Oriented Arrays of Nanocrystalline Magnetite in Polymer Matrix Produced by Biomimetic Synthesis

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Synthesis of nano sized magnetite particles has been carried out following a polymer matrix mediated process. The synthesis route, being akin to bio mineralization, yields elongated magnetite particles of uniform size and morphology. The produced particles were oriented perpendicularly with respect to polymeric tubules and showed a tendency of array formation as happens in magnetotactic bacteria.

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1. Introduction

The normal physical, electronic and magnetic properties of a material get dramatically altered when it is formed as discrete particles of approximately 10–100 nm in diameter.\(^1\,\,^2\) Magnetic properties of highly oriented and self-assembled nanoparticles, having the size of a single domain, have aroused a great interest among the solid-state physicists and the materials scientists. These particles possess a good potential for applications in magnetic tapes, printing inks, magnetic targeting of pharmaceuticals, cell separation, contrast enhancement agents in Magnetic Resonance Imaging and magnetic sensors. However, synthetically produced nanosized magnetic particles are generally non-uniform in shape, size and orientation. They are compositionally inhomogeneous, not fully crystallised and exist in an agglomerated state. The above limitations deteriorate the properties and the performance of the magnetic particles. On the other hand, the existence of naturally occurring magnetotactic bacteria, comprising of a bio-polymer bound chain of nanosized magnetite particles (35–80 nm) of uniform shape, size and orientation along the [111] axis, highlights the role of biomimetic process in achieving a high degree of sophistication in the synthesis of nanosized particles at room temperature.\(^3\) A high degree of orientation of magnetite particles in the polymer matrix makes the bacteria capable of sensing a small variation in the geomagnetic field, so that it decides the direction of swimming. The mechanism that transduces the magnetic information into the useful sensory signal, is still poorly understood, however, at the time of precipitation, the biologically induced orientation along the [111] direction maximise its magnetic moment.\(^4\) The four steps involved in the process of matrix mediated biomimetic (re)organization of supramolecular matrix, templating, nucleation-growth and cellular processing\(^5\) lead to the formation of magnetite crystals with the cubo-octahedral, rod-shaped, elongated and the rectangular morphologies. All these shapes are the derivatives of an octahedral [111], dodecahedral [110] or a cubic [100] forms compatible with Fd3m symmetry.\(^6\) Motivated with the in situ synthesis of self arranged and single domain sized magnetite particles, enabling a magnetotactic bacteria to sense small variations in geomagnetic field, we are attempting to in situ synthesise nanosized magnetite particles by a polymer matrix mediated process. The efforts to produce advanced inorganic materials by following a synthesis route akin to biomineralization are termed as “Biomimetic Synthesis”.\(^7\) This route has been employed for the synthesis of nanosized particles of different inorganic materials of technical importance by different groups of researchers.\(^8\)-\(^12\) The present paper describes the in situ synthesis of nanosized magnetite particles with high aspect ratio in a hydrophilic polymer matrix. The pre-organized polymeric surface provides a controlled environment for the nucleation and growth of magnetite crystallites with rod shaped morphology oriented almost perpendicular to the polymer chain. The paper deals only with the morphological aspects of the in situ precipitated magnetite particles and their structural characterization. The studies on the effect of size and morphology on the magnetic properties of these magnetite particles are on and will be reported later.

2. Experimental Procedure

Aqueous solutions of polyvinyl alcohol (PVA, crystalline powder, average molecular weight 125000 g), having concentration in the range of 0.25 to 2 mass% were prepared by dissolving weighed amount of PVA in doubly de-ionised water at 80°C. Similarly, mixed solutions of Fe (III) and Fe (II) ions [Fe (III)/Fe (II) = 1.5], having total iron concentration in the range of 0.005 to 0.5 mol were prepared by dissolving the required weight of FeCl\(_3\) and FeCl\(_2\) in doubly de-ionised water at ambient temperature. A number of experiments have been conducted involving the different concentrations of the polymer and the iron salt solutions to optimise the conditions for oriented growth of magnetite particles. However, this paper presents the results obtained by using 0.5 mass% PVA solution and 0.01 mol Fe(III)-Fe(II) solutions. The 0.01 mol solution of iron salts and 0.5% PVA solutions were filtered and mixed together in the volumetric ratio of 1:4 respectively. The system was stirred for 15 minutes and poured into a Petri dish. The dish was kept at 40°C for 24 h and an orange coloured polymeric membrane was obtained. The membrane was washed with distilled water and acetone in order to remove the metal salt adsorbed on the membrane surface. The orange coloured polymeric membrane was soaked in 10 mL of 0.006 mol solution of NaOH
at 40°C for 24 h following which a black coloured magnetic polymeric film was obtained and it was dried at room temperature. Entire experiment was conducted in a dust free environment. The film was structurally and morphologically characterised using X-ray diffraction (XRD Cu Kα, 35 kV, 25 mA), scanning electron microscopy (SEM, 10 kV) and transmission electron microscopy (TEM, 200 kV).

3. Results and Discussion

The inspirations obtained from the synthesis of inorganic materials by biological process has initiated a great momentum in the synthesis of inorganic materials following a biomimetic route. In situ synthesis of number of systems including nano sized calcite, hydroxyapatite, cadmium sulphide, zinc sulphide, titanium dioxide, copper and cobalt particles has been recently reported in literature.9-12 Most of the studies employed a supra molecular matrix having a strongly acidic functional group which leads to a strong chemical chelation of cations, however, our studies make use of a commonly available polymer, PVA, not popularly known for chemical chelation.13 Having a hydroxyl group attached with the alternate carbon atoms, associated with the polymeric backbone, PVA makes weak complexes with transition metal ions at a low pH with the help of secondary bonds.14 PVA, a monoclinic crystalline and water soluble polymer is known for its gelation power, degree of gelation being a function of temperature, time and concentration. Hydro-gel of the polymer comprises of self-organized, highly oriented polymeric chains, interconnected among themselves with the help of interchain hydrogen-bonds and forming a pre organized polymer matrix. PVA-matrix chelates the cations by a combined process of physical entrapment and weak chemical bonding leading to a highly controlled growth of different inorganic material in the form of nano sized dispersed particles as well as nanorods.15 UV-VIS spectra of FeCl3-FeCl2 solution used in the present experiment did not show any variation in the absorbance peak portion after mixing with PVA and ruled out any strong complexation in the system. XRD of the NaOH-soaked black film (after washing with distilled water to remove the sodium chloride, formed as a by product) did not show any sharp peak, however a hump in the diffracted intensity could be observed at around 43° which corresponds to 2.53 Å, indicating the possible formation of magnetite nanocrystalline phase (Fig. 1). No improvement in the XRD pattern could be observed even after aging the sample for one month. SEM analysis of this sample revealed the precipitation of magnetite particles falling in the size range of 100 to 200 nm and having a tendency to precipitate along the length of the underlying polymer chain [Fig. 2(a)]. However, it was not clear that whether the bigger particles are singles particles of 1.5 μm or agglomerated nano-particles. The same sample, after a week, when again observed under SEM, it showed an increase in the density of precipitated magnetite particles on the polymeric surface having a linear morphology with a high aspect ratio (length ~ 1 μm, width ~ 100 nm) [Fig. 2(b)]. This micrograph also revealed continuing precipitation of nano sized, almost circular particles as observed in earlier studies16 that can be attributed to the formation of linear structure of magnetite crystals lying parallel to each other on the polymeric surface. TEM studies of the sample confirmed the presence of aligned tubules of PVA having 1–2 μm length and 25 nm width [Fig. 3(a)]. These tubules are produced due to the folding of a polymeric strip along it’s axis and provides a functionalized surface for the chelation of Fe(III)-Fe(II) ions. A higher magnification picture revealed the precipitation of rod-shaped magnetite particles, 44 nm long and 11 nm wide,
Fig. 3  (a) TEM microstructure showing co-aligned PVA tubules forming pre-organized matrix. (b) Precipitation of nano sized magnetite rods (marked with *) on PVA tubules.

Fig. 4  (a) Precipitation of the bigger sized particles of magnetite (100–300 nm) in the defected region of the polymeric matrix. (b) Higher magnification view of the precipitated particles in the defected region of the matrix. The particles exhibited the faceted morphology. (c) Selected area diffraction pattern corresponding to particle A in Fig. 4(b). (d) Selected area diffraction pattern corresponding to crystal C in Fig. 4(b).

lying almost perpendicular to the tubular axis [Fig. 3(b)]. A close look of the microstructure demonstrates a high density of such nano-rods forming on the tubular surface and only a few number of such rods could be observed in the inter-
tubular space. Selected area diffraction patterns of these nano particles showed a number of rings of very weak intensity which could not be recorded. Another portion of the sample having a defect in the polymer matrix showed the precipita-
tion of relatively bigger magnetite crystals (100–300 nm) with faceted morphology [Fig. 4(a)]. In this region a chain of magnetite particles grown on matrix-interface defect could also be observed. On a higher magnification the bigger crystallites were found to be truncated cuboids with (100) plane lying perpendicular to the tube axis [A in Fig. 4(b)]. However, smaller crystallites did not show any truncation and found to be oriented along (111) axis [B in Fig. 4(b)]. Formation of nano-rods as recorded in the earlier microstructure [Fig. 3(b)] could also be confirmed in the area in vicinity of the defective region [C in Fig. 4(b)]. Single electron diffraction patterns obtained from the crystal A [Fig. 4(c)] corresponds to (011) zone axes of magnetite in the (444), (400), (844) reflections. Diffraction pattern corresponding to rod-shaped crystal [C in Fig. 4(d)] revealed the presence of sharp circular rings, superimposed with the diffraction spots of a single crystal [Fig. 4(d)]. The first ring corresponds to (220) reflection while the second one arises due to diffraction from (400) planes.

According to the available reports ferritin-like iron storage proteins contribute to the bio-mineralization of magnetite in biological structures, by providing fine sized chemical reactors working on the principle of molecular recognition, the mechanism involved in the synthetic-polymer mediated synthesis is also similar. The functional group of PVA having a lone pair of electrons makes weak coordinate complex bonds with cations leading to an earlier super saturation in the localized region of the polymer matrix. Precipitation of nanodots along the width of the polymeric tube followed by the diffusion-controlled growth leads to the formation of a linear nano structure (44 nm). Subsequent adsorption of the polymer on the crystal plane growing along the length of polymer limits it’s width to 10–11 nm. Hence the nucleation and growth of magnetite nano rods occur mainly on the tubular surface, however, due to hydrophilic nature of PVA, the surface of the polymer is diffused, which some times gives an impression of the growth in the inter-tubular space also.

4. Conclusions

Above mentioned studies demonstrates and discusses the PVA matrix mediated growth of linear nano structures of magnetite (44 nm × 11 nm), having a high aspect ratio. The process, derived from bio mineralization manifests a simple and economically viable route which is being refined to produce arrays of magnetite nano rods for several important applications like sensors and vector-assisted delivery of drugs.

REFERENCES