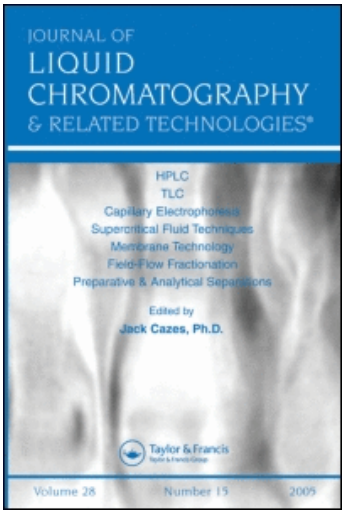

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Preparative Purification of Single Walled Carbon Nanotubes by High Speed Countercurrent Chromatography

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Abstract: The application of high speed countercurrent chromatography to the preparative purification of crude single walled carbon nanotubes is described. The purification was accomplished on the basis of an experiment that dispersed the single walled carbon nanotubes with aniline, the result mixture was separated by high speed countercurrent chromatography using the two phase system composed of chloroform/methanol/water = 4/4/2. The sizes of SWNTs separated were observed by scanning electron microscopy. The experimental results demonstrated that the high speed countercurrent chromatography possessed good efficiency for purification of single walled carbon nanotubes.

Keywords: High speed countercurrent chromatography, Preparative purification, Single walled carbon nanotubes

INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in the early 1990s by Iijima,[1] the unique chemical, mechanical, and electrical properties of

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CNTs promise numerous applications, including hydrogen storage,[2] probe tips,[3] quantum wires,[4] and electronic devices.[5] In fact, the synthetic method used dictates CNT properties such as the distribution of diameter and length, degree of entanglement, defects, chirality, and crystallinity, as well as the overall quality of the product. For many applications, they must be produced with high purity. Up to now, large scale synthesis routes, such as chemical vapor deposition[6] and gas phase decomposition of CO,[7] have been developed to produce CNTs materials with high yields, while it is still very difficult to get carbon nanotubes pure enough. Pursuit of these applications is hampered by a lack of means to produce bulk quantities of pure materials.

The purification of nanoparticles presents a significant challenge. There are many reports on the purification of single walled carbon nanotubes (SWNTs), and most of them involve filtration, centrifugation, or chromatography. Chromatography is attractive because of the power of the method.[8,9]

However, carbon nanotubes have poor dispersibility in solvents. Functionalization of CNTs is thus a mandatory task in order to be able to dissolve them in organic solvents and to prevent the aggregation of nanotubes. The chemical modifications of CNTs have been well summarized in several review articles.[10]

High speed countercurrent chromatography (HSCCC) is a liquid-liquid portioning chromatography method, and its stationary phase is immobilized by centrifugal force. HSCCC has two advantages: (A) it has no solid support matrix and can eliminate irreversible adsorption, which often happens in gas chromatography and liquid chromatography; (B) it has a higher sample capacity in preparative separation because of its particular mechanism of separation. In this paper, we report the purification of SWNTs dispersed in aniline by high speed countercurrent chromatography using a two phase solvent system of chloroform/methanol/water = 4/4/2 (v/v/v). The sizes of SWNTs separated were observed by scanning electron microscopy. To our knowledge, this is the first report that HSCCC is used for purification of nanoparticles.

EXPERIMENTAL

Apparatus

The HSCCC experiments were performed using a multilayer coil planet centrifuge constructed at the Beijing Institute of New Technology Application, China. The apparatus has a pair of column holders symmetrically placed on the rotary frame at a distance of 8 cm from the central axis of the centrifuge ($\beta = 0.5$–0.75). The multilayer coil was prepared by

winding a 1.6 mm I.D. polytetrafluoroethylene (PTFE) tube directly onto the holder hub with a total capacity of 260 mL. The system was equipped with a metering pump (Model NS-1007, Beijing Institute of New Technology Application, China), a UV detector (Model 8823A-UV, Beijing Institute of New Technology Application, China), a recorder, and an injection valve. The XL30ESEM-TMP Philips SEM was used to determine the purification.

Reagents

SWNTs (10–40%) were purchased from Aldrich. All organic solvents and other chemical reagents are of analytical reagent grade (Beijing Chemical Factory, China).

Preparation of Soluble SWNTs

The soluble SWNTs were prepared according to literature procedures.[11] Briefly, 5 mg of accurately weighed SWNTs were added to 3 mL of aniline and the mixture was heated at 160°C for 3 h in the dark. After being sonicated for about 1 h, the dark dispersion of soluble SWNTs for HSCCC separation was obtained.

Preparation of Two Phase Solvent System and Sample Solution

In the present studies, the two phase solvent system was composed of chloroform-methanol-water. Each solvent mixture was thoroughly equilibrated in a separating funnel at room temperature and the two phases were separated before use.

The sample solutions were prepared by adding soluble SWNTs in the above phase mixture consisting of equal volumes of each phase.

HSCCC Procedure

The multilayer coiled column was first entirely filled with the upper phase at a flow rate of 10.0 mL/min, the lower phase was pumped into the inlet of the column at a flow of 2.0 mL/min in the head to tail elution mode, and the apparatus was rotated at 800 rpm. When the front of the mobile phase elutes from the outlet of the column, 4.0 mL of sample solution containing 1 mg of SWNTs was introduced into the column through an injection valve. The effluent from the outlet of the column was

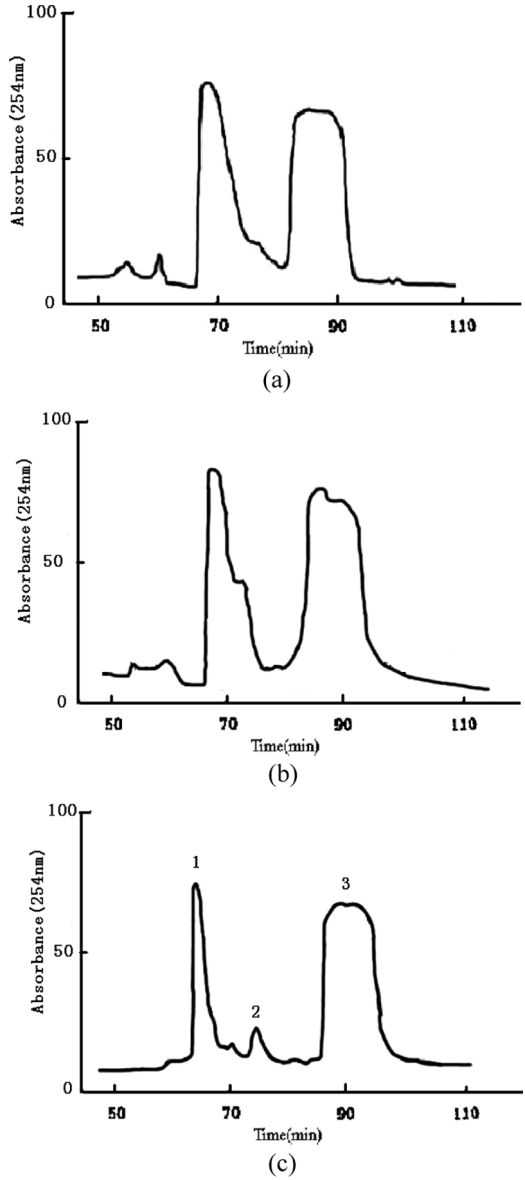
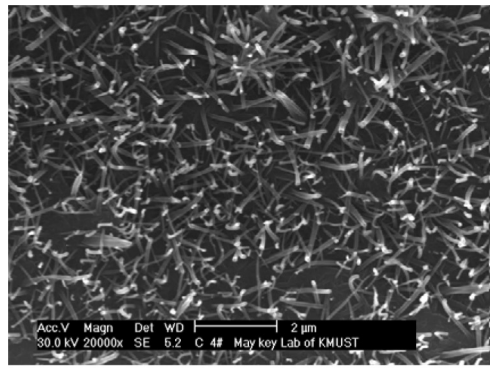
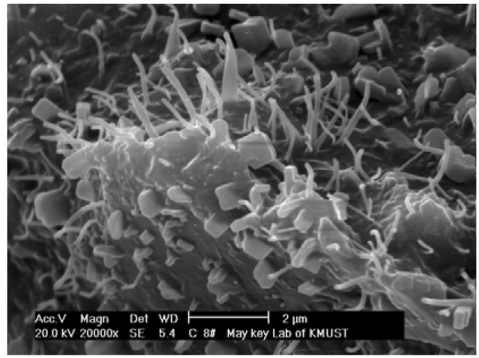


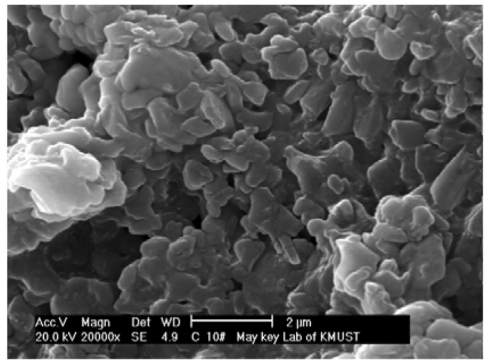
Figure 1. HSCCC chromatogram of SWNTs. Solvent system: (a) chloroform: methanol:water = 4:2:2; (b) chloroform:methanol:water = 4:3:2; (c) chloroform: methanol:water = 4:4:2.



(a)



(b)



(c)

Figure 2. SEM images of particles obtained from the peaks in Figure 1c. (a) peak 1; (b) peak 2; (c) peak 3.

continuously monitored with a UV detector at 254 nm. Fractions of peaks were collected according to the chromatograms.

RESULTS AND DISCUSSION

The selection of a solvent system is important for HSCCC, because selecting a solvent system means simultaneously choosing the column and the eluent. In the acetone, methanol, THF or DMF solvent, SWNTs dispersed in aniline possess a good solubility.[11] The $CHCl_3$-CH_3OH-H_2O solvent system contains the methanol and provides nearly equal volumes of the upper and lower phase with reasonably short settling times. Changing the ratio of methanol in the solvent system, permitted changing, simultaneously, the selectivity of upper and lower phase, as methanol can dissolve in chloroform and water and may change the dispersibility and partition characteristic of two phases.

The two phase solvent systems composed of chloroform:methanol: water = 4:2:2, 4:3:2, and 4:4:2 (v/v/v), respectively, were chosen to purify the SWTNs, and their three chromatograms are exhibited in Figure 1. As can be seen, Figure 1c gave the best separation result showing three main peaks. The top fractions of each peak were collected, in which the black color of fractions was obvious. In Figure 1c, the first peak eluted with a retention time of 68 min, and the second peak followed immediately. The third peak appeared around 98 min. Therefore, the best solvent ratio to separate SWNTs was 4:4:2.

To study the purification, three representative fractions in Figure 1c were analyzed by the scanning electron microscope. The SEM images in Figure 2 showed that from early to late fractions, there was a clear change in the particle shape. As can be seen, peak 1 contained high purity SWNTs (Figure 2a), Figure 2b (peak 2) showed some impurities, and no SWNTs were observed in Figure 2c (peak 3).

The structure of SWNTs resembles a graphite sheet rolled up into a cylinder, which consists of hexagonal graphite lattice on the wall and a few pentagons at the curve.[12] When the sample solution was injected into the separation column of the HSCCC, SWNTs had more solubility in the mobile phase than that of in the stationary phase, due to high surface area of SWNTs and solubility in organic solvent. Therefore, the first eluted particles were SWNTs, and then mixture of impurity and SWNTs, finally, impurity of sample.

CONCLUSION

We reported a new method to purify SWNTs dispersed in aniline using HSCCC. The sizes of SWNTs separated were observed by scanning

electron microscopy. The results demonstrated that the high speed counter-current chromatography possessed good efficiency for purification of SWNTs. This is the first report of the purification for nanoparticles in HSCCC.

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