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Metal–polymer nanocomposites based on Ni nanoparticles and polythiophene obtained by electrochemical method

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ABSTRACT

Polythiophene–nickel (PT–Ni) nanocomposites have been prepared by the electrochemical oxidative polymerization of thiophene in the presence of nickel nanoparticles. The metallic nickel nanoparticles were obtained by the chemical reduction of nickel chloride with hydrazine at 100–130 °C. Poly(*N*-vinylpyrrolidone) (PVP) was used as protective agent in the synthesis of nickel nanoparticles. Transmission electron microscopy data revealed the particle size to be in the range 6–20 nm. X-ray diffraction, scanning electron microscopy, thermal analysis, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were utilized to characterize the nanocomposites. XPS measurements for the PT–Ni nanocomposites showed that the nickel content varied between 0.43 and 1.3 at.% in the PT–Ni nanocomposites. The electrical conductivity of the composites increased from $4.5 \times 10^{-3}\ \Omega\,cm^{-1}$ to $1.25 \times 10^{-2}\ \Omega\,cm^{-1}$ as the amount of nickel was increased from 0.43% up to 1.3%, polythiophene–Ni nanocomposites exhibiting a good electrical conductivity response.

1. Introduction

In recent years, much attention has been paid to the investigation of mechanical, thermal and electrical properties of nanocomposite materials, such as polymer films, nanorods, nanotubes and nanowires. Nanocomposites based on metal-polymers present special interest in the nanoscience field and for nanotechnology applications. These nanostructures have a deep impact on both fundamental research and potential applications in nanoelectronics or molecular electronics, nanodevices, nanocomposite materials, bio-nanotechnology and medicine [1–4]. The electrodeposition method can be considered as a novel economical and viable technique with a potential for the large-scale production of such materials.

Inorganic particles not only provide mechanical and thermal stability, but also give new functionalities depending on their chemical nature, structure, size, and crystallinity (transition metal oxides, metallic phosphates, silica, nanoclays and metal chalcogenides). Indeed, inorganic particles can contribute to improving mechanical, thermal, electronic, magnetic and redox properties, as well as density, refractive index, etc. [5–8].

Generally, the reason for adding inorganic particles into polymers is to enhance the mechanical properties, such as tensile strength, modulus or stiffness by reinforcement mechanisms [9]. The optical properties of discontinuous metal or granular composite films, consisting of metal nanoparticles embedded in a polymer matrix, have long been of interest. Moreover, as the market of materials for optical applications is expanding, the request of novel materials with high functionality and transparency is increasing. Polymer-based inorganic nanoparticle nanocomposites represent a great promise, as they can provide the necessary stability and easy processability combined with interesting optical properties.

Conducting polymers with an extended π-conjugated system, such as polythiophene, polypyrole or polyaniline, are known to be widely utilized due to their interesting electrical, optical and chemical characteristics, good thermal and environmental stability, low toxicity, easy polymerization, adjustable electrical conductivity, etc. [10,11]. Among conductive polymers, polythiophene and its derivatives have received growing attention due to their high conductivity, ease of doping, redox properties, sensitivity to different gases, and applications in solar cells and organic field-effect transistors [12–14]. In order to expand the application range of polythiophenes, their nanocomposites with inorganic nanoparticles were developed [15–17]. The incorporation of inorganic

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nanoparticles can not only enhance the polythiophene characteristics, but also provide new performance, which cannot be achieved in their single counterparts due to the synergetic behavior of the components. Polythiophenes are one of the most valuable types of conducting polymers, which may be easily modified to afford a variety of useful electrical and physical properties, such as solubility, electrical conductivity, mobility and others.

In this paper, we report for the first time the synthesis of monodisperse nickel nanoparticles starting from nickel salts in a non-aqueous solution using poly(vinyl pyrrolidone) (PVP) as surfactant. Therefore, nickel nanoparticles were firstly obtained by the chemical reduction of nickel chloride with hydrazine hydrate ($N_2H_4{\cdot}H_2O$) and sodium hydroxide (NaOH) solution at a relatively low temperature. In the second step, the PT–Ni films deposited on the working electrode were subjected to electrochemical polymerization of thiophene in the presence of Ni nanoparticles. The as-prepared materials were characterized by X-ray diffractometry, transmission electron microscopy, X-ray photoelectron spectroscopy and scanning electron microscopy. The electrical conduction aspects of nanocomposites were analyzed as a function of temperature by determining electrical conductivity.

2. Experimental

2.1. Materials

Thiophene, hydrazine hydrate (100%), poly(N-vinylpyrrolidone) (PVP), sodium hydroxide, ethylene glycole, acetonitrile, methanol, ethanol, acetone, tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (all from Aldrich) and $NiCl_2{\cdot}6H_2O$ (Reactivul, Bucharest) were used as received.

2.2. Synthesis of Ni nanoparticles

An amount of 0.295 g of PVP was added to a solution of 0.297 g $NiCl_2{\cdot}6H_2O$ (0.05 M) in 25 ml ethylene glycol (EG) and the mixture was stirred until the total dissolution of PVP. After this, the resulting solution was heated up to 100–130 °C with constant stirring for 2 h. Then 1 M of hydrazine hydrate and 0.015 M NaOH solutions were added to the solution (without magnetic stirring). The absence of magnetic stirring minimized the problems related to the agglomeration associated with the superparamagnetic nature of nickel nanoparticles [18]. The initially green solution turned black, indicating the formation of Ni metal particles.

Nickel nanoparticles were collected, washed several times by ethanol. Some of these nanoparticles were dried at 60 °C and used for structural characterization, while the rest were kept in ethanol or acetonitrile solution and then utilized for nanocomposite synthesis. For comparison, a PT/Ni nanocomposite was prepared following the same procedure, but in the absence of PVP, in order to evidence the influence of the surfactant on the synthesis of Ni nanoparticles.

2.3. Electrochemical synthesis

Conducting polymer nanocomposites were prepared by the electrochemical method, using a Potentiostat–Galvanostat Bioanalytical System (BAS 100B/W). All the experiments were performed in a one-compartment cell, using a standard three-electrode cell arrangement with a working electrode (ITO glass purchased from Sigma Aldrich, 8–12 Ω, 2.0 cm × 2.5 cm area), an auxiliary electrode (platinum wire), and a reference electrode (consisting of silver wire coated with AgCl). Before each experiment, the ITO glass working electrode was sonicated for 10 min in a mixture of methanol and acetone using an ultrasonic bath, and rinsed with distilled water. All electrochemical experiments were carried out at room temperature. A continuous flux of argon was purged in the electrolytic solution for 15 min prior to each experiment. The electrochemical polymerization of thiophene and deposition of PT–Ni nanocomposites on the ITO electrode were carried out potentiostatically, applying a constant potential of 2.5 V for 120 s, in acetonitrile solution (10 mL) containing 1.9 mM thiophene, 0.002 g Ni nanoparticles and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as electrolyte (0.083 g). After polymerization, the polymer coated ITO substrate was washed thoroughly with acetonitrile to remove any residue.

2.4. Characterization

The structural analysis of Ni nanoparticles was performed by the X-ray diffraction (XRD) method, using a Bruker AD8 ADVANCE diffractometer (Cu K_α radiation, $\lambda = 1.54182$ Å). Infrared absorption spectra were obtained using a VERTEX 70/70 v FT-IR spectrometer between 4000 and 500 cm^{-1}. The Transmission Electron Microscopy (TEM) investigation was carried out on a Hitachi High-Tech HT 7700 instrument operated at 100 kV accelerating voltage in the high contrast mode. The samples were prepared on carbon coated copper grids of 200 mesh size. Microdrops of the nanoparticles dispersed in ethanol (0.1%) were placed on the grids, and then the solvent was removed in air. The morphology of the samples was examined by using an Environmental Scanning Electron Microscope (ESEM) type Quanta 200, operating at 20 kV with secondary electrons. Thermogravimetric analysis of the powders was carried out in a TGA/DTA STA 449 F1 Netzsch (Germany). The analysis was performed from room temperature (RT) to 700 °C at a heating rate of 10 °C/min in air flow. An X-ray photoelectron spectrometer (KRATOS *Axis Nova*) was used to probe the chemical state of PT–Ni nanocomposites. The pressure in the main chamber was below 10^{-8}–10^{-9} Torr during the analysis. Monochromatic Al K_α radiation (1486.6 eV) with 20 mA current and 15 kV voltage (300 W) was used as the X-ray source. The incident monochromated X-ray beam was focused on a 0.7 mm × 0.3 mm area of the surface. The XPS survey spectra for the samples were collected in the range of 10–1200 eV with a resolution of 1 eV and a pass energy of 160 eV. The high resolution spectra for all the elements identified from the survey spectra were collected using a pass energy of 40 eV and a step size of 0.1 eV.

The temperature dependencies of electrical conductivity, σ, were measured using a Keithley electrometer (model 6517) in the temperature range $\Delta T = 300$–423 K during a heat treatment consisting of two heating and cooling cycles. The thickness of the composite films was found to be between 1.5 and 5.0 μm. Electrical conductivity measurements as a function of temperature were performed on composite films equipped with two parallel thin film silver electrodes separated by a gap of about 6 mm. The width of each electrode was about 1 mm. The contact obmicity was verified and non-ohmic effects were not signaled.

3. Results and discussion

3.1. X-ray diffraction analysis

Firstly, experiments were carried out to optimize the deposition parameters for individual polythiophene and polymer composites incorporating Ni nanoparticles. Details of some representative samples from these two series are presented in Table 1.

The structural information about Ni nanoparticles has been investigated by X-ray diffractometry (XRD) and the results are given in Fig. 1. Wide angle XRD patterns show diffraction peaks

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