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Spectra of Radiation Emitted By Single-Walled and Multi-Walled Carbon Nanotubes During Multiple Microwave Irradiation and Cooling Cycles

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Abstract

Carbon nanotubes have been observed to emit ultraviolet, visible, and infrared radiation when exposed to microwave fields. We have performed experiments in which both single-walled (~1 nm diameters) and multi-walled carbon nanotubes (>50 nm diameters) were exposed to 2.45 GHz microwaves during several irradiation and cooling cycles at a pressure of ~10^{-6} torr. A comparison of the spectra of the radiation emitted by the nanotubes indicates that the intensity of radiation with wavelengths ranging from 700 to 1000 nm increased substantially during the course of five irradiation and cooling cycles. The data suggest that the mechanism responsible for the emissions is field emission-induced luminescence and that the intensity of the radiation emitted increased due to the opening of nanotube ends. Furthermore, the intensity of the radiation emitted by the multi-walled carbon nanotubes was much greater than the radiation emitted by the single-walled nanotubes. Scanning electron microscopy images indicate that most of the single-walled nanotubes were bundled together, while the multi-walled nanotubes were not. This bundling may have resulted in a lower field enhancement factor and/or screening effects which might help to explain the difference in the intensities of the radiation emitted by the samples.

Introduction

Carbon nanotubes (CNTs) have attracted much attention due to their unique mechanical and electrical characteristics. In particular, the behavior of CNTs in electromagnetic fields has been the subject of many investigations. Common processes to functionalize and purify CNTs involve microwave radiation, thus making CNTs' behavior in such a field a subject of interest. It has been previously observed by Imholt *et. al* [1] that when single-walled carbon nanotubes (SWCNTs) were

irradiated with 2.45 GHz microwaves, absorption resulted in the emission of infrared, visible, and ultraviolet radiation. During irradiation, Imholt *et al.* also observed that the SWCNTs were heated to a temperature of 2273 K. Wadhawan *et al.* [2] and Alvarez- Alvarez-Zauco *et al.* [3] observed the same phenomena in experiments involving SWCNTs and multi-walled carbon nanotubes (MWCNTs), respectively.

There has been some uncertainty concerning the mechanism that is responsible for the emission of the infrared, visible, and ultraviolet radiation by CNTs irradiated with microwaves [3, 4]. Initial reports attributed the phenomenon to the localized heating of metallic impurities in the CNT samples [2]. However, subsequent experimental investigations suggest that residual metallic catalysts do not play a significant role in the CNT samples' absorption of microwaves [5, 6]. Also, as a "perfect" one-dimensional CNT has been shown to be a ballistic conductor [7], any currents induced during the irradiation of CNTs would not be expected to heat the samples. However, due to the fact that structural imperfections present in CNT samples could result in the decay of ballistic transport [7], Joule heating has been mentioned as a possible mechanism responsible for the observed radiations. Ye *et al.* [8] developed a model that proposed that the heating of CNTs in microwave fields is due to the transformation of electromagnetic energy into mechanical vibrations. The model, which uses a nonlinear Mathieu equation to describe the vibrations, suggests that the polarization of CNTs in a microwave field results in transverse parametric resonance, which is responsible for the heating of the samples. Finally, a recent report claims that the response of CNTs in microwave fields is "an intrinsic property of the CNTs, which is directly determined by the microwave response of the growth substrate" [4].

The primary goal of this study was to gain information that might help us to understand the mechanism responsible for the emission of radiation by CNTs while being irradiated with microwaves. Specifically, we were interested in comparing the spectra of the radiation emitted by SWCNTs and MWCNTs, and also the spectra of the radiation emitted by CNTs during multiple irradiation and cooling cycles. We are aware of only one report [6] that has compared experimental data related to the microwave absorption properties of SWCNTs and MWCNTs, which indicated that both SWCNTs and MWCNTs were heated to ~3000 K during irradiation with 2.45 GHz microwaves. However, no comparison of the spectra was reported.

Experimental Procedure

Two types of CNTs were used in our experiments. According to specifications provided by the supplier [9], the first type had a SWCNT and double-walled carbon nanotube (DWCNT) content of > 90 wt%, a MWCNT content of > 5 wt%, and an amorphous carbon content of < 3 wt%. Raman spectroscopy analysis indicated that the outer diameters of the SWCNTs/DWCNTs were between 1 and 2 nm. The second type had a MWCNT content of > 95 wt% (diameters > 50 nm) and an amorphous carbon content of < 1.5 wt%. According to the supplier, the SWCNT lengths were between 5 and 30 μm and the MWCNT lengths were between 10 and 20 μm.

Samples with masses of 250 ± 1 mg were placed in a vertically-positioned Pyrex tube which was then pumped to a pressure of ~10^{-6} torr. A 700 W magnetron, with its antenna positioned approximately 1 cm from the tube containing the CNTs, produced microwaves with a frequency of 2.45 GHz. Data was collected using an Ocean Optics spectrometer probe, placed approximately 1 cm from the glass tube. The orientations of the magnetron antenna, Ocean Optics probe, and Pyrex tube were the same in all experiments.

In the first experiments performed, the radiation spectra produced by a SWCNT/DWCNT sample and a MWCNT sample during five irradiation and cooling cycles were obtained. Each of the samples were irradiated for 25 s and cooled for approximately 1200 s during each cycle. Then, a second set of experiments were performed in which three different samples of both SWCNTs/DWCNTs and MWCNTs were irradiated with microwaves for 25 s. During both sets of experiments, the spectra of the emitted radiation were integrated at 0.1 s intervals during the 25 s microwave irradiation periods.

Results and Discussion

Comparison of the radiation spectra produced by CNTs in microwave fields during multiple irradiation/cooling cycles:

The spectra produced by a single SWCNT/DWCNT sample during five irradiation and cooling cycles can be seen in Fig. 1 (with background radiation subtracted). Although a few peaks can be seen in the spectra, Fig. 1 suggests that the radiation emitted by the carbon nanotubes is essentially broadband in nature. The spectra also indicate that the intensity of the radiation emitted by the SWCNTs/DWCNTs does not decrease during multiple irradiation and cooling cycles as one would expect if the mechanism responsible for the emissions was a chemical process. Previous reports [1, 3, 10] have also noted that CNTs have been observed to consistently emit radiation throughout multiple microwave irradiation and cooling cycles. Perhaps the most surprising feature of the data shown in Fig. 1 is the increase in the intensity of radiation with wavelengths ranging from 700-1000 nm during the irradiation and cooling cycles. The ~900 nm-wavelength radiation emitted by the CNTs during the final microwave irradiation cycle is approximately three times more intense than radiation of the same wavelength emitted during the first irradiation cycle.

We believe that there is a simple explanation for the observed increase in the intensity of the radiation emitted by the CNTs during the irradiation and cooling cycles. It is well known that the caps of CNTs are more reactive than the cylindrical portions due to the presence of pentagonal structures [11]. When irradiated with microwaves, the ends of CNTs have been shown to open as they are heated [3]. As open-ended CNTs are known to have much better field emission properties than closed CNTs [12-14], the data shown in Fig. 1 suggests that the mechanism responsible for the emission of radiation by CNTs in microwave fields may be field emission-induced luminescence. We are aware of only one report [3] that mentions field emission-induced luminescence as a possible mechanism responsible for the radiation emissions of CNTs in microwave fields. This possibility is further supported

by the fact that the field emission currents (and the induced luminescence) have been shown not to decay over extended periods of time [12].

The field emission properties of CNTs have been studied extensively and the basic physics related to field emission are well understood. The field emission characteristics of CNTs are approximately described by a simplified version of the Fowler-Nordheim equation,

$$I = (aA\beta^2E^2/\Phi)\exp(-b\Phi^{3/2}/\beta E)" \quad (1)$$

where *a* and *b* are constants and *I*, *A*, *β*, *E*, and *Φ* are the current emitted by the CNTs, the emission area, the field enhancement factor, the applied electric field, and the work function, respectively. While the field enhancement factors for open and closed SWCNTs are similar [13], the existence of non-bonding valence electrons in open SWCNTs results in a lower work function than in the case of closed SWCNTs [13]. Experimental results suggest that the same is true for MWCNTs [14].

Fig. 2 shows the spectra produced by a single MWCNT sample during five irradiation and cooling cycles (with background radiation subtracted). The results were similar to those of the experiments involving the SWCNT/DWCNT sample. The spectra indicate that the ~900 nm-wavelength radiation emitted by the MWCNTs during the final microwave irradiation cycle is approximately two times more intense than radiation of the same wavelength emitted during the first irradiation cycle. The major difference between the spectra produced by the SWCNT/DWCNT and MWCNT samples is that the intensity of the radiation emitted by the MWCNTs is much greater. This topic is discussed in more detail in the next subsection of this report.

It is worth noting that, after each of the experiments, the interior of the Pyrex tube was almost completely coated with a layer of CNTs. During cooling, the exterior of the Pyrex tube was lightly tapped so as to remove the CNTs from the tube walls. However, some small portions of the sample were likely "lost" during each cycle. These slight decreases in the mass of the sample directly in front of the magnetron antenna may have resulted in small decreases in the intensity of the radiation emitted by the CNTs during each irradiation cycle.

Comparison of the radiation emitted by SWCNTs/DWCNTs and MWCNTs in microwave fields

Fig. 3 directly compares the sums of the spectra produced by three > 90 wt% SWCNT/DWCNT samples and three > 95 wt% MWCNT samples during 25 s microwave irradiations. Background radiation has been subtracted from the spectra shown in the figure. The comparison is in agreement with the data shown in Figs. 1 and 2, and indicates that the radiation emitted by the sample containing primarily MWCNTs is of much higher intensity than then radiation emitted by the sample composed of SWCNTs/DWCNTs.

We propose two possible reasons for this observed difference in intensities. One possible explanation is related to the way in which the SWCNTs/DWCNTs are bundled together. Fig. 4 is a scanning electron microscopy (SEM) image of the SWCNT/DWCNT sample, as purchased. It is typical of all SEM images of the SWCNT/DWCNT sample. The image clearly shows that the CNTs form bundles with

diameters between approximately 20 and 100 nm. While one might intuitively expect the smaller diameters of the SWCNTs/DWCNTs to result in a high field enhancement factor (due to the sharper cap geometry), it may be that the bundle diameters, rather than the individual CNT diameters, are what determine the factor [12]. Secondly, the field emission properties of the densely-packed SWCNTs/DWCNTs shown in Fig. 4 may suffer from screening effects. Previous reports suggest that the screening effect is minimized when the spacing of the individual CNTs is greater than their lengths [12] and that field emission properties are known to be strongly affected by the overall organization of CNTs [15]. Fig. 5 is a typical SEM image of the MWCNT sample after five irradiation/cooling cycles. The SEM image in Fig. 5 does not indicate that microwave irradiation causes any obvious defects in the MWCNTs. Previous reports have shown that at low currents, field emission-induced luminescence does not alter the structure of CNT walls [3]. Furthermore, it suggests that, unlike the SWCNT/DWCNT sample, the MWCNTs are not bundled together in the sample, which would minimize screening effects and could possibly help explain the difference in the emitted radiation intensities.

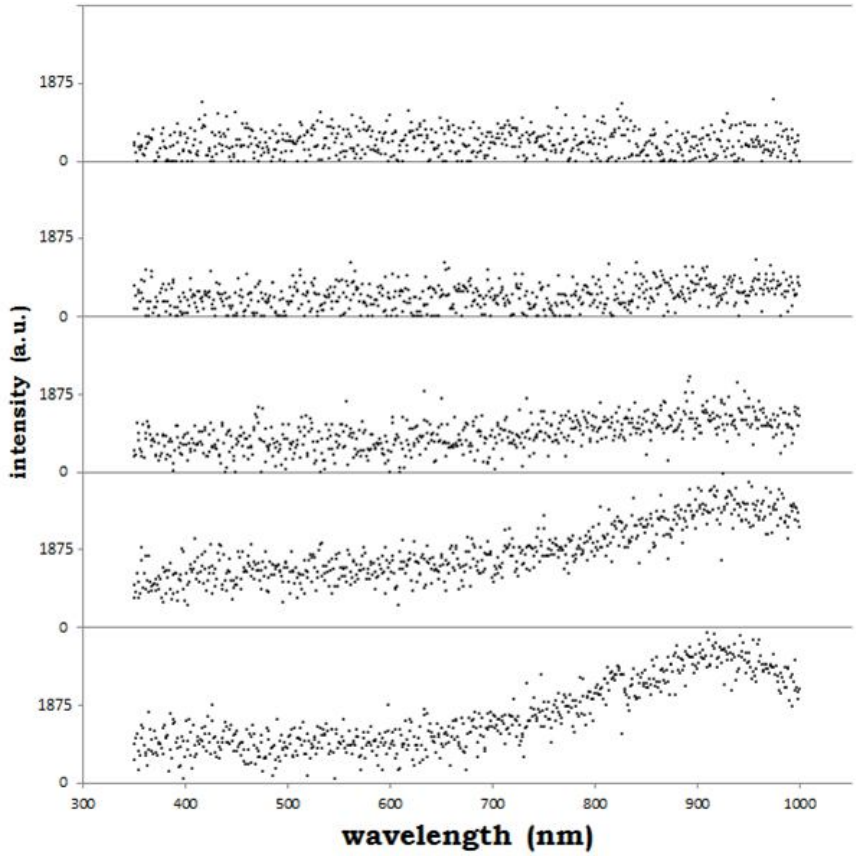

Fig.1. Spectra of radiation emitted by the SWCNTs/DWCNTs during several irradiation and cooling cycles (with background subtracted). From top to bottom, the spectra correspond to the first, second, third, fourth, and fifth cycles.

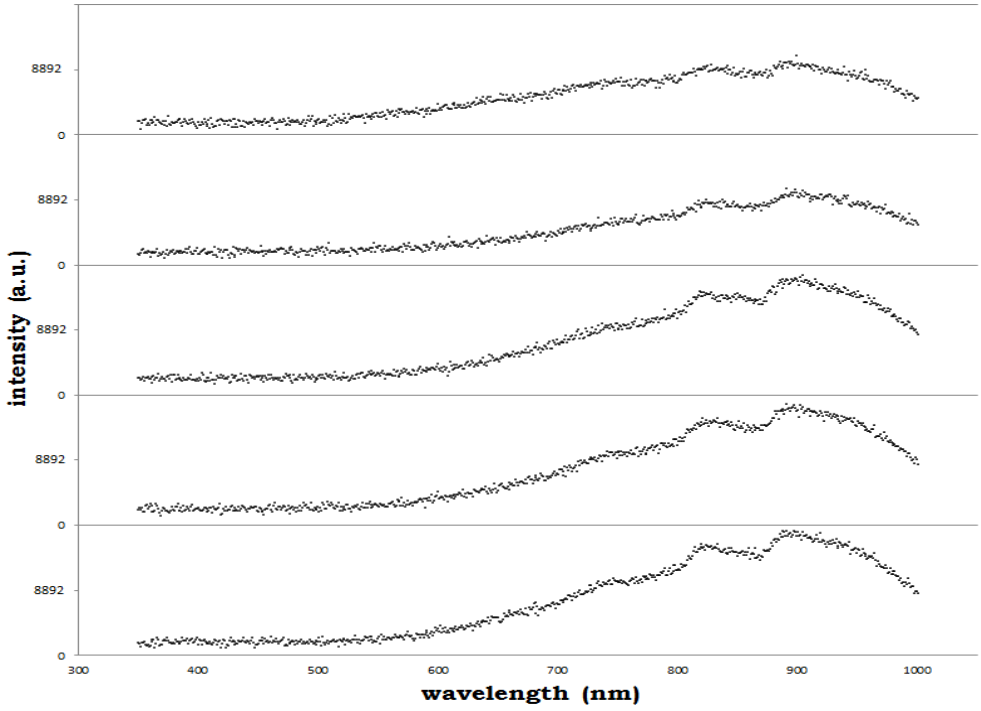

Fig. 2. Spectra of radiation emitted by the MWCNTs during several irradiation and cooling cycles (with background subtracted). From top to bottom, the spectra correspond to the first, second, third, fourth, and fifth cycles.

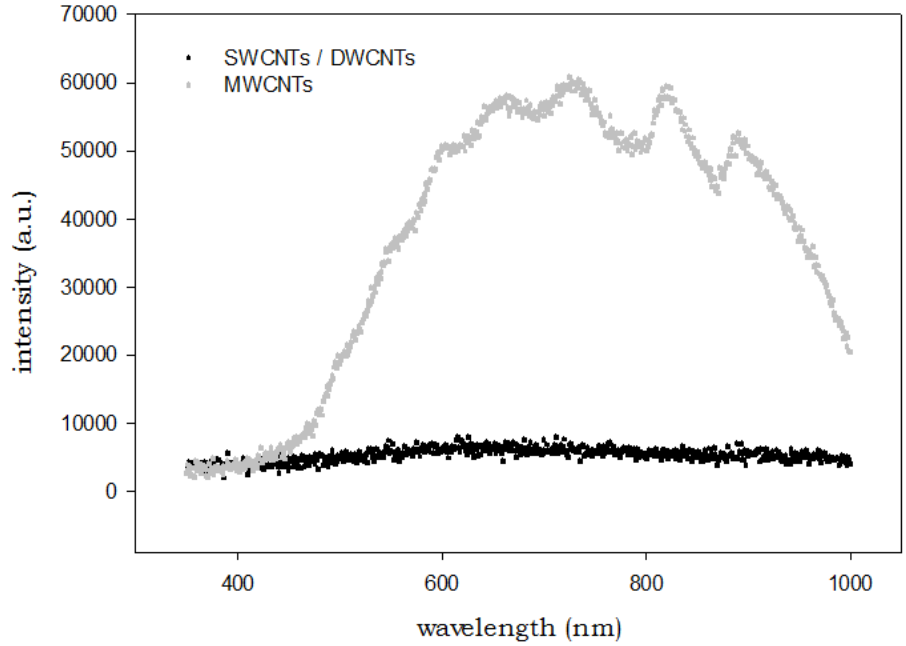

Fig. 3. Comparison of the sums of radiation spectra emitted by the > 90 wt% SWCNT/DWCNT and the > 95 wt% MWCNT (> 50 nm diameter) samples during three 25 s microwave irradiations.

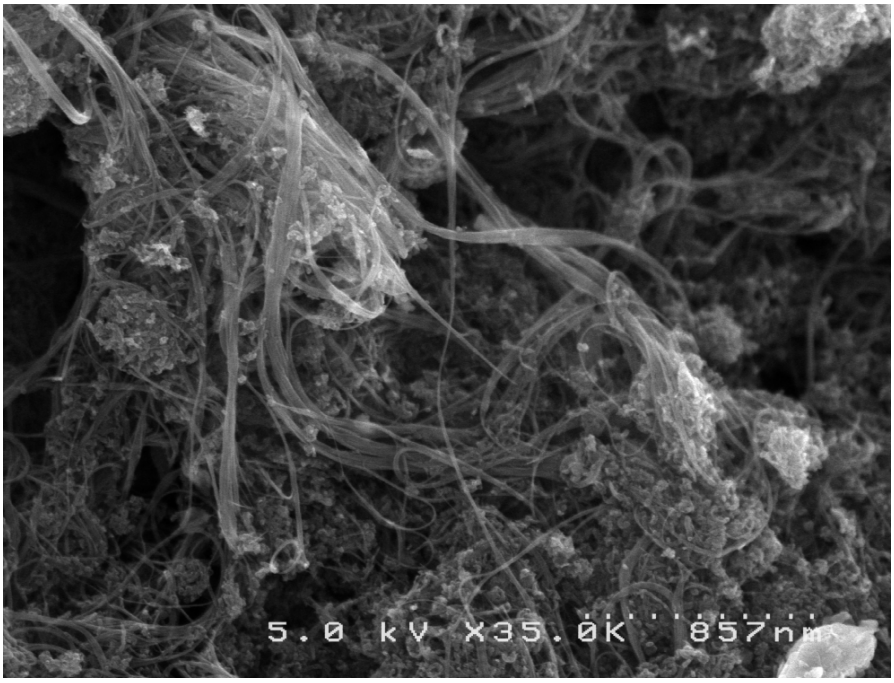

Fig. 4. SEM image of the SWCNT/DWCNT sample, as purchased.

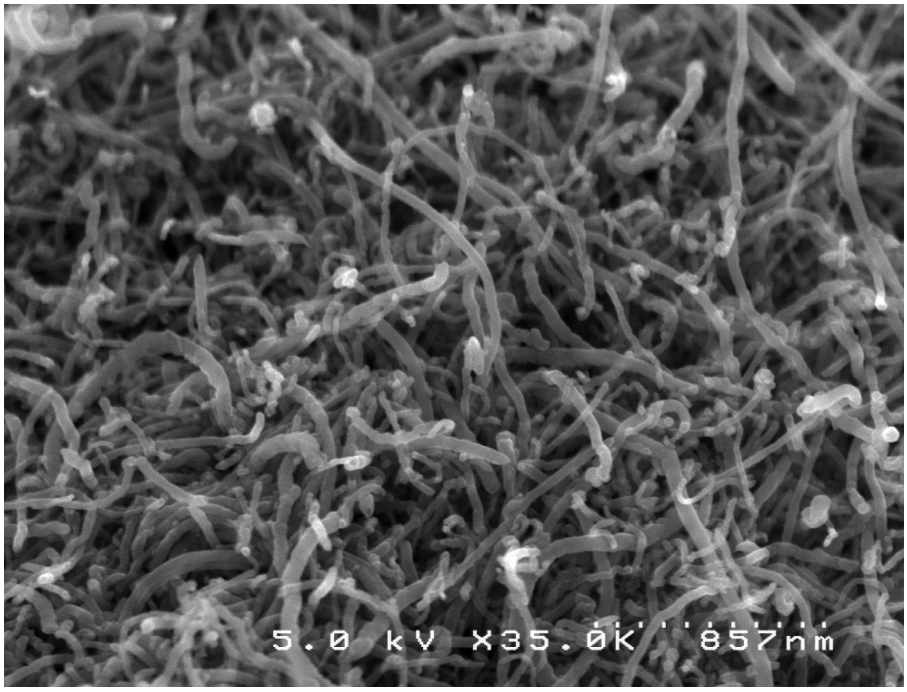

Fig. 5. SEM image of the MWCNT after five irradiation and cooling cycles.

Conclusions

Additional experimental and theoretical work needs to be done in order to adequately explain the behavior of CNTs in microwave fields. However, the data presented in this report indicates that the mechanism responsible for the emission of infrared, visible, and ultraviolet radiation from CNTs in microwave fields is likely field emission-induced luminescence. This possibility is supported by the fact that the intensity of the radiation emitted by the CNTs in our experiments increased during multiple microwave irradiation and cooling cycles, as the ends of the CNTs were opened. Furthermore, the difference in the intensities of the radiation emitted by the SWCNT/DWCNT and MWCNT samples can be explained by differences in their field emission properties. Finally, SEM images of the MWCNTs after five irradiation and cooling cycles do not indicate that the CNT walls are damaged in any obvious way during radiation emission, which also suggests that the mechanism responsible for the behavior of CNTs in microwave fields is field emission-induced luminescence.

In the future, experiments studying the behavior of isolated, individual SWCNTs and MWCNTs in microwaves should be performed in order to gain a better understanding of the mechanism responsible. Also, additional work should be done to assess any structural damage to CNTs as the result of microwave irradiation either by using a tunneling electron microscope to image the CNT walls (in order to confirm a recent report by Alvarez-Zauco*et al.* [3] which indicated that no damage was observed) or by analyzing the Raman spectroscopy G-band to D-band ratio.

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