National Institute of Standards & Technology

Report of Investigation

Reference Material 8281

Single-Wall Carbon Nanotubes
(Dispersed, Three Length-Resolved Populations)

This Reference Material (RM) is intended to provide a common set of single-wall carbon nanotube (SWCNT) dispersions of varying aspect ratios and purity for measurement comparisons. A unit of RM 8281 consists of four ampoules, three of the ampoules contain a single dispersion of average length SWCNTs and are labeled Long, Medium, and Short according to the population present in surfactant solution and the fourth ampoule labeled Blank which contains only surfactant solution. The surfactant is sodium deoxycholate and is present at a concentration of approximately 10 g/L in each of the four ampoules. Each ampoule contains approximately 2.5 mL of solution. The surfactant solution is subjected to the same processing as the nanotube dispersions and is included as a blank; no reference values are provided for this sample.

Reference Values: Reference values are provided in Table 1, for the ultraviolet-visible (UV-Vis) absorbance at specific wavelengths, and in Table 2 and 3 for the Raman G/D and G′/G ratios measured at 514.5 nm excitation for each nanotube population, respectively. Reference values are noncertified values that are the best estimate of the true value; however, the values do not meet the NIST criteria for certification [1].

Additional User Information: Spectra, images, and micrographs are provided in Figure 1 through 6. This additional information is considered to be of interest to the RM user.

Expiration of Value Assignment: RM 8281 is valid, within the measurement uncertainty specified, until **31 January 2023**, provided the RM is handled and stored in accordance with instructions given in this report (see "Instructions for Use"). This report is nullified if the RM is damaged, contaminated, or otherwise modified.

Maintenance of RM: NIST will monitor this RM over the period of its value assignment. If substantive changes occur that affect the value assignment before the expiration of this report, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Overall direction and coordination of the analyses was performed by J.A. Fagan of the NIST Materials Science and Engineering Division.

Technical measurements were conducted by J.A. Fagan and M. Zheng of the NIST Materials Science and Engineering Division, A.R. Hight Walker of the NIST Engineering Physics Division, R. Geiss formerly of NIST and E. Mansfield of the NIST Applied Chemicals and Materials Division.

Statistical consultation for this RM was provided by S.D. Leigh and D.V. Samarov of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this RM were coordinated through the NIST Office of Reference Materials.

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Certificate Revision History on Last Page

Steven J. Choquette, Director
Office of Reference Materials

NOTICE AND WARNING TO USERS

This material should be handled as recommended by the National Institute for Occupational Safety and Health (NIOSH). According to NIOSH, currently there are no studies reported in the literature of adverse health effects in workers producing or using carbon nanotubes or carbon nanofibers. The concern about worker exposure to these materials arises from results of animal studies. Several studies in rodents have shown an equal or greater potency of carbon nanotubes compared to other inhaled particles known to be hazardous to exposed workers in causing adverse lung effects including pulmonary inflammation and fibrosis [2]. Currently, the adverse effects of skin penetration or ingestion of nanoparticles have not been fully studied. For further information, refer to the Safety Data Sheet (SDS).

INSTRUCTIONS FOR USE

Individual ampoules of the SWCNT dispersion can be opened by holding the ampoule and applying pressure to the head of the ampoules above the score line. Opened ampoules should no longer be considered sterile, and the contents should be transferred to a clean, sealable, container for use subsequent to immediate withdrawal. Opened samples can be stored under refrigeration to slow bacterial growth; however, freezing conditions should be avoided.

The dispersant, sodium deoxycholate, is not compatible for direct use in many biological studies. The surfactant solution containing the nanotubes can be exchanged using filtration or dialysis using membranes rated for between 10 kDa MW and 100 kDa MW if needed for other measurements; a sufficient amount of dispersant must be present with the nanotubes at all times to maintain dispersion. However, the reference values are not valid after any exchange of dispersant or additional processing.

Stability: This material is considered stable when stored at room temperature and protected from exposure to strong ultraviolet radiation. However, its stability has not been rigorously assessed.

PREPARATION

The nanotube length populations were produced through a centrifugation-based length separation method [3]. After the separation, multiple length fractions were combined to form the three populations that comprise the RM. The dispersing medium was exchanged with fresh surfactant solution for each the three nanotube populations. The samples and Blank were dispensed into pre-cleaned glass ampules under an argon gas. The ampules were then irradiated to sterilize the contents. Additional details on sample preparation, methods, and sterilization process are provided in references 3 and 4.

REFERENCE VALUES

Reference values are assigned for the homogeneity of the finalized ampoule sets based on multiple measurements. Reference values are given for two ratios of peak features measurable using Raman scattering, and for the ratio of the optical absorbance measured at two different wavelengths in the ultraviolet and visible ranges of light. The uncertainty in the reference values, calculated according to the method described in the ISO/JCGM Guide [5], is expressed as an expanded uncertainty, U. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent the standard deviation. The coverage factor (k) is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and approximately 95 % confidence for SWCNT sample.

UV-Vis Absorbance Spectroscopy: The ratio of the absorbance values at two wavelengths, 571 nm and 785 nm, were measured using an UV-Vis-near infrared (UV-Vis-NIR) spectrophotometer in transmission mode using a one millimeter quartz cuvette. The addition of an integrating sphere detector was not used to complete these measurements and is not required for use with this material. The absorbance of the surfactant solution and cuvette were measured using the Blank and subtracted from the SWCNT dispersion absorbance before the ratio was calculated.

Raman Scattering Ratio: The Raman scattering measurements were done using a 514.5 nm Ar^+ laser with a spot size roughly 100 μm in diameter. At this excitation wavelength, the ratio of two distinct Raman scattering features of graphitic carbon, the G-band (located at approximately 1587 cm^{-1}) and the D-band (located at approximately 1320 cm^{-1}), is considered indicative of the fraction of defects in the graphitic carbon content, including nanotubes. The ratio of the G-band and an additional peak feature, the G′-band (located at approximately 2625 cm^{-1}), is indicative of the SWCNT carbon purity [3].

The homogeneity of RM 8281 was assessed by using both the G/D ratio and G′/G ratio. Completely homogenous nanotube containing material is expected to exhibit a consistent G/D ratio and G′/G ratio value for the Raman features at a given excitation wavelength. An inhomogeneous sample will exhibit varying ratios of nanotube to graphitic and amorphous carbon. Multiple subsamples were tested to assess homogeneity. Heterogeneity occurs over a length scale smaller than the measured volume of 100 μm^3. Tabulated values for the G/D ratio and G′/G ratio metrics appear in Tables 2 and 3, respectively.

Table 1. Reference UV-Vis Absorbance Ratios[(a)] Values

Population Length	A(571 nm)/A(785 nm)	Coverage Factor, *k*
Long	3.047 ± 0.022	2.78
Medium	2.140 ± 0.002	2.18
Short	1.535 ± 0.003	3.18

[(a)] Ratio is calculated after the subtraction of the absorbance of the Blank sample at the same measurement conditions.

Table 2. Reference G/D Raman Ratio Values at 514.5 nm

Population Length	G/D Ratio	Coverage Factor, *k*
Long	164.2 ± 20.8	2.07
Medium	104.2 ± 9.0	2.09
Short	55.7 ± 5.9	2.07

Table 3. Reference G′/G Raman Ratio Values at 514.5 nm

Population Length	G′/G Ratio	Coverage Factor, *k*
Long	1.100 ± 0.064	3.18
Medium	0.975 ± 0.024	2.09
Short	0.820 ± 0.031	2.07

ADDITIONAL USER INFORMATION

UV-Vis-NIR Absorbance Spectroscopy: The wavelength dependent UV-Vis-NIR absorbance spectra are provided in Figure 1. The absorbance spectrum was recorded in transmission mode through a 1 mm pathlength cuvette. The addition of an integrating sphere detector was not used to complete these measurements and is not required for use with this material. The absorbance spectrum of the Blank sample was measured independently and subtracted from the raw spectra recorded of the nanotube dispersions during data analysis.

The absorbance spectra of each SWCNT population displays multiple peak features identifiable to individual nanotube species. These species are often identified by their chiral vector indices (n,m), which describes the orientation of the tubular graphic structure. Readily observed species include the semiconducting (6,5), (7,5), (7,6), (8,3), (8,4), and (9,1) species; the metallic (6,6) and (7,4) nanotubes are also clearly observed. Other nanotube species may be present in the samples but are not readily identified from the absorbance measurement due to their low concentration levels, or due to overlapping absorbance features.

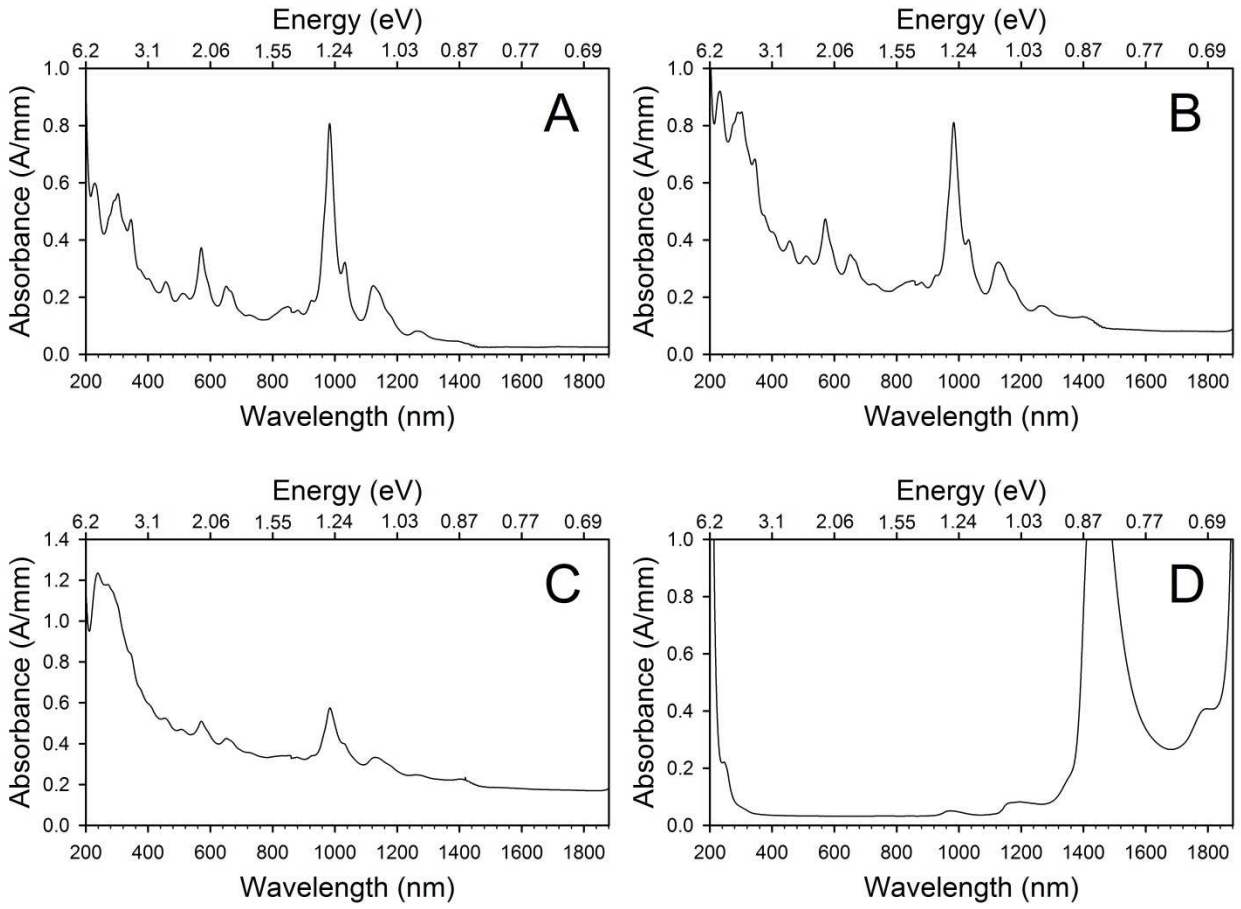


Figure 1. UV-Vis-NIR absorbance spectra for each population of RM 8281 in 10 g/L sodium deoxycholate solution measured through a 1 mm quartz cuvette. The panels are: A (Long population); B (Medium population); C (Short population); and D (Blank reference surfactant solution). The Blank spectra (panel D) is shown as measured and was subtracted from each of the spectra for the SWCNT populations displayed in this figure. Dominant peak features in each of the SWCNT populations are due to the semiconducting nanotubes (6,5) (343 nm, 568 nm, 982 nm). The large absorbance features at wavelengths greater than 900 nm in Blank spectrum (D) are due to the water content in the sample.

Raman Spectroscopy: Raman scattering data spectra for each length population with 514.5 nm excitation are presented in Figure 2. Additional Raman scattering spectra for excitation at 632.8 nm are given in reference 3.

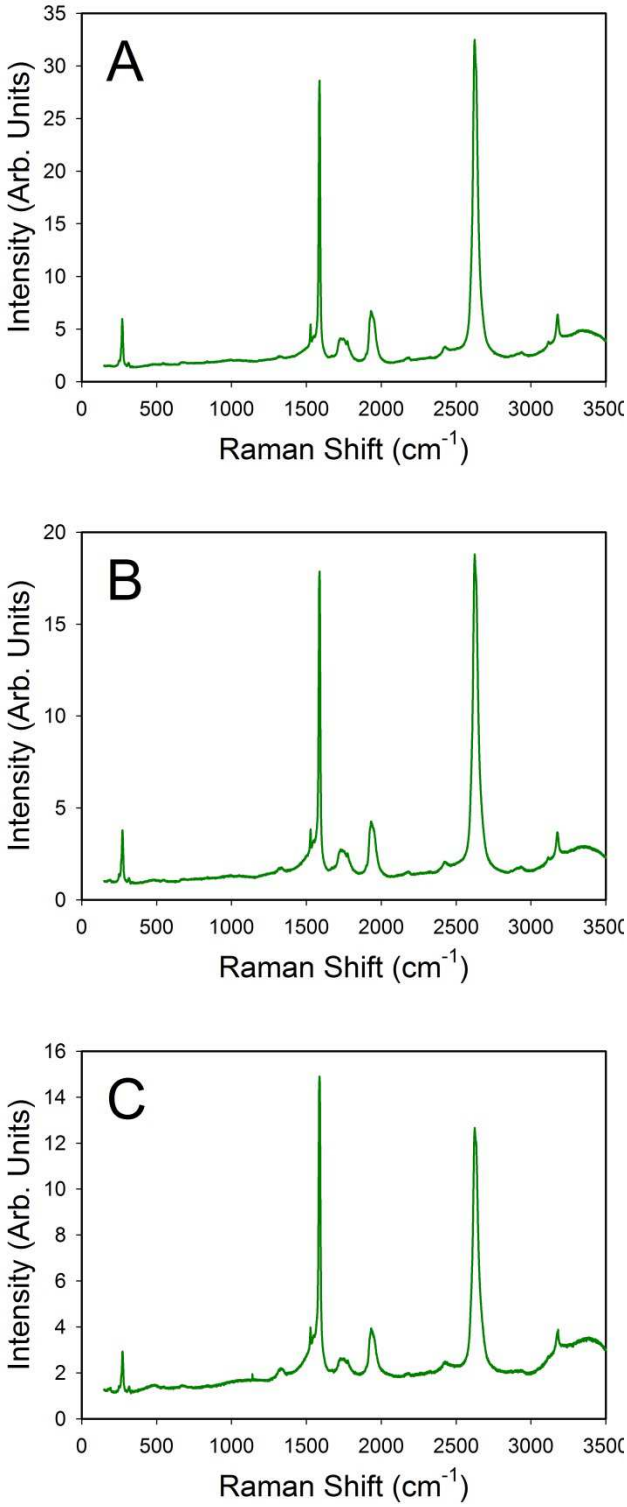
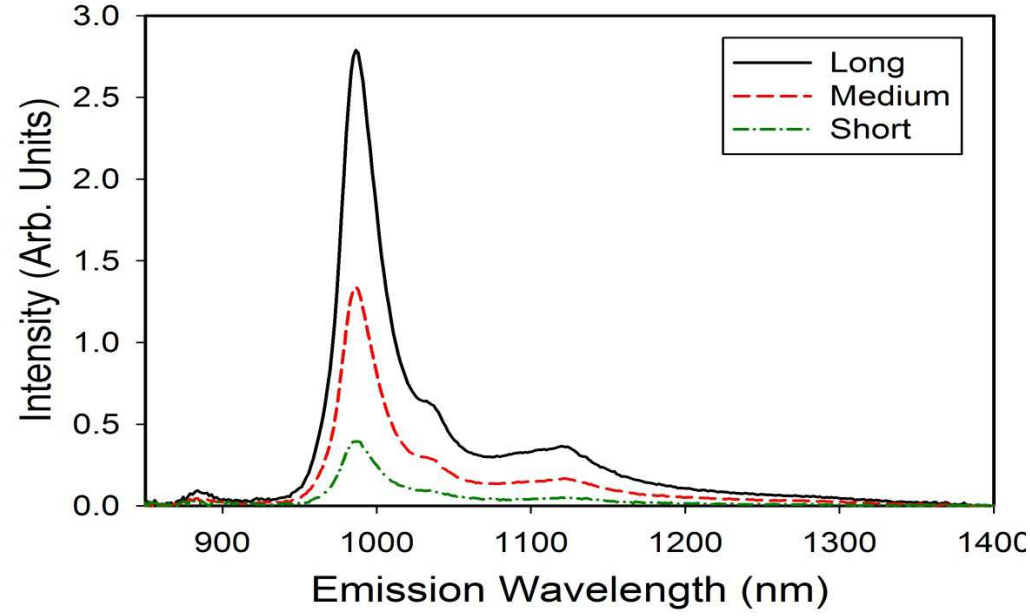
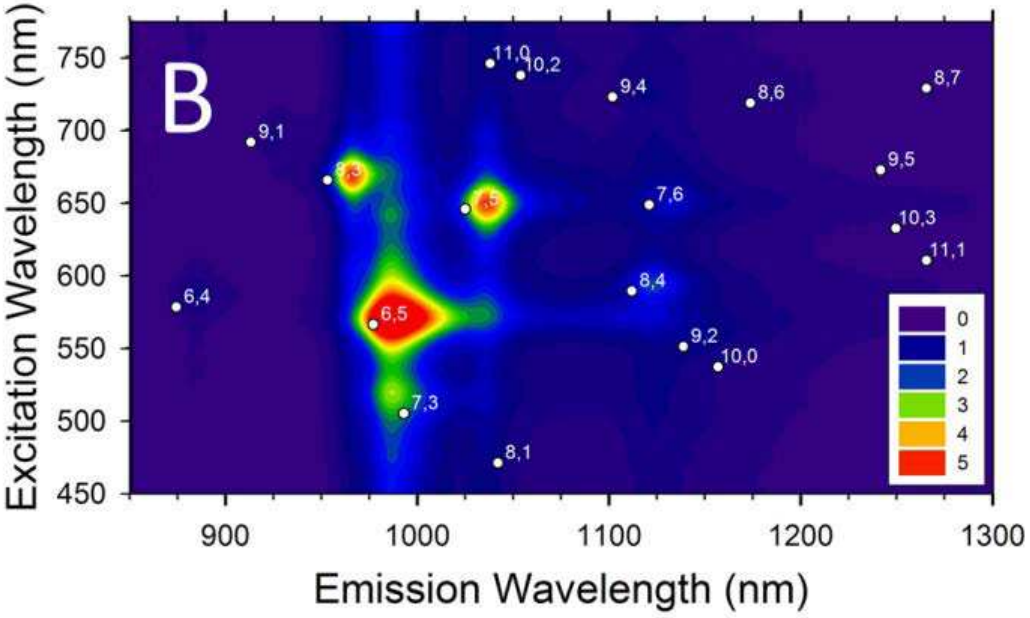


Figure 2. Raman scattering spectra for RM 8281 length populations with excitation at 514.5 nm. Peak features corresponding to different SWCNT Raman features, including several RBM modes, D-band, G-band, M and iTOLA, and G′ (2D)-bands, are visible in the SWCNT samples. The panels are: A (Long population); B (Medium population); and C (Short population). The D-band (≈1320 cm^{-1}) increases in size relative to the G-band (≈1587 cm^{-1}) comparing from the Long to the Short population spectra. The relative size of the G′-band (≈2625 cm^{-1}) to the G-band changes monotonically across the three samples as well.

Near Infrared Fluorescence: Excitation – emission contour plot intensities and a single-wavelength excitation line - emission line plot were measured for each of the nanotube populations and shown in Figure 3. Prior to analysis, samples were diluted to an absorbance of 0.12 cm^{-1} at 775 nm with the sodium deoxycholate solution from the Blank sample. The reported spectra are corrected for the emission train wavelength-dependent sensitivity and the wavelength-dependent excitation power, but not for the inner-filter effects of absorbance or Rayleigh scattering for the solution in the cuvette. Observation of specific peak features is an indication that specific semiconducting nanotubes are present in the sample, although the direct correlation between intensity and concentration is not fully established. The technique is not sensitive to metallic nanotubes or heavily chemically functionalized nanotubes.

In Figure 3, the emission intensity has been corrected for the excitation intensity and emission side wavelength-dependent sensitivity. Dominant peak features are emission from the (6,5), (7,5), and (8,3) chiralities. The (6,4), (7,6), (8,4), (9,1), (9,2), (9,4), (10,2) and (8,6) are also present in sufficient quantity to be detected, particularly in the Long population. Other chiralities are likely present, but in quantities too small to display fluorescence on this intensity scale (the intensity is normalized by the maximum of the (6,5) emission peak divided by 10). As a reference, empirical excitation – emission peak locations for different SWCNT structures as assigned in reference 6 are noted by white dots. The NIR fluorescence measurement technique is only sensitive to semiconducting nanotube chiralities.





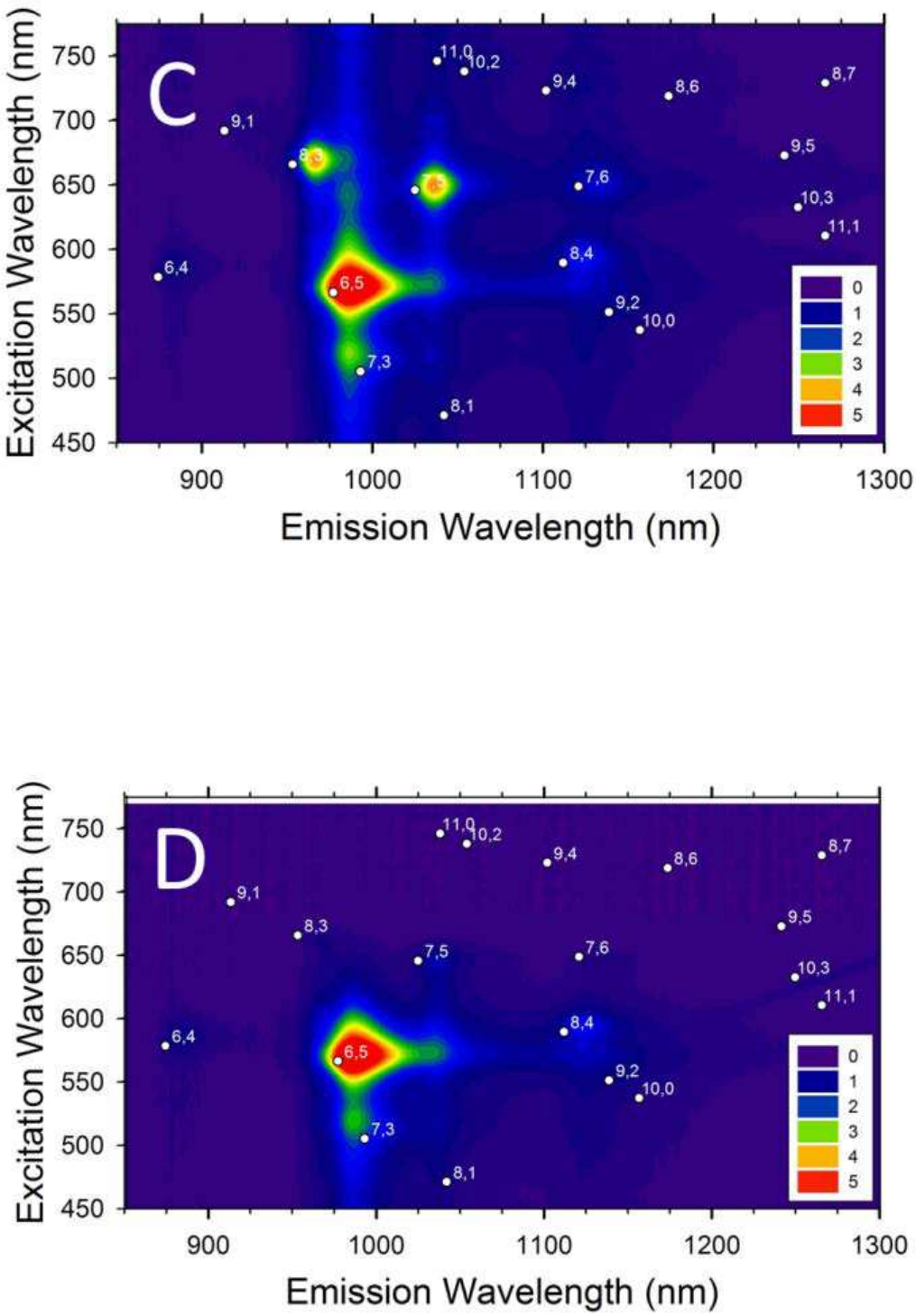


Figure 3. Information NIR fluorescence spectra for RM 8281 samples in 10 g/L sodium deoxycholate solution. The panels are: the fluorescence spectra of each sample under 570 nm excitation for A and the excitation – emission wavelength contour plot of the emission intensity for B (Long population), C (Medium population), and D (Short population).

Atomic Force Microscopy (AFM): Images of the contour lengths of RM 8281 populations were acquired using AFM and are shown in Figure 4. Prior to measurement, aliquots of each of the SWCNT length populations were washed with fresh 10 g/L sodium deoxycholate solution using an ultrafiltration membrane (30 000 Da molecular weight cutoff) in a stirred ultrafiltration cell to achieve a volumetric dilution of the irradiated surfactant solution of greater than 100 fold.

This step was necessary, because an artifact of the irradiation used for sterilization of the SWCNT populations is the formation of small particles in the surfactant solution that prevent the deposition of the SWCNTs on a surface for AFM measurement. In this surfactant exchange, the small particles pass through the membrane and are removed, but the nanotubes of all lengths are too large to pass through the pores and are retained for measurement. Figure 4 contains images of each of the populations.

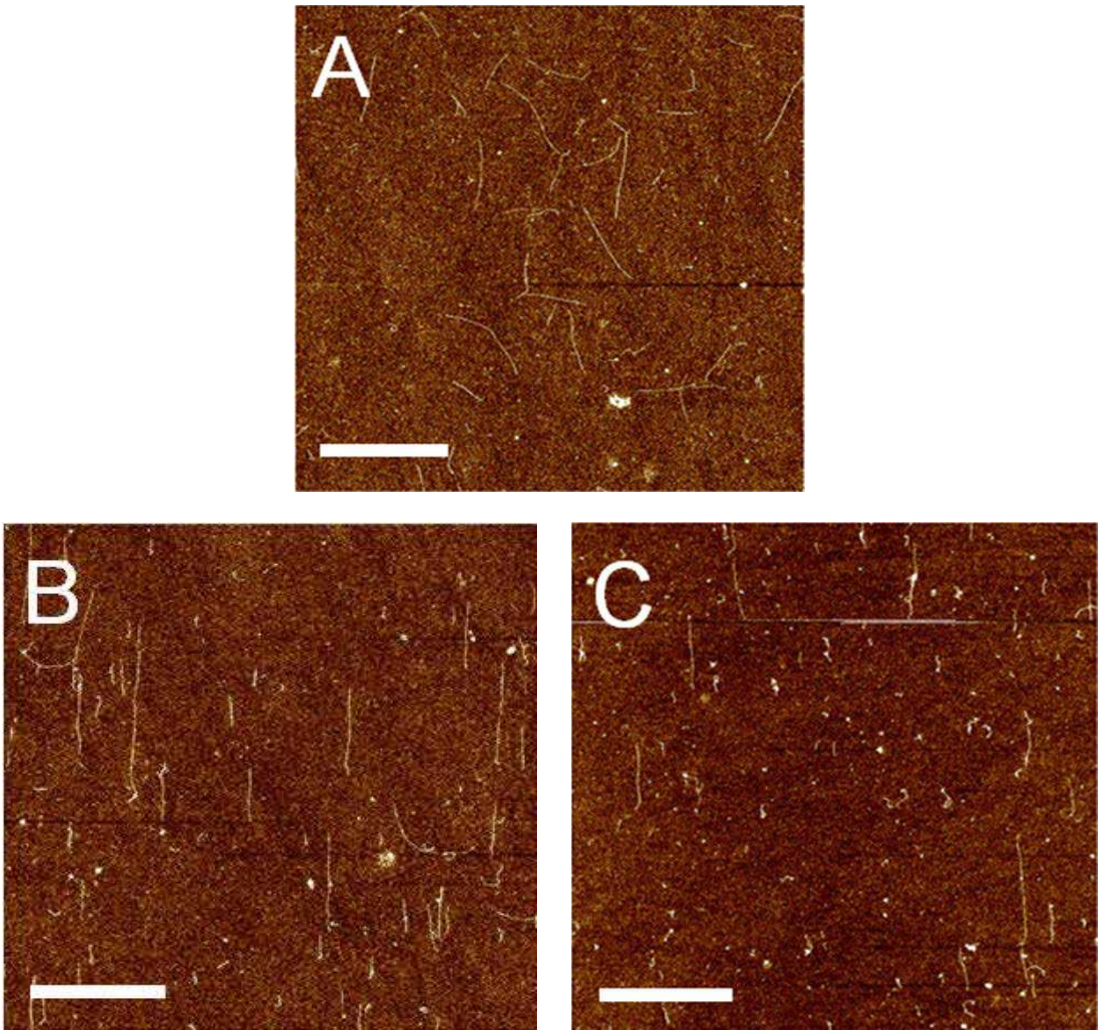


Figure 4. Representative AFM images of SWCNTs deposited onto an 3-(Ethoxydimethylsilyl) propylamine (APDMES) functionalized silicon wafer from each of the SWCNT samples. The panels are: A (Long population); B (Medium population); and C (Short population). The horizontal field of view is 4 μm, and the scale bar is 1 μm in each image.

In Figure 5, histograms of the measured nanotube lengths are shown for each of the RM 8281 SWCNT length populations. The length average and mode of the distribution increase from the Short to Long sample and decrease from Long to Short.

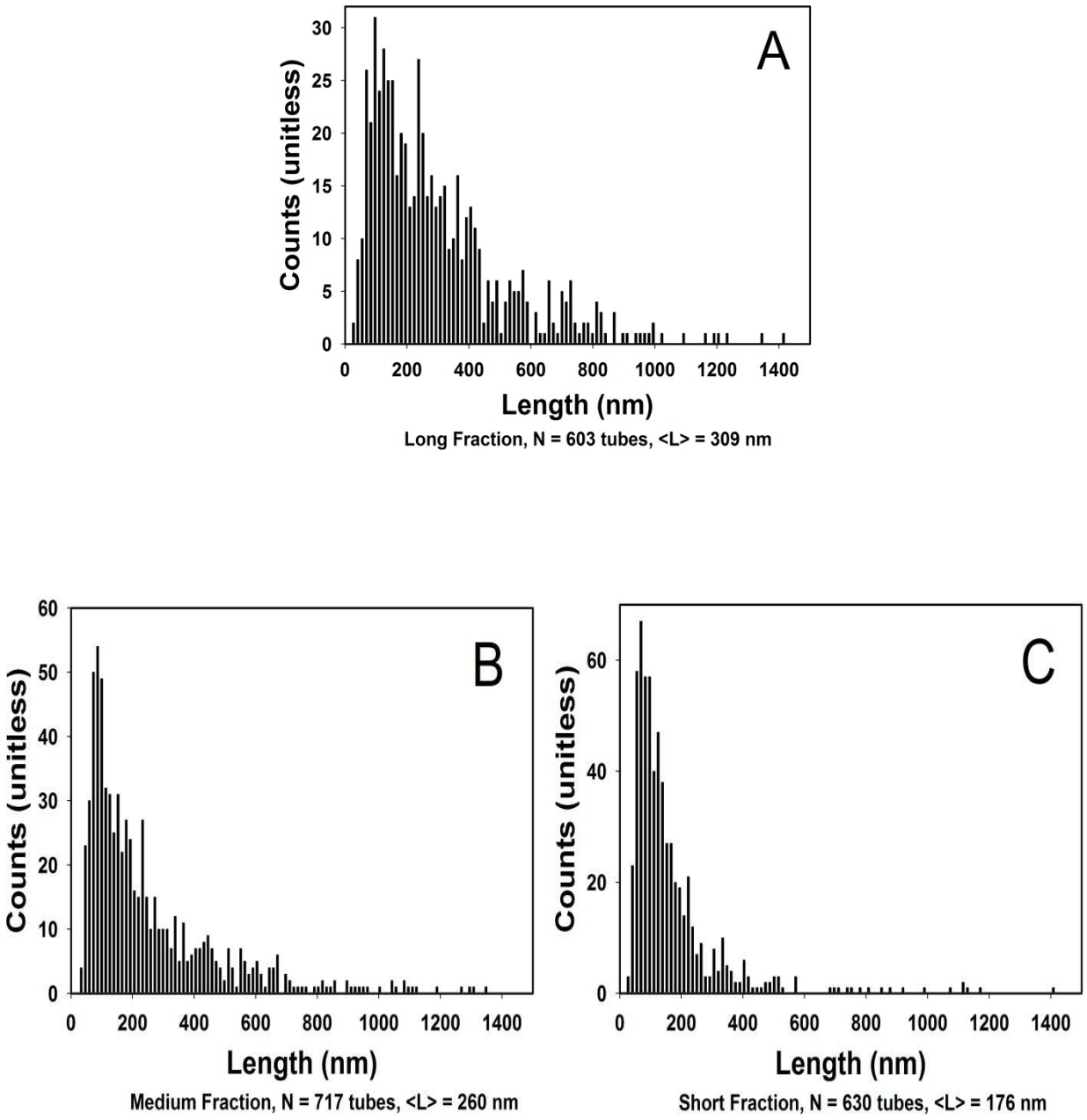


Figure 5. Histograms of SWCNT lengths measured from the AFM images of each SWCNT population deposited on an APDMES functionalized silicon wafers. The panels are: A (Long population); B (Medium population); and C (Short population).

Transmission Electron Microscopy (TEM): Figure 6 contains images of the TEM micrograph of SWCNTs from aliquots of RM 8281 deposited onto a TEM grid. Sample aliquots were prepared by diluting each of the three RM 8281 sample ampoules with ultrapure water, a 1:10 dilution. From each dilution, approximately 15 μL was deposited onto a copper grid and allowed to dry. A single-tilt sample holder was used for TEM observation. Images were taken on a TEM operated at 200 kV under low-dose operating conditions. Low dose means that the electron flux onto the samples was restricted with a small condenser aperture (typically 40 μm in diameter) and defocusing the illumination to the minimum that would allow an image to be captured with a 2 s exposure. All images were captured with a one megapixel CCD camera located below the viewing chamber. The SWCNT samples comprise primarily, on a dry-mass basis, the dispersing surfactant. Nanotubes are visible in each of the images mixed with the dried surfactant.

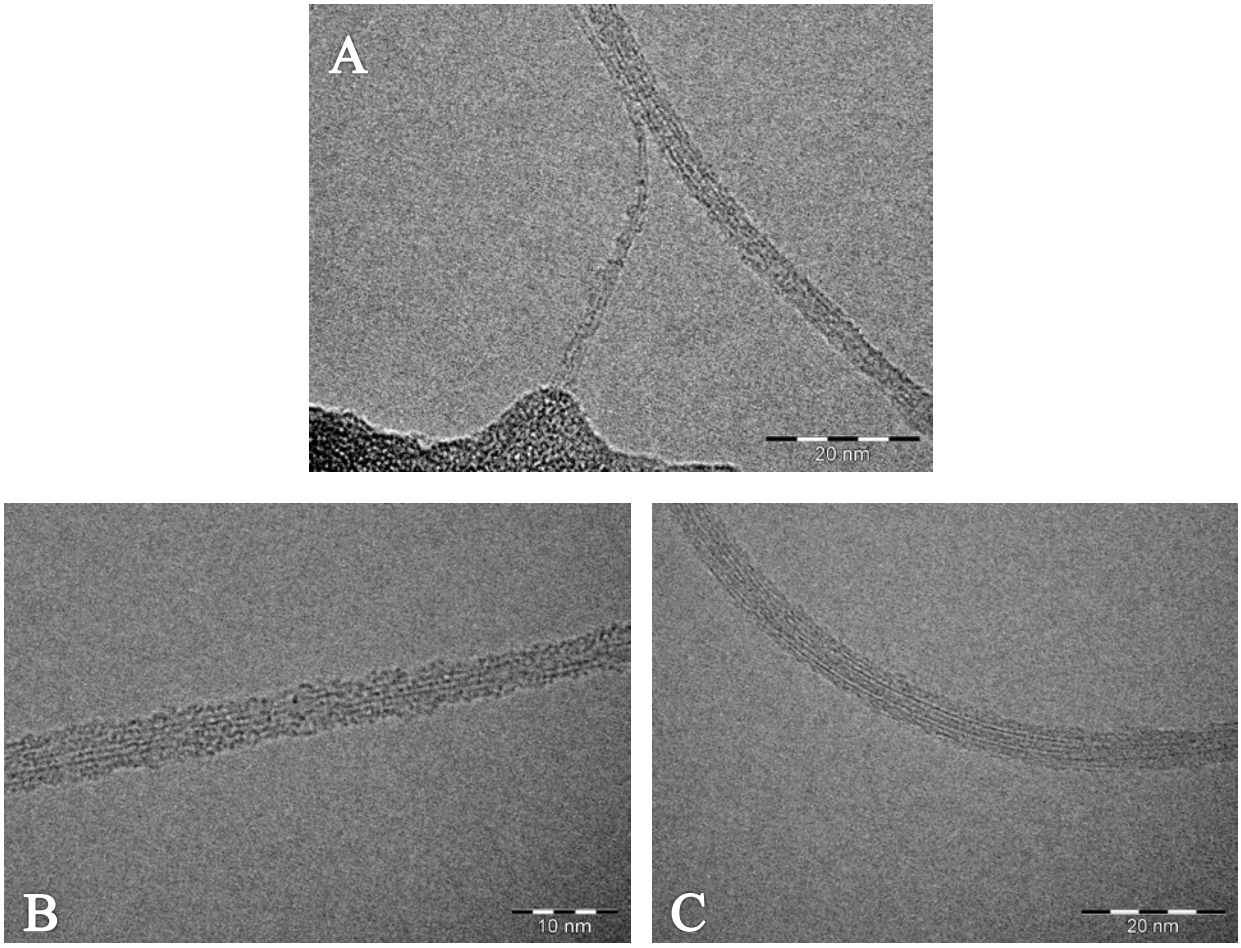


Figure 6. Micrographs of SWCNTs from aliquots of RM 8281 deposited onto a TEM grid. The SWCNT sample panels are: A (Long population); B (Medium population); and C (Short population). Bundled nanotubes are visible along with the surfactant in each image. On an individual basis, the nanotubes visible in the image are approximately 0.7 nm in diameter, consistent with the spectroscopic results. Significant quantities of surfactant are visible in the images due to the large quantity of surfactant in the liquid dispersions on a dry-mass basis.

REFERENCES

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[6] Weisman, R.B.; Bachilo, S.M.; *Dependence of Optical Transition Energies on Structure for Single-Walled Carbon Nanotubes in Aqueous Suspension: An Empirical Kataura Plot*; Nano Lett., Vol. 3, pp. 1235–1238 (2003).

Certificate Revision History: 03 November 2017 (Change of expiration date; editorial changes); **19 July 2013** (Original certificate date).

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