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Ma et al.

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(54) **NANOTUBE FILM STRUCTURE**

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(30) **Foreign Application Priority Data**

Mar. 26, 2014 (CN) 2014 1 0115685

(51) **Int. Cl.**
C01F 7/02 (2006.01)
C01B 32/158 (2017.01)

(52) **U.S. Cl.**
CPC ***C01F 7/02*** (2013.01); ***C01B 32/158*** (2017.08); *C01P 2004/13* (2013.01); *Y10T 428/24273* (2015.01); *Y10T 428/249921* (2015.04)

(58) **Field of Classification Search**
CPC .. C01F 7/02; C01B 31/022; Y10T 428/24273; Y10T 428/249921; C01P 2004/13; C01P 2004/50
USPC 428/113
See application file for complete search history.

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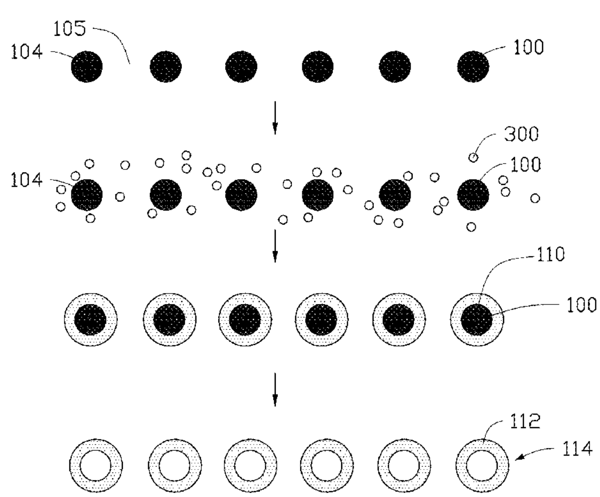
(74) *Attorney, Agent, or Firm* — Steven Reiss

(57) **ABSTRACT**

The disclosure relates to a nanotube film structure. The nanotube film structure includes at least one nanotube film. The at least one nanotube film includes a plurality of nanotubes orderly arranged and combined with each other by ionic bonds. The nanotube film is fabricated by using the template of carbon nanotube film. The carbon nanotube film is drawn from supper aligned carbon nanotube array and includes a plurality of carbon nanotubes joined end to end.

14 Claims, 23 Drawing Sheets



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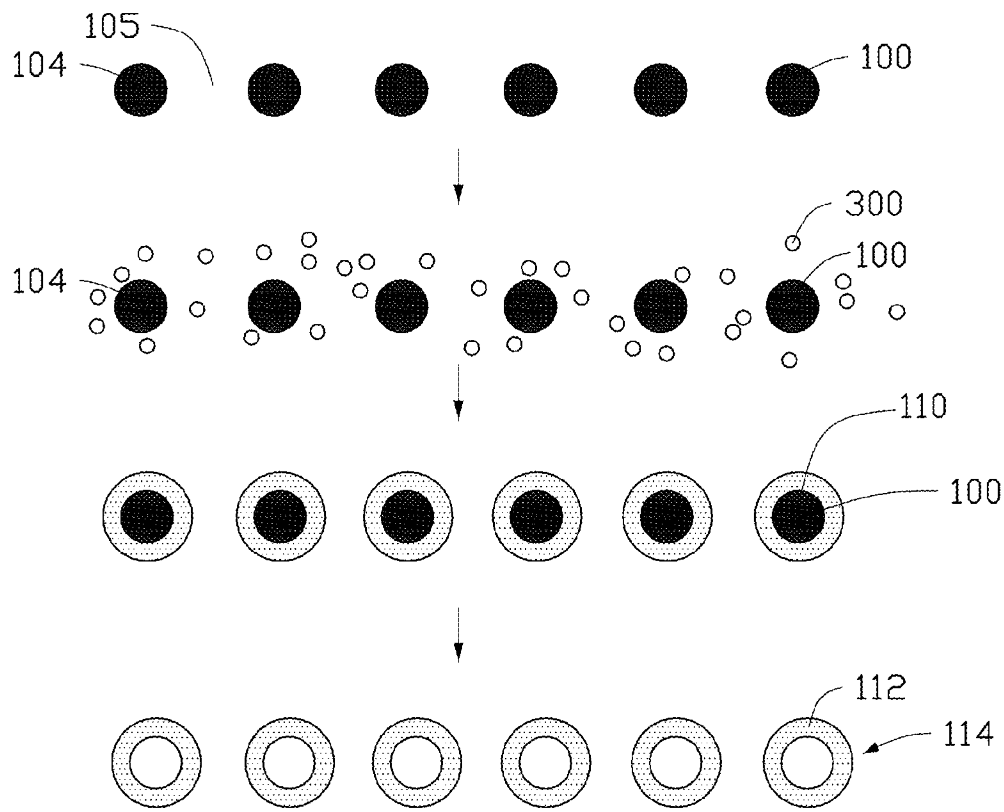


FIG. 1

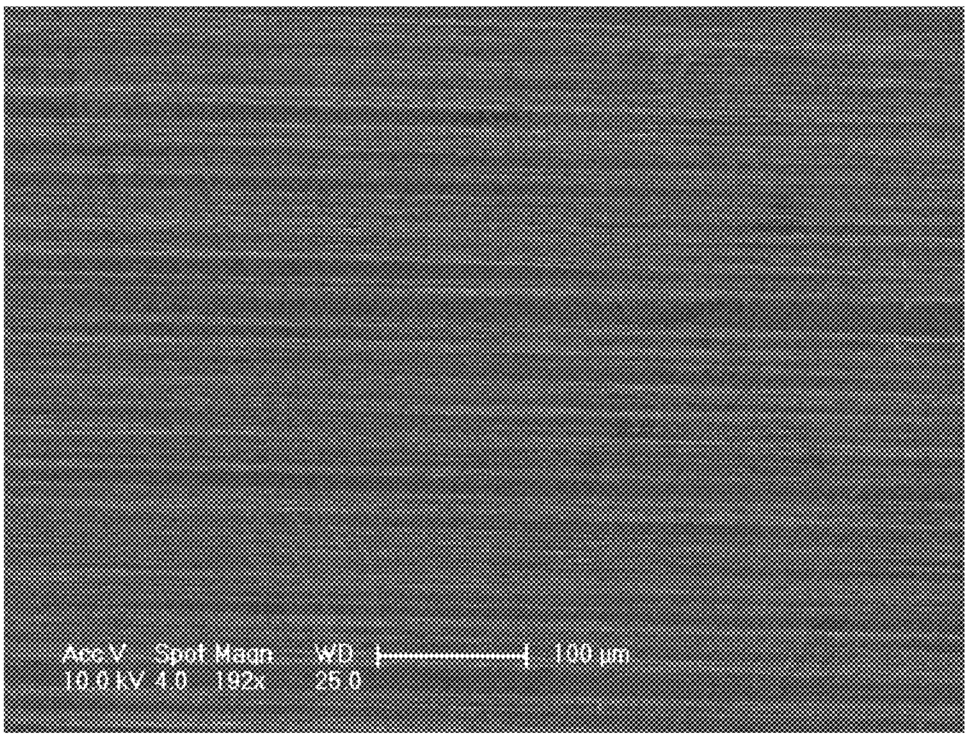


FIG. 2

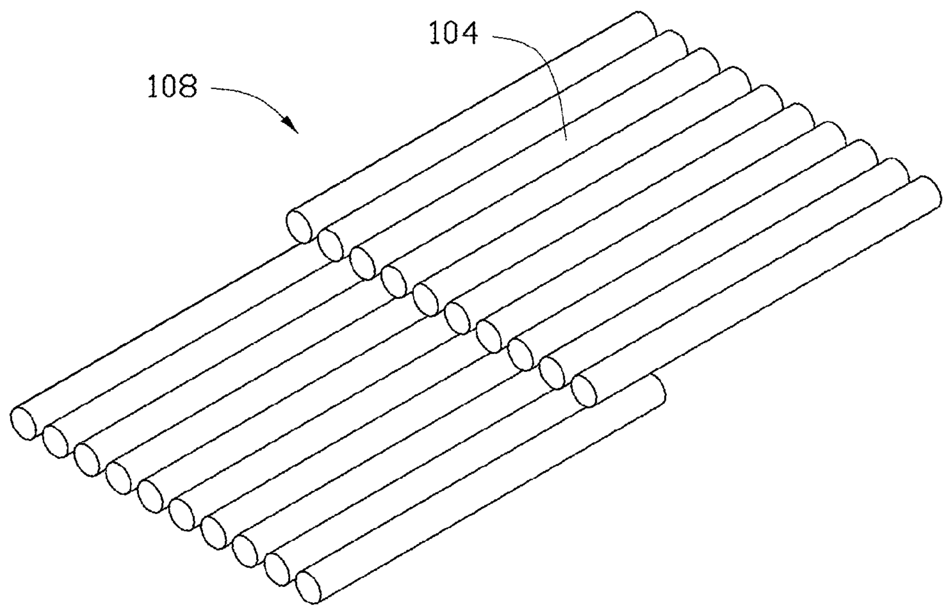


FIG. 3

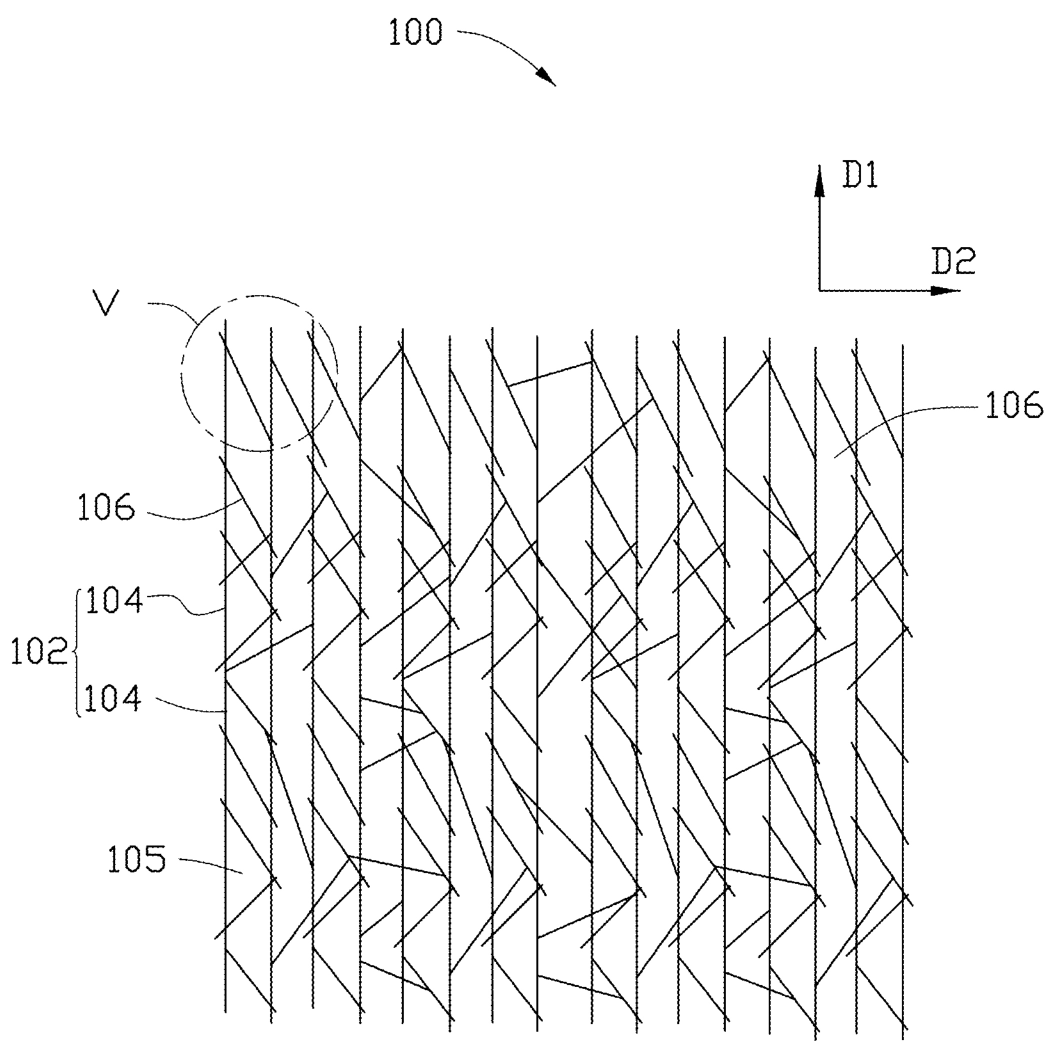


FIG. 4

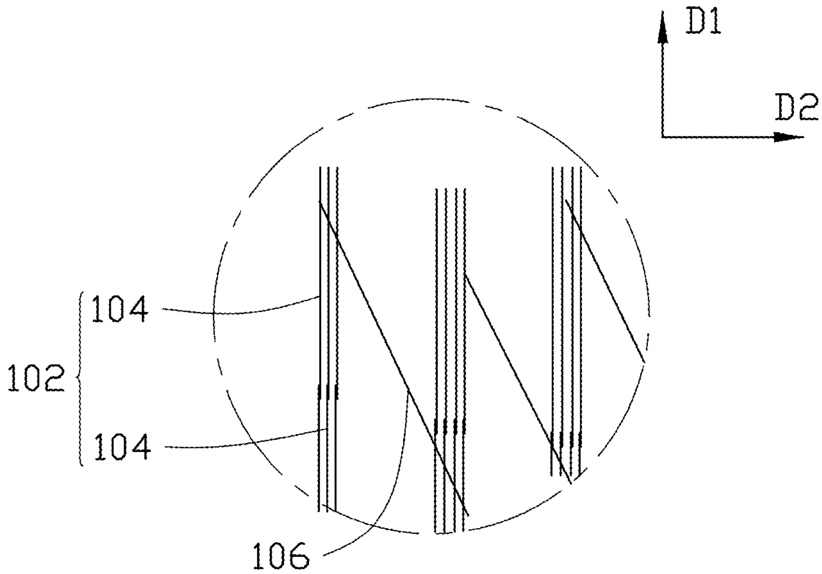


FIG. 5

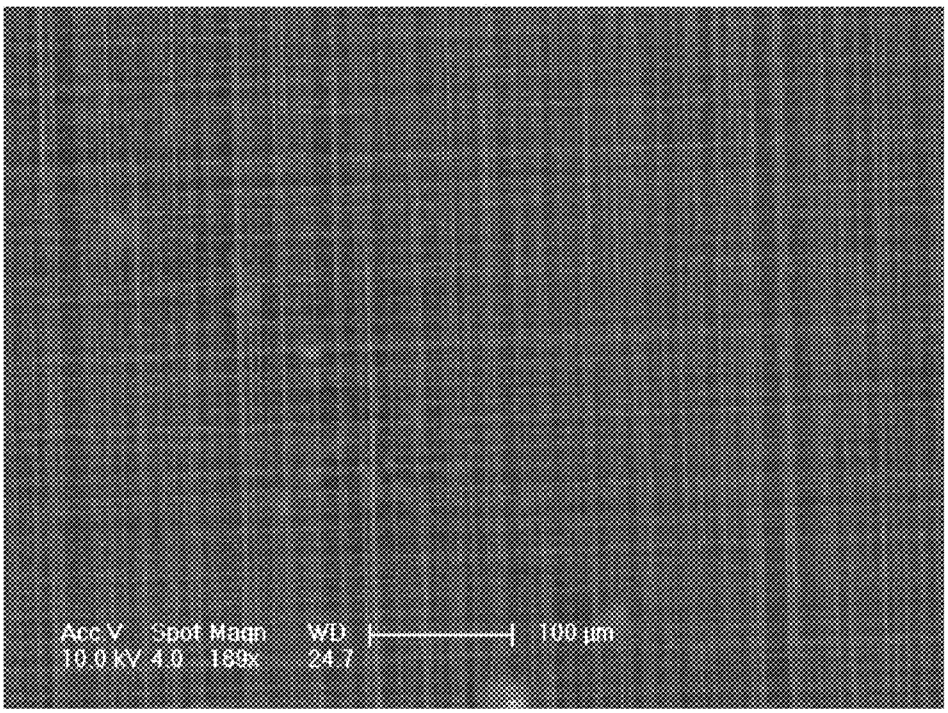


FIG. 6

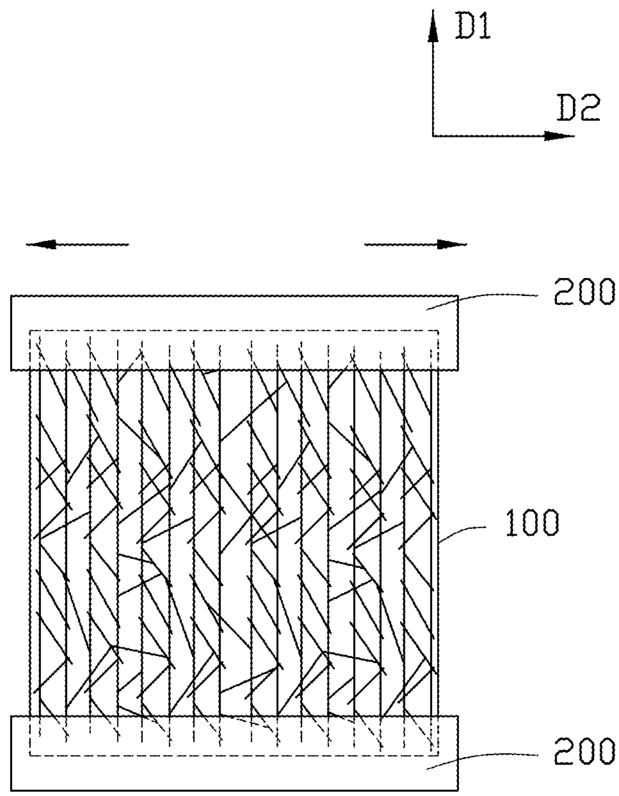


FIG. 7

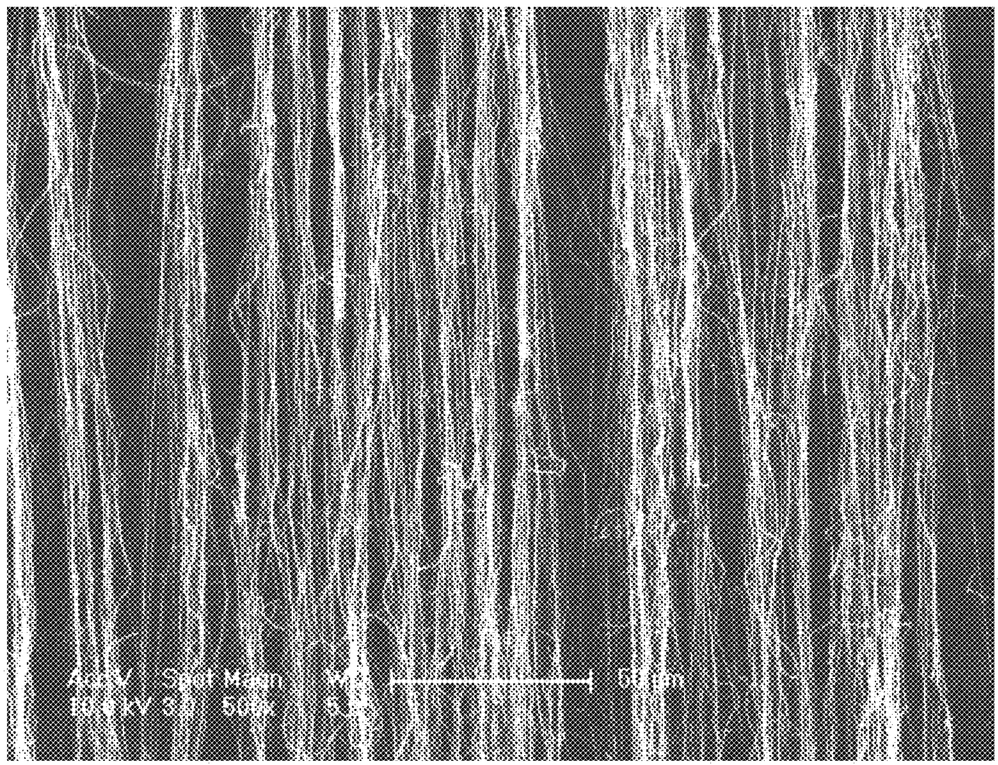


FIG. 8

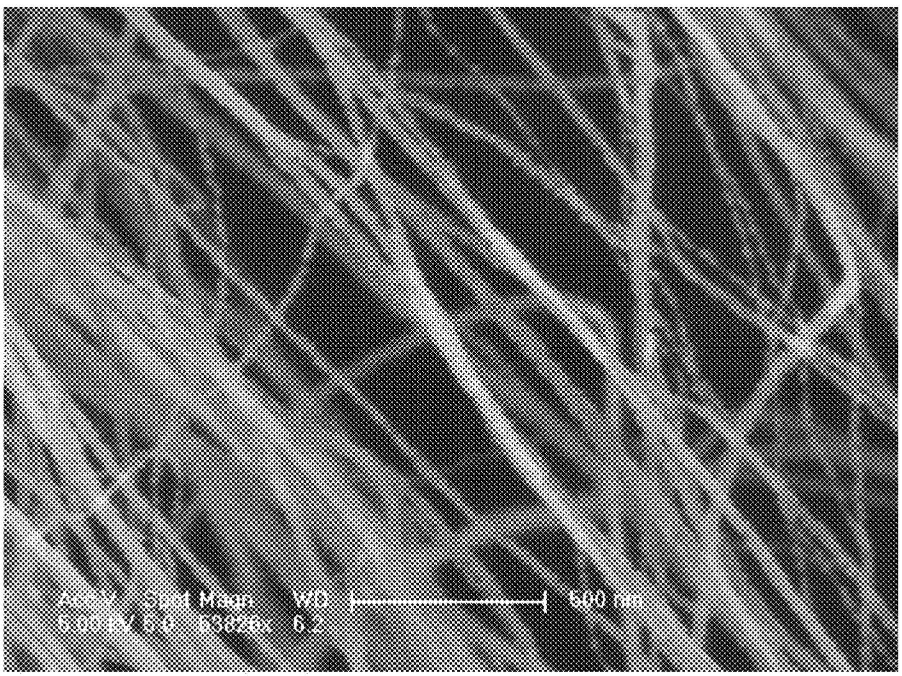
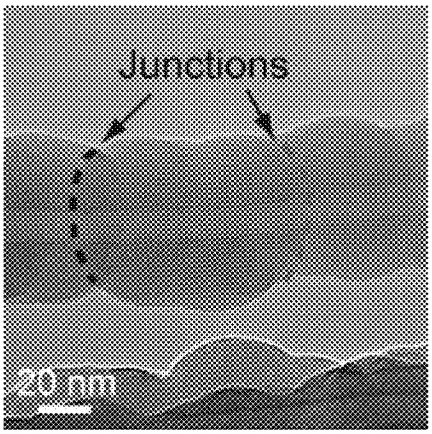
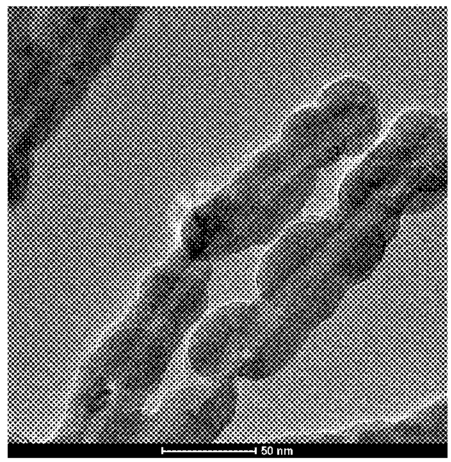


FIG. 9



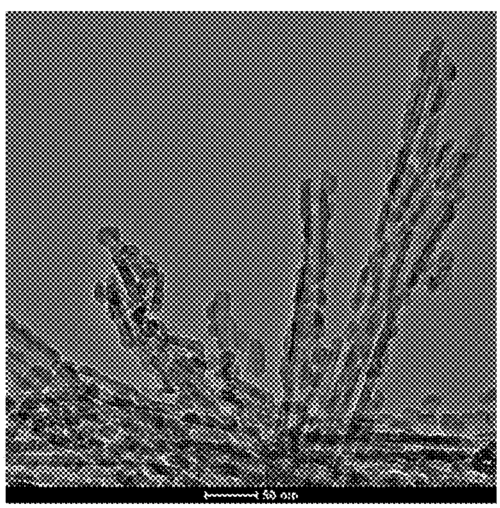
thickness of 30nm

FIG. 10A



thickness of 20nm

FIG. 10B



thickness of 10nm

FIG. 10C

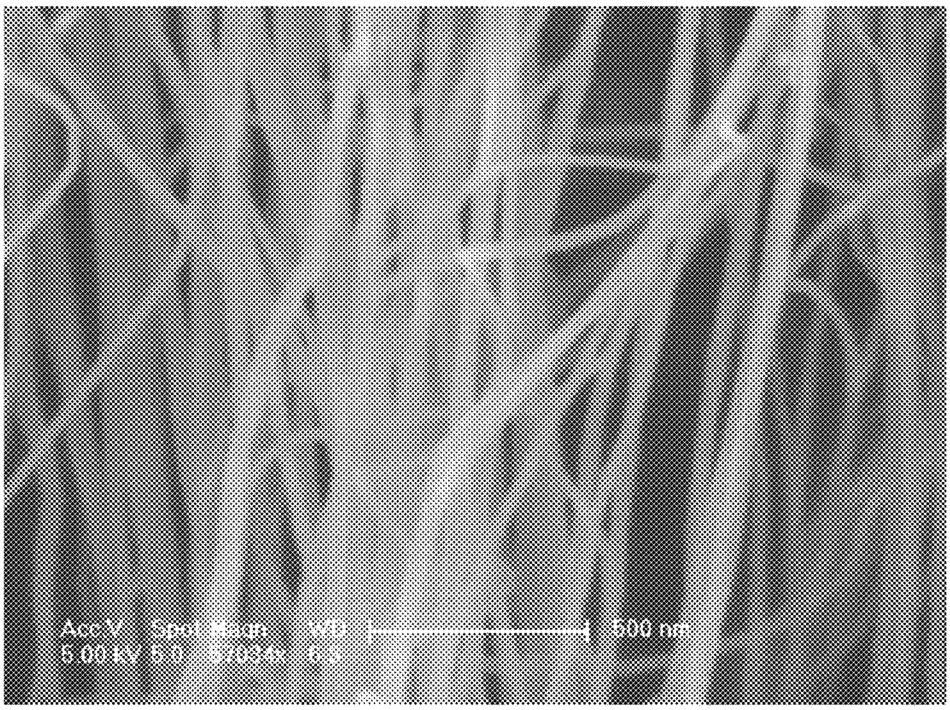
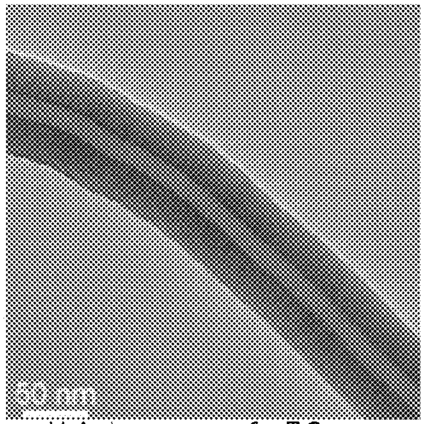
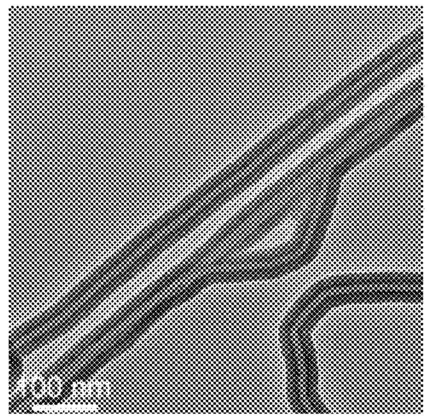


FIG. 11



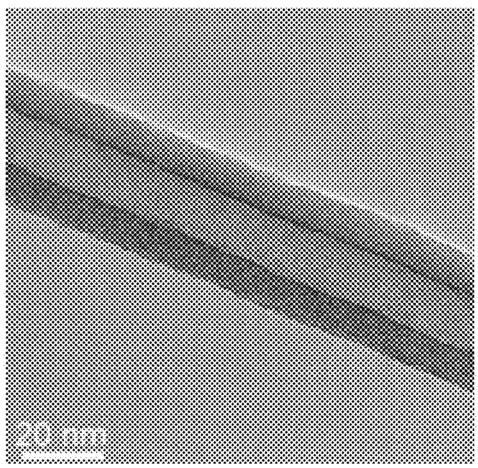
thickness of 30nm

FIG. 12A



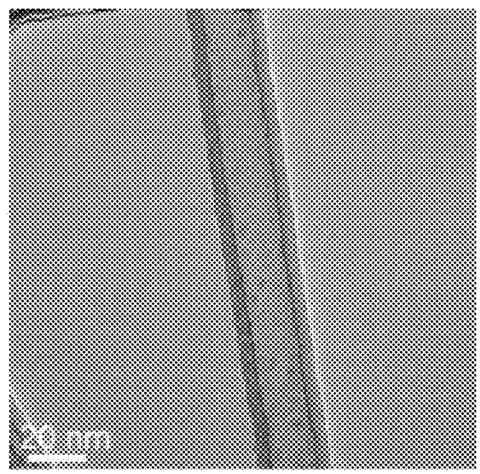
thickness of 20nm

FIG. 12B



thickness of 10nm

FIG. 12C



thickness of 5nm

FIG. 12D

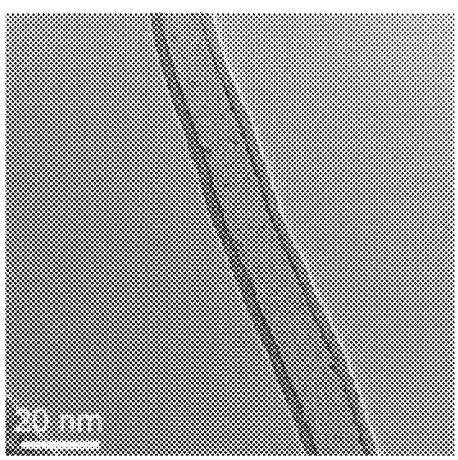


FIG. 12E

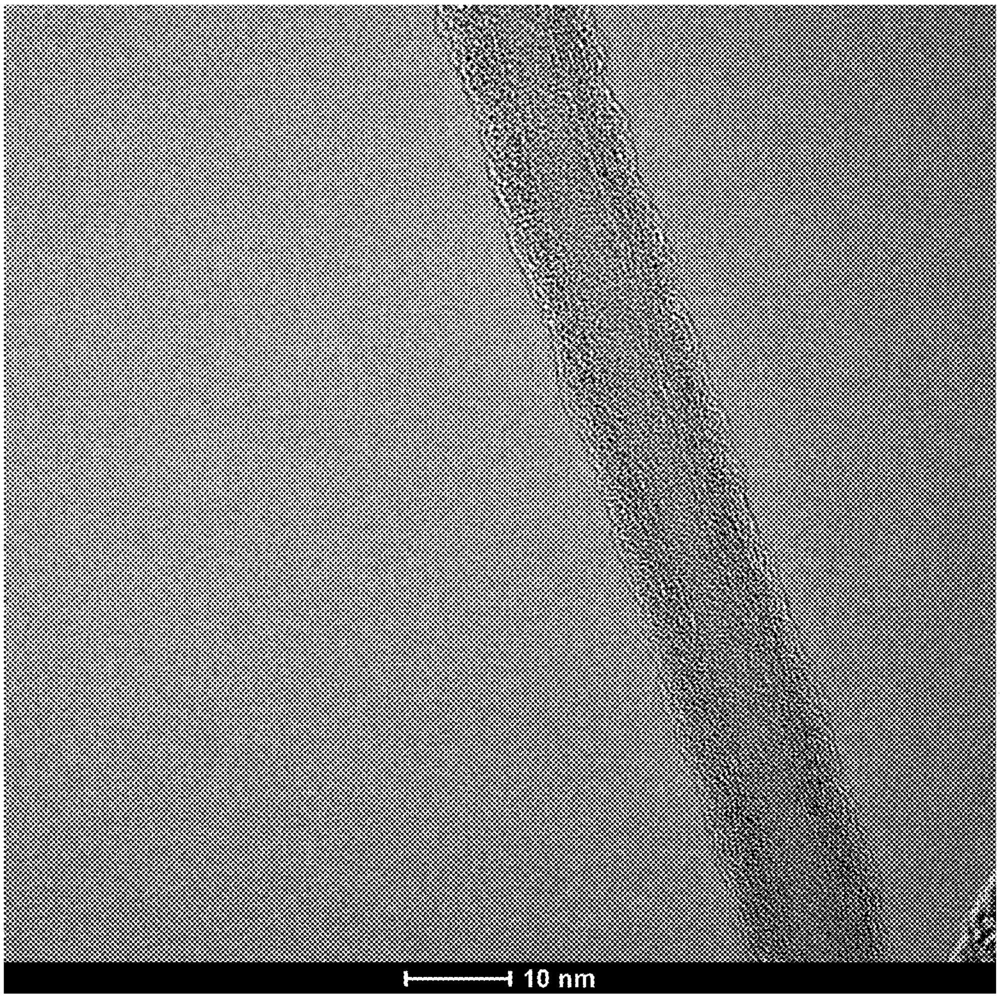


FIG. 13

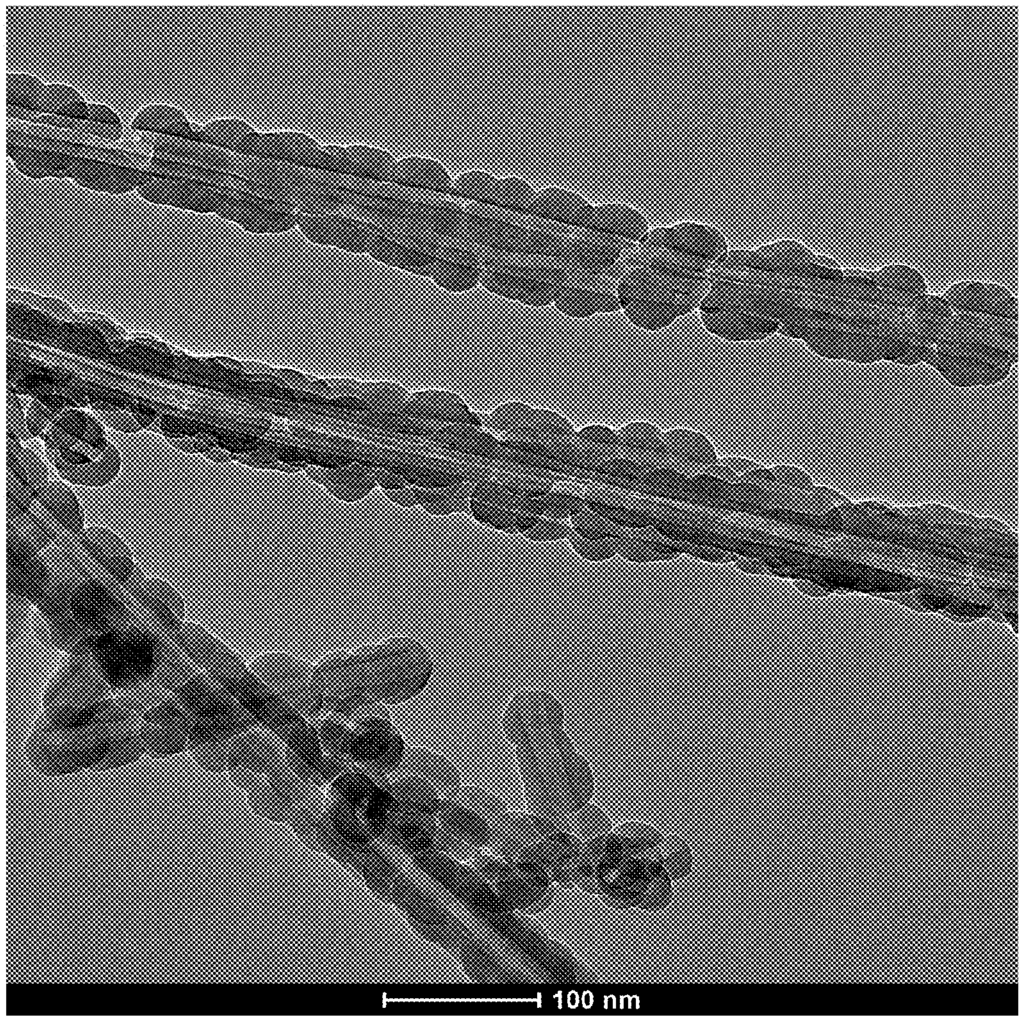


FIG. 14

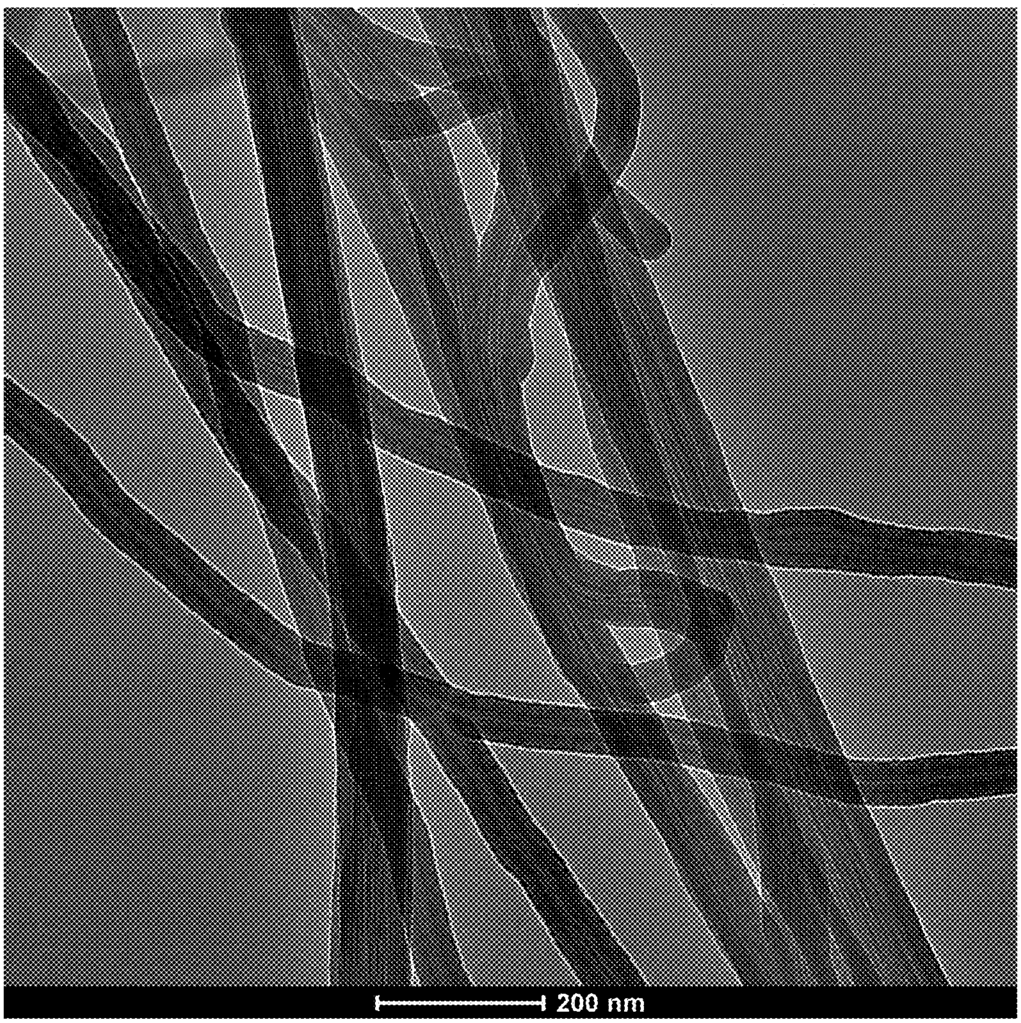


FIG. 15

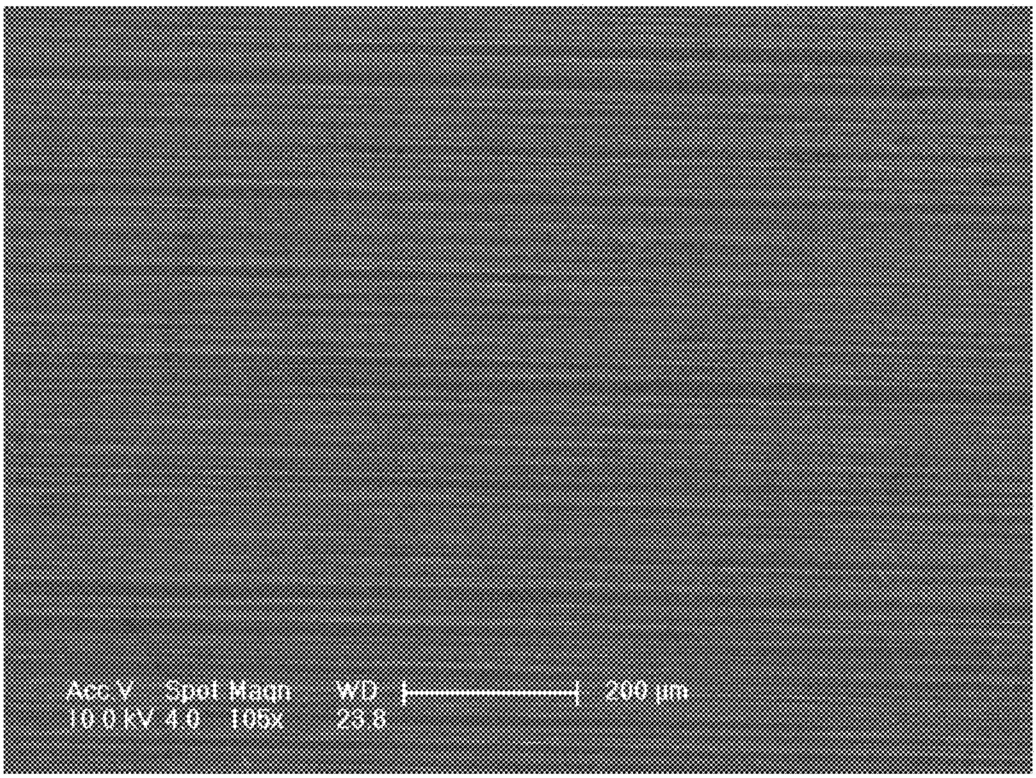


FIG. 16

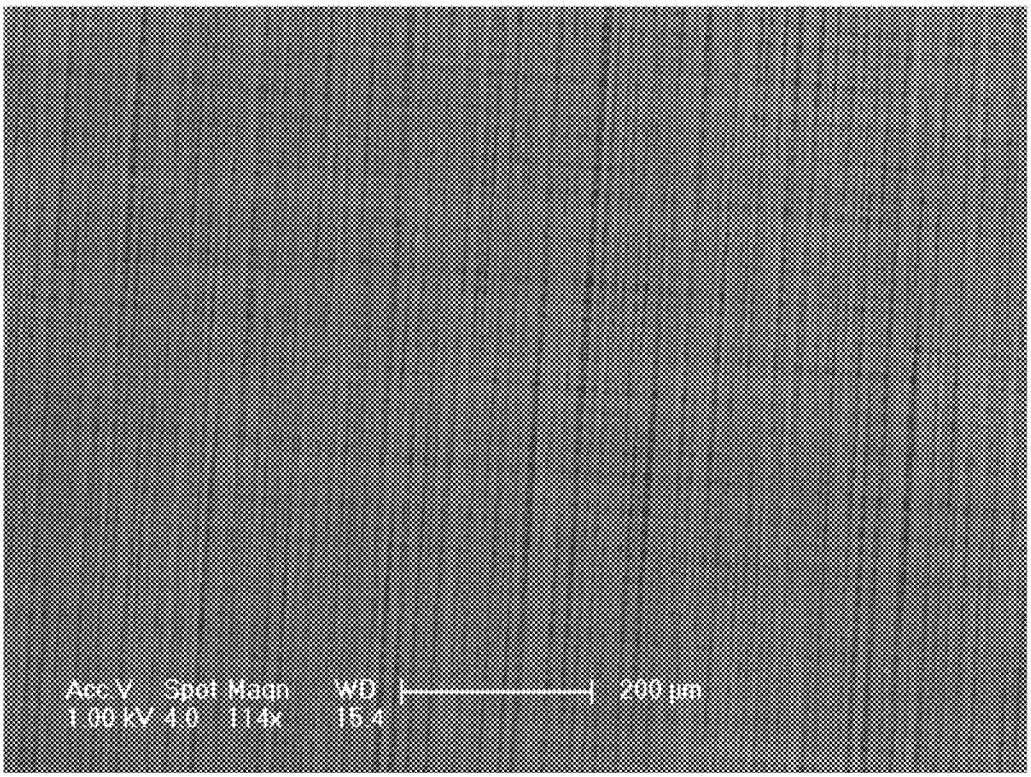


FIG. 17

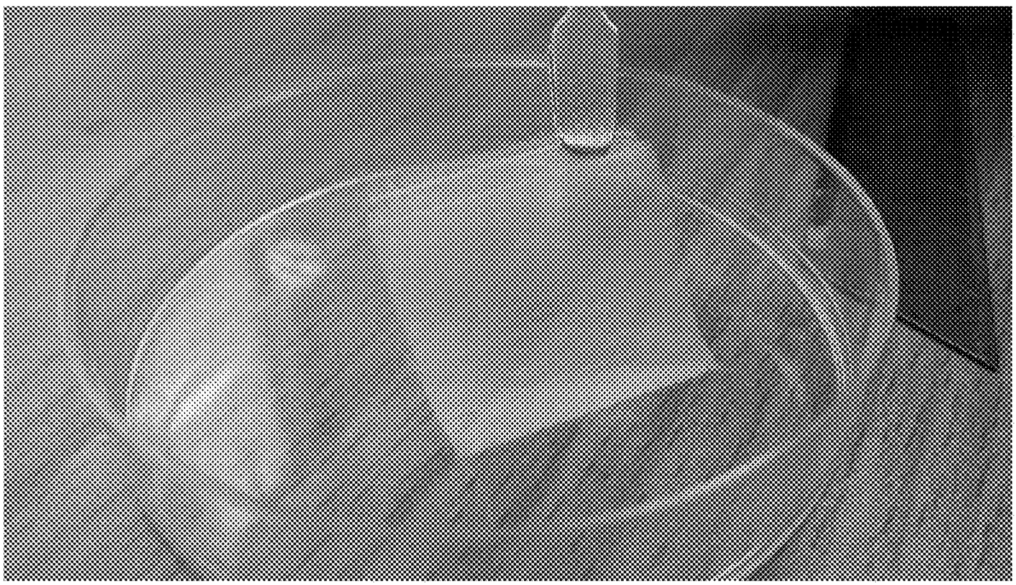


FIG. 18

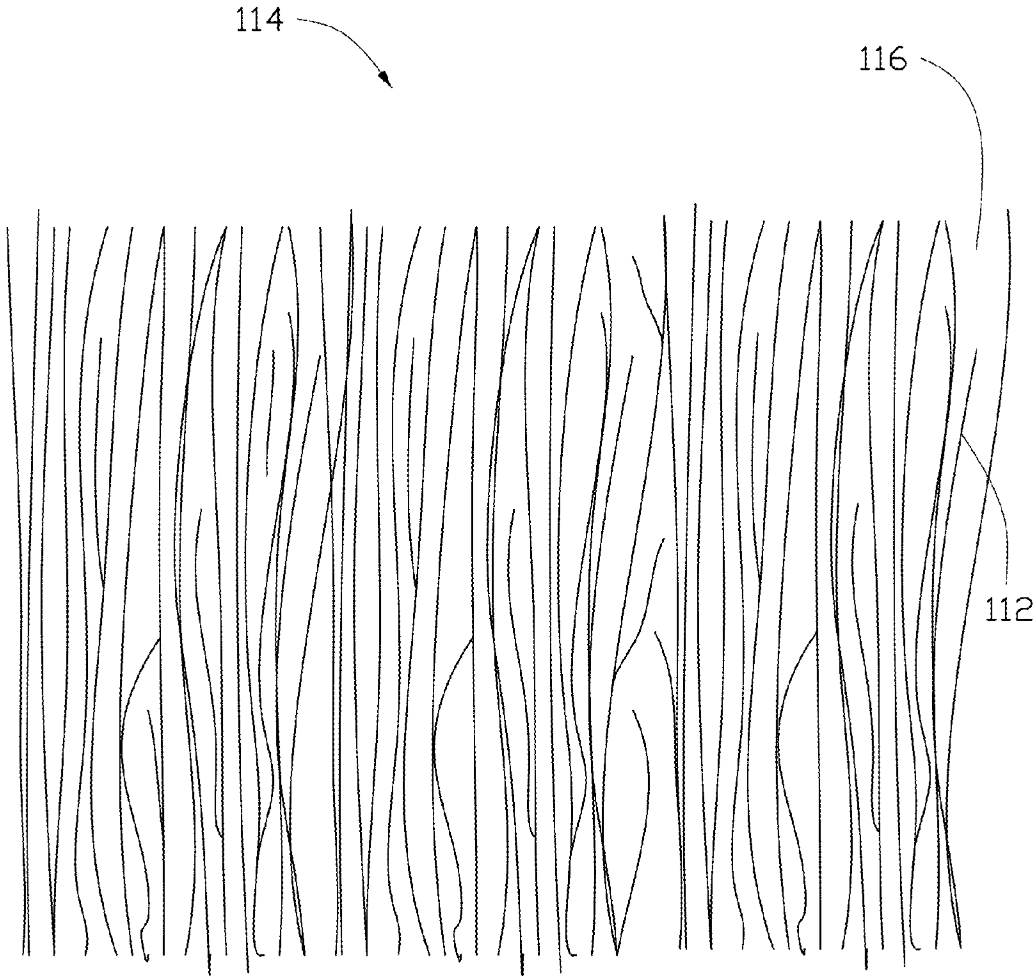


FIG. 19

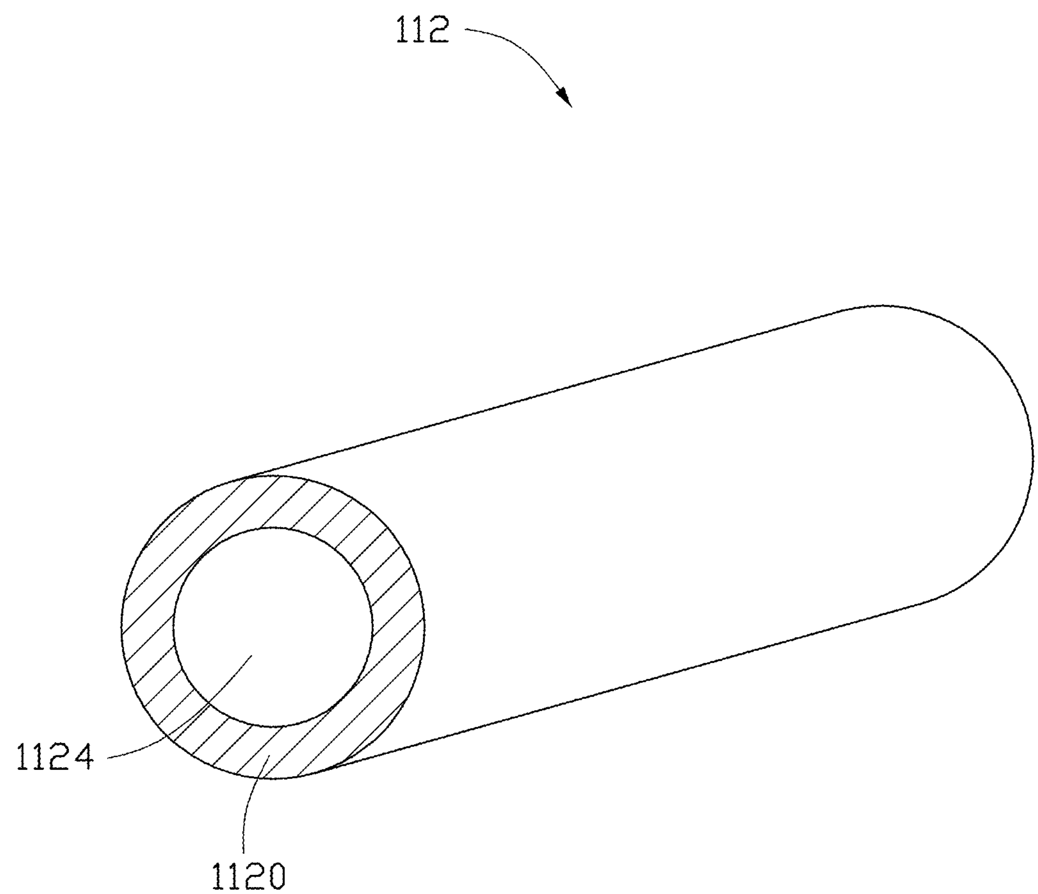


FIG. 20

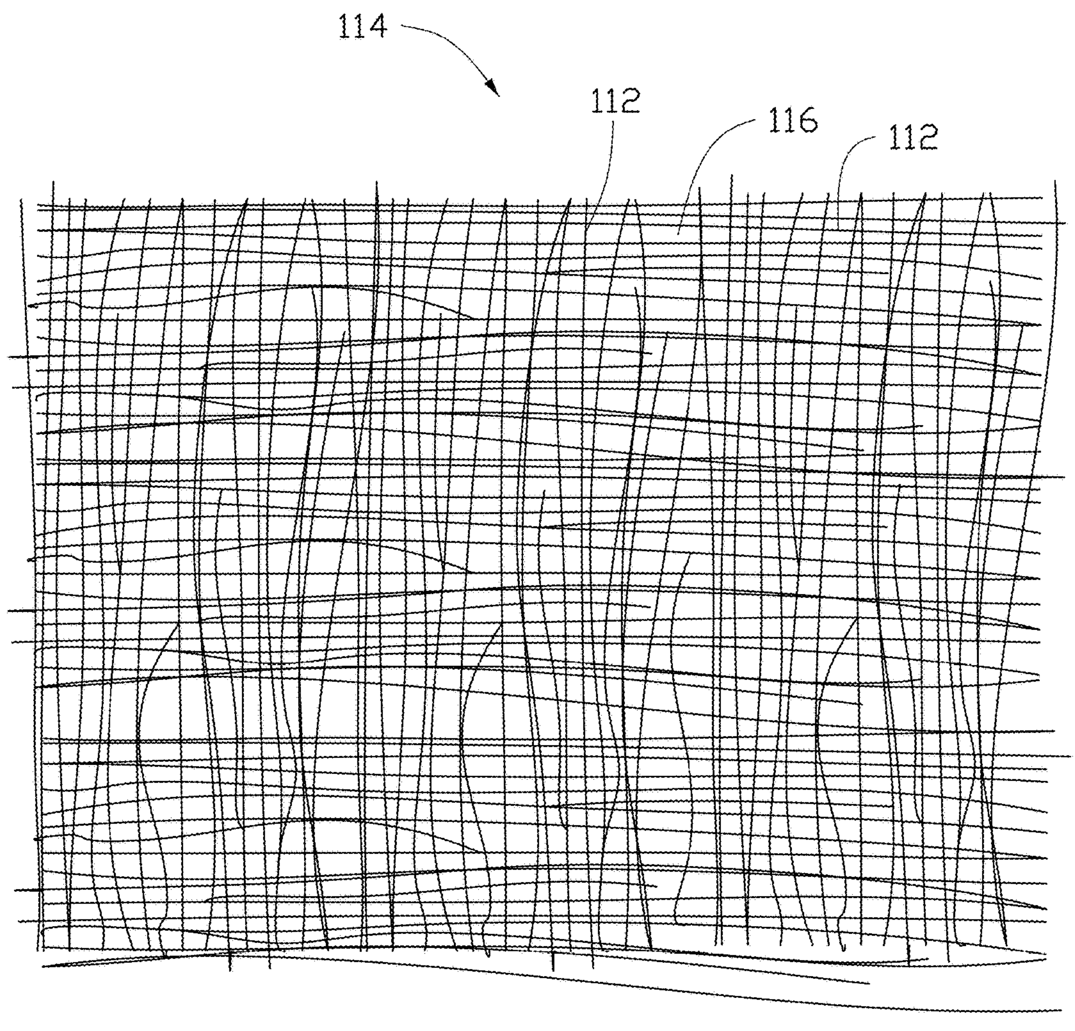


FIG. 21

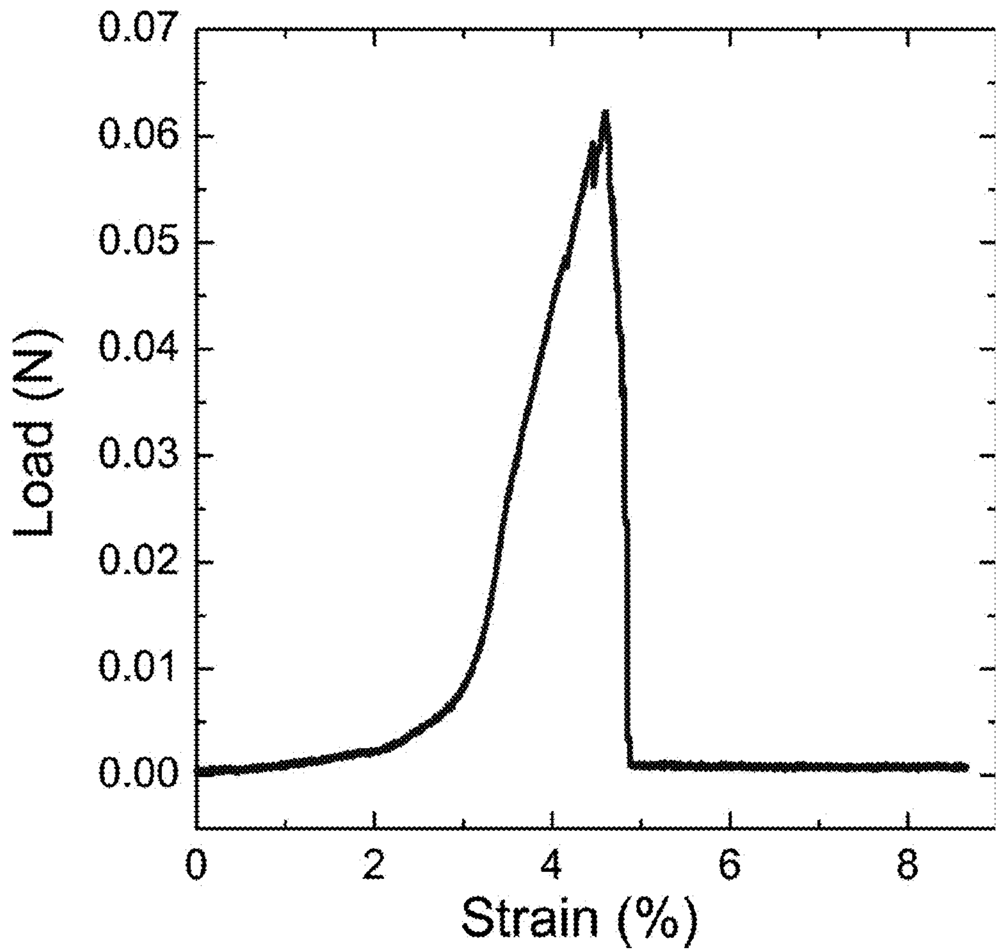


FIG. 22

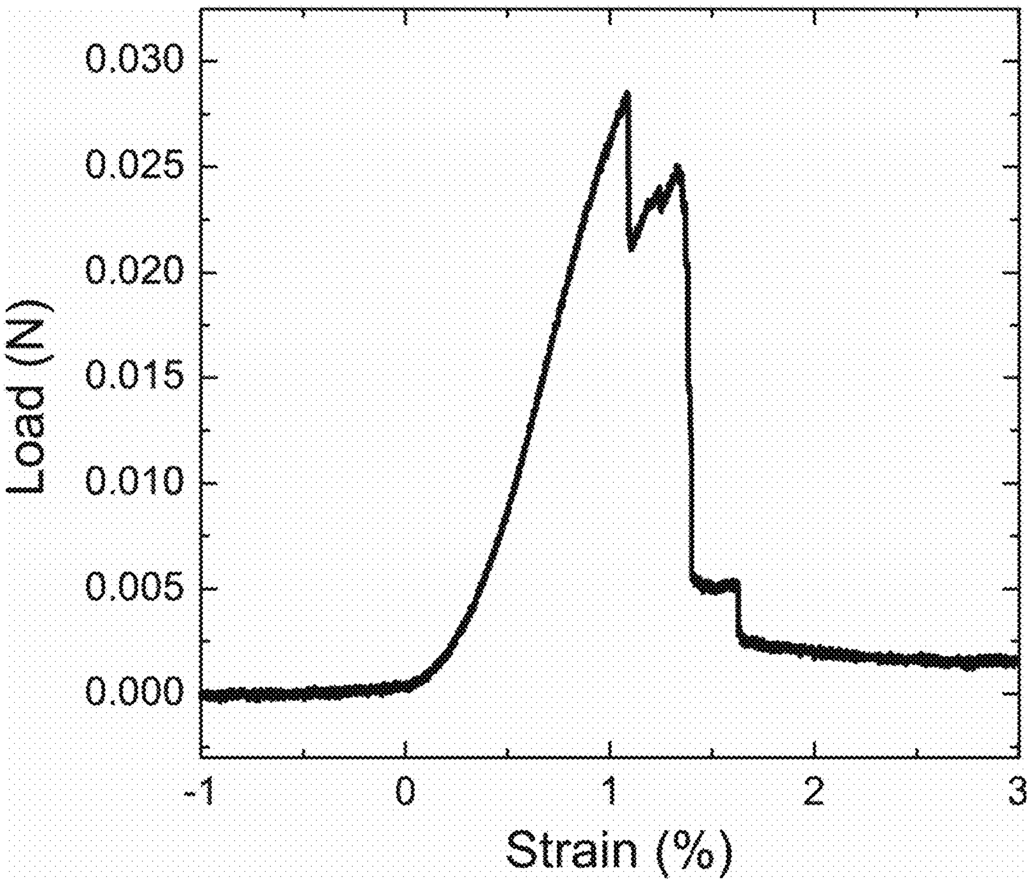


FIG. 23

NANOTUBE FILM STRUCTURE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to Chinese Patent Application No. 201410115685.4 filed on Mar. 26, 2014 in the China Intellectual Property Office, the contents of which are incorporated by reference herein.

FIELD

The subject matter herein generally relates to nanotube film and methods for making the same.

BACKGROUND

Many novel properties are beyond traditional theories of material science and properties when the materials are at a nanoscale. Nanomaterial has become representative of modern science and technology and future research because of their distinct catalytic reaction, electrical, physical, magnetic, and luminescent properties. Many methods have been developed to manufacture nanomaterial, such as spontaneous growth, template-based synthesis, electro-spinning, and lithography.

A carbon nanotube film has been fabricated by drawing from a supper aligned carbon nanotube array. The carbon nanotube film includes a plurality of carbon nanotubes joined end to end along the drawing direction. However, because each of the plurality of carbon nanotubes has a sealed end, the bonding force at joint between adjacent carbon nanotubes is only van der Waals force. Thus, the strength of the carbon nanotube film is relatively weak.

What is needed, therefore, is to provide a nanotube film and a method for solving the problem discussed above.

BRIEF DESCRIPTION OF THE DRAWINGS

Implementations of the present technology will now be described, by way of example only, with reference to the attached figures, wherein:

FIG. **1** is a flowchart of one embodiment of a method for making a nanotube film.

FIG. **2** is a Scanning Electron Microscope (SEM) image of a carbon nanotube film.

FIG. **3** is a schematic structural view of a carbon nanotube segment of the carbon nanotube film of FIG. **2**.

FIG. **4** is a schematic structural view of the carbon nanotube film of FIG. **2**.

FIG. **5** is a partially enlarged view of FIG. **4**.

FIG. **6** is an SEM image of two cross-stacked carbon nanotube films.

FIG. **7** is schematic view of one embodiment of a method for stretching the carbon nanotube film of FIG. **4**.

FIG. **8** is an SEM image of a stretched carbon nanotube film made by method of FIG. **7**.

FIG. **9** is an SEM image of one embodiment of an alumina (Al_2O_3) layer deposited on a pristine carbon nanotube film by atomic layer deposition (ALD).

FIGS. **10**A-**10**C show transmission electron microscope (TEM) images of alumina layers with different thickness deposited on pristine carbon nanotube films by atomic layer deposition.

FIG. **11** is an SEM image of one embodiment of an alumina layer deposited on a carbon nanotube film treated with oxygen plasma by atomic layer deposition.

FIGS. **12**A-**12**E show TEM images of alumina layers with different thickness deposited on carbon nanotube films treated with oxygen plasma by atomic layer deposition.

FIG. **13** is a transmission electron microscope (TEM) image of one embodiment of a carbon nanotube film treated by carbon accumulation.

FIG. **14** is an SEM image of one embodiment of an alumina layer deposited on a pristine carbon nanotube film by atomic layer deposition.

FIG. **15** is an SEM image of one embodiment of an alumina layer deposited on a carbon nanotube film treated by carbon accumulation by atomic layer deposition.

FIG. **16** is an SEM image of one embodiment of a single alumina nanotube film.

FIG. **17** is an SEM image of one embodiment of two cross-stacked alumina nanotube films.

FIG. **18** is a photo of an alumina nanotube film.

FIG. **19** is a schematic structural view of one embodiment of a single nanotube film.

FIG. **20** is a schematic structural view of one embodiment of a nanotube of the nanotube film of FIG. **19**.

FIG. **21** is a schematic structural view of one embodiment of two cross-stacked nanotube films.

FIG. **22** shows a relationship between a load and a strain of the cross-stacked alumina nanotube film made by template of a pristine carbon nanotube film.

FIG. **23** shows a relationship between a load and a strain of the cross-stacked alumina nanotube film made by template of a carbon nanotube film treated with oxygen plasma.

DETAILED DESCRIPTION

It will be appreciated that for simplicity and clarity of illustration, where appropriate, reference numerals have been repeated among the different figures to indicate corresponding or analogous elements. In addition, numerous specific details are set forth in order to provide a thorough understanding of the embodiments described herein. However, it will be understood by those of ordinary skill in the art that the embodiments described herein can be practiced without these specific details. In other instances, methods, procedures and components have not been described in detail so as not to obscure the related relevant feature being described. The drawings are not necessarily to scale and the proportions of certain parts may be exaggerated to better illustrate details and features. The description is not to be considered as limiting the scope of the embodiments described herein.

Several definitions that apply throughout this disclosure will now be presented.

The term "coupled" is defined as connected, whether directly or indirectly through intervening components, and is not necessarily limited to physical connections. The connection can be such that the objects are permanently connected or releasably connected. The term "outside" refers to a region that is beyond the outermost confines of a physical object. The term "inside" indicates that at least a portion of a region is partially contained within a boundary formed by the object. The term "substantially" is defined to be essentially conforming to the particular dimension, shape or other word that substantially modifies, such that the component need not be exact. For example, substantially cylindrical means that the object resembles a cylinder, but can have one or more deviations from a true cylinder. The term "comprising" means "including, but not necessarily limited to"; it specifically indicates open-ended inclusion or membership in a so-described combination, group, series and the like. It should be noted that references to "an" or "one" embodiment in this disclosure are not necessarily to the same embodiment, and such references mean at least one.

References will now be made to the drawings to describe, in detail, various embodiments of the present nanotube film and methods for making the same.

Referring to FIG. **1**, a method for making a nanotube film **114** of one embodiment includes the following steps:

step (S**10**), providing a free standing carbon nanotube film **100**, wherein the carbon nanotube film **100** includes a plurality of carbon nanotubes **104** orderly arranged and combined with each other via van der Waals force to form a plurality of apertures **105** extending along a length direction of the plurality of carbon nanotubes **104**;

step (S**20**), inducing defects on surfaces of the plurality of carbon nanotubes **104**;

step (S**30**), growing a nano-material layer **110** on the surfaces of the plurality of carbon nanotubes **104** by atomic layer deposition;

step (S**40**), obtaining a free-standing nanotube film **114** by removing the carbon nanotube film **100** by annealing, wherein nanotube film **114** includes a plurality of nanotubes **112** orderly arranged and combined with each other;

In step (S**10**), the carbon nanotube film **100** is drawn from a carbon nanotube array. Referring to FIGS. **2-5**, the carbon nanotube film **100** is a substantially pure structure consisting of a plurality of carbon nanotubes **104**, **106**, with few impurities and chemical functional groups. The carbon nanotube film **100** is a free-standing structure. The term "free-standing structure" includes that the carbon nanotube film **100** can sustain the weight of itself when it is hoisted by a portion thereof without any significant damage to its structural integrity. Thus, the carbon nanotube film **100** can be suspended by two spaced supports. The majority of carbon nanotubes **104** of the carbon nanotube film **100** are joined end-to-end along a length direction of the carbon nanotubes **104** by van der Waals force therebetween so that the carbon nanotube film **10** is a free-standing structure. The carbon nanotubes **104**, **106** of the carbon nanotube film **100** can be single-walled, double-walled, or multi-walled carbon nanotubes. The diameter of the single-walled carbon nanotubes can be in a range from about 0.5 nm to about 50 nm. The diameter of the double-walled carbon nanotubes can be in a range from about 1.0 nm to about 50 nm. The diameter of the multi-walled carbon nanotubes can be in a range from about 1.5 nm to about 50 nm.

The carbon nanotubes **104**, **106** of the carbon nanotube film **100** are oriented along a preferred orientation. That is, the majority of carbon nanotubes **104** of the carbon nanotube film **100** are arranged to substantially extend along the same direction and in parallel with the surface of the carbon nanotube film **100**. Each adjacent two of the majority of carbon nanotubes **104** are joined end-to-end by van der Waals force therebetween along the length direction. A minority of dispersed carbon nanotubes **106** of the carbon nanotube film **100** may be located and arranged randomly. However, the minority of dispersed carbon nanotubes **106** have little effect on the properties of the carbon nanotube film **100** and the arrangement of the majority of carbon nanotubes **104** of the carbon nanotube film **100**. The majority of carbon nanotubes **104** are not absolutely form a direct line and extend along the axial direction, some of them may be curved and in contact with each other in microcosm. Some variations can occur in the carbon nanotube film **100**.

Referring to FIG. **3**, the carbon nanotube film **100** includes a plurality of successively oriented carbon nanotube segments **108**, joined end-to-end by van der Waals force therebetween. Each carbon nanotube segment **108** includes a plurality of carbon nanotubes **104** parallel to each other, and combined by van der Waals force therebetween. A thickness, length and shape of the carbon nanotube segment **108** are not limited. A thickness of the carbon nanotube film **100** can range from about 0.5 nanometers to about 100 micrometers, such as 10 nanometers, 50 nanometers, 200 nanometers, 500 nanometers, 1 micrometer, 10 micrometers, or 50 micrometers.

Referring to FIGS. **4-5**, the majority of carbon nanotubes **104** of the carbon nanotube film **100** are arranged to substantially extend along the same direction to form a plurality of carbon nanotube wires **102** substantially parallel with each other. The minority of carbon nanotubes **106** are randomly dispersed on and in direct contact with the plurality of carbon nanotube wires **102**. The extending direction of the majority of carbon nanotubes **104** is defined as D**1**, and a direction perpendicular with D**1** and parallel with the carbon nanotube film **100** is defined as D**2**. The carbon nanotubes **104** of each carbon nanotube wire **102** are joined end-to-end along D**1**, and substantially parallel and combined with each other along D**1**. The plurality of apertures **105** are defined between adjacent two of the plurality of carbon nanotube wires **102** or the plurality of carbon nanotubes **104**.

The carbon nanotube film **100** is stretchable along D**2**. When the carbon nanotube film **100** is stretched along D**2**, the carbon nanotube film **100** can maintain its film structure. A distance between adjacent two of the plurality of carbon nanotube wires **102** will be changed according to the deformation of the carbon nanotube film **100** along D**2**. The distance between adjacent two of the plurality of carbon nanotube wires **102** can be in a range from about 0 micrometers to about 50 micrometers. The ratio of quantity or quality between the majority of carbon nanotubes **104** and the minority of dispersed carbon nanotubes **106** can be greater than or equal to 2:1 and less than or equal to about 6:1. The more the minority of dispersed carbon nanotubes **106**, the greater the maximum deformation of the carbon nanotube film **100** along D**2**. The maximum deformation of the carbon nanotube film **100** along D**2** can be about 300%. In one embodiment, the ratio of quantity between the majority of carbon nanotubes **104** and the minority of dispersed carbon nanotubes **106** is about 4:1.

The carbon nanotube film **100** can be made by following substeps:

step (S**100**), providing a carbon nanotube array on a substrate; and

step (S**102**), drawing out the carbon nanotube film **100** from the carbon nanotube array by using a tool.

In step (S**100**), the carbon nanotube array includes a plurality of carbon nanotubes that are parallel to each other and substantially perpendicular to the substrate. The height of the plurality of carbon nanotubes can be in a range from about 50 micrometers to 900 micrometers. The carbon nanotube array can be formed by the substeps of: step (S**1001**) providing a substantially flat and smooth substrate; step (S**1002**) forming a catalyst layer on the substrate; step (S**1003**) annealing the substrate with the catalyst layer in air at a temperature approximately ranging from 700° C. to 900° C. for about 30 minutes to 90 minutes; step (S**1004**) heating the substrate with the catalyst layer to a temperature approximately ranging from 500° C. to 740° C. in a furnace with a protective gas therein; and step (S**1005**) supplying a carbon source gas to the furnace for about 5 minutes to 30 minutes and growing the carbon nanotube array on the substrate.

In step (S**1001**), the substrate can be a P-type silicon wafer, a N-type silicon wafer, or a silicon wafer with a film of silicon dioxide thereon. A 4-inch P-type silicon wafer is used as the substrate. In step (S**1002**), the catalyst can be made of iron (Fe), cobalt (Co), nickel (Ni), or any alloy thereof. In step (S**1003**), the protective gas can be made up of at least one of nitrogen (N_2), ammonia (NH_3), and a noble gas. In step (S**1005**), the carbon source gas can be a hydrocarbon gas, such as ethylene (C_2H_4), methane (CH_4), acetylene (C_2H_2), ethane (C_2H_6), or any combination thereof. The carbon nanotube array formed under the above conditions is essentially free of impurities, such as carbonaceous or residual catalyst particles.

In step (S**102**), the drawing out the carbon nanotube film **100** includes the substeps of: step (S**1021**) selecting one or more of carbon nanotubes in a predetermined width from the carbon nanotube array; and step (S**1022**) drawing the selected carbon nanotubes to form nanotube segments at an even and uniform speed to achieve the carbon nanotube film **100**.

In step (S**1021**), the carbon nanotubes having a predetermined width can be selected by using an adhesive tape, such as the tool, to contact the super-aligned array. In step (S**1022**), the drawing direction is substantially perpendicular to the growing direction of the carbon nanotube array. Each carbon nanotube segment includes a plurality of carbon nanotubes parallel to each other.

In one embodiment, during the drawing process, as the initial carbon nanotube segments are drawn out, other carbon nanotube segments are also drawn out end-to-end due to van der Waals force between ends of adjacent segments. This process of drawing helps provide a continuous and uniform carbon nanotube film **100** having a predetermined width can be formed.

The width of the carbon nanotube film **100** depends on a size of the carbon nanotube array. The length of the carbon nanotube film **100** can be arbitrarily set as desired. In one useful embodiment, when the substrate is a 4-inch P-type silicon wafer, the width of the carbon nanotube film **100** can be in a range from about 0.01 centimeters to about 10 centimeters. The thickness of the carbon nanotube film **100** can be in a range from about 0.5 nanometers to about 10 micrometers.

Furthermore, at least two carbon nanotube films **100** can be stacked with each other or two or more carbon nanotube films **100** can be located coplanarly and combined by only the van der Waals force therebetween. As shown in FIG. **6**, two carbon nanotube films **100** are stacked with each other, and the majority of carbon nanotubes **104** of the two carbon nanotube films **100** are substantially perpendicular with each other.

Furthermore, in one embodiment, step (S**10**) further includes stretching the carbon nanotube film **100** along D**2** so that the apertures **105** have larger width. As shown in FIG. **7**, the stretching the carbon nanotube film **100** includes: fixing two opposite sides of the carbon nanotube film **100** on two spaced elastic supporters **200** so that a portion of the carbon nanotube film **100** are suspended between the two elastic supporters **200**, wherein two elastic supporters **200** are parallel with each other and extend along D**2**; stretching the two elastic supporters **200** along D**2** to obtain a stretched carbon nanotube film. As shown in FIG. **8**, the stretched carbon nanotube film has increased apertures. The two elastic supporters **200** can be elastic rubber, springs, or elastic bands. The speed of stretching the two elastic supporters **200** is less than 10 centimeters per second. The area of the carbon nanotube film **100** can be increased by stretching along D**2**.

Furthermore, in one embodiment, step (S**10**) can further include treating the carbon nanotube film **100** with organic solvent so that the apertures **105** have larger width. The organic solvent can be volatile, such as ethanol, methanol, acetone, dichloroethane, chloroform, or mixtures thereof. In one embodiment, the organic solvent is ethanol. The treating the carbon nanotube film **100** with organic solvent can be performed by applying the organic solvent to entire surface of the carbon nanotube film **100** suspended on a frame or immersing the entire carbon nanotube film **100** with the frame in an organic solvent.

In one embodiment, the treating the carbon nanotube film **100** with organic solvent includes soaking a suspended carbon nanotube film **100** with an atomized organic solvent at least one time. In one embodiment, the soaking a suspended carbon nanotube film **100** can include steps of: providing a volatilizable organic solvent; atomizing the organic solvent into a plurality of dispersed organic droplets; and spraying the organic droplets onto the surface of the suspended carbon nanotube film **100** and the organic droplets gradually penetrating onto the carbon nanotubes of the carbon nanotube film **100**, thereby making the suspended carbon nanotube film **100** be soaked at least one time by the organic droplets, and then make the carbon nanotube film shrink into a treated carbon nanotube film. The organic droplets are tiny organic solvent drops suspended in surrounding. The organic solvent can be atomized into the organic droplets by ultrasonic atomization method, high pressure atomizing method or other methods.

The organic solvent can be alcohol, methanol, acetone, acetic acid, and other volatilizable solvents. During the spraying process, a pressure is produced, when the organic droplets are sprayed, the pressure is small and can't break the carbon nanotube film **100**. The diameter of each organic droplet is larger than or equal to 10 micrometers, or less than or equal to 100 micrometers, such as about 20 micrometers, 50 micrometers. Thus, an interface force is produced between the carbon nanotube film **100** and the organic droplets. The interface force can ensure that the carbon nanotube film **100** is shrunk and the carbon nanotubes in the carbon nanotube film **100** are dispersed more uniformly.

The organic solvent is volatile and easy to be volatilized. When the organic droplets are sprayed onto the carbon nanotube film **100** and then penetrated into the carbon nanotube film **100**, the organic droplets are then volatilized, and the carbon nanotube segments **108** loosely arranged in the carbon nanotube film **100** are tightly shrunk. The diameter of each organic droplet is larger than or equal to 10 micrometers, or less than or equal to 100 micrometers, the soaked scope of the carbon nanotube segment of the carbon nanotube film **100** is limited by the small diameter of each organic droplet. Thus, diameters of the carbon nanotube segments **108** of the carbon nanotube film **100** can be shrunk into less than or equal to 10 micrometers, the carbon nanotube segments **108** are substantially invisible using naked eyes in the treated carbon nanotube film. The carbon nanotube film **100** is original black or grey. However, after the soaking with an atomized organic solvent, the carbon nanotube film **100** is shrunk into the treated carbon nanotube film which is more transparent.

In step (S**20**), the carbon nanotube film **100** can be suspended and treated by oxidization or carbon accumulation to induce defects. The carbon nanotube film **100** not treated by inducing defects is defined as a pristine carbon nanotube film **100**. In one embodiment, part of the carbon nanotube film **100** is suspended by attaching on a frame and oxidized by oxygen plasma **300** treating.

In the process of treating the carbon nanotube film **100** by oxygen plasma **300**, the carbon nanotubes **104**, **106** of the carbon nanotube film **100** are oxidized to form a plurality of dangling bond. In the process of oxygen plasma **300**, the carbon nanotube film **100** can be connected to a power and has an electric potential so that the carbon nanotube film **100** can be bombarded by the oxygen plasma **300** more strongly. When nano-material layer **110** are forming on the surface of the carbon nanotubes **104**, **106** by atomic layer deposition, the atoms of the nano-material layer **110** can stack on the surface of the carbon nanotubes **104**, **106** layer upon layer to form a compact nano-material layer **110** with high strength. Also, the thickness of the nano-material layer **110** is controllable so that a nano-material layer **110** with a thickness in nano-scale can be obtained. In the process of oxygen plasma **300**, the flow rate of the oxygen gas can be in a range from about 30 sccm to about 60 sccm, the pressure of the oxygen gas can be in a range from about 8 Pa to about 12 Pa, the treating time can be in a range from about 8 seconds to about 12 seconds, and the treating power can be in a range from about 20 W to about 30 W. In one embodiment, the flow rate of the oxygen gas is about 50 sccm, the pressure of the oxygen gas is about 10 Pa, the treating time is about 10 seconds, and the treating power is about 25 W. As shown in FIGS. **9**, **10**A-**10**C, when the alumina layer has a thickness less than 30 nanometers, the plurality of particles deposited on the pristine carbon nanotube film by atomic layer are discontinuous. When the alumina layer has a thickness above 30 nanometers, the plurality of particles deposited on the pristine carbon nanotube film by atomic layer are joined with each other to form a continuous alumina layer. However, lots of junctions are formed between adjacent two of the plurality of particles. Furthermore, the alumina layer deposited on the pristine carbon nanotube film by atomic layer has a smoothness at least above 10 nanometers. As shown in FIGS. **11**, **12**A-**12**E, when the alumina layer has a thickness less than 30 nanometers, the plurality of particles deposited on the oxygen plasma treated carbon nanotube film by atomic layer are a continuous and uniform layer structure. Furthermore, the alumina layer deposited on the oxygen plasma treated carbon nanotube film by atomic layer has a smoothness at least less than 10 nanometers. In one embodiment, the alumina layer deposited on the oxygen plasma treated carbon nanotube film by atomic layer has a smoothness less than 5 nanometers. In one embodiment, the alumina layer deposited on the oxygen plasma treated carbon nanotube film by atomic layer has a smoothness less than 3 nanometers even if the thickness of the alumina layer is less than 10 nanometers.

In the process of carbon accumulation, a carbon layer is coated on the surface of the carbon nanotubes **104**, **106**. The method of carbon accumulation can be physical vapor deposition (PVD), chemical vapor deposition (CVD), or spraying. In the process of carbon accumulation, an electric current can be supplied to flow through the carbon nanotube film **100** to produce heat to heat the carbon nanotube film **100** itself. In one embodiment, the carbon layer is coated on the surface of the carbon nanotubes **104**, **106** by magnetron sputtering. In the magnetron sputtering, the current can be in a range from about 100 mA to about 200 mA, the pressure can be in a range from about 0.05 Pa to about 0.2 Pa, the flow rate of Ar can be in a range from about 5 Pa to about 15 sccm, and the sputtering time can be in a range from about 1.5 minutes to about 7.5 minutes. In one embodiment, the current is about 150 mA, the pressure is about 0.1 Pa, the flow rate of Ar is about 10 sccm, and the sputtering time is about 5 minutes. As shown in FIG. **13**, the carbon layer is coated on the surface of the carbon nanotubes of the carbon nanotube film **100** by magnetron sputtering.

The carbon layer includes a plurality of carbon particles to form the defects on the surface of the carbon nanotubes **104**, **106**. Thus, when nano-material layer **110** are forming on the surface of the carbon nanotubes **104**, **106** by atomic layer deposition, the atoms of the nano-material layer **110** can stack on the surface of the carbon nanotubes **104**, **106** layer upon layer to form a compact nano-material layer **110** with high strength. Also, the thickness of the nano-material layer **110** is controllable so that a nano-material layer **110** with a thickness in nano-scale can be obtained. The thickness of the nano-material layer **110** can be in a range from about 3 nanometers to about 30 nanometers. If the carbon nanotube film **100** is not treated by carbon accumulation, the alumina layer deposited on the carbon nanotube film by atomic layer deposition can form a continuous layer structure only at the thickness above 30 nanometers. If the thickness of the alumina layer deposited on the carbon nanotube film by atomic layer deposition is smaller than 30 nanometers, the alumina layer is a plurality of discontinuous particles attached on the surface of the carbon nanotubes **104**, **106**. Thus, the alumina layer cannot form a compact layer structure. As shown in FIG. **14**, if the carbon nanotube film **100** is not treated with carbon accumulation, the alumina layer deposited on the carbon nanotube film by atomic layer deposition is a plurality of discontinuous particles. However, as shown in FIG. **15**, if the carbon nanotube film is treated with carbon accumulation, the alumina layer deposited on the carbon nanotube film by atomic layer deposition is a continuous layer structure.

In step (S**30**), the source material of the atomic layer deposition can be selected according to the material of the nanotubes **112**. For example, when the nanotubes **112** are metal oxide nanotubes **112**, the source material of the atomic layer deposition includes metal organic compound and water, and the carrier gas is nitrogen gas. The thickness of the nano-material layer **110** can be in a range from about 3 nanometers to about 100 nanometers. In one embodiment, the thickness of the nano-material layer **110** is in a range from about 20 nanometers to about 50 nanometers. The nano-material layer **110** can be coated on a surface of a single carbon nanotube to form a continuous layer structure and enclose the single carbon nanotube therein. The nano-material layer **110** can also be coated on a surface of two or more than two carbon nanotubes to form a continuous layer structure and enclose the two or more than two carbon nanotubes therein. The nano-material layer **110** can form a plurality of nanotubes **112** after the carbon nanotubes therein are removed because the nano-material layer **110** is a compact continuous layer structure. The plurality of nanotubes **112** can be combined with each other to form a free-standing nanotube film **114**. The nanotube **112** can be a single linear nanotube or a branch nanotube. The material of the nano-material layer **110** can be metal oxide, metal nitride, metal carbide, silicon oxide, silicon nitride, or silicon carbide.

In one embodiment, an alumina layer is deposited on the carbon nanotube film **100** by atomic layer deposition, the source materials of the atomic layer deposition are trimethylaluminum and water, and the carrier gas is nitrogen gas. The alumina layer is deposited on the carbon nanotube film **100** by following steps:

step (S**301**), suspending a portion of the carbon nanotube film **100** in a vacuum chamber of a atomic layer deposition device; and

step (S**302**), alternately introducing trimethylaluminum and water in to the chamber of the atomic layer deposition device.

In step (S**301**), the carbon nanotube film **100** is attached on a frame so that a portion of the carbon nanotube film **100** is suspended, and then placed into the vacuum chamber with the frame together. The frame can be a metal or ceramic frame. Because the carbon nanotube film **100** is free standing, the carbon nanotube film **100** can be directly placed on two spaced supporters located in the vacuum chamber. When the elastic supporters **200** mentioned above are made of thermostable material, the stretched carbon nanotube film **100** and the elastic supporters **200** can be placed in the vacuum chamber together.

In step (S**302**), the carrier gas is nitrogen gas. The flow rate of the carrier gas is about 5 sccm. The alternately introducing trimethylaluminum and water includes following steps:

step (S**3021**), first evacuating the vacuum chamber to a pressure of about 0.23 Torr;

step (S**3022**), introducing trimethylaluminum in to the vacuum chamber until the pressure of the vacuum chamber rises to about 0.26 Torr;

step (S**3023**), second evacuating the vacuum chamber to the pressure of about 0.23 Torr;

step (S**3024**), introducing water in to the vacuum chamber until the pressure of the vacuum chamber rise to about 0.26 Torr;

step (S**3025**), third evacuating the vacuum chamber to the pressure of about 0.23 Torr; and

step (S**3026**), repeating steps (S**3022**), (S**3023**), (S**3024**), (S**3025**) to start another cycle.

In each cycle, the second evacuating the vacuum chamber to the pressure of about 0.23 Torr takes about 25 seconds, and the third evacuating the vacuum chamber to the pressure of about 0.23 Torr takes about 50 seconds. The deposition velocity of the alumina layer is about 0.14 nm/cycle. The thickness of the alumina layer can be controlled by the cycle number.

In step (S**40**), the carbon nanotube film **100** coated with nano-material layer **110** is annealed to remove the carbon nanotube film **100** and obtain the plurality of nanotubes **112**. The plurality of nanotubes **112** are orderly arranged and combined with each other to form the free-standing nanotube film **114**. The annealing can be performed in oxygen atmosphere and at a temperature in a range from about 500° C. to about 1000° C. In one embodiment, the carbon nanotube film **100** coated with nano-material layer **110** is suspended in a quartz tube filled with air and heated to 550° C.

Referring to FIGS. **2** and **16**, the single alumina nanotube film and the single carbon nanotube film have substantially the same structure. Referring to FIGS. **6** and **17**, the two cross-stacked alumina nanotube films and the two cross-stacked carbon nanotube films have substantially the same structure. FIG. **18** shows that the alumina nanotube film is a free-standing nanotube film.

Referring to FIG. **19**, the nanotube film **114** of includes a plurality of nanotubes **112** orderly arranged and combined with each other. The nanotube film **114** is a layer structure having two opposite surfaces in macrocosm. In one embodiment, the plurality of nanotubes **112** are arranged to be substantially parallel with each other and extend substantially along the same direction. The plurality of nanotubes **112** are spaced from each other or in direct contact with each other. The length of the nanotube **112** is not limited and can be the same as the length of the carbon nanotube film **100** along the D**1** direction. In one embodiment, the length of the nanotube **112** is greater than 1 centimeter.

A plurality of openings **116** are defined by the plurality of spaced nanotubes **112**. The plurality of openings **116** extends through the nanotube film along the thickness direction. The plurality of openings **116** can be a hole defined by several adjacent nanotubes **112**, or a gap defined by two substantially parallel nanotubes **112** and extending along axial direction of the nanotubes **112**. The hole shaped openings **116** and the gap shaped openings **116** can exist in the patterned nanotube film **114** at the same time. The sizes of the openings **116** can be different. The average size of the openings **116** can be in a range from about 10 nanometers to about 500 micrometers. For example, the sizes of the openings **116** can be about 50 nanometers, 100 nanometers, 500 nanometers, 1 micrometer, 10 micrometers, 80 micrometers, or 120 micrometers. In one embodiment, the sizes of the openings **116** are in a range from about 10 nanometers to about 10 micrometers.

The adjacent nanotubes **112** are combined with each other by ionic bonds at the contacting surface and internal communicated. At least part of the plurality of nanotubes **112** extend from a first side of the nanotube film **114** to a second side opposite to the first side. The majority of nanotubes **112** of the nanotube film **114** are arranged to substantially extend along the same direction and in parallel with the surface of the nanotube film **114**. A minority of dispersed nanotubes **112** of the nanotube film **114** may be arranged randomly, crossed with and in direct contact with the adjacent nanotubes **112**. Thus, the nanotube film **114** is a free-standing structure.

Referring to FIG. **20**, the nanotube **112** includes a cylinder shaped cell **1122**. The cylinder shaped cell **1122** defines a cylinder shaped space **1124**. The thickness of the wall of the cylinder shaped cell **1122** can be in a range from about 3 nanometers to about 100 nanometers. The inside diameter of the cylinder shaped cell **1122** can be in a range from about 10 nanometers to about 100 nanometers. The material of the nanotube **112** can be metal oxide, metal nitride, metal carbide, silicon oxide, silicon nitride, or silicon carbide. In one embodiment, the nanotube **112** is an alumina nanotube with a thickness of about 30 nanometers and an inside diameter of about 20 nanometers.

As shown in FIG. **21**, two nanotube films **114** can be stacked with each other. The extending directions of nanotubes **112** in the two stacked nanotube films **114** form an angle α in a range from about 0° to about 90°. In one embodiment, the extending directions of nanotubes **112** in the two stacked nanotube films **114** are substantially perpendicular with each other so that the two stacked nanotube films **114** defines a plurality of openings **116**. The two stacked nanotube films **114** are combined with each other by ionic bonds to form a free standing structure with improved strength.

As shown in FIG. **22**, a mechanical strength of a first cross-stacked alumina nanotube film made by template of a carbon nanotube film treated with oxygen plasma is tested. The first cross-stacked alumina nanotube film can bear a load of about 0.06 N. As shown in FIGS. **22-23**, a mechanical strength of a second cross-stacked alumina nanotube film made by template of a pristine carbon nanotube film is tested. The second cross-stacked alumina nanotube film can bear a load of about 0.029 N that is greater than a greatest stretching force two stacked carbon nanotube film can bear. The first cross-stacked alumina nanotube film is much stronger than that of the second cross-stacked alumina nanotube film. Because the pristine carbon nanotube film is lack of active sites for alumina nanoparticles to grow on carbon nanotubes, with increasing the number of ALD cycles, although the alumina nanoparticles grow bigger and coalesce gradually to form tubular structure, a plurality of junctions are also formed as show in FIGS. **10**A-**10**C. These junctions in the alumina nanotube film serve as the weak joints and thus affect the mechanical strength seriously.

Furthermore, because the carbon nanotube film is drawn from supper aligned carbon nanotube array and includes a plurality of joints between adjacent two carbon nanotubes, adjacent two carbon nanotubes are joined only by van der Waals force. Thus, the strength of the carbon nanotube film is relatively weak. The second cross-stacked alumina nanotube film is made using the two stacked carbon nanotube film as a template, adjacent two nanotubes are joined by ionic bonds. Thus, the second cross-stacked alumina nanotube film has a relative high strength than that of the two stacked carbon nanotube films.

The embodiments shown and described above are only examples. Even though numerous characteristics and advantages of the present technology have been set forth in the foregoing description, together with details of the structure and function of the present disclosure, the disclosure is illustrative only, and changes may be made in the detail, including in matters of shape, size and arrangement of the parts within the principles of the present disclosure up to, and including, the full extent established by the broad general meaning of the terms used in the claims.

Depending on the embodiment, certain of the steps of methods described may be removed, others may be added, and the sequence of steps may be altered. The description and the claims drawn to a method may include some indication in reference to certain steps. However, the indication used is only to be viewed for identification purposes and not as a suggestion as to an order for the steps.

What is claimed is:

1. A nanotube film structure comprising: a nanotube film, wherein the nanotube film comprises a plurality of nanotubes orderly arranged and ionicly bonded to each other by direct contact with each other, and the nanotube film is free of carbon nanotubes.

2. The nanotube film structure of claim **1**, wherein adjacent two of the plurality of nanotubes are internally communicated such that interior of the adjacent two of the plurality of nanotubes are in communication with each other at a location where the adjacent two of the plurality of nanotubes are in direct contact with each other.

3. The nanotube film structure of claim **1**, wherein the plurality of nanotubes are substantially parallel with each other.

4. The nanotube film structure of claim **3**, wherein the nanotube film comprises two stacked nanotube films.

5. The nanotube film structure of claim **4**, wherein nanotubes of one of the two stacked nanotube films are perpendicular with nanotubes of the other one of the two stacked nanotube films.

6. The nanotube film structure of claim **4**, wherein the two stacked nanotube films are combined with each other by ionic bonds.

7. The nanotube film structure of claim **1**, wherein each of the plurality of nanotubes has a wall with a thickness in a range from about 10 nanometers to about 100 nanometers.

8. The nanotube film structure of claim **1**, wherein at least part of the plurality of nanotubes extend from a first side of the nanotube film to a second side opposite to the first side.

9. The nanotube film structure of claim **1**, wherein a length of the plurality of nanotubes is the same as a length or a width of the nanotube film.

10. The nanotube film structure of claim **1**, wherein a material of the plurality of nanotubes is selected from the group consisting of metal oxide, metal nitride, metal carbide, silicon oxide, silicon nitride and silicon carbide.

11. The nanotube film structure of claim **1**, wherein the nanotube film defines a plurality of openings.

12. The nanotube film structure of claim **1**, wherein the nanotube film is a free-standing structure.

13. A nanotube film structure comprising: a nanotube film, wherein the nanotube film comprises a plurality of nanotubes ironically bonded to each other by direct contact with each other and fabricated from a material selected from the group consisting of metal oxide, metal nitride, metal carbide, silicon oxide, silicon nitride and silicon carbide, and the nanotube film is free of carbon nanotubes.

14. The nanotube film structure of claim **13**, wherein the nanotube film is a free-standing structure.

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