Procedure for Dispersing SWeNT Single Walled Carbon Nanotubes

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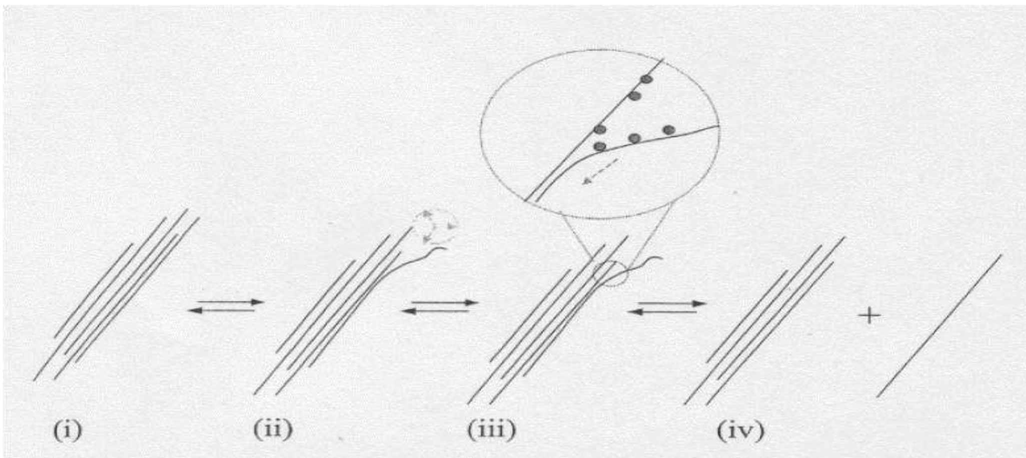
The dispersability and bundle defoliation of SWNTs produced through CoMoCAT process have been extensively investigated by SouthWest NanoTechnologies (SWeNT) and Professor Daniel Resasco at the University of Oklahoma [1]. The procedure employed to disperse single wall carbon nanotubes (SWNT) has a significant impact on its solution concentration, stability and fraction of individual tubes in the final suspension. To get a stable and homogeneous dispersion of SWNT, various technical approaches including covalent and non-covalent stabilization of SWNT can be adopted. Although each of them has some specific advantages, the non-covalent approach has been of particular interest since by this method the surface structure and properties of the tubes are preserved intact.

The non-covalent stabilization by surfactants or polymers approach has been widely used in the preparation of aqueous solution with higher concentration or with higher fractions of individually dispersed SWNTs than those produced by other methods. In a typical dispersion preparation procedure, after the surfactant has been adsorbed on the CNT surface by hydrophobic π-π interactions, ultra-sonication for minutes or hours will typically help surfactant debundling or exfoliation of the carbon nanotubes by Coulombic or hydrophilic interactions thereby overcoming the van der Walls forces between the individual tubes.

Since an individual nanotube covered by surfactant molecule has a density similar to that of water, centrifugation at about 20,000-170,000 g for long periods of time is needed to separate carbonaceous impurities and large SWNT bundles from clean SWNT. Small size bundles may be separated by an optional second sonication step, which can further increase the fraction of individual tubes in the suspension (Figure 1).

Figure 1: Proposed mechanism of nanotube isolation from bundles [2]

(i) Ultrasonic processing “frays” the bundle end
(ii) that then becomes a site for additional surfactant adsorption. This latter process continues in an “unzippering” fashion.
(iii) That terminates with the release of an isolated, surfactant-coated nanotube in solution (iv).



Among the various types of ionic surfactant, Sodium deoxycholate (NaDOCO), Sodium Cholate (NaCO), Sodium Dodecyl Benzene Sulfonate (NaDDBS) and Sodium Dodecyl Sulfate (SDS) are the most commonly used. NaDOCO and NaCO have been found to yield the best resolved spectral features. It has been reported in the literature that NaDOCO is about 25% to 30% more efficiency to exfoliate carbon nanotubes than NaCO [3]. Nonionic surfactants, with high molecular weight, are able to suspend larger quantities of SWNT. That is, surfactants with higher suspendibility do not necessarily results in sharper spectral features. At the same time, for a given SWNT sample, better resolved spectral features indicate a higher fraction of individual tubes in the suspension. Other surfactants are better or comparable to preferred NaDDBS.

In addition to more commonly reported operating conditions, such as type of surfactant and SWNT concentration, sonication and centrifugation times, other parameters such as the total amount of liquid, the shape and size of the vial, the depth of the probe under the solution during sonication, the procedure used to ovoid overheating the sample during sonication and different G-forces using centrifugation can be critical in determining the degree of dispersion. Abundant dispersion results have been published in the literature, however each laboratory has developed their own SWNT dispersion conditions and employed different techniques for characterizing the suspensions which makes it extremely difficult to establish direct comparisons.

During the first hour of sonication, a large degree of debundling (exfoliation) takes place. Between 1 to 2 hours sonication time appeared as the optimum treatment. Too long a sonication time can have the effect of shortening tubes.

Centrifugation greatly enhances the product quality because it removes from suspension several undesirable species (graphite, catalyst residue, amorphous carbon) as well as large bundles that remain in the sediment. Longer centrifugation times and higher g forces are effective at removing smaller nanotube bundles, narrowing the distribution in the final suspension. The greatest effect is observed during the initial hour of centrifugation. However, increasing RCF seems to be more efficient than increasing centrifugation time.

Critical Micelle Concentration (CMC) properties determine the surfactant concentration to be used. It is recommended to use about 2 to 5 times the CMC value of the surfactant employed for preparing a SWNT dispersion. We have found that in addition to NaDDBS surfactant, there are other surfactants that are as good or better than NaDDBS for SWNT suspension. The best performance surfactants as determined by FTNIR spectroscopy are Na-Cholate, Surfynol CT324, Aerosol OS and Dowfax 2A1 (Table 1).

Table 1: Comparison between different surfactant systems used for exfoliating and dispersing carbon nanotube materials [Reference 1].

Surfactant	Type	Surfactant Concentration (g/L)	FTNIR Resonance ratio
Sodium Cholate	anionic	20	0.147
Surfynol CT324	anionic/ non-ionic	15	0.144

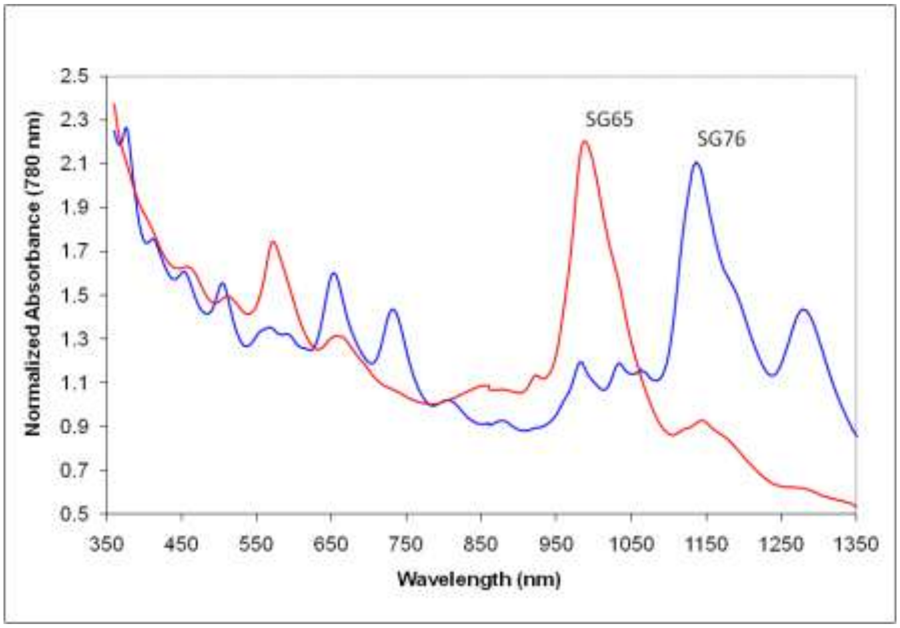
Aerosol OS	anionic	10	0.142
Dowfax 2A1	anionic	10	0.139
NaDDBS	anionic	5	0.132
Triton X-100	nonionic	5	0.112
SDS	anionic	10	0.084

A procedure that optimizes SWNT dispersability and spectra features is the following:

- Disperse 1-2 mg of purified SWNT in 7 milliliters of a surfactant solution containing 2 g/L Sodium Cholate solution in de-ionized water.
- Sonicate for 1 hour with horn sonicator using a microtip. Sonication should be done at a power density of about 1W/ml.
- Centrifuge for 30 minutes with a reltive centrifugal force RCF) of 25,000-32,000 G.
- Dilute the sample in surfactant solution until the value at 780 nm is less than 1 abs in double beam spectrometer equipment having a tungsten filament bulb in a standard 1cm path length optical glass cuvette. When using Sodium Cholate surfactant solution, the absorbance value < 1 can be obtained by diluting 1 ml of SWNT dispersion in 3 ml of de-ionized water.

The absorption spectrum of dispersed CoMoCAT nanotubes is remarkable. In Figure 2 shows a dispersion procedure used for the SWeNT- SG65 and SG76 samples. Clearly, CoMoCAT nanotubes have much more pronounced spectral features at 576 and 993 nm, and at 658 and 1141 nm corresponding to E11 and E22 transitions of the (6,5 and 7,6 tubes), previously identified as the most abundant semiconducting CNT in the samples.

Figure 2: Typical Optical Absorbance Spectrum for SWeNT SG65 and SG76



References.

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