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Particle−Wire−Tube Mechanism for Carbon Nanotube Evolution

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Abstract: The synthesis of carbon nanotubes (CNTs) has been proved to be greatly promoted by vapor metal catalysts, but the fast reaction feature and the required high-temperature environment involved in CNT evolution usually make it difficult for an insight into the evolution mechanism. Here, we successfully freeze the synthetic reaction at intermediary stages and observe the detailed morphologies and structures of the obtained intermediates and various objects related to carbon nanotubes. It is unveiled that there is a kindred evolution linkage among carbon nanoparticles, nanowires, and nanotubes in the vapor catalyst-involved synthetic processes: tiny carbon nanoparticles first form from a condensation of gaseous carbon species and then self-assemble into nanowires driven by an anisotropic interaction, and the nanowires finally develop into nanotubes, as a consequence of particle coalescence and structural crystallization. The function of metals is to promote the anisotropic interactions between the nanoparticles and the structural crystallization. An annealing transformation of carbon nanoparticles into nanotubes is also achieved, which gives further evidence for the evolution mechanism.

Introduction

Many processes have been developed for the syntheses of carbon nanotubes (CNTs), and metals, such as iron, cobalt, and nickel, have been proved highly active to promote nanotube growth. Clear understanding of underlying growth mechanisms is of basic importance in further technical improvements and innovations for massive syntheses and structural controls. In the case of metal-catalytic growth of multiwall carbon nanotubes (MWCNT), the mechanism has been extensively studied, and an adsorption−diffusion−precipitation (ADP) model[1−3] has been widely accepted.[4−12] In this model, C_n species are first adsorbed on the surface of a metal particle, then diffuse through the metal particle, and finally precipitate in crystalline tubular form. In this mechanism, all of the carbon species that participate in building nanotubes should be initially caught by the preexisting metal particles. The key step is the diffusion of carbon through the metal particle, as it determines the total growth rate and steers hollow structure evolution.[1−3,12] Such a situation might be realistic in the conventional chemical vapor deposition (CVD) process,[13−16] from which the mechanism was initially established by Baker et al.[1−3] on the basis of the observation of catalyst particles being located at the filament (or tubule) tips. In this process, solid metal catalysts, normally nanoparticles supported on porous materials, are specially prepared and preloaded into reactor before the supply of carbon species, which is normally confined by a careful control of the feed rate of gaseous carbon precursor.[13−16] Such operations keep the metal/carbon atomic ratio at a high level to facilitate the capture of carbon species, their diffusion within the metal particle, and thus the high-yield formation of nanotubes.

However, many metal-catalytic CNT-synthetic processes such as laser[17,18] or arc-discharge[19,20] evaporation of metal-mixed graphite, decomposition of organometallic compounds (so-called floating CVD),[21−23] and detonation-assisted CVD[24,25] have characteristics much different from those of the conventional

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CVD process. In these technologies (they are somewhat different in the nature of energy and/or carbon precursors), essentially, carbon and metal species are simultaneously formed in the vapor phase from the vaporization or decomposition of their premixed precursors, leading to quite chaotic vapor-phase environments, behind which nanotubes are constructed by a co-deposition of the carbon and metal species:

$$\text{(C+M) precursors} \rightarrow \text{(C+M) species (gas)} \rightarrow \text{carbon nanotubes}$$

For convenient description, here we nominate it as a gas−gas (GG) process and the conventional CVD process as a gas−solid (GS) process.

Although the GG process-involved technologies have been widely used and proved highly robust for nanotube synthesis, the related mechanism was scantly specialized and often referred ambiguously to the ADP model.[18,26−28] However, much preliminary information suggests that such a referring is highly doubtable. For instance, as required by the ADP model, catalytic nanoparticles should be first formed from the chaotic gaseous carbon−metal system in a GG process, but, theoretically, the condensation of metal species to nanoparticles should leastways not have precedence over carbon deposition because catalytic metals (such as Fe, Co, and Ni) have boiling points much lower than that of carbon.[29] Additionally, because more than 80% of the deposited carbons could assemble into tubular structures at a rather high carbon/metal atomic ratio (>50), it is difficult to imagine that the dense C_n species would be gradually captured by the sparse metal nanoparticles rather than immediately interact between themselves. Therefore, the evolution of carbon nanotubes in the GG processes likely follows a way different from that in the GS process.

Here, we observe in detail various locations of metal nanoparticles within carbon nanotubes and the morphologies and structures of the carbon nanotubes produced from two typical GG processes, floating CVD and detonation-assisted CVD, and suggest that an application of the ADP model to the nanotube growth in the GG processes is inappropriate. Particularly, we perform the synthesis under unoptimizable conditions to freeze nanotube growth at embryonic and intermediate states. The detailed observations of the embryonic and intermediate objects formed along with nanotubes show that the growth of nanotubes in a GG process abides by a particle−wire−tube evolution mechanism, which is further confirmed by a successful transformation of carbon nanoparticles into nanotubes.

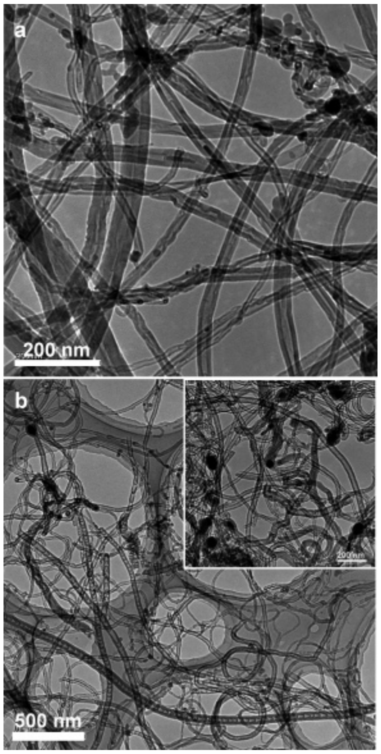

Figure 1. Carbon nanotubes obtained by (a) a floating CVD with starting material of acetylene and by (b) a detonation-assisted CVD with a recipe of picric acid, cyclohexane, and cobalt acetate. Inset of (b) shows the nanotubes obtained from a detonation-assisted CVD with a recipe of picric acid and ferrocene.

Experimental Section

Growth of CNTs by a Thermal Decomposition of a Mixture of Ferrocene and Acetylene. The synthetic procedure was similar to that reported elsewhere.[21] The experimental setup is a two-stage furnace system fitted with a quartz tubular reactor (25 mm i.d.). About 100 mg of ferrocene was placed in the first heating region and silicon substrate was placed in the second heating region, and then argon was flushed into the quartz tube at a flow rate of 100 sccm for 30 min to exchange air fully. Ferrocene was vaporized at 200 °C and carried by a mixture stream of argon (300 sccm) and acetylene (15 sccm) into the second heating region of the quartz tube where the pyrolysis was performed at 700 °C. After the consumption of ferrocene, we stopped feeding acetylene and allowed the reactor to cool to room temperature under argon. The materials produced on the substrates were collected for analyses. From the observation with transmission electron microscopy (TEM), the materials contain nanotubes of about 90% (Figure 1a).

Growth of CNTs by Detonation-Assisted CVD under Optimized Conditions. The starting materials, a mixture of 2.5 g of picric acid, 0.45 g of cyclohexane, and 0.06 g of cobalt acetate (or a mixture of 2.5 g of picric acid and 0.25 g of ferrocene), were premixed physically and loaded into a sealed stainless steal pressure vessel with a volume of 14 cm^3. The detonation was induced by heating to 583 K at a rate of 20 °C/min. The detonation reaction, lasting on a microsecond scale, generated pressure of about 45 MPa (shock wave, behind which the equilibrium pressure was about 15 MPa) and temperature of about 1200 K (note that the pressure behind the detonation was directly monitored by a pressure gauge fitted on the reactor, and the temperature was calculated on the basis of the pressure drop between the pressure behind the shock wave and the pressure at the time when the reactor was cooled to room temperature). After the reaction, the vessel was cooled to room temperature in air and emptied of gaseous products, and the solid products were collected. As analyzed by TEM, the cobalt catalysis is more effective than iron catalysis for nanotube growth, 90% versus 70% in nanotube yield (Figure 1b and the inset).

Freezing CNT Evolution at Intermediary Stages Using Detonation-Assisted CVD. The iron catalysis is less effective than the cobalt catalysis for nanotube growth as described above but leads to a more effective generation of intermediate objects; the picric acid−ferrocene system was selected for freezing the nanotube evolution at their

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intermediary stages. The primary experimental procedures were similar to those described above, while the freezing operation was carried out by releasing immediately (just after the detonation) the high-pressure hot gases from initial 15 to 5 MPa, which effectively reduces the system temperature and freezes the evolution at intermediary stages. After the operation, the reactor was cooled to room temperature naturally, the remaining gases were vented, and the solid products were collected for further characterization.

Reorganization of Iron-Encapsulated Carbon Nanoparticles into Nanotubes by Thermal Annealing. The detonation of the mixture of *m*-dinitrobenzene and ferrocene (molar ratio, 4:1) was purposively employed to prepare iron-encapsulated carbon nanoparticles (with the procedures similar to that employed for the above-described nanotube synthesis by detonation-assisted CVD); it effectively restrained the nanotube formation and resulted in pure nanoparticles as described later, which eliminated the possible intervention from the preexisting nanowires and nanotubes in the observation of the nanoparticle−nanotube transformation. The experiments of the thermal annealing of the iron-encapsulated carbon nanoparticles were performed in a horizontal tubular electrical furnace. 50 mg of the carbon nanoparticles was placed in a small quartz boat and put inside a quartz tube reactor (diameter, 25 mm; length, 600 mm), which was located in the electrical furnace. Argon was flushed into the quartz tube at a flow rate of 100 sccm for 30 min to exchange air fully, and, subsequently, the furnace was heated to 1000 °C (20 °C/min). The samples were treated at 1000 °C for 10 h in argon. Next, the furnace temperature was allowed to cool to room temperature, and the resulting materials were collected for further analyses.

Electron Microscopic Analyses. Electron microscopy studies were carried out with a JEM-2010 TEM (JEOL Ltd.) at an operating voltage of 200 kV. The obtained samples were dispersed supersonically in ethanol. A drop of the dispersed suspension was placed on a microgrid coated with a thin layer of amorphous carbon and dried in air before observation.

Results and Discussion

Morphological and Structural Features of CNTs Produced from GG Processes. To understand the mechanism of the nanotube growth in GG processes, we first examine the morphology and structure of nanotubes produced from the floating CVD and detonation-assisted CVD methods and observe the shape and location of the involved metal catalysts. Besides normal straight cylindrical structures, many nanotubes from the GG processes show distinctive morphologies and structures. Y-type tubular assemblies are frequently observed, in which the three channel ways sometimes communicated with each other (Figure 2a) and sometimes one of the channels was plugged by a graphitic wall (inset of Figure 2a). Many nanotubes often exhibit one or more “burls” (Figure 2b), which look like hollow spheres under high-resolution TEM (Figure 2c) and constantly make the tube turn to a sharp crankle. For some cases, a single nanotube, as shown in Figure 2d, has visibly different thickness and structures on two wall sides and/or exhibits a great change in channel wideness. Figure 2e shows a nanotube with a “bridge” across the channel, resulting in a Z-like structure. The “bridge” is constructed by some graphitic shells split from the inner part of tube wall. Figure 2f displays a bamboo-like tube, in which several disheveled long graphene ribbons split from the curved arch part. Based on these observations, many nanotubes produced by the GG processes are quite different in morphology and structure from those generated by the conventional CVD (GS process). The formation of such morphologies and structures is difficult to explain by the ADP mechanism and needs a new reasonable understanding.

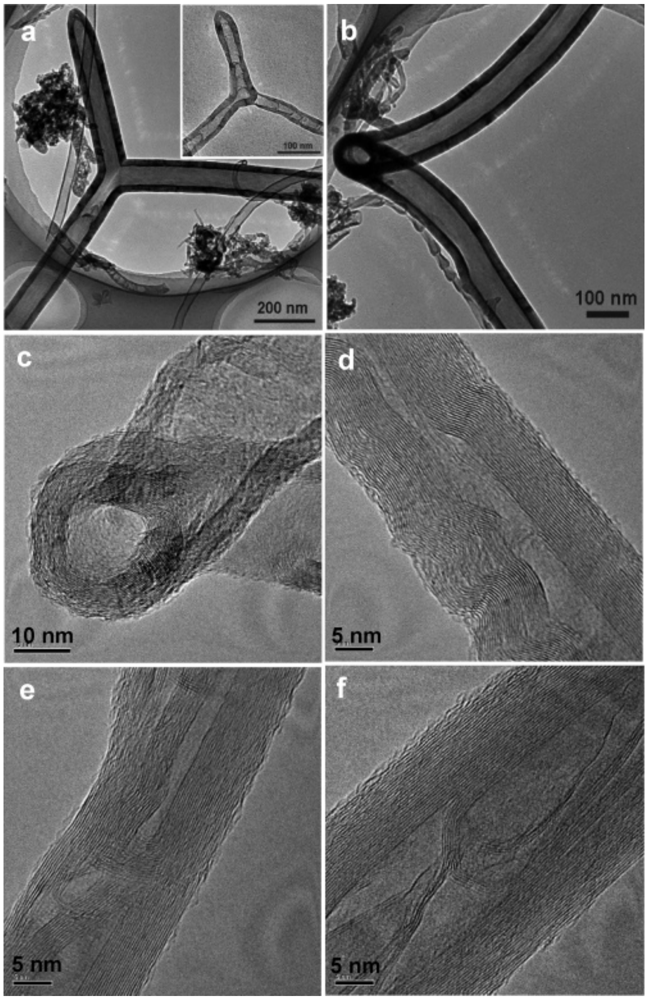

Figure 2. (a) A Y-type nanotube with communicated channels. In the Y-type nanotube shown in the inset, one of the channels is plugged. (b) A nanotube with a “burl”. (c) High-resolution image of a nanotube with a “burl”. (d) A nanotube with varying wall thickness, channel wideness, and structure. (e) A nanotube with an inner-shell-constructed “bridge” across the channel. (f) A bamboo-like tube with several disheveled long graphene ribbons splitting from the curved arch part. Note: the nanotubes in (a−c) were obtained from detonation-assisted CVD, and those in (d−f) were from floating CVD.

For the GS process, a nanotube usually contains a metal nanoparticle only at one of the two ends. Although a similar situation is also often evident (Figure 3a) for the GG process, the difference in metal catalyst-feeding mode between the two processes obviously leads to significant differences in the relative size and location of the metal particles connecting with nanotubes. Figure 3b−h illustrates several typical examples for the GG processes. The metal nanoparticles located at tube ends often have diameters quite larger than the diameters of the relative nanotubes (Figure 3b,c), inconsistent with the ADP mechanism in which metal diameter should determine tube diameter.[3,4,30] Furthermore, for the GG processes, metals are frequently located at both of the two tube ends as nanoparticles (Figure 3c) and/or filled within the tube channels as separated and elongated nanoparticles (Figure 3d−f,h) or as continuous nanowires (Figure 3b,g). The nanotubes completely filled with metals can also be observed (Figure 3g). Similar observations

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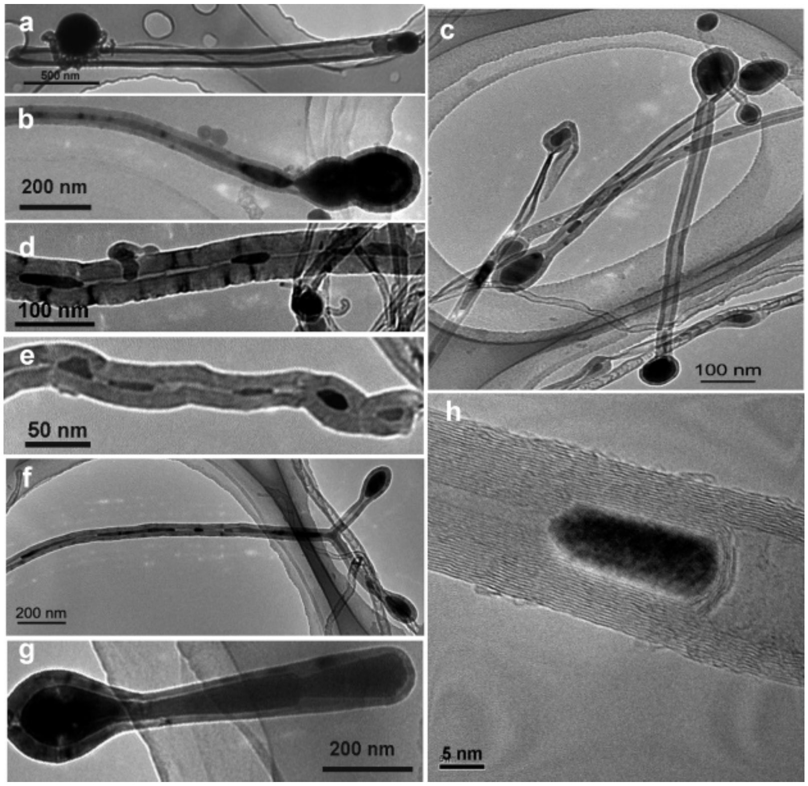

Figure 3. (a) A nanotube containing a metal nanoparticle only at one end. (b) A nanotube containing a large gourd-shaped metal nanoparticle at the end and a continuous metal nanowire within the channel. (c) Short nanotubes with large metal nanoparticles at both of the ends. (d,e) Nanotubes with multi-metal nanoparticles in the channel. (f) A Y-type nanotube with metal nanoparticles at two ends and in the channel. (g) A short nanotube with the channel completely filled with metals. (h) High-resolution image of a nanotube filled with a metal particle at middle part. The metal particle is bare at one side and covered by carbon layers at another side. Note: the nanotubes in (a), (b), (c), (f), and (g) were obtained from detonation-assisted CVD, and those in (d), (e), and (h) were from floating CVD.

were also previously reported by other authors.[23,31] These facts mean that the catalytic formation of the nanotubes in a GG process seems to not follow the ADP pathway in which a single metal particle is associated with the nucleation and growth of an individual nanotube.

For a GG synthetic process, because both carbon and metal species are in the gas phase before nanotube assembling and they are supplied and condensed simultaneously, necessarily, one should be careful in dealing with the linkage of nanotube evolution with the metal nanoparticles that one see in the final products (nanotubes). An understanding of how the metal nanoparticles form at tube ends and how they fill inside tubes would give valuable information for an insight into the real mechanism of nanotube evolution. As a preliminary consideration, there could be two possible situations: (1) the metal nanoparticles first form and then help nanotube nucleation and growth, following the ADP pathway; and (2) their formation accompanies nanotube evolution, as a consequence other than a causation of nanotube evolution. The measurements of the as-obtained nanotube samples with powder X-ray diffraction suggest that the metal nanoparticles have a single crystalline structure of parent metal other than metal carbides,[25] and the analyses by area-selected electron diffraction further confirm it and additionally reveal that the metal nanoparticles located at tube ends and those filled in tube channels have a similar structure. These basic facts make us doubt the possibility of a pioneered formation of the parent metal nanoparticles prior to the condensation of carbon species and nanotube assembling, because it required an unpractical selective deposition of gaseous metal species in the highly chaotic gas-phase carbon−metal system with a high carbon-to-metal ratio. On the other hand, a gradual formation of the metal nanoparticles along with nanotube evolution might be more reasonable, consistent with the actual situation that the nucleation and growth of nanotubes always go on in the intrinsic chaotic environment of the gaseous carbon−metal species. About this, further experimental observations and discussions are to be described later.

Evidence for a Linkage between Carbon Nanoparticles and Nanotubes. For the nanotubes produced by floating CVD, although most of them exhibit well-evolved structures (not shown here), many nanotubes still stay at semi-evolved state and leave behind visible traces about their evolution. Several examples of such nanotubes are illustrated in Figure 4. Unlike the well-evolved nanotubes, which exhibit smooth wall surfaces, these semi-evolved nanotubes, as shown by their low-magnification images (Figure 4a−c), have accidented surfaces and show protuberant "humps" on their walls. One can easily associate the "humps" with particle-like objects. Under high magnification, their images (Figure 4d−h) more clearly show that they have structures somewhat similar to that of the onion-like carbon nanoparticles,[32] metal-filling nanoparticles,[33] or elongated hollow nanoparticles, although there are structural distortions to different extents due to particle−particle interac-

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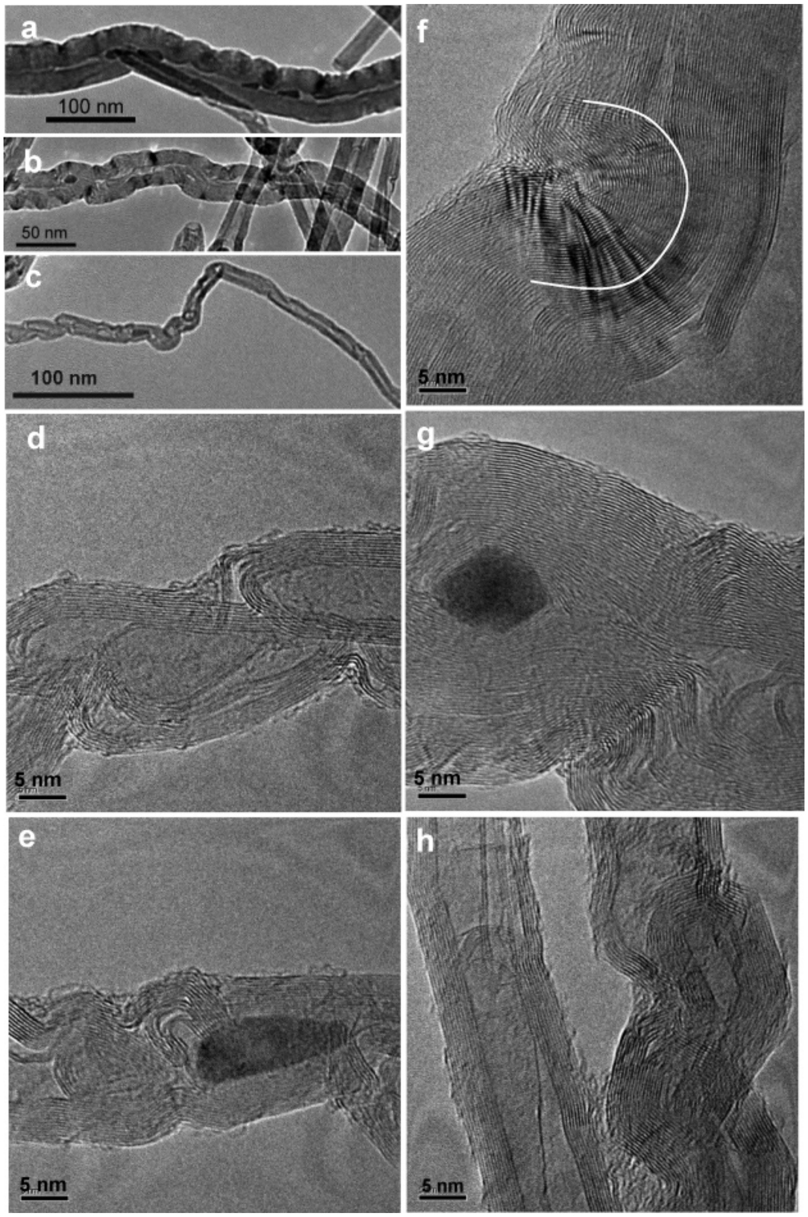

Figure 4. Semi-evolved nanotubes observed in the samples synthesized by floating CVD. (a,b,c) Low-magnification images of nanotubes with protuberant "humps" on their walls. (d,e) Magnification of the left parts of the nanotube shown in (c). (f) Magnification of a concave site on the wall of the nanotube shown in (a). (g) Magnification of the nanotube shown in (b). (h) A nanotube constructed by fused elongate hollow particles (the right one).

tion and fusion. The nanoparticles integrate together in one-dimension; between them superposing joints (likely through Van der Waals interactions) and wavelike chemically bonded connections are clearly visible. These traces of carbon nanoparticles on nanotubes suggest that the evolution of nanotubes is perhaps associated with carbon nanoparticles. The presence of metal-encaged carbon nanoparticles on the tubes (Figure 4e,g) further intensifies such an impression. The linkage of carbon nanoparticle to nanotube evolution also connects with the facts that carbon nanoparticles frequently exist in the channels of nanotubes and are the dominant byproducts in nanotube synthesis.

The next logical question is how the carbon nanoparticles evolve to nanotubes. To understand it, the observation of intermediates during the particle−tube transformation will undoubtedly give the most reliable information. However, it is often technically difficult to make nanotube growth stay at their intermediary stage, because nanotube growth is extremely fast.[34] We once performed the floating CVD process under varied conditions, but little valuable information was obtained about possible intermediates. Fortunately, the unique technical characteristics of the detonation-assisted CVD process provide an opportunity to freeze the nanotube evolution at their embryo and/or juvenile stages, as described below.

Evidence for a Particle−Wire−Tube Evolution. In the detonation-assisted CVD process for nanotube synthesis,[24,25] the quick decomposition of a carbon-containing explosive in a sealed pressure reactor releases huge energy and creates a high-temperature environment, in which premixed hydrocarbon and metal precursors are near immediately fragmentized into gaseous species and then condense and assemble as tubular structures.[24,25] In this process, the physical and chemical environment

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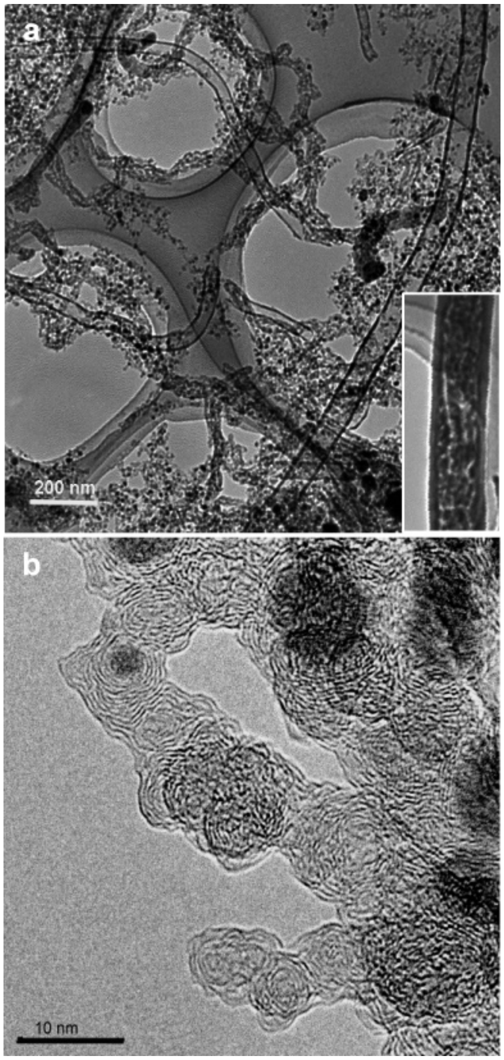

Figure 5. (a) TEM image of the materials obtained by the detonation-assisted CVD, using a freezing method. The materials contain carbon nanoparticles, nanowires, and nanotubes. The inset shows a nanowire with tube-wall-like ektexine. (b) Magnification of the nanoparticles.

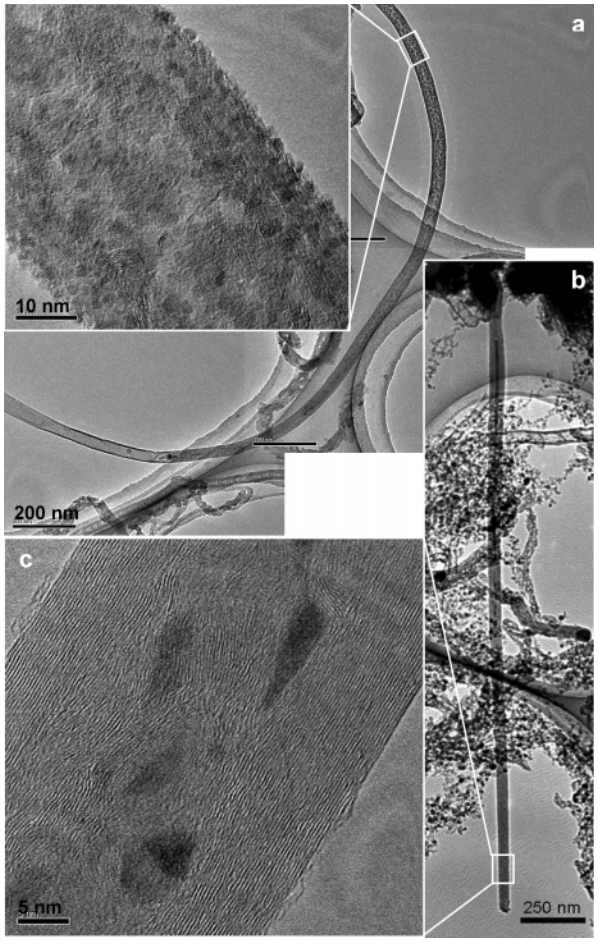

Figure 6. (a) A wire−tube-jointed intermediate object. The inset is the magnification of the sashed section at the wire moiety. (b) An iron-filled nanotube with a semi-evolved wirelike end. (c) Magnification of the wirelike end shown in (b).

and the energy required for the assembling of carbon species to nanotubes is dominantly derived from the detonation-generated high-pressure hot gases via the molecular collision between the gases and carbon species. These intrinsic features allow us to effectively generate the intermediates involved in nanotube evolution by a technical adjusting.

For this purpose, the picric acid−ferrocene reaction system is experimentally selected due to its facilitation for the generation of intermediate objects, as compared to the cobalt-catalytic system. To further maximize the generation of the intermediates, the high-pressure hot gases from the detonation are partially released immediately just after the detonation, which effectively reduces the system temperature and freezes the evolution at mid stages. The products resulting from such an operation contain MWCNTs of about 20% but plentiful isomerous objects such as carbon nanoparticles and wormlike nanowires (Figure 5a). The carbon nanoparticles have sizes of 10−20 nm and exhibit somewhat ordered layered structures far from graphitic crystals (Figure 5b). Their cores are hollow or filled with iron nanoparticles. Several or tens of particles often join together structurally in a one-dimension (1D) mode. The carbon nanowires exhibit accidented surfaces, on which granular objects and interspaces are visible clearly (Figure 5a). The sizes of the granular objects are comparative to those of the freestanding carbon nanoparticles, clearly indicating that they are formed by a 1D self-assembly of the carbon nanoparticles.

The diameters of nanowires (30−70 nm) are comparative to those of the nanotubes coexisting with them (Figure 5a). Furthermore, many nanowires have developed smooth ektexines (inset of Figure 5a), which are much similar to the walls of nanotubes. Simultaneously the inner nanoparticles involved in the nanowires exhibit a coalescence, leaving behind local large spaces, which can be viewed as the prophase of tube cavities. This information preliminarily suggests that nanotubes are likely evolved from the nanowires. This conjecture is supported by frequent observations of wire−tube-joined objects (Figure 6a,b). These objects can be viewed as frozen intermediates and reflect the proceeding state of the transformation. Figure 6a displays a typical wire−tube-joined object, composed of an underdeveloping nanowire moiety and a full-evolved nanotube moiety. The high-resolution images of the nanowire moiety (inset of Figure 6a) clearly show that the exterior of the wire has already evolved with multilayer graphitic structure but the interior is still filled with small disordered carbon particles. At this evolution stage, the wires are actually not totally solid, as meshlike inner spaces become visible due to a from-inner-to-outer structural shrinkage. Figure 6b demonstrates a nanotube filled with metal within its channel. This nanotube also contains a semi-evolved wirelike

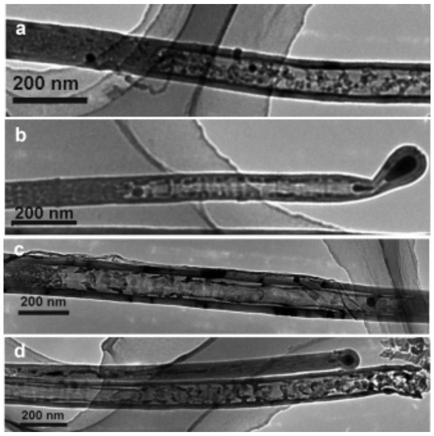

Figure 7. (a,b) Wire−tube-joined intermediate objects, showing the detailed transformation course from a solid nanowire to a hollow nanotube. (c,d) Tube-in-tube structures constructed by an outer thick tube and an inner thin tube. The total developing event of the inner tube at different stages is well kept down within the outer tube.

section, constructed by small carbon and metal particles (Figure 6c). The filling of integrated metals within the evolved tube channel seems a natural consequence of a fusion of the small metal nanoparticles during nanotube evolution.

More visibly, the wire−tube-joined intermediate object shown in Figure 7a records the detailed transformation course from a solid nanowire to a hollow nanotube. The left wirelike moiety of the intermediate already has continuous ektexine, but its core is still constructed by particles crowdedly. The right moiety has developed into a hollow cylinder, inside which particles obviously become sparse, as a consequence of the particle−particle coalescence and their adhering to tube wall. Such a structural transformation is approved by the event that, as compared to the wall at the wire moiety, the wall at the tube moiety significantly becomes thicker (Figure 7a). Figure 7b shows a similar situation, which additionally demonstrates that the small particles that are inside the tube moiety connect each other and rank in a line along the inner surfaces of the tube, apparently displaying a forming situation of the multi-shell wall and the channel spaces. Figure 7c and d illustrates two special tube-in-tube nanostructures; each of them is constructed by an outer thick tube and an inner thin tube. The evolution of the outer tube has been completed, while the inner tube is observably still under development. The total developing event of the inner tube at different stages is well kept down within the comfortable room of the outer tube, which allows us to get a more convincing insight into the tube evolution. Clearly, the inner tube is evolved from the small particles via their coalescence and reconstruction. Such a situation is similar to the previous observations: spherical fullerene molecules filled inside single-wall nanotubes can be coalesced and transformed into tubular structures.[35−38]

The above evidence unambiguously indicates that, in a GG process for nanotube synthesis, the evolution of the nanotubes follows a particle−wire−tube mechanism (Figure 8). This mechanism includes three key steps: (a) condensing gaseous C_n species as nanoparticles; (b) self-assembling the nanoparticles into nanowires; and (c) emptying the nanowires into tubular structures.

Discussion on the Key Aspects in the Particle−Wire−Tube Mechanism. In this section, we will discuss foundationally important issues related to the particle−wire−tube evolution mechanism, based on theoretical analyses and experimental observations. The first step of the mechanism, condensing gaseous C_n species as nanoparticles, is natural and comprehensible for a normal vapor deposition process; here, we will not discuss it in detail but focus our attention on the subsequent steps, which are believed to be more crucial for the entire tube evolution. The first key question is why the carbon nanoparticles assemble in a 1D mode to form nanowires. It is certain that what determine particles agglomerating irregularly or assembling in a confined 1D direction are their intrinsic structures, properties, and the feature of the interaction between them. It has been well known that the anisotropic properties of particles are generally responsible for their directional assembling.[39−42] Fully closed and graphitized spherical particles[32] are nearly isotropic and thus difficult to assemble orientationally. However, the incipiently formed carbon nanoparticles during the deposition of carbon species before nanotube formation exhibit ill-crystallized layered structures as described above (Figure 5b). Such structures are far from graphitized and predictably have lots of defects (such as sp^3 carbons, non-hexagonal rings, disconnected bonds, etc.)[43] especially at the two edges of the around-curved carbon (not graphite) layers, which would endow the layered structures strong anisotropy. Under proper conditions, the defective layered structures might be kinetically stabilized by defect−defect interactions, lip−lip interactions,[44] and possible metal−carbon conjugations,[45] which could obstruct their closure into the isotropic graphitic particles and competitively enhance the probability of directional particle−particle interaction and assembling. During the assembling, an anisotropy-induced dipole−dipole interaction and the defect−defect interaction between the defective and anisotropic nanoparticles likely give the primary driving forces. It is important to note that the 1D assembling of the particles can be in a one-by-one mode or in a rectangular array as shown in Figure 9a,b, which are presumedly determined by the nature of the particles and by the local environment and would lead to a control of the diameter of the evolved tubes. Another factor for the control of nanotube diameter is logically the diameter of the incipiently formed carbon nanoparticles, which is predictably dependent on the deposition conditions of the gaseous carbon species, such as the concentration, the energy carried by the carbon species, temperature of the local deposition region, etc. If proper conditions are available, very small and single-walled carbon particles (can be viewed as defective fullerenes) could be produced, and their 1D assembling would lead to the formation of single-walled nanotubes. Such a process might just be the practically synthetic situations in the arc discharge,[20] laser,[17]

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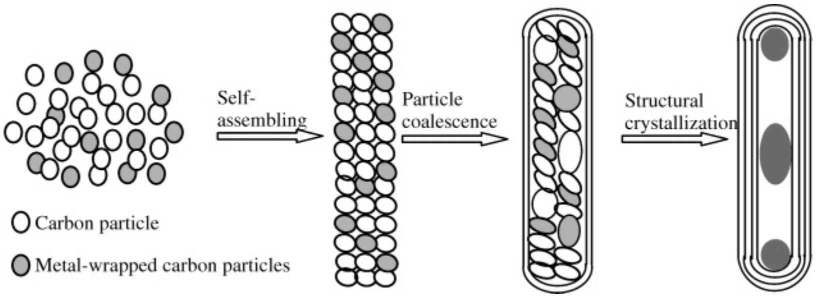

Figure 8. Schematic diagram of the proposed particle−wire−tube mechanism for nanotube evolution in a GG process.

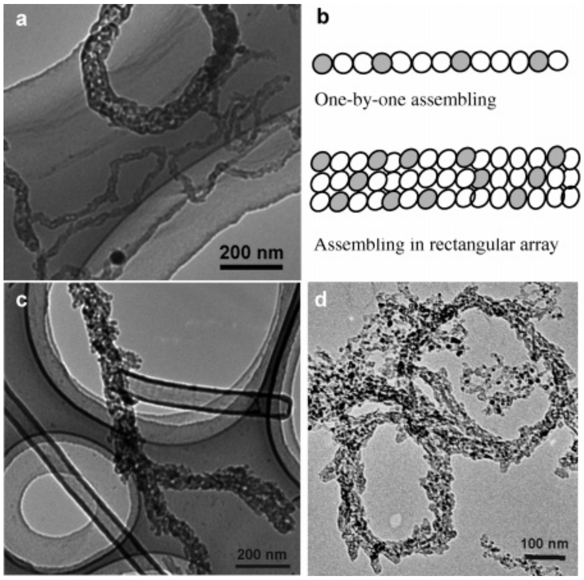

Figure 9. (a) TEM image and (b) schematic diagram of the carbon nanowires assembled by nanoparticles in a one-by-one mode and in a rectangular array. (c) A Y-type nanowire. (d) Two O-type nanowires.

floating CVD[46] processes and is supported by the facts that single-walled nanotubes are often generated accompanied with fullerenes[47] and that fullerene chains are frequently observed inside single-wall nanotubes and can be transformed into tubular structures.[36] In addition, as shown in Figure 9c and d, Y- and O-type wires can be also assembled due to the multiformity of the particles in shape and nature, which would provide a reasonable explanation for the spontaneous formation of the branched[27,28] and ringlike[48] nanotubes without using templates. For the formation of the aligned MWNTs (nanotube forest),[49−52] it is likely associated with directional interactions between the substrate surfaces and the anisotropic nanoparticles, and the directional interaction will then guide the particle−particle assembling along a defined direction, normally vertical to the substrate surfaces. Such an explanation is supported by the facts that the aligned nanotubes are generally produced by a usage of special substrates over which nanotubes grow and that aligned nanotubes exhibit a bottom-up growth mode, which is closely associated with the interactions between the substrate surfaces and reactants.

The next key questions are how a nanowire transforms to a nanotube and how the hollow channel of a nanotube forms. The driving force involved in nanowire−nanotube transfomation, we believe, is the structural crystallization and extension due to the relatively low stability of the carbon nanoparticles. Under external thermal annealing, they would exhibit a coalescence tendency and form more extended structures, accompanied with structural crystallization. Similar coalescences of carbon nanoparticles with Au in the cores have been in-situ observed with TEM by Sutter et al.[53] Such a coalescence might be mechanically similar to the coalescence of two thin single-wall nanotubes into a thicker nanotube,[54,55] which is induced by involved structural defects. More recently, Sunintaboon et al.[56] found that amphiphilic hollow particles exhibit a coalescence in aqueous solution and form tubular nanostructures. These observations imply that the coalescence of small nanoparticles seems a general phenomenon under proper conditions, connecting with a significant reduction of surface energy. Furthermore, because the thermal conduction rate across a carbon nanowire is limited by the weak interaction between the layers, the coalescence of the nanoparticles located in the nanowires most possibly starts at the outer edges and leaves behind an immobile cylindrical shell around the nanowire, similar to a bread-baking process. Additional shells formed from a subsequent coalescence of the inner particles would predictably attach (through Van der Waals interactions) to the inner surfaces of the initially formed shell, leading to a multi-shell structure. During the coalescence, it is imaginable that continuous inner spaces would be left behind within a nanowire through a unification of the inherent inner cavities and interspaces of the nanoparticles and a graphitization-induced structural shrinkage. So then, a multi-shelled and hollow carbon nanotube forms, as illustrated in Figure 8. Meanwhile, the small metal particles that are initially wrapped within the carbon nanoparticles would get free and agglomerate as larger particles (or even as metal wires if their amount is enough) within the tube channels (Figures 8 and 3).

Understanding the kinetic factors hiding behind nanotube growth is of importance for a further clarification of the

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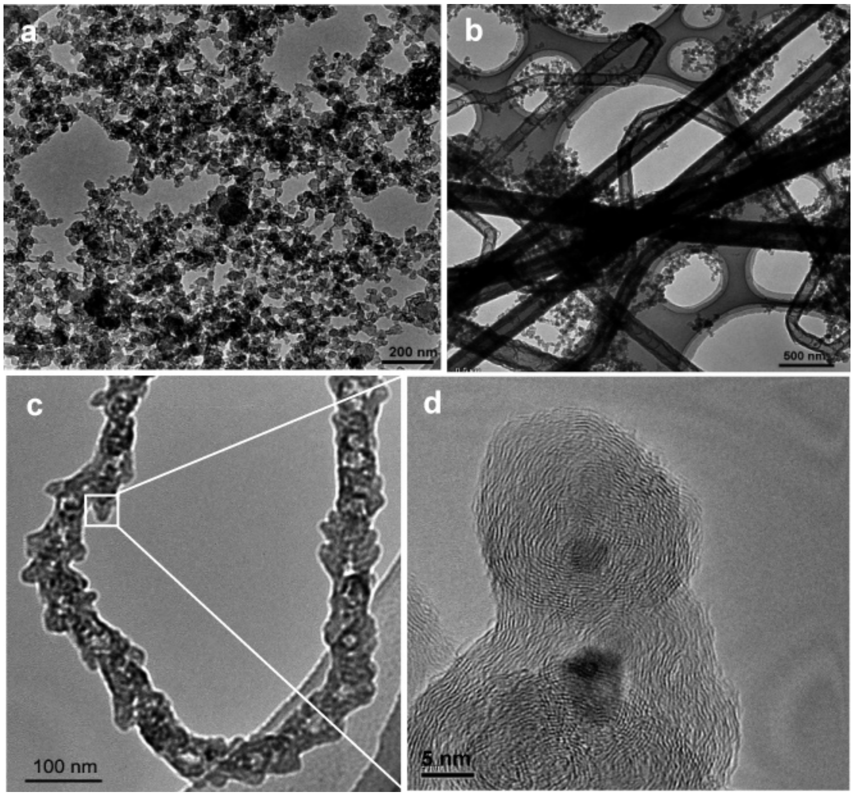

Figure 10. TEM images of carbon nanoparticles and the nanotubes transformed from them. (a) Carbon nanoparticles with diameter of 20−45 nm. (b) Nanotubes produced by a thermal transformation of the nanoparticles. (c) A nanowire organized by nanoparticles. (d) Magnification of the square section in (c), showing the presence of iron cores inside the nanoparticles.

particle−wire−tube evolution mechanism. As described above, we roughly presume the evolution mechanism includes three "elementary steps" (actually, each of the steps could be further divided into multisteps): (1) the formation of nanoparticles; (2) particle-to-wire assembly; and (3) wire-to-tube transformation. The first step, a vapor condensation process, is estimated to be very fast. The second and third steps are actually related to a solid−solid interaction and a reconstruction process, respectively, and are much likely associated with the rate-determining steps. Under the optimized conditions with high temperature, carbon crystallization would be fast, and the particle-to-wire assembly is possibly the rate-determining step, which is in agreement with the experimental observation that the synthesized products contain carbon nanotubes mainly and less nanoparticles but lack of nanowires, as shown in Figure 1. At low temperatures, carbon crystallization would be slow and becomes the rate-determining step, which is linked with the nanoparticles and nanowires remaining upon temperature reduction (Figure 5a). As shown in Figure 4a, the single nanotube shows a developing protuberant wall at one side and a well-evolved smooth wall at the other side, implying that, for a single nanotube, the structural crystallization could gradually develop radially and is kinetically slow.

Metals such as iron, cobalt, and nickel have been proved to play important catalytic roles in the nanotube evolution. Their detailed functions are estimated rather complex and still lack experimental or theoretical illumination. However, it is possible that their functions are embedded in the entire multistep evolution process, because in a GG system the transformation process of metals from gaseous species to solid particles or wires is always accompanied with the corresponding evolution scenario of carbons from the initial gas phase to final crystallized tubular forms. During the condensation of C_n species to nanoparticles, vapor metal species perhaps have a function to stabilize carbon species through a coordination interaction and to promote the formation of layered structure of carbon nanoparticles.[3,57] Such a function is in connection with the fact that the carbon layers covering metals are normally more ordered than those without metals. This promotion effect of metals subsequently improves the anisotropy of the carbon nanoparticles and thus the dipole−dipole interaction, contributing to the 1D assembling of carbon nanoparticles to nanowires. It is interesting to further understand whether the magnetic anisotropy of magnetic metals gives additional contribution to the 1D assembling of carbon nanoparticles, for which positive supports seem to be given by some experimental information: (1) the most active metals that catalyze nanotube growth are iron, cobalt, and nickel,[4,6,15] being the three metals with strong magnetism; and (2) the magnetic dipole interaction of the magnetic metal particles often leads to a 1D assembling of them into chains.[41,58−60] If carbon nanoparticles are filled with the magnetic metals, the magnetic dipole interaction can be predicted to help them assemble in a linear mode. Another function of metals is to catalyze the extension and crystallization of carbon structure involved in the particle coalescence and the transformation of nanowires into nanotubes. This function has been known for a long time,[3,57] although the detailed mechanism is still not very clear.

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Technical Guidance of the Particle−Wire−Tube Mechanism: Post-transformation of Carbon Nanoparticles into Nanotubes. As described above, a particle−wire−tube mechanism is proved to work in a GG nanotube evolution process. Based on this, a direct synthesis of carbon nanotubes from metal-catalyst-containing carbon nanoparticles (as starting materials) should be possible. On the other hand, if the synthesis is achieved, it will theoretically give an additional convincing support to the particle−wire−tube mechanism and technologically open a new way for CNT synthesis. With this purpose, the materials containing nanoparticles, nanowires, and nanotubes (∼20%) that are obtained from the freezing experiment with the picric acid−ferrocene system (Figure 5a) are first thermally annealed at 1000 °C. Such an annealing obviously makes some nanoparticles transform into nanotubes, enhancing nanotube from the initial 20% to final 60% (not shown); even so, the pre-existence of nanowires and nanotubes in the original materials makes the conclusion deduction somewhat foggy. Solid evidence should be from the data of pure nanoparticles, which can totally eliminate the interventions from the pre-existed nanowires and nanotubes in the observations of nanoparticle−nanotube transformation. We have carried out many experiments and found that replacing picric acid with low-energy-containing *m*-dinitrobenzene (employing a *m*-dinitrobenzene−ferrocene reaction system) effectively restrains nanotube formation and generates nearly pure uniform nanoscale particles with diameter of 20−45 nm (Figure 10a). Upon a thermal annealing of the nanoparticles at 1000 °C in argon atmosphere, as expected, more than 50% nanoparticles are transformed into carbon nanotubes (Figure 10b). Furthermore, 1D nanowires self-assembled by carbon nanoparticles (Figure 10c,d) are also observed frequently along with the nanotubes. Although there might be some structural differences between the nanoparticles obtained from the different conditions, it should not hinder one to obtain a conclusion that carbon nanoparticles can be transformed into nanowires and nanotubes, which gives a support for the particle−wire−tube model and may lead to a facile technology based on solid-state self-assembling and structural tailoring of nanoparticles for a massive synthesis of carbon nanotubes. Similar solid-phase transformations of carbonous particles to tubular structures were also achieved recently by Sinha et al.[61] using a cobalt-catalyzed vacuum annealing of amorphous carbons, and by Kanzow et al.[62] using a nickel-catalyzed annealing of fullerene blacks.

Conclusion

The morphologies and structures of carbon nanotubes as well as the related byproducts and intermediates produced by floating CVD and detonation-assisted CVD processes are studied in detail. The results show that the evolution of carbon nanotubes in the vapor-catalyst-involved synthetic processes disobeys the conventional adsorption−diffusion−precipitation mechanism, which was sketched from the solid-catalyst-involved synthetic process, but follows a particle−wire−tube evolution mechanism: tiny carbon nanoparticles first form from a condensation of gaseous carbon species and then self-assemble into nanowires driven by an anisotropic interaction; the nanowires finally develop into nanotubes, as a consequence of particle coalescence and structural crystallization. In this mechanism, an anisotropic interaction between the carbon nanoparticles with somewhat layered structure (far from graphite) and a crystallization-involved structural stabilization are the primary driving forces for the particle-to-wire and wire-to-tube transformations. The function of metals is to promote the anisotropic interactions between the nanoparticles and the structural crystallization. This mechanism is further experimentally validated by a successful transformation of metal-containing carbon nanoparticles into tubular structures. Although the outlined mechanism is mainly based on the experimental data obtained from detonation-assisted CVD technology due to its easily adjusted reaction environment for the generation and collection of intermediate objects, it seems to operate more generally because different GG processes are similar in basic reaction principles; the nanotubes obtained from floating CVD process are visibly related to particles as shown above, and various synthetic and structural phenomena seen in different synthetic processes could be reasonably explained with the present mechanism. Further systematic exploration of the particle formation and structure, the anisotropic interactions, the particle self-assembling, the related catalytic functions, and the involved thermodynamics and kinetics is necessary for deeper insights into the detailed and general nature of carbon nanotube evolution, which may be also highly valuable to understand the growth of the non-carbon 1D nanostructures.[41,42]

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