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Synthesis and Characterisation of Nanomaterials

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ABSTRACT

Development of synthesis protocols for realising nanomaterials over a range of sizes, shapes, and chemical compositions is an important aspect of nanotechnology. The remarkable size-dependent physico-chemical properties of nanoparticles have fascinated and inspired research activity in this direction. This paper describes some aspects on synthesis and characterisation of nanoparticles of metals, metal alloys, and oxides, either in the form of thin films or bulk shapes. A brief discussion on processing of two-phase nanocomposite magnets is also presented.

Keywords: Nanoparticle synthesis, self-assembly, thermal decomposition, liquid-liquid interface reaction, ball milling

1. INTRODUCTION

There is a tremendous research interest in the area of nanotechnology to develop reliable processes for the synthesis of nanomaterials over a range of sizes and chemical compositions. Although the conventional methods of synthesis of metal sols, known since the times of Michael Faraday, continue to be used for generating metal nanoparticles, there have been several improvements and modifications in the methods which provide a better control over the size, shape, and other characteristics of the nanoparticles[1,2]. These developments have enabled studies of quantum confinement as well as other properties dependent on size, shape, and composition[3]. Ligating nanoparticles with organic molecules and assembling these in one-, two-, or three-dimensional mesostructures have added another dimension to this field wherein collective properties of nanoparticles have been of special interest[4]. The exciting potential of nanomaterials can be *en routed* to nanodevice applications, only with a combination of nanobuilding units and strategies for assembling them. Self-assembly of nanoparticles synthesised by the colloidal route on suitable supports is one of the interesting techniques currently being investigated for realising such structures[5]. Though the synthesis and organisation of nanoparticles provide complementary tools for nanotechnology, processing of nanoparticles or nanopowders into bulk shapes, retaining nanosize is another challenging aspect, as far as structural and engineering applications are concerned.

Synthesis and assembly strategies of nanoparticles mostly accommodate precursors from liquid, solid or gas phase; employ chemical or physical deposition approaches; and similarly rely on either chemical reactivity or physical compaction to integrate the nanostructure building blocks within the final material structure. The variety of techniques that can be classified in top-down or bottom-up approaches are schematically illustrated in Fig. 1. The bottom-up approach of nanomaterials synthesis first forms the nanostructured building blocks (nanoparticles) and then assembles these into the final material.

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An example of this approach is the formation of powder components through aerosol and sol-gel techniques and then the compaction of the components into the final material. Nanoparticles with diameters ranging from 1 nm to 10 nm with consistent crystal structure, surface derivatisation, and a high degree of monodispersity can be processed by these techniques[6]. Gas phase synthesis or aerosol processing of nanoparticles is based on evaporation and condensation (nucleation and growth) in a subatmospheric inert-gas environment; and the processing mainly is by combustion flame, laser ablation, chemical vapour condensation, spray pyrolysis, electro spray, and plasma spray.

On the other hand, sol-gel processing is a wet chemical synthesis approach that can be used to generate nanoparticles by gelation, precipitation, and hydrothermal treatment. Besides, better size and stability control of nanoparticles can be achieved using inverted micelles, polymer-matrix architecture based on block copolymers or polymer blends, and *ex situ* particle-capping techniques. Additional nanoparticle synthesis techniques include sonochemical processing, hydrodynamic cavitation, and microemulsion processing. In sonochemistry, an acoustic cavitation process can generate a transient localised hot zone with extremely high temperature gradient and pressure[8]. Such sudden changes in temperature and pressure assist the destruction of the sonochemical precursor (e.g., organometallic solution) and the formation of nanoparticles. The technique can be used to produce a large volume of material for industrial applications.

In hydrodynamic cavitation, nanoparticles are generated through creation and release of gas bubbles inside the sol-gel solution[9]. By rapidly pressurising in a supercritical drying chamber and exposing to cavitational disturbance and high temperature heating, the sol-gel solution is mixed. The erupted hydrodynamic bubbles are responsible for nucleation, growth, and quenching of the nanoparticles. Particle size can be controlled by adjusting the pressure and the solution retention time in the cavitation chamber. Microemulsions are another important processing technique-extensively used for synthesis of metallic, semiconductor and magnetic nanoparticles[10,11]. By controlling the very low interfacial tension (~10^{-3} mN/m) by adding a cosurfactant (e.g., an alcohol of intermediate chain length), these microemulsions are produced spontaneously without the need for significant mechanical agitation. The technique is useful for large-scale production of nanoparticles using relatively simple and inexpensive hardware.

The top-down approach begins with a suitable starting material and then sculpts the functionality from the material. This technique is similar to the approach used by the semiconductor industry in forming devices out of an electronic substrate (silicon), utilising pattern formation (such as electron beam lithography) and pattern-transfer processes (such as reactive-ion etching) that have the requisite spatial resolution to achieve creation of structures at the nanoscale. This particular area of nanostructure formation has tremendous scope and is a driving issue for the electronics industry. Another top-

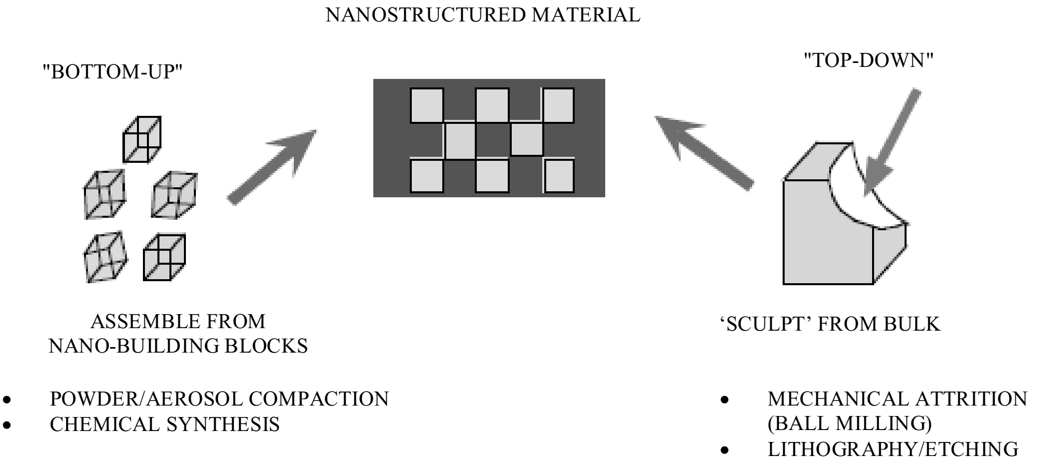


Figure 1. Schematic of a variety of nanostructure synthesis and assembly approaches.

down approach is ball milling, the formation of nanostructure building blocks through controlled mechanical attrition of the bulk starting material[12]. Those nano building blocks are then subsequently assembled into a new bulk material. The technique, already a commercial technology, has been considered dirty because of contamination problems from ball-milling processes. However, the availability of tungsten carbide components and the use of inert atmosphere and/or high vacuum processes have reduced impurities to acceptable levels for many industrial applications.

In fact, many current strategies for nanomaterial synthesis integrate both synthesis and assembly into a single process with efforts to have a better control over size, shape, and structure. Over the last several years, numerous physical and chemical methods have been employed to produce nanoparticles. The R&D status of these methods has gone up by an order of magnitude in the past five years due to the demand of the nanotechnology. A sampling of the leading institutions in India involved in various areas of nanomaterials research include, almost all the universities, IITs, IISc, JNCASR, DRDO, CSIR, DST, and other national laboratories. Each of these laboratories/institutions is involved in the core areas of research such as synthesis, assembly, and characterisation of nanoparticles, nanotubes, nanowires, nanoporous solids, nanostructured alloys, and DNA chips, etc. Some of the products being developed with the nanomaterials include NEMS-based thermal sensors, value-added fabrics, nanoparticle-based drug delivery systems, magnetic nanoparticles for therapeutic use, super-hard coatings, flexible display, biosensors, and nanopatterned surfaces.

The DMRL, being a metallurgical laboratory, is actively engaged in various activities of nanomaterials, which include, development of nanocomposite magnets through high-energy ball milling, piezoelectric ceramics by sol-gel method, metal-metal alloy particles by soft chemical method, and also characterisation of various nanomaterials by TEM and 3-D atom probe. In this paper, some of the important methods, highly suitable for either preparing films of nanoparticles or processing these into bulk shapes, are briefly presented.

2. SYNTHESIS OF NANOMATERIALS

The organisation of nanoparticles in a thin film form is often necessary to render these functional and operational. Two important chemical methods: (a) high-temperature thermal decomposition and (b) liquid-liquid interface reaction, suitable for preparing films of many metal and metal oxide nanoparticles, are illustrated with examples. In addition, the utilisation of a high-energy ball milling and spark plasma sintering process for the preparation and processing of nanocomposite powders into bulk magnets are also highlighted.

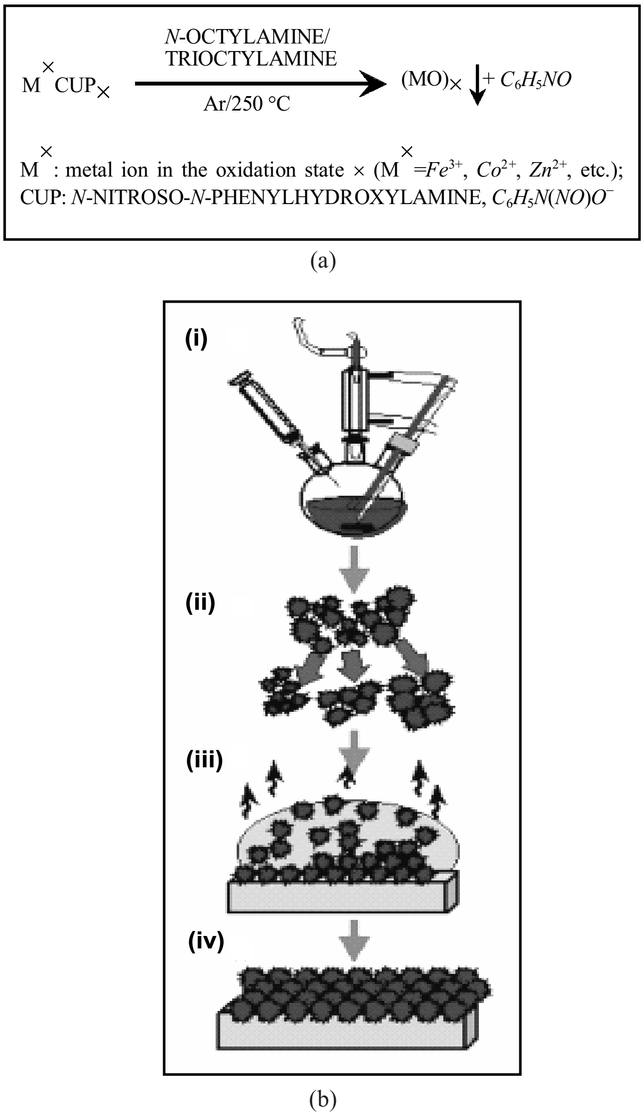
2.1 High-temperature Thermal Decomposition

A general scheme for preparing mono-disperse nanoparticles requires a single, temporally short nucleation event followed by slower growth on the existing nuclei. This may be achieved by quick addition of reagents into a reaction vessel containing a hot coordinating solvent. The temperature of the solution is sufficient to decompose the reagents, forming a supersaturation of species in solution that is relieved by nucleation of nanoparticles. High-temperature thermal decomposition provides a general route for preparing dispersable nanoparticles of most of the transition-metal oxides using metal cupferron complexes M^xCup_x (M: metal ion; Cup: *N*-nitroso-*N*-phenylhydroxylamine, $[C_6H_5N(NO)O^-]$ are used as single-molecular precursors[13]. In this non-hydrolytic route, the cupferron complex (which binds the metal ion through oxygen) is decomposed by releasing a leaving group such as nitrosobenzene at 250–300 °C in a hot coordinating solvent [Fig. 2(a)]. The resulting product forms a stable suspension consisting of oxide nanoparticles; each nanoparticle in a sample consists of an inorganic crystalline core surrounded by an organic monolayer (surfactant).

The nanoparticles so obtained are freely soluble in non-polar organic solvents and can be readily precipitated from solutions with polar solvents. Further, nanoparticles with uniform size distribution ($\sigma < 7\,\%$) can be achieved through size-selective precipitation procedures and the organic monolayer coordinating each nanoparticle surface enables to self-assemble into nanoparticle superlattices under controlled conditions. Thus, ordered nanoparticles assemblies/

monolayer thin films are obtained using this method. The experimental procedure is schematically represented in Fig. 2(b).

The characteristic advantages of this colloidal route are: (i) besides producing dispersable nanoparticles of almost all transition-metal oxides, this method enables to prepare ordered nanoparticle assemblies with appropriate choice of surfactants, (ii) using suitable ratio of bi-metal precursors, spinel ferrite nanoparticles can also be obtained, (iii) the reaction atmosphere employed in this method also plays critical role in determining the nature of the nanoparticles; and (iv) with the same precursor, one can prepare either oxide or sulphide nanoparticles by maintaining *Ar* or H_2S atmosphere during thermal decomposition. Following are some of the above facts demonstrated with specific examples:



$$M^{\times}CUP_{\times} \xrightarrow[\text{Ar/250 °C}]{\text{N-OCTYLAMINE/TRIOCTYLAMINE}} (MO)_{\times}\downarrow + C_6H_5NO$$

$M^{\times}$: metal ion in the oxidation state × ($M^{\times}=Fe^{3+}$, Co^{2+}, Zn^{2+}, etc.);
CUP: *N*-NITROSO-*N*-PHENYLHYDROXYLAMINE, $C_6H_5N(NO)O^-$

(a)

(b)

Figure 2. (a) Reaction scheme for the preparation of metal oxide nanoparticles, and (b) schematic representation of steps involved in obtaining ordered nanoparticle assemblies: (i) synthesis of nanoparticles by thermal decomposition, (ii) narrowing the nanoparticle sample by size-selective precipitation, (iii) deposition of nanoparticle dispersions to self-assemble, and (iv) ordered nanoparticle assemblies (superlattices).

At first, the precursor materials, i.e., metal cupferron complexes were prepared by aqueous precipitation, by cooling a solution of 5 g of respective metal chlorides in 100 ml of water to 0 °C and then adding 5 per cent by weight filtered aqueous cupferron solution, at suitable p*H*[14]. The obtained precipitates were washed several times with water and dried. The precursor materials were then recrystallised from methanol and characterised by thermogravimetry. Synthesis of several magnetic oxide nanoparticles including γ-Fe_2O_3, Fe_3O_4, and Co_3O_4 and semiconductor nanoparticles such as, *ZnO* and *ZnS* have been performed by decomposing respective metal cupferron complexes in the presence of a hot coordinating solvent.

In a typical synthesis yielding γ-Fe_2O_3 nanoparticles, a 0.3 mM solution of iron cupferron complex in *n*-octylamine was injected into a vigorously stirred 9 ml solution of tri-*n*-octylamine at ~300 °C in a round bottomed flask. The onset of reduction was marked by change in colour from red-brown to brown-black with brisk effervescence. The contents of the flask were maintained at ~225 °C and the stirring continued for another 45 min. To obtain Fe_3O_4 particles, the decomposition of cupferronates was carried out in H_2 atmosphere and the contents of the flask were maintained at ~250 °C till a colour change from brown to black was observed[15]. In a similar manner, Mn_3O_4, Co_3O_4, Cu_2O, and *ZnO* nanoparticles can be prepared by the thermal decomposition of respective cupferron complexes in *Ar* atmosphere[13].

Representative TEM images of typical magnetic oxides of γ-Fe_2O_3, Fe_3O_4, and Co_3O_4 (Fig. 3) show the successful synthesis of various uniform magnetic nanoparticles through this thermal decomposition method. The 2-D assembly of *n*-octylamine capped Co_3O_4 [Fig. 3(b)] and dodecylamine capped Fe_3O_4 [Fig. 3(d)] occurred spontaneously on the copper TEM grids after the evaporation of the solvents, indicating the regular shapes and narrow size distribution of these nanoparticles.

In Fig. 4, typical TEM micrographs of *n*-octylamine capped *ZnO* and *ZnS* nanoparticles obtained by thermal decomposition of zinc cupferron complex under *Ar* and H_2S atmosphere respectively, are shown[16]. Besides synthesising oxide and sulphide nanoparticles, by adopting bi-metal precursors in a certain mole ratio, composite oxide nanoparticles such as magnetic MFe_2O_4 (M represents *Fe*, *Co*, *Mg*, *Zn* or *Mn*) could be effectively prepared following this synthetic approach. Figure 5 depicts the typical micrographs of $CoFe_2O_4$ and $MnFe_2O_4$ spinel ferrite nanoparticles with dia ~10 nm, which formed 2-D patterns on the TEM grids and showed good uniformity[17]. The details of structural and magnetic properties of the nanoparticles prepared by this technique are described by Saravanan[15-16], *et al.* With the above examples, it is thus demonstrated that the thermal decomposition is one of the most general approaches for the preparation of transition metal oxide/sulphide colloidal nanoparticles.

2.2 Liquid-liquid Interface Reaction

Nanoparticles anchored to surfaces in the form of film are considered to be important because of their potential use in nanodevices. A liquid-liquid interface offers potential to synthesise nanoparticles, as well as casting them into a film. At a liquid-liquid interface, the particles are highly mobile and rapidly achieve an equilibrium assembly[18]. In contrast to the other techniques, this method is a one-step process enabling synthesis of nanparticle arrays at the liquid-liquid interface under ambient conditions.

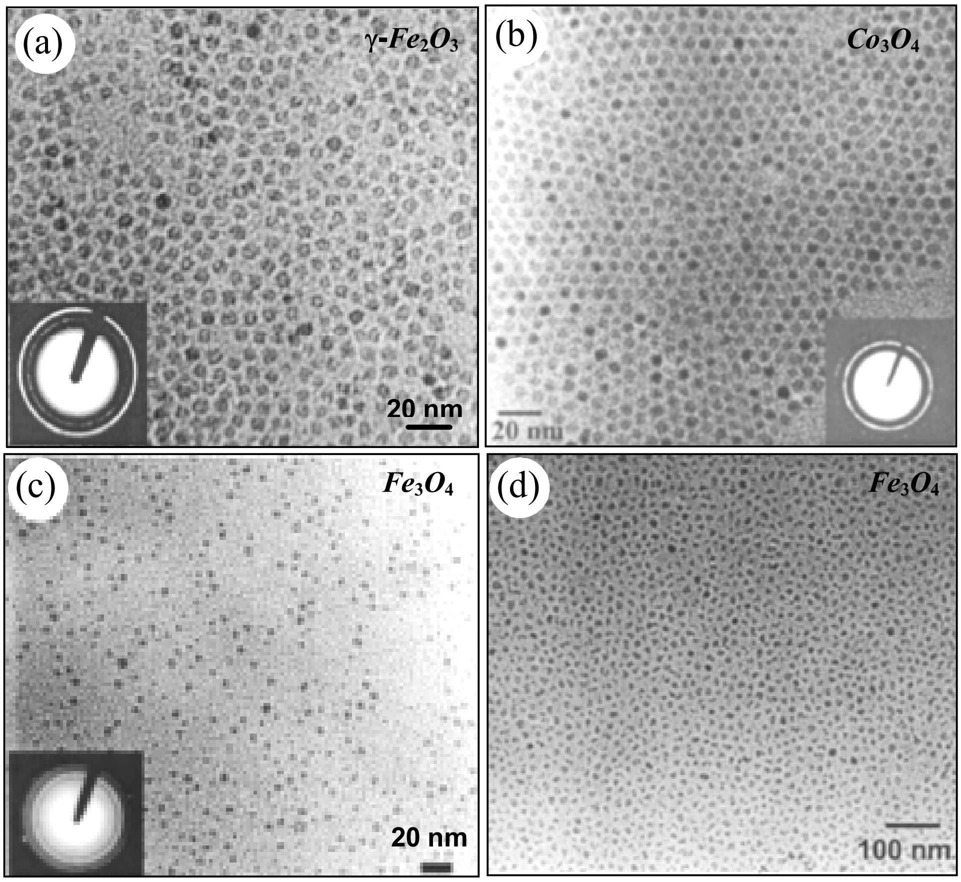


Figure 3. TEM micrographs of *n*-octylamine capped: (a) γ-Fe_2O_3 , (b) Co_3O_4 , (c) Fe_3O_4 , and (d) dodecylamine capped Fe_3O_4 nanoparticles, (Insets: SAED patterns).

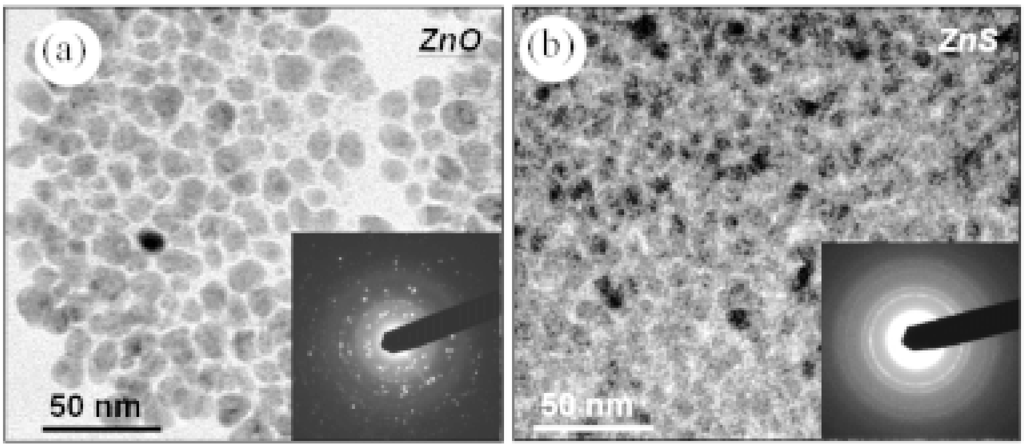


Figure 4. TEM micrographs of *n*-octylamine capped: (a) *ZnO* and (b) *ZnS* semiconductor nanoparticles, (Insets: SAED patterns).

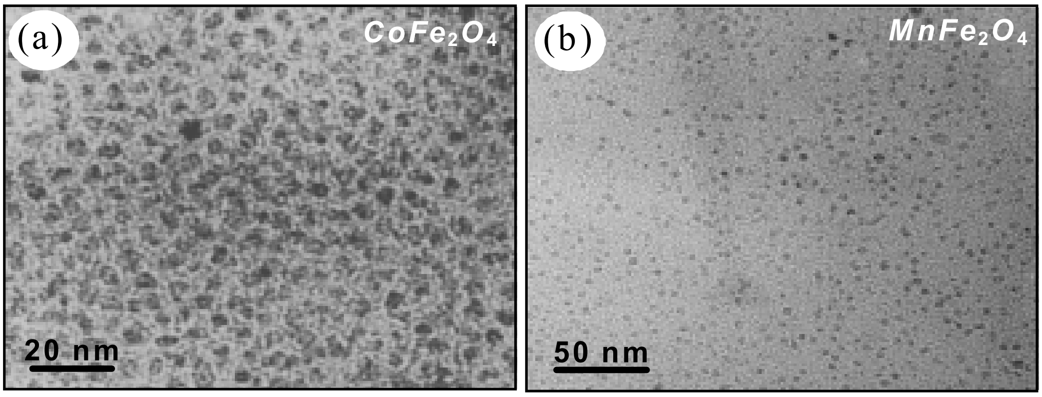


Figure 5. TEM micrographs of *n*-octylamine capped magnetic spinel ferrite nanoparticles: (a) $CoFe_2O_4$ and (b) $MnFe_2O_4$.

This method involves the reaction of an organometallic compound dissolved in the organic layer with a reducing, a sulphiding, or an oxidising agent in the aqueous layer. The material formed at the interface corresponds to an ultrathin nanocrystalline film consisting of closely- packed nanocrystals coated with the organic species present at the interface.

The novelty of this method is that it involves a finite growth rate of the ultrathin nanocrystalline film with controllable parameters such as temperature and concentration. The nanocrystals in the films can be readily extracted to aqueous or organic layers by adding suitable capping agents. Further, the nanocrystalline film obtained at the interface can be easily transferred onto a solid support such as mica or a polymer film. With appropriate choice of metal precursors and reducing agents, a variety of nanocrystalline films can be fabricated, and some of the typical results obtained by this method are presented to illustrate its versatility.

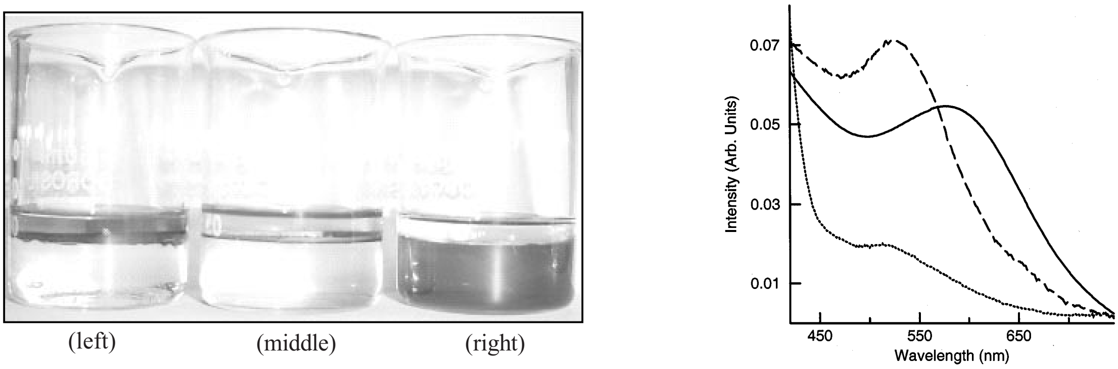
Nanocrystalline films of *Au*, *Ag*, and *Cu* have been prepared at the toluene-water interface by the interaction of their metal-triphenyl complexes in the organic layer with partially hydrolyzed tetra-kis-hydroxy-methyl-phosphonium chloride (THPC) in the aqueous layer[19]. In a typical preparation, 10 ml of 1.5 mM solution of $Au(PPh_3)Cl$ in toluene was allowed to stand in contact with 16 ml of 6.25 mM aqueous alkali in a 100 ml beaker under ambient conditions. Once the two layers got stabilised, 330 µl of 50 mM THPC was injected into the aqueous layer using a syringe with minimal disturbance to the toluene layer. The onset of reduction was marked by a faint pink coloration of the liquid-liquid interface. The reduction thus initiated was allowed to proceed without disturbance for several hours. With the passage of time, the colour became more vivid, finally resulting in a robust elastic film at the interface.

An important feature of the liquid-liquid interface method is that the nanocrystals at the interface can be transferred to either aqueous or organic phase using appropriate capping agents. For example, by adding of dodecanethiol to the organic layer, the *Au* nanocrystals could be transferred entirely to the organic layer, while the addition of mercaptoundecanoic acid transferred the nanocrystals to the aqueous layer.

The transfer of *Au* nanocrystals to the aqueous or the organic medium is marked by the acquisition of a vivid colour by the respective layer, as demonstrated in Fig. 6(a). The UV-visible spectra of the as-prepared *Au* film as well as of the hydrosol and organosol are shown in Fig. 6(b). All the spectra exhibit bands due to the surface plasmon, the position and intensity depending on several factors such as the diameter of the nanocrystals, the nature of the ligand, and the refractive index of the surrounding medium. The film on quartz substrate exhibits a broad band centred at 575 nm, while the sols show plasmon bands at ~530 nm.

Films of other metals such as *Ag* and *Cu* could be obtained by a similar procedure using $Ag_2(PPh_3)_4Cl_2$ and $Cu(PPh_3)Cl$, as metal precursors and the typical TEM images of nanocrystalline films of *Au*, *Ag*, and *Cu* are shown in Fig. 7. It can be seen that all the micrographs consist of close-packed nanocrystals with narrow size distribution, indicating that the effectiveness of this technique on required control of particle size distribution. Further, the size of the metal nanocrystals formed at the liquid-liquid interface can be controlled by adjusting the various reaction parameters such as contact time, temperature, and concentration of the reactants. By this means, the optical and electrical properties of the films can be varied[20].

Besides synthesising the films of *Au*, *Ag*, and *Cu* nanoparticles, films of *CuO* nanowhiskers with diameters in the range 50 nm to 300 nm and lengths of up to several microns could be prepared by employing reactions at the liquid-liquid interface[21].



(a) (b)

Figure 6. (a) Nanocrystalline film of *Au* formed at the toluene-water interface (middle). When dodecanethiol was added to the toluene layer, the film broke forming an organosol (left); while mercaptoundecanoic acid added to water produced a hydrosol (right), and (b) UV-visible spectra of the as-prepared standard film on a synthetic quartz substrate (dark line), octylamine capped nanocrystals in toluene (dashed line), and mercaptoundecanoic acid-capped nanocrystals in water (dotted line).

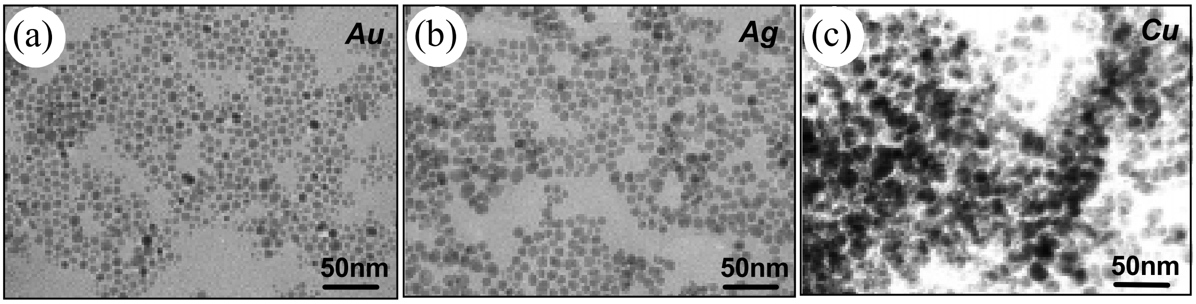
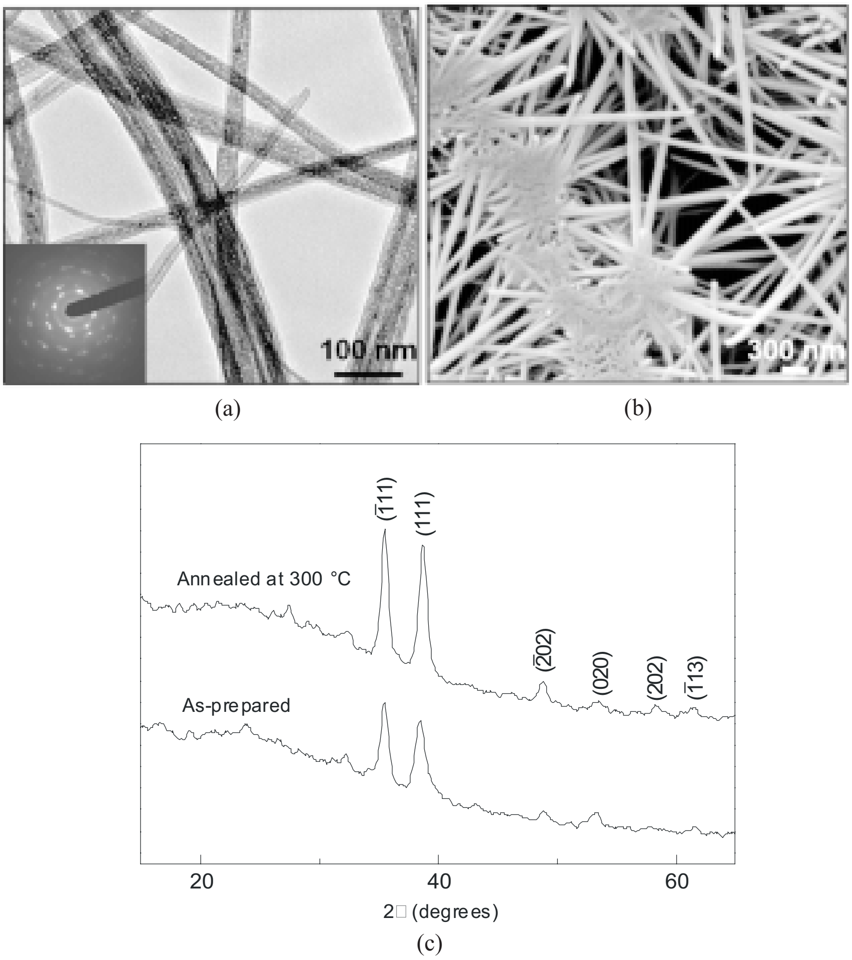


Figure 7. TEM micrographs of the as-prepared nanocrystalline films: (a) *Au*, (b) *Ag*, and (c) *Cu*.

In a typical preparation, 0.04 m mol of copper acetyl-acetonate in 10 ml of toluene was allowed to stand in contact with equal amount of aqueous layer containing 1 m mol of $NaOH$. Once the two layers were stabilised; the aqueous-organic interface was kept in a waterbath at 50 °C for 60 min, without disturbance. Reaction was complete, as could be evidenced by a colour change of the organic phase from blue to colourless, following which the appearance of a black-brown coloured CuO film at the liquid-liquid interface could be discerned. Figure 8(a) depicts typical TEM image of an as-prepared standard CuO film which reveals that the film consists of a rod-like structure, extending up to several hundred nm in length. Figure 8(b) shows a corresponding SEM micrograph of the CuO film, indicating dense-packing of needle- shaped nanowhiskers, with exceptionally large aspect ratios. The growth of these whiskers was scattered along the interface layer and the overall film morphology resembled a bamboo shoot-like structure.

Figure 8(c) shows the XRD pattern of the as-prepared nanocrystalline CuO film. All the diffraction peaks could be indexed to monoclinic CuO with lattice constants: a = 0.4689 nm, b = 0.34288 nm and c = 0.5142 nm, which are in good agreement with the bulk CuO. To further verify the phase of nanowhiskers, i.e., CuO or Cu_2O type, the as-prepared film was annealed to 300 °C in the air for about 6 h. The XRD analysis of annealed sample apparently showed no evidence of oxidation of the sample; indicating that the as-prepared film was purely that of CuO. It was demonstrated that the nature of the emerging film at the interface was dependent on the factors such as temperature of



(a) (b)

(c)

Figure 8. (a) TEM micrograph of as-prepared *CuO* nanowhiskers obtained from a toluene water interface at 50 °C, (Inset: SAED pattern), (b) SEM micrograph of as-prepared *CuO* film, and (c) XRD patterns of *CuO* film obtained at the interface.

the medium, contact time at the interface, relative amounts of reducing agent, and metal precursor. It is noteworthy that this simple approach requires neither sophisticated techniques nor metal catalysts and surfactants for the large-scale synthesis of monoclinic CuO nanowhiskers.

In addition to the above examples, the applicability of this technique in preparing a variety of nanocrystalline films of metals, oxides, chalcogenides[22], bi-metal and tri-metal alloys[23] has been recently demonstrated. So, undoubtedly the liquid-liquid interface can be considered as a promising method for the synthesis of films of nanocrystals.

2.3 High-energy Ball Milling

Despite the fact that the chemical methods have been widely employed for nanomaterial preparation; the utilisation of physical methods has also been given considerable attention; particularly in the area of nanoengineered materials, wherein large-scale fabrication of nanopowders is essential for processing these into bulk shapes[24]. Among the physical methods, mechanical milling has been widely utilised for the preparation of nanohard/nanocomposite magnetic powders owing to its versatility. Mechanical milling is a high-energy deformation process that progressively introduces defect structures (dislocations and vacancies), atomic-scale chemical disorder, and elastic strain energy into the initially crystalline starting powders through the shearing actions of ball-powder collisions. Milling can be used to produce a variety of effects in intermetallic alloys due to complex dependence of the nanostructure on milling intensity, temperature and other factors. The preparation of nanocomposite magnetic powders of $SmCo_5/Fe$ through high-energy ball milling method and their consolidation into bulk magnets using a spark plasma sintering method has been demonstrated.

Nanocomposite permanent magnetic materials consisting of hard ($SmCo_5$) and soft (Fe or Fe-Co) magnetic phases have immense potential to exhibit a higher energy product than the conventional single-phase hard magnets. It is predicted that the energy product, $[(BH)_{\max}]$ in a nanocomposite magnet can be enhanced from that of a single-phase hard magnet, using high saturation magnetisation of the soft phase and the high coercivity of the hard phase if the two phases are spring exchange coupled[25]. Since the magnetic properties and the degree of exchange coupling are strongly dependent on the microstructural parameters, such as crystallite size, phase distribution, and volume fraction of the hard and soft magnetic phases, many efforts have been made to synthesise and characterise the nanostructured magnets by mechanical milling, melt spinning, and thin-film techniques. However, the consolidation of nanocomposite powders into bulk-shaped magnets is a challenging one and the bulk-shaped magnets are very essential for any critical engineering application. Among all the techniques used for consolidation (hot isostatic pressing and plasma pressure compaction), the recently developed spark plasma sintering (SPS) technique has been successfully adopted to produce bulk nanocomposite magnets with high coercivity and excellent magnetic properties. In the SPS technique, simultaneous application of pressure and rapid heating rate (400–500 °C/min) by a pulsed electrical current with dc bias voltage helps in densification without causing grain growth.

The authors' recent investigation on the preparation of $SmCo_5$/x Wt per cent Fe nanocomposite powders by high-energy ball milling and their consolidation into bulk shape by SPS technique[26] has been presented. Figure 9 represents the various steps involved in the preparation of nanocomposite magnets. $SmCo_5$ alloys were prepared by induction melting of the elemental Sm and Co in Ar atmosphere. The as-cast alloy ingot was crushed into coarse powders with a typical particle size of ~300 μm. The alloy powders were then mixed with α-Fe powders of particle size < 10 μm and milled in a planetary ball mill with a ball-to-powder ratio of 10 : 1 for different milling time (4–50 h) at a constant speed (200 rpm). The ball milling was carried out using tungsten carbide balls and vial in toluene medium. The milling was stopped at regular intervals to collect the powders for intermediate structural and magnetic analyses. The milled powder (10 h) was packed in a graphite die of 15 mm inner dia for consolidation purpose and a magnetic field of 2T was applied to orient the powders prior to SPS. The aligned powders were then subjected to SPS in vacuum (10^{-3} Torr). The SPS conditions were as follows: (i) sintering temperature

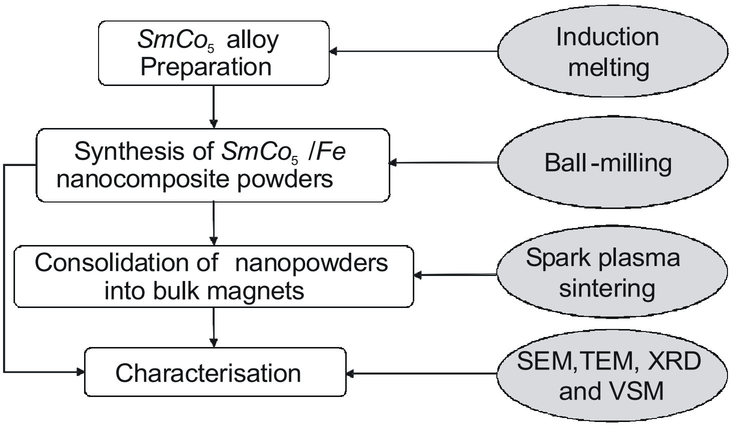
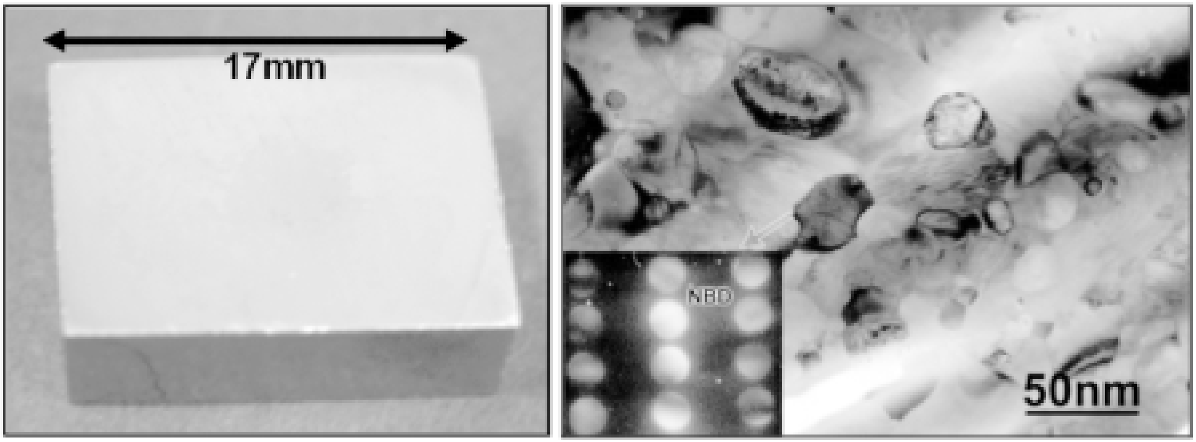


Figure 9. Flow chart showing various steps involved in the processing of nanocomposite magnets.

700–740 °C, (ii) pressure 10.0–10.5 kN, and (iii) sintering time 5 min.

A bulk magnet with density of about 8.1 g/cc (~96 %) was obtained after SPS compaction [Fig. 10(a)]. A typical TEM microstructure of SPS samples shown in Fig. 10(b), clearly reveals that the sample consists of randomly oriented nanograins, with an average grain size of 20 nm. The inset in Fig. 10(b) shows the nanobeam diffraction pattern taken along $[2\ 1\ \bar{3}\ 0\ ]$ zone axis of one of the $SmCo_5$ grains. Demagnetization curves of the spark plasma sintered nanocomposite $SmCo_5 + x$ Wt per cent Fe ($x = 5$ and 10) samples are shown in Fig. 11. The smooth demagnetisation curves and enhanced magnetisation of $SmCo_5$+Fe samples indicate the existence of strong exchange coupling between the hard and soft magnetic phases.

From Fig. 9, it can be seen that the $SmCo_5$ phase without addition of Fe has coercivity (H_c) of 12 kOe and saturation magnetisation (M_s) of 72 emu/g at a maximum applied field of 7T. The $SmCo_5$+5 Wt per cent Fe sample has H_c of 8.9 kOe and M_s of 86 emu/g, while $SmCo_5$+10 Wt per cent Fe sample showed a coercivity of 7 kOe and saturation magnetisation of 96 emu/g. It is clear from the magnetic characterisation that with the increase of Fe volume fraction, the magnetisation increases, revealing the existence of a strong exchange coupling between the nanosized hard ($SmCo_5$) and soft (Fe) magnetic phases. The energy products obtained in the SPS samples are in the range 8–10 MGOe. The relatively lower energy products obtained in the samples are attributed to the randomness of the nanograins as evidenced from TEM studies. To



(a) (b)

Figure 10.(a) Bulk $SmCo_5$ magnet after SPS compaction, and (b) corresponding TEM micrograph, (Inset: Nanobeam diffraction pattern of the $SmCo_5$ phase).

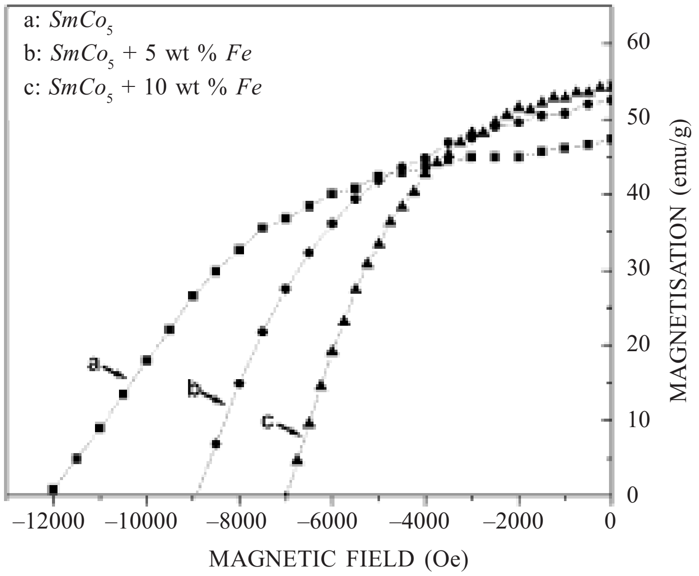


Figure 11. Demagnetisation curves of spark plasma sintered magnets.

conquer this problem, substantial efforts are being made to achieve anisotropic hard magnetic particles with nanosized grains by employing surfactant-assisted or magnetic field-assisted ball milling processes[27].

3. CONCLUSIONS

In this study, some salient aspects of chemical synthesis strategies such as high-temperature thermal decomposition and liquid-liquid interface reaction, and physical method such as high-energy ball milling suitable for either preparing films of nanoparticles or processing these into bulk shapes, have been presented. The potential of these techniques to prepare a variety of metal/metal oxide nanoparticles, films and two-phase nanocomposites has also been highlighted with suitable examples.

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