Communication

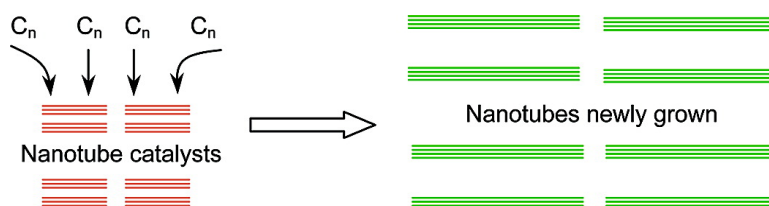# Self-Catalytic Behavior of Carbon Nanotubes

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Self-Catalytic Behavior of Carbon Nanotubes

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Growth of carbon nanotubes (CNT) is highly promoted by metal nanoparticles under mild conditions (below 1500 K), but the growth mechanism in the metal catalytic environments is still foggy on many critical aspects.[1] In the case of the multi-walled nanotubes, a mostly cited mechanism is based on the adsorption−diffusion−precipitation model;[1,2] C_n species are first adsorbed on the surface of the metal particle, then diffuse through the metal particle and precipitate in crystalline tubular form. In this mechanism, all of the C_n species that participate in building nanotubes should be caught by the metal particles, that is, metals operate in the entire growth process. However, such a situation is difficult to be imagined for many approaches, such as floating chemical vapor deposition (CVD)[3] and detonation (can be viewed as detonation-assisted CVD).[4] In these processes, since the generation and deposition of carbon and metal species are nearly synchronous and the carbon/metal atomic ratio can be higher than 50, an interaction of the dense C_n species should be more probable than their capture by the sparse metal nanoparticles, but the fact is that more than 80% of the deposited carbons could assemble into tubular structures.[3,4] A possible explanation is that assembling C_n species into CNTs is catalyzed not only by metals but also by growing tube embryos and/or juveniles.

Direct observation of nanotube self-catalysis in a metal-containing system is difficult since the growth environment is too chaotic to differentiate a tube-catalysis from a metal-catalysis. Using presynthesized nanotubes to examine their possible catalytic role meets new problems for conventional synthetic systems. For example, in a usual CVD system, CNTs could maintain their intrinsic forms, but C_n species for building new nanotubes are unavailable without metal catalysis. Conversely, under the conditions of the laser and arc-discharge processes,[5] any tubular carbons premixed into a graphitic starting material would not survive but be vaporized into small C_n species. Fortunately, the detonation synthetic system[4] can provide a unique environment, which ensures a survival of the pre-fed CNTs and simultaneously a ready generation of the C_n species. This advantage of the detonation system enables us to give an insight into the self-catalysis of CNTs under the conditions in which metal catalysis was previously figured to work only.

We use short nanotube pipes (CNT$_{catal}$) as catalysts to imitate growing tubes and to facilitate a distinction between the CNT$_{catal}$ and the newly formed nanotubes (CNT$_{new}$). They are prepared by opening and cutting the commercial CVD tubes with a ball-milling technology[6] and then by treatment with HCl solution and concentrated HNO_3 to remove originally existing iron (down to 0.2 mg/g) and thus to eliminate possible interference from metal catalysis. The pipes of CNT$_{catal}$ are end-opened, having lengths of 200−800 nm and diameters of 10−40 nm, averaging 30 nm (Figure 1). Their hollow channels are very narrow, with the ratios of channel diameter to tube wall thickness being usually less than 1.

To validate the stability of the CNT$_{catal}$ tubular form in a detonation environment, we mixed 20 mg of CNT$_{catal}$ into 2.5 g of
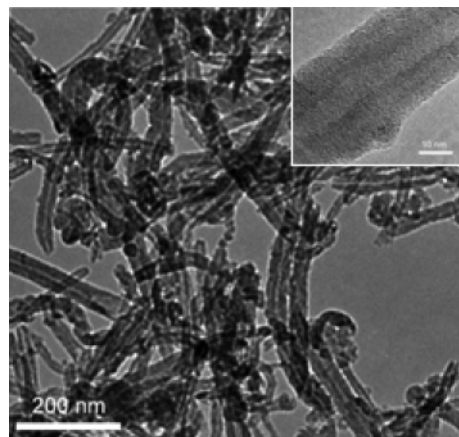

Figure 1. TEM images of the acid-treated nanotube pipes (CNT$_{catal}$). Note the narrow channels. The inset is a magnified tube.

trinitrophenol and let the mixture explode in a sealed reactor. The black solids left behind from the detonation mainly contain short CNTs with morphologies similar to that of the CNT$_{catal}$ (Figure S1), indicating that the short pipes can survive in the detonation environment.

Before the target examination, it is necessary to find proper experimental conditions for catalytic growth of nanotubes. A mixture containing 2.5 g of trinitrophenol, 0.45 g of cyclohexane, and 0.06 g of cobalt acetate has proved to be excellent for this purpose, its detonation produces CNTs with a purity of about 90% (Figure S2), despite the employed quite high carbon/cobalt atomic ratio (100, calculated from the amounts of cyclohexane and cobalt acetate). In this system, cyclohexane serves as carbon source and is decomposed into C_n species by the trinitrophenol detonation-produced thermal energy; cobalt acetate decomposes and gives cobalt nanoparticles to catalyze the assembly of the C_n species into nanotubes. Deporting cobalt acetate from the mixture leads to a material containing only amorphous carbon spheres and debris (Figure S3), which provides a blank mirror and indicates that the presence of a catalyst is crucial for nanotube formation under the employed conditions.

Adding 0.02 g of CNT$_{catal}$ (replacing cobalt acetate) into a trinitrophenol−cyclohexane mixture leads expectedly to a formation of new nanotubes (Figure 2a), about 50% of the resulted samples. The CNT$_{new}$ normally disjoint with the CNT$_{catal}$ (arrowed) and can be easily differentiated from the CNT$_{catal}$. Unlike the CNT$_{catal}$, the CNT$_{new}$ have large lengths (up to tens of micrometers) and large diameters (average of 70 nm). More typically, their inner channels are quite wide, and the ratios of channel diameter to tube wall thickness are usually larger than 2 (Figure 2a,b). The CNT$_{new}$ are often open at two ends. Their walls are well graphitized (Figure 2b), similar to that of the nanotubes produced by metal catalysis. Since a trace amount of iron brought from the CNT$_{catal}$ into the self-catalytic system is far insufficient to effectively catalyze tube
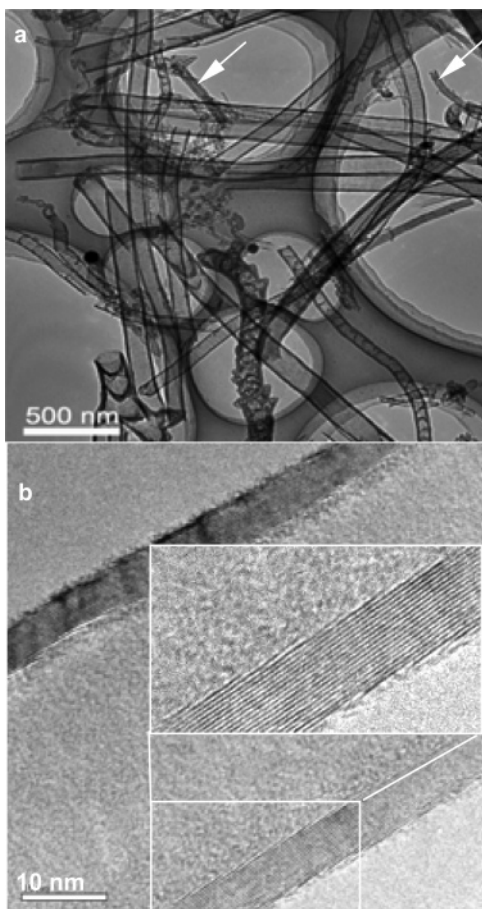
Figure 2. (a) TEM images of the newly formed nanotubes (CNT$_{new}$) produced by CNT$_{catal}$ catalysis. The arrowed objects are the remaining CNT$_{catal}$. (b) Graphitic microstructure of the walls of CNT$_{new}$.

growth, as evidenced by a special test, the above results unambiguously show that carbon nanotubes, themselves, really have an excellent self-catalytic property under the conditions in which metal catalysis was previously figured to work only. The large difference between the CNT$_{catal}$ and CNT$_{new}$ in their diameter and channel likely originates from the different growth environments, CVD for CNT$_{catal}$ and detonation for CNT$_{new}$. It is supported by the similarity of the channels of the nanotubes produced from the self-catalysis and from the metal catalysis (Figure S2) and by the fact that the nanotubes further produced by using the CNT$_{new}$, as catalysts, as particularly tested, resemble the original catalyst nanotubes in diameter and channel. In addition, compared with the metal catalysis grown nanotubes, which have closed ends that are stopped frequently by metal nanoparticles,[3,4] the end-opened feature of the nanotubes produced by the present nanotube self-catalysis implies that closing nanotubes is helped by metal catalysts, which are responsible for a growth termination, and thus this self-catalytic behavior may be further adjusted for a synthesis of long nanotubes.

The disjunctive feature of the CNT$_{catal}$ and CNT$_{new}$ and their great difference in diameter and channel suggest that a nanotube has the catalytic ability for the nucleation of a new one, probably via a seeding-like process. The fact that the CNT$_{new}$ are much longer than the CNT$_{catal}$ and exhibit multi-walled graphitic structures indicates that, in the absence of metal catalysts, carbon nanotubes, themselves, can adsorb and install free C$_n$ species at their opening edges and sidewalls and thus to grow axially and "fat" radially, similar to the situation in the high-temperature noncatalytic laser or arc-discharge processes.[5] For the radial fatting, the structural defects[7] on the tube walls probably serve as proper sites for the nucleation and development of new graphene layers. For the axial growth, the so-called "lip–lip" interactions[8] between the graphitic layers likely help to stabilize the opening edges to prevent tube ends from closure, which leads to a termination of tube growth. It is also of interest to note that the graphitic structures of the nanotubes are formed by a self-catalysis at temperatures of about 1200 K (see Supporting Information), different from the conventional view that graphitic structures are, without metal catalysts, formed at temperatures of higher than 2000 K. This result resonates with some recent results: pyrene group can be adsorbed onto the sidewall of a single-walled nanotube via π–π-stacking;[9] molecular graphene sheets can be self-assembled into graphitic nanotubes in wet mediums without any metal catalyst.[10] In a metal catalytic mild process, the initial nucleation of the graphitic nanotubes is likely helped by metal nanoparticles,[1,2] but once the nuclei are formed, they can intrinsically grow if C$_n$ species are available freely. Whether the curvature and/or low dimension of the nanotubes helps the formation of graphitic structures and the detailed information about how the self-catalysis perform is worth further regard.

In summary, a self-catalysis behavior of multi-walled carbon nanotubes is proposed for the first time and is experimentally validated under the conditions in which metal catalysis was previously figured to work only. The self-catalysis could support the nucleation and radial and axial developing processes. To better understand the growth mechanism of multi-walled nanotubes in a metal-involving process, the role not only of metal but of nanotubes, themselves, should be addressed. This conception may also bring a new viewport into the formation of single-walled nanotubes.[11]

Supporting Information Available: Experimental details and Figures S1–S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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