investigated.

Introduction

The reverse microemulsion (ME) based route is found to be highly versatile for the synthesis of a variety of nanomaterials as well-documented in several excellent reviews [1–7]. The effect of various ME parameters and components on the final size and morphology of these structures has been extensively investigated. Optimization of these components like surfactant, co-surfactant, organic phase and water to surfactant ratio (Wv) enables us to synthesize nanomaterials with controlled size and shape [6]. It is also well established that the physical properties, including their magnetic properties of nanostructures of the same composition differ with their size and morphology. Thus the control of shape and size in nanostructures is essential for obtaining the desired properties. Our group has over the past decade extensively investigated these systems by techniques like small angle x-ray scattering (SAXS), Fluorescence correlation spectroscopy (FCS) and time-resolved fluorescence studies by which we have been able to understand in detail the growth of bare ME systems as well as of the nanostructures that grow inside them [8–11]. The effect of various ME parameters were correlated with the final size and morphology of these structures. Nanostructured materials obtained by the ME method include metals, alloys, oxalates, carbonates, borates, succinates and oxides including niobates, tantalates and manganites.

Magnetic nanostructures have significant applications in several fields including data storage [12, 13], biomedical [14–18] sensor [19–21] and catalytic [22, 23] applications and thus it is highly desirable to tune the magnetic response of these nanostructures. Apart from the reverse-microemulsion (water-in-oil) systems (as we shall see in numerous examples below), the oil in water microemulsion [24] system has been extensively used for synthesis of nanostructures whose magnetic properties have been utilized for applications like magnetic resonance imaging (MRI) and drug delivery for therapeutic purposes [25, 26]. This current mini-review discusses the work done in our laboratory and other laboratories on the nanostructures obtained by the ME method whose magnetic properties were investigated. In several cases it is seen that the magnetic properties of
the nanostructures are critically dependent on the size, shape and alignment of the nanoparticles and are distinct from their bulk counterparts. We begin our discussion with a section on metal and alloy nanoparticles, followed by a review of oxide materials, composites and core-shell materials. To provide the reader a more holistic picture of the state of art in the field, some selected examples are also discussed where a combination of the ME method was used with a different synthetic technique to obtain magnetic nanostructures.

**Metal and alloy nanoparticles**

The ME method has been used extensively for the synthesis of metal and alloy nanoparticles with tailored size and morphology. In this section we shall comprehensively review the reports where the magnetic properties of metal and alloy nanoparticles synthesized by the ME method are investigated. Hexagonal cobalt (Co) and cobalt–nickel (1:1) alloy nanoparticles were obtained by the ME method [27]. Both the metal and the alloy nanoparticles were synthesized using CTAB (cetyltrimethylammonium bromide) as the surfactant, 1-butanol as the co-surfactant and isooctane as the oil phase. For the metal nanoparticles 0.1 M Co(NO₃)₂.4H₂O, 1.0 M N₂H₄.H₂O and 0.1 M NaOH was used as the aqueous phase while for the alloy particles, in addition to the above reagents, 0.1 M Ni(NO₃)₂.6H₂O was also added. Spherical nanoparticles of hexagonal and cubic forms of Co of sizes <10 nm is obtained by this method whereas normally fcc cobalt is predicted to be stable. These hcp cobalt nanoparticles when annealed in H₂ at 700 °C transform to fcc Co nanoparticles. Both cobalt (hcp and fcc) as well as the alloy (Co–Ni) nanoparticles exhibit ferromagnetism. It was observed that for the Co–Ni nanoparticles the saturation magnetization is reduced compared to the bulk and this was attributed to surface oxidation. Spherical Fe–Co alloy nanoparticles with compositions of Fe₇₅Co₂₅, Fe₆₇Co₃₃, Fe₅₀Co₅₀, and Fe₃₃Co₆₇ nanoparticles of sizes 20, 25, 10, and 40 nm respectively were synthesized by the ME method and found to be ferromagnetic in nature [28]. For the synthesis of these alloy particles, CTAB was used as the surfactant, 1-butanol the co-surfactant, and isooctane the oil phase. Three aqueous phase ME containing 0.1 M Cu(NO₃)₂, 0.1 M cobalt acetate, and 1.0 M NaBH₄ were prepared separately and slowly mixed. The weight fractions of various constituents in these ME were varied to obtain the different compositions. The obtained precipitate was separated, washed dried and calcined in a hydrogen atmosphere at 700 °C for 6 h to yield the alloy nanoparticles. Spherical core shell nanostructures with the core consisting of Cu–Co composite particles and a ~12 nm thick shell composed of Cu–Co alloy particles were synthesized [29] (figure 1). It is noteworthy that in the bulk, the Cu–Co binary system has practically no miscibility. For the synthesis of these core-shell particles, CTAB was used as the surfactant, 1-butanol as the co-surfactant, and isooctane as the oil phase. Four separate ME with aqueous phases containing 0.1 M Cu(NO₃)₂, 3H₂O, 0.1 M cobalt acetate, 20 M N₂H₄.H₂O, and 0.1 M NaOH were prepared, slowly mixed, dried and reduced in hydrogen atmosphere at 700 °C for 6 h to form the core-shell nanostructures. Cu–Co nanostructures (not alloys) were also obtained by using a lower concentration of reducing agent (1.0 M N₂H₄.H₂O). A ferromagnetic behavior at 4 K is exhibited by these Cu–Co nanostructures. The core-shell (Cu–Co composite @ Cu–Co alloy) nanostructures exhibit a saturation
anhydrous manganese oxalate

Calcination of these precursor nanomaterials yields the corresponding oxides. Transition metal oxalates, metal oxides are another important class of compounds that have structural and physical properties. Often the metal carboxylates and metal oxides obtained from them chain-like ones were ferromagnetic.

The advantage of this method was that reducing agents were not required. The magnetic properties were dependent on the structure of the nanoparticles. In another study by the same group, Nickel oxalate nanorods exhibited an antiferromagnetic transition at TN (∼470 nm) respectively leading to porous films, small nanoparticles and aggregates of nanoparticles each with varying magnetic properties.

Metal carboxylates and metal oxides obtained from them

Metal oxides are another important class of compounds that have structural and physical properties. Often the ME method is used to synthesize precursor nanomaterials (e.g. metal carboxylates) with tailored shape and size. Calculation of these precursor nanomaterials yields the corresponding oxides. Transition metal oxalates, anhydrous manganese oxalate (MnC2O4), nickel oxalate (NiC2O4·2H2O) and copper oxalate (CuC2O4·H2O) nanorods were synthesized by the ME route [34–36]. The manganese oxalate nanorod precursors, under specific reaction conditions yielded single phase nanoparticles of various manganese oxides such as MnO, Mn3O4 and Mn2O3 [34]. The size of MnO nanoparticles was 28 nm while that of α-Mn3O4 was 50 nm and both were cubic in phase. α-Mn3O4 shows a weak antiferromagnetic transition with a Néel temperature (TN) of 80 K, while the spinel Mn3O4 particles (100 nm in size) show a ferrimagnetic transition at 43 K. In another report nickel oxalate and copper oxalate nanorods were synthesized [35–37]. The nickel oxalate nanorods have a diameter of 250 nm and a length of the order of 2.5 μm while for the copper oxalate nanorods, the diameter and length are 130 nm and 480 nm respectively. The nature of the solvent was found to influence the aspect ratio of the nanorods. Nickel oxalate nanorods exhibited an antiferromagnetic transition at TN = 34 K while the copper oxalate nanorods show temperature independent paramagnetism. The magnetic properties were also found to be dependent on the synthesis techniques. For example in copper oxide nanoparticles synthesized by water-in-oil MEs with two different nonpolar solvents (isoctane and n-octane) the TN was found to be different [38]. The particles synthesized using isoctane have a grain size of 25–30 nm and exhibit a TN of 80 K while for the ones synthesized in the n-octane system have a grain size of 80–90 nm and a TN of ~220 K, similar to that of bulk sized particles. In another study, iron oxalate dihydrate nanorods ~470 nm long and having ~70 nm diameter were synthesized by the reverse micellar route [39]. These rods show an antiferromagnetic ordering at 27 K. Depending on the decomposition conditions, these oxalate rods act as suitable precursor for obtaining a variety of iron oxide nanoparticles with varying magnetic properties. When the iron oxalate nanorods were decomposed in air at 500 °C, spherical Fe2O3 nanoparticles (~50 nm) were obtained that exhibit a transition from a weakly-ferromagnetic to weakly anti-ferromagnetic behavior at ~225 K which is indicative of a Morin-like transition. However, on decomposition of the oxalate nanorods at 500 °C in vacuum (~10⁻⁵ torr) cuboidal Fe3O4 nanoparticles (~60–70 nm) were obtained which show a Verwey transition at 122 K [39].

We have also investigated the morphologies and properties of cobalt oxalate dihydrate nanorods obtained by the ME route [40]. The length of these rods can be modified with change in calcination temperature (from ~6.5 μm at 50 °C to ~2.5 μm at 150 °C) while maintaining a nearly constant diameter of 200–250 nm.
Nanoparticles of Co$_3$O$_4$ and Co are obtained on thermal decomposition of these rods in air and H$_2$, respectively, while a mixture of Co and CoO nanoparticles is obtained by carrying out the decomposition in a helium atmosphere. Antiferromagnetic ordering at 54 and 35 K is seen for the oxalate rods and Co$_3$O$_4$ nanoparticles respectively (figure 2). In another report [41], cobalt oxalate was obtained by the ME method that on decomposition at high temperatures yielded Co$_3$O$_4$ nanoparticles. These Co$_3$O$_4$ nanoparticles align under controlled kinetic parameters and specific decomposition temperatures to form anisotropic nanostructures with well-defined aspect ratios ranging from 1:5 to 1:13. It was observed that the temperature of decomposition influences the shape and size of the individual nanostructures while the cationic surfactant plays an important role in the assembly of these structures. The nanorods showed antiferromagnetic behavior and with decrease in the average size of the individual oxide nanoparticles the T$_N$ decreases proportionately. Nickel oxide (NiO) nanoparticles with an average size of 25 nm size having a narrow size distribution were obtained from nickel oxalate synthesized by the reverse-micellar route [42]. These particles exhibit a high magnetic moment as compared to the bulk NiO and also a nearly temperature independent paramagnetism.

Rod-shaped cobalt succinate sesquihydrate and spherical iron succinate trihydrate/pentahydrate were synthesized by the ME route [43]. These are excellent precursors for the synthesis of the respective metal and metal oxide nanoparticles and pure phase Co and α-Fe nanoparticles were obtained on heating in nitrogen atmosphere. Fe$_3$O$_4$ cubes of edge length ~150 nm and elongated particles of diameter ~200 nm were obtained. Use of a longer chain dicarboxylate ligand results in shorter rods. The Fe nanoparticles exhibit nearly 100% super para magnetism. The Fe$_3$O$_4$ nanoparticles show a Morin-like transition at 223 K while the Fe$_3$O$_4$ nanoparticles exhibit a Verwey transition at 115 K.

Grass like Fe$_3$O$_4$ nanostructures were reported by using a microemulsion assisted solvothermal method [44]. The magnetic hysteresis loops display superparamagnetic signature at room temperature with the saturation magnetization of 65.5 emu g$^{-1}$. Superparamagnetic silica modified iron oxide nanoparticles (8.8–12 nm) were synthesized [45] at room temperature in CTAB/butanol/cyclohexane/water ME system. The as synthesized particles exhibited fast response to applied magnetic fields and zero remanence and coercivity. In γ-Fe$_2$O$_3$ nanoparticles, nanorods and multi-pod nanostructure prepared by variation of reaction conditions the magnetic properties were found to be influenced by the morphology [46].

Magnetic studies on Co$_3$O$_4$ nanoparticles indicated an antiferromagnetic ordering at 20 K. ZnMn$_2$O$_4$ nanoparticles with the spinel structure were obtained from the decomposition of metal oxalate precursors synthesized by (a) the ME and (b) the coprecipitation methods [47]. It was seen that the shape, size and morphology of precursors and oxides vary significantly with the method of synthesis. The ME synthesis method...
resulted in the micron sized zinc oxalate rods whereas the coprecipitation method yielded spherical nanoparticles of size 40–50 nm. Low temperature (~450 °C) decomposition of oxalate precursors obtained from either of the methods yielded phase pure ZnMn$_2$O$_4$ nanoparticles. However, the size of the ZnMn$_2$O$_4$ nanoparticles obtained from the precursors made by ME method are relatively much smaller (20–30 nm) as compared to those obtained from precursors made by the co-precipitation method (40–50 nm). Antiferromagnetic ordering in the range of ~150 K was seen in nanocrystalline ZnMn$_2$O$_4$. NiMn$_2$O$_4$ nanospheres and hexagonal particles were synthesized by tuning the morphology of the nickel manganese oxalate precursor [48]. Variation of the surfactant, co-surfactant and non-polar phase in the ME route lead to the tuning of the aspect ratio from 2 to 24 in these nickel manganese oxalate precursors. With the decrease in the aspect ratio of the nanorods the ferrimagnetic transition temperature $T_c$ (126–72 K) and magnetization decrease. The lowest $T_c$ (72 K) and magnetization is shown by the hexagonal nanoparticles of NiMn$_2$O$_4$.

Ni$_{0.5}$Mn$_{0.5}$(C$_6$O$_7$)$_2$.2H$_2$O was synthesized by the ME route and crystallized as nanorods [49]. With the increase in the chain length of the cosurfactants (1-butanol, 1-hexanol and 1-octanol), the aspect ratio of the nickel manganese oxalate increased by up to four times. This was attributed to the reduction of film flexibility of the micelle on increasing the chain length of the co-surfactant in the presence of a non-ionic surfactant (Tergitol). The use of a cationic surfactant led to highly uniform nickel manganese oxide nanorods. These oxalate precursors on thermal decomposition yielded anisotropic nanostructures of nickel manganese oxide (NiMnO$_3$). It was observed that the NiMnO$_3$ nanostructures were all ferromagnetic. The Curie temperature ranged from 437 to 467 K and the saturation magnetization increased with increase in the aspect ratio of the nanorods. Nano-sized complex manganites LaMn$_2$O$_3$, La$_{0.67}$Sr$_{0.33}$MnO$_3$ and La$_{0.67}$Ca$_{0.33}$MnO$_3$ were synthesized using the ME route [50]. An average grain size of 68, 80 and 50 nm and ferromagnetic ordering at around 250 K 350 K and 200 K was observed for LAMn$_2$O$_3$, La$_{0.67}$Sr$_{0.33}$MnO$_3$ and La$_{0.67}$Ca$_{0.33}$MnO$_3$, respectively. These Curie temperatures correspond well with those reported for bulk materials with similar composition.

Anisotropic nickel borate nanostructures were obtained from a nickel boron precursor synthesized using MEs by a precursor-mediated route [51, 52]. Various co-surfactants (1-butanol, 1-hexanol and 1-octanol) were used and it was found a higher chain length leads to more uniform nanorods rather than nanospindles. The nanorods exhibit antiferromagnetic behavior with the $T_N$ ranging from 44 to 47 K. Additionally, the magnetic moment increases drastically with the anisotropy of nanorods (thinner rods) though there is no marked variation in $T_N$.

Tb-doped BiFeO$_3$ (Tb$_{0.1}$Bi$_{1-x}$Fe$_x$O$_3$) nanoparticles were synthesized using the micro-emulsion route [53]. SEM indicated the formation of 80–120 nm particles. On substitution of Bi$^{3+}$ by Tb$^{3+}$, the magnetic properties were found to be substantially altered. Among the synthesized compositions, the maximum saturation magnetization (Ms) of 0.6691 emu g$^{-1}$ was exhibited by Tb$_{0.02}$Bi$_{0.98}$FeO$_3$ while the maximum coercivity of 549 Oe was seen in BiFeO$_3$. In another study Tb$^{3+}$-doped 16–24 nm sized nanocrystalline zinc ferrites of a nominal composition of Zn$_{1-x}$Tb$_x$Fe$_2$O$_4$ (x = 0, 0.03, 0.06, 0.09, 0.12 and 0.15) were prepared [54]. The magnetic studies showed that these nanocrystalline terbium doped zinc ferrites are ferrimagnetic.

Hydroxyapatite-encapsulated cobalt ferrite (CoFe$_2$O$_4$) nanopowders were synthesized [55]. The obtained phases, morphology and magnetic properties were found to depend on calcining temperature. Nanoparticles calcined at 700 °C exhibit core–shell morphology. A maximum saturation magnetization of 7.8 emu g$^{-1}$ with a characteristic hysteresis loop was observed. On increasing the calcination temperature to 900 °C, cobalt ferrite reacts with hydroxyapatite leading to the formation of a new phase, Fe$_{12}$-PO$_4$·OH (1512), which results in decrease in saturation magnetization. The ME method was used to synthesize porous nickel ferrite (NiFe$_2$O$_4$) nanorods ~200 nm in diameter and ~2.5 to 3.0 µm long [56]. The structural defects like vacancies and surface disorder were investigated using positron annihilation spectroscopy while the cation distribution and magnetic hyperfine properties were probed by Mossbauer spectroscopy. As compared to the bulk composition, a reduced saturation magnetization ($M_s = 20.3$ emu g$^{-1}$) and an enhanced coercive field ($H_c = 37$ Oe) field was observed and this was attributed to the mixed spinel structure and the charge accumulated on the surface. The ME method followed by calcination was used to prepare MnFe$_2$O$_4$·Eu$^{3+}$ nanostuctures that are irregular in shape with an average diameter of 30–80 nm [57]. It was observed that the magnetic properties were greatly influenced by amount of Eu$^{3+}$ doping and increasing it from 0 to 1.0 mol 1$^{-1}$ the saturation magnetization (Ms) values decrease from 42.06 to 0.69 emu g$^{-1}$. CoFe$_2$O$_4$ nanoparticles (~49 nm) were prepared by the ME method [58]. At an applied magnetic field of 50 kOe and a temperature of 5 K, the coercivity and the maxismal magnetization were 15.1 kOe and 15.2 emu g$^{-1}$, respectively. The particles were found to be superparamagnetic at room temperature.

Yttrium iron garnet (YIG) and yttrium aluminum iron garnet (YAIG) nanoferrites were synthesized [59]. When sintered at 1100 °C, YIG nanoparticles show higher initial permeability and Q factor as compared to the YAIG nanoparticles. The saturation magnetization, remanence, and coercivity of YIG and YAIG samples varied when sintered at 900, 1000, and 1100 °C as seen from the hysteresis loops. The saturation magnetization and coercivity for the YIG and YAIG nanoparticles were observed in the range 11.56–19.92 emu g$^{-1}$ and
7.30–87.70 Oe respectively. Spherical maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticles of size 3.5 ± 0.6 nm were synthesized by a water-in-oil microemulsion method [60] were reported to have high saturation magnetization values. Mg$_{1-x}$Co$_x$Cr$_x$Fe$_{2x}$O$_4$ (x = 0.0–0.5) were prepared by ME method [61]. Hysteresis loops were recorded at temperatures of 300, 200, and 100 K up to 50 kOe. With decrease in temperature, both the saturation magnetization and the anisotropy coefficient increase with maximum values obtained at x = 0.3 and x = 0.2, respectively and this was explained on the basis of site occupancy of the substituting atoms.

Crystalline $\lambda$-MnO$_2$ nanodisks synthesized by a microemulsion route using polyvinylpyrrolidone (PVP) as a capping layer [62]. Temperature-dependent magnetization studies were carried out during zero-field-cooling and field-cooling (ZFC and FC) modes from 5 to 300 K. A discrepancy between these two curves indicates that an anisotropic potential barrier is present that blocks the magnetization reversal process. This potential barrier was attributed to the magnetocrystalline anisotropy of Mn$_2$O$_3$ nanoparticles (secondary phase) that was strong enough to camouflage the relatively weak antiferromagnetism of $\lambda$-MnO$_2$. Orthorhombic MnO(OH) nanoparticles (~7 nm) were obtained by a microemulsion method and were found to be ferromagnetic with a $T_c$ of 35 K and magnetic moment of $\sim$0.7 $\mu$B mol$^{-1}$ [63].

LiNiCo spinel ferrite nanoparticles of sizes 28 nm to 70 nm doped with rare earth metals Nd and Pr were prepared by the micro-emulsion method [64]. Magnetic properties were analyzed by VSM within applied magnetic field of $-10,000$ Oe and 10,000 Oe. $M_s$ and $M_H$ values decreased with the increase in concentration. The ferrites LiNi$_{0.35}$Co$_{0.15}$Pr$_{0.1}$Nd$_{0.5}$Fe$_{2}$O$_{4}$ were found suitable for applications in transformer core materials. X-type hexagonal nano-sized ferrites (Sr$_2$NiCo$\gamma$Fe$_{28}$O$_{46}$) doped with Yb were synthesized by the microemulsion method [65]. In these 29–41 nm crystallites the lattice strain increased from 3.62 × 10$^{-2}$ to 3.73 × 10$^{-2}$ with increased Yb content. The doping of Yb$^{3+}$ lead to decrease in remanence and saturation magnetization (figure 3). These ferrite materials would be useful for longitudinal recording media due to their thermal stability and higher coercivity.

Figure 3. Variation of magnetization (emu g$^{-1}$) and magnetic field for Sr$_2$NiCoYb$_{0.6}$Fe$_{24-x}$O$_{46}$ (x = 0.0–0.15). Reprinted from Journal of Alloys and Compounds Vol 708, ur Raheem, F, Khan, M A, Majeed, A, Hussain, A, Warsi, M F, & Akhtar, M N, ‘Structural, spectral, electrical, dielectric and magnetic properties of Yb doped SrNiCo-X hexagonal nano-structured ferrites’ pp 903–910 copyright (2017) with permission Elsevier.

The micro-emulsion technique was used to synthesize a series of nanocrystalline spinel ferrites with chemical formula Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) [67]. The lattice constant decreased from 8.39 to 8.34 Å as the Co concentration increased from x = 0 to x = 1 and this was attributed to the smaller ionic radii of Co(II) as compared to Zn(II). The M–H study indicates a ferrimagnetic behavior at room temperature. The magnetic properties were attributed to the effect of cation distribution and grain size. An $M_s$ of 21.29 emu g$^{-1}$ and an Hc of 1382.4 Oe was recorded for the CoFe$_2$O$_4$ nanocrystals. Cubic spinel Tb and Dy doped lithium-nickel ferrites, Li$_{0.2}$Ni$_{0.8}$Tb$_{0.5-x}$Dy$_{0.5}$Fe$_{2}$O$_{4}$ where (x = 0.00–0.08) of sizes in the range 30–42 nm was reported [67]. Doping Tb and Dy led to increase the coercive field (120–156 Oe) in these Li–Ni ferrites. Zr–Co doped nickel ferrites (NiZr$_{0.25}$Co$_{2}$Fe$_{2}$O$_{4}$ where x = 0, 0.2, 0.4, 0.6, 0.8) of sizes 10–15 nm having
an FCC structure were synthesized [68]. Though no clear trend is indicated, in general, the saturation magnetization (Ms) decreases from 47.9 to 13.09 emu g$^{-1}$ as x varies from 0 to 0.8. The high values of Ms of some compositions predicted the potential applications in high density recording media and microwave devices.

Silica-Fe$_2$O$_3$ composite nanostructures [69] with iron oxide nanoparticles having a wide size (4–50 nm) and a diverse morphology (spherical, ellipsoidal and rod-like) distribution were synthesized using a combination of microemulsion and sol-gel methods. ε-Fe$_2$O$_3$, a hard magnet phase with coercivity $\sim$2.13 T, was identified as the dominant crystalline phase via magnetic measurements. The samples were subject to post-annealing thermal treatment at various temperatures and a decrease in coercivity was seen for samples treated up to a temperature of 750 °C (to 1245 Oe). This was attributed to a change in phase from ε-Fe$_2$O$_3$ to α-Fe$_2$O$_3$. However, in samples treated at higher temperatures (1000 °C), an increase in coercivity $H_C \sim 1.5$ T was observed and this was attributed to the re-formation of the ε-Fe$_2$O$_3$ structure. On treatment at higher temperatures (1100 °C) the phase transformation (ε-Fe$_2$O$_3$ $\rightarrow$ α-Fe$_2$O$_3$) and crystallization of amorphous silica were observed.

Composites

Composite nanomaterials, due to a symbiotic effect among its components, may exhibit physical and chemical properties that are more suitable for specific applications than the individual components. Additionally, composites are of interest as they can be engineered to provide advantages like mechanical stability, corrosion resistance, increased solubility and alternate pathways for electron transfer to facilitate chemical, electrochemical and photoelectrochemical reactions. In this section, we shall discuss the composites prepared by the ME method whose magnetic properties were studied. Triton X-100 reversed-phase water-in-oil microemulsion encapsulation method was employed in coating the pre-prepared Fe$_3$O$_4$ nanoparticles with chitosan [70]. The resultant magnetic chitosan coated particles were 50 to 92 nm in size and the spinel structure of the Fe$_3$O$_4$ remained unchanged on coating. The saturated magnetization of these coated nanoparticles reached 18.62 emu g$^{-1}$, and showed these characteristics of superparamagnetism. A hydroxyapatite-magnesiumferrite (HA-MgFe$_2$O$_4$) nanocomposite was synthesized [71] by the ME route which exhibits a maximum saturation magnetization of 9.47 emu g$^{-1}$. Carbon nanotubes (CNTs) were decorated with magnetic M(II) Fe$_2$O$_4$ (M = Co, Ni, Cu, Zn) nanoparticles of sizes 15 to 20 nm [72]. Magnetic hysteresis loop measurements indicated that the nanocomposites displayed ferromagnetic behavior at 300 K which can be manipulated using an external magnetic field (figure 4). The CoFe$_2$O$_4$/CNTs nanocomposites exhibited the maximum value of saturation magnetization (37.47 emu g$^{-1}$).

A SDS/water/cyclohexane/n-pentanol microemulsion system was employed to synthesize functionalized polyaniline/Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ nanocomposites (PANI/MZFO NCs) that exhibited a superparamagnetic behavior [73]. Superparamagnetic Fe$_3$O$_4$/Ag nanocomposites with self-aggregated branch like nanostructures with sizes in the range of 10 ± 2 nm were synthesized by the ME route. The observed saturation magnetization of these nanocomposites were 40 emu g$^{-1}$. Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PANI nanocomposites were synthesized via ME method [74]. VSM measurements indicated ferromagnetic nature of the composite. A saturation magnetization of 3.95 emu g$^{-1}$ and low coercive force (39 Oe) was observed. The formation of a composite with PANI nanofibers results in transition of the magnetic properties of Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ crystals from superparamagnetic to ferromagnetic.

Inorganic nanocrystals combined with anticancer drugs to construct multifunctional hybrid nanostructures are a powerful tool for cancer treatment and tumor suppression [24]. The critical challenge is to reproducibility synthesize compact, multifunctional nanostructures with improved functionality. Magnetite hybrid nanostructures employing Fe$_3$O$_4$ nanoparticles to form multifunctional magnetite nanoclusters (NCs) were synthesized by combining an oil-in-water microemulsion assembly and a layer-by-layer (LBL) method. These nanostructures were shown to serve as improved magnetic resonance imaging (MRI) contrast agent. Fe$_3$O$_4$ nanoparticles and CdTe quantum dots (QDs) were directly incorporated into 50 nm diameter silica shell by reverse microemulsion method to produce water-soluble composites that were both magnetic and fluorescent [75]. By modifying the surface of MNs-QDs/SiO$_2$ composite nanoparticles with amino and methylphosphonate groups, biologically functionalized and monodisperse MNs-QDs/SiO$_2$ composite nanoparticles can be obtained. In this work, bi-functional composite nanoparticles were conjugated with FITC labeled goat anti-rabbit IgG, to generate novel fluorescent-magnetic-biotargeting tri-functional composite nanoparticles, which can be used in a number of biomedical application. Ferromagnetic Fe/Fe$_3$C–MWCNT composites were prepared by calcination of Fe$_3$O$_4$–MWCNT composite in a H$_2$ atmosphere. By electron microscopy it was seen that the Fe$_3$O$_4$ or Fe/Fe$_3$C nanoparticles both fill and surface decorate the MWCNTs [76]. The saturation magnetization and anisotropy field are particularly strong for Fe/Fe$_3$C–MWCNT.
Core-shell particles

Multiphasic, core-shell type nanoparticles comprise of an inner core structure and outer shell(s) with of different compositions. As a result of the composition of the core and the shell material as well as due to their design and geometry, these particles exhibit unique properties. Multifunctional nanocomplexes with a superparamagnetic iron oxide nanoparticle (SPIONs) core and an upconversion luminescent shell comprising of lanthanide ions were synthesized by the ME method [77]. Three distinct shells on SPIONs cores namely LaF₃:Yb⁺³/Er⁺³, NaYF₄:Yb⁺³/Er⁺³ and NaYF₄:Yb⁺³/Ho⁺³ were synthesized of which the first was obtained using the microemulsion and coprecipitation methods while the latter was obtained using the thermal decomposition method. VSM studies revealed a superparamagnetic character of the nanocomplexes. The saturation magnetization was 10.2 emu·g⁻¹ and 8.4 emu·g⁻¹ for SPIONs@LaF₃:Yb⁺³/Er⁺³ nanocomplexes with and without heat treatment, respectively. Multiphoton microscopy confirmed the upconversion process in these materials. For SPIONs@NaYF₄:Yb⁺³/Er⁺³, three peaks of emission were obtained, at 520 nm, 540 nm and 657 nm, while for SPIONs@NaYF₄:Yb⁺³/Ho⁺³ and SPIONs@LaF₃:Yb⁺³/Er⁺³ samples two peaks at 540 nm and 657 nm were observed. Xylan-Fe₂O₃ (QX-Fe₂O₃) core/shell nanocomposites were prepared by synthesis of γ-Fe₂O₃ nanoparticles by a solvothermal process and coating with QX via a reverse ME method. The particles
were further modified by polylysine (PLL) and folic acid (FA) to prepare PLL-QX-Fe$_2$O$_3$ and FA-QX-Fe$_2$O$_3$ nanoparticles. The Fe element content of QX-Fe$_2$O$_3$ was found to be 30–75 µg/ml$^{-1}$ and the saturation magnetization of QX-Fe$_2$O$_3$ nanoparticles was observed to be 1.49 emu g$^{-1}$. The spherical γ-Fe$_2$O$_3$ and QXFe$_2$O$_3$ nanoparticles had diameters of 50–100 nm and 60–150 nm, respectively. The FA-QX-Fe$_2$O$_3$ showed good performance as Magnetic Resonance (MR) imaging materials.

Gadolinium carbonate (Gd$_3$(CO$_3$)$_3$) hollow nanospheres were synthesized via a reverse ME method and their suitability for drug transport and magnetothermally-induced drug release was evaluated [78]. Tris (tetrathylcyclopentadienyl)gadolinium(III) and CO$_2$ were used as the starting materials and hollow spheres with an outer diameter of 26 ± 4 nm, an inner cavity of 7 ± 2 nm, with a wall thickness of 9 ± 3 nm are obtained. As a proof of concept study, the nanocontainers of Gd$_3$(CO$_3$)$_3$ hollow nanospheres were filled with anti-cancerogenic agent doxorubicin (DOX), via a ME strategy. The resulting DOX@Gd$_3$(CO$_3$)$_3$ nanocontainers provided the option of multimodal imaging including magnetic resonance imaging (OI, MRI), optical imaging as well as magnetothermal heating and drug release.

A dual contrast agent for computed tomography (CT) and magnetic resonance imaging (MRI) consisting of ~7 nm Fe$_3$O$_4$ particles forming the core with an iodine-carrying nanopolymeric shell, having an overall particle size ranging from 50 to 250 nm was synthesized via the microemulsion polymerization method. This contrast agent consists of (d = 7 nm) with 2-Methacryloyloxyethyl(2,3,5-triodobenzoate) was used as the monomer. The amount of the surfactant, sodium oleate was varied to control the overall particle size. The particles provided a highly visible contrast in CT and MR images. A template for biomedical applications was created by adding a comonomer and the particles were further functionalized with the somatostatin analogue Tyr3-octreotate. The particles were tested for specific uptake into somatostatin receptor-positive AR42J cells.

Fe@Au core-shell nanoparticles were synthesized by the microemulsion methods [79]. Most reports of Fe core based magnetic nanoparticles with an Au shell have iron oxides as cores which have a large lattice mismatch with Au. A Fe core be more appropriate, however, this is prone to oxidation, so this work is quite significant as it describes a method to circumvent this to produce stable core-shell Fe@Au nanoparticles. These 6 nm particles with 3 nm core have a saturation magnetization of 1.13 emu g$^{-1}$. Cobalt-silver (Co-Ag) core-shell nanoparticles (3–5 nm) with different shell thicknesses were synthesized in a two-step reduction process by the ME technique [80]. The observed magnetic properties were resultant of both superparamagnetic and ferromagnetic contributions. At room temperature, giant magnetoresistance values of 0.1% were observed. FeCo@C core-shell nanoparticles [81] were synthesized using a combination of the ME and catalytic CVD techniques. A lower saturation magnetization and higher natural–resonance frequency was observed in these core shell particles as compared with FeCo nanoparticles.

Biocompatible Superparamagnetic MnO@SiO$_2$ core/shell nanoparticles with a luminescent silica shell were synthesized by a combination of microemulsion techniques and common sol–gel procedures [82]. The presence of hydrophilic polyethylene glycol (PEG) chains on the SiO$_2$ surface, makes these nanocomposites soluble and stable in aqueous media, including physiological saline, buffer solutions and human blood serum. It was seen that the presence of a silica shell did not change the magnetic properties significantly, and cytotoxicity and biocompatibility studies indicated that these material are suitable for applications in biological imaging applications. The MnO@SiO$_2$ nanocomposite particles showed a T1 contrast with relitivity values comparable to those of the commonly used PEGylated MnO nanoparticles. Janus shaped plasmonic–magnetic silver–magnetite nanostructures were developed via a single phase microemulsion technique [83]. The measurements of response for bare magnetite as well as silver–magnetite nanoparticles in an alternating magnetic field reveal their suitability in hyperthermia applications.

Design of magnetic nanoparticles in useful in medicine as they can be directed to specific body sites by external magnetic fields. These magnetic nanoparticles may be used for magnetic resonance imaging and targeted drug delivery. Polymer coated manganese iron oxide nanoparticles were produced by the microemulsion method and used for treatment of medical device related infections [84]. Core-shell nanoparticles coated with the polymer, polyacrylamide (pAcDED), that is intrinsically antimicrobial, exhibits very desirable magnetic as well as antimicrobial properties. These particles were injected into the patients either soon after device implant or even after onset of infection and were able to prevent or remove the infection causing biofilm from the device.

**Miscellaneous**

A series of pentaalkylguanidinium-based magnetic room-temperature ionic liquids 1,1,3,3-tetramethyl-4-alkylguanidinium bromotrifluoromethanesulfonate(III) [C$_n$TMG][FeCl$_3$Br] (n = 2, 4, 6, 8) were used as the polar phase in a microemulsion system that had different aliphatic oils as a nonpolar phase, a mixture of nonionic surfactant Triton X-100 (TX-100) and different short-chain aliphatic alcohols as a cosurfactants [85]. Magnetic...
susceptibility and rheological measurements indicated that these microemulsion systems had low viscosity and strong magnetic susceptibility over the composition range where the system was optically clear. The ME method has also been used for polymerization reactions to synthesize nanomaterials whose magnetic properties have been utilized for medical applications [86]. For example, glycidyl methacrylate was utilized to derivitize dextran for the purpose of anchoring vinyl groups on the polysaccharides backbone. This enabled its utilization along with acrylic acid as a monomers for miniemulsion polymerization to form hydrogels. Separately magnetite particles (~5.2 nm) were synthesized by the co-precipitation method and encapsulated in the as prepared hydrogels. The magnetic nano-hydrogels were superparamagnetic and were stable under physiological conditions for a month.

Conclusions

The synthesis and characterization of a variety of nanomaterials by the microemulsion method and evaluation of their magnetic properties was reviewed. It was seen that the solvent and the decomposition temperature play a significant role in the size and morphology of the precursor oxalates and hence the magnetic properties of the resulting oxides. For example for copper oxide particles the solvent was seen to influence the size and corresponding magnetic properties. It is also observed that the decomposition temperature, (in iron oxide and cobalt oxide) and the surfactant, co-surfactant and the non-polar phase (for ZnMn2O4 particles) was found to influence the magnetic properties. Core-shell nanoparticles comprising of two immiscible metals could be formed by this method and the magnetic properties of the resulting particles exhibit magnetic properties that are distinct from composites of such materials. For particles such as nickel borate the co-surfactant influences the anisotropy and hence their magnetic properties. Applications in directed drug delivery, digital storage media, biomedical imaging applications were highlighted in this review. A class of materials that has been demonstrated to be useful in all these applications are nanoferries. Though various empirical relationships between the above factors and the size and morphology of the obtained nanomaterials have been deduced, it is seen that these relationships are usually composition dependent. Thus, more intensive research needs to be carried out, to deduce generalized conditions and protocols that may be applied to obtain nanostructures different compositions with well-controlled size and morphology.

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