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Multi-walled carbon nanotubes/polyaniline composites with negative permittivity and negative permeability

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A B S T R A C T

Intrinsic double negative metamaterials have been found in metal particles/ceramic composites, but polymer composites haven't achieved negative permittivity and negative permeability simultaneously until now. Negative permittivity and negative permeability appear simultaneously in multi-walled carbon nanotubes (MWCNTs)/polyaniline (PANI) composites in present study. No significant change in chemical bond and crystallization is found in MWCNTs/PANI composites through ATR and XRD tests. It is found from SEM analysis that MWCNTs/PANI composites form different morphology with the increase of MWCNT content. Occurrence of negative permittivity and permeability in MWCNTs/PANI composites derives for conductive network, closed circuit structure of MWCNTs and MWCNTs/PANI composite particles. The double negative property appears in the frequency range 955–1000 MHz in 40 wt% MWCNTs/PANI composites, 930–1000 MHz in 50 wt% MWCNTs/PANI composites, 925–1000 MHz in 60 wt% MWCNTs/PANI composites and 915–1000 MHz in 70 wt% MWCNTs/PANI composites. This study makes the properties of metamaterials no longer only depend on specific combination of structures, thus possesses great significance on research and development of metamaterials.

1. Introduction

Metamaterials are artificial composite structures or composite materials which possess physical properties without existing in natural materials proposed by Veselago in 1968 [1]. Their wave vector **k**, electric field **E**, and magnetic field **H** meet the left hand rule. J. B. Pendry predicted the periodic array models using artificial media including thin metal rods and split-ring resonators had equivalent negative permittivity and equivalent negative permeability in microwave band in theory in 1996 [2–4]. D. R. Smith prepared the first metamaterial through combined open resonator rings with a parallel array of metal rods [5]. The structural metamaterial has attracted considerable attention since then.

The special properties of structural metamaterial are derived from the arrangement of ordered structures. However, some composites without obvious periodic array were found possessing such negative permittivity in recent years [6–8]. Negative permittivity and permeability of these metamaterials obviously depended on their composition and distribution of components. These metameterials called intrinsic metameterials have greatly expanded the scope of metamaterials.

In the study of intrinsic metameterials, the development of metal composites is obviously faster than that of polymer composites. S. T. Chui theoretically predicted composites of magnetic metal particles with specific distribution could achieve double negative property in 2002 [6]. R. H. Fan et al. achieved double negative properties nearly 1 GHz with Ni or Fe nanoparticles grown on alumina foam 10 years later [7,8]. They believed that the negative permittivity behavior derived from the plasma oscillation of delocalized electrons in the conductive networks formed by Ni or Fe nanoparticles. Meanwhile, negative permeability was attributed to the plentiful conductive closed circuits formed by Ni or Fe nanoparticles in the composite. K. Hur et al. predicted that double negative property can be realized by three dimensional metal networks produced by a specific template [9]. The plasma oscillation of delocalized electrons in metal networks led to negative permittivity, meanwhile the strong diamagnetism of metal networks produced negative permeability. R. H. Fan injected Ag particles into porous $Y_3Fe_5O_{12}$ randomly and found the existence of double negative phenomena [10]. T. Tsutaoka et al. even mixed

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copper with yttrium iron garnet particles directly to prepare composite materials and achieved negative permittivity and negative permeability in microwave band [11], which was due to the negative permittivity of copper particles and negative permeability produced by yttrium iron garnet particles. So negative permittivity and negative permeability have been realized simultaneously in the composites of metal particles or ceramic particles (or networks).

The study of negative permittivity of polymer composites has also achieved some progress. Epstein reported that polyaniline doped with camphor benzene sulfonic acid showed negative permittivity in microwave frequency range in 2001 [12]. Gu et al. also found negative permittivity in PANI and polypyrrole (PPy) filled with WO_3, graphene, MWCNTs and $BaTiO_3$ in the frequency range of 20–10^3 Hz [13–19]. Qian et al. found negative permittivity in MWCNTs/phenolic resin composites, and the negative permittivity increased with the increase of MWCNT content in the range 10 M–1 GHz [20]. Zhang et al. showed MWCNTs/polypropylene (PP) composites with 2 wt% MWCNTs at 120 °C, 160 °C and 180 °C all had negative dielectric properties [21]. But double negative property similar with metal composites has not been realized in polymer composites. Our research group also made some laboratory investigation in nanoparticles/conductive polymers composites and proposed explanation of the negative permittivity of MWCNTs/PANI composites and oxide crystals/PANI composites using the “nano wire” theory [22,23]. The transition frequency of permittivity from negative to positive in MWCNTs/PANI composites was tested to move to high frequency with the increasing content of MWCNTs [22].

In present paper, MWCNTs/PANI composites with large content of MWCNTs are prepared and investigated. Negative permittivity and negative permeability are found simultaneously in MWCNTs/PANI composites in the frequency range of 915–1000 MHz and the relationship of negative permittivity and negative permeability with the structure of the MWCNTs/PANI composites is studied. Meanwhile, the generation mechanism of the negative permittivity and negative permeability in the MWCNTs/PANI composites is also explored. The MWCNTs/PANI composites have various advantages such as easy preparation, easy parameter adjustment and a wide range of use. This study provides a novel approach to develop metamaterials and will have a significant impact on the application of metamaterials.

2. Experimental

2.1. Chemicals

Aniline, ammonium persulfate (APS) and p-toluene sulfonic acid (PTSA) are purchased from Sinopharm Chemical Reagent Co. Ltd. China. Multi-walled carbon nanotube was purchased from Cheaptubes. All the chemicals were used as-received without any further treatment.

2.2. Fabrication of MWCNTs/PANI nanocomposites

Firstly, PTSA (proton acid, 5.167 g), APS (oxidant, 4.108 g) and different contents of MWCNTs were dispersed in 300 ml distilled water with ultrasonic for 40 min (power 320 W). The resultant dispersion was placed into a crystallizing dish containing a mixture of ice and water. Next, An (3.35 g) in 60 ml water was added dropwise into the dispersion solution under a magnetic stirring with 1000 r/min speed for 10 min when temperature of the dispersion solution about 0 °C. This dispersion with An was treated with ultrasonic for 6 h (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. Characterizations

Fourier transform infrared spectra (FT-IR) of the samples were recorded with a EQUINOXSS/HYPER FT-IR infrared spectrometer in the range of 4000–400 cm^{-1}. X-ray diffraction (XRD) analysis of the samples was by D/MAX 2550VB3+/PC under the test condition of diffraction angle 10–75°, continuous scanning 5°/min, tube voltage 40 kV and current 35 mA. 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 °C for 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 permittivity of PANI and MWCNTs/PANI composites filled with 10–90 wt% MWCNTs in the frequency range of 1–1000 MHz is shown in Fig. 1 (a). The permittivities of PANI and 10 wt% MWCNTs/PANI nanocomposites are all positive because their permittivities have turned from negative to positive in the range of 10^4–10^5 Hz [22]. Negative permittivity in MWCNTs/PANI composites appears in more than 20 wt% MWCNT content. The permittivities of MWCNTs/PANI nanocomposites with 20–50 wt% MWCNTs are all negative in the frequency range of 1–1000 MHz, as shown in Fig. 1 (b). The absolute value of negative permittivity of the MWCNTs/PANI composites increases with MWCNT content increasing,while the absolute value decreases in MWCNT content of 60–70 wt%, again increases in MWCNT content above 70 wt% and reaches the maximum in the MWCNTs/PANI composites with 90 wt% MWCNTs. Additionally, the permittivity transition from negative to positive appears in the frequency range of 100–1000 MHz when the content of MWCNTs is above 60%, as shown in Fig. 1 (b). The transition frequency becomes the lowest in the MWCNTs/PANI composites with 80% MWCNTs (181 MHz). The permittivities of MWCNTs/PANI composites with 60 wt% and 70% MWCNTs transform again to negative value after becoming positive value.

The permeabilities of PANI and MWCNTs/PANI composites with 10–90 wt% MWCNTs in the frequency range of 1–1000 MHz are shown in Fig. 1 (c). The permeability of PANI increases with frequency increasing, while the permeability of MWCNTs/PANI composites decreases with frequency increasing. The negative permeability is observed in MWCNTs/PANI composites with 40–80 wt% MWCNTs in the frequency range of 900–1000 MHz, as shown in Fig. 1 (d). In addition, the permeability does not transform from negative to positive in the measurement range, which indicates that the frequency of negative permeability is perhaps larger than 1000 MHz. The transition frequencies of MWCNTs/PANI composites with 10–70 wt% MWCNTs decrease with MWCNT content increasing, but they increase in more than 70 wt% MWCNT