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Controllable synthesis of leaflet-like poly (3,4-ethylenedioxythiophene)/single-walled carbon nanotube composites with microwave absorbing property

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ABSTRACT

Highly conductive leaflet-like poly (3,4-ethylenedioxythiophene)/single-walled carbon nanotube (PEDOT/SWCNT) composites were successfully synthesized via a facile method in a ternary phase system. Scanning electron microscopy and transmission electron microscopy observation denoted that SWCNT core was uniformly coated with PEDOT shell. More interestingly, on the surface of the resultant PEDOT shell a large number of PEDOT substructures were found to form by adjusting the molar ratio of water to the surfactant (defined as ***N***). The leaflet-like PEDOT/SWCNTs entangled together as a nanoporous conductive network. Measurements of microwave absorption revealed that the conductivity, layer thickness and mass fraction of the leaflet-like PEDOT/SWCNTs have great impacts on the microwave absorbing property. It was found that the sample with 10 wt% PEDOT/SWCNT content exhibited much more effective absorption performances.

1. Introduction

Microwave absorbing materials (MAMs) have wide applications on account of their ability to attenuate electromagnetic wave pollution and reduce the radar cross-section signals [1]. Therefore, significant attention has been devoted to explore effective microwave absorbers with lightweight properties, structurally sound ability and flexible ability as well as strong absorption in a wide microwave frequency range [2–8]. Recently, more and more attention has been drawn on the construction of unique microstructures of the absorbers and their influences on the improvement of microwave absorbing property. Wang et al. reported morphology-dependent electromagnetic properties and urchinlike nickel chains exhibited the best absorption performance with a peak of −25.29 dB at 9.6 GHz. The strong absorption was quantitatively illustrated as geometrical effect, multiple-absorption and point discharge effect due to the urchinlike microstructure [9]. Sun et al. has reported the morphology-dependent magnetic properties on iron-based dendrite-like materials with the reflection loss from −53 to −25 dB. The excellent microwave absorbing property associated to the dielectric and magnetic loss as well as the fine dendrite-like microstructures of the absorbers [10]. However most of these absorbers are inorganic materials and their weight content in the polymer matrix is over 50%, which limits their applications as lightweight microwave absorbers.

To meet the requirement of lightweight microwave absorbers, much attention has been put on CNT and its composites in the recent years [11,12]. Qi et al. reported the microwave absorbing property of bamboo-like carbon nanotubes over Fe/SnO_2 composite and the minimum reflection loss was −11.06 dB at 12.45 GHz [13]. A composite of epoxy-silicone filled with multi-walled carbon nanotubes (MWCNTs) and carbonyl iron particles was used as microwave absorber and showed a minimum reflection loss of −16.9 dB at 10.5 GHz. There were significant improvements in absorption bandwidth over the frequency range of 3.4–18 GHz with the reflection loss below −10 dB when it was filled with 0.5 vol% MWCNTs and 50 vol% carbonyl iron [14]. Nevertheless, the lightweight advantage of CNTs is still restricted due to the large weight or volume fraction (40–50%) of inorganic particles introduced into the polymer matrix [15–20].

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Conducting polymers combined with SWCNTs are quite promising for using as lightweight microwave absorbers. One of the most famous conducting polymers, poly (3,4-ethylenedioxythiophene) (PEDOT), is an appealing candidate to combine with SWCNT due to its high conductivity, low density and excellent electrochemical stability, which could be resistant to the corrosion as well as be favorable for the practical application in comparison to the metallic particles [11,21–24]. Moreover, the easy processibility of PEDOT allows to be designed for various nanostructures of the composites via numerous strategies [25].

In this work we propose a facile approach to the preparation of single-walled carbon nanotubes in-situ coated with PEDOT shell on which another PEDOT substructures formed afterwards. This novel leaflet-like PEDOT/SWCNT composite was controllably synthesized by simply adjusting the molar ratio of water to the surfactant (defined as ***N***). The novel leaflet-like PEDOT/SWCNTs blending with paraffin wax were investigated in respect to their microwave absorbing properties. The relative complex permittivity (ε_r) and the relative complex permeability (μ_r) of the microwave absorbers were measured by using HP8722ES network analyzer at the frequency range of 1–18 GHz. The obtained ε_r and μ_r are used to make calculations for the reflection loss of the composites. The obtained composites based on the leaflet-like PEDOT/SWCNTs exhibited excellent microwave absorbing property with the minimum reflection loss of −43 dB at 9.4 GHz.

2. Experimental

2.1. Materials

The EDOT monomer (⩾99.7%) was purchased from Aldrich. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 96%) was supplied by Acros Organics. The carboxyl purified single-walled carbon nanotubes (SWCNTs) with carboxyl content of 2.73 wt% were purchased from Timesnano (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, China). The SWCNTs had the diameter around 2 nm and length varying between 5 and 30 μm. The purity of the SWCNTs is >90% and the specific surface area equals to 380 $m^2\ g^{-1}$. Ferric chloride ($FeCl_3$) and other reagents were obtained from Chemical Reagent Company (Beijing). PEDOT (***N*** = 1.5) was prepared by using the method discussed in our previous work [21]. All of the reagents were used directly as received unless otherwise mentioned.

2.2. Preparation of leaflet-like PEDOT/SWCNT composites

The PEDOT/SWCNT composite was in-situ synthesized by chemically oxidative polymerization based on a ternary phase system. In a typical synthesis, the surfactant AOT was dissolved in p-xylene in a conical flask with a concentration of 1.5 mol L^{-1} and stirred for 20 min under ultrasonic irradiation to get a uniform solution. Then the carboxyl purified SWCNTs were added into the solution and made an ultrasonic treatment for another 1.5 h. Aqueous $FeCl_3$ solution (7 mol L^{-1}) was further added into the mixture afterwards and allowed to mix for 30 min with magnetic stirring. The molar ratio of water to the surfactant, namely ***N***, was varied with increasing volume of aqueous $FeCl_3$ solution. The definition of ***N*** in this case has been discussed in our previous report [21]. Here the values of ***N*** were 1.5 and 15, respectively. The addition of SWCNT differed with the ***N*** values. When the value of ***N*** was 1.5, 8.1 mg SWCNT was introduced into the system. Whereas 81 mg SWCNT was added as ***N*** was 15. Thereafter, 0.4 ml EDOT monomer was slowly dripped into the polymerization system whilst stirring and then left for 24 h at ambient temperature to undergo the reaction. Subsequently, the resultant dark solid product was isolated by centrifugation and washed several times with ethanol, followed by the process to remove the residual reagents by using a mixture of water and ethanol (1: 1, v/v) until the supernatant fluid appears colorless and transparent. Finally, the resultant product was collected and dried under vacuum at 80 °C for 24 h.

2.3. Characterization

The phase identification of PEDOT, SWCNTs and PEDOT/SWCNTs was performed by using Raman spectroscopy (inVia-Reflex, England Renishaw) with 532 nm excitation laser. Thermal gravity analysis (TGA) of PEDOT/SWCNT composites was measured with Q600-SDT (America). Scanning electron microscope (SEM) images of the as-prepared samples were obtained by using S-4800 (Japan) operated at 10 kV. Transmission electron microscope (TEM) images were taken by using JEM-2100F (Japan) and operated at 200 kV. For TEM measurements, the diluted sample powders in ethanol solution were dropped onto copper grids covered with holey carbon support films. The conductivity of the as-prepared samples was measured at room temperature with the standard four-probe method by using Keithley 2750. In the case of electromagnetic parameter measurement PEDOT/SWCNT composites mixed with paraffin wax at the weight fraction of 10 wt% were pressed into a toroidal shape with an outer diameter of 7 mm and an inner diameter of 3 mm. Subsequently, the measurements of relative complex permittivity (ε_r) and permeability (μ_r) were carried out by using HP8722ES network analyser at the frequency range of 1–18 GHz. The reflection loss was calculated from the obtained values of ε_r and μ_r.

3. Results and discussion

3.1. Structures and morphology

Raman spectroscopy is widely employed to probe the structure–property for both conjugated polymers and CNTs. In Fig. 1, the typical Raman spectra recorded using 532 nm excitation of the pristine SWCNTs, PEDOT and PEDOT/SWCNTs are presented in two band groups: (A) the radial breathing modes (R band) at 100–350 cm^{-1} [26]; (B) the tangential mode (TM) range at 1400–1700 cm^{-1} with D band around 1340 cm^{-1} and G′ band near 2660 cm^{-1} [27].

The Raman shifts of the observed bands for pristine SWCNTs, PEDOT and PEDOT/SWCNTs are listed in Table 1. The Raman spectra of polythiophene family display three main lines coupled to the electronic transition. So the dominant lines of PEDOT are around 1431 cm^{-1}, corresponding to C_α═C_β stretching region, which is absolutely symmetric, in-phase vibrations of thiophene rings that spreads over the entire polymer chain [28–30]. But a blue shift in the Raman peak is observed for PEDOT/SWCNT composite moving to 1433 cm^{-1}. Changes in the band positions are expected for high doping level of PEDOT due to the combination with carboxyl SWCNTs [31]. When the number of dopant ions in the pristine PEDOT increases, the symmetric C_α═C_β stretching band shifts to a higher wavenumber, leading to an enhancement in the proportion of the oxidized PEDOT structure. Thus the conductivity is elevated which is in agreement with the higher conductivity of PEDOT/SWCNTs in comparison to those of constituents as shown in Table 2. The similar results on shifting symmetric C_α═C_β stretching band with increasing polymerization potential have been discussed in previous reports, where the Raman band at 1414 cm^{-1} in the reduced PEDOT is shifted to 1445 cm^{-1} in the highly doped PEDOT [32–34]. The Raman band can be seen at 1363 and 694 cm^{-1}, which are assigned to C_β—C_β stretching and a C—H