

MULTI-WALLED CARBON NANOTUBES SYNTHESIZED AT AMBIENT PRESSURE FROM NICKEL COMPLEXES

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Abstract

Multi-walled Carbon nanotubes (MWCNTs) are formed from thermal decomposition of metal-containing organometallic compounds in the presence of a carbonizing compound at ambient pressure. The method permits the production of CNTs in a solid, film, fiber, or powdered form. Heat treatment of various precursor compositions up to 1300 °C results first in the decomposition of the organometallic compound and the formation of metal nanoparticles and ultimately the formation of carbon nanotubes during the carbonization process. X-ray diffraction, thermogravimetric analysis, Raman spectroscopy, transmission electron microscopy, and scanning electron microscopy studies confirmed the formation of CNTs in the developing carbon composition above 600 °C.

Introduction

Multi-wall carbon nanotubes (MWCNTs) are currently produced in bulk quantities and in high yield by chemical vapor deposition (CVD). In a typical experiment, a hydrocarbon gas reacts under heating with a metal nanoparticle catalyst in a quartz tube reactor at temperatures in the range of 600-800 °C under flowing argon. The MWCNTs are deposited on the wall of the quartz tube reactor from the thermal decomposition of organometallic compounds. Although the CVD method can produce high yields of CNTs, extensive purification and isolation still makes this methods cost prohibitive.

The possibility of using organometallic containing compounds or a mixture of an organometallic compound in the presence of an excess amount of a carbon precursor compound to produce CNTs in bulk solids at ambient pressures has recently been reported and offers a distinct advantage to the vapor phase methods. This potentially inexpensive method for the synthesis of MWCNTs in large quantities and in high yield within a shaped and highly dense solid domain has been developed in our laboratory. We have shown that small molecules containing both aryl and ferrocene units separated by a single alkyne group can be converted into a thermosetting polymer through the alkyne units. Further heating of the networked polymers resulted in the decomposition of the ferrocene units and the formation of CNTs in high yield during the carbonization process above 500 °C in the carbonaceous solid under ambient pressure. Our efforts have focused on developing polymeric precursors containing transition metals and the thermal conversion of such compositions through the melt process at elevated temperatures into shaped solid CNT-containing components under atmospheric pressure. Organometallic compounds or metal salts that decompose at fairly low temperatures below the carbonization process to initially produce metal atoms and clusters have been found to be a good source of metal particles. Our research activities have shown that only a small or catalytic amount of metal source is needed for the production of MWCNTs in a shaped carbonaceous bulk solid. In contrast to the CVD method that occurs from the gaseous phase, the MWCNTs are being formed in the solid carbonaceous phase during the carbonization process. The early interaction of the metal atoms with the precursor aromatic carbon source appears to be important in the formation of the nanotubes. The MWCNTs are formed in a non-ordered array within the carbonaceous solid domain.

In this paper, we describe the in situ synthesis of MWCNTs in high yield and in a bulk carbonaceous solid during the carbonization of a mixture of 1,2,4,5-tetrakis(phenylethynyl)benzene and Ni(COD)₂. Depending on the reaction conditions, the carbonaceous solid can be tailored to contain varying amounts of MWCNTs and Ni nanoparticles.

Experimental

General Procedures. All synthetic operations were carried out under an argon atmosphere using standard Schlenk techniques. All solvents were dried and distilled prior to use. 1,5-(C₈H₁₂)₂Ni [Ni(COD)₂] was purchased from Strem Chemical and used as received. 1,2,4,5-Tetrakis(phenylethynyl)benzene **1** was prepared according to a literature procedure. Thermal analyses experiments were performed using a TA Instruments SDT 2960 simultaneous thermogravimetric analysis (TGA)/differential thermal analysis (DTA) analyzer at a heating rate of 10 °C min⁻¹ and a nitrogen flow rate 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. Raman studies were carried out at room temperature using a Renishaw Raman Spectrometer equipped with a 514.5 nm argon-ion laser. Transmission electron microscopy (TEM) studies were performed on a Hitachi H-8100 electron microscope at 200 kV. Scanning electron microscopy (SEM) studies were performed on a Zeiss Model Supra 55 electron microscope.

Preparation of mixtures from various molar concentrations of Ni(COD)₂ and 1,2,4,5-tetrakis(phenylethynyl)benzene (1). A 1:20 molar mixture was prepared by the following procedure: **1** (1.7 g, 3.6 mmol) was placed in a Schlenk flask and transferred to a glove box. Ni(COD)₂ (0.05 g, 0.18 mmol) was weighed out and added to the flask. The flask was then placed under argon and 30 mL hexanes and 30 mL CH₂Cl₂ were added via syringe. After a few minutes, the reaction darkened from yellow to greenish-brown. The reaction remained heterogeneous and was allowed to stir for 3 h before removing the solvent under vacuum. The mixture was used as isolated in the studies. Several other precursor mixtures containing various amount of Ni(COD)₂ and **1** were prepared using the same procedure and the following amounts.

1:10 molar mixture: Ni(COD)₂ (0.10 g, 0.360 mmol) and **1** (1.7 g, 3.6 mmol)

1:50 molar mixture: Ni(COD)₂ (0.02 g, 0.072 mmol) and **1** (1.7 g, 3.6 mmol)

1:100 molar mixture: Ni(COD)₂ (0.01 g, 0.039 mmol) and **1** (1.9 g, 3.8 mmol)

Preparation of shaped MWCNT samples. A circular Al planchet was treated with teflon mold release. A sample (1.61 g) of the 1:20 molar mixture of Ni(COD)₂ to **1** was placed in the planchet on a hot plate preheated to about 220 °C inside a vacuum desiccator. The melt was degassed for 1.5 h to remove any volatile material. Following the degassing procedure, the sample was placed in a tube furnace, heated at 0.3 °C min⁻¹ to 1000 °C under an argon atmosphere, and cooled to room temperature at a rate of 0.5 °C min⁻¹.

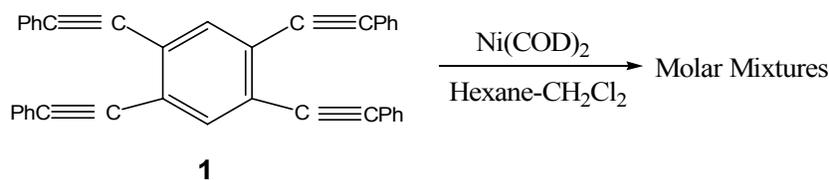
Preparation of small solid MWCNT samples for characterization studies. Milligram quantities of various mixtures (1:10 to 1:100 molar ratios) of Ni(COD)₂ to **1** were weighed into a TGA pan and heated at 10 °C min⁻¹ to 800, 1000 and 1300 °C (isotherm for 30 min) and then quickly cooled to ambient condition. The solid samples were used for x-ray diffraction, Raman, and magnetic studies.

Preparation of MWCNT samples for TEM studies. Samples of 1:10, 1:20 and 1:50 molar samples of Ni(COD)₂ and **1** were dissolved in a minimal amount of CH₂Cl₂ and dropped onto a clean silicon wafer to form a thin film before heating at 10 °C min⁻¹ to 1000 °C and holding for 1h. After cooling, the thin films, which were present on the silicon surface, were suspended in ethanol and dropped onto holey carbon grids for TEM studies. Thicker solid samples (30-50 mg) of the various molar precursor compositions were placed on a silicon wafer, heated to 1000 and 1300 °C, and held for 1 h at each temperature. After grinding the solid sample in a mortar and pestle, the powder was transferred to a beaker, 5 mL of acetone was added, and the mixture was sonicated in an ultrasonic processor (Sonics and Materials, 40 % amplitude) for 1 h at ambient temperature. The sample was solution deposited onto a holey carbon grid for TEM studies.

Preparation of MWCNT samples for SEM studies. A 1:20 molar sample of Ni(COD)₂ and **1** was deposited on a silicon wafer, melted to a film, heated to 1000 °C and held for 1 h yielding a thick film. To formulate a thin film, a 1:20 molar sample of Ni(COD)₂ and **1** was dissolved in CH₂Cl₂ and deposited on the silicon wafer. Heat treatment to 1000 °C afforded a thin carbonaceous film.

Results and Discussion

The growth of the CNTs proceeds in the solid phase during the carbonization process from pyrolysis of a mixture of **1** (excess) and Ni(COD)₂. When Ni(COD)₂ was used as the Ni source (Scheme 1), conversion to MWCNTs was found to readily occur in high yield from various concentrations of Ni(COD)₂ to **1** upon heat treatment to 1000 and 1300 °C. It has been previously reported that Ni(COD)₂ readily decomposes in CH₂Cl₂ in the presence of poly(vinylpyrrolidone) yielding Ni nanoparticles. During thermal treatment, the developing polycondensed aromatics react with the Ni species to produce MWCNTs. The amount of MWCNTs formed in the carbonaceous solid depends on the pyrolysis temperature, size and concentration of the Ni species, and the exposure time. Shaped MWCNT-containing carbonaceous compositions can be readily fabricated by the method. The composition can be tailored to have mainly MWCNTs or varying amounts of nanotubes and Ni nanoparticles. As formed without any purification, MWCNT compositions can be produced containing less than 1% Ni nanoparticles within the carbonaceous solid residue. However, the concentration of elemental Ni nanoparticles can be readily varied as a function of the amount of **1** and Ni(COD)₂ used in the initial synthesis of the precursor mixture. Such flexibility is necessary for the ability to vary specific properties of the carbonaceous composition. For some applications, the concentration and size of the Ni nanoparticles embedded within the MWCNT carbonaceous solid will be important.



Scheme 1. Reaction of Ni(COD)₂ with **1**

Figure 1 shows the TGA and DTA thermograms of a 1:20 molar sample of Ni(COD)₂ to **1** heated at 10 °C min⁻¹ to 1000 °C. The carbonization reaction resulted in a char yield of 82 %. An endothermic transition (Figure 1A) and an exothermic transition peaking at approximately 200 and 295 °C, respectively, are attributed to the melting point of **1** and to the reaction of the ethynyl units to a shaped solid or cross-linked polymeric system. Two small exotherms (Figure 1B) peaking at about 585 and 730 °C were assigned to the reaction of the Ni atom, clusters, and/or nanoparticles with the developing aromatic fused ring systems or carbon nanoparticles within the evolving carbonaceous solid composition. Further heat treatment above 800 °C resulted in the commencement of another exothermic transition, which was attributed to the formation of the nanotubes.

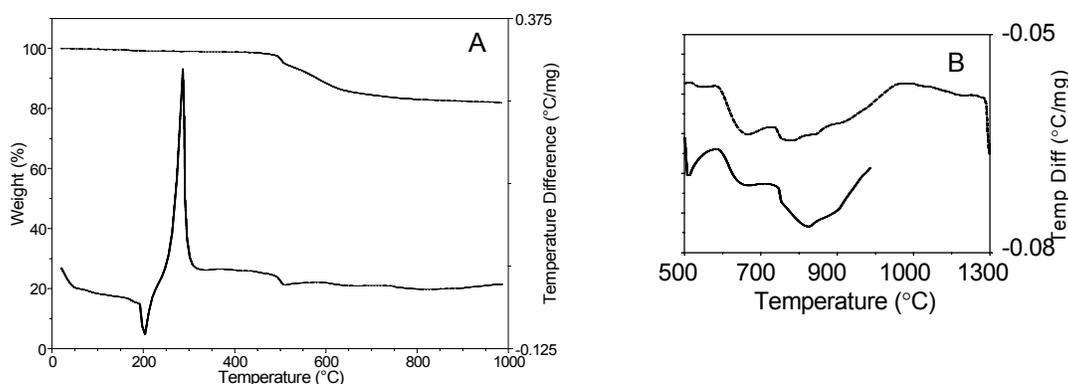


Figure 1. TGA/DTA thermogram of a 1:20 molar mixture of Ni(COD)₂ and **1** heated at 10 °C min⁻¹ to 1000 °C.

Raman studies were performed using a 514.5 nm argon-ion laser on the surface of the CNT-containing solid carbonaceous compositions prepared at various temperatures up to 1300 °C. Figure 2 shows the Raman spectra of a sample prepared from a 1:50 molar mixture of Ni(COD)₂ to **1** heated to 1300 °C and isothermed for 30 min. Samples exposed to high temperatures showed the first- and second-order peaks characteristic of MWCNTs. In these studies, the first- and second-order Raman spectra were obtained on the solid nanotube samples and analyzed in terms of the change in position, width, and relative intensity of the D and G peaks (first-order Raman), which lie at about 1347 and 1575 cm⁻¹, respectively, and the second-order scattering peaks between 2450 and 3250 cm⁻¹.

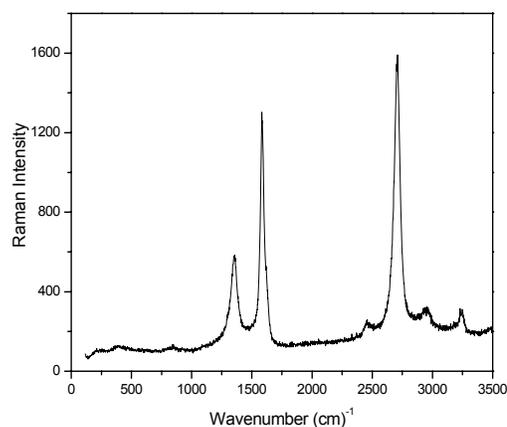


Figure 2. Raman spectra of a sample prepared from a 1:50 molar mixture of Ni(COD)₂ and **1** heated to 1300 °C for 30 min.

X-ray diffraction (XRD) studies were carried out on the Ni-based carbonaceous solids to confirm the presence of MWCNTs and to determine the dimensions of Ni nanoparticles. Figure 3 shows an overlay of the diffraction scans obtained

from samples in which Ni(COD)₂ and **1** are mixed in 1:10, 1:20, and 1:50 molar ratios and heated at 1300 °C for 30 min. The (111), (200), and (220) diffraction peaks for *fcc* Ni can be easily identified. The calculated particle sizes, based on the Scherrer's equation and neglecting the contributions due to strain broadening of the peaks, are in the 15-17 nm range for Ni nanoparticles. Similarly, the average diameters of the MWCNTs calculated from the FWHM of CNT (002) are in the 7.5-7.9 nm range. The diffraction peak at 25.61 degrees for MWCNT (002) is significantly deviated from either graphite-2H (002) peak at 26.38 or from graphite-3R (003) peak at 26.60. In previous studies involving Co and Fe catalyzed formation of MWCNTs in a carbonaceous solid, the MWCNT (002) was reported at 25.95 degrees. The observed intertubule distance of 3.44 Å for the (002) reflection in the Ni(COD)₂ and **1** carbonized samples is greater than the interlayer spacing found in graphite (3.35 Å). The expanded d-spacings for MWCNT (002) suggest an elongation along the c-axis, which may be due to Ni incorporation into the lattice. The c-parameter calculated from the (002) reflection is 6.93 Å in contrast to 6.72 Å reported for graphite-2H. The lattice parameter calculated from the (100) reflection is 2.45 Å compared to 2.47 Å for graphite. The saw tooth-shape of the (100) reflection arises due to two-dimensional periodicity of the layers. The asymmetry in the *hkl* reflections occurs from turbostratic stacking of the graphitic tubes resulting in a uniform tubular structure. For the polycrystalline samples, the diffraction pattern for the nanotubes consists of sharp edges on the low-angle side with a broad tail on the high angle side of the peak. In contrast, for a polycrystalline graphite sample, the diffraction peaks will be sharp with no tails extending for *hkl* reflections. Heat treatment of similar molar samples of Ni(COD)₂ and **1** to 1000 °C resulted in XRD pattern consisting of peaks from *fcc* Ni and MWCNTs.

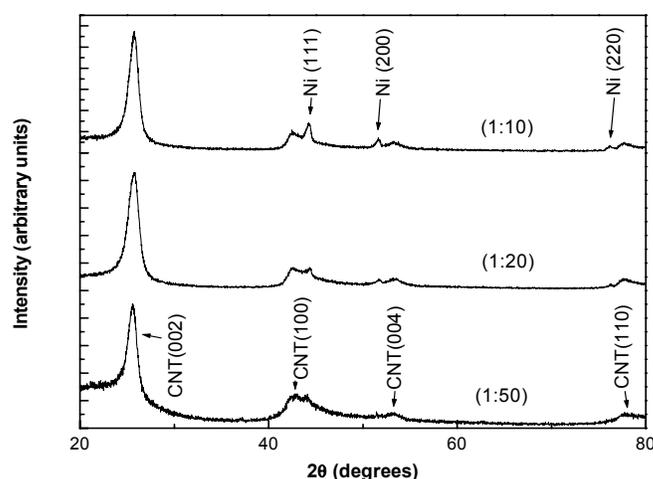


Figure 3. X-ray diffraction scans for 1:10, 1:20, and 1:50 molar mixtures of Ni(COD)₂ and **1** heated at 1300 °C for 30 min.

TEM studies were conducted on carbonaceous compositions obtained from pyrolysis of various samples of Ni(COD)₂ and **1** that had been heated at 1000 and 1300 °C, respectively. MWCNTs existed in abundance throughout thin film samples that were formulated on a silicon wafer. Figures 4A and 4B show the high magnification image of a MWCNT produced in a thin film from heat treatment of a 1:10 molar sample of Ni(COD)₂ and **1** to 1000 °C. The image shows a MWCNT with the Ni nanoparticle situated at the end or inside the end of the tubular structures. This MWCNT was found to have a diameter of 68.5 nm including 14 graphite layers and an outer layer of amorphous carbon. The inner diameter of the MWCNT was approximately 3.5 nm. The Ni nanoparticle was sealed in the end completely surrounded by graphite layers with a diameter of 21.5 nm and a length of 107.5 nm. Tubes of varying size and shape containing Ni nanoparticles were observed in other parts of the sample.

High-resolution TEM images (Figures 4C-E) show the existence of a copious amount of tube-like, ribbon shaped carbon nanostructures throughout an entire solid thick sample. The carbonaceous material is visible as a complex assortment of randomly oriented nanostructures and a small amount of amorphous carbon scattered throughout the sample. Due to the complexity of the graphitic structure, it is very difficult to view the entire image of an individual MWCNT. However, the graphite-like spacing of the MWCNT walls is discernible within the complexity of the isotropic network system. The interlayer distance between the graphitic layers was measured to be 0.34 nm, which was consistent with the d-spacing found from XRD analysis. The interlayer spacing within the graphitic patterns appears fairly uniform. Similar images were observed on the various turbostratic carbon solids that were produced from heat treatment of different concentration of Ni(COD)₂ and **1**. Upon heating at 1300 °C, there was a reduction in the quantity of amorphous carbon present in the samples.

SEM images were obtained on a CNT carbonaceous film that was formed on a silicon wafer by heating a 1:20 molar concentration of Ni(COD)₂ and **1** at 1000 °C for 1 h. Carbon nanotubes were found to have readily formed during the carbonization process. Figure 5A shows an abundant amount of MWCNTs and long individual MWCNTs in a random

arrangement extending from the edge of the thick film. The tubes are in various shapes and length. With an enhancement in the resolution (Figure 5B), individual nanotubes around 20-80 nm in diameter can be observed extending from the surface. From these images, we can conclude that the heat treatment of mixtures of Ni(COD)₂ and **1** at high temperatures results in the efficient, high-yield formation of MWCNTs within the carbonaceous solid.

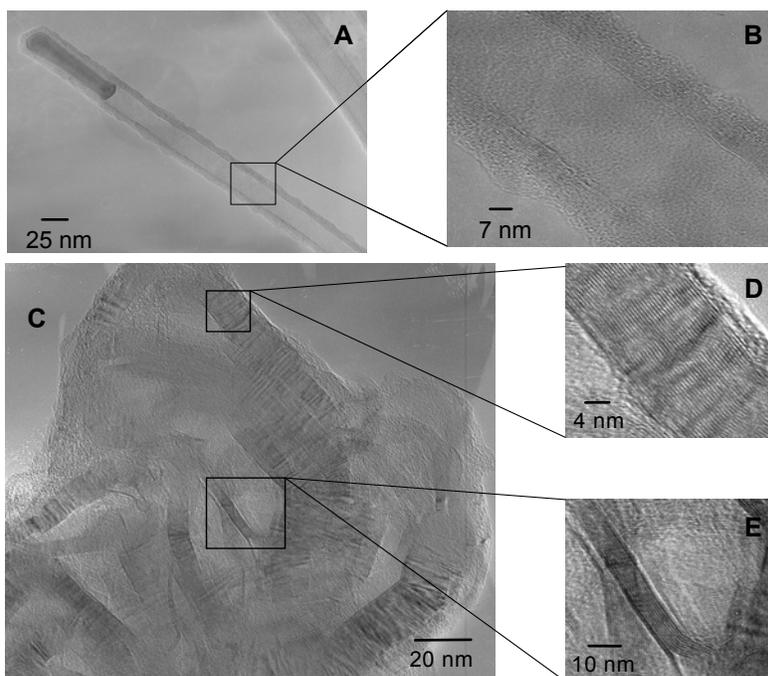


Figure 4. TEM images of 1:10 molar mixture of Ni(COD)₂ and **1** heated to 1000 °C on surface of silicon wafer: (A) low-resolution image of thin film showing Ni catalyst inside MWCNT; (B) high-resolution image of MWCNT; (C-E) high-resolution image of solid sample showing turbostratic carbon pattern

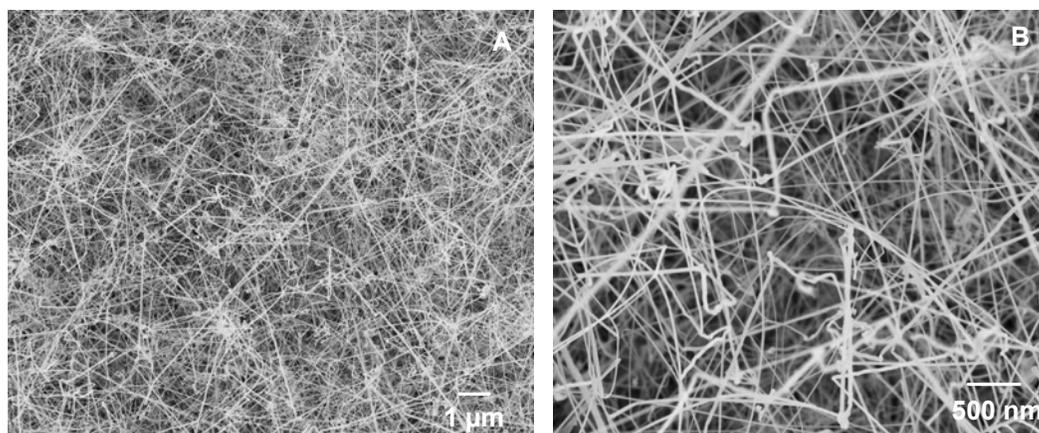


Figure 5. SEM images of CNT sample formulated from 1:20 molar amount of Ni(COD)₂ to **1** deposited on silicon wafer and heated to 1000 °C.

Conclusion

Carbon nanotubes are formed in high yield in a shaped carbonaceous solid at elevated temperatures under atmospheric pressure. X-ray diffraction, Raman, TEM, and SEM studies show the formation of MWCNTs within the dense carbon solids. Potential applications of CNTs depend on the development of large scale synthesis in high yield and an understanding of the growth mechanism. MWCNTs are produced during the carbonization process from heat treatment of a crosslinked polymer containing a small amount of Ni atoms, clusters, and/or nanoparticles as the precursor material. This synthetic method has the potential to produce large quantities of MWCNTs in any shape with varying amounts of Ni nanoparticles in the carbonaceous solid.

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