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Generation mechanism of negative dielectric properties of nano-Fe_3O_4/PANI composites

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HIGHLIGHTS

- Nano-Fe_3O_4/PANI composites have negative permittivity which is significantly affected with the nano-Fe_3O_4 content.
- Improved structure model of "crystal-nano wire" is used to explain the generation mechanism of negative permittivity.
- Negative dielectric phenomenon of nano-Fe_3O_4/PANI composites is explained from the point of structure.

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ABSTRACT

Polyaniline (PANI) composites filled with inorganic particles have been discovered to possess high negative permittivity in recent years. It has been proved that PANI filled with some inorganic particles had better performance in negative permittivity than pure PANI. In this paper, the negative permittivity of nano-Fe_3O_4/PANI composites is investigatedindetail. Nano-Fe_3O_4/PANI composites have negative permittivity which is significantly affected with the nano-Fe_3O_4 content. Structural analysis indicates that there is no chemical bonding between nano-Fe_3O_4 and PANI, and nano-Fe_3O_4 is evenly distributed in the PANI when the nano-Fe_3O_4content is less. Thereby the improved structure model of "crystal-nano wire" is used to explain the generation mechanism of negative permittivity. This study reveals the negative dielectric phenomenon of nano-Fe_3O_4/PANI composites from the point of structure.

1. Introduction

Since D. R. Smith et al. first constructed left-hand material in 2000, metamaterials have aroused wide attention of researchers for years. Researchers put forward the construction of the left-handed material theoretically, such as R. X. Wu who constructed the left-hand material based on polarization ferrite material and metal wire [1,2]. This study made metal resonant structure become the main method to obtain the left-hand material at present [3–5]. From 1996 to 1999, J. B. Pendry predicted that constructed periodic array models had equivalent negative permittivity and equivalent negative permeability in microwave band in theory [6–8], laying an important foundation for the construction of the left-hand material. Soon afterwards, D. R. Smith first prepared the left-handed material in microwave band by combining open resonator rings with a parallel array of metal wires [9]. At the same time, the ring structure of split-ring resonators (SRR) was changed to the square ring structure in order to facilitate the design and experiment [10]. S. O. Brien et al. proposed photonic crystal with nanoscale symmetric ring structures [11], which had the similar effect of SRR. On this basis, T.M. Grzegorczyk et al. constructed the left-handed material with symmetric ring structures [12]. Later, a variety of structures were designed by researchers.

The special properties of the traditional artificial metamaterials were 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. Copper composite materials prepared by mixing the Cu powder with Polyphenylene Sulfide (PPS) resin powder showed negative permittivity spectra below a characteristic frequency f0 indicating the low frequency

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plasmonic state [13]. Researchers even found double negative properties in metal composites like silver/zirconium nickel oxide nanocomposites and $Fe_{53}Ni_{47}$/Cu granular composites [14,15]

Doped conductive polymers were also discovered to possess negative permittivity. Recently researchers have reported that conductive polymers filled with inorganic nanoparticles possessed negative permittivity. Guo obtained negative permittivity in the surface initiated polymerization (SIP) synthesized β-silicon carbide (β-SiC)/polyaniline (PANI) metacomposites [16]. Tanrıverdi obtained negative permittivity in $CoFe_2O_4$/PANI nanocomposites by adding $CoFe_2O_4$ nanoparticles in polyaniline [17]. Pure polyaniline had a relatively large negative permittivity (1–10 Hz, about −1025). The negative permittivity of $CoFe_2O_4$/PANI nanocomposites gradually translated from a negative to a positive valueand then fluctuated between positive and negative values with the increasing of $CoFe_2O_4$ content. From authors' view, the negative permittivity of $CoFe_2O_4$/PANI nanocomposites may be due to the plasma resonance improving its conductivity at a relatively low frequency. There are free electrons and charged ions in the plasma, which has high conductivity thus can enhance the conductivity of the composites. Fe_3O_4 has unique electromagnetic properties, which often appears in the study of electromagnetic wave absorption [18], electromagnetic wave shielding [19], and metamaterials. Zhang et al. got a tunable negative permittivity based on an Fe-rich structure (Fe–Fe_3O_4–Al_2O_3) formed in an Al-rich structure (FeA-l_2O_4–Al_2O_3) [20]. Guo found the negative permittivity could only realize in the nanocomposites of polyaniline with more than 10% content of Fe_3O_4 [21]. The study of H. Kavas et al. also showed that the temperature exerted a great influence on the negative permittivity of Fe_3O_4/PANI nanocomposites [22]. Negative permittivity of the Fe_3O_4/PANI nanocomposite at 120 °C was 30 times as much as at 80°C and more than 60 times at room temperature, and it was considered that the negative permittivity was caused by the low frequency resonance. In addition to PANI, negative permittivity also appeared in polypyrrole (PPy) composed with magnetic particles. Guo et al. found negative permittivity in Fe_3O_4/PPy composites [23]. Whether these phenomenons are related with the crystal structure of fillers is worth investigating.

Our research group have studied negative permittivity in micronoxide crystal/PANI composites and nano-Al_2O_3/PANI composites and put forward the structure model of “crystal-nano wire” [24,25], which effectively explained the appearance and increase of negative permittivity in PANI and its composites. On the basis of the above researches, the negative dielectric properties of nano-Fe_3O_4/PANI composites are studied. The nano-Fe_3O_4/PANI composites have larger negative permittivity than that of nano-Al_2O_3/PANI composites. It is considered that the crystal structure in nano-Fe_3O_4 component has intrinsic conduction path, which leads to a certain extent of polarization voltage which can't continue to increase. Therefore, an improved structural model of “crystal-nano wire” is proposed to explain the effect of nano-Fe_3O_4 on the negative permittivity. This model explains the negative permittivity of nano-Fe_3O_4/PANI composites from the point of view of the material structure, which is more in-depth than the original interpretation of “low frequency resonance".

2. Experimental

2.1. Chemicals

Nitric acid, sulfuricacid, hydrochloric, potassiumdichromate, aniline, ammonium persulfate (APS), p-toluene sulfonic acid (PTSA), nano-ferriferrous oxide (nano-Fe_3O_4, 20–30 nm) were purchased from Sinopharm Chemical Reagent Co. Ltd. China. All the chemicals were used as-received without any further treatment.

2.2. Fabrication of nano-Fe_3O_4/PANI composites

Firstly, PTSA (proton acid, 5.167 g), APS (oxidant, 4.108 g) and nano-Fe_3O_4 (0-5 wt%) were dispersed in 300 ml distilled water with ultrasonic dispersion for 40min (power 320 W). The resulting dispersion solution was placed in a crystallizing dish containing a mixture of ice and water. Next, Aniline (An, 1.75 g) in 60 ml water was added dropwise into the dispersion solution under a 1000r/min speed magnetic stirring for 10min when temperature of the dispersion solution was lower than 10 °C. And then the dispersion with An was treated with ultrasonic for 60min (320 W) and reacted for 6 h 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. Nano-Fe_3O_4/PANI composites were obtained after drying for 6 h 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. Dielectric properties were investigated by a LCR meter (Agilent, E4980A) equipped with a dielectric texture (Agilent, 16451B) at the frequency of 20 Hz to 2×10^6 Hz at room temperature. The sample was a wafer with the diameter of 10 mm and thickness of 1–3 mm by moulding nano-Fe_3O_4/PANI 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 tested. Resistivity was tested by electrochemical workstation CHI660E in the frequency range of $1–1 \times 10^5$ Hz.

Nano-Fe_3O_4/PANI composites are synthesized by situ polymerization, and the situ polymerization method is similar with the polymerization of nano-Al_2O_3/PANI composites [25]. Fig. 1 (a) presents permittivity vs. frequency of PANI and nano-Fe_3O_4/PANI composites with 1 wt%-5wt% nano-Fe_3O_4. The permittivity of PANI shows a large negative value and converts to positive value with frequency increasing in the frequency range of $20–2 \times 10^6$ Hz at room temperature. The negative permittivity of PANI reduces from -2.3×10^4 to 0 in the frequency range of $20–2.3 \times 10^4$ Hz and becomes positive when above 2.3×10^4 Hz. In other studies, PANI had a smaller negative permittivity (close to −1200) [26] or positive permittivity [27]. The values of permittivity of nano-Fe_3O_4/PANI composites with 1 wt%-4wt% nano-Fe_3O_4 at 20 Hz are shown in Table 1, whose absolute values are more than 10 times of permittivity of PANI. But the negative permittivity of nano-Fe_3O_4/PANI composites is much smaller than that of nano-Al_2O_3/PANI composites [25]. Fig. 1 (b) presents imaginary part of permittivity vs. frequency of PANI and nano-Fe_3O_4/PANI composites with 1 wt%-5wt% nano-Fe_3O_4. PANI exhibits the largest negative imaginary part of permittivity. Except 1 wt% nano-Fe_3O_4/PANI composites, the negative imaginary part of permittivity decreases with increasing nano-Fe_3O_4/PANI content. The imaginary part of permittivity of all samples reduces and becomes positive when frequency increasing. The switching frequencies for each sample are quite consistent with that of permittivity.

Fig. 2 shows FT-IR curves of the nano-Fe_3O_4, PANI and nano-Fe_3O_4/PANI composites with 1 wt%, 4 wt%, 5 wt% nano-Fe_3O_4 respectively. The absorption peaks at 1564 cm^{-1} and 1483 cm^{-1} are attributed to C=C stretching vibration on the benzene rings. Peak at