

Growth of carbon nanostructures on carbonized electrospun nanofibers with palladium nanoparticles

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Received 2 February 2008, in final form 3 March 2008

Published 7 April 2008

Online at stacks.iop.org/Nano/19/195303

Abstract

This paper studies the mechanism of the formation of carbon nanostructures on carbon nanofibers with Pd nanoparticles by using different carbon sources. The carbon nanofibers with Pd nanoparticles were produced by carbonizing electrospun polyacrylonitrile (PAN) nanofibers including Pd(Ac)₂. Such PAN-based carbon nanofibers were then used as substrates to grow hierarchical carbon nanostructures. Toluene, pyridine and chlorobenzene were employed as carbon sources for the carbon nanostructures. With the Pd nanoparticles embedded in the carbonized PAN nanofibers acting as catalysts, molecules of toluene, pyridine or chlorobenzene were decomposed into carbon species which were dissolved into the Pd nanoparticles and consequently grew into straight carbon nanotubes, Y-shaped carbon nanotubes or carbon nano-ribbons on the carbon nanofiber substrates. X-ray diffraction analysis and transmission electron microscopy (TEM) were utilized to capture the mechanism of formation of Pd nanoparticles, regular carbon nanotubes, Y-shaped carbon nanotubes and carbon nano-ribbons. It was observed that the Y-shaped carbon nanotubes and carbon nano-ribbons were formed on carbonized PAN nanofibers containing Pd-nanoparticle catalyst, and the carbon sources played a crucial role in the formation of different hierarchical carbon nanostructures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon is a unique chemical element. Due to its special electronic structure, carbon is capable of forming covalent bonds with other elements, such as hydrogen, to form rings and long chains. It can also bond with other carbon atoms to form the well-known substances of graphite, diamond, and a wide variety of network-like structures, termed fullerenes. This has attracted consistently growing interest among researchers worldwide. Carbon nanotubes (CNTs) are tubular fullerenes which are among the strongest materials known to date [1–6]. CNTs were discovered and reported in the early 1960–1970s [7–12]. At that time they were called ‘thin filaments’ or

‘graphite whiskers’. These thin filaments or graphite whiskers were hollow tubular structures. The name ‘carbon nanotubes’ can be traced to Iijima’s seminal report published in *Nature* in 1990 [13]. Since then, reports on the methods of synthesis and structural properties of CNTs have sprung up in scientific periodicals worldwide.

Two major structural forms of CNTs are known to exist: single-walled CNTs (SWNTs), in which the tube is formed from a single layer of coaxial carbon atoms, and multi-walled CNTs (MWNTs), in which the tube consists of several layers of coaxial carbon tubes. Both types of CNTs can be synthesized by arc-discharge [13, 14], laser ablation [15] or chemical vapor deposition (CVD) [16–20]. Among these, the CVD method

has remarkable advantages and is able to synthesize CNTs with high yield, high purity and excellent self-assembling structures. So far, several CVD methods have been developed, e.g. plasma-enhanced CVD [18], template CVD [21], CVD on a preformed substrate [22] and CVD using a floating catalyst (CVD-ufc) [23–30], among others. In most cases, metal catalysts are required for the formation of CNTs. Transition metals (e.g. Fe, Ni, Co, Mo, etc) are usually used as catalysts for the synthesis of CNTs.

As a matter of fact, the mechanism of formation of CNTs based on CVD is not yet completely understood. So far, how CNTs are formed in synthesis has still been an intriguing topic attracting the attention of chemists and physicists worldwide. In past decades quite a few investigations have been dedicated to the mechanism of growth of CNTs [29, 31–37]. It has been well accepted that the formation of CNTs is a process of metal–catalytic carbon deposition based on either arc discharges [13, 14] or high temperature furnaces [16–20]. The metal nanoparticles serve as a catalyst for the formation of CNTs. It is still not known how the metal nanoparticles function in the formation of CNTs. Most researchers believed that the metal nanoparticles remained at the head of the growing CNTs and absorbed carbon species, which were generated by the pyrolysis of hydrocarbon compounds in the high temperature environment. The carbon species were dissolved into the metal particles. When the carbon-dissolved ‘metal particle solution’ was saturated, the carbon species crystallized in the shape of CNTs [37–40]. Meanwhile, other researchers believed that the metal nanoparticles were located at the root-end of the growing tubes during the formation of the tubes. In review of the technology, TEM was thought to offer a feasible tool for observing the actual location of the metal nanoparticles on the growing tubes [41, 42]. However, when sampling for TEM study, the samples had to be scratched off the substrate where the CNTs were growing and then dispersed in a solvent, such as ethanol or chloroform, using ultrasonication. Consequently, the dispersed CNTs in the solvent were sampled on a TEM copper grid sample holder for TEM observation. In such a case it is difficult to discern which end is the growing head and which the root-end of a CNT under TEM.

Therefore, in this paper we report a novel experimental scheme to resolve the above issue. In our study, to be described below, carbonized electrospun nanofibers [43–47] were used as the substrates and Pd nanoparticles as the catalyst for the formation of CNTs. For the purpose of concise expression below, the carbonized nanofibers containing Pd nanoparticles are called Pd/C nanofibers. As we know, metal Pd is an excellent catalyst used in organic synthesis, such as reduction of nitride compounds, coupling of aromatic ring compounds, and so on. Therefore, we expected that the Pd catalyst would show excellent performance in the formation of CNTs on Pd/C nanofibers. New types of hierarchical carbon nanostructures were anticipated in this study. Meanwhile, it was also expected that CNT growth on Pd/C nanofibers would provide us a feasible way to study the mechanism of formation of CNTs since the Pd/C nanofibers with untouched growing CNTs can be carried directly on the TEM sample holder for scanning.

By using this technique, it is possible for us to discern the growing head and root-end of the CNTs and to locate the metal nanoparticles on the growing CNTs. Furthermore, this experimental scheme also makes it clear how the catalytic metal nanoparticles formed and how the growth of CNTs started. Such observations will help us to understand the growth mechanism of CNTs.

2. Experimental details

2.1. Materials

As we know, polyacrylonitrile (PAN) has been used extensively to produce PAN microfibers, a common precursor for the mass production of commercial high performance carbon/graphite fibers. Carbon nanostructures formed on the surface of PAN-based carbon fibers may potentially provide an innovative interface toughening technique for advanced polymer composites based on high performance carbon fibers in a polymeric matrix. Thus, in this study, electrospun PAN nanofibers were selected as the precursor for producing carbon nanofibers that were to be utilized as substrates to grow CNTs. The PAN polymer was purchased from Aldrich ($M = 86\,000$, $M_w/M_n = 3.8$). Palladium acetate [$\text{Pd}(\text{Ac})_2$] (98%, Aldrich) was used as the precursor of the palladium particles, and *N,N*-dimethylacetamide (DMAc) (99%, Aldrich) was used as a solvent to dissolve both the polymer and the palladium acetate to make the solution used for electrospinning the precursor fibers. Toluene, pyridine and chlorobenzene were purchased from Aldrich (all 99.8%) and used as-received as carbon sources for the formation of carbon nanostructures.

2.2. Instrumentation

A high temperature furnace, purchased from Lindberg HEVI-Duty, was equipped with a 35 mm \times 950 mm tubular quartz reactor for the carbonization of polymer nanofibers and the formation of CNTs. An ES60-0.1P model HV power supply was purchased from Gamma High Voltage Research for the electrospinning of polymer nanofibers.

2.3. Electrospinning of composite nanofibers of PAN and [$\text{Pd}(\text{Ac})_2$]

The electrospinning process was performed with a solution containing 8 wt% PAN and 4 wt% $\text{Pd}(\text{Ac})_2$ in DMAc. An electric field with a magnitude of 100 kV m⁻¹ was adopted by applying a 30 kV electrical potential to a 25 cm gap between the spinneret and the collector.

2.4. Carbonization of the electrospun composite nanofibers and formation of Pd nanoparticles

The carbonization of the as-electrospun composite nanofibers, reduction of Pd^{2+} in the composite nanofibers, and formation of Pd nanoparticles in/on the carbonized electrospun nanofibers were completed in a high temperature furnace by the following steps: (1) 210 °C annealing for 1 h in air for the oxidation of PAN in the carbonization process; (2) heating

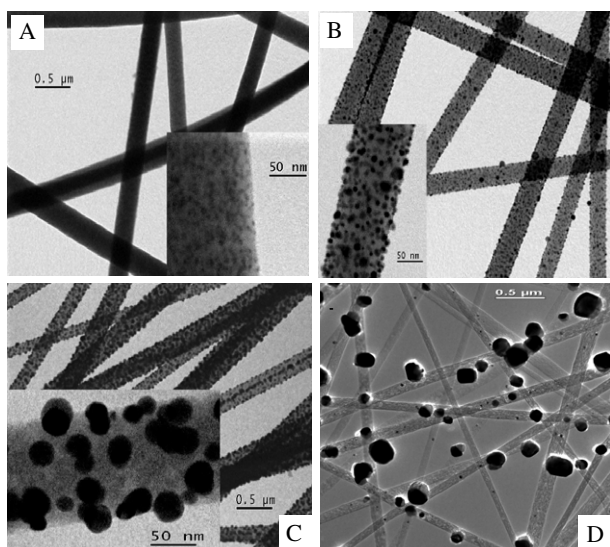


Figure 1. TEM images of Pd nanoparticles of varying size in/on the carbonized electrospun nanofibers with the process temperature: (A) 400 °C, (B) 600 °C, (C) 800 °C and (D) 1100 °C.

up to 400 °C at a rate of 5 °C min⁻¹ and annealing for 2 h in a mixture of H₂ and Ar (H₂/Ar = 1/3) environment for the reduction of Pd²⁺; (3) heating up to 600 °C at a rate of 5 °C min⁻¹ and annealing for 1 h in an Ar environment for the growth of large Pd nanoparticles; (4) heating up to 800 °C at a rate of 5 °C min⁻¹ and annealing for 30 min in Ar for the formation of Pd nanoparticles sitting on the nanofiber surfaces; (5) heating up to 1100 °C at a rate of 5 °C min⁻¹ and annealing for 60 min in Ar for the formation of large Pd nanoparticles on the nanofiber surfaces.

2.5. Formation of CNTs on carbon nanofibers

The formation of CNTs on carbon nanofibers was done at 800 °C by introducing either toluene, chlorobenzene or pyridine vapor into the tubular quartz reactor, which carried the carbonized electrospun Pd/nanofibers, via an Ar flow of 600 ml min⁻¹ through a carbon source (toluene, chlorobenzene or pyridine) bubbling chamber. The carbon source vapor supply was sustained for a pre-scheduled duration. The length of the CNTs growing on the carbon nanofibers was controlled by the amount of carbon source supply.

2.6. TEM observation

Small pieces of thin sheets of carbon nanofibers containing the possible mixture of Pd nanoparticles, CNTs and carbon nano-ribbons were put into ethanol. The sample used for TEM observation was prepared by mounting a piece of the thin sheet floating in ethanol on the TEM copper grid sample holder. TEM observation was performed using a 120 kV FEI Tecnai-12 and a 300 kV Jeol JEM 3010 model transmission electron microscope.

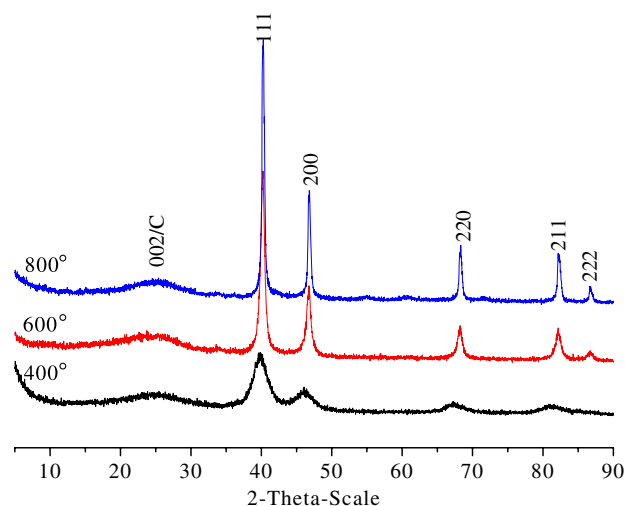


Figure 2. X-ray patterns of Pd/C nanofibers at the process temperatures of 400 °C, 600 °C and 800 °C, respectively.

3. Results and discussion

3.1. Carbonization of electrospun composite nanofibers and formation of Pd nanoparticles in carbon nanofibers

To examine the formation of Pd nanoparticles inside the carbonized nanofibers and on the fiber surfaces, several heating and annealing steps were adopted in the fabrication of Pd/C nanofibers. At the reduction stage, the precursor composite nanofibers stayed at 400 °C in the mixed H₂ and Ar atmosphere for 2 h, the Pd²⁺ was reduced into elemental Pd and aggregated into tiny particles inside the nanofibers. The diameter of the Pd particles is less than 5 nm, as shown in the TEM image (figure 1(a)). Following further heating and annealing at 600 °C, the Pd nanoparticles grew to a size of ~15 nm. Some particles were found to aggregate on the nanofiber surfaces (figure 1(b)). At the 800 °C stage, the Pd particles grew to a size of ~30 nm and almost all the particles aggregated onto the fiber surfaces. When heated to 1100 °C and annealed at this temperature for 1 h, the Pd particles continued to grow on the fiber surfaces. The final diameter of the Pd particles was between 50 and 350 nm. In this case, the diameter of most Pd particles was larger than that of the carbon nanofibers (figure 1(d)).

The x-ray diffraction pattern (figure 2) showed that the Pd particles inside the nanofibers were crystalline. The average size of the Pd particles, when heated up to 600 °C, was approximately three times greater than those formed at 400 °C. It is not known how the small Pd particles inside the fibers aggregated into particles of large size as the process temperature increased. In fact, the melting temperature of bulk Pd crystal is 1552 °C. Though there may exist a thermodynamic size effect, particularly at small sizes (diameters below 10 nm [48–50]), it seems an intriguing phenomenon that such tiny Pd particles melted inside the nanofibers at the experimental temperature of 600 °C and aggregated into large-sized ones. As a matter of fact, the temperature of 600 °C is much lower than the melting point

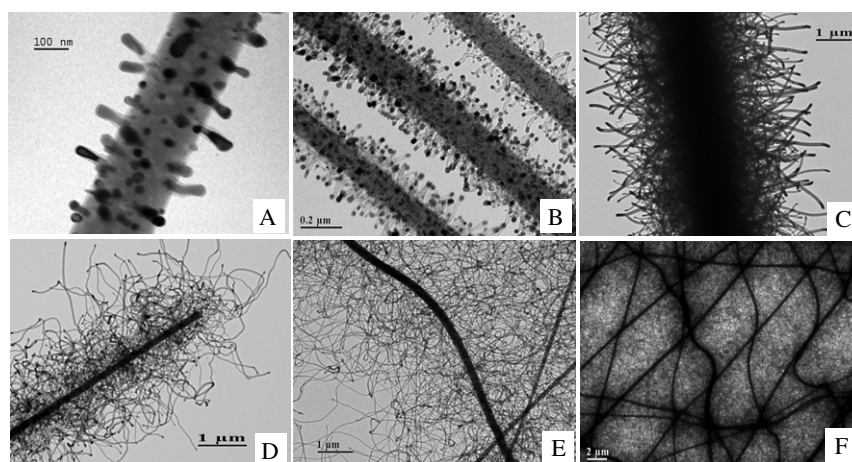


Figure 3. TEM images of CNTs of varying length on Pd/C nanofibers with varying durations of carbon source supply. The duration of toluene supply: (A) 15 s, (B) 30 s, (C) 50 s, (D) 100 s, (E) 240 s and (F) 600 s.

of bulk Pd crystals (1552 °C); and the carbonized nanofibers as carriers of the Pd particles would be a solid barrier to suppress the aggregation of the melts inside the fibers. Therefore, the aggregation of Pd particles may be reasonably considered as a process dominated by Pd atom migration. At high temperatures, the small Pd particles have a higher atom vapor pressure than the large ones. The atom vapor pressure is the driving force behind the aggregation of the Pd particles. In previous studies it was observed that the atoms of metallic elements (e.g. Cu, Au, Fe, etc) [51, 52] could diffuse through a carbon shell even with a thickness of a few tens of nanometers at high temperature. As evidence, Pd particles inside the carbonized nanofibers grew up with increasing process temperature. At temperature of 1100 °C, most Pd particles have aggregated onto fiber surfaces and the diameter of the particles reached a size of 50–350 nm.

3.2. The formation of CNTs on Pd/C nanofibers

3.2.1. Toluene as the carbon source. In the tubular quartz reactor at 800 °C, the Pd particles formed on the carbonized nanofibers functioned as a catalyst in the formation of CNTs, and toluene vapor was utilized as the carbon source for CNT growth. Bubbling Ar carried the toluene vapor into the high temperature tubular reactor. At 800 °C, the toluene molecules decomposed on the surface of the Pd nanoparticles due to the catalytic action of the metal. Carbon atoms were absorbed and then dissolved into the metal [23–26], and were further transported to the interfaces between the Pd particles and the growing end of the graphitic CNTs, finally assembling into the growing CNTs. The Pd particles were normally carried ahead of the growth of CNTs. The length of the CNTs depended on the duration of supply of toluene vapor. Longer supply durations usually yielded CNTs of larger length, while shorter durations led to shorter CNTs (figure 3).

Connections between the formed CNTs and the nanofiber substrates should be through chemical bonds. Figure 4 shows a typical linkage between an infant CNT and the supporting nanofiber. At the root-end of the CNT, one can find a layer of

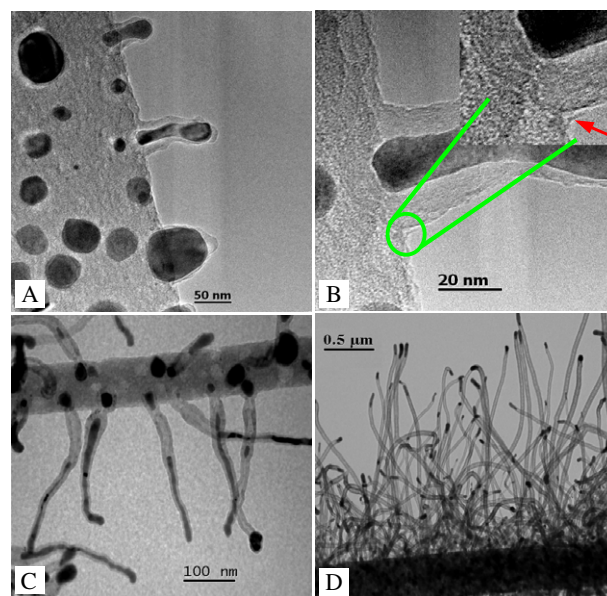


Figure 4. TEM images of the connections between the growing CNTs and carbonized nanofibers: (A) infant CNTs growing on the surface of a nanofiber; (B) a close view of the connection between a CNT and a nanofiber; (C) and (D) CNTs standing on the surface of nanofibers.

graphite ‘binding’ the CNT onto the surface of the nanofiber, as indicated by an arrow in figure 4(b). If the connections between the formed CNTs and the supporting nanofibers are types of physical linkage, one may easily detect the existence of CNTs lying on or separating from the surface of supporting nanofibers. However, no such evidence has been detected in our experiments (figures 4(c) and (d)).

3.2.2. Pyridine as the carbon source. In previous studies in the literature [53, 54], large-scale helical CNTs were formed by using pyridine as carbon source and iron pentacarbonyl as the catalyst precursor. In the present study it was expected that helical CNTs would be formed on the carbon nanofibers.

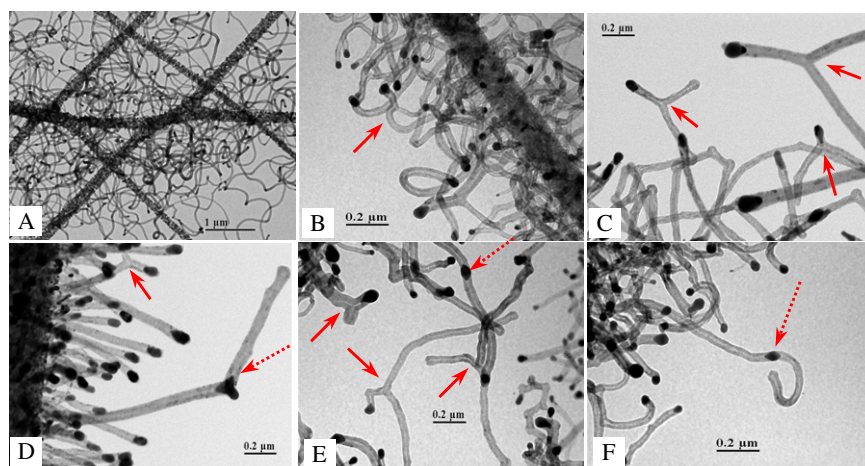


Figure 5. TEM images of coiled CNTs (A), Y-shaped CNTs on nanofiber substrates ((B)–(E), marked by solid arrows) and Pd catalyst particles located at the middle of the growing CNTs ((D)–(F), marked by dashed arrows).

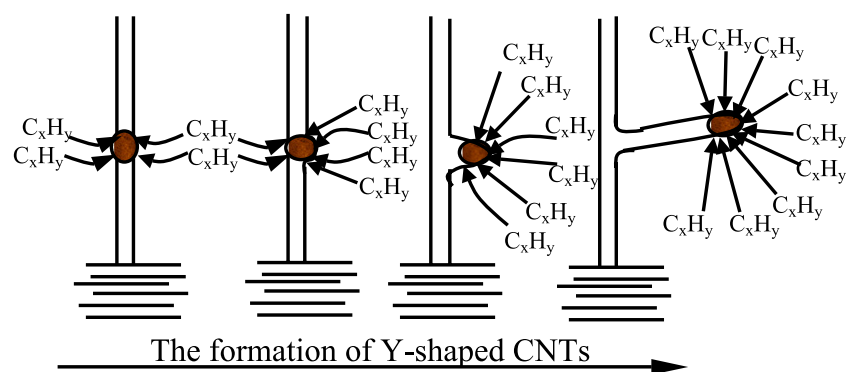


Figure 6. The schematic formation of a Y-shaped CNT based on a metal particle catalyst located at the middle of a growing tube.

However, when pyridine was used to replace the toluene as the carbon source, the products formed on the nanofibers exceeded our expectations. The products are tubular and coiled. There were no helical CNTs, but Y-shaped tubular structures were formed on the supporting nanofibers (figure 5). However, in this situation, some of the Pd catalysts were detected at the middle of the growing nanotubes. Without a doubt, Pd particles located in the middle of the growing tubes were responsible for the formation of Y-shaped nanotubes. This growth mechanism is illustrated by a diagram in figure 6.

Y-shaped CNTs have been reported in the last decade [55–60]. A high yield of Y-shaped tubes was obtained via a CVD method by using floating Fe/Ti composite catalyst [55]. The Ti composition in the metal particle catalyst was 1–3%, in which Ti was the key element responsible for the formation of Y-shaped tubes. The mechanism was triggered to form a Y-shaped tube when a floating Fe/Ti composite particle was attached at the middle of a growing tube. In our experiment, the catalyst was Pd nanoparticles, located at the root of the nanotubes at the start of CNT growth. During the course of tube growth, the Pd particle catalyst was mostly carried ahead as the nanotube grew longer and became located at the head of the growing tubes (figures 3(a)–(c), 4(d) and 5(d)). However, TEM observation showed that for

some unknown reason the metal catalyst might occasionally stay in the middle of the growing tubes (figure 6). In such a process, the Pd particle catalyst at the middle of the growing tubes could touch the pyridine molecules at a high temperature and therefore catalyze them to pyrolysis. In this case, the carbon atoms were absorbed and dissolved into the metal particles at the middle position, where the carbon atoms were incorporated into the graphitic carbon nanotubes, resulting in tube growth from the middle position. As a result, the tubes grew ahead of the metal particles. In this situation, the growing middle point may need a higher energy to sustain tube growth than when the metal particles are located at the ends of the growing tubes. In order to reduce the amount of extra energy required, a new growing point may develop on the catalyst particle with an angle between the growing direction of the infant tube and the fully grown tube. Newly absorbed carbon atoms were incorporated into the growing nanotube by both the top and bottom of the catalyst particle and therefore carried the particle ahead with growth of a newly developed branch nanotube in the third direction. As a result, a Y-shaped tube was formed as illustrated in figure 6. Also, figure 5(d) clearly demonstrates an example of the beginning of the formation of a Y-shaped tube (see the dashed arrow).

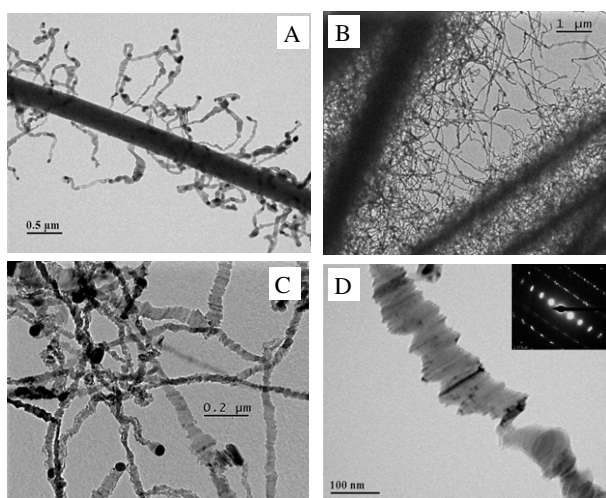


Figure 7. TEM images of the carbon nano-ribbons growing on carbonized nanofibers: (A) infant carbon nano-ribbons growing on the nanofiber substrates; (B) long nano-ribbons on the nanofibers; (C) and (D) high-magnification images of the nano-ribbons. The inset image (D) is the electron diffraction pattern of a single nano-ribbon.

3.2.3. Chlorobenzene as the carbon source. In our previous study [61] we obtained large-scaled aligned bamboo-like CNTs by using FeCl_3 as the precursor for the floating metal particle catalyst. The halogen element Cl was the key element responsible for the formation of the bamboo-like nanotubes. In fact, chlorobenzene contains a chlorine atom in each molecule. Large-scale bamboo-like nanotubes may therefore form on the nanofibers by adding the halogen element Cl to the Pd particle catalyst to alter the formation of CNTs. However, once again the experimental result exceeded our expectations. The carbon nanostructures formed on the nanofibers based with chlorobenzene as the carbon source were mostly carbon nano-ribbons (figure 7). The carbon nano-ribbons were highly graphitized with high crystallinity, revealed by electron diffraction patterns (figure 7(d)). The mechanism of formation of the nano-ribbons using chlorobenzene as the carbon source is still not clear. Detailed research is expected to further reveal the growth mechanism of the nano-ribbons.

4. Concluding remarks

The well-known metal catalyst Pd commonly used for organic synthesis has been employed successfully in the fabrication of carbon nanostructures. By electrospinning followed by carbonizing technology, Pd nanoparticles were prepared in/on the carbonized electrospun nanofibers. The size of the Pd particles was found to depend on the carbonizing temperature. Low temperatures yielded small Pd particles; while higher temperatures gave larger ones. The type of carbon nanostructure depended on the type of carbon source supplied. A toluene source resulted in straight CNTs; pyridine led to coiled nanotubes with a combination of partial Y-shaped tubes; and chlorobenzene yielded nano-ribbons. Furthermore, since electrospun nanofibers are essentially nano-scaled materials, the carbonized electrospun nanofibers with CNTs growing at

different stages can be directly used as CNT samples for TEM characterization without any disturbance. This is a simple but powerful method for exploring the mechanism of growth of carbon or other nanostructures.

Acknowledgments

Financial support is gratefully acknowledged from grant 2004CCA04700 of the '973' great fundamental research program of the Chinese Ministry of Science and Technology, grants DMI-0100354 and DMI-0403835 of the National Science Foundation, USA and grant 20464001 of the National Natural Science Foundation of China.

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