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Structure and growth of aligned carbon nanotube films by pyrolysis

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Abstract

Transmission electron microscopic study on the aligned carbon nanotubes has demonstrated a growth mechanism which involves two sizes of iron nanoparticles. While the small particle is catalytically active for the nucleation of the nanotube, the large particle produces the carbon atomistic species required for the growth of the nanotubes. The aligned nanotubes are believed to be the result of a competition growth process along the normal direction of the substrate. The surface diffusion of carbon atoms on the large iron particle leads to the formation of the observed bamboo-like structure. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Carbon nanotubes with a straight, curved, planar-spiral, and helical shape have been produced (see, e.g., Ref. [1]). These elongated nanotubes consist of carbon hexagons arranged in a concentric manner with both ends of the tubes normally capped by fullerene-like structures containing pentagons and possibly heptagons. They can exhibit semiconducting or metallic behavior depending on their diameter and helicity of the arrangement of graphitic rings in the walls. Dissimilar (carbon) nanotubes may be joined together allowing the formation of molecular wires with interesting mechanical, nonlinear optical, electrical and magnetic properties attractive for a number of potential applications (see, e.g., Ref. [2]). To mention but a few examples: carbon nanotubes have been proposed as new materials for electron field emitters in panel displays [3], single-molecular transistors [4], quantum wires [5], scanning probe microscope tips [6], gas and electrochemical energy storage [7], ultra-strong fibers [8], and molecular-filtration membranes [9,10]. The concept of filling the hollow cores of carbon nanotubes with foreign materials takes the nanotechnology one step further, by introducing various nanocomposites of properties characteristic both of the encapsulated and encapsulating materials with potential synergetic effects, and hence has additional significant impact on the potential applications of nanotubes. Carbon nanotubes filled with ferromagnetic nanoparticles (e.g., Fe, Ni or Co), for example, are attractive for the development of magnetic data storage devices, toners and

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inks for xerographyl [1,11]. For most of the above applications, however, it is highly desirable to prepare aligned carbon nanotubes.

A few approaches to aligned carbon nanotubes have recently been reported [12–14]. In particular, we have recently developed a technique for large-scale synthesis of carbon nanotubes (up to several square centimetres) aligned into the direction normal to the substrate surface (typically, quartz glass plates) by pyrolysis of iron(II) phthalocyanine (FePc) under Ar/H_2 (1:1–1:2 v/v) at 800–1100°C [15]. The aligned nanotubes thus produced are shown to contain iron nanoparticles. While the macroscopic structure and micropattern formation of the aligned nanotube films have been demonstrated elsewhere [15,16], the detailed growth mechanism of the aligned nanotubes is reported in this paper.

2. Experimental

The aligned carbon nanotubes were prepared by pyrolysis of iron(II) phthalocyanine, FePc, under Ar/H_2 atmosphere at a predetermined temperature using an appropriate substrate in a flow reactor consisting of a quartz glass tube and a dual furnace fitted with independent temperature controllers (fig. 1 of Ref. [15]). In a typical experiment, the quartz substrate is about 10–20 cm apart from the FePc source. There are two specimens used for this study, and they are prepared as follows.

For the specimen I, 0.3 g FePc and a clean quartz glass plate (ultrasonicated in aceton) were placed over the first and second furnaces, respectively, in the quartz glass reactor [15]. A flow of Ar/H_2 (1:1 v/v, 60–70 cm^3/min) was then introduced into the quartz tube while heating up the second furnace. After the second furnace reached a predetermined temperature of 850°C, the first furnace was heated at 650–750°C for ca. 10 min. Thereafter, both furnaces were kept at the pyrolysis temperature (850°C) for ca. 10 min to complete the pyrolysis process.

Specimen II was grown following a similar procedure as the first sample, but at a pyrolysis temperature of 900°C and using a self-assembled monolayer (SAM)-coated quartz glass plate. To prepare the SAM/quartz, a clean quartz glass plate was immersed into $CH_3(CH_2)_{16}SH$ for 30 min, rinsed with acetone, dried under a stream of nitrogen and used immediately. The detailed effect of the SAM layer on the growth of the branched nanotubes is still under investigation.

The microstructure of the carbon nanotubes was studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM was carried out at 15 kV using a Hitachi S800 equipped with a field emission source. The specimen used for SEM was either from the as-grown film or scratching a piece on a carbon tape. TEM was performed at 400 kV using an JEOL 4000EX and at 200 kV using a Hitachi HF-2000.

3. Experimental results

3.1. Microstructure of specimen I

To reveal the growth process of the carbon nanotubes, the general structural morphology was examined by SEM. From a piece of the scratched film (Fig. 1a), SEM clearly reveals the high density of the

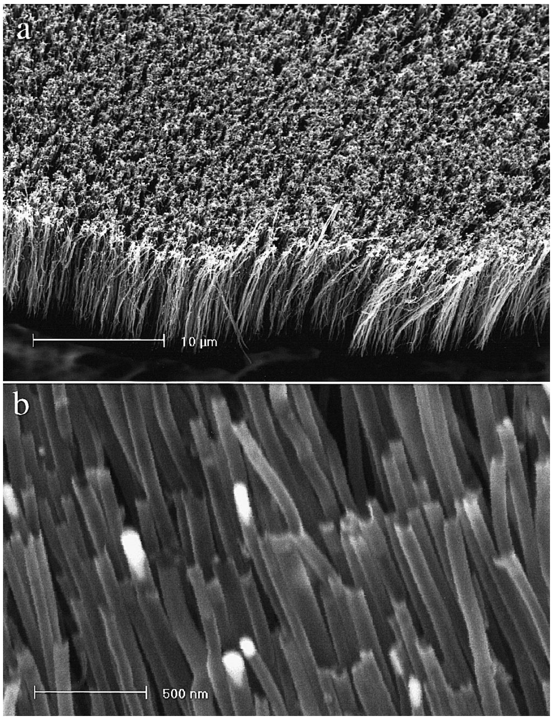

Fig. 1. (a) Low-magnification SEM image showing the uniformity of the aligned carbon nanotubes grown by pyrolysis. (b) SEM of the growth front after removing the iron particles, exhibiting the open-end structure of the carbon nanotubes.

aligned carbon nanotubes. The layer coating at the bottom surface of the carbon nanotubes is a layer of fine iron particles, whose chemical composition was identified by EDS. The large iron particles at the growth front can be removed chemically, resulting in carbon nanotubes with open ends (Fig. 1b). This is particularly attractive for chemical applications.

To reveal the details of the carbon nanotubes, a small quantity of the as grown film was dispersed on a holey carbon film supported by a copper mesh, which was inserted in TEM for examination. The carbon nanotube has an average length of ~ 10 μm and an average diameter of ~ 20 nm (Fig. 2a). The size of the nanotubes is rather uniform. From the TEM image, the iron particles distributed at the roots of the carbon nanotubes are small, and detailed TEM image reveals that the particle size is slightly larger than the inner diameter of the carbon nanotube (Fig. 2b, c). It can be clearly identified that the particles at the roots are mostly wrapped up by a carbon layer (see the particles indicated by arrowheads in Fig. 2c), suggesting that these particles are responsible for the nucleation of the carbon nanotubes but cannot be responsible for their growth. At the roots of the nanotubes (Fig. 3a), the marks left by the iron particles falling off the substrate are still visible, where the circular shape was produced by the contact of the iron particles with the nanotubes when the nucleation started.

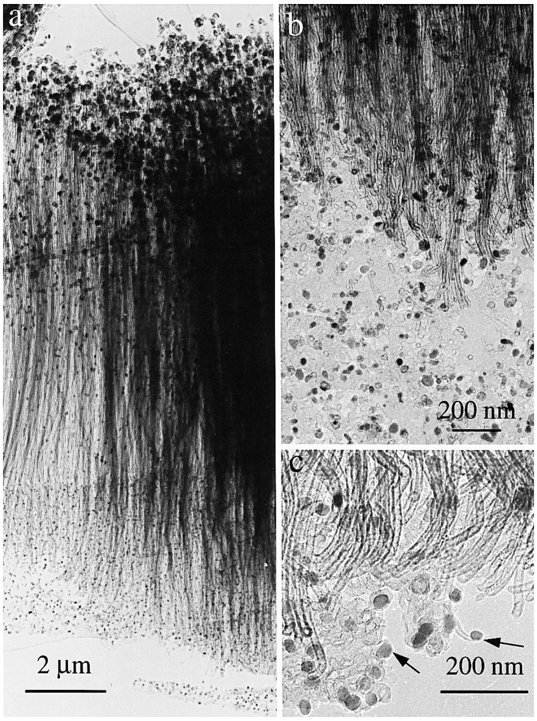

Fig. 2. TEM images showing (a) the full picture of the grown carbon nanotubes, and (b, c) the nucleation sites of the carbon nanotubes.

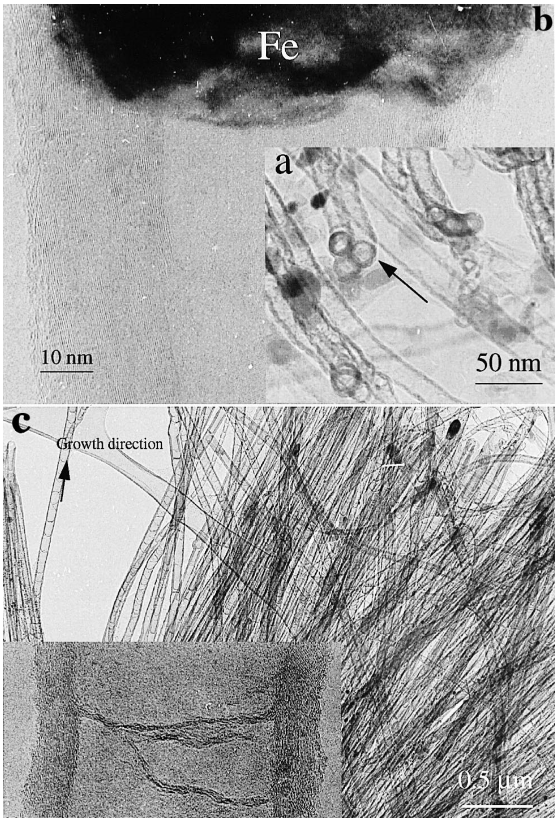

Fig. 3. (a) TEM image of the nucleation sites of the carbon nanotubes. (b) High-resolution TEM image of the growth front of a carbon nanotube, where the wall thickness is apparent and the large iron particle is at the forefront tip of the nanotube. (c) The bamboo-like interior structure of the grown carbon nanotubes.

The iron particles at the tips of the carbon nanotubes are significantly larger than the diameters of the nanotubes (Fig. 2a). High-resolution TEM image reveals that the larger particle at the growth front is partially attached to the nanotube, while a large portion of its surface is exposed to the reaction gases

(Fig. 3b). It is known that the presence of the catalysis is mandatory for the nucleation and growth of carbon nanotubes. The TEM image given in Fig. 3b apparently indicates that the large iron particles are responsible for producing the carbon atomistic species required for the growth of the nanotubes.

The carbon nanotube has a bamboo-like structure (Fig. 3c). The inner tube is almost empty but subdivided by single or double graphen layers. The wall thickness is ~9 nm. The nanotubes are believed to pertain a high density of defects as judged from their curly geometry. Removal of the iron particles at the growth front results in carbon nanotubes with open ends, which is an ideal structure for chemical functionalization of the nanotubes.

3.2. Microstructure of specimen II

Specimens grown at higher temperatures are also well aligned, and the top of the film is capped by iron particles (Fig. 4a and b). TEM images given in Fig. 4c apparently shows that the diameters of the nanotubes are significantly larger than those of the nanotubes grown at a lower temperature. The distribution of the diameters is also wider. The most striking feature to note is that the iron particles are

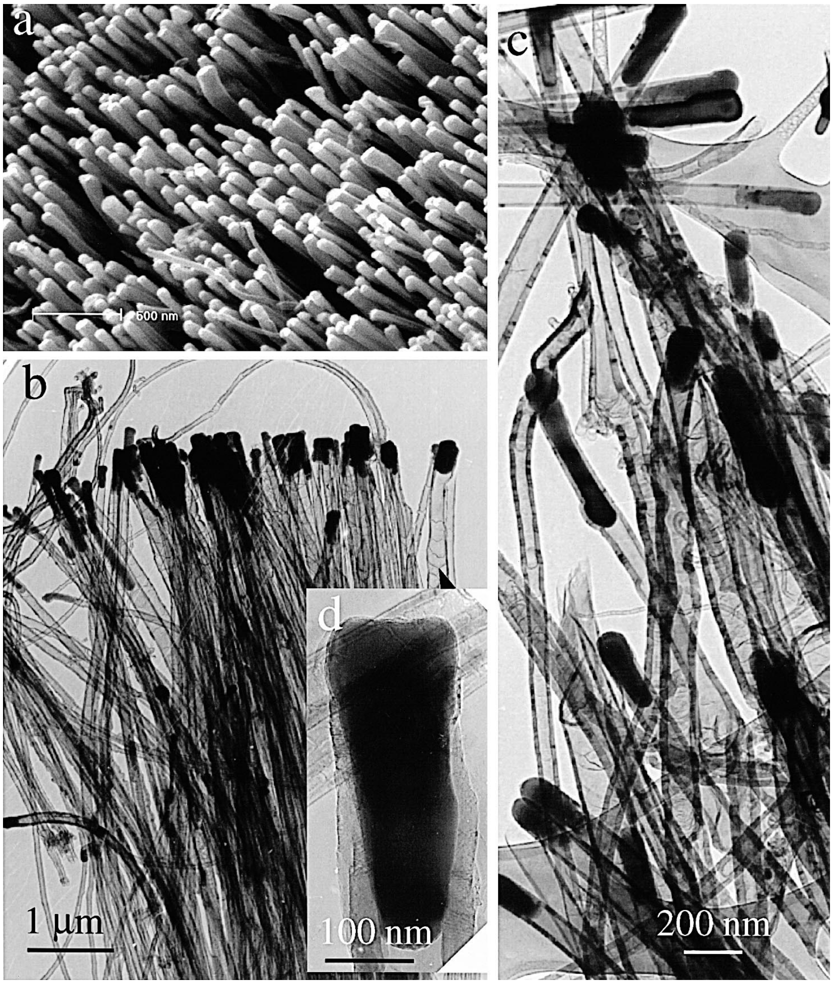

Fig. 4. (a) SEM image of the iron particle capped carbon nanotubes grown at a high temperature. (b, c) Corresponding TEM images of the carbon nanotubes showing the plugging of the iron particles into the carbon nanotubes. (d) The 'cork' structure of the iron particle.

mostly enclosed by the carbon tubes. A closer image of the iron particle reveals its 'cork' structure (Fig. 4d), where the particle has an elongated structure with an aspect ratio of ~ 3–5 and the carbon layers are closely wrapped on the side surface of the particle, while the carbon coverage on the tip surface is very thin.

4. Discussions

4.1. Growth mechanism of the aligned carbon nanotubes

To propose a growth mechanism of the carbon nanotubes, we speculated that FePc powder first evaporated from the first furnace to the second furnace, where it decomposed into atomic iron (from the reduction of Fe^{2+} by hydrogen) and phthalonitrile species under H_2/Ar at a high temperature (above 750°C). Almost simultaneously, the phthalonitrile decomposed into benzene rings and CN units while the iron atoms aggregated into nanoparticles on the substrate as catalytic centers for the growth of the aligned nanotubes. The benzene rings and CN units may fragment further, liberating C_n, CH_n, and N_2. These carbon species then precipitated on or diffused through the metal particles.

The growth of carbon nanotubes starts from the deposited catalysis layer, which is the iron in our case. The deposited iron film consists of larger particles and smaller ones. As mentioned above, the larger iron particles are mainly responsible for producing the carbon atomistic species required for the growth of the nanotubes, and the smaller iron particles are likely to be catalytically active because their higher surface energy facilitates the very first generation and accumulation of carbon atoms for the formation of a thin layer of graphitic film at the initial stage of the nanotube growth (Fig. 5a). The graphite layer thus formed could quickly enclose the iron particle, generating a concentric graphitic shell or a semi-spherical graphitic shell depending on the contact pattern of the particle with the substrate (Fig. 5b). The above conjecture is supported by our experimental observations of the nanotube roots shown in Fig. 2c and Fig. 3a. The coating of the smaller iron particles by carbon immediately stopped the catalytic activity of the particle, so that the only surfaces with active catalysis are the surfaces of the large iron particles.

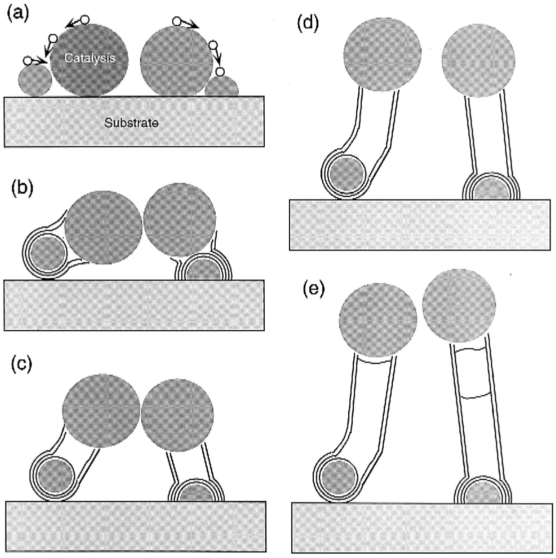

Fig. 5. Proposed growth mechanism of the carbon nanotubes on a flat substrate (see text).

Upon a full enclosure of the small iron particle by carbon, its surface catalytic activity for generation of carbon atoms was eliminated. The continuous generation of carbon atoms by the larger iron particles and their diffusion towards the neck region between the small and large particles (due possibly to a localized surface energy and/or temperature effect), however, led to a growth of cylindrical graphitic shells at the neck region (Fig. 5b). This can be considered as the beginning of the nanotube growth, and the contact area determines the inner diameter of the tube. As the nanotube growth proceeds, the large iron particle becomes further apart from the small iron particle, and the head-on contact between two adjacent large iron particles forces the nanotubes to grow vertically on the substrate surface (Fig. 5c). Remember the gravity plays little role here because any of these particles are rather small and light. There are three possibilities. One, the nanotubes growing parallel or nearly parallel to the substrate surface will be terminated at some length when they hit other nanotubes or iron particles. Second, the nanotubes growing along normal or nearly normal directions continue to growth to form large length nanotubes, thus the aligned nanotube film. This is the final produce we observed by SEM (see Fig. 1a). Finally, the nanotubes growing along a direction between the two cases will be aligned along the normal direction if the iron particle contacts another tube/particle and turns its growth direction (Fig. 5c). This competition growth process is similar to the growth of textured diamond film on a silicon substrate [17].

Since any newly-produced carbon atoms are 'inserted' into the nanotube structure at the contact region between the large iron particle and the *already formed* tubule segment, a uniform growth with a constant tube diameter and number of layers was observed (Fig. 5c). The insertion of pentagon and/or heptagon defects into the hexagonal graphite network, however, could curl the resulting nanotubes (Fig. 5d), as previously demonstrated [18]. Also, it is possible that some carbon atoms could diffuse on the surface of the iron particle and penetrate into the tube, forming a bridge structure across the nanotube wall, and hence the bamboo-like structure is formed inside a continuously growing nanotube (Fig. 5e). This is supported by the experimental image given in Fig. 3c, where the direction of the curly bamboo-layer is consistent with the expected result from the model.

4.2. Possible applications in magnetic data storage

From the two specimens prepared at pyrolysis at 850°C and 900°C, a big difference is seen in the microstructure of the tubes. The specimen prepared at the higher pyrolysis temperature contains larger size, cork-like Fe rods aligned along the longitudinal axis, possibly because of the increased coalescing. The iron is infiltrated into the top section of the nanotubes, and iron leakage is rarely seen. The aligned iron rods could be quite interesting in magnetic data storage. This issue is important in present recording technology with densities of around 100 megabits per square inch in the longitudinal magnetic recording (LMR), in which the direction of magnetization is parallel to the surface of the film, and it will be critical to the future development of ultrahigh density storage in the order of 10 Gbit/in^2, at which a single recording bit is expected to be 1 μm wide, only 70 nm long and the film thickness is only 30 nm. If the domain size is made smaller, a trend of increasing the density to more than 300 Gbit/in^2 is predicted in the 21st century [19] based on computer simulations [20] using the perpendicular magnetic recording (PMR) mode, in which the magnetization is perpendicular to the surface of the film. Moreover, the size of the domain determines the limit of information storage in high-density magnetic recording while the sharpness of the domain boundaries is closely related to the media noise. The noise reduction can be achieved by the segregation of a nonmagnetic phase at the grain boundaries, thus, the media are composed of at least two materials. The cork shape iron particles infiltrated into aligned carbon nanotubes with thin walls could be useful for this application. Detailed studies on the magnetic properties of the aligned carbon nanotubes are being undertaken.

5. Conclusions

In summary, our electron microscopic study on the aligned carbon nanotubes produced by the pyrolysis of FePc has clearly demonstrated a novel growth mechanism, which involves two iron nanoparticles of different sizes. While the small iron particle is catalytically active for the nucleation of the nanotube, the large iron particle produces the carbon atomistic species that are required for the growth of the nanotubes. The growth of the carbon nanotubes is a competition process, in which the nanotubes growing parallel or nearly parallel to the substrate surface will be terminated as they hit other tubes or particles, while those growing initially normal or nearly normal to the substrate will continue to grow, resulting in the formation of the aligned nanotubes. Therefore, the area density of the nanotube may be far less than the density of the iron particles on the substrate surface.

The surface diffusion of carbon atoms on the large iron particle across the nanotube wall leads to the formation of the observed bamboo-like structure. The removal of the iron particles at the growth front could lead to carbon nanotubes with open ends, a sort of structure which is ideal for chemical functionalization, whereas the presence of the larger size, cork-like Fe rods aligned along the longitudinal axis of certain aligned nanotubes should make the Fe encapsulated materials very attractive in the longitudinal magnetic recording (LMR) application.

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