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Synthesis and characterization of electromagnetic properties of polypyrrole nanorods prepared via self-reactive MnO_2 template

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ABSTRACT

Intrinsically conducting polymers (ICPs) due to special properties are promised in various applications, especially for radar absorbing materials (RAM). In the present paper, the dielectric and microwave absorbing properties of polypyrrole nanorods (PPyNR)/paraffin composite have been investigated in the frequency range of 2–18 GHz, for the first time. Also a simple route was successfully used for the chemical synthesis of PPy via a reactive template of α-MnO_2. For this purpose, the reactive template of MnO_2 was prepared by a facile hydrothermal method at 150 °C. The synthesized α-MnO_2 was used as oxidizing agent for polymerization reaction of PPy. The XRD patterns confirmed that the MnO_2 template consumed as an initiator almost completely. In the SEM images, the α-MnO_2 sample was composed of uniform nanorods and the PPy nanostructures were inherited their morphologies from the MnO_2 templates. Microwave absorbing studies of PPyNR/paraffin composite indicated the remarkable EM wave absorption property with the maximum reflection loss (around −50 dB) at about 10 GHz at a thickness of 3.1 mm. Microwave absorption result showed that these nanocomposites had excellent intrinsic potential for various microwave absorbing applications.

1. Introduction

Nowadays the rapid development of electronic and telecommunication systems as well as over usage of electromagnetic wave in microwave frequency range, discomfit in some critical fields such as military communication. So, finding materials with EM wave absorbing capability is very important. EM wave absorbers have many applications such as protecting electronic devices like mobile-systems against electromagnetic disturbances and camouflage of military equipment against enemy's radar. In the military applications, these materials are used as radar wave absorbers which are called radar absorbing materials. An ideal RAMs must have unique properties, such as low weight and thickness, high environmental stability, good mechanical characteristics and low cost [1,2]. Traditional RAMs have been fabricated by ferrites, metals and carbon black [1,3]. The carbon black mainly used as filler in radar absorbing coating due to its chemical resistance, electrical conductivity and low density. By utilization of carbon black in RAM coating, not only will not achieve to sufficient electrical conductivity and thus optimal performance of radar waves absorbing, but also the major drawback of these carbonaceous fillers are "peeling" [4]. Also, metals have good mechanical properties and reflection loss but they have disadvantages such as heavy weight, corrosion and poor processability. Because of these disadvantages and limitations, it is obvious that the RAMs with better properties are required [5]. The intrinsically conducting polymers (ICPs) seem to be good alternative for using in RAM coatings. Recently, application of ICPs and their composites have attracted attention in many fields of research due to their properties such as high electrical conductivity (compared with carbon), facile processability, low density (for example; polyaniline and polypyrrole densities compared with iron are 1.1, 1.2 and 7.8 g/cm^3, respectively), corrosion resistance (compared with metals), and preference for military purposes such as camouflage and stealth technology [3].

Polyaniline (Pani) and polypyrrole (PPy) have attracted specific interest among the conducting polymers known to date, because of their high conductivity, high flexibility, ease synthesis routes, high stability, low cost and good mechanical properties [6]. Lately, researchers attempt to design and synthesize predetermined structures of ICPs in nanoscale. Conducting polymers with nanoscale structures due to unique properties, exhibit improved performance in technological applications, such as high electrical

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conductivity; large specific surface area [7]; light weight and large aspect ratio, which arising from their nanoscale size. Template synthesis has offered a facile, controllable and efficient route to design and produce novel conducting polymer nanostructures. Soft-template methods (also named self-assembly method), hard-template methods, self-reactive template and electrospinning technology are several approaches for conducting polymer nanostructures synthesis with predictable morphologies [8]. In self-reactive template method, template not only must play the physical template role for polymer backbone formation, but also should have sufficient redox potential for beginning of polymerization reaction. Also, in this production method, most of the reactive template of MnO_2 is converted to soluble Mn^{2+} ions during the polymerization process. Since the PPy synthesize is in aqueous media, Mn^{2+} cations can be solved in media and then washed from PPy nanorods [8–10]. In the other words, the MnO_2 nanorods (as an oxidizing agent) have oxidized pyrrole to produce polypyrrole nanorods and they were reduced into Mn^{2+} cations, which were produced in solution as soluble species [9]:

$$nPy \rightarrow (Py^{0.33+})_n + 2nH^+ + 2.33ne^- \quad (1)$$

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \quad (2)$$

This redox mechanism can be represented by the following redox reaction:

$$7nMnO_2 + 16nH^+ + 6nPy \rightarrow 7nMn^{2+} + 14nH_2O + 6(Py^{0.33+})_n \quad (3)$$

As a result, to obtain the pure polymer, no special purification steps are required [8]. To the best of our knowledge, no systematic study has been reported to examine the effect of morphology on the PPy microwave properties. In previous work, we investigated the morphology effect of PPy microspheres consisted of interweaved PPy nanostructures on their microwave properties in the frequency range of 2–18 GHz [11]. In the present work, we study the morphology effect of PPy nanorods (PPyNR) on their microwave properties. In the work reported here, the PPyNR was synthesized with MnO_2 as an oxidizing agent and self-reactive template. The oxidation potential of MnO_2 was sufficient to initiate the polymerization of pyrrole, and polypyrrole nanorods formed on the surface of the MnO_2 nanorods. The morphology, external size and shape of PPy nanorods were similar to α-MnO_2 nanorods template. Also, the microwave properties of PPyNR/paraffin composite with 15 wt.% PPyNR was investigated in the frequency range of 2–18 GHz for the first time. The results demonstrated that using of polypyrrole with this morphology is a perfect choice to be a RAM in relatively low thickness. This can promise better radar absorbing coatings with low weight and low thickness.

2. Experimental

2.1. Materials

Pyrrole monomer (Py), potassium permanganate ($KMnO_4$, ≥ 99.0%), hydrochloric acid (HCl, 37%) and methanol were obtained from sigma-Aldrich. Py was distilled before use and all other chemicals were used as received. All the chemicals used here were of analytical grade and all aqueous solutions were freshly prepared by using high-purity water.

2.2. Synthesis of α-MnO_2 nanorods

The synthesis of α-MnO_2 nanorods were based on the previous work of Wang's group [12]. In brief, 4.1 mmol of $KMnO_4$ was dissolved into deionized water. Then, 1.5 ml of concentrated HCl (37%) was added to the above solution under stirring for 15 min to form a homogeneous mixture. Subsequently, the mixture was transferred into a Teflon-lined (PTFE) stainless steel autoclave with a capacity of 100 ml, sealed and maintained in an oven at 150 °C for 10 h when the autoclave cooled down and reached the room temperature, the resulting brown precipitates were collected by filtration and washed with distilled water until excess reagents were removed. The prepared MnO_2 was dried at 80 °C for 12 h in oven.

2.3. Synthesis of PPy nanorods

PPy nanorods were prepared almost similar to the previous work of Wang's group described in Ref. [10]. In a typical procedure, 100 mg of synthesized α-MnO_2 powders was dispersed in 0.1 M HCl solution by using an ultrasonic bath. Then the pyrrole monomers were then added drop wise into the above suspension under vigorous magnetic stirring at 0–5 ° C. After few minutes, the reaction rapidly initiated as the brownish MnO_2 suspension changed its color to black. After stirring for 2 h, the mixture was rest for 1 h. Finally, the resultant black PPy products were filtered and washed with deionized water and ethanol for several times, respectively.

2.4. Preparation of paraffin matrix absorber composite for electromagnetic measurements

The paraffin composite with 15 wt.% of the PPy nanostructures powder was manufactured according to the previous work of jazirehpour's group described in Ref. [13]. Briefly, the PPy together with paraffin were dispersed in toluene solvent by using ultrasonication. The resulting mixture was kept at 80 °C for 3 h to remove toluene from the blend. Then, the sample was cooled to reach the room temperature. The obtained paraffin homogenous mix was pressed into toroid shape with 7 mm outer diameter, 3 mm inner diameter and 2 mm thickness.

2.5. Characterization

Electromagnetic parameters of the mentioned paraffin matrix toroid sample were measured in frequency range of 2–18 GHz at room temperature. A Rohde & Schwarz ZVK vector network analyzer (VNA) was used in the measurement. The VNA was calibrated for the full two-port measurement with a modified SOLT calibration scheme. The relative complex permittivity of the specimen was then calculated, using the measured S-parameters based on ASTM D7449 standard. Structural characterizations of PPy was done by X-ray powder diffractometer (XRD, Bruker, D8 Advance), using Cu Kα radiation at 45 kV and 20 mA (k = 0.154056 nm). The Chemical structure of nanostructure was characterized by FTIR technique (Bruker, Tensor 27) and energy-disperse X-ray spectroscope (EDX). The morphology of the MnO_2 and PPy nanostructures were observed by a field-emission Scanning Electron Microscope (FESEM; MIRA3-XMU TESCAN). A thermo-gravimetric analysis (TGA) was carried out on samples about 15 mg with a LINSEIS model STS PT 16000 thermal analyzer under air atmosphere at a heating rate of 5 °C min^{-1}.

3. Results and discussions

3.1. Structural properties

The Fourier transform infrared spectra (FT-IR) analysis was conducted in order to investigate the chemical structure of the particles. The FT-IR of the PPy nanorods synthesized with MnO_2 as a self-reactive templates and α-MnO_2 nanorods are shown in