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Short communication

Microwave absorbing property of Fe-filled carbon nanotubes synthesized by a practical route

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Abstract

Fe-filled carbon nanotubes were prepared reliably and economically via pyrolyzing of ferrocene and activated carbon. The sample was characterized by high-resolution transmission electron microscopy, electron diffraction and fast Fourier transforms. The complex relative permittivity and permeability parameters were measured in a frequency range of 2–18 GHz and microwave absorbing behavior was investigated. The sample exhibits the maximum reflection loss and the widest bandwidth of below −5 dB is −11.29 dB and 4.13 GHz (matching thickness = 2.5 mm), respectively.

Keywords: Carbon nanotubes; Electromagnetic parameter; Microwave absorbers; Pyrolyzing synthesis

1. Introduction

Metal-filled carbon nanotubes have considerable potential for engineering applications because of the novel structure of encapsulating second phase inside carbon shells can immunize the encapsulated species against environmental degradation effects while retaining their intrinsic properties, which make the metal-filled carbon nanotubes exhibit unique electric, magnetic and nonlinear optical properties, and can also offer an opportunity to investigate dimensionally confined system. And it has been suggested that these striking properties might find their wide promising applications such as magnetic data storage, xerography and magnetic resonance imaging [1,2]. So far, various synthesis methods has been employed to prepare metal-filled carbon nanotubes, including wet-chemical methods [3,4], arc techniques [5,6], catalytic chemical vapor deposition [7,8] and pyrolysis of organometallic compound [9–11], etc.

Pyrolysis of metallocenes has been well proved to be a promising way in preparing not only multi-wall nanotubes, single-wall nanotubes [12,13], but also carbon nanotubes encapsulated metals [9–11]. This approach is based on the pyrolysis of metallocenes, which acts as the carbon resource and the important catalysts. Also, it offers the possibility of controlling the nanoscale and the microstructure of materials by changing the precursors or the reaction temperature, and the process is a relatively simple way of preparing chemically homogenous, high-purity and phase-pure powders at a lower temperature. A considerable amount of recent work has been devoted to synthesis and to probe new properties of composites prepared by pyrolysis of metallocenes process. The interest of hybrid materials carbon nanotubes encapsulation of metal thus simulated researchers to extensively enlarge the range of the carbon precursors from acetylene [12], benzene [13], thiophene [14,15] to C^{60} [16]. However, most procedures reported to date for carbon nanotubes encapsulated with nanoparticles have applied at least two steps, namely, preparation of CNTs followed by filling of the CNTs, and the carbon resource such as thiophene and C^{60} is so expensive. Therefore, the lack of a process by which these materials can be fabricated reliably and economically has severely hindered their applications.

In this paper, Fe-filled CNTs were prepared reliably and economically via a straightforward, one-step method by using activated carbon as carbon resource. CNTs modified by coating [17,18] or filling [19] with metal is commonly use as a good absorber for microwave absorbing technology. So we focus our attention on the microwave absorbing properties of Fe-filled carbon nanotubes. In addition, combining the promising properties of the encapsulated metal and carbon nanotubes, we believe that the Fe-filled CNTs composites are likely to be used in nanoelectronics devices, magnetic recording media and biological sensors.

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2. Experimental

The method for fabricating Fe-filled carbon nanotubes is as follows: activated carbon (C.P.) and ferrocene (A.R.) were used without further pre-treatment. In a typical synthesis, firstly, activated carbon and ferrocene were mixed physically with desired molar ratio and loaded into the cymbiform crucibles, then put into a conventional tube furnace. The reactor was heated at 21 K/min to the desired temperature (1000 °C) and was kept at this temperature for 3.0 h in a N_2 stream (~20–40 ml/min). After allowing it to cool naturally to ambient temperature, black powder-like solid was obtained from inside the cymbiform crucibles. The morphology of the sample was observed using a JEM-2010 (JEOL) high-resolution transmission electron microscope (HRTEM). Fast Fourier transforms and electron diffraction were taken and analyzed. The mixing ratio of Fe-filled MWNTs-to-olefin was fixed at 20 wt.%. The testing specimens have a toroidal shape with both thickness being 1 mm and outer and inner diameters being 7.0 and 3.0 mm, respectively. ε', ε'', μ' and μ'' are measured versus frequency range in the 2–18 GHz with a HP8722ES vector network analyzer. The absorbing properties with different thickness were calculated with equation as follows [20]:

$$\text{R.L. (dB)} = 20\log_{10}\left|\frac{Z_{\text{in}}-1}{Z_{\text{in}}+1}\right| \quad (1)$$

$$Z_{\text{in}} = \left(\frac{\mu_{\text{r}}}{\varepsilon_{\text{r}}}\right)^{1/2}\tanh\left[j\left(\frac{2\pi fd}{c}\right)(\mu_{\text{r}}\varepsilon_{\text{r}})^{1/2}\right] \quad (2)$$

where Z_{in} is the normalized input impedance relating to the impedance in free space, $\varepsilon_r = \varepsilon' - j\varepsilon''$ and $\mu_{\text{r}} = \mu' - j\mu''$ is the complex relative permeability and permittivity of the material, d is the thickness of the absorber, and C and f are the velocity of light and the frequency of microwave in free space, respectively. The impedance matching condition is given by $Z_{\text{in}} = 1$ to represent the perfect absorbing properties. The impedance matching condition is determined by the combinations of six parameters ε', ε'', μ', μ'', f and d. Also, knowing ε_{r} and μ_{r}, the R.L. value versus frequency can be evaluated at a specified thickness.

3. Results and discussion

3.1. Morphology observation

The obtained solid materials are black voluminous powder, exhibiting strong ferromagnetic property. Part filled and full filled CNTs were found in the low magnification TEM images as shown in Fig. 1(a) and (b), nanotubes with an average outer diameter and inner diameter between 60 and 80 nm and 30 and 50 nm, respectively, length up to 1–2 μm, and the purity of CNTs is more than 90%. Fig. 2 and the inset in Fig. 1(b) are high magnification image of the nanotubes shown by an arrow in Fig. 1(a) and (b), respectively. It is worth noticing that both multiwalled and double-lay CNTs were found, and full filled situation prefer to occur in the double-lay CNTs, as shown Fig. 1(b). Filled Fe nanowires are of similar diameters in cross section of carbon nanotubes, no obvious voids can be observed between the

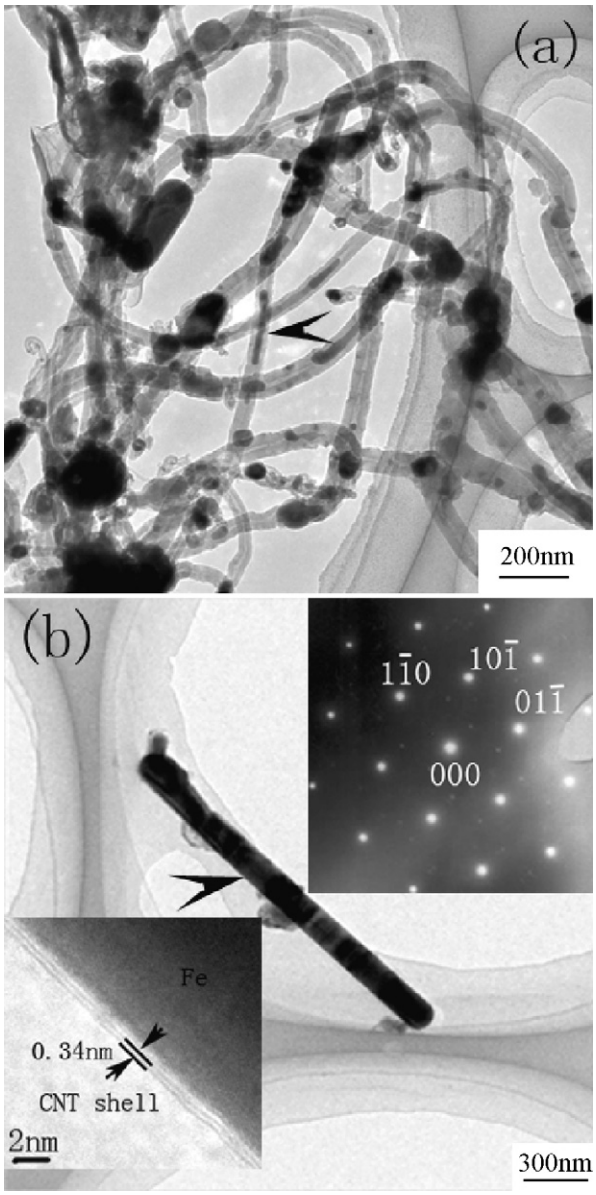

Fig. 1. TEM images of Fe-filled CNTs. The insets in (b) shows the electron diffraction pattern recorded perpendicular to the nanotube long axis and the high magnification image of the nanotubes shown by an arrow in (b), respectively.

nanowires and the shell. The tubular layers of both multiwalled and double-lay CNTs have the same spacing of lattice fringes (about 0.34 nm), which is close to that of the graphite (0 0 2) planes. The encapsulated iron nanowires are crystal and have lattice fringe spacing of 0.20 nm (Fig. 2), correspond to the (1 1 0) plane of the bcc-Fe crystal (JCPDS 6-0696). Combining with the electron diffraction pattern of the Fe-filled CNTs (Fig. 1(b)), confirm the filled iron nanowires are α-Fe.

3.2. XRD analysis

XRD characterization is performed to further validate the corresponding structure of the TEM data. Fig. 3 presents the profile of the as-synthesized product. The peaks at 44.9 and 65.7 °C can be identified as the (1 1 0) and (2 0 0) planes of bcc-Fe (JCPDS