Dispersion of single walled carbon nanotubes with biomacromolecules

Yan, Liangyu

2010

Yan, L. (2010). Dispersion of single walled carbon nanotubes with biomacromolecules.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/47465>

<https://doi.org/10.32657/10356/47465>

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DISPERSION OF SINGLE WALLED CARBON NANOTUBES WITH BIOMACROMOLECULES

YAN LIANGYU

School of Chemical and Biomedical Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2010

Acknowledgements

First, I would like to express my deepest appreciation to my advisor Prof. Chan Bee Eng, Mary for constant support and guidance, encouragement throughout my graduate study for years. I was always impressed by the plentiful and creative solutions she proposed for the problems that I encountered. She also set a good example of a hard-working leader in a research group and her commitment to training students has helped me both professionally and personally.

I would like to thank Prof. Judeh Zaher for guiding me in organic synthesis in the lab. Prof. Chen Yuan has been providing me support on my whole research work, in particular on characterization of experiments. I also want to thank Prof. Zhang qing for guidance of electrical measurement and Prof. Mu Yuguang helped me a lot in computer simulation. Thanks to Dr. Wang Xiujuan who gave me support on Raman measurements.

In addition I would like to thank many talented people in my research groups, including Dr. Poon Yin Fun, Dr. Zhang Jun, Dr. Zhou Wenxiu, Dr. Yan Yehai, Dr. Li Sai, Dr. Cai Qinjia, Dr. Chen Longqing, Dr. Zhou Chuncai, Dr. Qi Xiaobao, Pan Xiaoyong, Tan Yu Qian, Lee Koon Thye and Mr. Sharif; Wang Bo and Wei Li in Prof. Chen Yuan's group; Chen Fuming and Lee Chunwei in Prof. Lain-Jong Li's group.

I extend my thanks to my friends and colleagues for their support. For most, I would like to thank my parents for their endless love, support and understanding.

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List of Abbreviations

AFM	atom force microscope
^{13}C NMR	^{13}C Nuclear Magnetic Resonance
CD	circular dichroism
CS	chitosan
CVD	chemical vapor deposition
DCB	dichlorobenzene
D band	disorder band
DGU	density gradient ultracentrifugation
DMF	dimethylformamide
DOS	density of states
ECM	extra-cellular matrix
FET	field-effect transistor
FTIR	fourier transform infrared
GalNAc	N-acetyl-D-galactosamine
G band	tangential mode
GB	generalized Born
GDL	D-glucono- δ -lactone
GlcA	D-glucuronic acid
MWNT	multiwalled carbon nanotube
mSWNT	Metallic SWNTs
NMP	N-methylpyrrolidinone
OC	O-carboxymethylchitosan
OPEG	OC modified with poly(ethylene glycol)
PAA	poly (acrylic acid)

PEO	poly(ethylene oxide)
PFO	polyfluorenes
PLE	photoluminescence
PPO	poly(propylene oxide)
PSS	poly(styrene sulfonate)
PPVs	<i>p</i> -phenylenevinylene
PVP	poly(vinylpyrrolidon)
QC	quaternary ammonium chitosan
RBM	radial breathing mode
RCF	relative centrifugal force
SANS	small angle neutron scattering
SC	sodium cholate
SDS	sodium dodecylsulfate
SDBS	sodium dodecylbenzenesulfonate
SEM	scanning electron microscopy
SGC	sodium glycocholate
STC	sodium taurocholate
STM	scanning tunneling microscopy
SWNT	single walled carbon nanotube
sSWNT	semiconducting SWNT
TEM	transmission electron microscopy
THF	tetrahydrofuran
UV-vis-NIR	ultraviolet-visible-near infrared
VHS	van Hove singularities

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Summary

Dispersion of single walled carbon nanotubes with biomacromolecules

Student: Liangyu Yan

Supervisor: Associate Professor Chan Bee Eng, Mary

Single walled carbon nanotubes (SWNTs) are promising materials with exceptional electronic, mechanical and optical properties. A significant obstacle to the myriad applications of SWNTs is their tendency to aggregate into bundles. This thesis centers on the use of biomacromolecular dispersants for effective dispersion of SWNTs in aqueous solution into individual nanotubes or small bundles and extraction of specific chiral species.

In this thesis, we found several biomacromolecules which are highly effective dispersants of SWNTs: water-soluble chitosan derivatives O-carboxymethylchitosan (OC), and OC-modified polyethylene glycol (OPEG) and several glycosaminoglycans (GAGs), specifically heparin sodium salt, two isomers of chondroitin sulfate (chondroitin-4-sulfate (CS-A) and chondroitin-6-sulfate C (CS-C)) and hyaluronic acid (HA). Heparin and CS-A are easily removable and network field effect transistors (FETs) were made from them. Chitosan and its various neutral pH water-soluble derivatives were investigated for dispersing Hipco SWNTs. Chitosan (CS) can produce good dispersion of SWNTs but only in acidic pH condition. We synthesized two novel derivatives, O-carboxymethylchitosan (OC) and OC modified by poly (ethylene glycol) at the –COOH position (OPEG), which were able to produce highly effective debundling

and dispersion of SWNTs in neutral pH aqueous solution. AFM, TEM, PLE, UV-vis-NIR and Raman spectroscopy confirmed that SWNTs are present as individual nanotubes in the dispersions.

Heparin sodium salt was investigated as a dispersant for selective dispersion of SWNTs. We found that heparin sodium salt preferentially selects larger-diameter Hipco SWNTs. When used to disperse CoMoCAT® nanotube samples, heparin has a dramatic preference for (8, 4) tubes. After three-pass extraction of sodium dodecylbenzene sulfonate (SDBS)-dispersed CoMoCAT® SWNT samples with heparin sodium salt, (8, 4) species is found, using PLE, to be enriched from 7% to 60% of total abundance. Computer modeling verified that, of the various semiconducting species present, (8, 4) has the strongest binding energy with heparin sodium salt. Network FETs were successfully made with heparin-dispersed SWNTs, confirming the easy removability of heparin.

Glycosaminoglycans (GAGs) are interesting as SWNT dispersants. Three isomers of Chondroitin Sulfate (CS) ((chondroitin-4-sulfate (CS-A), dermatan sulfate B (CS-B) and chondroitin-6-sulfate C (CS-C))) were investigated as dispersants and were found to have differing abilities to debundle SWNTs. CS-C was found to be most effective at dispersing SWNTs and better than the commonly used sodium dodecylsulfate (SDS) surfactant. CS-B was found to be a poor dispersant. Computer simulation indicates that the intramolecular interactions of the three isomers are vastly different. The weak intramolecular hydrogen bonding in CS-C leads to its high dispersibility and the strongest binding energy of the

CS-C/SWNT complex while the strong intramolecular Coulombic interaction in CS-B results in its poor dispersibility and weakest binding energy of the CS-B/SWNT complex.

Finely dispersed SWNTs with OC and chondroitin sulfate solutions were successfully used for reinforcing alginate hydrogels and the compressive strength and moduli and electrical properties were dramatically enhanced. The compressive modulus and strain of the hydrogels was enhanced as much as two times by incorporation of a few weight percent SWNTs (based on alginate matrix).

Chapter 1 – Introduction

Progress in Single Walled Carbon Nanotubes (SWNTs) research has been remarkable since their discovery in 1993¹ due to their extraordinary mechanical, optical and electronic properties and thermal stability. Metallic SWNTs (mSWNT) have ballistic transport while semiconducting SWNTs (sSWNTs) have superior field-effect behavior and carrier transport mobility². These electrical properties of SWNTs make them excellent alternatives to metals and the present commonly used Si semiconductor. The Young's modulus of carbon nanotubes is about 300 to 1400 GPa, higher than that of steel of 208 GPa³. SWNTs are thought to be ideal reinforcing nanofillers and have been widely applied in polymer composites. Their high surface area (theoretically 1300 m²/g)⁴ also make them ideal for gas storage and as active sensing components in sensors.

1.1 Chiralities of SWNTs

SWNTs are one-dimensional (1D) cylinders of sp² hybridized carbon atoms (Fig. 1.1). The diameters of commonly synthesized SWNTs range from 0.5 nm to 2 nm, and their lengths can reach several micrometers. A SWNT can be thought of as a rolled-up sheet of graphene. SWNTs have different chiralities, depending on how each graphene sheet is rolled up and joined (Fig. 1.2). The direction of rolling up of the graphene sheet is defined by the vector $\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2$ (where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the graphene lattice vectors, Fig. 1.2). The chiral indices (n, m) define the degree

of twist in the nanotube as well as the nanotube diameter, both of which strongly influence the nanotube electronic properties. For $(n - m) = 3k$ with k an integer, the SWNTs are metallic; all other (n, m) belong to semiconducting SWNTs. One-third of SWNT chiralities are metallic and two-thirds are semiconducting (Fig.1.3).

Figure 1.1 Model of a (7, 5) single walled carbon nanotube

1.2 Challenges in SWNT solution processing

As synthesized SWNTs typically contain impurities such as metallic catalyst residual, catalyst support, amorphous carbon, multi-walled nanotubes *etc* and contain a mixture of chiralities. They will usually need to be purified before use and solution processing techniques such as acid treatment, centrifugation, sonication, *etc* are often applied. Further, SWNTs which are hollow with density $(\sim 1.3 \text{ g/cm}^3)^5$ approaching those of water and common organic solvents, unlike other solid inorganic nanowires, are thought to be ideal candidate materials for printed electronics.

Figure 1.2 (a) a ($n=5$, $m=0$) zigzag nanotube is shown. a_1 and a_2 are the graphene's lattice vectors. Cut a strip in the graphene sheet (blue) to roll into a carbon nanotube. (b) an ($n=2$, $m=2$) armchair carbon nanotube. (c) (n , m) carbon nanotube ⁶.

Figure 1.3 Metallic (open circles) nanotubes and semiconducting (closed circles) nanotube chiral indices ⁷.

However, one of the main challenges in SWNT solution processing is that

individual nanotubes easily form parallel bundles or ropes due to the extremely high aspect ratio (length/diameter > 1000)^{8, 9} and van der Waals forces. The solubility and mechanical strength of bundled SWNTs are poor^{10, 11}. More importantly, bundles typically consist of both metallic and semiconducting SWNTs. One of the main applications of SWNTs with huge market potential is in printed electronics. The market for printed electronics is estimated to be multiple billions of dollars in a decade or so as printing enable electronic products to be made flexible, thin, large-area and at low cost. Products based on printed electronics are expected to be pervasive, including portable electronic devices, energy storage devices *etc.* However, metallic nanotubes must be removed or suppressed for use of SWNTs as the semiconductor in printed transistors. Metallic SWNTs in the bundles also interfere with the optical and electronic property characterizations¹². Bundling results in poor removal or suppression. Therefore, the ability to disperse and debundle SWNTs into individuals is a pre-requisite for high yield purification of semiconducting nanotubes for use in new applications in electronics devices, biosensors, macroelectronics, *etc* ¹³.

There are two main approaches to overcome the problem of nanotube aggregation and bundling: covalent bonding of dispersants onto SWNTs and noncovalent functionalization. Both methods can be used to disperse SWNTs in aqueous or organic solvent. In covalent functionalization, the modifying compound is chemically reacted with the nanotubes, with the consequence that the graphene structure is altered or damaged after the chemical reaction and the intrinsic

physical properties of the SWNTs are modified. The chemically modified sites are scattering centers and impair the SWNT electronic and mechanical properties.

Surfactants and polymeric dispersants have been used as noncovalent dispersants for suspending and debundling SWNTs. Ionic surfactants in aqueous medium are thought to encapsulate SWNTs in micelles¹². However, surfactants tend to cause bubbles and foam and may present problems for the printing process. Polymer dispersants which interact noncovalently with the nanotubes have also been used to disperse SWNTs¹⁴. One family of polymeric dispersant is based on polycyclic aromatic polymers which have strong π - π interactions with the nanotube sidewall. A drawback to the use of polycyclic aromatic polymers for dispersing nanotubes is that the polymers are hard to remove afterwards so that an insulating polymer residual layer remains to wrap around each nanotube leading to deterioration of intertube and tube/electrode resistances in nanotube devices. Some amphiphilic polymers such as polystyrene-*b*-poly(acrylic acid)¹⁵ can form micelle with SWNTs to disperse them well. Biomacromolecules, such as DNA¹⁶ and protein¹⁷, and polysaccharides like starch¹⁸, have also been used to effectively disperse SWNTs. These biomacromolecules wrap around the SWNTs due to their amphiphilic nature. Their good solubility and the wrapping interaction rather than strong π - π interaction results in easy removability of some biomacromolecular dispersants. The biocompatibility, good nanotube dispersibility in aqueous medium and potentially easy removability of some biomacromolecules make them highly promising as SWNT dispersants for fundamental research as well as bioelectronic

and biosensor applications.

Polysaccharides belong to a class of biomacromolecules and possess unique advantages when used as dispersants of SWNTs. They possess multi-functional groups such as $-OH$, $-COOH$ and $-SO_3H$ (or their salt forms) making them highly water soluble, charged and relatively easily to be modified to many other types of derivatives^{19, 20}. Most polysaccharides such as chitosan are relatively cheap, mass-produced, biodegradable and biocompatible²¹. Polysaccharides are chain-like polymers and generally wrap SWNTs helically to fit the highly curved surfaces of SWNTs; according to the cavity size of the helical structure, polysaccharides can have some diameter selectivity of SWNTs. The aqueous polysaccharides-SWNT solutions are compatible with effective physical enrichment methods, like density gradient and gel electrophoresis^{22, 23}. Another advantage of polysaccharides as dispersants is that they have good solubility in water and can be easily removed during electrical devices fabrication.

1.3 Objectives of Thesis

Some polysaccharides, such as starch¹⁸, chitosan²⁴, cellulose derivatives²⁵, glucan²⁶ *etc* have been used to disperse SWNTs. Chitosan itself cannot dissolve in neutral water but can be dissolved in acid and chitosan solution has been used to disperse SWNTs²⁴. Other polysaccharides such as Inulin and Xanthan gum, cannot disperse SWNTs. Starch and glucan have been reported to helically wrap SWNTs^{18, 26}. Much remains to be understood of the forces driving the dispersability of

SWNTs by polysaccharides. Further, we seek to find novel polysaccharides which can yield high or selective dispersability of SWNTs.

The main objective of this thesis is to investigate the dispersibility of SWNTs in aqueous medium using polysaccharides. This project is divided into few sub-objectives.

The first sub-objective of this thesis is to debundle SWNTs in aqueous medium using novel polysaccharides and to develop understanding of the polysaccharide structure-dispersibility correlation. Novel water-soluble chitosan derivatives were designed and synthesized for individually dispersing SWNTs. Chitosan has several functional groups and can be modified into various water-soluble derivatives^{21, 27}. The chitosan amine or hydroxyl group can be selectively and controllably modified to help our understanding of the interaction between functional groups of chitosan-based dispersants and SWNTs.

Our second sub-objective is to selectively disperse certain (n, m) species of SWNTs. Different chiral species of SWNTs possess different band gaps and semiconducting behaviors³. As SWNTs are mixtures of various chiralities, dispersants which are chirality-specific are urgently needed. Heparin, a sulfated polysaccharide was found to select larger diameter tubes, and to extract certain chiral species of SWNTs.

Our third sub-objective is to develop easily removable SWNT dispersants. Ease of removability of the dispersants after dispersion of the nanotubes is critical to fabricating high-performance SWNT-based field-effect transistors (FETs).

Various glycosaminoglycans (GAGs) were evaluated and we found that chondroitin sulfate can disperse the SWNTs well and be removed fairly easily afterwards. We compared various GAGs to try to decipher the mechanism of polymer wrapping and dispersion.

Our fourth sub-objective is to use biomacromolecule-dispersed SWNTs as nanoscale reinforcement of hydrogels made with alginate matrix; the properties of the resulting gels were tested and analyzed.

1.4 Organization of Thesis

This report is organized into 8 Chapters. Chapter 1 is this introduction; Chapter 2 is the literature review; Chapter 3 is on SWNT source and characterization techniques used in the thesis; Chapter 4 is about dispersing SWNTs individually with chitosan derivatives; Chapter 5 reports our (n, m) selective dispersion of SWNTs with heparin; Chapter 6 compares various GAGs for dispersing SWNTs and studies in details the easily removable chondroitin sulfate dispersant; Chapter 7 discusses application of biomacromolecule-dispersed SWNTs in alginate hydrogel and Chapter 8 presents the conclusions and prospects for further research.

Chapter 2 – Literature Review

In 1991, Sumio Iijima at the NEC research lab in Japan published transmission electron micrographs of multiwalled carbon nanotubes (MWNTs)²⁸. Then in 1993, Iijima and coworkers¹ and Bethune and coworkers²⁹ separately and independently, but almost simultaneously, found single walled carbon nanotubes (SWNTs). Carbon nanotubes are tube-shaped configurations of sp^2 carbon atoms and can be thought of as 2-dimensional (2D) graphene sheets hypothetically rolled into cylinders. SWNTs belong to one class of allotropes of pure carbon known as fullerenes. The other allotropes of carbon are graphite and diamond. Carbons in diamond are sp^3 hybridized and bonded tetrahedrally while carbons in graphite are sp^2 hybridized and arranged in planar sheets.

2.1 Structures of SWNT

SWNTs are seamlessly rolled graphene sheets with diameters typically between 0.4 nm and several nanometers³⁰. The structure of SWNTs has been probed using transmission electron microscopy (TEM) and scanning tunneling microscopy (STM) techniques^{31, 32}. Electronic properties of an individual SWNT depend on how the graphene sheet is rolled up and joined lengthwise into a tube. The SWNT structure can be denoted by the chiral vector C_h ³³ (Fig. 2.1) which is perpendicular to the tube axis and defined as:

$$C_h = na_1 + ma_2 \quad (2.1.1)$$

where n is the number of a_1 units and m is the number of a_2 units of the C_h vector³⁴.

Fig. 2.1 shows the unrolled honeycomb lattice of a nanotube. When sites O and A, and sites B and B' were connected, a seamless nanotube can be formed. $\overline{OA}$ is defined as the chiral vector C_h and $\overline{OB}$ the translation vector T of the nanotube. Different ways of “rolling up” a graphene sheet affect not only the atomic structure, diameter and symmetry but also the electronic properties of individual SWNT^{35, 36}. The integers (n, m) uniquely define a SWNT.

Figure 2.1 The unrolled honeycomb lattice of a nanotube and definition of chiral vector C_h and chiral angle θ . a_1 and a_2 are the unit cell vectors of the two-dimensional hexagonal graphene sheet⁷.

The diameter of a nanotube can be defined by the integers (n, m) as follows:

$$d_t = C_h / \pi = \sqrt{3} a_{c-c} (m^2 + mn + n^2)^{1/2} / \pi \quad (2.1.2)$$

where a_{c-c} is the length of C-C bond which is usually 1.43 Å. The chiral angle θ can be defined as:

$$\theta = \tan^{-1}[\sqrt{3} m / (m + 2n)] \quad (2.1.3)$$

The range of chiral angle is between 0° and 30° . SWNTs with chiral angle of 0° and 30° are called armchair tubes and zigzag tubes respectively.

The unique electronic properties of a nanotube are due to its nearly one-dimensional structure and the consequent presence of van Hove singularities (VHS) in the density of electronic states (DOS)³⁷ (Fig. 2.2). According to tight-binding zone folding calculations³⁷, semiconducting SWNTs have bandgaps of 1-2 eV between their valence and conduction bands. For metallic SWNT, there is a continuum of states bridging the c_1 (first conduction) and v_1 (first valence) sub-bands in the density of states³. v_1 - c_1 is the first van Hove transition (E_{11}) and v_2 - c_2 is the second van Hove transition (E_{22}) and so on (Fig. 2.3). The band structure of a SWNT is sensitive to the precise way that the tube is joined longitudinally, that is to the precise values of n and m . If $(n - m)/3$ is an integer, nanotube is metallic, otherwise it is semiconducting³⁸. The bandgap energy E_{11} scale varies as the reciprocal of the nanotube diameter.

The Kataura plot (Fig. 2.4) was proposed in 1999 by Hiromichi Kataura³⁹ based on tight-binding calculation. Kataura plot shows the relationship between the electronic transitions E_{ii} (from i th valence band to the corresponding i th conduction band for both semiconducting and metallic tubes) and the diameter of the nanotube. Kataura plot has the oscillating shape of every branch which means that the properties of SWNT are strongly dependent on the chirality (n, m) of SWNT.

Figure 2.2 Density of states for armchair SWNTs⁴⁰

Figure 2.3 Electronic density of states of (a) a metallic SWNT and (b) a semiconducting SWNT⁴¹.

Figure 2.4 Electrical transition energies via diameter⁴²

2.2 SWNT Production Techniques

Main methods of SWNT growth are based on (a) arc discharge (b) laser vaporization (c) chemical vapor deposition (CVD) which includes High Pressure CO (HiPco) process and CoMoCAT® process. Although in practice each technique is quite different, the basic principle is similar: carbon is deposited onto nanometer-sized metal catalyst particles which catalyzes the formation and growth of nanotubes.

Arc-discharge method

Iijima *et al.*¹ reported CNT production with the arc discharge method in 1993. An electrical arc was passed between two graphite electrodes inside an atmosphere of inert gas. The electrical arc generated high temperature and carbon atoms were sublimated from the anode and deposited on the cathode. Typical catalysts are Fe, Co, Ni and Pt. SWNTs produced with this method usually have larger diameter (>1 nm).

The nanotube quantity produced with this method is high but the purity of SWNTs is usually low.

Laser Ablation

The laser ablation method to produce CNTs was first reported by Smalley *et al.* in 1995⁴³. A carbon target impregnated with metal catalyst (usually Ni or Co) was placed in a hot helium (He) or argon (Ar) atmosphere at about 1200 °C and vaporized with a high power laser so that carbon atoms would evaporate from the target. Carbon atoms condensed on the catalyst particles and formed SWNTs. The laser intensity and temperature are the key parameters for manipulating the nanotube properties. This method is costly because of the expensive high-purity graphite target and high power laser required.

Chemical Vapor Deposition (CVD)

With CVD, a gas containing carbon molecules is thermally decomposed on catalytic systems at high temperature (700 °C – 1000 °C) to produce CNTs. The catalysts are usually metals such as Fe, Ni, and Co and metal supports are Al₂O₃, Si, MgO *etc.* Hydrocarbons used for CVD are usually in gaseous state and these include methane, ethylene and acetylene. These hydrocarbons are passed through the catalyst so that they decompose into hydrogen and carbon at high temperatures. Carbon atoms diffuse onto the surface of catalysts and rearrange into a network like hexagons forming CNTs. The varying size of catalyst results in different diameter CNTs. Small catalysts yield small diameter CNTs while large catalyst particle size yields large diameter CNTs. CVD method is easily controlled and the composition of hydrocarbon,

catalyst system, decomposition temperature and flow rates of gases can be changed to make CNTs with varying properties.

Hipco^{44, 45} is a commercially successful CVD method that produces SWNTs with high purity at relatively high production rate. For Hipco method, CO is used as the continuous-flow gas and Fe(CO)₅ the catalyst precursor. The metal precursors (metal carbonyls) decompose to form metal clusters at high temperature. The decomposition of the metal carbonyl and the subsequent formation of catalyst particles occur in an atmosphere of carbon monoxide. The catalyst particles facilitate the decomposition of CO to CO₂ and produce SWNTs from carbon⁴⁴. Diameters of nanotubes can be controlled with the CO pressure. As Hipco SWNTs have high SWNT purity and small diameter SWNTs (0.7-2 nm)⁴⁴, they are good candidates for optical characterizations.

The CoMoCAT[®] CO disproportionation⁴⁶⁻⁴⁸ method has been well developed and CoMoCAT[®] SWNTs are commercially available. Both the diameter and chirality of produced SWNTs using CoMoCAT[®] CO disproportionation can be controlled. SWNTs are produced with disproportionation at 700 – 1000 °C. The catalyst is Co-Mo complex with a silica support and this catalyst system is only effective when both metals exist. The selectivity of the Co-Mo catalyst system is strongly affected by the stabilization of Co²⁺ species by Mo oxide species. At high temperatures, the Co-Mo interaction inhibits the Co sintering that is important for formation of CNTs. When Co particles are present at high ratio in the system, less impurities (such as MWNT, graphite and fibers) are produced. Only SWNTs are formed when the Co clusters are smaller than 2 nm. Typical CoMoCAT[®] SWNTs have narrow

diameter-distribution⁴⁹ and smaller diameter (< 0.9 nm) than any other bulk CNT synthesis method.

2.3 Properties and applications of SWNTs

SWNTs have many promising applications due to their high mechanical strength^{50, 51}, carrier mobility, ballistic transport, thermal conductivity^{52, 53}, and high aspect ratio.

The high carrier mobility of individual SWNTs (up to $20,000 \text{ cm}^2/\text{V}\cdot\text{s}$) makes them attractive for nanoscale electronic devices, especially field-effect transistor (FET) device⁵⁴⁻⁵⁶. In FETs, SWNTs are employed as the semiconducting material, a link between the source and drain. Due to the averaging effects of multiple tubes in networks, it is currently believed that network SWNTs shall be more viable than individual SWNTs as the semiconductor for printed electronics products though the former mobility is comprised. Recently, mobility of network SWNTs as high as $\sim 10 \text{ cm}^2/\text{V}\cdot\text{s}$ which is higher than typical values of semiconducting polymers (less than $1 \text{ cm}^2/\text{V}\cdot\text{s}$) has been reported despite a shorter history^{57, 58}. Greater strides in obtaining even higher purity semiconducting tubes separately from metallic tubes is expected to be achieved in the new few years in view of the great worldwide efforts in this aspect. Still higher mobility can be expected of network SWNTs in the foreseeable future. Large scale manipulation and placement technique with high precision, reliability and yield are other challenges⁵⁹.

The thermal conductivity of carbon nanotubes is due to nanotube lattice

vibrations, “the phonons”³. Biercuk *et al.* reported that in SWNT/epoxy composites, the thermal conductivity of samples loaded with SWNT is much higher than samples loaded with carbon fibers⁶⁰. Zhang *et al.*⁶¹ reported that the thermal conductivity of SWNTs depends on their length, diameter, chirality and temperature. The thermal conductivity of zigzag nanotube is the highest, while the chiral nanotube has the lowest heat conductivity.

SWNTs have attractive mechanical properties due to their strong carbon-carbon covalent bond and the van der Waals force between bundles. The perfect arrangement of the covalent bonds oriented along the nanotube axis makes this material exceedingly strong in the longitudinal direction. So SWNTs are used as excellent reinforcement material for polymer matrices. Young’s modulus of carbon nanotubes is about 300-1400 GPa compared to 208 GPa³ for steel.

The SWNT, with its nanoscale diameter and long hollow structure and concomitant high surface area, has been widely investigated as an energy storage material, such as for hydrogen storage in fuel cells^{62, 63}.

In medicine, SWNTs can be applied as drug delivery vehicles as they can easily enter living cells. SWNTs are very sensitive to the environment, making them ideal for sensing applications. SWNTs have also been widely used in biomolecular sensors where the nanotube atoms are exposed to the medium. In biomolecular sensors, SWNTs can detect a single molecule due their small size and bandgap sensitivity to nearby charges^{64, 65}. SWNTs also can be employed in gas sensor for detecting leakage of toxic gases⁴⁰. SWNTs have also been used as atomic force microscopy (AFM)

tips⁶⁶.

SWNT Field-effect transistors (SWNT-FETs)

SWNT-FETs were first reported in 1998 by both Dekker et al.⁵⁶ at Delft University and the IBM group⁶⁷. An individual or network of semiconducting SWNTs is connected to two metal electrodes - the source and drain. Earlier research on SWNT-FET focuses on individual nanotubes^{56, 68, 69} but recent work exploits the averaging effect of network electronics to minimize device to device variations^{70, 71}.

Fig. 2.5a is a typical SWNT-FET with an individual SWNT between the two electrodes. Fig. 2.5b shows the AFM image of an individual nanotube between the electrodes. Fig. 2.5c shows a network SWNT-FET in which two metal electrodes play the roles as source (S) and drain (D), and the bottom Si substrate is the insulated back gate (G). Applying a constant bias voltage (V_{sd}) between the source and drain and sweeping the gate voltage between negative and positive values modulate the current flow. Generally, when a semiconductor contacts with a metal, a Schottky barrier is formed at the semiconductor-metal interface. A typical current *versus* gate voltage curve (V_g) at constant source-drain voltage for SWNT-FET is shown in Fig. 2.6. When a very positive gate voltage is applied, the Schottky barrier at the SWNT-metal interface inhibits the hole transport from the metal to the SWNT resulting in small current (OFF-state). When the gate voltage is decreased to very negative values, holes-transport increases leading to increasing current until saturation (ON-state). FETs prepared with SWNTs in ambient condition are typically *p*-type, which means that the majority of charge carriers in SWNT are holes.

Figure 2.5 (a) Schematic of SWNT FET device (b) AFM image of single SWNT-FET device (c) Network SWNTs FET ⁷²

The important characteristics of a FET device are on-off ratio (I_{on}/I_{off}) (the ratio between the ON-state current versus the OFF-state current), mobility and hysteresis. Mobility indicates how fast the charge carriers respond to an external electric field. For network SWNTs, the effective FET mobility is calculated from the experimental transfer curve according to the following equation ⁷³:

$$\mu = (dI_d/dV_g) / (\epsilon V_d W / L_{ox} L) \quad (2.1.4)$$

where W and L are channel width and channel length, respectively; ϵ is the dielectric

constant of gate dielectrics; L_{ox} is the gate dielectric thickness and V_d is the source-drain bias. If the gate voltage is swept from positive to negative, then back to positive, a hysteresis can be found in the I_{sd} - V_g curve, shown in Fig. 2.6.

Figure 2.6 Typical current versus gate voltage at constant source-drain bias voltage ⁷² showing definitions of on/off states and hysteresis.

Network SWNTs can be fabricated using two main methods. One approach is based on solution deposition techniques; SWNTs are dispersed well in suspension and then deposited onto substrates by techniques such as solution casting, spin casting, ink-jet printing or printing from a stamp. Another method for fabricating network is direct SWNT growth on substrates by CVD. Solution deposition method is amenable for large-scale deposition and integration of other printing steps, while direct SWNT growth method causes less damage to the graphene structure of nanotube leading to high mobility devices.

For network SWNTs, when there is no applied gate field, the semiconducting SWNTs are insulating and only metallic SWNTs work for electric conduction. When

the ratio of metallic SWNTs increases to larger number, the network can transit from insulating to metallic. The critical density of metallic SWNTs for this transition is defined as the percolation threshold which is related to the length of SWNTs in the network. Above the percolation threshold, the network is metallic conductive. When a gate electrical field is applied to the network, the semiconductor SWNTs can be electrostatically doped so as to create new percolation paths for conduction in the network. The on-off ratio reflects the number of semiconducting versus purely metallic percolation paths. In general, the mobility of network increases with the number of SWNTs, but this will also increase the number of metallic SWNTs. A good device should have both high on-off ratio and mobility.

2.4 Methods for characterization of SWNT dispersions

This section describes standard techniques for characterization of SWNT dispersion, namely ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy, photoluminescence (PLE) spectroscopy⁴¹, atomic force microscopy (AFM), transmission electron microscopy (TEM), and Raman scattering.

2.4.1 Photoluminescence (PLE) spectroscopy

SWNTs are quasi one-dimensional (1D) electronic structures each with a large π -electron system. The van Hove singularities in the density of states (DOS) of these systems is related to the diameter of the SWNT⁷⁴. The energy of electronic transitions between the singularities is approximately proportional to the inverse of the tube diameter^{75, 76}.

Band gap fluorescence from individual SWNTs was first reported by Weisman's group at Rice University¹². Later, Bachilo *et al.*⁴¹ observed SWNT photoluminescence for E_{22} excitation followed by E_{11} fluorescent emission (Fig. 2.3). In this process, an electron is excited, via photon absorption from the second valence sub-band, v_2 , to the second conduction sub-band, c_2 . Then the excited electron non-radiatively relaxes to c_1 and later finally radiatively relaxes to v_1 with emission of a near infrared photon. Semiconducting nanotubes possess NIR photoluminescence features in the 800-1600 nm range which are related to the first van Hove transition energies (E_{11})¹². Each chiral species (*i.e.* (n, m)) of SWNT has distinct physical structure-dependent electronic structure and E_{11} and E_{22} energies⁴¹. Thus each semiconducting species can be identified by its photoluminescence energy, which is equal to the band gap energy. For metallic SWNTs, there is no excitonic luminescence. In metallic tubes, an electron can be excited through photon absorption, and the top of the valence band (v_1) touches the bottom of the conduction band (c_1), and the hole/electron pair recombines at zero energy, and so there is no distinctive fluorescent signal.

Photoluminescence spectroscopy is a powerful tool to identify specific semiconducting nanotube species and to characterize the distribution of semiconducting species in a sample. Different (n, m) SWNTs in a sample will show distinct E_{ij} transitions which have different excitation and emission wavelengths⁷⁷. A 2-D mapping of the photoluminescence features can be obtained by scanning across both the excitation wavelengths and emission wavelengths. PLE measurement in the NIR region is a powerful tool for characterizing the species abundance in SWNT

suspensions, though this method detects only semiconducting tubes and even these only as individuals or in small bundles¹². Bundling of SWNTs perturbs the electronic structure of the tubes. A further problem in PLE analysis of suspension of bundled tubes is that excitation transfer from excited semiconducting tubes to metallic tubes in the same bundle suppresses, or “quenches”, the PLE signal of the semiconducting tubes. For the most straightforward interpretation of photoluminescence data, it is necessary that the SWNTs be dispersed into individuals⁷⁸ and also other characterization methods are needed to provide complementary information for metallic SWNTs present in the mixture. Fig. 2.7 shows typical PLE maps of Hipco SWNTs and CoMoCAT[®] SWNTs dispersed with sodium dodecylbenzenesulfonate (SDBS). Hipco SWNTs have more chiral diversity and a distribution of diameters skewed toward larger nanotubes than CoMoCAT[®] SWNTs.

(a)

(b)

Figure 2.7 Typical PLE maps of (a) HiPco SWNTs and (b) CoMoCAT[®] SWNTs dispersed with SDBS¹⁰.

SWNT (n, m) Abundance Evaluation in PLE maps

Arnold *et al.*²² reported using photoluminescence spectra to determine the relative concentrations of different SWNT chiral species. Fig. 2.8a is a 2D mapping of photoluminescence intensity versus excitation and emission wavelengths. Fig. 2.8b shows emission versus excitation wavelength for a specific peak. This 1D cutout of the PLE map shows both a slowly varying background signal from off resonance

SWNTs (black arrow) and strong emission from the (7, 5) semiconducting SWNT species (red arrow)²². In order to reduce the influence of the slowly varying background in the determination of the peak amplitude, the authors suggested to calculate the partial derivative of photoluminescence intensity versus excitation wavelength (Fig. 2.8c and d). The amplitude of the partial derivative (black line AB in Fig. 2.8d) was used to determine the relative intensity of that specific chirality. This method was used in our study.

Figure 2.8 Method of abundance evaluation from photoluminescence spectra²² (a) a typical 2D PLE plot (b) a typical 1D PLE plot at a particular emission wavelength (c) partial derivative of PLE plot in 2D (d) partial derivative derivative of PLE plot at one emission wavelength.

2.4.2 UV-visible-near infrared (UV-vis-NIR) spectroscopy

The van Hove singularities of semiconducting and metallic SWNTs result in

sharp interband transitions with E_{11} ($v_1 \rightarrow c_1$), E_{22} ($v_2 \rightarrow c_2$) and E_{33} ($v_3 \rightarrow c_3$) energies. In a typical SWNT absorption spectrum, the 400-600nm region, 550-800nm region and 800~1400 nm region contain absorption features due to the lowest energy van Hove transition of metallic SWNTs (E_{11}^M), the second van Hove transition of semiconducting SWNTs (E_{22}^S) and the first van Hove transition of semiconducting SWNTs (E_{11}^S)¹². Fig. 2.9 shows typical UV-vis-NIR spectra of Hipco SWNTs and CoMoCAT[®] SWNTs dispersed with SDBS.

When SWNTs are present as individuals and/or very small bundles^{12, 79}, the absorption spectrum peaks are well-resolved. Broad peaks relative to the baseline indicate the existence of aggregated SWNTs because the intertube van der Waals interactions in bundles disturb the SWNT electronic structure, leading to line broadening^{12, 80-82}. Fig. 2.9c shows the difference between bundled and individual SWNTs samples when characterized using UV-vis-NIR spectroscopy. The bundles show broad and relatively lower amplitude absorption features while the individual SWNTs display sharp distinct peaks each corresponding to a different (n, m) species. Within these transition windows, the larger diameter (smaller band gap) SWNT transitions are observed at higher wavelengths.

Figure 2.9 Typical UV-vis-NIR spectra of (a) Hipco SWNTs⁸³ and (b) CoMoCAT[®] SWNT (from supplier's data sheet); (c) UV-VIS-NIR absorption of SWNT bundles and individual SWNTs⁸⁴.

One shortcoming of using UV-vis-NIR to identify the SWNT chirality in mixtures is that many SWNTs have similar E_{22} or E_{11} energies. There are overlaps in absorption energies resulting in broad peaks. UV-vis-NIR can be utilized together with photoluminescence to identify the chiralities present in SWNT mixtures.

SWNT purity from calculation of A(S)/A(T) ratio from UV-vis-NIR data

Haddon *et al.*⁸⁵ have proposed using solution-phase UV-vis-NIR spectroscopy to quantify the purity of SWNT dispersions (Fig. 2.10). The second semiconducting transition (E_{22}^S) was chosen for the evaluation because the S_{22} (E_{22}^S) transition is less susceptible to environmental influence. AA(S) is the area of the S_{22} (E_{22}^S) absorption spectral band after baseline subtraction and arises from dispersed SWNTs. AA(T) is the total area of the S_{22} (E_{22}^S) band, which includes contributions from SWNTs and carbonaceous impurities. A metric of the purity of dispersed SWNTs is then given by the $A(S)/A(T)$ ratio = $AA(S)/AA(T)$.

2.4.3 Raman spectroscopy

Raman spectroscopy is used to detect SWNT vibrational states and can provide information on the 1D properties of nanotubes, such as their phonon and electronic structures, as well as sidewall defects, through the resonant Raman effect⁸⁶. Raman spectroscopy detects both semiconducting and metallic SWNTs.

Figure 2.10 Schematic illustration of purity evaluation using UV-vis-NIR absorption spectroscopy of the SWNT S_{22} interband transition⁸⁷

SWNTs have three identifiable modes in the Raman range: one is the diameter-dependent radial breathing mode (RBM) between 100 cm^{-1} and 350 cm^{-1} which corresponds to the C atoms vibrations in the radial direction of the nanotube and the frequency of this mode has an inverse relationship to the diameters of nanotubes. A second mode is the higher frequency tangential mode (G band) between 1500 and 1600 cm^{-1} which is related to C-C bond planar stretching in the local plane of the nanotube sidewall. The third is the so-called disorder band (D band) between 1200 cm^{-1} and 1350 cm^{-1} which is due to defects (sp^3 hybridized carbon) in the

SWNT sidewall structure (Fig. 2.11) ⁸⁸⁻⁹⁰.

Figure 2.11 Raman spectrum exhibiting characteristic SWNT vibrational modes ^{75, 91}.

The G band has two important peaks: G^+ (around 1590 cm^{-1}) and G^- (around 1570 cm^{-1}) band. The G^+ peak is related to carbon atom vibrations along the SWNT axis. The G^- peaks is related to carbon atom vibrations along the circumferential direction of the SWNT (Fig. 2.11). The line shape of the G band can be used to distinguish between semiconducting and metallic SWNTs. The G band of semiconducting SWNTs has been well described with Lorentzian oscillators^{86, 92}. The Raman line shape of metallic SWNTs, on the other hand, is fitted well with the Breit-Wigner-Fano (BWF) line shape^{39, 93}. The lineshape of the G band is sensitive to metallic (Breit-Wigner-Fano lineshape) or semiconducting SWNT (Lorentzian lineshape)

content, as shown in Fig. 2.12.

Figure 2.12 Lineshape of G band for high oriented pyrolytic graphite (HOPG), one semiconducting SWNT and one metallic SWNT⁹⁴

The D peak can be used to check the extent of covalent functionalization⁷⁵. The intensity of the D band will increase relative to the G band after covalent functionalization since that disrupts the sidewall structure. Therefore, it is an important tool for confirmation of covalent functionalization of SWNTs.

When the incident laser energy matches the energy separation between van Hove singularities in the valence and conduction bands (e.g. E_{11}^S , E_{22}^S and E_{11}^M), a resonant Raman can be observed from that nanotube⁹⁴. Using different laser energies, one can probe distinct (n, m) species⁹⁵ and the degree of p - or n -doping⁹⁶. The RBM shift (ω_{RBM}) is inversely proportional to the SWNT diameter (d_t); the relation may be parametrized as $\omega_{\text{RBM}} = A/d_t + B$, where the A and B parameters are determined experimentally⁹⁴.

In this thesis, 633 nm laser (1.96 eV) and 514 nm laser (2.14 eV) were used for characterizing Hipco SWNTs and CoMoCAT® SWNTs. 633 nm laser can detect larger diameter ($d > 1$ nm) metallic SWNTs and smaller diameter ($d < 0.94$ nm) semiconducting SWNTs, while 514 nm laser can detect smaller diameter ($d < 1.03$ nm) metallic SWNTs and larger diameter ($d > 1.08$ nm) semiconducting SWNTs. The SWNTs which have band gaps similar to the incident laser energy can be excited. The Raman data can be analyzed by utilizing a Kataura plot⁹⁷.

2.4.4 Microscopy

The above described techniques necessarily characterize populations of nanotubes. Individual CNTs can be characterized by the techniques of atomic force microscopy (AFM) and transmission electron microscopy (TEM). These methods can be used to assess changes in the size of bundles and the length of tubes after suspension and purification treatments. Fig. 2.13 shows a typical AFM image. Such images can give direct evidence of the dissolution/dispersion state of the SWNTs and the degree of surfactant/dispersant removal. From the height profiles of AFM images, individually dispersed SWNTs or bundles can be recognized and the bundle size can be measured.

Figure 2.13 AFM height image and section analysis of modified SWNTs. The arrows point to a 2.3 nm height difference⁹⁸.

2.5 Dispersion of SWNTs

SWNTs in solution tend to aggregate into bundles due to their nano size and strong intertube interaction arising from van der Waals interaction and their hydrophobic nature^{9, 99}. Aggregation and/or bundling hamper the performance and applications of SWNT-based devices¹⁰⁰. In many applications, individually dispersed SWNTs are preferred. The dispersion of SWNTs bundles into individuals is a subject of intense interest and a variety of methods have been devised^{23, 101}.

SWNTs can be debundled into individual nanotubes in aqueous solutions via

covalent or noncovalent functionalization^{81, 102, 103}. In covalent functionalization, chemical reactions are used to attach molecules via sharing of electrons with the SWNT; this inevitably modifies the intrinsic physical properties and the aromatic structure of the SWNTs and limits the myriad applications which exploit the perfect graphene-like structure of SWNTs, especially in electronics. In covalent functionalization, a tradeoff between sufficient functionality and minimal tube damage often must be made. Non-covalent functionalization involves non-covalent bonding such as π - π interaction, charge transfer, hydrophobic interaction, helical wrapping *etc* and preserves the graphene structure of SWNTs.

Here, we mainly review dispersion of SWNTs with noncovalent functionalization methods.

Dispersion of SWNTs without surfactant

SWNTs can be dispersed into a colloidal suspension in some organic solvents, such as *N*-methylpyrrolidinone (NMP), dichlorobenzene (DCB) and *N,N*-dimethylformamide (DMF)¹⁰⁴⁻¹⁰⁶. However, suspension in organic solvents is typically not stable against SWNT re-aggregation over long periods¹⁰.

Dispersion of SWNTs with surfactant

SWNTs can be suspended as individual tubes in an aqueous water suspension using surfactants. Sodium dodecylsulfate (SDS) is the most commonly used surfactant and was reported by O'Connell *et al.* in 2002¹⁰⁷. It is used with sonication to promote separation of SWNT bundles into individual nanotubes (Fig. 2.14) and centrifugation to precipitate residual large bundles. Other reported surfactants that can disperse

SWNTs well include sodium dodecylbenzenesulfonate (SDBS)^{108, 109}, Triton X-100¹⁰⁹, Brij¹⁰⁸, and Tween¹⁰⁸ (Fig. 2.15). Smalley *et al.*¹¹⁰ have proposed that surfactants debundle SWNTs via an “unzipping” mechanism. Sonication provides a high shear environment which forms gaps or spaces at the bundle ends, into which dispersant molecules penetrate and wrap the tubes by physical adsorption. Subsequent centrifugation is typically performed to remove large bundles leading to a supernatant solution of small bundles and/or individually dispersed SWNTs (Fig. 2.14).

Figure 2.14 Mechanism of surfactant action in sonication¹¹⁰

Some biological surfactants such as bile salts have also been used for dispersing SWNTs in water. The most commonly used biological surfactant is sodium cholate (SC); others include sodium taurocholate (STC) and sodium glycocholate (SGC)¹¹¹⁻¹¹³ (Fig. 2.15). SWNTs individually dispersed with biosurfactants have been characterized with photoluminescence (PLE) and the results show that chemical structure of the biosurfactant modulates the SWNT chirality distribution in the supernatant¹¹³.

Figure 2.15 Chemical structures of surfactants

Various models of arrangements of SDS around the nanotubes have been proposed. O'Connell¹⁰⁷ have reported a model of SDS micelle as a hair-like structure arranged around the nanotube (Fig. 2.16 (a)). Later, other researchers proposed the hemi-cylinders shaped micelles around the nanotubes^{109, 114} (Fig. 2.16 (b) and (c)), the same shape of SDS adsorbed layer on flat graphite¹¹⁵.

Figure 2.16 Suggested Models for SDS Adsorption on CNTs^{107, 109, 114}. (a) SDS is the surfactant; (b) SDS, SDBS and Triton X-100 are the surfactants; and (c) A: The SDS molecules are adsorbed perpendicularly to the surface of the nanotube, forming a monolayer. B: The SDS molecules are organized into half-cylinders oriented parallel to the tube axis. C: The SDS molecules form half-cylinders oriented perpendicular to the tube axis.

SDS is unsuitable for dispersion of SWNTs for use in biomedical applications involving cell or tissue interaction. SDS is commonly used as a biological detergent for cell lysing. It disrupts polar interactions on the cellular membrane, forms complexes with proteins and lipids, and finally causes cell destruction and death.

Dispersion of SWNTs using polycyclic aromatic chemicals

Polycyclic aromatic molecules, such as anthracene and its derivatives¹¹⁶ and terphenyl¹¹⁷ which are dye molecules, perylene and its derivatives¹¹⁸ and phenanthrene¹¹⁹ have also been reported to disperse SWNTs via π -stacking onto the sidewalls of nanotubes in organic solvents (Fig. 2.17).

Figure 2.17 Structure of Polycyclic aromatic molecules

Nakashima *et al.*¹²⁰ reported pyrene-ammonium salt as a dispersant to disperse SWNTs in water. It has strong π - π interaction between the pyrene group and the CNT sidewalls. This has led to widespread use of many pyrene derivatives as dispersants for SWNTs¹²¹⁻¹²³. Dai *et al.*¹²⁴ demonstrated that a pyrene derivative can be used as

an interlinker for attaching protein onto the surface of SWNTs. Using the strong binding affinity of pyrene-based interlinkers for SWNT surfaces, Au nanoparticles¹²⁵, Fe_3O_4 ¹²⁶, poly(sodium styrenesulfonate)¹²⁷ *etc* have been immobilized onto SWNT surfaces.

Zn protoporphyrin¹²⁸ has also been reported to suspend SWNTs. Later many porphyrin derivatives have been reported for dispersing SWNTs in water^{129,130, 131}. Osuka *et al.*¹³² reported diporphyrin molecules (Fig. 2.18) as “chiral nano-tweezers” to extract either right- or left-handed SWNTs from raw samples.

Figure 2.18 Structure of chiral nano-tweezers¹³²

Dispersion of SWNTs using polymers

Amphiphilic block copolymers such as poly(ethylene oxide)-*b*-poly(propylene oxide) (PEO-PPO) copolymer can, like surfactants, micelle-encapsulate SWNTs¹³³. Amphiphilic polymers such as polystyrene-*b*-poly(acrylic acid)¹⁵ also have been reported to form micelles with SWNTs in DMF-water mixed solvents.

Since aromatic molecules have strong affinities for the sidewalls of SWNTs, pyrene^{134, 135} and porphyrin¹³⁶ have been attached to polymers as pendant groups so that the polymers can strongly wrap the tubes in order to disperse them. Fujigaya *et al.* reported a copolymer of pyrene-carrying acryl amide which can disperse SWNTs in

water¹⁰¹. Polyfluorenes (PFO)^{137, 138} have also been used for this purpose. PFO-based polymers possessing different side groups result in different (n , m) selectivity or specific diameter selectivity^{138, 139}.

p-phenylenevinylene derivatives (PPVs) which disperse SWNTs in chloroform are the first dispersant compounds reported to act via the π - π interaction between a polymer and the SWNT surface¹⁴⁰. The rigid conjugated polymer poly(aryleneethynylene)¹⁴¹ has been used to disperse SWNTs. The backbone of this polymer is rigid and aligns onto the sidewall of SWNTs via π -bond interaction. The π -conjugated polymer poly[(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)] (PmPV) has also been reported to disperse SWNTs¹⁴². Yi *et al.*¹⁴³ reported that PmPV has diameter selectivity of SWNTs. The polymer assumes a helical conformation with a certain cavity size, so that it can hold SWNTs up to a certain diameter.

O'Connell *et al.*¹⁴⁴ proposed the multi-helical wrapping of SWNTs with poly(styrene sulfonate) (PSS) and poly(vinyl pyrrolidone) (PVP). They postulated that there would be high-surface area coverage with low-backbone strain, and that the polymer would coil around the SWNT close to its backbone curvature.

Poly(vinyl alcohol)¹⁴⁵, poly (acrylic acid) (PAA)¹⁴⁶ and polyvinyl pyrrolidone (PVP)¹⁴⁷ can also disperse SWNTs very well. Polyaromatic amphiphiles have been designed to be selective to armchair SWNTs due to their supermolecular recognition of specific nanotube species¹⁴⁸.

Dispersion of SWNTs using biomacromolecules

Dispersion of SWNTs using biocompatible biomacromolecules would open up

new possibilities in the study of biological activities of biomacromolecule-SWNT complexes and applications in SWNT-based biomedical devices¹⁴⁹.

The use of Deoxyribonucleic Acid (DNA) to disperse SWNTs individually in water, was reported by Zheng *et al.*¹⁶. Helical wrapping of SWNTs by single-stranded DNA (ssDNA) was observed with AFM imaging¹⁵⁰. The mechanism of the DNA adsorption onto SWNT and the interaction between the SWNTs sidewall and the DNA has been studied through absorption and infrared (IR) spectroscopy¹⁵¹, and with theoretical methods¹⁵². The hydrophobic bases attach to the sidewall of nanotube with π -stacking interactions, and the negatively charged phosphate backbone is dissolved in water. Of particular interest is that, DNA-encapsulated SWNTs can be further separated by diameter, length and electronic type using ion-exchange chromatography^{16, 153}. Zheng *et al.*¹⁵⁴ also reported enrichment of certain chiral species for ssDNA/SWNT complexes using chromatography-based method.

Ishibashi *et al.*¹⁷ have used Ribonucleic Acid (RNA) to dissolve SWNTs in aqueous solution. Then a layer-by-layer technique was applied to fabricate a thin film from RNA/SWNT suspension on a substrate.

Wang *et al.*¹⁵⁵ used phage display to identify peptides with selective affinity for SWNTs. Diechmann *et al.*¹⁵⁶ synthesized an artificial α -helix amphiphilic peptide (labeled as “nano-1”). Due to charge-charge interactions, the peptide can self-assemble in aqueous solution and form fiber-like assemblies with SWNTs. Later, other synthesized peptides¹⁵⁷ and cyclic peptides¹⁵⁸ (Fig. 2.19) were reported for dispersing SWNTs. Two types of cyclic peptides have been designed with different

inner cavity size and they disperse SWNTs with diameter selectivity. In these systems, the hydrophobic interaction between the hydrophobic domains and CNT sidewalls plays a significant role in the dispersion¹⁵⁹.

Figure 2.19 Model (top view) of peptide with a (11,3) SWNT (C, green; H, white; N, blue; O, red; S, yellow; SWNT, pink)¹⁵⁸

Several natural proteins¹⁶⁰⁻¹⁶³ have been used to suspend SWNTs. The hydrophobic part of the protein has hydrophobic interaction with SWNTs. For example, lysozyme has been used to debundle SWNTs and also to form pH-sensitive dispersion with SWNTs (Fig. 2.20)¹⁶³. It can disperse SWNTs at pH<8 and pH>11; between these pH limits, SWNTs will aggregate. Poly-L-lysine¹⁶⁴ has been demonstrated to be effective in dispersing SWNT and poly-L-lysine-SWNT complex is also pH-sensitive.

Figure 2.20 Scheme of stabilization of SWNTs by lysozyme. Left: lysozyme in ribbon configuration. Right: secondary structure of lysozyme complexed with a SWNT¹⁶³.

Engineered carbohydrate-binding module (CBM) protein has also been reported for dispersing SWNTs¹⁶⁵. Natural polyelectrolytes, such as sodium lignosulfonate and humic acid, have also been reported to debundle SWNTs in aqueous solution¹⁶⁶.

Dodziuk *et al.*¹⁶⁷ have reported that η -CD (cyclodextrin), which has a 12-membered ring structure with an inner cavity of about 1.8 nm in diameter, can encapsulate individual SWNTs. Papadimitrakopoulos *et al.*¹⁶⁸ showed that flavin mononucleotide adopts helical structure when wrapping SWNTs via π - π interactions. Wrapping SWNTs in a helical pattern leads to efficient separation of aggregates into individuals. Flavin mononucleotide also exhibits chiral selectivity¹⁶⁸. Flavin moieties form a helical ribbon due to cooperative hydrogen bonding between them. The flavin mononucleotide assembly has higher affinity for (8, 6) SWNT as proven by PLE and modeling results¹³⁷.

Dispersion of SWNTs using carbohydrates

Chitosan and gelatin have been used to individually disperse SWNTs^{24, 169, 170}. Chitosan can disperse SWNTs well so that chitosan-SWNTs solution is stable even on

standing for prolonged periods of several months. However, the limitation is its non-solubility in neutral aqueous solution. Chitosan is soluble in acidic aqueous solution but the resulting solution viscosity tends to be high compared to those of other highly soluble polysaccharide (*e.g.* chondroitin sulfate) solutions. Dissolving chitosan in acidic pH precludes application of common physical SWNT enrichment methods (such as density gradient ultracentrifugation or gel electrophoresis^{22, 23} to increase semiconducting nanotubes proportion in the sample. Gelatin can disperse SWNTs in neutral aqueous solution while the dispersion cannot be stable for a long time.

Gum Arabic⁹⁹ and cellulose derivatives²⁵ have been found to effectively disperse SWNTs. Cellulose, a biodegradable polysaccharide, is insoluble in water and most organic solvents. The hydroxyl groups of cellulose can be modified to produce many kinds of cellulose derivatives. Sodium carboxymethylcellulose, a cellulose derivative, has been reported to be soluble in neutral aqueous solution and a good SWNT dispersant²⁵.

Glycoconjugate polymer with bioactive sugars⁸³ (Fig. 2.21), which has carbohydrate as the pendant side chain has been reported to disperse SWNTs well. Bioactive sugars as pendant groups make the glycoconjugate polymer highly soluble in water.

Figure 2.21 Scheme of glycoconjugate polymer-SWNT complex⁸³

Star *et al.*¹⁸ reported the use of starch to disperse SWNTs. They proposed a mechanism of helical amylose-wrapping of SWNTs (Fig. 2.22). Amylose, a glucose polymer, forms water-soluble complexes with left-handed helical conformation in the presence of guest molecules such as iodine. These amylose/guest molecule complexes when sonicated with SWNTs cause the amylose to helically wrap around the SWNTs.

Another helical natural polymer β -1, 3-glucans^{26, 171} has been reported to disperse SWNTs individually in water. TEM pictures of schizophyllan/SWNT hybrids clearly show that two-schizophyllan chain helically wraps one SWNT with right-handed helicity¹⁷¹. Later, Alginic acid¹⁷² has been reported to disperse CNTs with helical wrapping. We summarize the various fundamental mechanisms of SWNT dispersion by different types of compounds in Fig. 2.23.

Figure 2.22 Amylose chemical structure and scheme of the left-handed helix adopted by amylose¹⁸.

Figure 2.23 Schematic of dispersing SWNTs with different dispersants

Chapter 3 – Experimental Details: SWNT Sources and Characterization Techniques

This Chapter presents (1) a survey of the SWNT sources used to provide the raw materials of this research and (2) the specifics of the characterization methods for SWNTs employed in this project.

3.1 Carbon nanotube sources

Four main sources of SWNTs were used in this thesis.

Highly-purified HiPco SWNTs (super purified grade) were purchased from Carbon Nanotechnologies, Inc. (Houston, Texas, USA). The received SWNTs were heated in air at 350 °C for 1 h and refluxed in 3M HCl for 10 h. Then purified SWNTs were collected onto filter paper via vacuum filtration and washed with lots of de-ionized (DI) water until the washing water dripping from the filter paper was neutral in pH. The solid on the filter paper was freeze dried (Christ Alpha 1-2 plus Model) to a loose powder which was utilized for all subsequent purposes.

CoMoCAT[®] single walled carbon nanotubes (SWeNT[®]SG65 with at least 90 wt% carbon purity) were purchased from SouthWest NanoTechnologies, Inc. CoMoCAT[®] SWNTs were used directly without further purification.

Chengdu SWNTs with at least 90 wt% carbon purity were purchased from Chengdu Organic Chemicals Co. Ltd (China). The purification procedure was the same as with Hipco SWNT's purification process. The received SWNTs were heated in air at 350 °C for 1 h and refluxed in 3M HCl for 10 h. Then purified SWNTs were collected onto filter paper via vacuum filtration and washed with lots of de-ionized

(DI) water until the washing water dripping from the filter paper was neutral in pH. The solid on the filter paper was freeze dried (Christ Alpha 1-2 plus Model) to a loose powder which was utilized for all subsequent purposes.

P2 SWNTs with more than 90% carbonaceous purity were purchased from Carbon Solutions, Inc (USA). P2 SWNTs were used directly without further purification.

3.2 Details of our SWNT characterizations

Photoluminescence spectroscopy (PLE) measurements were conducted with a Jobin-Yvon Nanolog-3 spectrofluorometer equipped with an IGA (InGaAs) near-infrared (NIR) detector. PLE spectroscopy was used to determine the relative abundance of different species of semiconducting nanotubes in SWNT supernatant solutions obtained after centrifugation. The chiralities were determined by fitting the energy bandgaps from SWNT's E_{11} emission when the excitation energy match the nanotube E_{22} energy level (Fig. 2.3)⁴¹. The assignment of each chirality in the experimental data in our research was refer to the reported data⁴² (Table a1. Appendix A). For calculating the semiconducting (n , m) relative abundance distribution, the amplitude of the partial derivative of PLE intensity versus excitation wavelength was computed following the method proposed by Arnold *et al.*¹⁷³ (see Section 2.4.1).

Ultraviolet-visible-near-infrared (UV-vis-NIR) absorption spectroscopy was performed with a Varian Cary 5000 UV-vis-NIR spectrophotometer. A 10 mm light path quartz cuvette was used for characterization. The UV-vis-NIR data was used to

analyse SWNTs dispersibility, which is refer to the A(S)/A(T) ratio. A(S)/A(T) ratio is an index of the ability to disperse SWNTs into individuall and small bundles (A(S) is the area of the E₂₂ interband transition after baseline substraction and A(T) is the total area under the spectral curve⁸⁷.) (see Section 2.4.2). To assign the peaks in UV-vis-NIR with SWNT chirality, Table a1 (Appendix A) was used as reference.

Raman Spectroscopy was conducted using a Renishaw inVia Raman microscope with 514.5 nm (2.41 eV) and 633 nm (1.96 eV) wavelength lasers in a backscattering configuration. SWNTs dispersed in supernatant solutions were filtered onto 0.2 µm polycarbonate membranes (purchased from Whatman Ltd) to form homogenous films. Spectra were collected directly from these SWNT films. For analyzing each peak in RBM band of experimental Raman data, reported Kataura plot⁹⁷ was used to identified the chirality(Table a2 & a3. Appendix A).

Atomic Force Microscopy (AFM) was performed using a MFP 3D microscope (Asylum Research, Santa Barbara, CA) in AC (tapping) mode. For AFM measurement of polymer-SWNTs solutions, the SWNTs supernatant solution was deposited onto a silicon wafer (the silicon wafer was pre-cleaned by exposure in Ar plasma (PX-500TM, March Plasma Systems, Concord, CA) for 1 min with 100 W discharge power at 350 sccm Ar flow rate) and then rinsed for one day using neutral de-ionized (DI) water.

Transmission Electron Microscopy (TEM) was conducted using a JEOL JEM-2010 high-resolution transmission electron microscope (HR-TEM) at 200 kV. To prepare samples for TEM, 10 µL of supernatant solution of polymer-SWNTs after ultracentrifugation was dropped onto a 400 mesh Lacey Formvar/Carbon-grid

(PELCO, CA). Grids were dried at room temperature and then dipped into neutral DI water with shaking for 10 h to rinse away polymer.

X-Ray Photoelectron Spectroscopy (XPS) measurements were recorded using a Kratos Axis-ULTRA X-ray photoelectron spectroscope with a monochromatic Al-Ka x-ray source (1486.7 eV) in ultra high vacuum environment of 10^{-9} Torr. Survey spectra were made with a pass energy of 160 eV and a step size of 1 eV and high resolution spectra were made with a pass energy of 40 eV and a step size of 0.1 eV. The supernatant fraction of surfactant/dispersant-Hipco SWNT solution was filtered through a 0.2 μ m polycarbonate membrane. A large quantity of water was used to wash away the surfactant or dispersant. After drying, the nanotubes on the filter papers were used for the XPS tests.

Back-gated SWNT-FETs were made by drop-casting nanotube/dispersant solution on p-type silicon wafers (orientation: $\langle 1-0-0 \rangle$; thickness: 500 ± 25 μ m) capped with 300 nm thermally grown silicon dioxide layers. The source and drain electrodes pre-patterned on the Si wafer were made of 60 nm Au coated on top of 10 nm Ti. The channel width was 100 μ m and the length 20 μ m. The SWNT solution was dropped onto the devices which were then dried and rinsed with de-ionized water. The process was repeated until a percolation path in the active channel had been formed by measuring current. The device properties measurements were recorded with a Keithley semiconductor parameter analyzer Model 4200-SCS. The drain voltage was set at -2 V and the p-type silicon was the back gate.

Chapter 4 – Individually dispersing SWNTs with novel neutral pH water-soluble chitosan derivatives

4.1 Introduction

For dispersing SWNTs into individual nanotubes, noncovalent functionalization has the advantage of preserving the intrinsic electronic structure and properties but requires careful design to allow sufficient interaction of dispersant with the nanotubes¹⁷⁴. Individually dispersed SWNTs in biocompatible media is very important for many biomedical and nanomedicine applications¹⁷⁵⁻¹⁷⁷. Biopolymers such as starch¹⁷⁸, protein¹⁷⁹, α -GalNAC residues¹⁸⁰, lysozyme¹⁶³, poly-L-lysine-dispersed¹⁸¹ and DNA¹⁵⁵ have been demonstrated to be effective in dispersing SWNT and preparing biocompatible devices.

Chitosan (CS), a copolymer of 2-acetamido-2-deoxy- β -D-glucopyranose and 2-amino-2-deoxy- β -D-glucopyranose through a β -(1 $\rightarrow$ 4) linkage, is a naturally abundant polysaccharide¹⁸² which has been shown to be a good polymeric dispersant for SWNTs in acetic acid¹⁸³. It has also been shown to exhibit diameter-selectivity¹⁶⁹ in that “smaller-diameter” SWNTs are preferentially dispersed and wrapped by chitosan. CS has been applied in various biomedical areas due to its nontoxicity, biocompatibility and biodegradability. However, its limited solubility in acidic pH (< 6) restricts its applications.

We are interested in chitosan derivatives which are soluble in neutral aqueous media and which can serve as effective dispersants for SWNTs. To achieve highly

dispersed SWNTs, the dispersant needs to satisfy two conditions: it must possess (1) a head group which strongly anchors to the hydrophobic SWNT surface and (2) a tail group which imparts repulsive stabilizing forces to SWNTs¹⁸⁴. We expect that with suitable modification of the functional groups of chitosan, it can be made soluble in neutral pH aqueous solutions to extend the applicability of chitosan-derived dispersants. Various *N*- and *O,N*-substituted derivatives of CS, specifically *N*-succinyl chitosan, *O,N*-carboxymethylchitosan and *N*-hydroxypropyl- trimethylammonium chloride chitosan, have been reported to form small (4-9 nm) bundles of SWNTs over a range of pH, including neutral pH¹⁸⁵. However, all the derivatives used in that paper are substituted from the $-NH_2$ group. However, it is known that the electron-donating $-NH_2$ interacts strongly with carbon nanotubes¹⁸⁶. We are interested to ascertain the effects of various *O*- as well as *N*-substitutions of CS on the dispersibility of nanotubes.

In this chapter, we applied several derivatives of chitosan with different functional groups for dispersing SWNTs into individual nanotubes in neutral pH aqueous solutions. The derivatives investigated (Fig. 4.1) which are *O*-carboxymethylchitosan (OC), OC modified with poly(ethylene glycol) (OPEG) and quaternary ammonium chitosan (QC) obtained by introducing alkyl groups into the amine groups of chitosan, all have good solubility in neutral aqueous solutions. The dispersibility, stability and interaction of the dispersant-SWNT complexes were evaluated by photoluminescence, UV-vis-NIR, Raman spectroscopy, AFM and High-Resolution Transmission Electron Microscopy (HR-TEM). OC and OPEG were

found to be effective dispersants and Fourier-Transform Infrared Spectroscopy (FTIR) was used to investigate the nanotube-polymer interaction.

Figure 4.1 Structures of OC, CS, QC and OPEG

4.2 Experimental details

Materials

Hipco SWNTs were used in this chapter and the nanotube purification details are described in Chapter 3.1. Chitosan (CS) was from DaLian XinDie Chitin Co. Ltd, China. The CS degree of deacetylation was 81.79% and the number-average molecular weight was about 125,000 Daltons. All chemicals and solvents were purchased from Sigma-Aldrich (Singapore) at the highest commercially available purity and used without further purification.

Synthesis of O-carboxymethylchitosan (OC)

The process has been previously reported by us¹⁸⁷. Briefly, chitosan (2.0 g) was immersed into 25 ml of NaOH (50 wt %) solution for 24 h to swell and alkalize the polymer. Before addition of the acid, the alkalized chitosan was filtered under suction to obtain a dry cake. Monochloroacetic acid (3.0 g) dissolved in isopropylalcohol (25 ml) was then added dropwise into the alkalized chitosan for 20 min. The mixture was reacted for 8 h at room temperature. At the end of the reaction, the slurry was filtered to remove the solvent. The solid was dissolved in 100 ml of water, and then 2.5 M HCl was added to neutralize the pH of this solution. The reaction mixture was then centrifuged (4000 rpm for 15 min) and 400 ml of ethanol was added to the supernatant liquid, resulting in the precipitation of a white solid from the solution. The solid was filtered and rinsed several times with ethanol. The product was dried under vacuum at room temperature.

For OC, the degree of carboxymethylation was about 1.26. Alkalimetry was used to determine the degree of carboxymethylation (DC) of the OC samples^{188, 189}. DC was defined as the number of carboxymethyl groups per 100 anhydroglucosamine units of chitosan. In brief, OC samples were dissolved into 0.1 M NaOH solution with phenolphthalein as an indicator at room temperature. Titration was carried out using 0.1 M HCl until the pink coloration disappeared. DC was calculated as follows:

$$w_{-CH_2COOH} \% = \frac{[(V_{NaOH} \times C_{NaOH}) - (V_{HCl} \times C_{HCl})] \times 59}{W_{sample}} \times 100\% \quad (4.1)$$

$$DC = \frac{161 \times (w_{-CH_2COOH} \%)}{58 - (58 \times w_{-CH_2COOH} \%)} \quad (4.2)$$

where $w_{-CH_2COOH} \%$ is the weight percentage of carboxymethyl groups present in the sample. V_{NaOH} and V_{HCl} are the volumes of the NaOH and HCl respectively. C_{NaOH} and C_{HCl} are the concentrations (mol/l) of the standard solutions of NaOH and HCl respectively. W_{sample} is the sample mass (g) used for the titration. The constants used for DS are (i) the molecular weight of the anhydroglucose unit of chitosan (161), (ii) the net increase in the weight of the anhydroglucose unit for each carboxymethyl group substituted (58) and (iii) the molar mass of the carboxymethyl group (59).

Synthesis of QC

QC was synthesized according to literature^{190, 191}. Chitosan (1 g) was first suspended in *N*-methylpyrrolidone (50 ml). A 1.5 N NaOH solution (15 ml), sodium iodide (2.53 g) and iodomethane (19.45 ml) were added to this solution and its temperature was raised to 50 °C and maintained at this value for 12 h while stirring. The reaction mixture was then filtered to remove the insoluble portion and the filtrate was precipitated using a large excess of acetone (~500 ml).

For QC, the degree of quaternization of $-NH_2$ group was about 0.24. The degree of quaternization (DQ) was calculated from the relation:

$$DQ = \frac{\frac{C}{N} \text{mol}\% (QC) - \frac{C}{N} \text{mol}\% (chitosan)}{\frac{C}{N} \text{mol}\% (chitosan)} \times 100\% \quad (4.3)$$

where C% and N% are provided with elemental analysis data.

Synthesis of OPEG

Our OPEG was synthesized from reacting OC with mono-amine-terminated PEG according to carbodiimide chemistry¹⁹². Mono-amine terminated PEG (Mn 550) was synthesized using an established procedure¹⁹³.

Synthesis of carboxyl PEG monomethyl ether. 5.0 g PEG monomethyl ether (M_n 550) (I, Fig. 4.2) reacted with 0.91 g succinic anhydride in 60 ml toluene at 150 °C for 5 h. It was allowed to cool the mixture to room temperature, and pour the mixture into excess ether, resulting in the precipitation of crude products. Crude products were dissolved in dichloromethane (DCM) and the solution was applied filtration to remove unreacted succinic anhydride. The filtrate was concentrated to obtain a carboxy-terminated PEG (II, Fig. 4.2).

Activation of carboxyl groups. The carboxy-terminated PEG (11 mmol) was activated by *N*-hydroxysuccinimide (1.85 g, 16 mmol) and dicyclocarbodiimide (DCC) (3.33 g, 16 mmol) in a mixture of 1,4-dioxane and DCM (100 ml, 1:1 v/v) at room temperature for 12 h. The mixture was filtered to remove dicyclohexyl urea (by-product), and then the filtrate was concentrated. The product was redissolved in DCM and the solution stirred at room temperature for several hours before the solution was filtered to remove further the dicyclohexyl urea (by-product). The filtrate was concentrated to obtain the product.

Synthesis of amine PEG monomethyl ether. The activated PEG monomethyl ether (III, Fig. 4.2) (0.5 g, 0.68 mmol) was allowed to react with ethylene diamine (0.12 g, 1.99 mmol) in methanol (100 ml) at room temperature for 12 h. The mixture was

concentrated to obtain a yellow oil. The oil was dissolved in DCM and trace precipitate was filtered off. The filtrate was then concentrated and dried under vacuum to obtain amine PEG monomethyl ether (IV, Fig. 4.2).

Synthesis of OPEG. OCMCS (0.1 g, 0.55 mmol) was dissolved in water before 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (WSC) (0.20 g, 1.04 mmol) and amine PEG monomethyl ether (IV) (0.76 g, 1.04 mmol) were added. The reaction was stirred at room temperature for 24 h. After reaction, the solution was subjected to dialysis to remove salts and lyophilized. The lyophilized solid was washed with DCM three times to remove excess PEG and filtered. The product was then air-dried and 0.29 g of OPEG (V, Fig. 4.2) was obtained.

Figure 4.2 Schematic for the preparation of OPEG

OPEG had about 8.84 mol% PEG grafting to OC calculated according to the reported method¹⁹⁴ from the followed equation:

$$\text{PEG} = \frac{n \times 550}{m} \times 100 \quad (4.4)$$

Where n is concentration of PEG in the sample (mol/l) and m is the sample weight (g).

Polymer/SWNT solution preparation

2mg of Hipco SWNTs was added to 5 ml dispersant solutions (10 mg / ml D₂O) except for CS solution which was prepared in 1% v/v acetic acid. The mixtures were sonicated using a cup-horn ultrasonicator (SONICS, VCX-130) at 45 W for 15min in an ice-water bath, and then ultra-centrifuged for 2 h at 30,000 g. The supernatants obtained were stable at room temperature for months without precipitation. Characterizations of the supernatants using different dispersants were identified as SDS-SWNT, CS-SWNT, OPEG-SWNT, OC-SWNT and QC-SWNT respectively.

Solubility of polymer was measured by determining the saturation solubility. Certain amount of polymer (*e.g.* 10mg) was placed in a beaker and small amount of water (*e.g.* 20 μ L) was added dropwise and then the solution was then stirred for one hour with a magnetic bar. More water droplets were added until the polymer completely dissolved.

Gel Permeation Chromatography (GPC) was used to measure the molecular weight of chitosan and chitosan derivatives with respect to polyethylene oxide standards. GPC was performed on a Shimadza LC-20A Series GPC system equipped with a pump, PL-aquagel-OH column and Refractive Index (RI) detector. The samples were

analyzed at 40 °C with 0.2M acetic acid/ 0.2M sodium acetate buffer (pH=4.05) as eluent at a flowrate of 1.0 ml/min.

Surface tension was measured from the shape of a pendant droplet from a needle; the test was performed using First Ten Angstroms-200 Dynamic Contact Angle Analyzer. The concentration of SDS and polymer in neutral deionized water was 1 wt%.

Fourier-transform infrared (FTIR) spectra were recorded on a Nicolet OMNIC 5700 spectrometer at room temperature using a KBr pellet in the transmittance mode.

Zeta-potential was measured on a BROOKHAVEN-ZetaPALS system equipped with a solid state laser (660nm wavelength). OC, OPEG and QC (1 weight percent) was each dissolved in ultra pure deionized water obtained from a Millipore Ultrapure water system with a resistivity of $> 18.2 \text{ M}\Omega\text{-cm}$ at 25 °C. The polymer solutions were filled in the sample cell. All zeta-potential measurement was performed without additional electrolyte at 25 °C and then the classical Smoluchowski equation¹⁹⁵ was applied to obtain the zeta potential from the measured mobilities as follows: $\mu = \epsilon \xi / \eta$ where μ is the electrophoretic mobility, ϵ is the permittivity of liquid, ξ is the zeta potential and η is the viscosity of liquid.

The zeta potential of the polymer molecules enable us to identify the charge polarity of the polymer solutions. This is based on an assumption that the polymer molecules can be treated as “colloidal particles” (Appendix B).

The initial pH of the OC, OPEG and QC polymer solution were 6.90, 8.22 and 3.38 respectively. For CS, 1wt% polymer dissolved in 1% v/v acetic acid and the initial pH

value is 3.95. Zeta-Potential results of polymer solutions at different pH were also tested. The pH value was adjusted by adding 1M HCl or NaOH. The zeta potential values of OC, OPEG and QC at the initial point are negative, negative and positive respectively. We also obtained the Zeta-potential value at different pH values of each polymer.

SWNT characterizations. UV-vis-NIR, PLE, Raman, AFM and TEM were also used for characterizing the SWNT samples as described in Section 3.2.

4.3 Results and discussion

The chitosan (CS), OC, OPEG and QC have molecular weights of 125,000 Daltons, 126,000 Daltons, 129,000 Daltons and 122,000 Daltons respectively (Table 4.1). This shows that the the derivatization of chitosan has only a little effect on the main chain scission. Table 4.1 compares the solubility of OC, OPEG and QC in neutral water. It shows that our three novel derivatives are water-soluble and OPEG has the highest solubility (0.148 g/ml) and QC the lowest (0.013 g/ml).

Fig. 4.3 shows a photograph of SWNT dispersions prepared with SDS, CS, OC, OPEG and QC dispersants. The dispersions were prepared by sonication followed by centrifugation with these dispersants. The color of QC-SWNT supernatant solution is nearly the same as that of pure QC solution (data not shown) indicating that there are no or very few SWNTs in this supernatant solution. This is corroborated by results of UV-vis-NIR absorption and Raman spectroscopy showing no absorption peaks for

this QC dispersant (data not shown). We conclude that QC is not a suitable dispersant for SWNTs while SDS, CS, OC and OPEG can disperse SWNTs well.

Table 4.1 Properties of polymers and the solubilities of SWNTs in the supernatants

	SDS	CS	OC	OPEG	QC
Solubility in Deionized Water (g/ml)	N.A.	N.A.	0.059	0.148	0.013
Surface tension of 1wt% polymer solution (mN/m)	35.7	N.A.	67.0	64.9	67.7
Molecular Weight (Mn)	N.A.	125,000	126,000	129,000	122,000
SWNTs solubilities (g/L)	0.120 ^a	0.019 ^b	0.038	0.021	0.032
					N.A.

(a) Centrifugation speed at 30,000g is the optimal for polymer to debundle SWNTs (b) Optimal speed¹² according to literature to debundle SWNTs by SDS.

Figure 4.3 Photograph of supernatants of SWNT dispersions after sonication and centrifugation using various dispersants: (A) SDS, (B) CS, (C) OC, (D) OPEG and (E) QC

Fig. 4.4 (I) presents the absorbance spectra of SWNT dispersions using the four dispersants (*i.e.* SDS, CS, OC, and OPEG) that passed the initial suspension test. The total (*i.e.* resonance and non-resonance) absorbance is due to all carbonaceous materials including SWNTs (both single and bundled nanotubes), graphite and impurities. Compared with all the chitosan derivatives, SDS has significantly higher absorbance than the chitosan derivatives. Amongst the chitosan derivatives, CS and OPEG have higher total absorbance than OC.

The 400~600nm region, 550~800nm region and 800~1400 region are related to the lowest energy van Hove transition of metallic SWNTs (M_{11}), second van Hove transition of semiconducting SWNTs (S_{22}) and the first van Hove transition of semiconducting SWNTs (S_{11}) respectively¹². The peaks belonging to all four solutions are well-resolved due to interband transitions between van Hove singularities in the density of states (DOS) of individual SWNTs, indicating the presence of SWNTs as individuals and/or very small bundles with these dispersants¹². Broad peaks relative to the baseline would have indicated the existence of aggregated SWNTs because intertube van der Waals interactions in bundles disturb the electronic structure of SWNTs^{12, 80, 81}. In Fig. 4.4 (I), the intensity of peaks due to S_{11} increased as S_{11} peaks are easily affected by the SWNT chemical environment⁸⁵.

(I)

(II)

Figure 4.4 (I) UV-vis-NIR spectrum of SWNT-dispersed solution obtained after ultracentrifugation of homogenized supernatants of (a) SDS-SWNT in water, (b) CS-SWNT in acetic acid, (c) OC-SWNT in water and (d) OPEG-SWNT in H₂O (Baseline for SDS-SWNT in Figure 4.4 (I) has been shifted down by 0.2 a.u.). (II) A(S)/A(T) ratio of polymer-SWNT solution (calculated from original absorbance data in (I)).

Haddon *et al.*¹⁹⁶ have proposed the use of solution-phase NIR spectroscopy to quantitatively compare the purity of bulk SWNT materials. The S₂₂ interband transition is selected because it is less susceptible to incidental doping. A(S) is the area of the S₂₂ spectral band after linear baseline correction and is due only to dispersed SWNTs. A(T) is the total area of S₂₂ which includes contributions from

SWNTs and carbonaceous impurities¹⁹⁶ (see Section 2.4.2). Fig. 4.4 (II) shows the resonance ratio (*i.e.* $A(S)/A(T)^{85}$) and the higher values for the chitosan derivative dispersants suggest that these polymers (*i.e.* CS, OC and OPEG) have higher selectivity for SWNTs over other carbonaceous impurities compared to the small molecule SDS surfactant. The preferential ability of chitosan derivatives, as opposed to SDS, to suspend the high aspect ratio carbon nanotubes versus impurities is likely due to polymer wrapping around the SWNTs. This has been observed with other biopolymers such as sodium carboxymethylcellulose¹⁹⁷. We postulate that these chitosan derivatives possess helical conformations, as chitosan is known to possess^{198, 199}, which would effectively disperse nanotubes in a way analogous to nanotube-wrapping DNA¹⁵⁵. CS and OPEG, which have higher total carbon suspendability than OC, have O-substituted hydroxyl groups capable of forming hydrogen bonding and polar interactions with O atoms in oxidized SWNTs and in carbonaceous impurities. The presence of oxidation is confirmed by the XPS analysis of SWNTs, which shows O(1s) peak of 4 atomic percent and C(1s) peak of 96 atomic percent. No absorbance is observed in the QC-SWNT dispersion indicating there is no SWNT in the solution. This confirms that QC can not act as a dispersant to disperse SWNT.

The concentration of SWNTs in the supernatant was determined by measuring the absorbance of the SWNT/dispersant solution at 500nm (from Fig. 4.4(I)). Then Beer's law ($A=\epsilon bc$), where A is the optical density, ϵ is the extinction coefficient (*i.e.* $2.86 \times 10^4 \text{ cm}^2 \text{ g}^{-1}$ ²⁰⁰), b is the path length (b is 1 cm for our cell) and c is the

concentration, was applied. The SWNTs solubility with different dispersants are summarized in Table 4.1. The solubilities of SWNTs in neutral OPEG and OC (0.032 g/L and 0.021 g/L) are about the same as that with CS in acetic acid (0.038 g/L). For SDS, two centrifugation speeds were used. The centrifugation speed of 30,000g is the optimal condition for polymers to disperse and debundling SWNTs, but this speed cannot break the small bundles of SWNTs into individual nanotubes. In order to obtain the solubility of individually dispersed SWNTs in the supernatant using SDS, a higher centrifugation speed (120,000 g) according to the literature¹² was also used for the SDS-SWNT solution. The SWNT solubilities at low (30,000 g) and high (120,000 g) centrifugation speeds were found to be 0.12 g/L and 0.019 g/L respectively. The high speed SWNT solubility with SDS is comparable with those of chitosan derivatives.

Fig. 4.5 (I) shows fluorescence intensity versus excitation plots for OC-SWNT, OPEG-SWNT, SDS-SWNT solutions in D₂O and CS-SWNT solution in acetic acid with excitation scanned from 500 to 800 nm and emission collected from 900-1500nm. The resonance behavior of both excitation and emission results in spikes corresponding to a different semiconducting chiral (*n,m*) species⁴¹ (Metallic nanotubes do not photoluminescence because they have no bandgaps). The intense photoluminescence signals indicate the presence of the individual dispersion of SWNTs. The chiralities of the major peaks shown in Fig. 4.5 were assigned according to previous experimental and theoretical studies⁴¹. No photoluminescence signal was detected from the QC-SWNT solution, again confirming the inefficacy of QC as a

SWNT dispersant. The different (n, m) chiralities correspond to different nanotube diameters d , which are noted in the following. SDS-SWNTs showed strong peaks at chiralities (9, 4) ($d=0.916\text{nm}$), (8, 6) ($d=0.966\text{nm}$), (10, 2) ($d=0.884\text{nm}$) and (7, 6) ($d=0.895\text{nm}$) which corroborates with reported values of HiPco nanotubes by others^{41, 77, 201}. CS-SWNT has enhanced peaks at (8, 3) ($d=0.782\text{nm}$), (7, 5) ($d=0.829\text{nm}$) and (8, 4) ($d=0.84\text{nm}$) which mainly belong to small diameter tubes. OC-SWNT and OPEG-SWNT dispersions have more complete (n, m) distributions. OC and OPEG exhibit enhanced peaks at (8, 3) ($d=0.782\text{nm}$), (7, 5) ($d=0.829\text{nm}$), (8, 6) ($d=0.966\text{nm}$), (9, 5) ($d=0.976\text{nm}$) and (8, 7) ($d=1.032\text{nm}$). To roughly determine the chiral abundance distribution, the amplitude of the partial derivative of photoluminescence intensity versus excitation wavelength was computed following the method proposed by Arnold *et al.*¹⁷³ (See Section 2.4.1). The results are summarized in Fig. 4.5 (II) and Table 4.2. SDS shows selective enrichment of semiconducting SWNTs with diameter between 0.85 nm and 0.95 nm. CS can wrap more nanotubes with smaller diameter (36.9 % of semiconducting nanotubes with diameter less than 0.85 nm), but a smaller proportion of larger tubes (*i.e.* diameters $> 0.95\text{nm}$, Table 4.2). OC and OPEG can wrap nanotubes with the full range of diameters.

(I)

(II)

Figure 4.5 (I) Contour plots of photoluminescence intensities for polymer-SWNT dispersed solution (II) Diameter distribution calculated from (I) of each sample.

Table 4.2 Diameter distribution ratios of SWNTs in different polymer suspensions.

Ratio %	SDS	CS	OC	OPEG
$d < 0.85\text{nm}$	13.7	36.9	25.2	25.7
$0.85\text{nm} < d < 0.95\text{nm}$	63.2	45.7	40.2	43.5
$d > 0.95\text{nm}$	23.1	17.4	34.6	30.8

Fig. 4.6 shows Raman scattering spectra with 633 nm and 514 nm excitation laser wavelengths. The peaks of Raman are different from the excitation laser. In Fig. 4.6(I)a and 4.6(II)a, the G⁻ band (around 1550 cm⁻¹) of OC-SWNT and OPEG-SWNT slightly decreased compared to raw nanotubes using both excitation wavelengths. This might be due to enhanced selectivity of OC and OPEG dispersants for semiconducting *versus* metallic nanotubes¹⁶⁹ or to changes in the nanotube nanoenvironment arising from bundling/debundling²⁰². The chirality of nanotubes in the Radial Breathing Mode (RBM) has also been assigned according to experimental Kataura plots^{97, 203} in Fig. 4.6(I)b and Fig. 4.6(II)b. In the 633nm excitation spectrum, RBM features above 240 cm⁻¹ arise from semiconducting tubes which include (9,5), (8,6), (10,3), (9,4), (7,6) and (8,4) chiralities. These RBM results are corroborated by results of photoluminescence (PLE) (Fig. 4.5 (I). (The photoluminescence peaks with the stronger intensity (i.e. (9,4), (8,4)) show relatively low Raman scattering intensity; this is due to the fact that the resonant wavelengths of these chiralities are far away from the Raman laser wavelength used.) RBM features below 240 cm⁻¹ are due to metallic nanotubes which are mainly of chirality (12, 3), (8, 8), (11, 5) and (10, 7); these Raman results complement the PLE semiconducting tubes assignment. Fig.

4.6(II)b shows the Raman RBM spectra with 514 nm excitation. The peaks around 250 cm^{-1} and 270 cm^{-1} can be assigned to metallic nanotubes with chiralities (9, 3), (8, 5), (11, 2), (7, 7) and (10, 4). The weak peak at $\sim 185\text{ cm}^{-1}$ arises from semiconducting nanotubes. The peak around 210 cm^{-1} might be generated by (11, 7), (12, 5) and (12, 3) nanotubes. From the RBM range of both excitations, the peaks of dispersant-SWNTs show some up-shift compared to raw HiPco nanotubes, which can be attributed to debundling and change of dispersant environment surrounding the SWNTs (*e.g.* solvent and polymer wrappings)⁹⁴. SWNT-polymer interactions (hydrophobic interaction, van der Waals attraction, *etc.*) can change the SWNT free hole-carrier density in SWNTs, which is also reflected in the Raman peak shifts.

Figure 4.6 Raman spectra of raw HiPco SWNT and polymer-SWNT complex using (I) 633nm excitation source and (II) 514nm excitation source.

Fig. 4.7 is a TEM picture of an OC-SWNT sample showing individual SWNTs. The measured diameters of the nanotubes are in the range of 0.7 nm to 1.3 nm. OPEG has good solubility in neutral water but after water evaporation from OPEG-SWNT suspension on silicon wafer, it was difficult to re-dissolve OPEG and this prevented us from taking reasonable-quality AFM and TEM pictures. Hydrogen bonding present in OPEG causes the poor re-dissolution.

Figure 4.7 TEM image of OC-SWNT sample

AFM images show that OC-SWNTs are present as individual tubes as well as in very small bundles. Representative images are shown in Fig. 4.8. The measured heights with OC dispersant are in the range of 0.7nm to 1.5 nm. The AFM image of SDS dispersed SWNTs show that the nanotubes are in bigger bundles of 3-6 nm height. The relatively low centrifugation speed used (30,000g) has been found to be unable to separate small bundles from individual SWNTs with SDS¹² (For TEM and AFM samples preparation of OC-SWNTs, pH 1 HCl aqueous solution was used to wash away polymers).

Figure 4.8 (Cont'd)

Figure 4.8 (I)-(VI) AFM images in large area of OC-SWNT supernatant samples deposited on silicon wafer. (I)a AFM image of small area of the box in (I). (VII) AFM image of SDS-SWNT supernatant samples deposited on silicon wafer.

The interactions between the chitosan dispersants and nanotubes are related to the polymer's structure. SWNTs, which are structurally similar to fullerenes, are good electron acceptors^{96,204,205}, while the amine group present in the chitosan derivatives is a fairly good electron donor. Amine and amide functional groups have been reported to possess significant affinity for SWNT physisorption with attendant weak charge transfer to the graphene layer due to the high nucleophilicity of these N-based

groups¹⁸⁶. The degree of interaction between SWNTs and amines is correlated with the basicity of the amines. SWNT-amine interaction strength and consequently dispersibility decreases in the order of primary, secondary, and tertiary amines, suggesting that the interaction between SWNTs and amines is sensitive to steric hindrance around the nitrogen atom²⁰⁶. CS has been reported to be positively charged, with zeta potential of about 48.9 mV¹⁸⁷. The $-NH_2$ group on it is protonated in acetic acid forming $-NH_3^+$, which decreases the electron-donating ability. However, the cationic $-NH_3^+$ can form strong cation- π interaction with the nanotubes as observed in a study of protonated lysine as a nanotube dispersant¹⁸¹. We measured the zeta potential of QC to be about 50 mV (Fig. 4.9a). In QC, the hydrogen atoms in the chitosan R_2 group (Fig. 4.1) have been replaced by alkyl groups so that there is no lone electron pair. Further, the $-NR_3^+$ is sterically hindered from approaching to close proximity with nanotubes so that the cation- π interaction is minimal. OC has been previously reported by us to be negatively charged with zeta potential of about -20 mV (Fig. 4.9b) and the $-NH_2$ group is not protonated¹⁸⁷. With OC, the presence of lone electron pair donating $-NH_2$ in the R_2 -position leads to excellent dispersion of SWNTs²⁰⁷. Compared to CS and OPEG, OC has lower hydrogen bonding due to the absence of a primary hydroxyl group in the C6 position so that redissolution of the polymeric dispersant after individual SWNTs are deposited on wafer is possible. The zeta potential value of OPEG is negative, *i.e.* about -17mV (Fig. 4.9c). In neutral water, non-protonated $-NH_2$ group is present in OPEG contributing to very good dispersion of SWNTs. Hence, the adsorption of amide/amine from OC, OPEG and CS

dispersants onto the nanotubes leads to good dispersion; the adsorption is stabilized by donation of lone pair electrons or interaction of cations from sterically unhindered protonated primary amine groups to/with the graphene layer; these dominant interactions drive the tube debundling¹⁸⁶. The -COOH groups on the ends and sidewall of SWNT have low dissociation in the solution (since the zeta potential of SWNT is about -7 mV) so that electrostatic interaction through -COO^- is small.

(a)

(b)

(c)

Figure 4.9 Zeta-potential of (a) QC (b) OC (c) OPEG at different pHs

FTIR spectroscopy was used to confirm the charge transfer interaction between the nanotubes and polymers. Fig. 4.10 compares the FTIR spectra of the chitosan derivatives with that of the SWNT-chitosan derivative complexes; it shows the spectral region containing the -NH_2 bending vibration mode at around 1660 cm^{-1} for the three polysaccharide dispersants (CS, OC and OPEG). The -NH_2 groups belonging to OC and OPEG have a lone electron pair and donate negative charge to the SWNT in the polymer-SWNT complex. Upshift in the -NH_2 bending mode vibration frequency was observed in the spectra of OC-SWNT and OPEG-SWNT complexes due to partial escape from the low-lying anti-bonding acceptor orbital²⁰⁸. The OPEG polymer shows more upshift compared with the OC indicating stronger interaction; this is consistent also with the inability to re-dissolve OC from OC-SWNT complex. The FTIR spectra of CS-SWNT and CS show a slight downshift of the -NH_2 peak; there is no electron-donation from CS to SWNT.

Finally, these chitosan derivatives are nanotube dispersants and not surfactants, i.e. they do not significantly decrease the surface tension of the “solution”. Table 4.1 compares the surface tension of deionized water, SDS and the various CS derivatives. SDS decreases the surface tension of water from 72 mN/m to 35 mN/m while those of CS derivative solutions are still high at approximately 65 - 67 mN/m. To utilize SWNTs for network electronics, printing of the nanotube network will be an easy route to do so. For this process, it is known that surfactants will easily produce bubbles during the printing process and causes clogging and/or non-uniform printing. Our polymeric dispersants can overcome the bubble problem in SWNT printing.

Figure 4.10 FTIR spectra of pure polymer (CS, OC and OPEG) and polymer (CS, OC and OPEG) -SWNT complex. (The y-axis range of each individual spectrum is approximately 30-70%.)

In many applications including biosensors and SWNT-based transistors, individual nanotubes will be superior to even small-bundled nanotubes. For example, SWNT synthesis, thus far, can only produce mixtures of nanotubes with different

chiralities and electronic property (i.e. semiconducting versus metallic). To effectively separate the tubes into different fractions with distinct chiralities or electronic properties, the tubes must first be individually suspended^{175, 176, 209, 210}.

The toxicity of carbon nanotubes has, in recent years, been actively researched²¹¹. The nano-scale diameter of these nanotubes poses certain risks as these can be endocytosed by the cells. However, when the nanotubes are long, like in the range of few to tens of microns, then the probability of endocytosis of these nanotubes is small.

4.4 Conclusion

We have demonstrated that two derivatives of chitosan, specifically OC and OPEG, can effectively debundle SWNTs in neutral aqueous solutions using a mild and easy-to-implement process. The solubilities of individually dispersed SWNTs in neutral water are 0.021g/L and 0.032g/L for OC and OPEG respectively, which are comparable to 0.038g/L for SWNTs using CS in acetic acid. Solutions of 1 weight percent each of OC and OPEG in water have surface tensions of 65 - 67 mN/m compared to 72 mN/m for pure water. In contrast to SDS, these dispersants do not lower the surface tension of water making them useful dispersants for printing of nanotubes. UV-vis-NIR, photoluminescence, AFM and TEM confirm the debundling process and the presence of individual tubes. These two polymers (OC and OPEG) are believed to disperse SWNTs by way of a donor-acceptor interaction between the lone pair electrons in the primary amine groups in these polymers and the nanotubes; this mechanism is supported by our FTIR results. Like others, we also found that

unmodified chitosan can disperse SWNTs well in acetic acid aqueous solution. However, cationic QC cannot disperse SWNTs as the cation- π interaction between the polymer and the nanotubes is diminished by steric hindrance of the attached alkyl groups of the quaternary nitrogen. Our new dispersants, OC and OPEG which are able to disperse SWNTs in neutral pH aqueous solution, opens up new vistas in SWNT-based biomedical devices and the study of the biological activities of biomacromolecule-SWNT hybrids.

4.5 Acknowledgements

Part of the work presented in this chapter has been published in the *Journal of Physical Chemistry C* (10.1021/jp711039s).

Declaration:

Yan L.Y., Poon Y.F., Chan-Park M.B., Chen Y., Zhang Q., “Individually Dispersing Single-Walled Carbon Nanotubes with Novel Neutral pH Water-Soluble Chitosan Derivatives”, *J. Phys. Chem. C.*, 2008, 112, 7579-7587

Chapter 5 – Enrichment of specific chiralities of SWNTs through co-extraction with heparin

5.1 Introduction

SWNTs are seamless graphene sheets wrapped into tubes. Many possible tubular configurations, *i.e.* chiralities, exist with varying diameters and amounts of spiral winding of the carbon atoms; these configurations are commonly identified by their chirality indices (n, m) ²¹². The coexistence of nanotubes with different chiralities in commercially available SWNTs has been an obstacle to their large-scale practical applications and fundamental studies²¹³. Purification methodology that can yield chirality-specific SWNT is urgently needed.

Researchers have reported that large aromatic compounds such as pyrene, perylene and their derivatives can disperse nanotubes well due to their strong affinity to form π - π stacking with nanotube walls^{120, 214-218}. Some studies have been made on the selective (n, m) enrichment of SWNTs. Arnold *et al.*^{22, 219} reported density gradient ultracentrifugation (DGU) assisted enrichments of (6, 5) and (7, 5) CoMoCAT[®] nanotubes in the presence of sodium cholate (SC). During DGU, the SWNTs sediment through the density gradient until they reach their respective isopycnic points so that smaller-diameter SWNTs settle higher and larger-diameters and bundles settle lower in the centrifuge tube²³. Co-surfactant extraction has also recently been applied for selective enrichment of (6, 5) and (8, 3) nanotubes²²⁰. Flavin has been found to be chirality-selective to (8, 6) nanotube species^{168, 221}. Polyaromatic

amphiphiles have been shown to be selective to armchair SWNTs due to their supramolecular recognition of specific nanotube species²²². Left- and right-handed SWNTs separation also has been reported using enantiomers of the nano-tweezers¹³². Recently, density gradient ultracentrifugation using sodium cholate was reported to isolate different SWNT enantiomers²²³.

Polymer wrapping has also been used to perform chirality-selective nanotube enrichment. DNA²²⁴ and polyfluorenes (PFO)^{137, 138} have been used for this purpose. PFO-based polymers possessing different side groups result in different (n, m) selectivity^{138, 139}. However, dispersants important for bioelectronics which should be not just chirality-selective but also removable and biocompatible have been limited. Some of these biomolecules, *e.g.* starch¹⁸, alginic acid¹⁷², peptides¹⁵⁸, schizophyllan¹⁶⁸, flavin mononucleotide¹⁶⁸, β -1,3-glucan²²⁵, *etc* adopt helical structures when wrap around SWNTs.

In this chapter, we report a highly-sulfated glycosaminoglycan – heparin sodium salt (denoted “heparin” for brevity later in this chapter) (Fig. 5.1) – which can disperse SWNTs in aqueous solution and select certain (n, m) species. Heparin sodium salt is a linear polysaccharide consisting of a variably-sulfated repeating disaccharide unit²²⁶. The main disaccharide units that occur in our heparin sodium salt are shown in Fig. 5.1. The most common disaccharide unit in heparin sodium salt is composed of a 2-O-sulfated iduronic acid and 6-O-sulfated, N-sulfated glucosamine.

Figure 5.1 Chemical structure of heparin sodium salt²²⁶

In this research, heparin is used alone as a single dispersant with Hipco nanotubes and is found to preferentially suspend larger diameter nanotubes. Heparin is also used as an enrichment agent for specific chirality in CoMoCAT[®] nanotubes via single-/three-fold extractions from an initial dispersion with sodium dodecylbenzene sulfonate (SDBS) surfactant. Photoluminescence excitation (PLE) spectroscopy and UV-vis-NIR absorption spectroscopy were applied to characterize each sample. The PLE data exhibit dramatic increase in intensity of the (8, 4) peak. Computer simulation of the molecular interactions between different nanotube chiralities and heparin was performed to verify the affinity of heparin for the (8, 4) species. SWNT network field-effect transistors were fabricated using SDBS and heparin surfactants.

The dispersibility of the Heparin/Hipco SWNT solution was evaluated by PLE, UV-vis-NIR, AFM and TEM. Heparin was found to be preferable dispersing larger diameter nanotubes. Heparin and SDBS were used for co-extraction certain-chirality SWNT from CoMoCAT[®] SWNTs, and the results were confirmed with PLE, Raman and computer simulation results.

5.2 Experimental Procedure

Materials

Heparin sodium salt, SDS and SDBS were purchased from Sigma-Aldrich (Singapore) at the highest commercially available purity and used without further purification. Hipco, CoMoCAT[®] and P2 SWNTs were used in this chapter. The nanotube purification details were described in chapter 3.1.

5.2.1 Hipco SWNTS

Preparation of Hipco SWNT/SDS ultracentrifugation solution

To prepare Hipco SWNT/SDS ultracentrifugation solution, a mixture of 2 mg Hipco SWNTs material and 10 ml 1wt% SDS aqueous solution was agitated by cup-horn sonication (SONICS, VCX-130) at 100 W for 30 min in a water-ice bath. The suspension was then centrifuged for 1h at 120,000 *g* (Hitachi-Koki CS150GXL) to remove bundles of SWNTs. The homogeneous supernatant was examined spectroscopically with PLE and UV-vis-NIR spectroscopy.

Preparation of Hipco SWNT/Heparin ultracentrifugation solution

To prepare Hipco SWNT/Heparin solution, a suspension of 2mg Hipco SWNTs in 10 ml 4wt% heparin aqueous solution was sonicated (SONICS, VCX-130) at 100 W for 20 min in a water-ice bath. The suspension was centrifuged for 1h at 50,000 *g* (Sartorius, SIGMA@3K30). The supernatant was collected for testing.

5.2.2 CoMoCAT[®] SWNTs

CoMoCAT[®] SWNT/SDBS ultracentrifugation solution

To prepare CoMoCAT[®] SWNT/SDBS ultracentrifugation solution, a mixture of 2 mg CoMoCAT[®] SWNTs and 10 mL 1wt% SDBS aqueous solution was agitated by cup-horn sonication (SONICS, VCX-130) at 100 W for 30 min in a water-ice bath. Then the suspension was centrifuged for 1h at 60,000 g (Hitachi-Koki CS150GXL) to remove bundles of SWNTs. The homogeneous supernatant, denoted “CoMoCAT/SDBS”, was studied spectroscopically with PLE and UV-vis-NIR.

CoMoCAT[®] SWNT/SDBS-Heparin(x1) solution

To prepare CoMoCAT[®] SWNT/SDBS-Heparin solution, 4wt% heparin sodium salt aqueous solution was added into 3 mL supernatant after the SDBS-CoMoCAT[®] SWNT ultracentrifugation step. The mixture was sonicated (SONICS, VCX-130) at 100 W for 20 min in a water-ice bath. The suspension was centrifuged for 1h at 50,000g (Sartorius, SIGMA@3K30). The resulting supernatant, denoted “CoMoCAT/SDBS-Heparin”, was collected for testing.

CoMoCAT[®] SWNT/SDBS-Heparin(x3) solution

The CoMoCAT/SDBS/Heparin(x1) supernatant was filtered (0.05 μ m PC membrane, Whatman Ltd.) and washed with a lot of water to remove the SDBS and heparin. Then the solid on the filter paper was collected and redispersed with SDBS (sonication at 100 Watt for 30 minutes and centrifugation at 20,000 g). The supernatant was collected and re-dispersed with heparin. The heparin extraction cycle was repeated three times and finally the color of supernatant was pale grey color.

This supernatant is denoted CoMoCAT/SDBS/Heparin (x3) in the following discussion.

Computer Simulation of binding energies with Heparin and different chiralities

Four types of SWNT models with chiralities of (6,5), (8,3), (7,5) and (8,4) (matching those in Table 5.3) and length fixed at 60 Å were built using Nanotube Modeler.²²⁷

The initial structure of heparin was taken from a NMR model.²²⁸ All-atom GLYCAM/AMBER²²⁹ force field was used to represent heparin. The aromatic carbon type without partial charge was assigned to carbon atoms in the carbon nanotubes. A dodecahedral box with length of 76 Å contains one SWNT, one heparin molecule and around 9700 TIP3P²³⁰ water molecules. All simulations were run employing GROMACS package²³¹ with the help of Amb2gmx conversion utility tool.²³² All bonds involving hydrogen atoms were constrained in length according to LINCS protocol²³³. This allowed the use of an integration step 0.002 ps in simulations. Non-bonded pair lists were updated every 5 integration steps. The protein and the water were separately coupled to an external heat bath with a relaxation time of 0.1ps. Structure snapshots were output every 1 ps at 300 K for analysis. Electrostatic interactions were treated with particle mesh Ewald method²³⁴ with a cutoff of 9 Å, and a cutoff of 12 Å was used in the calculation of van der Waals interactions. Four different heparin-CNT simulations were run for 40 ns each. The binding free energy estimates were performed using generalized Born (GB) implicit solvent model developed by Onufriev *et al.*²³⁵ provided by the sander module in AMBER 9²³⁶.

5.2.3 P2 SWNTs

P2 SWNT/SDBS ultracentrifugation solution

To prepare P2 SWNT/SDS ultracentrifugation solution, a mixture of 2 mg P2 SWNTs and 10 mL 1wt% SDBS aqueous solution was agitated by cup-horn sonication (SONICS, VCX-130) at 100 W for 30 min in a water-ice bath. Then the suspension was centrifuged for 1h at 50,000 g (Hitachi-Koki CS150GXL) to remove bundles of SWNTs. The homogeneous supernatant, denoted “P2/SDBS”, was studied spectroscopically with UV-vis-NIR.

Preparation of P2 SWNT/Heparin ultracentrifugation solution

To prepare P2 SWNT/Heparin solution, a suspension of 2mg Hipco SWNTs in 10 ml 4wt% heparin aqueous solution was sonicated (SONICS, VCX-130) at 100 W for 20 min in a water-ice bath. The suspension was centrifuged for 1h at 50,000 g (Sartorius, SIGMA@3K30). The supernatant was collected for testing.

P2 SWNT/SDBS-Heparin(x1) solution

To prepare P2 SWNT/SDBS-Heparin solution, 4wt% heparin sodium salt aqueous solution was added into 3 mL supernatant after the SDBS-P2 SWNT ultracentrifugation step. The mixture was sonicated (SONICS, VCX-130) at 100 W for 20 min in a water-ice bath. The suspension was centrifuged for 1h at 50,000 g (Sartorius, SIGMA@3K30). The resulting supernatant, denoted “P2/SDBS-Heparin”, was collected for testing.

5.2.4 Characterizations

Circular dichroism (CD) measurement of heparin sodium salt was recorded on a Chirascan (Applied Photophysics Limited, UK) in a 0.2 mm path length fused quartz cell. Testing wavelength range is from 180 to 350 nm at 0.5-nm intervals. The scanning speed is 50 nm/min. The other parameters used are 0.5-s response time and 1-nm bandwidth. The concentration of polymer was 25.5 mg/mL D₂O.

UV-vis-NIR, PLE, Raman, AFM, TEM, XPS and FET device are also used for characterizing the samples and described in Section 3.2.

5.3 Results and Discussion

5.3.1 Conformation of heparin

Heparin solution was characterized with CD. Our CD spectrum (Fig. 5.2), which shows a positive band at 191 nm and a negative band at 210 nm, is similar to reported CD spectra of heparin²³⁷, confirming the linear loose helical structure of heparin in solution. Others have also confirmed the heparin linear helix structure using ¹³C NMR²³⁷.

Figure 5.2 Circular dichroism spectrum of heparin sodium salt in deuterium water.

5.3.2 Hipco SWNTs dispersion using Heparin

Heparin sodium salt is known to have good solubility in water due to its highly sulfated structure. For comparison, SDS, a widely used surfactant ¹², was also utilized for dispersion. The heparin concentration and sonication and centrifugation conditions were optimized to obtain well-dispersed SWNTs in heparin aqueous solution. We found that 4 wt % heparin, as opposed to 1 wt% SDS, was necessary to obtain well-dispersed Hipco SWNTs; with 1 wt % heparin, SWNTs settled out after sonication. With 4 wt% heparin, a black and stable solution was formed after sonication. Centrifugation was then applied to this solution. Different centrifugation forces (50,000 g, 40,000 g and 30,000 g) were tested, and 50,000 g centrifugation force was found to be the best for maximizing the ratio of A(S)/A(T) (Table 5.1) of

the UV-vis-NIR spectra (Fig. 5.3) which is reported to be an index of the ability to individually disperse the nanotubes ⁸⁷ (A(S) is the area of the E₂₂ interband transition after baseline subtraction and A(T) is the total area under the spectral curve.).

Table 5.1 SWNT solubility and A(S)/A(T) ratio of Hipco/Heparin supernatant solutions at different centrifugation force.

Relative Centrifugation Force RCF	30,000 g	40,000	50,000 g
SWNTs Solubility mg/L	81	68	48
A(S)/A(T)*	0.067	0.073	0.078

*A(S)/A(T) is an index of SWNT purity. A(S) is the area of the E₂₂ interband transition after baseline subtraction and A(T) is the total area under the spectral curve

Figure 5.3 UV-vis-NIR results of Hipco SWNT/Heparin samples

The Hipco SWNT/heparin solution remained transparent with no precipitation for months. Fig. 5.4a and 5.4b are representative HR-TEM and AFM images of Hipco SWNTs/Heparin solution. The images show that heparin can disperse SWNTs into small nanotube bundles and sometimes individual nanotubes with less than 1 nm

diameter.

Figure 5.4 Hipco SWNT/Heparin samples: (a) TEM image and (b) AFM image

PLE spectroscopy was used to determine the relative abundance of different species of semiconducting nanotubes in Hipco/SDS and Hipco/Heparin supernatant

solutions (Fig. 5.5a and 5.5b). The chiralities were determined by fitting the energy bandgaps from resonantly enhanced emission from the SWNTs' primary E_{11} electronic transitions when the excitation matches their secondary E_{22} electronic levels⁴¹. The relative intensity of each chirality in the PLE map was determined from the amplitude of the partial derivative of map intensity with respect to excitation wavelength, as described by Arnold *et al.* to minimize the effects of the slowly varying background²²,⁴¹ (See Section 2.4.1). The relative intensity analyses are reported in Table 5.2 and are illustrated in a qualitative way in Fig. 5.5c. The typical Hipco SWNTs suspended with SDS have a fairly wide distribution of diameter, between 0.7 and 1.0 nm, and of chiral angles from 0 to 30°. Fewer chiral species (six species) were observed in Hipco/Heparin solution than in Hipco/SDS solution (at least 10 chiral species) (Fig. 5.5a-b). The Hipco/Heparin supernatant is depleted, with respect to Hipco/SDS, in the smaller diameter tubes ((8, 4), (6, 5)), as evidenced by the much weaker signals in the smaller E_{11} wavelength range (*i.e.* smaller diameter, Fig. 5.5b, $\lambda_{em} < 1050\text{nm}$). The nanotube species selected by SDS and heparin are shown in Table 5.2 and the graphene sheet map (Fig. 5.5c). In the latter, red hexagons indicate carbon nanotube species present in the Hipco/SDS sample, and blue circles represent the species in the Hipco/Heparin solution; the thickness of each hexagon and circle is drawn proportional to the deduced concentration of that (n, m) species. The most prominent chiral species are (9, 4) and (7, 6) for both SDS and heparin, but the distribution of the heparin-suspended nanotubes is clearly weighted toward larger diameter tubes. The abundance of (9, 4) and (7, 6) is about 45% for both SDS and heparin, but tubes with

diameter larger than (9, 4) and (7, 6) account for 43% of the total in heparin compared with 23% in SDS (Table 5.2).

The intensity of the Hipco/Heparin PLE signal is significantly lower than that of Hipco/SDS (Compare Fig. 5.5b & 5.5a) and we think that heparin is not an excellent dispersant for dispersing SWNTs. This has been observed with PFO polymer, which has chiral selectivity when toluene, a relatively poor nanotube solvent, is used rather than chloroform¹³⁹.

Table 5.2 Relative PLE intensities of identified semiconducting species in Hipco-SWNT solutions with SDS and heparin

(n, m)	Diameter (nm)	Chiral Angle (Deg)	Relative Peak intensity	
			Hipco/ SDS	Hipco/ Heparin
(6,5)	0.757	27	9.22	i [†]
(7,5)	0.829	24.5	i [†]	i [†]
(8,4)	0.84	19	7.11	i [†]
(10,2)	0.884	9	13.67	11.7
(7,6)	0.895	27.5	19.13	19.7
(9,4)	0.916	17.5	27.16	25.0
(10,3)	0.936	13	7.92	9.1
(8,6)	0.966	25	10.72	17.5
(9,5)	0.976	21	5.07	10.2
(8,7)	1.032	27.8	i [†]	6.7

[†] i: insignificant

Figure 5.5 Contour plots of PLE of (a) Hipco/SDS solution and (b) Hipco/Heparin solution. (c) Graphene sheet map: red hexagons and blue circles are Hipco SWNTs wrapped by SDS and heparin, respectively. The thickness of each hexagon and circle is proportional to the deduced concentration of that (n, m) species of each sample.

5.3.3 CoMoCAT[®] SWNTs dispersion using Heparin

5.3.3.1 Co-extraction with SDBS and Heparin

To apply the large-diameter selectivity of heparin, we applied our heparin-extraction process on CoMoCAT[®] samples (with smaller average diameter

and narrower chirality distribution than Hipco nanotubes). In our commercial CoMoCAT[®] nanotubes (SWeNT[®] SG 65), the most abundant chirality is (6, 5), which accounts for about 47% of the total PLE intensity (Table 5.3). We postulate that starting with nanotubes having smaller diameters and a narrower diameter distribution for heparin extraction, which selects for larger diameter, will force a still narrower nanotube distribution. We used SDBS to initially disperse CoMoCat[®] nanotubes because SDBS binds slightly more (8, 4) than other common surfactants such as SC or SDS (data not shown).²³⁸ After adding heparin into the CoMoCAT nanotubes/SDBS supernatant, the supernatant was redispersed by 100 Watt sonication for 30 mins followed by ultracentrifugation at 50,000 g.

From the PLE plot (Fig. 5.6a), the dominant species in SDBS-dispersed CoMoCAT[®] tubes is (6, 5); other chiralities show low intensity. The CoMoCAT[®] sample obviously has a narrower chirality distribution and smaller diameter distribution (from 0.757 nm to 0.84 nm) than the Hipco sample. Heparin was added and some enrichment of (8, 4) was seen; (8, 4) increased from 7% in CoMoCAT/SDBS to 39% after one extraction with heparin (Fig. 5.6b, Table 5.3). The CoMoCAT/SDBS/Heparin(x1) supernatant was used as the starting material for subsequent extractions with heparin.

With three-time co-extraction with Heparin, the ratio of (8, 4) increased to 60% abundance (Fig. 5.6c and Table 5.3) in CoMoCAT/SDBS/Heparin(x3), compared with 7% in the starting CoMoCAT[®] samples. In the final CoMoCAT/SDBS/Heparin (x3) sample, only 2 species (6, 5) and (8, 4) are present (Table 5.3).

Table 5.3 Relative PLE intensities of identified semiconducting species in CoMoCAT®-SWNT solutions

<i>(n, m)</i>	Diameter (nm)	Chiral Angle ion)	Relative Peak intensity		
			CoMoCAT/ SDBS	CoMoCAT/ SDBS-Heparin(x1)	CoMoCAT/ SDBS-Heparin(x3)
(6,5)	0.757	27	47.4	53.2	40.0
(8,3)	0.782	15.3	28.9	i [†]	i [†]
(7,5)	0.829	24.5	16.4	7.6	i [†]
(8,4)	0.84	19	7.3	39.2	60.0

† i: insignificant

Figure 5.6 Using CoMoCAT nanotubes, (a) is the PLE map of CoMoCAT/SDBS; (b) PLE map of CoMoCAT/SDBS-Heparin(x1) solution after first heparin extraction (c) PLE map of CoMoCAT/SDBS-Heparin(x3) solution after third heparin extractions

Fig. 5.7 shows the absorption spectra of three samples normalized at the 990 nm peak. The (6, 5), (7, 5) and (8, 4) peaks are around 970 nm, 1024 nm and 1110 nm in the E_{11} region. The UV-vis-NIR also shows that the intensity of (8, 4) increased after one-/three-pass extraction with heparin. The overlap of (6, 5) and (7, 5) in absorbance affects the intensity of the peak at ~ 990 nm so that it is hard to precisely assign each peak of the UV-vis-NIR. We also used Raman spectroscopy with 633 nm laser to confirm the results and the radial breathing mode (RBM) (Fig. 5.8) indicates relative decrease of the (6, 5) chirality with successive heparin extractions.²³⁹ From these data, heparin appears to increase the relative abundance of the (8, 4) chiral species even in a single extraction, and multiple extractions further increase its abundance.

Figure 5.7 UV-vis-NIR spectra of these three samples normalized at 990nm (baseline of each curve was subtracted)

Figure 5.8 Raman spectra of raw CoMoCAT SWNTs, CoMoCAT /SDBS-Heparin(x1) after first heparin extraction and CoMoCAT /SDBS-Heparin(x3) after three heparin extractions.

We did circular dichroism (CD) characterization of CoMoCAT/SDBS, CoMoCAT/Heparin and CoMoCAT/SDBS-Heparin(x1) solutions and the results are shown in Fig. 5.9 below. For CoMoCAT/Heparin (red curve) and CoMoCAT/SDBS-Heparin(x1) (green curve) solutions, the peaks at 193nm and 210nm belong to heparin itself, and so there is no peak for CoMoCAT/SDBS (black curve) in the 190-220 nm range. According to the literature^{132, 223}, if there is enantiomeric selectivity of SWNTs, there would be peaks in the 300-800nm range. Our data show no peak of SWNTs in the 300-800nm range for three samples. We find no evidence of enantiomer selectivity for SWNTs with heparin, but heparin which carries various functional groups may potentially be modified to have enantiomer selectivity.

Figure 5.9 CD spectra of CoMoCAT/SDBS, CoMoCAT/Heparin and CoMoCAT/SDBS-Heparin(x1) solutions

5.3.3.2 Computer Simulation

To account for the enrichment of (8, 4) CoMoCAT[®] nanotubes by heparin, the interaction of SWNTs with heparin without SDBS surfactant was modelled numerically. The surfactant was omitted from the simulations since the concentration of SDBS used (1 wt%) was below the critical micelle concentration (cmc of SDBS is 55 wt% at room temperature). Also, heparin may displace the SDBS surfactant.

The heparin molecules were found to tightly wrap around SWNTs in a left-handed helical manner (Fig. 5.10). During the 40 ns simulations no dissociation events occurred. However, the heparin molecule can freely slide along and rotate around the SWNT. All SWNTs studied were found to bind with heparin in a similar manner (Fig. 5.10).

(a) (6, 5)

(b) (8, 4)

Figure 5.10 Structure models of heparin-SWNTs complex obtained from computer simulations: (a) (6, 5) SWNT; (b) (8, 4) SWNT. (Color labeling: C, gray; H, white; O, red; S, yellow; N, blue; SWNT highlighted in gray).

It is desirable to estimate the SWNT-heparin binding energy to shed light on how heparin molecules differentiate SWNTs with different chiralities. To this end, the binding energy of SWNT-heparin complex was calculated as:

$$E_B = E_c^{GB} - (E_H^{GB} + E_T^{GB})$$

where E_c^{GB} , E_H^{GB} and E_T^{GB} are the energies of complex, heparin and nanotube, respectively, based on the implicit GB model. The binding energies listed in Table 5.4

indicate that heparin preferably binds with (8, 4) SWNTs. Complex of heparin and (6, 5) SWNT is 4.8 kcal/mol less stable than that with (8, 4) SWNT. The binding of heparin with (8, 3) and (7, 5) SWNTs is much weaker than with (8, 4) and (6, 5) SWNTs. Considering the simplicity of the computational model employed here, *e.g.*, no partial charges on the SWNTs, the resolved differential binding of heparin on the SWNTs may root in the intrinsic rigidity of the heparin chain which preferably recognizes certain alignments of carbon atoms, *i.e.* the chirality of SWNTs.

Table 5.4 The binding energies of different heparin-SWNT complexes estimated by GB model.

Chirality (n,m)	E_B (kcal/mol)	$E_B - E_{B(8,4)}$ (kcal/mol)
(6,5)	-100.7 ± 7.2	4.8
(8,3)	-90.0 ± 8.4	15.5
(7,5)	-89.4 ± 9.4	16.1
(8,4)	-105.5 ± 6.5	0

We have repeated the processes reported here at least 5 times. All the results shown are reproducible. Many guest-induced wrapping examples have been reported for polysaccharides and other polymers^{225, 240}. However, most commonly reported bio-dispersants with helical structure, *e.g.* alginic-acid or starch, have no specific diameter or chirality selectivity. Interestingly, we show that heparin can narrow the diameter distribution of the nanotubes, either starting with broadly distributed Hipco tubes or more narrowly distributed CoMoCAT[®] tubes and also can shift the nanotube size distribution to larger tubes. Heparin shows the promising property of a specific chirality selectivity, for the (8, 4) species, suggesting the possibility of rational design of polymers with helical structure to achieve specific chiral selectivity through

nanotube wrapping. The rigidity/flexibility balance of the heparin backbone is an important factor. The flexibility of the backbone of heparin promotes wrapping on SWNTs because of a favorable energetic interaction between them since the backbone is rather hydrophobic. The intrinsic rigidity of heparin, partly due to the large sulfate groups, however, favors binding with relatively larger diameters and specific chirality of SWNTs. Single chirality nanotubes have many potential technological and fundamental applications. For example, calculations have shown that single chirality semiconducting SWNT have lower intertube resistance than heterogeneous SWNTs. Simultaneous measurement of electrical transistor properties and identification of chirality of individual SWNTs, particularly in the presence of certain chirality-selective molecules, will provide understanding of the subtle but fundamental differences between different SWNT chiralities. Such fundamental research requires identification of chirality or better still, single SWNT chirality. (8, 4) SWNT, a single-chirality semiconducting SWNT, promises future application in the fields of electronics, energy and sensing.

5.3.3.3 Application of heparin dispersant to FET

Another advantage of heparin extraction is that its removability after extraction. The Hipco/SDS and Hipco/Heparin solutions were filtered and washed with a large quantity of water. The filter paper was characterized with XPS. We found that in the heparin-Hipco SWNT sample, there was nearly no detectable S content (<0.005% of S, 26.63% of O, 67.31% of C and 6.06% of N). We believe most heparin has been

washed away.

In order to confirm the easy removability of heparin, we fabricated network field-effect transistor (FET) devices using CoMoCAT/SDBS, CoMoCAT/Heparin and CoMoCAT/ SDBS-Heparin(x3) solutions and measured their charge transport properties. Fig. 5.11(I)a and 5.11(I)b show typical transfer characteristics with forward and reverse sweeps of drain current (I_d) versus gate voltage (V_g) with the former two solutions. In Fig. 5.11(II) we show a histogram of the on/off ratios of devices made with CoMoCAT/SDBS, CoMoCAT/Heparin and CoMoCAT/SDBS-Heparin(x3) solutions. The device sample size for each of the three solutions is 50. Devices using CoMoCAT/Heparin have on/off ratios of order 10^1 - 10^3 , similar to those made using CoMoCAT/SDBS. Atomic force microscopy of the carbon nanotubes in the channel between the electrodes (inset, Fig. 5.11(I)) shows that the heparin has been mostly removed. After 3-fold extraction with heparin for CoMoCAT/SDBS-Heparin(x3), the nanotubes are expected to have thicker residual organic coatings than CoMoCAT/ SDBS or CoMoCAT/heparin, even after thorough rinsing, and the bundle size probably increases so that the number of devices with higher on-off ratio (10^3 to 10^4) decreases. The device performance can possibly be improved by patterning the nanotube network to suitable widths to decrease percolation of metallic nanotubes²⁴¹.

Typically, polymeric dispersants cannot be removed easily but heparin is more removable than other polymers that interact with nanotubes via π - π stacking.¹⁴³ Though polymers have been demonstrated to have metallicity or chirality based

selectivity^{138, 242}, no successful device fabrication has been reported using them; most polymers used thus far are difficult to remove even with aggressive organic solvents such as dimethylformamide; in contrast, heparin is easily removed with neutral water. Heparin, particularly with sodium counterion, has good solubility (50mg/mL) in water making it is easier to redissolve. Heparin forms helical structure around nanotubes but its interaction with nanotubes is not so strong as to prevent its removal. Removal of surfactant from nanotubes after dispersion is very important for applications in electronic devices. Compared to other agents for extracting specific chiralities of SWNT, biocompatibility is another advantage of heparin. This enrichment methodology can be used in biologically relevant areas.

One countervailing consideration of SWNT extraction using heparin is that the dispersion efficiency is not very high. Heparin is not a good at highly dispersing individual tubes but some selectivity is apparent and we have generally observed that a good dispersant will disperse and wrap all kinds of SWNT, so that good dispersants tend to be poor selective agents. Further work to modify the polymer side groups and elucidation of the relationship between selectivity and helical structure will be done in the future.

(I)a

(I)b

(II)

Figure 5.11 Typical transfer characteristics (I_d - V_g) of bottom-gated carbon nanotube network devices prepared by drop-casting with (a) CoMoCAT/SDBS and (b) CoMoCAT/Heparin (II) Histogram showing number of devices prepared from CoMoCAT/SDBS, CoMoCAT/Heparin and CoMoCAT/SDBS-Heparin(x3) solutions respectively versus the device on/off ratio. (Channel width is 100 μ m and channel length is 20 μ m for all devices.)

5.3.4 Arc-discharge (P2) SWNTs dispersion with Heparin

In the above, Heparin has been used to disperse Hipco and CoMoCAT[®] SWNTs, which are relatively small in diameter. We tried to use heparin to disperse large diameter SWNTs-Arc discharge SWNTs (P2 type SWNTs). SDBS and Heparin were used to disperse P2 SWNTs, and Heparin was also used for extraction of P2/SDBS solution once. From the UV-vis-NIR results, Heparin can disperse P2 SWNTs well, like SDBS (Fig. 5.12): well-resolved UV-vis-NIR peaks were observed for P2/Heparin and P2/SDBS/Heparin(x1), as for P2/SDBS. From the UV-vis-NIR data, there is one E_{11} peak at around 1700nm which is, however, out of the emission range of our PLE machine. Hence, we are unable to confirm if heparin has selective dispersion of semiconducting species of P2 or not. Heparin has strong affinity for

large diameter nanotubes and will probably suspend all large-diameter species fairly well. Our general conclusion is that a marginally good, rather than a very good, dispersant is needed for it to preferentially suspend certain nanotube species, whether the preference is based on diameter or metallicity.

Figure 5.12 UV-vis-NIR spectra of P2/SDBS, P2/Heparin and P2/SDBS-Heparin(x1) aqueous solutions.

5.3.5 Density gradient using Heparin as dispersant

It is clear that heparin yields some selectivity in the dispersion of SWNTs from former above Hipco and CoMoCAT[®] SWNTs results. Density gradient also is widely used for separation of SWNTs. We tried density gradient ultracentrifugation using heparin. For concentrating CoMoCAT/Heparin solution, 1 mL CoMoCAT/ Heparin solution was layered on top of 1.5 mL of an underlayer consisting of 2% w/v heparin

in 60% w/v iodixanol (Fig. 5.13a). The centrifugation parameters were 80k RCF for 10h. After centrifugation, all the SWNTs aggregated at the bottom of centrifugation tube (Fig. 5.13b) instead of suspending in the density gradient²². All the precipitated SWNTs were collected and 5mL water was added and the resulting mixture was tip sonicated at 100W for 30 mins. After sonication, the SWNTs settled in a short time (Fig. 5.13c). We believe that the heparin has separated out from SWNTs. The interaction of polymer and SWNTs is not too strong and this is probably why 1) the polymer is easily removed and 2) slight differences in affinity to wrap different chirality (or diameter) SWNTs results in differential suspension.

Figure 5.13 (a) Scheme of density gradient tube (b) photograph of ultracentrifugation tube after ultracentrifugation (c) photograph of precipitated SWNTs in water after sonication

5.4 Conclusion

In summary, heparin sodium salt, a water-soluble glycosaminoglycan, was applied to the dispersion of SWNTs. As a single dispersant, it preferentially wraps larger diameter nanotubes and forms helical structure around the nanotubes. In CoMoCAT/SDBS/ Heparin(x3), (8, 4) was enriched from 7% to 60% abundance as indicated by PLE, and substantiated by Raman and UV-vis-NIR results. Our computer

simulation shows that the helical structure of heparin sodium salt plays an important role in dispersing SWNTs and that the binding energy of (8, 4) is the lowest amongst the four chiral species of CoMoCAT[®] mixtures. The combination of small molecule surfactant, *i.e.* SDBS, with heparin provides a new approach for obtaining SWNTs with specific chirality. The easy removability of heparin was confirmed by successful fabrication of FETs made from CoMoCAT/Heparin and CoMoCAT/SDBS/Heparin(x3).

5.5 Acknowledgements

Part of the work presented in this chapter has been published in *Small*. Prof. Mu Yuguang and his team at the School of Biological Sciences, Nanyang Technological University, did the computing simulation in Section 5.2.2.

Declaration:

Yan L.Y., Li W.F., Fan X.F., Wei L., Chen Y., Kuo J-L., Li L-J., Kwak S.K., Mu Y.G., Chan-Park M.B., “Enrichment of (8, 4) Single-Walled Carbon Nanotubes Through Coextraction with Heparin”, *Small*, in press

Chapter 6 - Use of glycosaminoglycans as dispersants of SWNTs and removability of chondroitin sulfate

6.1 Introduction

Many polymeric dispersants for SWNTs (*e.g.* poly(9,9-dioctylfluorene) and pyrene-based polymers) interact with nanotubes via π - π stacking^{138, 143}. The polymer/nanotube interaction is typically strong due to the multiple sites of interactions between the polymeric dispersants and nanotubes, so that aggressive organic solvents are often needed to remove the insulating polymer afterwards but even then, substantial polymer residual remains stuck onto the nanotubes. The residual polymer on the nanotubes even after aggressive washing is a big hindrance to SWNTs' applications in electronic devices since it substantially increases resistance.

In Chapter 5, we studied a particular glycosaminoglycan (GAG) - heparin - which wraps around the SWNTs to preferentially suspend larger diameter or specific chirality nanotubes. Some polysaccharides such as starch have also been reported by others to form helical wrapping around SWNTs¹⁸. GAGs are a diverse family of biomacromolecules as shown in Table 6.1. GAGs are interesting as SWNT dispersants because they are water-soluble, contain abundant functionalizable sites and possess amine functional groups which are known to interact with carbon nanotubes²⁴³ (see also Chapter 4). Further, aqueous dispersions of SWNTS with GAGs are amenable to further aqueous-based post-dispersion physical separation techniques (such as density gradient ultracentrifugation and gel electrophoresis^{22, 244}).

Table 6.1 Types of GAGs²⁴⁵

GAG common name	Chemical name	Chemical structure
Hyaluronic acid	β -glucuronic acid-(1-3)- N-acetyl- β -galactosamine	
Keratan sulfate	β -galactose- (1 $\rightarrow$ 4)-N-acetyl- β -galactosamine-6- sulfate	
Heparin	α -L-iduronic acid-(1-4)-N-sulfo- β -galactosamine-6- -sulfate	
Chondroitin sulfate A	β -glucuronic acid-(1-3)- N-acetyl- β -galactosamine-4-sulfate	
Chondroitin sulfate B (also called dermatan sulfate)	β -Iduronic acid-(1-3)-N-acetyl- β -galactosamine-4-sulfate	
Chondroitin sulfate C	β -glucuronic acid-(1-3)- N-acetyl- β -galactosamine-6-sulfate	

GAGs can be classified into five types: chondroitin sulfate (CS), dermatan sulfate (DS), keratan sulfate, heparin and hyaluronic acid (HA) (Table 6.1). GAGs are linear unbranched polysaccharides consisting of repeating disaccharide units. Usually one sugar is uronic acid or D-galactose and the other sugar is N-acetylglucosamine or N-acetylgalactosamine. One or both of the sugars contain at least one anionic group (carboxyl or sulfate group). The extensive sulfation of most GAGs makes them highly hydrophilic in aqueous solutions. The sulfated groups can be attached at different positions. Among the different GAG types, only hyaluronic acid does not have sulfate groups.

Hyaluronic acid (HA) consists of β -D-glucuronic acid (GlcUA) (1 $\rightarrow$ 3)-linked to N-acetyl- β -D-galactosamine (GlcNAc). The disaccharide of keratan sulfate (KS) consists of β -D-galactose and N-acetyl β -D-galactosamine-6-sulfate connected by 1 $\rightarrow$ 4 linkages. For heparin, the disaccharide unit is α -L-iduronic acid (1 $\rightarrow$ 4)-linked to a glucosamine, while for heparan sulfate, the disaccharide unit is β -D-glucuronic acid (1 $\rightarrow$ 4)-linked to a glucosamine. There are three forms of chondroitin sulfate (CS): Chondroitin-4-sulfate (CS-A), Chondroitin sulfate B (CS-B) (also called dermatan sulfate) and Chondroitin-6-sulfate (CS-C) (Table 6.1). The disaccharide of CS-A and CS-C comprises β -D-glucuronic acid (GlcA) and N-acetyl- β -D-galactosamine (GalNAc). A galactosamine can be sulfated on the C-4 or C-6 or both positions. In CS-B, the β -D-glucuronic acid is replaced by α -L-iduronic acid.

In this Chapter, we (I) investigated more GAGs (CS-A, CS-B, CS-C and HA) as dispersants with the aim to understand the dispersibility and chemical structure

relationship and (II) investigated using chondroitin sulfate A (CS-A) as a removable dispersant of SWNTs. (heparin as dispersant has been investigated in Chapter 5)

6.2 Experimental Details

Materials

CS-A, CS-B, CS-C, HA and SDS were purchased from Sigma-Aldrich (Singapore) at the highest commercially available purity and used without further purification. Purified Hipco SWNTs were used in this chapter except for FET device fabrication. The details of the acid purification of Hipco SWNTs are described in Chapter 3.1. CoMoCAT[®] SWNTs (as supplied) were used for FET fabrication.

Preparation of SDS/Hipco SWNTs solution

To prepare Hipco SWNT/SDS ultracentrifugation solution, a mixture of 2 mg Hipco SWNTs material and 10 ml 1wt% SDS aqueous solution was agitated by cup-horn sonication (SONICS, VCX-130) at 100 W for 30 min in a water-ice bath. The suspension was then centrifuged for 1h at 50,000 g (Sartorius, SIGMA@3K30) to remove bundles of SWNTs. The homogeneous supernatant was examined spectroscopically with PLE and UV-vis-NIR spectroscopy.

Preparation of GAG/Hipco SWNTs solution

To prepare GAG/Hipco SWNTs solution, a mixture of 2 mg Hipco SWNTs and 10 ml 1wt% GAG (CS-A, CS-B, CS-C or HA) aqueous solution was agitated by cup-horn sonication (SONICS, VCX-130) at 100 W for 30 min in a water-ice bath. The suspension was then centrifuged for 1h (Sartorius, SIGMA@3K30) to remove

bundles of SWNTs; for comparison of various GAGs in Section 6.3.1, 50k g RCF was used whilst various centrifugation forces (40k g, 50k g and 60k g) were used for the optimization studies in Section 6.3.2. The homogeneous supernatant was examined spectroscopically with PLE and UV-vis-NIR spectroscopy.

SWNT Characterizations

UV-vis-NIR, PLE, AFM, XPS, TEM and FET devices were used for characterizing the SWNT samples as described in Section 3.2.

Computer Simulation to study binding of CS-A, CS-B and CS-C with SWNTs of different chiralities

Two types of SWNTs with chirality of (8, 4) and (9, 4) and length of 10nm were used in the simulation. The aromatic carbon type without partial charge was assigned to carbon atoms of SWNTs. Force field of the three kinds of Chondroitin sulfate (CS) was generated with *antechamber* program; partial charge was generated with *R.E.D.* *III* by performing quantum chemistry (QM) calculation with widely used commercial computer software package “Gaussian with HF (Hartree-Fock)/6-31G* basis” for quantum chemistry computations, and fitted by RESP (Restrained electrostatic potential) method. The SWNT was aligned along the *x* direction and a fully extended CS molecule (7-monomer length) was placed beside the SWNT. The SWNT-CS complex was placed in the center of a 12×6×6 nm box with ~13000 TIP3P²³⁰ water molecules. 14 sodium ions were added to neutralize the system because each CS monomer has 2 negative charges. All simulations were run employing GROMACS package²³¹ with the help of Amb2gmx conversion utility tool²³². All bonds involving

hydrogen atoms were constrained in length according to LINCS protocol ²³³. The position of SWNT was restrained at the center of the water box by applying a harmonic force on SWNT. This allowed the use of an integration step 0.002 ps in simulations. Non-bonded pair lists were updated every 5 integration steps. The protein and the water were separately coupled to an external heat bath with a relaxation time of 0.1ps. Structure snapshots were output every 1 ps at 300 K for analysis. Electrostatic interactions were treated with particle mesh Ewald method ²³⁴ with a cutoff of 9 Å, and a cutoff of 12 Å was used in the calculation of van der Waals interactions. Two independent simulations were carried out for each CS-SWNT pair and run for 20 ns. The binding free energy estimates were performed using generalized Born (GB) implicit solvent model developed by Onufriev *et al.* ²³⁵ provided by the sander module in AMBER 9 ²³⁶.

6.3 Results and discussion

6.3.1 Comparison of different GAGs

The four Hipco SWNTs solutions employing CS-A, CS-B, CS-C and HA dispersants were characterized by UV-vis-NIR and the results are shown in Fig. 6.1. We found that amongst the three forms of CS dispersants, CS-C can disperse SWNTs most effectively with highest A(S)/A(T) ratio of 0.152. HA and CS-A, with A(S)/A(T) ratios of 0.097 and 0.105 respectively, disperse SWNTs relatively well but are not as effective as CS-C though their A(S)/A(T) ratios are higher than SDS (0.072). CS-B cannot disperse SWNTs as witnessed by the more or less absence of peaks in the

UV-vis-NIR spectrum of CS-B/Hipco SWNT sample (A(S)/A(T) ratio=0.044).

(A)

(B)

Figure 6.1 GAG-SWNT and SDS/SWNT dispersions characterized by (A) UV-vis-NIR spectrum and (B) A(S)/A(T) ratio.

Photoluminescence was also used to characterize the GAG/Hipco SWNTs

supernatant solutions (Figs. 6.2 to 6.4, Table 6.2). The chiralities of different semiconducting SWNTs suspended with SDS, a typical surfactant, have a fairly wide distribution of diameter (between 0.7 and 1.0 nm) and chiral angles (0 to 30⁰); the most abundant chiral species is (9, 4) which account for 27% abundance for the SDS suspension. For CS-A, the medium-diameter species (*i.e.* (7, 5), (8, 4), (10, 2), (7, 6) and (9, 4)) have similar abundances which are less than 20% each and account for 76% of total abundance (Table 6.2). Compared to SDS, the selectivity of CS-A for a particular diameter is less significant and the population curve is flatter (Fig. 6.3). For CS-C, the diameter distribution of SWNTs is similar with CS-A/Hipco SWNT sample (Fig. 6.4). For HA as dispersant, there are mainly four species (7, 6), (7, 5), (9, 4) and (8, 4) suspended (Table 6.2), which have relatively larger chiral angle in the diameter range of 0.83 – 0.92 nm (Fig. 6.4).

Table 6.2 Relative PLE intensities of identified semiconducting species in Hipco-SWNT solutions with SDS, CS-A, CS-B, CS-C and HA

(n, m)	Diameter (nm)	Chiral Angle (Deg)	Relative Peak intensity				
			Hipco/ SDS	Hipco/ CS-A	Hipco/ CS-B	Hipco/ CS-C	Hipco/ HA
(6,5)	0.757	27	9.2	7.8	6.5	9.7	0
(7,5)	0.829	24.5	0	12.9	7.1	16.1	20.4
(8,4)	0.84	19	7.1	13.0	6.9	13.4	16.8
(10,2)	0.884	9	13.7	17.4	17.4	14.8	0
(7,6)	0.895	27.5	19.1	17.0	18.8	16.4	35.8
(9,4)	0.916	17.5	27.2	15.6	22.9	15.8	20.3
(10,3)	0.936	13	7.9	0	0	0	0
(8,6)	0.966	25	10.7	8.9	12.6	9.4	6.7
(9,5)	0.976	21	5.1	0	0	0	0
(8,7)	1.032	27.8	0	7.4	7.8	4.4	0

Figure 6.2 Photoluminescence spectra of GAGs/Hipco SWNTs solutions using (A) SDS (B) CS-A (C) CS-B (D) CS-C and (E) HA

(A) SDS

(B) CS-A

(C) CS-B

(D) CS-C

(E) HA

Figure 6.3 Plots of relative abundance of each chirality of SDS/Hipco, CS-A/Hipco, CS-B/Hipco, CS-C/Hipco and HA/Hipco

Figure 6.4 Graphene sheet map. The thickness of each hexagon and circle is proportional to the deduced concentration of that (n, m) species of each sample.

Hipco SWNTs dispersed with CS-A were analysed by Raman scattering spectra with 633 nm and 514 nm excitation laser wavelengths (Fig. 6.5). The acid purified Hipco SWNTs (details of purification is in Section 3.1) were used as the control. 633 nm laser wavelength probes the metallic nanotube in the range of diameters > 1 nm and semiconducting nanotubes in the range of diameters < 0.94 nm, while 514 nm laser wavelength mainly probes larger diameter ($d > 1.08$ nm) semiconducting and smaller diameter ($d < 1.03$ nm) metallic nanotube. For both excitation laser wavelengths, the G⁻ band (around 1550 cm^{-1}) of CS-A/Hipco SWNT solution slightly increased compared to raw nanotubes (Fig. 6.5(I)b and (II)b). The Raman G band shape slightly changes from the Lorentzian lineshape towards the Breit-Wigner-Fano (BWF) lineshape; the latter is characteristic of metallic nanotubes while the former is characteristic of semiconducting tubes. However, the difference is not obvious and the selectivity is not pronounced compared to other reported values¹⁶⁹.

The chirality of nanotubes in the Radial Breathing Mode (RBM) has also been assigned according to Kataura plots^{97, 203} (Fig. 6.5(I)a and 6.5(II)a). In the 633 nm excitation spectrum, RBM features above 240 cm^{-1} arise from semiconducting tubes which include (8, 6), (9, 4), (7, 6) and (8, 4) chiralities; these Raman results complement the PLE semiconducting tubes assignment (Fig. 6.3). RBM features below 240 cm^{-1} are due to metallic nanotubes which are mainly of chirality (12, 3), (8, 8), (11, 5) and (10, 7). Fig. 6.5(II)a shows the Raman RBM spectra with 514 nm excitation. The peaks above 220 cm^{-1} can be assigned to metallic nanotubes with

chiralities (8, 5), (7, 7) and (10, 4). The peaks around 210 cm^{-1} might be generated by (11, 7), (12, 5) and (12, 3) nanotubes which are rather large but their abundances are small. Both the Raman G band and RBM mode show no conclusive evidence of metallicity selectivity with CS-A dispersant.

(I) a

(I) b

(II) a

(II) b

Figure 6.5 Raman spectra of acid purified Hipco SWNT and chondroitin sulfate A-Hipco SWNT complex with (I) 633 nm source laser and (II) 514 nm source laser.

The RBM peaks of both excitations with CS-A/Hipco SWNTs show some up-shift compared to raw Hipco nanotubes and this can be attributed to debundling and change of dispersant environment surrounding the SWNTs (*e.g.* solvent and polymer wrappings)⁹⁴. SWNT-dispersant interactions (such as hydrophobic interaction, van der Waals attraction, *etc.*) can change the SWNT free hole-carrier

density in SWNTs leading to the Raman peak shifts.

To explain the different dispersibility of the three CS dispersants (CS-A, CS-B and CS-C) in Fig. 6.1, we carried out simulations with 7-mer CS molecules. We found that the interactions (specifically coulombic interaction and hydrogen bonding) in the three monomers are different (Fig. 6.6 A(i) & (ii), B(i) & (ii) and C(i) & (ii)) leading to different polymer conformations. Hydrogen bonding exists in CS-A and CS-C whilst coulombic interaction in CS-B (between the $-\text{SO}_3^-$ and $-\text{OH}$). The minimum value of radii of gyration (R_g) in a 10ns trajectory for the three CS molecules are 1.3 nm (CS-A), 1.0 nm (C-SB) and 1.4 nm (CS-C). The smaller value of R_g for CS-B indicates that it is more flexible and can be easily compacted into random coil in water. With all the CS molecules, the hydrophobic surface will be sealed in contact inside in contact with the nanotubes leaving hydrophilic groups (like $-\text{SO}_3$, and $-\text{COO}$) outside of the coil.

The CS molecules were found to tightly adsorb around SWNTs (Fig. 6.6 A(iii), B(iii) and C(iii)). During the 20ns simulations, no dissociation events occurred. Comparing the three CS molecules, CS-B with stronger intramolecular Coulombic interaction is more flexible and can wrap around the SWNTs in a tighter helical manner, while the wrap patterns of CS-A and CS-C around the nanotubes are more extended than that of CS-B. The conformation of CS-B is unfavorable for adsorbing on the surface of SWNT. For a sufficiently long chain, CS-A/CS-C molecule will also form a helix wrapping around SWNTs. CS-A and CS-C maintain more extended conformations in water so that their hydrophobic faces can approach and form stable

adsorptions on SWNT in a relatively easy way (Fig. 6.6). In the model of CS-A, CS-B and CS-C wrapping around nanotube, we found that $-\text{COOH}$, $-\text{OH}$ and $-\text{NHCOCH}_3$ groups extend in the solution, while $-\text{H}$ atoms of the backbone are inside the helical structures and have interaction with nanotube (Fig 6.6 D).

We also estimate the SWNT-CS binding energy to shed light on how different CS molecules differentiate the SWNTs with different chiralities. To this end, the binding energy of SWNT-CS complex was calculated as follows:

$$E_B = E_C^{GB} - (E_G^{GB} + E_T^{GB})$$

where E_C^{GB} , E_G^{GB} and E_T^{GB} are the energies of SWNT-CS complex, CS (or GAG) and nanotube, respectively, based on the implicit GB model. The binding energies listed in Table 6.3 indicate that the binding of CS-B with SWNTs is much weaker than CS-A/CS-C with SWNTs. There is not much difference between the bindings between CS-A and CS-C with SWNTs. Considering the simplicity of the computational model employed here, *e.g.*, no partial charges on the SWNTs, the resolved differential binding of different CS's on the SWNTs may root in the conformation of the CS chain resulting in different affinity in wrapping with SWNTs.

A(i)

A(ii)

A(iii)

B(i)

B(ii)

B(iii) (Cont'd)

Figure 6.6 (Cont'd)

Figure 6.6 Structure models of CS-A monomer (A) i and ii, CS-B monomer (B) (i) and ii and CS-C monomer (C) i and ii obtained from computer simulations (the blue dot line shows the interaction in the monomer); structure models of (a) iii CS-A + (8, 4) SWNT; (b) iii CS-B + (8, 4) SWNT and (c) iii CS-C + (8, 4) SWNT. (Color labeling: C, gray; H, white; O, red; S, yellow; N, blue; SWNT highlighted in green) and (D) is schematic of CS wrapping around nanotube (SWNT highlighted in green and polymer backbone highlighted in grey).

Table 6.3 The binding energies of different CS- SWNT complexes estimated by GB model.

Dispersant	SWNT Chirality	E_B (kcal/mol)
CS-A	(8, 4)	-89.2 ± 4.1
	(9, 4)	-92.8 ± 4.0
CS-B	(8, 4)	-85.3 ± 4.8
	(9, 4)	-85.2 ± 5.0
CS-C	(8, 4)	-89.9 ± 4.5
	(9, 4)	-91.5 ± 5.1

6.3.2 Optimization of centrifugation speed

The centrifugation speed for dispersing SWNTs was optimized to obtain well-dispersed SWNTs in CS-A aqueous solution. A 100-watt tip sonicator was first applied to the CS-A/Hipco SWNTs solution to obtain a black stable solution. Different centrifugation forces (40k g, 50k g and 60k g) were then applied to the solution. Using UV-vis-NIR (Fig. 6.7A), we found that 50k g provided the centrifugation force for maximizing the A(S)/A(T) ratio which is reported to be an index of the ability to individually disperse the nanotubes⁸⁷ (Fig. 6.7B). All the CS-A/Hipco SWNT solution remained transparent with no precipitation for months.

A

B

Figure 6.7 CS-A/Hipco SWNTs solutions prepared with different centrifugation speeds: (a) UV-vis-NIR spectra (b) $A(S)/A(T)$ ratio.

PLE spectroscopy was used to determine the relative abundance of different semiconducting species in CS-A/Hipco supernatant solutions made with different centrifugation speeds. The chiralities and their relative intensities were determined

from the PLE plot by the methods described in Sections 2.4.1.

Fig. 6.8 shows that there are no significant differences between PLE mappings of samples with the three different centrifugation speeds. We chose 50k g centrifugation force which leads to the highest A(S)/A(T) ratio in the UV-vis-NIR spectrum (Fig. 6.8B) for subsequent experiments. The relative abundance of different semiconducting species with 50k g was calculated and summarized in Table 6.4 and Fig. 6.3). SDS was used for comparison.

Figure 6.8 Contour plots of photoluminescence of (I) SDS, (II) CS-A/Hipco SWNT solutions with different centrifugation speeds (a) 40k RCF (b) 50k RCF (c) 60k RCF (relative centrifugal force)

6.3.3 Easily removable CS-A Dispersant

From Section 6.3.1, we note that CS-A, CS-C and HA have good dispersibility of SWNTs compared to SDS. The solubilities of CS-A, CS-C and HA in water are 100mg/ml (10 wt%), 10mg/ml (1 wt%) and 10mg/ml (1 wt%) (Sigma Aldrich)). We explored the use of CS-A as a water-removable dispersant in view of its much higher solubility and low cost. In this section, CS-A was used alone as a single dispersant with Hipco SWNTs and the solution and device properties were characterized.

Hipco SWNTs

The removability of CS-A from Hipco nanotubes with washing was examined by XPS and compared with SDS. SDS/Hipco and CS-A/Hipco solutions were filtered onto filter paper and washed with lots of water. Then the nanotubes on the filter papers were characterized with XPS. Table 6.5 shows that raw Hipco SWNTs and HCl-purified SWNT (details of purification are described in Section 3.1) both contain only C and O atoms. After HCl purification, the O atom relative content increased, possibly because small amounts of carboxyl groups are generated at the ends and sidewall of SWNTs²⁴⁶. In the CS-A/Hipco sample, there was nearly no detectable S content leading us to believe that most of the CS-A has been washed away. SDS data showed that SDS can be mostly washed away though some residual amount remains. Typically, polymeric dispersants cannot be removed easily but CS-A is more removable than other polymers that interact with nanotubes via π - π stacking¹⁴³. The sulfated CS-A has good solubility (100 mg/mL) in water making it is relatively easy to redissolve. By comparison with polymers having π - π interaction with nanotubes,

the interaction of CS-A with nanotubes is not so strong as to prevent its removal. Removal of surfactant from nanotubes after dispersion is very important for applications in electronic devices.

Table 6.5 XPS results of Hipco SWNT solutions with SDS and CS-A

Atom	Relative atomic concentration (%)			
	Raw Hipco	Acidified Hipco	SDS/Hipco	CS-A/Hipco
O	3.85	4.21	26.92	28.93
C	96.15	95.79	69.57	67.49
N	0	0	3.47	3.52
Na	0	0	0	0
S	0	0	0.04	0.06

Fig. 6.9 and Fig. 6.10 are representative AFM and HR-TEM images of CS-A/Hipco SWNTs. The AFM images show that CS-A can disperse SWNTs into small nanotube bundles and sometimes individual nanotubes with less than 1 nm diameter. From the AFM pictures, we need to specially mention that most polymers have been washed away by flowing water over the samples for 10 minutes. For the TEM pictures, there is some residual polymer as we cannot apply flowing water since the copper TEM grid is fragile and the polymer is easily stuck onto the carbon film of the copper grid. The TEM samples also show that the nanotubes are well dispersed into individuals or small bundles.

Figure 6.9 AFM pictures of washed CS-A/Hipco SWNT samples on Si

Figure 6.10 TEM image of washed CS-A/Hipco SWNT samples on carbon layer of TEM grid

CoMoCAT[®] samples

We also fabricated network field-effect transistor (FET) devices using CS-A/CoMoCAT solution to prove the easy removability of the polysaccharide; if a thick layer of residual polymer remains, the current going through the SWNT network will be negligible. For device fabrication, Hipco SWNTs without separation cannot make devices which are switchable as they have larger chirality distribution. CoMoCAT[®] SWNTs have few chiralities, higher semiconducting nanotube content as supplied and shorter tube length, so that some devices can be switched on and off even without metallicity-based separation. Fig. 6.11A shows the typical charge transfer properties of CS-A/CoMoCAT solutions with forward and reverse sweeps of drain current (I_d) versus gate voltage (V_g) at constant drain voltage. Fig. 6.11B shows a histogram of the percentage of devices with different on/off ratios (the data of SDBS/CoMoCAT solution was from chapter 5). Devices using CS-A/CoMoCAT have on/off ratios of 10^1 - 10^3 , similar to those made using SDBS/CoMoCAT. AFM of

nanotubes in the channel between the electrodes (Fig. 6.11A, right) shows that CS-A has been mostly removed. The good solubility of CS-A in water (100 mg/mL), particularly with sodium counter-ion, is believed to cause its easy re-dissolution. Removal of surfactant from nanotubes after dispersion is very important for applications in electronic devices. The device performance can possibly be improved by patterning the nanotube network to suitable widths to decrease the percolation of metallic nanotubes²⁴¹.

Figure 6.11 SWNT network device using CS-A/CoMoCAT SWNTs (a) a typical V_g - I_d graph (the channel width is 100 μ m and the length is 20 μ m). (b) The histogram of percentage of number of devices with various on/off ratios (SDBS/CoMoCAT solution is used as the reference and the number of devices tested for CS-A/CoMoCAT and SDBS/CoMoCAT are 30 and 50 respectively).

6.4 Summary

In summary, different GAGs disperse and debundle the SWNTs in aqueous solution to different extents though they seem to be chemically quite similar. The dispersibilities of SWNTs by the GAGs arranged in decreasing ability are as follows: CS-C, (CS-A, HA) (almost the same), SDS (control) and CS-B. CS-C has the highest A(S)/A(T) ratio of 0.152 which is about 2 times of SDS (0.072). The A(S)/A(T) ratios of CS-A and HA are 0.105 and 0.097 respectively which are still higher than that of SDS (0.072) and CS-B (0.044). From the UV-vis-NIR, there is starking difference between the SWNT dispersibility of CS-C and CS-B. Computer simulation comparing CS-A, CS-B and CS-C shows that the conformation of the polymer in solution affects its wrapping on SWNTs. Free CS-A and CS-C have loose helical confirmations in solution due to their weak intramolecular hydrogen bonding while CS-B has a tighter helical structure due to its stronger intramolecular coulombic interaction. The favorable energetic interaction between GAGs, particularly the extended CS-A and CS-C, and SWNTs is due to their hydrohobic backbone and energy mimization with the hybrids. In summary, with isomers of CSs, different intramolecular bonding causes their spiral angle of helicity to differ leading to different wrapping patterns and affinities for SWNTs.

CS-A can disperse SWNTs individually in aqueous solution. The effective debundling effect was confirmed with AFM and TEM pictures. CS-A also can be easily removed as confirmed by XPS results and successful network devices made from it. This dispersant can potentially be widely applied in bioelectronics FET

devices.

6.5 Acknowledgements

Professor Mu Yuguang and his team at the School of Biological Sciences, Nanyang Technological University, did the computing simulation in Section 6.2.

Chapter 7 – Polysaccharide-dispersed SWNTs reinforced alginate hydrogels

7.1 Introduction

Hydrogels are widely used in diverse biomedical applications such as tissue engineering, lubricous coating, implant (*e.g.* contact lens), and drug and protein delivery due to their high water content, biocompatibility and resemblance to native extracellular matrix (ECM). However, their poor mechanical properties often limit their applications²⁴⁷.

SWNTs have outstanding mechanical properties and may impart superior mechanical and electrical properties to hydrogels reinforced with them. Research about SWNTs applied to biocompatible polymeric hydrogels has been limited²⁴⁸⁻²⁵³. Bhattacharyya *et al.*²⁵⁰ reported the use of hyaluronic acid to disperse SWNTs for forming reinforced hydrogels using divinyl sulfone (DVS) cross-linking reagent. Kawaguchi *et al.*²⁵¹ reported alginate hydrogels reinforced with strong acid treated nanotubes and chemically crosslinked using ethylene-diamine-di-(hydroxyl-succinimide) (EDSI) and 1-ethyl-3-(3-dimethyl-aminopropyl-carbodiimide hydrochloride. CNTs treated with strong acid contained abundant carboxyl groups so as to enable them to disperse well in aqueous solution but the structure of CNTs would be damaged.

In Chapters 4 and 6, we studied OCMCS (OC) and chondroitin sulfate A (CS-A) as dispersants to finely disperse SWNTs in aqueous solutions. Both disperse SWNTs

well so that the nanotubes exist in solutions as individual tubes or small bundles. These dispersants noncovalently wrapped around SWNTs without damaging their structures. As OC and CS-A are biocompatible materials, they may potentially be suitable for reinforcing hydrogels for biomedical applications.

The purpose of this chapter is to study the effect of SWNTs on the enhancement of mechanical and electrical properties of alginate hydrogels. OC and CS-A (Fig. 7.1a and b) described in previous chapters were used as dispersants of SWNTs. SDS was used as the reference dispersant. Alginate (Fig. 7.1c) which we postulated to be compatible with OC and CS-A since they all belong to the polysaccharide family, was used as the matrix and was crosslinked with divalent Ca^{2+} so that the hardening process was very mild. Ionically crosslinked alginates are known to have diverse applications such as cell encapsulation and protein/drug delivery^{254, 255}.

Composite hydrogels comprising calcium alginate and SWNTs were made from the gelation of sodium alginate using divalent calcium ions supplied by calcium carbonate in the presence of D-glucono- δ -lactone (GDL) (Fig. 7.1d)²⁵⁶. We used SWNTs from Chengdu as the reinforcing nanofiller. As the Chengdu nanotube is fairly long, in the range of few microns, it would be highly effective for load transfer. Table 7.1 shows the proportions of various constituents of a typical hydrogel reinforced with 0.5 wt% SWNT dispersed with CS-A. The amount of solid was only about 1.7 wt% of total weight and SWNTs were varied from 0 to 5 wt% of alginate, *i.e.* SWNTs were added only in small amounts. The compressive properties, water swelling, electrical impedance and charge capacity of the composite hydrogels were

measured.

Figure 7.1 Chemical structures of (a) OC (b) CS-A (c) sodium alginate salt (d) GDL

Table 7.1 Composition of a typical SWNT-reinforced Alginate hydrogel (with 0.5 wt% SWNT based on Alginate)

	Constituent	Weight /mg	Percentage of total weight
Solid	SWNTs	0.15	0.007%
	Alginate	30	1.3%
	CaCO ₃	6.6	0.3%
Sum of solid		36.75	1.7%
Liquid	Water	2200	96.8%
	GDL	25.4	1.1%
	CS	10	0.4%
Sum of liquid		2235.4	98.3%
Sum of liquid and solid			100%
SWNTs/Alginate			0.5%
SWMTs/solid			0.41%

7.2 Literature Review (Alginate)

Alginate, a natural polysaccharide derived from purified seaweed, is biodegradable, biocompatible and widely used in biomedical applications such as cell encapsulation, drug delivery, and tissue engineering²⁵⁷. Alginate (Fig. 7.2a) is a linear copolymer consisting of β -D-mannuronic acid (**M**) and α -L-guluronic acid (**G**) residues with widely varying monomer composition and sequence (example, **MMMMMM**, **GGGGGG** and **GMGMGMGM**). The chemical and physical properties of alginate is dependant on the different compositions²⁵⁸. The proportion of M and G residues of alginate determines its physical properties.

Calcium alginate hydrogel can be made through ionic cross-linking with Ca^{2+} divalent ions. Low concentration of calcium ions in an alginate solution will increase its viscosity while larger amounts will cause gel formation. Guluronic acid has a “zig-zag” structure so as to be able to accommodate calcium ions and is the residue that has high affinity for divalent metal cations²⁵⁸. The divalent Ca^{2+} ions cooperatively bind blocks of guluronic acid (*i.e.* the G blocks) between alginate chains, thus forming ionically interlinked chains (Fig. 7.2b and 7.2c). A hydrogel is thus formed by the interaction of calcium cations with G blocks. Alginates with a high proportion of G blocks will form rigid gels. Alginates with a high proportion of M blocks (consisting of mannuronic acid) form gels gradually and the resulting gels are softer and more elastic²⁵⁸.

Figure 7.2 Alginate (a) chemical structure (b) gelation process (c) gel formation via G blocks: egg box model^{259, 260}

Several calcium salts (e.g. CaCl_2 , CaCO_3 and CaSO_4) have been used for gelation/crosslinking of alginate hydrogel²⁶¹. Calcium chloride (CaCl_2) causes fast gelation rate with alginate as CaCl_2 has good solubility in water and Ca^{2+} ions can be released instantly²⁶². However, the fast speed of gelation of alginate hydrogels with CaCl_2 often leads to irregular shape and inhomogeneous structure and properties. On the other hand, calcium carbonate (CaCO_3) together with D-glucono- δ -lactone (GDL) (Fig. 7.1d) leads to slow gelation. CaCO_3 is sparingly soluble in alginate solution and sonication is typically used to first break the CaCO_3 particles to smaller pieces²⁵⁶. With smaller CaCO_3 particle size, GDL (a hydrolyzing agent) can release the Ca^{2+} ions from the suspended calcium particles easily to crosslink the alginate hydrogel²⁶¹. With the CaCO_3 -GDL approach, structurally homogeneous gels can be achieved.

To improve the mechanical properties of alginate hydrogel, SWNTs have been applied as the reinforcing material^{51, 252, 253}. However, the large surface area associated with the nanoscale diameter, extremely high aspect area and intertube van der Waals forces typically cause the SWNTs to aggregate into bundles, diminishing their beneficial high real surface area to volume ratio⁹. Forro *et al*²⁶³ found out that the elastic modulus of individual CNT is about 1 TPa, but this number drops to 100 GPa when the CNTs exist in bundles. Their results show that the shearing effects in SWNT bundles due to weak intertube cohesion results in significantly lower modulus compared to individual SWNTs²⁶⁴. Hence, to fully exploit the high strength and stiffness of nanotubes in composites, the nanotubes should be debundled and well-dispersed, besides having strong interfacial coupling with the matrix. Suitable

dispersants or surfactants can be used to disperse SWNTs finely.

7.3 Experimental details

I) Materials

All the chemicals were purchased from Sigma-Aldrich (Singapore) at the highest commercially available purity and used without further purification. The synthesis procedure of OC was described in Section 4.2. SWNTs used in this chapter were bought from Chengdu Organic Chemicals Co. Ltd (China) and details of purification were described in Section 3.1. The 24-well cell polystyrene dish was bought from Fisher Scientific Inc.

II) Preparation of Alginate solution

To make 2 wt% alginate solutions, 0.9 g sodium alginate was added to 45 ml deionized water and stirred at room temperature for one day. This was to ensure that the alginate was completely dissolved to produce a homogeneous alginate solution. 198 mg calcium carbonate was added into 45 ml alginate solution (*i.e.* 1.5 ml alginate solution and 6.6 mg calcium carbonate was used for one gel sample). The mixture was sonicated (SONICS, VCX-750, 150 watt) for 30 minutes (10s on/10s off cycle in ice) in order to break calcium carbonate into small particles.

III) Preparation of polymer-SWNTs (SWNTs bought from Chengdu Organic Chemicals Co. Ltd (China)) solutions

2 wt% polymer (OC or CS-A) solution was used to disperse SWNTs. Using a 1 wt % SWNT in hydrogel as an example, 3 mg SWNTs were added into 5 ml polymer

solution. The mixture of SWNTs and polymer solution were sonicated at 100 watt with tip sonication in water-ice bath continuously for 1h (the concentration of SWNTs was based on the weight of alginate).

IV) Preparation of alginate hydrogels

The 24-well polystyrene cell culture dish was used as the gel formation mold. To make pure hydrogels without SWNTs, a pre-mixed solution comprising 1.5 ml alginate solution and 6.6 mg calcium carbonate as described above (Section 7.3II) was added into each well, followed by 0.5 ml pure polymer (OC or CS-A) solution and the mixture was stirred until homogeneous. Then 23.5 mg GDL was added into each well and the mixture was stirred again. The final mixture was left standing for 2 days at room temperature to harden.

To prepare SWNTs-reinforced hydrogels, the procedure was similar to above except that 0.5 ml polymer-SWNTs solution, rather than 0.5 ml pure polymer solution, was added into each well.

V) Swelling measurement

Hydrogels were freeze-dried for 24 h and then immersed in water to saturation. Then the hydrogels were taken out from water and quickly dried on filter paper to eliminate residual water on the surface. The percentage of swelling (S%) was calculated as follows:

$$S\% = (100 * (\text{Weight}_{\text{wet}} - \text{Weight}_{\text{dry}}) / \text{Weight}_{\text{wet}})\%$$

VI) Electrical properties measurement

All the impedance measurements were recorded in 0.01 M PBS at room temperature

on a CHI Electrochemical working station. Gold electrode was the working electrode, platinum electrode was the auxiliary electrode and saturated calomel electrode (SCE) was the reference electrode. The measurement frequency range was from 1 Hz to 100 kHz with AC amplitude of ± 5 mV. 25 ml of the prepared hydrogel precursor solution containing Ca^{2+} ions was dropped on the top of Au electrode (working electrode) using a micropipette and then kept there for two days in a humid environment before measuring the electrical properties.

Cyclic voltammogram of hydrogel was measured by applying potential difference in the range of -0.6V to 0.6V at a scan rate of 0.1V/s using the three point electrode system in an electrochemical workstation. Area of the cyclic voltammogram was calculated to measure the charge capacity of hydrogel.

7.4 Results and Discussion

7.4.1 Compressive Properties

Fig. 7.3 shows the alginate hydrogels made with and without SWNTs. The controls without SWNTs are transparent while the hydrogels containing SWNTs are homogeneous and black though no visible color difference was observed for the gels made with different SWNTs concentrations.

Figure 7.3 Photographs of typical hydrogels (a) control with OC dispersant (b) control with CS-A dispersant (c) with 0.5 wt% SWNTs using OC dispersant (d) with 0.5 wt% SWNTs using CS-A dispersant

The compressive properties of hydrogels with 0 to 5 wt% SWNTs were measured. Fig.7.4 shows typical stress-strain curves of hydrogels made with varying concentrations of SWNTs dispersed by CS-A. The ultimate compressive stress (σ_u), ultimate strain (ϵ_f), primary modulus (E_1) and secondary modulus (E_2) of hydrogels were summarized in Table 7.2 to Table 7.4 and Fig. 7.5 for OC, CS-A and SDS dispersants. (The calculation details are explained in Appendix C.)

Figure 7.4 Typical compressive stress (kPa) versus strain curve (%) for alginate hydrogels made with different concentration of SWNTs in CS-A/SWNTs solution.

Table 7.2 Compressive Properties of Alginate Hydrogels using SDS surfactant

	Ultimate Compressive stress(kPa)	Primary Modulus E ₁ (kPa)	Secondary Modulus E ₂ (kPa)	Strain at Ultimate compressive stress(%)
SDS control	6.9 ± 0.8	5.6 ± 0.7	14.8 ± 3.3	59.6 ± 4.8
0.5 wt% SWNT	9.1 ± 1.6	7.2 ± 1.1	20.6 ± 4.6	60.4 ± 6.6
1.0 wt% SWNT	6.9 ± 1.5	9.3 ± 3.0	24.7 ± 8.9	53.4 ± 7.0
2.0 wt% SWNT	11.8 ± 1.2	11.4 ± 2.1	40.5 ± 7.2	52.6 ± 2.4
3.0 wt% SWNT	9.7 ± 1.1	11.7 ± 2.5	40.0 ± 8.5	49.8 ± 3.8
3.5 wt% SWNT	8.4 ± 1.1	11.6 ± 4.4	34.4 ± 8.4	51.0 ± 6.5
5.0 wt% SWNT	6.1 ± 1.7	14.9 ± 4.2	29.0 ± 7.6	40.0 ± 1.4

Table 7.3 Compressive Properties of Alginate Hydrogels using OC dispersant

	Ultimate Compressive stress(kPa)	Primary Modulus E ₁ (kPa)	Secondary Modulus E ₂ (kPa)	Strain at Ultimate compressive stress(%)
OC control	8.5 ± 0.8	13.9 ± 3.5	38.9 ± 5.3	40.6 ± 5.0
0.5 wt% SWNT	14.0 ± 0.8	13.9 ± 2.2	49.8 ± 8.3	53.6 ± 3.0
1.0 wt% SWNT	14.3 ± 0.9	22.9 ± 4.2	62.9 ± 2.4	41.7 ± 3.2
2.0 wt% SWNT	14.6 ± 2.1	23.1 ± 3.4	61.4 ± 9.4	43.2 ± 3.3
3.0 wt% SWNT	17.2 ± 0.8	35.7 ± 8.1	68.4 ± 5.8	42.5 ± 3.7
3.5 wt% SWNT	18.1 ± 1.2	39.6 ± 7.9	84.3 ± 5.9	45.3 ± 2.8
5.0 wt% SWNT	17.6 ± 2.1	31.3 ± 9.1	66.1 ± 11.3	48.3 ± 5.5

Table 7.4 Compressive Properties of Alginate Hydrogels using CS-A dispersant

	Ultimate Compressive stress (kPa)	Primary Modulus E ₁ (kPa)	Secondary Modulus E ₂ (kPa)	Strain at Ultimate compressive stress (%)
CS-A control	8.4 ± 0.6	8.9 ± 0.9	35.3 ± 3.3	40.4 ± 2.2
0.5 wt% SWNT	11.5 ± 0.9	12.6 ± 2.1	50.9 ± 6.6	50.9 ± 3.9
1.0 wt% SWNT	12.2 ± 0.8	21.5 ± 5.3	53.7 ± 9.3	40.1 ± 2.9
2.0 wt% SWNT	11.8 ± 1.2	14.4 ± 2.2	55.0 ± 6.3	46.0 ± 2.0
3.0 wt% SWNT	14.6 ± 1.9	22.1 ± 4.1	70.9 ± 5.2	44.5 ± 3.2
3.5 wt% SWNT	11.0 ± 0.7	20.5 ± 4.0	49.8 ± 4.3	44.3 ± 3.0
5.0 wt% SWNT	9.9 ± 0.7	23.0 ± 2.3	45.4 ± 3.8	50.6 ± 3.1

(A)

(B)

(C)

Figure 7.5 Effect of SWCNTs dispersed with OC, CS-A and SDS on the (a) Ultimate Compressive Stress (σ_u) , (b) Primary Modulus (E_1) and (c) Secondary Modulus (E_2)

Fig. 7.5 (A) to (C) compare the compressive stress, primary modulus and secondary modulus of hydrogels made with different dispersants and SWNTs contents. Using SDS as the dispersant, the compressive strength and moduli of all the hydrogels (with and without SWNTs) are lower than those of hydrogels made with OC or CS-A dispersant. Interesting, the OC produces better compressive properties than CS-A too. Also, as SWNT concentration increases, these mechanical properties increase, though by different extent, till the optimum SWNT concentration and then decrease or plateau.

Using OC dispersant, σ_u , E_1 and E_2 of the hydrogels increase with SWNTs content and reached a maximum at around 3.5 wt%. With 3.5 wt% SWNTs content, the ultimate compressive stress (18.1 ± 1.2 kPa) and secondary modulus (84.3 ± 5.9 kPa) are more than two times those of pure alginate gel ($\sigma_u = 8.5 \pm 0.8$ kPa, $E_2 = 38.9 \pm 5.5$ kPa); E_1 (39.6 ± 7.9 kPa) increases to almost 3 times that of pure alginate gel (13.9 ± 3.5 kPa). Beyond 3.5 wt% SWNTs, the E_1 and E_2 moduli decrease and σ_u does not increase. We postulate that with more SWNTs, they begin to bundle leading to deterioration of compressive properties.

Using CS-A dispersant, σ_u and E_2 of the hydrogels increase with SWNTs content and reached a maximum at around 3 wt% so that the values ($\sigma_u = 14.6 \pm 1.9$ kPa and $E_2 = 70.9 \pm 5.2$ kPa) are around 2 times those of the CS-A control ($\sigma_u = 8.4 \pm 0.6$ kPa and $E_2 = 35.3 \pm 3.3$ kPa). E_1 plateaued at 3 wt% SWNT.

With SDS surfactant, at the optimum SWNT content of about 2 wt%, the σ_u (11.8 ± 1.2 kPa) and E_2 (40.5 ± 7.2 kPa) are nearly two times those of pure alginate gel

($\sigma_u=6.9\pm0.8$ kPa, $E_2=14.8\pm3.3$ kPa); E_1 plateaued at 2 wt% SWNT (to 14.9 ± 4.2 kPa) to 3 times of pure alginate (5.6 ± 0.7 kPa). (should not be drawn plateaued but increas)

Of the three dispersants, OC appears to be most effective and SDS the least effective in improving the compressive properties. We proposed that OC and CS-A dispersants, particularly the former, have O and N atoms to form hydrogen bonding with the alginate matrix. The less ionizable hydroxyl, carboxyl and amine groups on OC would afford more sites for hydrogen bonding than CS-A which contains highly ionizable sulfated group. The multiple sites of interaction on a single macromolecular OC or CS-A may account for their higher increase in compressive properties compared to small molecular SDS.

From the swelling data (Table 7.5 to Table 7.7), for all three families of gels, the water uptake capacities of the gels with different SWNTs content and dispersants are almost the same, which are about the same as those of pure alginate gels. This show that the presence of SWNTs or different dispersant has little influence on the gel's water uptake capacity.

7.4.2 Electrochemical measurement of hydrogels

Alginate hydrogel precursor solutions containing finely mixed SWNTs were dropped onto gold electrode surfaces and then gelled *in situ* for electrochemical measurements. The impedance was measured in phosphate buffered saline (PBS) solution at open circuit potential at room temperature. The impedance spectra of all the electrodes show similar trend on the Bode plots (Fig. 7.6). At low frequency range

($\leq 10^3\text{Hz}$), the impedance rapidly decreases with the increase of frequency. With frequency higher than 10^3Hz , the descending trend slows down. The electrode/electrolyte interface resembles a serial circuit made up of a resistance (R) and a capacitance (C). According to the impedance principle, its impedance (Z) could be calculated by the equation:

$$|Z|^2 = R^2 + (1/\omega C)^2$$

where R is the resistance of interface, ω is the frequency used and C is the capacitance of interface. Obviously at low frequency, the impedance is predominated by the capacitance. When ω is high, the impedance reaches plateaus.

Table 7.5 Swelling Values for Alginate Hydrogels (SDS as dispersant)

	Swelling (Wet Weight-Dry weight)/wet weight
SDS control	95.3% ± 0.2%
0.5% SWNT	95.1% ± 0.3%
1% SWNT	94.8% ± 0.9%
2% SWNT	95.1% ± 0.5%
3% SWNT	95.4% ± 0.8%
3.5% SWNT	95.1% ± 0.2%
5% SWNT	94.3% ± 0.4%

Table 7.6 Swelling Values for Alginate Hydrogels (OC as dispersant)

	Swelling (Wet Weight-Dry weight)/wet weight
OCMCS control	95.2% ± 0.5%
0.5% SWNT	94.4% ± 0.5%
1% SWNT	94.5% ± 0.9%
2% SWNT	95.3% ± 0.5%
3% SWNT	94.4% ± 0.2%
3.5% SWNT	94.1% ± 0.4%
5% SWNT	94.2% ± 0.2%

Table 7.7 Swelling Values for Alginate Hydrogels (CS-A as dispersant)

	Swelling (Wet Weight-Dry weight)/wet weight
CS-A control	95.1% ± 0.3%
0.5% SWNT	94.7% ± 0.2%
1% SWNT	94.5% ± 0.5%
2% SWNT	94.9% ± 0.2%
3% SWNT	94.5% ± 0.1%
3.5% SWNT	94.2% ± 0.7%
5% SWNT	94.6% ± 0.5%

From Fig. 7.6, the impedance of gel-modified electrode is lower than bare gold electrode, indicating increased capacitance. Hydrogels with different SWNTs concentration have similar trend of impedance curves. More importantly, when 0.5 wt% of SWCNTs dispersed with OC was incorporated into the gel, there is an evident decrease in the impedance. The incorporation of SWNTs could improve the electroactive area of the electrode, hence in turn improve the capacitance. According to the above equation, increase in capacitance by SWNTs results in lower impedance at low frequency range.

The cyclic voltammetries (CV) are shown in Fig. 7.7. All the CV curves display typical double-layer charging/discharging current. No evident redox peak could be found. The gel-SWNTs modified electrode give higher current compared with gel-modified electrode, which could be assigned to increased capacitance by the incorporation of SWNTs. The charge capacity of various SWNTs concentration, inferred from the area of the cyclic voltammetry versus SWNT content plot, is shown in Fig. 7.8. For OC and CS-A as dispersant, hydrogels with 0.5 wt% SWNTs has the highest charge capacity. For SDS, hydrogels of 1 wt% SWNTs has the highest charge capacity. When SWNTs reaches higher concentration (i.e. 3 wt% and 5 wt%), the charge capacity is not much higher than pure alginate hydrogels and we believe that the SWNTs are all bundles and interconnected in higher concentration leading to lower electrical properties²⁶⁵.

a

b

c

Figure 7.6 Impedance spectra of the hydrogels of (a) OC/SWNTs solution, (b) CS-A/SWNTs solution and (c) SDS/SWNTs solution

Figure 7.7 Typical cyclic voltammograms of hydrogels of (a) OC/SWNTs solution, (b) CS-A/SWNTs solution and (c) SDS/SWNTs solution at 0.5 wt% SWNTs

Figure 7.8 Area of Cyclic voltammograms curves of (a) SDS/SWNTs solution, (b) CS-A/SWNTs solution and (c) OC/SWNTs solution with different SWNTs concentrations

7.5 Conclusions

SWNTs were used to reinforce alginate hydrogels crosslinked through Ca^{2+} . Different ratios of SWNTs well dispersed with OC, CS-A or SDS (control) were added into the alginate hydrogels. Hydrogels reinforced with SWNTs show compressive properties (i.e. σ_u , E_1 and E_2) which increased as much as two times that of unreinforced alginate hydrogel controls. OC and CS-A, particularly the former, demonstrate much higher reinforcing enhancement than SDS. For electrical properties, hydrogels reinforced with 0.5 wt% SWNTs dispersed by OC have lower impedance and higher charge capacity compared with unreinforced alginate/OC hydrogel. The results show that SWNTs can improve the mechanical and electrical properties of alginate hydrogels.

Chapter 8 - Conclusion and Directions for Future Research

8.1 Conclusion

The development of efficient debundling, chiral-selective and easily-removable dispersants has been a major obstacle to widespread applications of SWNTs. In this thesis, we evaluated several polysaccharides for efficient dispersion and debundling SWNTs in aqueous solution, and performed in-depth studies to investigate the correlation between SWNTs dispersibility and the chemical structures of the dispersants.

Firstly, we synthesized novel water-soluble chitosan derivatives: O-carboxymethylchitosan (OC), OC-modified polyethylene glycol (OPEG) and quaternary ammonium chitosan (QC). OC and OPEG were found to be good dispersants of SWNTs in aqueous solution. Both OC and OPEG have amino groups which interact with SWNTs by electron transfer, which is confirmed by FTIR. The poor dispersibility of QC is due to protonation of its amino groups. We also found that several glycosaminoglycans (GAGs), specifically heparin sodium salt, three isomers of chondroitin sulfate (chondroitin-4-sulfate (CS-A), dermatan sulfate B (CS-B) and chondroitin-6-sulfate C (CS-C)) and hyaluronic acid (HA), can disperse the SWNTs into individual nanotubes or small bundles, though to different degrees. CS-C has the highest A(S)/A(T) ratio (0.15), even higher than SDS (0.072) (A(S)/A(T) ratio indicates individual or small bundle of SWNT content). Computer simulation results

show that heparin sodium salt and the three chondroitin sulfate isomers complex with SWNTs by helically wrapping them, though with different spiral angles and binding energies.

Secondly, we found that heparin sodium salt has selectivity for certain chiral species of SWNTs. Heparin sodium salt used alone as a dispersant of Hipco SWNTs is found to preferentially suspend larger diameter nanotubes. Heparin sodium salt was shown to be an effective enrichment agent for specific chiral species of CoMoCAT SWNTs. CoMoCAT, rather than Hipco, nanotubes are preferable for the chiral selection application of heparin because of the lower chiral diversity. We tested single- and three-fold extractions from an initial CoMoCAT dispersion using sodium dodecylbenzene sulfonate (SDBS) surfactant. PLE spectra exhibit dramatic increase in intensity of the (8, 4) peak, and the increase is greater with multiple successive extractions. After 3-fold extraction, the (8, 4) species was enriched to 60% abundance (from a pre-enrichment abundance of 7%). Our computer simulation shows that the helical structure of heparin sodium salt plays an important role in dispersing SWNTs and that the binding energy with (8, 4) tubes is the strongest amongst the four major chiral species ((8, 4), (6, 5), (7, 5), (8, 3)) in CoMoCAT mixtures. The combination of small molecule surfactant, *i.e.* SDBS, with heparin provides a new approach for obtaining SWNTs highly enriched in a specific chirality.

Thirdly, we found that heparin sodium salt and CS-A dispersants can be easily removed with DI water, which is an advantage compared with other reported polymeric dispersants. The easy removability was confirmed by successful fabrication

of FETs made from CoMoCAT/Heparin, CoMoCAT/Heparin(x3) and CoMoCAT/CS-A solutions. XPS data also showed that there is little sulfur residue in the enriched SWNT samples after removal of these dispersants. Residual polymer on SWNTs increases intertube resistance, and decreases the device mobility. Thorough removal of dispersant is important for application of SWNTs in high-performance electronics and is a benefit complementary to the high enrichment of a single chiral species.

Fourthly, we showed that the three isomers of chondroitin sulfate (CS), though chemically identical, have different abilities to disperse Hipco SWNTs. CS-B was found to very poorly suspend nanotubes because of its strong intramolecular Coulombic interaction. CS-C was found to be the most effective of these substances for SWNT dispersion because of its weak intramolecular hydrogen bonding and the favorable energetics of interaction of the hydrophobic CS backbone with nanotubes.

Finally, OC/SWNTs solution and CS-A/SWNTs solutions were used for preparation of alginate hydrogels. SWNTs are well known as reinforcement fibers; finely dispersed SWNTs solutions were mixed with alginate to form hydrogels. The compressive modulus and strain of the hydrogels was enhanced as much as two times by incorporation of a few weight percent SWNTs .

8.2 Directions for Future Research

8.2.1 Computer Modeling

Our research opens up new vistas for future study and application of

biomacromolecule-SWNT hybrids. A useful future direction would be detailed numerical modeling of polymer wrapping around SWNTs for further investigation of the mechanism(s) of interaction between polymers and SWNTs. Such research would provide information about which groups in the polymer chain have strong affinity for SWNTs, and other key parameters which affect the dispersibility and removability of polymer-based dispersants. This would help to guide rational design of highly effective chiral-selective polymeric dispersants.

8.2.2 SWNT selectivity by polysaccharides

We showed that polysaccharides complex with SWNTs in a helical configuration. The cavity size of a polymer's helical structure may accommodate different diameter SWNTs. The degree of alignment of the helical structure of a polymer with different SWNT chiralities may affect its chiral-selectivity. The rigidity of the polymer's backbone may also affect selectivity and the process of SWNT wrapping. Future systematic research into helical polymers with a range of cavity sizes and backbone rigidities which possess selectivities for different SWNT diameters and chiralities would be useful.

Our polysaccharides lack metallicity-selectivity, which is needed for SWNTs applications in FETs. It would be highly desirable to identify moieties which could confer metallicity-selectivity on helical polysaccharides.

CNT FETs are usually p-type in ambient conditions. Our biomacromolecules can be attached with moieties (e.g. $-\text{NH}_2$) which have electron transfer with nanotubes to

provide doping effect to SWNTs to make n-type devices.

We reported preliminary experiments on the application of density gradient ultracentrifugation (DGU) method for Hipco SWNT solutions (using Heparin dispersant). DGU is a well-known method for the separation of metallic and semiconducting SWNTs using sodium cholate. Combination of DGU with our biomacromolecular dispersants may also permit highly metallicity-selective separation of SWNTs.

Gel electrophoresis has been reported to be capable of separating metallic and semiconducting SWNTs²⁶⁶. However, the agarose gel employed is highly viscous and difficult to afterwards separate from the nanotubes. Alginate hydrogels, which may be liquefied afterwards, have the potential to be used as the matrix gel in this method. We have demonstrated that SWNTs can be homogeneously mixed in alginate hydrogels. However, applicability of alginate/SWNT in gel electrophoresis has yet to be demonstrated and the mixture would likely need to be optimized.

8.2.3 SWNTs applications

Hydrogels containing SWNTs can be used for future 3-D cell encapsulation studies.

Incorporation of carbon nanotubes into composite materials to achieve significant improvements in mechanical properties is an area of intense research^{265, 267}. A major challenge with SWNTs-reinforced composite materials is how to finely and thoroughly disperse SWNTs within polymers. Our biomaterials can disperse SWNTs

well and the dispersant can be chemically modified to crosslink with the hydrogel precursor. The SWNT-reinforced hydrogel with suitable dispersants, after drying, may result in high performance composites.

The biomaterial dispersants studied here can disperse SWNTs well without decreasing the surface tension. Some of the dispersants can be easily removed with neutral deionized water so that the dispersed SWNTs can be suspended in other organic solvents. These properties suggest a future research agenda of application of our SWNTs solutions in inkjet printing for large-scale fabrication of SWNT-based electrical devices. SWNTs solutions can be used to make flat and homogeneous thin films, in the form of either random networks or aligned arrays. This research has applications in thin film transistors and sensors.

Every atom of a SWNT is on the surface and exposed to the environment, and this very high surface area/mass ratio provides a great potential for biosensing applications. Amylose has been reported to solubilize¹⁸ SWNTs in water and it has been reported that SWNT-based FETs can detect the enzymatic degradation of starch²⁶³. We have reported several polysaccharides which disperse SWNTs well in water, and we can apply these solutions to make SWNT-based FETs to monitor enzyme-catalyzed reactions.

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Appendix A

In our thesis, chiralities assignments of PLE data and UV-vis-NIR data was according to reported Table a1⁴² by fitting the energy bandgaps from SWNT's E_{11} emission when the excitation energy match the nanotube E_{22} energy level . We mainly used Table a2 & a3 as reference⁹⁷ for the chiralities assignments of both semiconducting and metallic nanotubes in the RBM range.

Table a1. First and Second van Hove Optical Transition (E_{11} and E_{22}) for Semiconducting SWNT Structures with Diameters between 0.48 and 2.0 nm.

(n, m)	d (nm)	α (deg)	mod ^b	λ_{11} (nm)	$\bar{\nu}_{11}$ (cm ⁻¹)	E_{11} (eV) ^c	λ_{22} (nm)	$\bar{\nu}_{22}$ (cm ⁻¹)	E_{22} (eV)	(n, m)	d (nm)	α (deg)	mod ^b	λ_{11} (nm)	$\bar{\nu}_{11}$ (cm ⁻¹)	E_{11} (eV) ^c	λ_{22} (nm)	$\bar{\nu}_{22}$ (cm ⁻¹)	E_{22} (eV)
(4, 3)	0.483	25.28	1	700	14 283	1.771	398	25 147	3.118	(14, 12)	1.789	27.46	2	2059	4856	0.602	1181	8470	1.050
(5, 3)	0.556	21.79	2	720	13 884	1.721	522	19 147	2.374	(14, 13)	1.857	28.78	1	2141	4672	0.579	1208	8278	1.026
(5, 4)	0.620	26.33	1	835	11 974	1.485	483	20 697	2.566	(15, 1)	1.232	3.20	2	1426	7011	0.869	920	10 864	1.347
(6, 1)	0.521	7.59	2	653	15 323	1.900	632	15 828	1.962	(15, 2)	1.278	6.18	1	1622	6165	0.764	822	12 163	1.508
(6, 2)	0.572	13.90	1	894	11 183	1.387	418	23 900	2.963	(15, 4)	1.377	11.52	2	1589	6294	0.780	986	10 140	1.257
(6, 4)	0.692	23.41	2	873	11 452	1.420	578	17 312	2.146	(15, 5)	1.431	13.90	1	1752	5708	0.708	921	10 858	1.346
(6, 5)	0.757	27.00	1	976	10 244	1.270	566	17 667	2.190	(15, 7)	1.546	18.14	2	1779	5621	0.697	1064	9396	1.165
(7, 0)	0.556	0.00	1	962	10 397	1.289	395	25 318	3.139	(15, 8)	1.606	20.03	1	1907	5245	0.650	1035	9663	1.198
(7, 2)	0.650	12.22	2	802	12 468	1.546	626	15 977	1.981	(15, 10)	1.730	23.41	2	1987	5032	0.624	1156	8650	1.072
(7, 3)	0.706	17.00	1	992	10 083	1.250	505	19 820	2.457	(15, 11)	1.795	24.92	1	2086	4793	0.594	1158	8635	1.071
(7, 5)	0.829	24.50	2	1024	9768	1.211	645	15 496	1.921	(15, 13)	1.927	27.64	2	2207	4532	0.562	1259	7942	0.985
(7, 6)	0.895	27.46	1	1120	8930	1.107	648	15 441	1.914	(15, 14)	1.994	28.86	1	2287	4373	0.542	1288	7767	0.963
(8, 0)	0.635	0.00	2	776	12 886	1.598	660	15 146	1.878	(16, 0)	1.270	0.00	1	1623	6163	0.764	815	12 264	1.521
(8, 1)	0.678	5.82	1	1041	9603	1.191	471	21 226	2.632	(16, 2)	1.357	5.82	2	1561	6405	0.794	984	10 162	1.260
(8, 3)	0.782	15.30	2	952	10 508	1.303	665	15 029	1.863	(16, 3)	1.405	8.44	1	1746	5728	0.710	898	11 139	1.381
(8, 4)	0.840	19.11	1	1111	8997	1.116	589	16 981	2.105	(16, 5)	1.508	13.17	2	1732	5775	0.716	1055	9480	1.175
(8, 6)	0.966	25.28	2	1173	8525	1.057	718	13 928	1.727	(16, 6)	1.564	15.30	1	1884	5307	0.658	1000	9999	1.240
(8, 7)	1.032	27.80	1	1265	7908	0.981	728	13 727	1.702	(16, 8)	1.680	19.11	2	1925	5194	0.644	1138	8788	1.090
(9, 1)	0.757	5.21	2	912	10 964	1.359	691	14 466	1.794	(16, 9)	1.741	20.82	1	2046	4887	0.606	1115	8968	1.112
(9, 2)	0.806	9.83	1	1138	8790	1.090	551	18 155	2.251	(16, 11)	1.867	23.90	2	2134	4685	0.581	1233	8111	1.006
(9, 4)	0.916	17.48	2	1101	9086	1.126	722	13 843	1.716	(16, 12)	1.932	25.28	1	2231	4483	0.556	1238	8077	1.001
(9, 5)	0.976	20.63	1	1241	8055	0.999	672	14 883	1.845	(17, 0)	1.350	0.00	2	1552	6443	0.799	984	10 167	1.261
(9, 7)	1.103	25.87	2	1322	7567	0.938	793	12 610	1.563	(17, 1)	1.391	2.83	1	1744	5733	0.711	886	11 289	1.400
(9, 8)	1.170	28.05	1	1410	7093	0.879	809	12 362	1.533	(17, 3)	1.483	7.99	2	1699	5886	0.730	1050	9525	1.181
(10, 0)	0.794	0.00	1	1156	8652	1.073	537	18 606	2.307	(17, 4)	1.533	10.33	1	1873	5340	0.662	974	10 263	1.272
(10, 2)	0.884	8.95	2	1053	9493	1.177	737	13 574	1.683	(17, 6)	1.641	14.56	2	1875	5332	0.661	1125	8886	1.102
(10, 3)	0.936	12.73	1	1249	8006	0.993	632	15 834	1.963	(17, 7)	1.697	16.47	1	2019	4952	0.614	1079	9264	1.149
(10, 5)	1.050	19.11	2	1249	8006	0.993	788	12 695	1.574	(17, 9)	1.816	19.93	2	2072	4827	0.599	1212	8248	1.023
(10, 6)	1.111	21.79	1	1377	7262	0.900	754	13 262	1.644	(17, 10)	1.877	21.49	1	2188	4571	0.567	1195	8367	1.037
(10, 8)	1.240	26.33	2	1470	6805	0.844	869	11 502	1.426	(18, 1)	1.470	2.68	2	1682	5944	0.737	1048	9543	1.183
(10, 9)	1.307	28.26	1	1556	6428	0.797	889	11 248	1.395	(18, 2)	1.515	5.21	1	1868	5353	0.664	958	10 433	1.294
(11, 0)	0.873	0.00	2	1037	9644	1.196	745	13 431	1.665	(18, 4)	1.611	9.83	2	1838	5439	0.674	1118	8947	1.109
(11, 1)	0.916	4.31	1	1265	7906	0.980	610	16 388	2.032	(18, 5)	1.663	11.93	1	2003	4993	0.619	1052	9508	1.179
(11, 3)	1.014	11.74	2	1197	8353	1.036	793	12 617	1.564	(18, 7)	1.773	15.75	2	2020	4952	0.614	1197	8351	1.035
(11, 4)	1.068	14.92	1	1371	7295	0.904	712	14 036	1.740	(18, 8)	1.831	17.48	1	2156	4638	0.575	1159	8629	1.070
(11, 6)	1.186	20.36	2	1397	7157	0.887	858	11 661	1.446	(18, 10)	1.951	20.63	2	2218	4509	0.559	1288	7765	0.963
(11, 7)	1.248	22.69	1	1516	6597	0.818	836	11 968	1.484	(19, 0)	1.508	0.00	1	1867	5357	0.664	953	10 492	1.301
(11, 9)	1.377	26.70	2	1617	6183	0.767	947	10 564	1.310	(19, 2)	1.594	4.95	2	1816	5507	0.683	1114	8979	1.113
(11, 10)	1.444	28.43	1	1702	5877	0.729	969	10 320	1.280	(19, 3)	1.641	7.22	1	1994	5015	0.622	1033	9683	1.201
(12, 1)	0.995	3.96	2	1170	8549	1.060	799	12 516	1.552	(19, 5)	1.741	11.39	2	1979	5052	0.626	1187	8422	1.044
(12, 2)	1.041	7.59	1	1378	7255	0.900	686	14 575	1.807	(19, 6)	1.795	13.29	1	2135	4684	0.581	1130	8853	1.098
(12, 4)	1.145	13.90	2	1342	7452	0.924	855	11 693	1.450	(19, 8)	1.907	16.76	2	2164	4621	0.573	1271	7869	0.976
(12, 5)	1.201	16.63	1	1499	6670	0.827	793	12 605	1.563	(19, 9)	1.966	18.35	1	2295	4358	0.540	1238	8076	1.001
(12, 7)	1.321	21.36	2	1545	6473	0.803	930	10 751	1.333	(20, 0)	1.588	0.00	2	1808	5531	0.686	1113	8989	1.114
(12, 8)	1.384	23.41	1	1657	6036	0.748	917	10 910	1.353	(20, 1)	1.629	2.42	1	1990	5024	0.623	1023	9775	1.212
(12, 10)	1.515	27.00	2	1765	5666	0.703	1024	9763	1.210	(20, 3)	1.719	6.89	2	1952	5124	0.635	1181	8466	1.050
(12, 11)	1.582	28.56	1	1848	5412	0.671	1049	9535	1.182	(20, 4)	1.768	8.95	1	2122	4712	0.584	1108	9025	1.119
(13, 0)	1.032	0.00	1	1384	7228	0.896	677	14 770	1.831	(20, 6)	1.872	12.73	2	2121	4715	0.585	1258	7947	0.985
(13, 2)	1.120	7.05	2	1307	7651	0.949	858	11 661	1.446	(20, 7)	1.927	14.46	1	2269	4406	0.546	1208	8280	1.027
(13, 3)	1.170	10.16	1	1498	6676	0.828	764	13 095	1.624	(21, 1)	1.708	2.31	2	1938	5161	0.640	1178	8487	1.052
(13, 5)	1.278	15.61	2	1487	6723	0.834	922	10 843	1.344	(21, 2)	1.752	4.50	1	2116	4727	0.586	1095	9134	1.132
(13, 6)	1.336	17.99	1	1632	6127	0.760	874	11 441	1.419	(21, 4)	1.847	8.57	2	2090	4786	0.593	1250	8000	0.992
(13, 8)	1.457	22.17	2	1692	5909	0.733	1004	9956	1.234	(21, 5)	1.897	10.44	1	2253	4439	0.550	1184	8445	1.047
(13, 9)	1.521	24.01	1	1799	5558	0.689	997	10 027	1.243	(22, 0)	1.747	0.00	1	2114	4731	0.587	1090	9171	1.137
(13, 11)	1.652	27.25	2	1912	5230	0.648	1102	9071	1.125	(22, 2)	1.831	4.31	2	2070	4830	0.599	1245	8030	0.996
(13, 12)	1.719	28.68	1	1994	5015	0.622	1128	8862	1.099	(22, 3)	1.877	6.31	1	2243	4459	0.553	1168	8560	1.061
(14, 0)	1.111	0.00	2	1295	7721	0.957	859	11 640	1.443	(22, 5)	1.975	10.02	2	2229	4487	0.556	1320	7575	0.939
(14, 1)	1.153	3.42	1	1502	6660	0.826	748	13 364	1.657	(23, 0)	1.826	0.00	2	2064	4845	0.601	1244	8039	0.997
(14, 3)	1.248	9.52	2	1447	6910	0.857	920	10 867	1.347	(23, 1)	1.867	2.11	1	2238	4467	0.554	1160	8620	1.069
(14, 4)	1.300	12.22	1	1623	6162	0.764	842	11 875	1.472	(23, 3)	1.956	6.05	2	2205	4535	0.562	1314	7612	0.944
(14, 6)	1.411	17.00	2	1633	6123	0.759	902	10 078	1.250	(24, 1)	1.946	2.02	2	2193	4560	0.565	1311	7631	0.946
(14, 7)	1.470	19.11	1	1768	5655	0.701	955	10 476	1.299	(24, 2)	1.990	3.96	1	2365	4229	0.524	1231	8121	1.007
(14, 9)	1.594	22.85	2	1840	5435	0.674	1080	9261	1.148	(25									

Table a2. Summary of all observed RBM frequencies and transition energies of semiconducting tubes and their assignment.

ν	$la0la$	n_1	n_2	d (Å)	$\omega_{\text{RBM}}(\text{cm}^{-1})$	$E_{\#}$ (eV)	$\omega_{\text{RBM}}^{\text{exp}}(\text{cm}^{-1})$	$E_{\#}^{\text{exp}}$ (eV)	θ	Suscept.
-1	(12,1)	12	1	9.82	236.4	1.551	237	1.54	4.0	4.1
		11	3	10.00	232.6	1.570	233	1.55	11.7	2.0
		10	5	10.36	226.1	1.578	225	1.56	19.1	2.3
		9	7	10.88	216.0	1.564	215	1.55	25.9	1.3
-1	(11,0)	11	0	8.62	266.7	1.657	267	1.68	0.0	1.7
		10	2	8.72	264.6	1.690	264	1.69	8.9	2.3
		9	4	9.03	257.5	1.72	256	1.71	17.5	2.5
		8	6	9.53	246.4	1.73	243	1.72	25.3	1.4
-1	(9,1)	9	1	7.47	306.2	1.78	305	1.83	5.2	9.1
		8	3	7.72	297.5	1.857	296	1.88	15.3	35.8
		7	5	8.18	283.3	1.915	281	1.92	24.5	18.3
-1	(8,0)	8	0	6.27	352.2	1.99	361	1.97	0.0	0.1
		7	2	6.41			353	2.03	12.2	
		6	4	6.83			333	2.15	23.4	
+1	(14,1)	14	1	11.38	205.8	1.646	207	1.66	3.4	0.3
		13	3	11.54	203.3	1.610	204	1.62	10.2	0.6
		12	5	11.85	198.5	1.554	199	1.56	16.6	0.1
		11	7	12.31			192	1.47	22.7	
		10	9	12.90			185	1.38	28.3	
+1	(13,0)	13	0	10.18	230.8	1.84	229	1.85	0.0	0.2*
		12	2	10.27	228.1	1.82	227	1.82	7.6	12.2*
		11	4	10.54	221.8	1.76	222	1.74	14.9	0.1*
		10	6	10.97			214	1.64	21.8	
		9	8	11.54	204.0	1.535	204	1.52	28.1	0.5
+1	(11,1)	11	1	9.03	256.0	2.031	256	2.06	4.3	9.8
		10	3	9.24	252.1	1.945	251	1.98	12.7	3.6
		9	5	9.63			241	1.84	20.6	
		8	7	10.18	230.4	1.710	229	1.69	27.8	0.4
+1	(10,0)	10	0	7.83	291.4	2.38	292	2.35	0.0	
		9	2	7.95			288	2.28	9.8	
		8	4	8.29	280.9	2.10	277	2.11	19.1	0.3
		7	6	8.83	264.2	1.909	261	1.91	27.5	2.6
+1	(8,1)	8	1	6.69			339	2.69	5.8	
		7	3	6.96			327	2.48	17.0	
		6	5	7.47	308.6	2.20	305	2.18	27.0	

Table a3. Summary of all observed RBM frequencies and transition energies of metallic tubes and their assignment.

ν	$laola$	n_1	n_2	d (Å)	ω_{RBM} (cm ⁻¹)	$E_{\#}$ (eV)	ω_{RBM}^{comp} (cm ⁻¹)	$E_{\#}^{comp}$ (eV)	θ	Suscept.
0	(16,1)	16	1	12.94	182.0	1.81	184	1.81	3.0	0.5
		15	3	13.08	179.0	1.83	182	1.81	8.9	1.8
		14	5	13.36	174.5	1.83	179	1.81	14.7	1.9
0	(15,0)	15	0	11.75	200.4	1.908	201	1.93	0.0	0.7
		14	2	11.83	196.3	1.934	200	1.94	6.6	3.6
		13	4	12.06	193.5	1.944	196	1.94	13.0	2.5
		12	6	12.44	189.4	1.948	191	1.93	19.1	1.9
		11	8	12.94	183.2	1.936	184	1.92	24.8	1.9
		10	10	13.57	175.7	1.889	176	1.88	30.0	0.9
0	(13,1)	13	1	10.60	220.3	2.057	221	2.07	3.7	1.5
		12	3	10.77	217.4	2.075	217	2.07	10.9	2.6
		11	5	11.11	212.4	2.084	211	2.08	17.8	1.7
		10	7	11.59	204.0	2.067	203	2.07	24.2	0.9
		9	9	12.21	195.3	2.02	194	2.04	30.0	0.5
0	(12,0)	12	0	9.40	244.9	2.18	247	2.21	0.0	
		11	2	9.50			244	2.22	8.2	
		10	4	9.78			238	2.24	16.1	
		9	6	10.24			228	2.25	23.4	
		8	8	10.85			216	2.23	30.0	
0	(10,1)	10	1	8.25	276.3	2.38	278	2.35	4.7	
		9	3	8.47	272.7	2.43	272	2.40	13.9	
		8	5	8.90	262.7	2.47	259	2.45	22.4	
		7	7	9.50	247.8	2.45	244	2.46	30.0	
0	(9,0)	9	0	7.05			323	2.47	0.0	
		8	2	7.18	315.5	2.52	317	2.53	10.9	
		7	4	7.55	305.4	2.63	302	2.65	21.1	
		6	6	8.14			282	2.71	30.0	

Appendix B

For most applications, Zeta potential (ζ) is the electric potential that exists at the "shear plane" (which is approximately also the Stern Plane) - the interface between the hydrated surface and the bulk solution (see Fig. b1 below). Inside the shear plane, the ions move with the solid. It is the measurable potential of a solid surface and also called electrokinetic potential.

The polymer solution can be regarded as a "colloid solution". Charged polymer also form random coils in solution and can be treated as charged particles. The zeta potential of a polymer in solution will still be the electrical potential at the "shear plane". Depending on the polymer charge and the solubility in the solvent, the polymer can be extended or "collapsed". The shear plane would be a factor of the random coil diameter although the random coil will be distorted with shear.

Figure b1 The sketch of “surface of shear” (Figure is cited from supplier: Brookhaven.)

The zeta potential values of OC, OPEG and QC polymer solutions were about -20.0 mV, -17.5 mV, and $+50.0$ mV, respectively (chapter 4), suggesting that OC, OPEG and QC polymers prepared in this study are respectively negatively, negatively and positively charged. Having obtained such charge information, we are able to identify whether in these polymer solutions, the amine groups are protonation or not, and further we could propose the underlying mechanism for the interaction between SWNTs and amine groups (or protonation amine groups). For our aim, the charge information of the polymer solution is important not the magnitude of the Zeta-potential value.

Appendix C

Young's Modulus of elasticity

In this project, the alginate hydrogel will be subjected to compressive load and its Young Modulus will be measured. The slope of a stress-strain curve drawn from experimental data from tensile test can be used to determine Young's Modulus. Young's Modulus is the measure of the stiffness of isotropic elastic material. It is defined as the ratio of tensile/compressive stress to strain (change in length over original length). Thus:

$$E = \text{Tensile or compressive stress} / \text{strain}$$

$$= ((\text{Force})/(\text{original cross sectional area})) / (\text{change in length over original length})$$

Figure c1 Scheme of Stress-Strain curve

For many materials, the Young's modulus is generally constant for over a range of strain level up to yield point. This region obeys Hook's law. Steel is one example of linear materials. In Fig. c1, the slope of the linear curve is the modulus of elasticity or

Young's Modulus. After the yield point, stress increases in the strain hardening region until it reaches ultimate strength. This behavior is called the plastic behavior. Beyond this point, the material is thinning out (cross sectional area is decreasing), necking process forms. Finally, the neck becomes unstable and the sample fractures.

Mechanical Strength Test Analysis

Instron 5543 was applied for our mechanical strength test. Below shows an example of a typical stress-strain graph for pure alginate generated from the Instron 5543 (Fig. c2).

Figure c2 Typical curve of hydrogels generated from Instron 5543

Based on the above graph, the primary modulus is obtained from the slope of the tangent drawn at compressive strain of 20%. The secondary modulus can also be obtained from the slope of the tangent drawn at compressive strain of 40% (after the yield point). From the graph, the curve is in the elastic region where the strain increases proportionally with stress. Until strain reaches to about 15%, the alginate hydrogel exhibits the plastic properties (strain does not increase proportional to stress). This continues until the ultimate compressive stress is reached. The hydrogel finally

breaks at strain of 60%. This point is termed elongation at break in this report. Based on the results obtained, the graph for alginate hydrogels with different SWCNTs content exhibit similar trend as compared to pure alginate. From the plots, the primary modulus, secondary modulus, the ultimate compressive stress, and the elongation at break were averaged out and tabulated. For pure alginate hydrogels and alginate hydrogels with SWCNTs content from 0.5 wt% to 5 wt% were tested in chapter 7.

List of Publications

Journal Paper

1. Yan L.Y., Poon Y.F., Chan-Park M.B., Chen Y., Zhang Q., “Individually Dispersing Single-Walled Carbon Nanotubes with Novel Neutral pH Water-Soluble Chitosan Derivatives”, *J. Phys. Chem. C.*, 2008, 112, 7579-7587
2. Yan L.Y., Li W.F., Fan X.F., Wei L., Chen Y., Kuo J-L., Li L-J., Kwak S.K., Mu Y.G., Chan-Park M.B., “Enrichment of (8, 4) Single-Walled Carbon Nanotubes Through Coextraction with Heparin”, *Small*, in press
3. Yan L.Y., Li W.F., Mu Y.G., Chan-Park M.B., “Conformation effect in Dispersions of Single-Walled Carbon Nanotubes using Glycosaminoglycans ”, under preparations
4. Yan L.Y., Chan-Park M.B., “Novel Hydrogels of Single-Walled Carbon Nanotubes Dispersed with Biomaterials”, under preparations

Conference Paper

1. Yan L.Y., Poon Y.F., Chan-Park M.B., Abstracts of Papers, International Conference on Materials for Advanced Technologies, 2009
2. Yan L.Y., Poon Y.F., Chan-Park M.B., Abstracts of Papers, The International Symposium on Advanced Bio, Nano, and Pharmaceutical Science and Technology, 2009
3. Yan L.Y., Tina Tan. Y.Q., Chan-Park M.B., Abstracts of Papers, AsiaNano, 2008
4. Yan L.Y., Tina Tan. Y.Q., Chan-Park M.B., Abstracts of Papers, International Conference on Cellular & Molecular Bioengineering, 2007