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J. H. Xia, X. Jiang, and C. L. Jia

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The size effect of catalyst on the growth of helical carbon nanofibers

J. H. Xia,¹ X. Jiang,^{1,a)} and C. L. Jia²

¹Institute of Materials Engineering, University of Siegen, Paul-Bonatz-Str. 9-11, 57076 Siegen, Germany

²Institute of Solid State Research and Ernst Ruska Centre for Microscopy and Spectroscopy with Electrons, Research Centre Jülich, D-52425 Jülich, Germany

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Cu-catalyzed carbon nanofibers are investigated by means of transmission electron microscopy. Straight and helical carbon nanofibers are observed to connect to the catalyst particles of octahedron or triangular prism in the samples prepared using the same processing conditions. Statistic analysis of the results leads to evidence that the morphology of the nanofibers depends on the size of the catalyst particles. Small size of catalyst particles favors formation of the helical fibers, while large size of catalysts results in the straight fibers. Based on the observed results, growth, and morphology formation of the carbon nanofibers are discussed. The growth model in which the rotating catalysts catalyze the growth of the carbon nanostructure in a helical way is proposed. © 2009 American Institute of Physics. [doi:10.1063/1.3271031]

The growth mechanisms of catalytically grown helical carbon nanotubes and nanofibers have been previously proposed.¹⁻⁶ Growth of the helical structures is generally attributed to anisotropy and inhomogeneity of the crystalline catalyst.¹ Much attention has been paid to explore the material nature of the catalyst including its matter state (solid or liquid), crystallinity, and surface morphology. For example, the catalytic activities differ depending on the crystallographic planes terminating on the surface of the crystalline catalysts. As consequence, an anisotropic growth rate occurs on different crystallographic planes of surfaces, and thus leads to formation of helical morphology.

Besides the material nature mentioned above, can the size of catalyst particles under certain experimental conditions, i.e., catalyst treatment, growth temperature, and reactive gas pressure, be an effect factor on the morphology of nanofibers? So far, no report on this subject is available. On the other hand, there has been debate on which, diffusion process of surface or diffusion in bulk, is the critical step for the growth process.^{7,8} To investigate the size effects of catalyst on the growth of nanofibers may help in understanding the debate.

In the present letter we investigate the size effect of catalyst on the formation of helical nanostructures. The materials involved in this letter are Cu-catalyzed carbon nanofibers, which were synthesized by thermal chemical vapor deposition technique.⁹ Cu catalysts are prepared by the reduction in copper sulfate with sodium borohydride at 250 °C. Two different morphologies of carbon nanofibers namely straight and helical have been simultaneously synthesized in the same synthesis process. Statistical investigations of these carbon nanofibers are carried out by means of transmission electron microscopy (TEM). It is found that the morphology of the nanofibers is related to the size of the catalyst particles. The formation of the helical nanofibers is proposed as the result of the rotation of small catalyst particles.

Figures 1(a)–1(d) show TEM images of the carbon nanofibers with different morphologies. The fibers show a

brighter contrast than the catalyst particles. Each fiber consists of two branches which grow on opposite directions from the catalyst. Electron diffraction analysis indicates that the catalyst particles are crystalline Cu. The morphologies of the catalyst particles are determined using a method of particle tilting. This method has been used to determine the morphology of the Fe₃C catalyst of carbon nanohelices in our recent letter.⁶ It turns out that these Cu catalyst particles mainly have two kinds of morphologies, octahedron with eight {111} planes and triangular prism with two parallel {111} planes and three {224} planes as schematically shown in Figs. 1(e) and 1(f). Figures 1(g) and 1(h) display the projections of these polyhedrons along the Cu <110> direction

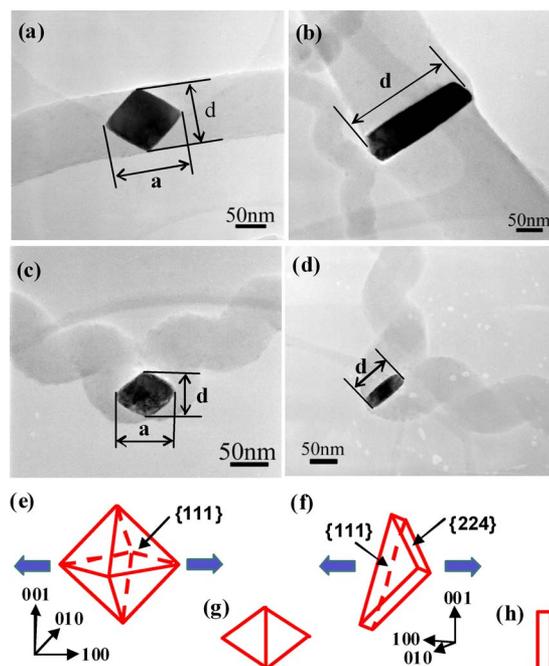


FIG. 1. (Color online) [(a)–(d)] TEM images of Cu-catalyzed carbon nanofibers recorded along the <110> zone axis of Cu crystal, showing different morphologies of the nanofibers. (e) and (f) Respective view of two catalyst polyhedrons: octahedron and triangular prism. (g) and (h) Projections of the polyhedrons in (e) and (f) along the <110> direction of Cu crystal.

^{a)}Author to whom correspondence should be addressed. Electronic mail: jiang@lot.mb.uni-siegen.de.

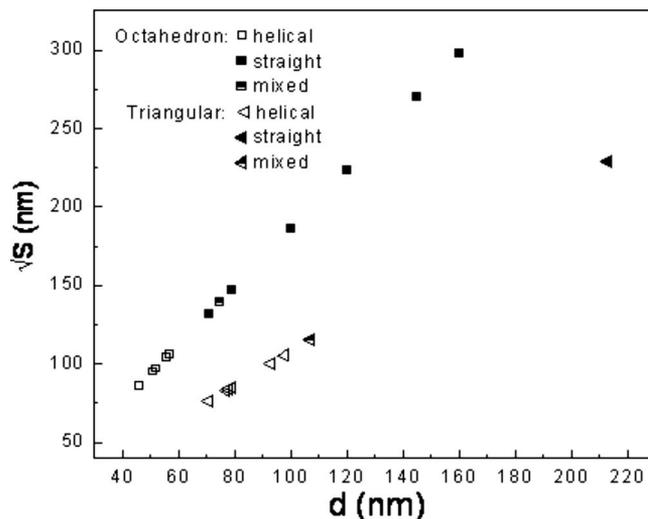
TABLE I. The measured and calculated values of a , d , and \sqrt{S} from 20 nanofibers are listed.

Nanofibers	d	a	\sqrt{S}
Oh ₁	56	79	104.2
Oh ₂	46	65	85.6
Oh ₃	52	74	96.8
Oh ₄	51	72	94.9
Oh ₅	57	81	106.1
Os ₁	120	170	223.3
Os ₂	100	141	186.1
Os ₃	71	100	132.0
Os ₄	79	112	147.0
Os ₅	160	226	297.8
Os ₆	145	205	269.9
Om ₁	75	106	139.6
Th ₁	78	90	83.8
Th ₂	98	113	105.3
Th ₃	93	107	99.9
Th ₄	71	82	76.3
Th ₅	79	91	84.9
Th ₆	77	89	82.7
Ts ₁	213	246	228.9
Tm ₁	107	124	115.0

which is the viewing direction of these particles in Figs. 1(a)–1(d). By comparing the TEM images with the corresponding catalyst polyhedrons, it is concluded that the nanofibers grow on the $\{111\}$ surface planes of the catalyst particles and that the growth directions are along the $\langle 100 \rangle$ [Figs. 1(a) and 1(c)] and the $\langle 111 \rangle$ [Figs. 1(b) and 1(d)] of the Cu particles. From the TEM images in Fig. 1, it is seen that both straight nanofibers [Figs. 1(a) and 1(b)] and helical fibers [Figs. 1(c) and 1(d)] can grow on octahedron and triangular prism catalyst particles. In a few cases nanofibers with a mixed character of straight and helical morphology are also found on the octahedron and triangular prism shaped catalysts.

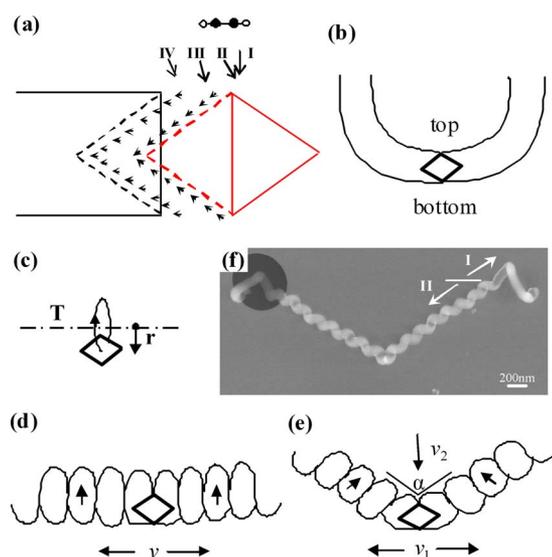
In order to quantify the size of the catalyst polyhedrons, we measure the polyhedrons with two orthogonal scales a and d as shown in Figs. 1(a)–1(d). In addition, the area S of the growth front of the fibers, i.e., the area contacting the catalyst polyhedron, is also calculated. For octahedron, $S = 2\sqrt{3}d^2$; for triangular prism, $S = 2\sqrt{3}d^2/3$. In statistics we investigate 20 nanofibers with different morphology along $\langle 110 \rangle$ or $\langle 100 \rangle$ zone axes of the Cu catalyst polyhedrons (see Ref. 10). The measured and calculated values of a , d , and \sqrt{S} (square root of the growth front area S) are listed in Table I. In the first row of Table I the first capital letters, O and T represent the type of polyhedrons (Octahedron or Triangular prism). The low case letters, h, s, and m, stand for the morphology of the nanofibers (helical, straight, or mixed character) and the subscripts for the number of the polyhedrons.

Analysis of these data results in an evidence for a relation between the size of the catalyst polyhedrons and the morphology of the nanofibers. For the investigated polyhedrons a linear relation is obtained between the values of d and \sqrt{S} . Figure 2 displays the values of \sqrt{S} and the morphology of the nanofibers as a function of the d values. In Fig. 2 squares represent the values for catalyst octahedrons and triangles for triangular prisms. The open symbols are the data of the polyhedrons resulting in the helical nanofibers and the solid ones are the values for the polyhedrons leading to the straight nanofibers. There are two values with half solid symbols which are the data for the polyhedrons connecting to the

FIG. 2. Dependence of nanofibers morphology on the size expressed by \sqrt{S} and d of the catalyst polyhedrons.

mixed character of nanofibers. For the two types of catalyst polyhedrons a critical value of d and a critical value of \sqrt{S} can be determined, respectively, for the change of the nanofiber morphology. Considering the fact that the straight and helical fibers are simultaneously synthesized in the same process conditions and that they grow on catalyst particles of both octahedron and triangular prism, the decisive factor leading to the different morphology of the nanofibers can be concluded to be the size of the catalyst polyhedrons. The small catalyst polyhedrons ($<$ critical values) favor formation of the helical nanofibers, and the large ones ($>$ critical values) promote formation of the straight fibers.

To understand the size effect, we select Cu catalyst octahedron as an example to discuss the interaction processes of acetylene with the catalyst particle. This discussion is also valid for the case of catalyst triangular prism. Figure 3(a) shows the schematic of the interaction process. It is well

FIG. 3. (Color online) (a) Schematic picture of the interaction processes of acetylene with the $\{111\}$ surfaces of Cu catalyst polyhedrons. (b) Coiled formation due to different growth velocities on the growth front of the catalyst particle. (c) Torsion T is created due to the stress in the growth front plane and makes the catalyst rotate. (d) The intermediate state of the helical formation. (e) The growth model of the helical nanofibers. (f) The SEM image of a typical helical nanofiber.

known that the interaction of hydrocarbons (acetylene in the present letter) with Cu surface does not lead to the rupture of the carbon-carbon bond,¹¹ which differs from the interaction on the surfaces of Fe, Co, and Ni catalysts. Our previous result¹² shows that acetylene molecules rapidly couple to form oligomers and polymers (process II) after their adsorption on a suitable Cu surface (process I). Further, these products diffuse accompanied by coupling each other (process III) on the Cu {111} planes, resulting in growth of nanofibers (process IV). Our infrared (IR) and C/H molar ratio analyses provide evidence that nanofibers have a polymer structure with C/H ratio equal to 1:1.

It has been proved that carbon diffusion on the catalyst surface¹³ is the rate-limiting step in the proposed growth path corresponding to the slowest process with the largest energy barrier. From the interaction processes described in Fig. 3(a), an ideal situation can be concluded as follows: The catalyst particle has morphology of a perfect polyhedron, and consequently the catalyst activity for adsorption as well as coupling of acetylene on its exposed faces is homogeneous. The rate-limiting surface diffusion (process III) for the coupling species take places in the same way with equal growth velocities on all {111} growth planes. Therefore, polymer structures can be stacked up with layer-by-layer incorporation in such a way that a layer is rapidly precipitated as soon as the growth faces with the area of S are completely covered by one layer of reaction species by surface diffusion. As a result, only the fibers with straight morphology either along the $\langle 100 \rangle$ direction for octahedron or along the $\langle 111 \rangle$ direction for triangular prism catalyst are formed.

In actual situation, the catalyst particle is, however, far from a perfect polyhedron and defects like atomic steps on the exposed faces and growth fronts affect its catalytic activities. Consequently, the adsorption and coupling interactions (process I and II) with the catalyst are anisotropic on the catalyst surface, which will further influence the following diffusion and precipitation processes. Ultimately, the differences of growth velocities on the growth front induce the formation of the fibers with variable morphologies. A simple growth model of the fiber with coiled morphology is shown in Fig. 3(b). The coiled fiber can be formed if the growth velocities in the bottom side of the catalyst are larger than those of the top side.

Stress is generated on the growth front when different parts of the fiber are grown with different growth velocities. The stress can be divided into σ_1 along the growth direction and σ_2 perpendicular to the growth direction. Because two branches of the fibers are oppositely grown on two growth fronts of the catalyst, the effect of σ_1 on the catalyst can be neglected. σ_2 can induce the torsion (T), which is inside the growth plane and perpendicular to the growth direction. T works on the catalyst and tends to rotate the catalyst along the direction parallel to the growth direction with a radius r [Fig. 3(c)]. The smaller the catalyst particle, the more asymmetrical is its imperfect feature. In addition, the smaller catalyst particles have less mass, which make them easily moved during the growth process. This interprets the phenomenon depicted in Fig. 2 which elucidates that straight fibers are formed with larger catalyst size while helical fibers are formed with smaller ones.

It can be expected that along with the rotation of a catalyst, two branches of the fiber will be helically grown on two growth fronts along the $\langle 100 \rangle$ direction for octahedron or the $\langle 111 \rangle$ direction for triangular prism catalyst. The corresponding growth model is depicted in Fig. 3(d). Here the influence of the fibers contacting with the substrate in the growing process must be considered due to the fact that the fibers are not suspended in the space but supported on the substrate. The scanning electron microscope (SEM) image of a typical helical fiber is shown in Fig. 3(f). The whole fiber consists of an irregularly grown part (part I) and a helix part (part II). It is supposed that in part I the fibers grow irregularly with the catalyst being turned randomly. During this process, the two branches grown are inclined to be in a triangle form instead of a straight line in order to grow steadily. At the beginning stage of part II, the torsion T that is imposed by the grown branches on the catalyst is balanced by the torsion defined as T_s , of the substrate working on the grown branches. T_s is generated from the friction force between the branches grown and the substrate. Consequently, the new growth state of equilibrium is created, in which the fibers are grown in v_1 direction over the catalyst rotating on the axis parallel to v_1 direction, combining with the movement of the catalyst in v_2 direction. The rotating catalyst catalyzes the growth of the carbon nanostructures in a helical way. Figure 3(e) shows the growth model of the helical fibers. The angle α is the stable angle with which the helical fibers grow steadily.

It is noted that the critical value of d is different due to the variability of catalyst morphology (Fig. 2). \sqrt{S} relevant to the catalyst morphology could be a factor to define the critical value of d for a certain polyhedron catalyst. In addition, the critical value of d can also be affected by the intrinsic factors of the catalyst such as its mass and catalytic characteristics of the growth fronts and the extrinsic factors such as the contacting situation with the substrate as well. Further investigations are required to elucidate the roles of those factors on the size effect of catalyst.

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¹⁰See EPAPS supplementary material at <http://dx.doi.org/10.1063/1.3271031> for the TEM images of carbon nanofibers along $\langle 110 \rangle$ or $\langle 100 \rangle$ zone axes of the Cu catalyst polyhedrons.

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