Chemical Vapor Deposition

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Full Paper

Relationship Between Geometric Structures of Catalyst Particles and Growth of Carbon Nanocoils**

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The relationship between the geometric structures of catalyst particles and the growth of carbon nanocoils (CNCs) is investigated. It is found that the CNCs usually consist of over two, but less than five tubules. The catalyst particles at the tips of CNCs are all polyhedron structures, in most cases, hexahedron. It is considered that a catalyst particle has two kinds of crystal facets, the catalytically active facet and the carbon precipitation facet. The active facet mainly plays the roles of decomposition of hydrocarbon and diffusion of the formed carbon atoms, while carbon tubules are grown from the precipitation facets and twisted to form a carbon coil. Catalysts with different numbers of active facets and geometric structures form different types of CNCs.

Keywords: Carbon nanocoils, Catalyst, Facet, Geometric structure, Growth mechanism

1. Introduction

CNCs have attracted much attention due to their unique three-dimensional helix morphology and outstanding mechanical and electromagnetic properties. They are expected to find applications as high-performance electromagnetic wave absorbers, field emitters, nanosprings, etc.[1–5] In the field of synthesis, the formation of CNCs and their morphologies have been reported in numerous papers.[4–7] Generally, CNCs are prepared by high-temperature catalytic decomposition of acetylene, methane, or benzene on metallic catalysts such as Fe, Co, Ni, and their alloys. They have been successfully synthesized in high yield using Fe–In–Sn–O or Fe–Sn–S–O as the catalyst,[4,5,8–10] which makes it possible to investigate the growth mechanism of CNCs and their physical and mechanical characteristics. To date, several kinds of carbon coils have been synthesized, such as coiled carbon nanotubes (CCNTs), coiled carbon nanofibers (CCNFs), and CNCs. We distinguish a CCNT from a CCNF in that the former comprises single- or multi-walled carbon nanotubes while the latter is a solid amorphous structure. Lying between the two kinds of materials mentioned above, CNCs are composed of several coiled hollow tubules with low crystallinity. The growth mechanism of these carbon coils has been reported by some researchers. Amelinckx et al. proposed a model of spatial-velocity hodograph to describe a formation mechanism for a catalytically grown CCNT.[2] Similarly, Kanada et al. have synthesized CCNTs with a higher crystallinity than CNCs, and proposed a possible base-growth mechanism which is similar to that of CNTs synthesized using a Fe catalyst.[11] Bandaru et al. proposed a plausible model for coiling in nanostructure growth motivated by both energy and entropic principles i.e., for a given volume of material, the helical form occupies the least amount of space.[12] Motojima and Chen proposed a three-dimensional growth model of carbon microcoils based on the anisotropy of the carbon deposition among three crystal facets; six fibers are grown from a Ni grain and coalesce to form two fibers, and then the two fibers entwine to form a double helix microcoil.[13] Zhang et al. proposed a four-step model to describe the formation of a CNC and considered that the symmetry of the crystal facet structure, together with other external factors, result in the growth of carbon coils with symmetrical morphology.[14] Qin et al. have synthesized CCNFs in a symmetric growth mode by the decomposition of acetylene with a copper catalyst, and proposed that this mirror-symmetric growth mode was induced by the shape changes in copper nanocrystals while catalyzing the decomposition of acetylene.[15] None of these can explain the growth of CNCs adequately, however, because the constitution and the geometric structure of the catalysts for CNCs are both different from those for CCNT, CCNF, or carbon microcoil. Pan et al. suggested that the non-uniformity of the carbon extrusion speed at different parts of the catalyst particle leads to the helical growth of nanocoils,[5] however the problems of why the carbon extrusion speed varies and how the structure of a catalyst

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particle affects the growth of a CNC have not yet been resolved. In this article, we report on our investigation of the relationship between the geometric structures of catalysts and the growth of CNCs based on the morphologies of the observed CNCs and the catalyst particles at their tips.

2. Results and Discussion

Figure 1 shows the representative scanning electron microscopy (SEM) image of the CNCs synthesized on the catalyst particles of Fe–Sn–O by a CVD method at the growth temperature of 700 °C for 10 min. Fine catalyst particles are observed at the tips of the grown CNCs, indicated by the arrows in Figure 1, suggesting a tip growth mechanism. The numbers of right-handed and left-handed CNCs are almost the same. The CNCs have coil diameters of 500 to 700 nm and coil pitches of 300 to 600 nm. The lengths of CNCs can reach up to several tens of micrometers for a 30 min growth.[9,10]

Figure 2a shows a transmission electron microscopy (TEM) image of a CNC twisted by two carbon tubules, each of which is also twisted by other two hollow tubules. It is observed that the catalyst particle at the tip of the CNC has an irregular polyhedral structure, and at least one flat facet is exposed to the outside without carbon precipitation, as indicated by an arrow. An energy dispersive X-ray (EDX) spectroscope was employed to study the elemental constitution of the single catalyst particle, as shown in Figure 2b. It was found that the catalyst is mainly composed of Fe, Sn, C, and O, in which the molar ratio of Fe/Sn is approximately 15:6, which is considered to be the optimal ratio for the growth of CNCs.

TEM observation reveals that the grown CNCs consist of two, three, or four carbon tubules, but no more than four tubules are found. The TEM images and the corresponding schematic illustrations of the CNCs are shown in Figure 3. It is observed from Figures 3a and 3b that a CNC consists of two coiled hollow carbon tubules with almost the same coil diameter and pitch. The two dashed lines in Figure 3b indicate the hollow parts in the two carbon tubules. These tubules have outer and inner diameters of approximately 50 and 9 nm, respectively. It is shown in Figures 3c and 3d that

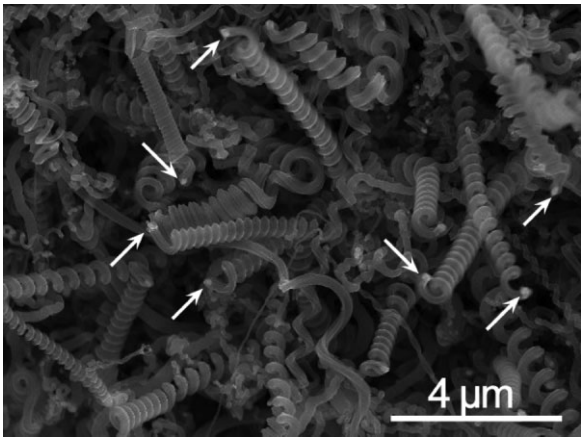

Fig. 1. SEM image of the CNCs grown at 700 °C for 10 min with the acetylene flow rate of 30 sccm. The white arrows point to the tips of CNCs.

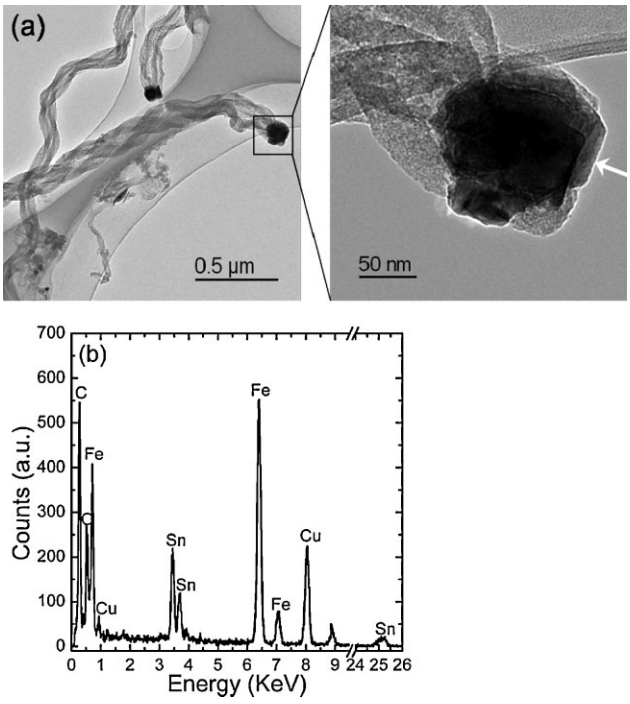

Fig. 2. a) TEM image of a CNC twisted by two fibers and the enlarged image of the catalyst particle at the tip of the coil. b) EDX spectrum of the catalyst particle in Fig. 2a.

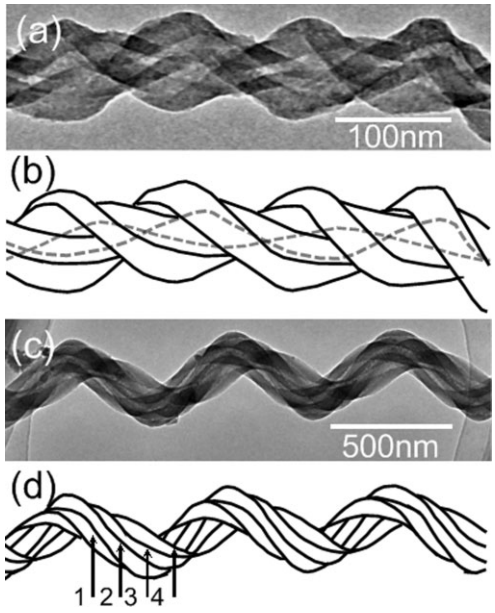

Fig. 3. TEM images and the corresponding schematic illustrations of two kinds of carbon coils. a) A CNC formed by two coiled hollow carbon tubules. b) Schematic illustration of a) where two dashed lines indicate two hollow

four tubules with different diameters and the same pitch form a perfect CNC with a coil diameter of 400 nm. It is difficult, though, to distinguish the hollow part of each tubule in the TEM image of Figure 3c because of the complex constitution of the CNC. Furthermore, the structures of all these CNCs are almost amorphous, which differs from those of CCNTs.

SEM images and the corresponding schematic illustrations of several CNCs with the catalyst particles at their tips are shown in Figure 4. It was observed that the catalyst particles were all polyhedral structures, most of which were hexahedron. The catalyst particle consists of two kinds of crystal facets, those with, and without, carbon precipitation. It was found that at least two adjacent flat facets without carbon precipitation are located at the tip of a coil, exposed to the gas atmosphere, which is also observed in Figure 2b. These facets are considered to be catalytically active facets which play the roles of adsorption and decomposition of hydrocarbon gas and diffusion of the formed carbon atoms. The other facets play a role of carbon precipitation, from which carbon fibers or tubules are grown out. In the growth process, carbon atoms are formed continuously on the adjacent catalytically active facets and migrate by surface and bulk diffusion to the precipitation facets where carbon tubules are grown. It is noted that the carbon atoms are diffused, not in an isotropic direction to only one precipitation facet, but to all the adjacent facets. It can be clearly seen in the SEM images, especially in Figure 4d, that a carbon tubule is bent along the direction from a catalytically active facet to its adjacent precipitation facet, suggesting that the rate of surface diffusion is larger than that of bulk diffusion. From this observation, we propose a growth model for the bending of a tubule as shown in Figure 5. The hydrocarbon gas is supplied to the surfaces of the adjacent catalytically active facets and decomposed to carbon atoms that are diffused to the precipitation facets and form carbon tubules. It is reasonable to consider that the rate of surface diffusion, V_s, has the largest value, and the rate of bulk diffusion is decreased by the increase of the diffusion distance, therefore a gradient of carbon precipitation rate is formed along the surface of a precipitation facet, leading to the bending of the grown carbon tubule. Carbon precipitation from one or two facets results in the growth of a single, coiled carbon tubule. On the other hand, the activity of hydrocarbon decomposition on the surfaces of the adjacent active facets is different/same, leading to the different/same carbon precipitation rates among the precipitation facets; carbon tubules formed from different precipitation facets would have different/same coil diameters and are coalesced together to form a three-dimensional CNC.

It is shown in Figure 4a that the catalyst particle at the tip of a CNC consists of three catalytically active facets. Three nanotubules are grown out from another three precipitation facets, and coalesce with each other to form the coils with triple carbon tubules. The catalyst particle in Figure 4b possesses a mirror-symmetric structure with over two active facets. In addition to the two adjacent side active facets, part of the upper facet is also active, surrounding which carbon has been precipitated. The underside facet would be the same as the upper side. In this case, only one tubule could be

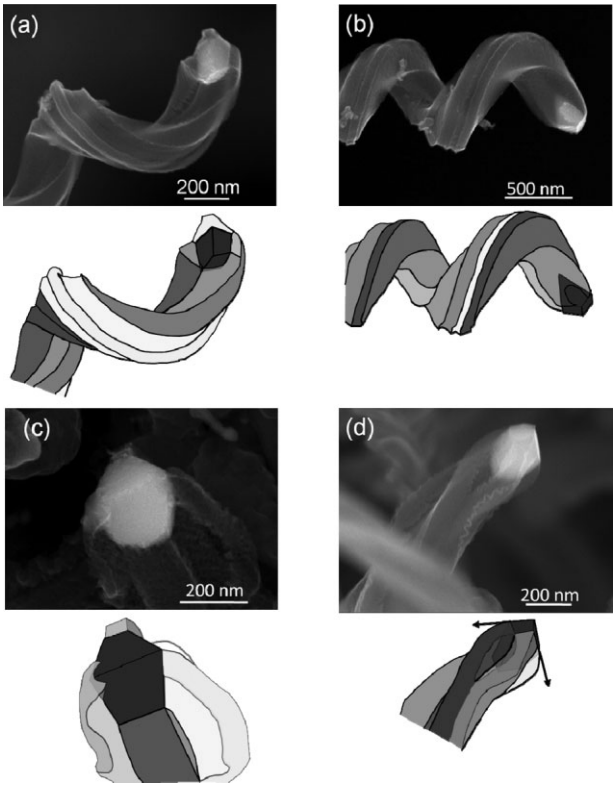

Fig. 4. SEM images and the corresponding schematic illustrations of several CNCs. a) A coil formed by three tubules with the catalyst consisting of three active facets on its tip. b) A coil formed by two tubules with the catalyst consisting of over two active facets on its tip. c) and d) Two coils formed by four tubules but grown out from the catalysts with two active facets and symmetric/asymmetric structures.

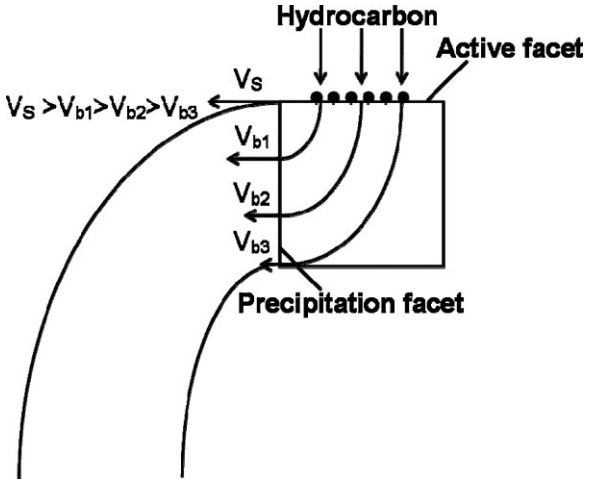

Fig. 5. Growth model for the bending of a tubule. V_s and V_b represent the rates of surface and bulk diffusion, respectively, where $V_s > V_b$.

grown from two adjacent facets, and this kind of catalyst particle is speculated to lead to the growth of two tubules with the same coil diameter and pitch, twisted to form a double-helix CNC. The catalyst in Figure 4c also possesses a mirror-symmetric structure but only two active facets. Each precipitation facet plays an independent role in forming a carbon tubule, which leads to the growth of a carbon coil consisting of four carbon tubules. For the same reason, in Figure 4d, four carbon tubules are grown out from the four precipitation facets of the catalyst particle with asymmetric structures and two active facets. Each two tubules grown from two adjacent facets are fused together to form twin tubules, then the two twin tubules are twisted round each other to form a nanocoil which has a similar structure to that shown in Figure 2a.

3. Conclusions

CNCs have been synthesized by catalytically thermal CVD using Fe–Sn–O as the catalyst. The grown nanocoils generally consist of over two carbon tubules with almost amorphous structures, and most of the catalyst particles are of a hexahedron structure. A growth model of CNCs is proposed such that the difference in the carbon diffusion through surface and bulk of a catalyst particle results in the difference of precipitation rates among the precipitation facets, from which the carbon tubules are formed and coalesced together to form a three-dimensional CNC. It is considered that a catalyst with three active facets leads to the growth of a CNC consisting of three tubules, while a catalyst with mirror-symmetric structure and over two active facets results in the formation of a CNC consisting of two tubules with the same coil diameter and pitch. Finally, the CNCs consisting of four tubules are grown out from the catalyst with symmetric/asymmetric structure and two active facets.

4. Experimental

$Fe_2(SO_4)_3/SnCl_2$ was selected as the catalyst precursor. The molar ratio of iron to tin was maintained at 3:1. A sol-gel process was used to prepare the catalysts, where 0.01 mol $Fe_2(SO_4)_3$, 0.0067 mol $SnCl_2$, and 0.03 mol-$C_6H_8O_7.H_2O$ were mixed with 100 mL ethanol, then the mixture was heated and stirred at 80 °C for 3 h to transform the solution into a sol, and then into a gel. The gel was heated in air at 700 °C for 3 h for the generation of catalyst particles containing the oxides of iron and tin (Fe–Sn–O). Catalyst particles with a mass of 0.010 g were dispersed on SiO_2 substrates (size: 10 mm × 10 mm). CNCs were synthesized on these substrates in a thermal CVD system at 700 °C for 30 min by introducing acetylene diluted by argon gas with a total flow rate of 260 sccm. Approximately 0.251 g deposits were collected after CVD.

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