Polyhedron 30 (2011) 1349–1359

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and characterization of poly(3-thiophenyl acetic acid) (P3TAA)–$BaFe_{12}O_{19}$ nanocomposite

Z. Durmus [a,*], B. Unal [b], M.S. Toprak [c], H. Sozeri [d], A. Baykal [a]

[a] Department of Chemistry, Fatih University, B. Cekmece, 34500 Istanbul, Turkey
[b] Department of Physics, Fatih University, B. Cekmece, 34500 Istanbul, Turkey
[c] Functional Materials Division, Royal Institute of Technology – KTH, SE16440 Stockholm, Sweden
[d] TUBITAK-UME, National Metrology Institute, P.O. Box 54, 41470 Gebze-Kocaeli, Turkey

ARTICLE INFO

Article history:
Received 8 December 2010
Accepted 16 February 2011
Available online 4 March 2011

Keywords:
Nanocomposite
Hexaferrite
Electrical properties
Polythiophene acetic acid
Magnetization

ABSTRACT

We have presented a method for the fabrication of poly(3-thiophenyl acetic acid) (P3TAA)–$BaFe_{12}O_{19}$ nanocomposites by the in situ polymerization of P3TAA in the presence of synthesized $BaFe_{12}O_{19}$ nanoparticles. The nanoparticles and the nanocomposite were analyzed by XRD, FTIR, TGA, TEM, VSM and conductivity techniques for structural and physicochemical characteristics. Crystallographic analysis revealed the phase as hexaferrite and X-ray line profile fitting yielded a crystallite size of 32 nm. The particles, observed by TEM, exhibit irregular shapes and sizes between 100 and 500 nm, revealing polycrystalline character when compared with the crystallite size from XRD. FTIR and TGA analysis results show that P3TAA is conjugated to the particle surface via a carboxylate group and that the composite has a polymer content of ~10%. Magnetic hysteresis curves do not saturate at high fields, which is a characteristic feature of fine particle systems with grain sizes smaller than 1 μm. Conductivity measurements showed a semiconductor character of the nanocomposite.

1. Introduction

M-type barium hexaferrite, with the hexagonal molecular structure $BaFe_{12}O_{19}$ (Ba hexaferrite), is a promising material for permanent magnet, advanced recording and microwave absorption because of its fairly large magnetocrystalline anisotropy, high Curie temperature, relatively large magnetization, excellent chemical stability and corrosion resistivity, whereas its magnetic and electric properties can be modulated to satisfy different applications [1–6]. Barium hexaferrite may be the most extensively investigated material among the family of hard ferrites having the general formula $MFe_{12}O_{19}$, where M = Ba, Sr, Pb. There are many approaches to manufacture Ba–M-type ferrites, including traditional ceramic sintering, the coprecipitation, microwave plasma and reverse micelle method, etc. [7].

Recently, conducting polymers have attracted considerable attention for their applications in electrochemical displays, sensors, catalysis, redox capacitors, electromagnetic shielding, as well as in secondary batteries, because of their promising electronic, magnetic and optical properties [8–12]. Their unique physical and chemical properties have made them considerably attractive materials for potential applications in the fields of drug delivery systems [13–16], electromagnetic interface (EMI) shielding [17], rechargeable batteries [18], electrodes and sensors [19], corrosion protection coatings [20], plastic transistors [21] and microwave absorption [22].

Among the conducting polymers, polythiophene (PTh) polymers are the most commonly studied electrically conducting conjugated polymers because of their excellent environmental and thermal stability. PTh polymers have been widely used in environmentally and thermally stable conjugated polymer materials such as electrical conductors, recording materials, nonlinear optical devices, polymer light-emitting diodes and displays, electrochromic or smart windows, photoresists, antistatic coatings, sensors, batteries, electromagnetic shielding and imaging materials, artificial noses and muscles, solar cells and transistors, electrodes, new types of memory devices, nanoswitches, optical modulators and valves, polymer electronic interconnects, DNA protection, and nanoelectronic and optical devices [23–32]. Recently, several interesting research papers have focused on PTh–metal oxide composites to obtain materials with advanced mechanical and chemical properties which can be used in many application fields [33–36].

Recently, conducting polymer composites containing ferrite nanoparticles, mainly hexaferrites, have been studied. Many methods have been reported for producing polypyrrole (PPy)-ferrites and hexaferrites. Thus, the incorporation of magnetic constituents and conducting polymeric materials into multifunctional composites opens new possibilities for the achievement of good shielding effectiveness for various electromagnetic sources.

---

[*] Corresponding author. Tel.: +90 212 866 33 00/20 70; fax: +90 212 866 34 02.
E-mail address: zhrdurmus@gmail.com (Z. Durmus).

0277-5387/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2011.02.044

To the best of our knowledge, no work has been done on the preparation and magnetic and electrical transport properties (electronic/dielectric) of P3TAA–$BaFe_{12}O_{19}$ nanocomposite. In the present study herein, we employed a simple one-pot in situ polymerization method to synthesize P3TAA–$BaFe_{12}O_{19}$ nanocomposite and studied its structural and physical properties in detail for the first time.

2. Experimental

2.1. Instrumentation

X-ray powder diffraction (XRD) analysis was conducted on a Rigaku Smart Lab operated at 40 kV and 35 mA using Cu Kα radiation ($\lambda = 1.54059$ Å).

Fourier transform infrared (FTIR) spectra of the samples were recorded with a Perkin–Elmer BX FTIR infrared spectrometer in the range 4000–400 cm^{-1}.

Transmission electron microscopy (TEM) analysis was performed using a FEI Tecnai G2 Sphera microscope. A drop of diluted sample in alcohol was dripped on the TEM grid. Scanning Electron Microscopy (SEM) analysis was performed, in order to investigate the microstructure of the sample, using FEI XL40 Sirion FEG Digital Scanning Microscope. Samples were coated with gold at 10 mA for 2 min prior to SEM analysis.

The thermal stability was determined by thermogravimetric analysis (TGA, Perkin–Elmer Instruments model, STA 6000). The TGA thermograms were recorded for 5 mg of powder sample at a heating rate of 10 °C/min, over the temperature range 30–800 °C under a nitrogen atmosphere.

VSM measurements were performed using a vibrating sample magnetometer (LDJ Electronics Inc., model 9600). The magnetization measurements were carried out in an external field up to 15 kOe at room temperature.

The electrical conductivity of P3TAA and P3TAA/$BaFe_{12}O_{19}$ nanocomposite were studied in the range 20–150 °C with 10 °C steps. The samples were used in the form of circular pellets of 13 mm diameter and 3 mm thickness. The pellets were sandwiched between gold electrodes and the conductivities were measured using a Novocontrol dielectric impedance analyzer in the frequency range 1 Hz – 3 MHz. The temperature was controlled with a Novocool Cryosystem, between −100 and 250 °C. The dielectric data (ε' and ε'') were collected during heating as a function of frequency.

2.2. Chemicals

Iron (III) nitrate nonahydrate, $Fe(NO_3)_3{\cdot}9H_2O$, barium nitrate, $Ba(NO_3)_2$, citric acid ($C_6H_8O_7$), triethanolamine (TEA), cetyl trimethylammonium bromide (CTAB) and ammonium persulfate (APS, $(NH_4)_2S_2O_8$) were all obtained from Merck and were used as received without further purification.

2.3. Procedure

2.3.1. Synthesis of $BaFe_{12}O_{19}$ nanoparticles

For the synthesis of $BaFe_{12}O_{19}$ (barium hexaferrite) nanoparticles, the citrate sol–gel combustion method was applied. Stoichiometric amounts of $Fe(NO_3)_3{\cdot}9H_2O$ and $Ba(NO_3)_2$ were dissolved in a small amount of deionized H_2O by stirring at 50 °C with a Fe/Ba ratio of 12:1. Citric acid was then added to the mixture solution of Ba^{2+} and Fe^{3+} to chelate these ions. The molar ratio of citric acid to metal ions used was 1:1. Ammonia was added to adjust the pH value to 7. The clear solution obtained was slowly evaporated at 80 °C under constant stirring, forming a viscous gel. By increasing the temperature up to 200 °C, the gel precursors were combusted to form brown loose powders. First the obtained powder was calcined at 450 °C for 4 h, and a final calcination was done at 1100 °C for 1 h. The hexaferrite $BaFe_{12}O_{19}$ particles were thus obtained.

2.3.2. Synthesis of poly(3-thiophenyl acetic acid) (P3TAA)–$BaFe_{12}O_{19}$ nanocomposite

Poly(3-thiophenyl acetic acid) (P3TAA)–$BaFe_{12}O_{19}$ nanocomposite was prepared via in situ polymerization. In a typical synthesis, 0.5 g $BaFe_{12}O_{19}$ nanoparticles and 2.06 g CTAB and triethanolamine (TEA, 5.27 g) were added into 50 mL water in a three-necked flask, and the mixture was sonicated at room temperature for 30 min. Then a pre-cooled ammonium persulfate (APS) solution was added dropwise into the mixture with constant stirring. The mixture was heated without stirring for 24 h at 70 °C. The composites were obtained by filtering and washing the reaction mixture with deionized water and methanol, followed by drying under vacuum at room temperature.

3. Results and discussion

3.1. XRD analysis

Phase investigation of the crystallized product was performed by XRD and the diffraction pattern is presented in Fig. 1. The XRD pattern indicates that the product is M-type $BaFe_{12}O_{19}$ and the diffraction peaks are broadened owing to the very small crystallite size. All of the observed diffraction peaks are indexed by the cubic structure of $BaFe_{12}O_{19}$ (JCPDS no. 84-0757), revealing a high phase purity of the hexaferrite. The mean size of the crystallites was estimated from the diffraction pattern by the line profile fitting method, using Eq. (1) given in [37,38]. The line profile, shown in Fig. 1, was fitted for the observed 15 peaks with the following miller indices: (0 0 6), (1 1 0), (0 0 8), (1 1 2), (1 0 7), (1 1 4), (1 0 8), (2 0 3), (2 0 5), (2 0 6), (2 0 9), (3 0 3), (1 1 1 2), (2 2 0), (2 0 1 4). The average crystallite size, D and σ, was obtained as 32 ± 3 nm as a result of this line profile fitting.

3.2. FTIR analysis

FTIR spectra of the $BaFe_{12}O_{19}$ nanoparticles, P3TAA and P3TAA–$BaFe_{12}O_{19}$ nanocomposite are presented in Fig. 2a–c respectively. In the spectrum of pure hexaferrite (Fig. 2a), the broad band between 3500 and 3100 cm^{-1} can be assigned to the ν_{O-H} vibration, while two characteristic peaks can be observed at 590 and 400 cm^{-1} which correspond to the Fe—O stretching modes of the magnetic lattice [39–44]. The structure of P3TAA is presented in Fig. 2d, where the carboxyl groups are exposed. Two major binding modes have been suggested for the surface carboxylate bonding [45,46]. According to Kirwan et al. [47], if there is C=O character in the spectrum and $\Delta\nu_{adsorbed}$ is greater than $\Delta\nu_{salt}$, then the adsorbed structure is monodentate. If there is no C=O character in the spectrum and $\Delta\nu_{adsorbed}$ is smaller than $\Delta\nu_{salt}$, then the adsorbed structure is bidentate chelating. If there is no C=O character in the spectrum and $\Delta\nu_{adsorbed}$ is similar to $\nu_{salt,}$ then the adsorbed structure is bidentate bridging [47–49]. It is worth noting that the C=O stretching band of the carboxyl group, which was present at 1690 cm^{-1} in the spectrum of pure P3TAA, was absent in the spectrum of the nanocomposite. In our case, $\Delta\nu_{adsorbed}$ (190 cm^{-1}) < $\Delta\nu_{salt}$ (314 cm^{-1}), therefore bidentate binding, as indicated in Fig. 2e, is suggested. All these modifications serve as direct evidence for the chemisorption of P3TAA on the hexaferrite nanoparticle surface. Fig. 2f shows the P3TAA–$BaFe_{12}O_{19}$ nanocomposite after calcination, which indicates a dendritic structure due to the long-range organization of the nanoparticles, dictated by the surface conjugated P3TAA.