US 20070116631A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2007/0116631 A1**

Li et al. (43) **Pub. Date: May 24, 2007**

(54) ARRAYS OF LONG CARBON NANOTUBES FOR FIBER SPINNING

(75) Inventors: **Qingwen Li**, Los Alamos, NM (US); **Yuntian T. Zhu**, Los Alamos, NM (US); **Paul Arendt**, Los Alamos, NM (US); **Raymond F. DePaula**, Santa Fe, NM (US); **James R. Groves**, Cupertino, CA (US)

Correspondence Address:
LOS ALAMOS NATIONAL SECURITY, LLC
LOS ALAMOS NATIONAL LABORATORY
PPO. BOX 1663, LC/IP, MS A187
LOS ALAMOS, NM 87545 (US)

(73) Assignee: **The Regents of the University of California**

(21) Appl. No.: **11/415,734**

(22) Filed: **May 1, 2006**

Related U.S. Application Data

(63) Continuation-in-part of application No. 11/051,007, filed on Feb. 4, 2005.

(60) Provisional application No. 60/620,088, filed on Oct. 18, 2004.

Publication Classification

(51) **Int. Cl.**
D01F 9/12 (2006.01)

(52) **U.S. Cl.** **423/447.3**; 502/263; 977/843

(57) ABSTRACT

An array of long carbon nanotubes (i.e. an array where the average length of the nanotubes is greater than 0.5 millimeters) is prepared by exposing a supported catalyst at elevated temperature to a gas mixture of hydrocarbon, inert gas, and a relatively low percentage of hydrogen. Addition of water vapor to the gas mixture may result in an increase in the length of the nanotubes, an increase the rate of growth, and a decrease in contamination of the array by amorphous carbon. The temperature and growth time are also chosen to minimize the amount of amorphous carbon that forms on the array. Fibers spun from the array have a higher tensile strength compared to known CNT fibers.

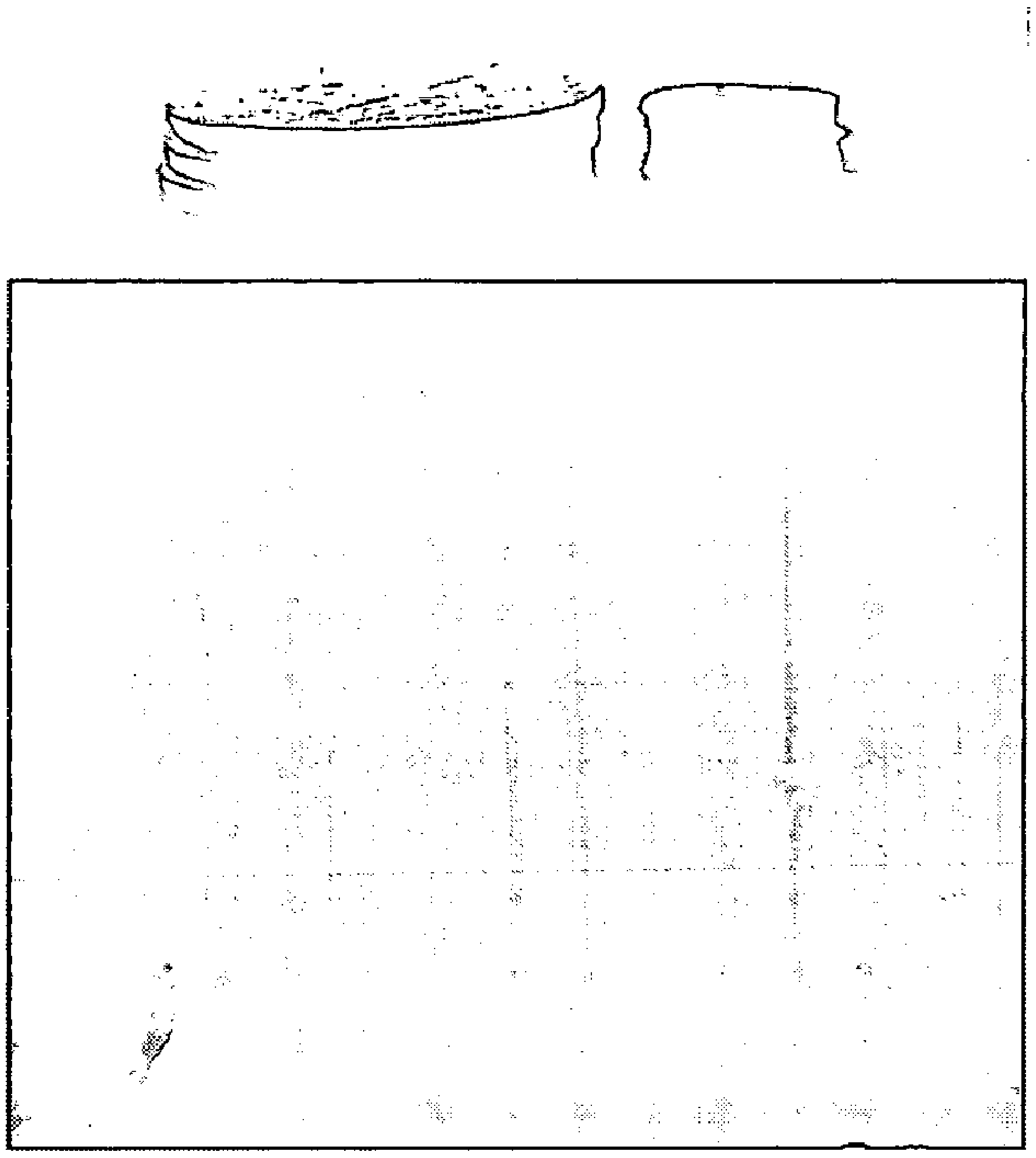

Fig. 1a

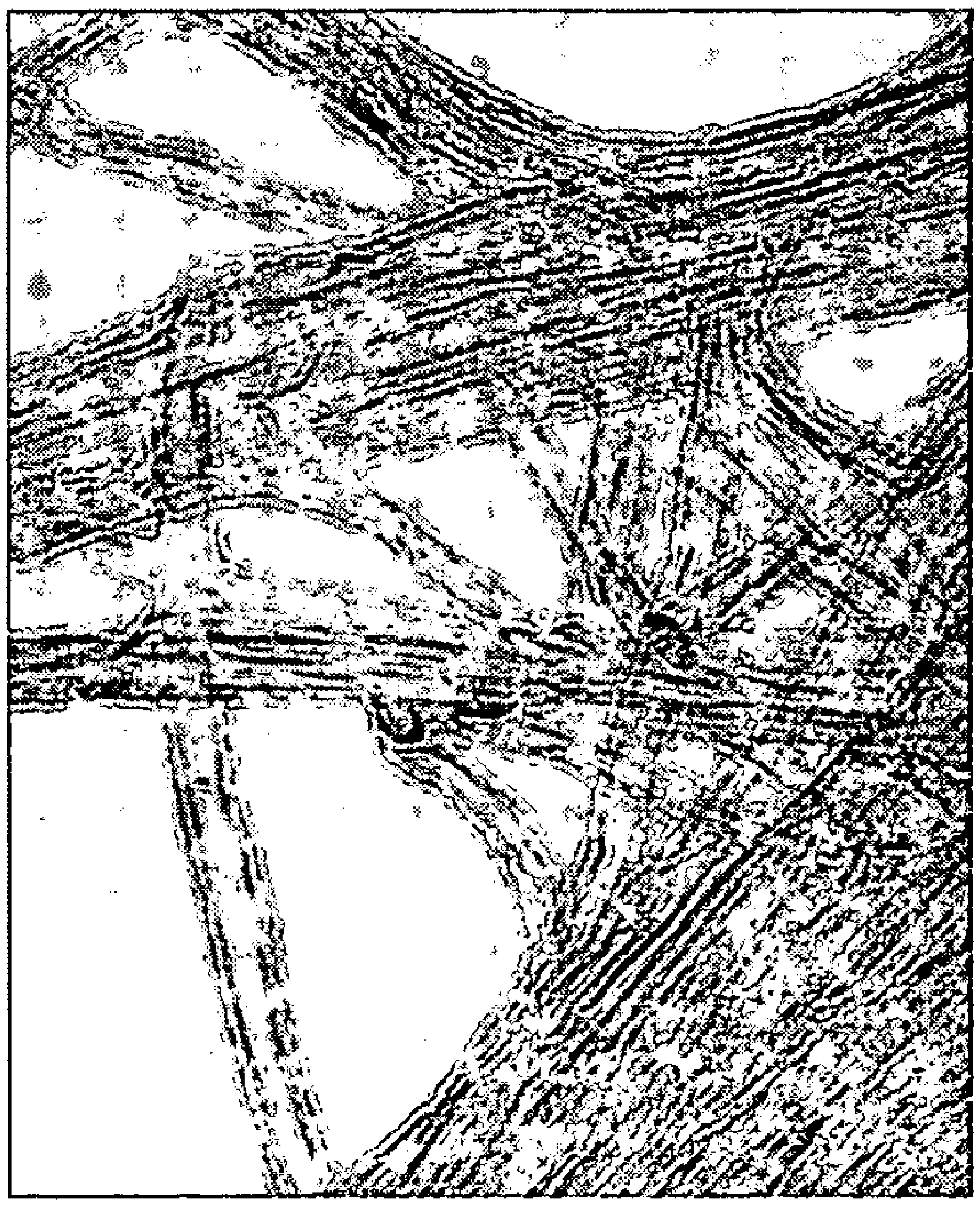

Fig. 1b

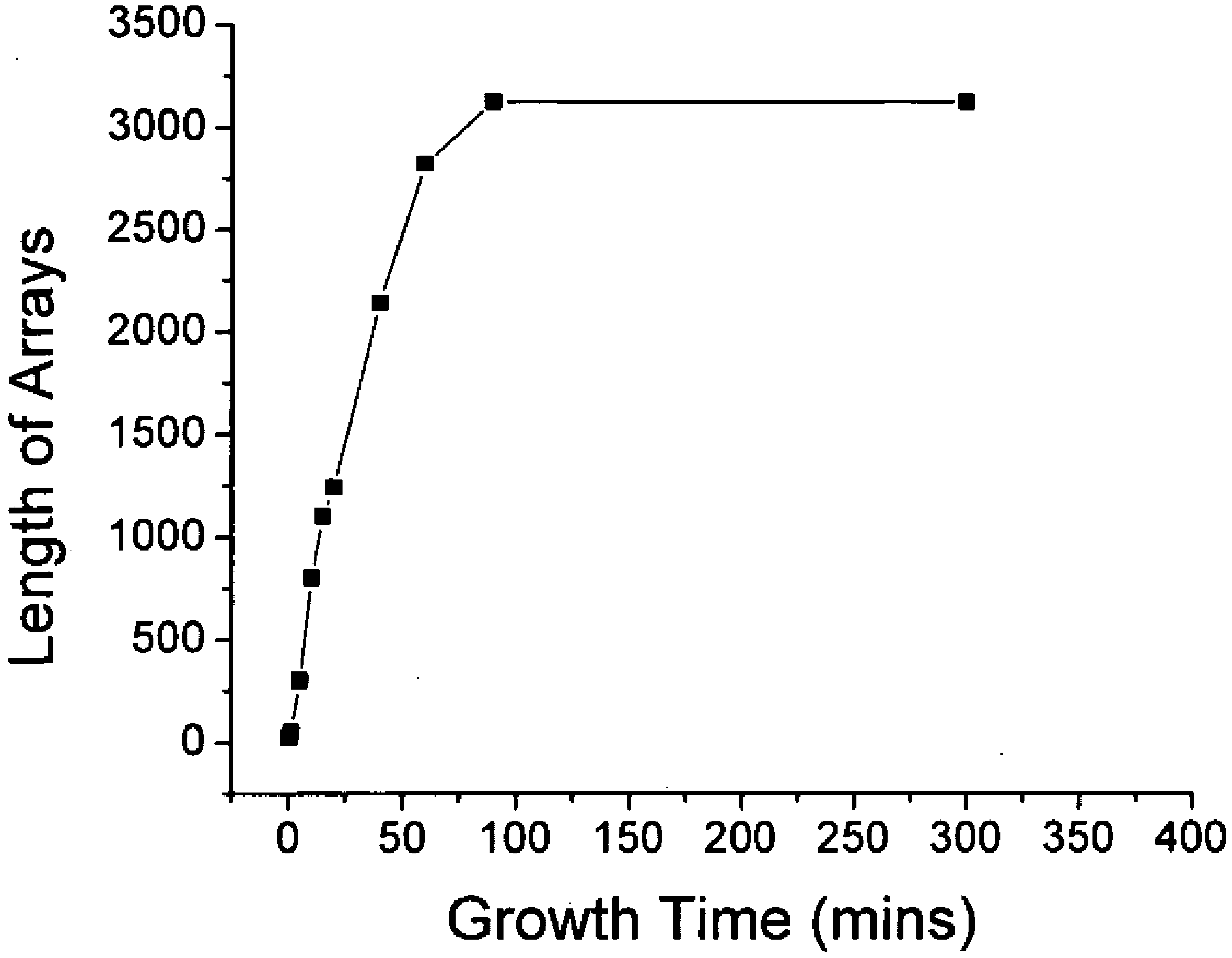
Length of Arrays
3500
3000
2500
2000
1500
1000
500
0
0
50
100
150
200
250
300
350
400
Growth Time (mins)

Fig. 2

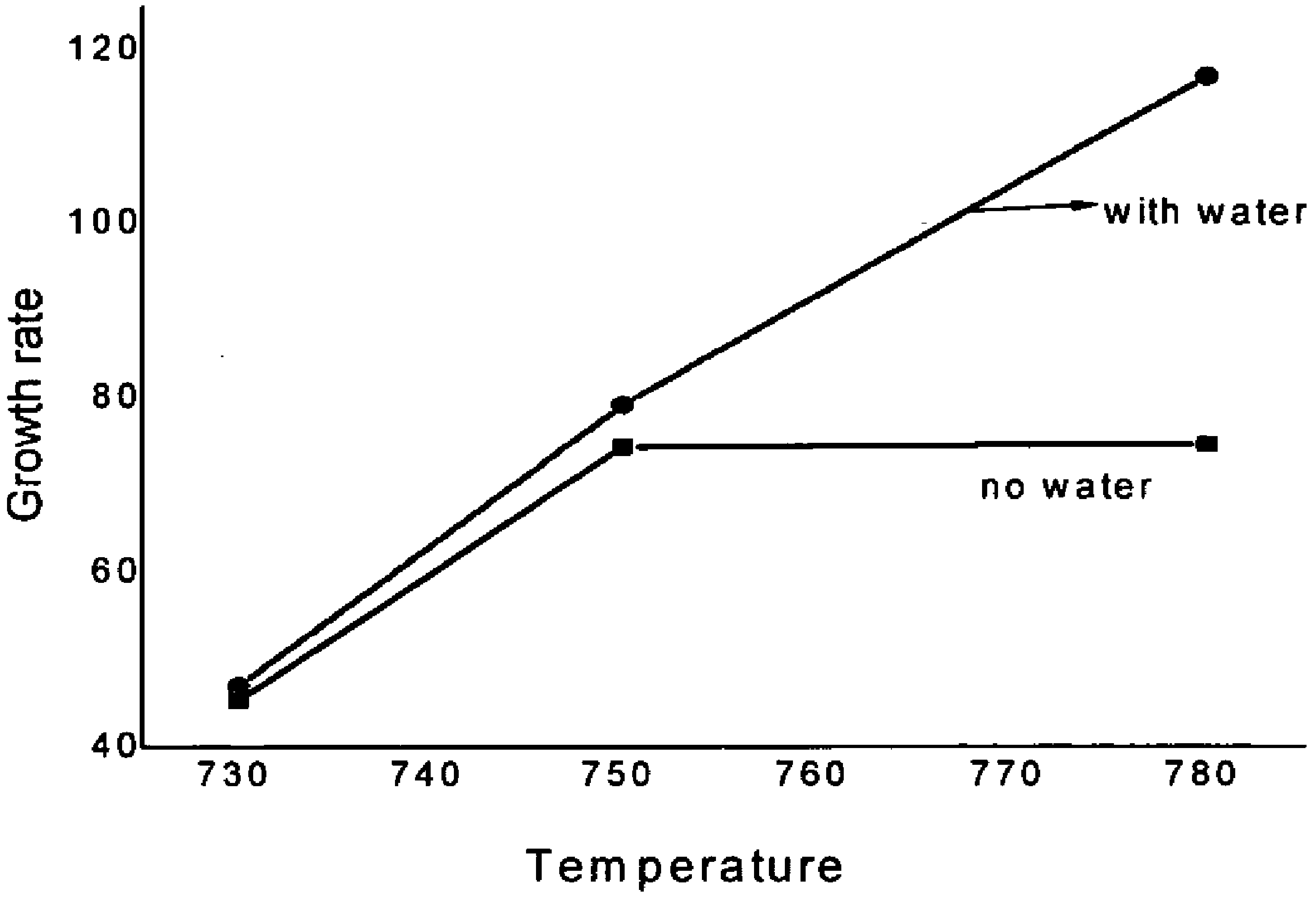
120
100
80
60
40
Growth rate
730
740
750
760
770
780
Temperature
with water
no water

Fig. 3

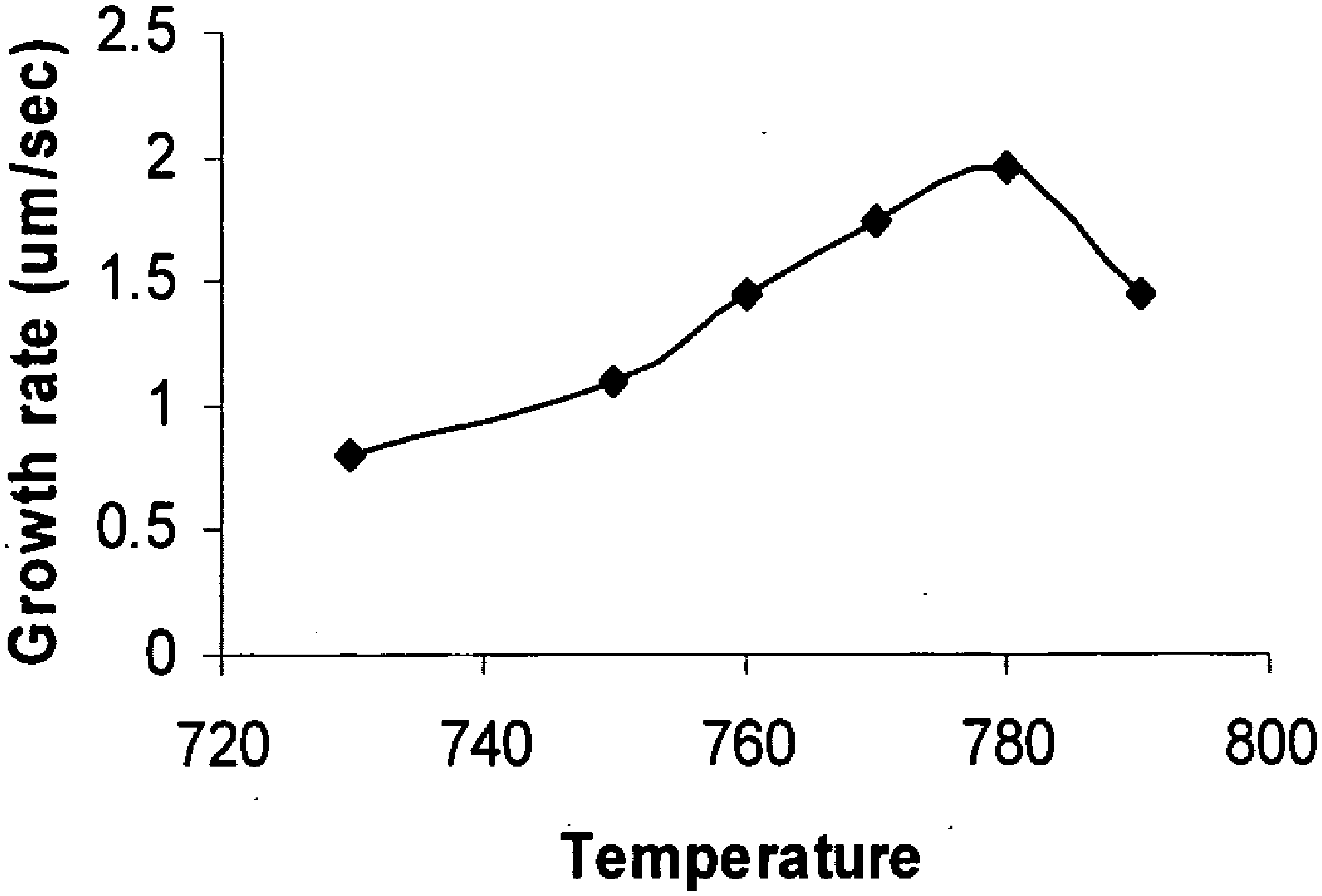
Growth rate (um/sec)
2.5
2
1.5
1
0.5
0
720
740
760
780
800
Temperature

Fig. 4

Fig. 5a

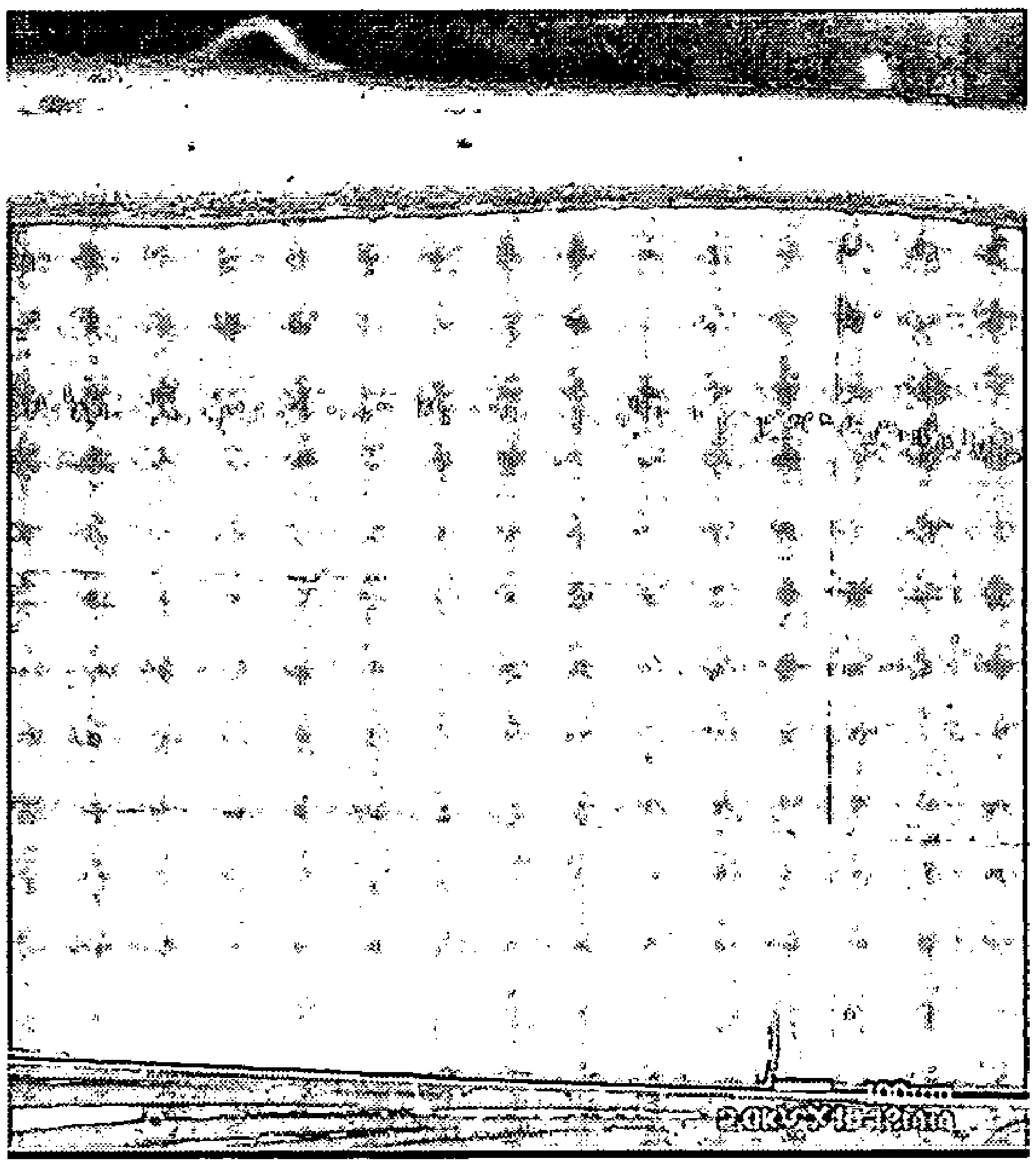

Fig. 5b

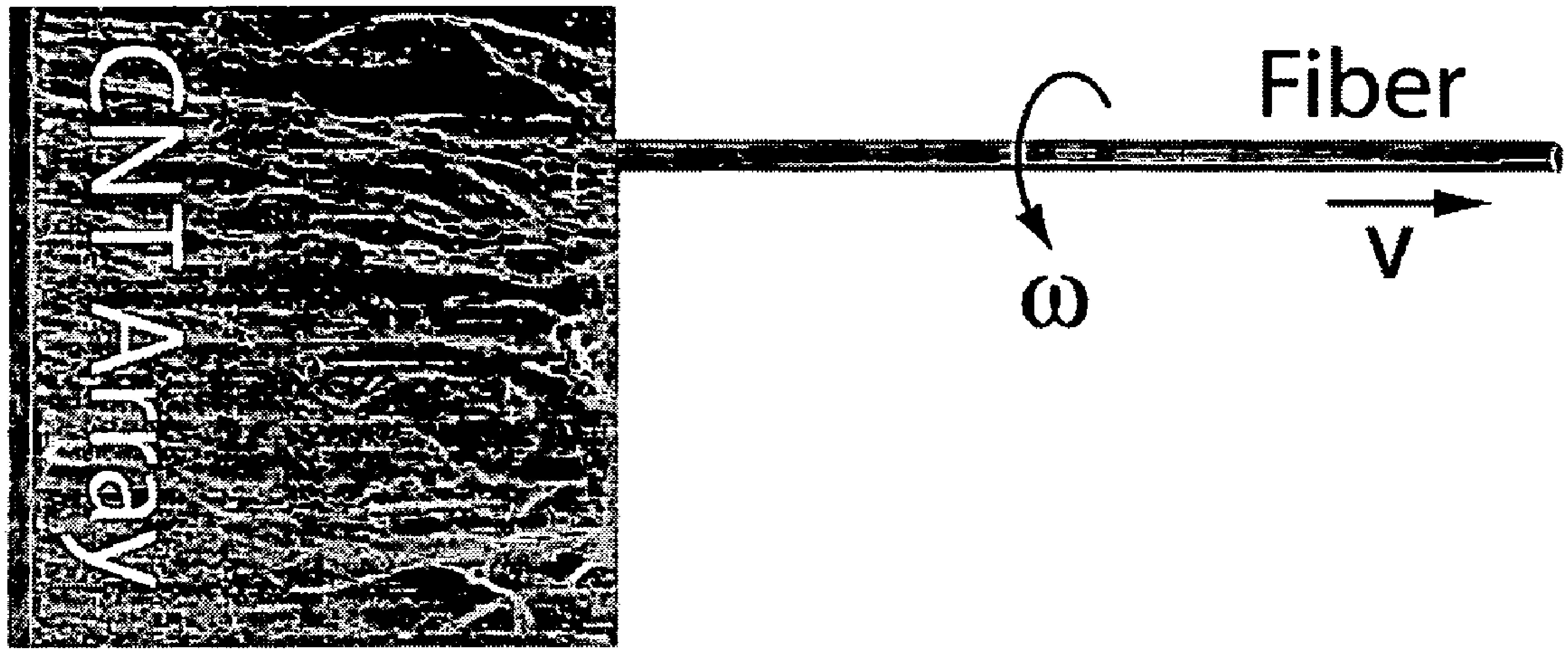

Fig. 6

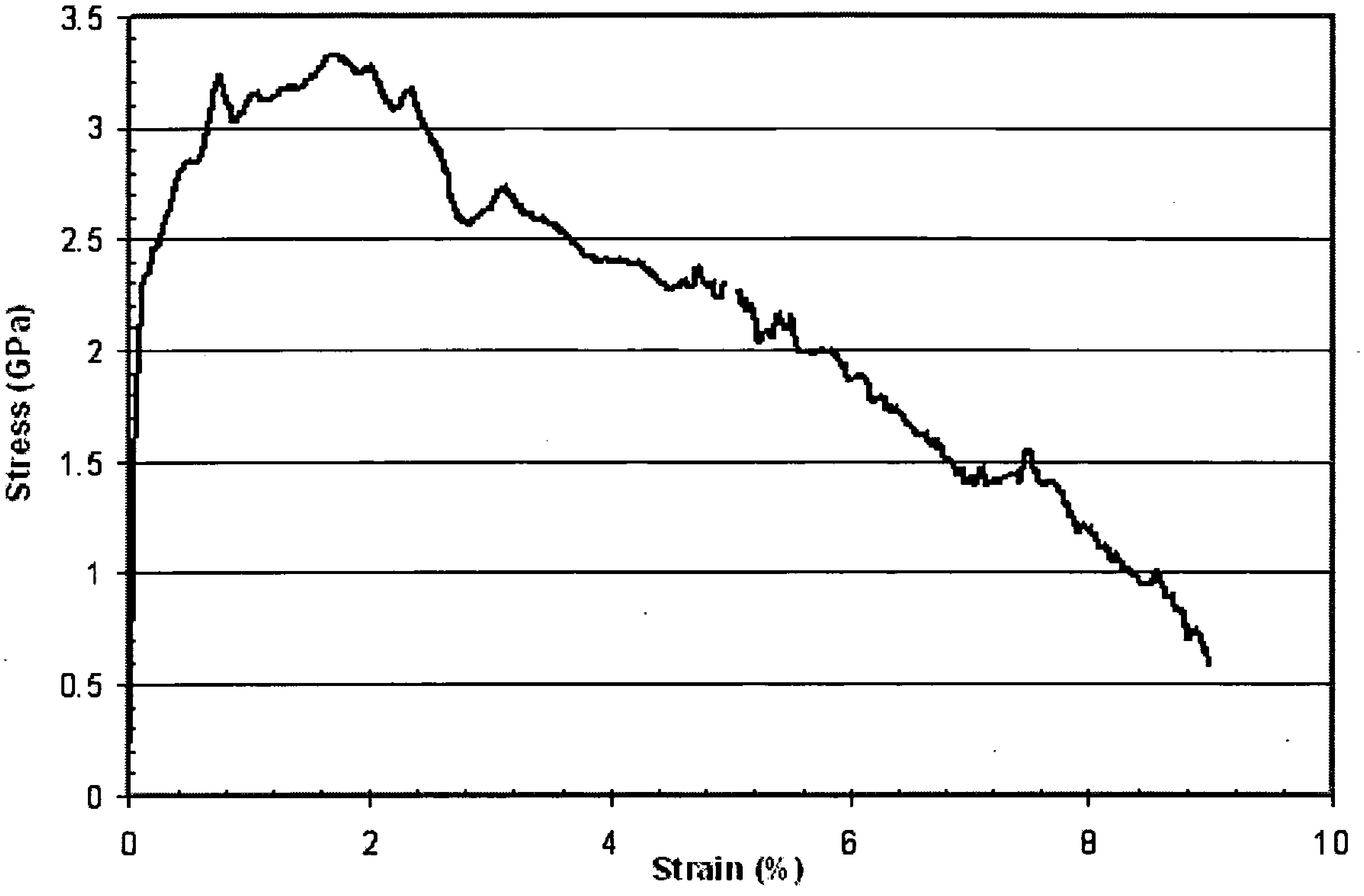

Fig. 7

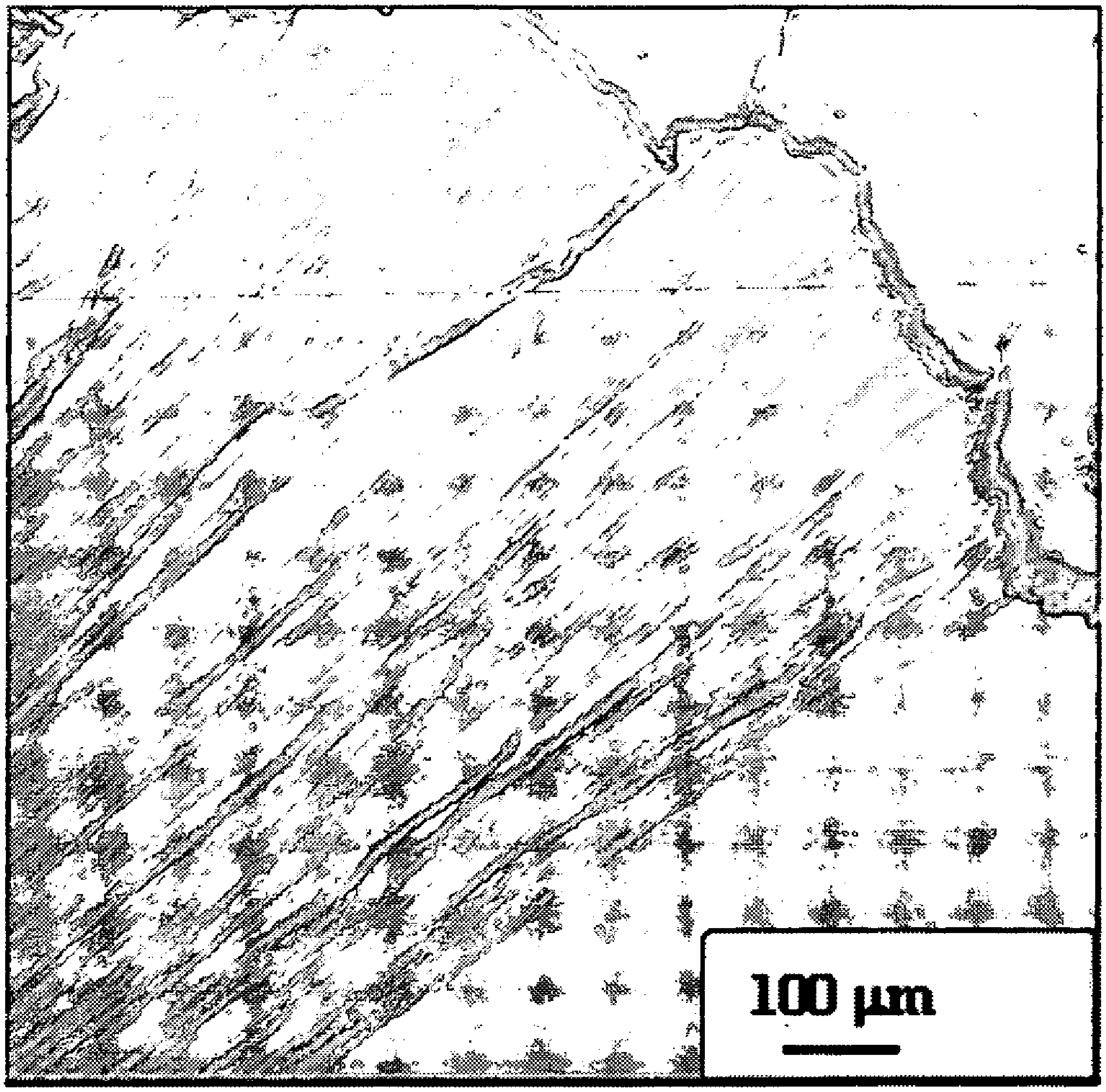

Fig. 8

ARRAYS OF LONG CARBON NANOTUBES FOR FIBER SPINNING

RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 11/051,007 filed Feb. 4, 2005, and also claims the benefit of U. S. Provisional Application Ser. No. 60/620,088 filed Oct. 18, 2004, both incorporated by reference herein.

STATEMENT REGARDING FEDERAL RIGHTS

[0002] This invention was made with government support under Contract No. W-7405-ENG-36 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] The present invention relates generally to carbon nanotubes, and more particularly to the preparation of a supported array of long carbon nanotubes, to a catalyst for preparing the array, and to fibers spun from the array.

BACKGROUND OF THE INVENTION

[0004] Individual carbon nanotubes (CNTs) are at least one order of magnitude stronger than any other known material. CNTs with perfect atomic structures have a theoretical strength of about 300 GPa [1]. In practice carbon nanotubes do not have perfect structures. However, CNTs that have been prepared have a measured strength of up to about 150 GPa, and the strength may improve upon annealing. For comparison, Kevlar fibers currently used in bulletproof vests have a strength of only about 3 GPa, and carbon fibers used for making space shuttles and other aerospace structures have strengths of only about 2-5 GPa [2].

[0005] Presently, CNT fibers can be drawn from CNT-polymer solutions or directly from CNT arrays. However, due to practical difficulties in dispersing, assembling and aligning carbon nanotubes using a CNT-polymer route, a strategy based on direct spinning of fibers from CNT arrays is more attractive.

[0006] The spinnability of CNT arrays depends greatly on the quality of the arrays, including CNT alignment, density, purity, length, and other factors. Due to difficulties in growing long CNT arrays that are conducive to spinning, CNT yarns so far can only be drawn from arrays of less than 300 μm long, and have a tensile strength of only around a few hundreds of MPa.

[0007] The preparation of suitable catalysts is important for synthesizing arrays of long CNTs. Hata et al., for example, recently reported the preparation of such a catalyst in "Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes," Science (2004) vol. 306, pp. 1362-1364, incorporated by reference herein. An array of long nanotubes by a water assisted chemical vapor deposition (CVD) procedure using ethylene as a carbon source was synthesized using a catalyst prepared by sputtering a thin layer of iron on a buffer layer of aluminum oxide. The aluminum oxide layer was previously deposited on the silicon dioxide surface layer of a silicon substrate. An abbreviation of this catalyst is SiO_2/Al_2O_3(10 nm)/Fe(1 nm), where the positions of the layers in the abbreviation indicate that the aluminum oxide layer is in between the silica layer and the iron layer. Using this catalyst, other researchers have prepared arrays of multi-walled CNTs with CNTs that are less than 2.2 mm in length. Arrays of long multi-walled CNTs can also be obtained using a catalyst structure having a buffering layer of MgO (instead of Al_2O_3).

[0008] A problem with current procedures for preparing CNT arrays is a requirement of a large amount of hydrogen gas in the precursor. Presently, it appears that a feed gas that includes hydrogen in an amount greater than 20 percent and as high as 50 percent hydrogen is required for the growth of long CNT arrays. Hydrogen is relatively expensive and can be dangerous when large amounts are used in the laboratory and industrially. Importantly, CNT arrays of the prior art are generally not good precursors for fibers because they tend to be contaminated with amorphous carbon.

[0009] There remains a need for long carbon nanotube fibers with improved strength, and for better methods for preparing arrays of carbon nanotubes that could be used as precursors for fibers of carbon nanotubes.

SUMMARY OF THE INVENTION

[0010] In accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention includes a method for preparing an array of long nanotubes. The method involves exposing a catalyst structure to a gaseous mixture for a chosen amount of time within a chosen temperature range, wherein the gaseous mixture comprises hydrocarbon, inert gas, and hydrogen, wherein the percentage of hydrogen in the gaseous mixture is P, wherein $P<20\%$, whereby an array of substantially aligned carbon nanotubes forms on the catalyst, the carbon nanotubes of the array having an average length of greater than about 0.5 millimeter.

[0011] The invention also includes an array of long carbon nanotubes prepared by a method comprising exposing a catalyst structure to a gaseous mixture for a chosen amount of time within a chosen temperature range, wherein the gaseous mixture comprises hydrocarbon, inert gas, and hydrogen, wherein the percentage of hydrogen in the gaseous mixture is P, wherein $P<20\%$, whereby an array of substantially aligned carbon nanotubes forms on the catalyst, the carbon nanotubes of the array having an average length of greater than about 0.5 millimeters.

[0012] The invention also includes a densely packed array of substantially vertically aligned long carbon nanotubes comprising an average nanotube length of at least 2.5 millimeters.

[0013] The invention also includes a method for preparing a fiber. The method involves exposing a catalyst structure to a gaseous mixture for a chosen amount of time at a temperature in a chosen temperature range, wherein the gaseous mixture comprises hydrocarbon, inert gas, and hydrogen, wherein the percentage of hydrogen in the gaseous mixture is P, wherein $P<20\%$, whereby an array of substantially aligned carbon nanotubes forms on the catalyst, the carbon nanotubes of the array having an average length of greater than about 0.5 millimeters; and spinning a fiber from the array.

[0014] The invention also includes a fiber prepared by a method comprising exposing a catalyst structure to a gaseous mixture for a chosen amount of time at a temperature in a chosen temperature range, wherein the gaseous mixture comprises hydrocarbon, inert gas, and hydrogen, wherein the percentage of hydrogen in the gaseous mixture is P, wherein $P<20\%$, whereby an array of substantially aligned carbon nanotubes forms on the catalyst, the carbon nanotubes of the array having an average length of greater than about 0.5 millimeters; and spinning a fiber from the array.

[0015] The invention also includes a spun fiber of carbon nanotubes having a tensile strength S, wherein $S \geqq 1$ GPa.

[0016] The invention also includes a ribbon prepared by a method comprising exposing a catalyst structure to a gaseous mixture for a chosen amount of time within a chosen temperature range, wherein the gaseous mixture comprises hydrocarbon, inert gas, and hydrogen, wherein the percentage of hydrogen in the gaseous mixture is P, wherein $P<20\%$, whereby an array of substantially aligned carbon nanotubes forms on the catalyst, the carbon nanotubes of the array having an average length of greater than about 0.5 millimeters; and pulling a ribbon from the array.

[0017] The invention also includes a composite structure that comprises a silicon substrate, a layer of silicon dioxide on the silicon substrate, a layer of aluminum oxide having a thickness of from about 2 nanometers to about 20 nanometers deposited by ion beam assisted deposition on the layer of silicon dioxide, and a layer of iron having a thickness of from about 0.1 nanometers to about 5 nanometers on the layer of aluminum oxide.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] The accompanying drawings, which are incorporated in and form a part of the specification, illustrate the embodiments of the present invention and, together with the description, serve to explain the principles of the invention. In the drawings:

[0019] FIG. **1***a* top shows a CNT array of the present invention next to a small stack of dime coins. FIG. **1***a* bottom shows a magnified scanning electron microscopy (SEM) image of the CNT array. FIG. **1***b* shows a transmission electron microscope (TEM) image of CNTs in the array.

[0020] FIG. **2** shows a graph that summarizes growth of a CNT array with the passage of time.

[0021] FIG. **3** provides a graph of the growth rate of a CNT array versus temperature with water (top graph) and without water (bottom graph).

[0022] FIG. **4** shows a graphical representation of the effect of temperature on the growth rate of CNT arrays.

[0023] FIG. **5***a-b* shows images of CNT arrays grown by a pulsed injection of ethylene at time intervals of 1, 2, 3, 4, and 5 minutes, each interval separated by 1 minute.

[0024] FIG. **6** shows a schematic diagram relating to spinning a fiber from an array of long CNTs according to the present invention.

[0025] FIG. **7** shows a stress-strain curve of a fiber spun from a CNT array of the invention. According to the curve, the fiber demonstrates a non-brittle behavior.

[0026] FIG. **8** shows a scanning electron microscopy (SEM) image of a ribbon of the invention.

DETAILED DESCRIPTION

[0027] Briefly, the invention is concerned with the preparation of an array of long (greater than 0.5 millimeters), substantially straight and aligned carbon nanotubes (CNTs). The invention is also concerned with a catalyst useful for preparing the array, and with fibers that are spun from the array. A very efficient, relatively long-lived catalyst useful for preparing a high purity, well-aligned array of multi-walled, long CNTs was prepared by depositing a thin film of iron (Fe) on a layer of aluminum oxide (Al_2O_3). An array of long CNTs was prepared by exposing the catalyst to a gaseous mixture of hydrocarbon, inert gas, and a relatively low percentage of hydrogen at an elevated temperature. The addition of water vapor to the gaseous mixture results in an increase in the final length of the CNTs in the array.

[0028] Arrays of long CNTs of this invention have been prepared with lengths of about 3 millimeters (mm), 3.5 mm, 4 mm, and 4.5 mm. A growth rate of about 120 μm/min was achieved, which is nearly ten times faster than the reported growth rates of CNT arrays that were grown from SiO_2 substrates [5]. These arrays of long CNTs (i.e. arrays where the CNTs have an average length greater than 0.5 millimeters) are preferred for spinning because they lead to fibers that can be used for carrying heavier loads than fibers prepared from arrays of shorter CNTs. Thus, fibers spun from these arrays of the invention have a tensile strength greater than that of known CNT fibers. These fibers may also have a higher electrical conductivity than fibers prepared from shorter arrays.

[0029] The catalyst used for synthesizing CNT arrays according to the invention was prepared using a silicon support having a thin surface layer of silicon dioxide (SiO_2). First, a layer of aluminum oxide (Al_2O_3), typically a layer having a thickness of about 10 nm, was deposited on the silicon dioxide, preferably by ion beam assisted deposition (IBAD). Although the layer of aluminum oxide could also be prepared using other techniques, such as but not limited to electron beam evaporation, the IBAD technique can deposit an Al_2O_3 layer that is fully, or at least partially amorphous. After the IBAD deposition, a thin layer (of about 1-3 nm in thickness) of iron was magnetron sputter deposited onto the aluminum oxide layer. It is believed that the aluminum oxide layer in some way improves catalytic activity and extends the lifetime of the catalyst. For the description that follows, unless specially mentioned, the catalyst used for preparing CNT arrays has a 1 nm thick Fe layer, a 10 nm thick aluminum oxide layer, and 1 micrometer (μm) thick silicon dioxide layer on a silicon substrate, wherein the aluminum oxide layer is deposited on the silicon dioxide layer by ion beam assisted deposition (IBAD), and the Fe layer is magnetron sputter deposited on the aluminum oxide layer.

[0030] The CNT arrays of the invention were prepared by chemical vapor deposition (CVD). A supported catalyst prepared as described above was placed in a quartz tube furnace. The diameter of the furnace used will depend on the size of the catalyst used. For the sizes of catalyst described in certain embodiments of this invention, a furnace with a diameter of about one inch was used. After placing the catalyst in the furnace, the furnace was heated to an elevated temperature and a nonflammable gaseous mixture of argon and about **6** percent hydrogen (the mixture is known in the art as "forming gas") and a source of carbon (ethylene, for example) were sent through the tube furnace. Sometimes, water vapor was included in the gaseous mixture by passing a small amount of Ar gas through a water bubbler.

[0031] Arrays of CNTs are prepared more safely using this invention than by other methods because the invention may employ a hydrogen concentration of about 6 percent or less, which is a lower concentration of hydrogen than what is used in current methods. The invention also employs a wider range of hydrocarbons (alkanes such as but not limited to methane and ethane; alkenes such as but not limited to ethylene; alkynes such as but not limited to acetylene; gaseous sources; liquid sources such as but not limited to hexane; functionalized hydrocarbons such as but not limited to alcohols and ketones (acetone, for example), and the like), a wider range of concentrations (from about 20 percent to about 80 percent of the hydrocarbon, and from about 20 percent to about 80 percent of an inert gas such as argon, helium, or an inert gas mixture) than known methods. For the purposes of this invention, hydrocarbons also include functionalized hydrocarbons (acetone, ethanol, and the like). The percentage of a particular hydrocarbon used may depend to some extent on the hydrocarbon employed.

[0032] The invention also employs a wider temperature range for the synthesis of an array of long nanotubes. A typical growth temperature is in the range of from about 700 degrees Celsius to about 800 degrees Celsius. A preferable growth temperature is in the range of from about 730 degrees to about 780 degrees.

[0033] Hydrogen is present in the feed in an amount less than 20 percent. More preferably, the hydrocarbon is present in an amount less than or equal to about 10 percent. More preferably, the hydrocarbon is present in an amount less than or equal to about 6 percent, which the amount present in forming gas. Other amounts of the hydrocarbon include about 5 percent or less, about 4 percent or less, and about 3 percent or less.

[0034] In an embodiment synthesis using forming gas, an array of CNTs having an average length of about 1 mm was prepared on a catalyst by placing the catalyst in a quartz furnace, adjusting the furnace temperature to a temperature of about 750 degrees Celsius, and sending a mixture of Ar and 6% H_2 gas at a flow rate of about 100 sccm and ethylene at a flow rate of about 100 sccm through the furnace for about 15 minutes.

[0035] In another embodiment synthesis, a catalyst was placed in a quartz furnace, the furnace temperature was adjusted to a temperature of about 750 degrees Celsius, and a mixture of Ar and 6% H_2 gas (flow rate of 100 sccm) and ethylene (flow rate of 100 sccm) and were sent through the tube for a period of about 2 hours, The result was an array of vertically aligned (with the catalyst structure on a horizontal surface) carbon nanotubes having an average nanotube length of 3.2 millimeters (mm). The top portion of FIG. **1***a* shows an image of the array. For a size comparison, the array was placed next to a small stack of coins (dimes). A closer inspection of the array by scanning electron microscopy (SEM, see the bottom portion of FIG. **1***a*) shows that the CNTs are densely packed, substantially straight, and well aligned in a direction substantially perpendicular to the surface of the corresponding substrate. A greatly magnified image of individual CNTs of the array using transmission electron microscopy (TEM) (see FIG. **1***b*) shows that the CNTs of the array are multi-walled, with an average diameter of about 10 nm.

[0036] FIG. **2** shows a graph of the growth of the CNT array. The growth temperature is about 750 degrees Celsius. According to FIG. **2**, over the first 20 minutes or so, the array grows at a substantially even growth rate of about 60 μm/min. Afterwards, the growth rate decreases gradually. After about 90 minutes, growth almost ceases, when the length of the CNTs of the array are about 3 mm.

[0037] In another embodiment synthesis, a catalyst was placed in a quartz furnace, the furnace temperature was adjusted to a temperature of about 750 degrees Celsius, and a flow of ethylene (flow rate of 100 sccm) and a mixture of Ar and 6% H_2 gas (flow rate of 100 sccm) and water vapor were sent through the **15** quartz tube for a period of about 2 hours. The addition of water vapor to the gaseous mixture did not appear to have any substantial effect during the first 20 or so minutes of growth. However, the final length of CNTs of the array was about 4.5 mm; the length of the CNTs of the array increased by about 50 percent when water vapor was included in the gaseous feed. The water added to the gaseous feed seems to play a role in maintaining the activity (i.e. the growth rate) and the lifetime of the catalyst.

[0038] In another embodiment synthesis, a growth rate of 46 μm/min for an array of CNTs was observed when catalyst was exposed to a combination of 100 sccm ethylene and 100 sccm forming gas (Ar+6% hydrogen) at a temperature of 730 degrees Celsius. In another embodiment synthesis of a CNT array, the growth rate increased to about 72 μm/min when the temperature was increased to about 750 degrees Celsius. When water (about 1000 ppm) was added to the feed by bubbling carrier gas through water at 8 sccm, the average growth rate did not substantially change in a temperature range of from about 730 degrees Celsius to about 750 degrees Celsius. However, when the synthesis was repeated in the absence and in the presence of water at a higher temperature of about 780 degrees Celsius, the growth rate with water was nearly twice the growth rate without water. FIG. **3** provides a graph of the growth rate versus temperature with water (top graph) and without water (bottom graph).

[0039] Raman characterization reveals that CNT growth with water leads to a lower D peak compared to a run at the same temperature but in the absence of water, indicating that less amorphous carbon was formed with water than without water. Further evidence to support this conclusion comes from an observation of the appearance of the arrays (with and without water) after about two hours of growth. In the absence of water, the top of the CNT array appeared brown after 2 hours, even at a temperature of 750 degrees Celsius when the CNTs of the array about 3.2 mm in length. By contrast, when water was added, the top of the array was still black after 2 hours when the CNTs were even longer, about 4.5 mm in length. From these observations, it is believed that the addition of water slows down the formation of amorphous carbon that contaminates the array and deactivates the catalyst.

[0040] FIG. **4** shows a graphical representation of the effect of temperature on the growth rate of CNT arrays. According to FIG. **4**, the highest growth rate achieved using an embodiment catalyst was approximately 120 μ/min at a temperature of about 780 degrees Celsius. At this rate, a 3 mm long CNT array may be grown in about 40 minutes. A longer growth time at this temperature, even with the addition of water to the gaseous feed, does not result in a longer array.

[0041] Under the synthesis conditions employed using the invention, CNT arrays appear to prefer to grow in a base growth mode (as opposed to a tip growth mode), with or without water added to the gaseous feed. FIG. **5***a-b* shows images of CNT arrays grown by a pulsed injection of ethylene at time intervals of 1, 2, 3, 4, and 5 minutes, each interval separated by 1 minute. Growth marks appear on the side of the array. The growth marks may be used as a simple and indirect indication of the growth mode. For a tip growth mode, the gap between two adjacent growth marks would gradually increase with increasing distance from the substrate. For a base growth mode, the opposite result would be seen. In this case, the largest gap between marks is found at the bottom of the array, which suggests a base growth mechanism. In addition, the size of each gap appears to be proportional to the growth time, indicating again that the growth evolves with time uniformly.

[0042] An aspect of the invention is concerned with controlling the thickness of the individual CNTs of an array of the invention. The CNT diameter, and the number of walls of the CNTs, may be adjusted by adjusting the thickness of the Fe catalyst layer. Although long CNT arrays may be synthesized using a catalyst structure having an Fe catalyst layer thickness in the range of 0.3-2 nm, the CNT diameter and the number of walls of the CNTs decrease when the thickness of the deposited Fe film decreases. Using a Fe film having a thickness of about 0.3 nm, for example, the majority of CNTs are double-walled and the average CNT diameter is about 6 nanometers (nm). This suggests that the microstructure of the CNTs can be tuned by adjusting the thickness of the catalyst (iron, for example) film.

[0043] It is currently believed that the longer it takes to grow an array of carbon nanotubes, the more amorphous carbon would be deposited on the CNT array. The presence of amorphous carbon on the array is detrimental for spinning fibers, and arrays with a substantial amount of amorphous carbon are unsuitable for spinning. A benefit of arrays prepared according to the present invention is that **25** such arrays include only a minimal amount of amorphous carbon. This is likely due to the speed at which arrays may be grown using the invention. CNT arrays can grow much faster (typically 10 times faster) than CNT arrays grown from SiO_2 substrates. Using a growth temperature of from about 720 degrees Celsius to about 790 degrees Celsius, a growth time from about 5 minutes to about 20 minutes, and a catalyst prepared as described above, long CNT arrays with lengths ranging from 700 μm to 1.5 mm were synthesized (using ethylene and forming gas). These arrays are useful for spinning fibers. Furthermore, the longer CNT arrays synthesized here will enhance the strength of fibers spun from the arrays.

[0044] Certain important aspects of the present invention that have been described in some detail thus far have been concerned with preparing catalysts and using them to synthesize arrays of CNTs. Another aspect of the invention is concerned with using the arrays to make strong fibers of CNTs. CNT fibers can be continuously spun out of suitable CNT arrays like a thread spun from a silk cocoon. However, not all arrays are conducive to spinning. Currently, it is believed that arrays with good alignment, high purity and therefore strong inter-tube interaction are favorable for spinning. We have tried to spin fibers from various CNT arrays with different diameters, different lengths and grown from different substrates. Most of the spinnable arrays prepared according to the prior art are shorter than 300 micrometers. We have found that CNT arrays with long CNTs (arrays with CNTs longer than 500 micrometers) having good alignment are preferred for spinning fibers. CNT arrays grown at a temperature of about 750 degrees Celsius for 10 to 15 minutes without water, for example, are excellent for spinning fibers. A longer growth time (greater than about 15 minutes) sometimes results in the formation of amorphous carbon and more rigid arrays. However, there appears to be a compromise among the array length, array purity, and array rigidity. Long, spinnable CNT arrays may be obtained at higher temperatures (780 degrees, for example) when water is added to the gaseous feed and when the growth is for a period of less than about 15 minutes.

[0045] FIG. **6** shows a schematic diagram relating to spinning a fiber from an array of long CNTs according to the present invention. As FIG. **6** shows, the fiber spins at a rate of ω while being pulled at a speed of v. The spinning parameters ω and v likely have an effect on the microstructural characteristics (e.g. the fiber diameter, the helix angle of individual CNTs in the fiber, and the like) of the resulting composite fiber. The spinning parameters can be adjusted to optimize the fiber structure for highest strength.

[0046] A spinning shaft with an end configured for nanotubes to stick on (a hooked end, an end with adhesive, and the like) may be used for preparing a fiber from the CNT array. When this end of the spinning shaft makes contact with nanotubes from the supported array, the nanotubes begin to twist around the shaft. Many thousands of nanotubes are likely twisted together at the beginning. A fiber begins to grow as the array moves relative to the spinning shaft, and additional nanotubes from the array can twist around the growing fiber to extend the length of the fiber.

[0047] The as-spun fiber can be stretched to improve alignment of the nanotubes.

[0048] An advantage of spinning the fiber from the supported array is that the long nanotubes from the array are generally aligned relative to one another before they are spun into a fiber. The spinning process spirally aligns the nanotubes, and this spirally aligned arrangement provides the CNT (or CNT/polymer composite) fiber with high strength. CNT, or CNT/composite fibers of this invention have a rope like structure that is made strong by twisting the carbon nanotubes together and around each other.

[0049] CNT fibers spun from a CNT array of the invention display an enhanced mechanical strength. Fiber samples were spun from 1 mm long CNT array. Each has a diameter in the range of from about 2 μm to about 3 μm. Tensile tests were performed with these fibers. For a tensile test, a fiber of about 1 cm in length was glued onto a hard paper with a fixed 8 mm long oval-shaped cavity in the center and then mounted in a commercial tensile test machine. A typical stress-strain curve for a fiber of the invention is shown in FIG. **7**. According to the curve of FIG. **7**, the fiber demonstrates a tensile strength of greater than 3.0 GPa. These fibers are much stronger than a fiber spun from a 300 μm CNT array. The enhancement of mechanical strength observed on fibers from the longer arrays may be because longer CNTs have a better interlocking ability during tensile testing and can therefore a carry higher load than fibers spun from shorter tubes. It should also be mentioned that the resistivity of as-made CNT fibers is $1.68\times10^{-3}\Omega\cdot$cm; thus, fibers prepared according to this invention have a higher conductivity than any spun MWNT fibers previously reported.

[0050] The nanotubes of the array may be coated with a polymer solution before they are spun into fibers or during the spinning process. The spinning process spirally aligns the polymer-coated nanotubes, and when the nanotubes are carbon nanotubes, the resulting fiber has a high volume fraction (60 percent of nanotubes, and higher), and the twisting improves mechanical interlocking between nanotubes.

[0051] CNT fibers spun from the array can also be infiltrated/coated with a polymer matrix to form composite fibers.

[0052] The spinning approach has several advantages over a drawing approach. One advantage relates to the relative ease a spinning process provides for preparing fibers compared to a drawing process.

[0053] Another advantage of the spinning approach versus the drawing approach relates to the helical orientation of the nanotubes that results from spinning the nanotubes and twisting them around each other. This helical orientation contributes to improving load transfer because the twisted nanotubes can squeeze radially against each other when the composite fiber is under load, which increases the bonding strength and consequently load-transfer efficiency. Untwisted carbon nanotubes/polymer composite fibers prepared by drawing are not strong fibers, presumably because the nanotube-polymer interface is slippery, making it difficult to transfer load onto the nanotubes.

[0054] Another advantage of spinning process of this invention is that the twisting squeezes out excess polymer so that individual CNTs can be closely spaced together. This close spacing increases the CNT volume fraction of the composite fiber.

[0055] Another advantage of the invention relates to using a substantially aligned array of carbon nanotubes to prepare a composite fiber. The alignment of the nanotubes prior to spinning guarantees alignment in the spun composite fiber.

[0056] Composite fibers prepared using nanotube arrays of the invention may be used for a variety of applications. These fibers could be used to prepare superior laminates, woven textiles, and other structural fiber composite articles. Fiber composites of this invention could be used to prepare strong and light armor for aircraft, missiles, space stations, space shuttles, and other high strength articles. The reduced weight would allow aircraft and projectiles to fly faster and for longer distances. These features are also important for spacecraft for future space missions (to the moon and to Mars, for example), where high strength and lightweight features of the composite fibers are very important.

[0057] Another advantage of this invention becomes apparent when metallic carbon nanotubes are used to prepare the composite fiber. Usually a fraction of carbon nanotubes in an array is metallic. Metallic carbon nanotubes have been shown to be highly electrically conductive [6]. Thus, composite fibers of this invention prepared using precursor carbon nanotubes would not only be very strong but also highly electrically conductive.

[0058] Composite fibers of this invention are prepared using a substantially parallel, aligned carbon nanotube array of the type illustrated in FIG. **1**. Arrays like these can be used after they are prepared, or they can be coated with a dilute solution of polymer by, for example, immersing the nanotube array in a polymer solution, and then ultrasonically vibrating the immersed array to promote wetting. Polymer solutions that have been used in the past to prepare carbon nanotube-polymer composites could be used with this invention and include, but are not limited to, polystyrene dissolved in toluene [8], low viscosity liquid epoxy [6], poly(methyl methacrylate) (PMMA) dissolved in PMF [9], polyvinyl alcohol (PVA) in water [10], and poly(vinyl pyrrolidone) (PVP) in water [10].

[0059] For the case involving polymer-coated nanotubes, after spinning and stretching, solvent is evaporated and the polymer is cured at an appropriate temperature. Detailed treatment parameters depend on the specific polymer and solvent that are used during the preparation. A vacuum oven may be used for solvent removal and curing.

[0060] The cured composite fiber of the invention can be evaluated in tension to obtain the strength, the dependency of the strength on the length (i.e. size effect), the Young's modulus, the ductility, and other properties. The fracture surface of the composite fiber may be examined using Scanning Electron Microscopy (SEM) to investigate the failure mode in order to evaluate the strength of the CNT/polymer interface. Transmission electron microscopy (TEM) may be used to examine individual CNT arrangements in the composite fiber and the CNT/matrix interface.

[0061] The invention is also concerned with the preparation of CNT ribbon from an array of the invention. FIG. **8** shows an SEM image of CNT ribbon prepared from an array of the invention.

[0062] In summary, arrays of long carbon nanotubes are prepared on a supported catalyst using a feed of hydrocarbon, inert gas, and a relatively small amount of hydrogen. Water may be added to the feed. The arrays are relatively rigid, of a high-purity, and have very good CNT alignment. A balance between length and quality of CNTs may be achieved to produce an array with a length of from about 500 μm to about 1.5 mm. Fibers spun from such long CNT arrays exhibit a mechanical strength and electrical conductivity greater than for known CNT fibers.

[0063] The foregoing description of the invention has been presented for purposes of illustration and description and is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching.

[0064] The embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

REFERENCES

The following references are incorporated by reference herein.

[0065] 1. Hata et al., Science, (2004) Vol. 306, pp. 1362-1364.

[0066] 2. Demczyk et al, Mater. Sci. Eng. A334, (2002) pp. 173-178.

[0067] 3. Concise Encyclopedia of Composite Materials, edited by A. Kelly, Pergamon, Oxford, UK (1995) pp. 42, 50, 94.

[0068] 4. Dalton et al., Nature, vol. 423 (2003) p. 703.

[0069] 5. Zhang et al., Chem. Phys. Lett., vol. 362, (2002) pp. 285-290.

[0070] 6. Jiang et al., Nature, vol. 419, (2002) p. 801.

[0071] 7. Penumadu et al., J. Mater. Res., vol. 18, (2003) pp. 1849-1853.

[0072] 8. Maruyama et al., Chem. Phys. Lett., vol. 360, (2002) pp. 229-234.

[0073] 9. Safadi et al., J. Applied Polymer Sci., vol. 84, (2002) pp. 2660-2669.

[0074] 10. Haggenmueller et al., Chem. Phys. Left., vol. 330, (2000) pp. 219-225.

[0075] **11**. Coleman et al., Appl. Phys. Lett., vol. 82, (2003) pp. 1682; and Cakek et al., Appl. Phys. Lett., vol. 81, (2002) pp. 5123-5125.

What is claimed is:

1. A method for preparing an array of long nanotubes, comprising:

exposing a catalyst structure to a gaseous mixture for a chosen amount of time within a chosen temperature range, wherein the gaseous mixture comprises hydrocarbon, inert gas, and hydrogen, wherein the percentage of hydrogen in the gaseous mixture is P, and wherein P<20%, whereby an array of substantially aligned carbon nanotubes forms on the catalyst, the carbon nanotubes of the array having an average length of greater than about 0.5 millimeter.

2. The method of claim 1, wherein the catalyst structure comprises a silicon substrate, a layer of silicon dioxide on the silicon substrate, a layer of aluminum oxide deposited by ion beam assisted deposition on the silicon dioxide layer, and a layer of metal on the aluminum oxide layer.

3. The method of claim 1, wherein the layer of aluminum oxide is amorphous.

4. The method of claim 1, wherein the layer of metal comprises iron.

5. The method of claim 1, wherein the hydrocarbon in the gaseous mixture is present in an amount in the range of from about 20 percent to about 80 percent.

6. The method of claim 1, wherein the hydrocarbon comprises ethylene, acetylene, hexane, acetone, or mixtures thereof.

7. The method of claim 1, wherein the inert gas is present in an amount in the range of from about 20 percent to about 80 percent.

8. The method of claim 1, wherein the inert gas comprises argon.

9. The method of claim 1, wherein P≦10%.

10. The method of claim 1, wherein P≦6%.

11. The method of claim 1, wherein P≦5%.

12. The method of claim 1, wherein P≦4%.

13. The method of claim 1, wherein P≦3%.

14. The method of claim 1, wherein the gaseous mixture further comprises water vapor.

15. The method of claim 1, wherein the gaseous mixture is a flowing gaseous mixture.

16. The method of claim 1, wherein the chosen amount of time and the chosen temperature are selected to minimize the formation of amorphous carbon on the array of substantially aligned carbon nanotubes.

17. The method of claim 1, wherein the chosen amount of time is in the range of from about 5 minutes to about 2 hours.

18. The method of claim 1, wherein the chosen amount of time is in the range of from about 10 minutes to about one hour.

19. The method of claim 1, wherein the chosen amount of time is in the range of from about 15 minutes to about 30 minutes.

20. The method of claim 1, wherein the chosen temperature range is from about 700 degrees Celsius to about 800 degrees Celsius.

21. The method of claim 1, wherein the chosen temperature range is from about 730 degrees Celsius to about 780 degrees Celsius.

22. The method of claim 1, wherein the temperature is about 750 degrees Celsius.

23. The method of claim 1, wherein the array of substantially aligned carbon nanotubes comprises a length of from about 20 μm to about 4.5 mm.

24. An array of carbon nanotubes prepared by a method comprising exposing a catalyst structure to a gaseous mixture for a chosen amount of time within a chosen temperature range, wherein the gaseous mixture comprises hydrocarbon, inert gas, and hydrogen, wherein the percentage of hydrogen in the gaseous mixture is P, wherein P<20%, whereby an array of substantially aligned carbon nanotubes forms on the catalyst, the carbon nanotubes of the array having an average length of greater than about 0.5 millimeters.

25. A densely packed array of substantially straight and aligned carbon nanotubes comprising an average nanotube length of at least 2.5 millimeters.

26. The array of claim 25, wherein the average nanotube length is at least 4 millimeters.

27. The array of claim 25, wherein the average nanotube length is at least 4.5 millimeters.

28. A method for preparing a fiber, comprising:

exposing a catalyst structure to a gaseous mixture for a chosen amount of time at a temperature in a chosen temperature range, wherein the gaseous mixture comprises hydrocarbon, inert gas, and hydrogen, wherein the percentage of hydrogen in the gaseous mixture is P, wherein P<20%, whereby an array of substantially aligned carbon nanotubes forms on the catalyst, the carbon nanotubes of the array having an average length of greater than about 0.5 millimeters; and

spinning a fiber from the array.

29. A fiber prepared by a method comprising:

exposing a catalyst structure to a gaseous mixture for a chosen amount of time at a temperature in a chosen temperature range, wherein the gaseous mixture comprises hydrocarbon, inert gas, and hydrogen, wherein the percentage of hydrogen in the gaseous mixture is P, wherein P<20%, whereby an array of substantially aligned carbon nanotubes forms on the catalyst, the carbon nanotubes of the array having an average length of greater than about 0.5 millimeters; and

spinning a fiber from the array.

30. The fiber of claim 29, wherein said fiber has a tensile strength S, wherein S≧1 GPa.

31. A spun fiber of carbon nanotubes having a tensile strength T, wherein S≧1 GPa.

32. A ribbon prepared by a method comprising:

exposing a catalyst structure to a gaseous mixture for a chosen amount of time within a chosen temperature range, wherein the gaseous mixture comprises hydrocarbon, inert gas, and hydrogen, wherein the percentage of hydrogen in the gaseous mixture is P, wherein P<20%, whereby an array of substantially aligned carbon nanotubes forms on the catalyst, the carbon nanotubes of the array having an average length of greater than about 0.5 millimeters; and

pulling a ribbon from the array.

33. A composite structure, comprising:

a silicon substrate;

a layer of silicon dioxide on the silicon substrate;

a layer of aluminum oxide having a thickness of from about 2 nanometers to about 20 nanometers deposited by ion beam assisted deposition on said layer of silicon dioxide; and

a layer of iron having a thickness of from about 0.1 nanometers to about 5 nanometers on said layer of aluminum oxide.

34. The structure of claim 33, wherein the aluminum oxide layer is at least partially amorphous.

35. The structure of claim 33, wherein the aluminum oxide layer is completely amorphous.

36. The structure of claim 33, wherein the aluminum oxide layer is comprised of fine grains.

* * * * *