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Polystyrene/magnetite nanocomposite synthesis and characterization: investigation of magnetic and electrical properties for using as microelectromechanical systems (MEMS)

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In this work, a novel polystyrene/Fe_3O_4 nanocomposite prepared by *in-situ* method is presented. Magnetic Fe_3O_4 nanoparticles were encapsulated by polystyrene. The FT-IR spectra confirmed polystyrene/Fe_3O_4 nanocomposite preparation. The electrical properties of prepared nanocomposite were investigated by cyclic voltammetry (CV). The CV analysis showed good electrical conductivity of the synthesized nanocomposite. Magnetic properties of the nanocomposite were studied by vibrating sample magnetometer (VSM). The VSM analysis confirmed magnetic properties of the nanocomposite. The morphology and the size of the synthesized nanocomposite were investigated by field emission scanning electron microscope (FESEM). According to the VSM and CV results, such nanocomposite can be used in microelectromechanical systems.

Keywords: *microelectromechanical system; polystyrene/Fe_3O_4 nanocomposite; magnetic nanoparticles; magnetite nanoparticles*

1. Introduction

Recently, inorganic-polymer composites have been studied widely because of their particular applications and properties [1, 2]. One of attractive nanocomposites is magnetite/polymer nanocomposite [3]. The iron oxide nanoparticles dispersed in the polymer matrix are used as superparamagnetic material. Because of the their magnetic properties the composites are used in many biomedical fields, such as drug delivery systems [4, 5], cell separation [6], cancer hyperthermia [7], magnetic resonance imaging (MRI) contrast agents [8], tissue engineering [9] and sensors [10].

Microelectromechanical systems (MEMS) are devices which are used to create tiny integrated devices or systems that combine mechanical and electrical components. The MEMS have sensing ability. They control and operate on the microscale and generate effects on the macroscale [11]. The use of these devices is increasing because they have low-volume-consumption and high-throughput [12]. Recently, MEMS attracted the biologists because of the ability of designing and controlling experiments on micrometer scale [13]. MEMS were first developed in the microelectronics industry. The rapid growth of integrated circuit (IC) industry is connected with MEMS which were used to produce tiny devices [14], such as sensors [15], switches [16], filters [17], and silicon gears [18]. Nowadays, in various markets, such as automotive, electronics, medical, communications and defensive technologies, MEMS find many applications [19].

Among different ferromagnetic materials, magnetite has attracted much attention because it is environmentally safe, inexpensive and chemically stable [20, 21].

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Various methods for magnetic nanoparticles preparation, such as sol-gel process [22], hydrothermal process [23] and co-precipitation [24, 25], have been reported in the literature.

For magnetite/polymer nanocomposite preparation, magnetite nanoparticles are coated or encapsulated by natural or synthetic polymer. Various studies have been performed to prepare magnetic polymeric particles [26]. In one of those methods, magnetic inorganic particles and polymer particles are synthesized separately and then mixed together for enabling either physical or chemical adsorption of polymer onto the magnetic particles [27]. Another method is to suspend magnetic particles in a solvent containing monomer and then polymerize the monomer in the presence of magnetic particles to form magnetic polymer particles by surfactant-free emulsion polymerization [28], dispersion polymerization [29], mini-emulsion polymerization [30], inverse emulsion polymerization [31], inverse microemulsion polymerization [32] and suspension polymerization [33].

Polystyrene is an environmental friendly inexpensive polymer which has a good capability to incorporate magnetite nanoparticles [30, 34]. Polystyrene is not conductive inherently but it can become conductive by adding critical amount of conductive nanoparticles to it [35].

In this study, a novel method for preparation magnetite/polystyrene nanocomposite is presented. Electrical properties of the nanocomposite were studied by cyclic voltammetry to know the usefulness of the nanocomposite for sensor applications. The FESEM images were taken to study the size and the shape of the nanocomposite. The properties of prepared nanocomposite were studied by VSM, XRD and FT-IR.

2. Experimental

2.1. Apparatus

Electrochemical experiments were performed with a 797 VA Computrace (Metrohm) for cyclic voltammetry studies (CVS). A conventional three-electrode system was used, including a platinum wire as an auxiliary electrode, Ag/AgCl (saturated KCl) as a reference electrode, and the prepared electrode made from the nanocomposite as the working electrode. A 1 M LiCl solution was used as an electrolyte. For characterization of the nanocomposite FT-IR (Fourier transform infrared) spectra were recorded on a Bruker Vector 22 FT-IR spectrophotometer and X-ray measurement was made on a Bruker D8 Advance XRD2 X-ray Powder Diffractometer (XRD) with a Cu electrode as anode. The morphology of the composite was investigated with a TESCAN MIRA3 scanning electron microscope (SEM). To detect the amount of Fe nanoparticles in the nanocomposite a Genesis FES model inductively coupled plasma (ICP) was used. To investigate the magnetic properties of the polystyrene/magnetite nanocomposite, a MDK-VSM vibrating sample magnetometer (VSM) was used. For sonication, an ultrasonic bath (Bandelin model D102H) with 120/480 W power and 35 kHz operational frequency was used.

2.2. Materials

All analytical grade chemicals containing polystyrene, $FeCl_2{\cdot}4H_2O$, $FeCl_3$, ethyl acetate and ethanol were purchased from Merck (Darmstadt, Germany) and used without further purification. Pure silicone grease was purchased from Greasil 4000 (Welwyn Garden City, England). In all preparation steps a Milli-Q water purification system from Millipore (Madrid, Spain) was used for preparing ultrapure water.

2.3. Preparation of Fe_3O_4 nanoparticles

$FeCl_3$ (1.29 g) and $FeCl_2$ (0.8 g) (molar ratio 2:1) was dissolved in 100 mL water. To dissolve the components completely, the solution was sonicated for 10 minutes. Then, 10 mL saturated NaOH was added to the solution under ultrasonic condition. The resulted precipitate was washed with water 3 times and centrifuged. The resulted nanoparticles were dried at 50 °C.

2.4. Preparation of polystyrene/Fe_3O_4 nanocomposite

For nanocomposite preparation, four different amounts of Fe_3O_4 nanoparticles (0.1 g, 0.2 g, 0.4 g and 0.8 g) were separately dispersed in 30 mL ethyl acetate for 5 minutes in an ultrasonic bath. 0.57 g polystyrene was dissolved in each mixture and sonicated for 15 minutes. Then, 15 mL ethanol was added to the mixture containing dissolved polystyrene and Fe_3O_4 nanoparticles. The deposited polystyrene encapsulated Fe_3O_4 nanoparticles. Finally, the resulted nanocomposite was washed twice with 30 mL water and dried at 50 °C.

2.5. Preparation of electrode

The obtained nanocomposite was mixed with a very low amount of silicone oil and deposited on a copper wire surface to use as the working electrode in cyclic voltammetry and investigate the possibility of using the nanocomposite in sensor fabrication.

3. Results and discussion

3.1. FT-IR studies

Fig. 1 shows the FT-IR spectra of polystyrene. The polystyrene was synthesized by purification of polystyrene. Polystyrene was dissolved in ethyl acetate and formed again by adding ethanol to the solvent. Absorption peaks at 3024 cm^{-1} and 3059 cm^{-1} are caused by aromatic C–H stretching vibrations. The peaks at 2649 cm^{-1} and 2921 cm^{-1} are caused by aliphatic C–H vibrations. The benzene overtones and the benzene C=C stretching vibrations are observed at 1451 cm^{-1} and 1492 cm^{-1}. The peaks observed at 696 cm^{-1} and 755 cm^{-1} are related to single substituted benzene.

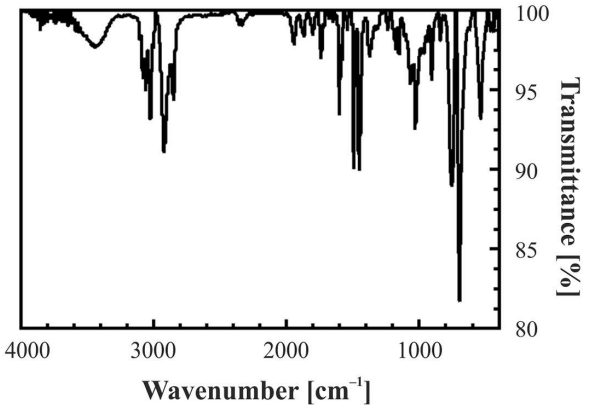


Fig. 1. FT-IR spectra of synthesized polystyrene.

Fig. 2 shows FT-IR spectra of polystyrene/Fe_3O_4 nanocomposite. Four different amounts of Fe_3O_4 nanoparticles were used for the nanocomposite synthesis (0.1 g, 0.2 g, 0.4 g and 0.8 g in 0.57 g polystyrene). Inductively coupled plasma (ICP) results show that the nanocomposites have 6.5 %, 16.4 %, 22.5 % and 39.9 % Fe, respectively. According to the amount of nanoparticles in the nanocomposites, they have been named as 6.5 % (0.1 g), 16.4 % (0.2 g), 22.5 %. As it was already said, the peaks at 696 cm^{-1}, 757 cm^{-1}, 1451 cm^{-1}, 1492 cm^{-1}, 2649 cm^{-1}, 2921 cm^{-1}, 3024 cm^{-1} and 3059 cm^{-1} correspond to polystyrene vibrations and the peak at 570 cm^{-1} proves that Fe_3O_4 has been introduced in the polymer. As can be seen in Fig. 2, by increasing the Fe_3O_4 content in the polymer matrix, the ratio of the peaks at 1492 cm^{-1} to those at 570 cm^{-1} has increased.

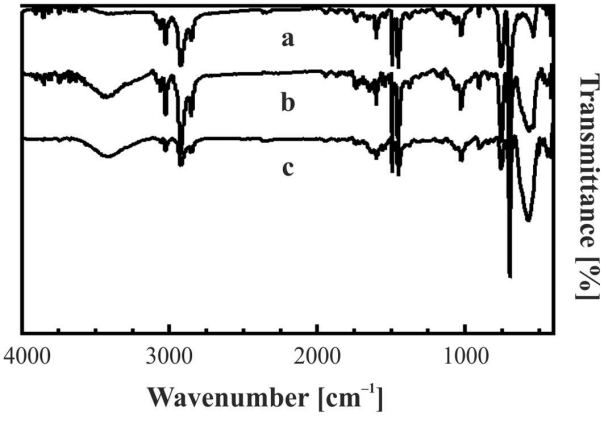


Fig. 2. FT-IR spectra of nanocomposites with different Fe content: 6.5 % (a), 22.5 % (b) and 39.9 % (c).

Fig. 3 shows the ratio of the peaks in the range of 1492 cm^{-1} to 570 cm^{-1} in the FT-IR spectra. As it is shown, the data from ICP confirm the IR results, which means that the peak at 1492 cm^{-1} is

related to the polymer and at 570 cm^{-1} corresponds to Fe_3O_4. These results confirm that reduction of Fe_3O_4 content causes an increase in 1492 cm^{-1} to 570 cm^{-1} ratio.

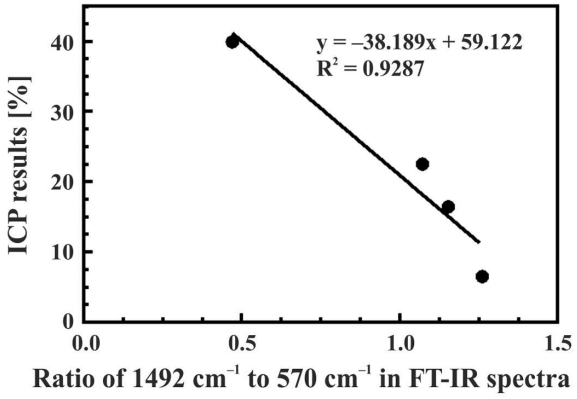


Fig. 3. Ratio of the peaks in the range of 1492 cm^{-1} to 570 cm^{-1} in the FT-IR spectra versus ICP results.

3.2. XRD study

The XRD analysis of prepared Fe_3O_4 nanoparticles was used for phase identification (Fig. 4). The main peaks in the XRD pattern (at $2\theta = 30°$, 36°, 43.5°, 54°, 57.3° and 63°) of the samples could be perfectly indexed to the phase of Fe_3O_4 (JCPDS Card No. 01-075-0449).

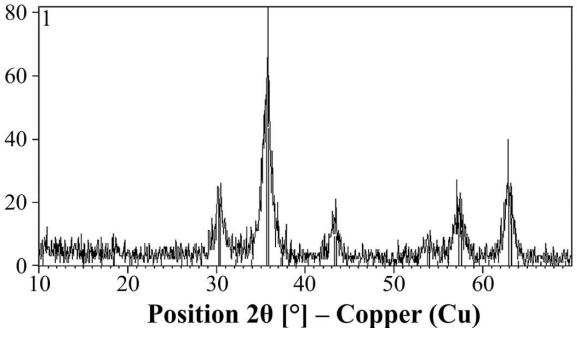


Fig. 4. XRD pattern of Fe_3O_4 nanoparticles.

3.3. FESEM studies

To investigate the morphology of the prepared samples, SEM technique was used. Fig. 5 shows the SEM image of prepared polystyrene. The SEM images of synthesized Fe_3O_4 nanoparticles are shown in Fig. 6. As can be seen, the nanoparticles have an average size about 50 nm. The SEM images prove that the Fe_3O_4 nanoparticles are encapsulated in the polymer matrix and they show that the polystyrene/Fe_3O_4 nanocomposite has a homogeneous morphology.

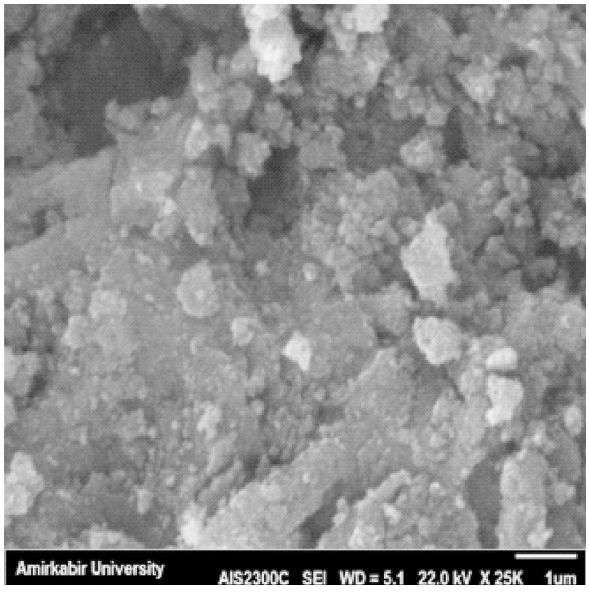


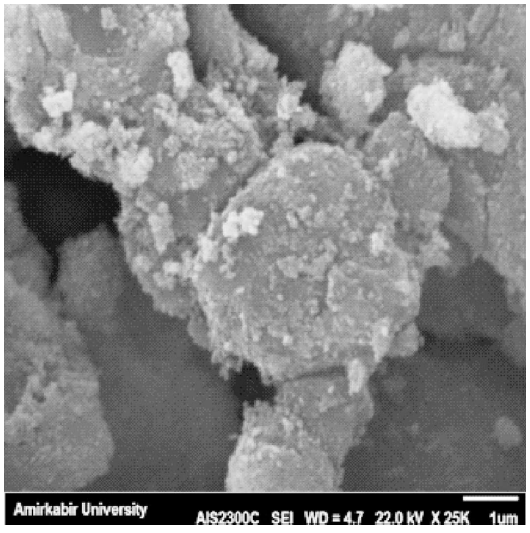
Fig. 5. FESEM image of Fe_3O_4 nanoparticles.

3.4. Cyclic voltammetry analysis

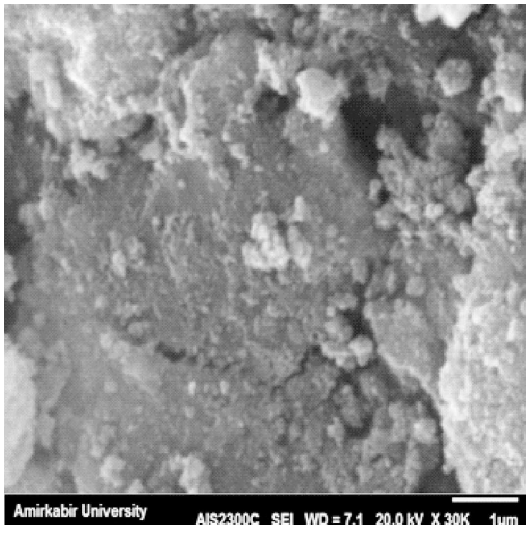
The cyclic voltammetry was conducted to investigate the electrical conductivity of the nanocomposite in 0.1 M LiCl electrolyte at 100 mV/S sweep rate. As Fig. 7 shows, the nanocomposite conductivity increases with increasing Fe_3O_4.

3.5. VSM analysis

Magnetization curves of the nanocomposites with different amounts of Fe_3O_4 (0.1 g and 0.8 g) are shown in Fig. 8a and Fig. 8b, respectively. The saturation magnetization of the nanocomposite (0.8 g) is 40 emu/g at 10 kOe. For the nanocomposite containing 0.1 g Fe_3O_4, magnetization decreases to 6 emu/g at 10 kOe. These results agree with literature implying that saturation magnetization decreases when nanoparticles are coated or covered by some ligands or material [20]. When



(a)



(b)

Fig. 6. FESEM images of nanocomposite containing 6.4 % (a) and 39.9 % (b) Fe_3O_4.

the amount of nanoparticles decreases in a nanocomposite, the magnetite amount decreases in the same ratio in measured samples and thus affects the total magnetic moment.

4. Conclusions

In this paper, a magnetic nanocomposite prepared by adding Fe_3O_4 nanoparticles to polystyrene has been studied. The synthesized nanocomposite showed good electrical

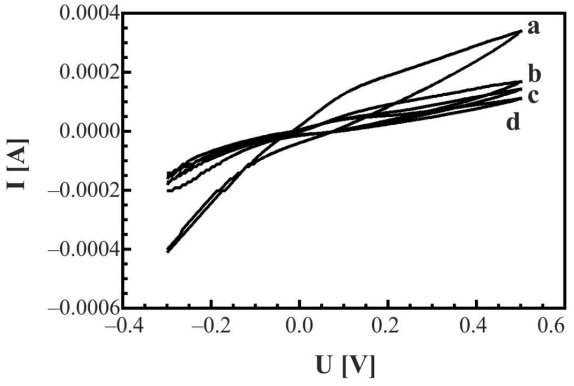
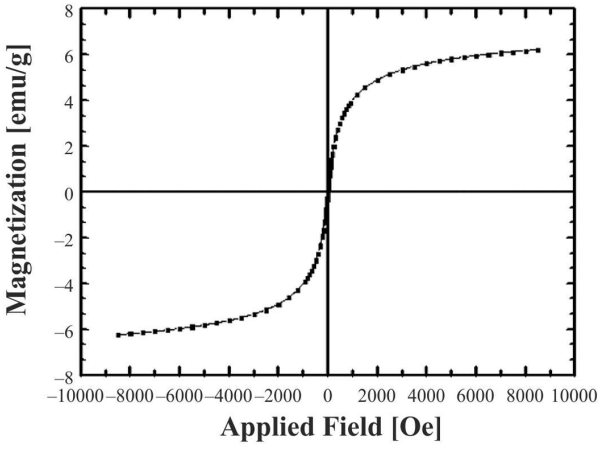
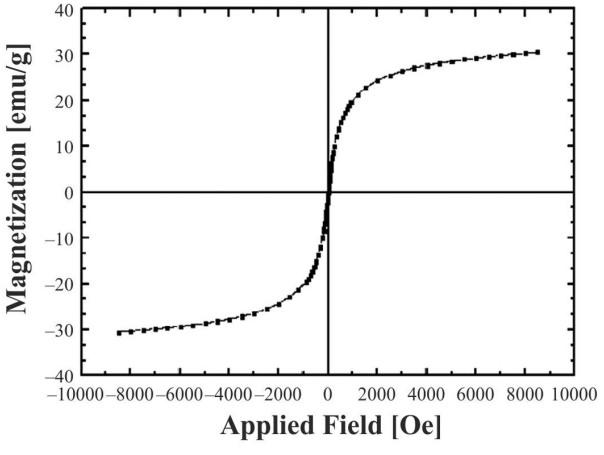


Fig. 7. Cyclic voltammograms of polystyrene/Fe_3O_4 nanocomposite containing 39.9 % (a), 22.5 % (b), 16.4 % (c) and 6.5 % (d) Fe.



(a)



(b)

Fig. 8. Magnetization curves of nanocomposite containing 0.1 g (a) and 0.8 g (b) Fe_3O_4 nanoparticles.

conductivity and magnetic properties, and the cost of its fabrication was low. Therefore, the nanocomposite seems to be promising for micro-electromechanical systems.

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