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Well-Aligned Carbon Nanotubules**

By *Jyun-Hwei Hwang, Wen-Kuan Hsu,
and Chung-Yuan Mou**

The recent discovery and bulk synthesis of carbon nanotubes have led to much speculation about their possible applications in electronics, composite materials and catalyst support.^[1, 2] The electronic properties of carbon nanotubes are strongly dependent on their morphology. For example, the electrical conductivity,^[3] being along the tube axis, can vary by orders of magnitude depending on the alignment of the carbon nanotubes. Since these transport properties are important to the application of carbon nanotubes in electronic devices, it is desirable to control nanotube morphology during synthesis. In this communication we present a method to influence the morphology of nanotubes by using copper-mixed graphite to form an ordered assembly.

The standard carbon-arc synthesis for fullerenes also produces abundant amounts of carbon nanotube fibers on the negative electrode under high helium pressure. When copper-mixed graphite is used as the electrode in arc production, many metal-catalyzed nanotubes are produced with very good directional alignment. SEM micrographs of samples show the directional growth of the tubes and show that most of them are bunched. TEM images of a typical sample show a multilayer structure with a hollow interior. Typical tube dimensions are 40–70 nm wide and 10 µm long. Energy-dispersive X-ray analysis shows that copper is incorporated into the graphite nanoparticles. Copper thus serves as a nucleation seed for the further growth of nanotube fibers. Thermogravimetric analysis (TGA) of the nanotubes show they are stable in air up to 800 °C.

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Kasokovskaya and Chernozatonskii^[4] have succeeded in making ordered arrays of tubules by electron beam evaporation of graphite in a high vacuum. The tubes are 10–100 nm long and 0.8 to 1.1 nm in diameter. However, the sample they obtained seems to be microscopic in size. More recently, Ajayan and Iijima^[5] have annealed tubes in the presence of molten lead resulting in the opening of the cap of the tube and capillary-induced filling of nanotubes. This is an indication of the strong metal–carbon interactions. It is known that copper can form small cluster compounds with carbon,^[6] and it would be interesting to investigate the type of tubule formation which takes place in the presence of copper atoms in plasma during the growth of nanotubes. Based on experience in the study of endohedral fullerenes, it is unlikely that copper would stay inside the tubule cage. The strong copper–carbon bond would probably lead to the incorporation of copper into the graphite nanoparticles, and promote their nucleation and growth.

The conventional method for the carbon-arc synthesis of carbon nanotube fibers involves the plasma discharge of pure graphite. In these cases, the nanotube fibers are predominantly randomly oriented. If copper-mixed graphite were used in place of graphite as the electrode, the carbon and copper atoms would be evaporated simultaneously. This gives rise to the possibility of copper incorporation and the copper atoms serve as nucleation sites for assembling carbon nanotubes.

In this study, we examine the idea of using the above mentioned catalysis to modify the morphology of carbon nanotubes. Several ratios of copper/graphite were used to examine the effect of metal on the growth of nanotubes.

Carbon nanotubes were prepared using the carbon-arc method and graphite, pure or mixed with copper, as the working electrode. All fibers were grown with power-supply control of the working electrode at 70 A and 25 V. The helium gas pressure was maintained at 500 Torr.

Three different compositions of copper were used: a) 0% (pure graphite), b) 23–25 wt.-% Cu, c) 73 wt.-% Cu (3% Pb, 24% C). The difference between (b) and (c) is that sample b was made by pressing copper powder (size: 325 mesh, 99.8%) in a hole (diameter 3 mm, depth 40 mm) in a graphite rod and in sample c copper powder was mixed with graphite powder and the mixture was pressed into a rod.

The carbon-arc was controlled to obtain a rod-shaped deposit about 1.5 cm long (diameter of about 7 mm). Under these conditions, about 75% of the consumed graphite rod is converted to a deposit of cylindrical shape of similar diameter. The rod-shaped deposit was then cut open with a knife to obtain the inner black fibers. Samples were sputter coated with gold before taking the scanning electron microscopic pictures. Scanning electron micrographs (Hitachi S-800 SEM) show the morphology of the fibers produced. Samples were sonicated in ethanol and a drop of the tube-containing liquid was dried over a nickel grid in preparation for the TEM micrographs. TEM (JEOL 2000FX with a Be holder) images (at 100 keV) of samples were taken to

investigate the detailed structure of fibers. An EDX analyzer was used to analyze the elements present in the specimen.

Figure 1 is a scanning electron micrograph of a sample produced with undoped graphite (sample a) inside a chamber that was previously uncontaminated by metal vapor. A sample was taken from near the tip of the carbonaceous deposit; most of the area shown in the micrograph is amorphous carbon. However, occasionally bundles of thin tubes sticking out of the surface can be seen. The diameter of the individual tubes is around 65 nm. When we cut open the same sample and examine the material inside, the tubes are oriented randomly and there is no bunching. The image (not shown here) is similar to those reported by Ebbeson and Ajayan.^[2] This observation indicates that well-aligned nanotubes can be formed by nucleation on a carbonaceous surface and that the strong electric field at the tip of the electrode probably influences the orientation of the tubules. There is no bunching of the nanotubes in the inner black core, and there are also few graphite nanoparticles. We therefore tried to produce more of these graphite particles by mixing graphite with copper, expecting the nanoparticles to be good nucleation sites for nanotubes.

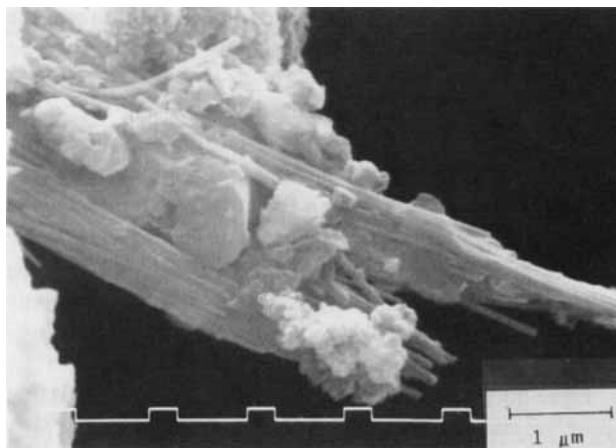


Fig. 1. Scanning electron micrograph of the tip of a rod-shaped deposit generated in arc production. Electrodes are graphite rods (sample a). The directional bunchy growth of carbon tubes is seen.

Figure 2 shows a scanning electron micrograph of a sample produced with copper-doped graphite (sample b). It was taken from the inner black core. The whole specimen shows well-aligned growth in most of the area examined, patches of about $20 \mu\text{m}^2$ containing aligned tubes (average diameter 52 nm). High-resolution TEM (not shown) shows these tubes have concentric buckytube structures. There are also more graphite particles in the inner core from which the tubes seem to grow. Figure 3 is an image for sample c where there are more graphite particles; in fact, many of the particles adhere to the nanotubes. The diameter of the individual tubes is also larger (average diameter 70 nm). In this sample, almost all the tubes are aligned.

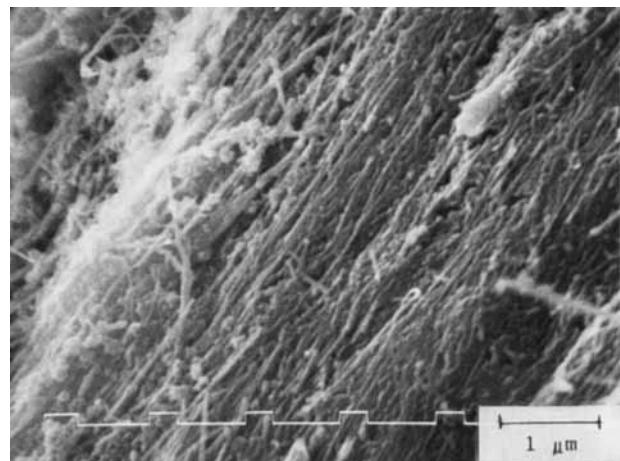


Fig. 2. Scanning electron micrograph of carbon nanotubes generated in arc production when copper-filled graphite (sample b) is used as the positive electrode.

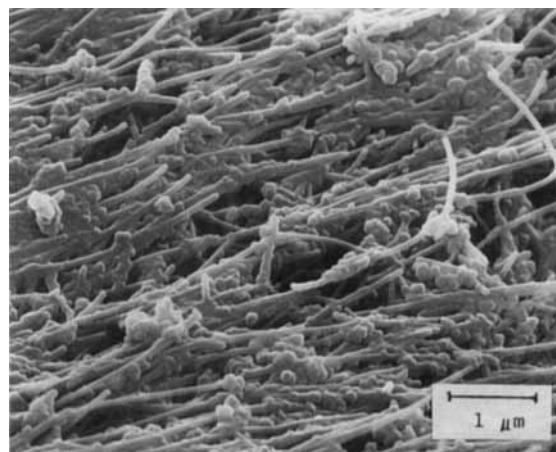


Fig. 3. Scanning electron micrograph of carbon nanotubes generated in arc production when copper-mixed graphite (sample c) is used as the positive electrode. There are many copper-containing nanoparticles serving as tube growth sites.

Examination of sample c by transmission electron microscopy showed that graphite particles are very dark (Fig. 4), an indication of metal incorporation. Energy-dispersive X-ray (EDX) analysis showed the presence of elemental copper. Figure 5 is an EDX spectrum taken from a nanoparticle sticking on a tube. Copper is present in the particle. The bigger nickel peak comes from nickel grid supporting the specimen. Further enlargement of the TEM image does not show any definite crystalline lattice fringe in the dark copper-containing region.

Ruoff and co-workers^[7] have observed single-crystals of LaC_2 encapsulated in carbon nanoparticles. It is likely that copper and carbon form clusters to initiate the growth of the nanoparticles. There are occasional dark stripes on the wall of the nanotubes. These dark stripes most likely come from copper, but we have not observed any filling of the hollow

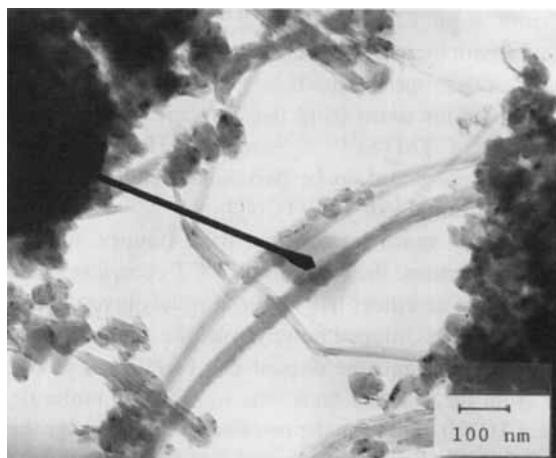


Fig. 4. Transmission electron micrograph of carbon nanotubes generated in arc production from a carbon/copper mixture (sample c).

inner space of the tubes although there is a high concentration of copper vapor present during the synthesis. Capillarity-induced filling of the nanotubes with lead, observed by Ajayan and Iijima,^[5] was performed at the much lower temperature of 400 °C with molten lead. The covalent nature of the carbon–copper bond^[6], and the fact that the operating temperature is much higher in the arc plasma, preclude the filling of the inner hollow region.

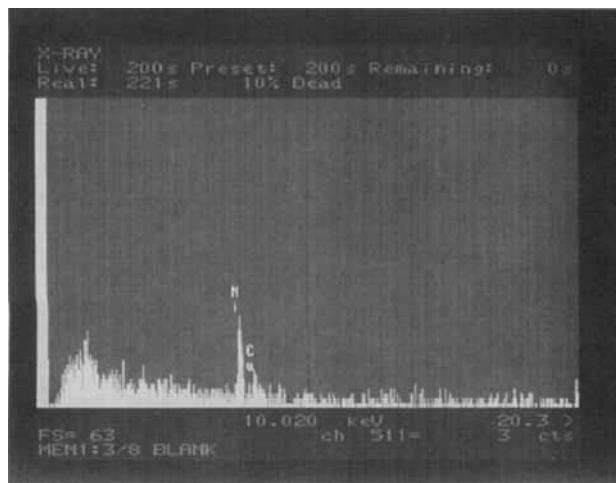


Fig. 5. Energy-dispersive X-ray data from copper-doped tubes, taken from the region indicated in Figure 4. The largest peak is due to the nickel grid that supports the specimen.

In every sample examined there are also many isolated nanotubes of smaller diameter, about 1–5 nm. However, the tubes in the bundles are wider and longer. It seems the more copper one uses the bigger the diameter of the tubes. Copper promotes both the nucleation and fattening of the tubes.

There are several proposals for the growth mechanism of nanotubes.^[8–10] Iijima and co-workers^[8] suggested that tubes grow thick by island formation and the extension of graphite basal planes. It is possible that the presence of copper helps this process and leads to thickened tubes. Saito and co-workers^[9] proposed that tubes grow from fluid-like elongated polyhedral particles under ion bombardment. This is consistent with our observation of simultaneous copious production of nanoparticles and tubes. It is not known whether some of the nanoparticles are the results of the fragmentation of buckytubes as suggested by Dravid and co-workers.^[10]

Since the nanotubes and nanoparticles are produced in a high-temperature environment, they should be very stable upon heating.

Thermogravimetric analysis (TGA) of the copper-promoted nanotubes shows that there is no weight loss in air up to 800 °C. Therefore, there is no bulk copper material or significant dangling carbon bonds in the sample.

It should be noted that there have been numerous reports over the years on carbon whiskers.^[11, 12] The whiskers are mostly obtained upon pyrolysis of carbon-containing gases at temperatures between 500 and 1000 °C. In particular, Tibbetts^[13] reported the formation of carbon tubules above 900 °C on decomposition of gaseous hydrocarbons on sub-micron catalytical metal particles. In these early studies, the whiskers, usually helical or curved, are not well-aligned due to the lack an orientational force field which is present in the arc method.

Metal particles were found on the tips of growing whiskers. It was proposed^[13] that the whiskers grow by precipitation from carbon-dissolving metal particles. In this approach, whiskers grow because of supersaturation of carbon in a catalytic liquid metal.^[14] However, in the present approach, the operating temperature is much higher, estimated to be 5000 K, such that metals evaporate completely. In fact, we have never found metal particles inside the growing tubule tips. The growth mechanism is vapor condensation. The tubules produced using our method are numerous, uniform in size, and well-aligned. These characteristics are not seen in the carbon whiskers produced by decomposition of hydrocarbons.

The use of metal as an agent to regulate the morphology of carbon nanotubes works well. Very significant modification of the carbon nanotube morphology has been achieved. The variation in the form and the extent of modification seen when using three different copper–graphite composition ratios are consistent with the hypothesis that the metal-promoted nanoparticles are necessary for copious production of aligned nanotubes.

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A New Conducting Charge Transfer Complex from a Model Thiophene Oligomer and a Keggin-Type Heteropolyanion**

By Bruno Fabre and Gérard Bidan*

The polythiophene family has been widely investigated as a typical class of conducting polymers because of their excellent stability and high conductivity. This family can include dopant anions, such as Keggin-type heteropolyanions (HPAs) $[\text{XM}_{12}\text{O}_{40}]^{n\ominus}$ ($\text{X} = \text{P}, \text{Si}$; $\text{M} = \text{W}, \text{Mo}$ and $n = 3, 4$).^[1] These inorganic and voluminous compounds give new properties to the conducting polymer to which they are linked (multiple redox exchanges, paramagnetism, electrochromism, catalysis, etc.). The material poly(3-methylthiophene) doped with $\text{PMo}_{12}\text{O}_{40}^{3\ominus}$ is very interesting because of the overlap in potential of the redox activity of both partners, which may result in the formation of a charge transfer (CT) complex between the conducting polymer and its dopant.^[2–4]

CT salts of the TTF/TCNQ family are well known and exhibit conducting properties ($\sigma_{298\text{K}} = 6 \times 10^5 \text{ S cm}^{-1}$).^[5–7] Compared to these synthetic metals, ones based on one-electron organic donor molecules with inorganic clusters, possibly in the mixed-valence state, have not been studied extensively. Recently, CT compounds derived from TTF and an inorganic acceptor such as a Keggin-type HPA: $\text{PMo}_{12}\text{O}_{40}^{3\ominus}$ (PMo_{12}) or $\text{PW}_{12}\text{O}_{40}^{3\ominus}$ (PW_{12}) have been prepared. They exhibited interesting conductivities: $\sigma_{298\text{K}} = 1.7 \times 10^{-2} \text{ S cm}^{-1}$ for a TTF/ PMo_{12} salt^[8] and $\sigma_{298\text{K}} = 3 \times$

$10^{-2} \text{ S cm}^{-1}$ for a TTF/ PW_{12} salt.^[9] The desire to prepare CT systems with increased dimensionality of structural, and hence electrical, properties has been prevalent in the work of many groups. This stems from the fact that the superconducting salts of $\text{TMTSF}^{[10–12]}$ and $\text{BEDT-TTF}^{[12–14]}$ were quickly recognized to be two-dimensional materials, not one-dimensional like TTF/TCNQ.

For molecules much longer than these donors, such as conducting polymers, the formation of CT complexes with organic electron acceptors has not been widely investigated. In the case of TCNQ-doped polypyrrole, the interaction between the polymer and the dopant can be either a charge transfer from the polymer backbone to a TCNQ molecule, creating a TCNQ anion, or the reaction of the nitrile group ($-\text{CN}$) of TCNQ with the hydrogen-deficient nitrogen site of the polymer backbone, creating a $-\text{N}=\text{C}=\text{N}-$ group.^[15]

The spontaneous reaction of polyaniline with organic acceptors, such as tetracyanoethylene (TCNE), *p*-benzoquinone (BQ) or TCNQ provides donor–acceptor CT complexes, although CT bands have not been found clearly and their conductivities are reported to be very low (10^{-9} to $10^{-4} \text{ S cm}^{-1}$).^[16] It appears that a CT complex between a polymer and its dopant anion has not yet been well defined.

We report in this paper the chemical synthesis and the characterization of a CT complex between the sexithienyl radical cation and a Keggin-type HPA.

Due not only to their well-defined chemical structure, chain and conjugation length, but also to their superior solubility and processability, conducting oligomers typified by oligothiophenes are ideal model compounds of the corresponding conducting polymer. Moreover, the fact that these oligomers give stable cation radicals and dications reveals the interest in considering these molecules as electron donors to prepare new CT complexes with organic or inorganic acceptors. Complexes prepared from α -conjugated oligothiophenes and TCNQ have been obtained in the form of

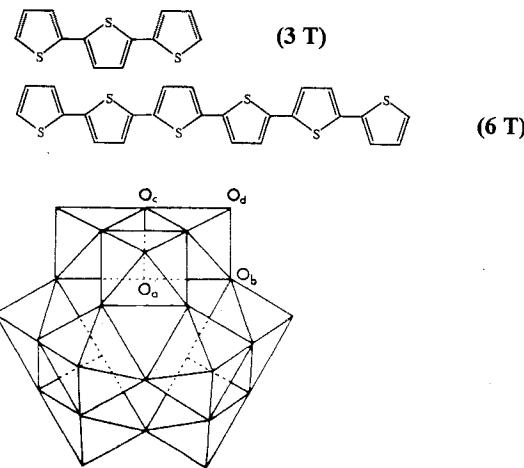


Fig. 1. Top) Chemical structures of the α -conjugated thiophene oligomers used in this study: 3T: thiophene trimer, 6T: thiophene hexamer. Bottom) Coordination polyhedron as a representation of the $\alpha\text{-PMo}_{12}\text{O}_{40}^{3\ominus}$ structure, the fourth Mo_3O_{13} set, the PO_4 tetrahedra are not shown for clarity [26].

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