PURIFICATION OF SINGLE-WALLED CARBON NANOTUBES AND THE PRODUCTION OF SWNT THIN FILMS AND SWNT/ELASTIN COMPOSITES

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Abstract

We report the purification of SWNTs and the production of SWNT-composite thin films. SWNTs were synthesized by the laser vaporization method and subsequently purified by treatments utilizing HNO_3 refluxing, water-extraction, thermal annealing, and H_2O_2 processing. The resulting purified SWNTs contain metal residues less than 1wt.% and carbonaceous impurities among the lowest ever reported, as assessed by optical techniques. Semitransparent SWNT thin films were produced by a filtration/transfer method to achieve sheet resistances less than 100 Ω/sq with transmittances of 65%. SWNT/elastin composites were produced by changing solution temperature and pH conditions, which show potential as biocompatible substrates, sensors, and tissue scaffolds.

Introduction

Since their discovery in 1993, single walled carbon nanotubes (SWNTs) have found numerous applications in chemistry, physics, material science, and biology on account of their unique structure, high aspect ratio, excellent strength and elasticity, and remarkable electronic properties. However, impurities in as-prepared SWNTs, such as amorphous carbon, metal catalysts, and carbon graphitic particles, largely affect the intrinsic properties of SWNTs. In the past decade, a large number of purification methods have been applied to obtain SWNTs with high quoted purities. Instrumental analysis techniques, such as electron microscopy, TGA, Raman spectroscopy, and NIR spectroscopy, have been developed and employed with varied success to assess the purity of SWNTs. Most of the purification methods are practically difficult to scale to industrial levels up. And from a fundamental level, samples of ultrapure SWNTs with quantified purity are still unavailable. Therefore, it is necessary to develop methods for both scalable purification and comprehensive purity evaluation for SWNTs.

SWNTs have long been of interest as additives to enhance the mechanical and electronic properties of polymers. Considerable progress has been made to produce functionalized SWNTs and SWNT polymer composites for biological applications. In this paper, we present purification and assessment methods of SWNTs produced by laser ablation on the 10 gram scale, and their processing for application in prototype conductive thin films and SWNT/elastin composites.

Experimental

An industrial grade Nd:YAG laser (600 W maximum average power, $\lambda = 1.06$ μm) was used to produce SWNTs by vaporizing graphite targets containing 1at.% of Ni and Co in a quartz tube located in a tube furnace similar to that used earlier by Puretzky et. al. (Puretzky, A. A. et al. 2000). The as-prepared SWNTs (AP-SWNT) contained 10-15 wt% of metal catalysts. In the purification, 10 grams of AP-SWNTs were refluxed in 12M HNO_3 for 6 hours. The acidic mixture was extracted by 3-4 cycles of a repeating centrifuging, decanting, and washing procedure. The resulted black paste was then refluxed in 30% H_2O_2 for 10 hours. After cooling to room temperature, the mixture was filtered through 1μm pore-size membrane. The cake on the filter paper was washed and dried overnight. The dried SWNTs were annealed at 450°C for 20 minutes. The final yield of purified SWNTs (P-SWNTs) was about 5% compared to the raw material.

The production of SWNT transparent conductive thin films followed the method of Wu et al. (Wu, Z. et. al. 2004). Generally, P-SWNTs were dispersed in 1% SDS aqueous solution via sonication to generate a homogeneous dispersion. The SWNT dispersion was filtered through a 0.1μm pore-size membrane. The SWNTs deposited on the membrane were washed with water to remove the SDS residue in the SWNTs. After drying, the SWNT thin film on filter membrane was transferred to a glass coverslip by washing away filter membrane with acetone.

The production of SWNT/elastin composites were produced as follows. First, 1 gram of elastin (purchased from Aldrich) was dissolved in 10 mL of deionized water to form a slightly yellow solution. P-SWNTs powder was then added to the solution and the mixture was sonicated for 30 minutes. The pH of the solution was adjusted to 5 by adding 0.1M NaOH and the dispersion was heated to 37°C. Yellowish-gray precipitates were formed in the dispersion and could be carefully removed from the reaction vial. This SWNT/elastin composite material was dried at room temperature overnight for further characterization and application.

Results and Discussion

Figure 1 shows SEM images of AP-SWNTs and P-SWNTs. The P-SWNTs contain highly reduced amounts of amorphous carbon, as assessed by near-infrared optical absorption spectroscopy. NIR spectroscopy is a useful method to evaluate the carbonaceous purity of SWNTs (Itkis, M. et. al. 2003). Briefly, this method is based on the comparison of the areal absorption of the second semiconducting interband transition of SWNTs versus a selected reference sample to obtain a relative purity. By using this method, the relative purity of P-SWNTs was estimated at levels as high as 230% (against the original reference sample of Itkis, M. et. al. 2003), significantly higher than that estimated for AP-SWNTs (30-50%). TGA data shows the metal residue in AP-SWNTs and P-SWNTs are 15 wt% and 1 wt%, respectively. The intensity ratio of the disorder mode to the tangential mode (D/G ratio) measured by Raman spectroscopy of SWNTs can reflect the amount of disorder in graphitic carbon, giving a measure of amorphous carbon and SWNT defects in the sample. The D/G ratio of P-SWNTs is only 0.03, which is smaller than that of AP-SWNTs (D/G=0.11). Therefore, the P-SWNTs have the highest fraction of nanotube vs. amorphous carbon yet reported and very low metal residue, and can therefore be regarded as a new standard sample for the assessment of SWNT purity.

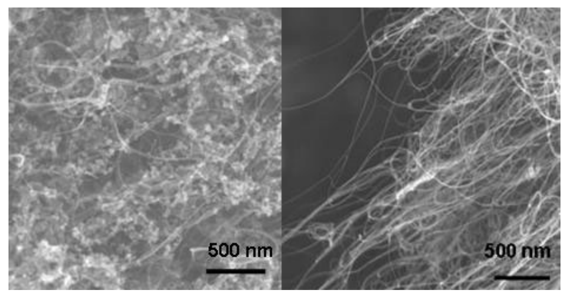

Figure 1. SEM images of (a) AP-SWNTs and (b) P-SWNTs.

Transparent conductive SWNT thin films have great potential as transparent electrodes nano-electronic devices such as organic light emitting diodes. It is desirable to produce SWNT thin films with low surface resistance and high transmittance. Following the reference method, we can produce SWNT thin films with transmittance from 60% to above 90% at 550nm by controlling the amount of SWNT/SDS solution during the preparation. The SWNT thin films can be doped with thionyl chloride to decrease the surface resistance (Dettlaff-Weglikowska, U. et al 2005). The surface resistance of a 65% transmittance SWNT film after doping can be as low as 97 Ω/sq, which is comparable to that reported for other SWNT films. Figure 2 shows a TEM image of SWNT thin film on a TEM grid, in which small SWNT bundles are uniformly deposited to form a network.

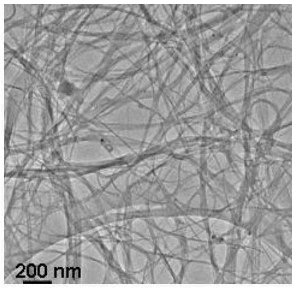

Figure 2. TEM image of a semitransparent purified film of SWNTs on a TEM grid.

Elastin is an elastic bio-polymer which is composed of amphiphilic peptide sequences. The morphology of elastin is largely depended on the solution pH and temperature. At high temperature and pH, the hydrophilic lysine linker in elastin shrinks which results in the hydrophobic property of elastin. Based on this property, SWNT/elastin composites can be produced by controlling the pH and temperature of their solution. Figure 3 shows a SEM image of an elastin /SWNT composite, in which SWNTs were uniformly embedded in elastin. This composite material shows potential as biocompatible substrates, sensors, and tissue scaffolds. Future research will focus on the mechanical properties measurement of SWNT/elastin composites.

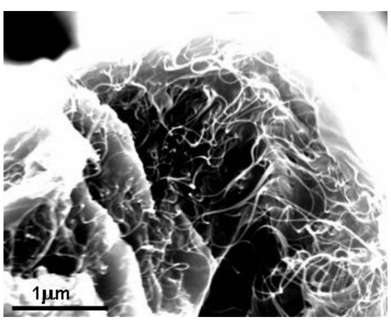

Figure 3. SEM image of a SWNT/elastin composite mat.

Conclusion

Laser-vaporization-produced SWNTs were purified by a multi-step procedure yielding SWNT reference samples with carbonaceous purity 2.3 times higher than that of Itkis et al. and metal contents < 1 wt.%. Semitransparent SWNT thin films were produced by filtration/transportation method to achieve sheet resistances lower than 100Ω/sq with transmittance of 65%. SWNT/elastin composites were produced by adjusting solution temperature and pH conditions.

References

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