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Effect of ultrasonication on particle size and magnetic properties of polyaniline $NiCoFe_2O_4$ nanocomposites

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ABSTRACT

Polyaniline nanocomposites (PANI/$NiCoFe_2O_4$) have been synthesized by *in-situ* chemical polymerization of aniline in the presence of $NiCoFe_2O_4$ nanoparticles (20%, 10% w/w of fine powders) with and without ultrasonic treatment. The average particle size of $NiCoFe_2O_4$ synthesized by auto-combustion method is 32 nm. The particle size of the PANI nanocomposites synthesized vary in the range of 24–41 nm. The structure, morphology and magnetic properties of PANI and nanocomposites are characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and Vibrating sample magnetometer (VSM). The nanocomposites are further characterized by Fourier transform infrared spectra (FTIR), Thermogravimetric analysis (TGA) and second harmonic generation (SHG) activity. The nature of PANI/$NiCoFe_2O_4$ is visualized through the SEM and TEM images and also the presence of $NiCoFe_2O_4$ on PANI is confirmed with FTIR spectra. XRD patterns of $NiCoFe_2O_4$ have higher intense diffraction peaks than PANI/$NiCoFe_2O_4$ nanocomposites. Hysteresis measurements revealed that the saturation magnetization (M_s) increases with increase in ferrite content whereas, coercivity decreases. Ferromagnetic nature of PANI/$NiCoFe_2O_4$ nanocomposites are confirmed by VSM. FTIR investigation indicates that the main absorption peaks corresponding to the spinel structure appeared at around 600 cm^{-1}; it is due to the $NiCoFe_2O_4$ tetrahedral and octahedral stretching vibrations.

1. Introduction

Over the past few decades, polymer-inorganic nanocomposites have attracted considerable attention due to their unique electrical, mechanical and optical properties and their wide range of potential applications in hybrid materials [1–4]. Polymers of these composites are conducting polymers such as polyaniline, polypyrrole and polythiophene [5,6] and their derivatives. Conducting polymers exhibit considerable attention, because of their potential applications in various fields [7]. Among the known conducting polymers, polyaniline (PANI) is one of the most promising material, due to its high conductivity, excellent environmental stability and rather simple preparation, good processibility [8], and potential applications in various fields such as catalysis, sensors, biosensors, recharchable batteries, electronical technology [9] and microwave absorbing materials [10]. By coating of iron oxides on conducting polymers anti corrosion activity of metals can be improved [11]. Various polyaniline-inorganic nanocomposites have been reported including inorganic oxides, sulfide, and nitride [12,13]. Nanocomposites based on ferrite-polymer have been an active area, owing to their wide range of applications in electromagnetic interference shielding (EMI), drug delivery [14–16], drug targeting and as contrasting agents in magnetic resonance imaging [17]. Ferrites are mainly focused due to their applicability in various fields [18]. Recently, spinel ferrites are used as the most convenient materials in various forms. Among these ferrites, cobalt ferrite is a common spinel ferrite material which creates considerable interest because of their high coercivity at room temperature [19,20] and high capacity magnetic storage [21,22]. PANI/ferrite nanocomposites have been reported by using different methods, namely a mechanical milling method which was used to prepare PANI/NiZn ferrite [23] and oxidative electrochemical polymerization of aniline in an aqueous solution in the presence of ferrites. Ferrites are ferromagnetic oxides, crystallizes into two magnetic sub-lattices namely, tetrahedral site and octahedral site. The electrical and magnetic properties can be altered by the cation distribution among these two sites. Ferrites are high resistivity materials with low eddy current losses which make them potential materials for high frequency applications such as microwave devices.

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The electrical resistivity of ferrites has been normally found to increase on doping or substituting with other oxides. A number of articles have been observed that the magnetic properties of ferrites are influenced by coating of a conducting polymer [24–26]. Nickel ferrite possessed high resistivity at room temperature on substituting 1% or 2% cobalt concentration. There are only few studies and literatures of polymer nanocomposites about the effect of ultrasonic on the performance of nanocomposites. Ultrasonic treatment was used to be feasible in mixing nano clay in epoxy [27]. The breakup of clay agglomerates can be assisted by the vibration of ultrasonic waves [28–30]. However, the longer time of ultrasonic treatment may lead to early polymerization and degrade the properties of nanocomposites due to increased temperature during sonication. The longer time of ultrasonic treatment will result in increased viscosity of polymer mixture.

In this present work, ultrasonic treatment is used to prepare PANI/$NiCoFe_2O_4$ nanocomposites by *in-situ* chemical polymerization. The role of ultrasonication on structural, morphological and magnetic properties of PANI/$NiCoFe_2O_4$ nanocomposites is also discussed. In PANI/$NiCoFe_2O_4$ nanocomposites, the particle size and magnetic properties are decreased under the ultrasonication treatment.

2. Experimental

2.1. Materials

Aniline (AR) monomer was distilled under reduced pressure and stored below 0 °C. Ammonium persulphate [APS, $(NH_4)_2S_2O_8$], Hydrochloric acid (HCl), $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and urea were of analytical purity and used without further purification.

2.2. Synthesis of $NiCoFe_2O_4$ nanoparticles

Nanocrystalline $NiCoFe_2O_4$ particles were prepared by an auto-combustion technique with the chemical formula $Ni_{1-x}\,Co_x\,Fe_2O_4$. In this preparation 0.4 mol of nickel nitrate, 0.6 mol of cobalt nitrate and 2 mol of ferric nitrate were dissolved in 50 ml of deionized water. 50% of urea was added in distilled water to the above solution and then heated at 160 °C under constant stirring using magnetic stirrer. Urea has been used for the combustion process. On ignition in air at room temperature, the dried gel was burnt in a self-propagating combustion, giving rise to the evolution of a large amount of gases and producing a dry and loose ferrite powder.

2.3. Synthesis of PANI/$NiCoFe_2O_4$ nanocomposites

Two sets of PANI/$NiCoFe_2O_4$ nanocomposites with and without ultrasonication are synthesized by adopting the previously described method. A mixture containing 1.35 ml aniline in 70 ml of 2 M HCl and 0.3 g of $NiCoFe_2O_4$ nanoparticles was subjected to mechanical stirring for 2 h. The polymerization of aniline was initiated by dropping 2.94 g of APS in distilled water with constant stirring for 6 h at room temperature. The reaction mixture was filtered, washed with HCl, deionized water and dried under vacuum at 60 °C for 24 h. PANI/$NiCoFe_2O_4$ nanocomposites with varying ferrite content were synthesized by using two different ratios (10% and 20% w/w of fine powders) of $NiCoFe_2O_4$ nanoparticles with respect to aniline monomer which is indicated as PN1 and PN2. The nanocomposites PN1S and PN2S were also synthesized by adopting the above procedure and composition with 6 h of ultrasonication before filtration. The composition details and conditions of the synthesized nanocomposites are presented in Table 1.

2.4. Characterization

The PANI/$NiCoFe_2O_4$ nanocomposites were subjected to XRD analysis with Rigaku X-ray diffraction unit (Model ULTIMA III) to explore the structural properties. Infrared spectra were recorded in the range 400–4000 cm^{-1} using a Perkin-Elmer FTIR spectrometer by a KBr pellet technique. A scanning electron microscope (SEM), JEOL 5600LV microscope at an accelerating voltage of 10 kV was used to examine the particle morphology. High resolution Transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) was recorded on a Technai G20-stwin using an accelerating voltage of 200 kV. The thermal stability of nanocomposites were observed with a PTC10A, Rigaku Thermoflex thermal analyzer at 10 °C min^{-1} heating rate under N_2 atmosphere. The SHG activity of the sample was performed by the Kurtz Perry powder technique using Q-switched Nd: YAG laser. The magnetic properties of the samples were investigated by using a Vibrating sample magnetometer (Lakeshore VSM 7410).

3. Results and discussion

3.1. X-ray diffraction

The XRD pattern of $NiCoFe_2O_4$ is shown in Fig. 1. The reflection peaks correspond to the characteristic inter plannar spacing between (220), (222), (311), (400), (422), (511), (440) and (531) planes of the spinel ferrite with a cubic symmetry, demonstrating the formation of $NiCoFe_2O_4$ and PANI/$NiCoFe_2O_4$ as per JCPDS card nos. 00-001-1121 and 00-003-0875. The particle size of the samples was calculated by using the Debye–Scherrer formula $t = 0.9\lambda / \beta\cos\theta$. The XRD pattern of PANI (Fig. 2a) does not show any sharp peaks confirming the amorphous nature of PANI. The polymer displays only a diffuse broad peak ranging from 20° to 30°. The broad peak at about $2\theta = 25°$ shows amorphous nature ascribed to the periodically parallel PANI chains. Fig. 2b–d shows the XRD pattern of PANI/$NiCoFe_2O_4$ nanocomposites with decreasing order of ferrite content, which contain the characteristic peaks of PANI and polycrystalline $NiCoFe_2O_4$. The XRD pattern of the nanocomposites PN1S and PN2S is shown in Fig. 2c and e which corresponds to the decreased particle size due to ultrasonication when compared with XRD pattern of PN1 and PN2 shown in Fig. 2b and d synthesized without ultrasonication. The particle sizes of the nanocomposites are listed in Table 2.

Table 1
Sample details of PANI/nanocomposites.

Samples	Code	$NiCoFe_2O_4$ (g)	PANI(ml) monomer	$NiCoFe_2O_4$/ PANI (w/w)	Method (*in-situ* polymerization)
PANI	P	–	1.35	–	Without ultrasonication
$NiCoFe_2O_4$/ PANI	PN1	0.3	1.35	1:5	Without ultrasonication
$NiCoFe_2O_4$/ PANI	PN1S	0.3	1.35	1:5	With ultrasonication
$NiCoFe_2O_4$/ PANI	PN2	0.15	1.35	0.5:5	Without ultrasonication
$NiCoFe_2O_4$/ PANI	PN2S	0.15	1.35	0.5:5	With ultrasonication