Separation of Mixed SWNTs and MWNTs by Centrifugal Force -- an Experimental Study

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***Abstract* — For eventual commercial applications of carbon nanotubes (CNTs) in nanoscale devices, it will be very important to realize effective separation of mixed single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). We have developed a new method to separate a mixture of SWNTs and MWNTs by centrifugal force in an aqueous solution of glycerol. The method proposed in this paper takes advantage in the difference of the density and diameter of the SWNTs and MWNTs, which effectively produce a difference of sedimentation velocity between them along the direction of spinning radius when centrifugal force is exerted. The inert gradient agent acts to both stabilize the fluid environment of the centrifuge tube and facilitate sharp resolution of zones of the centrifuge fluid in the tubes after the centrifugation. Experiments show that SWNTs and MWNTs subside at different speeds during the procedure of centrifugation and suspend at different levels in the centrifugal tube, due to difference in their buoyant densities, at the end of centrifugation. Our results indicate that the centrifugal technique can provide a rapid and repeatable separation of mixtures of SWNTs and MWNTs.**

Keywords ***— CNT Separation,Centrifugal Separation, SWNT, MWNT***

I. Introduction

Carbon nanotubes (CNTs) have recently attracted much attention due to their nanometer-scale electronic structures and outstanding material properties [1, 2]. Specifically, SWNTs can exhibit either metallic or semiconducting behavior depending on their diameters and chiralities. Semiconducting SWNTs that exhibit distinct characteristic of ballistic conductor and insulator is considered one of the most ideal materials for a wide range of potential applications such as DNA biosensors and CNT-based field effect transistors [3, 4]. A great challenge to efficiently realize the full potential of SWNTs is the need to synthesize defect-free SWNTs and purify them. Currently, the method of large-scale synthesis of SWNTs using electric arc discharge from raw MWNTs can obtain defect-free SWNTs that range from 0.9 to 2 nm in diameter and range from 1 to 5 μm in length [5, 6]. However, as-synthesized SWNTs not only vary in their diameters, but also include some impurities such as particles of metal catalyst, amorphous carbon and MWNTs [5]. Although the existing purification methods could effectively remove the impurities such as particles of metal catalysts and amorphous carbon, MWNTs could not be effectively removed by the methods presented in [5] and [7]. Therefore, it is necessary to develop a reliable method to separate mixed SWNTs and MWNTs after SWNTs are purified.

Several methods have been reported recently for sorting CNTs, including an approach using alternating current dielectrophoresis to separate semiconducting SWNTs and metallic SWNTs, and a technique utilizing the density-gradient ultracentrifugation based on density differentiation [8-11]. However, these methods all focus on sorting SWNTs by diameter, density, or electronic behavior. Few methods have been reported for separation of mixed SWNTs and MWNTs. Though the improvement of techniques to decrease the content of MWNTs in as-synthesized SWNTs is possible, even a small amount of MWNTs is fatal to the characterization of nano sensors or nano electronic devices based on SWNTs. To resolve the problem of separation and to attain highly homogeneous SWNTs, we have developed a general approach for separating the mixture of CNTs by centrifugal force. In general, the diameter and density of MWNT is much higher than those of SWNT. Additionally, the diameter and density of CNT is similar to molecular entitles such as DNAs and RNAs, so we propose to separate mixtures of SWNTs and MWNTs by adapting a similar technique of centrifugation which is already a powerful tool for separating and purifying DNAs and RNAs [12, 13].

In the present study, we will focus on the application of centrifugal force to separate mixtures of SWNTs and MWNTs. In this paper, we will describe the basis of centrifugation theory, the dynamic model of CNT in a centrifugal filed and the detailed procedure of how we utilize the centrifugal technique to separate mixtures of SWNTs and MWNTs.

II. Theoretical Backgroud and Modeling

A. Dynamic Model of CNT in a Centrifugal Field

For CNTs in a centrifugal field, CNTs will move outward from the center of rotation. During the centrifugal process, the total force acting on CNTs is the sum of several independent forces. Because the direction of Gravitational Force and the

This project is funded by the Chinese National 863 Plan (Project Code: 2006AA04Z320), the National Natural Science Foundation of China (Project Codes: 60635040 and 60675060), and the Hang Kong Research Grant Council (Project Code: 413906).

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direction the sedimentation movement of CNTs are vertically reciprocal, Gravitational Force can be neglected in horizontal direction. With negligible Gravitational Force, CNT in a centrifugal field experience three major forces. The three dominate force components are Centrifugal Force (F_c), Buoyant Force (F_b), and Frictional Force (F_f) (see Figrure.1).

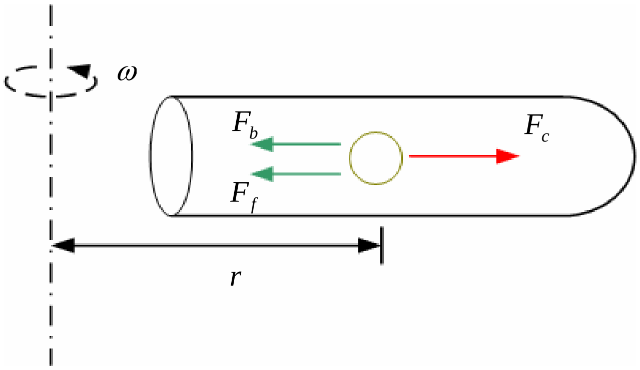


Figure 1. Schematic diagram of CNT during a centrifugal process. Centrifugal Force produced during centrifugation will move CNTs outward from the center of rotation. For CNTs in a centrifugal filed, CNTs also experience another two forces, Buoyant Force (F_b) and Frictional Force (F_f). F_f is opposite to the movement direction of CNTs and F_f is proportional to the viscosity coefficient of the medium solution and the sedimentation velocity of CNTs. If F_c is greater than F_b, CNTs will move towards the bottom of the centrifugal tube. By contrast, CNTs will move towards the top of the centrifugal tube. The difference between F_c and F_b will determine the sedimentation velocity of CNTs.

Centrifugal Force refers to the force produced during centrifugation that moves CNTs outward from the center of rotation. The force is proportional to the radial distance and the square of the rotor speed. The Centrifugal Force value is determined by the following formula:

$$F_c = m\omega^2 r \tag{1}$$

where m is the mass of CNTs, ω is the angular velocity of the centrifugal tube and r is the distance between CNTs and the spinning axis. For CNT, $m = V\rho_p$, where V is the volume of CNT, and ρ_p is the density of CNT.

The main external influence on CNTs suspended in a fluidic environment is the buoyant force. For CNTs in a fluidic environment, Buoyant Force is given by

$$F_b = -m_o\omega^2 r \tag{2}$$

where m_0 is the mass of the displaced solution. For the solution $m_0 = V\rho_m$, where ρ_m is the density of the fluid.

For simplicity, we can consider CNT to be spherical. Assuming the surface area of a spherical particle is equal to the surface area of CNT. Consider the equation $\pi d^2 = \pi ab$, the equivalent diameter d of CNT can be written as

$$d = \sqrt{ab} \tag{3}$$

where a is the diameter of CNT, and b is the length of CNT.

According to Stoke's Law, Frictional Force can be written as

$$F_f = -3\pi\sqrt{ab}\eta_m \frac{dr}{dt} \tag{4}$$

where η_m is the viscosity of the solution medium, $\frac{dr}{dt}$ is sedimentation velocity of CNT in the process of centrifugal sedimentation. In this expression, the actual frictional force exerting on the CNT will be much great than the frictional force calculated through equation (4) in theory, because the shape of CNT is cylindrical rather than spherical.

For CNTs in a centrifugal tube spinning around a fixed axis, the kinetic equation of CNTs in centrifugal sedimentation can be written as

$$m\frac{d^2 r}{dt^2} = F_c - F_b - F_f \tag{5}$$

where $\frac{d^2 r}{dt^2}$ is the acceleration of CNTs in the process of centrifugal sedimentation. Based on equation (5), the movement of CNT in a fluidic environment is governed by F_c, F_b and F_f .

Substituting $\frac{1}{4}\pi a^2 b = V$ and let $m = V\rho_p$ and $m_0 = V\rho_m$, then (5) becomes:

$$\frac{1}{4}\pi a^2 b\rho_p \frac{d^2 r}{dt^2} + 3\pi\eta_m\sqrt{ab}\frac{dr}{dt} - \frac{1}{4}\pi a^2 b(\rho_p - \rho_m)\omega^2 r = 0 \tag{6}$$

Substituting $p = 12\eta_m \frac{1}{\rho_m a\sqrt{ab}}$ and $q = \frac{(\rho_p - \rho_m)}{\rho_p}\omega^2$, then equation (6) can be simplified as

$$\frac{d^2 r}{dt^2} + p\frac{dr}{dt} - qr = 0 \tag{7}$$

where p is a constant coefficient subjected to the viscosity of the medium, the density of CNTs, the diameter of CNTs, and the length of CNTs; q is also a constant coefficient subjected to the densities of the CNT and the medium, and ω is the angular velocity of the centrifugal tube.

B. *Simulating the Sedimentation of the CNT in a Centrifugal Process*

The sedimentation of SWNTs and MWNTs are directly related to the centrifugal angular velocity, the density and the viscosity coefficient of the solution medium. Since glycerol has relatively high viscosity, we used glycerol as the gradient solution in the centrifugal process.

In our modeling analyses, the densities of SWNTs and MWNTs are greater than the density of the solvent of glycerol. Figure 2 shows that the sedimentation velocity of CNTs will increase when the viscosity coefficient of the gradient solution decreases. Figure 3 shows that the sedimentation velocity of CNTs will augment when the centrifugal speeds increases. Hence, in a same fluidic environment, the sedimentation velocity of MWNTs is much greater than that of SWNTs.

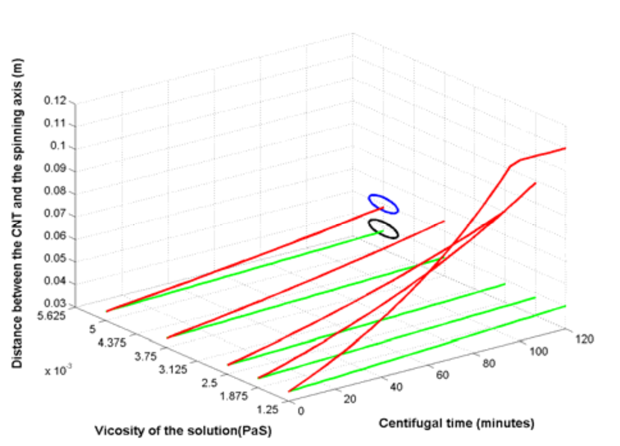


Figure 2. The sedimentations of SWNTs and MWNTs at different viscosity coefficients. The density of the medium solution is 1.15g/cm3 and the centrifugal speed is 27,000rpm. The red lines suggest the sedimentation process of MWNTs and the green lines explain the sedimentation process of SWNTs at different viscosities. The blue ellipse is the real experiment result of the sedimentation of MWNTs and the black ellipse is the actual experiment result of the sedimentation of SWNTs.

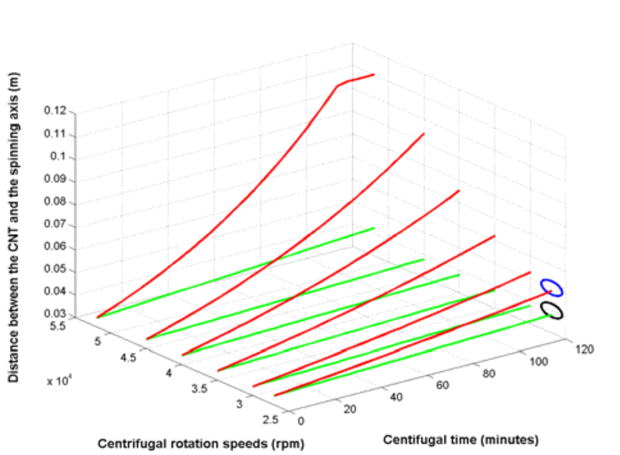


Figure 3. The sedimentations of the SWNTs and the MWNTs at different centrifugal speeds. The density of the medium solution is 1.15g/cm^3 and the viscosity coefficient is 0.005PaS. The red lines suggest the sedimentation process of MWNTs and the green plots suggest the sedimentation process of SWNTs at different centrifugal speeds. The blue ellipse is the real experiment result of the sedimentation of MWNTs and the black ellipse is the actual experiment result of the sedimentation of SWNTs.

III. EXPERIMENTAL

Rather than attempting a complete description of synthesis, purification and classification of the SWNT, this paper concentrates mainly on a possible solution to separate the mixture of SWNTs and MWNTs, an absolutely necessary process before sorting the SWNTs based on their electronic type. In our experiment, the raw samples of CNTs we used was produced by using the technique of hydrogen electric-arc described in [5]. Because the raw samples of CNTs include the metal catalyst, amorphous carbon, the samples of as-synthesized SWNTs and MWNTs need first be purified using the methods reported in [7]. In general, the morphology of the purified CNTs is in the form of bundles of a few nanotubes and weblike substances, so we also needed to disperse CNTs before using them.

In the centrifugal experiment, we used two sorts of CNTs, purified SWNTs (including some residual MWNTs from purification process) and MWNTs, to investigate the proper rotating speed, centrifugal force and centrifugal time required for SWNT-MWNT separation. The purity of SWNTs was about 95 wt%. The residual 5 wt% material mixed with purified SWNTs were mainly MWNTs. The purity of MWNTs was 95 wt%. The purified MWNT contained the residual 5 wt% material of the catalyst particles and other nanoparticles that were not yet removed in the purification process.

Based on the centrifugal theory, the sedimentation velocity of a material will be subjected to many factors such as the dispersing condition of the particle and concentration of the particle in solution. For the preparation of the individual suspension of SWNTs and MWNTs, purified CNTs were first dispersed by utilizing the technique of sonication [8]. The sample (10mg) of the purified MWNTs were dissolved in 20 ml of alcohol and sonicated for two hours at a frequency of 57 KHZ, and the upper 80% of the supernatant was then carefully decanted. The typical mass concentration of the resulting MWNT solution was ~20 mg/liter. To attain the same mass concentration of SWNT solution, 10 mg of purified SWNTs and 0.2g surfactant sodium dodecyl sulfate (SDS) were suspended in 20ml di-water, using a similar technique described in [8]. Then, the SWNT solution was sonicated for three hours, and the upper 80% of the supernatant was then carefully decanted. The resulting SWNT solution has a typical mass concentration of ~20mg/liter.

In our experiment, another very important procedure is to prepare the proper gradient solution. The inert gradient agent acts to both stabilize the fluid environment of the centrifuge tube and facilitate sharp resolution of zones of the centrifuge fluid in the tubes after the centrifugation. The solutes of gradient solution used in our centrifugal experiments include sucrose, glycerol and cesium chloride. The gradient solution we eventually adopted was the aqueous solution of glycerol. The 8 ml of glycerol solution was respectively transferred to four centrifugal tubes that were labeled from A to D. Because the glycerol dissolves with water each other, the 80 wt% of glycerol solution can be obtained. Approximately, 2ml of SWNT/aqueous solution was laid on the top of the glycerol solution in Tube A, and 2ml of MWNT/alcohol solution was laid on the top of the glycerol solution in Tube B. The mixture of 1ml of SWNT/aqueous solution and 1ml of MWNT/alcohol solution were laid on the top of the glycerol solution in Tube C and D. The samples were then centrifuged at 25,900 rpm for two hours. The rotational velocities can produce an acceleration of 56,977g. Our approach has a distinct difference from the method reported on density-gradient centrifugation in [2]. In our approach, the density of the SWNT and the MWNT are all higher than the density of gradient solution.

IV. Results and Discussion

A. *Record of the Centrifugal Process*

Figure 4 shows the sedimentation results of MWNTs, SWNTs, and the mixture of SWNTs and MWNTs. By contrast of Tube B and A, we find that the sedimentation velocity of MWNTs is much more than that of SWNTs. In Tube C, SWNTs and the MWNTs have a clearly formed two detached layers. After centrifugation, the samples in Tube C were removed, layer by layer, for the following AFM scanning analyses.

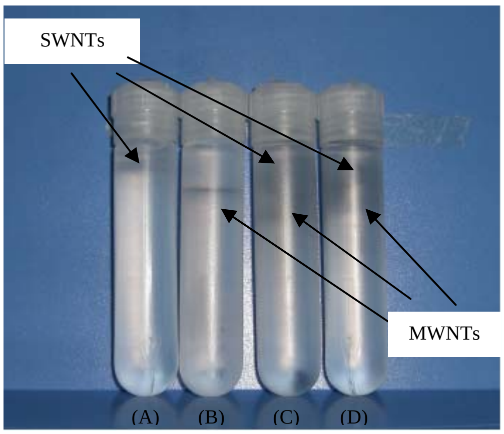
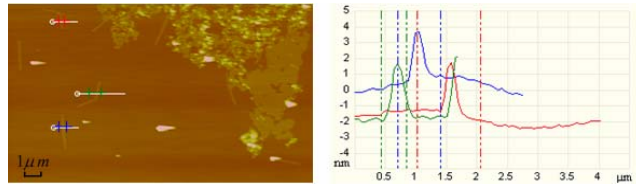


Figure 4. The sedimentation results of MWNTs, SWNTs, and mixtures of SWNTs and MWNTs. Tube A shows the sedimentation result of SWNTs in the aqueous solution of glycerol and Tube B shows the sedimentation result of MWNTs in the aqueous solution of glycerol after two hours of centrifugation. By contrast of Tube A and Tube B, we find that the sedimentation velocity of MWNT is much more than the sedimentation velocity of SWNT in the same fluidic environment. Tube C and Tube D show that the sedimentation results of mixtures of SWNTs and MWNTs after two hours of centrifugation. In Tube C and D, SWNTs and MWNTs have assembled at different levels in the tube.

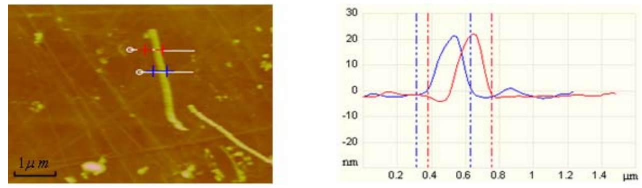
B. *AFM Analyses*

According to the rule of sedimentation velocity, heterogeneous band of molecules or particles of different sizes and densities should settle into a gradient when centrifugal force is applied. To observe the distribution of CNTs in Tube C, we used an AFM to scan the samples that we removed from Tube C. Figure 5 shows that the first layer samples in Tube C are SWNTs and Figure 6 shows that the second layer samples in Tube C are MWNTs. The AFM scanning results suggest that we realized the effective separation of SWNTs and MWNTs by use of the method of centrifugation.



(a) (b)

Figure 5. SWNTs lie in the first layer of Tube C. a) SWNTs spread on the surface of mica. b) The cross-section of SWNTs. The diameter of SWNTs is less than 3 nm.



(a) (b)

Figure 6. MWNTs lie in the second layer of Tube C. a) MWNTs spread on the surface of mica. b) The cross-section of MWNTs. The diameter of MWNTs is more than 20 nm.

V. Conclusion

The difference of the density (*effective*) between SWNTs and MWNTs is increased by centrifugal force, so that the sedimentation velocity of MWNT is much more than that of SWNT in the same centrifugal tube. To separate a mixture of SWNTs and MWNTs, the proper centrifugal speed should be ~30,000 rpm, and the acceleration of the centrifuge should be ~60,000g. The mass concentration of the glycerol solution should be ~80%. Finally, when the viscosity coefficient of the glycerol solution is 0.005PaS, the resolution of zones of the centrifuge fluid in the tubes is higher.

Acknowledgment

The authors acknowledge Shenyang National Laboratory for Materials Science for their supply of SWNTs and MWNTs. The authors would also like to thank Department of Laboratory & Equipment Management for the centrifuge and centrifugal experiment.

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