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Polyaniline/$Co_{0.6}Zn_{0.4}Fe_2O_4$ core-shell nano-composites. Synthesis, characterization and properties

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ABSTRACT

Magnetic nano-composites having different percentages of polyaniline (PANI) and $Co_{0.6}Zn_{0.4}Fe_2O_4$ nanoparticles have been synthesized using in-situ polymerization process. The utilized $Co_{0.6}Zn_{0.4}Fe_2O_4$ nanoparticles were prepared via sucrose auto-combustion route. The structural, thermal, magnetic and electrical properties were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), transmission electron microscopy (TEM), thermo-gravimetric analysis (TG), vibrating sample magnetometer (VSM), Ac-conductivity and dielectric measurements. XRD, FT-IR and TEM measurements showed the existence of some interactions between PANI and ferrite nanoparticles resulted in the formation of nano-composites with core–shell structure. TG measurements exhibited the improvement of the thermal stability by increasing ferrite content. VSM experiments indicated ferromagnetic properties of the entire studied nano-composites with an obvious increase in the magnetization by ferrite addition. On the other hand the gradual decrease in the coercivity with increasing ferrite ratio was attributed to the core-shell structure formed. The ac conductivity as well as the dielectric properties were studied as a function of temperature and frequency. The ferrite addition increases the dielectric properties as well as the conductivity of pure PANI as a result of increasing thermal stability.

1. Introduction

Materials possessing both electrical and magnetic characteristics are of great importance in many advanced applications such as electrical, magnetic shielding, molecular electronic, sensors, nonlinear optics and microwave absorbent [1]. Of these materials, the magneto-conducting polymers comprise an advanced generation of multifunctional materials that combine the properties of ordinary conducting polymers (high conductivity, flexibilities and processability) and magnetic inorganic compounds (high susceptibility, mechanical strength and hardness) [2].

Recently, many investigators focused their attentions on the preparation and characterization of polyaniline/ferrite nano-composites having complementary synergy characteristics of PANI and ferrite nanoparticles [3–10]. Polyaniline (PANI) is considered as one of the most conducting polymers because of its low coast, ease of preparation, thermal and chemical stability besides controllable conductivity [9]. On the other hand, spinel cobalt ferrite nano-particle ($CoFe_2O_4$) has been received great attentions than other magnetic inorganic materials due to its high magnetization, strong anisotropy, high coercivity, mechanical hardness and chemical stability [11].

$CoFe_2O_4$ is a well-known inverse spinel in which Fe^{3+} ions are distributed equally between octahedral and tetrahedral sites. On the other hand, $ZnFe_2O_4$ is considered as one of the most well-known normal spinels in which all Fe^{3+} ions preferably occupy octahedral sites, leaving Zn^{2+} ions bonded to O^{2-} anions on the tetrahedral sites [12]. Thus, it will be expected that Co-Zn ferrites will have mixed spinel structure in which all Zn^{2+} ions occupy tetrahedral sites whereas Co^{2+} ions preferably occupy octahedral sites. In this context, many investigators [13–19] concluded that the cation distribution in Co-Zn ferrites could be affected by the preparation conditions, microstructure as well as temperature.

Generally, it was observed that the magnetic properties of ferrites were greatly influenced by coating with conducting polymer [6,7]. This is can be due to the physical or electronic interactions occurring at the interface between the ferromagnetic material and the conducting polymer as well as possible chemical interactions. Therefore, it is very interesting to prepare and characterize

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nanostructures of PANI composites in which ferrite particles are adhering to the polymer surface in order to shy light on the expected improved properties.

In literature, many investigations concerning the synthesis, characterization and properties of PANI/$CoFe_2O_4$ nano-composites are reported [20–25]. In spite of the presence of some investigations dealing with PANI/substituted ferrites [4–8], the researches studying PANI/Co-Zn ferrites are very few [9,10] and still needs further investigations.

Ma et al. [9] prepared polyaniline (PANI)/$Co_{0.5}Zn_{0.5}Fe_2O_4$ nano-composite via an in situ polymerization. The nano-composites were characterized using XRD, FT-IR, TEM and UV–Visible spectra. The average particle sizes of the PANI and PANI/$Co_{0.5}Zn_{0.5}Fe_2O_4$ nanocomposites were 50 and 70 nm, respectively. The reflection loss of the nanocomposites was improved than that of pure PANI.

Kumar et al. [10] synthesized $Co_{0.5}Zn_{0.5}Fe_2O_4$/PANI nano-composites by reverse microemulsion. Structural characterizations were carried out using XRD, FT-IR and TEM measurements. VSM measurement confirmed the ferromagnetic behavior of nano-composite with saturation magnetization of 3.95 emu/g and low coercive force (39 Oe).

As it was already shown [13–19], the magnetic performance of Co-Zn ferrites ($Co_{1-x}Zn_xFe_2O_4$, where $x = 0.0–1.0$) are varied dramatically with x. in our previous work [26], it was proved that, the optimum value of saturation magnetization could be obtained in this system (prepared via sucrose combustion method) for $x = 0.4$. Therefore, the $Co_{0.6}Zn_{0.4}Fe_2O_4$ nano-ferrite will be used in the present study to construct nano-composites with PANI.

In this manuscript, $Co_{0.6}Zn_{0.4}Fe_2O_4$ magnetic nanoparticles, prepared via simple, economic and environmentally friend sucrose method was coated by conducting polyaniline using in-situ polymerization method. The obtained core-shell structure was discussed and an appropriate mechanism for the PANI/ferrite nano-composites formation was suggested. Different percentages of $Co_{0.6}Zn_{0.4}Fe_2O_4$ nanoparticles with respect to the aniline monomer (10, 30, 50, 70 and 90% w/w) were prepared to investigate and discuss the effect of changing ferrite ratio on the structural, morphological, thermal, electrical and magnetic properties of PANI matrix. To the best of our knowledge, no such integrated study was conducted in literature especially, with the using of ferrites prepared via this novel sucrose auto-combustion route.

2. Experimental

2.1. Samples preparation

The sucrose assisted auto-combustion method [26] was adopted for the preparation of $Co_{0.6}Zn_{0.4}Fe_2O_4$. Stoichiometric amounts of $Co(NO_3)_2 6H_2O$, $Fe(NO_3)_3 9H_2O$ and $Zn(NO_3)_2 6H_2O$ were used. In this method, entire metal nitrates, acting as an oxidant are mixed with sucrose reductant solution (12 g dissolved in 50 ml distilled water) at 60 °C under constant stirring for 30 min. Ammonia hydroxide was then added to adjust pH to 7. The obtained viscous gel was evaporated on hot plate till self-combustion exothermic reaction is propagated with the evolution of large quantities of gases. The produced black powder was grounded and stored without any further heat treatments.

Pure PANI was prepared via polymerization method as described in Refs. [27,28]. 1 ml of aniline monomer was dissolved into 35 ml 0.5 mol/L H_3PO_4 solution and sonicated for 30 min. 2.78 g of ammonium persulfate dissolved in 20 ml 0.5 mol/L H_3PO_4 solution was added during constant stirring at 0 °C under nitrogen atmosphere for 24 h. The obtained green precipitate was filtered, washed using deionized water and ethanol then dried under vacuum at 50 °C for 24 h.

PANI/$Co_{0.6}Zn_{0.4}Fe_2O_4$ nano-composites were prepared through a simple in situ polymerization method of PANI in the presence of different percentage of $Co_{0.6}Zn_{0.4}Fe_2O_4$ nanoparticles (10, 30, 50, 70 and 90% w/w) with respect to the aniline monomer using the same procedure mentioned above.

2.2. Characterization

The crystal structure was identified by X-ray diffraction (XRD) measured using a Bruker D8 Advance X-ray diffractometer (40 kV, 25 mA and CuKα irradiation source) in the 2θ range of 4°–70° with scanning rate 1°/min.

The structure changes were monitored using Fourier transform infrared (FT-IR, Brucker- Vector 22 spectrometer) and the KBr pellet technique in the wavenumber range from 4000 to 400 cm^{-1}.

The particles morphology were characterized using transmission electron microscopy (TEM, JEOL-1011) running at an accelerating voltage of 100 kV.

The thermal stability was estimated using thermo-gravimetric analysis (TG) carried out using a Perkin Elmer thermal analyzer, at a heating rate of 5 °C min^{-1} in air having a flow rate of 30 ml/min.

The different magnetic parameters were investigated at room temperature using a vibrating sample magnetometer (VSM, Lake Shore, Model 7400) under applied magnetic field strength up to 10 kOe.

Electrical properties as a function of temperature (up to 570 K) and frequency (100 Hz–5 MHz) were measured by a two-probe method using a Hioki LCR high tester 3531 on samples compressed into pellets, 1 cm in diameter and ca. 1 mm thickness.

3. Results and discussion

X-ray diffraction patterns of PANI and PANI/$Co_{0.6}Zn_{0.4}Fe_2O_4$ nano-composites are shown in Fig. 1. The low crystallinity broad peaks appeared at about 20.8° and 25.5° suggesting the amorphous structure of PANI and could be assigned to the periodicity parallel of PANI chains [6]. The appearing of the characteristic diffraction peaks attributed to the well-crystalline ferrites indicated the successive preparation via sucrose auto-combustion route.

The presence of these diffraction peaks assigned to both ferrite and PANI matrix in the diffraction pattern attributed to 10% composition confirmed the nano-composite formation. The weakening of the diffraction peaks characteristic of PANI by increasing ferrite content followed by their disappearance at higher contents

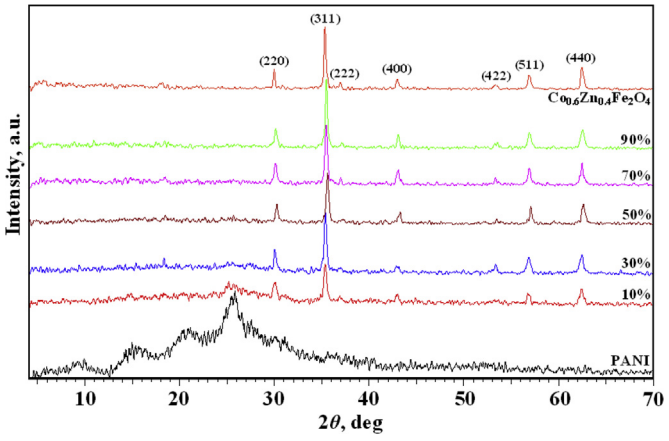

Fig. 1. XRD patterns of pure components and PANI/$Co_{0.6}Zn_{0.4}Fe_2O_4$ nano-composites.