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SYNTHESIS AND CHARACTERIZATION OF CARBON AEROGEL NANOCOMPOSITES CONTAINING DOUBLE-WALLED CARBON NANOTUBES

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Introduction

Carbon aerogels (CAs) are novel mesoporous materials with applications such as electrode materials for super capacitors and rechargeable batteries, adsorbents and advanced catalyst supports.[1-3] To expand the potential application for these unique materials, recent efforts have focused on the design of CA composites with the goal of modifying the structure, conductivity or catalytic activity of the aerogel.[4-8] Carbon nanotubes (CNTs) possess a number of intrinsic properties that make them promising materials in the design of composite materials. [9-11] In addition, the large aspect ratios (100-1000) of CNTs means that small additions (less than 1 vol%) of CNTs can produce a composite with novel properties. Therefore, the homogeneous incorporation of CNTs into a CA matrix provides a viable route to new carbon-based composites with enhanced thermal, electrical and mechanical properties. [12]

One of the main challenges in preparing CNT composites is achieving a good uniform dispersion of nanotubes throughout the matrix. CAs are typically prepared through the sol-gel polymerization of resorcinol with formaldehyde in aqueous solution to produce organic gels that are supercritically dried and subsequently pyrolyzed in an inert atmosphere. Therefore, a significant issue in fabricating CA-CNT composites is dispersing the CNTs in the aqueous reaction media. Previous work in the design of CA-CNT composites have addressed this issue by using organic solvents in the sol-gel reaction to facilitate dispersion of the CNTs. [5,13] To our knowledge, no data has been published involving the preparation of CA composites containing CNTs dispersed in aqueous media. In this report, we describe a new method for the synthesis of monolithic CA-CNT composites that involves the sol-gel polymerization of resorcinol and formaldehyde in an aqueous solution containing a surfactant-stabilized dispersion of double-walled carbon nanotubes (DWNT). One of the advantages of this approach is that it allows one to uniformly distribute CNTs in the CA matrix without compromising the synthetic control that is afforded by traditional organic sol-gel chemistry over the CA structure. We will describe the physical characterization of these novel materials as well as the influence of DWNT loading on the electrical conductivity of the CA composite.

Experimental

Materials. All reagents were used without further purification. Resorcinol (99%) and formaldehyde (37% in water) were purchased from Aldrich Chemical Co. Sodium carbonate (anhydrous) was purchased from J.T. Baker Chemical Co. Sodium dodecylbenzene sulfonate (SDBS) was purchased from Fluka Chemical Corp., Inc. Purified DWNTs were purchased from Carbon Nanotechnologies, Inc.

Sample Preparation. The DWNT-CA composites were prepared using traditional organic sol-gel chemistry.[1] In a typical reaction, purified DWNTs (Carbon Nanotechnologies, Inc.) were suspended in an aqueous surfactant solution containing SDBS and thoroughly dispersed using a Bronwill Biosonik IV tip sonicator operating at 25% of maximum power at high frequency. To determine the optimal conditions for DWNT dispersion, a range of sonication times (1 to 4 hrs) and SDBS-to-DWNT ratios (10:1, 5:1 and 2.5:1) were evaluated. Once the DWNT were dispersed, resorcinol (1.235 g, 11.2 mmol), formaldehyde (1.791 g, 22.1 mmol) and sodium carbonate catalyst (5.95 mg, 0.056 mmol) were added to the reaction solution. The resorcinol to catalyst ratio (R/C) employed for the synthesis of the composites was ~ 200. The sol-gel mixture was then transferred to glass molds, sealed and cured in an oven at 85°C for 72 h. The resulting gels were then removed from the molds and washed with acetone for 72 h to remove all the water from the pores of the gel network. The wet gels were subsequently dried with supercritical CO_2 and pyrolyzed at 1050°C under a N_2 atmosphere for 3 h. The composite materials were isolated as black cylindrical monoliths. Carbon aerogel composites with DWNT loadings ranging from 0 to 8 wt% (0 to 1.3 vol%) were prepared by this method. For comparison purposes, pristine CAs as well as SDBS-loaded CAs were also prepared using the method described above, except without the addition of the DWNT.

Characterization. Bulk densities of the DWNT-CA composites were determined from the physical dimensions and mass of each sample. The volume percent of DWNT in each sample was calculated from the initial mass of DWNTs added, assuming a CNT density of 1.3 g/cm^3, and the final volume of the aerogel. Scanning electron microscopy (SEM) characterization was performed on a JEOL 7401-F. SEM sample preparation included sputtering a few nanometer layer of Au on the aerogel sample. Imaging was done at 5-10 keV (20μA) in SEI mode with a working distance of 2-8 mm. Electrical conductivity was measured using the four-probe method similar to previous studies. [14] Metal electrodes were attached to the ends of the cylindrical samples. The amount of current transmitted through the sample during measurement was 100 mA and the voltage drop along the sample was measured over distances of 3 to 6 mm.

Results and Discussion

Our objective in this work was the design of monolithic CA composites that exhibit enhanced electrical properties through the incorporation of CNTs into the CA matrix. Previous work has shown that the addition of a critical volume fraction of carbon nanotubes to various matrices, if uniformly dispersed, yields significant increases in the electrical conductivity. [14] To achieve uniform distribution of CNTs in CA materials, our approach was to disperse the CNTs in the sol-gel reaction prior to polymerization so that the CNTs can be readily incorporated into the network structure as the polymer framework forms. The resulting RF polymer network containing the CNTs could then be dried and carbonized to afford the CA composite. The main challenge associated with this approach was dispersing the CNTs in water, the reaction medium for the sol-gel reaction, and maintaining the dispersion during polymerization to avoid settling or agglomeration of the CNTs. Since the DWNTs used for this work were very hydrophobic, an effective dispersion process was required. Previous work [15-20] had identified various methods for the dispersal of carbon nanotubes in water, including the suspension of carbon nanotubes in aqueous solutions of surfactants via sonication. For the synthesis of the DWNT-CA composites, we investigated various surfactants as well as sonication methods to disperse the DWNTs in the sol-gel reaction. Based on our initial results, we found that tip sonication of DWNTs in aqueous solution of sodium dodecyl benzene sulfonate (SDBS) provided the most uniform dispersion of DWNTs in the CA matrix and, therefore, this approach was used to prepare the nanocomposites presented in this report. In a typical synthesis, the DWNT were added to a solution of SDBS in water and dispersed using a tip sonicator. Resorcinol, formaldehyde and the reaction catalyst were then added to the solution and the reaction mixture was cured at elevated temperatures, during which time, black monolithic gels formed. These wet gels were then supercritically-dried and carbonized to afford the DWNT-CA composites. Interestingly, during the solvent exchange step prior to supercritical drying, the fluid washed from the pores of the wet gel was clear, indicating that the majority of DWNTs had been incorporated into the aerogel structure. Using this approach, a series of CA composites with DWNT loading ranging from 0 to 8 wt% (0 to 1.3 vol%)were prepared.

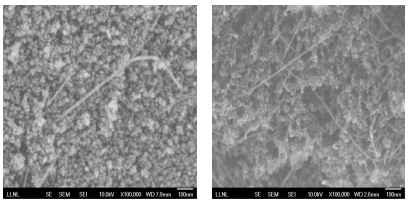

Figure 1. SEM images of DWNT-CA with a) 1 wt% and b) 8 wt% DWNTs.

The microstructures of the DWNT-CA composites were evaluated using scanning electron microscopy. As shown in **Figure 1**, the network structures of the CAs consist of interconnected networks of primary carbon particles, as would be expected based on the sol-gel reaction formulation. This observation is important as it shows that the formation of the aerogel network is not negatively impacted by the presence of either the surfactant or the DWNTs. These images also show the distribution of DWNTs throughout the CA framework. Clearly, the combination of SDBS surfactant and sonication was

effective in maintaining the dispersion of DWNT during the sol-gel polymerization reaction. Based on the SEM images, the DWNTs are dispersed as bundles with diameters of less than 10 nanometers, while the lengths of these bundles are on the order of ~ 1 micron. Not surprisingly, the composites prepared with higher loading levels of DWNTs clearly show a higher population of nanotubes in the SEM images.

To determine the effect that incorporation of DWNTs into the CA matrix has on the electrical properties of these materials, the electrical conductivity of the DWNT-CA composites were determined using the four-point probe method. As shown in **Figure 2**, the electrical conductivity of each composite material is enhanced relative to their respective pristine CA reference. The electrical conductivity enhancement, $\sigma_{enhanced}$, is given by

$$\sigma_{enhanced} = \frac{\sigma_{DWNT-CA} - \sigma_{CA}}{\sigma_{CA}} \quad (1)$$

where $\sigma_{DWNT-CA}$ and σ_{CA} are the measured electrical conductivities of the DWNT-CA composite and the pristine CA, respectively. This relative enhancement in electrical conductivity was chosen over absolute electrical conductivity so that samples of different densities could be directly compared. In general, the electrical conductivity of the nanocomposites increases as a function of DWNT concentration (Figure 2). The most consistent increases across the range of DWNT concentrations are for the DWNT-CAs prepared using 10:1 and 5:1 SDBS:DWNT ratios. In general, samples prepared with SDBS:DWNT ratio of 10:1 showed slightly larger improvements in conductivity than the 5:1 ratio in this case, but the 2.5:1 ratio was decidedly inferior to both. This observation is likely due to improved dispersion of the DWNTs in the reaction mixture at higher surfactant concentrations, as has been seen in previous work with aqueous suspensions of CNTs. [15-20]

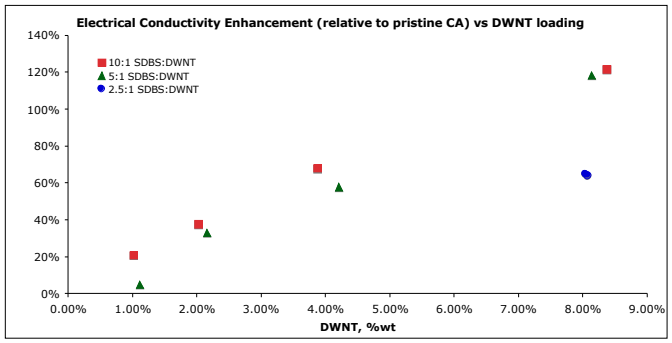

Figure 2. Enhancement in electrical conductivity relative to pristine CA as a function of DWNT concentration for a range of SDBS:DWNT ratios.

The largest improvements in electrical conductivity were observed in DWNT-CAs with 8 wt% (1.3 vol%) DWNTs, showing a twofold increase in conductivity. To verify that these enhancements were attributable to the incorporated DWNTs and not the SDBS surfactant, we also measured the electrical conductivity of reference CA materials that were prepared with SDBS and without the DWNTs. While the data for these materials show modest improvements in conductivity relative to the pristine CA, the effect is small relative to the overall enhancements seen in the CA-DWNT composites. Therefore, these improvements can be attributed to the incorporation of DWNTs into the CA framework.

Conclusions

This paper describes the synthesis and characterization of monolithic DWNT-CA prepared by the sol-gel polymerization of resorcinol and formaldehyde in an aqueous solution containing a surfactant-stabilized dispersion of DWNTs. Results from SEM imaging showed that the DWNTs were uniformly dispersed in the CA matrix and the aerogel network was not negatively disrupted by the presence of the DWNTs. The electrical conductivity enhancement as a function of DWNT loading did not show a percolation effect. The electrical conductivity of DWNT-CAs with 8 wt% (1.3 vol%) DWNTs were improved by a factor of two compared to pristine CA.

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