Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 223 (2004) 389–394

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Effect of synthesis method of nanocopper catalysts on the morphologies of carbon nanofibers prepared by catalytic decomposition of acetylene

Yong Qin,[a,b] Qian Zhang,[a] and Zuolin Cui [a,*]

[a] *Key Laboratory of Nanomaterials, Qingdao University of Science and Technology, Qingdao, 266042, People's Republic of China*
[b] *College of Environmental Science and Engineering, Ocean University of China, 266002, Qingdao, People's Republic of China*

Received 16 December 2003; revised 20 January 2004; accepted 7 February 2004

Abstract

Regularly coiled carbon nanofibers with a novel "V"-type symmetric growth mode were synthesized by the decomposition of acetylene with nanocopper catalysts. These were obtained from an aqueous copper sulfate solution by borohydride reduction and from the decomposition of copper tartrate, butyrate, oxalate, and lactate precursors, whereas copper nanoparticles prepared by the hydrogen-arc plasma only revealed ribbon-like fibers under identical reaction conditions. The morphology of the catalyst particles before and after fiber growth has been investigated and the effect of the synthesis method on the morphology and growth of the fibers is discussed.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Carbon fibers; Nanocopper; Decomposition; Growth mode

1. Introduction

Carbon fibers, prepared by metal-catalyzed decomposition of hydrocarbons such as acetylene, benzene, and methane, present various growth modes, including whisker-like, branched, bidirectional, and multidirectional types of growth [1–3]. The addition of additives or a second metal to the metal catalyst, the use of a support, the pretreatment of the catalyst in a particular environment, and the catalyst source may have considerable effects on the carbon deposition. Bernardo and co-workers observed whisker-like growth from catalyst particles containing less than 80% copper and multidirectional carbon deposits at higher copper concentrations [4,5]. Bidirectional growth was reported for several binary catalysts, for example, Fe–Sn and Fe–Ni [6,7]. Multidirectional carbon deposits were also observed in filaments formed on nickel catalysts of high sulfur content [8–10]. Motojima and co-workers prepared microcoiled carbon fibers by metal powder-activated pyrolysis of acetylene containing a small amount of H_2S or thiophene as an impurity [11–13]. The effect of the metal catalyst source and presulfidation of the metals on the growth of the coiled carbon fibers were examined in detail. These coils are double-coiled forms in which two fibers intertwine with each other as in a double helix of a DNA. In addition, variation of the catalyst precursor and the presence of impurities have an effect in the synthesis of coiled carbon nanotubes [14,15]. It was proposed that small metal particles could be prepared in a particular orientation favorable toward carbon deposition by selecting the optimum catalyst precursor, and that the pretreatment of metal in a particular environment would result in the formation of oxide, nitride, or sulfide and so on, being precursor for small metal particles [1].

In this paper, we describe the synthesis of carbon nanofibers by the decomposition of acetylene with nanocopper catalysts under mild reaction conditions. The effect of synthesis method of the catalyst on the morphologies of carbon nanofibers obtained was examined.

2. Methods

Nanocopper catalysts were prepared by these methods as follows:

1. *Copper tartrate catalyst precursor*. To prepare the precursor, 100 ml of 0.02 M sodium hydroxide aqueous solution was added to 100 ml of well-stirred 0.01 M tartaric acid aqueous solution. Then 100 ml copper dichlo-

---

[*] Corresponding author.
E-mail address: cuizl@public.qd.sd.cn (Z. Cui).

0021-9517/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2004.02.004

ride aqueous solution (0.01 M) was slowly added to the obtained sodium tartrate solution under vigorous stirring. A light blue precipitate (copper tartrate) was formed. The precipitate was filtered and washed with anhydrous ethanol. Then it was dried for 1 h at 110 °C and transferred to the reaction tube.

2. *Copper butyrate, oxalate, and lactate catalyst precursors*. These were prepared in analogous ways.
3. *Borohydride reduction of cupric ion*. An amount of 100 ml of aqueous solution of copper sulfate (0.01 M) was brought in a conical flask and purged with nitrogen for 10 min to remove the dissolved oxygen. Then 100 ml of 0.01 M ice-cold sodium borohydride aqueous solution was added under stirring. Metallic copper particles formed immediately and were filtered, washed with anhydrous ethanol, and then transferred to the reaction tube.
4. *Hydrogen-arc plasma method*. This method was described in detail in a previous publication [16].

The catalytic decomposition of acetylene was carried out at atmospheric pressure in a horizontal quartz tube (9 cm in diameter, 90 cm in length) which was heated from the outside through an electric furnace. A ceramic plate containing the catalysts was placed in the reactor. After the tube was heated to 250 °C in a vacuum (for catalyst precursor, holding at 250 °C for 30 min in order that all the precursor particles decomposed to form metallic copper particles), acetylene was introduced into the reactor for a selected reaction period.

For transmission electron microscopy analysis (TEM), the sample powders were dispersed in ethanol, agitated in an ultrasonic bath, and finally 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. High-resolution transmission electron micrographs (HRTEM) were obtained by imaging samples on carbon mesh copper grids using a JEOL JEM 2010F microscope operated at an accelerating voltage of 200 kV. The carbon nanofiber specimens for field-emission scanning electron microscopy (FE-SEM) were platinum-coated using a JEOL JFC-1600 auto fine coater prior to imaging. Samples were examined on a JEOL JSM-6700F operating at an accelerating voltage of 10 kV. Energy-dispersive X-ray (EDX) analysis was performed on an Oxford Inca X-ray energy detector. XRD patterns of the nanocopper catalysts were obtained on a Philips X'Pert MPD diffractometer using K_α radiation.

3. Results and discussion

TEM images showed that the copper particles, obtained from the thermal decomposition of copper tartrate precursor, had a rather irregular shape and a size of 30–80 nm (see Fig. 1A). Differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis revealed that copper tartratre, butyrate, oxalate, and lactate precursors all start to decompose at a temperature of about 250 °C. According to TEM results, copper nanoparticles prepared from aqueous copper sulfate solution by borohydride reduction, and from decomposition of copper butyrate, oxalate, and lactate precursors were all identical to copper tartrate-derived particles. However, the nanocopper particles prepared by the hydrogen-arc plasma method have a spherical or ellipsoidal shape and a grain size ranging from 50 to 100 nm (Fig. 1B). These particles exhibit a chain-like shape due to the interaction between the particles. Powder XRD analysis was used to examine the crystal structure of the samples. The copper nanoparticles obtained by all the above methods were crystalline. As an example, the XRD pattern of the copper nanoparticles derived from copper tartrate decomposition is shown in Fig. 1C. The diffraction pattern shows the standard copper reflections, indicating that the sample is highly crystalline. No peaks due to impurities were found.

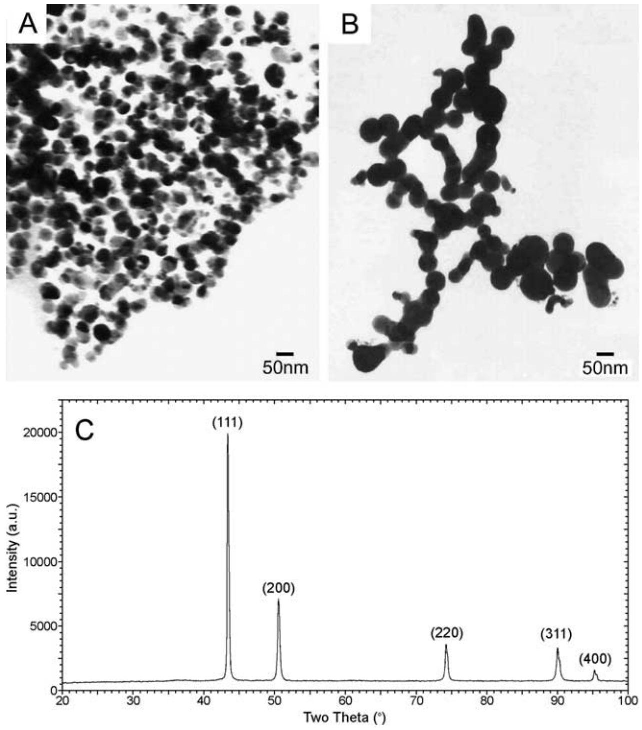

Fig. 1. TEM image of the nanocopper particles, (A) obtained from the thermal decomposition of copper tartrate at 250 °C, and (B) prepared by the hydrogen-arc plasma method. (C) XRD pattern of copper nanoparticles.

The experiments showed that the copper nanocrystals, prepared by all the above methods, possess good catalytic activity for the growth of carbon nanofibers under selected reaction conditions, enabling high fiber yields to be obtained. There was no obvious difference in fiber yields when copper nanocrystals of different source were used as a catalyst. In general, the fiber yield of a gram of copper nanocrystals or an equimolar amount of precursor was about 75 g for a 2-h reaction period at a reaction temperature of 250 °C.

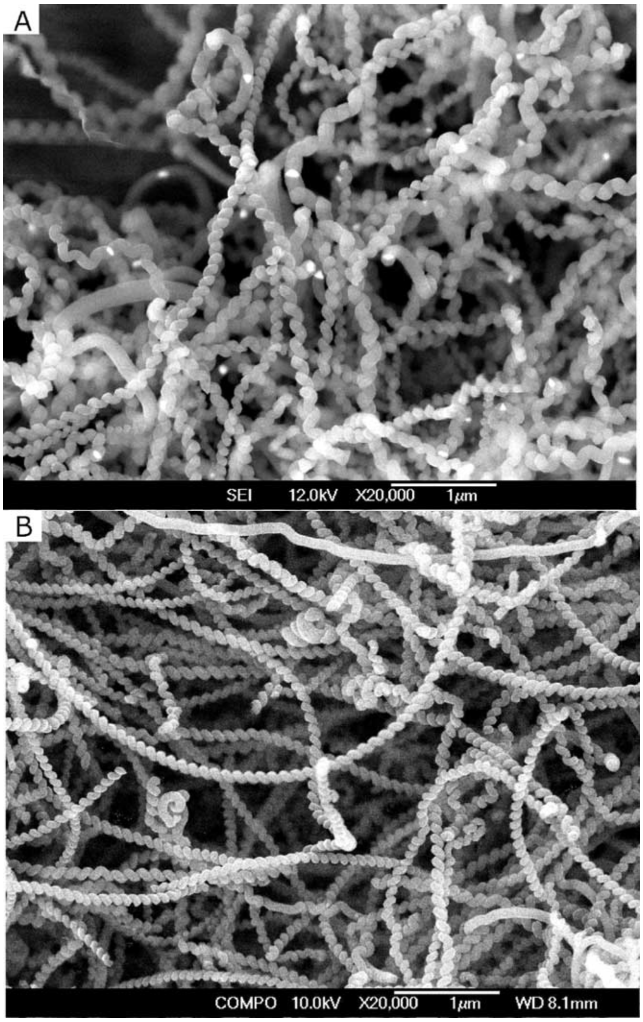

Fig. 2. Field-emission secondary electron microscopy (FE-SEM) images of representative coiled carbon nanofibers prepared using copper tartrate as a catalyst precursor. (A) After a growth period of 3 min, and (B) after a growth period of 2 h.

FE-SEM investigations revealed that the copper nanocrystals, obtained from the decomposition of copper tartrate precursor, were extraordinarily effective for the growth of regularly coiled carbon nanofibers. The coiled-fiber content in the resulting fibers was very high and reproducible. The FE-SEM images of Figs. 2A and B show representative coiled nanofibers after a growth period of 3 min and 2 h (the residual acetylene was pumped off immediately after reaction), respectively. The catalyst particles were included in the coiled fibers and are clearly seen in Fig. 2A. Almost all these fibers are regular coiled in the form of single coils. They are tightly coiled, and hence have very short coil pitches. These fibers are about 100 nm in coil diameter. Every fiber exhibited constant coil diameter, coil pitch and fiber diameter, indicating that the fiber growth was stable and not sensitive to external influence. XRD analysis showed that the coiled fibers prepared at 250 °C were amorphous (not graphite-like). The C/H molar ratio of the fibers was 1.11/1 (by Flash EA 1112), demonstrating that the products contain hydrogen. This indicates that the growth of the fibers occurs by both decomposition and polymerization of acetylene.

Fig. 3 shows the TEM and FE-SEM images of coiled nanofibers obtained using copper tartrate precursor as a catalyst for a reaction period of 3 min. Fig. 3A shows that two regularly coiled fibers have grown over the rhomb-shaped copper nanocrystal, which is about 50 nm in size. The fibers have identical coil number, coil length, coil pitch, coil diameter, and fiber diameter. Most important of all, it must be noted that the helical senses of the two coiled fibers are different, as one fiber coils left-handed and the other right-handed. The fiber diameter is approximately equal to the grain size of the copper nanocrystal, and the coil diameter is about twice the size of the particle. Generally, two coiled fibers grown from a single particle have opposite helical sense, resulting in the occurrence of helical reversals. As shown in Fig. 3B, the two fibers both have 42 beautiful coils and change their helical senses at the 21st coil (numbered from the catalyst particle). This induces that the two fibers coil always in opposite helical senses. Therefore, we conclude that the two fibers follow a mirror-symmetric growth mode.

The catalyst particles included in the fibers (located at the nodes of the two fibers) always exhibit regularly faceted shapes. In addition to rhombic particles (Fig. 3C), copper nanocrystals of a variety of faceted shapes, such as triangular (Fig. 3D) and quadrangular (Fig. 3E), were also observed. Selected area electron diffraction patterns indicated that they were single crystalline. Because these particles exhibited irregular shapes (Fig. 1A) before fiber growth, we conclude that they changed from an irregular to a regular faceted shape during fiber growth. Detailed TEM investigations revealed that only two coiled fibers, with identical fiber diameter, coil diameter, coil number, coil pitch, and different helical sense, grow from a single copper nanocrystal, irrespective of the shape it had originally. Thus, the faceted shape of the catalyst particle is not the determining factor for the helical morphology and symmetric growth mode of the fiber. Multidirectional (including tridirectional) growth has not been observed in our work. Of course, the symmetrical relationship between the twin nanohelices resulted in an identical number of left- and right-handed coils. EDX analysis of catalyst particles included in the coiled fibers gave no evidence for impurities (in particular Ni or Co). Therefore, the copper nanocrystals had high purity and were indeed responsible for the growth of the fibers.

The FE-SEM images, given in Figs. 3F and G, show the nodes of two coiled fibers at which catalyst particles located. The two nodes were imaged in different directions, that is, Fig. 3F presented the concave of one node and Fig. 3G the convex of the other. We infer that the helical morphology of the fibers results from the dispersion of the growth rate of fibers over the catalyst particles. The magnitude of the dispersion could be embodied by and large via the FE-SEM image of the node, from the curvature of the convex or con-

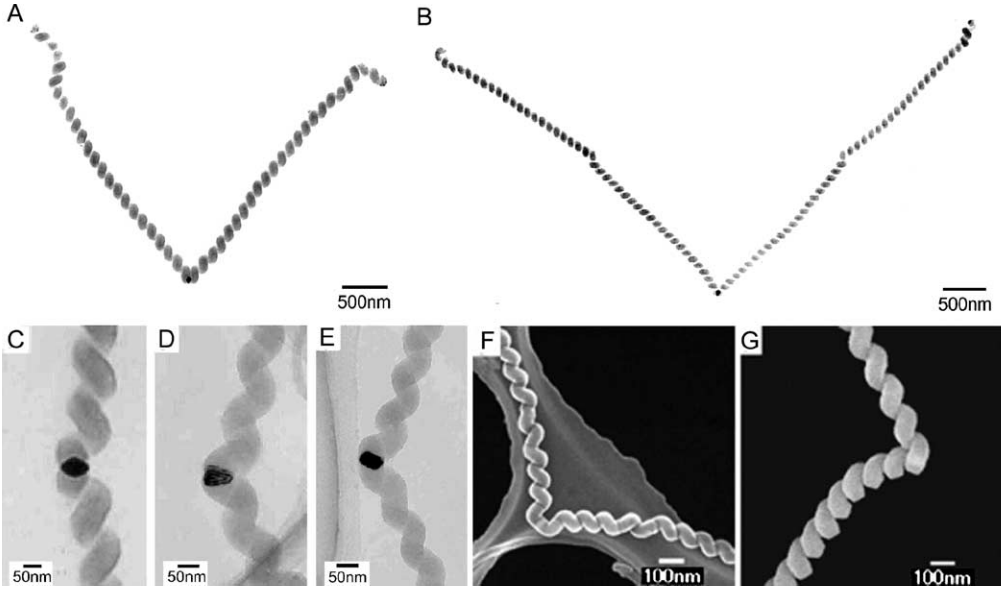

Fig. 3. (A and B) TEM images of two coiled fibers grown over single copper nanocrystals. (C–E) TEM image of copper nanocrystals located at the node of two coiled fibers. (F and G) FE-SEM images of the node at which catalyst particles are located.

cave nodes. The considerable dispersion of growth rate over the surface of catalyst particle induced a curly node, small coil diameter, and tight coil pitch of the fibers [17].

In order to examine the effect of carboxyl anion of precursor on the growth forms of carbon nanofibers, copper nanoparticles derived from the decomposition of copper butyrate, oxalate, and lactate precursor were also used as catalysts to catalyze the carbon deposition. In brief, the results revealed that the fibers obtained were coiled and had an identical symmetric growth mode. Further examination by FE-SEM and TEM indicated that coiled nanofibers of symmetric growth mode could also be produced with nanocopper catalysts obtained from the borohydride reduction of copper sulfate. Thus, we conclude that the form of the coiled morphology and the symmetric growth mode were not induced by carboxyl anions of precursor.

Fibers from nanocopper particles prepared by hydrogen-arc plasmas are shown in Fig. 4. Comparing the FE-SEM images of Fig. 4A and Fig. 2 shows that the morphologies of the resulting fibers are different, as under identical reaction conditions, only ribbon-like fibers with a width of about 100 nm were obtained. TEM investigations showed that after fiber growth the catalyst particles were also faceted and had a variety of shapes with a grain size of about 100 nm. Selected area electron diffraction patterns indicated that they were also single crystals. The majority of these particles exhibited irregular shapes, as shown in Figs. 4B–D. In addition, very few particles seemed to have a regular projected faceted shape, such as rhombic (Fig. 4E) and triangular (Figs. 4F and G). Besides bidirectional growth, the tridirectional growth form was usually found (Figs. 4D and G). Obviously, the copper nanoparticles prepared by the hydrogen-arc plasma method also changed from initial spherical or ellipsoid to faceted shapes after fiber growth. However, their

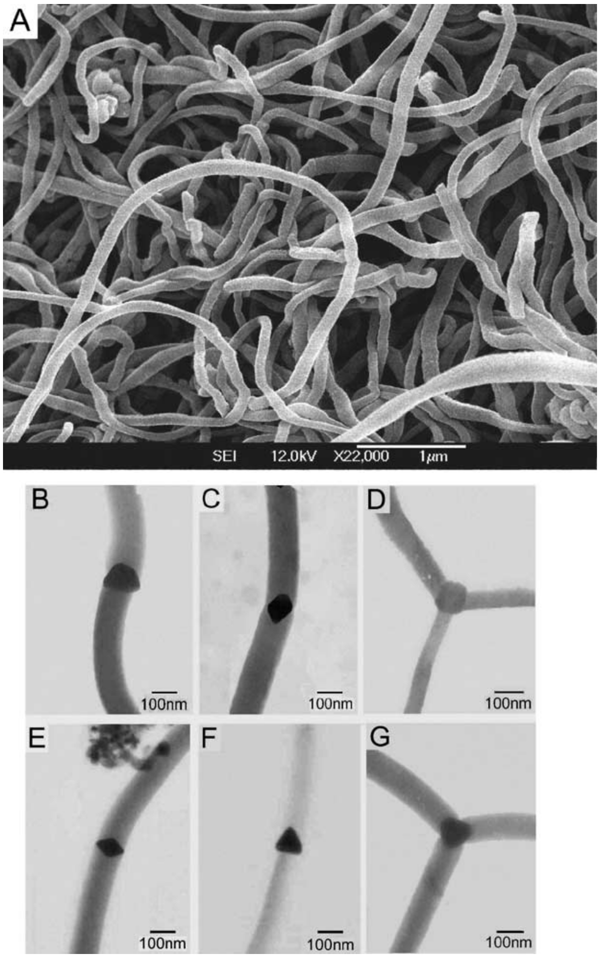

Fig. 4. (A) FE-SEM image of ribbon-like carbon nanofibers obtained using nanocopper catalysts prepared by the hydrogen-arc plasma method. TEM images of copper nanocrystals included in the fibers with (B–D) irregular shapes and (E–G) regular projected shapes.

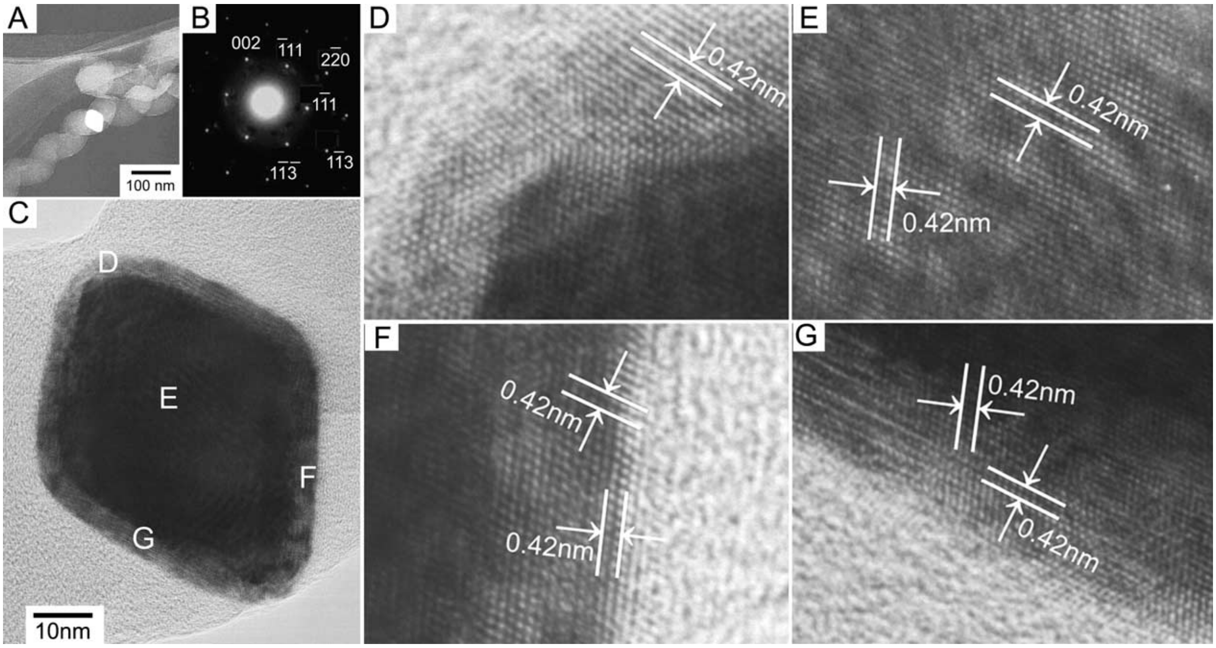

Fig. 5. Microstructure of a rhombic-projected copper nanocrystal located at the node of two coiled fibers. (A) TEM image. (B) Selected area electron diffraction pattern. (C) HRTEM image. (D–G) Magnified images of those corresponding positions marked in (C). (The carbon fibers are amorphous because of the low reaction temperature.)

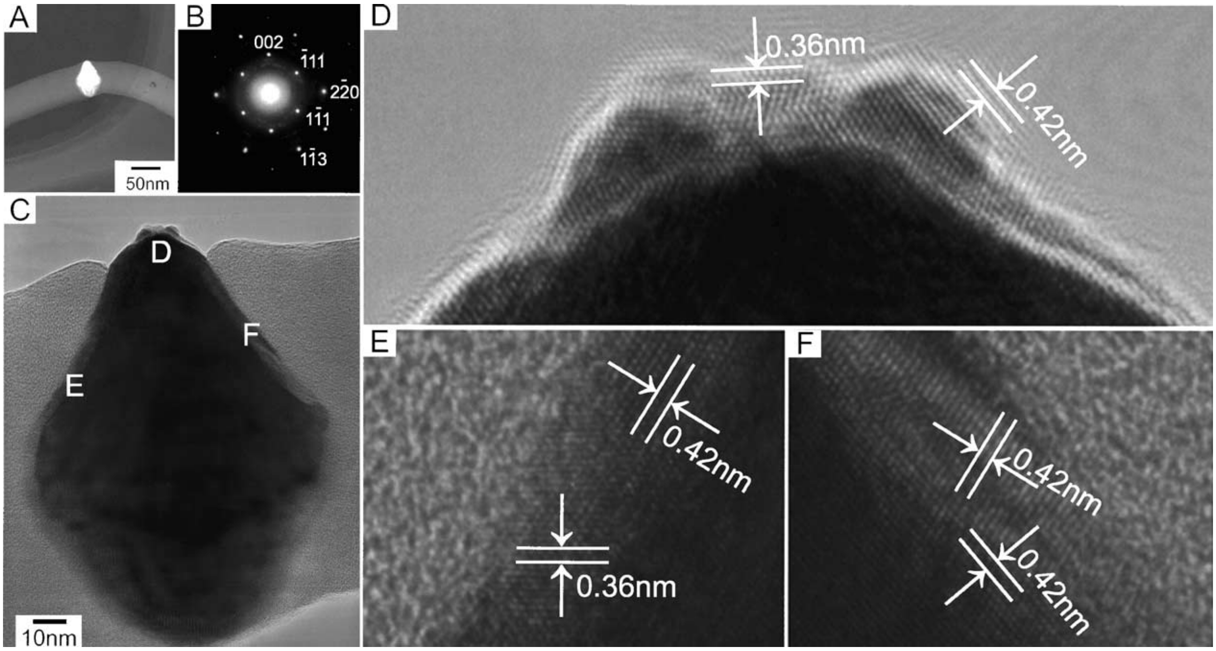

Fig. 6. Microstructure of a rhombic-projected copper nanocrystal included in a straight fiber. (A) TEM image. (B) Selected area electron diffraction pattern. (C) HRTEM image. (D–F) Magnified images of those corresponding positions marked in (C).

faceted shapes were generally irregular and the resulting fibers had a ribbon-like shape.

Regularly faceted catalyst particles were suited for the growth of regularly coiled fibers [17]. In order to clarify the reason why very few copper nanocrystals prepared by the hydrogen-arc plasma method seemed to have a regularly faceted shape after fiber growth, although ribbon-like fibers formed, HRTEM analysis was applied. Figs. 5 and 6 show the microstructure of a rhombic-projected copper nanocrystal located at the node of two coiled fibers, and one included in a straight fiber, respectively. Obviously, the two particles have identical rhombic shapes according to TEM investigation (Figs. 5A and 6A). Also, they exhibit nearly identical electron diffraction patterns (Figs. 5B and 6B). This reveals that the two copper nanocrystals exposed their crystal faces in the same form, as (111) index faces.

The HRTEM images (Figs. 5C–G and 6C–F) further confirm this. The HRTEM images indicate that the carbon fibers were mainly extruded from the (111) planes. At the same time, the HRTEM investigations revealed that the rhombic particle located at the node of two coiled fibers had a uniform thickness (Fig. 5C) and a relatively clean and structurally perfect surface (Figs. 5D–G). The lattice fringes were visible throughout the whole particle (Fig. 5E). However, the rhombic-projected particle included in the straight fibers had a variable thickness (Fig. 6C). Its lattice fringes were visible only at the thicker part of the particle. It did not have a clean and structurally perfect surface (Figs. 6D–F). Based on these analyses we conclude that even if this rhombic-projected particle included in the straight fibers had a regular projected shapes, it did not possess a regular shape as to a three-dimensional structure.

Many researchers described the deposition of hydrocarbon over metal catalysts and the possible growth mechanism for the fibers. The metal particles were usually faceted after the growth of carbon filament. Yang and Chen reported that small particles of Ni, Fe, and Co were faceted single crystals upon carbon filament growth by reaction with methane and the faceting was caused by the surface reconstruction due to precipitation of graphite. All particles, however, had an irregular shape [3]. Motojima et al. reported the synthesis of carbon microcoils by metal-catalyzed pyrolysis of acetylene and the effect of the source of metal powder catalyst on the coil yield [11]. After the growth of the coiled fibers, the catalyst particles were regular rhombic single crystals (micrometer sized) and the fibers grown over them had a DNA-like form. A three-dimensional growth mechanism was proposed for the fibers based on the three-dimensional structure of the rhombic catalyst particles [12]. Baker and Waite reported that platinum–iron alloy particles underwent a rapid change from an irregular to a more spheroidal form while catalyzing the carbon deposition of acetylene [2]. In our study, nanocopper catalysts, obtained by borohydride reduction of copper sulfate and by thermal decomposition of precursors including copper tartrate, butyrate, oxalate, and lactate, all catalyzed the formation of coiled carbon nanofibers from acetylene. These fibers exhibited a symmetric growth mode. TEM investigations showed that the catalyst particles changed from an irregular to a regular faceted shape after fiber growth. However, nanocopper particles prepared by the hydrogen-arc plasma method could only catalyze the growth of ribbon-like fibers. These particles showed irregular faceted shapes after fiber growth. Therefore, it could be concluded that the helical structure and the symmetric growth mode of coiled fibers synthesized in our study were not induced by carboxyl anions of the precursor and the grain size of copper nanoparticles. However, the original shape of the catalyst particles seems to have a considerable effect on the morphology of the fibers obtained. We infer that the decomposition of precursors and borohydride reduction of copper sulfate could produce a special form of metastable copper nanocrystals, which would change from irregular to regular faceted shapes in a way that favors the growth of coiled fibers upon contacting the acetylene gas. In this case a large number of regularly coiled fibers was obtained. Copper nanoparticles prepared by the hydrogen-arc plasma method also change shape during growth of fibers. However, these particles changed to irregular shapes and were not suited for the growth of regularly coiled fibers; only ribbon-like fibers formed.

4. Conclusion

Nanocopper catalysts were prepared by the decomposition of several copper carboxylate precursors, by borohydride reduction of copper sulfate, and by the hydrogen-arc plasma method. These copper nanoparticles catalyze the carbon deposition of acetylene to yield regularly coiled fibers with a novel symmetric growth type, whereas ribbon-like fibers formed over nanocopper particles prepared by the hydrogen-arc plasma method. The copper nanocrystals change from irregular or spherical shape to faceted shapes after fiber growth. The regularity of the shapes of the faceted catalyst particles included in the fibers accounts for the different morphologies of the resulting products.

Acknowledgment

The Natural Science Foundation of Shandong Province supported this work financially.

References

[1] R.T.K. Baker, Carbon 27 (1989) 315.
[2] R.T.K. Baker, R.J. Waite, J. Catal. 37 (1975) 101.
[3] R.T. Yang, J.P. Chen, J. Catal. 115 (1989) 52.
[4] C.A. Bernardo, I. Alstrup, J.R. Rostrup-Nielsen, J. Catal. 96 (1985) 517.
[5] M.T. Tavares, C.A. Bernardo, I. Alstrup, J.R. Rostrup-Nielsen, J. Catal. 100 (1986) 545.
[6] R.T.K. Baker, J.J. Chludzinski, J. Catal. 64 (1980) 464.
[7] R.T.K. Baker, P.S. Harris, S. Terry, Nature 253 (1975) 37.
[8] J.R. Rostrup-Nielsen, J. Catal. 85 (1984) 31.
[9] M. Audier, M. Coulon, A. Oberlin, Carbon 18 (1980) 73.
[10] M. Audier, A. Oberlin, M. Coulon, J. Cryst. Growth 55 (1981) 549.
[11] S. Motojima, Y. Itoh, S. Asakura, J. Mater. Sci. 30 (1995) 5049.
[12] S. Motojima, X.Q. Chen, J. Appl. Phys. 85 (1999) 3921.
[13] S. Motojima, S. Asakura, T. Kasemura, S. Takeuchi, H. Iwanaga, Carbon 34 (1996) 289.
[14] W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, Science 274 (1996) 1701.
[15] Y. K Wen, Z.M. Shen, Carbon 39 (2001) 2369.
[16] Z.L. Cui, Z.K. Zhang, C.C. Hao, L.F. Dong, Z.G. Meng, L.Y. Yu, Thin Solid Films 318 (1998) 76.
[17] S. Amelinckx, X.B. Zhang, D. Bernaerts, X.F. Zhang, V. Ivanov, J.B. Nagy, Science 265 (1994) 635.