Separation of Single-Walled Carbon Nanotubes with a Gel Permeation Chromatography System

Benjamin S. Flavel,[†,*] Katherine E. Moore,[†] Moritz Pfohl,[†] Manfred M. Kappes,[†,‡] and Frank Hennrich[†,*]

[†]Institute of Nanotechnology, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany, and [‡]Institute of Physical Chemistry, Karlsruhe Institute of Technology, 76128 Karlsruhe, Germany

ABSTRACT A gel permeation chromatography system is used to separate aqueous sodium dodecyl sulfate suspensions of single-walled carbon nanotubes (SWCNTs). This automated procedure requires no precentrifugation, is scalable, and is found to yield monochiral SWCNT fractions of semiconducting SWCNTs with a purity of 61−95%. Unsorted and resulting monochiral fractions are characterized using optical absorption and photoluminescence spectroscopy.

The development of new techniques for the preparation of monochiral single-walled carbon nanotube suspensions in a scalable, reproducible, and simple manner remains an ongoing challenge to the carbon nanotube community. Although chirality selective growth has been shown to be possible, direct synthesis methods remain limited to only a handful of different nanotube species such as (6,5), (7,6), or (9,8).[1−3] In order to gain access to the richly varying optical properties of SWCNTs, emphasis has therefore been placed upon the separation of raw carbon nanotube material. These raw materials are typically synthesized by techniques such as arc discharge, laser ablation, or the HiPco process and contain a complex mixture of metallic (m) and semiconducting (s) SWCNTs of varying diameter (D_t), chiral angle, or (n, m) index.

Previously separation of (n, m) pure SWCNTs has been achieved by various groups utilizing such techniques as the wrapping of SWCNTs with short sequences of single-stranded DNA (ssDNA) and subsequent ion exchange chromatography (IEX),[4] the suspension of SWCNTs with surfactants followed by density gradient ultracentrifugation (DGU),[5−7] or gel filtration.[8−11] Despite providing promising routes for the separation of SWCNTs, each of the above methods has drawbacks, be it the use of extended ultracentrifugation time, expensive density gradient medium and ssDNA, or the large amount of gel and gel columns required in the preparation of (n, m) pure SWCNT material. These factors combined with difficulty in often reproducing research results among groups have led to (n, m) pure SWCNT suspensions remaining on the small research scale and accessible to only a few groups. To this end, research has begun to develop new scalable methods for the preparation of SWCNT suspensions. For example Khripin et al.[12] have recently used immiscible polymer phases to spontaneously separate metallic and semiconducting SWCNTs on the liter scale. Likewise Tvrdy et al.[13] have also successfully separated liter volumes of mixtures of (7,5) and (8,3) and chirality pure (6,5), which was then used in the fabrication of a carbon nanotube based solar cell.[14] Liu et al.[15] achieved a single-chirality separation of seven (n, m) SWNT species using temperature-controlled gel chromatography. This method used temperature to selectively control the interaction between the SDS-wrapped SWCNTs and the allyl dextran-based Sephacryl gel. The control of the temperature enhanced the

differences in the interactions of various (n, m) SWCNTs with the gel, enabling the separation of seven (n, m) species (purities between 56% and 93%). The authors speculate on the influence of temperature on the separation mechanism. They suggest that reducing the temperature may enhance the interactions between the adsorbed SDS molecules and nanotubes of certain specific chiralities (e.g., near-armchair SWCNTs) and therefore that this may result in the reassembly of the SDS molecules on the nanotube surfaces, thus altering the dielectric constant around the SWCNTs and the absorbability of SWCNTs on the gel.

In our contribution to scale up, we have recently shown that the number of required Sephacryl gel columns can be reduced to one by altering the pH of the sodium dodecyl sulfate (SDS) eluent and demonstrated the separation of 15 different nanotube (n, m) species with a purity of 17−72%.[16] In that work we took a centrifuged 1 wt % SDS suspension of HiPco raw material and added it to a 14 cm high Sephacryl gel column. By changing the pH of the SDS eluent we showed that hydrolysis of SDS led to small quantities of 1-dodecanol being formed in solution. 1-Dodecanol is then incorporated into the SDS micelle of the SWCNTs. As it has been shown on graphite surfaces,[17,18] the integration of 1-dodecanol into the SDS micelle results in a structural conversion from a continuous parallel semicylindrical structure to a herringbone pattern. We expect a similar structural change for SWCNTs and attribute this structural change to a reduction in the SWCNT/gel interaction and the mechanism responsible for the elution of different SWCNT species. As discussed by Kataura and co-workers,[10] the initial SDS micelle of SWCNTs is strongly curvature-dependent[19] (hence also the nanotube gel/interaction strength) due to differences in the surface π-electron states. In other words, as the curvature of the SWCNT increases (smaller diameter), the SDS concentration/density decreases. Subsequently Duque et al.[20] have also experimentally confirmed the curvature-dependent wrapping of SDS. Hence our method was shown to have a strong dependence of elution order on nanotube diameter. In a recent paper, Kataura and co-workers follow on from our work varying the pH of SDS but provide an alternative explanation for the separation mechanism.[21] In their work they also observed the adsorbance of SWCNTs to the Sephacryl gel to be reduced under acidic pH conditions; however they describe the adsorbability as being related to a band structure dependent oxidation of SWCNTs, where oxidation confers positive charges onto the SWCNTs, and these charges enhance the electrostatic interactions of the SWCNTs with SDS, thereby leading to the condensation of SDS on the SWCNTs. This increase in SDS density around the SWCNT then reduces interaction between the SWCNTs and the gel.

Despite the exact mechanism of separation with variations in pH remaining under debate, both explanations share one commonality, namely, changes in pH induce changes in the SDS micelle structure, which in turn reduces the SWCNT/gel interaction strength.

In this contribution we further build on our separation of SWCNTs by varying pH; however we apply our approach to a gel permeation chromatography (GPC) system. In doing so, we gain precise control over the pH of the SDS eluent and can utilize computer-controlled pH gradients in the separation of (n, m) SWCNT species. This allows us to reproducibly elute different (n, m) species with control over when (time-based) different fractions should be collected. This is a significant advantage over previous methods, where a vast number of fractions would need to be collected followed by absorption or photoluminescence spectroscopy to find the few (n, m) pure fractions. Our method also has the advantage of requiring no centrifugation; all raw materials are simply sonicated prior to use. This reduces the required infrastructure for (n, m) SWCNT sorting to a probe sonicator, a small amount of Sephacryl gel, and any pump system capable of dual solvent mixing.

RESULTS AND DISCUSSION

As outlined in our previous work,[16] the high-throughput separation of (n, m) pure s-SWCNTs with a single-column size exclusion chromatography (SEC) approach involved the use of a centrifuged 1 wt % SDS in H_2O suspension of raw HiPco-SWCNT material that was added to a Sephacryl S-200 gel bed under 1 wt % SDS in H_2O. This resulted in a starting material containing over 14 different (n, m) species, as shown by a photoluminescent contour map in Figure S1(a) of the Supporting Information. In this case centrifugation at ~100000g for 1.5 h was also necessary to remove any remaining catalyst particles and bundled carbon nanotubes and most importantly produce an SWCNT raw material with a reduced length distribution that is ideal for SEC sorting. Despite this preparatory centrifugation step, the resulting (n, m) suspensions afforded from our previous sorting effort were often intermixed with other (n, m) species and had a purity (by absorption spectroscopy) of 17−72%. In the current work we utilized the same raw HiPco material as before; however by tailoring the wt % of SDS we were able to limit the number of (n, m) SWCNT species absorbed on the gel for sorting to 1−6 species and this required no centrifugation. By dramatically reducing the number of species absorbed on the gel for a separation experiment, (n, m) species intermixing was therefore reduced and allowed for the preparation of much higher purity suspensions.

Preselection. As outlined in the Methods section, 80 mL of a 2 wt % SDS in H_2O suspension of raw HiPco-SWCNT material was prepared by 15 h sonication

at constant temperature. Such a long sonication time is typical for the gel separation technique, where short nanotubes are required. In this work, no attempt was made to optimize the sonication time and thereby find the upper or lower bound length; however sonication represents an important third dimension to our separation process and will be investigated in the future. The raw material was then adjusted to 1.6 wt % SDS by the addition of H_2O, and 15 mL of the solution was added to the Sephacryl S-200 gel. The raw material was washed through the gel with a further 1.6 wt % SDS and collected. The diode array detector was used to monitor the washing process, and collection was stopped once a drop in intensity was observed. Although trace amounts of unbound SWCNTs are washed from the gel over the equilibrium time, collection of this entire volume would result in a weakly concentrated SWCNT suspension and make subsequent experiments difficult. The SWCNT material that remained absorbed to the gel is then the "starting material" for sorting with the GPC system. However, in order to initially understand which (n, m) species remained on the Sephacryl gel, 5 wt % SDS was added to the column to elute all adsorbed SWCNTs. An analogous process was then used to allow for preselection of adsorbed SWCNTs. Specifically, the SDS concentration of the SWCNTs initially washed through the gel (flow through) was adjusted in decrements of 0.2 wt % to cover the range 1.6−0.4 wt % SDS. As shown in the absorption spectroscopy in Figure 1, this resulted in a series of "starting materials" with increasing SWCNT diameter, where SWCNTs with a small, medium, and large D_t are designated to have a first optical transition (S11) in the regime 900−1050, 1050−1200, and 1200−1350 nm, respectively. Furthermore, it can be seen in Figure S2 of the Supporting Information that as the SDS concentration is reduced from 1.6 to 0.4 wt % SDS the relative concentration of small-diameter SWCNTs is reduced or completely removed. Interestingly, from the complex HiPco mixture, a suspension enriched in the (6,5) SWCNT, the species with the smallest diameter (D_t = 0.747 nm) can easily be prepared by adding the raw HiPco material to a column with 1.6 wt % SDS. From absorption measurements this material clearly also contains (7,5) and (7,6) species; however such a purity level may be useful to certain research groups.

The observation that changes in SDS concentration can control the adsorption of SWCNTs on the Sephacryl gel was also recently seen in work by Blanch et al.[11] In their work the SDS concentration of raw HiPco material was varied from 0.5 to 3.5 wt %, and it was found that for low SDS concentrations (0.5−1 wt % SDS) almost all SWCNT species in solution were absorbed on the gel and could be eluted with sodium deoxycholate. Alternatively for high SDS concentrations (2−3 wt % SDS) only small-diameter species such as (6,5), (8,3), and (7,6) were absorbed to the gel. For SDS concentrations
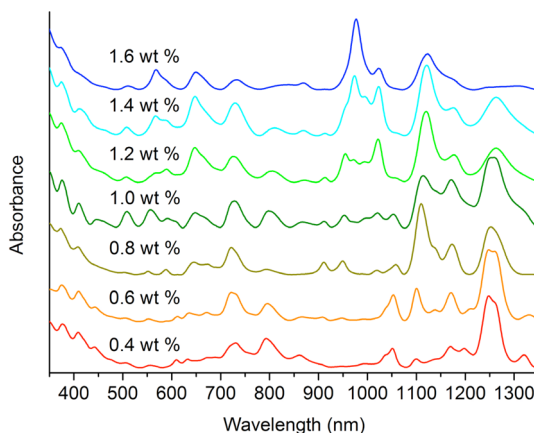

Figure 1. Absorption spectroscopy of "starting materials" (SWCNTs absorbed on the Sephacryl gel) obtained by sequentially reducing the SDS concentration from 1.6 to 0.4 wt %.

below 0.5 wt % complete and irreversible adsorption to the gel was observed. However, in the work of Blanch et al.[11] they took "fresh" HiPco raw material and adjusted the SDS concentration sequentially instead of collecting the "flow-through" material and reducing the concentration. This is an important point differentiating our work from the work of Blanch et al. and is likely the reason for the missed potential to sequentially adsorb certain (n, m) species to the gel, as we have done. Likewise, Liu et al.[15] investigated the effect of SDS concentration on the adsorbance of SWCNTs to the Sephacryl gel. They described the decreased adsorbance at higher SDS concentrations as being related to a higher coverage and/or thickness of SDS around the SWCNT, which leads to a reduced interaction with the gel. With this in mind and the knowledge that the SDS micelle is strongly curvature-dependent,[19] it is therefore a logical conclusion that smaller diameter SWCNTs are less coated at relatively higher SDS concentrations and give rise to the sequential adsorption shown in our work. However, this is not forgetting one important requirement for the preparation of these "starting materials", namely, the sequential removal of smaller diameter SWCNT species. There exists a specific number of Sephacryl binding sites (secondary amide groups along the polymer backbone), which may bind to an s-SWCNT. This adsorption process has been shown to be a kinetically driven, competitive, process[13] with larger diameter SWCNTs passing through the gel if the adsorption sites are already taken by smaller diameter SWCNTs. Initially this would suggest that it is not necessary to adjust the SDS concentration and that the same result would be achieved through simply using multiple, sequential columns. Indeed we have tried this approach; however we note that this does not lead to complete removal of the smaller (n, m) species before proceeding to the subsequent column. Furthermore, and in agreement with the work of Tvrdy et al., the concentration of
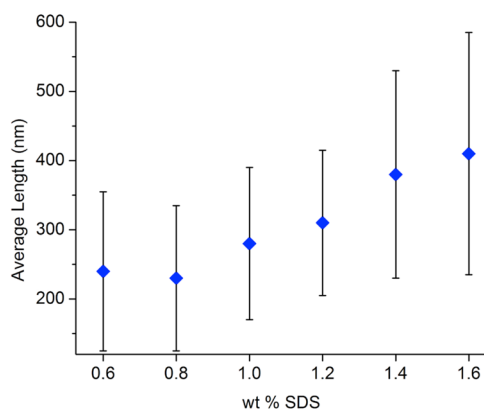
Figure 2. Average length of the SWCNT "starting material" as determined by AFM measurements.

SWCNTs absorbed on the gel dramatically decreases with sequential columns.[13] The SDS concentration must be reduced to ensure high concentration and (n, m) species removal. The importance of (n, m) species removal is also discussed by Liu et al., who use temperature control to sort SWCNTs and note that it is necessary to completely remove (6,4) (D_t = 0.683 nm) before proceeding to collect (6,5) (D_t = 0.747 nm).

In an attempt to further understand the observed selective adsorption we performed atomic force microscopy (AFM) measurements of the material absorbed to the gel for concentrations of 1.6−0.6 wt % SDS. These measurements are summarized in Figure 2, where the average length of the "starting material" is shown for each SDS concentration. The complete set of measurements for each SDS concentration can be found in the Supporting Information in Figure S3. For each "starting material" a Gaussian was fitted to the histogram to obtain the average length. It can be clearly seen that the relatively smaller diameter SWCNTs absorbed to the Sephacryl gel at higher SDS concentrations have relatively longer lengths compared to the SWCNTs absorbed at lower SDS concentrations. The implication of this observation for the adsorption of SWCNTs to the gel still requires investigation and remains speculative. However, this is an observation that is in agreement with the work of Clar et al.,[22] who discussed the SDS/SWCNT interface as being highly intricate. The surfactant shell around a SWCNT is dynamic, not well-defined and is expected to be heterogeneous, with some areas of the SWCNT completely exposed to the gel.[22] Therefore the strength of the SWCNT/gel interaction is likely controlled by not only nanotube diameter and SDS concentration but also length due to the interfacial area. This is also in agreement with Heller et al.,[23] who achieved simultaneous separation of SWCNT length and diameter by gel electrophoresis and column chromatography conducted on individually dispersed, ultrasonicated SWCNTs. They proposed a diameter-selective cutting mechanism with ultrasound treatment that was later confirmed by Hennrich et al.[24]

In their mechanism the smaller diameter SWCNTs are cut to a lesser extent compared to the larger diameters due to the fact that strain forces associated with sonication induced cavitation scales with the square of the nanotube length and is also supposed to be diameter dependent. Scission of SWCNTs then stops when the strain force falls below a critical value for nanotube disruption.

Automated SWCNT Sorting. Upon having a defined "starting material" obtained from different SDS concentrations, we then used the GPC system to apply a pH gradient to the gel, which allowed us to separate the trapped SWCNTs (rather than simply washing all species off the column with 5 wt % SDS). At this point it important to note that the pH of the parent and daughter "starting materials" was between 7 and 8, and all experiments were performed at 23 °C. Figures 3 and 4 show photoluminescence (PL) contour maps corresponding to the "starting material" (1.6−0.6 wt % SDS) absorption spectra shown in Figure 1. A PL contour map of the 0.4 wt % SDS "starting material" can be found in Figure S1(b) of the Supporting Information. Upon looking at the PL contour maps the dependence of diameter adsorption of SWCNTs to the Sephacryl gel on changes in SDS concentration is further made clear. For example the "starting material" obtained at 1.4 wt % SDS (consisting primarily of (7,5), (6,5), (7,6), and (8,4) SWCNTs) has an average diameter of 0.818 nm compared to 0.6 wt % SDS (consisting primarily of (9,4), (9,5), (10,2), (10,3), (11,1), (8,6), and (8,7) SWCNTs), which has an average diameter of 0.933 nm. The SWCNT diameter values were taken from the data of Weisman et al.[25] Accompanying the PL contour map of each "starting material" the corresponding elution profile can also be found in Figures 3 and 4. In order to record these elution profiles, the GPC system was fitted with a diode array detector capable of measuring full spectra between 190 and 950 nm. Despite the ability to extract full spectral data at the completion of an experiment, during a run only two fixed wavelengths could be monitored. To ensure sensitivity to all (n, m) species in the second optical transition (S22) regime either 590, 650, or 720 nm was monitored with a resolution of ±10 nm.

Explanation of the elution diagrams and (n, m) separation is best served by beginning with the most simple situation of SWCNTs absorbed to the Sephacryl gel in 1.6 wt % SDS. In this instance the number of SWCNTs to be sorted is limited to essentially (6,5) with a small amount of (7,5) and (7,6) (as shown by absorbance measurements in Figure 1). In performing the separation the GPC system was operated isocratically in 1.6 wt % SDS with a quaternary pump mixing 1.6 wt % SDS (defined pump A) and 1.6 wt % SDS adjusted to pH 3 upon addition of HCl (defined pump B). The separation was then performed in the following manner: In preparation the Sephacryl gel was placed
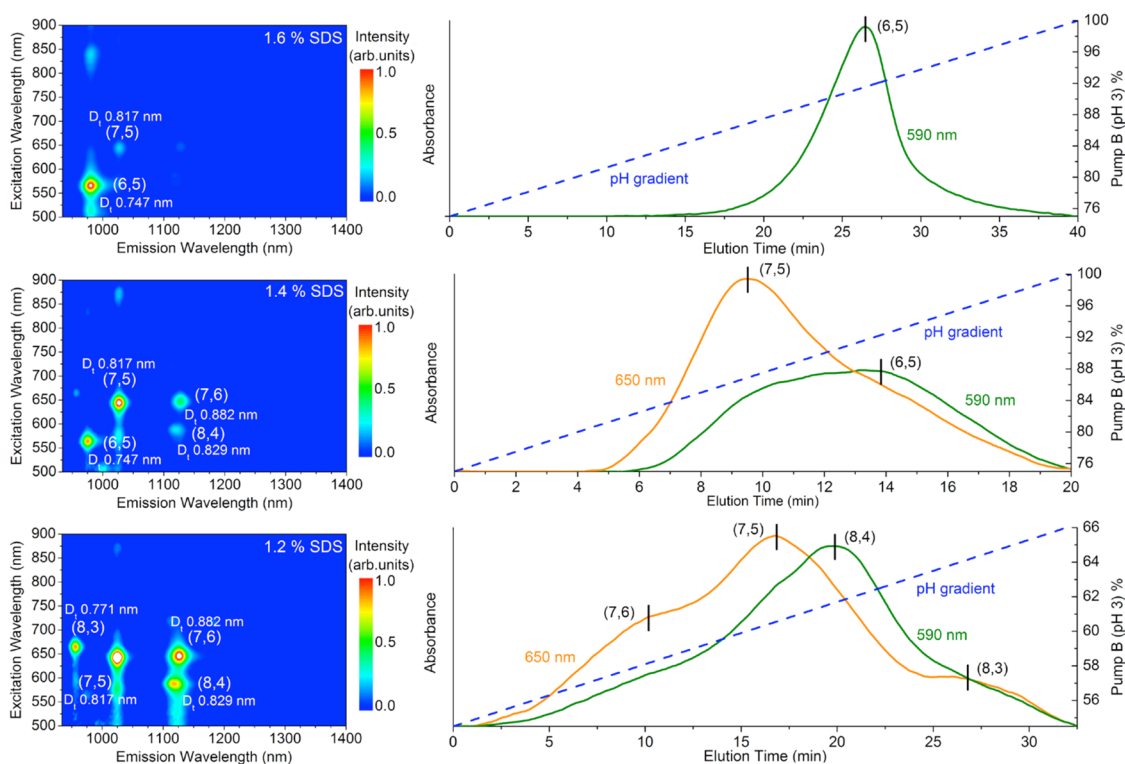
Figure 3. Photoluminescence contour maps of SWCNTs absorbed to the Sephacryl gel at 1.6, 1.4, and 1.2 wt % SDS ("starting materials") and the corresponding elution profile diagram.
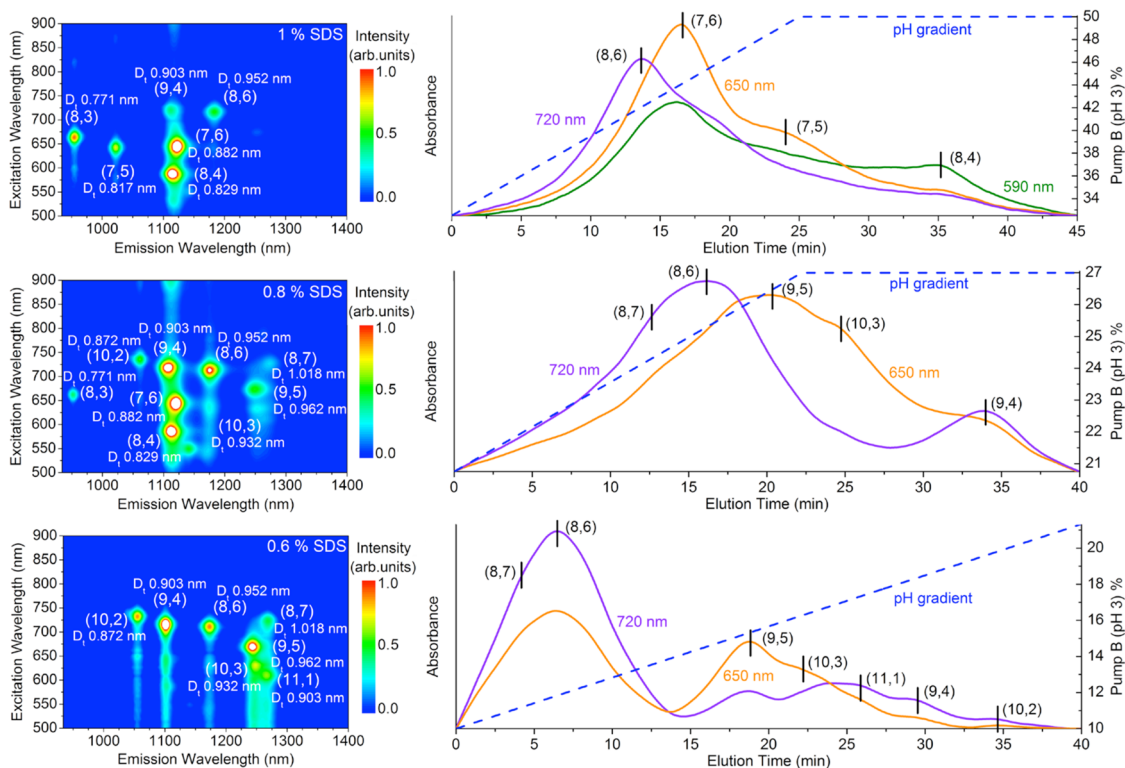

Figure 4. Photoluminescence contour maps of SWCNTs absorbed to the Sephacryl gel at 1, 0.8, and 0.6 wt % SDS ("starting materials") and the corresponding elution profile diagram.

under 1.6 wt % SDS by setting pump A to 100% at a pumping rate of 2 mL/min for 1.5 h. Fifteen milliliters of raw HiPco material (adjusted to 1.6 wt % SDS) was

then pumped onto the Sephacryl gel and washed through with a further 1.6 wt % SDS. Importantly the "flow through" material was collected for subsequent

separation steps. While maintaining a flow rate of 2 mL/min the quaternary pump was then used to bring the column under reduced pH conditions by setting pumps A and B in a ratio of 15:75% and holding there for 1.5 h. As depicted in Figure 3 the pumping ratio was then linearly varied to 100% pump B (pH 3, 1.6 wt % SDS) over a period of 40 min. By setting the diode array detector to 590 and 650 nm the elution of (6,5) SWCNTs can then be seen as a peak centered at 26 min (pH = 3.04) beginning at approximately 20 min (pH = 3.06) and ending at 35 min (pH = 3.01). Despite the presence of (7,5) and (7,6) in the "start material", these species were not observed to elute from the column in this region, a typical observation for (n, m) species in low concentration, such as (7,6) and (8,4) in the 1.4 wt % SDS separation. However, upon comparison of the absorption spectra for (6,5) presented in Figure 1 (1.6 wt % SDS) to that of Figure 7, it can be seen that the purity of (6,5) is dramatically improved due to the removal of (7,5) and (7,6). This procedure was then repeated for SDS concentrations of 1.4−0.6 wt % SDS upon sequentially adjusting the SDS concentration of the "flow through" material. In each case the SDS concentrations of pumps A and B were also adjusted. Upon looking at the 1.4 wt % SDS separation, a "start material" with now significantly more (7,5) and less (6,5) is obtained. This is reflected in the elution diagram with a larger peak of (7,5) eluting at 9.5 min (pH = 3.06) and a smaller peak for (6,5) at 14 min (pH = 3.03). In reading the elution diagrams in Figures 3 and 4, it is important to keep in mind that despite the pump ratio being varied linearly the real pH gradient is in fact asymptotic in nature. Furthermore time 0 is after the 1.5 h equilibrium time.

Despite 1.6 and 1.4 wt % SDS "start materials" being separated in the same pH window, i.e., a linear gradient between 75% pump B (pH = 3.12) and 100% pump B (pH = 3), as the SDS concentration was further reduced from 1.2 to 0.6 wt % SDS the required pH window for elution was observed to shift. For example 1.2, 1, 0.8, and 0.6 wt % SDS "start materials" were separated in the linear pump regime of 55−66% (pH 3.25−3.18), 33−50% (pH 3.48−3.30), 20−27% (pH 3.69−3.56), and 10−21% (pH 4−3.67) pump B. This is in agreement with our previous work,[16] where we showed that the elution of relatively small diameter SWCNTs scaled relative to reductions in pH. However, in our previous work we varied the pH from 4 to 1 in order to elute the entire HiPco (n, m) ensemble, whereas in the current work we can work in the pH regime 4−3. This difference is attributed to previously working with a much larger Sephacryl gel column (14 cm instead of a 2 cm bed height) and an underestimation of the solvent volume required to equilibrate such a large gel to a set pH value and the speed at which SWCNTs transverse through the column. The use of the GPC system to apply a controlled gradient, a smaller column, and the ability to monitor UV in situ have allowed us to now be
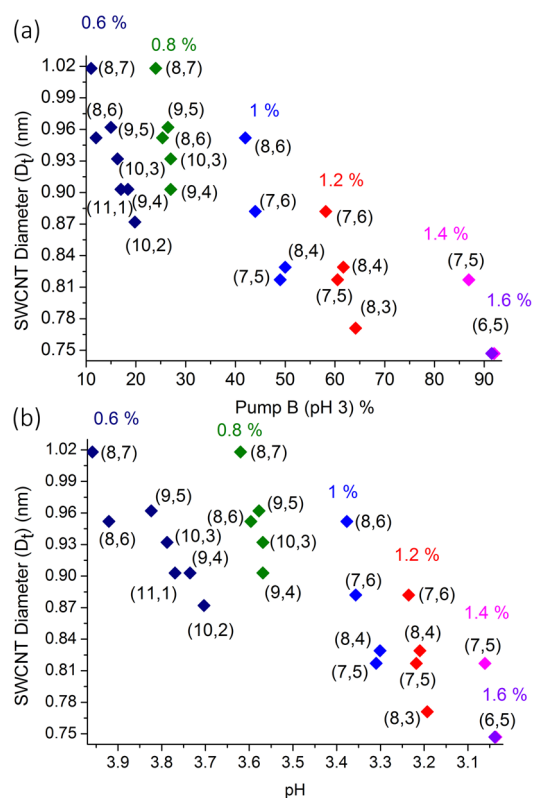

Figure 5. Single-walled carbon nanotube (SWCNT) diameter (D_t) dependence upon (a) the pumping rate of pump B and (b) the corresponding pH. The SDS concentration is color-coded.

more precise with the required pH for (n, m) species elution. This is summarized in Figure 5, where the SWCNT diameter is plotted against (a) the required percentage of pump B (pH 3) and (b) the corresponding pH, where the peak position for each (n, m) species was taken from the elution diagram.

Closer examination of the elution diagrams in Figures 3 and 4 reveals the presence of certain (n, m) species across multiple SDS concentration regimes. A good example is the (7,5) SWCNT, which is present in 1.4, 1.2, and 1 wt % SDS. Rather than having a fixed pH for elution, the position of (7,5) shifts from pH 3.06 to pH 3.22 to pH 3.30 for 1.4, 1.2, and 1 wt % SDS concentrations, respectively. This shift in position tends to rule out the possibility for SWCNT doping or band structure dependent oxidation[21] being responsible for (n, m) species elution. Rather we hypothesize in agreement with the AFM data presented in Figure 2 that there exists different types of (7,5) within the raw HiPco material following sonication. This (7,5) material has different lengths and more importantly different surfactant wrapping of the nanotube and consequently different overall interaction strength and (interfacial area per length) with the Sephacryl gel. With this in mind, it is therefore unsurprising that the elution point of (7,5) at different SDS concentrations can change. Of course, another possible explanation is
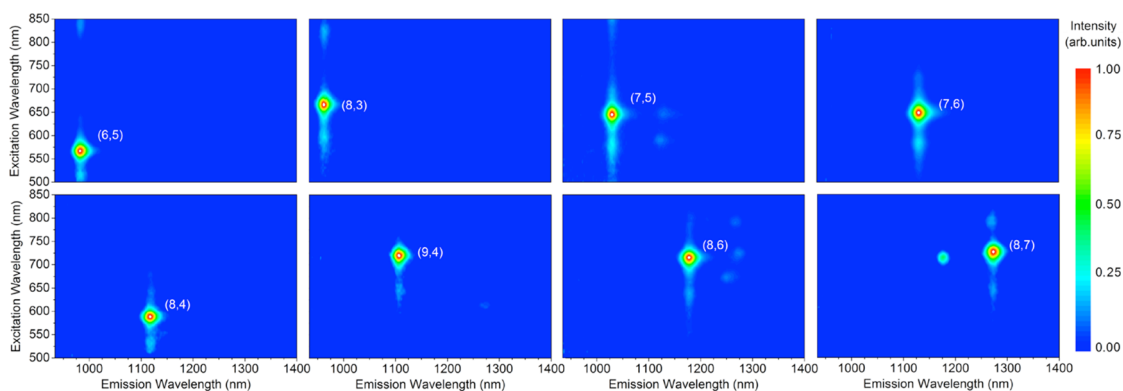
Figure 6. Photoluminescence contour maps of (*n*, *m*) fractions obtained from an automated gel permeation chromatography (GPC) system.

simply the differing size, shape, and or thickness of the SDS micelle around the SWCNT at different SDS concentrations. The interaction strength of the SWCNT will therefore also be different and may require reduced micelle modification, be it through band structure dependent oxidation or 1-dodecanol addition, for (*n*, *m*) species elution. However, we note that it is occasionally possible to elute the same (*n*, *m*) species at two different pH points in a fixed SDS concentration. For example (7,5) in 1 wt % SDS is often found to elute at pH 3.30 (23 min as shown in Figure 4) and also at pH 3.22, which would be the same pH point as required for 1.2 wt % SDS. Such an observation gives further weight to our speculation that the interfacial area and nonmonotonic length distribution of SWCNTs are also important. Another possible explanation is the potential for enantiomers; however we have made no attempt to verify this and believe it to be unlikely.

Contrary to typical elution diagrams from standard GPC separations the various peaks associated with different (*n*, *m*) species are seen to have a large degree of overlap, making it not immediately obvious how this method is conducive to the preparation of (*n*, *m*) pure samples. The trick lies in choosing the appropriate "starting material" for the (*n*, *m*) species desired. For example, it is always much easier to harvest an (*n*, *m*) species that has either the smallest or largest diameter in an ensemble under investigation. The largest diameter species always elutes first from the Sephacryl gel and the smallest last. These fractions are typically free of all other (*n*, *m*) species in the "starting material", and an automated collection of beginning or end conditions is easily achieved. For example if (7,5) was the desired SWCNT, this is better prepared from 1.4 wt % SDS, where it is the leading species compared to 1.2 and 1 wt % SDS, where (7,5) is surrounded by other (*n*, *m*) species. Likewise (8,6) is much better prepared from 1 wt % SDS compared to 0.8 or 0.6 wt % SDS. In the case of "starting materials" with many more (*n*, *m*) species present the separation can begin to break down due to the presence of multiple SWCNT with very similar or indeed the same diameter such as (9,4)

and (11,1) as present in 0.6 wt % SDS. In this case we were unable to successfully separate these species, regardless of how finely the pH gradient was adjusted. Therefore when attempting to purify (9,4), it is better to choose a 0.8% SDS "starting solution" where it represents the smallest diameter SWCNT species. It should be noted that (7,6) and (8,4) were not found to elute in this pH regime. Furthermore, it should be noted that due to the decreased concentration of the "starting material" and the strong interaction of the SWCNTs, we were not able to perform a separation with 0.4 wt % SDS "starting material". Work to prepare the larger diameter SWCNTs is now under way; however it is expected that this goal is best achieved by choosing a different raw material such as that from laser ablation, where the larger diameter SWCNTs are in greater proportion.

Despite the inability to prepare pure suspensions of the larger diameter SWCNTs, we are now able to reproducibly sort eight different (*n*, *m*) species from the HiPco raw material as shown by photoluminescence contour maps in Figure 6 and the corresponding absorption measurements in Figure 7. Normalized raw absorbance data can also be found in Figure S4 of the Supporting Information. Furthermore, the fitted peak area from absorption measurements was used to calculate (*n*, *m*) purity, where the major (*n*, *m*) contribution was taken as a ratio of all other peaks. For this calculation only the first optical transition peak (S_{11}) was taken and the absorbance cross section was assumed to be identical across all (*n*, *m*) species. Purity data can be found in Table 1. In this work we have managed to routinely prepare eight (*n*, *m*) species with a purity of 61−95%. This is an improvement compared to our previous work, where we isolated 10 (*n*, *m*) species with a purity of 19−30%, with only two species ((8,6) and (6,5)) on the level of 60−70%. This highlights the benefit of having a reduced (*n*, *m*) species "starting material" and also precise control over the pH. It should be noted that between 450 and 550 nm nanotube-related transitions are seen in the absorption spectra. This absorption regime is typically associated with
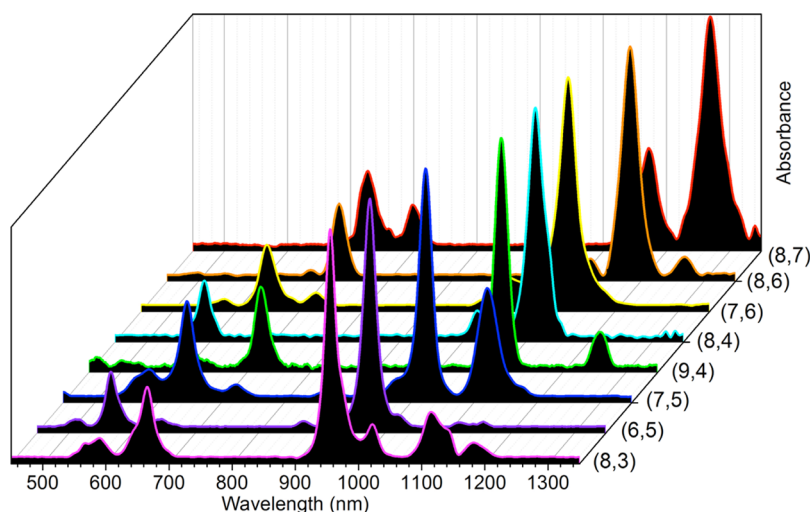
Figure 7. Absorption spectra corresponding to fractions displayed in Figure 6.

TABLE 1. Purity of (n, m) Species Obtained from the Gel Permeation Chromatography (GPC) System

	(n, m) species							
	(8,3)	(6,5)	(7,5)	(9,4)	(8,4)	(7,6)	(8,6)	(8,7)
purity (%)	64	92	61	76	76	95	88	77

m-SWCNTs; however, due to an overlap of the third interband transition (S33) of the HiPco s-SWCNTs, it is difficult to estimate the m-SWCNT concentration. Preliminary electrical transport measurements indicate a metallic/semiconducting-SWCNT ratio equivalent to standard Sephacryl S-200 separations. That is to say that 90% of all fabricated devices showed semiconducting behavior with an on/off ratio of at least 1 order of magnitude. Our fabricated devices had a gap width comparable to the average nanotube length and a 1 μm contact width with a nanotube density of 10−20 CNTs/μm. From this we estimate the degree of metallic/semiconducting-SWCNT separation to be >95%. In comparison to the initial work of Liu et al.,[10] who were able to obtain 13 different (n, m) species with purities of 39−94% our method is shown to afford superior purities. However, in comparison to the latest work in 2013 of Liu et al.,[15] who modified their initial approach to include temperature control and were able to prepare seven (n, m) species with a purity of 56−93%, our work is equivalent to the current state of the art. A trend also seen upon comparison to the work of Tvrdy et al.,[13] who prepared (6,5), (7,3), (7,5), and (7,6) with purities of 96, 87, 56, and 64%, respectively. For an effective sorting method it is also important to assess the yield of the various (n, m) species. While we did not measure this directly, it is noted that the starting solution has a mass on the milligram level and the final (n, m) fractions were below the μg level. This obvious problem in yield is due to only collecting beginning or

end material, with a large portion of the eluent discarded. In the future we hope to be able to have less overlap of the individual (n, m) species and hence dramatically improve our yield. Upon eliminating the need for centrifugation in our method, a question is also raised as to the fate of impurity carbon and/or non-SWCNT material. This material is typically removed by centrifugation and must show up somewhere in our separation. We note that during the 1.5 h equilibration time (prior to the collection of (n, m) species) material is observed to elute from the column. Upon measuring absorbance spectra, this material is typically poorly defined or has no SWCNT absorption characteristics, and we have therefore attributed it to be such impurity carbon material.

Our method allows for routine time based separation (dependent on set pump conditions) of (n, m) species, where the users know in which region of the elution diagram they must collect pure (n, m) fractions. This is something that can easily become automated, as in our case where we plan to take an automated fraction collector and have a completely automated process from the injection of raw HiPco material through to the collection of (n, m) pure species. Upon maintaining the sonication conditions constant, the elution time and position of each (n, m) species at a set SDS concentration remained constant between experimental runs. Additionally, the gel column was found to be reusable with preliminary tests, showing the gel to be reusable up to 10 times. This is important if such a method is to become industrially applicable. As discussed by Strano et al.,[13] the (n, m) separation of SWCNTs is a process that is easily scalable to arbitrary large volumes of Sephacryl gel and raw material, and we believe our automated method will therefore form a crucial step toward the routine separation of SWCNTs. However, it is important to remember that upon increasing the separation volume (amount of gel and

raw material) the elution timing will need to be adjusted/optimized to accommodate for the larger gel volume and the time required for the gel to reach pH equilibrium. In our initial experiments a 3-fold increase in gel volume has resulted in roughly a 3−4-fold increase in pH equilibrium time and therefore also the time required for a separation. Furthermore, factors such as flow rate and pressure applied to an increased gel bed volume will need to be optimized before a truly large-scale separation can be realized. Ideally one should keep the column length the same and scale the area with a fixed flow rate per area of gel. It is also likely that the next step in (n, m) purity will also come by combining the methodology of several groups into one process, for example, the use of a gel permeation chromatography system to vary not only pH and SDS concentration but also gel/eluent temperature.

CONCLUSION

In conclusion, we have shown the (n, m) separation of eight different SWCNT species with a purity of 61−95%. This separation was achieved without the use of centrifugation and with the use of a gel permeation system. The ability to achieve high-purity (n, m) suspensions routinely with use of a computer-controlled and automated system, without the need for specialist equipment, will hopefully allow many new research groups access to pure (n, m) suspensions and further foster development in the field of SWCNTs.

METHODS

HiPco SWCNT raw material (NanoIntegris) was used throughout this work. In order to prepare starting suspensions, 20 mg of raw SWCNT material was suspended in 80 mL of H_2O with 2 wt % sodium dodecyl sulfate using a tip sonicator (Weber Ultrasonics, 35 kHz, 500 W, in continuous mode) applied for 15 h at ∼20% power. During sonication, the suspension was placed in a water-circulation bath to aid cooling.

Gel filtration was performed using 7 mL of the Sephacryl S-200 gel filtration medium (Amersham Biosciences) in a commercially available water-jacketed liquid chromatography column (XK 16/20, GE Healthcare) with 16 mm inner diameter and 20 cm length. After applying slight compression the gel yielded a final height of 2 cm. An Accel 250 LC water chiller (Thermoscientific) was then used to maintain the column temperature at 23 °C. Separation was performed with a SECcurity gel permeation chromatography 1260 Infinity system (Agilent Technologies). This consisted of a quaternary pump (G1311B), an autosampler (G2258A), a diode array detector (G1315D), and a fraction collector (CHF122SC, Advantec). The GPC system was controlled via the WinGPC UniChrom v.8.1 software (Polymer Standards Service GmbH). The diode array detector was used to monitor two fixed wavelengths at either 590, 650, or 720 nm during an experimental run with complete spectra measured from 190 to 950 nm with a bandwidth of 10 nm and a step width of 8 nm. Following sonication the SDS concentration of the raw material was adjusted to the appropriate concentration by the addition of H_2O. A 15 mL amount of SWCNT suspension was then pumped onto the gel column and washed through with further SDS. Importantly the "flow through" material was collected for subsequent dilution and separation steps. After loading the gel with SWCNTs the quaternary pump was used to mix SDS (pump A) with SDS at pH 3 (pump B) (prepared through the addition of the appropriate concentration of HCl). While maintaining a flow rate of 2 mL/min the quaternary pump was then used to bring the column under reduced pH conditions by setting pumps A and B to the appropriate ratio and holding there for 1.5 h. Once the gel reached equilibrium conditions, an appropriate pH gradient was applied to the gel over a period of 20−40 min, and 2 mL fractions were collected.

For spectroscopic characterization, the doping effect of reduced pH was removed by addition of 1 drop of 25% w/w tetramethylammonium hydroxide aqueous solution (Alfa Aesar) to each 2 mL fraction. This resulted in a SWCNT suspension that was slightly basic and ensured no spectroscopic features were missed. UV−vis−NIR absorption spectra were recorded on a Varian Cary 500 spectrophotometer. For ease of comparison, background subtraction of the UV−vis spectra was performed using the freeware fityk (http://fityk.nieto.pl/). Photoluminescence maps were measured in the emission range ∼900−1700 nm and excitation range 500−950 nm (scanned in 3 nm steps) using a modified FTIR spectrometer (Bruker IFS66) equipped with a liquid nitrogen cooled Ge-photodiode and a monochromatized excitation light source as described elsewhere.[26]

Atomic force microscopy was performed in an air environment with a multimode head and Nanoscope III controller (Digital Instruments), operating in tapping mode. Commercially available silicon cantilevers with fundamental resonance frequency of 320 kHz were used. Images of 10 × 10 μm topographic (height) and amplitude were collected simultaneously at a scan rate of 0.5 Hz with the parameters' set point, amplitude, and feedback control optimized for each sample. A 0.7 μL sample of SWCNT solution was then dropped onto a 1 cm^2 silicon wafer and spin coated at 1500 rpm for 60 s.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Photoluminescence contour maps of raw HiPco SWCNT material and SWCNTs absorbed to the Sephacryl gel at 0.4 wt % SDS. Absorption spectra of raw HiPco SWCNT material (flow through) following sequential reduction of the SDS concentration and separated (n, m) species. Histograms of the SWCNT length distribution for the various "starting materials", as determined by AFM. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

1. Wang, H.; Wang, B.; Quek, X. Y.; Wei, L.; Zhao, J. W.; Li, L. J.; Chan-Park, M. B.; Yang, Y. H.; Chen, Y. A. Selective Synthesis of (9,8) Single Walled Carbon Nanotubes on Cobalt Incorporated TUD-1 Catalysts. *J. Am. Chem. Soc.* **2010**, *132*, 16747−16749.
2. Liu, J.; Wang, C.; Tu, X. M.; Liu, B. L.; Chen, L.; Zheng, M.; Zhou, C. W. Chirality-Controlled Synthesis of Single-Wall Carbon Nanotubes Using Vapour-Phase Epitaxy. *Nat. Commun.* **2012**, *3*, 1199.
3. Bachilo, S. M.; Balzano, L.; Herrera, J. E.; Pompeo, F.; Resasco, D. E.; Weisman, R. B. Narrow (n,m)-Distribution of Single-Walled Carbon Nanotubes Grown Using a Solid

Supported Catalyst. *J. Am. Chem. Soc.* **2003**, *125*, 11186–11187.

4. Tu, X. M.; Manohar, S.; Jagota, A.; Zheng, M. DNA Sequence Motifs for Structure-Specific Recognition and Separation of Carbon Nanotubes. *Nature* **2009**, *460*, 250–253.

5. Arnold, M. S.; Stupp, S. I.; Hersam, M. C. Enrichment of Single-Walled Carbon Nanotubes by Diameter in Density Gradients. *Nano Lett.* **2005**, *5*, 713–718.

6. Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. Sorting Carbon Nanotubes by Electronic Structure Using Density Differentiation. *Nat. Nanotechnol.* **2006**, *1*, 60–65.

7. Ghosh, S.; Bachilo, S. M.; Weisman, R. B. Advanced Sorting of Single-Walled Carbon Nanotubes by Nonlinear Density-Gradient Ultracentrifugation. *Nat. Nanotechnol.* **2010**, *5*, 443–450.

8. Moshammer, K.; Hennrich, F.; Kappes, M. M. Selective Suspension in Aqueous Sodium Dodecyl Sulfate According to Electronic Structure Type Allows Simple Separation of Metallic from Semiconducting Single-Walled Carbon Nanotubes. *Nano Res.* **2009**, *2*, 599–606.

9. Blum, C.; Sturzl, N.; Hennrich, F.; Lebedkin, S.; Heeg, S.; Dumlich, H.; Reich, S.; Kappes, M. M. Selective Bundling of Zigzag Single-Walled Carbon Nanotubes. *ACS Nano* **2011**, *5*, 2847–2854.

10. Liu, H. P.; Nishide, D.; Tanaka, T.; Kataura, H. Large-Scale Single-Chirality Separation of Single-Wall Carbon Nanotubes by Simple Gel Chromatography. *Nat. Commun.* **2011**, 2.

11. Blanch, A. J.; Quinton, J. S.; Shapter, J. G. The Role of Sodium Dodecyl Sulfate Concentration in the Separation of Carbon Nanotubes Using Gel Chromatography. *Carbon* **2013**, *60*, 471–480.

12. Khripin, C. Y.; Fagan, J. A.; Zheng, M. Spontaneous Partition of Carbon Nanotubes in Polymer-Modified Aqueous Phases. *J. Am. Chem. Soc.* **2013**, *135*, 6822–6825.

13. Tvrdy, K.; Jain, R. M.; Han, R.; Hilmer, A. J.; McNicholas, T. P.; Strano, M. S. A Kinetic Model for the Deterministic Prediction of Gel-Based Single-Chirality Single-Walled Carbon Nanotube Separation. *ACS Nano* **2013**, *7*, 1779–1789.

14. Jain, R. M.; Howden, R.; Tvrdy, K.; Shimizu, S.; Hilmer, A. J.; McNicholas, T. P.; Gleason, K. K.; Strano, M. S. Polymer-Free Near-Infrared Photovoltaics with Single Chirality (6,5) Semiconducting Carbon Nanotube Active Layers. *Adv. Mater.* **2012**, *24*, 4436–4439.

15. Liu, H. P.; Tanaka, T.; Urabe, Y.; Kataura, H. High-Efficiency Single-Chirality Separation of Carbon Nanotubes Using Temperature-Controlled Gel Chromatography. *Nano Lett.* **2013**, *13*, 1996–2003.

16. Flavel, B. S.; Kappes, M. M.; Krupke, R.; Hennrich, F. Separation of Single-Walled Carbon Nanotubes by 1-Dodecanol-Mediated Size-Exclusion Chromatography. *ACS Nano* **2013**, *7*, 3557–3564.

17. Paruchuri, V. K.; Nalaskowski, J.; Shah, D. O.; Miller, J. D. The Effect of Cosurfactants on Sodium Dodecyl Sulfate Micellar Structures at a Graphite Surface. *Colloid Surf. A* **2006**, *272*, 157–163.

18. Paruchuri, V. K.; Nguyen, A. V.; Miller, J. D. Zeta-Potentials of Self-Assembled Surface Micelles of Ionic Surfactants Adsorbed at Hydrophobic Graphite Surfaces. *Colloid Surf. A* **2004**, *250*, 519–526.

19. Tummala, N. R.; Striolo, A. Curvature Effects on the Adsorption of Aqueous Sodium-Dodecyl-Sulfate Surfactants on Carbonaceous Substrates: Structural Features and Counterion Dynamics. *Phys. Rev. E* **2009**, *80*, 021480.

20. Duque, J. G.; Densmore, C. G.; Doorn, S. K. Saturation of Surfactant Structure at the Single-Walled Carbon Nanotube Surface. *J. Am. Chem. Soc.* **2010**, *132*, 16165–16175.

21. Hirano, A.; Tanaka, T.; Urabe, Y.; Kataura, H. pH- and Solute-Dependent Adsorption of Single-Wall Carbon Nanotubes onto Hydrogels: Mechanistic Insights into the Metal/Semiconductor Separation. *ACS Nano* **2013**, *7*, 10285–10295.

22. Clar, J. G.; Silvera Batista, C. A.; Youn, S.; Bonzongo, J. C.; Ziegler, K. J. Interactive Forces between Sodium Dodecyl Sulfate-Suspended Single-Walled Carbon Nanotubes and Agarose Gels. *J. Am. Chem. Soc.* **2013**, *135*, 17758–17767.

23. Heller, D. A.; Mayrhofer, R. M.; Baik, S.; Grinkova, Y. V.; Usrey, M. L.; Strano, M. S. Concomitant Length and Diameter Separation of Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* **2004**, *126*, 14567–14573.

24. Hennrich, F.; Krupke, R.; Arnold, K.; Stutz, J. A. R.; Lebedkin, S.; Koch, T.; Schimmel, T.; Kappes, M. M. The Mechanism of Cavitation-Induced Scission of Single-Walled Carbon Nanotubes. *J. Phys. Chem. B* **2007**, *111*, 1932–1937.

25. 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.* **2003**, *3*, 1235–1238.

26. Lebedkin, S.; Hennrich, F.; Kiowski, O.; Kappes, M. M. Photophysics of Carbon Nanotubes in Organic Polymer-Toluene Dispersions: Emission and Excitation Satellites and Relaxation Pathways. *Phys. Rev. B* **2008**, *77*, 165429.