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Sol–gel mediated surface modification of nanocrystalline $NiFe_2O_4$ spinel powders with amorphous SiO_2

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Abstract

Surface modification of nanocrystalline $NiFe_2O_4$ spinel particles with amorphous SiO_2 by the sol–gel process at 350 °C was demonstrated. Amorphous phase of the SiO_2 layer was evaluated by X-ray diffraction technique. Structural coordination of the pristine and SiO_2 coated $NiFe_2O_4$ particles as investigated by employing FTIR analysis. Thickness of the SiO_2 layer was investigated through transmission electron microscopy and it was identified to be ~10–23 nm over nanocrystalline $NiFe_2O_4$ particles. The magnetic behavior of pristine and surface modified $NiFe_2O_4$ particles were investigated using vibrating sample magnetometer (VSM). Magnetic studies showed the retention of magnetic property of surface modified $NiFe_2O_4$ particles with the reduced saturation magnetization and coercivity compared to the pristine $NiFe_2O_4$ particles, which is respectively due to the lower fraction of the magnetic component and the formation of interfacial structure.

Keywords: A. Sol–gel processes; B. Electron microscopy; C. Magnetic properties; D. Ferrites

1. Introduction

Nanocrystalline $NiFe_2O_4$ and their related materials have been were widely investigated for their unique magnetic properties including superparamagnetism and quantum tunneling of magnetization, which are significantly influenced by their size/shape and their combination with other materials [1–4]. These materials found applications in numerous fields including catalysis, sensor technology, electromagnetic shielding, water treatment, biomedical and biotechnology fields [5–10]. The common challenge in utilizing nanocrystalline magnetic materials including $NiFe_2O_4$ in various device applications is the retention of their physicochemical/magnetic properties, because of their strong tendency to aggregate and corrode due to the large surface reactivity [11]. In addition to that, the nanofabrication lowers the coordination between atoms in surface, which caused the reduction in magnetic moment compared to their respective bulk structures [12]. This can be addressed by introducing a coating structure on thesurfaces of magnetic particles, which suppresses the surface effect and also controls the inter-particle interactions. Guang-She et al. successfully demonstrated the reduction of this surface effect by dispersing nano-sized $NiFe_2O_4$ structures in a silica matrix [13].

Hence, surface modification of the magnetic materials receives great attention in the field of material research [14,15]. In addition to that, surface engineering of such magnetic materials creates additional functional properties that can be utilized for many diversified applications.

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In general, shell structure has been made from either various kinds of polymers or silicates depend on the application requirements. Among them, silica is found to be an effective choice for the surface modification of magnetic core as a protective layer, which exhibits an enhanced corrosion resistance for the core materials, wide range of temperature operations, compatibility with bio-systems, non-toxicity, dielectric property, etc. [16]. Furthermore, the coating of SiO_2 layer over magnetic nanoparticles provides an effective encapsulation of the individual magnetic particles, which can prevent the interactions between the closely spaced magnetic particles. This will helps in inhibiting the nucleation and agglomeration of the magnetic particles during the additional processing [17]. As the demand for monodispersed magnetic materials increases surface modification of various types of magnetic materials received significant attention. Several groups have reported the fabrication and characterization of silica coated Fe_2O_3 [18,19], $CoFe_2O_4$ [20] and $NiFe_2O_4$ [21] nanomaterials. In addition to magnetic materials, SiO_2 coating was performed for various other metals [22,23], metal oxides [16,24] and metal chalcogenides [25,26] in literatures in order to improve their performance.

Fabrication process plays a key role in controlling the properties of SiO_2–magnetic materials interfaces and hence many processes were developed and explored. Sol–gel [4,27], poly-condensation procedure [28], microemulsion route [18], laser pyrolysis [29], etc., are a few common methods, which have been investigated for the surface modification of magnetic nano particles with SiO_2 layer. Among them, the sol– gel process is found to be a simple low temperature route, which has been extensively investigated for the uniform coating of SiO_2 layer on various types of nanostructure materials including magnetic particles with the better control of layer thickness [4,27]. However, very few reports are available for the sol–gel mediated synthesis of SiO_2:$NiFe_2O_4$ structures which are commonly called as composite materials, in which $NiFe_2O_4$ phase was dispersed in the SiO_2 matrix [4,13,30–33]. Recently, Larumbe et al. reported the auto-combustion method for the synthesis of SiO_2 coated $NiFe_2O_4$ using citric acid as fuel [21]. Their extensive microscopic study indicates the formation of $NiFe_2O_4$ phase in SiO_2 matrix. However, the surface modification/coating of $NiFe_2O_4$ particles with SiO_2 layer was not reported so far. Hence, in the present investigation, the surface modification of nanocrystalline $NiFe_2O_4$ particles with amorphous SiO_2 by the sol–gel process is reported. The surface modification process was investigated through TG/DTA, FTIR, XRD, SEM–EDS and TEM analysis. The magnetic properties of the pristine and SiO_2 coated nanocrystalline $NiFe_2O_4$ particles were identified through VSM studies.

2. Experimental

Nanocrystalline $NiFe_2O_4$ powders were prepared by polyacrylic acid and ethylene glycol assisted combustion route reported earlier [34]. Initially, 5 g of nanocrystalline $NiFe_2O_4$ powders was dispersed in acetone and sonicated for 30 min to remove agglomerations. Further, the particles were collected through centrifugation and the excess acetone was removed at 75 °C in hot air oven. 2 ml of TEOS was mixed with ethylalcohol by keeping them in equal volume under constant stirring. The obtained clear solution was mixed with water by keeping the TEOS and water mole ratio as 1:16, which is labeled solution A. Dried $NiFe_2O_4$ powders were dispersed in ethylalcohol and labeled as mixture B. Solutions A and B were mixed under constant stirring and the obtained sol was allowed to evaporate the excess water and alcohol. Further evaporation led to the formation of brown colored gel and the obtained gel was dried at 125 °C. Continuous drying resulted in the formation of dried mass; further it was calcined at 350 °C for the stabilization of SiO_2 shell on the surface of $NiFe_2O_4$ particles. Collected particles were used for further characterization. Schematic representation of the sol–gel process for the fabrication of SiO_2 coated nanocrystalline $NiFe_2O_4$ particles is shown in Fig. 1.

Thermal behavior of the evaporated gel coated $NiFe_2O_4$ particles were investigated using a TG/ DTA, Lybsys thermal analyzer, Setaram, France. Approximately 3 mg of SiO_2 xerogel coated $NiFe_2O_4$ particles was heated at the rate of 10 °C/ min from room temperature to 600 °C in flowing oxygen and the TG/ DTA thermograms were recorded . The Fourier-Transform Infrared Spectroscopy (FTIR) spectra were obtained employing Shimadzu FTIR - 8000 spectrometer. Synthesized specimens were mixed with KBr powder and the pressed pellets were examined between 400 and 4000 cm^{-1}. Scanning electron micrographs and elemental

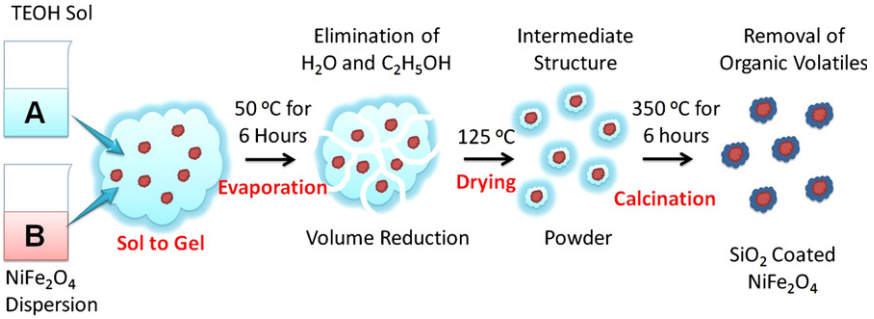

Fig. 1. Schematic representation of the solgel process for the surface modification of nanocrystalline $NiFe_2O_4$ powders with SiO_2.