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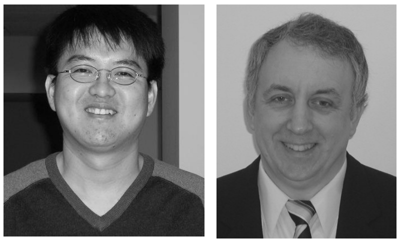
SYNTHESIS AND CHARACTERIZATION OF CARBON NANOTUBE MATERIALS (REVIEW)



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ABSTRACT

This paper provides a survey of synthesis, purification, and characterization of carbon nanotubes. Resent results obtained at the University of Cincinnati on growth and study of carbon nanotube arrays are presented and discussed. The reported achievements in this area will open up more applications for carbon nanostructured materials in many areas of emerging nanoscale science and nanotechnology.

Keywords: carbon nanotubes, nanostructured materials, nanotechnology.

TECHNIQUES FOR GROWING CARBON NANOTUBES

The number of publications and patents on carbon nanotube (CNT) synthesis is rapidly increasing. Still there are many remaining challenges that need to be addressed. One of them is the production of large scale and low cost single-wall carbon nanotubes (SWCNT) and multi-wall carbon nanotubes (MWCNT). Another field of interest comprises the pursuit of controlled CNT growth in terms of selective deposition, orientation, and pre-selected metallic or semi-conducting properties. Our understanding of the CNT growth mechanism has been rapidly evolving, but more consideration is still required to explain the variety of the observed growth features and experimental results. A significant amount of information covering these aspects of CNT research, along with other related topics can be found in [1-5].

There are three principal techniques to produce high quality SWCNT, laser ablation [6], electric arc discharge [7, 8], and Chemical Vapor Deposition (CVD) [9, 10]. Laser ablation and arc-discharge are modified Physical Vapor Deposition (PVD) techniques and involve the condensation of hot gaseous carbon atoms generated from the evaporation of solid carbon. However, the equipment requirements and the large amount of energy consumed by these methods make them mostly suitable for laboratory research [9, 10]. Both the laser ablation and arc discharge techniques are limited in the volume of sample they can produce in comparison to the size of the carbon source. In addition, more impurities accompany the nanotubes in the form of amorphous carbon and catalyst particles because of the high temperature nature of the heat source. Since the growth is difficult to control, the final product consists mostly of MWCNT with poor alignment.

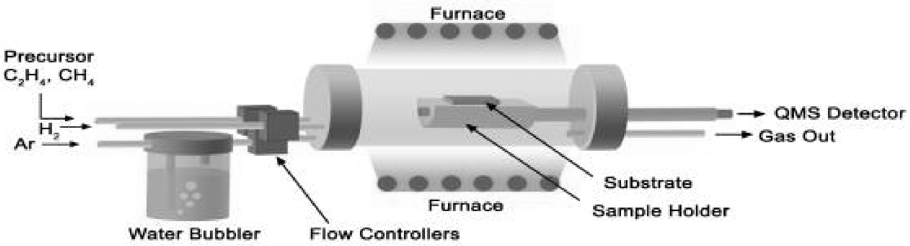

Fig. 1. Schematic of a CVD reactor for carbon nanotube growth. (Sketch by S. Yarmolenko from NCA&T State University)

Chemical Vapor Deposition has become the most important commercial approach for manufacturing carbon nanotubes. CVD is known as irreversible deposition of a solid from a gas or a mixture of gases through a heterogeneous chemical reaction. This reaction takes place at the interface of gas-solid substrate, and depending on the deposition conditions, the growth process can be controlled either by diffusion or by surface kinetics. CVD is the preferred technique for fabrication of thin layers of metals, insulators and semiconductors on different substrates [11, 12, 13]. This method can be easily scaled up to industrial production. CVD is a continuous process and currently is the best-known technique for high yield, and low impurity production of CNT at moderate temperatures. It offers better growth control because of the equilibrium nature of the chemical reactions involved. In addition, CVD has the capability to control the size, shape and alignment of the nanotubes through a carefully designed patterning of the catalysts on the substrate's surface [10]. CVD of CNT uses carbon precursor gases such as methane, ethylene, acetylene, benzene, carbon monoxide or ethanol. The process usually involves high temperature decomposition of hydrocarbons in hydrogen over the catalyst, which is pre-deposited on the solid substrate.

A typical schematic illustrating a CVD reactor for growing CNT is shown in Fig. 1. The precursors in the drawing are ethylene or methane. The bubbler provides water vapor carried by argon gas into the reactor. Water serves as an oxidizing agent helping to remove amorphous carbon from the surface of the catalyst particle. In addition, hydrogen and argon are added to the gas mixture for better control of the carbon concentration in the gas phase. A sample holder accommodates the substrate with patterned catalysts on its surface. The reactor is heated by a resistance furnace and the gas phase is monitored via a quadrupole mass spectrometer.

Transition metals such as Fe, Co, and Ni are frequently used as catalysts. In addition to these catalysts, other metals such as: Sc, Ti, V, Cr, Mn, Y, Zr, Nb, Mo, Hf, Ta, W, Re or a combination of them are also included into the family of catalysts for CNT growth. The metal catalyst can stay on top of CNT forming a cap encapsulating the CNT [14]. In some cases, it remains at the bottom of the CNT, which may promote a bamboo-shaped morphology [15]. The growth mechanism postulates that carbon atoms from the gas phase are transported through the melted carbon-catalyst solution to the growth surface of the CNT. This process is based on the Vapor-Liquid-Solid (VLS) mechanism [16]. The selection and preparation of the substrate and catalyst are important aspects affecting the nanotube yield, and the ability to purify the product of the synthesis.

The CVD synthesis of CNT can be divided into two major groups: bulk synthesis and surface synthesis on flat substrates [10]. Frequently used substrates for bulk synthesis are ceramic particles such as magnesium oxide (MgO), aluminum oxide (Al_2O_2), and in some cases mixed with SiO_2 to form hybrid materials for bulk synthesis [17-21]. Surface synthesis of SWNT requires flat substrates such as polished or porous Si wafers, patterned with metal catalysts by various lithographic techniques [22-27]. Glass, ceramic or metal wafers are also employed for surface synthesis. An advantage of this technique is that the final CNT product is much cleaner than the one grown by bulk synthesis. In addition, the surface synthesis provides better control of the diameter and the alignment of the carbon nanotubes, which makes it attractive for device fabrication. The size and the pattern of the metal-catalyst islands on the Si substrate predetermine their orientation, geometric dimensions and selective growth. Fig. 2 shows a multilayered Si substrate patterned with Fe particles, which

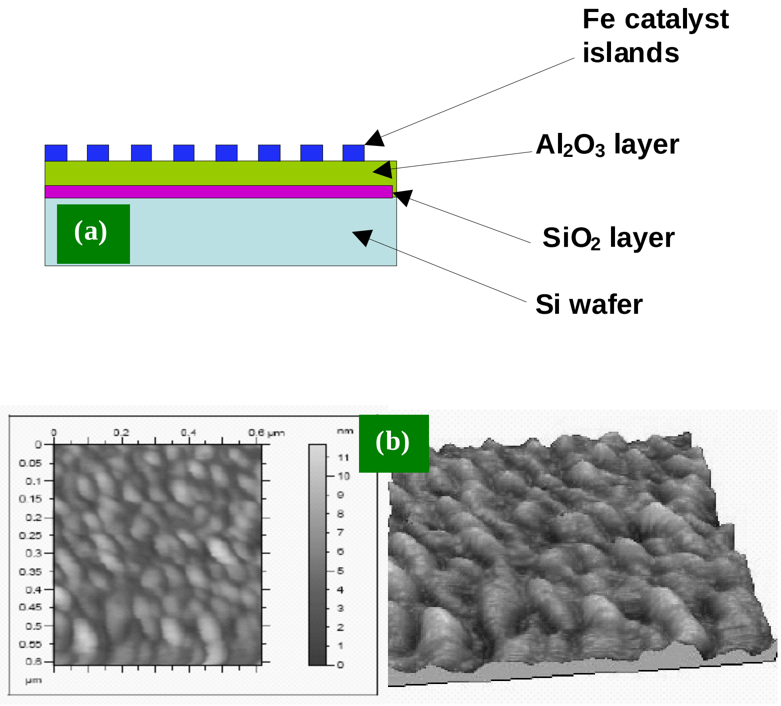

Fig. 2. Substrate design: (a) Substrate design for growing of CNT arrays; (b) AFM images of iron clusters on $Si/SiO_2/Al_2O_3$ multi-layered substrate prepared for CVD of CNT arrays.

are uniformly distributed on the substrate's surface. Each catalyst cluster is about 40 nm diameter and promotes growth of one multiwall CNT with a diameter of about 20 nm. An AFM (Nanosurf-Easyscan 2) was used in a taping mode to study the substrate surface.

The choice of the bulk or surface approach affects the morphology of the CNT synthesized on ceramic particles or on flat substrates patterned with catalyst. This is illustrated in Fig. 3 which compares "spaghetti" type CNT synthesized on MgO particles with aligned CNT arrays grown on Si substrates patterned with Fe nanoclusters (as shown in Figure 2).

There are two different pathways to synthesize CNT by Chemical Vapor Deposition. The first one, as previously described, involves a solid catalyst supported by a substrate. The catalyst can be introduced as a vapor in the CNT growth zone. This pathway is known as the floating catalyst approach, which provides nanosize particles of the metal catalyst [28-31]. A typical floating catalyst compound, which has been studied extensively, is ferrocene. The reaction takes place at about 1,100^{T}C depending on the stability of the hydrocarbon.

CVD FACILITY FOR GROWING CNT AT THE UNIVERSITY OF CINCINNATI

An EasyTube™ Nanofurnace shown in Fig. 4 is used at the University of Cincinnati for the synthesis of carbon nanotubes [32]. The furnace utilizes a thermally driven CVD process and consists of two main units: the control unit, and the process unit. The process unit with the controller is shown in Fig. 4(a). The furnace and a quartz tube reactor with a loader are displayed in Fig. 4(b). A computer controller regulates the furnace temperature and the gas flow. The computer uses the Microsoft Windows environment and LABVIEW as the programming language. The system uses four process gases: methane, ethylene, hydrogen, and argon, which are involved in

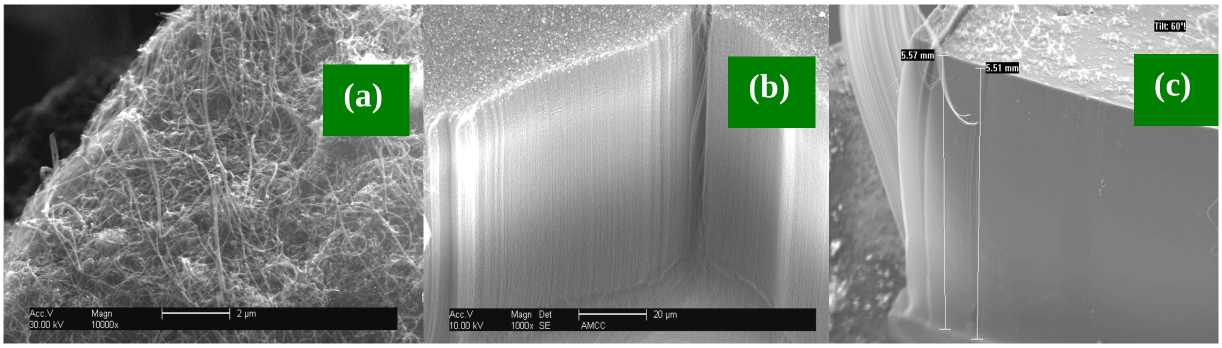

Fig. 3. SEM images of CNT grown on ceramic particles and or Si substrates: (a) bulk synthesis of "spaghetti" type CNT on powdered MgO substrate coated with Fe catalyst; (b) 50 mm CNT array grown on patterned with Fe nanoclusters Si; (c) 0.5 cm long CNT array grown on Si in collaboration with CVD Equip. Inc. by an UC optimized process.

the synthesis of nanotubes. Nitrogen is used for operating the pneumatic gas valves in the furnace. Methane and ethylene are the carbon precursor gases. Hydrogen is used for moderating the chemical reaction of the hydrocarbon decomposition. Argon creates an inert atmosphere during the purging and cooling process steps. Safety is a concern when using the EasyTube™ System and combustible gases. In addition, leak detectors for hydrogen and hydrocarbons are installed in the gas cabinet and all along the gas supply lines to the furnace.

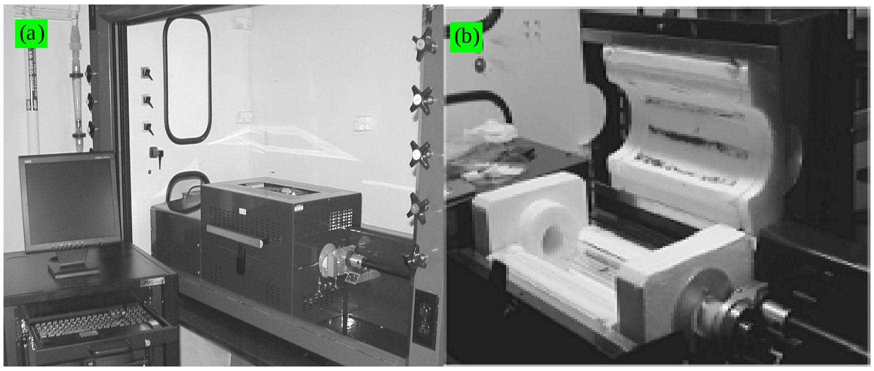

Fig. 4. CVD system for CNT growth: (a) controller and furnace, (b) quartz tube in furnace.

In-situ Quadrupole Mass Spectroscopy (QMS) is a very useful technique for monitoring the species in the CVD reactor, and the related studies can improve the quality of the CNT. This technique was successfully tested during plasma CVD growth of polycrystalline diamond films [33]. To investigate the gas phase environment during nanotube growth, the EasyTube™ System was modified by incorporating a Quadrupole Mass Spectrometer, VISION 1000 P-M (300 amu), made by MKS Instruments. This instrument samples from the reactor during the deposition, and provides quick feedback information about the species in the reaction zone. This approach helps to optimize the process variables in terms of quality of the CNT.

PURIFICATION OF AS-GROWN CNT AND ANALYSIS OF THE PURITY

As deposited CNT are frequently contaminated with metal catalysts, ceramic particles, amorphous carbon, and graphitic nanoparticles. Purification of the as-grown CNT is a complex procedure. The first step of purification includes removal of the impurities by wet chemical oxidation. Acids such as hydrochloric and nitric acid are frequently used for this purpose. Additional steps include decanting, centrifugation or filtration, followed by rinsing in de-ionized water. Gas or vapor phase oxidation is also used for deeper refinement. Finally, gentle treatment in an ultrasonic bath helps to continuously break up agglomerated nanotubes. These approaches are frequently combined to achieve more comprehensive purification and a higher CNT yield.

Most of the purification efforts are based on “wet-chemical” treatment [19, 20]. This approach offers large scale processing. The involvement of strong acids causes a lot of defects on the nanotubes. The procedures such as filtering and drying after chemical etching substantially lower the yield.

Another simple approach for “dry” purification of carbon nanostructured materials is high temperature oxidation (325-425°C) in air [34]. It is important to note that when using this technique the metal catalyst should be removed first by wet oxidation. The last step is required, since in the presence of oxygen the metal particles catalyze low temperature oxidation of the CNT, which decreases the yield dramatically.

UC is also exploring “dry” plasma purification”. This method is clean, efficient, can be done at low-temperatures and offers minimum loss during the treatment.

Fig. 5. UC plasma system for CNT purification

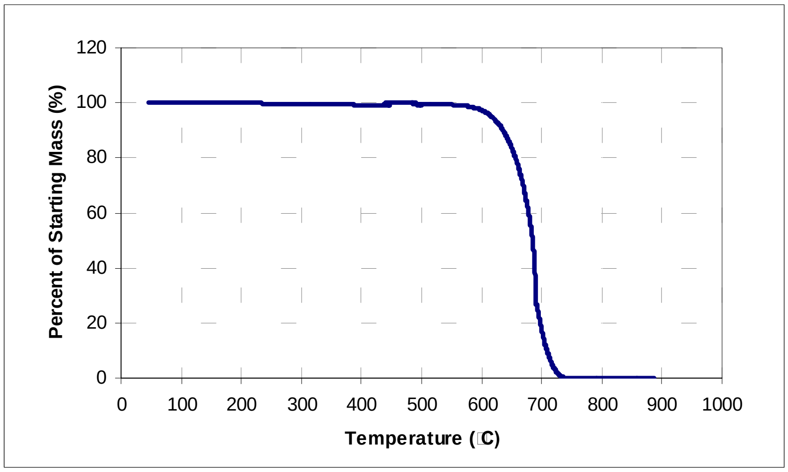

Fig. 6. TGA of a CNT array synthesized and purified at UC. Starting mass of the CNT is 3.371g.

Plasma etching for removal of amorphous carbon that poisons the catalyst or to etch out the remaining catalysts has been tested using water-plasma with or without additional hydrogen [35]. However, prolonged plasma processing may damage the graphitic structure of the nanotubes. There are several reactors reported in the literature for plasma processing of nanostructured particles: a vibrating bed reactor, fluidized bed reactor and a rotary drum reactor. The one used at UC (Diener Electronic, PICO Model) includes a cylindrical tumbler and is shown in Fig. 5. Additional information on purification of CNT synthesized by different methods is revealed in [36-39].

Measuring the CNT contaminant can be done by thermo gravimetric analysis (TGA). Burning the CNT sample in air up to 1000°C removes all the carbonaceous material and the metal catalysts in the original sample convert to oxides. Purity evaluation of the CNT is not a simple procedure. The metal catalyst weight in as-grown CNT can be up to 30 % depending on the synthesis method. Thermo Gravimetric analysis (TGA) is frequently used to measure material weight loss or gain as a function of temperature. This type of analysis provides information related to phase changes, and oxidation or chemical reactions that result in weight loss or gain. TGA is one of many method used to characterize the purity of carbon nanotubes. Amorphous carbon burns in air at a lower temperature than graphitic carbon. Therefore, if high amounts of amorphous or other non-crystalline carbon are present, appreciable weight loss should occur below 400°C. After this initial weight loss, a second weight change should occur when the graphitic carbon comprising the CNT walls oxidizes and converts to CO_2. Fig. 6. shows the TGA curve for a CNT array synthesized and purified at UC. The graph indicates high purity due to low weight loss in air below 400°C which corresponds to loss of amorphous carbon.

Measuring the carbonaceous purity is a much more difficult procedure. Most of the qualitative and quantitative techniques have been based on spectroscopy. The ideal technique has to distinguish between graphitic and amorphous carbon phases in the CNT. A very promising approach for this is solution-phase near infrared (NIR) spectroscopy [34]. In addition, Micro-Raman spectroscopy can indicate defects in the graphitic structure of the CNT along with the presence of amorphous carbon. This approach is discussed in detail later in the paper.

CHARACTERIZATION OF CNT

Carbon nanostructured materials have at least one dimension smaller than 100 nanometers, which makes their characterization complicated and requires sophisticated instruments.

Scanning Electron Microscopy

The morphology of CNT, their dimensions, and orientation can be easily revealed using Scanning Electron Microscopes with high resolution [6, 10, 17, 18, 23-26]. Appropriate is the use of an Environmental SEM (ESEM), which does not need preparation of the samples using a conductive coating. A description of the ESEM and its use for our research are given below. A FEI XL-30 ESEM FEG made by Philips has been employed to study the morphology of the CNT. A Shottky hot-field emission tip is employed as an electron source and has an ultimate resolution of 1.2-1.5nm. A large specimen chamber housing a motorized stage with an internal CCD camera allows observation of fairly large specimens. Thanks to the variable pressure limiting apertures, the ESEM chamber can be operated at a pressure of 1 to 20 Torr. Gaseous detection systems are used in imaging the samples. Partial ionization of the chamber gas causes charge neutralization at the sample surface, with the oppositely charged species being collected by the gaseous secondary detector through a cascade effect. The overall outcome is an improved image of samples regardless of the nature of the samples.

The CNT samples described below were grown at UC and are studied by ESEM. The first group represents bulk synthesis of CNT on powdered ceramic carriers, and the second includes specimens synthesized on a flat Si substrate. ESEM is a perfect technique to reveal the orientation of the CNT and to distinguish between the "spaghetti" type and aligned CNT arrays. In addition, it can focus on fine features related to the CNT morphology as shown in the figures below.

The samples are directly mounted onto a standard aluminum fixture using double sided carbon adhesive tape. No further sample preparation or metallization is carried out, allowing the nanotubes to be imaged in their natural condition. The following set of parameters is used to obtain high resolution images of CNT: working distance between 8-10 mm, accelerating voltage of 10-30 KV, and a chamber pressure between 0.9-1.3 Torr. The images in Fig. 6 are taken using the ESEM and illustrate unpurified nanotubes grown on alumina particles coated with the Fe-Mo catalyst patterned on a Si substrate. The images reveal CNT dimensions of about 1 μm long and 2-3 nanometers in diameter, which suggests that the specimens are SWCNT. The nanotubes form a spaghetti-type pattern with tubes lying over each other. Fig. 7(a) displays typical morphology of SWCNT grown on alumina supported catalyst particles. Excessive catalyst is present below the nanotubes, which can be removed by purification with acids. Fig. 7(b) shows growth of SWCNT between catalyst particles on a silicon substrate, indicating that CNT could be synthesized by bridging catalyst particles. It is observed that long SWCNT originate from one mound of catalyst and terminate at a different mound of catalyst running over the dark silicon substrate.

CNT arrays grown on multilayered Si substrate with Fe catalyst are shown in Fig. 8. Fig. 8(a) reveals that the array is compact and slightly detached from the substrate. The CNT array is easily separated from the Si substrate. Fig. 8(b) shows selective growth of CNT containing towers separated from each other.

Another advanced approach for morphological observations of nanostructureed materials is Atomic Force Microscopy (AFM), which provides the opportunity to study features and properties of CNT that are not available with other techniques [10]. The resolution of the new generation Atomic Force Microscopes (AFM) is dramatically improved. This allows observation of the overall morphology of CNT with unprecedented detail.

Transmission Electron Microscopy

High Resolution Transmission Electron Microscopy (HRTEM) is the most powerful instrument that reveals the diameters of the single-wall and multi-wall CNT, the number of walls, and the distance between the walls [8, 9, 15, 17, 18, 20, 40-42]. In addition, the electron diffraction mode of the TEM helps to identify the nature of the cap on top of the CNT, which is usually composed of the metal catalyst [14, 23, 24].

In Transmission Electron Microscopy, a thin solid specimen ($\leq$ 200 nm thick) is bombarded in vacuum with a highly focused, monoenergetic beam of electrons.

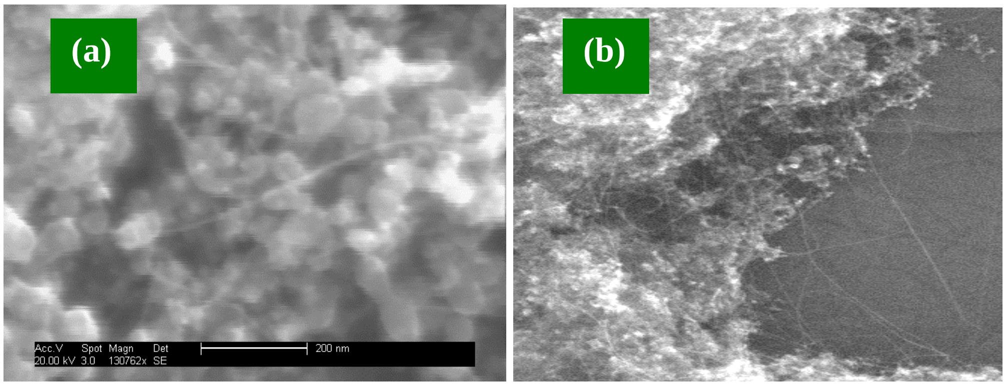

Fig. 7. SEM images of "as grown" SWCNT on alumina particles supported Fe-Mo catalyst patterned on Si substrate: (a) SWCNT at magnification of x 130,000, (b) SWCNT grown between catalyst particles at magnification of x 50,000.

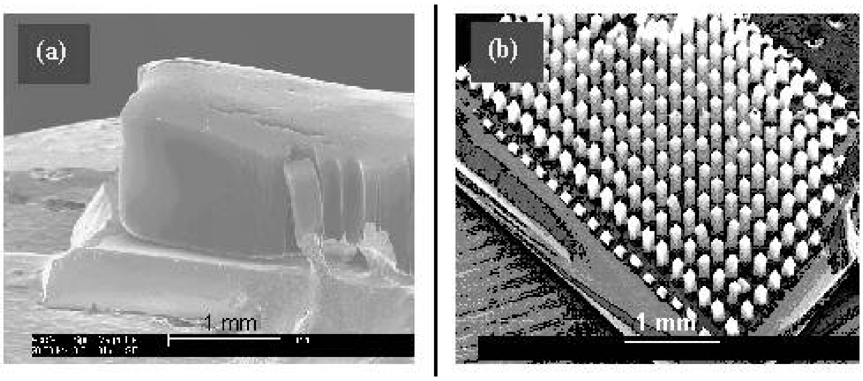

Fig. 8. ESEM Images of CNT arrays grown at UC by CVD on a multilayered Si substrate using Fe catalyst: (a) CNT array on non-patterned substrate; (b) Selectively grown 0.5 mm towers of MWCNT on patterned with catalyst substrate. Growth conditions: 200 SCCM of H_2 flow, 200 SCCM of C_2H_4 flow, 100 SCCM Ar flow through a bubbler with water, 750 C growth temperature, 30 minutes growth time.

The beam is of sufficient energy to propagate through the specimen. A series of electromagnetic lenses then magnifies this transmitted electron signal. Diffracted electrons are observed in the form of a diffraction pattern beneath the specimen. This information is used to determine the atomic structure of the material in the sample. Transmitted electrons form images from small regions of the sample that contain contrast, due to several scattering mechanisms associated with interactions between electrons and the atomic constituents of the sample. Analysis of transmitted electron images yields information both about the atomic structure and defects present in the material. The lateral resolution is better than 0.2 nm on some instruments [41].

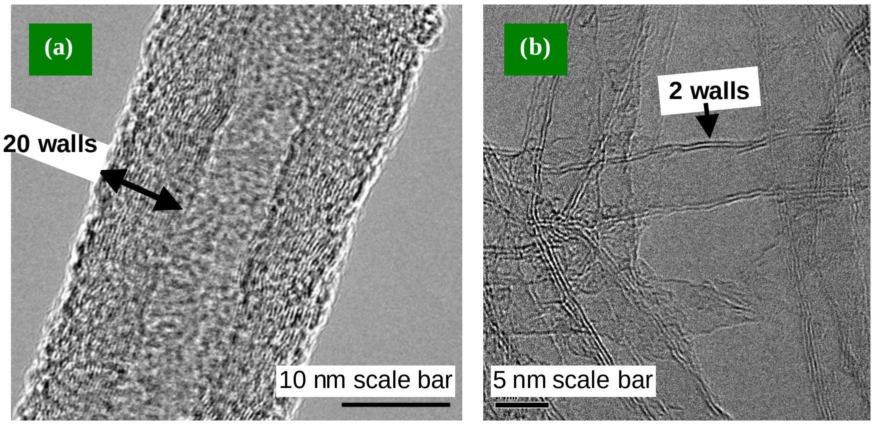

Fig. 9. High Resolution TEM images of CNT synthesized at UC: (a) MWCNT with 15-20 nm outer diameter and 7 nm inner diameter; (b) Double wall CNT found with about 5 nm diameter.

The internal structure of the CNT synthesized at UC was examined by a HRTEM, JEOL JEM-2010, operated at 200 KV. For TEM study, the nanotube arrays were harvested from the substrate, and dispersed in dimethylformamide using tip ultrasonification. The samples were prepared by placing a droplet of the suspension onto a *Leci™* carbon coated grid and dried in air. Fig. 9(a) displays a HRTEM image of a 20 wall MWCNT, and Fig. 9(b) shows a double wall CNT.

The internal structure of the nanotubes and their dimensions are clearly revealed in Fig. 10, where the encapsulated catalyst particle is revealed inside the MWCNT.

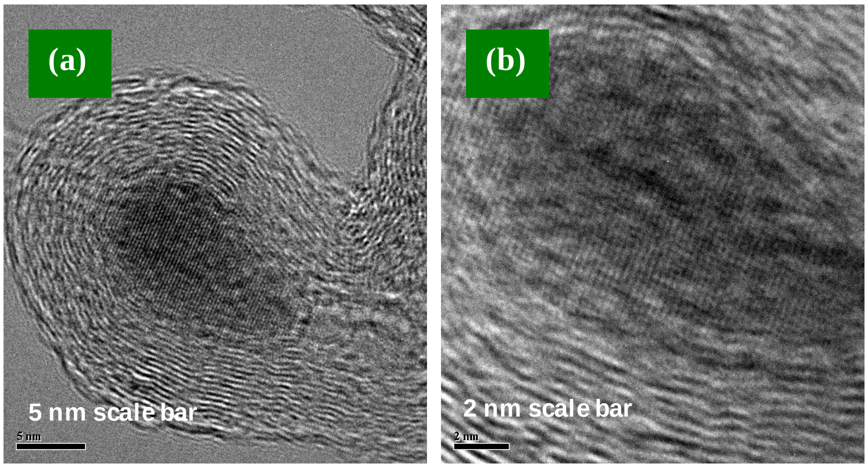

Fig. 10. Internal structure of the CNT by TEM: (a) Multi-Wall CNTs with encapsulated catalyst particle; (b) Lattice structure of the catalyst particle is visible.

Raman Spectroscopy

Micro-Raman Spectroscopy is frequently employed to study the quality of the carbon nanotubes [20, 21, 27, 43]. The tube configuration, including their diameter, can be investigated in detail using this technique [8]. It also provides information about the number of the walls, and the presence of crystalline or amorphous carbon, including the diameter of SWCNT. The Raman technique is used in qualitative and quantitative analysis of carbon nanotubes. When a beam of light traverses a dust-free, transparent sample of a chemical compound, a small fraction of the light emerges in directions other than that of the incoming beam. Most of this scattered light is of unchanged wavelength. However, a small part has wavelengths different from that of the incident light, and its presence is a result of the Raman effect. The pattern of the Raman spectrum is characteristic of the particular molecular species and the intensity is proportional to the number of scattering molecules in the path of the light. Resonance peaks are also observed in the spectrum, which symbolize the presence of a particular specie type that is in abundance. Comprehensive information on the Raman technique and its application can be found in [44-46].

Micro-Raman spectroscopy is used for characterization of CNT with a typical excitation wavelength of 632.8 nm (He–Ne laser) or of 514.5 nm (Ar ion laser). The diameter of SWCNT can be determined by SEM/TEM measurements and additionally verified by Micro-Raman Spectroscopy. The characteristic spectrum of SWCNT exhibits three main zones at low (100–250 cm^{-1}), intermediate (300–1300 cm^{-1}), and high (1500–1600 cm^{-1}) frequencies [8, 20]. These bands can be reduced by the presence of other carbon forms like MWCNT or amorphous carbon [20, 27]. Other carbon materials produce other types of spectra [47].

The high-frequency bands can be decomposed in one main peak around 1580 cm^{-1}, with a shoulder around 1540 cm^{-1}. This shoulder is more important in the case of SWCNT produced by arc discharge, where a separate peak can be observed [20, 27]. In carbon-based materials, typically two main first order peaks are present. One is the D peak, observed around 1300 cm^{-1} (for excitation with He-Ne laser) or at 1350 cm^{-1} when using an Ar ion laser. The D peak is related to the presence of defects [21]. The other one is the G peak at about 1580 cm^{-1}, which is associated with the in-plane vibrations of the graphene sheet [43,48]. In addition to the *G*- line, the appearance of a side peak at about 1540 cm^{-1} indicates the existence of single-wall nanotubes with different diameters [27, 49]. Ratios of the D peak to the G peak have been used as an indicator of the amount of disorder within nanotubes [21, 50]. A small I_D/I_G ratio, typically in the range of 0.1- 0.2, indicates that the defect level in the atomic carbon structure is low, which suggests reasonable crystalline quality [43].

The high-resolution spectrum obtained in the low-frequency domain shows several components within the range of 100–250 cm^{-1} [20, 21]. Prominent low energy peaks around 191 and 216 cm^{-1} are the breathing modes of nanotubes vibrating along the radial direction [49], and can be clearly revealed using a He-Ne laser [27]. The spectrum in the low frequency domain reflects the SWCNT diameters and can be used to evaluate it. In general, the frequency increases with decreasing tube diameter (d). These bands are due to the A_g symmetry mode. The frequency v of these modes is known to be inversely proportional to the diameter of the SWCNT. Based on the equation v (cm^{-1}) = 223.75/d (nm), the diameter of the SWCNT can be determined [51]. The calculated (d) values reflect a distribution in the diameters of the CNT. The peaks ranging from 400 to 1000 cm^{-1} are usually observed in single-wall nanotubes studied using an excitation wavelength of 632.8 nm and could be related to the finite length of the carbon nanotubes [27, 52].

In the case of MWCNT studied using excitation with a He-Ne laser, the *G* line reveals a small bump at the higher energy side around 1620 cm^{-1} and it is attributed to the multi-wall structure. In addition, breathing modes are significantly diminished [27]. The Raman spectrum of nanotubes grown by thermal CVD on Co-coated Si substrates clearly shows the *G*-line peak at 1587 cm^{-1} [27]. The observed broad peak near 1337 cm^{-1} indicates the existence of defective graphitic layers on the wall surfaces due to the relatively low growth temperature. Prominent peaks on the lower energy side cannot be observed. [27]. Another study claims investigation of low frequency spectra of multi-walled CNT [53]. Low frequency modes between 115 and 220 cm^{-1} are obtained after purification of the carbon nanotubes and excitation with a red laser line of 676 nm and a green line of 514 nm. These radial-breathing modes originating from individual walls can be used for characterization of multi-walled CNT. The excitation energy of the laser sources can be used to explore the spectrum in the range 1400-1700 (cm^{-1}) and find variations in the metallic or semi conducting nature of the fabricated CNT. If the light excitation energy is between 1.7 and 1.9 eV, and resonance is observed in the 1400-1700 cm^{-1} wave number range, it is an indication of metallic nanotubes. If the light excitation energy is above 2.2eV or below 1.5eV, and resonance peaks are observed in the 1400-1700 cm^{-1} wave number range, it is an evidence of the semi-conducting nature of the CNT [54].

An inVia Raman microscope was employed for obtaining the CNT spectra synthesized at UC. The Renishaw spectrometer is a 250 mm focal length system. For the 514.5 nm laser excitation, 1800 l/mm grating and 50 micron slit width, the spectral resolution is about 5.5 cm^{-1}. This spectrometer is coupled with a RenCam high-performance cooled CCD detector, which is an all-in-one compact unit. It uses thermoelectric cooling to operate at -70°C without the need for expensive cryogenic coolants. Its detector chip and electronics are carefully engineered to offer users ultra-low noise and low dark current. A Raman spectrum from 0 to 300 (cm^{-1}) obtained from non-aligned ("spaghetti"- type) SWCNT synthesized at UC is shown in Fig. 11. As indicated earlier, the relationship between diameter and resonance wave number is: v (cm^{-1}) = 223.75/d (nm). From this equation is easy to calculate the CNT diameter which is found to be about 1.2 nm.

Aligned CNT arrays prepared at UC were also characterized by Raman spectroscopy using the instrument described above.

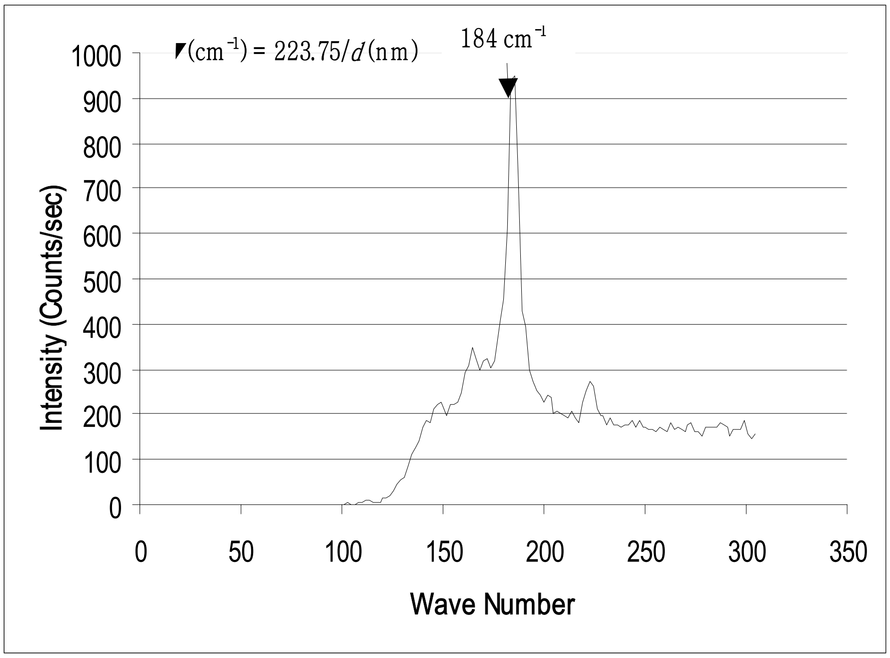

Fig. 11. Raman spectrum of CNT grown at UC from alumina supported Fe-Mo catalyst on a patterned silicon substrate.

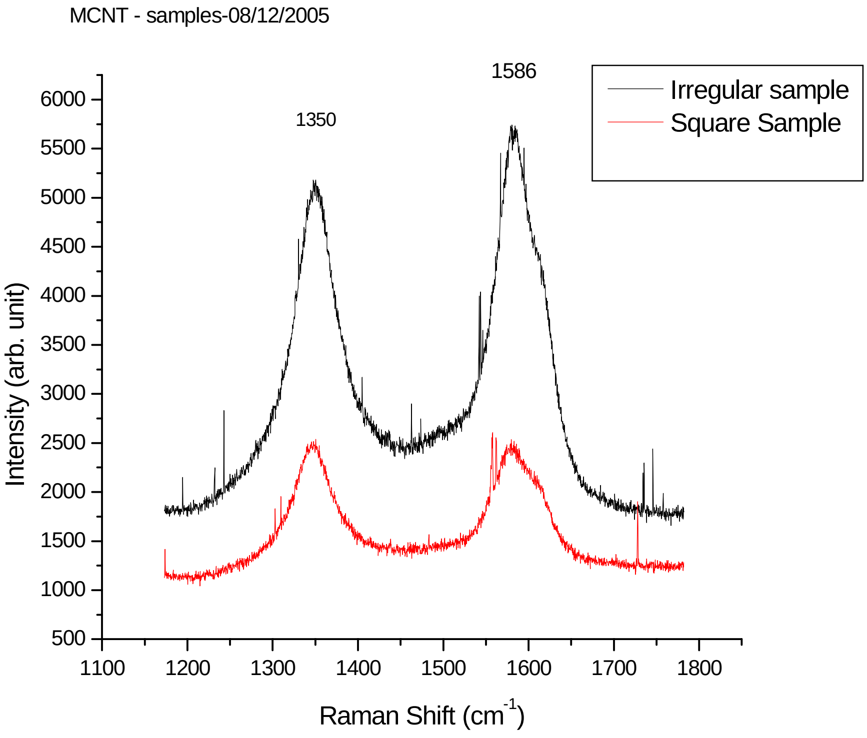

Fig. 12. Raman spectra of aligned CNT arrays.

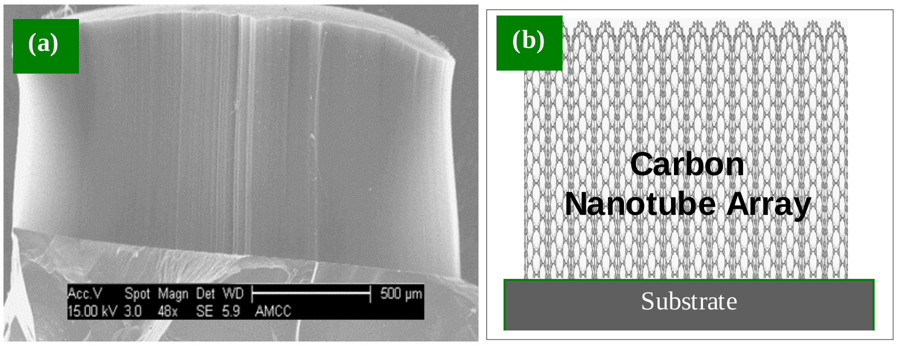

Fig. 13. CNT array: (a) 1.4 mm CNT array with (b) alignment shown schematically.

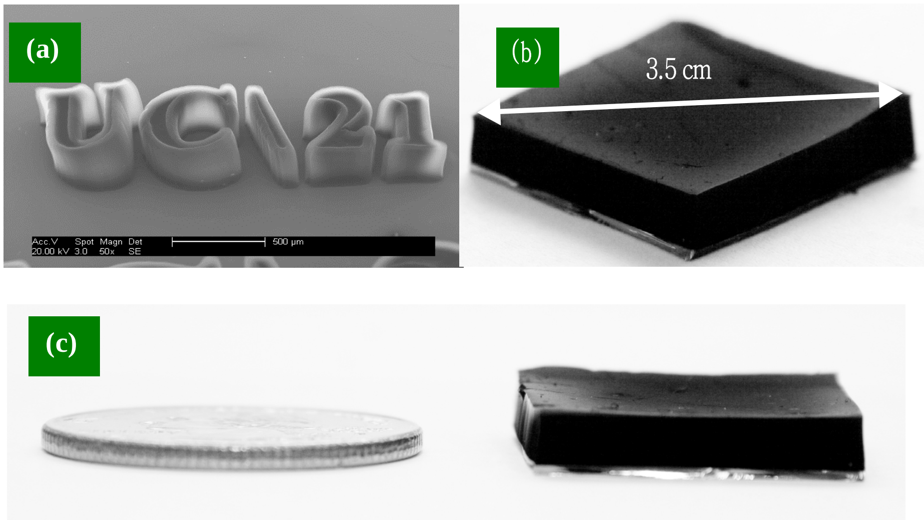

Fig. 14. Large area CNT arrays grown at UC with a novel substrate preparation approach and CVD process: (a) The UC logo made by selectively grown CNT array on a Si substrate; (b) and (c) Large area CNT arrays grown on a Si substrate.

Two samples, one with irregular and one with square shape, were analyzed. The samples were post-processed by an acid reflux method in an attempt to remove any metal and amorphous impurities. Raman spectra of the aligned MWCNT arrays are shown in Fig. 12. Both the 1350 cm^{-1} (D band) and 1586 cm^{-1} (G band) peaks are very strong and appear in the two samples. In addition, a week band around 1615 cm^{-1} (D$^{/}$ band) also appears as a shoulder of the G band.

The existence of the strong D band peak is not fully understood. There might be several reasons for its appearance [55, 56]. The first one is a presence of amorphous carbon on the CNT side surface of highly compacted arrays. The second one is the relatively low crystallization degree of the CNT arrays along with turbostratic structures formed in some carbon sheets. It is also assumed that there is a large crystalline domain with very small (nanometer scale) dimensions that enhances the D peak. It seems that the strong D peak is a feature of highly dense CNT arrays. Similar results are reported in [55-57]. The growth time along with the concentration of the carbon precursor, and the deposition temperature is very important for reducing the D band. Any growth time above 50-60 minutes may not contribute substantially to the length of the CNT but will accumulate amorphous carbon. This explains why our Raman spectrum shows a strong D-band for samples grown longer than 30 minutes. Post thermal treatment in vacuum helps to decrease the D peak [58]. The large D peak seems to be an attribute or characteristic of highly dense CNT arrays, and may not be of too much concern.

GROWTH OF MILLIMETER LONG MWCNT ARRAYS

The short length of CNT has been a roadblock to many of their applications. Growth of CNT with controlled morphology is an intensively investigated area [55-57, 59-65]. Below we report synthesis of highly aligned MWCNT arrays with millimeter length- Fig. 13. Oxidized Si wafers, were used as substrates. E-beam deposition was employed to form a top Al layer, which was subsequently oxidized. Finally, a catalytic iron film of controlled thickness was deposited through a shadow mask on top of the Al$_2$O$_3$. The CNT were grown by thermal CVD from an H$_2$-C$_2$H$_4$-H$_2$0-Ar gas mixture at 750^{o}C in an EasyTube™ furnace [65]. The gas composition of the growth zone was monitored by a QMS [64]. An optimal set of conditions, including substrate preparation and growth, allowed us to synthesize CNT arrays with length above 5 mm as shown in Fig. 14.

By using a novel substrate preparation approach and CVD process we were able to control precisely the growth of the CNT array, as shown in Fig. 14(a), and to deposit aligned CNT over large substrate areas as shown in Figs. 14(b) and 14(c).

CONCLUSIONS

The CVD technique is a powerful approach for synthesis of CNT with controlled properties. The length of the CNT array was found to be critically sensitive to the substrate design. Water vapor was proved to assist the growth, and longer growth time was used to increase the nanotube length. The optimized conditions produced vertically aligned MWCNT arrays over 5 mm in length with high purity and weak adhesion to the substrate. The long nanotubes grown on large areas opens up new applications for oriented nanotubes in development of advanced materials, sensors, and active devices.

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