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Solid-phase transformation of glass-like carbon nanoparticles into nanotubes and the related mechanism

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ABSTRACT

Multi-walled carbon nanotubes have been synthesized through the solid-phase transformation of metal-containing glass-like carbon nanoparticles by heating at temperatures of 800–1000 °C. From microscopic observations on the morphologies and structures of the nanotubes and various intermediate objects, it is shown that the transformation occurs by nanoparticles first assembling into wire-like nanostructures, and then transforming into nanotubes via particle–particle coalescence and structural crystallization.

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1. Introduction

Carbon nanotubes (CNTs) exhibit excellent properties and have wide potential applications, and their properties are highly dependent upon their structure and dimension, which make their large-scale synthesis and structure control become central topics in this field. For CNT synthesis, current technologies are mainly based on a gas-phase assembly of carbon species (C_n) that are produced from various carbon precursors by alterable methods, such as arc discharge [1] and laser [2] vaporization of pure carbons, catalytic [3,4] or detonation-assisted [5,6] cracking of hydrocarbons, and the decomposition of organometallic compounds [7,8]. There are growing experimental evidences, showing that the formation of both multi-walled and single-walled nanotubes involves a solid-phase transformation in the gas-phase synthesis processes [9–11]. It implies that a direct synthesis of CNTs by a transformation of solid carbons under mild conditions is possible, if accessible, it would be quite beneficial for a large-scale synthesis due to the intrinsic high-feeding-density characteristic of the solid-phase reaction process.

Recently, successful syntheses of CNTs by the solid-phase transformation of granular carbon materials, such as carbon black, amorphous carbon, and fullerene soot, have been reported [10–18], achieved at extremely high temperatures (2000–3000 °C). However, further technical improvement for practical access and clear understanding of the transformation mechanism for rational process design and control are still necessary and challengeable.

Herein, we show that glass-like carbon nanoparticles (GCNPs) can be successfully transformed into multi-walled nanotubes under an annealing at relatively low temperatures (800–1000 °C), assisted by metal catalysis. More importantly, the detailed observation of the morphologies and structures of the nanotubes and the related intermediate objects unveils that the transformation obeys following mechanism: nanoparticles first self-assemble into wire-like nanostructures, and then transform into nanotubes via particle–particle coalescence and structural crystallization, much similar to the mechanism we suggested in the gas-phase processes [9]. Furthermore, the observations also preliminarily display the detailed evolution scenarios about the wire-to-tube transformation.

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2. Experimental

The GCNPs containing iron catalysts were prepared by the detonation-assisted CVD technology as described elsewhere [5,6]. Shortly, *m*-dinitrobenzene (1.5 g) and ferrocene with molar ratio of 12:1 were mixed physically and loaded into a 14 ml stainless steel pressure vessel. The detonation of explosive was initiated by heating (20 °C/min) and occurred at ~310 °C, which was evidenced by pressure break (up to 40 MPa). After the detonation, the vessel was cooled in air and emptied of gaseous products, and the solid products were collected. For the transformation of the carbon nanoparticles into nanotubes, 100 mg of the GCNPs, loaded in a small quartz boat, were placed at the central part of a quartz tube reactor (diameter, 25 mm; length, 600 mm), which located in a horizontal tubular electrical furnace. The reactor was first flushed with oxygen-and-water-removed high pure argon stream (100 ml/min) to make the reaction system free of air and then heated up to desired temperatures at a rate of 10 °C/min. After a continuous reaction (800 °C for 1 h or 1000 °C for 10 h), the reactor was allowed cooling to room temperature under the argon stream, and the resulted material was collected for further analyses by transmission electron microscopy (TEM). The TEM analyses were carried out with a JEM-2010 TEM (JEOL Ltd.) at an operating voltage of 200 kV. The obtained samples were dispersed ultrasonically in ethanol. A drop of the dispersed suspension was placed on a microgrid coated with thin layer of amorphous carbon and dried in air before fitting into the TEM machine.

3. Results and discussion

3.1. Characteristic of the glass-like carbon nanoparticles

The carbon nanoparticles we employed (Fig. 1), containing 5 wt% iron catalysts, were prepared by the detonation-assisted CVD technology as described elsewhere [5,6], employing a mixture of *m*-dinitrobenzene and ferrocene. The particle sizes are rather small, below 45 nm. Some of the particles are filled with iron nanoparticles (inset of Fig. 1a), but

most of them are free of metal and exhibit mesh-shape porous structures in their cores (Fig. 1b), much similar to the microstructure of glass-like carbon [19]. The GCNPs exhibit irregular shapes and show somewhat ordered layered structures on their outer shells. The structures are obviously far from graphitic crystals and contain numerous structural defects (Fig. 1b). The structural defects, associated with a high reactivity, are expectably favorable to a desired interaction between the particles and facilitate their assembly. The irregular shape and the layered structure predictably endow the GCNPs with special anisotropic properties, which support a possible orientable assembly of the particles.

3.2. Self-assembly of the GCNPs into nanowires

Thermal annealing of the GCNPs at 800 °C for 1 h leads to a visible assembly of most particles into plenty of wire-like nanoassemblies (Fig. 2a) and minority of tube-like nanoobjects (Fig. 2b). From the high magnification images of the nanowires as shown in Fig. 2c and d, it is clear that the nanowires are organized by carbon nanoparticles. Some of the particles are filled with iron nanoparticles, which are obviously larger than those in the starting GCNPs, 7 nm vs. 4 nm in average diameter. Most of them are free of iron and completely hollow (Fig. 2c and d), and the cores losing the initial mesh porous structure (Fig. 1b). The tube-like objects (Fig. 2b) are apparently constructed by 1D-connected hollow compartments with large cavities, much similar to the bamboo-like nanotubes previously observed from the gas-phase processes [20,21]. They are surely derived from a particle assembly because our starting materials consist of particles only (Fig. 1a), which is further supported by their accidented morphologies, which clearly display 1D-assembling appearance of hollow granular from-inner-to-outer structural shrinkage of the initial mesh porous particles (Fig. 1b). Elongated cavities are also evident in the tube-like objects, likely deriving from the coalescence and reconstruction of the hollow particles under the annealing. Briefly, under an annealing at 800 °C, a normal temperature level in many gas-phase synthesis processes [3,22], the mesh porous GCNPs can readily reform into hollow particles and self-assemble into

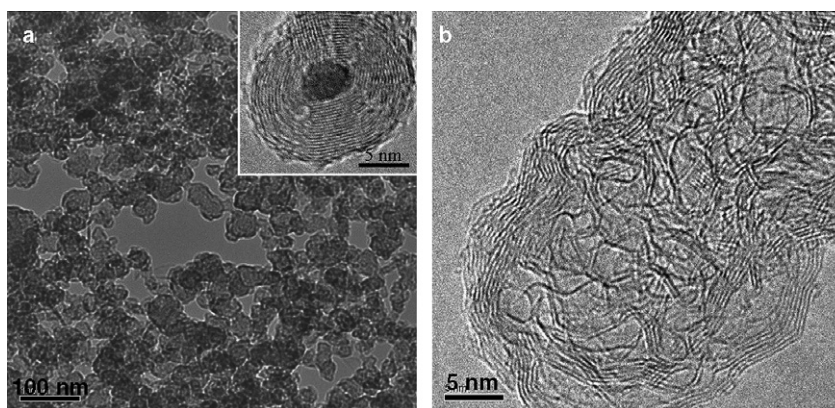


Fig. 1 – (a) TEM images of the GCNPs prepared by a detonation method. Inset: a carbon nanoparticle containing an iron core with diameter of about 4 nm. (b) High-resolution image of a typical carbon nanoparticle, showing somewhat ordered layered structure on the shell and glass-like carbon structure in the core.

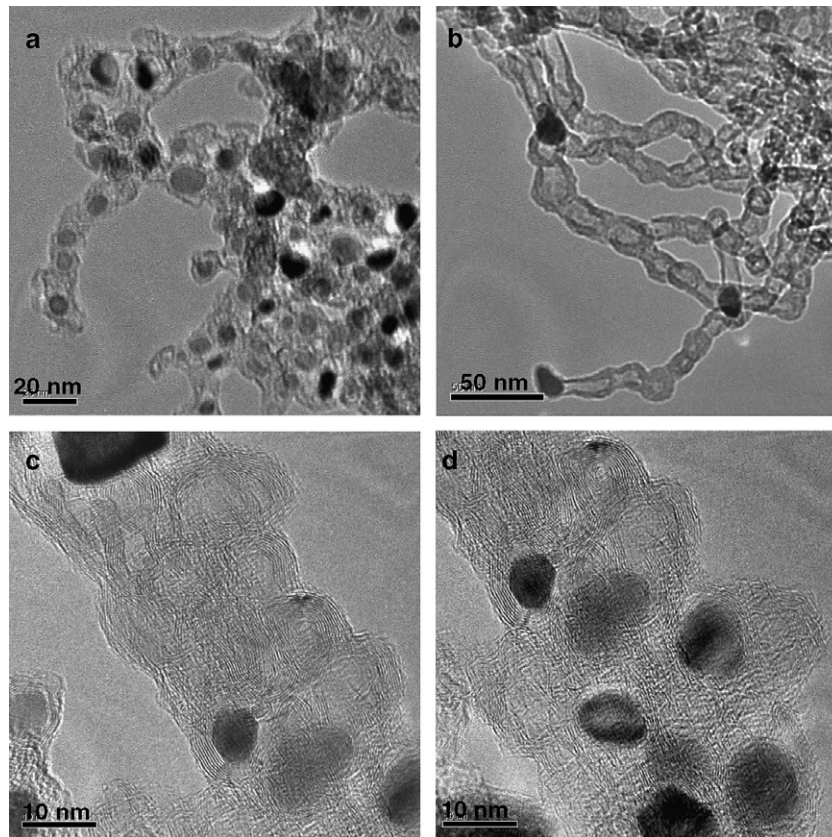


Fig. 2 – Materials obtained by an annealing of the carbon nanoparticles at 800 °C. (a) Carbon nanowires, encapsulated with iron particles (average diameter of 7 nm). (b) Tube-like structures. (c and d) High-resolution images of the carbon nanowires, showing that the nanowires are assembled by empty or iron-encapsulated carbon nanoparticles.

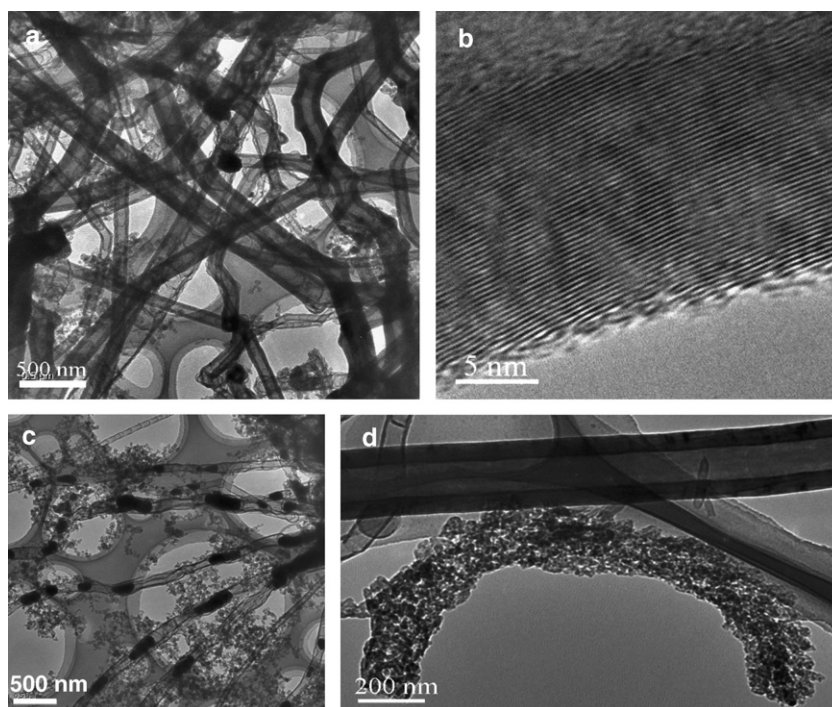


Fig. 3 – Materials obtained by an annealing of the carbon nanoparticles at 1000 °C. (a) Carbon nanotubes with remained nanoparticles. (b) High-resolution image of a typical tube wall with well-crystallized graphitic structure. (c) Nanotubes with more than one iron nanoparticles filled inside the channels. (d) Carbon nanowires organized by nanoparticles.

wire- and tube-like nanostructures, although the tube structures are constructed not very well.

3.3. Transformation of the GCNPs into nanotubes

Considering of the relatively difficult contact and interaction between solid objects, we further performed the thermal annealing of the GCNPs at a higher temperature (1000 °C) for longer duration (10 h) to improve nanotube evolution. As expected, such an operation effectively increases CNT yield from about 10% to 60% and, more interestingly, results in well-constructed nanotubes (Fig. 3a). Although bamboo-like nanotubes are also present under the reinforced annealing, majority of the formed nanotubes are completely hollow (Fig. 3a) and exhibit well-crystallized graphitic structure (Fig. 3b). Some of the nanotubes are filled with iron nanoparticles at the ends or within the channels (Fig. 3c), but many of them are empty along entire tube length, free of metal. It should be emphasized that along with the nanotubes, wire-like assemblies are also observed frequently (Fig. 3d), they are clearly self-assembled by numerous small nanoparticles in 1D mode. Above-described results indicate that carbon nanoparticles containing metal catalysts can be readily transformed into nanotubes in solid-phase under annealing conditions with relatively low temperatures.

3.4. Mechanism of the solid-phase particle-to-tube transformation

What we most interest in is how the nanotubes are evolved from the carbon nanoparticles. Since there is a great morphological difference between the 0D particles and the 1D hollow tubes, it is expectable that a successful transformation between them must undergo a complex transitional process, in which the formation of intermediate objects is necessary to bridge and facilitate the transformation. Therefore, an observation of possibly survived intermediate objects would be helpful to find credible evidences and to trace the underlain evolution pathway. The 1D wire-like assemblies, normally formed for the mild annealing at 800 °C (Fig. 2a, c and d) and partially survived for the reinforced annealing at 1000 °C (Fig. 3d), might be just the representative intermediate objects to morphologically bridge and link the two distinct forms, nanoparticle and nanotube. It is strongly supported by the facts that the nanowires are constructed by 0D nanoparticles and exhibit diameters similar to those of the nanotubes presented along with them (Fig. 3d). A self-assembly of the nanoparticles into the nanowires can be readily attributed to an orientational interaction driven by the anisotropic properties of the nanoparticles [9,21–26], while a wire-to-tube evolution seems more difficult to be understood due to the imaginable complexity hid behind the evolution process. How do the short-range-structured shells of the nanoparticles located on the nanowires transform into the continuously-structured walls of the nanotubes? How are the cavities or channels of the nanotubes evolved? What are the driving forces behind the evolutions? These questions are of crucial importance for a clear understanding of the entire nanotube evolution pathway.

Fortunately, the annealing at 1000 °C leaves behind various special intermediate objects (Fig. 4), which provide plentiful

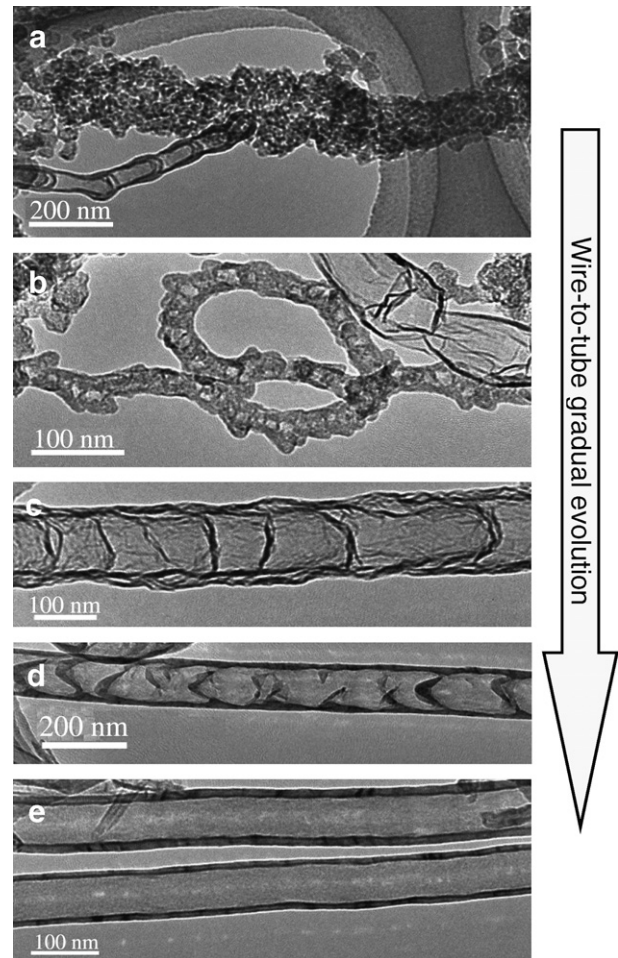


Fig. 4 – Some special tube-related structures contained in the sample annealed at 1000 °C, showing a possible evolution scenario from nanowire-to-nanotube. (a) A nanowire organized by nanoparticles. (b) The nanoparticles on the wire have highly coalesced, which leaves behind enlarged inner spaces but still exhibits many protuberant knots on the wire walls. (c) A bamboo-like tubular structure forms preliminarily with the inner spaces fully developed and the knots tailored off, but the wall has not integrated well yet. (d) The tube wall has been well integrated and the arch parts between the compartments of the bamboo tubes start to be tailored, which results in well-evolved tubes (e).

structural information for an insight into the wire-to-tube evolution. As shown in Fig. 4a, the small-particle-assembled 1D nanowires initially exhibit rough surfaces, on which granular objects and interspaces are still visible clearly. The curvature-induced high surface tension and the defect-based high reactivity of the small particles imply that under suitable conditions such as annealing, the particles involved in the wires would interact each other and coalesce together to form more stable and extended structures [27–29], which simultaneously results in an amalgamation of the original small cavities of the particles into larger ones (Fig. 4b). The interval spaces between the original particles can be imagined to give additional contribution to the cavity enlargement. At this initial wire-to-tube evolution stage, the walls are not well developed

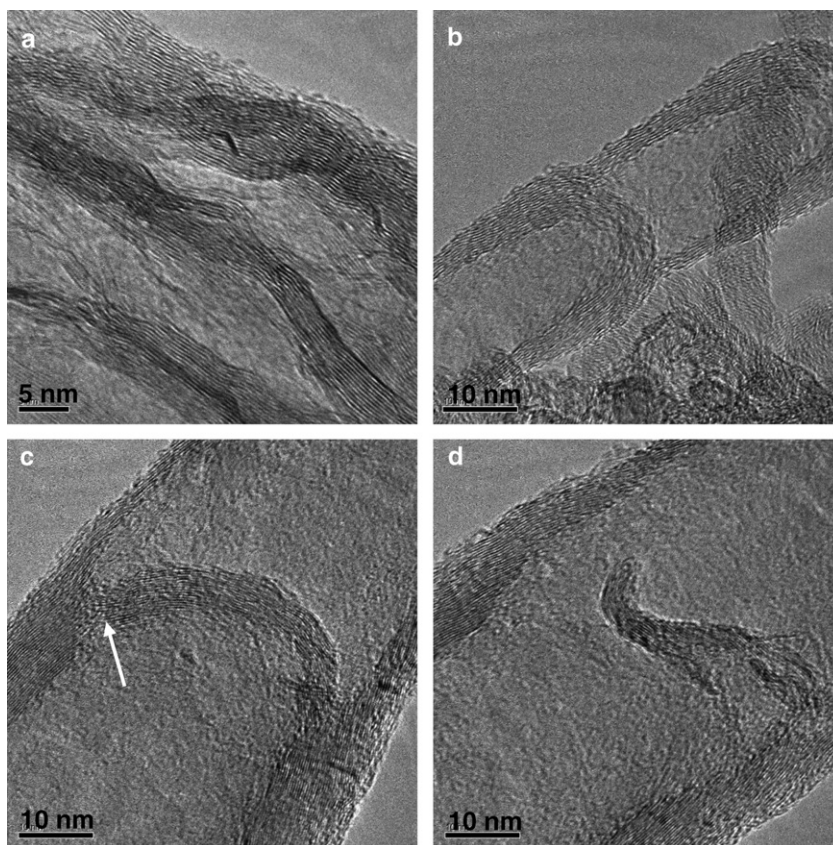


Fig. 5 – (a) A high-resolution image of the wall of bamboo tube shown in Fig. 4c, showing a split structure. **(b, c and d)** The situation of the transformation of a bamboo tube into a fully hollow tube. **(b)** A bamboo tube with compartment arches closely attaching to the tube wall. **(c)** An arch starts to disconnect with the tube wall at one end (arrowed). **(d)** An arch has completely disconnects with the tube wall at one end.

and exhibit many protuberant knots on them (Fig. 4b). Under further annealing, bamboo-like tubular structures, with highly developed inner spaces and relatively smooth wall surfaces, are preliminarily formed (Fig. 4c), likely resulting from further structural coalescences and reconstructions driven by the crystal stabilization. The crystal stabilization may link up the entire tube evolution processes, including the combination of multiple split layers (Figs. 4c and 5a) into an integrated graphitic wall (Fig. 4d). The compartment arches of the bamboo-like tubes intrinsically contain relatively unstable non-hexagonal cells and thus tend to rebuild into more stable hexagonal cells, which may show as a breakage of the arches and then an amalgamation into the hexagon-constructed tube wall (Fig. 4d, see Fig. 5b and d for more details) and finally lead to well-constructed tubes with completely hollow channels and uniform tube-diameter and wall-thickness (Fig. 4e). On all accounts, the solid-phase transformation of nanoparticles into nanotubes is bridged by the formation of nanowires, which gradually evolve into hollow tubular structures via particle coalescence and structural crystallization.

It should be pointed out that metal plays important catalytic role in this solid-phase particle-to-tube evolution process. There have been not direct evidences yet to clearly understand which step metal works at and how the metal works. However, it is sure that the large metal particles pre-

sented in the final nanotube products (Fig. 3c) are not the real catalysis-running forms but just a terminal state behind a successive change of practically functioned forms, as suggested by the observation that the sizes of the metal particles significantly increase, from starting 4 nm (an average value, hereafter) in the GCNPs (inset of Fig. 1a) to 7 nm for the annealing at 800 °C (Fig. 2a) and further 70 nm for the annealing at 1000 °C (Fig. 3c). Additionally, the phenomenon of more than one large metal particles presenting within final nanotubes (Fig. 3c) means that numerous smaller catalytic metal particles are actually involved in the evolution process of a single nanotube. The promotion effect of metals (especially Fe, Co, and Ni) on the extension and crystallization of carbon structures has been known for a long time [30,31], although the detailed mechanism is still not very clear. Such a metal function might operate in the entire particle-to-tube evolution process, including particle-to-wire assembly and wire-to-tube development, because the extension and crystallization of carbon structures are always involved in these steps, as described above. It is worthy to note that even if metal catalysts are present, a self-induced interaction between carbon structures might also contribute to the particle-to-tube evolution, as supported by following observations. (1) Many of the original GCNPs, the resulted nanotubes, and the related intermediate structures are completely free of metal (Figs. 1a, 3a and 4). (2) A self-catalytic growth ability of carbon nanotubes

[32] and a metal-free transformation of amorphous carbons into nanotubes [12] have been reported recently.

Above-described wire-bridging solid-phase particle-to-tube transformation is in good agreement with the CNT growth mechanism recently proposed for gas-phase CNT synthesis processes [9], suggesting that there is a common intrinsic factor to control carbon structural evolution, which might be the anisotropic interaction and the crystal stabilization. Compared with the gas-phase processes, the present solid-phase process technically seems to require higher temperature and longer transformation time for a successful nanotube assembly, theoretically associated with the intrinsic difficulty of moving and transporting building blocks for an orientation assembly in a solid-phase process. Based on this, a further technical improvement for the solid-phase process may be achievable by employing fluid-bed reactors, in which the gas stream would help the movement of the nanoparticles and thus facilitate their assembly. Such a design would also be highly beneficial for a successive practical operation. For a control of the diameter and channel wideness of nanotubes, a technical modification could be deduced from the proposed mechanism and achieved by employing starting particles with desired diameters and cavities. In addition, the bamboo-like tubes observed here are morphologically similar to those obtained previously from other synthesis techniques [33–36]. For the later case, the formation of the bamboo-like tubes was proposed being induced by the changed kinetic environment of synthesis systems [33–36]. In the present particle-to-tube transformation process, bamboo-like tubes seem to be the intermediates of the transformation, which give a new viewport for a clearer insight into the formation mechanism of bamboo-like tubes. Following these ideas, the related works are underway in our laboratory.

4. Conclusion

Multi-walled carbon nanotubes have been synthesized through the solid-phase transformation of metal-containing glass-like carbon nanoparticles by heating at temperatures of 800–1000 °C. It provides a possibility of controlling the diameters of the nanotubes by controlling the diameters of the nanoparticles or the assembly way of the nanoparticles. More importantly, from microscopic observations on the morphologies and structures of the nanotubes and various intermediate objects, it is indicated that the transformation occurs by nanoparticles first assembling into wire-like nanostructures, and then transforming into nanotubes via particle–particle coalescence and structural crystallization. Furthermore, the observations also preliminarily display the detailed evolution scenarios about the nanowire-to-nanotube transformation. The new mechanistic information, we believe, would guide and promote further technical improvement of the solid-phase synthetic process.

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