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Growth of coiled amorphous carbon nanotube array forest and its electromagnetic wave absorbing properties

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ABSTRACT

Coiled amorphous carbon nanotube (CACNT) array was prepared by chemical vapor deposition method. The experimental results indicated that the length of as-prepared CACNT array was about 30 μm. The electromagnetic wave absorbing properties were studied through comparison among CACNTs, CACNT-$La(NO_3)_3$, CACNT-(Fe, Co, Ni) and CACNT-reduced graphene oxide (RGO). The experimental results showed the maximum frequency bandwidth of CACNT-(Fe, Co, Ni) was 6.4 GHz below −5 dB and 2.3 GHz below −10 dB separately. Compared to the pure CACNTs, all the frequency bandwidth had been broaden after adding the modified agent. Meanwhile, the additive of rare earth ions La^{3+} could effectively increase the maximum absorption peak (−17.94 dB at 8.96 GHz).

1. Introduction

Recently, electromagnetic wave absorption materials [1–5] with favorable properties such as low density, low cost, strong absorption and thin thickness within a wide frequency range are strongly needed, because of the rapid development of electronic devices, electromagnetic wave communication and the pollution of electromagnetic interference. Using the relative complex permittivity to both real (dielectric constant) and imaginary (magnetic loss) components, the parameter requirements for electromagnetic wave absorption are well established. The performance of electromagnetic wave absorption is dominated by the complex permittivity and the microstructure of absorber material. The materials used as electromagnetic wave absorbers must have higher energy loss with high imaginary component of permittivity and enable better absorption of incident radiation in synchronized frequencies by dissipating it as heat. So, the commonly used carbon materials have 3 kinds: U carbon, carbon black and carbon nanotube (CNT), and these carbon materials added with 15 wt% were used to prepare the samples, the maximum absorption peak of U carbon is −12 dB, while that of carbon black is −6 dB, and carbon nanotube is −11 dB [6].

In fact, CNTs have both metal and semiconductor characteristics [7]. Meanwhile, CNTs have special helical structures and chirality [8], which will produce special new electromagnetic effects. As for the performance, the unique mechanical, electrical and magnetic characteristics of CNTs indicate that it will surely have a broad application in the new stealth materials for electromagnetic wave absorption [9,10]. What's more, the electromagnetic wave absorption material prepared by CNTs has a wide frequency band, good controllability, great compatibility, light quality and thin thickness, which is easy to satisfy the command of microwave absorbing material: “thin, light, wide and strong”.

Coiled amorphous carbon nanotube (CACNT) array with unique three-dimensional spiral structures [11–14] has drawn much attention due to their potential applications such as high-performance electromagnetic wave absorbers, micro-/nano-scale solenoids, heaters and springs, electromechanical sensors, tactile sensors, and novel reinforcements in high-strain and semiconductive composites. The forest as well as the spring structure can cause the multiple reflections of incident waves and consume the waves into resistance heat.

In this work, CACNT forest was fabricated through CVD method. The electromagnetic wave absorbing properties were studied through comparison with CACNTs, CACNT-$La(NO_3)_3$, CACNT-(Fe, Co, Ni) and CACNT-reduced graphene oxide (RGO). The influence and mechanism of the forest or spring structure were discussed. The possible assumptions were proposed to explain the

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electromagnetic properties of the spring forest structures. The experiments mainly focused on the influence of combining different materials into CACNTs. So we set the same mass ratio of the efficient materials. As for the impact of other CACNT amounts, we will explore it in the later study.

2. Experimental

The growth of CACNTs was performed by floating catalyst CVD [15] in a quartz tube reactor (length 80 cm and diameter 5 cm). The reaction temperature was set at 750 °C, and argon gas controlling the flow speed of 200 sccm was used as the carried gas. The xylene, ferrocene and nickelocene solution (the mole ratio of C: Fe: Ni is 30: 1: 0.8–1.6) was used as carbon sources and the catalyst precursor was injected into the reactor by a syringe pump at the speed of 0.3–0.6 ml/min. The samples were obtained from the tube reactor and collected for further characterization. In order to obtain CACNT-$La(NO_3)_3$, CACNT-(Fe, Co, Ni) and CACNT-RGO composites, CACNT was mixed with $La(NO_3)_3$, Fe-Co-Ni particles and RGO by ball milling method. The mass ratio of CACNTs and the additive was set as 10:1. The obtained powder was heated to 700 °C under Ar protection gas for 1 h.

Transmission electron microscope (TEM, Tecnai G2 F30, FEI), field emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL), and X-ray diffraction patterns (XRD, X'Pert PRO MPD, PANalystal, $\lambda = 0.154$ nm) were used for qualitative analyses on the surface morphology, structural properties and component composition of all samples. The samples which were used for the characterization of electromagnetic wave absorbing properties were prepared by mixing 15 wt% CACNT composite with 85 wt% molten bismaleimide resin (BMI), then made into a doughnut-shaped sample (φ_{out}: 7.03 mm, φ_{in}: 3.00 mm). The complex permittivity (ε', ε'') and permeability (μ', μ'') components as the function of frequency of a sample were measured using a E8562B vector network analyzer (Anritsu: 10 MHz-20 GHz).

3. Results and discussion

Fig. 1(a) is SEM image of CACNT sample scratched from the quartz tube. As can be seen from Fig. 1(a), the length of the CACNT array is about 30 µm. The array formation is due to the high density of the CACNTs, because there is not enough space for CACNTs to grow into other directions but squeeze each other into vertical direction. Fig. 1(b) is SEM image of CACNTs. The screw pitch is about 250 nm and the coil diameter is about 200 nm. The spiral structure is due to the nonuniform evolution speed of carbon atoms from the catalysts. The reason is mainly because that compared with the pure iron particles, the additive of nickel may make the structure and morphology of the catalyst unsymmetrical, leading to the uneven growth rate and the helical structure. Fig. 1(c) is the TEM image of CACNT-$La(NO_3)_3$. The mean radius of $La(NO_3)_3$ wrapped by carbon nanotubes is about 300 nm. $La(NO_3)_3$ and CNTs are well connected. Fig. 1(d) shows TEM image of CNT-RGO. CNTs are interconnected with RGO. The black block inside the tube is the catalyst. Fig. 1(e) and (f) are the TEM images of CACNTs. The curvature of the CACNT is obvious. There are a large number of carbon atoms with random arrangement proving the amorphous structure. The catalyst shows cubic shape. Fig. 1(g) and (h) are XRD spectra of CACNT-$La(NO_3)_3$, CACNT-(Fe, Co, Ni), CACNT-RGO and graphite. The XRD spectrum of CACNT-(Fe, Co, Ni) is similar with CACNT-RGO, except the peak of Co. CACNT-RGO composite has the residual Fe-Ni catalyst, which explains the Fe and Ni peaks. $La(NO_3)_3$ peak is mild and not obvious, which might be due to the quantity is smaller compared with CACNTs. Fig. 1 (h) clearly exhibits that the structures of CACNT-$La(NO_3)_3$, CACNT-(Fe, Co, Ni), CACNT-RGO are amorphous compared to the crystal of graphite. It is in agreement with the amorphous structure in Fig. 1(f). Fig. 1(i) further proves the amorphous and defective states of CACNTs. Compared with the graphite curve, the D-mode and G-mode in curve CACNTs are wider, and D-mode is larger than that of G-mode, and the relative intensity (I_D/I_G) of D-mode and G-mode is larger, showing the amorphous structure of CACNTs. A high D-mode and a relatively low 2D-mode further indicate that this structure has many defects, and the reason for the formation of the amorphous structure D-mode is attributed to the tensile vibration modes of C-H bonds formed by hydrogen impurity introduced during high temperature oxidation. The above results confirm that the coiled CNTs have amorphous structure.

The electromagnetic wave absorption properties are correlated with their relative complex permeability ($\mu_r = \mu'$- $j\mu''$) and permittivity ($\varepsilon_r = \varepsilon'$ - $j\varepsilon''$) [16–18]. The frequency dependence of complex permeability and permittivity of four composites are measured using a network analyzer. The real permittivity (ε') and real permeability (μ') present the storage ability of microwave energy, while the imaginary permittivity (ε'') and imaginary permeability (μ'') represent dissipation ability of microwave energy [19–25]. The complex permittivity (ε', ε'') and permeability (μ', μ'') spectra of CACNT composite *vs* frequency are shown in Fig. 2(a-d). The permittivity and permeability are used for characterization of dielectric constant and magnetic loss properties of the absorbing materials [26–28]. In Fig. 2(a and b), the dielectric constant (ε') and dielectric loss (ε'') of the three modified composite are better than that of CACNT. The CACNT-$La(NO_3)_3$ curve fluctuates versus the frequency and the other three samples appear a more stable trend. This might be due to that when the electromagnetic field changes faster than the charge carrier number, the electron may obtain more energy with the frequency increasing, leading to the tunnel effect and obvious conductivity change. In Fig. 2(a and b), the dielectric constant (ε') and dielectric loss (ε'') of CACNT-RGO and CACNT-(Fe, Co, Ni) are higher than that of CACNTs, which can be explained by the good conductivity of RGO and Fe-Co-Ni. The CACNT-$La(NO_3)_3$ composite has better dielectric polarization and relaxation effects. Noticeably, the ε' values of the CACNT-$La(NO_3)_3$ sample are the highest among other samples, which suggests the more energy storage and polarization. Furthermore, one can observe that the CACNT-$La(NO_3)_3$ sample shows the largest ε'' values in the four samples, which indicates the superior dielectric loss [19]. When the conductive phase is distributed in the insulating matrix to form composite materials, the free charge gathering will exist in the insulation/conductor interface due to the difference in the two phase conductive performance. The interfaces can induce additional interfacial polarizations, which is beneficial for the dissipation of electromagnetic wave energy. Moreover, based on the free electron theory, $\varepsilon'' \approx 1/(\pi\varepsilon_0\rho f)$, where ρ is the resistivity. The conductivity of the CACNT-$La(NO_3)_3$ composite is higher than that of other composite samples [19–23]. The high tube density of the array structure may increase the probability for the tubes to overlap and twine each other for forming conductive network inside $La(NO_3)_3$ to improve the dielectric polarization properties. In Fig. 2(b), the real permeability of CACNT-(Fe, Co, Ni) is lower than others, the reason why CACNT-(Fe, Co, Ni) including magnetic composition is smaller than others containing non-magnetic constituents is the limit of this experiment itself. This experiment is a compared experiment. The mass ratio of CACNTs and the additive was set as 10:1, which causes the volume of the additive in the composites is not the same. The volume of the non-magnetic constituents may be much bigger than that of the magnetic composition when having the same mass, which means that