

Separating Single-Walled Carbon Nanotubes by Length

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ABSTRACT

Single-walled carbon nanotubes (SWNTs) are typically microns in length. However, intermediate lengths between small spheroidal fullerenes and long SWNTs could have significant scientific and technological importance in molecular electronics and sensing applications. Existing methods are limited by factors such as scalability, polydispersity and cost. Here we describe a simple, yet powerful technique for sorting SWNTs by length. It is based on a scalable two-phase liquid-liquid extraction process which is capable of transferring water-soluble SWNTs into an organic phase. The extraction utilizes electrostatic interactions between a common phase transfer agent and the sidewall functional groups on the nanotubes. Large length-dependent van der Waals forces for nanotubes allow the ability to control the length of nanotubes extracted into the organic phase as demonstrated by AFM.

Keywords: carbon nanotubes, length, phase transfer, separation

1 INTRODUCTION

In order to utilize single-walled carbon nanotubes as structural components for various applications, uniform SWNT building blocks of specific length are needed. This aids dispersibility control and facilitates their use in many important fields including medicine, molecular electronics and advanced materials. Common ways of synthesizing SWNTs [1, 2], however, only allow for a very limited degree of length control. Therefore, typical as-produced SWNT samples are highly polydisperse with a wide length range.

Cutting SWNTs into shorter pieces is one way to narrow down length distributions and attain shorter nanotubes. While many reagents and cutting schemes have been developed that significantly shorten SWNTs [3-6], the products are not yet monodisperse. Also, cutting methods consume the product material and are inherently undesirable when long SWNTs are required.

Several methods have been proposed to separate carbon nanotubes by length. It has been demonstrated that common

instrumental techniques for analytical separations based on chromatography [7, 8], capillary electrophoresis [9, 10] and field flow fractionation [11, 12] can be employed for SWNT separation. For these methods, SWNTs are suspended in surfactants such as sodium dodecyl sulfate, poly(vinylpyrrolidone) or DNA strands. This limits the use of these techniques to a microgram-scale as only very dilute concentrations of SWNTs can be processed at one time. Therefore, we have focused our efforts on the development of an effective large-scale method.

2 METHOD

The technique demonstrated here is based on a simple separation principle. If the dispersibility of nanotubes in a given solvent can be altered in a way that specific length nanotubes are less dispersible than others, they can be extracted and separated from the others using a phase-transfer procedure. Such extractions are facile processes and can be scaled up since they do not require any sophisticated machinery.

A common phase transfer agent, tetraoctylammonium bromide (TOAB), is used to induce a length-dependent dispersibility change in SWNTs. TOAB is known to form ion-pairs with carboxylate and sulfonate moieties. It has been widely used for extractions of gold nanoparticles from aqueous media into organic solutions [13]. These phase transfer reactions were found to be size-selective [14]. It has been our goal to establish such size selectivity for a SWNT/TOAB system. Our choice of SWNTs has sulfonate containing functional groups since they are dispersible in water. By electrostatic interactions with TOAB's quaternary ammonium cation, nanotubes are selectively extracted into an organic phase.

2.1 Experimental

Single-walled carbon nanotubes obtained from the HiPco process were purified by SF₆/O₂ oxidation according to Xu et al. [15] and then functionalized twice with chloroaniline sulfonate to attain highly water-dispersible nanotubes [16]. The tubes were then dispersed in water. In a separate vial, TOAB was added to an organic solvent

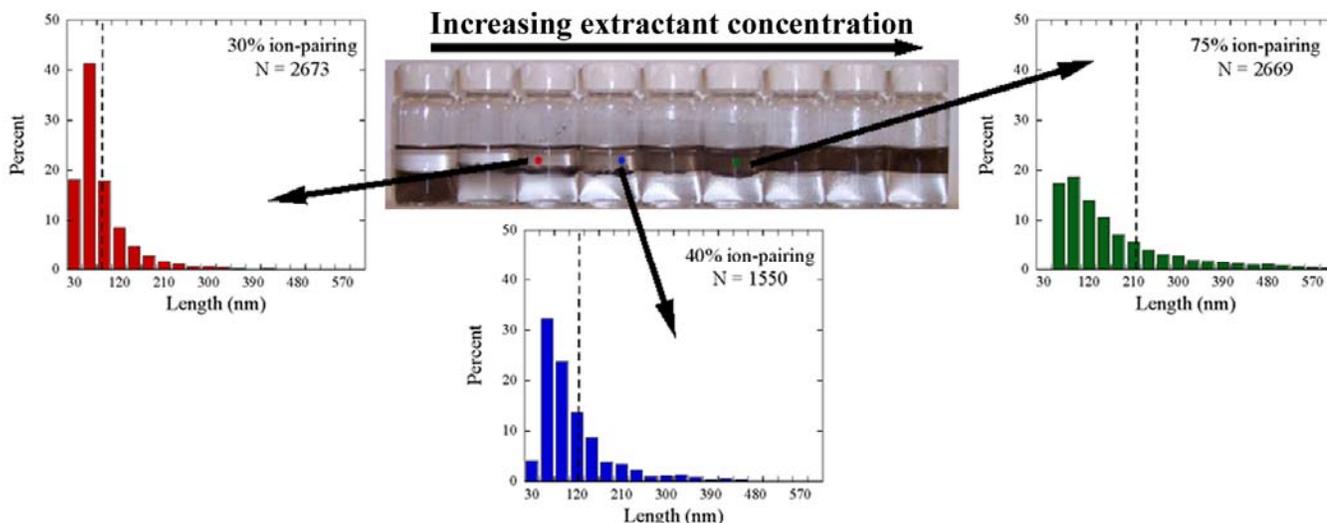


Figure 1: The effect of TOAB concentration on SWNT phase transfer. As the $\text{TOA}^+/\text{SO}_3^-$ ion pairing ratio is raised, (from left to right 0, 15, 30, 40, 60, 75, 90, 100 and 200 %), increasingly longer SWNTs get extracted into the organic phase.

(e.g., ethyl acetate). Subsequently both solutions were mixed vigorously. The emerging emulsions were broken up by freezing and thawing the samples. The binding of TOAB to nanotubes collected from the organic phase was reversed by washing with excess acetic acid. The removal of the TOAB leads to aggregation and settling of the nanotubes. The collected nanotube product can be re-suspended in water, methanol, or ethanol by short ultrasonication. Further details can be obtained elsewhere [17].

2.2 Analysis

For all length measurements, SWNT solutions were dispersed on freshly cleaved mica and imaged with a tapping mode atomic force microscope (Digital Instruments Nanoscope IIIA). Then, length distributions were obtained using SIMAGIS software. This technique delivers statistically accurate results as described earlier [18]. UV-Vis-NIR spectra were recorded of undiluted SWNT solutions in cuvettes with a path length of 1 cm using a Shimadzu UV-3101PC spectrometer.

3 RESULTS AND DISCUSSION

Tetraoctylammonium bromide was able to facilitate a phase transfer of SWNTs from the aqueous medium into the organic. On the basis of the previously described electrostatic interaction of sulfonate and other anions with the TOA^+ cation that leads to an increase in organophilicity of the substrate, it becomes evident that this must also be the case for the SWNT/TOAB system. Control samples with pristine tubes (i.e., they contain no anionic functional groups) as well as functionalized SWNTs without TOAB show no extraction of nanotubes.

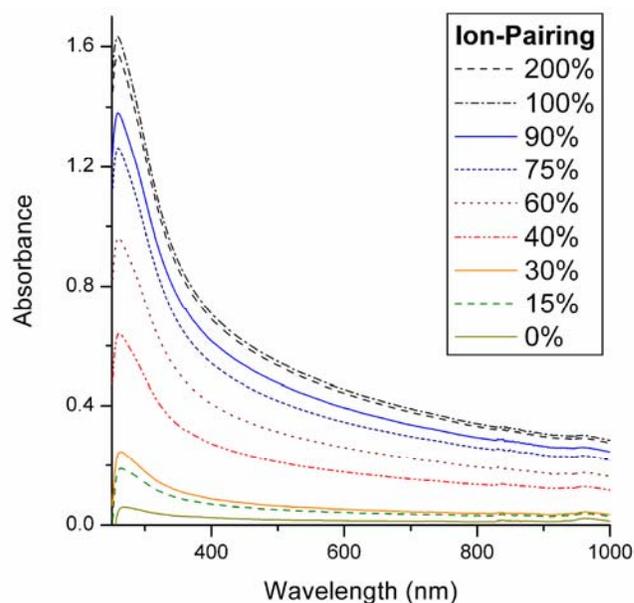


Figure 2: UV-Vis absorbance spectra of organic phase after extraction

As shown in Figure 1, the amount of material transferred to the organic phase is dependent on the concentration of TOAB, in particular on the amount of $\text{TOA}^+/\text{SO}_3^-$ ion pairing. Higher TOAB concentrations lead to a larger SWNT transfer and therefore to a higher absorbance intensity of the organic phase, as seen in Figure 2. Eventually, complete ion pairing with all sulfonate groups results in the extraction of all nanotubes. This corresponds to a 1:1 stoichiometric electrostatic interaction of TOA^+ with every SO_3^- group. The UV/Vis data also shows that at low TOAB concentrations ($\text{TOA}^+/\text{SO}_3^-$ ratio of 0.15 and 0.3) very few nanotubes are extracted, suggesting that insufficient ion pairing occurs to render the SWNTs organophilic. Instead, they form emulsions or

accumulate at the interface. The partially ion-paired functional groups yield amphiphobic SWNTs that contain both anionic charges as well as hydrophobic octane tails on the sidewall. Therefore, salts like ammonium chloride were added to eliminate some of the charge on the nanotubes and aid the phase transfer into the organic medium.

Length distributions of the starting material as well as the extracted SWNTs were obtained to evaluate TOAB's performance as a size selective extraction catalyst for SWNTs. The starting material shows a broad distribution of SWNT lengths. The average length is 275 nm. When a sufficient amount of TOAB is added to pair up 30% of the sulfonate groups, only very short SWNTs get extracted. The average length drops to 73 nm. At higher concentrations of TOAB longer SWNTs get extracted. Finally, with most sulfonate moieties electrostatically bound to TOA⁺ ions, the length distribution approaches that of the starting material. When the nanotube average length in the organic phase is plotted versus ion pairing, a graph like the one in Figure 3 is obtained. The average length of the nanotubes shows a linear correlation with the predicted amount of ion pairing.

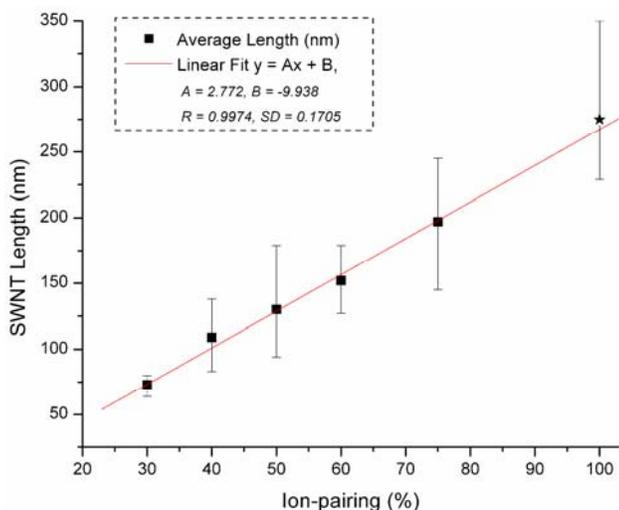


Figure 3: Fitted length averages of extracted SWNTs as a function of ion-pairing. The starred data point (100%; 275 nm) corresponds in fact to the starting material.

A comparison of nanotube length distributions for a TOAB concentration equivalent to 50% ion pairing was performed by recovering SWNTs from both organic and aqueous phases after the separation. The distributions and AFM images as seen in Figure 4 show that after a single extraction step a length sorting has taken place. Most carbon nanotubes longer than 600 nm remain in the water phase, while the majority of short SWNTs are transferred to the ethyl acetate extract. Therefore, this data suggests that step-wise extractions could provide narrowed length distributions.

Although the data and AFM images clearly indicate a significant degree of separation, the fidelity of the separation is hindered by inadequacies in removing the organic phase near the phase boundary. Improvements in the removal of the organic phase from the aqueous phase will likely produce better fidelity separations.

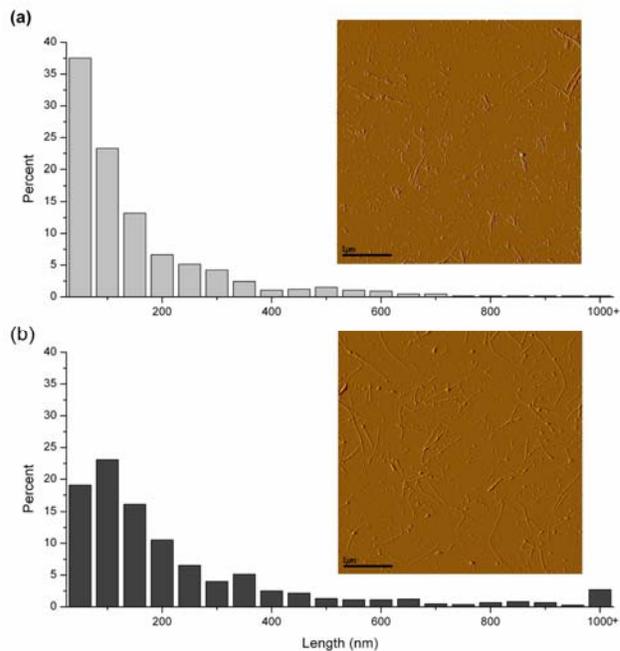


Figure 4: Length distributions and AFM images for 50% ion pairing. (a) Ethyl acetate extract, (b) Water extract.

The length selectivity of the separation is a result of noncovalent interactions between SWNTs and TOAB ions in solution. Attractive van der Waals forces are additive and therefore are greater between larger particles. In fact, an attractive energy of $36 k_B T$ per nm has been determined for nanotubes [19]. As the shortest SWNTs have the least attractive van der Waals interactions, the hydrophobicity associated with alkyl chains of the TOA⁺ bound sulfonates is sufficient to transport short nanotubes to the organic layer already at low stoichiometric ratios. The amount of TOAB required depends on the degree of functionalization of SWNTs. In fact, the method relies on highly water soluble SWNTs with high degrees of functional groups.

4 CONCLUSION

The separation of carbon nanotubes based on length has been demonstrated with a simple and scalable liquid phase extraction. The length of extracted nanotubes is tunable by the degree of sidewall functionalization as well as the amount of phase transfer catalyst present. Also, the separation process is much easier and cheaper than all methods known to date. The SWNT material can be completely recovered from both phases. This is because the

separation technique is entirely based on reversible, non-covalent interactions, such as the attractive van der Waals forces between SWNTs and the ion pairs formed between sidewall sulfonate groups and the quaternary ammonium ion of TOAB. Preliminary evidence suggests that the length distributions can be narrowed down further by performing several controlled extractions in a step-wise procedure.

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