The Complex Optical Response of Arrays of Aligned, Multi-walled Carbon Nanotubes

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ABSTRACT

The optical properties of periodic and nonperiodic arrays of aligned multiwalled carbon nanotubes are presented. Experimental analysis indicates a complex optical response that is attributed to both the individual carbon nanotube scatterers and also to the array ensembles. These studies indicate that by controlling the geometry and spacing of the arrays, it is possible to create structures that respond very strongly to specific wavelengths or bands of wavelengths. Structures such as these may form the basis for numerous applications in energy conversion. This would include highly efficient solar energy conversion as well as sensitive, finely tuned detectors that can respond to predetermined wavelength bands ranging from the ultraviolet to the infrared region. Experimental, theoretical and modeled results are discussed as they apply to these applications. Challenges and issues are discussed.

Key Words: Band-gap, carbon nanotubes, periodic honeycomb arrays, reflectance data, polarization effects, self-assembly nanosphere lithography, light antenna, dipole antenna

1. INTRODUCTION

In recent years the optical properties of carbon nanotubes (CNTs) have attracted much attention due to their unique physical characteristics. They can be grown on the order of a wavelength of light, which suggests strong interaction with the visible electromagnetic spectrum. Efforts were undertaken to understand this interaction in multi-walled carbon nanotubes (MWCNTs) beginning with a study of diffraction effects[1, 2]. Early on, however, it was clear that the optical response from MWCNTs could not be understood solely in terms of Bragg diffraction. This lead to a series of trials where different geometries were tested to prove whether the nanotubes were behaving like light antennas[3]. During these trials a number of optical responses were recorded including: coherent backscattering, plasmonic resonance, and photonic band gap behavior[4, 5].

In order to isolate the antenna effect, it was necessary to eliminate Bragg diffraction and other optical responses due to the periodicity of the samples (figure 2a). Non-periodic arrays were grown (figure 2b) where the distance between tubes ranged from $\lambda/2$ to λ. Spectroscopic studies were performed that related the length of the nanotubes to their resonant responses. These data matched very well to predicted antenna theory response, similar to the way in which a radio antenna responds to radio waves. Polarization studies were also conducted. It was shown that nanotubes give a maximum response when the polarization of the incoming radiation is parallel to its longitudinal axis. The resonant length and polarization studies indicate that the nanotubes behave like dipole antennas.

These effects set the potential for highly efficient energy conversion. In the early 1970s Robert Bailey performed research that took advantage of the electromagnetic nature of solar radiation. Contrary to standard photovoltaic devices, which are dependent on the photovoltaic effect, Bailey proposed the use of antennas to convert solar energy to d.c. electricity. Unlike photovoltaic devices, an antenna would not be dependent on the band-gap of the semiconductor from which it was made[7,9]. Bailey and Fletcher submitted the first patent describing an antenna-based device that would convert electromagnetic wave energy into electricity in 1973[8]. Theoretical work on these devices continued through the 1970s. W. C. Brown, doing research at Raytheon, first used the term rectenna to describe a rectifying antenna. Brown is recognized as a pioneer in microwave power transmission through the use of antennas[10]. In 1988, Farber, at University of Florida's Solar Energy and Energy Conversion Laboratory, used pyramidal antenna arrays to receive and rectify microwave radiation in the 2-3GHz range[6].

There are many challenges involved in applying the idea to visible radiation. In this paper we will review previous work showing that CNTs behave like light antennas and show further evidence, both theoretical and experimental, confirming the antenna behavior. We will also discuss the potential of making them into effective solar antennas. Challenges and problems that need to be addressed in order to bring this idea to reality will also be discussed.

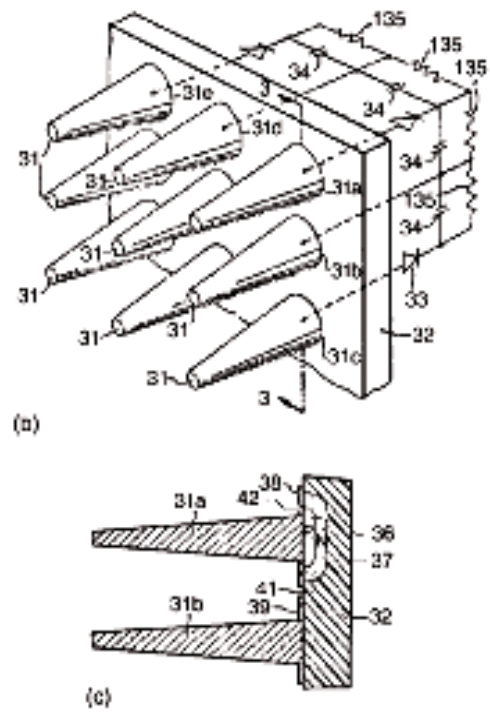


Figure 1. Diagram from Fletcher and Bailey's 1973 patent[8].

2. Sample Preparation and Review

Two samples were used to study the antenna response of MWCNTs, both of which were non-periodic and aligned. The first sample was prepared by depositing a thin film of Ni onto the Si substrate in a dc magnetron sputtering system. The sample was then placed into a plasma-enhanced chemical vapor deposition (PECVD) chamber where it was heated to 550-600˚C, which breaks the Ni film into small catalyst particles. A mixture of NH_3 and C_2H_2 is introduced into the chamber and a dc glow discharge plasma is generated and maintained by a bias voltage of 500-550 V. In this way, 1000nm length tubes are grown in about 1-2 minutes[3, 11, 12].

The second sample was prepared in a similar way. A 25x25 mm Corning 1737 aluminosilicate glass substrate was sputter coated with a 15nm Cr layer which gave a conductive yet transparent layer. Ni dots were randomly distributed through electrochemical deposition. The sample was then briefly used as a cathode in an electrolytic bath, with an aqueous solution of 0.01M $NiSO_4$ and 0.01 M H_3BO_4 as the electrolyte, and a graphite electrode as an anode. The sample was then placed in the PECVD chamber and grown to the required heights[3, 11, 12].

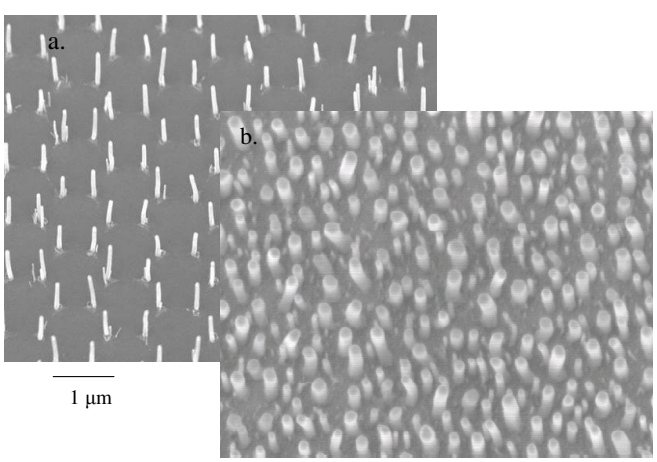


Figure 2. SEM images of periodic (a) and nonperiodic (b) MWCNT arrays used during experiments.

2.2 Polarization Effects

Using samples prepared in the first manner described, experiments were done to show two main antenna properties. The polarization effect, which suppresses the response of an antenna when the incoming electric field is polarized perpendicular to the antennas axis, and the length dependence, which states that when the length of the antenna is a multiple of $\lambda/2$, the response is maximized. In order to demonstrate the polarization effect, a sample was prepared such that one half was coated with a thin film of Cr and the other half was

prepared to grow MWCNTs as described above. The sample was then illuminated with unpolarized white light, and observed in a specular direction through a rotating polarizer. Starting with the polarizer parallel to the nanotube axis (Θ=0˚) and rotating until the polarizer is perpendicular (Θ=90˚) revealed the graph in figure 3. When the polarizer's axis is parallel to the nanotubes' axis, it was observed that the portion of the sample containing nanotubes was clearly visible, while the Cr coated side appeared dark. As the polarizer was rotated the nanotube portion of the sample darkened while the Cr coated side became brighter.

This behavior can be explained by considering the excitation of currents in the nanotubes and in the film. In the nanotubes, currents are excited along the longitudinal axis, while in the film currents are parallel to the surface. As the axis of polarization rotates it changes the projected electric field by $E' = E_0 \cos\theta$. Each nanotube acts like an antenna reradiating light with polarization parallel to its axis. The observed intensity changes can be described in terms of Malus' Law.

$$I_{NT}(\Theta) = \frac{c\varepsilon_0}{2} E_0^2 \cos^2 \Theta \qquad (1)$$

$$I_{Cr}(\Theta) = \frac{c\varepsilon_0}{2} E_0^2 \sin^2 \Theta \qquad (2)$$

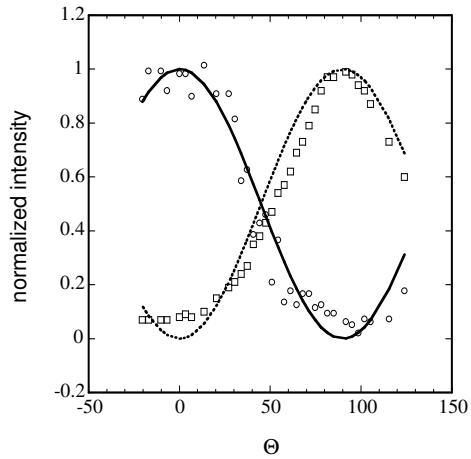


Figure 3.Polarization Effects: The circles represent the light intensity of the nanotubes, and the squares of the thin film of Cr. The lines represent expected functional dependencies[3].

The top equation represents the variation of intensity from the nanotubes and the bottom corresponds to the Cr film. The light reflected from the two regions of the sample are completely out of phase of with one another, thus confirming the re-radiation of light polarized perpendicular to the nanotube axis, and the suppression of light polarized perpendicular to the axis.

2.3 Length Effect

As stated earlier, antenna theory predicts that the maximum response of an antenna occurs when its' length is on the order of nλ/2. In order to observe this property, a random array of MWCNTs was produced for which the nanotubes increased length from left to right (see inset in figure 4). Using an Ocean Optics USB2000 Fiber Optic Spectrometer (FOS), white light was focused on the surface at an angle of 30˚ with a spot size on the order of .5mm diameter[5]. Several different points on the sample were measured -- each with a different length. The relative intensity was plotted as a function of wavelength in figure 4. This plot confirmed that the observed colors were, in fact due to the resonant response of the nanotubes. Further studies were undertaken to confirm this evidence.

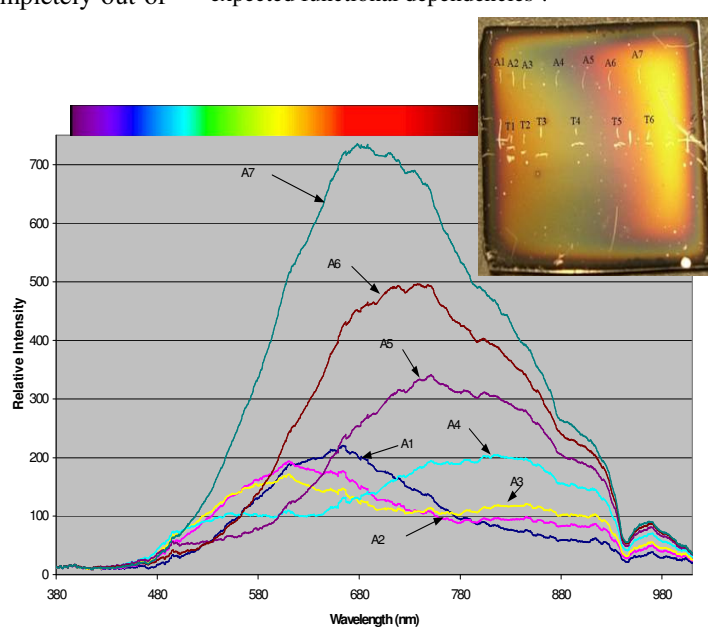


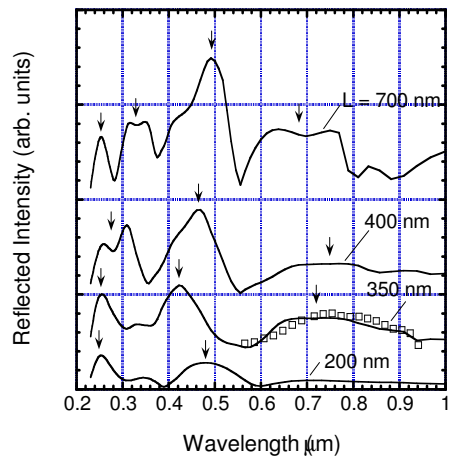
Figure 4. Resonance Maxima at Various Locations. Each location was measured to confirm the resonance response of the nanotubes. The inset is a photograph of the actual sample.

Computer simulations were also performed regarding the electromagnetic response of a random array of dipoles antennas. At each location where a spectrophotometric curve was recorded, a small scratch was made in the sample. SEM was used to measure the length of the nanotubes at each scratch location. Using the nanotube array dimensions, the simulation was run with the same interantenna spacing, height, and diameter. The number of antennas, however, was reduced to 10. These data are displayed in figure 5 (a)[3]. Here is shown the reflected light intensity, the squares represent experimental data used for comparison. This clearly shows that the nanotubes closely match conditions corresponding to dipole antennas.

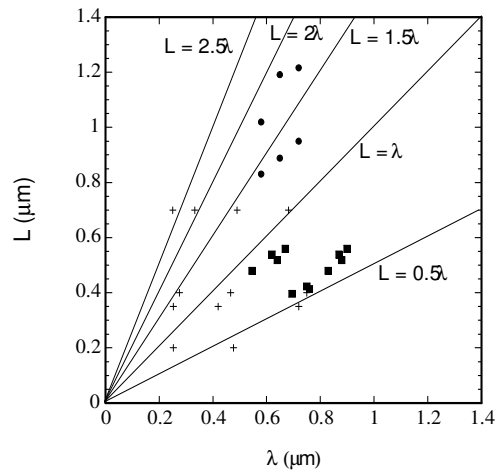
An additional simulation was performed and compared with experimental data[3]. The results are shown in figure 5 (b). The solid lines correspond to the following equation describing scattering maxima of a random array of dipole antennas[3].

$$L = m\frac{\lambda}{2} f(\theta, n) \tag{3}$$

Where f(θ, n)=1 for the ideal dipole condition[3]. Under this condition, various lengths were plotted. Actual measured data using the scratch/SEM technique are shown as squares and circles on the graph. It can be seen that the experimental measurements closely match the ideal dipole condition. The crosses correspond to distinct maxima marked with arrows in Figure 5 (a). These experiments and the corresponding computer simulations indicate that the MWCNTs do indeed behave like dipole antennas.



(a)



(b)

Figure 5. The length effect. (a) Theoretical reflected light intensity spectra from a model array of random antennas. (b) Average length vs. wavelength[3].

3. Optical Antennas and Lobe Patterns

During the experiments described above another interesting phenomenon was observed and has recently been studied in much greater detail. The MWCNTs project radiation patterns similar to the way radio antennas respond to radio waves. In order to study this attribute, a small slot was cut into a screen and a sample of randomly distributed MWCNTs was produced using the electrochemical deposition method described above. The incident beam was normal to the plane of the screen and passed through the slot in order to illuminate the sample, which was mounted on a rotating stage. At θ_i=0 the sample was coplaner to the screen, it was then rotated in ten-degree increments until θ_i=50. A camera was placed next to the sample to photograph the projected images. The results of this experiment are displayed in figure 6.

The nanotubes project patterns similar to concentric cones. The way in which the screen intersects the cone is equivalent to the well-known theory of conic sections. Rotating the sample is equivalent to changing the angle at which the screen intersects the cones by θ_s=180º-θ_i. This produces the various conic sections that are seen at different angles. The upper series in figure 6 corresponds to nanotubes of length l~3.5μm~6.5λ and the lower to l~850nm~2λ. When the sample is at θ_i=0 the pattern appears as a number of concentric rings. The number of rings is dependent upon both the length of the nanotubes and the angle of incidence. As the angle of incidence increases so does the number of rings behind the main lobe.

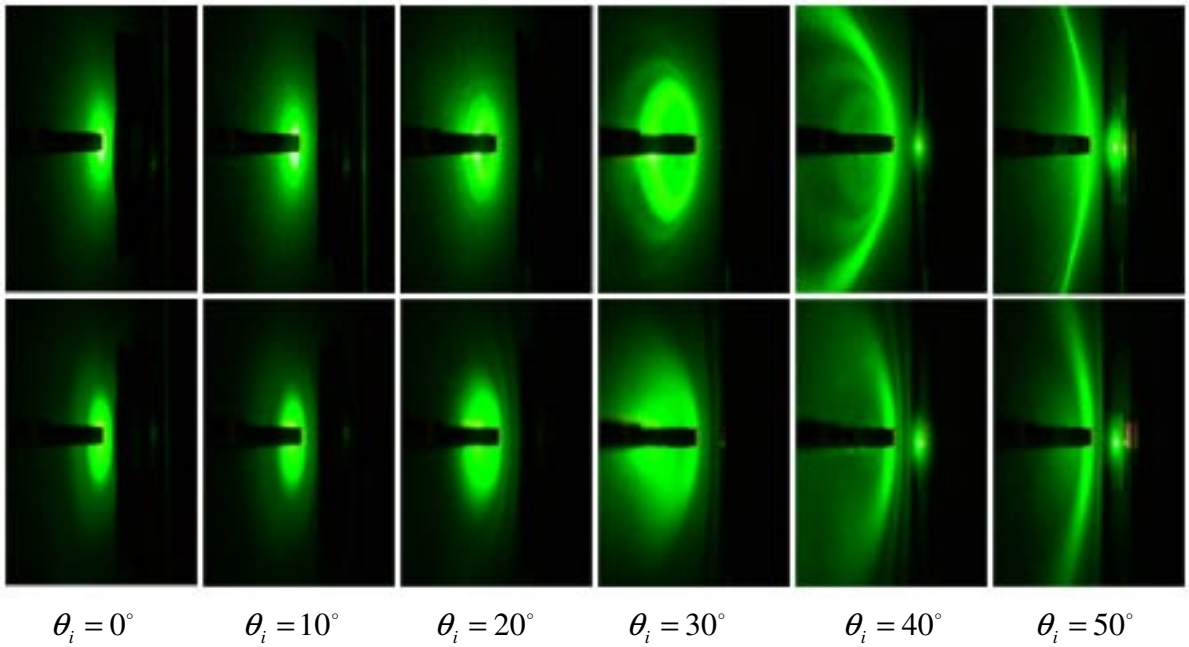


Figure 6. Projected lobe patterns at increasing angle of incidence. Upper series corresponds to nanotubes of length l~3.5μm~6.5λ; lower series to l~850nm~2λ. Incident wavelength λ=543.5nm.

In order to understand the nature of these lobe patterns it is necessary to consider the two properties that contribute to it. The principle of pattern multiplication states that any pattern is the sum of the pattern due to each element and the pattern due to the array. If the nanotubes are considered to be simple dipole antennas then the pattern projected by them in polar coordinates is described by,

$$F_{dipole}(\theta) = \sin(\theta) \ . \tag{4}$$

For ease of calculation, and with no loss of generality, the nanotubes are considered to be a uniform linear array. The pattern for such an array is described by,

$$F_{line}(\theta) = \sin(\theta)\sin\left[\left(\frac{\pi L}{\lambda}\right)\cos(\theta)\right] \Big/ \left[\left(\frac{\pi L}{\lambda}\right)\cos(\theta)\right]. \tag{5}$$

This equation, however, does not account for the array being excited by an outside source. Consider a uniformly excited, equally spaced, linear array of point sources. Each point source is radiating isotropically and positioned on the horizontal axis. If they are spaced some distance d apart, the incoming wavelength is λ, and θ is the polar angle then the intensity radiated is the linear sum of the intensities of the individual sources. A phase difference, δ, will be introduced because the arriving radiation will excite each element successively. This phase difference will be,

$$\delta = \left(\frac{2\pi d}{\lambda}\right)\cos(\theta). \tag{6}$$

The total emitted intensity will then be,

$$AF(\theta) = I_0 + I_1 e^{i\delta+\alpha} + I_2 e^{2i\delta+2\alpha} + \ldots = \Sigma I_n e^{in(\delta+\alpha)}. \quad (7)$$

Next we may assume that each element emits at an equal intensity, therefore $I_0=I_1=\ldots=I_n$. We may also define Ψ such that it contains all the phase information about the array.

$$\Psi = \delta + \alpha \quad (8)$$

Where α is the phase difference between the excited currents in the successive elements of the array. Finally the normalized array factor can be written as,

$$F_{array} = \sin(N\Psi/2)N\sin(\Psi/2), \quad (9)$$

where N is the number of elements in the array. This equation describes the total number of maxima due to constructive interference in the array. These are the bright lines seen in figure 6. Because this equation is both periodic in Ψ and bound by δ, the total number of maxima, or lobes, seen will be (N-1)d/λ, as N increases the number of lobes will increase linearly. Furthermore, if d is allowed to decrease, such that the length of the array remains constant, then (N-1)d=L, if the limit as N→∞ and d→0 is taken, the equation returns to that of a uniform line of length L[13]. By using the small angle approximation on (9), setting α=0, and multiplying be sinθ, the full pattern may be written,

$$F(\theta) = \sin(\theta)\sin\{(\pi L/\lambda)[\cos(\theta)-\cos(\theta_0)]\}/\{(\pi L/\lambda)[\cos(\theta)-\cos(\theta_0)]\}^{5,\,13}. \quad (10)$$

Where θ_0 is the angle that produces the maximum intensity.

To confirm this behavior a study was performed to compare the photographed patterns to computer models. The results are shown in figure 7. This fully confirms the fact that MWCNTs can and do act like dipole antennas, receiving and transmitting light in the same manner that a radio antenna receives and transmits radio waves.

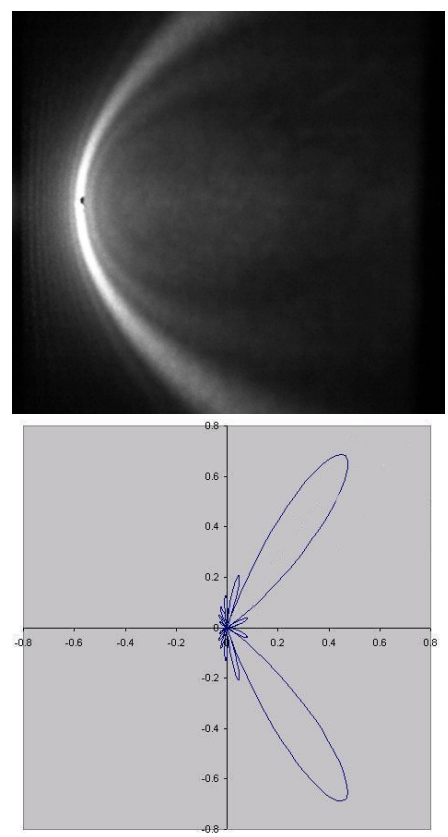


Figure 7. Lobe pattern comparison. The top photograph, shown in black and white for detail, is exactly the same as the predicted computer model.

4. Electromagnetic Wave Energy Conversion

The photovoltaic effect, which exploits the particle nature of light, is traditionally used for solar energy conversion. Though partially successful, this method has not provided the level of efficiency necessary to allow for mass usage. Furthermore, many photovoltaic devices require years of usage to produce an amount of energy equivalent to the amount required for their fabrication. It has even been reported that some devices can take up to thirty years to recoup that energy. Besides these manufacturing problems, they are also dependent on the band gap of the semiconductor from which they are made. The energy of the impinging photons must be within, or an integer multiple of, the bandgap or they will reflect off or pass through the device. The combination of these problems has only allowed incremental efficiency increases since the 1960s.

In 1971 Robert Bailey of The University of Florida proposed a different idea for the conversion of solar energy[9]. Opposite to the photovoltaic effect this idea takes advantage of the wave properties of light. Using antennas of a specific length and shape, theoretically one can absorb incoming electromagnetic radiation and then rectify it into usable energy. In a

technical report submitted to NASA in 1975, Bailey further analyzed this concept and showed that devices of this nature could have 100% conversion efficiency[7].

However, it was well recognized that an electromagnetic wave energy conversion was going to be difficult to produce. The calculations that Bailey performed assumed that the absorber had no rectifier built in. It also assumed that there were antennas small enough to absorb light in the visible spectrum. In Baileys own words one would need "… a forest of small relatively closed-spaced conoids or pyramids[7]." Since we now know that antennas can be produced of the required size and scale we feel this holds out the potential for such a device to be created.

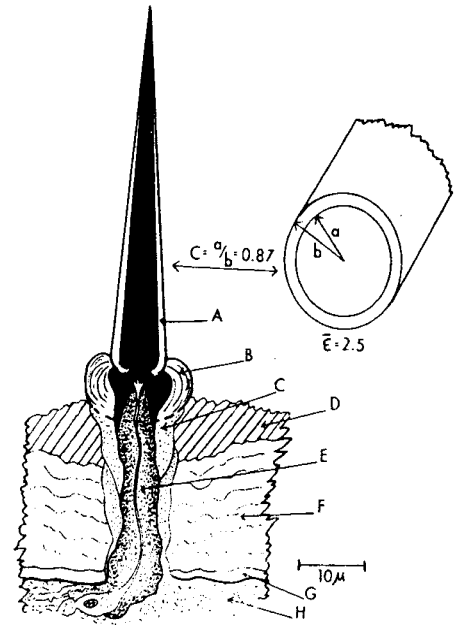


Figure 8. Diagram of insect waveguide spine[14].

Bailey was also quick to point out a theory presented by Philip Callahan, an entomologist for the USDA. It seems nature has endowed many insects with the ability to absorb, and in some cases, to rectify electromagnetic signals. Callahan postulated that the antennas on many insects were polytubular dielectric waveguide antennas[14, 15]. Figure 8 shows one of Callahan's original diagrams. To test this hypothesis, he inserted electrodes into a live moth, one in its thorax and another into the main antennal nerve, and then irradiated the antennae with a HeNe laser. From this experiment he was able to show that the moth antenna did respond to radiation by measuring with a dual beam oscilloscope. The difference between nature's antennas and CNTs is that the CNTs are metal, and metals are very lossy at visible frequencies. However, it could be possible to coat the CNTs to allow for absorption and then direction of a current into a rectifying device.

Bailey and Callahan also performed a theoretical comparison of insect antenna and their man-made equivalent. Figure 9 shows two of the eight geometries that they considered.

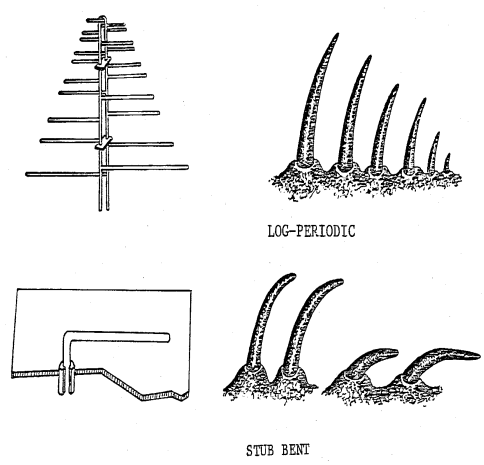


Figure 9. Comparison of insect antenna to their man-made equivalent[7].

Through the 1960s, and well into the 80s, research was also being conducted on microwave power transmission. During this re2search, which was mainly conducted at the Raytheon Corporation under the supervision of William Brown, and with funding from the United States Airforce, the idea of rectenna was introduced, which is simply a rectifying antenna. A simple rectenna is a Schottky diode placed in the middle of two dipole antennas. Brown and his group were able to use this concept to power a small helicopter by receiving and rectifying a microwave beam. Farber continued work in the microwave regime, and in 1988, using a pyramidal antenna structure, he was able to power a small motor.

5. Summary

Our previous studies involving the optical properties of MWCNTs have been reviewed. These studies reveal antenna-like effects, specifically the length effect and the polarization effect. We have proposed that MWCNTs behave like phased arrays of dipole antennas. Further evidence has also been presented, both theoretical and experimental showing the radiation lobe patterns. We feel that this

provides convincing evidence that MWCNTs interact with light waves in the same manner in which radio antennas interact with radio waves.

We have also reviewed concepts that would enable the use of this interaction to produce usable d.c. electricity. The electromagnetic wave energy converter concept, originally conceived and designed by Bailey in the 70s, was introduced and compared to the arrays of MWCNTs. With further research into rectification techniques, it may be possible to realize highly efficient and inexpensive energy conversion devices. Devices of this nature hold the potential to provide a permanent, clean, and reusable source of electricity to address the worlds growing energy crisis.

A review of similar research using microwave frequencies was also conducted. Through the work of Brown, Bailey, Farber, and others, it has been shown that microwave radiation can be rectified using antennas and power small electronic devices. Now that structures can be produced, in a controlled fashion, that are small enough to interact with the visible spectrum, it is reasonable to consider the possibility of visible light rectification.

Finally, an interesting insect antenna comparison, originally made by Bailey, was presented. The pioneering work of Callahan shows that nature has been using antennas for energy conversion for eons. The authors note that, often times, nature has in principle, simple solutions to complex problems, and perhaps it is time to take a page from it's book.

The properties discussed above hold the potential for a new class of electro-optic devices, photonic band-gap structures, efficient energy conversion, optical computing, UV/VIS/NIR detectors, and imaging devices.

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