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RESEARCH ARTICLE

Y-Junction Multibranched Carbon Nanofibers

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Multibranched carbon nanofiber (CNF) is produced by a thermal chemical vapor deposition method using camphor as precursor. Nickel and cobalt catalyst was deposited on silicon substrate by e-beam evaporation and used as substrate for the growth of carbon nanomaterials. Branched carbon nanofibers were grown on the nickel thin film at 900 °C, whereas spherical carbon beads formed on the cobalt thin film. These fibers followed base growth mechanism devoid of any catalyst particle at the tip of fibers.

Keywords: Y-Junctions, Carbon Nanofibers, CVD, Camphor.

1. INTRODUCTION

Branched nanostructure has great potential for use in nanoelectronic devices. The rectification behavior and ballistic switching property of Y-junctions have been theoretically and experimentally studied.[1–3] For the device perspective, controlled and high-yield production of Y-junctions is required. Although a template gives a more uniform Y-junction by CVD, pyrolysis of hydrocarbon in the presence of catalyst can only produce multiple Y-junctions along with a single nanotube or nanofiber. Occasionally these Y-junction carbon nanotubes (CNTs) are formed as a byproduct while synthesizing carbon nanotubes. Successful efforts have been made to increase their yield by Rao et al.[4,5] Branching in CNT occurs due to the topological defects at the junction, i.e., introduction of pentagonal and heptagonal rings in a hexagonally made CNT.[6] Formation of such pentagonal and heptagonal rings during pyrolysis probably needs a crucial parameter, which drives the creation of more junctions in the CNT/CNF. Hence, synthesis of any specific nanostructure needs sensitive reaction parameters. Camphor has been used to synthesize different forms of carbon, viz., fullerene, CNTs, octopus shaped nanofibers, etc.[7–9] In addition, since camphor is a natural precursor and contains both pentagonal and hexagonal rings, it could be an appropriate choice of precursor for Y-junction CNT/CNF.

In this paper, we report the formation of very high yield (~90%) multibranched carbon nanofibers along with very few straight fibers without any amorphous or other carbon structures. There is no such report of the formation of multibranched carbon nanofibers to the best of our knowledge. All previous reports on the junction were based on carbon nanotubes.

2. EXPERIMENTAL DETAILS

Two electric furnaces were used for the purpose, where one furnace was used to vaporize camphor and the other for pyrolysis of camphor vapors over catalyst-supported substrates. Nickel and cobalt metal of thickness 100 nm was coated on a silicon (100) substrate by the e-beam evaporation method. This silicon substrate was used as a catalyst. Known weight of camphor was taken and vaporized slowly. Pyrolysis of vaporized camphor gas was carried out at 900 °C over the catalyst-coated substrate for 30 min in a hydrogen and argon (1:3) at atmospheric pressure. After pyrolysis, the furnace was cooled to room temperature in an argon atmosphere, and the sample was taken out for characterization. SEM study of samples was carried out with a JEOL machine (Model JSM 840). TEM analysis was done with TECNAI G2 12 at an accelerating voltage of 120 kV.

3. RESULT

Figures 1a, b shows SEM images of carbon materials grown from camphor (30 g) on nickel- and cobalt-coated silicon substrates after 30 min of pyrolysis at 900 °C,

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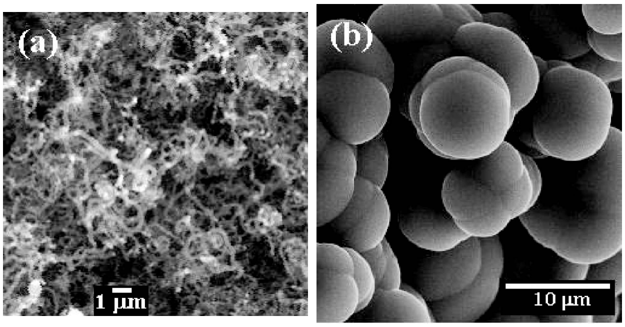

Fig. 1. SEM images of branched carbon nanofibers on nickel-coated Si substrate (a); merged carbon beads formed on cobalt-coated Si substrate (b) after 30 min of pyrolysis.

respectively. A dense growth of CNFs was observed when the nickel-coated substrate was used, whereas the cobalt catalyst produced merged carbon beads. Pyrolysis of vaporized camphor gas for a short time (5 min) taking 2 g of camphor produced carbon fibers in the presence of nickel catalyst but with a less density. Instead of merged carbon beads, isolated small size (diameter 0.5–1.0 μm) carbon beads formed on the cobalt-coated substrate in a short pyrolysis process (5 min).

Figure 2 shows TEM images of branched carbon fibers at different magnifications. The diameter of these carbon fibers was in the range 80–100 nm (length could not be measured). All the fibers formed in this case had a branched structure. A few of these fibers were almost nanotube type, having a clear inner diameter of around 25 nm and the same outer diameter of 80–100 nm as fibers. Branching occurred uniformly and at regular intervals (∼50–100 nm). In a few places, branching continued and measurement was difficult because the electron beam may not be exactly perpendicular to the plane of the branches.

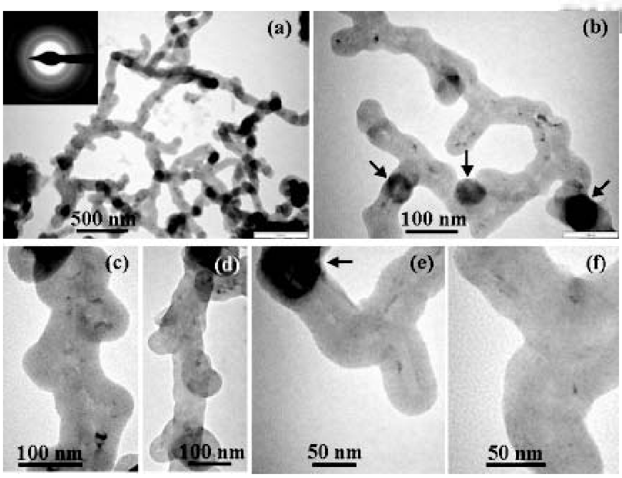

Fig. 2. TEM images of branched carbon nanofibers at a lower magnification (a, b), images at the commencement of branching (c, d), and higher magnification image at the junction (e, f). The inset of (a) shows a SAD pattern indicating the polycrystalline nature of these fibers.

Moreover, this kind of multiple branching at quite regular intervals on a single CNF suggests possible multitunnel devices.[6] Figures 2c, d shows that accurate angle branching occurred (of Fig. 2b). But on the average, the branched fiber was not found to grow more than 200 nm from the base of the main CNT/CNF stem. The contrast black portions shown with an arrow in Figures 2b, e are branched fibers parallel to the electron beam of the TEM, which shows that branched arms were growing in every direction from the main CNF trunk. This thickness contrast should not be confused here with a catalyst particle inside the CNT/CNF, because the selected area diffraction (SAD) pattern and magnified image at this place did not shows any catalyst particle. The angle between each branch was nonuniform in the present study. It varies from 45′ to 120′ to the inception of branching. Figures 2e, f shows a magnified image at the junction of the fiber. These branching fibers may find better application in composites, where they can hold and lock other fibers like a network with enhanced mechanical properties.

Use of conventional catalysts (Ni, Fe, and Co) and precursors (benzene, methanol, acetylene, etc.) occasionally produced a junction or kink in carbon nanostructures, whereas most of the time straight carbon tubes or fibers are grown from these catalysts and precursors. A good yield of branched structures has not been reported, without sensitive reaction conditions. Rao et al. and Zhu et al. consider thiophene to be a critical factor in the formation of Y-junction nanotube,[5, 10] whereas Gan et al. believed copper is the main catalyst for the formation of Y-junction CNTs.[11] However, in the present study, branched CNFs were formed in the absence of both thiophene and copper. So it is not correct to give a single reason behind the formation of Y-type junction. In contrast to all previous studies, the occurrence of branching in this case is rampant and at regular intervals. Like all other previous results and unlike Li et al.,[12] there were neither catalyst particles at the junction center of the branched structure nor at the tip of fibers in the present study.

It has been widely accepted that pentagonal and heptagonal rings are required to create defects in CNT/CNF, which leads to formation of junctions in CNTs. Almost all precursors used so far by others are either aliphatic hydrocarbon gases or aromatic solvent and do not contain 5- or 7-membered rings in their mother structure. So there is less possibility for the formation of 5- and 7-membered rings from those precursors. As a result they had to use stringent reaction conditions to help the formation of 5- and 7-membered rings. Camphor, on the other hand (used in the present study), has two pentagonal and one hexagonal ring. So little extra effort is needed to form 5- and 7-membered rings. Figure 3 elucidates the formation of 5-, 6-, and 7-membered carbon rings from camphor. Hence, it has been possible to grow these Y-junction branched CNFs easily with camphor.

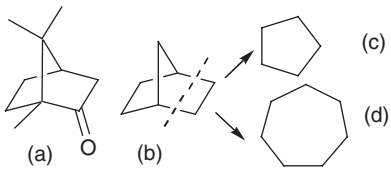

Fig. 3. A camphor molecule (a), a 7-membered skeleton after removal of all side chains (b), on expelling two side carbon atoms from "b" pentagon forms (c), on rearrangement of 7-membered "b" can give a heptagon (d), and on expelling the top carbon of the "b" hexagon remains (not shown in figure). These three 5-, 6-, and 7-membered rings are building block of Y-junction CNFs.

4. CONCLUSION

It has been shown possibility to synthesize in high yield branched carbon nanofibers from a natural precursor "camphor." These branched fibers don't contain the catalyst. A mechanism is proposed to suggest the formation of 5-, 6-, and 7-membered rings from camphor, which drives the junction formation during the growth process.

References and Notes

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