

CARBON NANOTUBE FORMATION IN BULK CARBONACEOUS SOLIDS VIA IN-SITU CARBONIZATION OF LOW-COST ORGANIC PRECURSORS IN THE PRESENCE OF METALLIC NANOPARTICLES

Teddy M. Keller,¹ Matthew Laskoski,¹ Jeffrey W. Long,² and Syed B. Qadri³

¹Code 6127, Chemistry Division

²Code 6171, Chemistry Division

³Code 6360, Materials Science and Technology Division
Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375

Introduction

Carbon nanotubes (CNTs) are formed in bulk solids from the thermal decomposition of melt-processible organometallic compounds or metal salts in the presence of an excess amount of an aromatic carbon precursor, such as a multi (ethynyl) compound or any polymeric material or resin that forms a char, followed by carbonization [1-4]. The nanotubes obtained by this patented method [5] are not formed from gaseous components, as is common with the current CNT production based on chemical vapor deposition methods (CVD), but rather evolve from metal and carbon nanoparticles that form within the carbonaceous solid during the carbonization process. The principal advantage of this novel synthetic approach is that nanotube compositions can be achieved in bulk solid, moldable forms, using relatively low-cost precursors and processing equipment, thereby reducing economic barriers that are inherent with carbon nanotube materials produced by the more conventional CVD method. This highly flexible synthetic method also offers the ability to incorporate heteroatoms (e.g., nitrogen, oxygen, and/or boron) into the carbon nanotube solid via the initial carbon precursors. Following carbonization, the carbonaceous solids are composed of varying amounts of nanotubes and amorphous carbon, depending on such synthetic parameters as the metal catalyst concentration, carbonization temperature, and the specific organic precursors used. The amorphous carbon phase is readily removed via selective combustion (calcination) at temperatures from 300-450°C, producing a highly porous, purified, and high surface area CNT composition [4]. In this paper, the *in-situ* synthesis of multi-walled carbon nanotubes (MWNTs) is described in high yield within a carbonaceous solid during the simple carbonization of high temperature polymers and metal carbonyls. The amount of CNTs obtained depends on the pyrolysis temperature with larger quantities being formed at the higher temperatures.

Experimental

Thermal properties were determined on a TA SDT 2960 simultaneous thermogravimetric(TGA)-differential thermal (DTA) analyzer. All thermal analyses were performed using heating rates of 10°C min⁻¹ under a nitrogen atmosphere with flow rates of 100 cm³ min⁻¹. X-ray analysis was performed using a Rigaku 18 kW x-ray generator and a high resolution powder diffractometer. X-ray diffraction scans of the samples were measured using CuK α radiation from a rotating anode x-ray source. Scanning electron microscopy (SEM) was performed on a Zeiss Model Supra 55 electron microscope. Transmission electron microscopy (TEM) was performed on a Libra 120 electron microscope at 120 kV.

Formation of MWNT-containing carbonaceous shaped solid. Commercially available resins/polymers such as novolac epoxy resins, polyacrylonitrile (PAN), and phthalonitrile resins were mixed in an appropriate solvent in the presence of Fe₂(CO)₉ and Co₂(CO)₈ and used in the formation of the CNTs. In a typical experiment, a 1:20 molar amount of Fe₂(CO)₉ and phthalonitrile resin was mixed by stirring in CH₂Cl₂ for 3 hr followed by removal of the solvent at reduced pressure. The Fe₂(CO)₉-phthalonitrile composition was then thermal converted to the CNTs by heating to 1200°C under inert conditions. The amorphous carbon was removed by heating either the pulverized or solid composition between 300-450°C in a flow of air.

Results and Discussion

Multi-walled carbon nanotubes (MWNTs) are formed in shaped, porous carbonaceous solids from the thermal decomposition of metal carbonyls (Fe₂(CO)₉ or Co₂(CO)₈) in the presence of carbon sources such as epoxy resins, PAN, phthalonitriles, and basically any organic material that forms a char, ultimately forming the MWNTs during the carbonization process. The metal nanoparticles are the key to the formation of the MWNTs. The ultimate size and separation of the metal nanoparticles (Fe or Co) is dependent on the molar ratio of metal carbonyl to carbon source used and on the time to gelation at a given temperature and whether decomposition of the metal carbonyl occurs in the melt phase or after solidification. Comparing the molar ratios of Fe and Co, the Co affords smaller diameter MWNTs with higher surface areas.

Compositions with various molar concentrations (1:1 to 1:100) of Fe₂(CO)₉ or Co₂(CO)₈ and a high temperature novolac epoxy resin-amine mixture, PAN, or a phthalonitrile are melted and thermally converted into a shaped solid polymeric component at elevated temperatures. During the heat treatment, degradation of the salt (Fe₂(CO)₉ and Co₂(CO)₈) will occur above 200 °C producing initially metal atoms and ultimately metal clusters and nanoparticles embedded in the network polymeric system. As the temperature is increased above 500 °C in an inert atmosphere, carbonization to a CNT-containing carbonaceous solid readily occur. The extent of the CNT formation depends on the pyrolysis temperature and time of

exposure at the upper temperature. The solid CNT composition can also be easily pulverized and converted into a powdered form. In addition, CNT compositions can be readily obtained containing various quantities of Fe or Co nanoparticles.

Thermogravimetric analysis was used to monitor the thermal transitions and the thermal stability of the CNT precursor source during the heat treatment to 1200°C in an inert atmosphere. Fig. 1 shows a TGA-DTA thermogram of precursor polymer, formulated from a 1:20 molar ratio of Fe₂(CO)₉ to the novolac epoxy resin, cured in the presence of an aromatic diamine, and heated to 1200°C in a flow of nitrogen. The TGA thermogram displayed thermal stability to about 325°C and a weight retention of about 35% at 1200°C. The sample exhibited exothermic transitions peaking at 365°C and 810 and 1025°C, attributed to the degradation of the epoxy polymer and reaction of the Fe nanoparticles with the developing carbonaceous matrix and the formation of the CNTs, respectively.

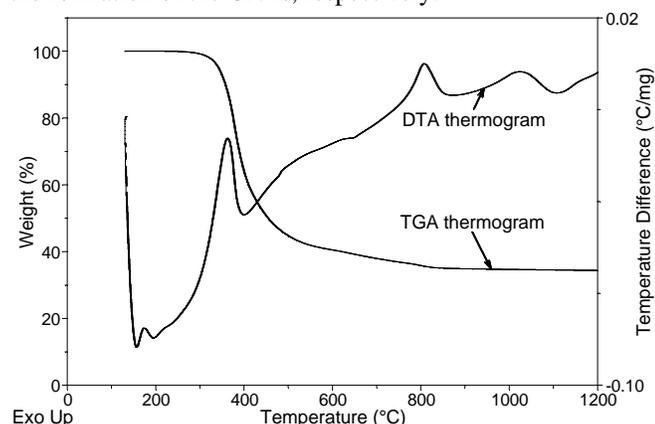


Fig. 1 TGA-DTA thermograms of 1:20 molar ratio of Fe₂(CO)₉ to novolac epoxy resin/polymer heated to 1200°C.

Transmission electron microscopy (TEM) on purified sample, formulated from the epoxy resin, showed that two types of CNTs could be formed depending on whether Fe or Co nanoparticles were used during the carbonization step (Fig. 2). The Fe nanoparticle composition afforded only bamboo CNTs upon thermal treatment to 1000°C and 1200°C. The Co catalyzed system displayed both the bamboo-type CNTs and MWNTs under identical conditions. The metal nanoparticles (Fe and Co) embedded within the carbonaceous solid are converted to their respective oxides during the purification (calcination) step.

Conclusions

The conversion of a highly aromatic thermosetting resin into MWNTs is a significant milestone in the development of an inexpensive route to CNTs. Since the MWNTs are not produced in the vapor phase using a complex high pressure, high temperature apparatus but in the solid phase during a simple carbonization process under atmospheric conditions, a potentially cost-effective method can be realized for their

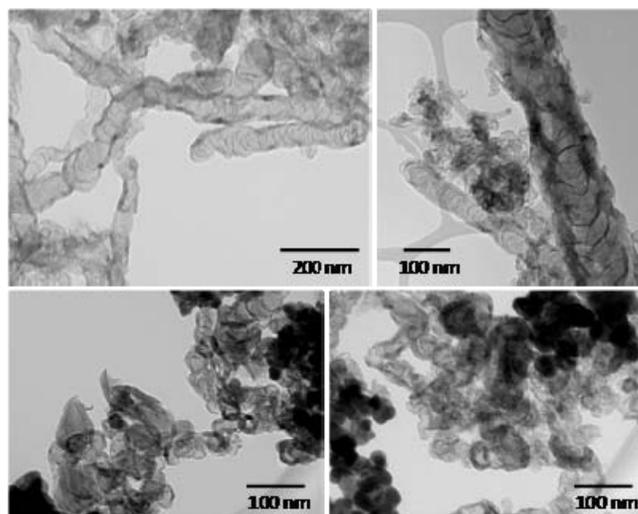


Fig. 2 TEM images of the novolac epoxy/Fe₂(CO)₉ (top) and novolac epoxy/Co₂(CO)₈ systems (bottom).

production in large quantities. By controlling the choice of precursor, metal nanoparticle size, temperature of carbonization, and time of thermal exposure, shaped CNT compositions with varying porosities and surface areas can be readily obtained. The bamboo CNTs and MWNTs formed by this method are currently being evaluated for various applications in energy (battery and fuel cell), nanoelectronic, air filtration, and structural applications. Since the CNT-containing carbonaceous solid also contain magnetic Fe and Co nanoparticles in a homogeneous array, devices utilizing both the nanotubes and metal nanoparticles could be important. By using standard resin processing techniques, various shaped carbonaceous configurations containing a large percentage of CNTs can be realized.

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- [5] See U.S. Patent #6,846,345 and #6,890,504.