

# Effect of purification of the electrical conductivity and complex permittivity of multiwall carbon nanotubes

C. A. Grimes<sup>a)</sup>

*Department of Electrical Engineering & Materials Research Institute, 208 Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802*

E. C. Dickey

*Department of Materials Science & Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802*

C. Mungle and K. G. Ong

*Department of Electrical Engineering & Materials Research Institute, 204 Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802*

D. Qian

*Department of Materials Science & Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802*

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In this work we report on the complex permittivity spectra and electrical conductivity of both as-fabricated and graphitized multiwall carbon nanotubes (MWNTs). The high-temperature annealing removes the Fe<sub>3</sub>C catalyst particles present in the as-fabricated material, enabling the intrinsic MWNT properties to be measured. The permittivity spectra of 1 wt % MWNT-polystyrene composite films are measured from 75 to 1875 MHz. Comparison of measurements with an appropriate effective medium model shows that the residual catalyst inclusions in the core of the nanotube increase the average electrical conductivity by approximately a factor of 3.5. © 2001 American Institute of Physics. [DOI: 10.1063/1.1400100]

## INTRODUCTION

Carbon nanotubes have received considerable attention due to their interesting electrical and physical properties.<sup>1–15</sup> For example, the ability to produce nanotubes in semiconducting or metallic form offers the possibility of molecular circuit devices,<sup>7</sup> while their size and electrical properties make them ideally suited for application in field effect devices.<sup>8</sup> The outstanding mechanical properties of nanotubes offer the potential for fabrication of high-strength composite materials,<sup>9</sup> while nanotube composites with a near-unity value of compressive-to-tensile strengths appear possible.<sup>10</sup> The dispersal of such high aspect ratio conducting or semiconducting nanotubes into dielectric hosts also offers an exciting opportunity for producing strong, lightweight electromagnetic devices such as antennas or shielding materials.

To date the lack of an economical high-volume fabrication technique capable of producing high purity multiwall nanotubes (MWNTs) and single-wall nanotubes (SWNTs) has significantly hindered experimental measurement of intrinsic nanotube properties and development of commercial applications. High temperature annealing, or graphitization, of nanotubes has, however, recently been shown to be a successful, low-cost procedure for removing the residual catalyst particles<sup>16–20</sup> and increasing the graphitic perfection of the nanotubes.<sup>20</sup> Analysis of these pure materials allows the measurement of intrinsic nanotube properties, whereas the

bulk of the reported nanotube literature,<sup>1–15</sup> including our own earlier work,<sup>9,15</sup> has been on characterization or application of nanotubes still containing catalyst residue, which are in themselves composite materials. We are therefore motivated to examine the permittivity and electrical properties of purified nanotubes, tubes from which the residual catalyst particles have been removed.

In this article we measure the low frequency, 75 to 1875 MHz, complex permittivity spectra of 1 wt % MWNT loaded polymer composites, using either as-fabricated MWNTs that still contain Fe<sub>3</sub>C catalyst particles<sup>20</sup> or MWNTs that have been purified through high-temperature annealing (graphitization). The experimental results are simulated using an effective medium theory (EMT) developed for predicting the electromagnetic properties of composites comprised of elongated stick-like conducting inclusions, e.g., nanotubes, within a dielectric matrix;<sup>21</sup> comparison of experiment and theory allows for a quantitative analysis of the intrinsic electrical properties of the nanotubes. Briefly summarizing the key points of the model presented in Ref. 21 and used here, the frequency dependent complex permittivity,  $\epsilon = \epsilon' - i\epsilon''$  of the conductive inclusions, dielectric host, and resulting composite material are given as

$$\frac{p}{3} \frac{f(\Delta)\epsilon_m/\epsilon_e}{1 + f(\Delta)(\epsilon_m/\epsilon_e)(b^2/a^2)\ln(1 + a\epsilon_d/b\epsilon_e)\cos\Omega} + 3(1-p) \frac{\epsilon_d - \epsilon_e}{2\epsilon_e + \epsilon_d} = 0, \quad (1)$$

<sup>a)</sup>Electronic mail: cgrimes@enr.psu.edu

where the  $\epsilon$ 's are complex numbers,  $2a$  is the length of the conductor,  $b$  is the radius of the conductor, and  $p$  is the packing fraction. The subscript  $e$  indicates the composite material (nanotubes and binder), subscript  $d$  indicates the dielectric host (polystyrene binder), subscript  $m$  indicates the MWNTs, and  $f(\Delta)$  and  $\Omega$  are given as

$$f(\Delta) = \frac{(1-i) J_1[(1+i)\Delta]}{\Delta J_0[(1+i)\Delta]}, \quad (2)$$

$$\Omega^2 = \epsilon_d (a\omega/c)^2 \frac{\ln(a/b) + ia\omega/c \sqrt{\epsilon_d}}{\ln(1 + a\epsilon_d/\epsilon_e)}, \quad (3)$$

where  $\Delta = b(\sqrt{2\pi\sigma_m\omega/c})$ ,  $i$  denotes a complex number,  $\omega$  is the radian frequency,  $c$  is the speed of light, and  $J_0$  and  $J_1$  are Bessel functions of the zero and first order. In our work, the input parameters for Eq. (1) were the packing fraction, the dimensions and aspect ratio of the MWNTs, and the complex permittivities and conductivity of the dielectric binder and resultant composite. The only unknown left in Eq. (1), the complex permittivity and conductivity of the MWNTs, was determined by solving the equation with an optimization code to best fit the experimental measurements. Note we assume that in this frequency range: (1) The polystyrene dielectric host has a complex, frequency independent form, i.e.,  $\epsilon = \epsilon'_d - i\epsilon''_d$ , where  $\epsilon'_d$  and  $\epsilon''_d$  are constants. (2) The effective dielectric response of a MWNT (the conductive inclusion) is given by

$$\epsilon_m = \epsilon'_m - \epsilon''_m = \epsilon'_m - i \frac{\sigma_m}{\omega\epsilon_o}, \quad (4)$$

where  $\epsilon_o$  is the permittivity of free space. The usual frequency dependence of the complex part of the permittivity of a metal has been used, with the real part of the MWNT permittivity  $\epsilon'_m$  and the dc conductivity  $\sigma_m$  treated as constants.

## EXPERIMENTAL METHOD

The MWNTs used in this work were created by a chemical vapor deposition method using a floating catalyst.<sup>22-24</sup> A xylene-ferrocene mixture was continuously injected into a  $\approx 200^\circ\text{C}$  preheat chamber and the vapor was carried into the furnace reaction zone by an Ar/H<sub>2</sub> (10%) carrier gas that also served to control the reactor partial pressure. The MWNTs grew perpendicular to the surface of both the quartz reactor walls and quartz plates inserted into the chamber, forming thick mats that were easily collected. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) observations showed that the nanotubes used in this work were  $\approx 50\ \mu\text{m}$  long and 30 nm in diameter, with an aspect ratio of 1667. A portion of the nanotubes from the same fabrication run were graphitized in a horizontal electric resistance tube furnace.<sup>20</sup> After a dry nitrogen purge the samples were heated in nitrogen from ambient to  $1000^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ . Upon reaching  $1000^\circ\text{C}$  the furnace was put under automatic control (optical pyrometer) and heated at  $12.5^\circ\text{C}/\text{min}$  to  $3000^\circ\text{C}$  where it was held for 45 min. As determined by inductively coupled plasma-optical emission spectroscopy the as-fabricated MWNTs

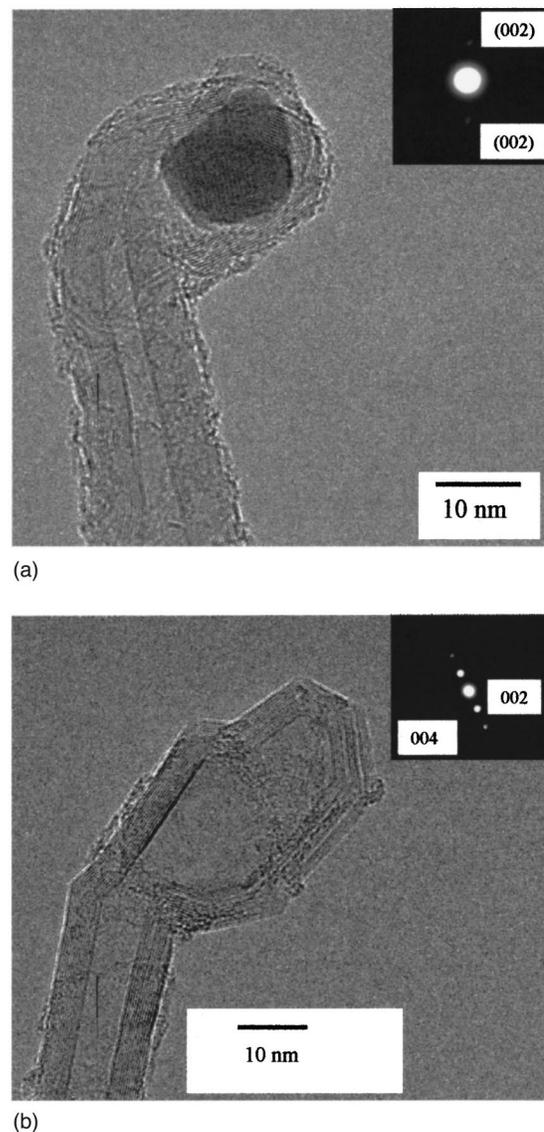
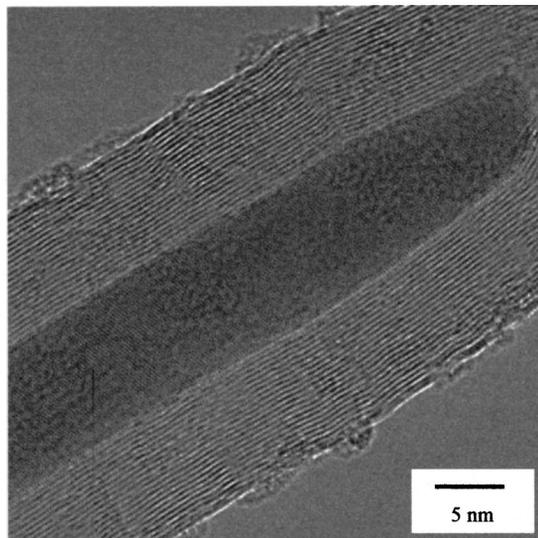


FIG. 1. HRTEM images and microelectron diffraction patterns of MWNT tips (a) as-fabricated containing Fe<sub>3</sub>C catalyst particles and (b) annealed at  $3000^\circ\text{C}$  with no residual catalyst. The inset microdiffraction patterns taken from the MWNT walls show the enhanced crystallinity in the annealed tubes.

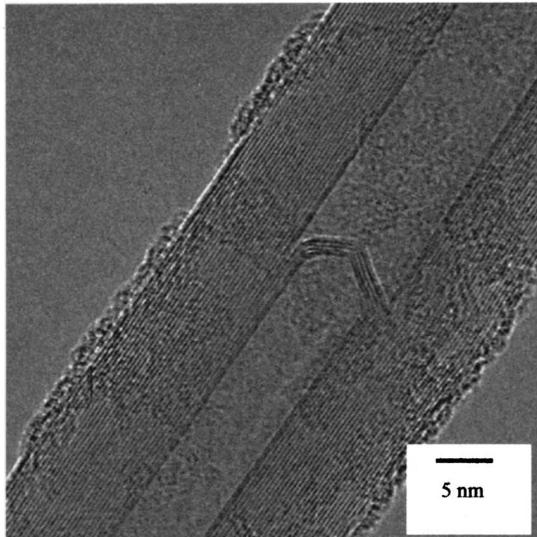
contained 7.10 wt% Fe and the graphitized tubes  $<0.01$  wt%.<sup>20</sup> X-ray diffraction confirmed the Fe to be in the form of Fe<sub>3</sub>C.<sup>20</sup>

The polymer matrix used in this work, 280 k molecular weight polystyrene, was loaded with 1 wt% MWNTs. An ultrasonic wand dismembrator (Fischer Scientific 550) was used to disperse the nanotubes in toluene. Each batch was sonicated for a total of 35 min in on/off increments of 30 s. The polystyrene was dissolved in toluene, then combined with the nanotube suspension and placed in a bath sonicator for 30 min. The resulting mixture was cast into a culture dish and allowed to dry completely over a period of 1 week before testing.

Complex permittivity measurements were carried out using a resonant stripline cavity.<sup>25-27</sup> The cavity used for these measurements has a fundamental resonant frequency of 75



(a)



(b)

FIG. 2. HRTEM images of MWNTs (a) as-fabricated, containing  $\text{Fe}_3\text{C}$  inclusions in the tube core and (b) annealed at  $3000^\circ\text{C}$  free from inclusions.

MHz; permittivity measurements are obtained at each odd harmonic of the fundamental, up to the 25th at 1875 MHz. The measured test samples were  $25.0 \times 3.0 \times 0.4$  mm strips. The strips were cut from the composite films along multiple directions, and in different locations on the sheet, to ensure that the as-cast film was isotropic. The data for six different individual strips did not differ significantly, confirming a random orientation and even distribution of the MWNTs within the polystyrene.

## RESULTS AND DISCUSSION

Transmission electron microscopy images of MWNTs before and after graphitization are shown in Figs. 1 and 2 and demonstrate the successful removal of catalyst particles from the nanotube ends and cores upon graphitization. Not

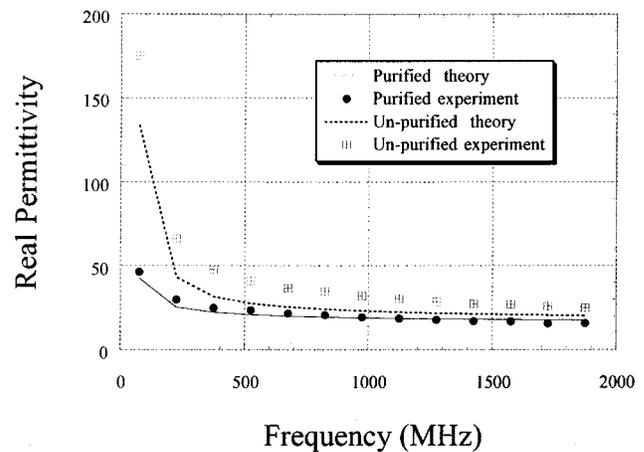


FIG. 3. Comparison of the real permittivity spectra  $\epsilon'$  of polystyrene loaded with unpurified and graphitized (catalyst particles removed) MWNTs. Symbols are used to denote measured values and lines theoretical simulation.

only did the graphitization remove the catalyst particles but it also improved the crystallinity of the nanotubes as evidenced by x-ray and electron diffraction.<sup>20</sup>

Figures 3 and 4 show, respectively, the measured real  $\epsilon'$  and imaginary  $\epsilon''$  permittivity spectra of the unpurified and purified MWNT composites; EMT best fits to the experimental data are also plotted. The magnitude of the permittivity spectra is decreased with graphitization, with both samples showing a permittivity steadily declining with frequency.

For the EMT modeling an aspect ratio of 1667 was used throughout, corresponding to the dimensions of the MWNTs. As reported in Ref. 28 MWNTs show a substantial spread in measured electrical conductivities; Ebbesen *et al.*<sup>28</sup> measured seven MWNTs and found a spread in dc conductivity values of  $10^6$ . The macroscopic electrical response of the composite test samples is largely determined by the MWNTs having the greatest conductivities, with the remaining tubes serving to increase the permittivity of the binder from that of polystyrene,  $7 + 0.3j$ , to a slightly higher value.<sup>15</sup> To account for this effect the binder was assigned a permittivity of 17

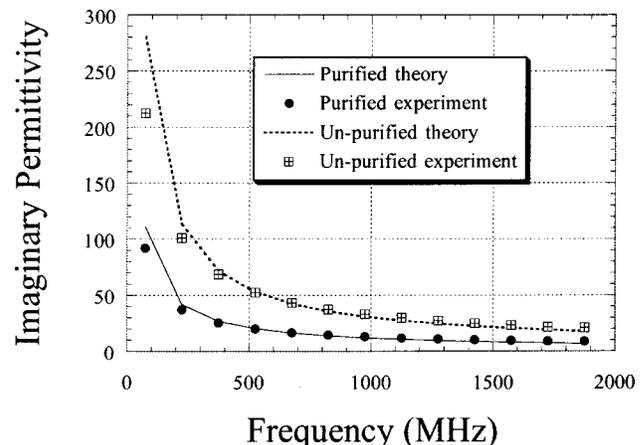


FIG. 4. Comparison of the imaginary permittivity spectra  $\epsilon''$  of polystyrene loaded with unpurified and graphitized (catalyst particles removed) MWNTs. Symbols are used to denote measured values and lines theoretical simulation.

+0.3j in the EMT calculations, which enabled a more accurate fit to the high frequency end of the spectra. Optimal agreement between theory and experiment are obtained using 0.1% volume packing fraction, corresponding to 1 out of 5 nanotubes being significantly more conductive than the other nanotubes; higher packing fraction values did not as accurately match the lower frequency measurement data. With these model inputs, the only adjustable parameter is the MWNT permittivity; for both unpurified and graphitized samples a real permittivity  $\epsilon'$  of approximately 100 produced the best results, with values between 70 and 140 predicting similar spectra. For the unpurified MWNTs a conductivity of  $7.78 \times 10^4$  S/m produced optimal results, while for the purified nanotube sample optimal agreement was obtained with a conductivity value of  $2.22 \times 10^4$  S/m.

## CONCLUSIONS

The low frequency complex permittivity spectra of polystyrene thick films containing as-fabricated and graphitized MWNTs are measured. Graphitization is found to reduce the magnitude of the MWNT composite permittivity spectra, which is attributed to a net decrease in the conductivity of the MWNT-catalyst composite. Since high temperature annealing increases the graphitic nature of the tubes and eliminates microstructural defects,<sup>20,24</sup> both of which act to increase the conductivity, it appears that the electrical response of as-fabricated MWNTs are significantly influenced by the residual catalyst particles present. Certainly the core of the tube shown in Fig. 2(a) appears filled with  $\text{Fe}_3\text{C}$ , which acts in some measure to increase the tube conductivity. Unfortunately, measuring the electrical conductivity of the  $\text{Fe}_3\text{C}$  nanoparticles<sup>29</sup> is a challenging prospect and to our knowledge has not been accomplished. With graphitization this presumably conductive core is removed, restricting the electrons to a narrower path thus acting to decrease the tube conductivity. In contrast, the graphitized walls should have enhanced conductivities.<sup>20,24</sup> The net result of the competing effects is an apparent net drop in the electrical conductivity by approximately a factor of 3.5 with graphitization.

In examining the magnitude of the predicted conductivity values,  $2.22 \times 10^4$  S/m for the purified MWNTs and  $7.78 \times 10^4$  S/m for the as-fabricated, it should be remembered that the effective medium theory addresses randomly oriented conductors within the matrix. The conductivity of graphite is highly anisotropic, with the *c*-axis conductivity over  $10^3$  less than the in-plane value.<sup>30</sup> Therefore the predicted conductivity based on the composite values will be a smaller (averaged) value since only tubes aligned with the exciting voltage contribute to the conductivity measurement. Hence it is reasonable to assume that the actual longitudinal MWNT

conductivity values may be a factor of 10 higher than the calculated values based upon our characterization of randomly oriented composites. Future work will focus on the characterization of aligned MWNT composites to resolve this enigma.

## ACKNOWLEDGMENT

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