Manipulation of Nanoparticles via Dielectrophoresis

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Abstract

While nanoscale device prototypes using carbon nanotubes abound, no mass production-scale technique exists for examining properties of a batch of nanotubes. Dielectrophoresis, on the other hand, has received much attention in the press as a method of separating and trapping particles. In this research, a method of developing mass production-scale tests of carbon nanotubes using dielectrophoresis without the need to grow them in situ is proposed. While reliability of placement is low at present, this method holds promise, warranting further investigation.

Introduction

Richard P. Feynman's[1] 1960 speech "There's Plenty of Room at the Bottom" brilliantly predicted the advent of research at the nanoscale. Sumio Iijima's 1991 discovery of carbon nanotubes was a major step forward in the genesis of this new field.[2] Carbon nanotubes have since been found to have exceptional mechanical and electrical properties, including tensile strength, temperature stability, resilience, and heat conduction. Depending upon their helicity, they can be conductive or semiconductive.[3] This host of desirable characteristics has led to proposed applications ranging from nanoscale circuits and transistors, to chemical sensors, to structural reinforcement of polymers.[4]

Measurement of these properties has proven difficult, however. Determining torsional response, for instance, involved distributing nanotubes onto a silicon wafer and patterning metal pads according to the dispersion.[5] This, obviously, is inconvenient and slow, as it requires separate patterns for each wafer.

Another technique has been to grow nanotubes directly using carbon vapor deposition.[6] Since this technique can only measure the properties of nanotubes grown locally, it is woefully inadequate for testing nanotubes grown in separate batch processes. Verifying a batch sample's metallic properties or determining whether defects in a batch grown for structural reinforcement are rare require a different method.

The challenge, then, is a delicate balancing act: to devise a method using a generic device that can almost customize tests. This method requires the versatility to examine electrical, mechanical, and electromechanical properties of nanotubes while maintaining the efficiency of large-scale production.

Background

When a neutral particle is placed in an electric field, it polarizes, forming a dipole. If the field is uniform, the field on each end of the dipole is equal, and no net motion occurs (Figure 1). In a nonuniform field, however, the fields on opposite ends of the dipole are unequal, and a net translational motion called *dielectrophoresis* (Figure 2) occurs. Unlike electrophoresis — the movement of charged particles in an electric field — dielectrophoresis does not depend on the polarity of the applied field (Figure 3), allowing AC fields to be used as well.

Dielectrophoretic force can be expressed as

$$F_{DEP} = \frac{1}{2}\mathrm{Re}\left[(\bar{m}(\omega)\cdot\nabla)\vec{E}^{*}\right]$$

where $\bar{m}(\omega)$ is the dipole moment of the particle, ∇ is the del vector, and $\vec{E}^{*}$ is the complex conjugate of the applied electrical field. For the simplest case, a spherical particle, the dipole moment $\bar{m}(\omega)$ can be expressed as

$$\bar{m}(\omega) = \frac{1}{3}v\varepsilon_m K(\omega)\vec{E}\,,$$

where v is the volume of the particle, and $\tilde{\varepsilon}_m$ is the relative permittivity of the surrounding medium. $K(\omega)$ is the Clausius-Mossotti factor, described by

$$K(\omega) = \frac{\tilde{\varepsilon}_p - \tilde{\varepsilon}_m}{\tilde{\varepsilon}_p + 2\tilde{\varepsilon}_m}\,.$$

$\tilde{\varepsilon}_p$ and $\tilde{\varepsilon}_m$, in turn, are the complex permittivities of the particle and medium, respectively, described by

$$\tilde{\varepsilon}_p = \varepsilon_p - j\frac{\sigma_p}{\omega}$$

$$\tilde{\varepsilon}_m = \varepsilon_m - j\frac{\sigma_m}{\omega}$$

j is the imaginary, $\sqrt{-1}$, σ the conductivity, and ω the angular frequency of the applied electric field. The time-averaged dielectrophoretic force, then, for a spherical particle of radius a is given by

$$\left\langle \vec{F}_{DEP} \right\rangle = 2\pi a^3 \varepsilon_m \,\mathrm{Re}\left[\frac{\tilde{\varepsilon}_p - \tilde{\varepsilon}_m}{\tilde{\varepsilon}_p + 2\tilde{\varepsilon}_m}\right]\nabla\left|\vec{E}_{RMS}\right|^2.$$

For detailed derivations including those of nonspherical particles, the reader is referred elsewhere.[7,8] As shown by Zhang et al.,[9] a nanotube in the presence of an electric field will preferentially orient

itself with its longitudinal axis parallel to the field.

Key implications of these results are threefold. First, for small particles, dielectrophoretic force is very small, necessitating large field gradients to overcome Brownian motion. Second, dielectrophoretic force is greatest at regions of high field gradient, such as sharp edges (Figure 4). Third, the direction of force depends not on the field but on the Clausius-Mossoti factor. Figure 5 shows a plot of all terms of dielectrophoretic force except the gradient of the field as a function of frequency for 510 nm latex beads suspended in water. Note that at low frequencies the force is positive, while it is negative at higher frequencies; this implies that the beads will be attracted toward regions of high field strength at low frequencies and repelled at high frequencies.

Approach

To exploit this powerful, versatile method of particle manipulation, conventional microfabrication techniques were used to construct a device to trap single nanotubes between reflective conductive electrodes using dielectrophoresis. Different geometries of electrodes are patterned onto a surface to accommodate various types of experiments. The device in this experiment, 1 cm on each side, accommodates 20 pairs of electrodes, 10 with spacing of 1 µm and 10 with spacing of 2 µm (Figure 6). SU-8 photoresist is patterned on the surface, around the electrodes (Figure 6), to create a well with two channels in which the experiment can be run. This well can be covered with a glass cover slip during an experiment to minimize electrohydrodynamic flows associated with evaporation. The channels allow limited evaporation. If necessary, capillaries can be inserted to inject a sample or to flush sample remnants.

A set of electrodes was connected to the circuit of Figure 7. The circuit, similar to that used by Chung and Lee,[10] serves to diminish the field substantially after a nanotube bridges the gap and to detect the bridging event by monitoring the voltage drop across the resistor. The gap, which can be modeled as a small capacitor, prevents flow of direct current; thus, the DC component of the source voltage is applied exclusively across the gap. The large impedance of the gap relative to the large capacitor ensures that most of the AC voltage is applied across the electrodes. Nanotubes are attracted toward the high field gradient at the electrode

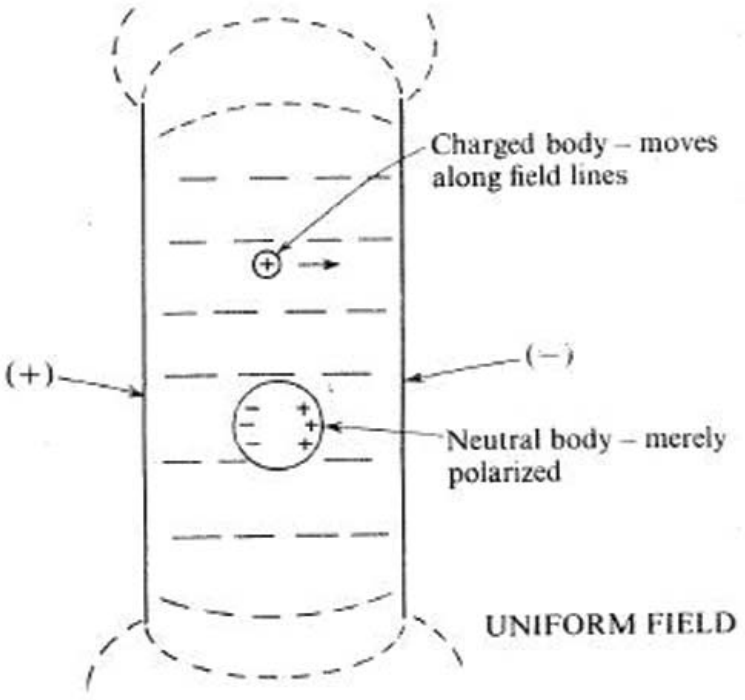

Figure 1: Neutral and charged particles in a uniform electric field.[12]

tips; when one bridges the gap, the impedance (assuming a metallic nanotube) drops dramatically, and nearly all source voltage is measured as a drop across the resistor/capacitor series. The electric field in the gap is substantially diminished, and the operator can gauge the success of the experiment before using scanning electron microscopy or similar methods to image the positions of carbon nanotubes.

The capacitance of the electrode gap was estimated, using finite element analysis software, to be between 0.1 and 1 pF. This result, though probably only accurate to a few orders of magnitude, allows selection of a capacitor large enough for the electrode gap. Values of 1 GΩ and 22 µF were selected for the resistor and capacitor, respectively.

After trapping, the nanotube can be affixed to the electrodes using e-beam lithography, and a myriad of tests can be performed. The electrodes are conductive, allowing electrical, mechanical, or electromechanical tests.

Results

Use of the trapping device has made it possible to demonstrate that carbon nanotubes are attracted toward the electrode tips — the region of high field gradient. Furthermore, this research has demonstrated correct orientation of carbon nanotubes toward another electrode. As seen in Figure 8, nanotubes are attached to one electrode and oriented with their longitudinal axis along the electric field lines. Figure 9 shows that nanotubes are preferentially attracted toward the electrode tips. Both results were expected and are reproducible.

The attempt to trap a single nanotube proved unsuccessful. The experimental results seen in Figure 11 show a single nanotube oriented correctly and bridging the electrode gap. However, some debris, as well as other nanotubes, were collected with one electrode. The research was able to reproduce bridging, but never without the presence of other nanotubes, debris, or both. Debris and/or other nanotubes made it difficult to secure the nanotube using an electron beam.

Placement of nanotubes was very sensitive to variation in the frequency of the applied field and concentration of suspension. Frequencies as low as 10 kHz

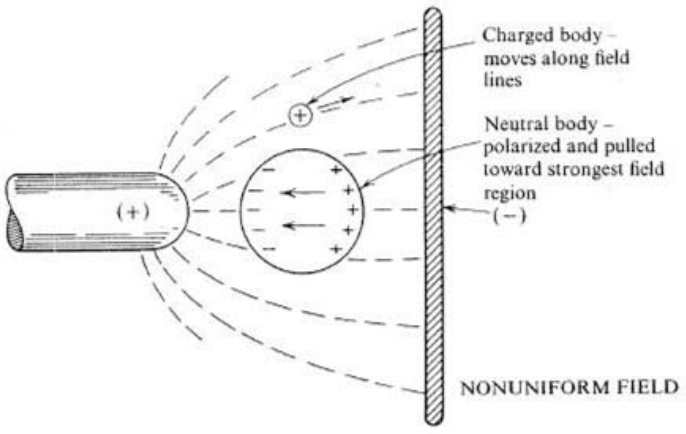

Figure 2: Neutral and charged particles in a nonuniform field.[12]

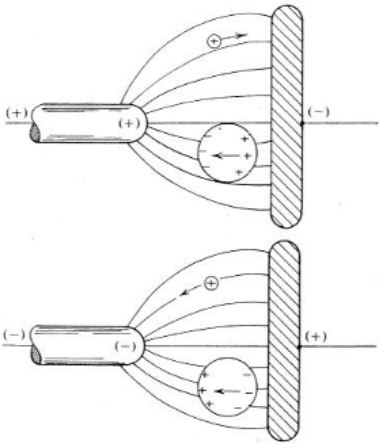

Figure 3: Neutral and charged particles in an alternating field.[12]

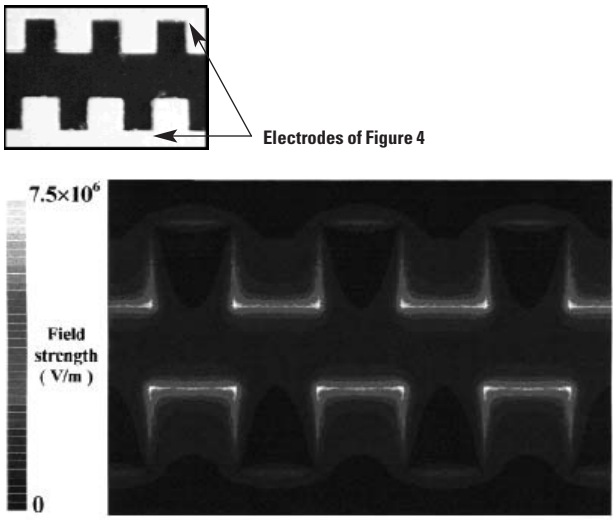

Figure 4: Electric field distribution for a plane immediately on top of the electrode array above. Note the extremely high gradients at the corners of each.[13]

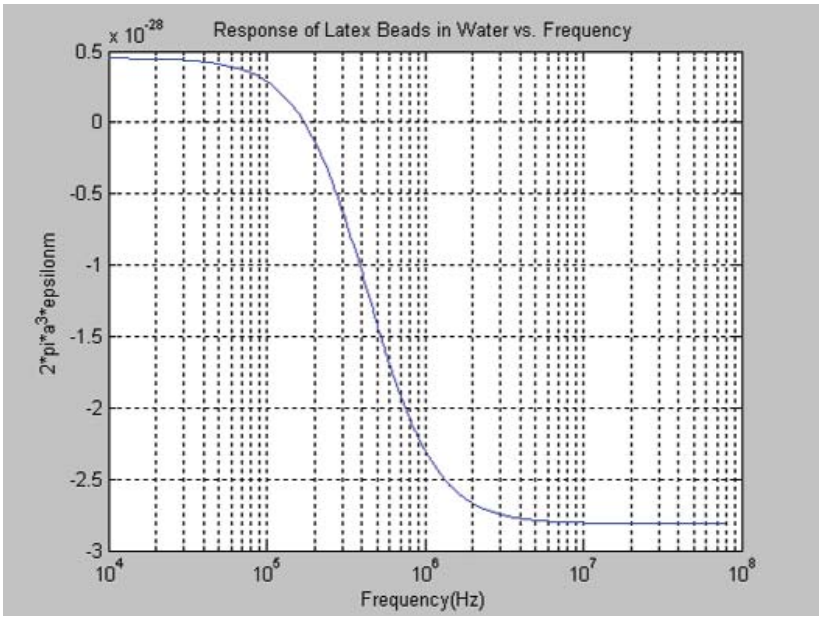

Figure 5: $\frac{\langle F_{DEP} \rangle}{V|E_{RMS}|^2}$ **as a function of frequency.**

resulted in large agglomerations of debris, including nanotubes, around the electrode tips, even with moderate concentrations (Figure 10). Higher concentrations, meanwhile, resulted in similar agglomerations of nanotubes — but not necessarily debris — at all frequencies investigated (<10 MHz). Note that in Figure 9 a lower voltage but higher concentration was used than in the experiment of Figure 8. The results shown in Figure 10, meanwhile, use the same concentration as the experiment shown in Figure 11, with frequency varied. Results are summarized in Table 1.

Additionally, when nonactivated electrodes were investigated, some were found to have nanotubes present, as seen in Figure 12. Achieving a nearly perfect result on even two sets of electrodes, as was the case in this experiment, is puzzling and warrants further investigation.

The research also explored the possibility of removing some excess nanotubes after dielectrophoretic deposition. If many are deposited with the correct orientation across an electrode gap, removing most could statistically leave a single nanotube at the desired location. To test this, a PDMS film was placed on an electrode gap known to have attracted a number of nanotubes, and subsequently the film was peeled away. This is similar in technique to soft lithography. Results were irregular; nanotube bunches were completely removed from some gaps and left nearly intact at others.

Similarly, reliability and reproducibility are issues in dielectrophoretic placement. As demonstrated, a single nanotube has not been completely isolated across an electrode gap. Further work is required to determine the exact repeatability of results. The technique still holds much

potential if it can be refined to allow placing a nanotube at will. While not presently possible, such a scenario is at least conceivable.

Also yet to be studied are the relative efficiencies of dielectrophoretic placement and placement using an atomic force microscope (AFM) integrated into a scanning electron microscope (SEM) chamber. As demonstrated, such a device can be used to place individual nanotubes directly.[11] It may be more efficient to place nanotubes in this fashion rather than via dielectrophoresis.

Conclusion

By combining dielectrophoresis with a versatile electrode device and a simple circuit, one can trap carbon nanotubes for testing. While the results are far from perfect, given the vast number of parameters that affect dielectrophoretic force, near-perfect results do not seem out of the question. Further exploration of different frequencies, AC and DC combinations, and suspension media (both different permittivities and conductivities) is necessary. Additionally, accurate values of conductivity and permittivity of nanotubes would give a method of predicting the effects of varying such parameters. After more exploration of this method's reproducibility and parametric effects, an efficiency comparison should be performed with an integrated SEM/AFM.

While mass production-scale testing of carbon nanotubes is still in the distant future, given nanotubes' wide range of potential applications, there is little doubt of their continued key role in miniaturization.

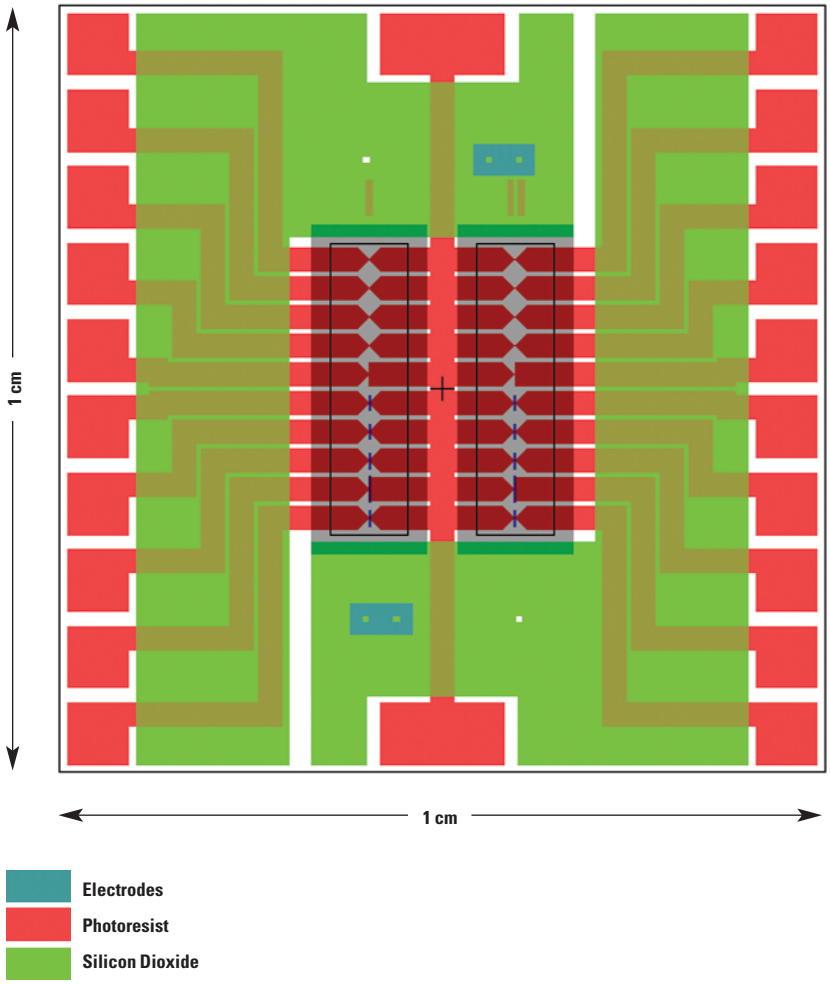

Figure 6: The device used in this experiment. Electrodes in the left column have 1 µm between them, while those on the right are spaced 2 µm apart.

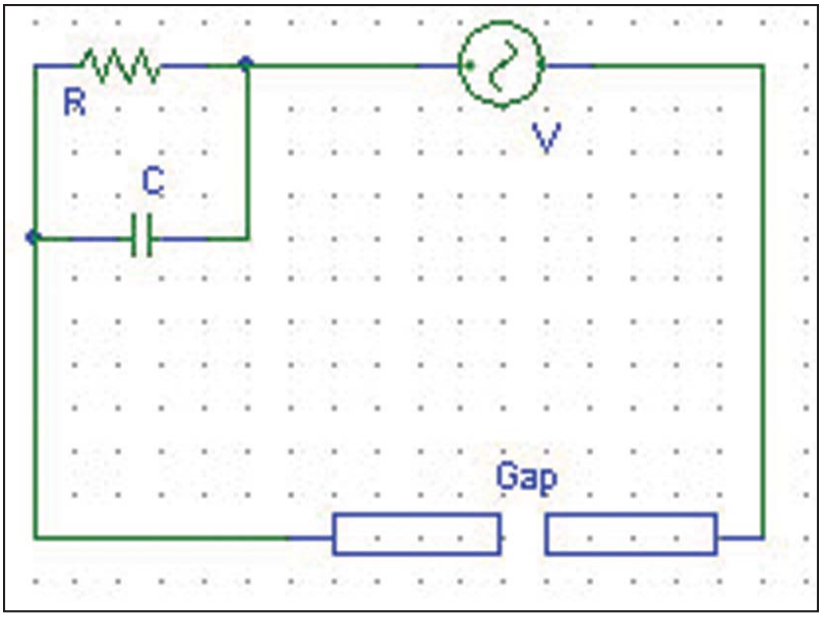

Figure 7: Schematic of circuit used to trap single nanotubes across a set of electrodes.

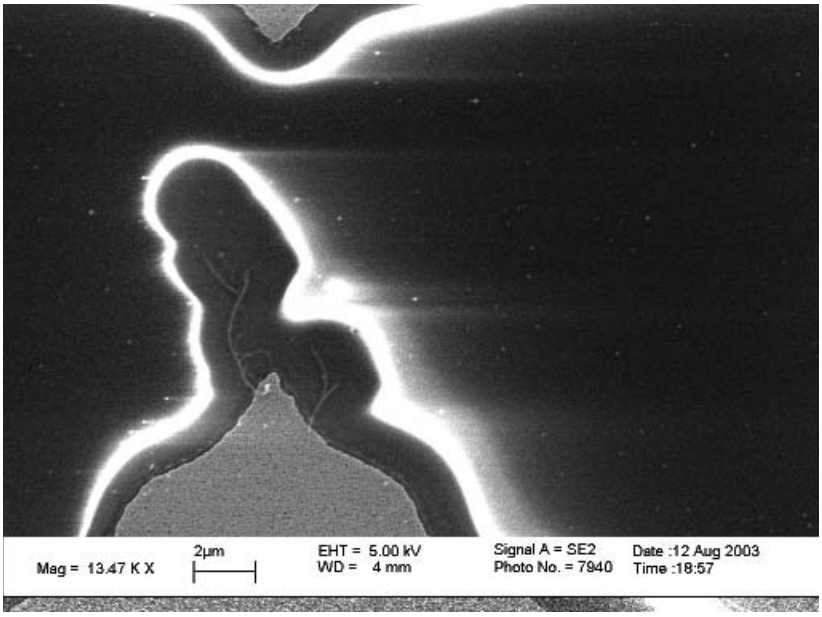

Figure 8: SEM image demonstrating correct orientation of nanotubes using an applied signal of 3 volts of direct current (VDC) and 3 volts of alternating current (VAC) at a frequency of 5 MHz.

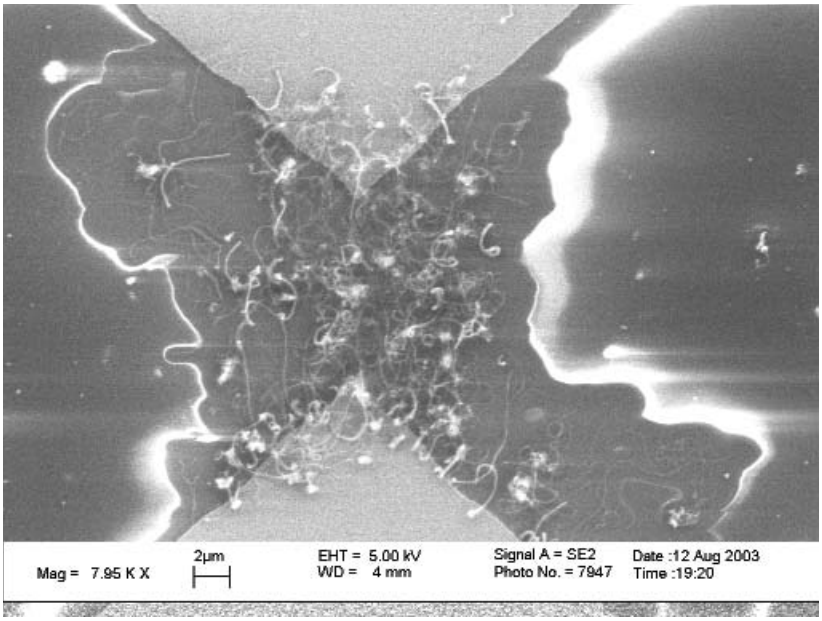

Figure 9: Attraction of nanotubes to electrode gaps using a 2.5 VDC, 2.5 VDC 5 MHz signal.

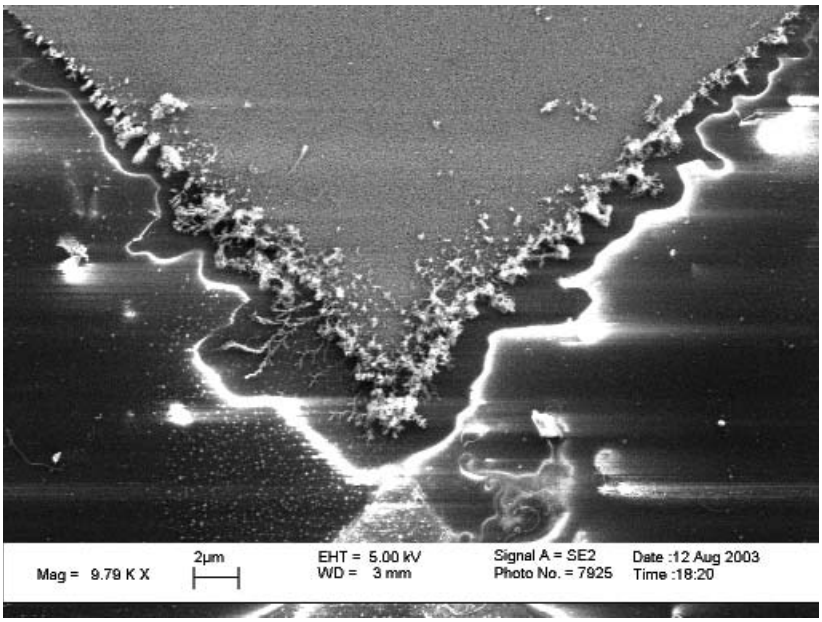

Figure 10: Attraction of assorted debris to the electrode gap using a 3 VDC, 3 VAC 10 kHz signal.

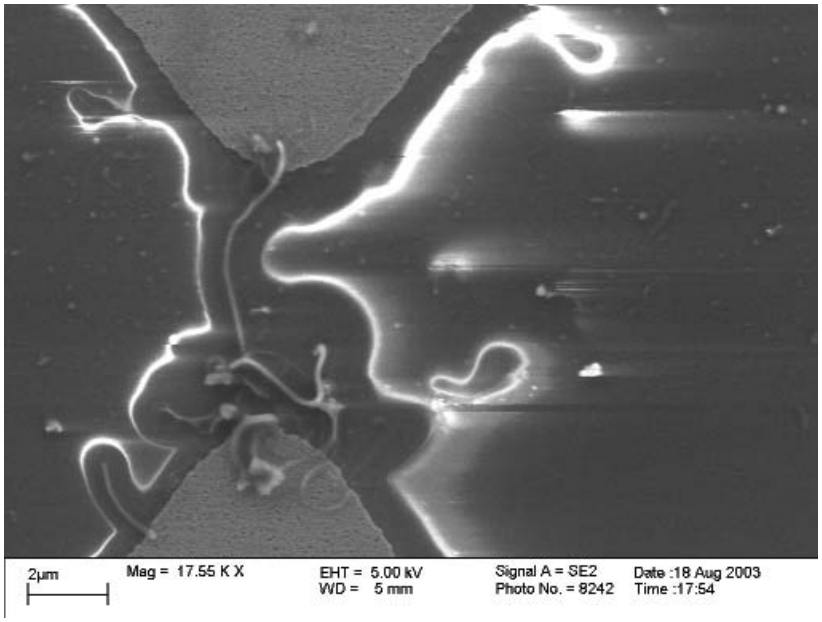

Figure 11: A single nanotube almost bridging the electrode gap.

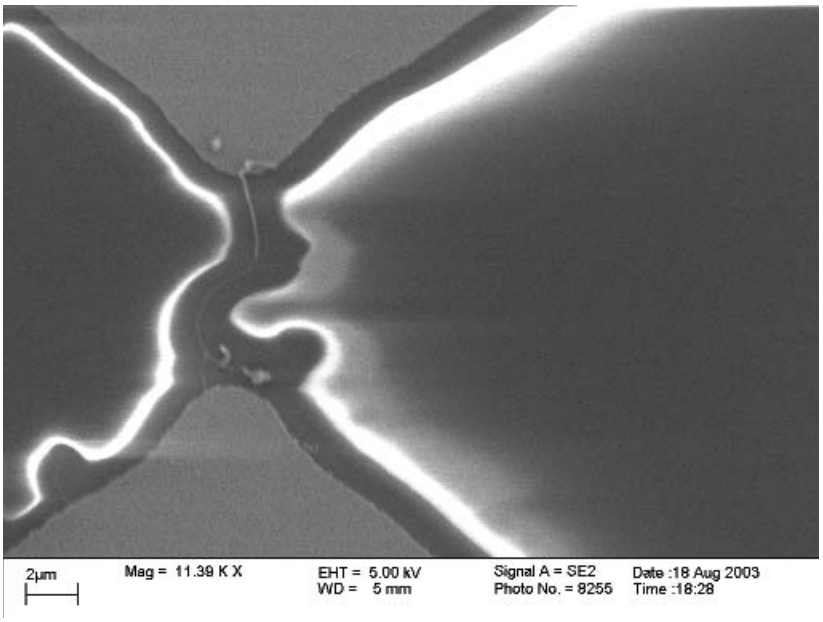

Figure 12: Electrode without voltage applied.

Table 1: Summary of above results

Figure	DC Signal	AC Signal	Frequency	Summary of Results
8	3	3	5 MHz	Correct orientation of nanotubes, lack of debris
9	2.5	2.5	5 MHz	Nanotubes attracted in bunches to electrode gap
10	3	3	10 kHz	Debris and nanotubes attracted to electrode gap
11	2	2.5	Varied	Nearly perfect bridging of a single nanotube
12	-	-	-	Nearly perfect bridging of a single nanotube

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