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Research paper

Electropolymerization and multifunctional properties of novel polypyrrole films embedded with Co nanoparticles

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ABSTRACT

A novel electropolymerization process has been presented to prepare compact polypyrrole (PPy) polymer films embedded with different cobalt nanoparticle (Co NP) loadings by using cyclic voltammetry. An electropolymerization mechanism is suggested and further confirmed by Fourier transform infrared (FT-IR) spectroscopy and Raman spectroscopy of pure PPy and PPy polymer nanocomposites (PNCs). The PPy/Co PNCs exhibit unique multifunctional properties. Firstly, they are superparamagnets at room temperature, whose saturation magnetization can be controlled by modifying the concentration of Co NPs in the electrolyte solution. Secondly, they show not only semiconductor transportation behavior but also a negative magnetoresistance under external magnetic field. The permittivity of the PPy/Co PNCs switches from negative to positive with the increasing frequency. Both the outstanding magnetic and electrical properties make the PPy PNCs promising as one kind of microwave absorbing materials.

1. Introduction

Nowadays polymer nanocomposites (PNCs) prepared by dispersing magnetic nanoparticles (NPs) into a conducting polymer are proposed to have wide applications because of their many advantages, such as low cost, environmental stability, light weight, and unique electromagnetic properties [1–4]. Among diverse conducting polymers, polypyrrole (PPy) has attracted great attention due to its tunable conductivity by various ways of doping, easy preparation under different conditions, and outstanding pseudocapacitance as electrode materials [5–8]. In the past decades, PPy kept on the hottest research topics list and has already been used as microwave absorbing materials, adsorption materials, electrocatalytic reagents, magnetic-controlled switches, biomedical materials, biosensors, and corrosion inhibitors [9–15].

PPy PNCs could get intrinsic magnetic properties by controlling their molecular structure by directly adding dopants consisting of iron species during polymerization [6,7]. However, this kind of intrinsic magnetism is very weak and hardly meets practical applications. PPy PNCs can also obtain external magnetic properties through compositing with magnetic metal or alloy crystal additives. For this kind of PPy PNCs, the magnetic properties become reasonably better, and thus has been extensively studied [9,16–19]. The magnetic additives are normally focused on Ni, Fe, Fe_3O_4, γ-Fe_2O_3, $BaFe_{12}O_{19}$ [9,16–19], etc. However, there are only a very few reports about PPy PNCs doped with cobalt (Co), even though Co is a very classical magnetic metal.

Face-centered-cubic (fcc) Co has a very high saturation (166 emu/g) being much larger than Fe_3O_4 (97 emu/g) which is one of the most common magnetic materials in practice [20]. While reducing their size, the saturation magnetization of Co NPs could become even larger [20], which indicates a better performance to some extent in their composites. Besides, Co NPs have better oxidation-resistance than Fe NPs although the later has a higher saturation magnetization (~213 emu/g). Thus PPy/Co PNCs can be expected to have wide applications in the future.

There are at least four methods to prepare PPy NPCs, including simple blending, in situ polymerization, one-step chemical method, and electrochemical deposition [21]. The first three methods are reported frequently, yet they are technically possible to produce PPy NPCs powders only [9–19]. Considering that the PPy PNCs hardly dissolve in any inorganic or organic solvents, they would be used inconveniently in most situations where PPy PNCs are supposed to form films or coat upon machines' surface. By contrast, electrochemical processing could directly deposit a large

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area of PPy film on metal surface uniformly, which makes it one reliable method to use PPy NPCs industrially. Among those relatively fewer reports, Watanabe et al. have successfully prepared Co nano-clusters embedded in the PPy matrix by two-step electrodeposition, which firstly polymerized PPy films at a positive potential and then reduced Co nano-clusters at a negative potential [22]. This kind of PPy/Co PNCs indeed combined the characteristics of parent constituents, nonetheless the Co nano-clusters could only stay on the surface of the PPy and disperse unevenly. Therefore, other synthesis process needs to be developed to prepare PPy/Co NPCs with improved properties. Here, we present a novel electrochemical process to prepare PPy films embedded with Co NPs and the mechanism of electropolymerization process is explained. The composite exhibits multifunctional properties.

2. Experiment

All reagents are of analytical grade. Pyrrole is purified by vacuum distillation method before using. Other chemicals are not further purified. The synthesis process includes two steps as below.

2.1. Preparation of water dispersible Co NPs

Firstly, the monodispersed Co NPs were synthesized by the chemical method of decomposing $Co_2(CO)_8$ in phenyl ether [23]. The Co NPs were dispersed in 10 mL of hexane after being purified for two times. Mercaptoacetic acid ($C_2H_4O_2S$) was dropped into the dispersion of Co NPs until Co NPs were observed to agglomerate gradually and deposit from the solution. The dispersion was centrifuged and the precipitate was re-dispersed in 5 mL of deionized water.

2.2. Electropolymerization of PPy films embedded with Co NPs

All electropolymerizations were performed at room temperature in a conventional three-electrode cell with a Pt counter electrode, a saturated calomel electrode (SCE) and Pt-coated silicon substrates as the work electrode, which has been reported in our previous work [24]. This electropolymerization process was developed by modifying the method of preparing PPy [25]. The typical electrolyte was composed of 0.1 M sodium sulfate, 0.001 M sodium dodecylbenzenesulfonate, and 0.1 M pyrrole while the pH value was adjusted to 3 by adding sulfuric acid. The electropolymerization of PPy/Co PNCs achieves at a lower pH value than that of pure PPy. In order to reduce the time of Co NPs staying in acidic solution, several drops of well-dispersed Co NPs suspension, such as 6, 26, 50 and 100 drops, should be added into the electrolyte after all other experimental procedures were ready. After stirring the mixture for about 1 min, electropolymerization started at once. One drop of Co NPs suspension contained about 0.6 μg of Co NPs. The electropolymerization was carried out by cyclic voltammetry for 15 successive cycles. The potential was applied in the range of +0.5 V to +1.0 V and the scan rate was 25 mV/s. The films were washed by deionized water several times and dried in the air.

The surface morphology of the films were examined by using a LEO-1450 scanning electron micro-scope (SEM).The chemical structures were analyzed by NICOLET iS10 Fourier transform infrared spectra (FTIR) and Renishaw inVia Raman spectra. The electrochemical tests of the films were carried out on an LK98BII microcomputer-based electro-chemical analyzer. Magnetic and electronic properties of the films were studied by a physical property measurement system (PPMS) at room temperature. The dielectric property was measured by a TH2828S impedance analyzer.

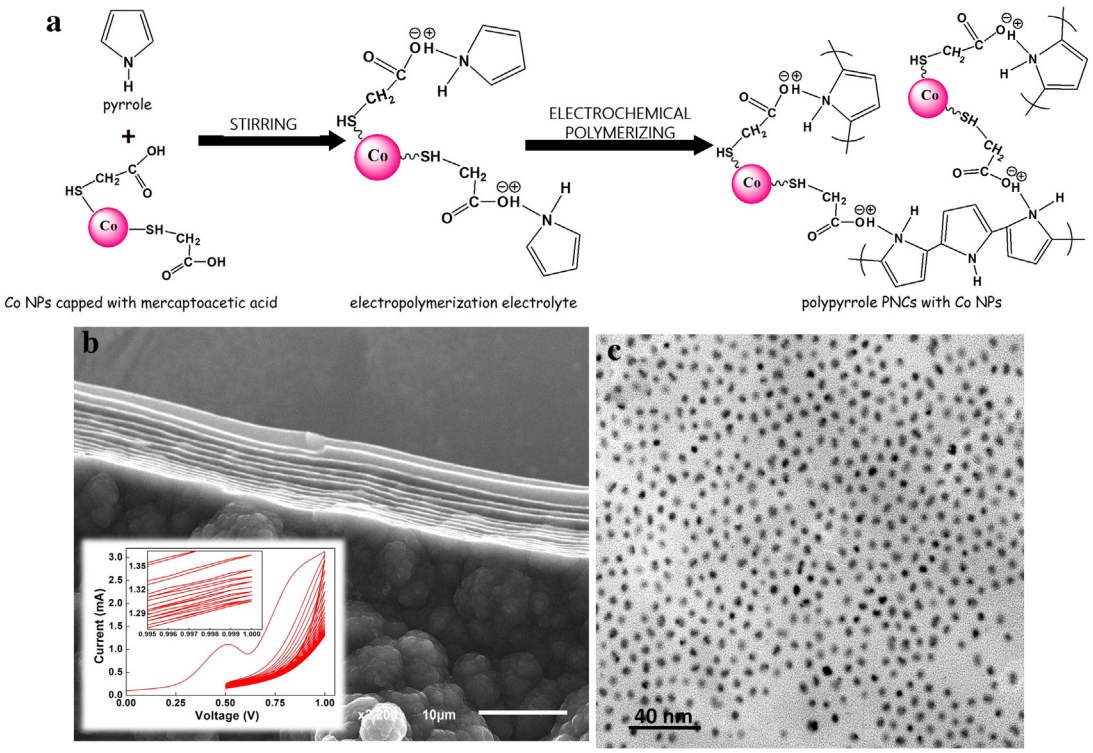

Fig. 1. (a) Schematic diagram of the electropolymerization of PPy/Co PNCs. (b) Sectional view of the PPy/Co films. (c) TEM image of the Co NPs. The inset in (b) is the cyclic voltammetry curve of the electropolymerization.