

Reply to “Comment on ‘Using the Selective Functionalization of Metallic Single-Walled Carbon Nanotubes to Control Dielectrophoretic Mobility’”

Nitish Nair and Michael S. Strano*

Department of Chemical & Biomolecular Engineering,
University of Illinois, 118 Roger Adams Laboratory,
Box C-3, 600 South Mathews Avenue,
Urbana, Illinois 61801-3602

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Dielectrophoresis (DEP) is a process in which micro- and nanoscale particles can be manipulated by the application of a nonuniform electric field.¹ A large electric field gradient can be applied between lithographically created gold electrodes on a silicon substrate, for example. A dipole moment is then induced within a neutral particle in the vicinity of the electrode gap. Depending on the frequency of the alternating current (ac) field, an attractive (positive DEP) or repulsive (negative DEP) force acts on the particle. This characteristic of dielectrophoresis has been reportedly harnessed in separating semiconducting carbon nanotubes from metallic ones.^{2,3}

The separation of metallic and semiconducting carbon nanotubes is a continuing research area. With regard to dielectrophoresis, the claim is that metallic nanotubes always experience positive DEP while semiconducting nanotubes are repelled toward the regions of lowest field gradient at frequencies above the crossover frequency, ω_c . This is about 3 MHz for a 1% sodium dodecyl benzene sulfonate (SDBS) suspension of nanotubes and 1 MHz for a 0.1% SDBS–nanotube suspension.³ Other approaches have been proposed, including methods based on chemical differences. Diazonium reagents apparently functionalize single-walled carbon nanotubes (SWNTs) suspended in aqueous solution with selectivity toward their electronic structure.⁴ These reagents have also been used in the fabrication of semiconductor-only single-walled carbon nanotube network devices.⁵ DNA-coated carbon nanotubes have been found to separate into different fractions with different electronic structures by ion-exchange chromatography.^{6,7} The affinity of amine groups for semiconducting SWNTs, as opposed to their metallic counterparts, has been used for the apparent selective precipitation of metallic nanotubes, as suggested by Raman investigations.⁸ Despite the activity in this area, an unambiguous, scalable method of separating single-walled carbon nanotubes in this way remains elusive.

In their comment, Krupke and co-workers mischaracterize our previous work⁹ as a “failed [dielectrophoresis] experiment” apparently because we draw very different conclusions from spectroscopic measurements on dielectrophoretically deposited material. In our original manuscript, we performed the deposition using the exact same frequency, voltage, electrode gap size, and surfactant suspended solution as the authors in their ref 1. Also, our data are very similar to their observations in ref 2. For example, we obtain the same high density of aligned nanotubes by scanning electron microscopy (SEM): compare, for example, Figure 2a of Baik et al.⁹ and Figure 2 of Krupke et al.² We also observe a very similar enhancement of metallic Raman features when Raman spectroscopy is performed on the DEP deposited material. Compared to a control formed from drying the same starting solution on a microscope slide, the

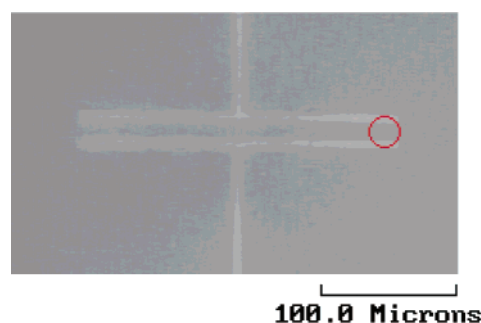


Figure 1. Photograph of the 10 μm electrode gap that was used in the dielectrophoresis experiment.

DEP material shows enhancement of metallic features at 633 nm excitation.

A major conclusion of our manuscript is that environmental factors contribute to changes in the radial breathing mode (RBM) spectra, and this complicates their use to benchmark a potential separation. In Baik et al.,⁹ we compare the DEP deposited material to two different control samples with differing average SWNT bundle sizes. In previous work,¹⁰ we demonstrated and modeled the systematic change in Raman spectral features with an increase in bundle size. In ref 9, we show conclusively that the apparent enrichment of metallic features can be completely attributed to the fact that DEP creates smaller bundles of nanotubes compared to the drop-dried control used by Krupke et al.² We also provide electrical transport measurements that confirm that both metallic and semiconducting nanotubes are still present after DEP. Because the only evidence in the literature^{2,3,12} to date for DEP separation of SWNTs relies on very similar changes in the Raman spectra, as we investigate in ref 9, we assert that the case for this separation remains unconvincing.

In their recent comment on our article, the authors suggest that our results are somehow different than those of ref 2, although it is not clear what aspects of the data are inconsistent with their work. They suggest that our electrode geometry included a much larger surface area that may have led to sample heating. They also raise the possibility that our sample was contaminated. Spectra of a supposedly enhanced DEP separation are then provided where the metallic features of DEP deposited material are considerably larger than what has been published previously.² The point that is implied here is that their DEP process has now produced an even greater apparent enhancement of metallic modes over semiconducting ones and this is evidence of high frequency DEP separation of metallic versus semiconducting nanotubes. The tacit assumption is that Raman mode enhancement based on morphology or aggregation cannot produce an enhancement this large.

To address these assertions, we changed our electrode design to adopt a narrower geometry similar to ref 2. The electrodes were fabricated by photolithography using the same gap size of 10 μm . The contacts were formed on a SiO_2 –Si substrate by evaporating 10 nm of titanium and 300 nm of gold (Figure 1). The wafer–electrode setup was then fitted on a dual inline package and connected to the electrical pads on the latter using a wedge-bonder (Hybond). HiPco SWNTs were dispersed in 1% aqueous solution of the surfactant, sodium dodecyl sulfate (SDS), according to the protocol outlined in ref 11. This was the same protocol as that used in refs 2, 3, and 9. In the dual

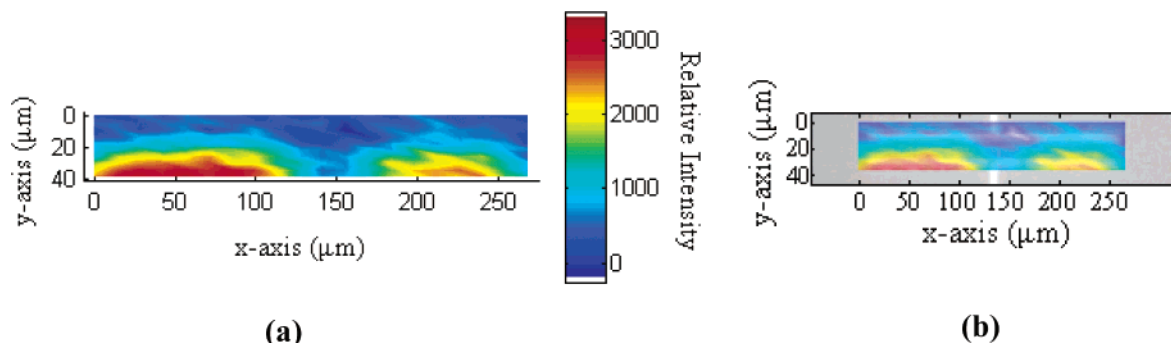


Figure 2. 2-D Raman map of the area in the electrode gap at 785 nm: (a) Raman map with the color scale; (b) white light overlay (the color plot is superimposed on the electrode gap).

inline package, the silicon substrate was situated in a cavity which was filled with the nanotube–SDS suspension and covered with a glass slide to prevent evaporation from taking place. When the aim of the dielectrophoresis process is to deposit aligned carbon nanotubes in the electrode gap, only a drop of the suspension is required, which is blown after the field has been applied for the requisite period of time. The focus of our experiment was to observe the effect of the ac electric field on the suspension and to test the claim of preferential deposition of metallic nanotubes. The ac field was applied using a function generator at a frequency of 10 MHz and a peak-to-peak voltage of 10 V for a period of 5 min. This procedure was repeated six times for the same chip. Afterward, instead of blowing the solvent away, the chip was rinsed successively with SDS solution, methanol, and water. The purpose of this was to remove any surfactant that was adhered to the deposited nanotubes.

The Raman spectrum of the material in the gap is very similar to Figure 1 of the Krupke et al. comment at 633 nm, showing dramatically enhanced metallic features and barely detectable semiconducting features. The area in the gap between the electrodes was then mapped using the Raman spectrometer at a laser wavelength of 785 nm. Individual spectra along the electrode edges were also taken at 633 nm. The laser power at the sample was 41.3 mW for the 785 nm laser and 5.26 mW for the 633 nm laser. The diameter of the beam-waist was approximately 3 μm .

The Raman map in Figure 2 shows the regions with the highest concentrations of nanotubes, based on the area underneath the RBM peaks in the spectrum (213–237 cm^{-1}). The following nanotubes can be detected in this range: (9,7), (10,5), (11,3), (10,6), (12,1), and (12,2). The peaks corresponding to the first three were observed in the Raman spectrum of the starting solution. Since the Raman map was taken using the 785 nm laser at which these semiconducting tubes are detectable, it is clear that they have been deposited and hence experienced positive dielectrophoresis. Raman spectra at 633 nm were also taken in the same regions of nanotube concentration, as visible in the 2-D map to probe for metallic tubes. Figure 3 shows that metallic carbon nanotubes are also present, based on the (13,4) and (12,3) metallic nanotube peaks. They are also concentrated in the same regions as their semiconducting counterparts and correspond exactly to the peaks observed in the comment that Krupke et al. had published in response to ref 9, in which dielectrophoresis had been carried out at 10 MHz. The corresponding semiconducting peaks that were observed at 785 nm are shown in Figure 4 in comparison with the silicon peak. The relative intensities for the RBM and the silicon peak are shown on different scales so as to make the former more prominent. We see that the relative intensities of the Raman modes at both

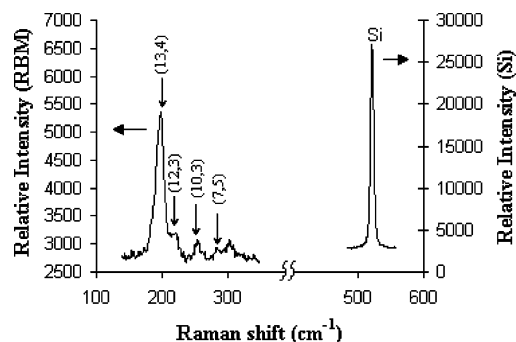


Figure 3. The 633 nm Raman spectrum shows the (13,4) metallic nanotube peak in comparison with the Si peak. As in the comment of Krupke et al. to ref 9, diminished semiconductor peaks, corresponding to the (10,3) and (7,5) nanotubes, are also visible.

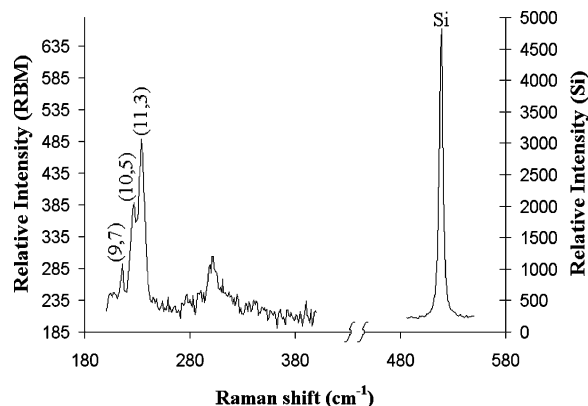


Figure 4. The 785 nm Raman spectrum shows semiconducting nanotubes with the Si peak as a standard for comparison to estimate the concentration of material deposited. The spectrum was taken in the same region as the one in Figure 3.

633 and 785 nm excitation are comparable using the Si peak as a reference in each spectrum.

Because the DEP process described here yields very similar spectra to those presented by Krupke et al. in their comment, we remain unconvinced that the latter is due to enrichment of metallic species. A convincing measurement can be made by studying the electrical conduction through the electrode gap in detail, as we have done in our previous work.⁹ Photoabsorption should also yield unambiguous results. Spectroscopy on the remaining (undeposited) material in the mixture which should be enriched in semiconductors should also answer these questions.

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