

Purification of SWNTs Using High-Speed Centrifugation

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Abstract — For eventual commercial applications of single-walled carbon nanotubes (SWNTs) in nanoscale devices, it will be very important to realize effective purification of SWNTs. We have developed a simple method to purify as-synthesized SWNTs by centrifugal force in an aqueous solution of sodium dodecyl sulfate (SDS). The method proposed in this paper can effectively remove impurities such as metal catalyst particles, graphitic nanoparticles and amorphous carbon. Our method takes advantage of the fact that more massive particles sediment faster than less massive particles. Through adjusting relative centrifugal force, we can respectively remove metal catalyst particles and carbon nanoparticles from SWNTs by centrifugation. SEM results indicate that the concentration of the SWNT solution decreased when the number of times of centrifugation is increased. Raman spectra suggest that the purity of the SWNT solution increased when the number of times of centrifugation is increased. These experimental results indicate that the centrifugal technique can provide a rapid and repeatable purification of SWNTs.

Keywords — Centrifugation, CNTs, Dispersion, Purification, SWNTs

I. INTRODUCTION

Since carbon nanotubes (CNTs) were discovered by Iijima in 1991, CNTs have attracted strong attention due to their nanometer-scale electronic structures and outstanding material properties [1, 2]. Depending on their diameters and chiralities, single-walled carbon nanotubes (SWNTs) can exhibit either metallic or semiconducting behavior [3-5]. Metallic SWNTs possess high electrical and thermal conductivity can be used to fabricate chemical, thermal, and flow sensors [2, 6]. Moreover, semiconducting SWNTs that exhibit distinct characteristic of ballistic conductor and insulator is considered one of the most ideal materials for the application of CNT-based field effect transistors [7, 8]. To efficiently realize the full potential applications of SWNTs, the need to synthesize defect-free SWNTs and to remove the impurities such as metal catalyst particles and carbon nanoparticles is critical [9]. Currently, the method of large-scale synthesis of SWNTs using electric arc discharge can obtain defect-free SWNTs that range from 0.9 to 2 nm in diameter and range from 1 to 5 μm in length. However, it is a large challenge to effectively remove the impurities such as metal catalyst particles and carbon nanoparticles, without destroying the structure and the electrical and material properties of SWNTs. Usually, the process to purify as-synthesized SWNTs is very complicated, which includes gas- or vapor-phase oxidation, wet chemical oxidation or treatment,

filtration, etc. The impurities such as metal catalyst particles and carbon nanoparticles can be removed after the purification [9-12]. However, the traditional purification process to purify as-synthesized SWNTs will possibly damage the mechanical structure of SWNTs and even change the electrical and material properties of SWNTs. Recently researchers paid much attention to purify as-synthesized SWNTs using the method of centrifugation to remove the impurities such as metal catalyst particles and carbon nanoparticles. A method utilizing centrifugation in a two step process for the bulk purification of SWNTs was described in [13]. And, another method for purifying chemically modified SWNTs was reported in [14]. However, as-prepared SWNTs were firstly treated by nitric acid or oxidant in these methods, so that the mechanical and material properties of acid-treated SWNTs would possibly change [14].

Therefore, we propose a new and simple method to directly purify as-synthesized SWNTs by using centrifugation. This approach differs from reported method in [13], in which as-synthesized SWNTs were firstly treated with nitric acid. In this study, we will focus on the dynamic model of particles in a centrifugal field and experimental results of centrifugal purification of SWNTs.

II. THEORETICAL BACKGROUND AND MODELING

A. Dynamic Model of Particles in a Centrifugal Field

For a particle in a centrifugal field, the particle will move outward from the center of rotation. During the centrifugal process, the total force acting on the particle is the sum of several independent forces. If the gravitational force is neglected, the particle in a centrifugal field experiences three major forces: the centrifugal force (F_c), the buoyant force (F_b) and the frictional force (F_f) (see Figure 1). As described previously in [15], the dynamic model of the particles in a centrifugal field can be written as

$$\frac{d^2 r}{dt^2} + 18 \frac{1}{D^2 \rho} \eta_m \frac{dr}{dt} - \frac{\rho - \rho_0}{\rho} \omega^2 r = 0 \quad (1)$$

where r is the distance between the particle and the spinning axis, t is the time of centrifugation, D is the diameter of the particle, η_m is the viscosity of the solution medium, ρ is the density of the particle, ρ_0 is the density of the solvent and ω is the angular velocity.

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From the above equation, we find that the sedimentation velocity is relevant to the density and diameter of the particle. So it is feasible to separate SWNTs from the impurities such as metal catalyst particles and carbon nanoparticles.

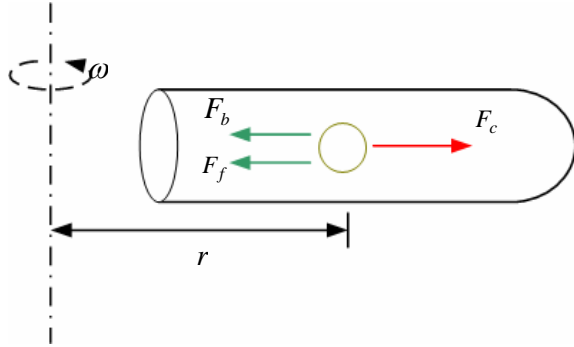


Figure 1. Schematic of a particle during the centrifugal process. The centrifugal force produced during centrifugation will move the particle outward from the center of rotation. If F_c is greater than F_b , the particle will move towards the bottom of the centrifugal tube. By contrast, the particle will move towards the top of the centrifugal tube, if F_b is greater than F_c . In our experiment, the density of the particles separated is greater than the density of the solvent. Separation is based upon mass (i.e., larger particles will sediment faster). The advantages of the method are that run times are short, and the quality of the separation is good.

B. Simulating the Sedimentation of the Particles in a Centrifugal Process

A fundamental requirement of using centrifugation to purify SWNTs is to determine the run conditions. So, we made use of the dynamic model of the particles to simulate the sedimentation motion of the particles in the centrifugal field. In our simulation, we used the following estimated parameters as shown in Table 1.

Table 1. Parameters of SWNTs, bundles of SWNTs, metal catalyst particles and carbon nanoparticles.

Parameters	Nanoparticles			
	SWNTs	Bundles of SWNTs	Metal catalyst particles	Carbon nanoparticles
Diameter (nm)	90	200	1~50	1~100
Density (g/cm^3)	<1.9~2.3	<1.9~2.3	~7.8	>1.9~2.3

For simplicity, we considered SWNT to be spherical. Assuming the surface area of a spherical particle is equal to the surface area of a tubular SWNT, the equivalent diameter of SWNT was obtained. The diameters of the metal catalyst particles and the carbon nanoparticles were observed by AFM in our experiments. Additionally, we assume that the density of SWNTs is less than that of graphite ($1.9\sim 2.3 \text{ g}/\text{cm}^3$) and the density of carbon nanoparticles is more than that of graphite. And the density of metal catalyst nanoparticles is similar to that of iron ($\sim 7.8 \text{ g}/\text{cm}^3$). The standard viscosity of pure water at 4°C is assumed to be $1.787\text{E}-3 \text{ Pas}$.

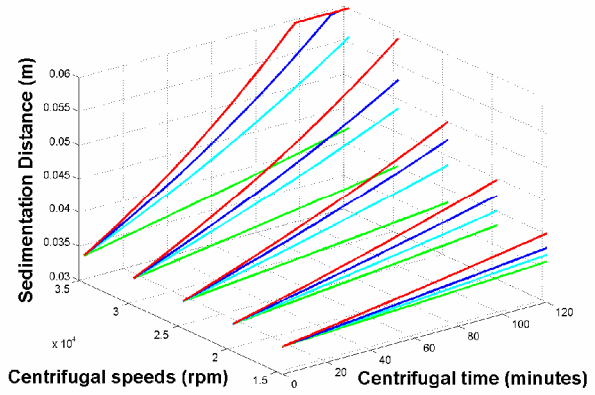


Figure 2. Simulation analysis of the sedimentation process of SWNTs and impurities at different centrifugal speeds. The green, cyan, blue and red curves respectively suggest the sedimentation process of SWNTs, bundles of SWNTs, carbon nanoparticles and metal catalyst particles at different centrifugal speeds.

Figure 2 shows that the sedimentation velocity of the particle increases when the centrifugal rotation speed is increased. When working at the speed of 35,000 rpm, centrifuge provides a better resolution of separation of these particles. However, the speed of 25,000 rpm was applied in our real experiments due to the limit of the centrifuge we used.

C. Observing the Sedimentation of SWNTs in a Centrifugal Process

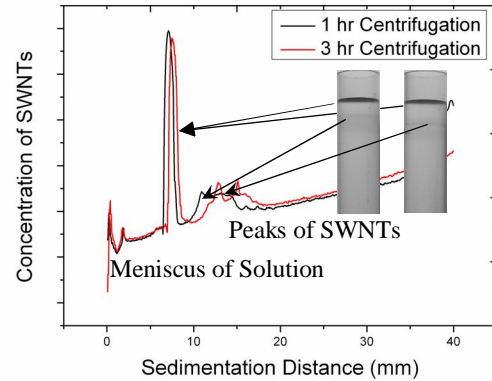


Figure 3. The concentration curves of SWNT solution in the centrifugal tube. The movement of peaks of SWNTs explains the sedimentation process of SWNTs in the centrifugal tube.

In order to make the simulation of the sedimentation of these particles reflect the real experiments, it is important to observe the sedimentation process of the particles. However, since the main aim was to separate SWNTs from the impurities in our experiment, we only needed to observe the sedimentation process of SWNTs. We used purified SWNTs to perform the process of centrifugation while applying the same run conditions as used in the simulation. Figure 3 shows the resulting sedimentation process of purified SWNTs after applying a centrifugal rotation speed of 25,000rpm. The run

time for the experiment was three hours. The centrifugal process was recorded by a camera every hour. By comparing the simulation and the experimental results, we find that the sedimentation velocity of SWNTs in our experiments was more than the sedimentation velocity of SWNTs in the simulation. However, the experiment does demonstrate that our simulation of the sedimentation of the particles in the centrifugal process provides useful information on the run conditions necessary to purify SWNTs using high-speed centrifugation.

III. EXPERIMENTS AND RESULTS

A. Dispersing and Purifying SWNTs

The raw sample of SWNTs used in our experiments was synthesized by the hydrogen arc-discharge method. These as-prepared SWNTs were then dispersed. From the simulation analysis we found that the difference of the sedimentation velocity between the bundles of SWNT and the impurities was very small. Therefore, in order to separate SWNTs from the impurities, it is very important to get stable and homogeneous dispersion of SWNTs. The typical dispersion procedure used in our experiments is that 2.5 mg of raw SWNTs and 1% weight of the surfactant sodium dodecyl sulfate (SDS) are added into 5ml DI-water, and the dilution is then sonicated for 3 hr at room temperature.

In our experiments, we adopted the DI-water as the gradient solution. The aim of using the gradient solution was to improve the resolution of centrifugation through increasing the sedimentation distance of the particles. The DI-water was firstly filled in the centrifuge tubes. Then, the as-dispersed SWNTs were added on the top of the gradient solution. It was very important to choose the proper centrifugal run conditions. In our experiment, the sample of as-dispersed SWNTs was centrifugated for half an hour at a relative centrifugal force of 45,000 g (25,000 rpm). The centrifugation was carried out at 4 °C. We controlled the sedimentation position of SWNTs by adjusting the centrifugal time. After centrifugation, the supernatant solution of SWNTs was collected. To improve the purity of the solution of SWNTs, the process was repeated three times. The concentration of SWNTs in the solution decreased when centrifugation was repeated. The sediment included bundles of SWNTs which could be dispersed and centrifugated again so that more SWNTs could be utilized effectively.

B. SEM Observation

SEM was used to identify and characterize as-dispersed SWNTs. Figure 4 shows that SWNTs were homogeneously dispersed. It also shows that the solution of SWNTs consisted of a large number of metal catalyst particles and a number of carbon nanoparticles. However, if the centrifugal process is applied, metal catalyst particles and carbon nanoparticles were removed, which will be discussed in the following section.

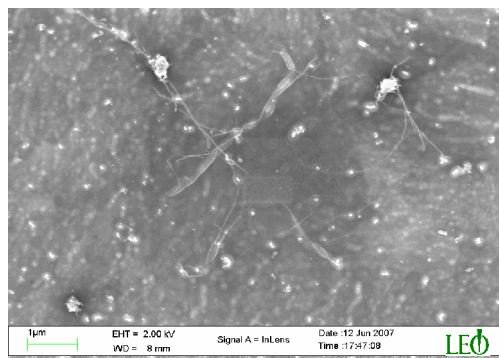


Figure 4. SEM image of materials collected from the supernatant solution of dispersed SWNTs.

C. Raman Spectra

Raman spectrum is a very useful tool to characterize the purity of SWNTs and to estimate the diameter of SWNTs. As shown in the inset of Figure 5, the characteristic mode of SWNTs is called as the radial breathing mode (RBM) which ranges from 100 to 300 cm^{-1} . The frequency of the RBM is inversely proportional to the diameter. And the characteristic mode of SWNT at high frequency of around 1580 cm^{-1} is the tangential stretching mode. Another characteristic mode is the

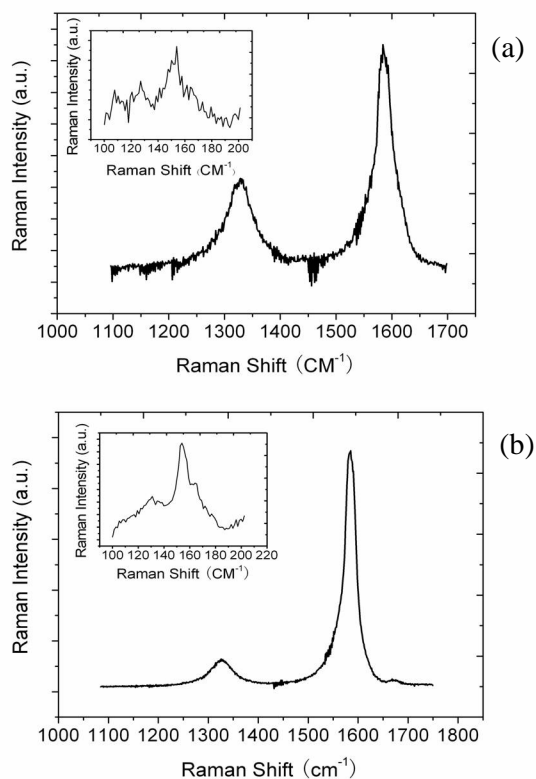


Figure 5. Raman spectra of materials collected from: (a) the supernatant solution of dispersed SWNTs, (b) the supernatant solution which was centrifugated 3 times.

D mode at high frequency of around 1350 cm^{-1} , which is sensitive to carbon nanoparticles and defective SWNTs. In Figure 5a, the peak of Raman spectrum of dispersed SWNTs is at $\sim 1350\text{ cm}^{-1}$, which means that the dispersed SWNTs included some carbon nanoparticles. By contrast, Figure 5b shows that a majority of carbon nanoparticles had been removed after 3 times of centrifugation.

D. AFM Analyses

The metal catalyst nanoparticles and the bundles of SWNTs can not be characterized by Raman spectrum, so we used AFM to observe the metal catalyst nanoparticles after centrifugation. Figure 6 presents the typical AFM images of SWNTs after 1 time of centrifugation and 3 times of centrifugation, respectively. According the results of AFM analyses, a number of metal catalyst nanoparticles were removed (Figure 6a) after 1 time of centrifugation. However, almost no metal catalyst nanoparticles were observed (Figure 6b) after 3 times of centrifugation.

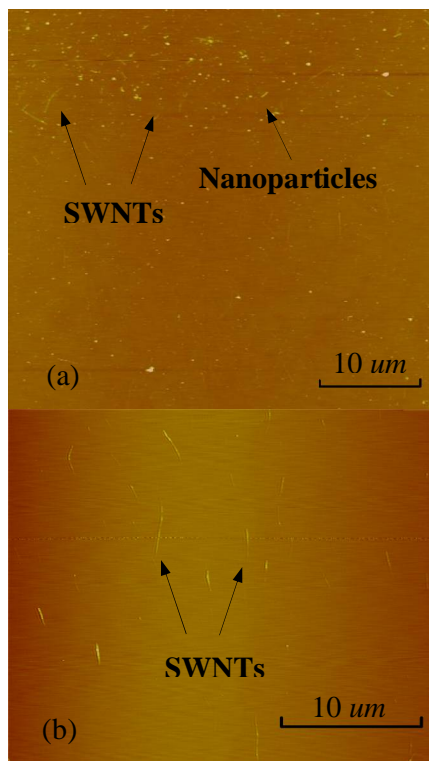


Figure 6. AFM image of SWNTs. (a) Some nanoparticles lied on the surface of mica after 1 time of centrifugation. (b) Almost no particles lied on the surface of mica after 3 times of centrifugation.

IV. CONCLUSION

In summary, we have shown that the differences of density and diameter among SWNTs, metal catalyst nanoparticles and carbon nanoparticles, provide a possibility to purify as-synthesized SWNTs directly by using the centrifuge method. The predicted run conditions based on the dynamic model of nanoparticles during the centrifugal process could ensure an

optimum purification process of SWNTs in a minimum amount of time. The experimental results indicate that high speed centrifugation is a very effective technique to purify SWNTs.

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