Solubilization of Single Wall Carbon Nanotubes with Salmon Sperm DNA
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ABSTRACT

Single wall carbon nanotubes (SWCNTs) have been highlighted among scientific communities due to their potential to advance numerous application areas, such as in nanoscale circuits, ultrathin, flexible, and transparent conductors, supercapacitors, field emitters, actuators, nanosized electrochemical probes, transistors, photovoltaic devices, and nanoscale sensors. Aside from their immense technological importance, enhancing the structural purity and homogeneity by obtaining well dispersed and fractionated samples could also enable us to better characterize and model the SWCNTs. Recently, it has been possible to separate and/or enrich fractions of SWCNTs according to metallicity and diameter (d). Deoxyribonucleic acids (DNAs), specifically in synthetic oligomeric form, have been playing an important role in the exfoliation and subsequent d and metallicity dependent separation of SWCNTs. However, their extreme high price for the synthesis needs to be overcome for the cost-effective and bulk scale solubilization and separation of SWCNTs. In this paper, we present a solubilization study of commercially available SWCNTs by using the DNA extracted from waste materials of the salmon fishing industry through an enzyme isolation process. The optical properties, including NIR and circular dichroism spectra, are also presented.

Keywords: single wall carbon nanotubes, DNA, dispersion, solubilization, spectroscopy

1 INTRODUCTION

Single wall carbon nanotubes can be pictorially presented as the cylindrical roll-up of a simple flat graphene sheet containing carbon atoms in a hexagonal lattice, with a circumferential rolling vector of \( C_h = n \mathbf{a}_1 + m \mathbf{a}_2 \), where \( n \) and \( m \) are integer and \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are unit vectors. Typically, their diameter varies from 0.4 to 3 nm and length ranges from tens of nanometers to micrometers by controlling the growth conditions and/or applying appropriate post-growth chemical treatments, such as oxidative shortening. The large scale growth of structurally perfect single wall carbon nanotubes has been typically performed via arc discharge, laser ablation, chemical vapor deposition (CVD), and plasma enhanced chemical vapor deposition (PECVD) methods. Among the growth processes, CVD and PECVD methods have appeared to be particularly important processes for the production of SWCNTs that contain minimal concentrations of graphitic nanoparticle contaminations. However, the extreme SWCNTs inter-tube aggregation forces, along with inhomogeneity in the chirality, pose significant obstacle in the achievement for technological breakthroughs where nanotubes of precisely defined length, diameter, and chirality are used.

By wrapping and/or groove-binding with SWCNTs via hydrophobic interactions, DNA has been recognized as one of the most efficient dispersion media that enables us to acquire both individually exfoliated samples and chirality-fractionated carbon nanotubes according to their diameter and metallicity. From a series of experiments, single stranded d(GT)\(_n\) DNA has been recognized to exhibit not only individual-level nanotube dispersion, but also effective SWCNT chirality separation when eluted from an anion exchange column at various salt concentrations. However, the typical synthetic oligomer price for a d(GT)\(_{20}\)NIR and circular dichroism spectra, from the solubilized nanotube samples will be presented along with the chirality dependent separation results from SaDNA mediated SWCNT dispersion.

2 EXPERIMENTS

2.1 DNA preparation

Synthetic d(GT)\(_{20}\) DNA was purchased from IDT and used to compare the solubility of SWCNTs to SaDNA
solution. The SaDNA used for this research was purified DNA provided by the Chitose Institute of Science and Technology (CIST)\(^8\), through an Asian Office of Aerospace Research and Development (AOARD) supported effort. It is marine-based, extracted from frozen salmon milt and roe sacs through a homogenization process. It goes through an enzymatic treatment to degrade the proteins by protease. Proteins are then removed by controlling the pH level. The saDNA undergoes a carbon treatment for decolorization, is filtered, and precipitated by adding acetone. The purified saDNA is finally filtered from the acetone and freeze dried. The molecular weight of the purified saDNA typically measures \(>8,000,000\) Daltons (Da), via gel phase electrophoresis. The saDNA material purity measures ~96% and the protein content measures ~2%.

### 2.2 SWCNT dispersion and spectroscopy

Commercial SWCNTs (HipCo, CNI) were ultrasonicated with a horn sonicator at the concentration of 1mg/ml in D\(_2\)O with 1mg of DNA for each sample. The dispersed SWCNTs were further centrifuged at 14,000g for 90 min, and the supernatants were carefully taken for further spectroscopic measurements.

A Renishaw inVia Raman microscope was used for resonance Raman spectroscopy (RRS) measurements, equipped with a 1.96 eV excitation laser line focused on a 1 \(\mu\)m spot by using a 50x objective. All samples were subjected to the same laser intensity, focus, exposure time, and collection scan number for the given laser line. To enhance the sampling signal and uniformity, the RRS data were collected and averaged out from 30 different individual spots.

A JASCO J-815 circular dichroism (CD) spectrometer equipped with 0.2mm path length sample holder was used for circular dichroism measurements.

### 3 RESULTS AND DISCUSSION

The first electronic transition energy \(E_{\text{M-S}}^{\text{ii}}\) of van Hove singularity (VHS) in sem-SWCNTs \(E_{\text{S}}^{\text{i1}}\) have been well characterized by both theory and experiments. Since this distinctive excitation energy is not overlapped by other higher electronic transitions, such as \(E_{\text{S}}^{\text{i2}}\) and \(E_{\text{M}}^{\text{i1}}\), and the SWCNT peaks are widely spread for HipCo nanotube samples, the detailed feature of the NIR peak can not only provide the degree of solubilization, but also reveal the relative enrichment information about the dispersed tubes. Figure 1 shows normalized NIR absorption spectra obtained from oligo d(GT)\(_{20}\) DNA and SaDNA dispersed HipCo SWCNTs. Characteristic \(E_{\text{S}}^{\text{i1}}\) peaks from \{9,7\}, \{11,1\}, \{10,3\}, \{11,3\}, \{8,4\}, \{9,2\}, \{9,4\}, \{10,2\}, \{7,5\}, \{11,0\}, and \{8,3\} SWCNTs were observed (marked as diamond shape from left to right in each spectrum).\(^9\) SaDNA dispersed SWCNTs show relatively comparable peak features, and even better isolated peaks from \{11,3\} and \{8,4\}, \{9,2\}, \{9,4\} groups of tubes than the spectrum from d(GT)\(_{20}\) oligomer dispersed SWCNTs. This indicates that the natural SaDNA product enables us to obtain individually dispersed SWCNTs in solution at a comparable or even enhanced level than d(GT)\(_{20}\) DNA oligomer.

![Figure 1: Normalized NIR absorption spectra from oligo d(GT)\(_{20}\) DNA and SaDNA dispersed HipCo SWCNTs.](image1)

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Figure 2 shows NIR spectra profile changes from SaDNA dispersed HipCo SWCNTs at various ultrasonication times. A Sigmoid-like 0.97 eV NIR absorption change was observed (Figure 2a). By extrapolating this curve with a sigmoid function (not shown) fitted from the above profile, we could estimate a saturation ultrasonication time of 90 min with an absorption of 0.173. When the NIR spectra from 10, 30, and 50 min sonicated samples were normalized with respect to the

![Figure 2: (a) 0.97 eV NIR absorption profile with respect to sonication time, and (b) Normalized NIR absorption spectra from SaDNA dispersed HipCo SWCNTs at various ultrasonication times. The star indicates the absorption from the \{11,1\}, \{10,3\} SWCNT group. The up arrows indicate the increase of the absorption from the \{8,4\}, \{9,2\}, \{9,4\} groups of tubes than the spectrum from d(GT)\(_{20}\) oligomer dispersed SWCNTs. The numbers on the top x-axis indicate the average diameter (nm) from each SWCNT group.](image2)

Figure 2: (a) 0.97 eV NIR absorption profile with respect to sonication time, and (b) Normalized NIR absorption spectra from SaDNA dispersed HipCo SWCNTs at various ultrasonication times. The star indicates the absorption from the \{11,1\}, \{10,3\} SWCNT group. The up arrows indicate the increase of the absorption from the \{8,4\}, \{9,2\}, \{9,4\} groups of tubes than the spectrum from d(GT)\(_{20}\) oligomer dispersed SWCNTs. The numbers on the top x-axis indicate the average diameter (nm) from each SWCNT group.
absorption from \{(11,1), (10,3)\} tubes (indicated as a star in Figure 2b) and baseline-corrected by subtracting the plasmonic and scattering lines, the absorption from \{(8,4), (9,2), (9,4)\}, \{(11,3)\} and \{(7,5), (11,0)\} (indicated as arrows) SWCNTs showed an increase in relative intensity, implying their enrichment in the dispersion as the ultrasonication time increased. Meanwhile, the relative absorption from \{(9,7)\} tubes diminished indicating their decrease in abundance.

RRS is particularly important to analyze SWCNTs with respect to their chirality. When the electronic transitions between the VHSs of a given SWCNT are within the resonance window (~ 0.2 eV) of excitation laser energy, the phonons from this one dimensional system are strongly coupled with electrons, generating clear and distinctive SWCNT peaks in RRS. When SWCNTs \(d_t\) is correlated with the \(\text{lower frequency radial breathing mode (RBM)}\)

The ideal \(d_t\) of a SWCNT can be calculated from a simple relation, \(d_t = (a/\pi)(n^2 + m^2 + nm)^{1/2}\), where \(a\) is an average carbon-carbon distance (1.44Å in this paper). It is clear from the NIR absorption profile that smaller diameter \((d_t<0.9 \text{ nm})\) SWCNTs are becoming more abundant as the ultrasonication time increases, meanwhile the larger diameter \((d_t>1.0 \text{ nm})\) tubes are becoming less stable in the dispersion. Further CD study from these samples has shown a matching trend in the helicity of the SaDNA, where small \(d_t\) tubes are stabilized as the DNA configures from high near-complete A- (NCA) form to an intermedia or mixture of A- and B- (A&B) form. Circular dichroism has been typically utilized to estimate the representative secondary structures of DNA, A- and B-form, by monitoring the intensity changes from the negative and positive peaks at 290-260 nm and 260-230 nm, respectively. The SWCNT-induced changes of DNA CD characteristics have been investigated by several groups. By using heavily acid-treated commercial SWCNTs, Li et al. reported carbon nanotubes induce a B-A transition of DNA. In Figure 4, this stabilization of A-form DNA structure is clearly shown in the CD measurement from SaDNA dispersed HipCo SWCNTs. At the initial ultrasonication of 10 min, SaDNA is in NCA-form, and moves to A&B-form as the sonication time increases. Typically, DNA helical structure exhibits the diameters of 2.6 nm and 2.0 nm at A- and B- forms, respectively. Assuming the SaDNA are wrapping around SWCNTs, the enrichment trend of small \(d_t\) nanotubes at prolonged sonication (50 min) matches surprisingly well with the decrease in diameters of surfactant DNA.

4 CONCLUSION

The NIR study revealed that single wall carbon nanotubes were dispersed into the D_2O media at a level comparable to or better than that of d(GT)_{20} DNA oligomer. Moreover, selective stabilization of smaller \(d_t\) SWCNTs was observed as the sonication time increased. 1.96 eV RRS measurement on (7,5) and \{(11,1), (10,3)\} tubes showed agreeing enrichment trend with the observation.
from NIR study. CD measurements on the SaDNA dispersed SWCNTs and SaDNA revealed that SaDNA preferred A-form when sonicated with SWCNTs. Also the NCA to A&B transition trend matches well with the small d, SWCNT stabilization at longer sonication time. More precise determination of solubilization and separation degree in SaDNA dispersion is under progress by using a UV-VIS-NIR fluorometer. Ion exchange, gel permeation, density gradient and agarose-gel electrophoresis can be good candidates for further SWCNT separation studies using this SaDNA. In addition, with optimally chirality-separated nanotube samples, the immense number of possible DNA oligomeric-structures available in SaDNA will enable us to investigate the kind of DNA strands that are interacting with each specific \((n,m)\) SWCNT. For this, a conventional separation and amplification technique from DNA research, such as polymerase chain reaction, can be used to identify the sequences of preferentially interacting DNAs.

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**REFERENCES**