Dielectrophoretic separation of metallic arc-discharge single-walled carbon nanotubes in a microfluidic channel

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Electronic type-dependent separation of single-walled carbon nanotubes (SWNTs), preserving pristine crystallinity and length, is of great interest since mixtures of semiconducting and metallic species are produced by current synthesis methods. Here we separated highly-enriched metallic SWNTs, synthesized by the arc-discharge method, by dielectrophoresis in a microfluidic channel. The design of microelectrodes was optimized to prevent the nanotube deposition on the electrodes for prolonged operation of the microfluidic chip. The average length of separated high crystalline metallic SWNTs was relatively long (2–2.4 μm).

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1. Introduction

Single-walled carbon nanotubes (SWNTs) have demonstrated great potential as building blocks for nano-electronics and thin film devices due to their outstanding mechanical, optical and electrical properties [1–4]. However, existing synthesis methods produce mixtures of metallic and semiconducting species creating needs for post-synthetic separation processes according to electronic types. The selective destruction strategies such as gas-phase etching, nitronium ion reaction, oxidation, and ultraviolet irradiation were explored in early stages of development [5–10]. More recently, nondestructive separation methods have been actively investigated including dielectrophoresis (DEP), density gradient ultracentrifugation (DGU), and agarose-gel-based separation [11–21]. The single-chirality separation of SWNTs was demonstrated by DGU, and nanotubes separated by DGU are commercially available [2,11,12,14,20]. The agarose-gel-based method can separate nanotubes with high yield and low cost eliminating the ultracentrifugation step [16,17,21].

The difference in dielectric constant and conductivity between metallic and semiconducting SWNTs is utilized by DEP to separate nanotubes under an alternating-current electric field [13,18,19]. We previously demonstrated the separation of metallic SWNTs by DEP in an H-shaped microfluidic channel [18]. Nearly pure metallic SWNTs were obtained at one outlet whereas mixtures of metallic and semiconducting species existed at the other port [18]. One limitation was that metal-enriched nanotubes deposited on the electrodes located at the bottom of the fluidic channel due to dielectrophoretic attraction prohibiting prolonged operation of the microfluidic device. Here we designed vertically-aligned electrodes at the opposite side-wall of the channel preventing nanotube deposition over a total of 1000-h operation and successfully separated the arc-discharge generated metallic tubes which were relatively long.

2. Experimental

Fig. 1a shows an optical image of the microfluidic chip with two inlets and two outlets, and a schematic is provided in Supplementary Figure S1. The microfluidic chip was composed of...
a polydimethylsiloxane (PDMS) cover and a vertical glass sub-
strate (Seoulin Bioscience). A platinum layer with a thickness
of 100 nm and a titanium adhesion layer with a thickness of 50 nm
were deposited on the glass substrate by optical lithography to
form microelectrodes. The gap and width of the electrodes were
30 and 60 μm, respectively. An oxide layer with a thickness of
150 nm was formed on top of the electrodes to prevent deposition
of SWNTs. A PDMS layer with a thickness of a few micrometers
was also applied to enhance adhesion between the substrate and
PDMS cover. The fluidic channel was defined in the PDMS cover
using an SU-8 negative photoresist. The height and width of
the channel were 300 and 150 μm, respectively. The lengths of
the embedded electrodes and the junction, where two channels meet
without any barrier between channels, were 2.45 and 5 mm, respec-
tively. Two inlet and two outlet holes were mechanically punched
through the PDMS cover. The holes were connected to four syringe
pumps (Harvard 11Plus, USA) by Polytetrafluoroethylene (PTFE)
tubes. The PDMS cover and glass substrate were bonded after the
oxygen plasma treatment. The oxygen plasma process generates
silanol groups (OH) on the surface of PDMS enhancing adhesion
[22].

SWNTs produced by the arc-discharge method were obtained
from Hanwha Nanotech (HANOS ASP-100F). Nanotubes were
suspended in a sodium dodecyl sulfate aqueous solution (SDS,
Sigma–Aldrich, 436143, 1 wt%) by ultrasonication (BRANSONIC
5510R-DTH) for 20 min at 540 W [18]. The nanotube suspen-
sion was ultracentrifuged (Beckman coulter LE-80K) for 4 h at
170,000 × g, and the supernatant was used for further experiments.
The nanotube suspension was supplied into inlet 1. A buffer solu-
tion, prepared by the identical procedure without nanotubes, was
introduced at inlet 2. The vertically-aligned electrode was located
at the side-wall of the buffer stream. The nanotubes are dielec-
trophoretically attracted from the nanotube stream to the electrode
on the opposite side. The buffer stream between the electrode and
nanotube stream prevented deposition of nanotubes on the electro-
de during the separation process.
3. Results and discussion

The flow rate of each stream was firstly optimized by finite element simulation and dye release experiments without application of an electric field. A detailed description is provided in Supplementary Figure S2, and the simulated nanotube concentration at the exit of the separation region of the microfluidic channel is shown in Fig. 1b. There was convective and diffusive mixing between the nanotube and buffer stream when the flow rate was identical. Therefore, the inlet flow rate of the buffer stream was increased (3 μl/min) compared with that of the nanotube suspension (1 μl/min) to minimize cross-over of nanotubes without application of an electric field. This also prevents the cross-over of semiconducting SWNTs due to a small positive dielectrophoretic force as will be discussed shortly. The simulation was also confirmed by dye-release experiments (Supplementary Figure S2). The flow rate at the outlet of each port was set at 2 μl/min.

Fig. 1c shows the calculated dielectrophoretic force over the gradient of electric field strength square using Eq. (1) [13,19,23,24].

$$F_{DEP} = \frac{\pi \alpha^2 \varepsilon_0 \varepsilon_m \text{Re} \left( \frac{\varepsilon_i^* - \varepsilon_m^*}{\varepsilon_m^* + (\varepsilon_i^* - \varepsilon_m^*)D} \right) \nabla E^2}{8}$$  (1)

where $d = 1.3$ nm and $l = 2.4$ μm denote the diameter and length of a nanotube, $\varepsilon^*$ is the complex dielectric constant, $\varepsilon$ is the real part, $K$ is the conductivity, $\omega$ is the frequency, $E$ is the electric field strength and $D$ is the depolarization factor defined as $D = d^2/4l[ln(2l/d) - 1]$. Subscripts $i$ and $m$ represent the suspending nanotube and medium, respectively. The term

$$\text{Re} \left( \frac{\varepsilon_i^* - \varepsilon_m^*}{\varepsilon_m^* + (\varepsilon_i^* - \varepsilon_m^*)D} \right) d$$

is known as the Clausius Mosotti (CM) factor [13]. The permittivity of SWNTs is inversely proportional to the square of the band gap energy [13,19,23]. The permittivity of semiconducting SWNTs was assumed to be 5 whereas that of metallic species should be large [13,19,23].

The medium conductivity can be directly measured (MALVERN, Nano-ZS, $K_m = 0.137$ S/cm). The particle conductivity, $K_p$, can be obtained from the sum of intrinsic conductivity ($K_{int}$) and surface conductivity. A detailed derivation was published previously, and a brief summary is provided below [19,23,24].

$$K_p = K_{int} + \frac{2\lambda_s}{a}$$  (3)

where $\lambda_s$ is the surface conductance, and $a$ is the radius of a spherical particle [23,24]. We assumed that $a = 2.7$ nm for micellized-SWNTs [23]. The intrinsic conductivity of semiconducting nanotubes is very small ($K_{int} \approx 0$) whereas that of metallic species is large ($K_{int} \approx 13,000$) [23,25]. There are two components in $\lambda_s$,

$$\lambda_s = \lambda_{s,d} + \lambda_{s,\infty}$$  (4)

where $\lambda_{s,d}$ is the diffuse layer conductance, and $\lambda_{s,\infty}$ is the Stern layer conductance. The $\lambda_{s,d}$ can be obtained using the zeta potential of carbon nanotubes ($\zeta$), and $\lambda_{s,\infty}$ was estimated using the typical ratio of $\lambda_{s,\infty}$ and $\lambda_{s,d}$ [19,23,24,26].

$$\lambda_{s,d} = \frac{4q^2n_a z^2 F}{10^7 K_B T k} \left( 1 + \frac{3m}{z^2} \right) \left( \cosh \left[ \frac{2qz}{2k_B T} \right] - 1 \right)$$  (5)

$$\frac{\lambda_{s,\infty}}{\lambda_{s,d}} = 0.56$$  (6)

where $q$ is the charge of an electron, $n_a$ is the bulk concentration of an ion, $z$ is the valence of an ion, $k_B$ is the Boltzmann constant, $T$ is the temperature, $F$ is the diffusion constant, $\kappa$ is the reciprocal Debye length, and $m$ is the contribution from electroosmotic transport. The experimentally obtained $\zeta$ of SDS-stabilized nanotubes was $-51.3$ mV (MALVERN, Nano-ZS). The same $\zeta$ was assumed for both metallic and semiconducting nanotubes. Other parameters used for the calculation were published previously [19,23]. Finally, $K_p = 1.448$ S/cm was obtained for semiconducting SWNTs. $K_p = 13.001$ S/cm was calculated for metallic SWNTs similar to a value in literature [19,25].

The simulation results are shown in Fig. 1c. When the particle conductivity is smaller than 0.091 S/cm, the dielectrophoretic force of semiconducting tubes (permittivity ~ 5) becomes negative whereas nanotubes with a higher permittivity (e.g., metallic tubes with a permittivity > 5000) experience positive force. However, the difference in permittivity becomes insignificant as the particle conductance increases. A significantly greater positive dielectric force was induced for metallic SWNTs, primarily due to the greater particle conductivity, enabling selective cross-over of metallic species from the stream of nanotube suspension to the buffer side. The flow rate was adjusted to prevent cross-over of semiconducting SWNTs since they also experience a small positive dielectrophoretic force due to the induced surface conductivity. It is important to note that this separation design is targeted to obtain pure metallic tubes at one outlet rather than semiconducting species [18].

A control experiment was carried out using a microfluidic chip with microelectrodes located at the bottom of the fluidic channel (see Supplementary Figure S3 for details) [18]. As shown in Fig. 1d, nanotubes deposited on the electrodes after application of an electric field ($V_{pp} = 10$ V, 10 MHz) prohibiting prolonged operation of the microfluidic chip. The deposited nanotubes were mostly metallic as confirmed from the G-mode of Raman spectra (Fig. 1e, Renishaw, inVia Raman microscope) [27]. The strong asymmetric Breit–Wigner–Fano (BWF) line is an indication of metal-enrichment [27]. In order to prevent the nanotube deposition, the electrodes were placed at the side-wall of the buffer side (Fig. 1a and f). Nanotubes could not be observed on the electrodes even after a total of 1000-h operation. However, the distance between nanotubes and electrodes was increased decreasing the induced dielectrophoretic force of nanotubes. A stronger electric field had to be applied ($V_{pp} = 60$ V, 5 MHz), generated by a function generator (Agilent, 33250A) and an amplifier (NF HAS-4101), to attract metallic SWNTs selectively. Nevertheless, the concentration of separated tubes was low as will be discussed shortly. A shorter channel width may increase the separated tube concentration in the future.

Fig. 2a compares the radial breathing mode (RBM) of pristine and metal-enriched SWNTs (sample M). The pristine sample exhibited peaks related with metallic (140–195 cm$^{-1}$) as well as semiconducting (200–220 cm$^{-1}$) species [27]. The semiconducting peak was negligible for the sample M, collected at the metallic port, demonstrating selective cross-over of metallic species after application of the dielectrophoretic force. As shown in Fig. 2b, the tangential G’ mode associated with atomic vibration along the circumferential direction (BWF line) was also broadened for the sample M compared with that of the pristine sample [27]. The diameter distribution of arc-discharge SWNTs is narrow making the Raman characterization more reliable [5,12]. The semiconducting peak was also negligible for the sample M when the characterization was carried out at 514 and 633 nm (Fig. 2c and d). The optical absorption of suspended tubes was too small to make a comparison. Instead, the optical absorption spectra of TCFs were compared as shown in Fig. 2e. The detailed film preparation method is provided in Supplementary Information. Both metallic (M11, 550–850 nm) and semiconducting (S22, 800–1000 nm; S33, 390–550 nm) peaks
were observed for the pristine sample [5,12]. Semiconducting peaks were negligible whereas metallic peaks could be observed for the sample M. This is consistent with the Raman characterization. It is interesting to note that two major peaks in E\textsuperscript{M11} transitions of metallic SWNTs were observed in the pristine sample. The corresponding tube diameters were 1.25 and 1.4 nm [28]. However, the separated metallic sample showed only one major peak at 773 cm\textsuperscript{-1}, having the larger diameter. According to the calculation of Eq. (1), the dielectrophoretic force over the gradient of electric strength square of the 1.4 nm diameter tubes was 119.5% greater than that of the tubes with a diameter of 1.25 nm. It is possible that larger diameter metallic tubes were preferentially separated by dielectrophoresis.

The electrical transport characteristics are compared in Fig. 2f. A drop (20 \mu L) of nanotube suspension (pristine or sample M) was placed on an electrode with a gap of 2 \mu m. A detailed geometry of the electrode was published previously, and a brief description is provided below [18,19]. A titanium/gold layer with a thickness of 5/200 nm was deposited on a SiO\textsubscript{2}/Si substrate as a top electrode. The thickness of the SiO\textsubscript{2} layer was 300 nm. The droplet was blown off using nitrogen gas after 1 min. The source–drain current was measured as a function of the back-gate voltage (V\textsubscript{G}), using a semiconductor parameter analyzer (Agilent, E5262A) and a probe station (Cascade, RF-1), after rinsing with de-ionized water to remove surfactant. The source–drain bias was 1 V. The pristine sample showed the typical behavior of mixtures of metallic and p-type semiconducting species [18]. The current was 52.5 \mu A at 30V\textsubscript{G} which increased with decreasing V\textsubscript{G}. However, there was no gate-dependence for the sample M demonstrating metallic characteristics. The electrical transport phenomena were consistent with the absorption and Raman analysis.

The low concentration of metal-enriched sample is one disadvantage of the dielectrophoretic separation in a microfluidic channel. The separation yield of metallic tubes would be 40.32 \times 10\textsuperscript{-3} g/day at the current experimental condition which may be improved by employing multiple fluidic channels in the future. However, long metallic arc-discharge SWNTs were obtained in this study. Fig. 3a and b compares the length of commercial metallic nanotubes separated by DGU (Nanointegris, IsoNanotubes-M) and metallic SWNTs separated by DEP in a microfluidic channel. The atomic force microscopy images (AFM, Veeco, dINNOVA 840-012-711) are shown in Fig. 3c and d. The
4. Conclusions

Arc-discharge metallic SWNTs were separated by dielectrophoresis in a microfluidic channel. The design of microfluidic chips was optimized to prevent the nanotube deposition on the electrodes for prolonged operation. Highly-enriched metallic tubes were obtained at one port whereas mixtures of metallic and semiconducting species were present at the other outlet. Longer metallic tubes could be obtained although the suspended nanotube concentration was low.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.synthmet.2013.09.024.

References


