Negative permittivity and negative permeability of multi-walled carbon nanotubes/polypyrrole nanocomposites

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ABSTRACT

Multi-walled carbon nanotubes(MWCNTs)/polypyrrole(PPy) nanocomposite particles were synthesized by in-situ polymerization. Negative permittivity and negative permeability appeared simultaneously in MWCNTs/PPy nanocomposites with different content of MWCNTs. It was found from SEM analysis that MWCNTs/PPy nanocomposite particles were randomly packed with a large number of micropores, and formed a lot of conductive loops around the micropores, some MWCNTs could be cross the micropores and increase the number of conductive loops. In the meantime, MWCNTs themselves in MWCNTs/PPy composite also formed many conductive networks. The negative permittivity behavior stem from the plasma oscillation of delocalized electrons in the conductive networks, and the negative permeability was attributed to the diamagnetic response of ring currents in the plentiful conductive loops. This study should initially find a double negative metamaterial in polymer composites.

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1. Introduction

Double negative materials are metamaterials with simultaneously negative permittivity and permeability, which can be applied to perfect lens, miniaturization microwave devices, antennas, cloak of invisibilities and so on. Because of its negative refraction effect, inverse Doppler effect and other singular characteristics, double negative materials have attracted extensive attention in recent years. As early as 1968, basic theories of electromagnetic metamaterials were proposed by Veselago [1]. In 1996, J. B. Pendry [2] predicted constructed periodic array models using artificial media including thin metal rods and split-ring resonators (SRR) had equivalent negative permittivity and equivalent negative permeability in microwave band in theory. According to the theoretical model of J. B. Pendry, D. R. Smith [3] prepared the first metamaterial in microwave band through combined open resonator rings with a parallel array of metal wires, whose equivalent permittivity and equivalent permeability were all negative. Metamaterials in X band were also successfully produced in 2001 by D. R. Smith [4], and the real existence of negative refraction effect was proved by a prism experiment [5]. Since then, various electromagnetic metamaterials were constructed to achieve double negative property [6–8]. However, the special properties of the traditional artificial double negative materials are derived from the periodic ordered structures rather than the materials themselves. The metamaterials without periodic ordered blocks are so-called "intrinsic metamaterials", whose performances significantly depend on their composition and component distribution.

Intrinsic metamaterials has been confirmed and developed rapidly in composites with metal particles. In 2002, S. T. Chui [9] theoretically predicted composites of magnetic metal particles with specific distribution could achieve double negative property. In 2012, R. H. Fan et al. achieved double negative properties in microwave frequency range via nano Ni or Fe particles grown on foamed alumina [10,11]. However, the research of intrinsic metamaterials with double negative property in polymer composites developed slowly. In 2001, Epstein [12] reported that polyaniline(PANI) doped by camphor benzene sulfonic acid showed negative permittivity in the range of microwave frequency. The study incorporated doped conductive polymers into the field of electrical metamaterials. Zhu et al. [13] found negative permittivity in graphene/polyaniline composites or MWCNTs/polyaniline composites. MWCNTs had an excellent amplification effect on the negative permittivity of polyaniline. Gu et al. [14] reported β-SiC/polyaniline nanocomposites with negative permittivity. W. Zhong [15] reported negative permittivity in carbon nanofibers(CNFs)/

polyetherimide composites. X. Zhang [16] found negative permittivity in Polypropylene (PP)/carbon nanotubes (CNTs) nanocomposites. In addition to PANI, negative permittivity in PPy and its composites also appeared. Zhu et al. [17] showed negative permittivity of WO_3/PPy composites in certain frequency range. Following this study, PPy with CNFs and graphene with different sizes also obtained negative permittivity [18]. Moreover, Guo et al. [19] found negative permittivity in Fe_3O_4/PPy composites. But double negative property in polypyrrole composites has not been found until now.

In present paper, MWCNTs/PPy nanocomposite particles were synthesized by in-situ polymerization. Interestingly, negative permittivity and negative permeability appeared simultaneously in the frequency range of 945–1000 MHz of 20 wt%MWCNTs/PPy nanocomposites, 885–1000 MHz of 30 wt%MWCNTs/PPy nanocomposites, 870–1000 MHz of 40 wt%MWCNTs/PPy nanocomposites and 880–1000 MHz of 50 wt%MWCNTs/PPy nanocomposites. Such wide range of double negative properties in polymer composites has not been reported. We believe that double negative polymer composites have a wide application in medical, ultrashort wave and other fields.

2. Experimental section

2.1. Chemicals

Pyrrole, ammonium persulfate (APS), p-toluene sulfonic acid (PTSA) were purchased from Sinopharm Chemical Reagent Co. Ltd. China. Multi-walled carbon nanotubes were purchased from Cheaptubes (outer diameter: 30–50 nm, length: 10-20μm). All the chemicals were used as-received without any further treatment.

2.2. Fabrication of PPy and MWCNTs/PPy composite

Firstly, PTSA (proton acid, 10.271 g), APS (oxidant, 7.393 g) and different contents of MWCNTs (0-80 wt%) were dispersed in 600 ml distilled water with ultrasonic for 40min (power 320 W). The resultant dispersion was placed into a crystallizing dish containing a mixture of ice and water. Next, pyrrole (Py, 4.347 g) in 120 ml water was added dropwise into the dispersion solution under a magnetic stirring with 1000r/min speed for 10min when temperature of the dispersion solution about 0 °C. This dispersion with Py was treated with ultrasonic for 60min (320 W) in the ice/water mixture. Finally, the product solution was filtrated in a sand core funnel and washed with deionized water and ethanol until the supernatant was transparent. MWCNTs/PPy composites were obtained after 6 h of drying in an air blast oven at 80 °C.

2.3. Characterization

Scanning electron microscope (SEM) images were taken on a Quanta FEG 250 field emission scanning electron microscopy. Dielectrical properties were investigated by an LCR meter (Agilent, E4991A) equipped with a dielectric detector (Agilent, 16453A) at the frequency of 1 MHz to 1 GHz at room temperature. The sample was a wafer with the diameter of 20 mm and thickness of 2–4 mm prepared by moulding composite powder in 8.0 MPa pressure. The wafer was coated with conductive silver paste on top and bottom surface and dried in vacuum at 80°Cfor 4 h in order to form two electrodes before testing. Permeability properties were investigated by an LCR meter (Agilent, E4991A) equipped with a permeability detector (Agilent, 16454A) at the frequency of 1 MHz to 1 GHz at room temperature. The sample was a toroidal core structure wafer with the inner diameter of 5 mm and outer diameter of 15 mm and thickness of 4–7 mm prepared by moulding composite powder in 8.0 MPa pressure.

3. Results and discussion

The real permittivity of PPy and its composites filled with 10–80 wt%MWCNTs in the frequency range of $1-1 \times 10^3$ MHz at room temperature is shown in Fig. 1 (a). The permittivity of PPy and MWCNTs/PPy nanocomposites with 10–50 wt% MWCNTs is negative in the test range, and absolute value of their negative permittivity decreases with the frequency increasing. No permittivity transition from negative to positive is observed. Although absolute value of negative permittivity of MWCNTs/PPy nanocomposites with 60–80 wt% MWCNTs also decreases with frequency increasing, permittivity transition from negative to positive occurs. Moreover, the transition frequency decreases with the increase of MWCNTs content, respectively 565 MHz, 286 MHz, 191 MHz, as shown in Fig. 1(b). In lower frequency range, the trend of negative permittivity with MWCNTs content is not pronounced when MWCNTs are added less than 60 wt%, while the absolute value of the negative permittivity of composites increases with the increase of MWCNTs when MWCNTs are added more than 60 wt%. The negative permittivity of MWCNTs/PPy nanocomposites with 80 wt% MWCNTs reaches the maximum absolute value (-408936.5 at 1 MHz). Similar negative permittivity properties also appear in the WO_3/PPy composites, graphene/PPy composites and Fe_3O_4/PPy composites [17–19].

Fig. 1(c) presents the real permeability of PPy and its composites filled with 10–80 wt%MWCNTs in the frequency range of $1-1 \times 10^3$ MHz at room temperature. The permeability of PPy and its composites decreases with frequency increasing in the test range. Negative permeability surprisingly appears in MWCNTs/PPy nanocomposites with 20–80 wt% MWCNTs, as shown in Fig. 1(d) (transition frequency: 945 MHz, 885 MHz, 870 MHz, 880 MHz,875 MHz, 865 MHz, 880 MHz).

Fig. 1 (e) dielectric loss of PPy and its composites filled with 10wt-80 wt%MWCNTs in the frequency range of $1-1 \times 10^3$ MHz at room temperature. In lower frequency, dielectric loss increases with the increase of absolute value of negative permittivity. High dielectric loss reflects well conduction in MWCNTs/PPy nanocomposites. The dielectric loss is not changed obviously in the frequency band with negative permeability. Moreover, no loss peak appears in the composites.

The ATR curves of MWCNTs, PPy and MWCNTs/PPy nanocomposites are shown in Fig. 2 (a). MWCNTs has no obvious absorption peak, while PPy and its nanocomposites show the same peak locations at 1541 cm^{-1} and 1456 cm^{-1}, which corresponds to C=C and C–N stretching. The peak near 1301 cm^{-1} and 1209 cm^{-1} can be assigned to the C–H in-plane and out-of-plane deformation vibration, and the peaks at 1155 cm^{-1} and 964 cm^{-1} present C–C stretching and C–C out-of-plane deformation vibration respectively. These absorption peaks of PPy are almost consistent with the references [17,19]. The almost same peak locations of PPy and its nanocomposites demonstrate that the negative permittivity and negative permeability of MWCNTs/PPy nanocomposites are not aroused by the chemical reaction between MWCNTs and PPy.

The XRD curves of MWCNTs, PPy and MWCNTs/PPy nanocomposites are shown in Fig. 2 (b). The wide peak of PPy from 15° to 30° proves its amorphous structure,which is basically consistent with the references [19]. The diffraction peaks of MWCNTs at 25.6° and 43.5° indicates (002) and (100) crystal plane respectively. The intensity of the peak at 25.6° increases with the increase of MWCNTs, and no new diffraction peak appears. These indicate that the negative permittivity and negative permeability of MWCNTs/PPy composites are not attributed to the change of crystal structure.