Nano-octopus: A New Form of Branching Carbon Nanofiber

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A new multibranched octopus-type structure of carbon nanofibers is synthesized from a natural precursor, camphor, by a thermal chemical vapor deposition technique. An alloy of Cu:Ni catalyst is prepared by electrochemically coating nickel on a copper sheet, with nickel sulfate as an electrolyte, and heating that nickel-coated copper sheet to a higher temperature. Deposition of carbon on these substrates leads to the formation of a branched nanostructure in the temperature range of 923 K to 1023 K. The fiber diameter increases from 30 nm to 250 nm with increasing pyrolysis temperature. Detailed morphology and the internal structure of these fibers are studied by scanning and transmission electron microscopy.

Keywords: Camphor, Branched Nanofibers, CVD, Ni:Cu Alloy.

Branching structure is a new interest in nanoscience.[1–4] In recent days many types of carbon nanomaterials have been synthesized, either by arc vaporization or by chemical vapor deposition.[5–8] Their potential applications are well recognized in many promising fields.[9–11] The structure of these nanocarbons has been found to be very sensitive to the reaction conditions and catalyst preparations. So finding deposition parameters for synthesizing a particular nanostructure is a quite difficult task. Here we report the formation of branched carbon nanofibers with very high density and in a wide temperature range of deposition. Another striking feature of this study is the use of a natural hydrocarbon precursor, camphor, ($C_{10}H_{16}O$), for the formation of these carbonaceous materials. The camphor tree, native to Asia, is found in many parts of the world and cultivated successfully in subtropical countries, such as India, Australia, and Ceylon. It has been thriving in Egypt, Formosa, Madagascar, the Canary Islands, southern Europe, California, Florida, and Argentina. So this natural precursor can replace any fossil-related hydrocarbon for the synthesis of carbon materials. The same precursor has previously been used for the synthesis of fullerene,[12] carbon nanobeads,[13] and carbon nanotubes.[14]

As a catalyst is an important control factor for the production of carbon nanomaterials, here we have coated a 0.15-mm-thick copper sheet electrochemically with nickel, with the use of nickel sulfate as an electrolyte. This nickel-coated copper sheet acts as a substrate for the growth of carbon nanomaterials. The deposition was done in a dual-furnace system, in which precursor (camphor) and substrate were kept inside a quartz tube in the first and second furnace zones, respectively. Before the second furnace was heated to a set temperature, the whole reaction tube was purged with nitrogen gas for 15 to 20 min, and then camphor (1 g) was vaporized when the temperature of the first furnace was raised to 473 K. The vaporized camphor molecules are pyrolyzed in the high-temperature zone of the second furnace and form a branched nanostructure in the presence of nickel-coated copper catalyst. The carbon deposits are collected and examined with a Topcon (ABT-150F) scanning electron microscope and a Hitachi (HU-12A) transmission electron microscope.

In Figure 1a, b, and c we show nanofibers grown on a nickel-coated copper sheet by the pyrolysis of camphor at temperatures of 923 K, 973 K, and 1023 K, respectively. In the image, bright spots are catalyst particles that are lifted from the substrate. The substrate temperatures taken in this deposition are sufficient to break up nickel islands formed in the electrochemical coating into Ni nanoparticles, which leads to the formation of branched nanofibers. With increasing pyrolysis temperature, diameters of these fibers are found to increase from 30 nm to 250 nm. Li et al.[15] have reported a more complex method of preparation of Ni:Cu:Al catalyst for the growth of branched carbon fibers and nanotubes from a methane and nitrogen mixture. But those fibers were not uniform in a wide range of temperatures. Gan et al.[16] have reported the production, with another deposition technique (HFCVD system), of branched carbon nanotubes in the presence of copper catalysts. This reveals that the presence of copper plays an important role for branched structures. However, the

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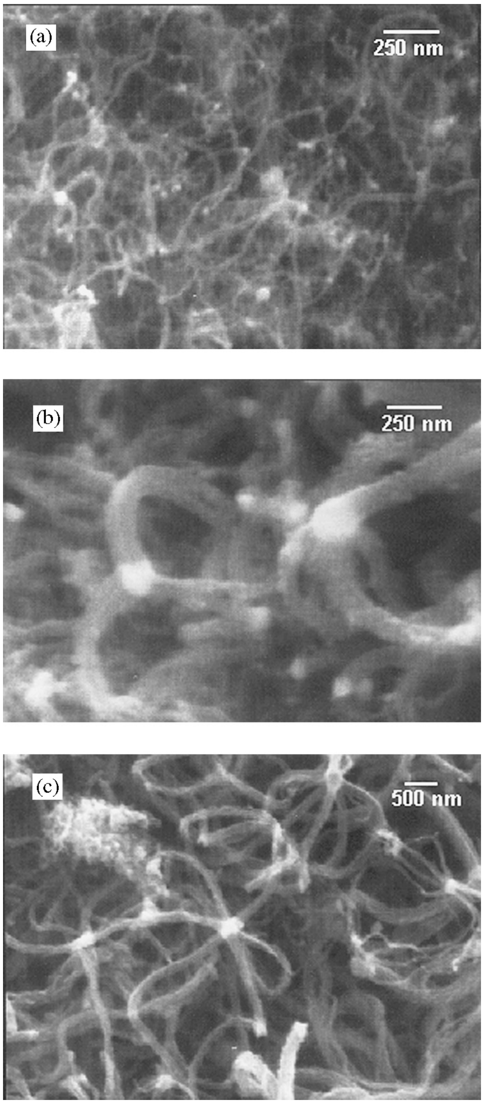

Fig. 1. SEM images of branched carbon fibers obtained at temperatures of (a) 923 K, (b) 973 K, and (c) 1023 K.

method of catalyst preparation and deposition parameters greatly influence the structure of the resulting product. Adveeva et al.[17] have also reported this kind of branched fiber, but under conditions different from those reported here. In this study, uniform branched nanofibers are found on the substrate at all of the deposition temperatures. This may be due to the formation of Ni:Cu alloy at the surface of nickel-coated copper at high temperatures, which has been confirmed by XRD. The presence of aluminum in the catalyst does not have any effect on the formation of branched structures. But the present electrochemical coating of copper substrates is a much simpler method of obtaining Cu:Ni alloy for the synthesis of branched nanofibers. Moreover, the growth of branched structures from Ni:Cu alloy does not completely follow traditional growth mechanisms of carbon nanofibers,[18] that is, neither the base-mode nor the tip-mode growth mechanism. Our observation suggests that these fibers probably first grow by the tip-growth mechanism, lifting up the catalyst particle, and then the lifted catalyst particle acts as a multidimensional nucleation center that forms many branches. Otherwise, it may happen that many branches emerge from the catalyst particle at the beginning of growth. However, more evidence is sought to support this idea.

In recent years, both multijunction[19] and Y-junction[3, 16, 20–22] carbon nanotubes have been reported. But nowhere have catalyst particles been observed at the junction of nanotubes. The presence of five- and seven-member rings at the junction leads to negative curvature of Y-junction carbon nanotubes, but their exact mechanism is still unknown. It is quite difficult to predict the effect of only catalyst in the formation of branched nanostructures ignoring the role of other stringent deposition parameters. Nevertheless, in the present studies, catalyst particles are essentially observed at the junctions supporting the results reported by Li et al.[15]

Figure 2 shows transmission electron micrographs of multibranched carbon fibers of octopus-type growth. Here the term “octopus” is symbolic and should not be considered as really eight-armed. Usually these are five- to six-armed structures with an appearance that approximates that of an octopus. A new feature, which was not clearly distinguished in the scanning electron microscope, is that the arm of this so-called octopus is not a single arm but a bunch of many fine fibers, self-organized into a rope-like structure. The magnified TEM image (Fig. 2b) reveals this feature. To look into the crystal structure of these fibers, while taking the TEM images, we took a selected area diffraction pattern of the same. Clear rings observed in its diffraction pattern (inset of Fig. 2b)

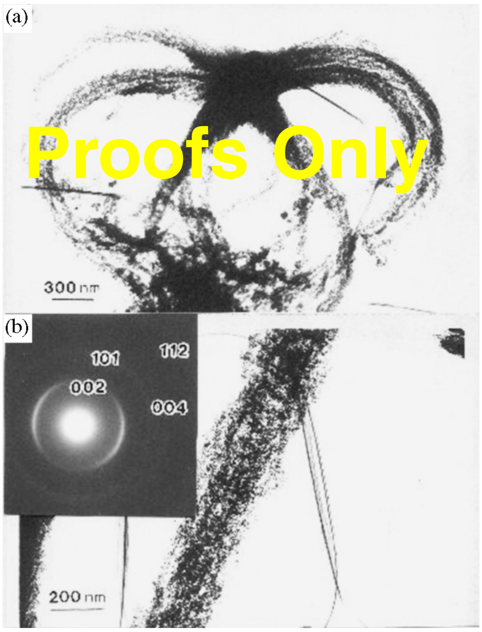

Fig. 2. TEM images of (a) branched octopus-type fibers and (b) an arm of fibers (inset, SAD pattern).

suggest that these fibers possess considerable polycrystallinity. By measurement of the ring diameters and the TEM camera length, the concentric rings around the central bright spot were indexed as graphite's (002), (101), (004), and (112) planes, respectively.

In summary, octopus-like branched carbon fibers are obtained from a natural precursor, camphor, by a simple thermal chemical vapor deposition method. Each arm of these fibers can be seen as a well-organized rope of nanofibers. The multifaced branching of these crystalline fibers is attributed to the use of electrochemically catalyst-coated substrate. With increasing pyrolysis temperature, the fibers diameter tends to increase from 30 nm to 250 nm. This leads to the possibility of growing thinner nanofibers at still lower temperatures, with further optimization of other preparative conditions.

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