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Low-temperature synthesis of carbon nanofibers by decomposition of acetylene with a catalyst derived from cupric nitrate

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ABSTRACT

Carbon nanofibers have been synthesized by the thermal decomposition of acetylene with a copper nanocatalyst derived from cupric nitrate trihydrate at a low temperature of 260 °C. The resultant carbon nanofibers were characterized using transmission electron microscopy and X-ray power diffraction. The copper nanoparticles changed from initial irregular shapes to regular shapes during the growth of nanofibers. The copper nanoparticle size has a considerable effect on the morphology of carbon nanofibers. Helical carbon nanofibers with a symmetric growth mode were grown on copper nanoparticles with a grain size less than 50 nm. When the catalyst particle size was in the range of 50–200 nm, straight carbon nanofibers were obtained dominantly.

1. Introduction

Carbon nanofibres and carbon nanotubes, as the important carbon materials, have attracted much attention due to their potential applications as hydrogen storage [1], electromagnetic wave absorber [2], electrodes [3,4], filter media [5], catalyst supports [6], electron sources [7,8], electronic and mechanical devices [9,10], fuel cell [11,12], building blocks [13], helical sensors [14] and templates [15]. Since the discovery of carbon nanotubes by Iijima in 1991 [16], many methods have been applied for the growth of carbon nanomaterials. Among growth conditions of carbon nanofibers, types and particle sizes of catalysts undoubtedly play a key role in the structures of carbon nanofibers. Carbon fibers are usually synthesized by the high-temperature catalytic decomposition of hydrocarbons with metallic catalysts such as Fe, Co, and Ni [17–23], or their alloys [17,24]. In addition, nickel–copper–aluminum takovite [25], mixture of $Ni(OH)_2$–$Mg(OH)_2$ [26], ferrocene [27], copper tartrate [28], and cobaltocene [29] have been used as catalyst precursors. In this work, we report a simple approach to carbon nanofibers by the decomposition of acetylene with a copper nanocatalyst derived from cupric nitrate trihydrate at a temperature as low as 260 °C. Two morphologies (helical and straight) of carbon nanofibers were obtained.

2. Experimental

For the synthesis of carbon nanofibers, cupric nitrate trihydrate (analytical pure) was used as a catalyst precursor. Acetylene was used as the carbon source. The decomposition of acetylene was carried out with a special apparatus at atmospheric pressure, which consists of a horizontal quartz tube (9 cm in diameter, 90 cm in length), an intelligent temperature control system and tail gas system. The catalyst precursor was placed in a ceramic boat, which was situated at the middle of the reaction tube. When the tube was pumped to 10^{-3} Pa, acetylene was introduced into the reaction tube and temperature was raised from room temperature to temperature of 260 °C with a heating rate of 15 °C/min. The fiber growth was carried out for 30 min. The resultant carbon nanofibers were characterized using transmission electron microscopy (TEM) and X-ray power diffraction (XRD). The TEM analysis of carbon nanofibers was carried out on a JEOL JEM-2000EX operating at an accelerating voltage of 160 KV. The XRD pattern was detected by a Philips X'Pert MPD diffractometer using Kα radiation.

3. Results and discussion

Fig. 1 shows the typical TEM image of as-prepared regularly helical nanofibers with a symmetric growth mode. The following characteristics of the helical carbon nanofibers were discovered. First, there are always only two helical nanofibers symmetrically grown over a single catalyst nanoparticle, which is below 50 nm in size (30 nm in Fig. 1). According to our TEM observation, the

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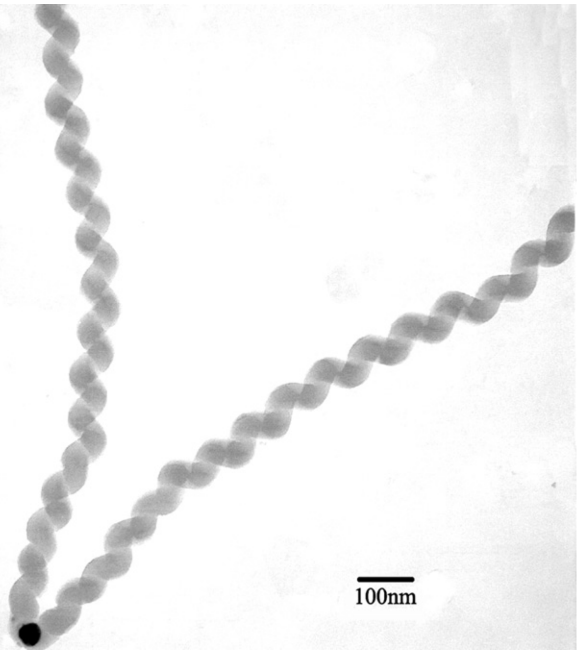

Fig. 1. TEM image of typical helical carbon nanofibers.

majority of these catalyst nanoparticles located at the nodes of two helical nanofibers have rotundity-shapes and a grain size of less than 50 nm. Second, the two helical nanofibers have absolutely opposite helical senses, one is left-handed coiled, and the other is right-handed coiled. Third, the two helical nanofibers are identical in coil diameter, coil length, fiber diameter, cycle number, coil pitch and cross section. Finally, the fiber diameter of the helical nanofibers is approximately equal to the grain size of the nanocatalyst particle responsible for their growth, but the coil diameter almost twice the size of the catalyst nanoparticle. Therefore, based on the information mentioned above, we conclude that the two helical fibers follow a mirror-symmetric growth mode. Ding et al. [24] reported that the carbon nanocoils had specific growth characteristics closely related to the symmetroid or surface symmetry of the Ni–P and Ni–X–P (X = W, Co, Cu) alloy catalyst particles. Kim et al. [30] used electron tomography to study the 3D structures of helical or zigzagged GaN, $ZnGa_2O_4$, and Zn_2SnO_4 nanowires. They found that the GaN nanowires adopted a helical structure that consists of six equivalent <0 1 1 1> growth directions with the axial [0 0 0 1] direction. They also confirmed that the $ZnGa_2O_4$ nanosprings had four equivalent <0 1 1> growth directions with the [0 0 1] axial direction.

In addition to the typical helical nanofibers, several special morphologies were observed. Fig. 2 shows the TEM image of two helical nanofibers with different coil pitches symmetrically grown over a single nanoparticle. Compared with the typical helical nanofibers shown in Fig. 1, the two helical nanofibers have different coil pitch. The two nanofibers both have 11 coils. From 1 to 4 coils (numbered from the catalyst particle), each fiber has tight coil pitch, from 4 to 11 coils, their coil pitches become looser. No matter how loose their coil pitches become, the two nanofibers follow a mirror-symmetric growth mode, namely, they are identical in coil pitch in the same position. In our experiment, the helical reversals were also observed. As shown in Fig. 3A, the two helical nanofibers both have two helical reversals (denoted by arrows), which appear at the coil position of the same cycle number. Interestingly, a few very long (1–1.5 μm) and straight sections appear in the helical nanofibers. As can be seen from Fig. 3B, there are several frequent helical reversals in two fibers. When the helical reversals are at slow rate, it would give rise to long and straight parts.

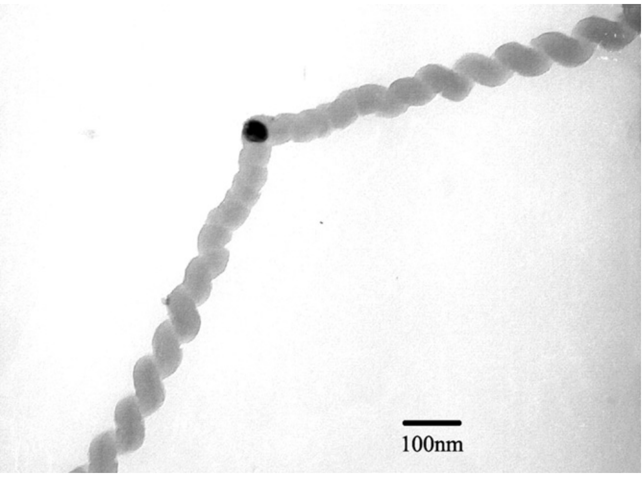

Fig. 2. TEM image of two helical nanofibers having different coil pitches.

In order to investigate the microstructure of the catalyst particles, a lower reaction temperature was chosen, i.e., the temperature was raised from room temperature to 220 °C. After being cooled, the catalyst samples were then examined using TEM and XRD. Fig. 4 shows the microstructure of the nanoparticles obtained from the thermal decomposition of the cupric nitrate trihydrate crystal under acetylene atmosphere at 220 °C. The XRD pattern of these catalyst nanoparticles is shown in Fig. 5. XRD analysis of these nanoparticles shows the standard copper reflections, indicating that the sample is highly crystalline. No peaks due to impurities were found. As can be seen from Fig. 4, these copper nanoparticles show irregular shapes. Compared with these copper nanoparticles on which two helical nanofibers symmetrically grow, it is obviously that the copper nanoparticles changed from initial irregular shapes to regular shapes during the course of reaction and the shape changes were caused by the changes of surface energy resulting from the acetylene adsorption on the catalyst. Fig. 6 shows the schematic diagram of growth mechanism of helical nanofibers. The mechanism of morphological changes of copper catalysts and the growth of carbon nanofibers are proposed in five steps: (1) the dehydration of cupric nitrate trihydrate, (2) the decomposition of cupric nitrate into Cu oxide, (3) the reduction of Cu oxide, (4) the formation of Cu nanoparticle before the growth of carbon nanofibers, and (5) the reaction with acetylene for the growth of carbon nanofibers. Hansen et al. [31] reported that copper nanocrystals would undergo dynamic reversible shape changes in response to changes in the gaseous environment, and the shape changes were caused both by adsorbate-induced changes in surface energies and by changes in the interfacial energy. They found that gas adsorption on the surface of Cu nanoparticles and the surface energy of different crystallographic planes of a single crystal were the main driving force for the gas-induced surface reconstruction and reshaping of the Cu nanoparticles. In a small metal particle, surface energies associated with different crystallographic planes are usually different. The catalyst particles undergo surface reconstruction to form geometrical shapes, which were able to promote the formation of carbon nanofibers with certain growth conditions of catalysts, gas, and temperature [32–34]. Based on Hansen's and above results, it was inferred that the shape changes of copper nanoparticles were induced by the adsorption of gases on the surfaces of particles. During the reaction, the active sites of the copper nanoparticles were changed from one place to another by following the surface reconstruction.

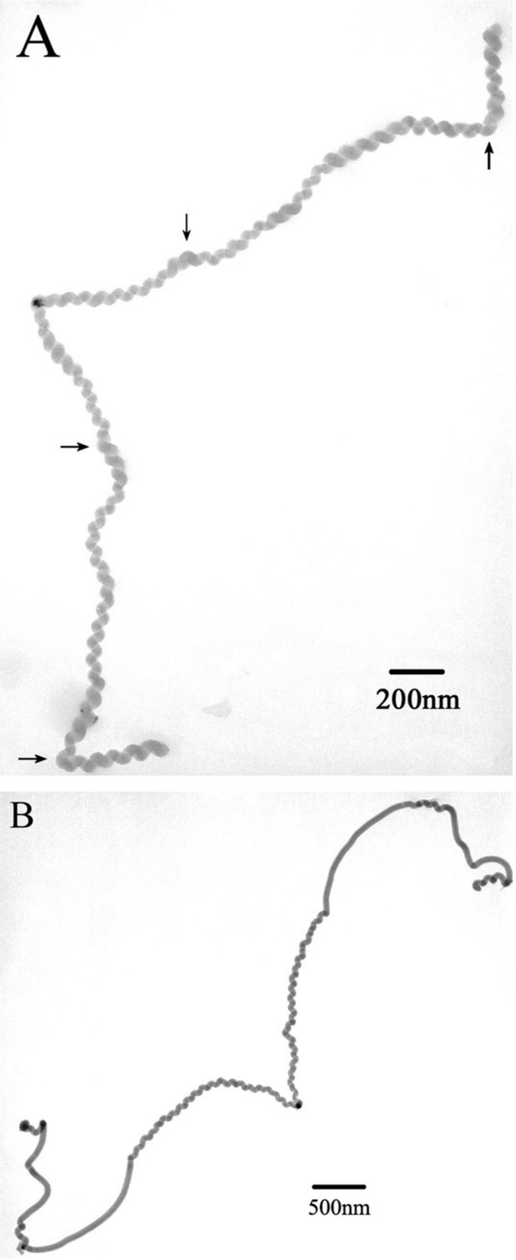

Fig. 3. TEM image of two helical nanofibers with (A) helical reversals and (B) long and straight parts.

It was observed that cupric nitrate was effective for the growth of carbon nanofibers under selected reaction conditions. Moreover, the reaction showed good reproducibility and high yields were obtained. On average, 6.8 g of carbon nanofibers could be obtained if 1 g of cupric nitrate was used as catalyst precursor for a 1 h reaction period at a reaction temperature of 260 °C. In order to investigate the effect of change of growth condition on the yield of carbon fibers, different reaction temperatures, such as 260, 300, and 340 °C were employed. The results revealed that the yield of carbon fibers reduced by increasing the reaction temperature, which showed an optimum yield of carbon nanofibers could be achieved on an optimally reaction temperature.

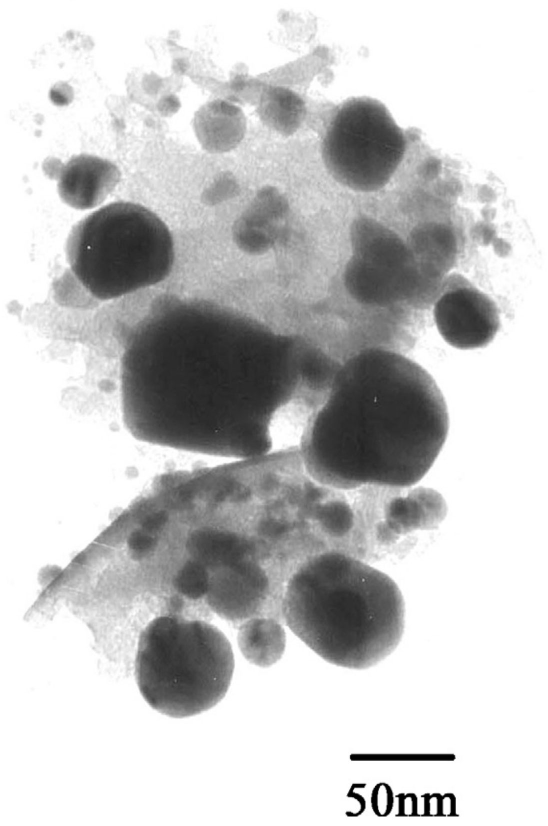

Fig. 4. TEM image of copper nanoparticles obtained from the thermal decomposition of cupric nitrate trihydrate in acetylene at 220 °C.

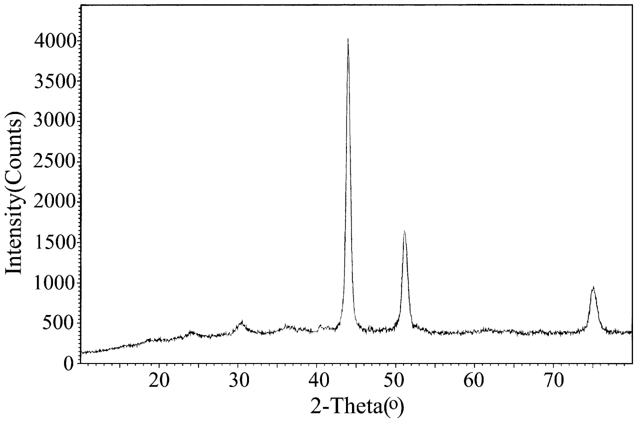

Fig. 5. The XRD pattern of catalyst nanoparticles.

Fig. 7 shows the TEM image of a few resultant straight nanofibers. As can be seen, two club-shaped fibers with a diameter of about 200 nm grow over a single copper nanoparticle, which has an irregular rotundity-shape and a grain size of about 200 nm being approximately equal to the diameter of the fiber. According to our statistic, the majority of nanocopper particles that located at the node of two straight nanofibers have a distribution in grain size ranging from 50 to 200 nm and irregular shapes. Therefore, we inferred that the catalyst particle sizes had a considerable effect on the morphology of grown carbon nanofibers. When the cata-

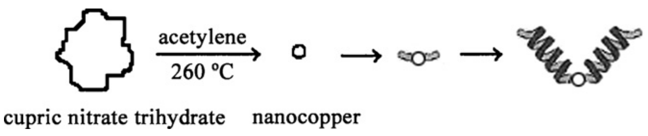

Fig. 6. The schematic diagram of growth mechanism of helical nanofibers.

Fig. 7. TEM image of club-shaped fiber.

lyst nanocopper particles have a grain size less than 50 nm, the nanofibers by catalytic synthesis had helical morphology with a symmetric growth mode, while ones sized around 50–200 nm grew straight carbon nanofibers. The catalyst particle size plays a key role in the growth of carbon nanofibers. During the growth process of carbon fibers, catalytic activity of every crystal face of the catalyst particles is anisotropic and inhomogeneous by reason of the anisotropy of the particle surfaces, which was the essential condition that carbon fibers could be grown in a helical morphology [28,35,36]. Catalyst particles with regular shapes and small grain sizes were suitable for the growth of regular helical fibers. The results from research on formation of carbon nanofibers through methane decomposition showed that Co metal particles with diameters from 10 to 30 nm grew carbon nanofibers preferentially, while ones larger than 30 nm were inactive for the growth [19].

4. Conclusion

Carbon nanofibers have been synthesized by the decomposition of acetylene with a copper nanocatalyst derived from cupric nitrate trihydrate crystal at a low temperature of 260 °C. The copper nanoparticles changed from initial irregular shapes to regular shapes during the growth of nanofibers. The mechanism of morphological changes of Cu catalysts and the growth of carbon nanofibers are proposed in five steps: (1) the dehydration of cupric nitrate trihydrate, (2) the decomposition of cupric nitrate into Cu oxide, (3) the reduction of Cu oxide, (4) the formation of Cu nanoparticle before the growth of carbon nanofibers, and (5) the reaction with acetylene for the growth of carbon nanofibers. The copper nanoparticle size has a considerable effect on the morphology of carbon nanofibers. The helical carbon nanofibers with a symmetric growth mode were grown on copper catalyst nanoparticles with a grain size less than 50 nm. When the catalyst particle size was around 50–200 nm, straight carbon nanofibers were obtained dominantly. It is reasonable to assume that it is possible to control the diameter of carbon nanofibers by controlling the size of the catalyst particle.

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