Carbon Nanotubes

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Separation and Diameter-Sorting of Empty (End-Capped) and Water-Filled (Open) Carbon Nanotubes by Density Gradient Ultracentrifugation**

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Ever since the discovery of single-wall carbon nanotubes (SWCNTs),[1] their unique and remarkably diverse electronic and optical properties, which depend critically on their exact diameter and chiral structure,[2] have proven to be both a blessing and a curse, as synthetic methods invariably produce mixtures of structures, while applications demand more uniform properties. The sorting of SWCNTs by buoyant density through solubilization as individually isolated tubes using bile salt surfactants,[3] followed by ultracentrifugation to equilibrium in a density gradient (DGU), is definitely the most promising technique for separating SWCNTs that have different diameters and chiral structures.[4] However, the diameter-sorting is still not well understood, and the isolation of few or even individual SWCNT species has been limited to SWCNTs with relatively small diameters. In the present work, we have obtained an unprecedented insight into the sorting mechanism by showing that each individual SWCNT chirality actually does not concentrate at one, but rather at two different densities, which correspond to empty and water-filled nanotubes (Figure 1): the intact (end-capped, and therefore empty) SWCNTs, which are present mainly in carefully solubilized samples,[5] can be separated from water-filled SWCNTs by DGU. Remarkably, these empty tubes possess far superior properties than the water-filled tubes used in previous nanotube research, and the overall reversed trend of buoyant density with increasing diameter enhances sorting of large-diameter tubes.

In recent years, important progress has been made toward the preparation of monodisperse SWCNT samples, at least for small-diameter tubes, both by more selective synthesis and by post-synthesis purification methods.[4e,f] The sorting of SWCNTs by DGU was pioneered by Arnold et al.,[4a,6] and has been further developed and emerged as the most widely used and most versatile technique for sorting different SWCNT species by length, diameter, electronic type, and handedness.[4,7] In DGU,[8] particles sediment in a solution of spatially varying density under a high centrifugal acceleration (ca. 10^5 times the standard gravitational acceleration g), until they reach their equilibrium position where their buoyant density matches that of the solution. Counterintuitively,[9] Arnold et al. (and many other DGU studies reported since[4]) found that tubes with larger diameters float at layers that have higher density. A hydrodynamic model, which empirically incorporates a diameter dependence of the surfactant monolayer packing density, has been used to

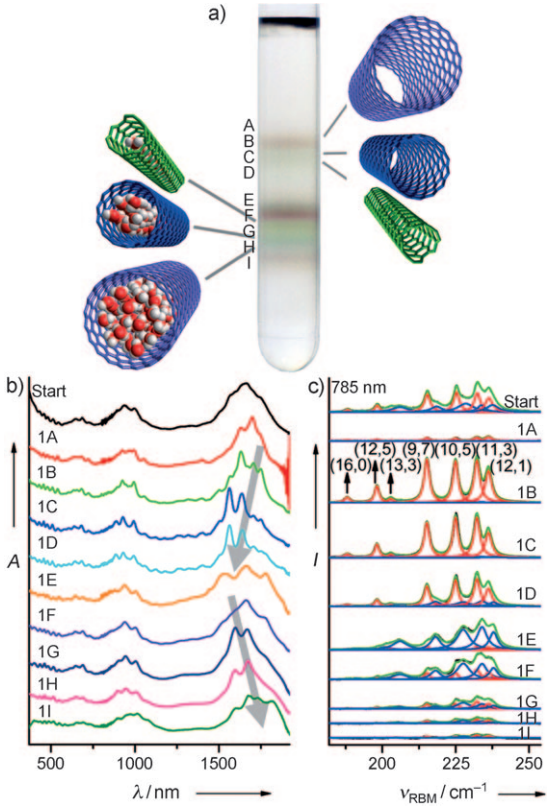

Figure 1. Sorting of empty and water-filled Arc SWCNTs (2% w/v SC). a) Centrifuge tube containing Arc SWCNTs sorted by a 24 h DGU run at 122000 g in 2% w/v SC solution. Bundles were removed beforehand by medium-speed centrifugation without gradient. b) Absorption spectra of the original solution and of the sorted fractions 1A–1I. Spectra are background-subtracted, normalized, and offset for clarity. c) Resonance Raman spectra (black) of the different fractions excited at 785 nm. Fits (green) are superpositions of the known RBM peaks of empty (red) and filled (blue) tubes. Spectra obtained by excitation at other wavelengths are given in the Supporting Information.

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describe this reversed order.[10] Theoretical analysis later showed that this model was not sufficient to explain the observed sorting, and prompted the assumption that the SWCNTs are filled with water.[11] This filling is indeed possible, despite the hydrophobic nature and small diameter of SWCNTs, and has been the subject of many theoretical[12] and experimental studies.[13] In fact, high-resolution Raman spectroscopy of the radial breathing mode (RBM) vibration of SWCNTs has shown that both empty (closed) and water-filled (opened) SWCNTs occur in aqueous solutions,[5] and that SWCNTs can be filled down to extremely thin diameters ($d = 0.548$ nm).[14] Furthermore, it was shown that water-filled tubes dominate in solutions of chemically purified tubes or tubes that have been dispersed by using heavy ultrasonication,[5] as is almost universally applied in DGU work (even though also high concentrations of individual SWCNTs can be achieved using bile salt surfactants without ultrasound[3]).

Very importantly, the possible occurrence of empty tubes has not been taken into account in DGU separations, and we hypothesized that it would be beneficial to use intact, empty SWCNTs in DGU sorting for at least two reasons: 1) As the resolution in DGU separations is determined by the counteracting effects of gravity and diffusion, it improves with increasing molecular mass (for a given density),[8] and is therefore expected to be best for the empty SWCNTs (as these are end-capped, and therefore intact, full-length tubes). 2) A larger dependence of buoyant density on SWCNT diameter may be expected for empty tubes, at least for tubes with sufficiently large diameters where the volume of the internal (empty) channel plays a dominant role. The latter behavior can be qualitatively described by a very simple geometric model that treats the internal water molecules as hard spheres in a cylinder[15] and the surfactant as a concentric cylindrical layer around it (see Section 2 in the Supporting Information). This model results in a diameter dependence of the density which reverses at some intermediate diameter, but eventually, as intuitively expected, converges towards the density of water for large water-filled tubes, whereas it continues to decrease for empty tubes.

We first demonstrate that empty SWCNTs can be successfully separated from water-filled SWCNTs by DGU and that both species (empty and filled) can be further sorted by diameter in a single DGU run. To this end, we used SWCNTs synthesized by the arc-discharge method, which have a relatively large diameter d and narrow diameter distribution ($d = (1.33 \pm 0.1)$ nm). The SWCNTs were solubilized in D_2O with sodium cholate (SC) surfactant using only mild sonication to obtain solutions that contain both empty and water-filled SWCNTs. The solutions were first centrifuged at medium speed to remove any bundles so that only the individually solubilized SWCNTs remained. When such solutions were then ultracentrifuged in a gradient of iohexol[16] in D_2O, we observed a clear separation into two series of colored bands, which we collected into fractions labeled 1A–1D and 1E–1H (Figure 1a). High-resolution Raman spectra of these fractions (e.g., Figure 1c; analyzed by fitting the well-resolved peaks of empty and water-filled tubes by using the accurately determined peak positions and widths from Ref. [5]) showed that the lower-density fractions 1A–1D indeed contain only empty SWCNTs, whereas the higher-density fractions mainly contain water-filled SWCNTs (of the same chiral structures), and the original solution contained a mixture of both SWCNTs. The fact that colored bands are observed in both series already indicates that a separation of different SWCNT structures occurs among both empty and water-filled tubes. In fact, this observation also clearly excludes the fact that either series would correspond to remaining bundles or aggregates of SWCNTs[17] (which are actually found to band as a single, black band at even higher density when not removed beforehand; see the Supporting Information). Interestingly, this macroscopic separation evidently also implies that empty and water-filled tubes are largely present as fully separate entities, as opposed to the occurrence of empty and water-filled domains within the same nanotube (a behavior which could not be excluded from previous measurements on mixed samples[5,14]): any defect large enough to allow water molecules to pass causes the entire SWCNT to be water-filled. The structure separation is further supported by the absorption spectra (Figure 1b), which show a sequence of highly resolved features, especially within the range of the lowest-energy transition of the semiconducting SWCNTs at approximately 1500–1800 nm (not resolved in the original solution). As the wavelength of this transition is roughly related to diameter, the absorption spectra already hint at an opposite diameter–density relation among empty and water-filled tubes. However, the transition wavelengths of SWCNTs also depend to some extent on the exact chiral structure, and therefore more unequivocal information is obtained from 2D IR band-gap fluorescence excitation spectroscopy, which allows for resolving each individual SWCNT structure (identified by its chiral indices (n,m)).[18] An example of a 2D fluorescence map of a fraction of empty tubes is given in Figure 2a, and shows a band-gap emission that has a sharp peak at approximately 1550 nm (a technologically very important wavelength widely used, for example, in optical telecommunications). Three-color overlays of three empty SWCNT fractions of increasing densities (Figure 2b) and three water-filled SWCNT fractions of increasing density (Figure 2c) immediately show that 1) the optical transitions of the empty tubes are much more resolved (both in excitation and in emission) and 2) the sorting of SWCNT structures is based mainly on diameter and is influenced less by their chiral angle (compare with the superimposed diameter/chiral angle grid), but follows an order among empty and filled SWCNTs, with the largest diameter tubes at the lowest densities in the case of empty tubes (within the diameter range of these arc-discharge SWCNTs). This trend can be visualized more synoptically (similar to the absorption data, but with a more direct relation with diameter) by projecting the 2D fluorescence data along curves of constant diameter to obtain the 1D curves of fluorescence intensity as a function of diameter as shown in Figure 2f (see also Section 7 in the Supporting Information). Comparing 2D fluorescence maps for fractions of empty tubes with corresponding fractions of water-filled tubes (e.g., the two-color overlay in Figure 2d) reveals not only the dramatic broadening but also a significant red-shift of the electronic transitions induced by the water-filling, both in

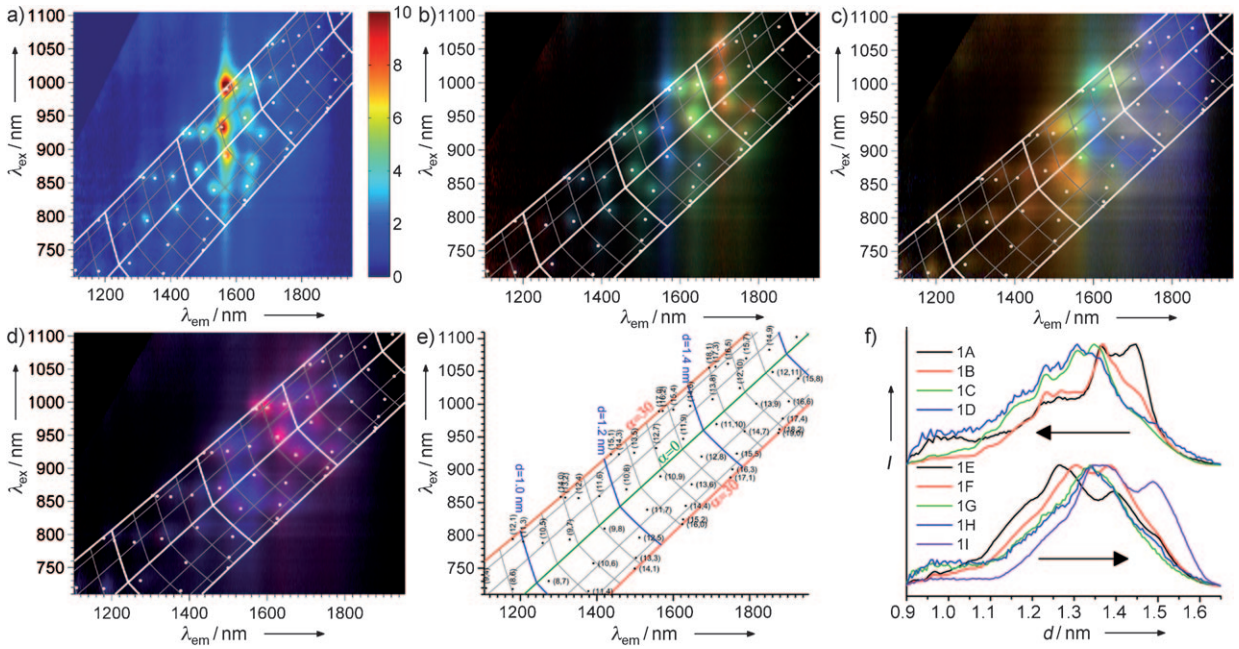

Figure 2. 2D IR fluorescence-excitation maps of fractions 1A–1I a) Example of a 2D IR fluorescence-excitation spectrum of fraction 1C, revealing the chirality distribution of the semiconducting tubes in this fraction. Empirical peak positions and a grid, visualizing the lines of constant density and chiral angle, are superimposed on the 2D spectrum. b) Three-color overlays of three empty fractions 1A (red; $\langle\rho\rangle = 1.163\ g\,mL^{-1}$), 1B (green; $\langle\rho\rangle = 1.175\ g\,mL^{-1}$), and 1C (blue; $\langle\rho\rangle = 1.182\ g\,mL^{-1}$), clearly revealing the diameter-based sorting for empty tubes. c) Three-color overlay of filled fractions 1E (red; $\langle\rho\rangle = 1.199\ g\,mL^{-1}$), 1F (green; $\langle\rho\rangle = 1.204\ g\,mL^{-1}$), and 1I (blue; $\langle\rho\rangle = 1.267\ g\,mL^{-1}$), showing the opposite diameter vs. density relation for filled tubes. d) Two-color overlay of fraction 1B (red) and fraction 1E (blue), evidencing the electronic red-shifts and broadening for water-filled SWCNTs. e) Labeled SWCNT peak positions (chiral indices (n,m)) and diameter/chiral angle grid over the same range as the 2D IR fluorescence spectra, all derived from the adapted empirical relations (Equation S2) for empty tubes. f) Integrated fluorescence intensity of the different fractions, integrated along strips of constant diameter, that reveal the opposite diameter versus density relation for empty (upper spectra) and filled SWCNTs (lower spectra).

excitation (second transition of semiconducting tubes E_{22}^S) and in emission (E_{11}^S).

To obtain a more detailed picture of the structure–density relation, we performed extensive resonance Raman and 2D fluorescence-excitation measurements, which both have the advantage of providing intensities (that are proportional to the concentrations, which were kept sufficiently low to avoid reabsorption) of each individual SWCNT structure present in the different fractions. This procedure allowed us to determine at which buoyant density each (empty and filled) tube structure (n,m) is concentrated (Figure 3). The result is in remarkable agreement with the qualitative predictions of the simple hard-sphere model, indeed showing a divergence between the densities of empty and water-filled tubes at increasing diameters, and the onset of the reversal of the diameter–density relation for empty SWCNTs. The Raman data also includes results for metallic SWCNTs, and shows that there are no significant density differences between metallic and semiconducting tubes of similar diameter. Superimposed on these general trends, significant oscillations are observed, which we attribute to packing effects of the surfactant molecules around SWCNTs of different diameters, which were already suggested to play an important role by Arnold et al.,[4a] and which can also help in the optimization of the separation of specific SWCNTs, albeit in a less predictable way, by using different surfactants, surfactant concentrations, or by adding electrolytes.[4a,d,h,19] In fact, it was

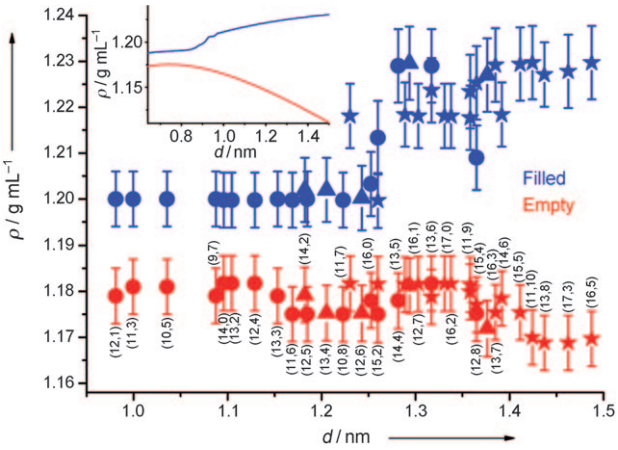

Figure 3. Density of empty and water-filled SWCNTs. Density of empty (red) and filled (blue) SWCNTs obtained from comparing resonance Raman intensities of semiconducting (circles) and metallic (triangles) tubes and IR fluorescence intensities (stars) of fractions 1A–1I. Error margins are determined by the density differences between subsequent fractions. Densities of fractions were determined from optical absorption spectrometry of the iohexol absorption at 2272 nm. The inset shows the calculated density vs. diameter relationship using the geometric model described in the Supporting Information.

recently found that reducing the surfactant concentration also improved the DGU-based sorting of thinner SWCNTs,[4c] which may be attributed to a reduction of the surfactant

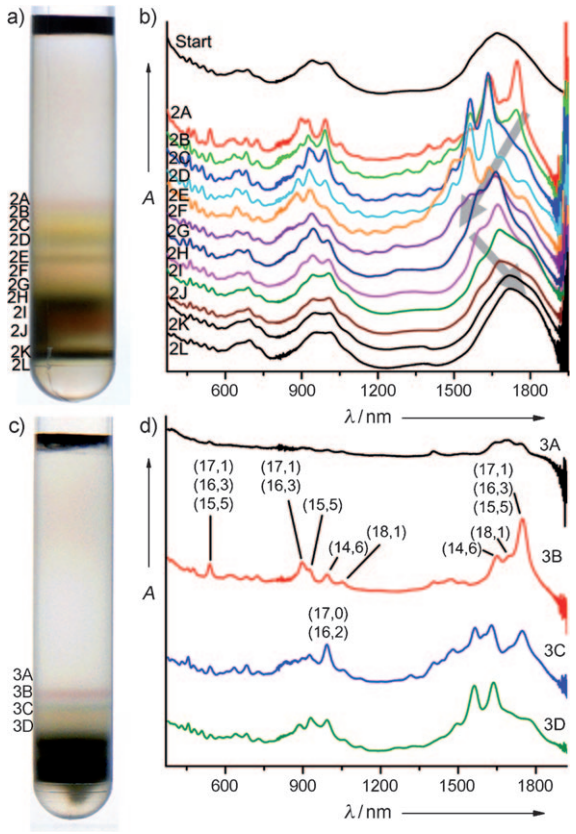

Figure 4. Sorting of Arc SWCNTs using 0.7% w/v SC. a) Centrifuge tube containing Arc SWCNTs sorted by a 24 h single DGU run at 122 000 g in 0.7% w/v SC. Bands 2A–2E are empty SWCNTs, bands 2H–2J are water-filled tubes, and bands 2K–2L contain bundles. b) Absorption spectra of the unsorted and sorted fractions. Spectra are background-subtracted, normalized, and offset for clarity. c) Image of centrifuge tube containing Arc SWCNTs sorted by a 48 h single DGU run at 122 000 g in 0.7% w/v SC. d) Absorption spectra of the sorted fractions showing very narrow chirality distributions. Indicated chiral indices are determined by combining absorption and fluorescence spectroscopy.

layer thickness (possibly from a double layer to a monolayer). Repeating our experiments with this lower surfactant concentration (0.7% SC; Figure 4) particularly enhances the oscillations (Figure 5b), which is consistent with the concept of a thinner surfactant layer that reduces the total volume and increasing the relative effect of the SWCNTs and of the surfactant monolayer packing on the effective buoyant density. These oscillations result in a more complex non-monotonous diameter sorting (Figure 5b,c), and help in the excellent sorting yielding only a few chiralities in separate fractions of empty tubes (see Figures 4c, 5a, and Figure S11 in the Supporting Information), but the same general trend is confirmed for an opposite diameter–density relation for empty and filled SWCNTs. Interestingly, use of a slightly different bile salt surfactant (sodium deoxycholate; DOC) results in much reduced oscillations and thus a more systematic general trend in the diameter–density relation that more clearly shows the opposite behavior for empty and filled tubes (see Figures S18–S20). While both bile salts are known to be very efficient surfactants (among which DOC is better than SC),[3] and both form a very homogeneous, unperturbing coating around the nanotubes, as indicated by the unusually narrow SWCNT spectral linewidths,[3] the present results show that slight variations of the structure of the surfactant (one extra OH group for SC), result in a different packing around the SWCNTs that is more critically dependent on the exact diameter in the case of SC, and is believed to be the dominant mechanism in the sorting of small-diameter SWCNTs (see the Supporting Information, Section 10).[4a]

The separation of empty and water-filled SWCNTs with a much wider diameter distribution, including thinner tubes (as produced by the high-pressure carbon monoxide (HipCO) process; $d \approx 0.7$–1.4 nm) at first seemed more challenging, as the buoyant density range of filled thin tubes may overlap with that of empty thicker tubes. This is indeed the case, but nevertheless we achieved a good separation of empty and water-filled tubes, both for the thinnest diameters (ca. 0.548 nm) and for the larger diameters (ca. 1.1 nm), especially when using DOC, which minimizes the surfac-

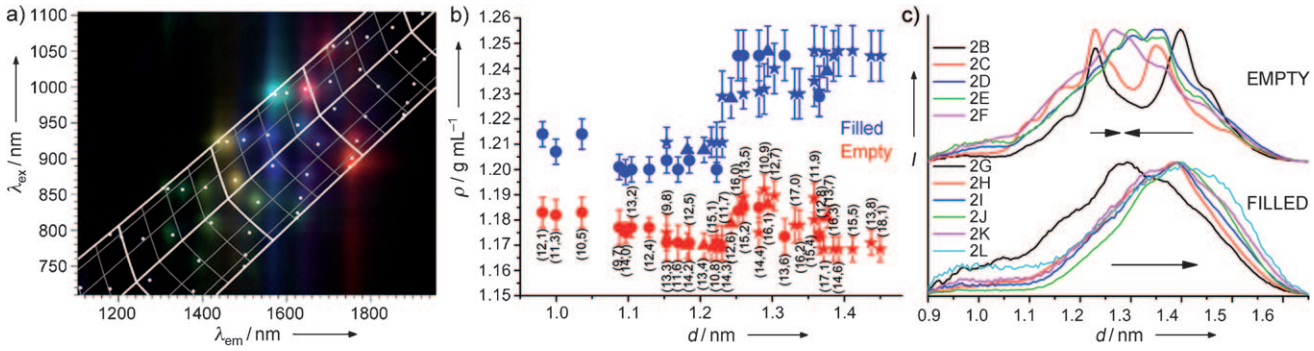

Figure 5. 2D IR fluorescence of sorted Arc SWCNTs using 0.7% w/v SC. a) Three-color overlay plot of the 2D IR fluorescence spectra of fractions 3B (red; $\langle\rho\rangle = 1.176\ g\,mL^{-1}$), 3C (green; $\langle\rho\rangle = 1.194\ g\,mL^{-1}$), and 3D (blue; $\langle\rho\rangle = 1.204\ g\,mL^{-1}$) clearly showing a very good sorting with only a few chiralities present in the fractions 3B and 3C. b) Density of empty (red) and filled (blue) SWCNTs obtained from comparing resonance Raman intensities of semiconducting (circles) and metallic (triangles) and IR fluorescence intensities (stars) of fractions 2A–2L. c) Integrated fluorescence intensities versus diameter for the fractions 2A–2L, showing the diameter-sorting and a turning point around 1.25 nm, which is attributed to the surfactant-induced fluctuation in the diameter–density relation.

tant-induced density modulation (see the Supporting Information).

The electronic and vibrational transitions of the SWCNTs, which are already extraordinarily sharp because of the very regular, unperturbing bile salt micellar coating,[3] are even narrower for the empty SWCNTs than for the water-filled SWCNTs.[5,14] Therefore, isolation of the empty SWCNTs results in solutions with by far the most resolved Raman spectra reported to date for carbon nanotubes (see for example, fraction 1B in Figure 1c and Section 5 and Figures S18 and S16 in the Supporting Information), with RBM linewidths as low as 1.16 cm^{-1} (e.g., the (6,4) tube in fraction 6B; see Figure S18d). This result implies very long phonon lifetimes (setting a lower limit of 4.6 ps for the empty (6,4) tube), which suggest improved thermal conductivities of these intact, empty SWCNTs. Also the electronic transitions are clearly much narrower (e.g., Figure 2 and Section 7 and Figures S3, S4, S14, and S19 in the Supporting Information), thus indicating that the electronic properties are much less perturbed. This result is indeed also confirmed by dramatically improved fluorescence efficiencies. A relative measure of fluorescence quantum efficiency is obtained by normalizing the fluorescence intensity to the absorbance (see the Supporting Information). The fluorescence quantum efficiency drops steeply with increasing diameter for both empty and water-filled tubes, but that of empty tubes is approximately twice as high as that of the more commonly used water-filled tubes. Likewise, the resonance Raman cross-section is found to be 4–5 times higher for the empty SWCNTs, which, when combined with the fact that the Raman scattering is also concentrated in much narrower RBM lines, results in extraordinarily strong peak intensities in Raman spectroscopy. Thus, all observations point at considerably enhanced electronic and vibrational (and thus thermal) properties for empty SWCNTs.

In conclusion, the fact that each SWCNT chirality may be observed at two different buoyant densities that correspond to empty and water-filled tubes, each of which has a different diameter–density relation, is not only essential to the understanding of the diameter-sorting process, but also provides an important new degree of freedom in the DGU separation of carbon nanotubes. It will be particularly important for the sorting of very large diameter SWCNTs to prepare these tubes in a pristine, closed (and therefore empty) state, as the density of water-filled tubes becomes essentially constant at large diameters. Moreover, the pristine empty tubes isolated by using this method not only have the largest possible aspect ratios but also display far more ideal, unperturbed properties than the filled tubes, as exemplified by the much narrower electronic and vibrational transitions and enhanced quantum efficiencies, and will thus be preferable in most applications.

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