Novel Purification Procedure and Derivatization Method of Single-Walled Carbon Nanotubes (SWNTs)

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Abstract. A new purification procedure is introduced, which uses the advantages of both, column-chromatography and vacuum-filtration. Potassium polyacrylate was used as a stationary phase. This method is based on the idea that the size of the existing cavities in the polymer increases during a swelling process in distilled water. The cavities are big enough to entrap nanoparticles, but allow for a free movement of nanotubes and bundles. The procedure starts with an oxidation step to remove part of catalyst and nanoparticles. In this step a chemical modification of the SWNTs occurs, namely the oxidation of cage carbon atoms to carboxylic groups as well as to hydroxyl- and carbonyl-groups.[1] In contrast to Haddon,[2] we use an alternative derivatziation of carboxylic acid groups in making amides in water. AFM images of the reaction products show clearly that the SWNTs have also been oxidized on their sidewalls.

INTRODUCTION

SWNT raw material prepared via arc discharge consists of tubes which are different in diameter and length. During the preparation of SWNTs, other carbon species such as fullerene polyhedra and other graphitized carbon structures, as well as amorphous carbon are formed simultaneously. There are also metal cluster impurities, sticking on the tips of the ropes and interconnecting the SWNTs. Therefore, effective purification methods are very important,[3] in order to explore the enormous potential of proposed applications. Further efforts concern the chemical behavior of SWNTs. For example, it is still unclear what really happens during the oxidation step. Another big obstacle is to obtain stable solutions in organic solvents. All these open questions constitute a serious challenge to synthetic chemists.

RESULTS AND DISCUSSION

The process involves three steps. First, raw material is treated in 65% nitric acid for 3h under reflux (typically 150 ml of acid *per* 100 mg of raw material). During this time a weight loss of about 20% takes place.

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The next step is the treatment of the SWNTs with an ultrasonic tip for 1 min. This treatment reduces the size of the nanoparticles. Tubes and bundles are shortened as well, but to a lower extend. As a consequence, the size difference between SWNTs and degraded particles increases.

The final and most important step is a chromatographic separation using a stationary phase consisting of potassium polyacrylate swollen in distilled water. In contrast to common chromatographic procedures, the speed of this method can be increased by the application of vacuum. In this way, the swollen polymer particles are squeezed like a sponge until elution stops. SWNTs which are too big to be encapsulated by the cavities move through the space between the swollen polymer particles and elute in high quantity (more than 40 %mass) as the first fraction. The remaining material still contains a considerable amount of SWNTs which can be eluted in lower quality (Figure 2) by repeated swelling of the gel with distilled water and application of vacuum. Most of the degradation products remain within the cavities of the polymer.

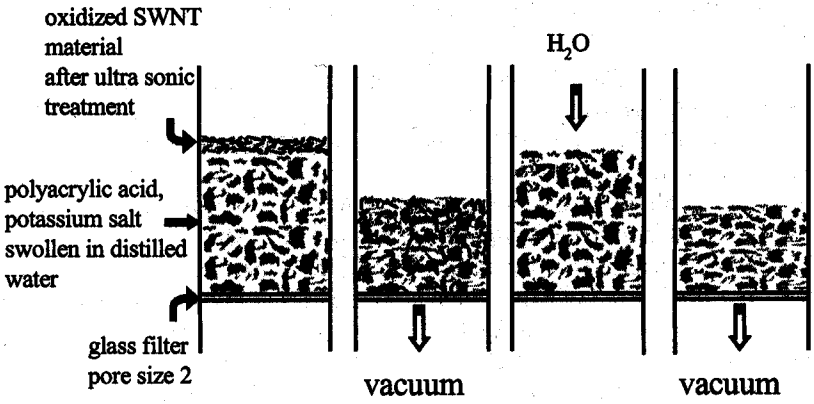
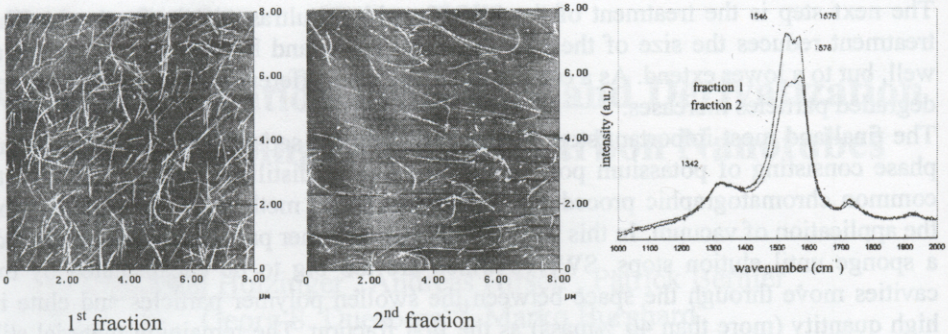


Figure 1: Schematic representation of the filtering procedure using potassium polyacrylate swollen in distilled water.

Raman spectroscopy was performed to monitor the purification process. The D-line around 1350 cm^{-1} and the G-line, centered at 1580 cm^{-1}, is normally attributed to the carbon impurities and the SWNTs in a sample, respectively. Their relative intensities provide a measure for the purity of the sample.



1st fraction 2nd fraction

Figure 1. AFM images and Raman spectra of the two collected fractions. The first fraction shows a large number of SWNT bundles and only a very small amount of impurities (single dots). These impurities mostly consist of amorphous carbon. On the right side, Raman spectra of the two collected fractions are shown. The different intensities of the G-line about 1560 cm^{-1} compared to the similar (scaled) intensities of the D-line at 1342 cm^{-1} reveal the decreased amorphous carbon content in the collected fractions.

The resulting purified dispersions were directly used to prepare SWNTs with chemically modified carboxylic acid groups under aqueous conditions. This goal could be achieved with the aid of EDC (1-ethyl-3-(3-dimethylamino-propyl)carbodiimide) as a water soluble coupling reagent. The addend is a Newkome dendron, that has already been used to solubilize C_{60} in water.[4][5] A vast molecular excess of EDC and the dendron is needed to obtain a significant amount of product.

Th reaction was carried out by using a 0.5 mg/ml dispersion of purified SWNTs, which was stirred for 3 d at ambient temperature and pH 5 together with 10 mg/ml each of the Newkome dendron and EDC. The weakly acidic mixture was subsequently centrifuged, leaving a black sediment, which was washed with water and ethyl acetate to remove by-products and non-reacted components. The sediment was then dispersed in ethanol by ultrasonic agitation and centrifuged again. Finally, the supernatant solution, containing soluble tubes, was decanted.

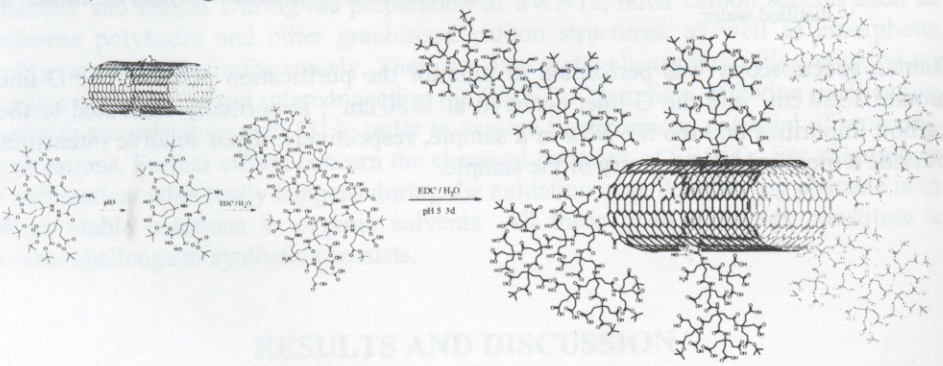


Figure 2. Amide coupling with dendritic amines in water.

In order to obtain solutions in organic solvents, the Newkome dendron was allowed to react in a weakly acidic aqueous dispersion. A very pleasant effect in this case is the partial polymerization of the dendron. Caused by the partial deprotection of the *tert*-butylic esters, generating free carboxylic acid groups, forming amide bonds with other dendra. Thus formed large dendra are eventually then attached to the carboxylic acid groups of the SWNTs both at the ends and the sidewalls.
As shown in Figure 4, the resulting dendritic polymer, which is covering the SWNTs, is sufficiently big to be detected by AFM.

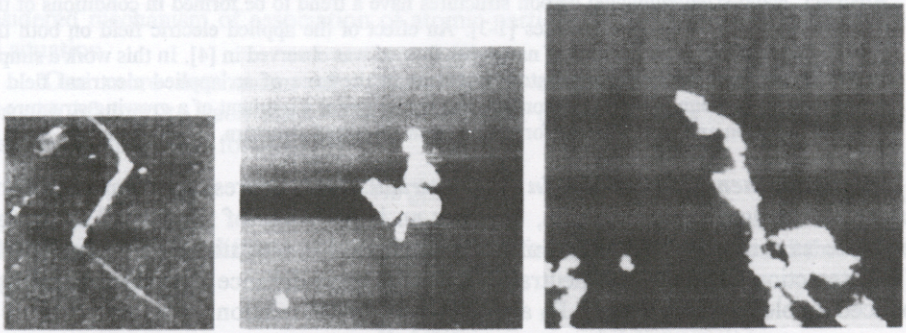


Figure 3. AFM images of modified, ethanol soluble SWNTs.

In conclusion, a straightforward purification procedure and a new method to functionalize SWNTs have been developed. As for the purification, there is no need for expensive filter systems which makes it possible to purify a large amount of raw material within hours. The resulting SWNTs show high purity in neutral aqueous environment. No surfactants or additives are required to obtain highly dispersed, stable suspensions. Amide linkage was successfully employed to decorate the dispersed and partially oxidized SWNTs with the Newkome dendra.

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