Progress towards total structure control in SWCNT populations

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ABSTRACT

As-synthesized single-wall carbon nanotube (SWCNT) populations contain substantial distributions of SWCNT structures, including in the distribution of species ((n,m) chiralities) and enantiomers (*i.e.* the handedness of the lattice vector), as well as in their lengths, modifications to the pristine lattice, and environmental factors such as the endohedral filler. A driving challenge for the field is the scaled separation of these polydisperse materials into homogenous populations to enable optimal application. Multiple technologies and strategies have been developed over the last decade to address this challenge, however total structure control is still a work in progress. In our lab we are demonstrating the power of the aqueous two-phase extraction (ATPE) method to resolve SWCNTs by their metallic/semiconducting nature, diameter and even their enantiomeric handedness. This technique, which can be readily applied to process bench scale quantities of well-specified SWCNTs, and combined with other separation schemes for length and filler specification, holds promise for providing long desired materials for application development. An overview of the separation method and an update on its development and incorporation into a larger strategy of separation will be presented.

Keywords: carbon nanotubes, SWCNT, SWNT, purification

1 INTRODUCTION

Projected high value applications of nanoparticles and nanoparticle materials rely on the availability of well-defined populations of such materials with specific properties. In general, structurally homogenous populations of a given material are expected to yield the best, *i.e.*, most intense, properties, regardless of whether the desired property is optical, electrical, magnetic, *etc*… in nature. This assumption is based on the idea that variations in nanoparticle structure, size, surface chemistry, or defect density, *etc*… will all affect the material properties on a per particle basis, and thus reduce the achievable intensity of any property when integrated across the entire population. Efforts for purification and separation of nanoparticles based on variations in these characteristics have thus been a focal point of nanoparticle research. Single-wall carbon nanotube (SWCNT) materials in particular have engendered substantial efforts towards the development of separation and purification methods due to the large number of structures in any as-synthesized batch of material, and the tremendous differentiation in material properties for even highly similar nanotube structures.

A single structure (chemical species) of a SWCNT is typically described by a pair of indices, n and m, that define the chiral vector of a graphene lattice that if brought together to "roll up" the hexagonal lattice would generate the particular cylindrical structure. In general, the (n,m) indices are the primary parameter that define a SWCNTs properties; $n = m$ SWCNTs are metallic; SWCNTs for which Mod(n-m,3) = 0, with $n \neq m$, are semimetals; the remaining ≈ $2/3^{rds}$ of species are semiconducting in electronic nature. However, it is important to note that all but $n = m$, and $m = 0$ species are chiral in nature, and thus the structure can have either a left or a right-handed twist. Although the electronic properties of the SWCNT itself are unaffected by its enantiomeric structure, the two structures are likely to interact differently with other chiral molecules. A partial map of SWCNT structures is shown in Figure 1.

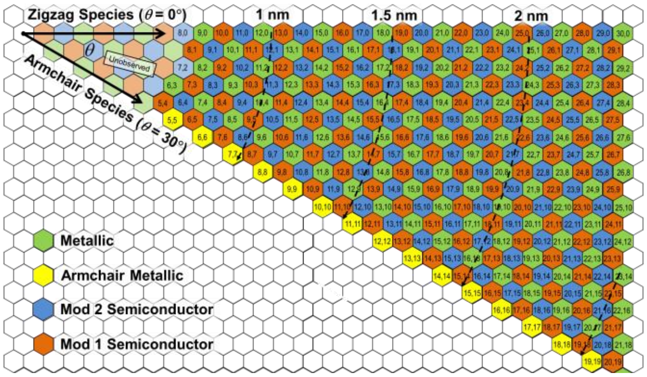

Figure 1: SWCNT structure map showing a partial range of stable SWCNT structures and their semiconducting or metallic nature. Only the armchair, n=m species are true metals. Each structure has its own unique material properties; reflection of the shown map along the horizontal, "zigzag," axis generates structures with identical material properties but opposite enantiomeric handedness, *e.g.*, opposite twist.

Additionally, for any given (n,m) structure, the SWCNTs in the population will typically have a wide distribution in tube lengths, with typical lengths ranging from < 50 nm to >2 μm when dispersed in solution. The average length of the populations appears to depend both on factors in synthesis as well as in dispersion processing.

Although length generally only affects optical and electronic properties weakly, transport and processing characteristics, as well as interactions with biological systems can be strongly affected by SWCNT length.

Finally, additional polydispersity in SWCNT populations comes from factors that modify the SWCNT structure and/or what comprises its effective nanoparticle form during processing. Several important examples include the presence of specified or uncontrolled chemical moieties, structural defects, the presence/absence of an end cap, and what if, any material, is located inside the SWCNT. Figure 2 graphically shows the orthogonal vectors possible for SWCNT purification.

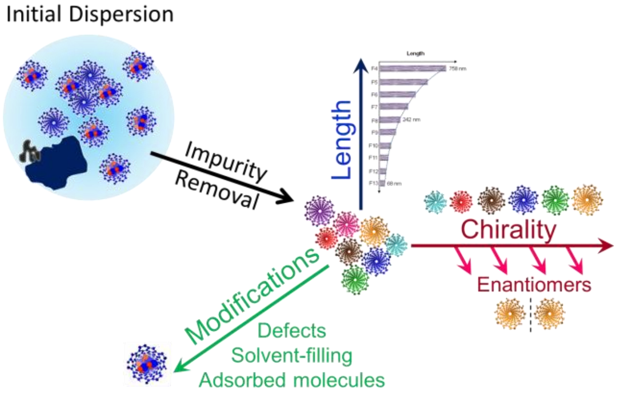

Figure 2: Orthogonal vectors for separation of an initially polydisperse SWCNT population through liquid phase separations.

2 GENERATING PURE MATERIALS

As discussed above, commercially available SWCNT powders contain a highly polydisperse mixture of SWCNT structures in addition to impurities such as residual catalyst and non-SWCNT carbon. Research into selective synthesis is an ongoing and exciting front-end manner for addressing the polydispersity problem. Recent reports describe synthesis of single species and/or reduced polydispersity SWCNT populations through SWCNT cloning [1], synthesis and growth from endcap seeds [2], or through tightly constrained geometry tungsten catalysts [3] hold substantial promise for reducing the back-end processing needed currently to generate pure populations. Additionally, advances in product development from SWCNT manufacturers over the last decade has dramatically improved the mass fraction of SWCNTs in as-sold powders, as well as reduced in many cases the cost of the material. Both these developments imply that less processing may be necessary in the future to generate well-defined SWCNT materials. However, processing is likely to always have a substantial role in generating these well-defined materials simply due to the number of differentiating vectors, species, enantiomer, length, chemical modifications, that affect the eventual material properties.

From the manufacturer, SWCNT powders can generally be purchased at several different price points and with different degrees of purification. Common variations available are as raw soot, chemically purified to remove most catalyst and sometimes non-SWCNT carbon, and chemically modified to attach specific functional chemical moieties. It should be noted that the most desirable material for purchase will entirely depend on the end application and its requirements for material properties. As will be briefly noted later, the unique optical, electronic, magnetic and thermal properties of any SWCNT species could be optimal for a given application, and thus a focus on broadly applicable processing techniques has been followed at NIST.

Post-procurement, processing that enables separation of individual nanotube populations, rather than selection through destruction of unwanted material, will involve liquid phase processing. Separation methods have been developed for processing in both aqueous and non-aqueous liquids, however, methods in aqueous conditions are currently more flexible and well-developed. In the next section the variety of the developed methods available for separating nanotubes will be described.

Before reaching that step, however, dispersion of the SWCNTs must first be achieved. At the most efficient limit, dispersion of the nanotubes will result in rapid and full individualization of each SWCNT in the source powder in a robust manner without affecting the length distribution or causing chemical modification to the nanotube. In general, SWCNTs are not thermodynamically stable as pure components in the aqueous and non-aqueous liquids useful for separation, and so do not generate solutions. Instead, small molecule surfactants or macromolecular dispersants are utilized to coat the SWCNTs in the liquid and generate kinetically stable dispersions. Fortunately, these coating dispersants also often provide chemical “handles” that can be utilized to drive the selectivity in our separation processes.

3 SWCNT SEPARATIONS

The focus of separation method research at NIST has been on methods useful for separation in aqueous dispersions. [4] Separation methods based on relative stability of SWCNTs and on selective dispersion have been demonstrated in non-aqueous systems, but are not a focus of this contribution. Broadly, separation methods can be broken down into three classes, those that separate on the basis of species/enantiomer, those that separate populations by length, and separations targeting modifications to the basic SWCNT structure. Of these classes, by far the most effort has focused on separation by SWCNT species, and particularly on the broader sub-class of separating metallic from semiconducting species.

3.1 Species and Metal/Semi Separations

Extensive effort since 2002 has focused on the difficult problem of single SWCNT species, or at least separating metallic from semiconducting species using aqueous processing. A nonexhaustive list of methods developed for this purpose includes ion-exchange chromatography (IEX) [5], density gradient ultracentrifugation (DGU) [6], solid-phase adsorption [7], gel chromatography (GC) [8], electrophoresis driven separation [9], and aqueous two-polymer phase extraction (ATPE) [10-16].

Detailed reviews and descriptions of each technique exist in the literature, in general however, each technique utilizes the interactions of the adsorbed surfactant/dispersant to translate the underlying structure of the SWCNT into a property difference of the combined hybrid object that is then used to enable separation. The nature of these interactions can be broken down further into two classes; adsorbed layers determined by competition for surface adsorption on the SWCNT, and differentiation of adsorbed layers by recognition-based packing *versus* semi-random adsorption. DGU and GC exploit the first strategy near-exclusively, IEX utilizes the second, and ATPE utilizes both.

At NIST, the focus of recent efforts is on the development of ATPE [10,11,13-16]. ATPE utilizes the phenomena of spontaneous phase separation above a critical concentration line for pairs of water soluble polymers to generate spatial separation of dispersed solutes with differing chemical affinities for the two split phases. Advantages of ATPE are that it is rapid, scalable, utilizes dispersants that enable high concentration processing, and is exquisitely tunable. A schematic of ATPE is shown in Figure 3.

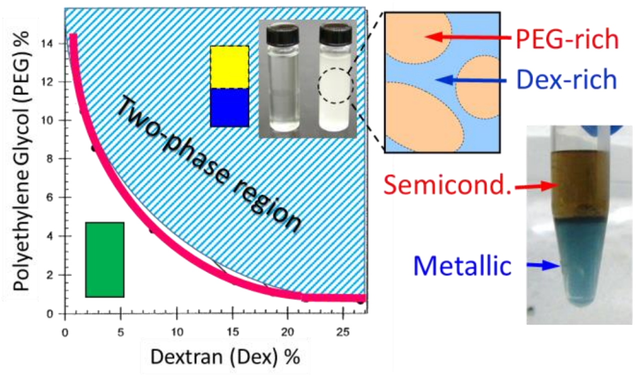

Figure 3: A schematic of a batch ATPE separation. Above a critical concentration of polymers the system spontaneous phase separates; solutes within the mixture distribute between the two phases on the basis of their affinity difference between the two phases. In the example shown, semiconducting nanotubes are selected into the top phase, and metallic nanotubes into the bottom phase.

For APTE we have developed three modes of separation: 1) metallic/semiconducting separation based on the competition of sodium cholate (SC) and sodium dodecyl sulfate (SDS) for the nanotube surface [10,13]; 2) species separation based on competition of sodium deoxycholate (DOC) and SDS at several concentrations in a multistage process [11,14]; 3) recognition based separation utilizing the ability of specific single stranded DNA sequences to form a highly-defined complexes with specific SWCNT species [15,16]. The common polymer systems that we utilize are poly-ethylene glycol (PEG) – dextran (DEX) and PEG – polyacrylamide (PAM).

Separation of semiconducting from metallic nanotubes is a key requirement for digital logic applications, as well as for fluorescence-based sensors or for producing conductive fibers. Our primary strategy for M/S separation *via* ATPE relies on the competition of the surfactants SC and SDS for the nanotube surfaces. At a composition near ≈ 0.9 mass % SC and 0.7 mass % SDS, the surface coverage of the metallic and semiconducting SWCNTs is distinctly different; the semiconducting SWCNTs become predominantly SDS covered, and are selectively extracted into the PEG phase, while the metallic SWCNTs are SC covered and select for the dextran phase [10]. Recently we determined that control of the oxidation/reduction environment during a metallic-semiconducting SWCNT separation was a key factor for achieving highly effective separations [13], and that addition of small quantities of an oxidant such as NaClO enabled repeatable separations of > 90 % effectiveness per step. Repeated extractions can be performed to reach very high semiconducting purities, particularly by utilizing temperature cycling to overcome mass transport limitations.

Separation of SWCNT species in multistage surfactant gradient ATPE uses the same polymers, and in simplified description selects for extraction between the two phases on the basis of the SWCNT diameter [11,14]. To achieve this selection the bile salt surfactant SC is replaced by the more tightly binding DOC. At a constant DOC concentration, variation in the SDS concentration then selects the threshold diameter to be extracted into the upper phase. Larger diameter SWCNTs require less SDS for extraction, smaller diameter SWCNTs more. By repeated fractionation at multiple SDS concentrations a narrow diameter range, consisting of only a single chirality can be selected. In practice, the handedness of the DOC molecule and specific packing effects add complexity to the idea that there is a direct monotonically increasing diameter selected with increasing SDS concentration, but these details enable separation of enantiomers and identical diameter nanotube structures in a practical manner. Automated, chromatographic, implementation of the ATPE gradient method [17] should be sufficient to extract species and enantiomers at high resolution, and is a goal of future work.

Separation of SWCNT species and enantiomers by ssDNA recognition is different in operation from the multistage gradient extraction. Instead of a competition between surfactants on the SWCNT interface, all SWCNTs are dispersed by the same DNA sequence, however it is hypothesized that only on the target SWCNT is a highly ordered interfacial structure formed. This structure, by the conditions of its discovery, is then well-separated in solvation energy from all of the other SWCNT-DNA structures in the dispersion, and is selected by itself into one of the two polymer phases. The exquisite sensitivity of the DNA-SWCNT recognition results frequently in the selection of only single enantiomeric (n,m) structures, as recently demonstrated through circular dichroism measurements [16].

3.2 Length Separation

Length separation is limited by the initial length distribution after dispersion, and is much less commonly performed than species separation. Several methods are available for length separation. Hydrodynamics based separations include size-exclusion chromatography (SEC) [18], asymmetric field flow fractionation (AFFF) and rate-zonal ultracentrifugation (RZU) [19]. Of these SEC is the most common and has the greatest mass throughput, although its effective range extends only to only those SWCNTs less than ≈ 700 nm in length. RZU can isolate longer SWCNTs at lower resolution but is limited in mass throughput. Separately, a thermodynamic method based on excluded volume can be used to separate length populations using polymer driven precipitation. Length fractions are not as narrow as in SEC, but the method can be applied to all SWCNT lengths.

3.3 Modification Control

Beyond the species and length of the SWCNT, modifications to the structure of the nanotube, whether by structural defects, chemical defects, or environmental factors can substantially alter the achievable properties of a nanotube. A common example is that any significant degree of covalent chemical modification disrupts the extended sp2 structure of the nanotube lattice and at significant doping completely suppresses the intrinsic optical features of the nanotube. Beyond the scope of this contribution, the addition of a sparse number of controlled defects can yield tailored improvements to nanotube properties and is an area of active research.

The broadest known, and frequently ignored, environmental modification is what fills the inside of a SWCNT in solution. SWCNTs with both endcaps and few chemical defects are effectively empty inside, and exhibit significantly narrower optical peak linewidths and greater fluorescence intensities than open ended nanotubes [20,21]. The reason for this is that water in an aqueous system will fill even the smallest diameter SWCNTs, raising the effective dielectric constant of the environment felt by the SWCNT and acting as quenching site for excited states. Recently, specific predispersion filling with water insoluble compounds has enabled control of the interior environment and can avoid the degrading effects off water ingestion [23]. For nanotubes in which part of the population is water-filled and part is empty or contains a controlled filler, density differences between the two populations can be used as a handle to separate them through appropriately constructed DGU or RZU processing.

4 SUMMARY

In summary, dramatic progress has been made in the past decade on separation methods to enable production of highly specified SWCNT populations. It is now also possible to arbitrarily combine multiple separation methods in series to produce populations specified in all vectors of their structural characteristics and modifications. These populations will feed emergence of direct applications in computation, energy, and health sectors that rely on tight property control for performance. Ongoing challenges including process scaling, improvements in initial dispersion, increasing species separation resolution in the large diameter limit, development rapid quality control methods in the high-purity limit, arbitrary surface functionality control, and controlled assembly into specified structures for application all appear overcomeable. It is anticipated that the adoption and commercialization of any highly purified SWCNT population will provide strong impetus for addressing these remaining barriers.

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