Determination of relative concentrations of metallic and semi-conducting SWNTs in suspension via dielectrophoresis

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ABSTRACT

Dielectrophoresis (DEP) is a phemomenon of induced particle motion in non-uniform electric fields. The effect is frequency dependent; by monitoring the motion of particles in AC fields and ananlysing the change in motion with frequency, it is possible to determine the electrical properties of nanoparticles in lab-on-a-chip systems. In this paper, we demonstrate how DEP can be used to determine the ratio of semiconducting and metallic carbon nanotubes in solution, by monitoring the frequency-dependent impedance change between two electrodes as a function of energising frequency.

Keywords: dielectrophoresis, chirality, characterisation, impedance

1 INTRODUCTION

In the years since their discovery [1], carbon nanotubes (CNTs) have been shown to have remarkable properties [2-4] that make them applicable in a broad range of applications as components in nanoelectronic applications. However, one significant disadvantage is that when CNTs are produced, single-wall carbon nanotubes (SWNTs) can behave either as a metal or a semi-conductor depending on their diameter and chirality at time of formation [5]. As this process is random, SWNTs of both kinds are produced simultaneously and much effort has been applied to separating them. Perhaps the most effective separation technique so far, dielectrophoresis (DEP) - the movement of particles in non-uniform electric fields - has been used to separate mixtures of semi-conducting and metallic SWNTs [8-10] However, assessment of the efficacy of separation has been limited by the investigation methods available; generally, measurement of the frequency-dependent collection of dielectrophoresis has been based on Raman spectroscopy, which offers low frequency resolution and requires some complex interpretation of results [11-14].

In this paper, we report the application of combined dielectrophoresis and impedance measurements to provide real-time rapid, accurate measurement of dielectrophoretic collection of SWNTs. Using this method, we are able to quantify not only the precise dielectrophoretic collection behavior of SWNTs of both varieties, but also the proportions of tubes of both types within the sample.

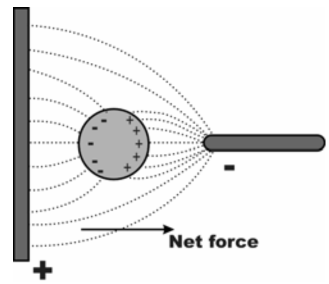

Figure 1. Dielectrophoresis is the force induced on a polarisable particle suspended in a non-uniform electric field.

We demonstrate that this can be used to provide an accurate assessment of the optimum conditions of DEP separation and determination of the dielectric properties of the carbon nanotubes. Our results indicate the sample analyzed in this study contains 21.5 % of metallic and 78.5 % of semi-conducting carbon nanotubes before separation, and that the range 1 MHz-15 MHz is optimal to collect only the metallic type of SWNTs.

2 MATERIALS AND METHODS

We used a suspension of SWNTs (laser ablation) in a TritonX-100 solution (0.6 % Triton X-100, 0.16 % SWNTs in weight). The suspension has been sonicated and then centrifuged for 2 h at 16000 g to remove the large impurities (catalyst particles, amorphous carbon). The electrodes were prepared from a 20 nm chromium film deposited by sputtering on glass. The patterning was made by photolithography and etching.

Measurements were performed on needle-shaped electrodes with an inter-electrode gap of 10 μm and energized with a sinusoidal 10 $V_{pk\text{-}pk}$ voltage, at 5 frequencies per decade over the range 10 kHz-20 MHz. A resistance of 4.33 kΩ was connected in series with the electrodes, and the voltage measured across the resistor and resistor/electrode combination using an ISO-TECH IDS710 digital oscilloscope. The output of the oscilloscope was digitised, and a MATLAB program (The Mathworks, Natick, MA, USA) was used to calculate the impedance of the inter-electrode gap at 1-second intervals. The recording process preceded the SWNT containing suspension being placed on the electrodes, and continued for typically 5 min.

The time constant of the change of resistance as a function of time was then obtained. A control experiment with a Triton solution free of carbon nanotubes was also performed to observe as a zero collection reference.

3. RESULTS

The control solution was weakly conductive ($1.4mSm^{-1}$ compared with deionized water $0.75mSm^{-1}$). After the application of triton solution without nanotubes, a 30 % decrease was observed in the impedance between the electrodes. When the solution contained nanotubes, two different types of behavior were observed. In the first, corresponding to the group of curves recorded at high frequencies, an initial drop in impedance at the application of the sample was followed by an exponential decrease to a stable value after approximately 200 s. In the second set, observed at low frequencies, the reduction is much more significant and rapid. At 20 MHz, the response indicated that the impedance change was due to the medium alone – that is, the result was identical to the control measurement, indicating no collection of nanotubes was occurring.

4. DISCUSSION

If we hypothesize that the time taken for the impedance to change due to the collection of nanotubes is inversely proportional to the force acting on those tubes, then the reciprocal of the time constant would indicate the magnitude of the force. Across a population of particles, this reciprocal also indicates the relative population of particles where multiple populations are present. By modeling the population using known models of dielectrophoretic behavior, it is possible to determine both the electrical properties of each population and the relative number [15]. Two dielectric dispersions were evident, centered approximately at 250 kHz and 13 MHz. We observe that this is consistent with behavior we would expect for a heterogeneous mix of metallic and semi-conducting SWNTs.

It is possible to predict the behaviour of nanoparticles in DEP fields, and hence to infer their properties from their observed DEP response. For a spherical particle of radius r the DEP force is given by equation (1):

$$F_{sphere} = 2\pi r^3 \varepsilon_m Re\left[\frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*}\right]\nabla E^2 \qquad (1)$$

where, ε_m is the absolute permittivity of the suspending medium, E is the local (rms) electric field, ∇ is the differential vector operator, ε_p^* and ε_m^* are the complex permittivities of the particle and medium respectively, $\varepsilon^* = \varepsilon - j\sigma/\omega$, where, ε is the permittivity, σ the conductivity, ω the angular frequency of the applied field, $j = \sqrt{-1}$, and Re denotes the real part. For the case where the 'spherical' particle is replaced with a rod whose major axis is r_1 and minor axis r_2, the force is given by the equation (2):

$$F_{rod} = \frac{2\pi r_1 r_2^2 \varepsilon_m}{3} Re\left[\frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_m^*}\right]\nabla E^2 \qquad (2)$$

According to the relative magnitudes of ε_p^* and ε_m^*, which are in turn related to ω, the DEP force causes particles to move either towards or away from high-field regions at electrode edges. These two effects are termed *positive* and *negative* DEP respectively.

A best fit was found when the population of SWNTs was modeled as two subpopulations of nanotubes, superimposed to determine the net frequency-dependent SWNT collection. A spherical model, postulated by Krupke et al. [8] to account for ballistic ion transport, was found to provide a good fit for the conducting nanotubes, when the nanotubes were assigned a conductivity of $130\ mSm^{-1}$ and a relative permittivity of less than $40\varepsilon_0$. We were able to obtain a unique set of parameters that enabled us to model semi-conducting nanotubes either as spheres or as long, thin ellipsoids – an approach that has been used successfully for dielectrophoretic modeling of rod-shaped nanoparticles in the past [16]. In the case of a spherical model, the nanotubes had a conductivity of $2.2\ mSm^{-1}$, and for the prolate ellipsoid model, $2.5\ mSm^{-1}$. As with the conducting nanotubes, the model indicates a permittivity of less than $40\varepsilon_0$. Notably, this permittivity is considerably lower than the near-infinite value suggested in the literature [17].

Once the electrical properties of the SWNTs populations have been obtained, we can further determine the relative populations of the particles by determining the relative multiples of each required to match the spectra. Our calculations indicate that where the semi-conducting nanotubes are modeled as prolate ellipsoids, the proportions of the two subpopulations indicate the population contains (78.5 ± 1 %) semi-conducting SWNTs, with the remainder being metallic. This proportion appears high at first, but is commensurate with the findings of Samsonidze et al. [18] who showed that semi-conducting nanotubes dissolved preferentially in ODA; if similar effects are present in Triton-dissolved nanotubes, we would anticipate the result described here.

In conclusion, we have demonstrated a rapid, precise and low-cost method for performing dielectric spectroscopy of single-walled carbon nanotube suspensions. This has allowed the determination of the dielectric properties of the SWNTs with good precision, and also the rapid determination of the proportions of metallic and semi-conducting SWNTs. Moreover, the precision afforded by the system presented here has potential for providing more accurate control over defining the optimal conditions for the large-scale separation of SWNTs that is required for the adoption of nanotubes as a material of choice in the semi-conductor industry.

3 REFERENCES

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