

Using Nonionic Surfactants for Production of Semiconductor-type Carbon Nanotubes by Gel-based Affinity Chromatography

Invited Article

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Abstract Single-wall carbon nanotubes (SWCNTs) have remarkable properties based on their electronic properties, i.e., metallic or semiconducting types, but as-grown SWCNTs contain a mixture of both types. Presented here is an improved and detailed method for producing highly enriched semiconducting SWCNTs from a colloidal suspension of as-grown SWCNTs through agarose gel column-based affinity chromatography. After a 2 wt% sodium dodecyl sulphate (SDS) aqueous dispersion of SWCNTs is passed through the gel column, metal-type SWCNTs preferentially elute out using a 1.5 wt% SDS solution. Semiconductor-type SWCNTs are subsequently recovered from the column using a 2 wt% Pluronic F77 surfactant solution eluent. The semiconductor-enriched fraction purity is in the 90-95% range, based on detailed UV-vis-NIR absorption and resonant Raman spectroscopy

characterization of the particulate suspension. Semiconductor-type SWCNTs are recovered in solid form by evaporating the suspension fluid, and heating the dried sample in air to a temperature just above the Pluronic decomposition temperature. Using Pluronic and other nonionic-type surfactants can aid the scalability of the chromatographic production of semiconducting SWCNT samples.

Keywords Carbon Nanotube, Semiconductor, SWCNT, Separation, Affinity Chromatography

1. Introduction

Single-wall carbon nanotubes (SWCNTs) have remarkable properties such as high electrical conductivity

and chemical reactivity based on whether they are metallic or semiconducting. Metallic SWCNTs are the best electrical conductor on a unit mass basis, and semiconducting SWCNTs have potential applications as fluorescent tags in nanomedicine and as nanoelectronic devices such as field effect transistors (FETs) [1-7]. However, SWCNTs are normally synthesized containing metallic and semiconducting types, and are handled as a powder comprised of huge aggregates of individual nanotubes. Methods to produce individual, unaggregated nanotubes of mostly one type exist, but the quantities produced are small. These methods are based on various separation schemes [8-12].

One approach to circumvent the low-yield problem of separation processes is to synthesize SWCNTs of only the semiconductor type. There exists one commercial source of preferentially semiconducting SWCNTs (with some metallic SWCNTs present, especially from the (6,6) and (7,7) families), which is synthesized by SouthWest NanoTechnologies through the "CoMoCAT" process [13, 14]. These SWCNTs have very small diameters (~0.7 nm), and larger-diameter semiconducting SWCNTs are not available. The second approach to circumvent the low-yield problem of separation processes is to improve the separation efficiency. The separation of SWCNTs into metallic and semiconducting types (metal/semiconductor or "M/S" separation) has been studied for the better part of the last decade, yet there is still no established method that can provide high-purity M- and S-enriched SWCNT samples in large quantities. Column chromatography is a scalable technique potentially capable of producing highly enriched semiconducting SWCNTs through a purification approach, using SWCNTs synthesized from HiPco, laser ablation, and other processes.

Agarose gel has been used to separate DNA strands and proteins through techniques such as column affinity chromatography and gel electrophoresis [15-19]. The dimensional similarities of SWCNTs and DNA/proteins suggest the possible use of agarose gel column chromatography for SWCNT separation. In 2009, Tanaka *et al.* reported the successful use of agarose gel column chromatography to perform M/S separation of SWCNTs [20]. A SWCNT suspension in a sodium dodecyl sulphate (SDS) solution was prepared by sonication of as-grown SWCNTs in the fluid and ultracentrifugation to remove bundles of aggregated SWCNTs and impurities such as the SWCNT growth catalyst. The SWCNT suspension was subjected to agarose gel column chromatography to produce purified suspensions of metallic and semiconducting SWCNTs after elution with SDS and sodium deoxycholate (DOC) aqueous solutions, respectively (Figure 1). This separation protocol took >24 hours to perform (including preparation of the SWCNT parent sample), yielding reported purities of 90-95% for the S-enriched suspension.

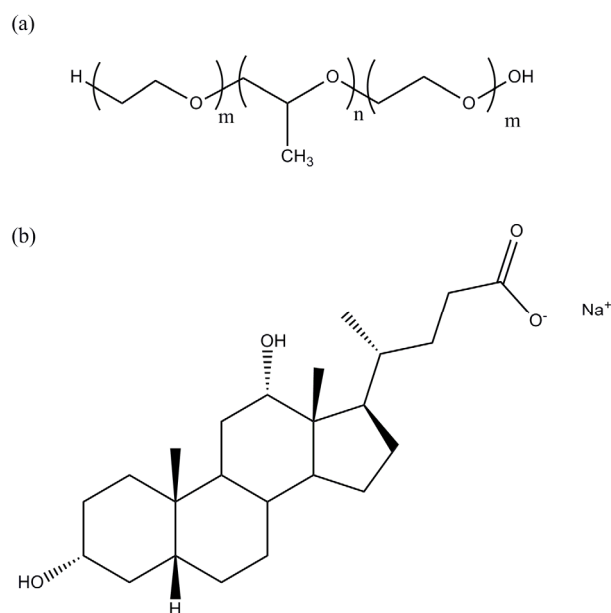


Figure 1. General structure of (a) Pluronic triblock copolymer and (b) sodium deoxycholate (DOC) compounds

Here, we demonstrate an improved method that takes less than six hours and that consistently yields S-enriched fractions with purity levels ~ 95%. We prepared SDS suspensions of HiPco SWCNTs and used SDS and Pluronic surfactants to elute out the M- and S-enriched fractions, respectively. Recently, Ziegler and co-workers reported how selective adsorption of surfactant-stabilized SWCNTs onto agarose gel is responsible for M/S separation [12]. Pluronic is a family of commercially available nonionic polyethylene oxide-polypropylene oxide-polyethylene oxide surfactants that have not been used for chromatographic purification of SWCNTs before, and in this research we hypothesized that Pluronic is more effective than DOC at displacing the surfactant-stabilized SWCNTs bound to the agarose gel. We performed UV-vis-NIR and resonant Raman scattering spectroscopies to assess the SWCNT types and to quantify the purities of the resulting suspensions. We recovered surfactant-free S-enriched SWCNTs by calcining the dried SWCNT suspension, eliminating the need for vacuum filtration.

2. Materials and Methods

2.1 Materials

HiPco SWCNTs (nanotubes produced through the High Pressure Carbon Monoxide process, Batch HPR 94 with average diameter 1.1 ± 0.1 nm) were obtained from Rice University and laser ablation SWCNTs (Average diameter 1.3 ± 0.1 nm) were obtained from NanoPower Research Labs at the Rochester Institute of Technology. The as-produced HiPco SWCNTs are comprised almost entirely of bundles [16]. Sodium dodecyl sulphate (SDS,

NaC₁₂H₂₅SO₄, >99%), Pluronic F68 (>99%), Pluronic F77 (>99%) and Pluronic F108 (>99%) were purchased from Sigma-Aldrich. Agarose gel (Sephacrose 2B, 60-200- μ m mean bead diameter) was procured from GE Healthcare. Deionized water from a Barnstead NANOpure Diamond purifier (resistivity > 18 M Ω cm⁻¹) was used for all experiments. All chemicals were used as received unless otherwise noted.

2.2 SWCNT Parent Sample Preparation

The SWCNTs (20 mg) were dispersed in a 2 wt% SDS aqueous solution (20 mL) at an initial SWCNT concentration of 1 g-SWCNT L⁻¹-solution. Bath sonication using a Cole-Palmer 60W ultrasonic cleaner (Model #08849-00) for 30 min was followed by probe sonication for 2 hr using a Cole-Palmer 500W ultrasonic processor (Model #CPX-600, 1/4" probe, 35% amplitude) at a water bath temperature of 15 °C (Figure S1). 10 mL of the resulting suspension was ultracentrifuged in a PN 7030 centrifuge tube from Seton Scientific for 2 hr at 208,400 g (average) using a Sorvall Discovery 100SE ultracentrifuge with a TH-641 swinging-bucket-type titanium rotor, which removed large SWCNT bundles and SWCNT impurities. The upper 7.5 mL of the supernatant was used as the stock SWCNT suspension, i.e., the SWCNT parent sample used for separation.

The SWCNT concentration was determined by performing a mass balance between the top 7.5 mL and the discarded 2.5 mL. We account for the increased weight due to the surfactant by having a control of just the surfactant solution undergoing sonication and ultracentrifugation and weighing this sample. This calculation gave us a value of ~0.265 g-(SWCNT+SDS) L⁻¹-solution in the stock suspension. We then performed thermogravimetric analysis of the suspension to plot derivative wt% vs. temperature. The peak for SDS and SWCNT were fitted using a Lorentzian-type fitting algorithm in OriginPro 8.5 and the ratio of area under each peak was used to calculate the approximate ratio of SDS to SWCNT in the suspension to get a SWCNT concentration ~0.25 g-SWCNT L⁻¹-solution in the parent sample.

2.3 SWCNT M/S Separation

A 10 mL medical plastic syringe was used as the chromatography column. Agarose gel was added to the top of the syringe with the plunger removed. Cotton was used to plug the bottom of the syringe to prevent agarose gel loss. The gel was added to an initial height of 9 cm in the column, followed by passing 15-20 mL of 1.5 wt% SDS solution through the column. The gel column was then left to settle and dry to give a final column height of ~5-7 cm, with a 6 cm column providing the best M/S

separation performance. 1 mL of the SWCNT parent sample was carefully added to the top of the column, followed by a series of 2 mL eluent (1.5 wt% SDS solution) until no more colour was seen in the eluate by eye (Figure 2). The collected fluid was pink in colour. A series of 2 mL eluent (2 wt% Pluronic F77 solution) was then used until no more colour was seen in the eluate, generating a fluid that was green in colour. The separation takes no more than an hour once the gel has been added to the column.

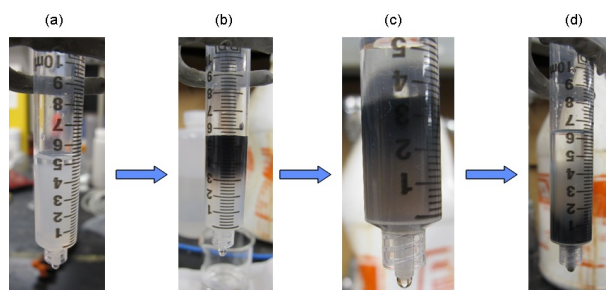


Figure 2. Illustration of agarose gel column chromatography applied to the SWCNT parent sample: (a) Agarose gel added to the column and equilibrated with SDS/H₂O, (b) 1 mL SWCNT parent sample added to the top of the column, (c) SDS solution preferentially elutes metallic SWCNTs and (d) Pluronic solution preferentially elutes semiconducting SWCNTs

2.4 Characterization Techniques

Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectroscopy: UV-vis-NIR absorption spectroscopy of the samples was performed using a Shimadzu UV-3101PC double beam scanning spectrophotometer in the range of 400-1350 nm with 1 nm interval and a quartz cuvette (10 mm path length).

Resonant Raman spectroscopy: Resonant Raman spectroscopy of all samples was performed in a Renishaw *inVia* Raman microscope fitted with a liquid sample holder. The samples were placed in quartz cuvettes and spectra were collected at excitation laser wavelengths of 514, 633, and 785 nm. All measurements were performed at room temperature and atmospheric pressure with an exposure time of 60 s with each measurement collected across 15 accumulations in a spectral range of 100-500 cm⁻¹.

Photoluminescence (PL) spectroscopy: Photoluminescence (PL) spectroscopy of the samples was performed using a NS1 NanoSpectralyzer (Applied NanoFluorescence) at 660 nm and 785 nm excitation wavelengths and emission spectra were collected in the range of 900-1400 nm using a 250 ms integration time across 10 acquisitions for each sample.

Thermogravimetric analysis (TGA): TGA was carried out with a TA instruments Q-600 Simultaneous TGA/DSC.

The samples were first heated to 100 °C in an ambient environment to remove most of the water present and the concentrated suspension was cooled to room temperature to be used for TGA. Samples were heated at a ramp rate of 10 °C/min from 25 °C to 100 °C, kept isothermal for 10 minutes, and then heated again at a ramp rate of 5 °C min⁻¹ to a final temperature of 800 °C. All measurements were made under air (Matheson Trigas, research purity) at a flow rate of 90 standard centimetres cubed per minute (sccm).

3. Results and Discussion

The SWCNT suspension yielded two eluate suspensions after performing the chromatographic separation (Figure 1). The first eluate (Sample A, from SDS) was pink-coloured and the second eluate (Sample B, from Pluronic F77) was green (Figure 3). The colours were consistent with those reported for M-enriched and S-enriched HiPco SWCNT suspensions [21, 22]. The SWCNT concentrations were determined to be ~0.10 and ~0.15 g-SWCNT/L-solution, respectively, for samples A and B using a technique similar to the determination of SWCNT concentration for the parent sample. This separation method, from beginning (i.e., preparation of SWCNT/SDS parent sample) to end (i.e., recovery of two coloured suspensions), took <6 hr to perform, a significant time saving over the 25 hr duration of the recent methods described by Tanaka and co-workers [23, 24]. As another point of comparison, density gradient ultracentrifugation (DGU) was used to generate suspensions of chirally pure SWCNTs with concentrations to the order of ~10 mg L⁻¹ after ≥24 hr of processing time [7]. Our process readily yields 10× higher concentrations using 4× less time, but it is not chiral selective like DGU.

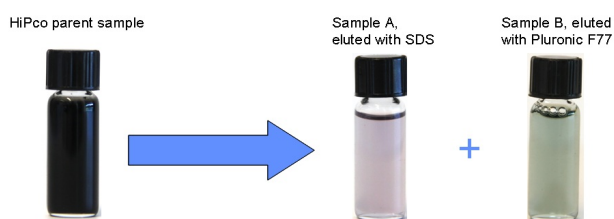


Figure 3. Pictures of the HiPco parent sample (~0.25 g-SWCNT/L-solution) and the separated samples obtained post-chromatography. Sample A (~0.10 g-SWCNT/L-solution), appears pink and Sample B (~0.15 g-SWCNT/L-solution) appears green.

3.1.1 UV-vis-NIR absorption spectroscopy analysis

UV-vis-NIR absorption spectroscopy was performed to verify that Sample A was metallic SWCNT-enriched and that Sample B was semiconducting SWCNT-enriched. The absorption spectrum of the parent sample showed peak features throughout the entire

wavelength range (Figure 4). The absorption peaks in the 400-650 nm range were assigned to the first optical transition of metallic SWCNTs of different diameters (M₁₁ band region) [20]. The peaks in the 620-920 nm and 920-1320 nm range were assigned to the second and first optical transitions of semiconducting SWCNTs of different diameters (S₂₂ and S₁₁ bands, respectively).

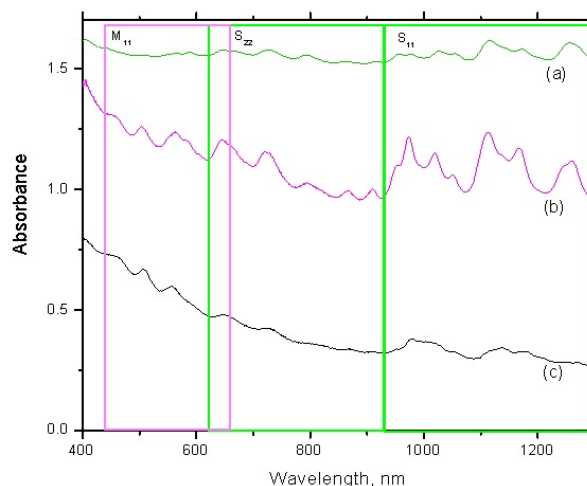


Figure 4. UV-vis-NIR spectra of (a) Sample B (eluted with Pluronic), (b) HiPco parent sample, and (c) Sample A (eluted with SDS). The spectra have been offset for clarity.

The spectra of Figure 4 are offset but not normalized or re-scaled; spectra without the offset are shown as Figure S2. Relative to the M₁₁ peaks, the S₁₁ and S₂₂ peaks of the HiPco sample diminished significantly in absorbance in Sample A, confirming that Sample A was M-enriched (Figure 3b). Sample B was S-enriched because the M₁₁ peak intensities decreased to nearly the background absorbance levels (Figure 3c). The M-enriched and S-enriched samples were determined to be 75-80% pure in metallic SWCNTs and 90-95% pure in semiconducting SWCNTs, respectively, using a fitting protocol described in the Electronic Supplementary Material (Figure S3). The SWCNT parent sample was 35-40% pure in the metallic type and the remainder the semiconducting type.

3.1.2 Resonant Raman spectroscopy analysis

Resonant Raman spectroscopy provided additional information about the M-enriched and S-enriched samples. "Small-diameter" metallic SWCNTs resonate at an excitation wavelength of 514 nm, such that Raman spectra collected at this excitation wavelength can reveal their presence, as seen in Figure 5(a) [25]. The spectrum of the parent sample showed three distinct peaks corresponding to the radial breathing modes of three different metallic SWCNTs. Based on the Kataura plots for HiPco SWCNTs [6, 25-27], the

following SWCNT types were identified: (7,7) (with a diameter of 0.95 nm), (8,5) (0.89 nm) and (9,3) (0.85 nm) (Figure 5a). The diameter of SWCNTs with a known chirality was calculated from the corresponding (n,m) index using the equation $d = \frac{0.246}{\pi} \sqrt{(n^2 + nm + m^2)}$ [25]. The electrical conduction type of SWCNTs was assigned in the following manner: metal-types are those with the difference between n and m to be a multiple of three (with the so-called "armchair" SWCNTs with $n = m$), and semiconductors are those with a difference not being a multiple of three [25]. The M-enriched sample contained all the metallic SWCNTs, and the S-enriched sample did not.

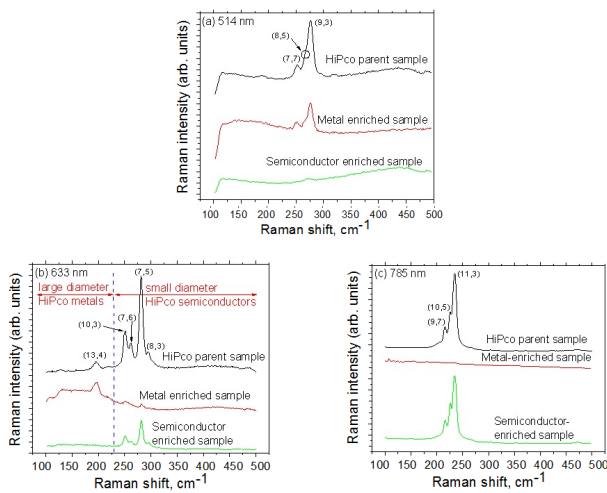


Figure 5. Resonant Raman spectra of the parent, M-enriched, and S-enriched samples collected at laser excitation wavelengths of (a) 514 nm, (b) 633 nm, and (c) 785 nm

Resonant Raman spectroscopy performed at 633 nm laser excitation can reveal the presence of "large-diameter" metallic SWCNTs and "small-diameter" semiconducting SWCNTs if radial breathing modes are detected, respectively, below and above the empirically chosen Raman shift of 233 cm^{-1} [28]. The parent sample contained (13,4) metallic SWCNTs and (10,3), (7,6), (7,5), and (8,3) semiconducting SWCNTs, as seen in Figure 5(b). The M-enriched sample contained the (13,4) metallic SWCNTs and very little of the semiconducting SWCNTs. The (13,4) metallic SWCNTs were absent from the S-enriched sample. The data of Figures 5(a) and (b) support UV-vis-NIR absorption spectroscopy results, i.e., the S-enriched SWCNT sample is highly pure in semiconducting SWCNTs.

Resonant Raman spectroscopy performed at 785 nm laser excitation, which revealed the presence of "large-diameter" semiconducting SWCNTs, indicated that the M-enriched sample lacked the "large-diameter" (9,7), (10,5) and (11,3) semiconducting SWCNTs detected in the parent sample and in the S-enriched sample (Figure 5(c)). This data, combined with Figure 5(b) data, leads us to conclude the M-enriched sample is also very pure, consistent with the purity estimates from UV-vis-NIR spectroscopy.

Table 1 summarizes the detected SWCNT types found in the M- and S-enriched eluates. This improved method is applicable to HiPco SWCNTs and also laser ablation-type SWCNTs (Figures S4 and S5).

SWCNT types detected in parent sample	SWCNT diameter (nm) ^a	Excitation wavelength (nm)	S- or M- type ^b	Found in the M-enriched sample?	Found in the S-enriched sample?
(7,7)	0.95	514	M	✓	
(8,5)	0.89		M	✓	
(9,3)	0.85		M	✓	✓
(13,4)	1.20		M	✓	
(10,3)	0.92	633	S	✓	✓
(7,6)	0.88		S		✓
(7,5)	0.82		S	✓	✓
(8,3)	0.77		S		✓
(9,7)	1.10	785	S		✓
(10,5)	1.00		S		✓
(11,3)	1.00		S		✓

^a SWCNT diameter = $\frac{0.246}{\pi} \sqrt{(n^2 + nm + m^2)}$

^b If $\text{mod}[(n-m),3] = 0$, then SWCNT is considered metallic. If $\text{mod}[(n-m),3] = 1$ or 2, then SWCNT is considered semiconducting

Table 1. SWCNT types detected through resonant Raman spectroscopy (excitation wavelengths of 514, 633 and 785 nm) in the parent and purified samples

3.1.3 Photoluminescence (PL) spectroscopy analysis

From photoluminescence spectroscopy we can identify semiconductor-type SWCNTs in a sample by chirality, whereas metallic SWCNTs are not seen. This is a supporting means for confirming semiconducting SWCNT content in the separated samples. We chose to perform PL studies at 660 and 785 nm excitations because most, if not all, semiconducting HiPco SWCNTs of average diameter 1 nm show emission at these two wavelengths. There is a redshift in the spectra of the semiconductor-enriched sample compared to the parent sample due to the different surfactant present. Figure 6(a) and 6(b) show that the metal-enriched sample has very little “small-diameter” and “large-diameter” semiconducting SWCNTs and the relative intensity of semiconducting SWCNTs in the semiconductor-enriched sample has greatly increased compared to the parent sample. This supports our results from UV-vis-NIR and Raman spectroscopy, and also shows that we have no loss of semiconducting SWCNTs of specific chirality after the separation process.

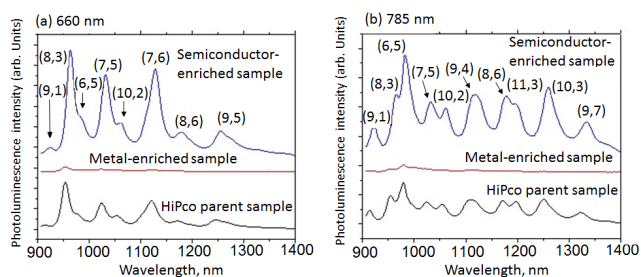


Figure 6. Photoluminescence (PL) spectra of the parent, M-enriched, and S-enriched samples collected at laser excitation wavelengths of (a) 660 nm and (b) 785 nm. The spectra have been offset for clarity.

3.1.4 Separation mechanism

To understand the mechanism of separation, we recognize that SWCNTs do not undergo reversible adsorption to the gel (i.e., partitioning from the mobile phase to the solid phase). Rather, they adsorb irreversibly onto specific binding sites on the gel surface. The gel-based process used here and by others is a form of affinity, or displacement, chromatography, wherein the parent SDS-suspended SWCNT sample is passed through the gel column, leading to the SDS-coated SWCNTs to bind to the column material. Then, a SDS solution is passed through the column, causing the metallic SWCNTs to be desorbed from the surface and eluted out with the SDS phase. Our results imply that the semiconducting SWCNTs have a stronger affinity to bind to the stationary agarose gel phase rather than SDS surfactant head groups, and the metal ones prefer the SDS surfactant head groups to the agarose surface.

Kataura and co-workers also suggested that metal SWCNTs have a more polarizable surface than semiconducting SWCNTs, allowing the anionic SDS surfactant to attach more favourably to metallic SWCNTs than to semiconducting ones [29]. This is consistent with the observation that other anionic surfactants like sodium dodecane sulphonate and sodium dodecyl phosphate also preferentially enrich metal SWCNTs [30]. The Kataura group recently concluded that the metallic- and semiconductor-SWCNTs had different free energies of adsorption on agarose gel, with the latter binding more strongly than the former; this is consistent with the affinity chromatography concept [31]. The concentration of SDS has also been shown to play a role in facilitating metal-semiconductor SWCNT separation [32]. It is likely that a combination of these different effects causes the M-SWCNTs to displace from the agarose surface more readily than the S-SWCNTs during the passage of the SDS eluting fluid through the column. Recent work from Strano and co-workers indicated that different chiral SWCNTs have different affinities to the gel surface and that single-chirality SWCNT separation is possible by adjusting the surfactant-SWCNT binding energy [33]. This theory is further supported by work from Ziegler and co-workers [34] who recently performed a comprehensive study of the various interaction forces of adsorption between SWCNTs suspended with SDS and agarose: ionic, hydrophobic and π - π . They concluded that a large permanent dipole moment associated with agarose combined with the dissimilar packing of SDS on the SWCNT surface resulted in SWCNTs of different chiralities having different affinities to the agarose gel surface.

Semiconducting SWCNTs remain bound to the gel until a surfactant more effective than SDS can dislodge them, such as DOC or Pluronic. We used DOC in a comparison experiment to replace Pluronic, and found that the resulting semiconducting eluate was not as pure (80%) as the Pluronic case (95%). We do not believe there are any SWCNT bundles/impurities remaining behind in the column after SDS has been passed through and so it is unlikely that DOC could have pulled off the semiconducting-SWCNTs along with bundles giving a lower impurity of final s-SWCNTs. Perhaps the reason DOC performed in such a way is due to Pluronic having a stronger binding affinity to SWCNTs than DOC when suspending SWCNTs. We verified this when we prepared SWCNT suspensions using DOC and F77 in place of SDS: DOC led to a concentration of ~ 0.33 g-SWCNT L⁻¹ solution and F77 led to a higher concentration of ~ 0.41 g-SWCNT L⁻¹ solution. Another possible explanation is that Pluronic binds more strongly to the agarose gel than DOC does, thereby displacing more SWCNT from the surface and increasing the semiconducting content of the eluate.

3.1.5 Use of different Pluronic surfactants

Less expensive than DOC and also biocompatible, Pluronic surfactants have been used to suspend SWCNTs in water [35, 36]. Hersam and co-workers recently reported using Pluronic in density gradient ultracentrifugation to obtain S-enriched SWCNTs [37]. We studied two more Pluronic surfactants (F66 and F108) for any structural effects on separation efficacy. UV-vis-NIR spectroscopy results showed that the eluates were S-enriched with similar purities (90-95%) as calculated earlier for the F77-derived eluate, suggesting little effect of Pluronic molecular structure (Figure 7).

The relative hydrophilicity and hydrophobicity of Pluronic (as characterized by its hydrophilic-lipophilic balance, or HLB, value) depends on the content of poly(propylene oxide) (PPO) linkages as compared to poly(ethylene oxide) (PEO) blocks for Pluronic [38], and plays an important role in determining how the polymer behaves in a suspension of organics and water. The HLB values calculated for all three Pluronics used (29 for Pluronic F68, 26 for Pluronic F77 and 27 for Pluronic F108) were similar [39]. We chose Pluronic F77 to represent the Pluronic family of polymers because its number of PPO units was between that for Pluronic F68 and Pluronic F108. We found that another nonionic surfactant type, called Tetronic surfactants (HLB of 7) [39], was able to generate semiconducting-enriched SWCNT's of similar purities, indicating polymer surfactants with a wide range of HLB values can be used (Figures S6 and S7). In fact, Tetratics have recently been shown to be able to disperse grapheme [40] as well as have a pH-dependent interaction [41] with SWCNT sorting via DGU, which agrees with our findings.

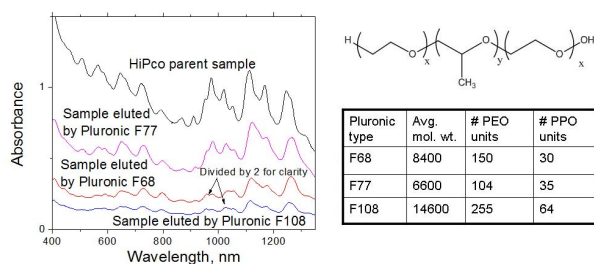


Figure 7. UV-vis-NIR absorption spectra of S-enriched samples eluted by three different Pluronic surfactants. PEO and PPO units are designated as x and y, respectively, in the general structure.

A concentrated Pluronic-eluted, S-enriched SWCNT suspension was dried at 100 °C, and the residue was analysed through TGA under flowing compressed air (Figure 8a). The first major mass loss by 300 °C was due to Pluronic combustion and the second mass loss by 400 °C was due to SWCNT combustion, based on a comparison of

TGA profiles of Pluronic and of dried HiPco powder (Figure S8). The TGA results were similar for the other Pluronic types. The residual material at 800 °C (~17 wt%) was attributed to the now-oxidized growth catalyst.

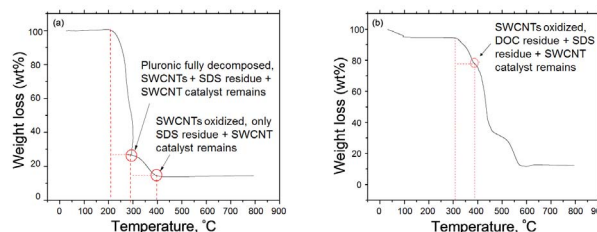


Figure 8. TGA profiles of dried S-enriched SWCNTs eluted with (a) Pluronic F77 and (b) DOC.

A concentrated DOC-eluted, S-enriched SWCNT suspension was prepared and dried at 100 °C, and an analogous TGA study was performed (Figure 8b). In this case, the first major loss occurred by 400 °C, which was due to SWCNT combustion and DOC decomposition. The second weight loss occurred by 550 °C, which was also due to DOC decomposition (Figure S7).

The implication of the TGA results is that Pluronic-eluted, S-enriched SWCNT suspensions can be treated to remove the Pluronic by drying and calcining under air above 200 °C and below 300 °C. DOC-eluted SWCNTs cannot be treated in the same manner, because DOC does not fully decompose at a temperature below the combustion temperature for SWCNTs.

4. Conclusions

Agarose gel column-based affinity chromatography is a scalable technique towards high efficiency separation of metallic and semiconducting single-wall carbon nanotubes. The separation mechanism is based on the affinity differences of metallic and semiconducting SWCNTs towards the agarose gel surface. The existing methods rely on anionic surfactants in a process that takes more than one day to complete and requires physical methods such as vacuum filtration after separation to recover pristine SWCNTs. We improved this process by reducing the total time to less than six hours through the use of biocompatible, nonionic surfactants to elute the semiconducting SWCNTs adsorbed to the gel phase after SDS elution of the metallic SWCNTs. SWCNT suspensions with a semiconductor-type purity level of up to 95% can be achieved, as quantified through UV-vis-NIR absorption and resonant Raman spectroscopy. Pluronic-free SWCNTs can be generated by removing the water and heating the dried material to a temperature at which Pluronic thermally decomposes, but below the decomposition temperature of SWCNTs. The use of nonionics increases the availability of semiconductor-type SWCNTs and could

improve chiral-specific semiconductor-type SWCNT separations.

5. Acknowledgments

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