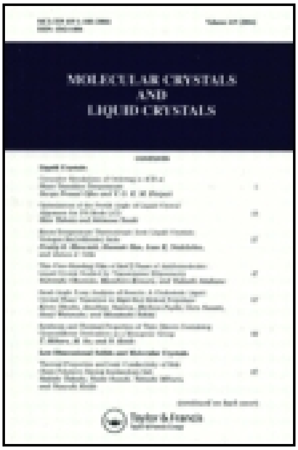

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Structure and Electrochemical Properties of Carbon Nanotube Intercalation Compounds

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Structure and Electrochemical Properties of Carbon Nanotube Intercalation Compounds

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This article summarizes the current status of carbon nanotube intercalation compounds. It focuses on the structure and electrochemical properties of intercalated single-walled carbon nanotubes (SWNTs). Materials synthesis, purification and characterization methods are also discussed. This article draws mostly from works performed at UNC.

Keywords: carbon nanotube; intercalation; structure; electrochemistry; synthesis

INTRODUCTION

Intercalation compounds of different carbon allotropes have been investigated intensively for scientific interests and technological applications. Metal intercalated C_{60} fullerides show novel electronic properties and high superconducting transition temperatures[1]. Graphite and carbonaceous materials are currently used as anodes for commercial Li-ion batteries[2]. Two types of nanotubes can now be synthesized. Multi-walled nanotubes (MWNTs) are composed of concentric and, in the ideal case, seamless and capped graphene tubules[3]. Single-walled nanotubes (SWNTs) produced by the laser ablation and arc-discharge methods form bundles with a close-packed 2D triangular lattice[4]. The structure and chemical bonding of the carbon nanotubes suggest that they can host guest species in their hollow inner cores, the van der Waals interstitial channels between the SWNTs within the bundles, and in the inter-shell spaces in the MWNTs when defects are present. Intercalation chemistry has been explored since the discovery of carbon nanotubes[5] and has drawn increasing attention[6-8] after relatively homogenous materials were made available by the advances in materials synthesis.

Compared to graphite and C_{60} counterparts, very little is known about intercalation in carbon nanotubes. Progress is still limited by materials issues. Early studies on MWNTs showed, surprisingly, intercalation of alkali metals to the same saturation composition of

AC_8 (A=K, Rb and Cs) as observed in graphite[5]. This result can only be reconciled if there are high concentration of defects on the walls of the MWNTs. Several groups have investigated SWNT intercalation compounds [7-11]. Although experimental results--weight up-take, conductivity and Raman--clearly indicate intercalation and charge transfer from the guest species to the host, the structure of the intercalated compounds is still unknown. This paper summarizes our recent results on SWNTs. Given the importance of materials, we start this article by first describing synthesis and purification.

SYNTHESIS and PURIFICATION of SWNTS

SWNT bundles used in this study were synthesized at UNC by ablating a graphite target containing Ni/Co catalysts at 1150°C using a 1064nm pulsed Nd:YAG laser. The experimental set-up is similar to that first reported by the Rice group[4] except in our case only one laser beam is used[9]. The quality and morphology of the products were determined by electron microscopy, Raman and X-ray diffraction techniques and were found to vary considerably depending on the actual ablation conditions. Several parameters such as furnace temperature, gas pressure and flow rate, laser power, and laser wavelength were varied separately in attempt to optimize the yield and control the nanotube diameters. Measurements on materials synthesized in our lab indicate the furnace temperature affects mainly the production rate and purity. Samples synthesized in the temperature range of 800-1200°C have essentially the same average diameter. A ~10% increase in the average SWNT diameter was observed when the wavelength of the laser used for ablation was changed from 1064nm to 532nm (the power density was normalized)[9]. The quality of the target such as mechanical strength and dispersion of the metal catalysts plays a major role in both the production rate and materials purity. Large amounts of graphite flakes were observed when the targets were not well sintered.

The precise purity of the SWNT-containing materials is difficult to determine. A rough estimate can be obtained by taking micrographs over relatively large areas by TEM The purity of the materials synthesized in our lab varies from 20% to 60%. The impurity phases are amorphous carbon, carbon nano-particles and metal catalysts which are usually encapsulated by the nano-particles. Several techniques have been developed to purify the raw materials, including filtration either assisted by ultrasonication or surfactants, preferential oxidation using various acids. Although most of the amorphous carbon and carbon nano-particles can be separated through these treatments, it has been very difficult to remove all the magnetic metal catalysts. This is in part because they are encapsulated by the nano-particles and some of them are inside the bundles. In addition, the structural integrity of the SWNTs can also be damaged by strong ultrasonic agitation and oxidation by strong acid. Our early samples were purified by the filtration method. Recent experiments were performed on materials purified by a two-step process involving first refluxing the SWNTs in 20 vol.% of H_2O_2 in H_2O for 12 hours at 100°C. Amorphous carbon phase was preferentially oxidized by the hydrogen peroxide to yield CO_2 gas. The remaining materials (~40wt% of the starting material) were rinsed first in CS_2 to remove C_{60} and then in methanol. They were then filtered through 0.8-2μm pore-size membranes. A significant fraction of the nano-particles and magnetic catalysts can be removed by repeating the filtration process several times till the liquid passing through the filter is clear. The final product contains ~90% of SWNT bundles. Figure 1 shows the representative TEM micrographs taken at different steps of the purification process. Powder x-ray diffraction experiments and intensity simulations show that the average diameter of the SWNTs is 1.3-1.5nm and bundle diameter 10-40nm. The bundles are randomly oriented

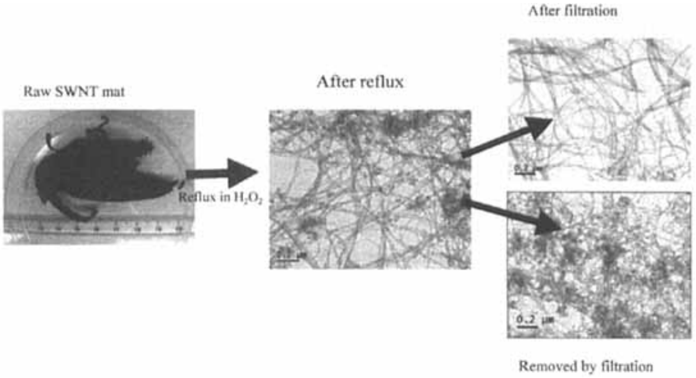

Figure 1. Representative TEM micrographs of the SWNTs at different steps of the purification process.

STRUCTURE OF INTERCALATED SWNT BUNDLES

Carbon nanotubes are intercalated using the same synthesis methods developed for graphite and C_{60}, including vapor-transport, solution, electrochemical, and solid state reactions. Weight-uptake measurements on as-made SWNT mats/powder reacted with alkali metal vapor show a saturation composition of AC_8 (A=K, Rb and Cs), the same as that of graphite and MWNTs[7-9]. No crystalline Bragg peaks from the SWNT lattice was observed by x-ray diffraction experiment, indicating that intercalation induces disorder within the bundles[7,9]. We have performed in-situ intercalation and TEM experiments to study the structural evolution of the SWNT bundles[10]. An analytical TEM with an attached reaction chamber was used which allows transferring of air-sensitive samples to the TEM chamber without exposing to air. As shown in Figure 2, the clear lattice fringes and diffraction spots originated from the inter-nanotube translational correlation within the same bundle became blurred after exposure to Cs vapor, indicating disorder. Regions with higher contrast were observed in some bundles that may be due to intercalated Cs ions located in-between the nanotubes. The bundles were found to maintain their tubular geometry. In contrast to the MWNTs[5], there is no evidence of structural damage on the individual nanotubes. The reaction is reversible. The bundles were de-intercalated and the lattice fringes and diffraction spots recovered after exposing the sample to air.

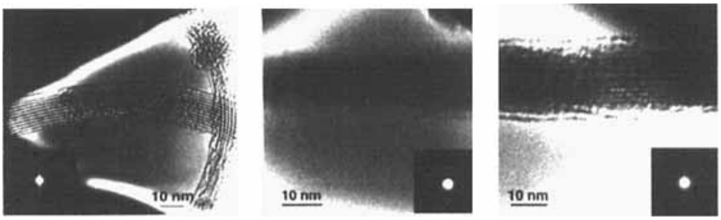

FIGURE 2. A sequence of TEM micrographs and electron diffraction patterns taken from *one* SWNT bundle at different stages of the intercalation reaction. Left: a pristine SWNT bundle; middle: 8 hours after exposed to Cs vapor at room temperature; right: a Cs-intercalated bundle after air exposure.

A reversible expansion of the inter-nanotube spacing was observed in HNO_3 intercalated SWNTs[11]. As shown in Figure 3, the position of the (10) peak of the pristine SWNT 2D triangular lattice shifted from 0.39A^{-1} to 0.36A^{-1} in Q ($Q=4\pi\sin\theta/\lambda$) after the sample was immersed in concentrated HNO_3 for 2 hours and air-dried. The relative intensities are noticeably different while the peak width remains the same as before. *Assuming* there is no change in the unit cell symmetry, the amount of shift in the (10) position corresponds to an approximately 1.85A expansion in the lattice constant. A simple space-filling model shows that the 1.85A expansion is required to fill the interstitial channels in the bundle with the HNO_3 molecules[11]. Due to the limited number of experimental observations, no further structural analysis was carried out.

Raman measurements showed an up-shift in the positions of the SWNT tangential modes (Figure 3) indicating oxidation of the SWNTs by nitric acid. A two-probe electrical measurement performed on a SWNT film showed over a factor of ten increase in the conductivity when the sample was reacted nitric acid, similar to that observed in the alkali metal reacted SWNTs[7].

FIGURE 3. Left: Powder x-ray diffraction patterns of SWNT bundles before (bottom), after (middle) reaction with HNO_3 and after de-intercalation (top). Middle: A simple unit cell model of the HNO_3 intercalated SWNTs that is consistent with the x-ray result. Right: Raman spectra of pristine and HNO_3 intercalated SWNTs. See color plate IV at the back of this issue.

ELECTROCHEMICAL INTERCALATION

Since their discovery, the carbon nanotubes have been speculated to be promising electrode materials. An early experiment demonstrated reversible electrochemical intercalation of SWNTs with lithium[12]. We investigated both MWNTs and SWNTs. The results show that purified SWNTs have a reversible Li capacity (C_{rev})of ~550-650mAh/g[13], much higher than the ideal value for grahite (372mAh/g) and is similar to that of disordered carbon[14]. By processing, C_{rev} can be increased to as high as 1000mAh/g [13].

In the electrochemical experiments, 3-4mg of nanotubes were deposited on flat 1cm diameter metal plates (Cu or stainless steel) and were dried in vacuum after deposition. A Swagelok-type cell was used with Li foil and the nanotube film as the two electrodes. A polypropylene filter soaked with standard liquid electrolyte was placed between the anode and cathode. The cell was discharged and charged at 50mA/g current between 0-3V. The specific Li capacities (amounts of Li intercalated per unit of carbon) were calculated from the time and the current used. In some cases, the SWNTs were first ball-milled for 0-20 minutes before deposition on the current collectors.

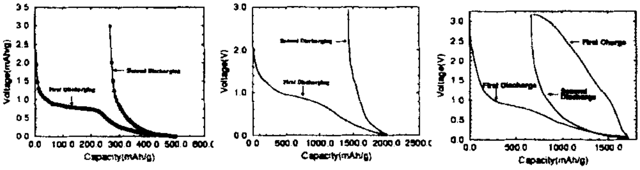

Figure 4. The charge-discharge data collected from as-synthesized MWNTs (left), purified SWNTs (middle), and SWNTs after 10-minutes of ball-milling (right). The data were collected under galvanostatic mode at 50mA/g current.

Figure 4 shows the typical charge-discharge data collected from as-synthesized MWNTs, purified SWNTs, and SWNTs after 10-minutes of ball-milling. The MWNTs exhibit a C_{rev} of ~250mAh/g, similar to that reported in another study[15]. A large number of SWNT samples were measured, C_{rev} was found to be in the range to 550-650mAh/g, larger than the ideal value for graphite (372mAh/g). A large irreversible capacity (C_{irr}) and voltage hysteresis were also observed which are detrimental for battery applications. The large C_{irr} is assumed to be related to the large surface areas of the SWNTs and the formation of solid-electrolyte-interface (SEI) in the first discharge. The origin of the large voltage hystersis is not clear. Upon 10-minute ball-milling, C_{rev} increased to 1000mAh/g and C_{irr} reduced to 600mAh/g. The reversible capacity is among the largest observed for carbon materials. No reduction in C_{rev} was observed after 5 cycles.

SUMMARY

The results presented in this paper show that SWNT bundles are interesting 1D host materials for intercalation. They can be intercalated with both electron donors and acceptors. Because of the low crystallinity and disorder within the SWNT bundles due to intercalation, the structure of the intercalated compounds is still unknown. Preliminary experiments on electrochemical intercalation of lithium demonstrate high specific lithium capacity in the processed SWNTs. The origin of this high capacity is not unclear and requires further investigation.

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