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Electrical and optical properties of nickel ferrite/polyaniline nanocomposite

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ABSTRACT

Polyaniline–$NiFe_2O_4$ nanocomposites (PANI–$NiFe_2O_4$) with different contents of $NiFe_2O_4$ (2.5, 5 and 50 wt%) were prepared via in situ chemical oxidation polymerization, while the nanoparticles nickel ferrite were synthesized by sol–gel method. The prepared samples were characterized using some techniques such as Fourier transforms infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Moreover, the electrical conductivity and optical properties of the nanocomposites were investigated. Pure (PANI) and the composites containing 2.5 and 5 wt% $NiFe_2O_4$ showed amorphous structures, while the one with 50 wt% $NiFe_2O_4$ showed a spinel crystalline structure. The SEM images of the composites showed different aggregations for the different nickel ferrite contents. FTIR spectra revealed to the formation of some interactions between the PANI macromolecule and the $NiFe_2O_4$ nanoparticles, while the thermal analyses indicated an increase in the composites stability for samples with higher $NiFe_2O_4$ nanoparticles contents. The electrical conductivity of PANI–$NiFe_2O_4$ nanocomposite was found to increase with the rise in $NiFe_2O_4$ nanoparticle content, probably due to the polaron/bipolaron formation. The optical absorption experiments illustrate direct transition with an energy band gap of $E_g = 1.0$ for PANI–$NiFe_2O_4$ nanocomposite.

Introduction

The study of nanocomposite materials is a rapidly developing subject of research. This fast growing area is generating many inspiring new high-performance materials with new properties. Nanocomposite materials extensively cover a large range of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, made of definitely different components and mixed at the nanometer size. Large attempt is focused on the capability to attain rule of the nanoscale structures via new preparation methods. The properties of nanocomposite materials based not only on the properties of their particular parents, but also on their morphology and interfacial types [1]. The applications of nanocomposites are quite promising in the fields of microelectronic packaging, optical integrated circuits, automobiles, drug delivery, sensors, injection molded products, membranes, packaging materials, aerospace, coatings, adhesives, fire-retardants, medical devices, consumer goods, etc. [2]. Polymer materials in the form of nanocomposites are useful due to certain advantages such as high surface area to volume ratio.

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There has been a growing interest in new ways of producing conducting polymer nanocomposites that can exhibit some novel properties. A number of groups have reported studies on the electrical conductivity of composites of a variety of conducting polymers [3]. They found that the conductivity depends on several factors such as the type of filler, its concentration, size, concentration and the strength of the interaction between the filler molecules and the polymer macromolecules [4,5].

The conducting polymers are a new group of synthetic polymers which combines the chemical and mechanical properties of polymers with the electronic properties of metals and semiconductors [6]. Nowadays, conducting polymers have several applications in different areas such as microwave absorption, electronic displays, corrosion protection coating, electrochemical batteries, super capacitors, sensors, and electrodes [7–11]. They have extended p-conjugation with single- and double-bond alteration along its chain. They behave as a semiconductor material with low charge carrier mobility [12] and their conductivity is increased to reach the metallic range by doping with appropriate dopants [12]. Polyaniline is the most widely studied conducting polymer because of its facile synthesis, low synthetic cost, good environmental and thermal stability. There are three forms of PANI, namely, the fully reduced (leucoemeraldine), the fully oxidized (pernigraniline) state and the more conducting emeraldine base (half-oxidized). Emeraldine is the most conductive form when doped to form emeraldine salt [12].

Polyaniline can be easily prepared either chemically or electrochemically from acidic aqueous solutions [13,14]. The chemical method has a large significance because it is very reasonable method for the mass production of PANI. The most common preparation method is by oxidative polymerization with ammonium peroxodisulfate as an oxidant.

Ferrites belong to a special class of magnetic materials, which have a wide range of technological applications. Due to their low cost, ferrite materials are used in various devices like microwave, transformer cores, magnetic memories, isolators, noise filters, etc. [15–18]. The spin-glass state in ferrites exhibits the most interesting magnetic property that causes high field irreversibility, shift of the hysteresis loops, and anomalous relaxation dynamics [19,20].

Nickel ferrite ($NiFe_2O_4$) is one of the most important spinel ferrites that have been studied. Stoichiometric $NiFe_2O_4$ considers as n-type semicoductor [21]. It exhibits different kinds of magnetic properties such as paramagnetic, superparamagnetic or ferrimagnetic behavior depending on the particle size and shape. Also, it exhibits unusual physical and chemical properties when its size is reduced to nano size.

Recently, significant scientific and technological interest has focused on the PANI–inorganic nanocomposites. The use of nano sized inorganic fillers into the PANI matrix produces materials with complementary behavior between PANI and inorganic nanoparticles. These novel materials find applications in many industrial fields. The nanocomposites of polyaniline can be synthesized by polymerization of aniline in the presence of dispersed inorganic material. This can be done by three different routes [22]. The first route consists of direct solid-state mixing between the inorganic particles and the polyaniline macromolecules. The second one is in situ chemical polymerization of aniline in an acidic medium with dispersion of inorganic material in the presence of an oxidant at low temperature. The third route includes the dipping of the partially oxidized PANI in a suspension of the metal oxide.

The present study reports the synthesis, characterizations and effects of nano sized $NiFe_2O_4$ addition on structural, thermal stability, optical and electrical properties of polyaniline.

Experimental

Materials

Aniline (Adwic 99%) was used after double distillation. Other chemicals used were of AR grade. Water used in this investigation was de-ionized water.

The nickel ferrite nanopowder was synthesized by sol–gel method. An appropriate amounts of nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) and ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) were mixed together with citric acid and polyethylene glycol (PEG) with 1:2:4.44:8.88 molar ratio of $Ni(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, citric acid and PEG, respectively. The solution obtained was vigorously stirred during heating from room temperature to 90 °C, and kept for two hours. The solution became viscous and gel is formed. The gel was then washed with de-ionized water several times to remove possible residues and then dried at 110 °C for 24 h and calcined at 400 °C for 2 h.

$NiFe_2O_4$–PANI composite was prepared by the oxidation of aniline with ammonium peroxydisulphate in an aqueous medium. Aniline (0.2 M) was dissolved in 100 mL of HNO_3 (1 M) and stirred well in an ice bath. Certain amounts of $NiFe_2O_4$ nanopowder were suspended in the above solution and stirred for about one hour. As an oxidizing agent, 20 ml of pre-cooled solution of ammonium persulfate (0.25 M) was then slowly added drop wise to the mixture with a constant stirring over a period of 2 h. The reaction was then left at 0 °C for 4 h. The product obtained was collected by filtration and washed several times by acetone and distilled water until the filtrate was colorless. The product was dried at 80 °C for 24 h. Three different PANI–$NiFe_2O_4$ composites were prepared by using 2.5, 5 and 50 wt% $NiFe_2O_4$ with respect to the aniline monomer. Pure polyaniline was synthesized in the same manner without adding $NiFe_2O_4$.

Characterization

XRD spectra of pure PANI, $NiFe_2O_4$ and PANI–$NiFe_2O_4$ composites were performed at room temperature in the range from $2\theta = 10$–$80°$ on a Diano (made by Diano Corporation, USA), using Cu Kα radiation ($\lambda = 1.5406$ Å). The infrared spectra of the specimens were recorded using a KBr pellet on a Brucker-FTIR (Vector 22), made in Germany. SEM of the pure PANI and PANI–$NiFe_2O_4$ composite was recorded using JEOL JSM 6400 microscope. TGA thermograms of pure PANI, $NiFe_2O_4$ and PANI–$NiFe_2O_4$ composites were recorded under nitrogen atmosphere and in a temperature range of 25–600 °C and at a heating rate of 10 °C/min using Shimadzu DT-50 thermal analyzer. Conductivity measurements were performed on pellets of 1.3 cm and 0.15 cm thickness in the temperature range of 30–250 °C. The optical absorption of composites dissolved in dimethyl sulfoxide (DMSO) was measured at room temperature on UV/vis spectrophotometer (T80 + PG) in the range of 400–1100 nm.