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Enhanced magnetic properties of polymer-magnetic nanostructures synthesized by ultrasonication

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ABSTRACT

Polymer based nickel (Ni) and cobalt (Co) co-doped ferrites were prepared by adept ultrasonication route. Different concentrations of polymer [polyvinyl alcohol (PVA)] (0.2 g and 0.5 g) was added as a surfactant to the magnetic particles. The phase purity of Ni-Co ferrites (spinel structure) was confirmed by X-ray diffraction (XRD). Enhanced saturation magnetization of polymer based magnetic nanoparticles due to shape anisotropy and size. 0.2 wt% doped ferrite showed superparamagnetic characteristics with blocking temperature above room temperature. Hence, ultrasonication route is a rapid and effective technique for tailoring size and morphology of magnetic nanostructure that could be useful in magnetic-sensor applications.

1. Introduction

Nanosized particles possess distinct chemical and physical properties owing to their surface-to-volume ratio [1]. Generally, nanocomposites contain nanometric metals or metal oxide particles embedded in polymer matrices that provide a diverse range of magnetic and electrical properties. Cobalt ferrite ($CoFe_2O_4$) is a familiar hard magnetic material which has been widely studied due to its exciting magnetic properties [2]. However, nickel ferrite ($NiFe_2O_4$) is a soft ferrite which possesses low magneto-crystalline anisotropy but high electrical resistivity, and is used for power applications [3]. Inorganic ferrite materials were embedded in organic matrix for wide range of applications in electromagnetic interference (EMI), shielding [4,5], drug delivery [6] and magnetic resonance imaging (MRI) [7–10]. Various techniques have been suggested to synthesize nanophase materials such as mechanical milling [11], reversed micelles [12] and self-assembled monolayer [13]. Apart from above mentioned techniques, ultrasonication is a homogenizer to diminish particles size in a liquid to improve uniformity and stability. It is an efficient method to reduce the size of soft and hard magnetic particles. Dispersion and deagglomeration of particles in liquids are the significant application of ultrasonicator. Ultrasound can be employed to aid extraction, homogenization, freezing, crystallization, filtration and drying process [14]. Ultrasonication method has been employed in the prepared of uniform sized nanostructures of metals, metal oxides, graphene, and polymer nanocomposites for several applications.

Particle size, distribution of particles and morphology may not be controlled during conventional synthesis process. This could be solved by employing polymers, surfactants or capping agents. However, it is indistinguishable to comprehend the mechanism of variation in particle size, distribution and morphology of the particles. Polymers were coated on the surface of nanoparticles for protecting oxidation and to provide well controlled growth to tailor

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morphology of the nanoparticles. Nathani et al. reported the magnetic behavior of mechanical milling of nickel ferrite and polyethylene by in-situ polymerization of nickel ferrite polystyrene nanocomposites with core-shell morphology of particles [15]. Xiang et al. reported on polyvinyl pyrrolidone based cobalt–nickel ferrite nanofibers by electrospinning route. They found that the saturation magnetization and coercivity lie in the range 29.3–56.4 emu. g^{-1} and 210–1255 O_e, respectively [16]. Zhang et al. reported decrease in coercivity and increase in magnetization of $NiFe_2O_4$ magnetic nanorods via a Poly (ethylene glycol) PEG-assisted route [17]. Polyvinyl alcohol (PVA) is semi-crystalline, non-toxic, biocompatible, biodegradable polymer with good chemical resistance which is employed for biomedical applications [18]. In literature, very few studies related to magnetic polymer nanocomposites via ultrasonication assisted technique are reported. Chitra et al. reported ultrasonication on polyaniline/$NiCoFe_2O_4$ which showed spherical morphology with increase in magnetic saturation [19]. However, to the best of our knowledge, no reports available on polyvinyl alcohol (PVA) based hard soft ferrites synthesized by ultrasonication route to examine physicochemical and magnetic properties.

2. Materials and methods

Polymer based nickel-cobalt co-doped ferrites ($NiCoFe_2O_4$) was prepared by ultrasonication route using precursors such as ferric chloride (Merck), nickel (II) chloride hexahydrate (Merck), cobalt chloride hexahydrate and poly-vinyl alcohol (PVA) (CDH laboratory reagents). Solutions of $FeCl_3$ (0.4 M), $NiCl_2 \cdot 6H_2O$ (0.1 M) and $CoCl_2 \cdot 6H_2O$ (0.1 M) were mixed at 60 °C for 30 min. Subsequently, hydrazine hydrate is added drop wise to the solution which transformed into black colored solution. Final solution was ultrasonicated using Sonics-Vibra-Cell VCX (750W) 750 probe ultrasonicator with pulse time (3 min) for 30 min. Ultimately, the solution was dried in hot air oven at 80 °C and grounded to obtain fine powders. Hereafter, it is referred as UNCF. The polymer (PVA) with different concentrations (0.2 gm and 0.5 gm) was added separately to Ni-Co ferrites solution to synthesize polymer based magnetic nanostructure and the samples are labeled as 0.2PUNCF and 0.5PUNCF, respectively.

3. Results and discussion

3.1. XRD analysis

X-ray diffraction (XRD) of the samples was carried out using Bruker XRD CuK_α radiation (0.154 nm). Fourier transform infrared spectroscopy (FTIR) and Raman analysis of the samples were examined using BOMEMDA-8 FTIR and Jobin Yvon, respectively. The surface morphology was analyzed by scanning electron microscopy (SEM) (Carl Zeiss MA15/EVO18). Magnetic properties of the magnetic nanostructures were carried out by vibrating sample magnetometer (VSM) in a physical property measurement system (PPMS) from Quantum design.

The XRD patterns of (a) UNCF, (b) 0.2PUNCF and (c) 0.5PUNCF are shown in Fig. 1A. The major peaks are associated with (220), (311), (400), (422), (511) and (440) planes of $NiCoFe_2O_4$ using JCPDS (03-0864) and JCPDS (10-0325) values. The average crystallite size and lattice parameter were calculated using MAUD (Material Analysis Using Diffraction) software and the values are shown in Table 1. The crystallite size was around 105 nm for UNCF sample. The decrease in crystallite size was observed for 0.2PUNCF which could be due to high temperatures and pressures at microscopic level of the sonicated composite in colloidal solution by the formation of acoustic cavitation [20]. As the polymer incorporation increases to 0.5 wt% of PVA to UNCF, the crystallite size was enhanced which might be due to the increase in chemical activity of polymer chains. The chemical activity is increased by the acoustic cavitation by creating radical reactions in the solutions [19]. The lattice parameter decreased upon incorporation of polymer into Ni-Co ferrites. Wang et al. reported increased lattice parameter (8.366 Å) for $CoFe_2O_4$ and 8.342 Å for $NiFe_2O_4$ [3]. For 0.5PUNCF, the (220) plane is a prominent compared to other planes which could be due to growth kinetics plane directions. The intense (311) plane was attained for 0.2PUNCF. Ultrasonication and polymer incorporation change the growth rate which could modify the plane orientation as observed in 0.2PUNCF and 0.5PUNCF samples.

3.2. FTIR

FT-IR spectra of UNCF and 0.5PUNCF are shown in Fig. 1B. A broad absorption band was observed between 3841 cm^{-1} and 3200 cm^{-1} which corresponds to O-H stretching band of complex metal-hydroxyl groups. The bands at 3435 cm^{-1} and 1609 cm^{-1} could be due to OH stretching vibration through hydrogen bonding in metal oxides. Adsorbed atmospheric CO_2 in trace level was confirmed by absorption peak at around 2367 cm^{-1} which assigned to C═O stretching vibrations of carboxylate group of CO_2 gas. The peak at 1403 cm^{-1} was attributed may be also due to adsorption of carbonate group [21]. The peak at 1200 cm^{-1} is attributed to C-OH stretching vibrations [22]. The peak at 1380 cm^{-1} is assigned to symmetric stretching of CO_3^{2-} [23]. The peak at about 1560 is attributed to the NH_2 group may be due to hydrazine [24]. The Fe–O bond in tetrahedral and octahedral sites in $NiCoFe_2O_4$ was observed at 638 cm^{-1}.

The metal oxygen band at 590 cm^{-1} was observed which corresponds to intrinsic stretching vibration of metal at tetrahedral site. Cobalt ion substitution in spinel ferrites was observed at the peak 1087 cm^{-1}. The band of stretching mode of the metals was found to be in the range of 600–500 cm^{-1} [12]. The bands in the range 600–500 cm^{-1} and 1087 cm^{-1} were suppressed upon addition of PVA into $NiCoFe_2O_4$ which confirmed the functionalization of Ni-Co ferrites with PVA by forming hydrogen bond [13].

3.3. Raman analysis

Raman spectra of (a) UNCF, (b) 0.2PUNCF and (c) 0.5PUNCF are shown in Fig. 1C. Five Raman active modes ($A_{1g} + E_g + 3F_{2g}$) are observed in Ni-Co ferrites. The less intense peak at 680 cm^{-1} corresponds to symmetric stretching of oxygen atoms with Fe-O (and Ni-O) bonds in the tetrahedral sites. E_g mode was observed at 320 cm^{-1} which corresponds to symmetric bending mode of oxygen bonding to metal ions. The peaks at 480 cm^{-1} and 530 cm^{-1} are ascribed to asymmetric bending mode of oxygen [$F_{2g}(3)$] and asymmetric stretching mode of iron (nickel, cobalt) and oxygen [$F_{2g}(2)$] modes, respectively. Translational movement of tetrahedron [$F_{2g}(1)$] was observed at 210 cm^{-1} [14,19]. Addition of polymer to Ni-Co ferrites, suppressed all four Raman modes and except the mode $F_{2g}(3)$ which confirmed surface functionalization of the polymer to metal oxides by forming hydrogen bonding. Raman modes of the polymer were observed at 1362 cm^{-1} and 1604 cm^{-1} which corresponding to C-H bending mode of polymer and the first-order scattering (E_{2g} mode), respectively [25].

3.4. SEM analysis

The SEM images of $NiCoFe_2O_4$ without and with polymer incorporation are shown in Fig. 2. Spherical nanoparticles of $NiCoFe_2O_4$ were in the range of 500 nm–700 nm in the absence of polymer (PVA). Wang et al. reported the synthesis of cubical spinal