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Two opposite growth modes of carbon nanofibers prepared by catalytic decomposition of acetylene at low temperature

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Abstract Helical carbon fibers were synthesized by the catalytic decomposition of acetylene as carbon source at low temperature of 240–260 °C with two nanocopper catalysts prepared by the hydrogen-arc plasma method and thermal decomposition of copper tartrate. Two growth modes for helical carbon fibers were obtained. One is mirror-symmetric growth mode, and the other is asymmetric growth mode. In the two growth modes, there were always only two helical fibers in regular shapes that were grown over a single copper nanoparticle. The two helical fibers had identical coil diameter, coil length, fiber diameter, cycle number, tight coil pitch, and cross section. In mirror-symmetric growth mode, the two helical fibers had absolutely opposite helical senses. The catalyst particle size was less than 50 nm and the coil diameter was <100 nm. Whereas in asymmetric growth mode, the two helical fibers had absolutely identical helical senses. The catalyst particle size was larger than 200 nm and their coil diameters reached 1 μm. The catalyst particle size had considerable effect on the growth mode for helical carbon fibers.

Introduction

Coiled carbon nanofibers and carbon nanotubes have attracted much attention due to their potential applications and remarkable electronic, magnetic, chemical, physical, thermal, and mechanical properties [1–10]. Since the discovery of carbon nanotube by Iijima in 1991[11], a good many methods have been applied for the growth of carbon nanomaterials. It is obvious that the types and particle size of catalysts, types of carbon resources, and reaction temperature may greatly affect the growth process of carbon nanofibers. Among these growth conditions, types and particle size of catalysts would undoubtedly play a key role to affect the structure properties of carbon nanofibers. Highly crystalline nanofibers with controlled structure may be prepared over Fe and Fe–Ni alloy catalysts [12]. The incorporation of as little as 2% copper into the cobalt could create a major modification in the conformation of the carbon nanofibers [13]. Very regular single-helix carbon microcoils were prepared by the WS_2-catalyzed pyrolysis of acetylene in the presence of thiophene impurity. The effects of reaction temperature and thiophene gas flow rate on the growth of single-helix carbon microcoils and the morphology were examined in detail [14]. Baker et al. [15] reported the fabrication of twisted carbon filaments with a symmetric growth style formed from acetylene on Fe/Sn alloy particles at temperatures >1,073 K. Hansen et al. [16] reported that copper nanocrystals would undergo dynamic shape changes in response to changes in the gaseous environment and that the shape changes were caused by adsorbate-induced changes in surface energy and by changes in the interfacial energy. Gorbunov et al. [17] argued the role of catalytic metal nanoparticle size in the synthesis of single-wall carbon nanotubes. The effect of Ni crystal size on the growth of carbon nanofibers prepared by catalytic decomposition of methane has been studied [18].

In this article, we report the synthesis of helical carbon fibers synthesized by the catalytic decomposition of acetylene with two nanocopper catalysts prepared by different

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methods. Two opposite growth modes for helical carbon fibers obtained were described in detail.

Experimental

Nanocopper catalysts used in this study were prepared by two methods as follows:

Copper tartrate catalyst precursor

In a typical experiment, 100 mL copper dichloride aqueous (0.01 M) was slowly added to 100 mL of 0.01 M sodium–potassium tartrate aqueous solution under vigorous stirring. A light blue precipitate (copper tartrate) was formed. The obtained precipitate was filtered and washed with anhydrous ethanol. After washing, the copper tartrate was dried in a furnace at 110 °C for 1 h, then allowed to cool to room temperature.

Hydrogen-arc plasma method

The metal nanoparticle manufacturing apparatus used consists of the following parts [19]: (I) a stainless steel vacuum chamber that is cooled by circulating water; (II) a water-cooled and rotatable copper anode, on which the derby to be evaporated is placed; (III) a water-cooled and moveable tungsten cathode; (IV) a cold surface collector; (V) a gas flow system; (VI) two stage vacuum pump system; and (VII) a DC power supply. Before preparation, the vacuum chamber was pumped to 10^{-3} Pa, then backfilled with a working gas (hydrogen/argon mixture). The arc plasma was initiated and the copper billet was melted and evaporated by the high temperature of the plasma. The nanoparticles were formed by the nucleation and growth processes through collision of the metal atoms with gas atoms (molecules).

The decomposition of acetylene was carried out with a special apparatus at atmospheric pressure, which consists of a horizontal quartz tube heated from the outside through an electric furnace, an intelligent temperature control system, and tail gas system. The catalyst was placed in a ceramic plate, which was situated at the middle of the tube. The fiber growth occurred at 240–260 °C.

The morphology and microstructure of the carbon nanofibers were studied by TEM. For TEM analysis, the sample after ultrasonic dispersion in ethanol was deposited on a copper grid, which was coated with a carbon film. TEM was carried out on a JEOL JEM-2000EX operating at an accelerating voltage of 160 KV.

Results and discussion

The representative transmission electron microscope (TEM) images of regularly helical nanofibers with a “V”-type symmetric growth mode are shown in Fig. 1a and b. As can be seen from Fig. 1a, there are only two helical nanofibers symmetrically grown over a single rhomb-shaped nanocopper particle derived from the thermal decomposition of copper tartrate, which is about 50 nm in size. The two helical nanofibers have absolutely opposite helical senses, namely, one is left-handed coiled, the other is right-handed coiled, but they are identical in coil diameter, coil length, fiber diameter, cycle number, tight coil pitch, and cross section. Therefore, we conclude that the two helical fibers follow a mirror-symmetric growth mode. This mirror-symmetric growth mode is induced by the shape changes in nanocopper particles during catalyzing the decomposition of acetylene, namely, the nanocopper particles used as catalyst underwent a change from an irregular to a regular faceted form after fiber growth, and

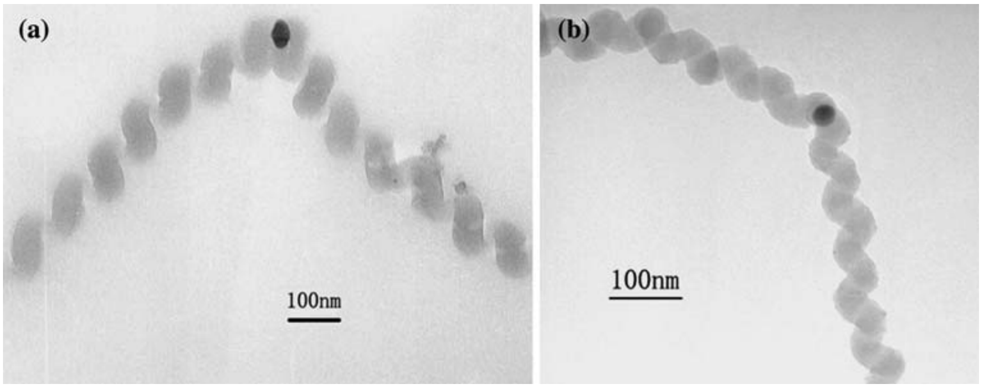

Fig. 1 TEM images of regularly helical nanofibers, symmetrically grown on a single nanocopper particle derived from the thermal decomposition of copper tartrate. (**a**) rhombic and (**b**) circular nanocopper particles

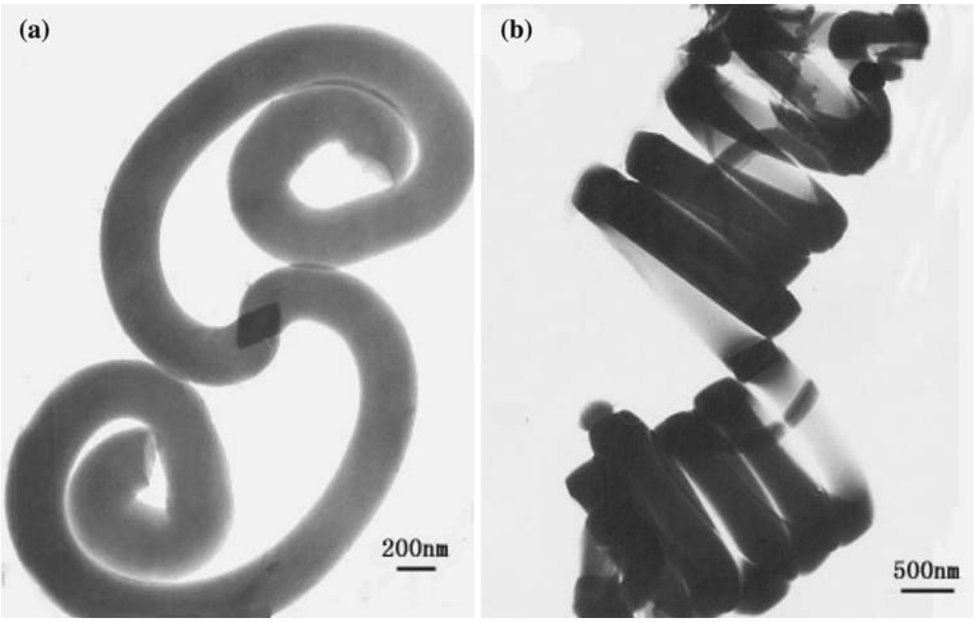

Fig. 2 Helical carbon fibers with identical helical senses and a large coil diameter (copper nanocatalysts are prepared by hydrogen-arc plasma method). (**a**) parallelogrammic and (**b**) rectangular copper nanoparticles

the shape changes were caused by the changes in surface energy resulting from the acetylene-adsorption on the nanocopper particles. Surprisingly, the fiber diameter of the coiled nanofibers is approximately equal to the size of the nanocopper particle responsible for their growth, but the coil diameter of about 100 nm has size about twice as much as the nanocopper particle.

In contrast with Fig. 1a, b shows that the nanocopper particle derived from the thermal decomposition of copper tartrate, over which two helical nanofibers symmetrically grown, is circular in shape. The particle size is about 30 nm, which is approximately equal to the fiber diameter of the coiled nanofibers, and the coil diameter is about 60 nm. Further investigation revealed that most nanocopper catalyst particles in the node of two helical nanofibers with mirror-symmetric growth mode were <50 nm in size, and the coil diameter was <100 nm. Therefore, it can be inferred that apart from the shape changes in copper nanoparticles during catalyzing the decomposition of acetylene, the small size of the nanocopper catalyst particles is also responsible for the mirror-symmetric growth mode. Namely, the symmetrical growth mode depends on the catalyst particle size, and dominates when the catalyst particle size is <50 nm.

Figure 2a and b present helical fibers with identical helical senses and a large coil diameter, which were synthesized by the catalytic decomposition of acetylene with nanocopper catalysts prepared by hydrogen-arc plasma method. In Fig. 2a, we can see clearly that there are only two helical fibers grown over a single parallelogram shaped nanocopper particle, which is about 220 nm in size, whereas the coil diameter is much larger than the particle size and reaches about 1 μm. Similarly, the two helical fibers possess the same coil diameter, coil length, fiber diameter, cycle number, tight coil pitch, and cross section. Most important of all, it must be noted that the helical senses of the two coiled fibers are identical, as the two fibers coil right-handedly. Therefore, we conclude that the two helical fibers follow an asymmetric growth mode. As is shown in the Fig. 2b, the rectangle-shaped copper nanoparticle reaches about 500 nm in size, and their coil diameters are also about 1 μm. Compared with Fig. 2a, the two helical fibers shown in Fig. 2b coil left-handedly. The catalyst particle size plays a key role in the production of carbon nanofibers. Chen et al. [18] reported that Small Ni crystals would yield a low growth rate and fast deactivation, and thus a low final yield of carbon nanofibers, and large Ni crystals would reduce the growth rate due to low surface area. An optimum growth rate and yield of carbon nanofibers could be achieved on optimally sized Ni crystals around 34 nm. Ermakova et al. [20] reported that the yield of filamentous carbon prepared by methane decomposition was possibly related to the average size of the Ni catalyst particles, and that the maximum yield was obtained at a distribution in grain size ranging from 20 to 60 nm. Otsuka et al. [21] reported that the Co catalysts prepared carbon nanofibers with relative diameters from 10 to 30 nm through the reaction at 773 K irrespective of the kind of catalytic supports.

From the above results, we found that even though the shape of single catalyst particles was not identical, the two helical fibers grown on it were still helical and had a mirror-symmetric growth mode or asymmetric growth mode. Therefore, the shape of catalyst particles was not the determinating factor that caused the growth modes of the two helical fibers. It is obvious that the nanocopper particle size has a considerable effect on the helical senses of grown helical nanofibers.

Conclusion

Nanocoppers as catalysts were derived from the thermal decomposition of copper tartrate and prepared by the hydrogen-arc plasma method. Regularly helical carbon nanofibers with two growth modes were synthesized by the decomposition of acetylene with these resultant nanocopper catalysts. There were always only two helical fibers grown on a single copper catalyst particle. It is found that copper particles with diameters <50 nm grew carbon nanofibers with the mirror-symmetric growth mode, while ones from 220 to 500 nm in diameters grew carbon nanofibers with the asymmetric growth mode. The size of the nanocopper particle as catalyst for fiber growth is an important factor that determines the growth mode of helical carbon fibers.

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