Award Number: DE-SC0003727

Award Recipient: TetraGchem, LLC

Award title: Recovery Act – Large Scale SWNT Purification and Solubilization

P.I.: Dr. Linda B. McGown

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Subcontractee: Rensselaer Polytechnic Institute

Subcontract P.I.: Dr. Linda Schadler

Executive Summary

The unique properties of Single-Walled Carbon Nanotubes (SWNTs) including exceptional mechanical strength, electron mobility and nanoscale dimensions make them excellent candidates for use in wide-ranging applications including polymer additives, transparent conductive films, nanoelectronics, sensing, nano-optics, transistors, filters, hydrogen storage, drug and gene delivery, oscillators, field emitters and even space elevators [1-5]. Progress towards the commercial development of SWNT-based technologies has been severely impeded by the poor availability and high cost of pure SWNT products. Existing bulk synthesis methods produce a mix of SWNTs of various diameters and chiralities, other carbonaceous species and residual catalyst. Moreover, many of the most promising applications of SWNTs require a highly purified SWNT product that has been further sorted by electronic behavior (i.e. metallic vs. semiconducting), diameter, or chirality. Industrial-scale processes for this type of separation are not currently available, and existing laboratory-scale methods are severely limited by small batches, low yields, lengthy processing and in some cases, expensive reagents such as DNA or peptides. Moreover, the extensive and often harsh conditions required for SWNT purification and separation of SWNT subfractions may result in degradation of the quality of the final product, including introduction of surface defects, tube breakage and irreversible surface modification. All of these alterations can compromise the desired behaviors of the SWNTs.

In order to realize the commercial potential of SWNTs there is a critical need for practical, economical, scalable, non-destructive and environmentally benign methods to (1) purify SWNTs from concomitants (multi-wall carbon nanotubes (MWNTs), amorphous carbon, metals, carbon nanoparticles) in the raw synthetic products, (2) disperse individual SWNTs in biocompatible and environmentally safe materials and (3) fractionate SWNTs according to their various physical, chiral and conductive properties [6-10].

The P.I.'s group at Rensselaer Polytechnic Institute discovered a new, reversible biogel medium [11] that can readily disperse high concentrations of individual SWNTs in aqueous solution without modifying, damaging, or destroying them (PCT/US2007/004866, EPO appl. #: 07861249.6, and U.S. appl. #: 12/234,257). The medium

is formed by simple, commercially available biological compounds that undergo reversible self-assembly in aqueous solution to form higher-ordered gel phases. The gel is formed by binary mixtures of guanosine monophosphate (GMP) and guanosine (Guo) and is referred to as “binary G-gels). No synthesis, chemical polymerization, non-aqueous solvents or potentially toxic materials are involved. The medium is inherently scalable and capable of processing nanotubes at very high concentrations without chemically altering or physically compromising their structure. Key to these abilities is the solubilization mechanism afforded by the medium, namely, that the medium solubilizes SWNTs as individual tubes instead of as bundles that is common to other bulk solubilization methods. In some compositions, the medium not only solubilizes but also aligns the individual SWNTs. The self-assembled medium is readily removed from the SWNTs simply by washing and gentle filtration under conditions that reverse the forces that stabilize the gel and reduce it to the monomeric, small molecules.

The goal of this Phase I project was to establish a quantitative foundation for development of binary G-gels for large-scale, commercial processing of SWNTs and to develop scientific insight into the underlying mechanisms of solubilization, selectivity and alignment. In order to accomplish this, we performed systematic studies to determine the effects of G-gel composition and experimental conditions that will enable us to achieve our goals that include (1) preparation of ultra-high purity SWNTs from low-quality, commercial SWNT starting materials, (2) separation of MWNTs from SWNTs, (3) bulk, non-destructive solubilization of individual SWNTs in aqueous solution at high concentrations (10-100 mg/mL) without sonication or centrifugation, (4) tunable enrichment of subpopulations of the SWNTs based on metallic vs. semiconductor properties, diameter, or chirality and (5) alignment of individual SWNTs.

Comparison of Actual Accomplishments with Project Goals and Objectives

As described in the following section, we demonstrated made significant progress towards goals 1, 3 and 4. Plans were set in place for experiments towards goals 2 and 5 but work has not yet been performed. The results are consistent with our expectations for purification and selective enrichment of SWNTs using the binary G-gel media.

Summary of Project Activities for Entire Funding Period

The project start date was December 7, 2009. Funds for Phase I were received in March 2010. Our first task upon receiving the funds was to set up our laboratory since this is the first award received by TetraGchem, LLC (having been recently established in March 2009). We were up and running within a few weeks and began to prepare samples of commercial low purity and high purity SWNTs in different G-gels and under different processing conditions. The samples, summarized in Table 1, were characterized by thermogravimetric analysis (TGA) and microRaman spectroscopy by the Schadler laboratory at RPI (the subcontractee).

We found that there is a striking difference among the results for the different G-gels in both purification and selectivity among metallic vs. semiconducting tubes, ranging from no purification or discrimination to the results discussed below. Our processing is currently at the scale of 50 mL per batch with approximately 1 mg SWNT per mL G-gel (50 mg total). Since there is no need for ultracentrifugation, it is possible to run many 50 mL samples in parallel a single day, which is a significant improvement over existing purification methods that require extensive ultracentrifugation (which imposes limits on volume per sample, parallel sample processing, and may also cause SWNT damage).

SWNT purification

Figure 1 shows the best results to date for purification of commercial, “as received” low purity HiPco SWNTs as evaluated using Thermogravimetric Analysis (TGA) [12]. The amount of catalyst in the sample is indicated by the weight remaining in the sample above 900 °C. Assuming the iron has oxidized to Fe_2O_3 , the remaining weight can be used to determine the initial iron content. In addition, as the carbonaceous material is removed, the temperature of the onset of sample degradation (indicated by weight loss) increases. For highly pure SWNT, this does not occur until about 600-650 °C whereas low purity samples start to lose weight at 400 °C.

Figure 1A shows typical TGA for the low purity SWNTs before any processing. Figure 1B shows typical TGA for the “as received” high purity SWNTs, for comparison with the G-gel purified product. Figure 1C shows the low purity SWNTs after gentle treatment with dilute HCl and a few hours of wet air heat treatment at relatively low temperature (250 °C). This treatment is designed to remove bulk impurities without damaging or altering the SWNTs [13]. Figure 1D shows the TGA for the treated sample corresponding to Figure 1C but after processing using the G-gel.

The results show that G-gel processing removes substantial impurities, as indicated by reduced contributions from impurities that are volatilized at lower temperatures. The apparent % metal catalyst is higher after G-gel processing, but this may be due to the decrease in other species that contribute to the total weight in Figure 1C. Further optimization of the processing to improve purity is needed.

Table 1. Summary of samples tested in Phase I.

Sample	Molar Composition			SWNT (type)
	GMP	Guo	KCl	
1	0.3	0.01	0	low purity
2				low purity
3				0
4				low purity
A Pure	0.3	0.01	0	0
A1				low purity
A2				low purity
B Pure	0.3	0.01	0.05	0
B1				low purity
B2				low purity
C Pure	0.3	0.03	0	0
C1				low purity
C2				low purity
D Pure	0.3	0.03	0.05	0
D1				low purity
D2				low purity
A1	0.15	0.03	0.05	high purity
A2				high purity
B1	0.15	0.04	0.05	high purity
B2				high purity
C1	0.15	0.05	0.05	high purity
C2				high purity
D1	0.1	0.03	0.05	high purity
D2				high purity
E1	0.1	0.04	0.05	high purity
E2				high purity
F1	0.2	0.07	0.05	high purity
F2				high purity
13 mL	0.3	0.01	0	high purity
13 mL Raw	0.3	0.01	0	low purity
AA1	0.15	0.03	0	high purity
AA2				high purity
BB1	0.15	0.04	0	high purity
BB2				high purity
EE1	0.1	0.04	0	high purity
EE2				high purity
FF1	0.2	0.07	0	high purity
FF2				high purity
13mL Raw2	0.3	0.01	0	low purity
AA1*	0.15	0.03	0	AA1 ppt
AA2*				AA2 ppt

Sample	Molar Composition			SWNT (type)
	GMP	Guo	KCl	
G1	0.3	0.03	0	low purity
G2				low purity
H1	0.3	0.03	0.05	low purity
H2				low purity
I1	0.25	0.03	0	low purity
I2				low purity
J1	0.25	0.03	0.05	low purity
J2				low purity
K	0.3	0.03	0	low purity
L	0.25	0.02	0	high purity
M	0.15	0.03	0	low purity
N	0.15	0.03	0	low purity
O	0.15	0.03	0	low purity
P	0.3	0.01	0	low purity
Q	0.3	0.03	0	low purity
R	0.25	0.03	0	low purity
S	0.1	0.02	0	low purity
T1	0.3	0.03	0	low purity
T2				low purity
U1	0.25	0.03	0	low purity
U2				low purity
W1	0.3	0.03	0	high purity
W2				high purity
X1	0.25	0.03	0	high purity
X2				high purity
Y	0.3	0.03	0	low purity
Z	0.15	0.03	0	0
AA	0.25	0.03	0	0
AB1	0.25	0.03	0	high purity
AB2				ppt from AB1
AC1	0.15	0.03	0	ppt from AB2
AC2				ppt from AC1
AD1	0.25	0.03	0	low purity
AD2				ppt from AD1
AE1				low purity
AE2				ppt from AE1
AF1				low purity
AF2				ppt from AF1
AG1				low purity
AG2				ppt from AG2
AH	0.3	0.01	0	low purity

Figure 1. Thermogravimetric Analyses (TGA) of SWNT samples. (A) “As Received” low purity SWNT; (B) “As Received” high purity SWNT; (C) “As Received” low purity SWNT after gentle acid washing and wet air treatment; (D) SWNTs from (C) after G-gel processing (Sample AG in Table 1).

Selective enrichment of metallic and semiconducting SWNTs

Figure 2 compares the microRaman spectra of “as received” low purity SWNTs to the precipitate of the low purity SWNTs after G-gel processing according to Sample Composition Q in Table 1. According to the literature [14], at 514 nm excitation, semiconducting SWNTs have radial breathing mode (RBM) peaks in the range of 170-220 cm^{-1} while metallic SWNTs have RBM peaks in the range of 220-300 cm^{-1} . After the raw SWNT is processed by the binary G-gel, the precipitate shows significant enrichment of semiconducting SWNTs. The G-band also shows the same effect, in which the broad peak at lower frequencies that corresponds to metallic SWNTs [14] is stronger for “as received” SWNTs, indicating that the precipitate is enriched in semiconducting SWNTs. *The results suggest that the binary G-gel preferably disperses the metallic SWNTs, which have smaller diameter, in the supernatant while leaving the precipitate highly enriched in larger diameter, semiconducting SWNTs.*

Figure 2. MicroRaman spectra of precipitate of G-gel processed low purity SWNTs (sample Q) vs. “as received” low purity SWNTs. (a) RBM at 785 nm excitation; (b) RBM at 514 nm excitation; (c) G-band at 785 nm excitation; (d) G-band at 514nm laser excitation.

Comparison between the microRaman spectra of SWNTs in the precipitate and the supernatant (Figure 3) supports the conclusion that the precipitate is enriched in semiconducting SWNTs and further indicates that the supernatant is enriched in metallic SWNTs. However, comparison between the microRaman spectra of the supernatant from the G-gel (see Figure 3) and the “as received” SWNTs (see Figure 2), does not show the expected enrichment of the supernatant in metallic tubes. One possible explanation is that vacuum filtration is used to retrieve the tubes from the supernatant, and because metallic SWNTs are fully solubilized as individual tubes in the binary G-gel and have small diameter (0.7-1.0 nm), it is easier for them to go through the filter paper. As a result, there may be a loss of metallic SWNTs during the filtration process to collect the tubes from the supernatant. Further work is needed to refining our collection method to ensure retention of the smaller, individual metallic tubes and testing the discard solution in the filtration step for the presence of metallic tubes that may have slipped through the filter paper.

Figure 3. MicroRaman spectra of precipitate vs. supernatant of G-gel processed low purity SWNTs (sample Q). (a) RBM at 785 nm excitation; (b) RBM at 514 nm excitation; (c) G-band at 785 nm excitation; (d) G-band at 514nm laser excitation.

In summary, the results indicate that there is a striking difference among the results for the different G-gels in both purification and selectivity among metallic vs. semiconducting tubes, ranging from no purification or discrimination to the results in Figures 1-3. Our processing is currently at the scale of 50 mL per batch with approximately 1 mg SWNT per mL G-gel (50 mg total). Since there is no need for ultracentrifugation, it is possible to run many 50 mL samples in parallel a single day, which is a significant improvement over existing purification methods that require extensive ultracentrifugation (which imposes limits on volume per sample, parallel sample processing, and may also cause SWNT damage).

Products Developed and Technology Transfer Activities

None

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