Methods for TEM analysis of NIST's single-walled carbon nanotube Standard Reference Material[1]

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ABSTRACT

The National Institute of Standards and Technology (NIST) will soon release a series of single-walled carbon nanotube (SWCNT) reference materials (RMs) to provide users with a well-characterized material for their applications. The SWCNT reference material will be introduced as a series of three types of material: (1) raw soot characterized for composition, which will be certified as a Standard Reference Material, (2) purified (greater than 90 % SWCNT by weight) bucky paper and (3) dispersed, length-sorted populations characterized by length. The instrumental characterization of NIST's SWCNT reference materials is extensive, and this paper aims to provide researchers with dispersion preparation methods for TEM (transmission electron microscopy) analysis of the SWCNT raw soot. A selection of dispersing solvents, including organic solvents, aqueous surfactants and DNA dispersions, were prepared and examined by TEM. Recommendations for sample preparation of the SWCNT SRM 2483 to yield images similar to those presented here are given. Examples of images of the length-sorted SWCNT reference material are also shown. These results illustrate the importance of optimal dispersion to enable imaging of SWCNT characteristics.

Keywords: Reference material, Single-walled carbon nanotubes, TEM

1. INTRODUCTION

The unique combination of optical, thermal, mechanical, and electrical properties of single-walled carbon nanotubes (SWCNT) has led to substantial development activities in numerous applications such as composites,[(1)] nano-electronics,[(2)] chemical and biosensors,[(3)] and platforms for drug delivery.[(4)] The performance of SWCNT in each of these applications depends on the properties and purity of the SWCNT material. Variability in these materials can occur, depending on the manufacturing process used (e.g., chemical vapor deposition, laser ablation) and the conditions within a manufacturing run (e.g., temperature, catalyst concentration). Post-production purification of materials can also impact the variability by introducing surface functionality to the outer shell of the carbon nanotubes. While the uses for SWCNT samples varies widely from being used as a bulk composite additive to being used as a microelectronic circuit component, most of the applications of SWCNTs require well characterized pure samples.

The National Institute of Standards and Technology (NIST) is developing a series of single-walled carbon nanotube reference materials (RMs) to provide researchers with well characterized materials for their applications. The SWCNT reference materials will be introduced as a series of three types of material: (1) raw soot characterized for composition, (2) purified (> 90 % SWCNT) bucky paper and (3) dispersed, length-sorted populations characterized by length. The first material, bulk raw soot, is expected to be certified for atomic composition by NIST's highest standards, making it a Standard Reference Material (SRM). For the second material, the raw soot will be further processed through dispersing, filtration and washing to yield a bucky paper sample, which will be certified for composition. In the third material, raw soot will be taken through a purification and length-sorting procedure[(5,6)] to yield a series of surfactant-suspended, length sorted tubes classified as "long," "medium," and "short." General measurements made on these materials include transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and Raman, ultraviolet-visible-near infrared and fluorescence spectroscopy.

As mentioned above, one aspect of the SWCNT SRM characterization is the TEM imaging of the raw soot and length sorted materials. TEM is used in the analysis of SWCNT as a qualitative technique which provides a measure of purity

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Instrumentation, Metrology, and Standards for Nanomanufacturing III, edited by Michael T. Postek, John A. Allgair,
Proc. of SPIE Vol. 7405, 74050A · © 2009 SPIE · CCC code: 0277-786X/09/$18 · doi: 10.1117/12.825406

for a given sample.[7] TEM has a much higher resolution than that of SEM, that allows for the characterization of nanotube type (i.e., multi-walled, single-walled) and the degree of bundling in the structures. Electron-diffraction information from isolated SWCNT samples using the TEM can also be used to characterize the chirality of the individual nanotubes.[8] To prepare a sample for TEM, SWCNT raw soot is suspended in a solvent, in which the concentration of a solution is determined by its color (e.g., a small tweezer pinch of nanotubes in solvent yields a light gray solution). The solution is deposited onto a carbon-coated copper TEM grid by pipette and allowed to dry by air.

This paper provides examples of TEM images from a variety of sample preparations of the SWCNT SRM 2483 raw soot. A selection of dispersing solvents, including organic solvents, aqueous surfactants, and DNA dispersions, were examined. Recommendations for sample preparation of the SWCNT SRM 2483 to yield similar images are given. Examples of TEM images of the length-sorted SWCNT reference material are also shown.

2. CARBON NANOTUBE SAMPLE PREPARATION

2.1 Carbon Nanotubes

All carbon nanotubes used for this study were samples taken from NIST's single-walled carbon nanotube raw soot Standard Reference Material SRM 2483. This particular Standard Reference Material was grown through the cobalt-molybdenum-catalyst (CoMoCat) process and then further refined to meet NIST's standards. From the raw soot material, a length-sorted material was produced by dispersing the nanotubes in a sodium deoxycholate surfactant solution. Once suspended, the carbon nanotubes were subjected to a series of ultracentrifugation steps to yield a length-separated product. This product was characterized for length by atomic force microscopy (AFM) and dynamic light scattering.

2.2 Organic Solvent Dispersions

To prepare chloroform samples, SWCNT SRM 2483 was added to chloroform in a 2 mL glass vial. The solution was sonicated in a bath sonicator for 15 minutes to suspend CNTs in solution. The solution was used immediately after sonication to minimize settling of the material. It should be noted that the SWCNT Standard Reference Material is difficult to disperse in toluene. SWCNT soot was added to a 2 mL glass vial and 1 mL of toluene is added. The solution was sonicated in a bath sonicator for 15 minutes. When sonicating, the carbon nanotubes appear to be well dispersed within the toluene, but upon removing them from the sonicator, SWCNT will settle out of solution. The vial was shaken vigorously after sonicating and prior to depositing the sample on the TEM grid.

2.3 Surfactant Dispersions

A 1 % sodium dodecyl sulfate (SDS) solution was prepared in ultrapure water. Carbon nanotubes and SDS were added to a 2 mL vial and sonicated in a bath sonicator for 10 minutes to yield a light gray solution of carbon nanotubes. This solution was diluted to 0.25 % SDS with more ultrapure water prior to depositing the sample on the TEM grid. A 0.25 % solution of sodium deoxycholate (DOC) was also prepared in ultrapure water. This solution was added to SWCNT in a 2 mL vial and sonicated to yield a light grey solution for 10 minutes in a bath sonicator. After the sample was well dispersed, it was diluted to a concentration of 0.625 % DOC and deposited on the sample grid. A 1 mg/mL solution of L-α-phosphatidylcholine (PC) and SWCNT was sonicated for 45 minutes until the lipid solution was no longer cloudy. The light grey dispersion was deposited on the TEM grids via micropipette.

2.4 DNA Dispersions

Single stranded DNA (ssDNA) with the sequence $(GT)_{15}$ was used for dispersions. SWCNT were added to a suspension of 1 mg/mL ssDNA in ultrapure water and sonicated 10 minutes to yield a light grey solution of dispersed nanotubes.

2.5 Length Sorted Dispersions

Length sorted dispersions were prepared as presented in the literature.[6] Briefly, SWCNT raw soot was dispersed in a 2 % w/w sodium deoxycholate solution and separated by use of a transient ultracentrifugation approach described in detail elsewhere.[6] In brief, a layer of dispersed nanotubes was density modified and placed underneath a column of dense liquid such that the dispersed SWCNTs travel up the liquid in response to the applied centrifugal acceleration. Due to differences in the scaling with length of the buoyancy and frictional forces, longer nanotubes traveled faster up the liquid column under transient conditions; eventually after enough separation was obtained the liquid column is fractionated. Separated fractions were then dialyzed to remove the density modifying agent by use of a forced dialysis cell.

3. TEM EXPERIMENTAL CONDITIONS

3.1 Sample preparation for the TEM

All the samples were prepared for analysis in the TEM by depositing small drops of the various SWCNT dispersions onto a thin holey carbon TEM grid by use of a micropipette. The drop was allowed to dry completely overnight in most cases. The grid was then mounted in a single-tilt sample holder for TEM observation.

3.2 TEM observation

All images presented here were taken at 200 keV under low-dose operating conditions in the TEM. Low dose means that the electron flux onto the samples was restricted with a small condenser aperture (typically 40 micrometers in diameter) and underfocusing the illumination to the minimum that would allow an image to be captured with a two second exposure. All images were captured by use of a one megapixel CCD camera located below the viewing chamber. Most were captured at a TEM optical magnification of 300 kX with the objective lens at or near the Scherzer defocus condition, which in our microscope is -76 nm.

4. RESULTS AND DISCUSSION

4.1 Chloroform Solutions

Dispersions of SWCNT raw soot in chloroform appear to be slightly clumped, but remain suspended after sonicating for approximately 10 minutes. Figure 1 shows a typical image obtained from a chloroform dispersion. Throughout the image, ropes of SWCNT are seen, as well as a few isolated tubes approximately 0.8 nm in diameter. Ropes of SWCNT are seen as the thicker structures with multiple lines running through the center. Figure 2 shows an end-on view of a rope of SWCNT, verifying that the ropes consist of multiple single-walled tubes. In this image, the ends of the individual tubes are seen and range from 0.7 nm to 0.8 nm in diameter. From a chloroform dispersion, we observed what appears to be a graphene sheet (Figure 3). This sheet is approximately 2.5 nm in width, which would be the expected size if a 0.8 nm single-walled carbon nanotube "unzipped" to a flat graphene sheet.[9,10]

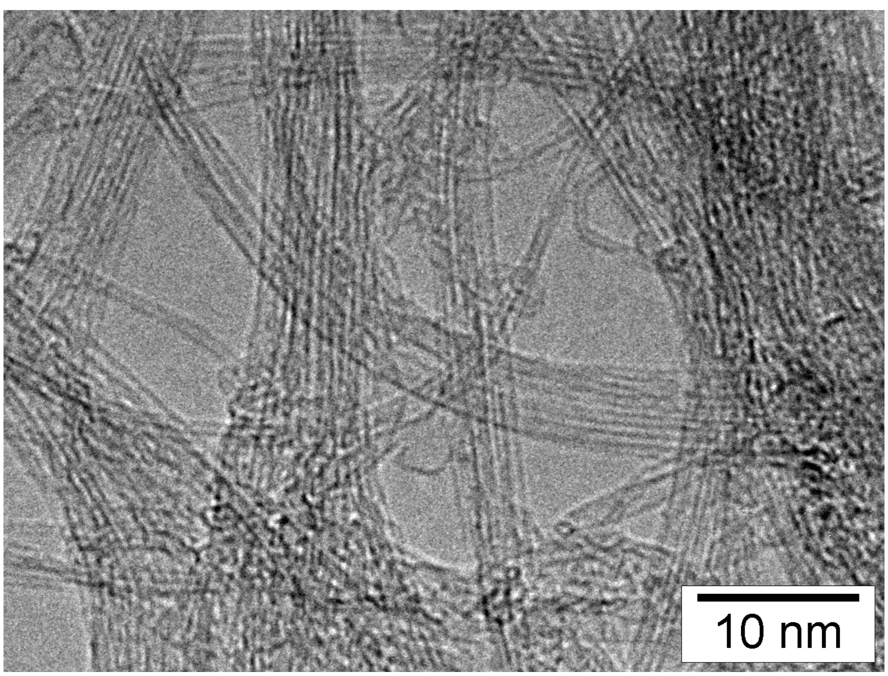

Figure 1: SWCNT deposited from chloroform. A representative area shows ropes and single nanotubes dispersed with one another. Single nanotubes are on the order of 0.7 to 0.8 nm in diameter.

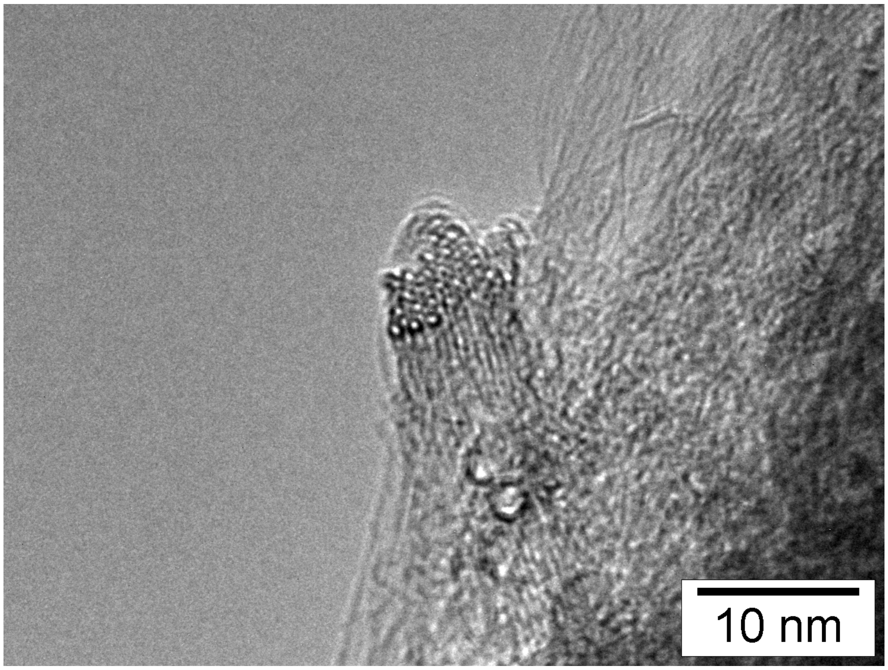

Figure 2: End on view of a rope of SWCNTs from a SWCNT sample deposited from chloroform. The little circles seen in the center of the image are individual CNT ends of tubes projecting out from a rope structure.

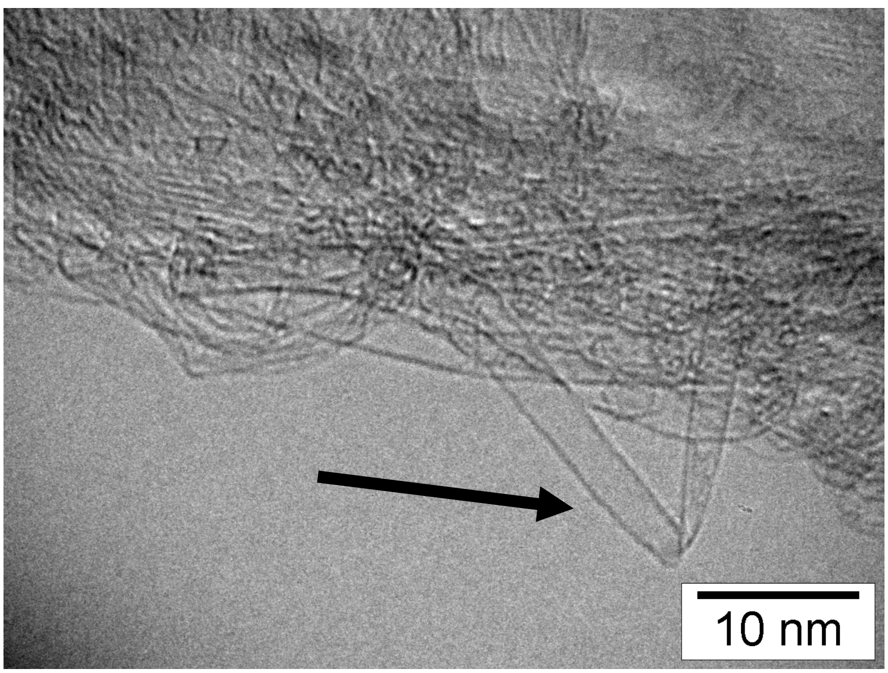

Figure 3: SWCNT sample deposited from chloroform. The arrow denotes a graphene sheet, approximately 2.5 nm in length, is seen protruding from a CNT bundle.

4.2 Toluene Dispersions

Dispersions of SWCNT in toluene yield a clumpy dispersion in which the nanotubes do not appear to be well dispersed in the solvent. When they are deposited on the TEM grid, it is difficult to find sections of isolated carbon nanotubes or isolated ropes of carbon nanotubes. Figure 4 shows a typical image obtained from a toluene dispersion. This image was enhanced by use of Fourier Transform processing to highlight the SWCNT ropes that were hidden in background noise.

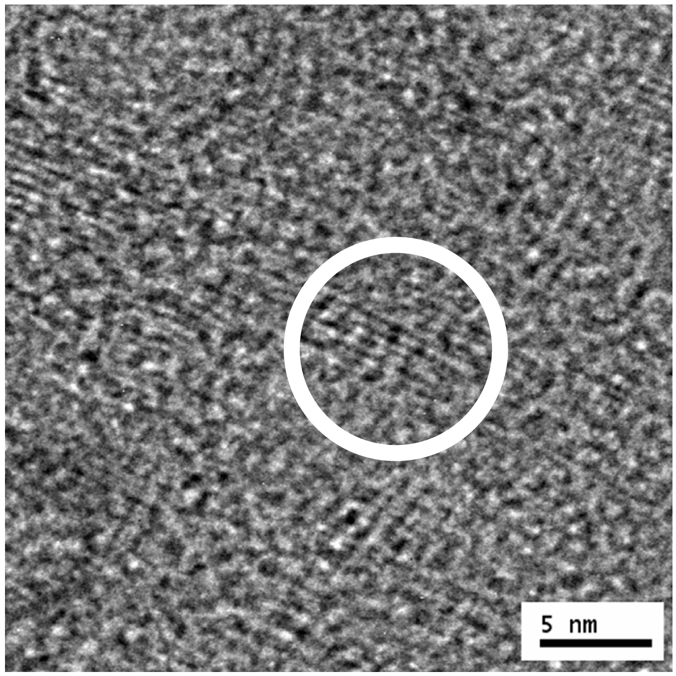

Figure 4: SWCNT deposited from a toluene dispersion. The white circle denotes a region where SWCNT ropes can be seen.

4.3 DOC Dispersions

Sodium deoxycholate (DOC) has been used as the preferred dispersing agent for length-sorted material because it yields a well dispersed material.(6) Figure 5 is a low magnification image of a sample deposited from DOC where the carbon nanotubes span the two areas of dried surfactant. The nanotubes in Figure 5 span approximately 500 nm in length. Figure 6 is a high-magnification image of a small rope of SWCNT deposited in DOC. Figure 7 shows two SWCNT fused together on the left of the image, then separated to form two separate SWCNT tubes. The surface of the SWCNTs in Figures 6 and 7 appear to be coated with another material when compared to the surfaces of the nanotubes in Figure 1. The coating on the nanotubes in Figures 6 and 7 is attributed to the deoxycholate remaining on the surface of the CNT as the sample dries.

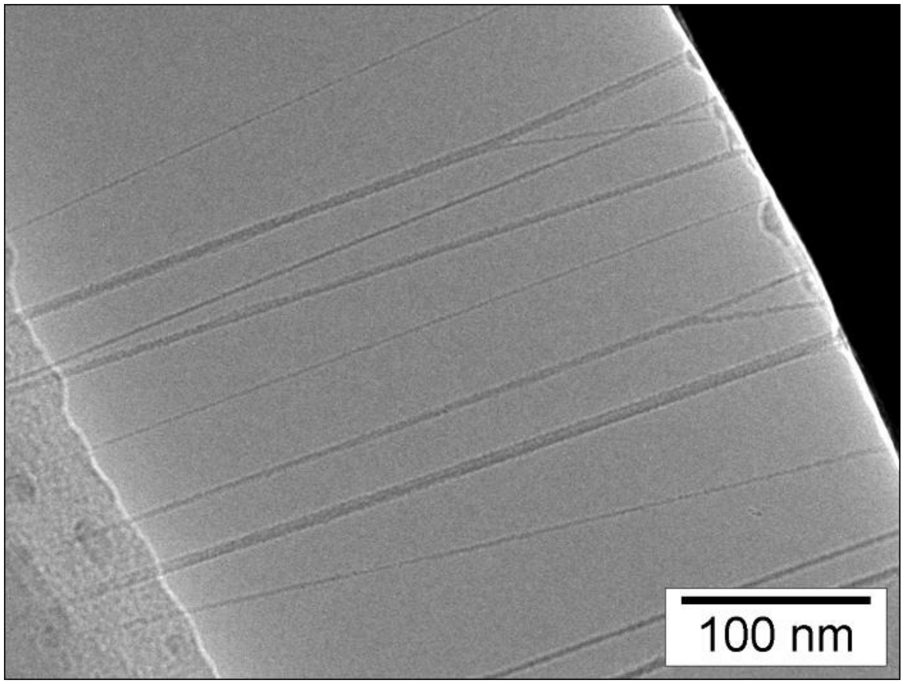

Figure 5: Low magnification view of a sodium deoxycholate deposited sample. The length of tubes shown is greater than 500 nm.

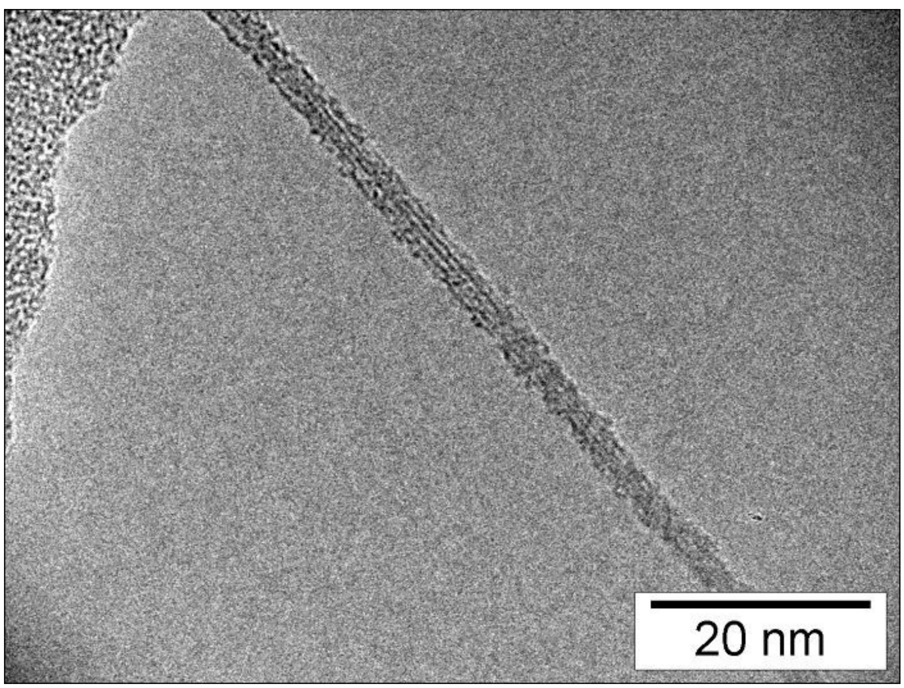

Figure 6: Image of a rope after deposition from a sodium deoxycholate sample.

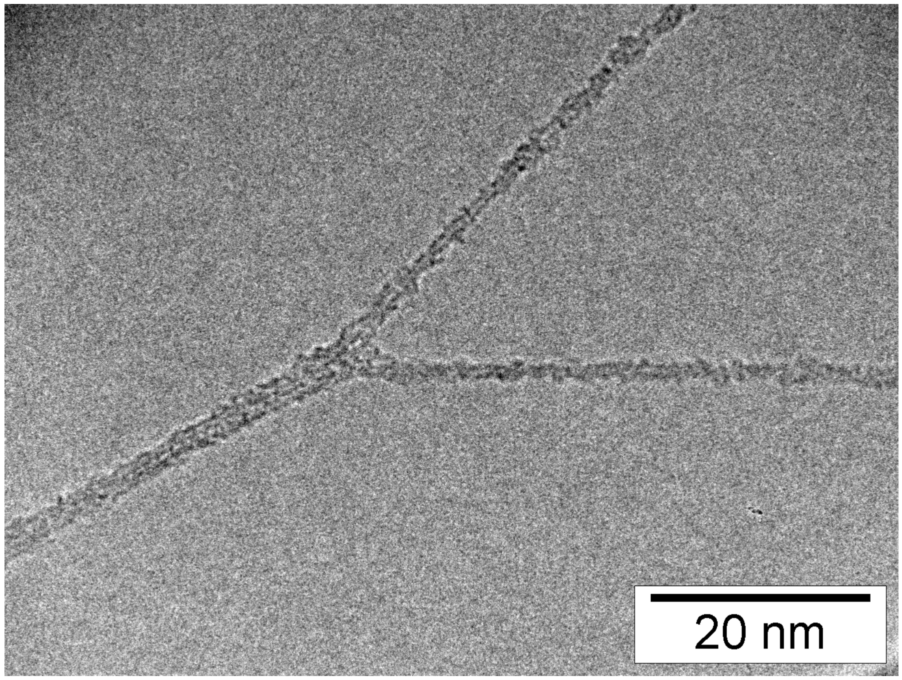

Figure 7: Two single-walled carbon nanotubes branch off from one another in a sodium deoxycholate sample.

4.4 Sodium Dodecyl Sulfate Dispersions

SWCNT were dispersed in sodium dodecyl sulfate (SDS) and dried on sample grids. The samples were beam sensitive, and under minimum exposure to the electron beam the surfactant flowed over the SWCNTs, making it virtually impossible to capture a satisfactory TEM image with a two-second exposure period. This method of dispersion is not recommended for preparing specimens that will be exposed to electron beams.

4.5 Phospholipid Dispersions

Figure 8 shows an image obtained when SWCNT are suspended in a lipid solution. As seen with the toluene, the lipid does not isolate the carbon nanotubes from the one another, or from the bulk aggregates that form. It appears that lipid vesicles associate with the surface of the carbon nanotube bundles, but will not help to isolate individual tubes.

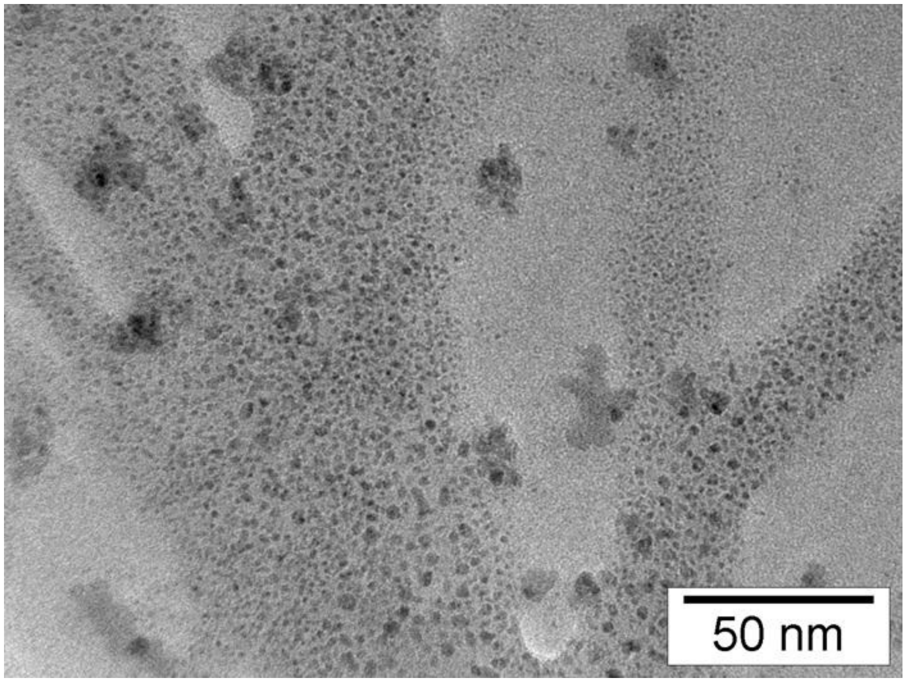

Figure 8: Low magnification of carbon nanotube ropes, with associated lipid vesicles.

4.6 DNA Dispersions

Figure 9 shows a low magnification view of a sample of single-walled carbon nanotubes suspended in a DNA solution. The ropes of single-walled nanotubes are evident, with some isolated tubes seen at the ends. The length of ropes are in the range of 300 nm long.

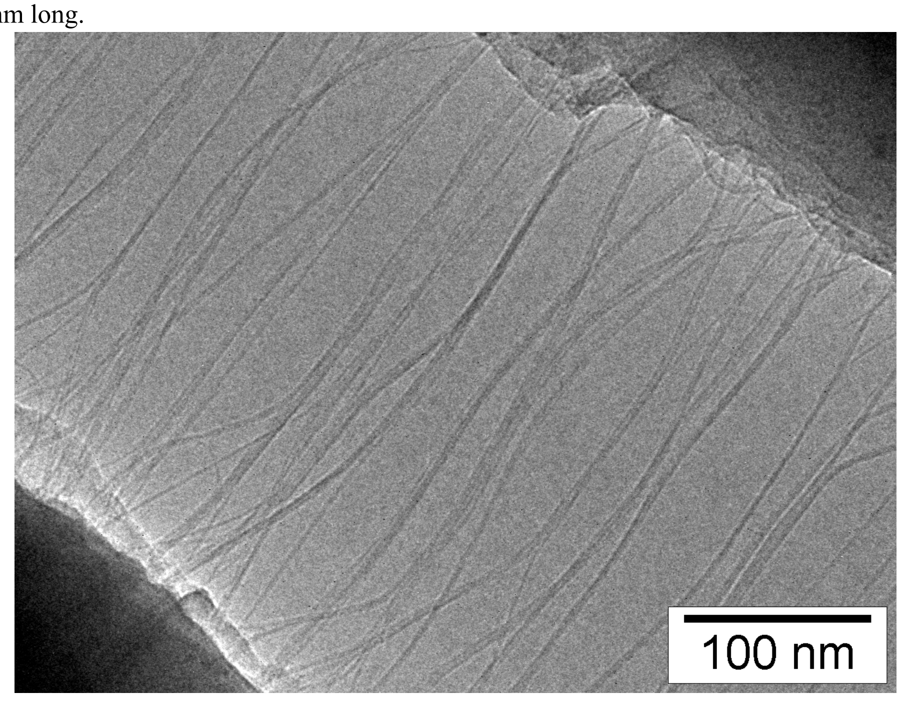

Figure 9: Low magnification view of DNA-isolated SWCNT. Ropes and some single tubes are present. Length of the nanotubes is approximately 300 nm.

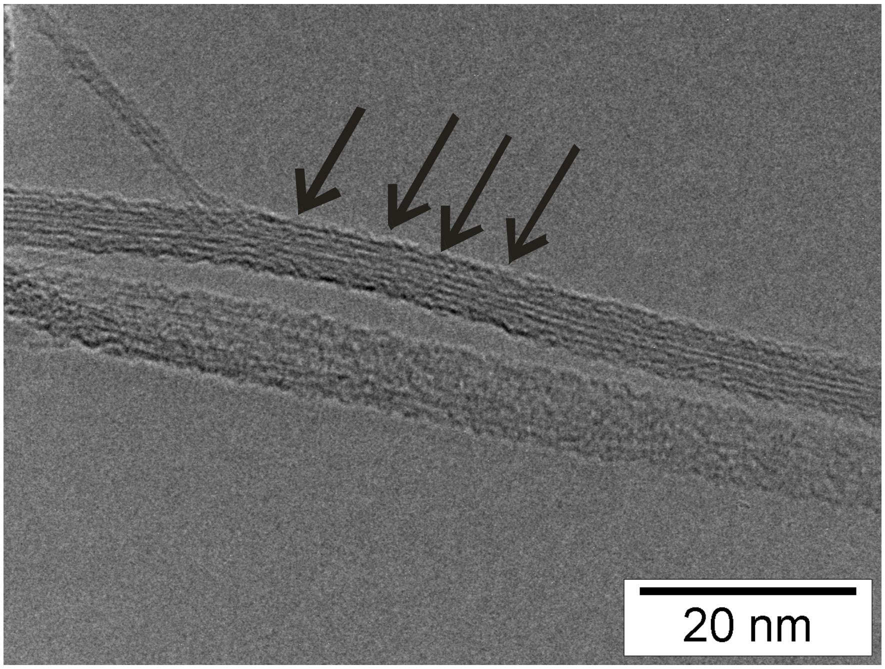

Figure 10: High magnification image of DNA-SWCNT. The arrows point out DNA draping the SWCNT rope.

Figure 10 is a high magnification view of the DNA-SWCNT sample. Arrows point to regions where a material is deposited orthogonal to the surface of the SWCNT ropes. We attribute this to the DNA wrapped around the CNT rope, as single-stranded DNA is expected to take on this configuration from previous DNA/CNT studies.[11,12]

4.7 Length-Sorted Materials

The length-sorted materials for the SWCNT material (Figure 11) show characteristics similar to those of the sodium deoxycholate solutions seen in Figures 6 and 7. The length-sorted materials also consist of ropes of SWCNT, with some individual tubes isolated from the ropes. The coating on the SWCNT attributed to the DOC surfactant (see Figures 6 and 7) is still apparent on the tube surface for the length-sorted fractions (Figure 11). This TEM work was not used to measure length of the SWCNT in this instance, but aimed to examine the quality of the nanotube surface (e.g., coated with surfactant) and the state of the material (e.g., bundled ropes of single-walled nanotubes).

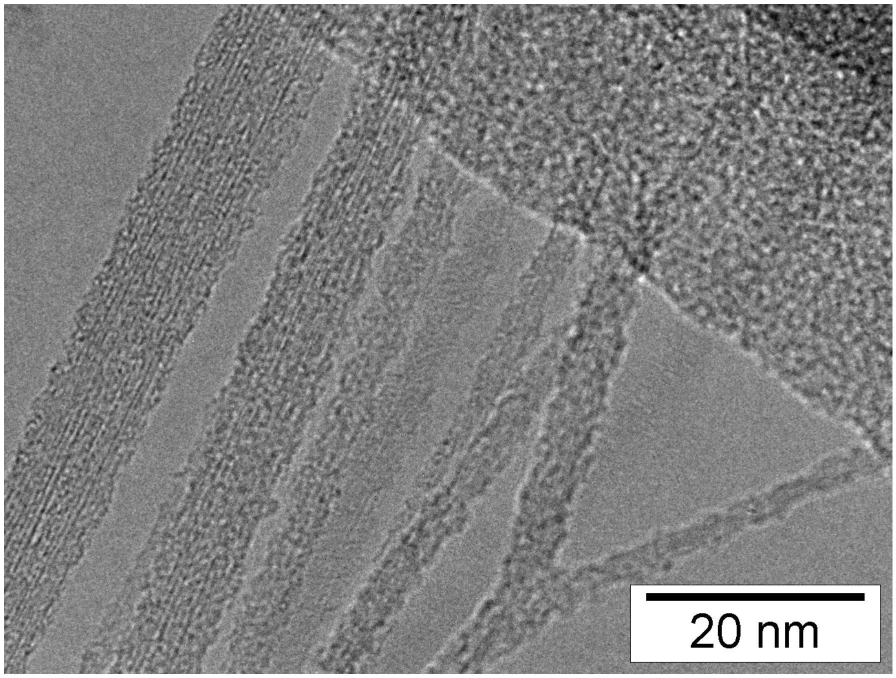

Figure 11: Ropes and SWCNT in a length-sorted fraction deposited from sodium deoxycholate solution.

5. CONCLUSIONS AND RECOMMENDATIONS

We have presented a selection of dispersing agents, including organic, aqueous, and DNA dispersions, for preparing TEM samples of the NIST SWCNT Standard Reference Material. This material should be representative of a clean SWCNT sample obtained by the cobalt-molybdenum catalyst process that has undergone some post-production purification by the manufacturer. When organic solvents are used, chloroform yields a clean sample with some isolated tubes and clean ropes consisting of SWCNT. This preparation method gives the most representative look at the SWCNT material and is the preferred method for TEM studies of the reference material. For surfactant preparations, sodium deoxycholate will yield well-separated nanotubes, although they remain coated in surfactant after the sample preparation is complete. DNA suspensions allow the samples to be imaged as ropes, but have evidence of associated DNA along the length of the tube. Toluene and L-α-phosphatidylcholine (PC) provide a means to deposit the SWCNT on the TEM grid, but do not provide separation of the ropes. In the case of the PC, lipid vesicles tend to aggregate on the SWCNT surface, which could prevent further studies of these materials. Other solvents used, such as sodium dodecyl sulfate, prevent the imaging of the SWCNT sample altogether. These results illustrate the importance of dispersion preparation to enable optimal imaging of SWCNT characteristics.

6. REFERENCES

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