

Length Separation of Zwitterion-Functionalized Single Wall Carbon Nanotubes by GPC

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The drive toward single wall carbon nanotube (SWNT) based molecular electronics¹ renders their separation according to length and type (metallic (*met*-) or semiconducting (*sem*-)) pivotal for nanoscale devices.² Schlittler et al.³ recently demonstrated a synthetic methodology to fabricate SWNT single crystals. Although both tube diameter and chirality are identical within each crystal, such properties vary between crystals. SWNT postsynthesis separation presents an alternative route, which however is associated with an array of challenges stemming from their poor solubility and natural tendency to aggregate in solution.⁴ Although various strategies have been developed for dispersing⁵ and solubilizing⁶ SWNTs, fractionation according to length remains to be demonstrated. Size exclusion chromatography has primarily been focused on the purification of surfactant-stabilized⁷ and covalently functionalized nanotubes⁸ (NTs) as a means of removing graphitic impurities. In the present communication we demonstrate that not only size-fractionation of shortened (250 to 25 nm) SWNTs is possible by GPC, but such fractions permit direct observation of all optically allowed transitions for both *met*- and *sem*-SWNTs.⁹ Such transitions have been previously observed only by scanning tunneling microscopy (STM),¹⁰ electron energy loss spectroscopy (EELS),¹¹ and Rayleigh scattering¹² of individual or ropes of NTs.

Purified SWNTs^{13,14} (tubes@rice)¹⁴ were acid functionalized and shortened by sonicating in a mixture (7:3) of HNO₃ and H₂SO₄.¹⁵ The carboxy-terminated shortened SWNTs (sSWNTs) were zwitterion-functionalized with octadecylamine (ODA) according to previously established procedures.^{6a} A 100 μ L sample of the sSWNTs-zwitterion complex in tetrahydrofuran (THF) was injected into a Waters 150-C Plus GPC. A total of 40 fractions were collected (1 fraction every 15 s) during the elution of the broad multimodal band shown in the chromatogram of Figure 1. Comparing this elution profile to GPC polystyrene standards, retention times of 36.8, 42.4, 46.7, and 48.5 correspond to 30.0, 4.00, 1.00 and 0.470 kDalton, respectively. sSWNTs were found to be present in all 40 elution fractions, as monitored by UV-vis, near-IR (NIR). Atomic force microscopy (AFM) was used to obtain the sSWNTs length distribution per fraction. This was achieved by depositing them on surface-modified silicon substrates and assessing their length as described elsewhere.¹⁶ Figure 2 depicts the weight-averaged length and distribution (shown with error bars) as a function of fraction number. Typical AFM-generated histograms for fractions 1 and 40 demonstrate a relatively narrow length distribution within each fraction. The length of sSWNT gradually decreases from 232 nm in fraction 1 to about 29 nm in fraction 40.

The noncovalent functionalization of sSWNTs was specifically chosen because the reaction yields are moderately high (~60%) and it has previously shown not to alter the intrinsic electronic

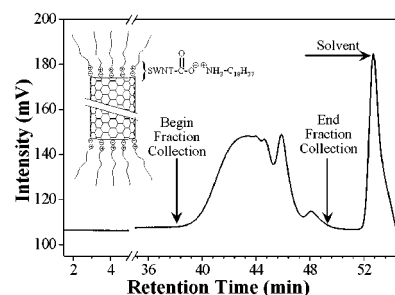


Figure 1. The chromatogram of sSWNTs/zwitterions in THF (Waters 600-996, styragel HMW7 column, refractometer detector).

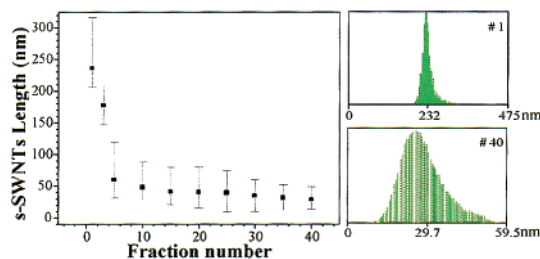


Figure 2. Distribution of sSWNTs lengths after fractionation, as monitored by AFM. The solid squares indicate weight-average length of nanotubes in each fraction whereas the error bars manifest the length distribution within 98% accuracy. The AFM-generated length histograms for fractions 1 and 40 are also illustrated.

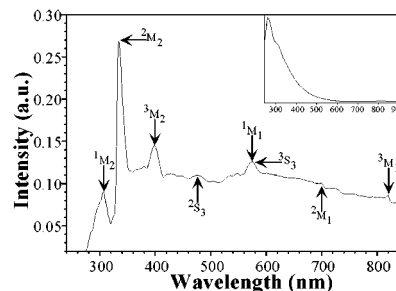


Figure 3. Typical UV-vis spectrum of the fractionated sSWNTs in THF (fraction 10). The inset illustrates the spectrum of the sSWNT/zwitterion suspension before fractionation.

properties of SWNTs.^{6a} Dispersion of SWNTs in THF has been demonstrated, where the majority of the bundles were exfoliated in small ropes (2–5 nm in diameter) and individual nanotubes. Assuming the dissolution is a result of the repulsive interaction induced by the ionically attached ODA end-groups, in the case of shortened-SWNTs, the flow-induced shearing through the GPC columns could further reduce aggregation and lead to length fractionation. The UV-vis spectrum of a typical eluting fraction of sSWNTs in THF is presented in Figure 3. This spectrum markedly contrasts that of the injected suspension (Figure 3 inset), which was obtained after extensive sonication in THF and filtration

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Table 1. Peak and Corresponding SWNT Diameter Assignments (from Figure 3), Based on Theoretical Prediction for the Optically Allowed Transitions between Pairs of Singularities in the DOS for *met*- and *sem*-SWNTs¹⁷

symbol ^a	DOS transitions	abs wavelength	calcd dia. (nm)	energy (eV)	
				obsd	calcd
¹ M ₁	metallic 1st pair	585	~1.2 ₂	2.1 ₂	2.0 ₈
² M ₁	metallic 1st pair	690	~1.3 ₃	1.8 ₀	1.8 ₈
³ M ₁	metallic 1st pair	820	~1.6 ₀	1.5 ₁	1.4 ₇
¹ M ₂	metallic 2nd pair	310	~1.2 ₂	4.0 ₀	4.1 ₀
² M ₂	metallic 2nd pair	340	~1.3 ₃	3.6 ₅	3.5 ₈
³ M ₂	metallic 2nd pair	396	~1.6 ₀	3.1 ₃	3.1 ₃
² S ₃	semiconducting 3rd pair	490	~1.3 ₃	2.5 ₀	2.5 ₁
³ S ₃	semiconducting 3rd pair	585	~1.6 ₀	2.1 ₂	2.0 ₈

^a Symbol: ^{no.}TYPE_{transition}.

through a 10 μm Teflon filter. The profound difference in these two spectra might originate from either the complete exfoliation of the 2–5 nm diameter SWNTs ropes or fractionation by length and possibly type (diameter and/or chirality). The latter two can be easily excluded based on the spectral resemblance and the presence of *met*- and *sem*-nanotubes of various diameters in all 40 fractions (as elaborated later in Table 1). Therefore, the most likely cause for such enhanced spectral resolution is currently attributed to total unbundling of sSWNTs, leading to complete “solubilization”.

The indicated absorptions in Figure 3 can be ascribed to the interband transitions between the mirror image spikes in the density of states (DOS) of SWNTs.¹⁸ As shown in Table 1, these absorption maxima corroborate the presence of at least three metallic *met*-SWNTs with differing diameters (1.22, 1.33, and 1.6 nm) and two different semiconducting *sem*-SWNTs (with 1.33 and 1.6 nm diameters). The relative intensities are in agreement with both the narrow diameter distribution and mean value (~ 1.3 nm) for laser ablated SWNTs.^{14,15} In the UV–vis region, both of the optically allowed transitions for *met*-SWNTs are accounted for along with one of the three transitions (3rd pair of singularities) for *sem*-SWNTs. The remaining two transitions are also accounted for in the NIR region (Figure S1, Supporting Information). In the case of the inset of Figure 3, the sharp absorption maximum at 270 nm has been related to the π -plasmon frequency (~ 5 eV).^{11,12} This has been argued to correspond to the collective excitation of the π -electron system polarized along the NT axis,¹¹ and to the first approximation, it provides a good indication of NT aggregation.¹² The absence of this π -plasmon peak in all GPC collected fractions (Figure 3) further supports the “solubilization” argument.

However, this “solubilization” is a dynamic process, and if the fractions are left undisturbed for a few weeks, their spectrum reverts back to that before fractionation. To better elucidate the importance of the pendent ODA groups in preventing NT aggregation, we replaced the low dielectric constant THF solvent ($\epsilon_{\text{THF}} = 7.6$) with a DMF, a higher dielectric constant ($\epsilon_{\text{DMF}} = 36.5$), capable of dissociating the ionically attached ODA groups.^{19,20} Figure 4 illustrates the UV–vis spectra of fraction 10 in DMF prior to and after sonication for 1 h. As expected, this was accompanied by a dramatic loss in spectral resolution and the reappearance of the 270 nm π -plasmon peak. Subsequent sonication allowed the observation of only the strongest optically permitted transitions at partial expense of the π -plasmon peak.

In conclusion, a unique GPC-assisted length separation of zwitterion-functionalized shortened SWNTs (sSWNTs) has been demonstrated. The resulting flow through the GPC column led to a shear-induced solubilization, clearly demonstrated by the exceptionally resolved UV–vis spectra of each fraction. This nondestructive and highly versatile method could prove pivotal in sorting

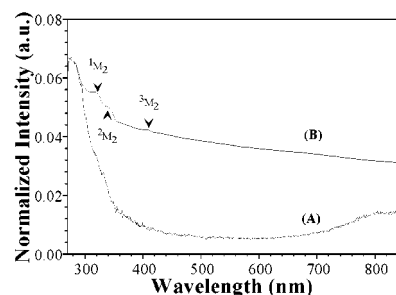


Figure 4. UV–vis spectra of fraction 10 in DMF (A) prior to and (B) after sonication for 1 h.

sSWNTs by diameter and possibly by chirality, opening up an array of possible applications for SWNT-based nanostructured devices.

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Supporting Information Available: Figure S1, typical NIR spectra of the sSWNTs/zwitterion complex upon fractionation (fraction number 10) and equations used for estimating interband transition energy and SWNTs diameter (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (20) The presence of unbound ODA can be observed from its 240 nm absorption, which is absent in the case of zwitterion functionalized NTs.

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