

Coiled carbon nanotubes: Synthesis and their potential applications in advanced composite structures

Kin Tak Lau^{a,*}, Mei Lu^{a,b}, David Hui^c

^a Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, China

^b College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, People's Republic of China

^c Department of Mechanical Engineering, University of New Orleans, New Orleans, LA 70148, USA

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Abstract

Since the discovery of carbon nanotubes, their applications benefit to a wide range of engineering, applied physics and biomaterials areas, because of their superior mechanical and electrical properties. In the advanced composite society, substantial works including the synthesis of different types of nanotubes, manufacturing process of nanotube-related composites, mechanical characterizations of these composites, have been conducted in the past few years. One of the major focuses, has not yet been solved, is on how to ensure a good bonding between straight nanotubes and their surrounding matrix, and also the integrity of the nanotubes' structures, in their atomic scale level after being bonded with the matrix. Physical nanotube pullout and push in tests can be used to determine the interfacial bonding properties of the nanotube/polymer composites. However, due to their size constraint, it is impossible to precisely conduct such tests, based on current testing technology. Although molecular dynamics (MD) simulations are another alternative to roughly estimate the bonding behaviour of the composites, the results are highly dependent on the basic assumptions applied to models. Recently, the development of coiled carbon nanotubes opens a new alternative to reinforce the traditional composites. The coiled configuration of the nanotubes can enhance the fracture toughness as well as mechanical strength of the composites even there is no direct chemical bonding between the nanotubes and matrix. Their coiled shape induces mechanical interlocking when the composites are subjected to loading. In this paper, a critical review on the synthesis of the coiled nanotubes and their applications in advanced composites is given.

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1. Introduction

The discovery of carbon nanotubes by the Japanese researcher Sumio Iijima in 1991 marks the beginning of over a decade of intensive research into the properties of the one-dimensional (1D) tubular molecules [1–4]. As a peculiar matter with outstanding mechanical, optical, and electronic properties, carbon nanotubes have played a central role in leading the overall progress of nano-science and nano-technology in both academic research and industry applications. The extent of this interest is evident by the fact that carbon nanotubes is the subject of study of about seven research papers each day, excluding book chapters and reviews.

Carbon nanotubes can be geometrically described as a seamless cylinder of a rolled graphene sheet (single-walled

nanotubes) or multiple nested cylinders consisting of rolled graphene sheets (multi-walled nanotubes) of varying shapes [5,6]. In the advanced composite society, substantial works including the synthesis of different types of straight nanotubes, manufacturing process of nanotube-related composites, mechanical characterizations of these composites, have been conducted in the past few years. One of the major focuses, has not yet been solved, is on how to ensure a good bonding between straight nanotubes and their surrounding matrix, and also the integrity of the nanotubes' structures, in their atomic scale level after being bonded with the matrix. Physical nanotube pullout and push in tests can be used to determine the interfacial bonding properties of the nanotube/polymer composites. However, due to their size constraint, it is impossible to precisely conduct such tests, based on current testing technology. Although molecular dynamics (MD) simulations are another alternative to roughly estimate the bonding behaviour of the composites, the results are highly dependent on the basic assumptions applied to models. Besides, using straight carbon nanotubes may cause the

* Corresponding author. Tel.: +852 2766 7730; fax: +852 2365 4703.

E-mail address: mmkklau@polyu.edu.hk (K.T. Lau).

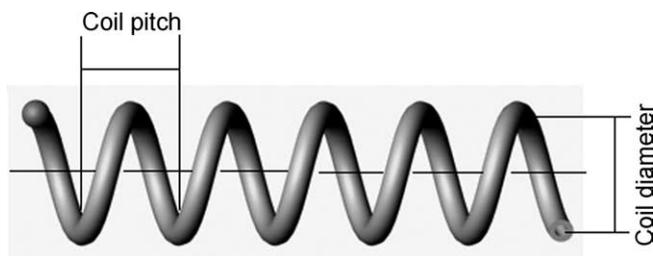


Fig. 1. Schematic illustration of coil pitch and coil diameter of coiled carbon nanotube.

over-stiff of composite materials since these ultra-strong nanotubes, because of their high Young's modulus (1 TPa), may reduce the toughness and ductility of the composite materials.

Recently, the development of coiled carbon nanotubes opens a new alternative to reinforce the traditional composites. The coiled carbon nanotubes were first predicted to exist in the early 1990s by Ihara et al. and Dunlap [7–10] and experimentally observed in 1994 by Zhang et al. [11]. Coiled nanotubes are generally described by coil diameter and coil pitch, the distance between adjacent corresponding points along the axis of the helix, as shown in Fig. 1. On a micro-scale, periodic incorporation of pentagon and heptagon pairs into the predominantly hexagonal carbon framework for creating positively and negatively curved surfaces, respectively, can generate a carbon nanotube with regular coiled structure [12]. Computer simulation with molecular dynamics calculations has shown that coiled nanotubes are energetically and thermodynamically stable [13]. As such, the coiled structure is believed to have exceptional properties and versatile applications, hence tremendous theoretical and experimental researches have been devoted to the studies of this intriguing carbon material. This review provides an examination of a decade of work on the synthesis of coiled carbon nanotubes and its potential applications.

2. Synthesis of coiled multi-walled carbon nanotubes

The production of straight carbon nanotubes is generally achieved via electric arc-discharge, laser evaporation, or chemical vapor deposition (CVD) [14]. While samples derived from arc discharge and laser evaporation methods will contain only straight nanotubes owing to the growth temperature of each method, CVD has been found to be the most efficient in terms of obtaining coiled carbon nanotubes in nanotube samples. In the arc discharge and laser evaporation process, the very high growth temperature (>2000 °C) required for the vaporization of solid graphite for nanotube growth will result in a higher mobility of carbon atoms and thus forming the perfect hexagonal graphite for the growth of only straight nanotubes. On the other hand, the growth temperature with the CVD method (500–1000 °C) results in lower mobility of carbon atoms, favors the formation of non-hexagon carbon rings in the growing nucleus and results in a poor crystalline graphitic structure. From a microscopic point of view, all curvatures of

nanotubes, such as bending, branching, closed ring, plane buckling, coils, etc. originate from the introduction of pentagon–heptagon pairs in the hexagonal network on the straight nanotube walls [7–10,15]. A regularly orientated nucleation of heptagons and pentagons along the nanotube body would produce a coiled nanotube.

CVD process involves the pyrolysis of a hydrocarbon (e.g. methane, acetylene, benzene, propane, etc.) over transition metal catalysts (e.g. Fe, Co, Ni) at high temperatures (500–1000 °C) to produce fullerene, carbon fibers, carbon nanotubes, and other fascinating sp^2 -like nano-structures. The structure, morphology and size of carbon materials critically depend on the catalyst preparation and deposition conditions. CVD method was first used by Motojima et al. [16,17] in the early 1993 to synthesize regular micro-coiled carbon fibers. Acetylene or propane was used as carbon source gases to form the deposition of carbon atoms on micron-sized Ni particles in the presence of thiophene as an impurity gas. Since then, three major CVD-based methods have been investigated with the goal of finding the optimal condition to obtain coiled carbon nanotubes on a large scale, support-based, on substrate, or template-based CVD growth.

2.1. Supported CVD growth

The first experimental observation for the production of coiled nanotubes was in 1994 [11,18,19], when Zhang et al. in a Belgium research group observed the multi-walled coiled carbon nanotubes with inner and outer diameter of 15–20 nm in the sample grown by catalytic decomposition of acetylene over silica-supported Co catalyst at 700 °C. The tube walls of coiled nanotubes contained concentric cylindrical graphene sheets separated by the graphitic interlayer distance. The study on the morphology and internal structure of the coils by high-resolution transmission electron microscopy (HRTEM) and electron diffraction revealed the regular polygonized characteristic of the coiled nanotubes and the existence of pairs of pentagon–heptagon carbon rings among the hexagonal network. Thereafter, Amelinckx et al. [12] proposed the concept of a spatial-velocity hodograph to describe quantitatively the extrusion of helix-shaped carbon nanotube from a catalytic particle. A growth mechanism at a molecular level was described by Fonseca et al. [20,21] to explain the formation of knees, tori and coils using the heptagon–pentagon construction proposed by Dunlop. In 1998, coiled nanotubes were imaged by scanning tunneling microscopy (STM) for the first time [22]. The electrical resistance and elastic deformation of the coils were found to play a significant role in the image formation process, such as the line cut and dip effect. Hernadi et al. [23] investigated the correlation among the pH of the catalyst solution, asymmetry of the catalyst particle, and the curvature of the coiled nanotubes. The described growth mechanism for the spiral suggests a potentially controlled synthesis of coiled nanotubes with the catalyst/support combination design. With benzene as the carbon source, Diaz et al. [24] observed coiled nanotubes in the nanotube sample obtained by CVD on Co/SiO₂ catalyst-support system at 500 °C. Further detailed investigation shows a crucial

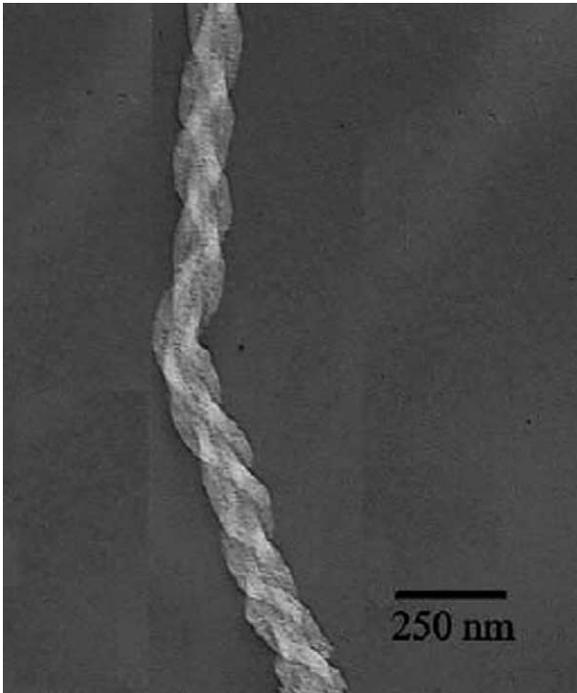


Fig. 2. TEM image for carbon nano-ropes consisting of three coiled multi-walled nanotubes with the pitch and the diameter about 480 and 120 nm, respectively.

relationship between the active catalytic particle as well as the reactive environment and the growth of the coil structures.

An interesting structure of carbon nano-ropes consisting of three helically coiled multi-walled nanotubes with a constant coil pitch over several microns (Fig. 2) was reported by Su et al. [25], in which the aluminophosphate ($\text{AlPO}_4\text{-5}$) supported lanthanide oxide was employed for the catalytic decomposition

of acetylene. It was presumed that the self-organized twist within the three nanotubes was kept by both the spontaneous curvature and van der Waals attraction. Huang and Dai [26] found coiled, spring like, regular helical, and double-helical carbon nanotubes in the pyrolysis of iron phthalocyanine (FePc) proceeded at a relatively low temperature with an insufficient of carbon source (Fig. 3). By using commercial kerosene and methane as the carbon sources, Pradhan [27] and Takenaka's [28] group obtained the coiled nanotubes by CVD over Ni and Co/ Al_2O_3 under an adjusted pyrolysis temperature, respectively. Takenaka's also suggested a dominant mechanism of the base growth for coiled nanotubes at higher temperature based on the observation of the metal particles and the strong interaction of metal with support at higher temperature.

Using both thermal filament and micro-wave catalytic CVD methods, Xie et al. [29] synthesized regular coiled nanotubes over three types of catalyst/support, Fe/magnesium carbonate, Fe/silica, and Ni/zeolite. They believed that the anisotropic catalytic properties for coiled nanotube growth in thermal filament CVD was caused by the impurity gas of thiophene, while the same was caused by the great temperature gradient around the catalyst particles in the micro-wave CVD method. PCl_3 was also used as an impurity gas mixed with acetylene for the coiled nanotube growth [30]. The obtained regular coiled nanotubes was believed to have grown catalytically with Ni-P-Cl co-crystal based on the 'anisotropy of carbon deposition' theory (Fig. 4). Most of the CVD fabrications of coiled nanotubes were carried out under atmospheric pressure and high gas flow rate, which may cause safety concerns and environmental issues due to the inefficient use of hydrocarbon gas. Lu et al. [31] explored an efficient and secure CVD method to prepare coiled nanotubes on silica-supported Co

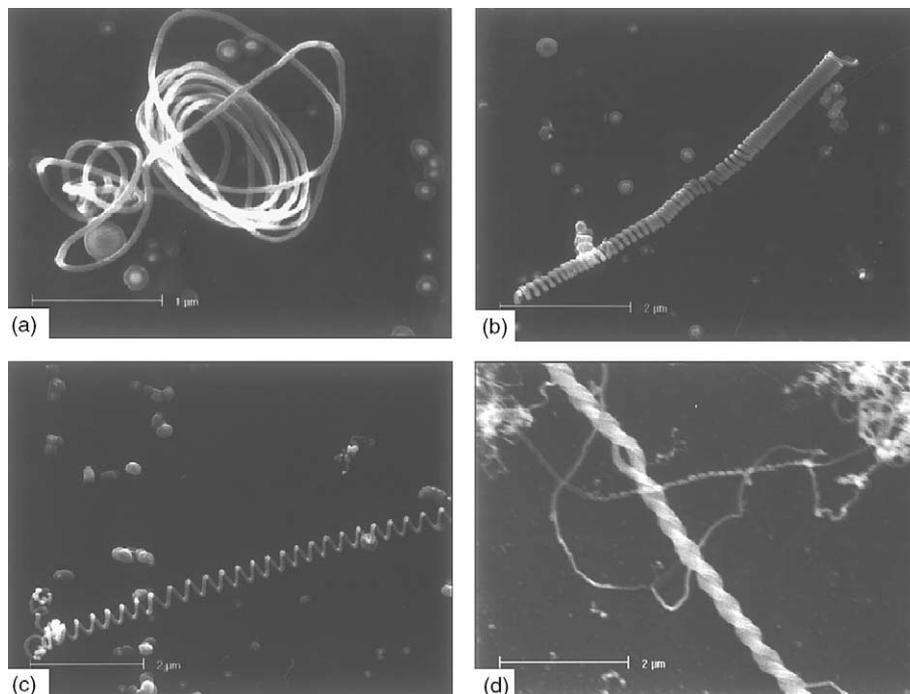


Fig. 3. SEM images of individual carbon nanotube having (a) coiled; (b) spring-like; (c) regular helical; and (d) double-helical structure.

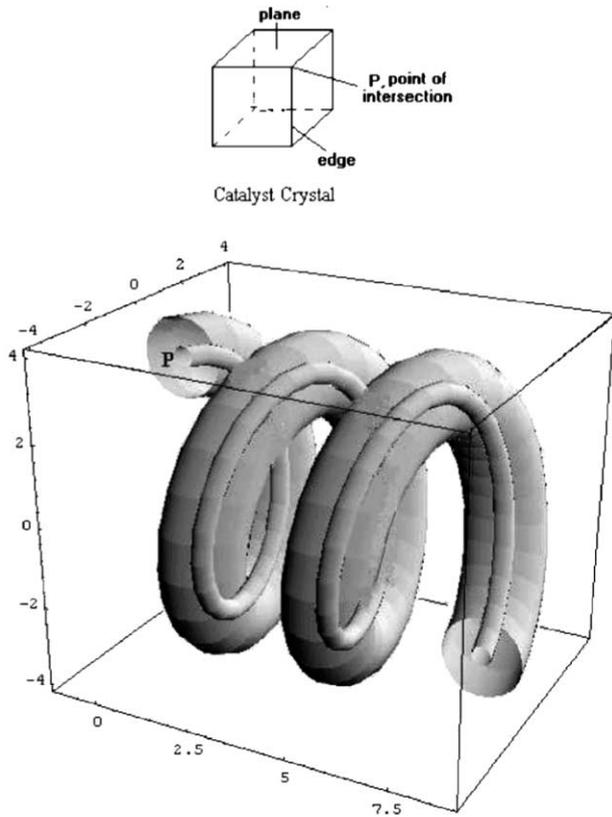


Fig. 4. 3D model for growth mechanism of coiled carbon nanotubes.

nano-particles under reduced pressure and at lower gas flow rates. In their nanotube samples, they observed the regular coiled nanotubes such as slightly curved, spring-like, highly compressed, and loop-wire shaped, as well as other nanotubes of irregular coils with various shapes (Fig. 5). Also proposed was a helix formation mechanism involving a carbon core formation centering on a catalytic particle followed by carbon helices growth controlled by kinetics on the basis of the heptagon–pentagon construction theory (Fig. 6).

The drawbacks of the present supported CVD synthesis of coiled nanotubes are in three aspects: (1) the obtained coils have only been as by-products of multi-walled nanotubes; (2) the manufacturing of coiled nanotubes have not realized the large-scale production for industrial and device applications as that of straight nanotubes; (3) the coil growth is difficult to control precisely via CVD process conditions and catalyst features. For almost 10 years, controlled synthesis of regular coiled multi-walled nanotubes in high yield had been one of the major challenges to researchers.

2.2. Substrate CVD growth

Grobert et al. [32] observed coiled nanotubes and nano-fibres in the preparation of aligned carbon nanotube bundles and films by pyrolysis of solid organic precursors on laser-patterned catalytic silica substrates. They noted that melamine pyrolysis over aged Ni and Co substrates are capable of generating coiled nanotubes within the eroded tracks as well as on the surface of the metal films close to these channels

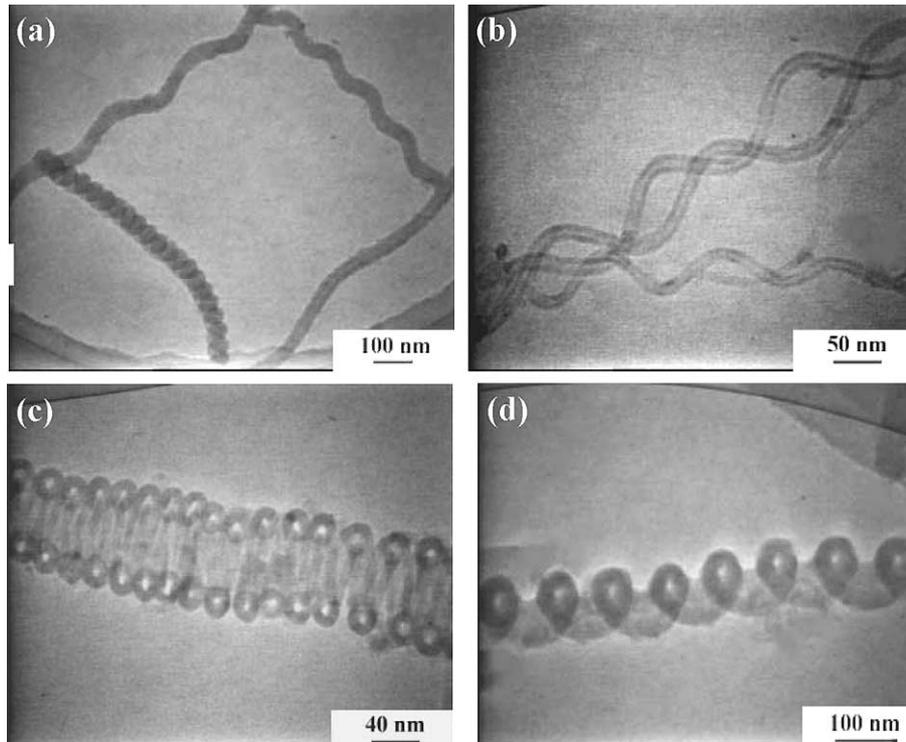


Fig. 5. (a) Four coils with various pitch and diameter; (b) several wavy nanotubes twisted with each other; (c) highly compressed coiled nanotubes with nodes; (d) loop wire shaped nanotube (all these coils were produced by reduced pressure CVD).

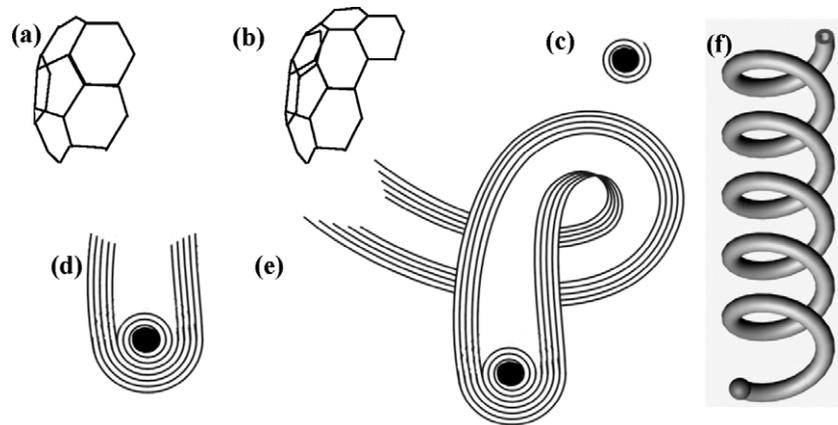


Fig. 6. (a) Nucleation of a pentagon; (b) growth of a quasi-icosahedral shell; (c) formation of a spiral shell carbon encapsulated catalyst particle; (d) growth of a straight carbon nanotube; (e) formation of a node along the straight carbon nanotube; (f) formation of a coiled nanotube.

(Fig. 7). They also believed that the formation of coiled nanotubes depended critically on the dimensions of small catalyst clusters modified by surface effects and the non-symmetrical fashion of diffusion path lengths in the catalyst particle. High-yield production of coiled multi-walled nanotubes was attempted on indium tin oxide (ITO) glass substrate by Nakayama's group in Japan [33–35]. They synthesized coiled nanotubes by decomposition of acetylene on patterned Fe film-coated ITO glass and achieved a high yield of over 95% at a growth temperature of 700 °C (Fig. 8). The resulted carbon coil usually consisted of two or more nanotubes and each of them grew with its own diameter and pitch. It was believed that Fe played a role in the growth of carbon tubes while Sn/O enhanced the growth rate and In/O contributed to the formation of coils. Another great breakthrough in the large-scale synthesis of coiled nanotubes was made by Hou et al. [36], in which the CVD process was accomplished by pyrolysis of a vapor mixture of $\text{Fe}(\text{CO})_5$ and pyridine or toluene on a silicon substrate at a temperature of 1050–1150 °C under H_2 flow. The resulting product was composed of mainly multi-walled coiled nanotubes with different coil diameter and coil pitch, which showed no significant differences in Raman spectrum and

X-ray diffraction pattern from the normal multi-walled nanotubes. The metal nano-particles were found in various shapes (Fig. 9) at the tips of nanotubes for the growth of coiled nanotubes, which led to the conclusion that tube growth could occur by the tip-growth model. The explanation for the coil formation is that the carbon dimer C_2 was inserted or added in a hexagonal ring without any C_5 ring neighbor on the fullerene-like carbon cap to form two C_5 and two C_7 rings at high temperatures (Fig. 10).

In many cases, aligned coiled nanotube arrays are required to facilitate their structural–property characterization, individual nanotube assessment, and the efficient device incorporation for practical applications. Bajpai et al. [37] presented a method that combined Hou's technique for producing large-scale non-aligned coiled nanotubes and their existing method for the construction of aligned/micro-patterned straight nanotubes arrays. They successfully fabricated large-scale aligned coiled nanotubes arrays perpendicular to the substrate surface by copyrolysis of $\text{Fe}(\text{CO})_5$ and pyridine onto the pristine quartz glass plates at 900–1100 °C, under a flow mixture of Ar and H_2 . The obtained nanotubes are 70% helical in the densely packed aligned nanotubes arrays (Fig. 11). However, the growth process still needs further optimization for producing aligned



Fig. 7. SEM image of the coiled carbon nanotubes generated by pyrolysis of melamine over Co 'aged' catalytic substrates (in air).

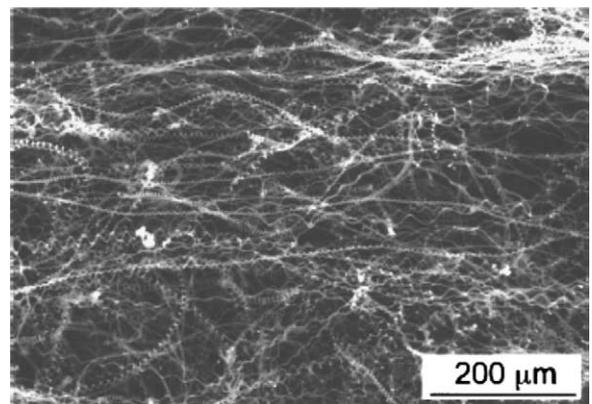


Fig. 8. SEM image of the carbon nano-coils grown on an iron-coated ITO substrate at the reaction temperature of 700 °C for 60 min.

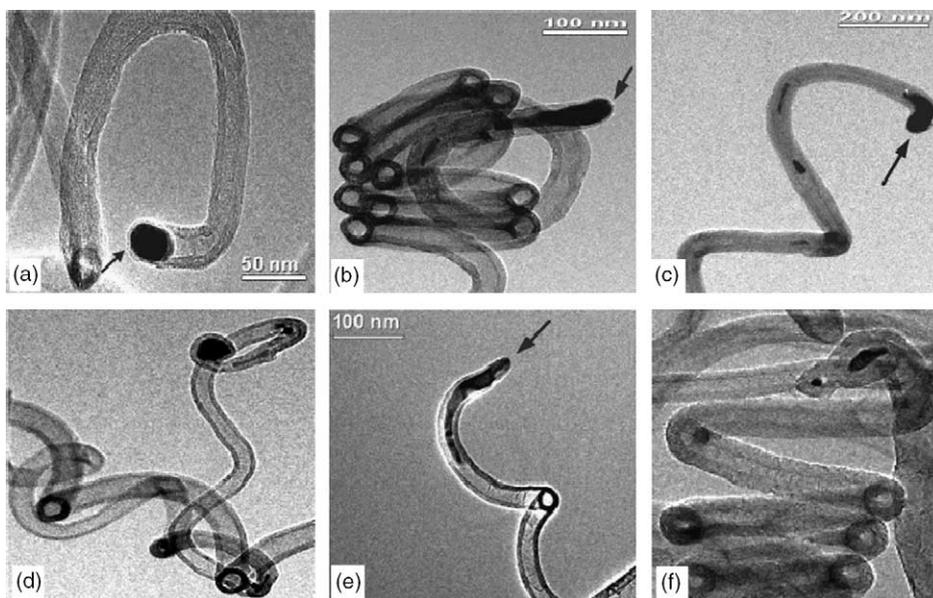


Fig. 9. TEM images of various shaped metal catalyst particles at the tips of coiled nanotubes: egg-like shape (A); taper shape (B); droplet-curved shape (C); peach shape (D); worm shape (E); and beak shape (F).

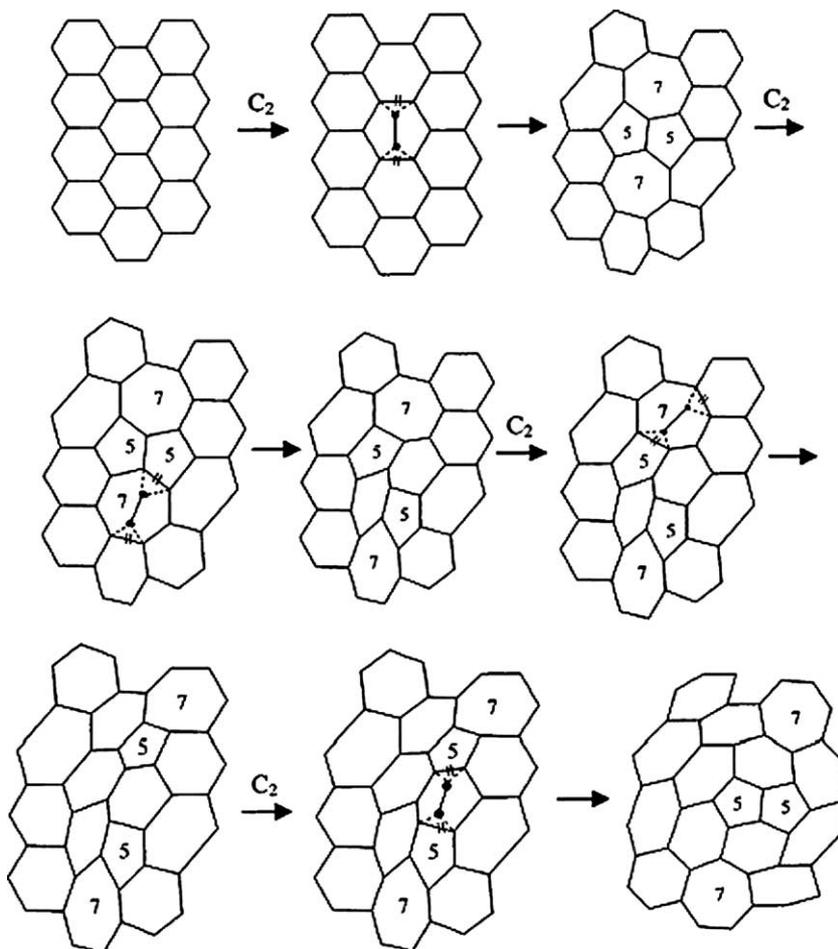


Fig. 10. Schematic illustration for the insertion of a C_2 cluster to a C_6 ring without any C_5 ring neighbors to form C_5 rings and C_7 rings and how the C_5 and C_7 rings move on the semifullerene cap.

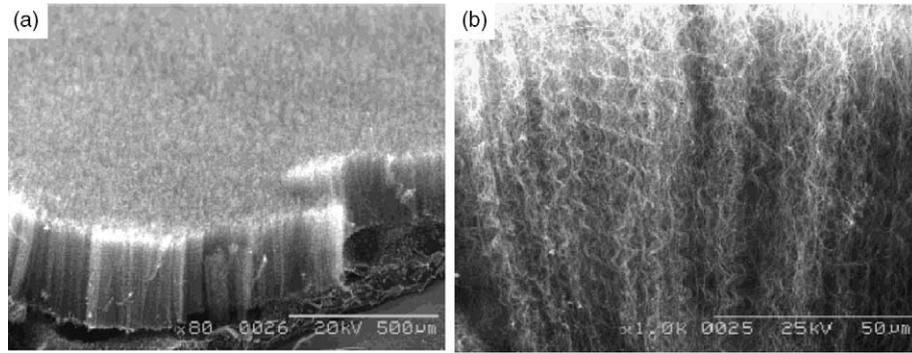


Fig. 11. (a) Typical SEM image of the aligned coiled nanotube array; (b) enlarged cross-section view of densely packed aligned coiled nanotubes [37].

coiled nanotubes with a predetermined helical pitch and/or other structural parameters.

Another peculiar structure in coiled nanotubes is the zigzag shaped nanotubes with small radii of curvature. AuBuchon et al. [38] utilized dc plasma enhanced chemical vapor deposition (PECVD) to produce nanotubes with sharply defined zigzag structure on Ni film-sputtered Si (100) substrate with a tip growth mechanism and a mixed gas of ammonia and acetylene. The obtained nanotubes bends with very sharp radii of curvature of only ~ 25 nm were introduced primarily by dramatically manipulating the electric field lines through controlled movement of field-concentrating conductor plates (molybdenum slab). The zigzag shaped nanotubes arrays had a density of $\sim 2 \times 10^9$ nanotubes/cm² (Fig. 12). With similar setups, more complicated three-dimensional structures, such as regular coils, segmental helices, box-helices, or horizontal-vertical 90-degree zigzag shapes, were anticipated to be obtainable by designing the movement of field-concentrating metal plates.

2.3. Template CVD growth

To date, there are two published works related to template growth of coiled nanotubes. Bai's [39] template growth method

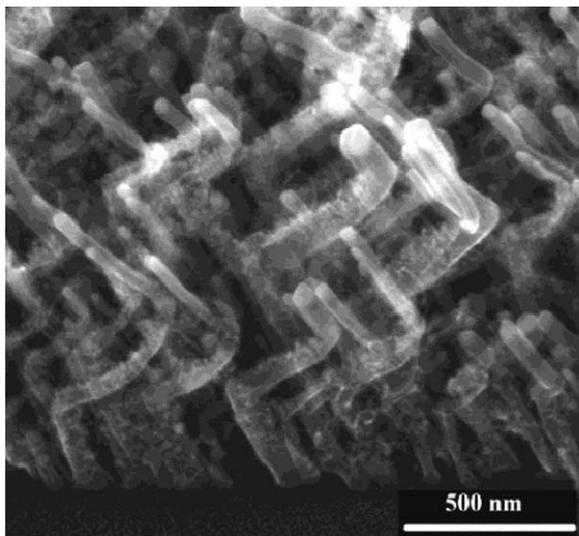


Fig. 12. Zigzag shaped nanotube array grown with PECVD by manipulating the electric field.

used porous aluminum oxide (PAO) template with linear, cylindrical pores of uniform diameters, in which monodispersed nano-structures of the desired material can be obtained in each pore. Through the careful choice of pore size of the PAO template and the electrochemical deposition conditions of metal catalyst, it is possible to produce coiled carbon structure with more or less controlled morphology with acetylene as the carbon source at 650 °C. It has been found that a fine-coiled nanotube with coil diameter of 50 nm, coil pitch of 130 nm and nanotube diameter of 10 nm was produced with very fine catalyst particles in the pores of 5–15 nm under several second AC electrochemical deposition conditions, while larger coiled nanotubes with coil diameter of 200 nm, coil pitch of 160 nm, and nanotube diameter of 160 nm was produced with rather large particles under about 30-s DC deposition conditions. Also can be obtained are micro-coiled carbon nano-fibres with larger metal particles under 1 and 2 min DC deposition conditions (Fig. 13).

The second template CVD growth of coiled nanotubes was reported by Zhong et al. [40]. The aligned straight nanotubes arrays were used as a template for controlled synthesis of coiled nanotubes. The process involved initial growth of three-dimensional regular columns of straight nanotubes with a width of 40 nm on the patterned catalyst stripes and the secondary re-growth of coiled nanotubes with pitches and coil diameters from 100 to 300 nm (Fig. 14). This is accomplished with micro-wave plasma enhanced CVD (MPECVD) method on the straight nanotube arrays. The possible mechanism for the novel formation of coiled nanotubes was attributed to the



Fig. 13. SEM image of the micro-coiled carbon nano-fibres by template CVD.

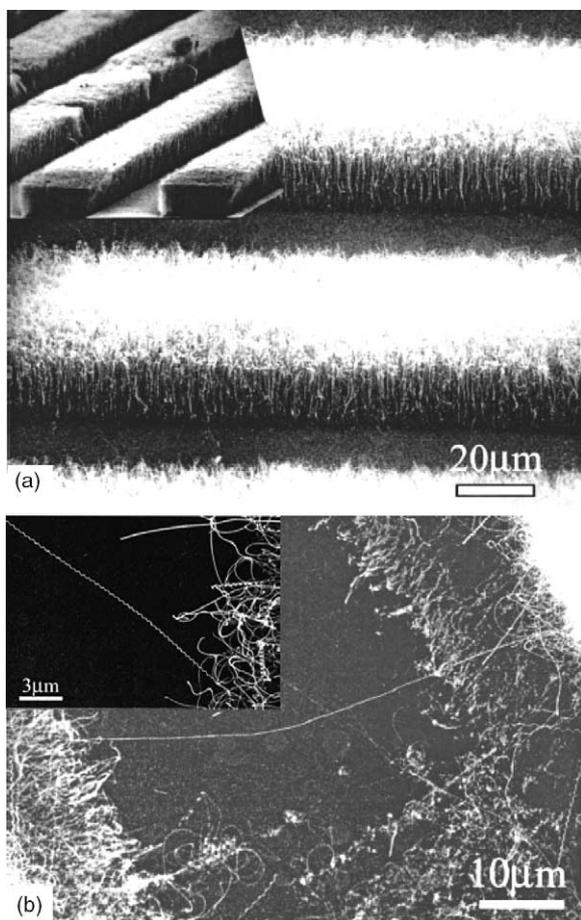


Fig. 14. (a) SEM image of the regular columns of aligned nanotubes (inset: sideview of the nanotube columns); (b) SEM image of the coiled nanotubes (inset: a coiled CNT (> 20 μm in length) extending out from the nanotube array template).

asymmetric growth rate around the catalyst particles induced by the mesoporous template structure of the straight nanotube arrays.

2.4. Other growth methods

In addition to the dominating CVD growth of multi-walled coiled nanotubes, coils have also been found with other methods that had been proven to be effective for producing straight nanotubes. Koos et al. [41] reported coiled nanotubes growth by laser evaporation of a fullerene/Ni particle mixture in vacuum using 532 nm laser pulses of 12–28 μJ from Nd YAG laser on a freshly cleaved graphite (HOPG) surface. The samples were examined by STM and atomic force microscopy (AFM) without further manipulation and revealed a regular coiled structure as well as stable coiling over distances in the order of 100 nm. Saveliev et al. [42] detected regular coiled nanotubes and ribbon-like coiled nano-fibers with rectangular cross-section in the straight multi-walled nanotubes samples obtained from opposed flow flame combustion method. The catalytic support made of Ni-alloy with composition of 73%Ni–17%Cu–10%Fe was positioned at the fuel side of the opposed flow flame formed by fuel (96%CH₄–4%C₂H₂) and

oxidizer (50%O₂–50%N₂) streams. The diversity of formed carbon nano-structures was attributed to the strong variation of flame properties along the flame axis including temperature, hydrocarbon and radical pool. It is also worth-mentioning that coiled carbon nanotubes were observed by accident in an electrolysis of molten salt (NaCl) at 810 °C in the synthesis of single-walled and multi-walled nanotubes [43].

3. Synthesis of coiled single-walled carbon nanotubes

Based on molecular dynamic simulations, single-walled coiled carbon nanotubes were predicted by Ihara et al. in 1993 [8] (Fig. 15). The coiling of the proposed structures is constructed by periodically incorporation of pentagonal and heptagonal carbon rings into the perfect hexagonal network of the graphitic sheet along the tube axis. Although computer simulation made by Terrones et al. [44] has shown that single-walled coiled nanotubes could be observed by HRTEM, no conclusive evidence was found after much efforts of finding single-walled nanotubes during HRTEM observation. This failure may be due to the fact that such thin free-standing coil-like objects will likely be mechanically unstable under e-beam irradiation. The first experimental observation of tightly wound, single-walled coiled nanotubes was achieved in CVD growth samples with STM by Biro et al. in 2000 [45]. The STM imaging of some of these coils was possible only in point contact regime, with indication of semiconducting behavior in accordance with theoretical calculations [46]. Two years later,

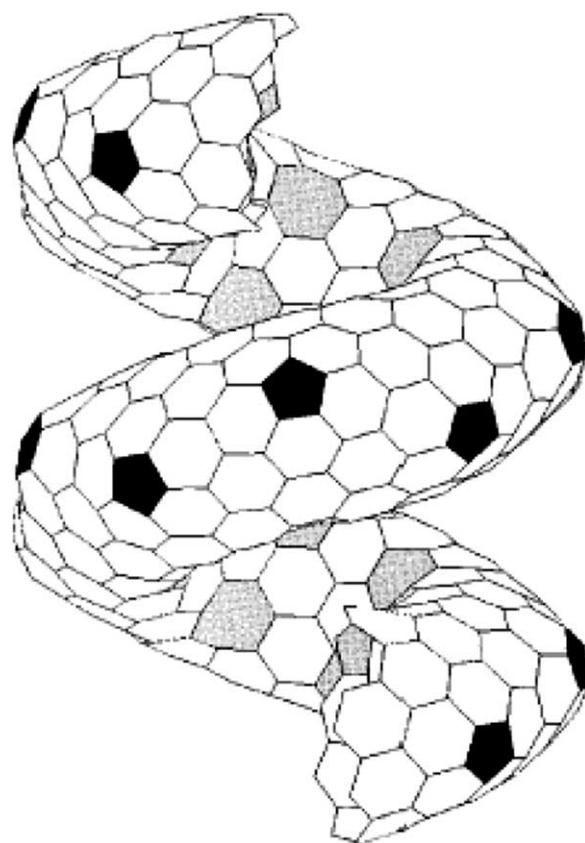


Fig. 15. Molecular model of a coiled single-walled nanotube.

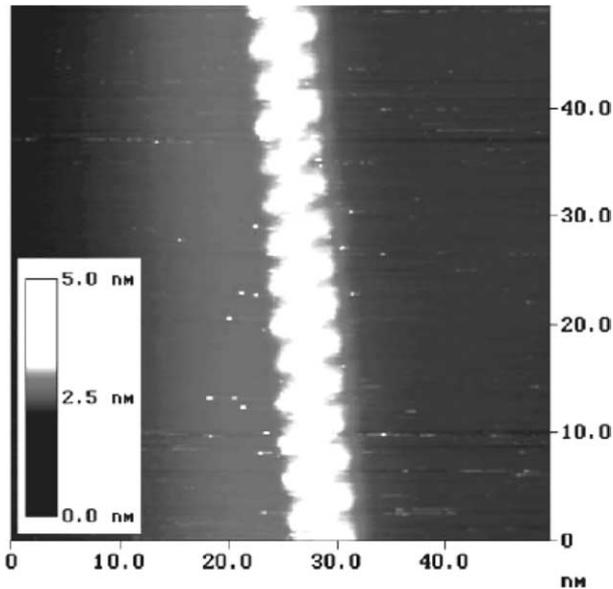


Fig. 16. Constant current, topographic STM image of a coiled single-walled nanotube [47].

further progress was reported by Biro's group [47] again that single-walled nanotubes were grown on a graphite substrate at room temperature by decomposition of fullerene under moderate heating at 450 °C with 200-nm Ni particles as the catalyst. The as-grown coiled structure was investigated without any further manipulation by STM (Fig. 16). The belief was that the formation of the single-walled coiled structures was attributed partly to the template effect of the HOPG substrate, and partly to the room temperature growth, which enhanced the probability of quenching-in for pentagonal and heptagonal carbon rings.

4. Properties and potential applications of coiled nanotubes in advanced composite structures

Based on theoretical studies, regular coiled nanotubes exhibit exceptional mechanical, electrical, and magnetic properties due to the combination of their peculiar helical morphology and the fascinating properties of nanotubes. Coiled nanotubes is believed not only to be of importance in the study of basic science but also possess great potential for

applications in nano-composites, nano-electronic devices and nano-electromechanical systems (NEMS). However, in comparison to the numerous recognized manufacturing techniques for straight nanotubes, the lack of large-scaled synthesis method for coiled nanotubes in the past 10 years has hindered measurement of precious properties of coiled nanotubes, as well as further realizing their potential applications on an industrial scale. Thus far, studies on the properties of the coiled nanotubes have only been limited to the theoretical estimation of the electrical properties and experimental measurement of the mechanical properties.

For straight nanotubes with small diameter, it has been demonstrated that they exhibit either metallic or semiconducting electrical conduction depending on their chiral vectors and independent of the presence of dopant or defects [5,6]. Unlike the straight nanotubes, the earliest theoretically study by Akagi et al. [46,48] has indicated that coiled nanotubes can show even semimetallic characteristics, in addition to the metallic and semiconducting behaviors, which could not be manifested in straight nanotubes. This is due to the fact that according to the simple tight-binding models, the electronic structures of coiled nanotubes vary with the position of pentagon–heptagon pairs in the perfect hexagonal network after folding the energy bands of the constituent carbon nanotubes. The calculations also imply that coiled nanotubes could be a candidate as a superconductor because of the sharp peak of the corresponding densities of states (DOS) of coiled nanotubes at the Fermi level. The unique change in chirality in coiled nanotubes could have potential applications in nano-electronic devices by inducing the pentagon–heptagon pairs defect and associated metal/semiconductor heterojunctions.

Straight carbon nanotubes as discontinuous reinforcement for polymer matrices is regarded as the ultimate carbon fiber with break strengths as high as 200 GPa and elastic moduli in the 1 TPa range [49,50]. Individual nanotube can accommodate extreme deformations without fracturing [51]. Carbon nanotubes also have aspect ratios of around 103, ~500 times more surface area per gram, and possess extraordinary capability of returning to their original, straight structure following deformation [52]. Coiled nanotubes, with all the advantages of straight nanotubes in addition to the peculiar spring-like shape would be another promising candidate as

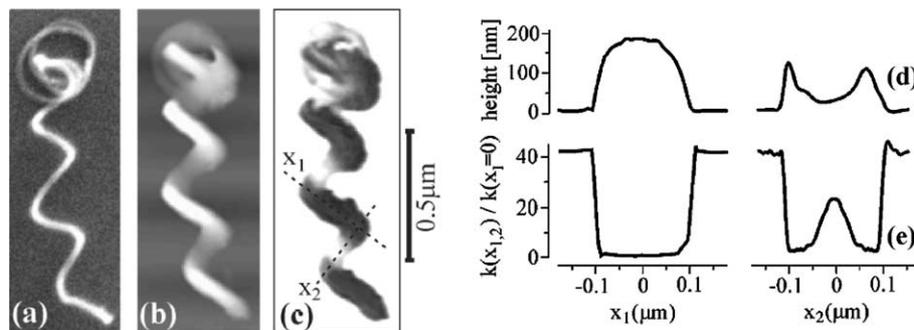


Fig. 17. (a) Electron micrograph of a coiled nanotube; (b) topographic AFM image recorded simultaneously with the FMM image shown in (c); (d) AFM topography of the upper part and the lower part of a winding of the coiled nanotube (cross-sections x_1 and x_2 in (c), respectively); (e) corresponding spatial dependence of the normalized stiffness [53].

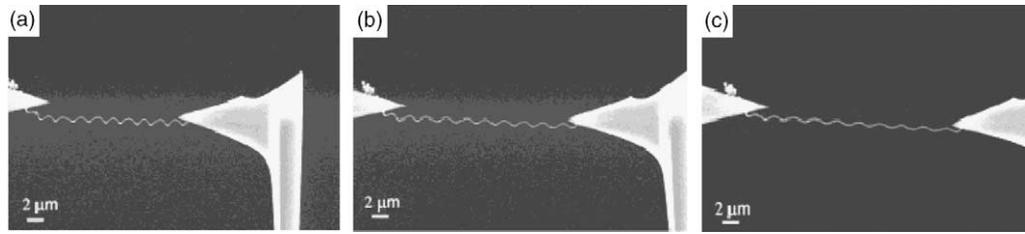


Fig. 18. (a) Relaxed coil prior to loading; (b) coil at a relative elongation of 20%; (c) coil at a relative elongation of 33% [54].

advanced reinforcement fillers in nano-composites. Volodin et al. [53] conducted the first AFM measurement of mechanical properties of coiled multi-walled nanotubes which were deposited on oxidized silicon substrate via catalytically decomposition of acetylene at 700 °C at atmospheric pressure. Their force modulation measurements (FMM) in the tapping mode of operation allowed one to probe the local elastic response along the length of the coil (Fig. 17). The FMM results nicely agreed with the classical theory of elasticity and showed a high Young modulus around 0.7 TPa for the coiled nanotubes, comparable to that of straight nanotubes. By adding a small amount of coiled nanotubes to a polymer matrix to form nano-composites, the configuration of the coils' surface should enhance the bonding strength between the coils and the matrix due to mechanical interlocking, therefore, favor a better load transfer from the coils to the matrix than in the case of straight nanotubes. The resilient property of these spring-like nanotubes can also increase the fracture toughness of polymer-based nano-composites. Due to the uncertainty of the interfacial bonding between the straight nanotubes and the matrix, i.e. the outermost layer of multi-walled nanotubes always pulls out from the matrix after a tensile test, the coiled nanotubes as nano-fillers may provide an efficient way to investigate the interfacial bonding behavior and the failure mechanism of nano-composites.

Another AFM investigation on the mechanical properties of coiled nanotubes was performed by Chen et al. [54], in which the CVD synthesized coiled nanotubes grown from the ITO glass substrate were used as their research object. An individual nano-coil was clamped between two AFM cantilevers and loaded with tension to a maximum relative elongation of $\sim 42\%$ (Fig. 18). The results indicated elastic spring behavior of the coil with a spring constant K of 0.12 N/m in the low-strain regime and an upturn in K in the high-strain regime. The mechanical properties of the coiled nanotubes were characterized on the basis of a non-linear relationship between the spring constant K of the coil and the shear modulus G in which the contributions of all of the components of the restoring force were included.

The use of coiled nanotubes as mechanical resonant sensor recently reported by Alexander et al. [55] is a significant achievement among the many promising applications. Previous studies have shown that straight nanotubes as mechanical resonant sensors involved a complicated sample preparation technique and sophisticated measurements of mechanical vibration of nanotubes in an electron microscopy. The intrinsically coiled nanotubes with remarkable mechanical

properties enabled one to avoid the above complications to attach electrode directly as self-sensing mechanical resonators under AFM study. The coiled nanotubes produced from the decomposition of acetylene were adsorbed on a silicon substrate and then narrow (~ 150 nm) gold electrodes were deposited on the nanotube surface. When the nanotube windings were excited either electrically or acoustically, the gold contacts were discovered to be extremely sensitive to vibrations, to the point of being able to detect fundamental resonances ranging from 100 to 400 MHz. This meant thus produced nanotubes could be useful as a tool to detect mass change as small as a few tens of attograms. Furthermore, the authors anticipated being able to measure even smaller forces and masses in the femtogram range with self-sensing coiled nanotubes, obtained through tinier coils with radii and pitches smaller than a few tens of nanometers, or by creating an artificial tunneling barrier between the coils and the contacts such as the self-assembled organic molecules around the coiled nanotubes.

Coiled nanotubes could have even more interesting applications in various areas than their straight counterparts. For example, the conduction of electricity through coiled nanotubes will generate an inductive magnetic field, an indication that coiled nanotubes, unlike straight nanotubes, are of use as electromagnetic nano-transformers or nano-switches. Due to their unique 3D structure, coiled nanotubes may also be possible as mechanical components such as resonating elements, nano-springs, high-performance electromagnetic absorbers, and nano-actuators. For in-plane nano-interconnection between device components or contact pads, routing of circuit connections often requires not just a straight but curved or sharp-turn conductor circuit lines. Coiled nanotubes may be suitable for this purpose. In addition, coiled nanotubes, especially the vertically straight portion of a zigzag shaped nanotube, can serve as a high-resolution nanotube scanning tip, because the bent portion can provide a sufficient contact length for enhanced bonding to the AFM pyramid sidewall.

5. Conclusion

The development of coiled carbon nanotubes provides a new alternative to the advanced composite industry. Traditional straight carbon nanotubes have been well recognized as strong reinforcements to substantially enhance the strength of composites. However, the drawbacks on the decrease of fracture toughness and subsequently increase the brittleness of the composites may restrict the utilization of these

reinforcements for some composite structures. Coiled carbon nanotubes, due to their coiled configuration, have a great potential to be used for any kinds of composite materials. In this review article, detail of the synthesis of the coiled nanotubes and their potential applications in advanced composites is clearly addressed. The coiled nanotubes indeed are ideal reinforcements for composite and polymer-based materials. These reinforcements can provide moderate strength improvement as well as enhance the fracture toughness of the composites without substantially increasing the weight and damaging the nanotubes' structures.

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