

Small angle neutron scattering study of isolated single wall carbon nanotubes in water

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1. Introduction

As an effort to provide more practical approaches to a wide range of potential applications of carbon nanotubes, we report a new type of noncovalently functionalized isolated single-walled carbon nanotube (SWNT) which is easily dispersible in water by only ten minutes of mild vortex mixing. The structure and quality of dispersion have been investigated using small angle neutron scattering (SANS) technique.

2. Methods and Results

In this section a method to prepare non-covalently functionalized SWNT powders is described. The structure of the isolated SWNT system is analyzed with cylindrical core-shell model using SANS results.

2.1 Sample Preparation

In water, super purified HiPco SWNTs (2 mg/mL, purity > 98 wt%, CNI) were mixed with the cationic surfactant cetyltri-methylammonium 4-vinylbenzoate (CTVB, 5mg/mL, synthesized in house), which has polymerizable counterions.[1,2] Individually isolated SWNTs with an adsorbed layer of CTVB were produced by sonicating the mixture of SWNTs and CTVB for one hour. The CTVB monolayer on the SWNT surface was tightly fixed by in situ free-radical polymerization of the counter ions of CTVB at 60 °C (by injecting the free-radical initiator 2,2'-azobis[2-(2-imidazolin-2-yl) propane] dihydrochloride (VA-044). [Fig.1] To separate the isolated SWNTs from the bundled ones, the polymerized mixture was ultra-centrifuged (~ 111000 g) for 4 h, and the upper 70 % of the solution, which showed homogeneous dispersion of SWNTs, was decanted.[3] The decanted solution contained isolated SWNTs coated with polymerized CTVBs (*p*-SWNT) and polymerized CTVB micelles (*p*-CTVB) which were not involved in SWNT coating. To reduce the content of *p*-CTVB, the decanted mixture was filtered through a membrane with pores of 0.22 μm. Typical sharp van Hove transition peaks were observed in the UV-vis-NIR spectra indicating individually isolated SWNTs in solution.[3] The absorption spectra were also used to estimate the concentration of SWNTs (0.08mg/mL) and CTVB surfactants (2.6mg/mL) in the solution after filtering. This *p*-SWNT dispersion was diluted or concentrated for further characterization. The easily re-dispersible powder form of *p*-SWNT was

prepared by freeze drying the decanted and filtered dispersion of *p*-SWNT (SWNT 0.13 mg/mL), which was easily dissolved in water at the same concentration as before freeze drying with only 10 minutes of mild vortex mixing.

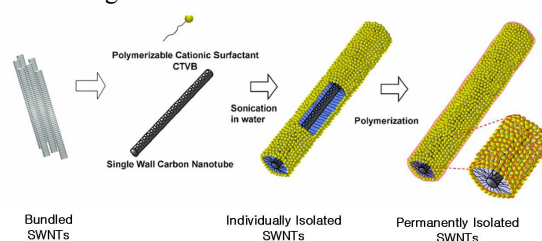


Figure 1. Procedure to make the *p*-SWNT. The free-radical polymerization was performed by injecting 5 mol% (relative to the CTVB concentration) VA-044 initiator at 60 °C.

2.2 SANS Measurements

To understand the microstructure of the polymerized surfactant layer on SWNTs, small angle neutron scattering (SANS) measurements were performed using the NG7 30m SANS instrument at NIST for a *p*-SWNT dispersion in D₂O (SWNT 0.03mg/mL and CTVB 1.2mg/mL).

First, as shown in Fig. 2, it should be noted that in the low *q* region, the intensity of *p*-SWNT dispersions do not show $q^{-\alpha}$ ($2 < \alpha < 3$, $q=4\pi/\lambda \sin(\theta/2)$ where λ is the neutron wavelength and θ is the scattering angle) behavior which is typical for networked SWNTs as found in all the previous SANS studies[4-6] of SWNT dispersions in aqueous solution. In fact, α is 0.94, slightly smaller than 1. If the *p*-SWNTs are fully dispersed without forming any network, they can be understood as rigid core-shell cylinders freely dispersed in water and their SANS intensity should show q^{-1} behavior in the low *q* region (represented with a core-shell cylinder model in Fig. 2). However, some amount of *p*-CTVB, which has a flattened SANS intensity in the low *q* region (represented with a cylinder model in Fig. 2), still exist in the *p*-SWNT dispersion, thus make α slightly less than one (red circles in Fig. 2). Even at higher *p*-SWNT concentrations (SWNT 0.5 mg/ml), α was 0.95, still slightly less than one. This clearly indicates that the *p*-SWNTs are well dispersed in a purely isolated way without forming any network.

Second, The SANS intensities of a *p*-SWNT dispersion measured when freshly prepared and then 3 months after preparation were exactly identical, indicating long-time stability without any structural changes (Fig. 2).

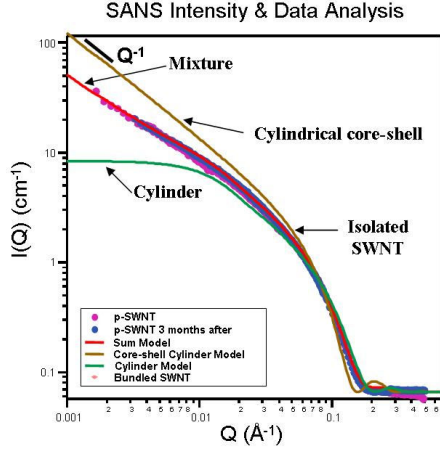


Figure 2. SANS intensities and model calculations of *p*-SWNT dispersion in D₂O.

2.2 SANS analysis

We simulated the scattering intensity of *p*-SWNT dispersion using a sum of two models, a core-shell cylindrical form factor $P_{cs}(Q)$ and a cylindrical form factor $P_{cyl}(Q)$ to describe the *p*-SWNT and *p*-CTVB, respectively. Since the dispersion is very dilute, the interparticle interaction can be ignored and hence the SANS intensity can be simplified as [7]

$$\frac{d\Sigma}{d\Omega} = n_{cyl}P_{cyl}(Q) + n_{cs}P_{cs}(Q) + bkg$$

where

$$P(q)_{cyl} = \int_0^{\pi/2} f_{cyl}^2(q, \alpha) \sin \alpha d\alpha$$

$$f_{cyl}(q, \alpha) = 2(\rho_{cyl} - \rho_{solv})Vj_0\left(\frac{qL \cos \alpha}{2}\right) \frac{J_1(qR \sin \alpha)}{(qR \sin \alpha)}$$

$$P(q)_{cs} = \int_0^{\pi/2} f_{cs}^2(q, \alpha) \sin \alpha d\alpha$$

$$f_{cs}(q, \alpha) = 2(\rho_{core} - \rho_{shell})V_{core}j_0\left(\frac{qL_{core} \cos \alpha}{2}\right) \frac{J_1(qR_{core} \sin \alpha)}{(qR_{core} \sin \alpha)} + 2(\rho_{shell} - \rho_{solv})V_{shell}j_0\left(q\left(\frac{L_{core}}{2} + t\right) \cos \alpha\right) \frac{J_1(q(R_{core} + t) \sin \alpha)}{(q(R_{core} + t) \sin \alpha)}$$

$$j_0 = \sin(x)/x$$

$$V = \pi R^2 L, V_{core} = \pi R_{core}^2 L_{core}, V_{shell} = \pi(R_{core} + t)^2(L_{core} + 2t).$$

n_{cyl} and n_{cs} are the number densities of cylindrical particles and core-shell cylindrical particles, respectively. L and R are the length and radius of the cylindrical particle. L_{core} and R_{core} are the length and radius of the core, and t is the shell thickness. ρ_{cyl} , ρ_{core} , ρ_{shell} , and ρ_{solv} are scattering length densities of cylindrical particles, the core and shell of core-shell particles and solvent, respectively. $J_1(x)$ is the first order Bessel function and α is the angle between the cylinder axis and the scattering vector, q .

Prior to the analysis of SWNT dispersion (mixture of *p*-SWNT and *p*-CTVB), the SANS intensity of the *p*-CTVB alone in D₂O was analyzed to determine the *p*-CTVB cylinder dimensions which were a radius and length of 2.0 nm and 70 nm respectively. When modeling the mixture, these values were held fixed for

the *p*-CTVB as well as the core radius (0.5 nm), shell thickness (2.0 nm, radius of the cylindrical *p*-CTVB micelle) and length (500 nm, typical length of sonicated SWNTs) of the core-shell cylinder (*p*-SWNT). In this simulation the volume fractions ϕ_{p-CTVB} and ϕ_{p-SWNT} were adjusted to match the SANS intensity. The number of CTVB molecules adsorbed per unit length of SWNT was calculated to be 21/nm using the estimated volume fractions and the head group area of CTVB (66 Å²) [1, 2]. This value is reasonably consistent with 24/nm which was obtained assuming cylindrical monolayer of CTVB on SWNT as illustrated in Figure 1.

3. Conclusion

In summary, we have successfully developed non-covalently functionalized and individually isolated SWNTs that are readily re-dispersible in water even after freeze drying. The SANS measurements showed that, unlike the previous SWNT dispersions, the *p*-SWNT does not form any network at the concentrations investigated in this study. In addition, the microstructure of *p*-SWNT was also investigated using the SANS results.

ACKNOWLEDGEMENT

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