Purification of Carbon Nanotubes through an Electric Field near a Microelectrode

H C Shim¹, H W Lee², S J Yeom¹, Y K Kwak¹, S S Lee¹ and S H Kim¹, ³

¹ Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology(KAIST), 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, Republic of Korea
² Massachusetts Institute of Technology(MIT), Micro & Nano Systems Laboratory, 77 Massachusetts Ave. Room 5-008, Cambridge, MA 02139, US
³ E-mail : scacos@kaist.ac.kr

Abstract. In this work, we attempt to purify multi-walled carbon nanotubes (MWNTs) using electrophoresis induced by application of an ac electric field to a set of microelectrodes in a microliquid channel. This purifying method is different from conventional methods based on chemical processes. We observed that the most of the MWNTs could pass along the microliquid channel without attaching to the electrode under specific conditions of 1 kHz, 0.2 Vrms/µm. On the other hand, the majority of the carbon impurities attached to the electrodes under same condition. Field emission scanning electron microscopy (FESEM) images confirm that this condition is beneficial for removing the carbon impurities. We aligned and attached this purified MWNTs and raw materials to extra electrodes with 5 MHz, 0.8 V rms/µm. This experimental FESEM images show a clear difference between before and after purification. The proposed approach has potential applicability to the development of microdevices that can simultaneously perform purification and fabrication of MWNTs.

1. Introduction
Since their discovery in 1991, carbon nanotubes (CNTs) have drawn the considerable attention not only for their unique physical properties but also because of their potential for use in various applications [1, 2, 3, 4, 5]. The beneficial characteristics of CNTs include their high mechanical strength and unusual electronic properties, which make them suitable for field emission displays, their capability to store a large amount of hydrogen, a high modulus, and structural diversities, which make band gap engineering possible [6].

However significant problems with putting these applications to practical use and mass production remain. In particular, it is difficult to control CNTs for their nano size. Furthermore, they sometimes display irregular mechanical or electrical properties, as well as impurities which are inevitably included when a synthetic process is not employed in the manufacture of CNTs. These impurities include fullerene, amorphous carbon, etc., and they act as defects in development and research with CNTs. Study on purification of CNTs has occupied a considerable portion of the research field related to CNTs, and a variety of methods to purify CNTs have been reported including chemical oxidation [7], thermal oxidation [8, 9, 10], filtration [11], and chromatography [12, 13]. Among these methods,
chemical or thermal oxidation processes are simple but can potentially result in destruction or transformation of CNTs. Chromatography, meanwhile, has limited practical applicability because of the limited solubility of CNTs.

In the present study, we have attempted to purify CNTs through an approach involving application of an electric field. The proposed method is simple, fast and nondestructive. To this end, we fabricated a set of microelectrodes in a microliquid channel, and attempted to identify specific purifying conditions through adjustment of voltage and frequency. We also assessed experimental results with field emission scanning electron microscopy (FESEM) images.

2. Apparatus and theory

2.1. Background theory
Dielectrophoresis or electrophoresis can be generated by applying an alternating current (AC) or direct current (DC) electric field between electrodes. Dielectrophoresis is quite different from electrophoresis. Dielectrophoresis is the motion of neutral particles caused by a polarization effect or dipole in a nonuniform electric field. On the other hand, electrophoresis is caused by electrostatic force, generated by applying an AC or DC electric field between an electrode and a charged body. Electrophoresis can be generated regardless of the electric field’s uniformity.

Figure 1. shows the motion of neutral and charged particles in a uniform electric field, and it also describes the general aspects of electrophoresis. A charged particle is pulled along the field lines towards the electrode carrying the charge opposite to that of the particle. In the same field, a neutral body will merely be polarized. The result may produce a torque, but not a net translational force, without which the body as a whole will not move toward either electrode. Electrophoresis can be appreciable even when the free charge per unit weight of the particle is quite small. It is different from dielectrophoresis in that it does not depend upon the particle volume, but rather upon the free charge on the particle [14]. Therefore, it is possible to purify the CNTs using an electric field by utilizing the difference of motion between CNTs, a neutral body in a physical sense and carbon impurities, charged particles.

2.2. Apparatus

2.2.1. Fabrication of purifying device
As shown in Figure 2., the purifying device used in experiment, is composed of a set of microelectrodes having a gap of 30 μm in a microliquid channel whose size is 200 μm. We placed 12 symmetric gold electrodes on a silicon oxide plate, and covered plate with SU-8 with a thickness of 100 μm, which having shape of microliquid channel. The whole process of fabricating purifying device was achieved by a simple photolithography method. The ends of the purifying device are termed the outlet and inlet. Multi-walled carbon nanotubes (MWNTs) solution could the flow along the channel from the inlet to outlet by capillary force.

2.2.2. Experimental set-up
Figure 3. is a schematic diagram of the experimental apparatus for purifying the MWNTs. The apparatus consists of two parts, an approaching part, and an inducing part. The approaching part is composed of 12 probes and gold electrodes on a purifying device as counter electrodes. To support the purifying device, we fixed a holder to the translation stage of the z-axis. The 12 probes apply the voltage and frequency to the each electrode on the purifying device through the function generator, and each probe can be adjusted using the xyz-stage.

The inducing part of the apparatus is composed of a signal generator and a signal detector. We used an oscilloscope as the signal detector. The electric field can be generated by ac voltage, and we can check the signal with the oscilloscope.
3. Experimental section

3.1. Pre-treatment of MWNTs

We obtained MWNTs from Iljin Nanotech. These MWNTs were synthesized by the arc-discharge method, and had a diameter of 30 nm, and a length of 5~10 \( \mu \text{m} \). Figure 4. shows an FESEM image of MWNTs in the raw state. As shown in this image, many carbon impurities are located near the MWNTs. These MWNTs had been dispersed in water with sodium dodecyl sulphate (SDS); consequently, this polymer structure obscured the FESEM image. Hence, we removed the SDS using acetone, and sonicated MWNT solution for 5 minutes with 70 W, 45 kHz after dispersing MWNTs in chloroform (CHCl\(_3\)) and isopropanol (IPA) at a ratio of one to one. The concentration of MWNT solution was fixed at 5 \( \mu \text{g/ml} \), and the volume of droplets was fixed at 4 \( \mu \text{l} \) based on consideration of the inlet volume.

3.2. Determination of purifying condition

We supplied only ac voltage to the purifying device. Through previous research, the approximate range of conditions under which CNTs attached and aligned well to the electrode had been determined, i.e., voltage of 0.3~1.3 \( V_{\text{rms}}/\mu \text{m} \), and frequency of 0.1~20 MHz [15]. Hence, it is necessary to avoid these conditions to purify the MWNTs, as the goal is to attach carbon impurities to electrodes rather than the MWNTs. First, we varied the voltage in the range of 0.1~0.3 \( V_{\text{rms}}/\mu \text{m} \), while utilizing a fixed frequency of 100 kHz in order to assess the influence of voltage amplitude. Based on previously obtained experiment data, we subsequently varied the frequency in the range of 0.01~100 kHz under fixed voltage. The range of purifying conditions, with the appropriate voltage and frequency, was the narrowed on the basis of formerly obtained experiment data.

3.3. Verification of degree of purity through fabrication of MWNTs

We added a pair of extra electrodes having a gap of 20 \( \mu \text{m} \) to the outlet of the purifying device, and applied a voltage of 0.8 \( V_{\text{rms}}/\mu \text{m} \), and a frequency of 5 MHz [15] as the purified MWNT solution passed by these electrodes. The above conditions, which are applied by another function generator, are chosen for the attachment and alignment of MWNTs. Hence, the degree of purity through could be verified based on an assessment of the difference between images taken before and after purification of the MWNTs attached and aligned on the extra electrodes, added to end of the outlet.
4. Results and discussion

Electrostatic force is increased as the applying voltage is increased. As shown in Figure 5., more MWNTs and carbon impurities are attracted to the electrodes with increasing voltage. Through iterations of the experiment we could observe that not only carbon impurities but also many MWNTs are attracted to the electrodes at the voltage greater than 0.2 V\textsubscript{rms}/\mu m. However, as the goal of the study is to filtrate carbon impurities by the electrodes rather than MWNTs, we determined the maximum voltage, i.e. 0.2 V\textsubscript{rms}/\mu m.

We also found that more MWNTs relative to the amount of carbon impurities attached and aligned to the electrodes at a frequency of more than 100 kHz, as shown in Figure 6. The amount of attached carbon impurities also decreased at a frequency of less than 100 kHz. In other words, the amount of carbon impurities attached to the electrodes are decreased at less or more than 100 kHz. This result can be explained by the following phenomenon. Carbon particles are in a colloidal state in a mixture of IPA and CHCl\textsubscript{3}, positively charged and covered with negative ions. Negative ions slip off positively charged particles at a low frequency of less than 100 kHz, and therefore carbon impurities could move along the electric field line. However, at a high frequency of more or too less than 100 kHz, carbon impurities do not readily move along the field line, because charged particles covered with negative ions. MWNTs could be attracted to the electrodes in a nonuniform electric field, which could be induced by imperfectly symmetric electrodes or irregular interface shape of the electrodes on a micro-scale. As shown in Figure 7., the MWNTs could be purified with increasing voltage, but also lost their quantity at the outlet area, because of the attachment of MWNTs. However, most MWNTs flowed through the apparatus without attachment to the electrodes, along the microliquid channel at a voltage of 0.2 V\textsubscript{rms}/\mu m, and a frequency of 1 kHz.
In order to verify the difference between before and after purification of the MWNTs, we aligned and attached each before and after purifying MWNTs to the electrodes, added to the outlet of the purifying device. The added electrodes had gap size of 20 \mu m. As shown in Figure 8., there is clear a difference between the MWNTs before and after purification. When we aligned and attached the MWNTs purified through an electric field generated by a voltage of 0.2 V/\mu m, and a frequency of 1 kHz to extra electrodes, almost no carbon impurities were found near the MWNTs. But it was not in case of not to generate electric field when MWNTs passed along the microliquid channel. Therefore, the experiment results show that this purifying device can be used not only for purification of MWNTs but also in the fabrication of impurity-free MWNTs.

Acknowledgement
The authors would like to express their appreciation to the Brain Korea 21 project in 2006 for partly financial support of this work.

References
[1] Iigima S 1991 Nature 354 56-8
[2] Lee SM, Lee YH. 2000 Appl. Phys. Lett. 76 2877–9.
[3] Collins PG, Bradley K, Ishigami M, Zettl A 2000 Science 287 1801–4.
[4] Deheer WA, Chatelain A, Úgarte D 1995 Science 270 1179–80.
[5] Journet C, Maser WK, Bernier P, Loiseau A, Chapelle ML, Lefrant S, et al. 1997 Nature 388 756–8.
[6] Fu-Hsiang Ko, Chung-Yang Lee, Chu-Jung Ko, Tieh-Chi Chu 2005 Carbon 43 727
[7] Rinzler AG, Liu J, Dai H, Nikolaev P, Huffman CB, Rodriguez-Macias FJ, et al. 1998 Appl. Phys. A: Mater. Sci. Process 67 29–37.
[8] Ebbesen TW, Ajayan PM, Hiura H, Tanigaki K. 1994 Nature 367 519.
[9] Hiura H, Ebbesen TW, Tanigaki K. 1995 Adv. Mater. 7 275.
[10] Dujardin E, Ebbesen TW, Krishnan A, Treacy MJ. 1998 Adv. Mater. 10 611–3.
[11] Bandow S, Rao AM, Williams KA, Thess A, Smalley RE, Eklund PCJ. 1997 Phys. Chem. B 101 8839–42.
[12] Shelimov KB, Esenaliev RO, Rinzler AG, Huffman CB, Smalley RE. 1998 Chem. Phys. 282 429–34.
[13] Murphy R, Coleman JN, Cadek M, McCarthy B, Bent M, Drury A, et al. 2002 J. Phys. Chem. B 106 3087–91.
[14] Herbert A Pohl, 1978 Dielectrophoresis (Lodon: Cambridge university press).
[15] Lee, H. W 2005 A Study on Alignment and Attachment of Carbon Nanotube Using Electric Field (Daejeon: Korea Advanced Institute of Science and Technology press).