

Chirality Separation of single walled carbon nanotube using microfluidic

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ABSTRACT

Highly pure metallic single-walled carbon nanotubes were continuously extracted from a mixture of semiconducting and metallic species using a non-destructive, scalable method. Two laminar streams were generated in an H-shaped microfluidic channel with two inlets and two outlets. The flow conditions were carefully controlled to minimize diffusive and convective transport across the boundary between the two flows. Dielectrophoretic force from the embedded electrode at the junction extracted metallic nanotubes from a stream of nanotube suspension toward the other stream of buffer solution without nanotubes. The highly pure metallic and enriched semiconducting nanotubes were obtained simultaneously at each outlet using this novel approach. Excellent selectivity was verified by electrical transport measurement, absorption, and Raman spectroscopic analysis.

Keywords: carbon nanotube, chiral separation, dielectrophoresis, microfluidics chip

1 INTRODUCTION

Single-walled carbon nanotubes (SWNTs) have attracted considerable attention due to their size and exceptional material properties [1,2]. Metallic SWNTs can function as conductive additives in composites and nanoscale leads in integrated circuits [3–5], while semiconducting SWNTs can be used as field effect transistors [6]. However, all current synthesis methods produce only heterogeneous mixtures of semiconducting, semi-metallic, and metallic electronic types [7]. Various approaches have been explored for the separation of metallic from semiconducting SWNTs, including the selective synthesis of narrow chiral distribution nanotubes, the preferential destruction of one type of nanotubes in a mixture, and separation by chemical and physical methods [8–10]. However, none of these approaches allow bulk-scale separation with high selectivity. Here, we report a completely nondestructive, scalable separation method in a microfluidic channel using dielectrophoretic force fields. Near-complete selectivity was achieved for bulk quantities of metallic nanotubes, while semiconducting nanotubes were significantly enriched in the other outlet [11]. In

addition, the results demonstrated that the metallic nanotubes could potentially be separated by diameter via frequency tuning.

2 EXPERIMENTAL

Figure 1 shows a schematic of an H-shaped microfluidic channel with two inlets and two outlets. Microelectrodes were deposited on a glass substrate and the flow channel was patterned in the polydimethylsiloxane (PDMS) cover. An oxide layer 150 nm thick formed on top of the electrode, preventing the deposition of nanotubes there. The depth and width of the channel were 150 μ m and 500 μ m, respectively, and the length of the junction with embedded electrodes was 2.45 mm. The nanotube suspension was injected into one inlet, and the buffer solution without nanotubes was introduced into the other through tubes connected to the PDMS cover. A dual syringe pump generated an identical flow rate for both streams. The nanotube suspension was prepared using HiPco SWNTs and 1 wt% cetyltrimethylammonium bromide (CTAB), as described previously. The buffer solution was prepared using the same procedure without introducing nanotubes.

The flow conditions were carefully simulated using a finite element method (COMSOL, Multiphysics), to minimize diffusive and convective transport of nanotubes across the boundary between two flows. The diffusive mixing of nanotubes at the junction of the flow channel was governed by the diffusivity and the flow rate. For the randomly moving prolate ellipsoid, diffusivity D is governed by the following equations

$$D = 3k_B T / f \quad (1)$$

$$f = 3\pi\eta l / \log(l/r) \quad (2)$$

here k_B is Boltzman constant, T is the absolute temperature, f is the friction factor, η is the fluid viscosity, l is the length of a nanotube, and r is the radius of a nanotube. The diffusivity of nanotubes in water was estimated to be 9×10^{-12} , assuming the length and radius of a micelle-coated HiPco SWNT to be 1 μ m and 2 nm, respectively. Based on the simulation results, a flow rate of 0.001 ml/min was chosen to minimize the diffusive transport of nanotubes. In addition, dye release experiments demonstrated two laminar streams in the channel, without any convective mixing across the interface.

3 RESULT AND DISCUSSION

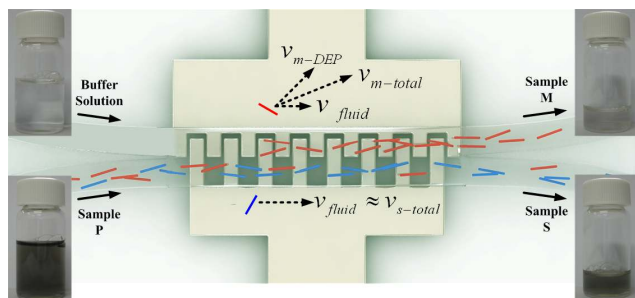


Figure 1: Schematic of the experimental setup. The separation mechanism based on dielectrophoresis is shown. Metallic SWNTs (red rods) were subjected to a significantly larger dielectrophoretic force, perpendicular to the direction of the flow, than semiconducting SWNTs (blue rods).

If the dielectrophoretic force is pretty larger than the viscous force, the nanotube can move across the boundary between two flows before the arrival of flow exit. Otherwise, the nanotube moves through its original flow and goes to the lower exit in Figure 1b.

We employed a dielectrophoretic force field with a peak-to-peak voltage (V_{pp}) of 10 V at 10 MHz, to separate the metallic SWNTs from the nanotube suspension stream, even though the separation mechanism of the conventional H-type filter is based on diffusion. Most of the previous dielectrophoretic separation methods involved the selective deposition of metallic nanotubes on electrodes or remnants of the solution after metallic deposition. Previous separation mechanism was based on the large difference in dielectric constants of metallic and semiconducting nanotubes, which led to positive and negative dielectrophoresis [10, 12, 13]. Our method was based on the deliberate combination of the positive dielectrophoresis and the viscous force of the fluid. The embedding electrode in the microfluidic channel and fine control of the flow rate contributed to achieve the careful modulation of the separation condition. Our recent theoretical and experimental investigations revealed that a small positive dielectrophoretic force could be induced even for semiconducting nanotubes, depending on the surface charge conditions. Nevertheless, metallic SWNTs are subject to a significantly larger dielectrophoretic force in the perpendicular direction than that of the semiconducting SWNTs, as shown in Figure 1. In our method, the dielectrophoresis (DEP) force dominates over viscous drag and Brownian motion, causing the preferential movement of metallic species toward the buffer stream. The separated nanotube suspensions in vials are shown next to the schematic in Figure 1. These were collected from the continuous streams over 35 h, using a microfluidic separation device.

Figure 2a shows the ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra of aqueous suspended nanotubes before and after separation. The first (S_{11}) and second (S_{22}) van Hove transitions of semiconducting SWNTs are shown at 830–1600 nm and 600–800 nm, respectively. The first van Hove transitions of metallic SWNTs (M_{11}) in the 440–645 nm range are magnified in Figure 2b. Sample P was the nanotube suspension before separation. Samples M and S, which contained pure metallic and enriched semiconducting SWNTs, respectively, were obtained at each outlet of the microfluidic channel.

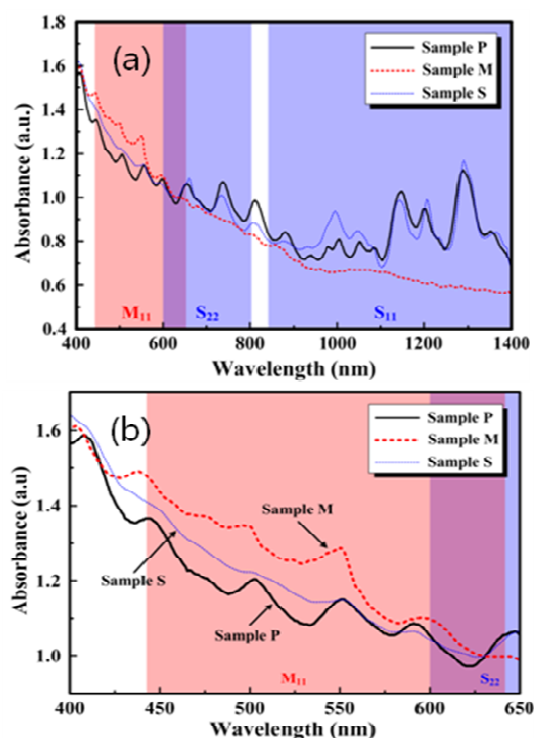


Figure 2: UV-Vis-nIR spectra of nanotube suspensions before and after separation. (a) The spectra were normalized for comparison. (b) The first valence to conduction electronic transitions of metallic nanotubes were magnified.

The nanotube concentration of sample P was approximately 15 mg/L. The absorption spectra were measured to have an identical absorptivity at 632 nm. The absorptivities of samples M and S were 23 and 77% that of sample P, respectively. The theoretical concentrations of metallic and semiconducting SWNTs were about 33 and 67%, respectively. If the absorptivity at 632 nm was approximately proportional to the nanotube concentration, a large portion of metallic SWNTs were collected in sample M, whereas sample S contained a mixture of enriched semiconducting and metallic SWNTs. This hypothesis was

supported by absorption and Raman, as will be discussed shortly. Sample P showed sharp transitions in the optical absorption spectra, corresponding to van Hove singularities. This indicated a well-dispersed nanotube suspension. The metallic transitions of sample M were significantly increased, while the semiconducting transitions, S_{11} and S_{22} , were negligible. The semiconducting transitions of sample S were similar to those of sample P. However, the metallic peaks were substantially decreased. This remarkable selectivity suggested that pure metallic and enriched semiconducting species were collected at each outlet. The color observation of the separated sample together with absorption data is very simple method to effectively judge the separation quality of the sample¹⁸. In our experiment, the separated sample had no color as shown in Figure 1. Comparing the above study, the reason might be due to the separated metallic nanotubes composed of various diameters as shown in Figure 2, and then they make the sample no color.

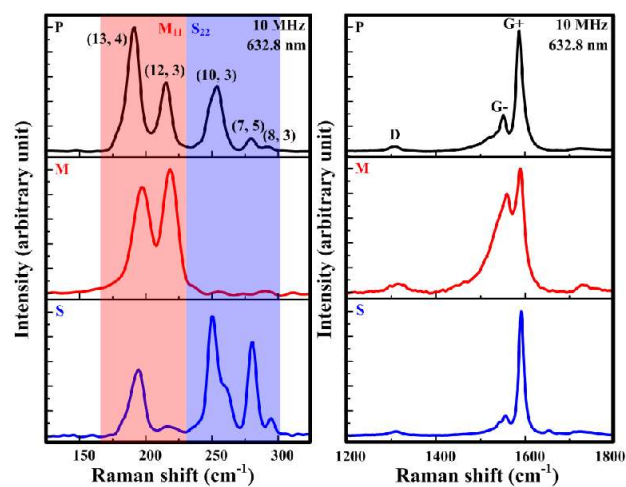


Figure 3: Raman and near-infrared fluorescence spectra before and after separation. (a) The radial breathing mode and G mode spectra were measured at an excitation wavelength of 632.8 nm. The data from top to bottom correspond to samples P, M, and S.

Figure 3 shows the radial breathing mode (RBM) and tangential G mode of Raman spectra (Renishaw) before and after separation. A drop of nanotube suspension was air-dried on a silicon substrate, and Raman spectra were obtained at 632.8 nm excitation (1.96 eV). All the samples were carefully prepared using the same procedure, because the resonance conditions depended on the sample morphology. Sample P showed features related to metallic SWNTs at lower frequencies ($\omega_{\text{RBM}} = 160\text{--}230\text{ cm}^{-1}$), and to semiconducting SWNTs at higher frequencies ($\omega_{\text{RBM}} = 230\text{--}300\text{ cm}^{-1}$). After separation, the peaks associated with semiconducting SWNTs disappeared completely, while metallic modes were still clearly apparent in sample M. Sample S showed significantly enriched semiconducting

peaks. These changes in the relative intensities of RBM indicated that a large number of the metallic SWNTs were selectively moved to the buffer stream by the dielectrophoretic force.

The Raman-allowed tangential G mode in SWNTs showed a multi-peak feature, including G^+ for atomic displacement along the tube axis, and G^- for modes with atomic displacement along the circumferential direction. The G- mode is broadened for metallic SWNTs, exhibiting an asymmetric Breit-Wigner-Fano (BWF) line shape, instead of the Lorentzian shape seen for semiconducting tubes. This is because of the coupling of a discrete phonon with a continuum related to conduction electrons. Sample P showed typical G modes associated with a mixture of metallic and semiconducting species. The G^- mode of sample M had a BWF line shape, while that of sample S retained a Lorentzian shape, supporting the RBM observation.

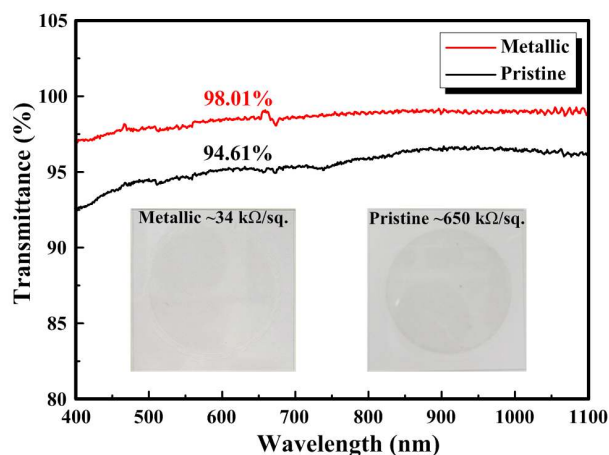


Figure 4: Transmittance and sheet resistance of transparent conductive films made of pristine (black line) and separated metallic (red line) nanotubes. The contrast of the film images in the inset has been increased.

Transparent conductive films were fabricated by a vacuum filtration method to implement the excellent conducting properties of separated metallic nanotubes as fillers for composite materials. As shown in Figure 4b, the film of pristine nanotubes exhibited a sheet resistance of 650 k Ω /square (four-point probe) at a transmittance of 94.6% (UV-vis spectrometer). The film of separated metallic nanotubes had a sheet resistance of 34 k Ω /square, which was 19 times lower than that of the pristine SWNT film, even at a higher transmittance of 98%. The inset images show both transparent conductive films.

4 CONCLUSION

The H-shaped microfluidic channel, combined with the dielectrophoretic force field, could separate pure metallic

and enriched semiconducting nanotubes. The separation phenomenon was due to a positive dielectrophoresis of metallic SWNTs, and was not caused by a significant diffusion in combination with a negative dielectrophoresis of semiconducting SWNTs. This nondestructive separation method could be scaled up by connecting multiple channels in parallel and/or by using larger fluidic channels. In addition, we expect that a serial combination of microfluidic devices would enhance the separation efficiency of semiconducting species. Separated pure metallic nanotubes would have a variety of applications, such as conductive fillers for composites and leads for electronic circuits.

5 ACKNOWLEDGEMENT

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REFERENCES

- [1] McEuen, P. L. *Phys. World* 2000, 13, 31-36.
- [2] Baughman, R. H.; Zakhidov, A. A.; de Heer, W. *Science*, 297, 787, 2002.
- [3] Collins, P. G.; Arnold, M. S.; Avouris, P. *Science*, 292, 706, 2001.
- [4] Lee, M.; Im, J.; Lee, B. Y.; Myung, S.; Kang, J.; Huang, L.; Kwon, Y. K.; Hong, S. *Nat. Nanotechnol.* 1, 66, 2006.
- [5] Rao, S. G.; Huang, L.; Setyawan, W.; Hong, S. *Nature*, 425, 36, 2003.
- [6] Misewich, J. A.; Martel, R.; Avouris, Ph.; Tsang, J. C.; Heinze, S.; Tersoff, J. *Science*, 300, 783, 2003.
- [7] Wu, Z.; Chen, Z.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Herbard, A. F.; Rinzler, A. G. *Science*, 305, 1273, 2004.
- [8] An, K. H.; Park, J. S.; Yang, C.; Jeong, S. Y.; Lim, S. C.; Kang, C.; Son, J.; Jeong, M. S.; Lee, Y. H. *J. Am. Chem. Soc.*, 127, 5196, 2005.
- [9] Strano, M. S.; Dyke, C. A.; Usrey, M. L.; Barone, P. W.; Allen, M. J.; Shan, H.; Kittrell, C.; Hauge, R. H.; Tour, J. M.; Smalley, R. E. *Science*, 301, 1519, 2003.
- [10] Krupke, R.; Hennrich, F.; Löhneysen, H.; Kappes, M. M. *Science*, 301, 344, 2003.
- [11] D. H. Shin, J.-E. Kim, H. C. Shim, J.-W. Song, J.-H. Yoon, J. Kim, S. Jeong, J. Kang, S. Baik, and C.-S. Han, *Nano Lett.*, 8, 4380, 2008.
- [12] Pohl, H. A. *Dielectrophoresis*, Cambridge Univ. Press: Cambridge, 1978.
- [13] Jones, T. B. *Electromechanics of Particles*, Cambridge Univ. Press: Cambridge, 1995.