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Separation of carbon nanotubes by frit inlet asymmetrical flow field-flow fractionation

Flow field-flow fractionation (flow FFF), a separation technique for particles and macromolecules, has been used to separate carbon nanotubes (CNT). The carbon nanotube ropes that were purified from a raw carbon nanotube mixture by acidic reflux followed by cross-flow filtration using a hollow fiber module were cut into shorter lengths by sonication under a concentrated acid mixture. The cut carbon nanotubes were separated by using a modified flow FFF channel system, frit inlet asymmetrical flow FFF (FI AFIFFF) channel, which was useful in the continuous flow operation during injection and separation. Carbon nanotubes, before and after the cutting process, were clearly distinguished by their retention profiles. The narrow volume fractions of CNT collected during flow FFF runs were confirmed by field emission scanning electron microscopy and Raman spectroscopy. Experimentally, it was found that retention of carbon nanotubes in flow FFF was dependent on the use of surfactant for CNT dispersion and for the carrier solution in flow FFF. In this work, the use of flow FFF for the size differentiation of carbon nanotubes in the process of preparation or purification was demonstrated.

Key Words: Flow field-flow fractionation; Carbon nanotube; SWCNT; Separation; Size characterization; Frit-inlet asymmetrical flow FFF channel; Cut CNT

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1 Introduction

Carbon Nanotubes (CNTs) are of great interest because of their electrical properties and their potential applications in nanoscale materials and devices [1–3]. The structure of the carbon nanotube resembles a graphite sheet rolled up into a cylinder which consists of hexagon rich sp^2 carbon at the wall and a few pentagons at the curve [3]. Single wall carbon nanotubes (SWCNTs) are about 1–2 nm in diameter and up to few micrometers in length. Since carbon nanotubes have high chemical stability, thermal conductivity, and high mechanical strength, these materials are thought to be a potential source for field emitters.

Recently, it was reported that carbon nanotubes were used as field emitters in the fabrication of a flat panel display [4]. Due to the low voltage needed to turn a field emission display (FED) on, and the brightness with stability, much effort is being made to incorporate CNTs into a new generation of display materials. Since the raw CNT materials prepared by the arc discharge method are a mixture of CNT ropes, amorphous carbon particles, and metal

particles used as catalysts, purification of CNT by removing those impurities is sometimes needed if CNTs are to be used in sophisticated nanoscale devices. It may also be necessary to cut the endless and highly tangled ropes into shorter lengths. The purification of nanotubes by treatment with acid mixtures or by air oxidation has been described [5–10]. Cut CNTs are often difficult to identify when examined microscopically, since nanotubes are only a few hundred nm in length and less than 10 nm in thickness and they easily form bundles or layered agglomerates upon drying.

Flow field-flow fractionation (FIFFF), a member of the FFF family, is a separation technique applicable to the size characterization of nanoparticles, colloids, and macromolecules [11–14]. FFF techniques utilize a fluid flow to transport particulate materials down a thin empty channel having a rectangular cross section, in most cases, and each subtechnique uses a characteristic external field force which is directed perpendicular to the flow axis in order to retain sample components within the channel. In FIFFF a secondary flow stream (cross flow) driven across the channel is employed as field force [13]. Due to its versatile applications, FIFFF has become a universal technique for separating particulate materials and macromolecules [15–18]. When a sample component is located in the cross-flow field in FIFFF, it is driven toward one side (accumulation wall) of the

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channel walls and, simultaneously, is pushed away from the wall due to particle diffusion. The two counteracting forces acting on the sample material are balanced at an equilibrium position that is at a short distance from the accumulation wall and depends on the particle size or on molecular weight. Thus, particles are differentiated by size at different equilibrium heights above the wall. When separation flow is applied to the particles at their equilibrium, a small particle located at a higher mean elevation will be transported down the channel earlier than a large particle due to the parabolic properties of flow streamlines in a thin FFF channel. Therefore, separation is achieved by increasing diffusion. In flow FFF, retention time, t_r , in normal mode is inversely proportional to the diffusion coefficient, D , of the analyte, and directly proportional to the square of the channel thickness, w . For highly retained sample components, the retention ratio, R , is expressed as [11, 16, 17].

$$R = \frac{t^0}{t_r} \cong \frac{6D}{w^2} \frac{V^0}{\dot{V}_c} \quad \left(D = \frac{kT}{3\pi\eta d_s} \right) \quad (1)$$

where t^0 is the void time, V^0 the channel void volume, \dot{V}_c the cross-flow rate at the channel wall, kT the thermal energy, η the viscosity of carrier solution, and d_s the Stokes' diameter. From this relationship, it is possible to calculate the diffusion coefficient or Stokes' diameter of a particle from an experimental retention time, provided that the experimental run conditions are known.

In this work, a modified form of flow FFF frit inlet asymmetrical flow FFF (FI-AFIFFF) channel [21–23], has been employed to separate carbon nanotubes during the purification process. Flow FFF was utilized to fractionate carbon nanotubes in an earlier publication [2], but it was only given with a brief mention and no detailed work has been reported. In FI-AFIFFF, a sample injection is made directly into the flowing streamline and sample relaxation, which is an important procedure used for establishing equilibrium conditions of particles in most FFF techniques, is achieved hydrodynamically by the use of a high speed frit flow that is introduced through a small inlet frit nearby the injection point (see **Figure 1.a**). Compared to a conventional flow FFF system, which utilizes a stop flow procedure in which separation flow is temporarily halted for a certain period of time during relaxation and is then resumed, operation of a FI-AFIFFF is simple since it is unnecessary to stop the flow or to use flow converting valves. In this report, carbon nanotubes, before and after the cutting process, were examined using a FI-AFIFFF channel. The elution profiles of carbon nanotube samples were investigated using different carrier solutions with or without surfactant. During a FIFFF run, narrow volume fractions of eluted nanotubes were collected for confirmation by Raman spectroscopy and field emission scanning electron microscopy.

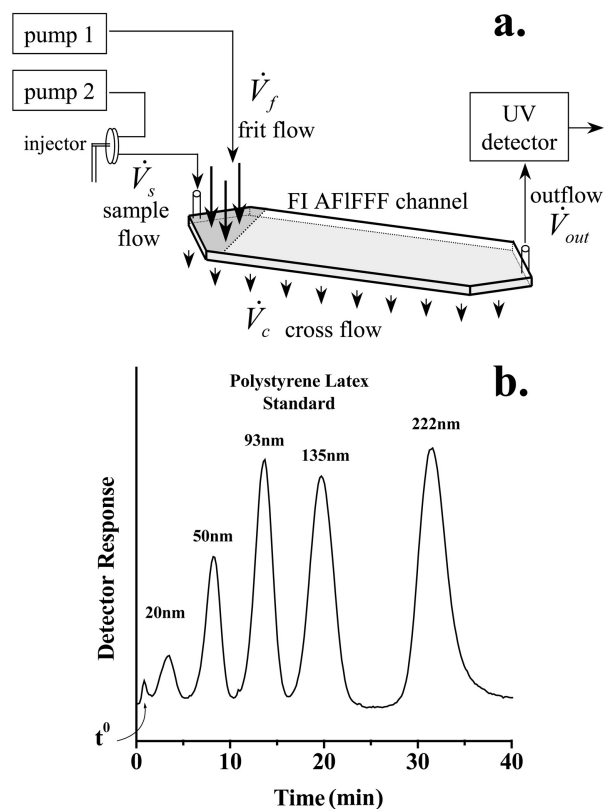


Figure 1. Diagram of frit inlet asymmetrical flow field-flow fractionation (FI-AFIFFF) system (a) and the size separation of polystyrene latex spheres (b). Flow rate conditions are 0.20/4.04 for injection flow/frit flow rate and 0.37/3.87 for outflow/crossflow rate in mL/min.

2 Experimental methods

2.1 Purification and cutting of carbon nanotubes

The raw carbon nanotube materials were obtained from Carbox Inc. (Lexington, KY, USA) and were treated with acid to isolate CNTs from the impurities in the mixture. The isolated CNTs were cut into shorter lengths by the following procedure similar to the literature [5]. First, 250 mg of raw CNT material was suspended in 70 mL of deionized water and sonicated with a horn at 80 A for 20 min. Then the suspended solution was mixed with nitric acid to give 1.5 M total concentration and was refluxed at 100°C for 24 h with stirring. After reflux, the acidified CNT solution was filtered by using 0.2 μm pore sized PTFE membrane and rinsed with water several times to remove acid. The filtered CNT cake was dispersed in 10 mL of 0.05% Triton X-100 solution containing 0.02% NaN₃ as a source of salt as well as a bactericide by using a tip sonicator for 10 min. Then the suspended solution was diluted with the same Triton X-100 solution to give 5 L total volume and adjusted to pH 10 by using NaOH. The diluted suspension was treated with cross-flow filtration using a MidGee MM01 (pore size 0.2 μm) hollow fiber filtration module

obtained from A & G Technology Corp. (Needham, MA, USA). Since the hollow fiber filtration module operates with tangential flow filtration, blockage of membrane pores can be minimized and the suspended CNT mixture solution can be concentrated by circulation of the retentate solution. During the circulated filtration, amorphous particles and other impurities were expected to be removed with the permeate and the CNT ropes were concentrated in the retentate. To circulate the flow, a Minipulse3 peristaltic pump from Gilson (Villiers-le-Bel, France) was used and the ratio of flow rates was adjusted to 10:1 for the retentate and the permeate. The treatment was processed for about 24 h. The flow rate was regulated by controlling the length of a narrow inner diameter tubing at the permeate side. When all that remained of the CNT solution was about 100 mL, the concentrated solution was filtered through 0.2 μm pore sized PTFE membrane to remove the retentate solution.

The filter cake was transferred to 100 mL of 3:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ in a beaker and sonicated in a water bath for 2–4 h at 35°C in order to cut the CNT ropes into smaller lengths. After sonication, the resultant suspension was diluted to 200 mL of deionized water and the cut CNTs were collected by a 0.2 μm pore sized PTFE membrane and then rinsed with 0.1 mM NaOH solution. The cut nanotubes with a PTFE membrane were re-dispersed in the following solutions: a) 0.05% Triton X-100 (nonionic surfactant) with 0.02% NaN_3 , b) 0.05% FL70, a nonionic and anionic surfactant from Fischer Scientific (Fairlawn, NJ, USA), solution with 0.02% NaN_3 , and c) 0.02% NaN_3 solution without a surfactant. The volume of final nanotube suspension was adjusted to about 3 mL of each preparation and each was sonicated using a horn at 80 A for 10 min for the flow FFF analysis.

2.2 Flow field-flow fractionation

A FI-AFIFFF channel built in house was used and the system configuration was described elsewhere [21–23]. The schematic diagram of FI-AFIFFF channel is shown in Figure 1.a. The channel blocks were made of Plexiglass and a 130 μm thick spacer to provide a separation chamber is layered over the usual membrane and these were stacked over the porous ceramic frit wall mounted inside a channel block. A sheet of membrane was made from regenerated cellulose (YM-30 type) having MW cut-off of 30,000 from Amicon (Beverly, MA, USA). The channel was rectangular having a constant breadth ($b = 2.0$ cm) except for the triangular end pieces at both the inlet and the outlet. The length from tip to tip is 27.2 cm with the inlet frit extending 3.1 cm from the injection end.

To deliver the carrier solution to FI AFIFFF channel, two HPLC pumps of a model M930 from Young-Lin Co. (Seoul, Korea) were individually used for sample injection and for frit flow. To control outflow (leading to detector)

and cross-flow rates, a needle valve was placed at the channel outlet to provide back pressure. Injection was made with a model 7125 loop injector from Rheodyne (Cotati, CA, USA) having a 20 μL loop and sample amounts for injections were about 0.5–2.0 μg for each polystyrene latex standard and about 10 μg for cut CNTs. Eluted samples were detected by a model M720 UV detector from Young-Lin Co. at a wavelength of 254 nm and the detector signals were recorded by AutochroWin data acquisition software from Young-Lin Co. The eluted CNT nanotubes were collected after the detector during FFF runs in short time intervals (0.1–1 min) by using a Dynamax FC-2 fraction collector from Rainin Instrument Co. Inc. (Woburn, MA, USA) for analysis with Raman spectroscopy and SEM.

2.3 Field emission scanning electron microscopy

Purified CNTs and cut CNTs were examined by a model S-4200 field emission scanning electron microscope from Hitachi Ltd. (Tokyo, Japan). The raw CNT materials were directly mounted on conductive carbon tape and examined by SEM without sputtering. For the CNT ropes (or bucky paper) and the cut CNTs dispersed in an aqueous media, an electrodeposition method was used instead due to the difficulty in mounting CNTs in aqueous solution on a stub. Suspended CNTs and the cut CNTs collected at the end of flow FFF runs were electrodeposited onto a graphite disk (5 mm in diameter) with a well polished surface. About 10 μL of collected fraction was added to a 5 mm long Teflon tube ending with a polished graphite disk and the tube was filled with 0.02% NaN_3 solution for the electrophoretic migration of CNTs onto the surface of graphite disk. A 5 V DC current was applied for 5 min between the graphite disk (positive electrode) and a small stainless steel plate covering the aqueous solution. Afterwards, CNTs were expected to be deposited on the graphite disk, the surface of the graphite electrode was washed with ethanol and dried. SEM observations were made at an applied voltage of 15 kV for most measurements. When graphite was used, the specimen was not sputtered; however, when using carbon grid as a replacement for graphite disk, Pt sputtering was applied for 2 min.

3 Results and discussion

The ability of a FI-AFIFFF system to separate nano-sized particles was demonstrated with polystyrene standard latex spheres shown in Figure 1.b. The separation of standard beads was accomplished at a flow rate ratio of sample flow to frit flow, V_s/V_f , as 0.2/4.04 in mL/min and a ratio of outflow to cross flow as, V_{out}/V_c , 0.37/3.70 by stopless flow separation. Figure 1.b showed a high resolution separation of five different latex mixtures in a 10-fold diameter range. By utilizing the run condition used in Figure 1.b, CNT samples prepared by the purification and

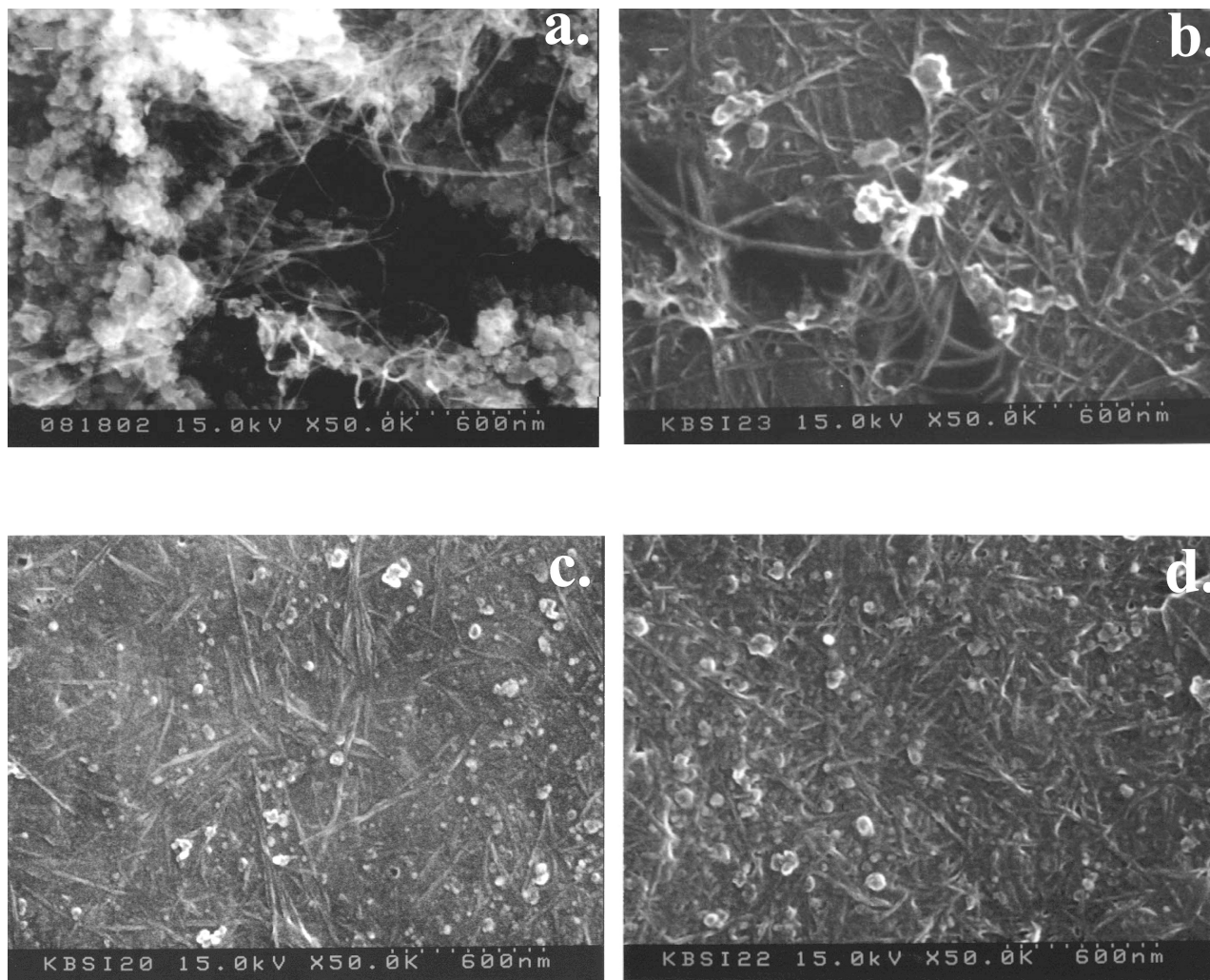


Figure 2. Electron micrographs of carbon nanotubes: a) raw CNT, b) CNT ropes before cutting process (after acid reflux and cross-flow filtration), c) CNT cut by 2 h of sonication under acid mixtures ($\text{H}_2\text{SO}_4+\text{HNO}_3$), and d) CNT cut by 4 h of sonication.

cutting process were separated using the FI-AFFFF system.

Figure 2 shows the electron micrographs of the CNT samples: a) raw CNT materials, b) CNT ropes after reflux in 1.5 M HNO_3 for 24 h followed by cross-flow filtration, c) cut CNTs obtained by sonication of sample b for 2 h in 3:1 $\text{H}_2\text{SO}_4:\text{HNO}_3$, and d) CNTs cut by sonication for 4 h. Samples b–d were mounted on a graphite surface by the electrodeposition method, as described in the experimental section. As shown in micrograph b, CNT ropes seem to be well purified since most particulate impurities appear to have been removed. However, the carbon nanotubes in the micrograph b were shown to be thicker than they

appeared in micrograph a, which implied that CNTs bundled with each other into clumps as thick as 20 nm in diameter. Micrographs c and d clearly showed that CNTs were cut into shorter lengths along with some particle residue. The cut nanotubes were a few hundred nanometers in length but those in sample d seemed to be slightly shorter than those in sample c. Since the samples shown in Figure 2 were not treated by sputtering, the image showed the real dimensions without being thickened by Pt.

Retention profiles of the carbon nanotube samples b–d were examined by varying the carrier liquid solution in flow FFF. **Figure 3** shows the superimposed fractograms of

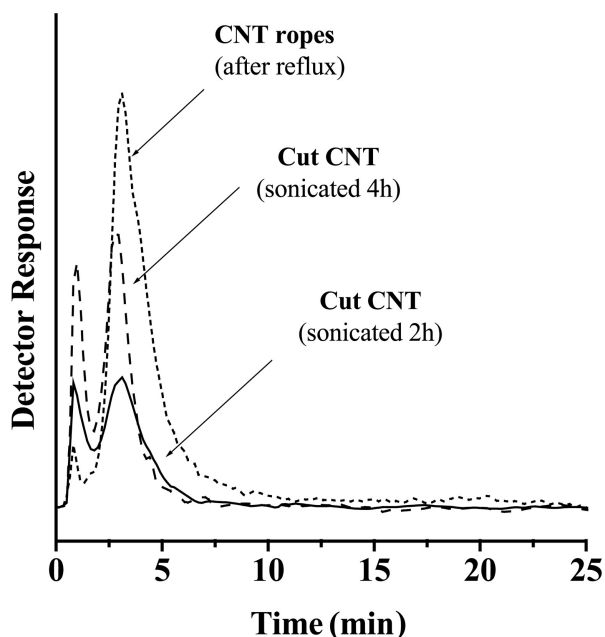


Figure 3. Fractograms of CNT samples before and after cutting process obtained by FI AFIFFF using a carrier solution, 0.05% Triton X-100 plus 0.02% NaN_3 . Experimental conditions are the same as used in Figure 1.

CNT samples obtained by using a carrier solution containing 0.05% Triton X-100 added with 0.02% NaN_3 ($I = 3.1 \text{ mM}$). The run conditions were the same as those used for Figure 1.b. Apparently, the three fractograms in Figure 3 did not seem to show any significant difference in retention profiles among them. Similar results were obtained with the same surfactant solution without adding any salt but they were not included in the figure. In order to check the effect of added surfactant in the elution of carbon nanotubes, FL-70, which was a mixture of nonionic and ionic surfactant, was utilized as a carrier solution for flow FFF. Tests were made with or without adding FL-70 to the carrier solutions and both contained the same amount of sodium azide as used in Figure 3. The three fractograms at the top of **Figure 4** were obtained from 0.05% FL-70 solution with 0.02% NaN_3 and they showed a clear difference in the elution profiles of nanotubes before and after they were cut. While the fractogram of CNT ropes showed a broad peak in which the effective spherical diameter reached up to over a hundred nm (as compared with the PS separation peaks at the bottom of Figure 4), elution of both cut CNT samples appeared to be shifted toward shorter time scales with narrow distributions. These resulted from the increase in the diffusion coefficient of the cut nanotubes due to the short length of the nanotubes. The retention profiles of the two cut CNT samples did not appear to be significantly different from each other. However, the CNT sample sonicated for 2 h seemed to show a slightly higher distribution for the sec-

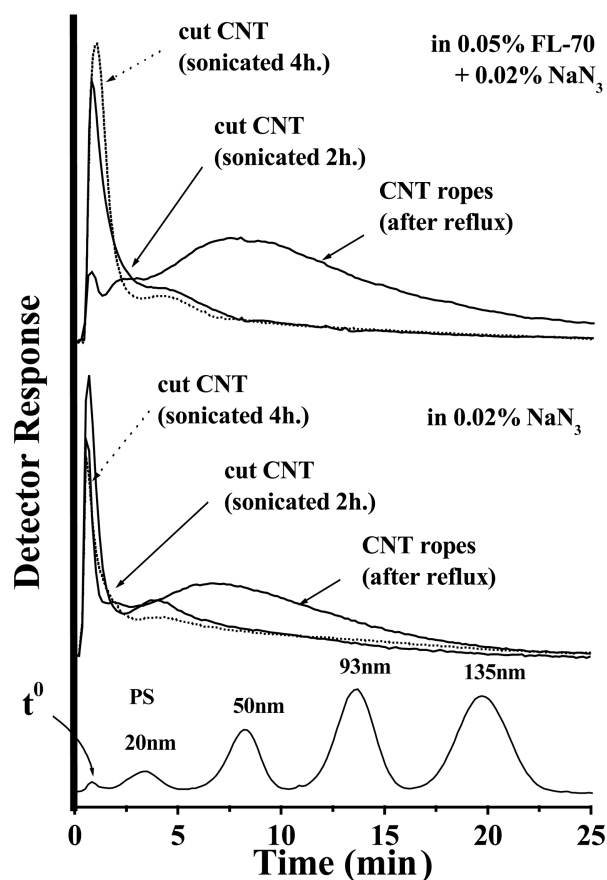


Figure 4. Comparison of FI AFIFFF separations for three CNT samples (before and after cut) which were run with carrier solutions containing 0.02% NaN_3 a) with or b) without 0.05% FL-70. Flow rate conditions are 0.2/4.04, for injection flow/frit flow rate and 0.37/3.87 for outflow/crossflow rate in mL/min.

ond peak (a shoulder after the sharp peak) as compared to the sample obtained after 4 h. The apparent similarity in the retention of the two cut CNT samples can be explained by the fact that the difference between the average lengths of the two samples was not large enough to induce a significant difference in diffusion. Similar results were observed in the middle part of the superimposed fractograms in Figure 4 which used a carrier solution having only 0.02% NaN_3 but the relative intensities of the sharp eluting peaks were bigger due to the slight shift of all of the peaks into a shorter time scale.

In order to confirm the elution of cut nanotubes, the eluted sample components were collected during a flow FFF run at two different time intervals as shown in **Figure 5.a** and are examined by FT-Raman spectroscopy. Since the concentration of the collected nanotubes was too dilute, the injection amount was increased several times over that previously injected. In this case, separation was carried out at a weak field strength, $\dot{V}_s/\dot{V}_f = 0.10/2.50$, $\dot{V}_{out}/\dot{V}_c = 0.22/2.37$ in mL/min, which led to a fast elution. In **Fig-**

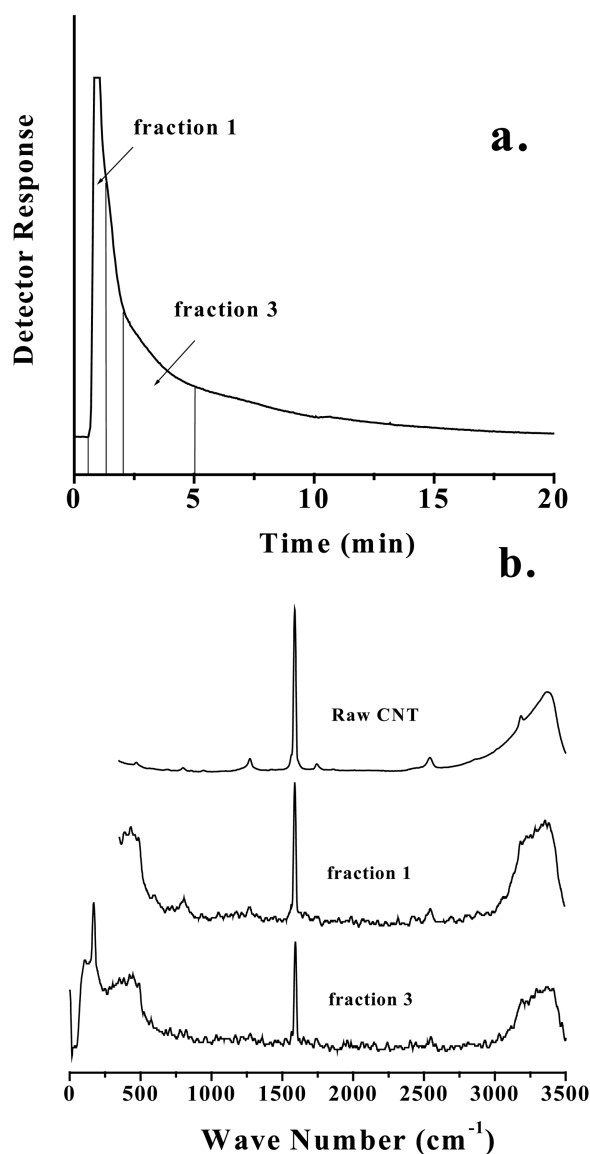
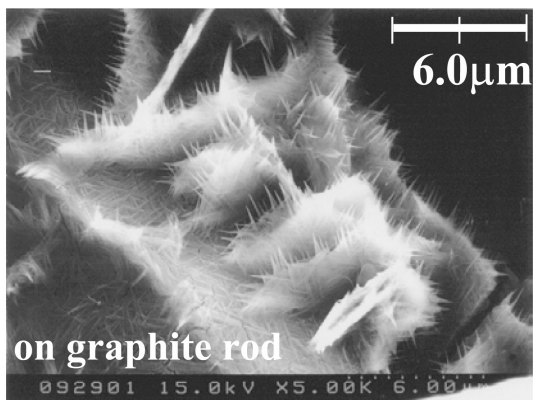


Figure 5. a) Fractogram of cut CNT sample (4 h of sonication in acids followed with curing in $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$) along with b) FT-Raman spectra for the two fractions collected after the FI FIFFF run. Carrier solution used is 0.05% FL-70 mixed with 0.02% NaN_3 . Run conditions are 0.1/2.5 for injection flow/frit flow rate and 0.22/2.37 for outflow/crossflow rate in mL/min.

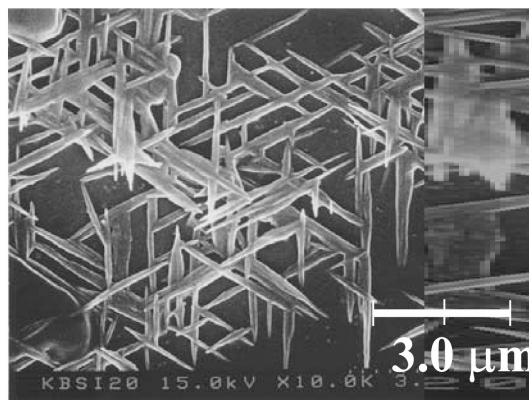
ure 5.b. FT-Raman spectra of the two fractions are shown together with that of the raw CNT material for comparison. Apparently, both fractions showed characteristic peaks at 1580 cm^{-1} originating from carbon nanotubes. To examine the cut nanotubes by FE-SEM, the eluted samples were collected in similar fashion. **Figure 6** and **Figure 7** show fractograms of the two cut CNT samples (sonicated for 2 h and 4 h) along with the respective electron micrographs. Both separations were obtained under the same run condition as used in Figure 4 and with a carrier solution containing no surfactant (containing only 0.02% NaN_3).

When a surfactant (either FL-70 or Triton X-100) was present in a collected fraction, the collected nanotubes were not successfully identified since a thick layer of presumably dried surfactant molecules seemed to cover all the nanotubes. Figure 6 shows a fractogram of the CNT sample sonicated for 2 h along with micrographs taken at each fraction collected during run. Collected nanotubes suspended in the carrier solution were transferred to a graphite disk for electrodeposition, as explained in the experimental section. On looking at the micrograph of the original sample shown in Figure 6, nanotubes appeared to be cut into shorter lengths. It was also noted that some of the cut nanotubes were arranged vertically over the nanotube layers which were laterally aligned with each other. It was likely that the cut nanotubes were arranged into specific directions when they approached each other above the graphite surface. This phenomenon was observed in the micrographs of collected fractions which were relatively dilute in their concentrations after a flow FFF run. Fraction 1, collected during 1.5–2.0 min of the elution, showed that carbon nanotubes were arranged into thick bundles just few micrometers long. It was noteworthy that the cut CNT bundles were arranged into three different alignments. Since the nanotubes were mounted on a graphite surface that has sp^2 carbons bonded hexagonally with each other, similar to CNTs, nanotubes were thought to be attracted to the graphite lattice 120° to each other during electrodeposition. Due to the formation of bundles, it was rather difficult to measure the individual length of the nanotubes in the current fraction. When late eluting nanotubes were collected in fraction 2 (time interval of 6.0–6.5 min), the micrograph showed a more complicated network of nanotubes. However, individual nanotubes in fraction 2 were expected to be longer in length than those observed in fraction 1 since the decreased diffusion led them to elute at a longer retention time in flow FFF. In addition, they appeared to be bundled less severely than those in the fraction 1, but they gather together forming a texture. It was thought that the relatively longer nanotubes were not as likely to form huge bundled structures during electrodeposition due to a decreased mobility.

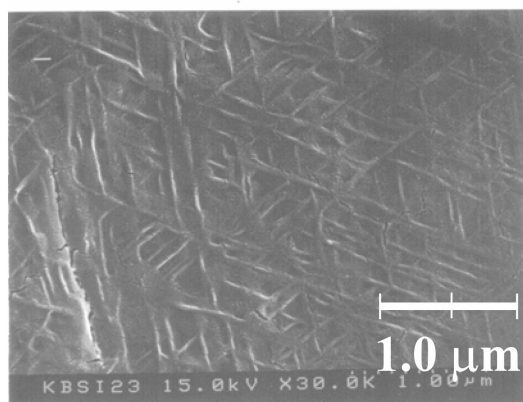
When the nanotubes were mounted on a carbon grid by an electrodeposition method, microscopic identification of individual nanotubes was rather straightforward. This is obtained from a CNT fraction collected during 3.7–4.2 min for another cut CNT sample (sonicated for 4 h) in flow FFF as shown in Figure 7. A same run condition was used as in Figure 6. For the microscopic examination, the cut nanotubes were mounted on a carbon grid by the same electrodeposition method. When this method was used, the tendency of nanotubes to align 120° to each other disappeared and individual cut nanotubes were clearly shown with a random arrangement. Upon measuring the dimensions of apparent nanotube rods, the aver-



**Cut CNT
(sonicated 2h.)**



fraction 1



fraction 2

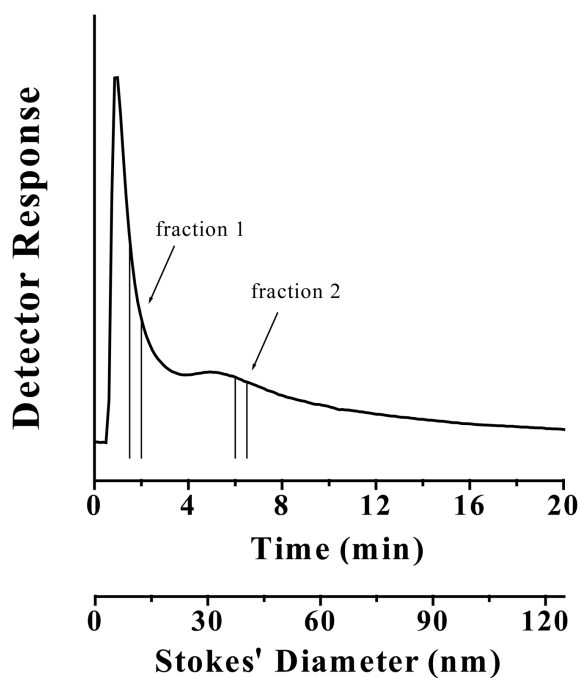


Figure 6. FI FIFFF separation of cut CNT sample (sonicated for 2 h) along with electron micrographs of the fractions collected during run. Carrier solution contains only 0.02% NaN_3 . Flow rate condition is the same as used in Figure 4.

age tube length was 182 ± 37.4 nm with an average thickness of about 29 ± 7.0 nm. Since the nanotubes were rod-shaped, an accurate calculation of nanotube length from FFF theory was not easy to obtain due to the effect of shape on retention in flow FFF. In addition, the cut nanotube fraction shown in Figure 7 was mounted on a carbon grid followed with Pt sputtering for 2 min for an improved microscopic examination and thus, the apparent nanotube bundles appeared to be thicker than the actual image.

In this work, it was demonstrated that FIFFF was applicable to the separation of carbon nanotubes. Also shown was the

possibility of examining nanotube fractions of similar lengths for further physical analysis. The current study suggested that appropriate use of surfactant was required for carbon nanotubes of short length in a well dispersed state. On utilizing an FI-AFIFFF channel, sample injection and separation can be performed continuously; this gives such channels a definite practical advantage over other conventional FIFFF channels. Since separation of nanoparticles or nanotubes using FIFFF was achieved in a few minutes, FIFFF can potentially be utilized in monitoring the preparation or purification of nanoparticles as well as carbon nanotubes, as well as the dispersion or agglomeration behavior of nanotubes and their derivatives.

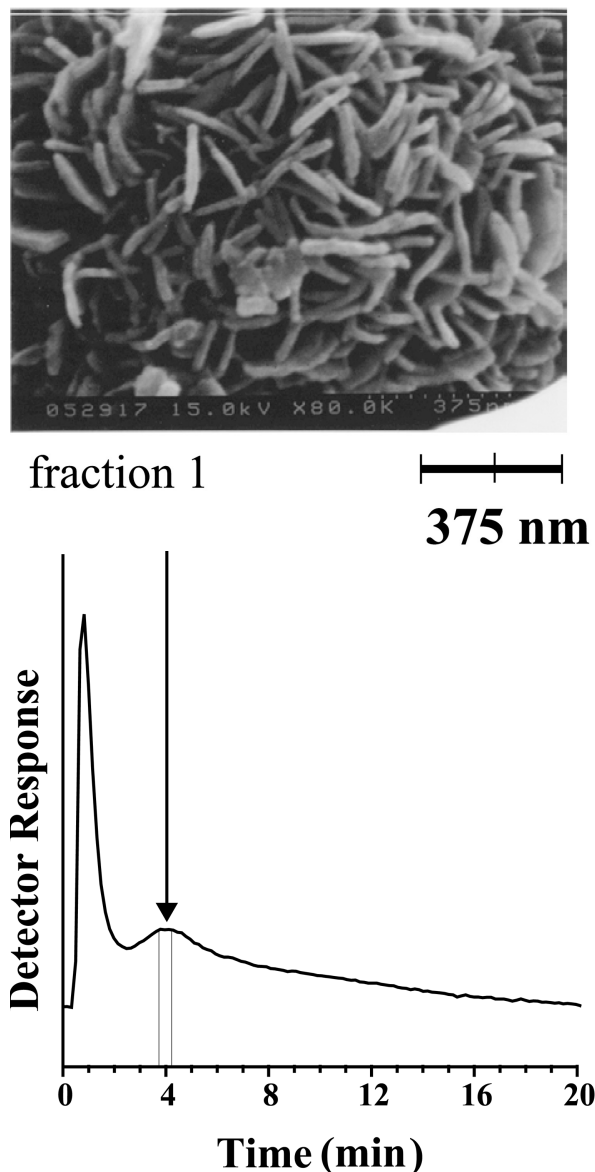


Figure 7. Fractogram of cut CNT sample (sonicated for 4 h) along with micrograph of the fraction. Run condition is the same as used in Figure 6.

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