PREPARATION OF NANOPARTICLES OF SILVER HALIDES, SUPERCONDUCTORS AND MAGNETIC MATERIALS USING WATER-IN-OIL MICROEMULSIONS AS NANO-REACTORS

V. PILLAI, P. KUMAR, M.J. HOU, P. AYYUB and D.O. SHAH

Center for Surface Science & Engineering, Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, USA

CONTENTS

Abstract ..................................... 241
I. Introduction .................................. 242
II. Reactions in Microemulsions .................. 244
III. Particle Synthesis in Microemulsions ......... 246
IV. Synthesis of Silver Halides .................. 247
V. Synthesis of Magnetic Oxides ................ 249
   A. Synthesis of Barium Ferrite ............... 249
   B. Synthesis of γ-Fe₂O₃ ...................... 253
VI. Synthesis of Superconductors ............... 256
   A. Synthesis of Y-Ba-Cu-O (123) Superconductors 256
   B. Synthesis of Bi-Pb-Sr-Ca-Cu-O (2223) Superconductors 261
VII. Summary .................................. 263
VIII. Future Directions .......................... 264
IX. Acknowledgements ........................... 265
X. References .................................. 265

ABSTRACT

Water-in-oil microemulsions have been used for the synthesis of a variety of nanoparticles since the technique was first introduced in 1982. In this paper we have reviewed several articles pertaining to the synthesis of nanoparticles in microemulsions and described in some detail our research efforts in the past decade in the field of synthesis of nanoparticles of silver halides, superconductors and magnetic materials using water-in-oil microemulsions as nano-reactors.
I. INTRODUCTION

A microemulsion may be defined as a thermodynamically stable isotropic dispersion of two immiscible liquids consisting of nano-size domains of one or both liquids in the other, stabilized by an interfacial film of surface active molecules [1]. Microemulsions may be classified as water-in-oil (w/o) or oil-in-water (o/w) depending on the dispersed and continuous phases. In both cases, the dispersed phase consists of mono-dispersed droplets in the size range of 100–1000 Å [2]. It has now been shown that when microemulsions contain comparable amounts of oil and water, some of these systems may show a bicontinuous structure [3,4].

Microemulsions were first introduced by Schulman and his co-workers in 1943 [5]. They explained that microemulsions were spontaneously formed with the uptake of water or oil due to the negative transient interfacial tension which allows the free energy to decrease as the total oil–water interfacial area increases [5,6]. At equilibrium, the oil/water interfacial tensions become zero or a very small positive number of the order of $10^{-2}$–$10^{-3}$ mN/m.

During the past fifteen years, studies on both theoretical and experimental aspects of microemulsions have provided a better understanding of the formation, properties, and phase behavior of microemulsions [7–13]. Due to their importance in various technological applications such as enhanced oil recovery, pharmaceutics, cosmetics, and nanoparticle synthesis, the structure and structural transitions of microemulsions have been extensively studied using X-ray and light scattering, ultracentrifugation, spin label probes, dielectric relaxation, fluorescence probes, and neutron scattering [14–27].

As many applications depend on the dynamics of microemulsions, the characterization of the size and shape of microemulsion droplets and their inter-droplet interaction has been vigorously pursued recently. Many techniques such as light scattering, small angle neutron scattering, fluorescence quenching, stopped-flow, and electrical conductivity have been used to study the dynamics of microemulsions [28–34].

Microemulsions are industrially relevant due to their applications in a number of areas [35]. The interfacial and rheological properties of microemulsions are important to exploit surfactant-enhanced tertiary oil recovery methods. There are also obvious applications in the food and cosmetics industries, particularly using phospholipid surfactants. The ability to precisely control the size and stability of the microstructure
domains of microemulsions makes them useful for applications in liquid membrane technology [35,36]. Microemulsions also provide compartmentalized liquid structures having high surface area and can therefore be used as novel and versatile media for chemical synthesis. This is significant for potential applications in enzymic reactions in microemulsions [36]. Another potential use of the fluid but structured nano-size domains of microemulsions is in the preparation of sub-micron or nano-particles of a desired size or shape, reflecting the structure and environment of the aqueous droplets [35].

Sub-micron or nanometer sized particles are of increasing scientific and technological interest [37]. There is clear evidence that small atomic clusters (10–1000 atoms) exhibit novel and hybrid properties between the molecular and bulk solid-state limits. These nanophase materials, which may contain crystalline, quasicrystalline, or amorphous phases, can be metals, ceramics, or composites with rather unique and improved mechanical, electronic, magnetic and optical properties, than normal, coarse-grained polycrystalline materials. Because of their ultrafine sizes, and high surface area, these particles can easily overcome conventional restrictions of phase equilibria and kinetics, leading to lowering of sintering and solid-state reaction temperatures, and increase in sintering rate. The large fraction of atoms residing at the surfaces and grain boundaries of these materials also leads to materials with novel properties. Such nanoparticles are not only of basic physical interest, but have also resulted in important technological applications such as: (a) catalysis, (b) high-performance ceramic materials, (c) micro-electronic devices, and (d) high density magnetic recording [37–39].

These potential technological applications have led to the development of several new techniques for the synthesis of various types of nanoparticles in recent years. These include gas-phase techniques such as gas-evaporation, laser vaporization, and laser pyrolysis [40–44]; vacuum synthesis techniques like sputtering, laser ablation, and ionized beam deposition [45–48]; and liquid phase techniques like precipitation from homogeneous solutions, sol–gel processing, freeze drying [49–53], etc. This article focuses on the use of the aqueous cores of water-in-oil microemulsions as reactors for the synthesis of nanoparticles. Precipitation reactions in microemulsions offers a novel and versatile technique for the synthesis of a wide variety of nanophase materials with the ability to precisely control the size and shape of the particles formed [35,54,55]. It also offers a unique method to control the kinetics of particle formation.
and growth by varying the physicochemical characteristics of the microemulsion system.

II. REACTIONS IN MICROEMULSIONS

In water-in-oil microemulsions, the aqueous droplets continuously collide, coalesce and break apart resulting in a continuous exchange of solute content [32,56]. The collision process depends upon the diffusion of the aqueous droplets in the continuous media, i.e. oil, while the exchange process depends on the attractive interactions between the surfactant tails and the rigidity of the interface, as the aqueous droplets approach close to each other [32].

For reactions in water-in-oil microemulsions involving reactant species totally confined within the dispersed water droplets, a necessary step prior to their chemical reaction is the exchange of reactants by the coalescence of two droplets. When chemical reaction is fast, the overall reaction rate is likely to be controlled by the rate of coalescence of droplets [32]. Therefore, properties of the interface such as interfacial rigidity are of major importance. A relatively rigid interface decreases the rate of coalescence, and hence leads to a low precipitation rate. On the other hand, a substantially fluid interface in the microemulsion enhances the rate of precipitation. Thus, by controlling the structure of the interface, one can change the reaction kinetics in microemulsions by an order of magnitude [57]. It has been further shown that the structure of oil, alcohol and ionic strength of the aqueous phase can significantly influence the rigidity of the interface and the reaction kinetics [28,57].

Conceptually, if one takes two identical water-in-oil microemulsions and dissolves reactants A and B respectively in the aqueous phases of these two microemulsions, upon mixing, due to collision and coalescence of the droplets, the reactants A and B come in contact with each other and form AB precipitate. This precipitate is confined to the interior of the microemulsion droplets and the size and shape of the particle formed reflects the interior of the droplet. This is one of the principles utilized in producing nanoparticles using microemulsions (see Fig. 1a). However, nanoparticles can also be produced in microemulsions by the adding a reducing or precipitating agent, in the form of a liquid or a gas, to a microemulsion containing the primary reactant dissolved in its aqueous core. Figure 1b shows the formation of metallic nanoparticles by adding reducing agents such as hydrazine or hydrogen gas in the microemulsion.
Fig. 1. Schematic representation of synthesis of nanoparticles in microemulsions (a) using two microemulsions, (b) by adding a reducing agent to a microemulsion, and (c) by bubbling gas through a microemulsion.

containing the metal salt. Figure 1c shows the formation of oxide, hydroxide or carbonate precipitates by bubbling gases like O₂, NH₃, or CO₂ through a microemulsion containing soluble salts of the cations. In the past decade or so, several researchers have used these techniques to synthesize nanoparticles in microemulsions. These articles are briefly described in the next section.
Synthesis of ultrafine particles using reactions in microemulsions was first reported by Boutonnet et al. [54] when they obtained monodispersed metal particles (in the size range 3–5 nm) of Pt, Pd, Rh and Ir by reducing corresponding salts in water pools of water-in-oil microemulsions with hydrazine or hydrogen gas. Since then, there have been several reports in literature where microemulsions have been used for the synthesis of a variety of nanoparticles.

Metallic nanoparticles and metal clusters have a wide range of applications, including their use in catalysis, as biological stains, and as ferro-fluids. Touroude et al. [58] synthesized bimetallic particles of platinum and palladium by reduction of $\text{H}_2\text{PtCl}_6$ and $\text{PdCl}_2$ with hydrazine in water/pentaethylene glycol dodecyl ether/hexadecane microemulsions. Similarly, platinum particles have also been synthesized in aerosol-OT (AOT) and cetyl trimethyl ammonium bromide (CTAB) based microemulsions for applications in catalysis [59]. Colloidal gold and silver particles have potential applications as condensers for electron storage in artificial photosynthesis. This has led to studies by Kurihara et al. [60] on laser and pulse radiolytically induced colloidal gold formation in w/o microemulsions. Colloidal gold and silver particles have also been synthesized by reduction of corresponding metal salts in water-in-oil microemulsions using sodium borohydride [61,62].

Colloidal semiconductor particles, especially cadmium sulfide, have invoked a lot of interest due to their unique photochemical and photophysical properties. These properties are drastically dependent on the size of the semiconductor nanoparticles. Several researchers have therefore used water-in-oil microemulsions for the synthesis of such nanoparticles. Meyer et al. [63] have generated platinized colloidal cadmium sulfide in situ in AOT based microemulsions. Several studies have recently been published on the synthesis, growth and characterization of cadmium sulfide [64–70] and cadmium selenide [71] particles in microemulsions.

Colloidal particles of calcium carbonate, stabilized by surfactants, constitutes an important class of additives for oils used in lubrication for internal combustion engines. Water-in-oil microemulsions thus provide an ideal media for the synthesis of such particles. This has been exploited for the synthesis of calcium carbonate [72–75], barium carbonate [76], and strontium carbonate [M] particles by carbonation of their respective
salts or hydroxides in the aqueous cores of water-in-oil microemulsions.

Microemulsions have also been used for the synthesis of monodisperse particles of nickel, iron and cobalt boride particles, which have applications in heterogeneous catalysis, by the reduction of metal salts using sodium borohydride [78,79]. Other nanoparticles synthesized in water-in-oil microemulsions include monodisperse silica particles [80–83], nano-size molybdenum sulfide particles [84], and magnetic particles such as magnetite [85,86] and maghemite [87].

In recent years, we have been successful in synthesizing a variety of nanoparticles using different microemulsion systems. These include in situ synthesis of nanoparticles of AgCl [88] and AgBr [57]; and microemulsion mediated synthesis of highly dense and microhomogeneous Y-Ba-Cu-O (123) and B-Pb-Sr-Ca-Cu-O (2223) high temperature ceramic superconductors [89–91], high coercivity barium ferrite for high-density perpendicular recording [92,93], superparamagnetic γ-Fe₂O₃ nanoparticles [94] and zinc oxide based varistors [95]. The synthesis of these materials and their structure and properties are described in the following sections.

IV. SYNTHESIS OF SILVER HALIDES

Nanoparticles of silver halides are extremely important for applications in photographic emulsions [96,97]. It is, however, difficult to obtain nanosize, monodispersed particles of silver halides by conventional methods. We have synthesized nanoparticles of AgCl [88] and AgBr [57] using water/AOT (sodium di-2-ethylhexyl sulfosuccinate)/alkane microemulsion systems. Two microemulsions with the same composition but differing only in the nature of the aqueous phase were taken. Microemulsions were prepared by solubilizing the aqueous solutions into AOT/alkane mixtures under vigorous stirring. The concentration of AOT in alkane (for example n-heptane) was 0.15 M. The aqueous phase in the first microemulsion was silver nitrate (AgNO₃, 0.4 M) whereas the aqueous phase in the second microemulsion was either NaCl or NaBr (0.4 M). The microemulsions had identical compositions and each solubilized 8 moles of aqueous phase per mole of surfactant (AOT). These two microemulsions were then mixed under constant stirring. This led to the precipitation of AgCl or AgBr particles within the aqueous droplets due to the reaction between the two reactants as the aqueous droplets collide.
coalesce, and break again. The growth of the particles is restricted by the size of the aqueous droplets resulting in the formation of nano-size particles.

Transmission electron microscopy (TEM) was used to study the size and size distribution of these particles. Samples were prepared by dropping a small amount of particles dispersed in the microemulsion onto a TEM grid. Figures 2a and b show nanoparticles of AgCl precipitated in
water/AOT/heptane microemulsions, observed 1 day and 1 week respectively after the start of the reaction. These micrographs show that the particles formed in the microemulsions are in the size range of 50–100 Å in diameter with very uniform size distribution. These nanoparticles appear to have a spherical shape. It can also be seen that these dispersions are very stable with little or no aggregation of AgCl particles even after a week. This has been explained on the basis of a low attractive interaction between the microemulsions droplets containing the AgCl nanoparticles [57,88].

Electron diffraction was used to identify the crystal planes of the AgCl nano-crystals. Four d-planes of the fcc lattice structure of AgCl, namely, (111), (200), (220) and (420) were identified based on the analysis of the diffraction pattern.

Thus, water-in-oil microemulsions can be used for in situ synthesis of stable dispersions of nanoparticles of silver halides.

V. SYNTHESIS OF MAGNETIC OXIDES

Finely divided magnetic nanoparticles are widely used in high density magnetic recording media and magnetically responsive fluids, novel seals and magnetically directed printing inks. The magnetic oxides commonly used for magnetic recording are γ-Fe₂O₃, Fe₃O₄, cobalt modified Fe₂O₃ and CrO₂ for longitudinal recording, and hexagonal ferrites like BaFe₁₂O₁₉ for high density perpendicular recording. The magnetic characteristics of these particles depend crucially on their shape and size and they should be essentially single domain [98,99]. These requirements can be satisfied if these particles are synthesized using water-in-oil microemulsions.

A. Synthesis of Barium Ferrite

Barium ferrite (BaFe₁₂O₁₉) has been traditionally used in permanent magnets because of its high intrinsic coercivity and fairly large crystal anisotropy [100]. However, in the past decade, it has emerged as an important magnetic media for high density perpendicular recording [101]. Such technological applications require materials with a strict control of homogeneity, particle size and shape, and magnetic characteristics [102].
The classical ceramic method for the preparation of barium ferrite consists of firing mixtures of iron oxide and barium carbonate at high temperatures (-1200°C) [103,104]. Furthermore, the ferrite must then be ground to reduce the particle size from multi-domain to single-domain. This generally yields mixtures which are non-homogeneous on a microscopic scale. Milling introduces lattice strains in the material, whereas high reaction temperatures induce sintering and coagulation of particles, both of which can be damaging if specific properties like uniform and reduced particle sizes, and high coercivities are required in the final product [105,106].

In order to achieve a homogeneity of ions at the atomic level, and to overcome the effects of milling, various techniques such as chemical coprecipitation [107,108], glass crystallization [101,109], organometallic precursor method [110,111], aerosol synthesis [112,113], and colloidal synthesis [114] have been developed to prepare ultrafine barium ferrite. We have used the aqueous cores of water-in-oil microemulsions as reaction media to produce uniform-sized, microhomogeneous nanoparticles of carbonate precursors for the synthesis of ultrafine barium ferrite [92,93].

We selected a microemulsion system with cetyl trimethyl ammonium bromide (CTAB) as the surfactant (12% by wt); n-butanol as the co-surfactant (10% by wt); n-octane (44% by wt) as the continuous oil phase; and a salt solution (34% by wt) as the dispersed aqueous phase. This system solubilizes a relatively large volume of aqueous phase in well-defined nano-size droplets of stable, single-phase water-in-oil microemulsions [89].

Microemulsions were prepared by solubilizing different salt solutions into CTAB/n-butanol/n-octane solutions. We took two microemulsions (microemulsion I and microemulsion II) with identical compositions but different aqueous phase. The aqueous phase in microemulsion I was a mixture of barium nitrate and ferric nitrate solutions. The aqueous phase in microemulsion II was the precipitating agent, ammonium carbonate. These two microemulsions are then mixed under constant stirring. Due to the frequent collisions of the aqueous cores of water-in-oil microemulsions [32,56], the reacting species in microemulsions I and II come in contact with each other. This leads to the precipitation of barium-iron-carbonate within the nano-size aqueous droplets of the microemulsion. The aqueous droplets act as constrained nano-size reactors for the precipitation reaction, as the surfactant monolayer provides a barrier restricting the growth of the carbonate particles. This surfactant mono-
Fig. 3. Transmission electron micrograph of barium ferrite precursors synthesized in water/CTAB/1-butanol/octane microemulsions.

layer also hinders coagulation of particles.

The barium–iron–carbonate precipitate was separated in a centrifuge at 5000 rpm for 10 minutes. The precipitate was then washed in a 1:1 mixture of methanol and chloroform, followed by pure methanol to remove any oil and surfactant from the particles. The precipitate was then dried at 100°C. The dried precipitate was heated (calcined) at 950°C for 12 hours to ensure complete conversion of the carbonates into the hexaferrite (BaFe_{12}O_{19}).

Transmission electron microscopy (TEM) was used to study the size and size distribution of the precursor particles (carbonates) as well as the calcined particles. Samples were prepared by ultrasonically dispersing the particles (precursors and calcined powder) in methanol prior to depositing it onto a carbon coated TEM grid. Figure 3 shows that the precursor particles formed within the aqueous droplets of the microemulsion were in the size range of 5–15 nm. On the other hand, the TEM of
the calcined powder (Fig. 4) shows that these particles are in the size range of 50–100 nm, implying that growth of particles has taken place during calcination.

X-ray diffraction for the calcined powder showed all the characteristic peaks for barium ferrite marked in the diffractogram. No other phases were detected. This confirmed the complete conversion of the precursor carbonates into the hexagonal ferrite BaFe$_{12}$O$_{19}$.

Room temperature magnetic property measurements for the calcined powder were carried out on a vibrating sample magnetometer (VSM) using an unoriented, random assembly of particles. The magnetization curve (Fig. 5) thus obtained yielded an intrinsic coercivity ($H_c$) of 5397 Oe, a saturation magnetization ($M_s$) of 61.2 emu/gram, and a remanent magnetization ($M_r$) of 33.3 emu/gram for the microemulsion synthesized barium ferrite particles. This high value of coercivity indicates that these barium ferrite particles are essentially single domain. This observation is also confirmed by the fact that the particles formed by us are in the size range of 50–100 nm. Haneda et al.[115] have shown that using the theory of Kittel [116], the critical domain size for barium ferrite particles is about 1 μm. Also, direct observation of the domain structure of barium ferrite particles at room temperature by Goto et al. [117] confirms that the critical domain size is indeed in the region of 1 μm.
In summary, we have presented a new, microemulsion mediated process for the synthesis of ultrafine particles of barium ferrite. This process yielded high coercivity, single domain barium ferrite particles, which are phase pure as confirmed by X-ray diffraction. These phase pure, single domain particles can be doped by Co and Ti to reduce the coercivity and large anisotropy to make these particles suitable for high density perpendicular recording [101].

B. Synthesis of $\gamma$-Fe$_2$O$_3$

Magnetic pigments with particles in the nanometer size range have potential applications in information storage [118], color imaging [119], bioprocessing [120], ferrofluids [121], magnetic refrigeration [122] and magnetic resonance imaging [123]. The magnetic oxide commonly used for these applications is $\gamma$-Fe$_2$O$_3$.

A microemulsion system, similar to the one used for the synthesis of barium ferrite precursors was used [94]. The first microemulsion had a 0.15 M solution of ferrous sulfate as the dispersed aqueous phase. To this microemulsion, a 2.0 M solution of tetra ethyl amine (TEA) in octane was
added. Diffusion of TEA through the surfactant monolayer into the aqueous droplets results in the hydrolysis of Fe$^{2+}$ ions. A second microemulsion, containing sodium nitrite as the dispersed aqueous phase, was added to this suspension. This system was maintained at 45 ± 5°C for one hour under constant stirring. The hydrolyzed Fe$^{2+}$ ions reacted with sodium nitrite due to the frequent collision and coalescence of the droplets. This led to the oxidation of the hydrolyzed product and the formation of iron oxide within the aqueous core of the microemulsion. The barrier provided by the surfactant monolayer restricted the growth of the particles. Transmission electron microscopy of these particles revealed that they were spherical, with a narrow size distribution and a size range of 22–25 nm (see Fig. 6). X-ray diffraction of the dried powders showed characteristic peaks corresponding to the crystalline γ-Fe$_2$O$_3$ phase. No other impurities corresponding to the α-Fe$_2$O$_3$ or Fe$_3$O$_4$ were detected in the diffractogram.
Fig. 7. Room temperature magnetization curve for $\gamma$-Fe$_2$O$_3$ particles synthesized in microemulsions.

Room temperature magnetization curve for the dried powder, obtained on a VSM, is shown in Fig. 7. This curve shows no hysteresis and zero coercivity indicating that these particles were superparamagnetic at room temperature. These measurements also yielded a saturation magnetization of 46.6 emu/g. As particle size decreases to the nanometer size range, the thermal energy becomes sufficiently large at room temperature to overcome the magnetic anisotropy energy, and the bulk magnetic properties (coercivity and retentivity) vanish at room temperature, leading to superparamagnetism (as shown for $\gamma$-Fe$_2$O$_3$ particles synthesized in microemulsions).

If microemulsions are used for in situ synthesis of superparamagnetic, nanometer sized, gamma iron oxide magnetic particles, these particles
can be isolated easily in powder form for their use in magnetic imaging. These powders can also be dispersed in aqueous or non-aqueous media for potential applications as ferrofluids, or they can be incorporated in a polymer or glass matrix for their use in magnetic refrigeration.

VI. SYNTHESIS OF SUPERCONDUCTORS

The discovery of a superconducting temperature ($T_c$) near 30 K in La-Ba-Cu oxide by Bednorz and Muller [124], prompted many efforts to study perovskite-like oxide superconductors. This led to the discovery of new superconducting materials in the Y-Ba-Cu-O system with $T_c$ above the boiling point of liquid nitrogen [125,126]. Recently, even higher $T_c$ (>110 K) superconductors were discovered in the Bi-Sr-Ca-Cu-O [127] and Tl-Ba-Ca-Cu-O [128] systems.

It is now well recognized that the properties of high temperature oxide superconductors are critically dependent on the microstructure of the sample. Control of particle size, size distribution, morphology of precursors, and heat treatment conditions are critical to obtaining a desired microstructure. The conventional method for the preparation of oxide superconductors by solid state reaction has many inherent problems like poor homogeneity, large particle size, lack of reproducibility, and longer heat treatment times. In order to achieve a better level of homogeneity, wet chemical techniques such as coprecipitation [129–132], freeze drying [133], amorphous citrate process [134,135], and chelation [136] have been used. One can achieve an even better level of homogeneity and smaller particle sizes if the wet chemical reactions are carried out in constrained nanosize reactors, like the aqueous droplets of water-in-oil microemulsions. We have used water-in-oil microemulsions for the synthesis of nanoparticles of oxalate precursors of both Y-Ba-Cu-O (123) and Bi-Pb-Sr-Ca-Cu-O (2223) superconductors.

A. Synthesis of Y-Ba-Cu-O (123) superconductors

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors were synthesized by the co-precipitation of oxalates of yttrium, barium and copper in the aqueous cores of water/cetyl trimethyl ammonium bromide/1-butanol/octane microemulsion systems [89]. Two microemulsions (each consisting of 29 wt.% surfactant plus cosurfactant phase, 60 wt.% hydrocarbon phase, and
11 wt.% aqueous phase), one containing an aqueous solution of yttrium, barium and copper nitrates in the molar ratio 1:2:3, and the other containing ammonium oxalate solution as the aqueous phase, were mixed. This led to the precipitation of the oxalate precursors within the aqueous cores of the microemulsion. Since the two microemulsions are identical in composition, there is no destabilization of the microemulsion phase on mixing. The barrier provided by the surfactant monolayer restricts the growth of the particles and hinders inter-particle coagulation. Serial precipitation of the cations (which may occur in other wet chemical synthesis processes) is avoided in this approach due to the size of the “nanoreactors”, which was about 130 Å in the present case. The particles are also expected to be microhomogeneous due to mixing of the cations at the nano-scale level in the microemulsion droplets. The oxalate precipitate was separated, washed, dried and then calcined at 820°C for 2 hours for complete conversion to the oxide. This powder was then pressed into pellets and sintered at 925°C for 12 hours.

As a comparison, we also studied co-precipitation of yttrium, barium, copper oxalates in a bulk aqueous solution using ammonium oxalate. The oxalate precipitate thus obtained was calcined and then sintered under similar conditions as the microemulsion precipitate to produce the YBa$_2$Cu$_3$O$_{7-x}$ superconductor.

DC magnetic susceptibility measurements as a function of temperature were performed on a superconducting quantum interference device magnetometer (SQUID). This revealed that the microemulsion synthesized sample had a superconducting transition temperature (T$_c$) of 93 K and showed 90% of the Meissner shielding as that expected from an ideal sample (−1/4π). This sintered disk also had 98% of theoretical single crystal density. This high density is due to the ability of the nanoparticles to pack closely with very few voids and upon sintering, these well-packed particles are able to form large grains (15–50 μm) with very low porosity. This can be seen from the scanning electron micrographs (SEM) of the sintered disk shown in Fig. 8a and b. On the other hand, the bulk co-precipitated sample showed a Meissner shielding of 14% of that expected from an ideal sample. This can be explained by the fact that this sample was more porous (lower density) than the microemulsion synthesized material due to the fact that the precursor particles were large and therefore did not pack well. This resulted in smaller grains (0.5–2.0 μm) in the sintered pellet with more pores (see Fig. 8c and d). A comparison of all properties of the microemulsion synthesized and bulk co-precipi-
Fig. 8. Scanning electron micrographs of sintered YBa$_2$Cu$_3$O$_{7-x}$ pellet synthesized using microemulsions (a,b) and bulk co-precipitation (c,d). The magnifications used were (a) 1000, (b) 5000, (c) 5000, and (d) 20000.
TABLE 1
Comparison of selected physical properties of YBa$_2$Cu$_3$O$_{7-x}$ synthesized using microemulsions and by bulk co-precipitation

<table>
<thead>
<tr>
<th>Property</th>
<th>Microemulsion synthesis</th>
<th>Bulk aqueous synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESD of Y-Ba-Cu oxalate precursor</td>
<td>47.4 nm</td>
<td>380.6 nm</td>
</tr>
<tr>
<td>ESD of Y-Ba-Cu-O powder</td>
<td>274.8 nm</td>
<td>626.6 nm</td>
</tr>
<tr>
<td>Calcination conditions</td>
<td>820°C, 2 h</td>
<td>860°C, 6 h</td>
</tr>
<tr>
<td>Grain size of sintered pellet</td>
<td>15–50 μm</td>
<td>0.5–2.0 μm</td>
</tr>
<tr>
<td>Sintering conditions</td>
<td>925°C, 12 h</td>
<td>925°C, 12 h</td>
</tr>
<tr>
<td>Percent of theoretical density of sintered pellet</td>
<td>98% (±3)</td>
<td>90% (±2)</td>
</tr>
<tr>
<td>Fraction of ideal Meissner signal (–1/4π)</td>
<td>90.5%</td>
<td>14.4%</td>
</tr>
<tr>
<td>Superconducting T$_c$</td>
<td>93 K</td>
<td>91 K</td>
</tr>
</tbody>
</table>

ESD – Estimated spherical diameter.

tated samples are shown in Table 1. Based on these results we can say that the microemulsion derived 123 superconductor is seven times better than the one formed by bulk co-precipitation, on the basis of the Meissner shielding results for the two samples.

YBa$_2$Cu$_3$O$_{7-x}$ superconductors have also been synthesized using water-in-oil microemulsions based on a nonionic surfactant Igepal CO 430 (nonylphenoxypropyly (ethyleneoxy) ethanol) with cyclohexane as the oil phase [90]. In this process, the aqueous phase in one microemulsion consisted of yttrium acetate, barium carbonate and copper acetate, in a cationic ratio of 1:2:3 (based on 10 mM of Y$^{3+}$) dissolved in a 50/50 (v/v) acetic acid/water mixture. The second microemulsion had oxalic acid dissolved in a 50/50 (v/v) acetic acid/water mixture. Mixing of the two microemulsions resulted in the precipitation of oxalates of Y$^{3+}$, Ba$^{2+}$ and Cu$^{2+}$ in the ratio 1:2:3 (as confirmed by EDAX) within the aqueous cores of the microemulsion. These oxalate precursors were calcined at 800°C for 12 hours in air for conversion to the oxide. The calcined powder was pressed into a pellet and sintered at 930°C for 12 hours in flowing oxygen atmosphere.
Fig. 9. Scanning electron micrograph of sintered YBa$_2$Cu$_3$O$_{7-x}$ pellet synthesized using water/Igepal CO-430/cyclohexane microemulsions.

Powder X-ray diffraction of the sintered sample showed only peaks for the orthorhombic superconducting phase of YBa$_2$Cu$_3$O$_{7-x}$. All diffraction peaks were accounted for by an orthorhombic unit cell with $a = 3.818$ Å, $b = 3.881$ Å and $c = 11.679$ Å. The sintered pellet had a density corresponding to 97.8% of single crystal density which is quite remarkable for superconductors sintered under ambient pressure. This is also observed in the morphology of the sintered pellet shown in Fig. 9. These highly dense, large grains result from the ultrafine nature of the precursors.

Superconducting transition temperature measurements on a SQUID revealed a $T_c$ of 92 K. The diamagnetization corrected value of zero-field cooled signal (Meissner shielding) is 93.2% of that expected from an ideal sample ($-1/4\pi$). This high value is explained on the basis of the high density and large grain sizes in the sintered superconductor.
B. Synthesis of Bi-Pb-Sr-Ca-Cu-O (2223) superconductors

Recently, we have also used water-in-oil microemulsions for the synthesis of Bi-Pb-Sr-Ca-Cu-O (2223) superconductors [129]. A nonionic surfactant Igepal CO-430 or nonylphenoxypoly (ethyleneoxy) ethanol was used for the formation of the microemulsion with cyclohexane as the external oil phase. The aqueous phase in the first microemulsion was a solution of salts of Bi, Pb, Sr, Ca, Cu in the molar ratio 1.84:0.34:1.91:2.03:3.06 dissolved in a 50/50 (v/v) mixture of acetic acid and water. This aqueous solution was prepared by dissolving Bi$_2$O$_3$, Pb(CH$_3$COO)$_2$, SrCO$_3$, CaCO$_3$ and Cu(CH$_3$COO)$_2$ in the acetic acid/water mixture in the cationic ratio given above. The aqueous phase in the second microemulsion was a solution of oxalic acid in a 50/50 (v/v) acetic acid and water mixture. Both the microemulsions consisted of 15 grams of surfactant, 50 ml of oil, and 10 ml of aqueous phase. Mixing of these two microemulsions led to the formation of the oxalate precursor within the aqueous cores of the microemulsion. These precursors were in the size range of 2–6 nm (see Fig. 10). These oxalate particles were calcined at 800°C for 12 hours and then pressed into a pellet and sintered in air for 96 hours at 850°C.

DC magnetic susceptibility measurements as a function of temperature (shown in Fig. 11) indicated that this superconductor had a $T_c$ of 112 K. The zero field cooled signal (diamagnetic shielding) corresponded to 93% of the Meissner shielding expected from an ideal sample ($-1/4\pi$). Phase analysis by X-ray diffraction showed characteristic peaks of the 110 K phase; (002) and (0010) at $2\theta = 4.8^\circ$ and 23.9$^\circ$ respectively. This confirmed that the material was phase pure 2223 superconducting oxide.

The sintered disk also had large, lamellar grains as can be seen from the scanning electron micrograph (Fig. 12). This disk has very low porosity and had a density corresponding to 97% of the theoretical value. As in the case of the 123 superconductor, the ability of the nanoparticles to pack closely, with very few voids, results in high density disks with low porosity, and high Meissner shielding.

Thus, we have shown that uniform sized nanoparticles of precursors of superconductors precipitated in microemulsions, upon heat treatment, lead to the formation of microhomogeneous, high density superconductors which show properties that are superior to those synthesized by most wet chemical methods.
Fig. 10. Transmission electron micrograph of oxalate precursors for 2223 superconductors synthesized in water/Igepal CO-430/cyclohexane microemulsions.

Fig. 11. DC magnetic susceptibility measurements as a function of temperature for 2223 superconductor synthesized using microemulsions.
VII. SUMMARY

The importance of nanophase technology has resulted in tremendous research efforts towards the development of new techniques for the synthesis of nano-size particles. One such technique, developed a decade or so ago, was to use water-in-oil microemulsions as a reaction medium. The aqueous cores/water pools of these microemulsions can be used as nano-size reactors for the precipitation of a wide variety of nano-particles. For this technique to be successful, the reactants should be confined to the aqueous cores of the microemulsions and should not interact with the other components of the microemulsion (namely oil and surfactant).

In this paper, we have presented some of our recent research efforts in the field of synthesis of nanoparticles using water-in-oil microemulsions. We have described the synthesis of silver halides, barium ferrite, gamma iron oxide and Y-Ba-Cu-O and Bi-Pb-Sr-Ca-Cu-O superconductors using microemulsions. All these materials synthesized in microemulsions exhibit unique properties unlike those of materials synthesized using conventional techniques.
VIII. FUTURE DIRECTIONS

Over the past decade or so, researchers all over the world have been successful in synthesizing a variety of inorganic and organic nanoparticles using microemulsions as reaction media. However, attempts have to be made to make this process commercially and economically feasible. The process, as it currently exists, is expensive since microemulsions require the use of oil, surfactant and cosurfactant in high quantities. After separation of the particles from the microemulsion, the supernatant which is left over should be separated to recover the oil, surfactant and cosurfactant so that these materials can be used again for making microemulsions. This would significantly lower the cost of the process and will make it commercially more viable than at present.

Another aspect that needs to be explored is the effect of components of the microemulsion (oil, surfactant, cosurfactant) on the kinetics of particle formation and size of nanoparticles formed in microemulsions. We have shown that the interfacial rigidity of droplets in microemulsions can be controlled by the structure of the oil, surfactant or cosurfactant [28,57]. A high interfacial rigidity leads to a low inter-droplet attraction and low rate of precipitation, while a fluid interface leads to a higher rate of precipitation. However, a detailed and systematic study to reveal the effect of microemulsion components on reaction kinetics of particle formation and the effect this has on the morphology and properties of the particles formed would be very useful.

Most of the reports in literature on the synthesis of nanoparticles in microemulsions involve the formation of spherical particles. It would be of great scientific and technological interest to form asymmetrical particles like needle, disk, and egg-shaped particles in situ within the aqueous cores of water-in-oil microemulsions and to have the ability to precisely control the size and shape of these particles.

Finally, another area of interest would be in the synthesis of nanoparticle composites where one material (50–100 Å) may be coated by a thin layer (10–20 Å) of another material. Technologically, these types of materials have several applications, for example, in the synthesis of cobalt surface doped iron oxide particles which are used in magnetic recording media.

These are some of the main areas which should be the focus of research, in the near future, in the field of synthesis of nanoparticles using microemulsions.
IX. ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support provided by the National Science Foundation (Grant nos. CBT 8807321 and CTS 8922574), the Electric Power Research Institute (Grant no. RP 800922), and the Alcoa Foundation. We would also like to thank Prof. M.S. Multani and Dr. L.M. Gan with whom we had stimulating discussions on these topics.

X. REFERENCES

84 E. Boalye, L.R. Radovic and K. Osseo-Asare, J. Colloid Interface Sci., 163 (1994) 120.
268