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(54) **CARBON NANOTUBE CHAIN AND PRODUCTION PROCESS FOR THE SAME, TARGET DETECTOR, AND TARGET DETECTION METHOD**

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D01F 9/12 (2006.01)(52) **U.S. Cl.** 423/447.1(57) **ABSTRACT**

To provide a carbon nanotube chain consisting of a row of carbon nanotubes, the carbon nanotube chain being suitably used for instance as a target detector or sensor, and an efficient production process for the same. The carbon nanotube chain includes a support, and a plurality of carbon nanotubes bonded at one end to a surface of the support, wherein the plurality of carbon nanotubes is oriented in a direction substantially orthogonal to the surface of the support.

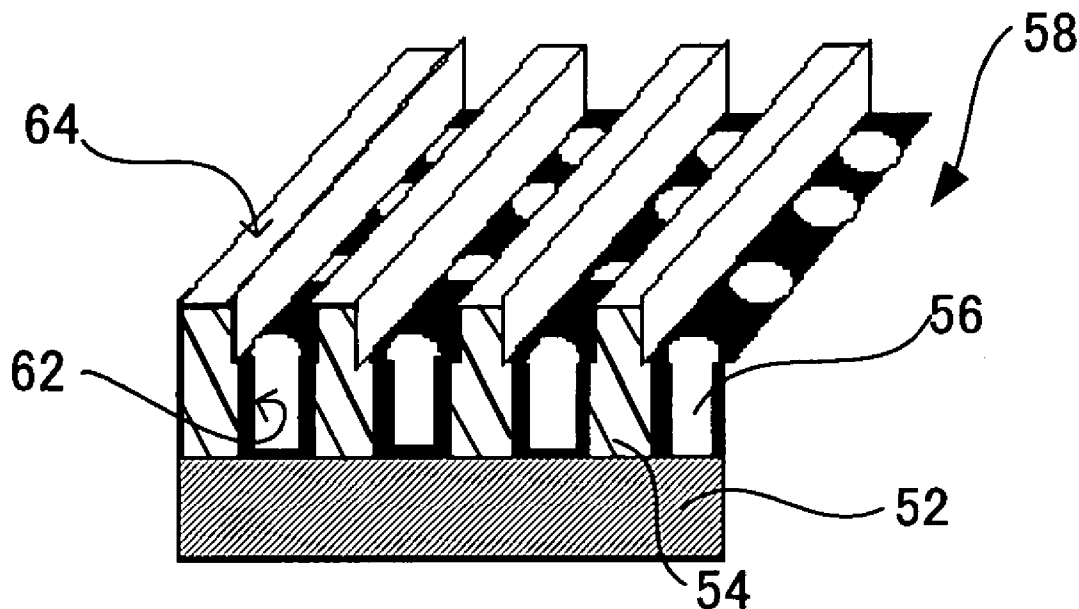


FIG. 1A

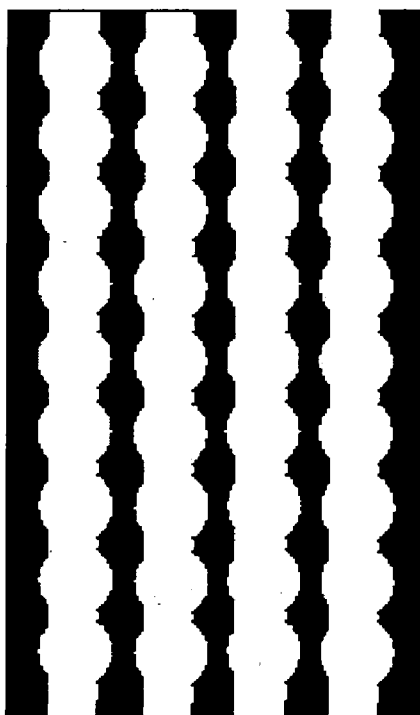


FIG. 1B

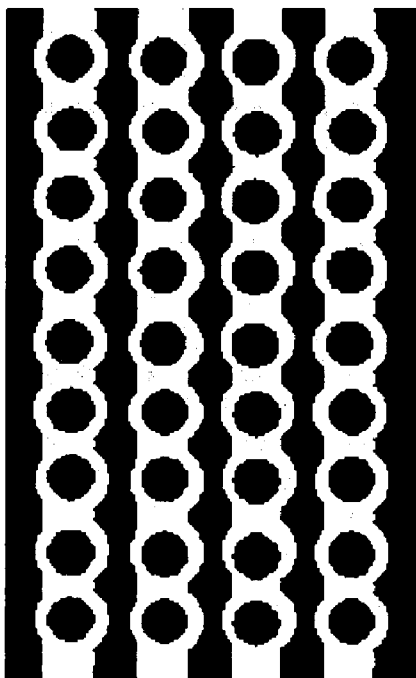


FIG. 2A

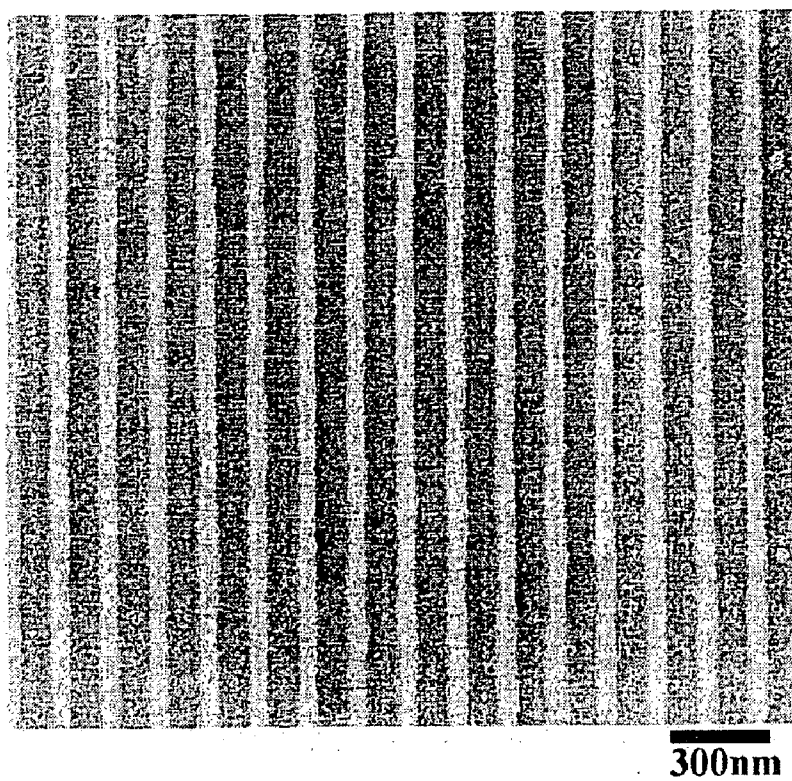


FIG. 2B

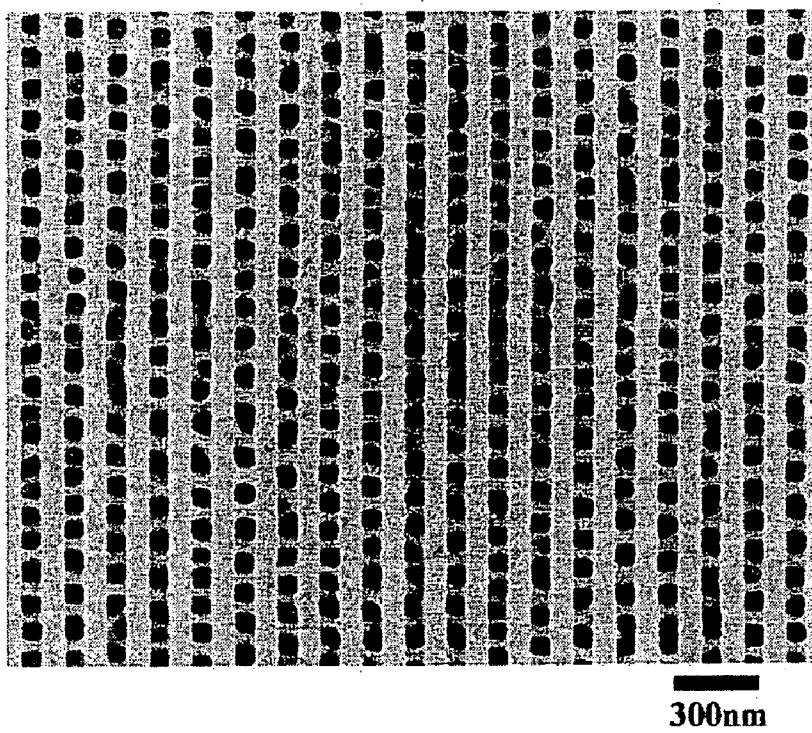


FIG. 3A



FIG. 3B

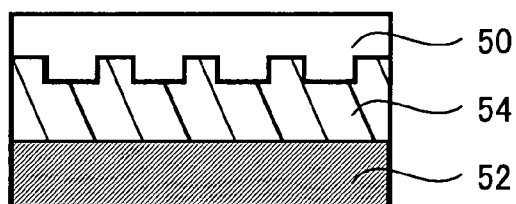


FIG. 3C

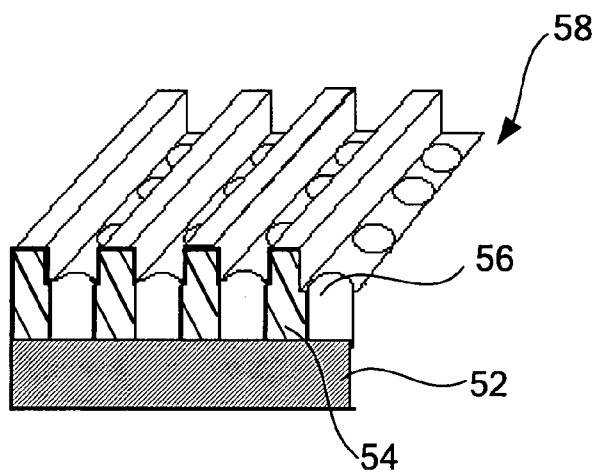


FIG. 3D

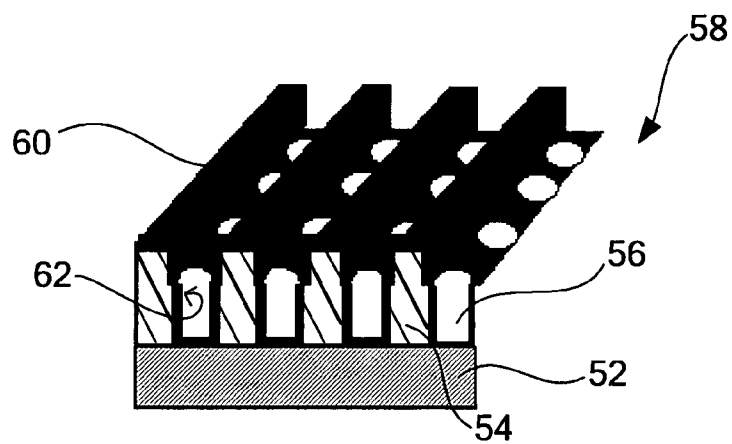


FIG. 3E

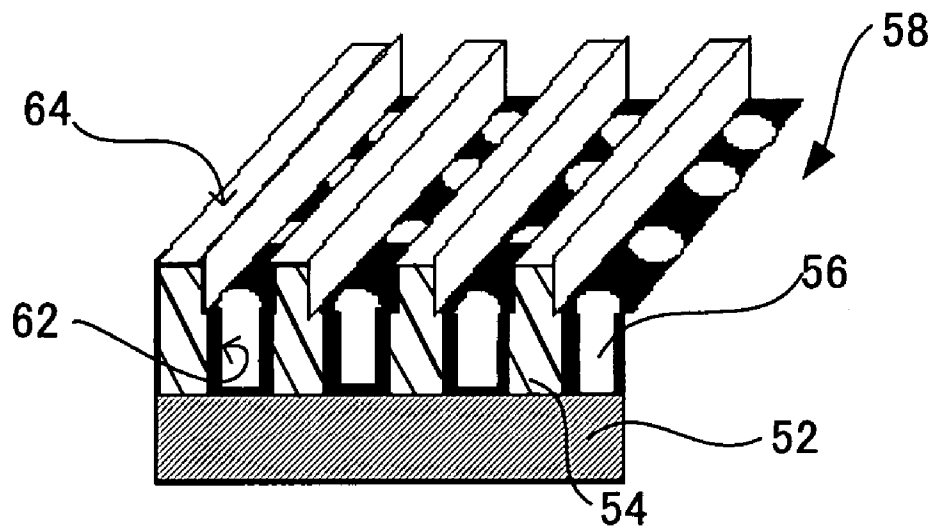


FIG. 3F

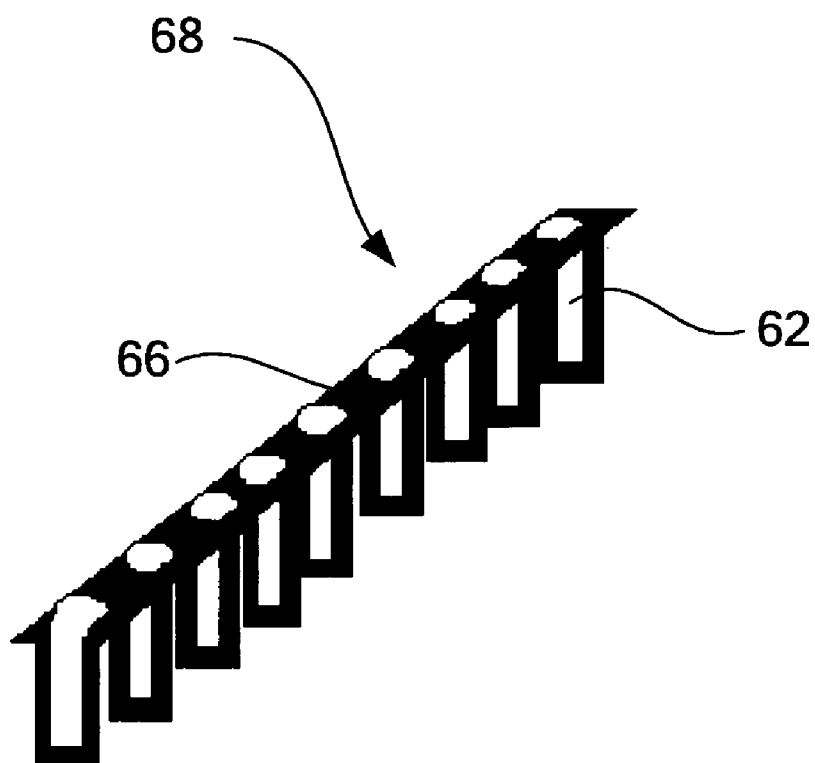


FIG. 4

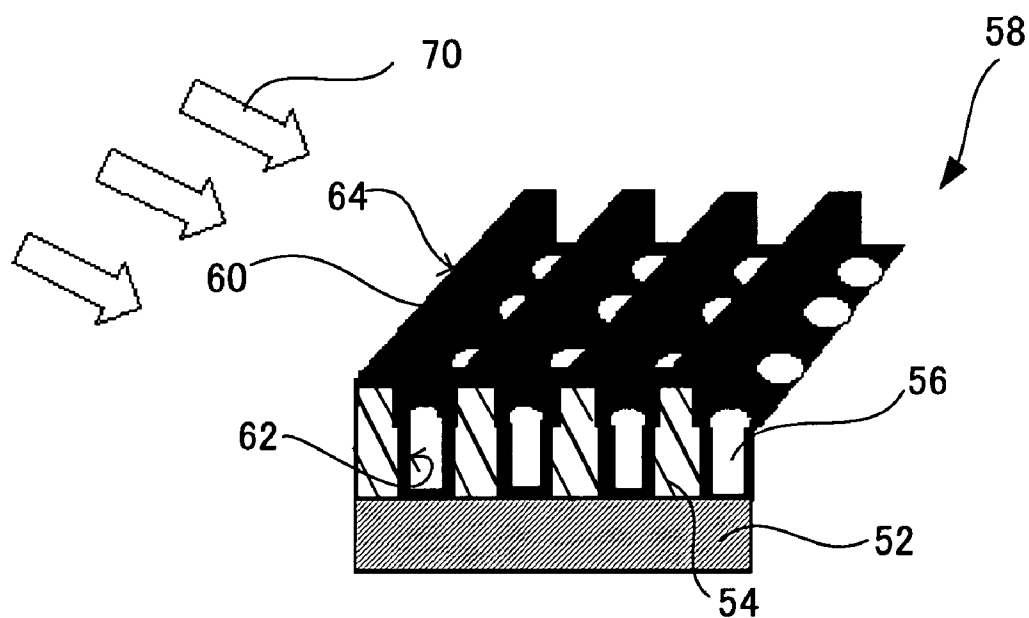


FIG. 5

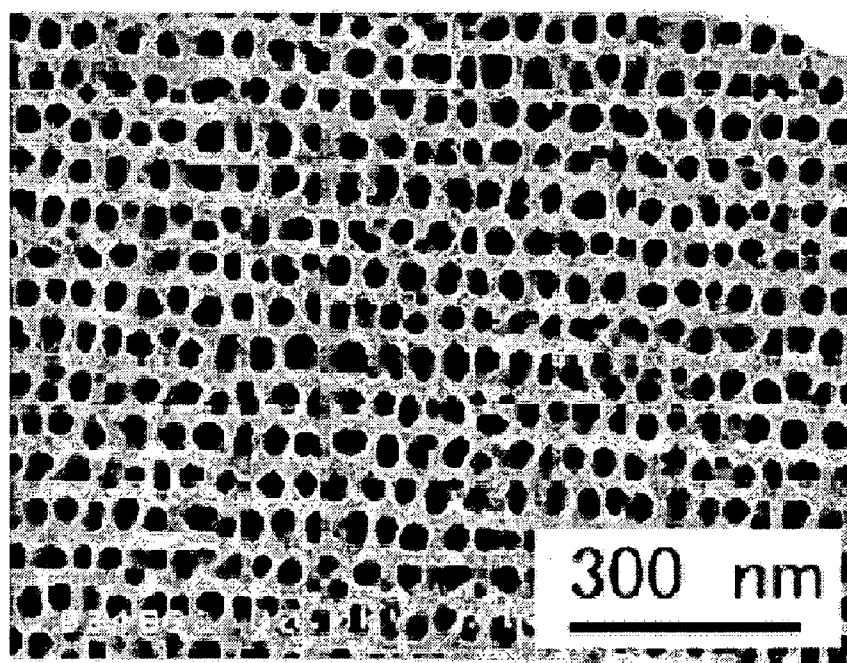


FIG. 6

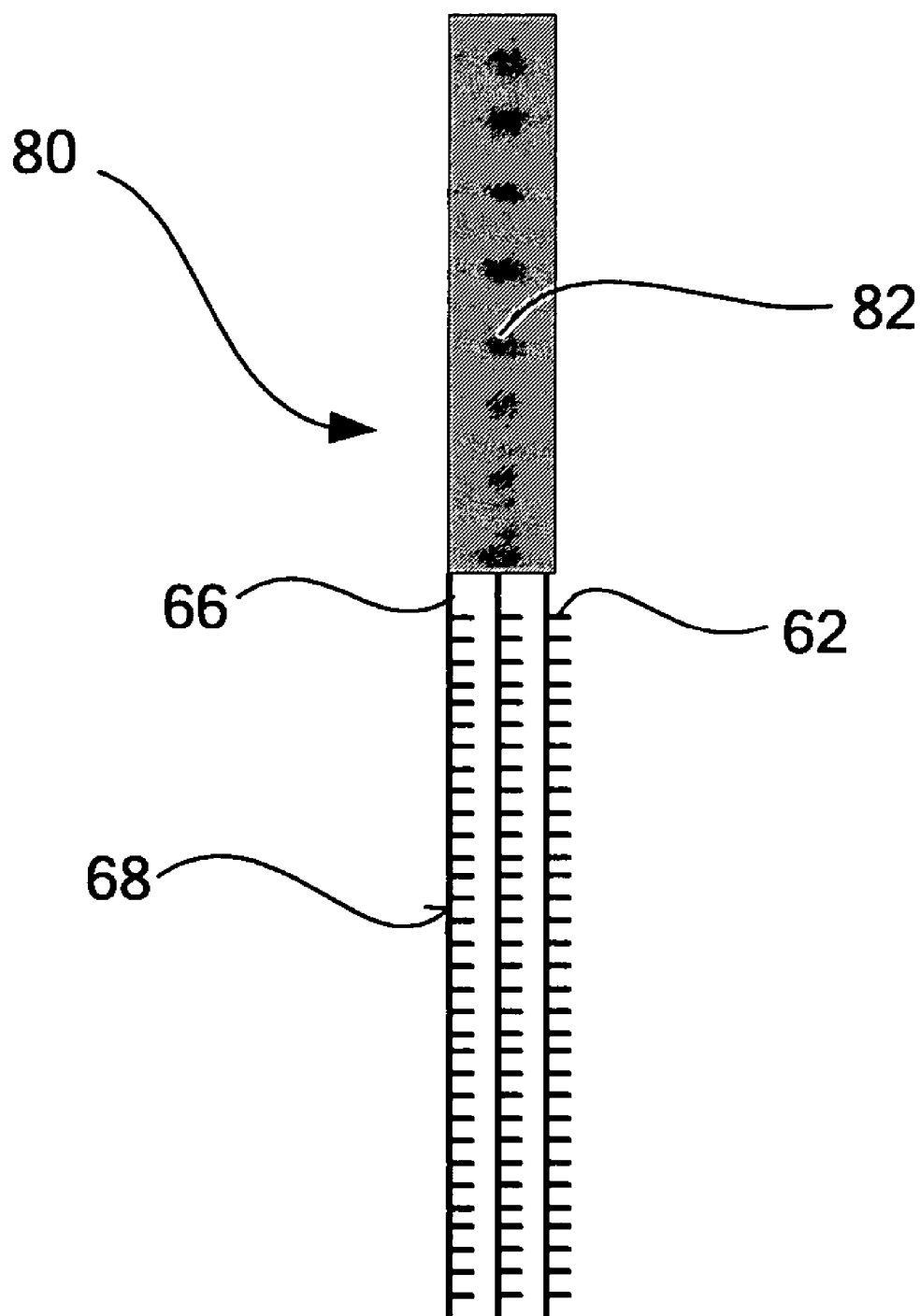


FIG. 7A

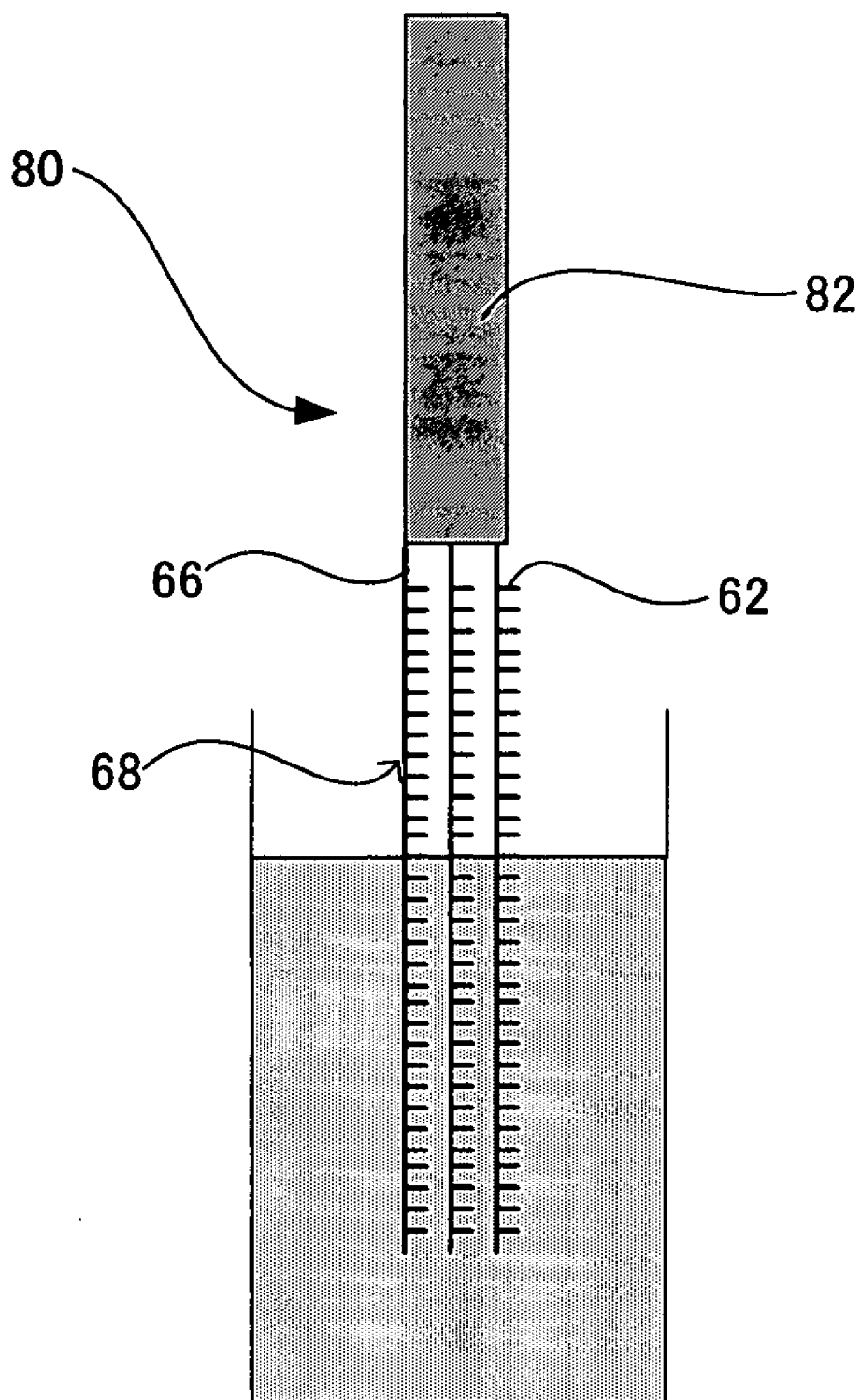
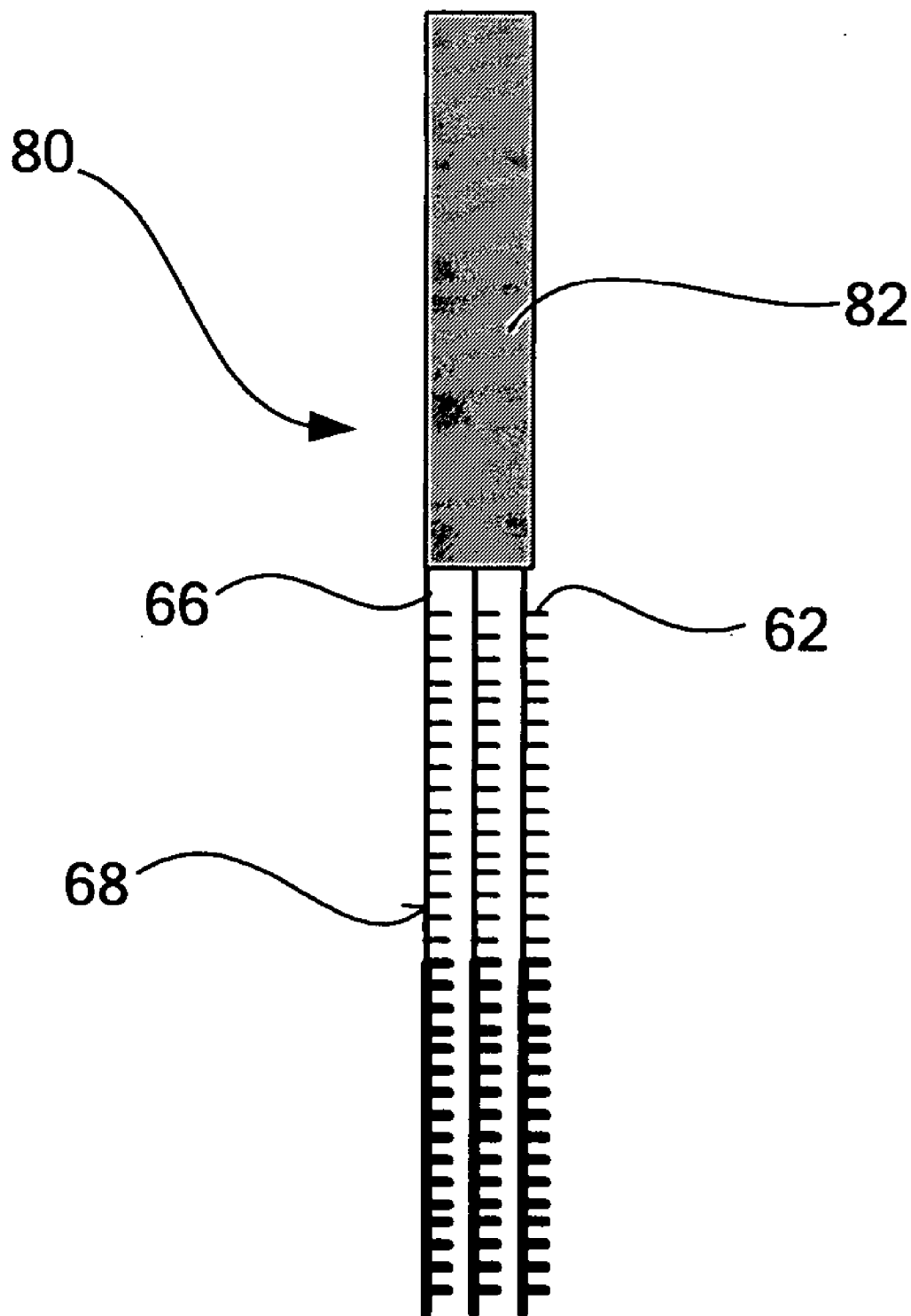


FIG. 7B



CARBON NANOTUBE CHAIN AND PRODUCTION PROCESS FOR THE SAME, TARGET DETECTOR, AND TARGET DETECTION METHOD

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is based upon and claims the benefits of the priority from the prior Japanese Patent Application No. 2006-100656 filed on Mar. 31, 2006, the entire contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a carbon nanotube chain consisting of a row of carbon nanotubes, a production process for the carbon nanotube chain, a target detector using the carbon nanotube chain, and a target detection method using the target detector.

[0004] 2. Description of the Related Art

[0005] Carbon nanotubes (hereinafter may be referred to "CNT") have been used as novel materials in various fields including electronics and electric industries, and have been produced for instance by arc discharging, laser vaporization, thermal chemical vapor deposition (thermal CVD) or plasma chemical vapor deposition (plasma CVD). Known carbon nanotubes produced by these methods are broadly classified into single-layer carbon nanotubes (single wall nanotube; SWNT) comprising a single graphene sheet, and multilayer carbon nanotubes (multi-wall nanotube; MWNT) comprising a plurality of graphene sheets.

[0006] Excellent physical properties of carbon nanotubes have made them fit for practical use in various applications, including micro devices such as integrated circuits, electrical connectors used in semiconductor chips in computers, batteries, high-frequency antennas, scanning tunnel microscopes, atomic force microscopes, and scanning probe microscopes. Moreover, there is an expectation that carbon nanotubes will find their application in many other fields. When multiple carbon nanotubes are to be used particularly in nanotechnology where high definition, high accuracy, etc., are required, it is desired that the carbon nanotubes be regularly spaced for use.

[0007] Carbon nanotubes prepared by arc discharging or the like, however, are not uniform in length, thickness, etc., and are produced as discrete fine particles; therefore, it is difficult to take a given number of the carbon nanotubes and align them at regular intervals.

[0008] To overcome this difficulty there is proposed a process for producing a carbonaceous nanostructure, the process including the steps of growing carbon nanofibers by vapor phase carbonization in anodized aluminum oxide (alumina) nanoholes used as a template, removing carbon deposited on the surface of the alumina layer, and dissolving away the anodized aluminum oxide (alumina) nanoholes (see Japanese Patent Application Laid-Open (JP-A) No. 2004-243477). This method has the advantage of being capable of precise control of the size of nanoholes under the anodization condition, as well as the size of the carbon nanotubes produced in the nanoholes. The produced anod-

ized aluminum oxide (alumina) nanoholes, however, are arranged two-dimensionally as with hexagonal closest packed structures and the like, and therefore, the resulting carbonaceous nanostructure is a two-dimensional aggregate of carbon nanotubes. For this reason, this method cannot provide carbon nanotubes that are arranged regularly (e.g., in a row).

[0009] An object of the present invention is to solve the foregoing conventional problems and to achieve the object described below. That is, an object of the present invention is to provide a carbon nanotube chain consisting of a row of carbon nanotubes of 1 μm or less in length, the carbon nanotube chain being suitably used for instance as a target detector or sensor; an efficient production process for the carbon nanotube chain; a target detector which is capable of high-sensitivity detection, and qualitative and quantitative analysis, of various types of targets including disease-causing substances, biological substances and toxic substances by using the carbon nanotube chain, and which can be suitably used as a biosensor and gas sensor; and a target detection method capable of easy, high-sensitivity detection of targets by using the target detector.

BRIEF SUMMARY OF THE INVENTION

[0010] The means of solving the foregoing problems are recited in the appended claims. That is, the carbon nanotube chain of the present invention includes a support and a plurality of carbon nanotubes bonded at one end to a surface of the support, wherein the plurality of carbon nanotubes is oriented in a direction substantially orthogonal to the surface of the support. As described above, the carbon nanotubes are bonded at one end to the support in such a way that they are oriented in a direction substantially orthogonal to the surface of the support. For this reason, when the support is a sheet-shaped article, a band-shaped article, or a linear article, it results in the formation of a sheet-shaped carbon nanotube chain, a band-shaped carbon nanotube chain, or a linear carbon nanotube chain, respectively. Moreover, since the carbon nanotube chain has an adsorption capability and releasing capability, it is capable of detection of various types of targets including disease-causing substances, biological substances and toxic substances, and of being suitably applicable to various fields including sensors such as target detectors, biosensors, and gas sensors.

[0011] The process of the present invention for producing a carbon nanotube chain is directed to the production of the carbon nanotube chain of the present invention, the process including forming grooves in a metallic layer and performing a nanohole formation treatment to form a nanohole structure in which a row of nanoholes is formed in each of the grooves, the nanoholes being oriented in a direction substantially orthogonal to a surface of the metallic layer (nanohole structure formation step); forming a carbon nanotube in each of the nanoholes (carbon nanotube formation step); removing carbon deposited on surfaces of lands of the metallic layer between the grooves (carbon removal step); and dissolving away the metallic layer (metallic layer dissolving step).

[0012] In the nanohole structure formation step of the process of the present invention, grooves are formed in a metallic layer, followed by nanohole formation treatment to the metallic layer. In this way, a nanohole structure is

obtained in which rows of nanoholes that are oriented in a direction substantially orthogonal to the surface of the metallic layer are formed in the grooves. In the carbon nanotube formation step, carbon nanotubes are formed in the nanoholes. In the carbon removal step, carbon deposited on surfaces of lands of the metallic layer between the grooves in the carbon nanotube formation step is removed. In the metallic layer dissolving step, the metallic layer is dissolved away. Through these steps, the carbon nanotube chain of the present invention is efficiently produced.

[0013] The target detector of the present invention includes the carbon nanotube chain of the present invention and a holder, wherein the carbon nanotube chain includes a capturing portion capable of capturing a detection target. Since the carbon nanotube chain of the present invention in the target detector includes such a capturing portion, various types of detection targets can be captured by the capturing portion. Moreover, since the carbon nanotube chain is immobilized to the holder, the target detector can be operated by hand. When two or more of the carbon nanotube chains are immobilized to the holder, it is possible to impart different functions to each carbon nanotube chain, and further to impart different functions to different sets of carbon nanotubes in each carbon nanotube chain. Accordingly, the target detector of the present invention is capable of high-sensitivity detection, and qualitative and quantitative analysis, of various types of targets including disease-causing substances, biological substances and toxic substances, and can be suitably used in various fields including sensors such as biosensors and gas sensors.

[0014] The target detection method of the present invention includes causing the target detector of the present invention to act on a sample containing a detection target. Since the target detection method of the present invention involves use of the target detector of the present invention that includes the carbon nanotube chain of the present invention, various types of detection targets act on the carbon nanotubes. Accordingly, the detection target in the sample can be detected with high sensitivity and with ease. When the target detector has two or more of the carbon nanotube chains, it is possible to impart different functions to each carbon nanotube chain, and further to impart different functions to different sets of carbon nanotubes in each carbon nanotube chain. Accordingly, different detection targets can act on the carbon nanotube chains or carbon nanotubes, thereby allowing simultaneous analysis of multiple detection targets.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0015] FIG. 1A is a schematic diagram showing a state before rows of nanoholes are formed that vary at regular intervals in width.

[0016] FIG. 1B is a schematic diagram showing a state after rows of nanoholes have been formed that vary at regular intervals in width.

[0017] FIG. 2A is a picture showing an example of a surface of an aluminum layer bearing a imprinted pattern of a mold.

[0018] FIG. 2B is a picture showing an example of rows of nanohole formed by anodizing the aluminum layer shown in FIG. 2A.

[0019] FIG. 3A is a first step view for explaining a step of the process of the present invention for producing a carbon nanotube chain.

[0020] FIG. 3B is a second step view for explaining a step of the process of the present invention for producing a carbon nanotube chain.

[0021] FIG. 3C is a third step view for explaining a step of the process of the present invention for producing a carbon nanotube chain.

[0022] FIG. 3D is a fourth step view for explaining a step of the process of the present invention for producing a carbon nanotube chain.

[0023] FIG. 3E is a fifth step view for explaining a step of the process of the present invention for producing a carbon nanotube chain.

[0024] FIG. 3F is a schematic diagram showing an example of the carbon nanotube chain of the present invention.

[0025] FIG. 4 is a schematic diagram showing an example of the carbon removing step in the process of the present invention for producing a carbon nanotube chain.

[0026] FIG. 5 is a picture showing an example of the arrangement of nanoholes formed over the surface of the anodized metallic layer.

[0027] FIG. 6 is a schematic diagram showing an example of the target detector of the present invention.

[0028] FIG. 7A is a first schematic diagram showing an example of an experimental technique for evaluation of the adsorption capability of the target detector of the present invention.

[0029] FIG. 7B is a second schematic diagram showing an example of an experimental technique for evaluation of the adsorption capability of the target detector of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

(Carbon Nanotube Chain and Production Process for the Same)

[0030] The process of the present invention for producing a carbon nanotube chain includes a nanohole structure formation step, a carbon nanotube formation step, a carbon removal step, and a metallic layer dissolving step, and further includes additional step(s) where necessary that are appropriately selected.

[0031] The carbon nanotube chain of the present invention can be suitably produced by the process of the present invention for producing a carbon nanotube chain. Hereinafter, the details of the carbon nanotube chain of the present invention will be provided in connection with the description of the process of the present invention.

<Nanohole Structure Formation Step>

[0032] The nanohole structure formation step is a step wherein grooves are formed in a metallic layer followed by nanohole formation treatment to form rows of nanoholes in

the grooves that are oriented in a direction substantially orthogonal to the surface of the metallic layer, to thereby form a nanohole structure.

[0033] The material, shape, size, etc., of the metallic layer are not particularly limited and can be appropriately determined depending on the intended purpose. Any material can be used as long as it is capable of forming nanoholes upon subjected to the nanohole formation treatment; examples include elementary metals, oxides thereof, nitrides thereof and alloys thereof, and among them, alumina (aluminum oxide) and aluminum are preferred.

[0034] The metallic layer may be formed on a substrate. In this case, the substrate may be made of any suitable material and may have any suitable shape, structure and size according to the intended purpose. Examples of the materials includes metals, glass, silicon, quartz and SiO_2/Si obtained by forming a thermally oxidized film on the surface of silicon. These materials can be used alone or in combination. Among them, metals are preferred in view of the fact that they can be used as an electrode upon anodization for nanoholes. Note that the substrate may be purchased ready-made or may be prepared as needed.

[0035] When nanoholes are to be produced by anodization, an electrode layer may be disposed between the substrate and metallic layer.

[0036] The material of the electrode layer can be any suitable material according to the intended purpose; examples include Nb, Ta, Ti, W, Cr, Co, Pt, Cu, Ir, Rh, and alloys thereof. These elements or alloys can be used alone or in combination. The electrode layer can be formed in accordance with any suitable procedure, such as vapor deposition or sputtering.

[0037] The thickness of the metallic layer is not particularly limited and can be appropriately determined depending on the intended purpose. The thickness of the metallic layer directly corresponds to the length of carbon nanotubes, and therefore, the metallic layer preferably has a thickness of 1 μm or less for the purpose of obtaining carbon nanotubes that are 1 μm or less in length. The thickness of the metallic layer can be made equal to the desired length of carbon nanotubes to be produced. Thus the length of the carbon nanotubes in the carbon nanotube chain of the present invention can be readily controlled by adjusting the thickness of the metallic layer. This is advantageous in that it is possible to equalize the lengths of the carbon nanotubes and to achieve uniform quality and physical properties.

[0038] The metallic layer can be formed in accordance with any suitable known procedure, such as vapor deposition or sputtering. In particular, sputtering is preferable because it is capable accurate and easy control of the thickness of the metallic layer.

[0039] The metallic layer can be suitably formed by sputtering of a sputtering target which is made of the same metal as the metallic layer to be deposited. The sputtering target can have any suitable purity according to the intended purpose, but preferably has a high purity. When the metallic layer is made of aluminum, the purity of aluminum in the sputtering target is preferably 99.990% or more.

[0040] Prior to anodization of the metallic layer, it is necessary to form rows of concaves (grooves) therein where

the nanoholes are to be formed. The use of anodization for the formation of nanoholes is advantageous because the nanoholes can be efficiently formed only in the grooves.

[0041] The cross section of the groove, a surface of the groove obtained by cutting the groove along its width, is not particular limited and can be appropriately determined depending on the intended purpose; for example, the cross section may be rectangular, V-shaped, or semicircular.

[0042] The method of forming grooves is not particularly limited and can be appropriately selected depending on the intended purpose; examples are: (1) a method wherein a mold with a pattern of regularly spaced rows of lands on its surface is imprinted (transferred) to a metallic layer (e.g., an alumina or aluminum layer) to thereby form thereon a line-and-space pattern comprising rows of alternating grooves and spaces (lands) arranged at regular intervals; (2) a method wherein a resin layer or a photoresist layer is formed on the metallic layer, patterned by normal photolithography and by imprinting using a mold, and etched to form rows of grooves in the surface of the metallic layer; and (3) a method wherein grooves are directly formed in the metallic layer.

[0043] By changing the widths of the rows of lands in the mold, the widths of the grooves in the photoresist layers, etc., at specific intervals (at regular intervals) along their length, it is possible to change (widen and narrow) the widths of the nanohole rows at regular intervals along their length correspondingly, whereby the intervals between adjacent nanoholes can be advantageously made equal in synchronization with the constant change in the groove width.

[0044] The mold can be any suitable one according to the intended purpose, but is preferably made of silicon, silicon dioxide, or combination thereof in view of the fact that these films are most widely used as the materials for manufacturing fine structures in the semiconductor field; in addition, for example, a silicon carbide substrate and a Ni stamper that is generally used in the molding of optical discs can be used in view of their high durability in continuous use. The mold can be used multiple times. The method of imprinting is not particularly limited and can be appropriately selected from those known in the art. Examples of the resist material for the photoresist layer include not only photoresist materials, but electron beam resist materials. The photoresist material for use herein can be selected from any suitable materials known for instance in the semiconductor field; examples are materials to which near-ultraviolet light and near-field light can be applicable.

[0045] The nanohole formation treatment is not particularly limited as long as it is capable of formation of nanoholes in the metallic layer, and can be appropriately selected for instance from anodization, etching, etc., depending on the intended purpose.

[0046] Among them, anodization is particularly preferable because it is capable of formation of a number of nanoholes in the metallic layer that are arranged at substantially regular intervals while causing the nanoholes to be oriented in a direction substantially perpendicular to the surface of the substrate.

[0047] Anodization can be carried out at any suitable voltage but preferably at such a voltage that satisfies the following equation: $V=I/A$, wherein V is the voltage in the

anodization; I is the interval (nm) between adjacent nanoholes; and A is a constant (nm/V) ≈ 2.5 .

[0048] When the anodization is carried out at a voltage satisfying the above equation, the resulting nanoholes are advantageously arranged in the rows of grooves.

[0049] The type, concentration and temperature of an electrolyte and the time period for anodization are not particularly limited and can be appropriately set according to the number, size and aspect ratio of the nanoholes to be formed. For example, the electrolyte is preferably a diluted phosphoric acid solution when the interval (pitch) of the adjacent rows of nanoholes ranges from 150 nm to 500 nm; is preferably a diluted oxalic acid solution when the interval ranges from 80 nm to 200 nm; and is preferably a diluted sulfuric acid solution when the pitch ranges from 10 nm to 150 nm. In either case, the aspect ratio of the nanoholes can be controlled by immersing the anodized metallic layer for instance in a phosphoric acid solution following anodization for increasing the diameter of the nanoholes (alumina pores).

[0050] When the nanohole structure formation step is carried out by anodization, it may result in the undesirable formation of a barrier layer at the bottom of each of the multiple nanoholes formed in the metallic layer, but the barrier layer can be easily removed by conventional etching using a conventional etchant like phosphoric acid.

[0051] Thus, in the nanohole structure formation step, a nanohole structure is formed in which multiple nanoholes are oriented in a direction substantially perpendicular to the surface of the metallic layer.

[0052] The nanoholes in the nanohole structure are not particularly limited in terms of shape, and any shape can be adopted depending on the intended purpose; however, they may be formed as holes or dents, more preferably as through holes.

[0053] The interval between adjacent rows of nanoholes is not particularly limited and can be appropriately determined depending on the intended purpose; however, the interval is preferably 5 nm to 500 nm, more preferably 10 nm to 200 nm.

[0054] An interval of less than 5 nm makes the formation of nanoholes difficult, whereas an interval of greater than 500 nm makes it difficult to arrange them at regular intervals.

[0055] The ratio of the interval between adjacent rows of nanoholes to the width of a row of nanoholes is not particularly limited and can be appropriately set depending on the intended purpose; for example, the ratio preferably ranges from 1.1 to 1.9, and more preferably from 1.2 to 1.8.

[0056] A ratio (interval/width) less than 1.1 may cause hole fusion between adjacent nanoholes and it may result in failure to produce discrete nanoholes, whereas a ratio exceeding 1.9 may result in the formation of nanoholes in portions other than the grooves during anodization.

[0057] The width of the rows of nanoholes is not particularly limited and can be appropriately set according to the intended purpose; for example, the row width is preferably 5 nm to 450 nm, and more preferably 10 nm to 200 nm.

[0058] A row width of less than 5 nm makes the formation of nanoholes difficult, whereas a row width of greater than 450 nm makes it difficult to arrange them at regular intervals.

[0059] In addition, the row width may be constant along the length or may vary (widen or narrow) at specific intervals as shown in FIG. 1A. The latter case is preferable because it becomes likely that nanoholes are formed at regular intervals along the nanohole row at areas that are larger in width than other areas, as shown in FIG. 1B.

[0060] The depth of the nanoholes is generally 10 μm or less but is not particularly limited and can be appropriately set depending on the intended purpose; however, the nanohole depth is preferably 1 μm or less in view of the fact that it corresponds to the length of the carbon nanotubes in the carbon nanotube chain of the present invention.

[0061] The opening diameter of the nanoholes is not particularly limited and can be appropriately set depending on the intended purpose; the opening diameter is generally one-third the nanohole interval that is determined depending on the anodization voltage, but the opening diameter can be increased as needed by treatment with phosphoric acid solution.

—Carbon Nanotube Formation Step—

[0062] The carbon nanotube formation step is a step for forming carbon nanotubes inside the nanoholes.

[0063] The carbon nanotubes can be formed according to any suitable procedure, such as chemical vapor deposition (CVD).

[0064] Examples of chemical vapor deposition (CVD) procedure are thermal CVD (also simply referred to as “CVD”), hot filament CVD, plasma-enhanced CVD (also referred to as “plasma-assisted CVD or plasma CVD”), plasma-enhanced hot filament CVD, and laser-enhanced CVD (also referred to as “laser CVD”). Among them, thermal CVD and plasma CVD are preferred.

[0065] In thermal CVD, a reaction tube containing a nanohole structure is heated to around 400° C. to 2,000° C. in an electrical furnace, followed by introduction of material gas into the tube to decompose the material, allowing carbon or carbon nanotubes to deposit in the nanoholes.

[0066] In plasma CVD, the material gas is decomposed by reaction with a plasma excited by radio-frequency (RF) waves of about 0.1 to 1,000 W/cm², thereby allowing carbon to deposit. Instead of the plasma excited by radio-frequency (RF) waves, plasmas excited for example by low-frequency waves, microwaves (MW) or direct current (DC) can also be used.

[0067] The conditions used for the formation of carbon nanotubes by CVD are not particularly limited and can be suitably selected depending on the intended purpose. For example, it is preferable to control the flow rate of the material gas and to use as the material gas a mixture gas of carbon-source gas and carrier gas.

[0068] Examples of the carbon-source gas are methane, ethylene, propylene, acetylene, benzene, butane, methanol, ethanol, propanol, isopropanol, C₁₀H₁₆, CS₂, and C₆₀ gases. Examples of the carrier gas are nitrogen, argon, hydrogen and NH₃ gases.

[0069] The proportions of the carbon-source gas and carrier gas in the mixture gas are not particularly limited and can be set depending on the intended purpose. For example, where propylene gas is used as the carbon-source gas and

nitrogen gas as the carrier gas, the mixture gas is preferably fed under the condition that the ratio of the flow rate of propylene gas to that of nitrogen gas is about 1:99 to 5:95 and that the total flow rate is 100 cm³/min to 300 cm³/min. The temperature at this point is preferably 500° C. to 900° C., and most preferably around 800° C.

[0070] When carbon nanotubes are to be produced, for example, by CVD in the carbon nanotube formation step, the material of the metallic layer serves as catalyst for forming the carbon nanotubes, and thus an extra catalyst is not required. For example, when the metallic layer is made of aluminum, the alumina present at the exposed surface of the metallic layer serves as catalyst by which the formation of carbon nanotubes is facilitated.

[0071] The carbon nanotubes produced by the carbon nanotube formation step are substantially identical in diameter, length, and the number of layers, and when the thickness of the metallic layer is made 1 μm or less, the carbon nanotubes have an average length of 1 μm or less, with one end of each nanotube being closed.

<Carbon Removal Step>

[0072] The carbon removal step is a step for removing carbon deposited on surfaces of lands between the grooves in the carbon nanotube formation step.

[0073] The formation of grooves in the metallic layer in the nanohole structure formation step results in the formation of lands of metallic layer between the grooves. Subsequently, in the carbon nanotube formation step, carbon nanotubes are formed in the nanoholes in the grooves, and at the same time, carbon is deposited on the lands. The carbon removal step is directed to remove carbon deposited on the surfaces of the lands. By performing a metallic layer dissolving step to be described later, it results in the formation of carbon nanotube chains of the present invention of any of sheet shape, band shape, string shape, etc., each of which consisting of regularly spaced carbon nanotubes bonded to a carbon layer derived from carbon deposited over the groove of the metallic layer (nanohole structure). In each of the carbon nanotube chains, the carbon nanotubes are oriented in a direction substantially perpendicular to the surface of the carbon layer.

[0074] The method of carbon removal is not particularly limited and can be appropriately determined depending on the intended purpose; for example, a method of etching away carbon deposited on the lands of the metallic layer by wrapping or chemical mechanical polishing (CMP) is used. In particular, methods of removing carbon deposited to the side walls of the lands are: (1) a method that involves application of oxygen plasma (including application of voltage to the substrate) at angles with respect to the length and height of the lands of the metallic layer to etch away deposited carbon; (2) a method that involves application of an ion beam (e.g., an oxygen ion beam) at angles with respect to the length and height of the lands of the metallic layer to remove deposited carbon; (3) a method that involves control of an oxygen atmosphere and application of an ion beam at angles with respect to the length and height of the lands of the metallic layer to remove deposited carbon; and so forth.

[0075] Note that the condition used in the carbon removal step is not particularly limited and can be appropriately set

depending on the intended purpose. In addition, the angle at which the plasma is applied to the lands of the metallic layer with respect to their length and height in the method (1), and the angle at which the ion beams in the methods (2) and (3) are applied can be determined appropriately.

<Metallic Layer Dissolving Step>

[0076] The metallic layer dissolving step is a step of dissolving away the metallic layer (nanohole structure). By performing this step, it is possible to obtain the carbon nanotube chain of the present invention.

[0077] The condition, etc., used in the metallic layer dissolving step are not particularly limited and can be appropriately determined depending on the intended purpose. In the case of alumina nanoholes, specific examples of procedures employed in this step are immersion in hydrogen fluoride (HF) and hydrothermal treatment with sodium hydroxide (NaOH).

<Additional Steps>

[0078] The additional steps are not particularly limited and can be appropriately selected according to the intended purpose; examples are a washing step and a drying step.

[0079] The carbon nanotube chain of the present invention is efficiently produced by the process of the present invention described above for producing a carbon nanotube chain.

[0080] The carbon nanotube chain of the present invention consists of a row of multiple carbon nanotubes bonded at one end to a support in such a way that they are oriented in a direction substantially perpendicular to the surface of the support.

[0081] The material, shape, structure, size, thickness, etc., of the support are not particularly limited and can be appropriately determined depending on the intended purpose; however, the material is preferably carbon. If the support is made of carbon, the carbon nanotube chain can be readily formed. To be more specific, a carbon layer is deposited on the metallic layer (nanohole structure) upon formation of carbon nanotubes in the nanoholes during the carbon nanotube formation step, and the carbon layer deposited on the grooves of the metallic layer is then integrally bonded to the carbon nanotubes that are oriented in a direction substantially perpendicular to the surface of the carbon layer. The obtained single piece article corresponds to the carbon nanotube chain described above.

[0082] Examples of the shape of the support include a sheet shape, band shape, and linear shape. Among these shapes, the support is preferably of linear shape because it can be readily designed and can be applicable to a wide range of fields.

[0083] The thickness of the support is not also particularly limited as long as it is capable of holding carbon nanotubes; for example, the thickness is preferably 2 nm to 20 nm.

[0084] The number of carbon nanotubes present in the carbon nanotube chain is not particularly limited; it varies depending on the intervals between nanoholes in the nanohole structure and on the length of the carbon nanotube chain, and can be appropriately determined depending on the intended purpose.

[0085] In the carbon nanotube chain, it is preferable that an end of each carbon nanotube to be bonded to the support be opened, with the other end being closed. A carbon nanotube chain having this configuration offers excellent chemical stability and never undergoes oxidation or the like with time. Accordingly, the carbon nanotube chain can be suitably used in various applications.

[0086] The carbon nanotubes in the carbon nanotube chain are preferably identical in at least one of length, size, and outer diameter. When such a carbon nanotube chain is used for target detection or as a sensor, each carbon nanotube acts to a similar extent, thus achieving a stable operation.

[0087] The length of each carbon nanotube can be made equal to the thickness of the metallic layer, and therefore, it is possible to readily obtain a carbon nanotube chain having small carbon nanotubes of 1 μm or less in length. Again, since the length of the carbon nanotubes corresponds to the thickness of the metallic layer (e.g., an aluminum layer or alumina layer), it is possible to control the carbon nanotubes so as to have a desired length readily, precisely, and uniformly, by controlling the thickness of the metallic layer.

[0088] The carbon nanotube is preferably covered with a functional material; examples thereof include biological molecules such as antibody. Although the carbon nanotube itself exhibits adsorption capability and releasing capability, covering the carbon nanotube with such a biological molecular makes detection of various targets possible by means of the biological molecule.

[0089] Use applications of the carbon nanotube chain of the present invention are not particularly limited and can be appropriately selected depending on the intended purpose; for example, the carbon nanotube chain of the present invention is preferably used for capturing a detection target. In this application, the carbon nanotube chain preferably has a target capturing body.

—Target Capturing Body—

[0090] It is preferable for the target capturing body to have a binding portion capable of being bound to the carbon nanotube chain, and a target capturing portion capable of capturing a detection target. The reason for this is that it is possible to efficiently to achieve separate functions in one molecule.

[0091] The form in which the carbon nanotube chain is bound to the target capturing body is not particularly limited and can be appropriately determined depending on the intended purpose; however, they are preferably held together by chemical bonds because they can be bonded together more firmly.

[0092] The target capturing body is not particularly limited as long as it is capable of capturing a detection target at the target capturing portion, and can be appropriately selected according to the intended purpose.

[0093] The manner in which the target capturing body capture a target is not particularly limited; capturing may be achieved by physical adsorption, chemical adsorption or the like, which are realized by hydrogen bonding, intermolecular force (van der Waals force), coordination bonding, ionic bonding or covalent bonding.

[0094] Suitable examples of the target capturing portion include those formed from enzymes, coenzymes, enzyme

substrates, enzyme inhibitors, clathrate compounds (hereafter may be referred to as “host compounds” or “hosts”), metals, antibodies, antigens, proteins, microorganisms, viruses, cell debris, metabolites, nucleic acids, hormones, hormone receptors, lectins, sugars, physiologically active substances and physiologically active substance receptors, allergens, blood proteins, tissue proteins, nucleic substances, virus particles, neurotransmitters, heptanes, parasites, endocrine-disturbing chemicals, and chemical species or derivatives thereof.

—Detection Target—

[0095] When the target capturing portion is an enzyme, the detection target is for example a coenzyme of this enzyme; when it is a coenzyme, the detection target is for example an enzyme for which this coenzyme functions as a coenzyme; when it is a clathrate compound, the detection target is for example a guest compound (component to be contained) of this clathrate compound; when it is an antibody, the detection target is for example a protein which is an antigen against this antibody; when it is a protein, the detection target is for example an antibody recognizes this protein as an antigen; when it is a nucleic acid, the detection target is for example a nucleic acid complementary to this nucleic acid; when it is a hormone receptor such as tubulin or chitin, it is for example a hormone received by this hormone receptor; when it is a lectin, it is for example a sugar received by this lectin; and when it is a physiologically active substance receptor, it is for example a physiologically active substance received by this physiologically active substance receptor.

[0096] Samples containing the above-noted detection targets are not particularly limited and can be appropriately selected depending on the intended purpose; examples include pathogens such as bacteria and viruses; blood, saliva, tissue sections, which are isolated from living organisms; and excreta such as feces and urine. Upon prenatal diagnosis, some embryo cells in the amniotic fluid or some in vitro dividing egg cells can also be used as sample. The sample may be directly, or after being condensed as sediment by centrifugation or the where necessary, subjected to cell destruction treatment (e.g., enzyme treatment, heat treatment, surfactant treatment, ultrasonic treatment or any combinations thereof) before use.

[0097] The clathrate compound is not particularly limited as long as it has molecular recognition capability (i.e., host-guest binding capability), and can be appropriately selected according to the intended purpose; examples include those with a cylindrical (one-dimensional) hollow, those with a stratified (two-dimensional) hollow, and those with a cage-shaped (three-dimensional) hollow.

[0098] Examples of clathrate compounds comprising a cylindrical (one-dimensional) hollow include urea, thiourea, deoxycholic acid, dinitrodiphenyl, dioxytriphenylmethane, triphenylmethane, methyl naphthalene, spirochroman, PHTP (perhydrotriphenylene), cellulose, amylose and cyclodextrin (in solution, the hollows are cage-shaped).

[0099] Examples of detection targets which can be captured by urea include n-paraffin derivatives.

[0100] Examples of detection targets which can be captured by thiourea include branched and cyclic hydrocarbons.

[0101] Examples of detection targets which can be captured by deoxycholic acid include paraffins, fatty acids and aromatic compounds.

[0102] Examples of detection targets which can be captured by dinitrodiphenyl include diphenyl derivatives.

[0103] Examples of detection targets which can be captured by dioxytriphenylmethane include paraffins, n-alkenes and squalene.

[0104] Examples of detection targets which can be captured by triphenylmethane include paraffins.

[0105] Examples of detection targets which can be captured by methylnaphthalene include n-paraffins and branched paraffins, both having up to 16 carbon atoms.

[0106] Examples of detection targets which can be captured by spirochroman include paraffins.

[0107] Examples of detection targets which can be captured by PHTP (perhydrotriphenylene) include chloroform, benzene and various polymer substances.

[0108] Examples of detection targets which can be captured by cellulose include H_2O_2 , paraffins, CCl_4 , dyes and iodine.

[0109] Examples of detection targets which can be captured by amylose include fatty acids and iodine.

[0110] Cyclodextrins are cyclic dextrins generated by decomposition of is starch by amylase, and there are three known types: α -cyclodextrin, β -cyclodextrin, and γ -cyclodextrin. Cyclodextrins used in the present invention also include cyclodextrin derivatives wherein some of their hydroxyl groups are replaced by other functional groups, such as alkyl groups, allyl groups, alkoxy groups, amide groups and/or sulfonic acid groups.

[0111] Examples of detection targets which can be captured by cyclodextrins include phenol derivatives such as thymol, eugenol, resorcinol, ethylene glycol monophenyl ether and 2-hydroxy-4-methoxy-benzophenone; benzoic acid derivatives such as salicylic acid, methyl parahydroxybenzoate and ethyl p-hydroxybenzoate and esters thereof; steroids such as cholesterol; vitamins such as ascorbic acid, retinol and tocopherol; hydrocarbons such as limonene, allyl isothiocyanate; sorbic acid; iodine molecule; methyl orange; Congo Red; and 2-p-toluidinylnaphthalene-6-sulfonic acid potassium salt (TNS).

[0112] Examples of the stratified (two-dimensional) clathrate include clay minerals, graphite, smectite, montmorillonite and zeolite.

[0113] Examples of detection targets which can be captured by clay minerals include hydrophilic substances and polar compounds.

[0114] Examples of detection targets which can be captured by graphite include O, HSO_4^- , halogens, halides and alkali metals.

[0115] Examples of detection targets which can be captured by montmorillonite include brucine, codeine, o-phenylenediamine, benzidine, piperidine, adenine, guanine and ribosides thereof.

[0116] Examples of a detection target which can be captured by zeolite include H_2O and the like.

[0117] Examples of the cage-shaped (three-dimensional) clathrate compound include hydroquinones, gaseous hydrates, tri-o-thymotide, oxyflavane, dicyanoamine nickel, cryptands, calixarenes and crown compounds.

[0118] Examples of detection targets which can be captured by hydroquinones include HCl, SO_2 , acetylene and rare gas elements.

[0119] Examples of detection targets which can be captured by gaseous hydrates include halogens, rare gas elements and lower hydrocarbons.

[0120] Examples of detection targets which can be captured by tri-o-thymotide include cyclohexane, benzene and chloroform.

[0121] Examples of detection targets which can be captured by oxyflavane include organic bases.

[0122] Examples of detection targets which can be captured by dicyanoamine nickel are benzene and phenol.

[0123] Examples of detection targets which can be captured by cryptands include NH_4^+ and various metal ions.

[0124] Calixarenes are cyclic oligomers wherein phenol units are linked together by methylene groups, which can be prepared from phenol and formaldehyde under suitable conditions; 4- to 8-mers are known. Among these, examples of detection targets which can be captured by p-t-butylcalixarene (n=4) include chloroform, benzene and toluene. Examples of detection targets which can be captured by p-t-butyl calixarene (n=5) include isopropyl alcohol and acetone. Examples of detection targets which can be captured by p-t-butyl calixarene (n=6) are chloroform and methanol. Examples of detection targets which can be captured by p-t-butyl calixarene (n=7) include chloroform.

[0125] Examples of crown compounds include not only crown ethers having oxygen as an electron-donating atom, but also as analogues large ring compounds having electron-donating atoms such as nitrogen and sulfur as ring components, and also include complex cyclic crown compounds having two or more rings such as cryptands typified by cyclohexyl-12-crown-4, dibenzo-14-crown-4, t-butylbenzo-15-crown-5, dibenzo-18-crown-6, dicyclohexyl-18-crown-6, 18-crown-6, tribenzo-18-crown-6, tetrabenzo-24-crown-8 and dibenzo-26-crown-6.

[0126] Examples of detection targets which can be captured by the crown compounds include various metal ions from alkali metals such as Li, Na and K; metal ions from alkaline earth metals such as Mg and Ca; NH_4^+ ; alkylammonium ions; guanidium ions; and aromatic diazonium ions. The crown compounds form a complex with these ions. Examples of other detection targets which can be captured by the crown compounds include polar organic compounds containing a C—H unit that has a relatively large acidity (e.g., acetonitrile, malonitrile and adiponitrile), a N—H unit (e.g., aniline, aminobenzoic acid, amides and sulfamide derivatives) and an O—H unit (e.g., phenols, acetic acid derivatives), the crown compounds also form a complex with these polar organic compounds.

[0127] The size (diameter) of the hollow of the clathrate compounds is not particularly limited and can be appropriately set according to the intended purpose, but in order for the clathrate compounds to offer a stable molecular recog-

nitration capability (host-guest binding capability), the diameter is preferably 0.1 nm to 2.0 nm.

[0128] In addition, clathrate compounds can be classified into monomolecular host compounds, polymolecular host compounds, polymer host compounds and inorganic host compounds, for example.

[0129] Examples of monomolecular host compounds include cyclodextrin, crown compounds, cyclophane, azacyclophane, calixarene, cyclotrimeratrylene, spherand, cavitan and oligopeptides.

[0130] Examples of polymolecular host compounds are urea, thiourea, deoxycholic acid, perhydrotriphenylene and tri-o-thymotide.

[0131] Examples of polymer host compounds include cellulose, starch, chitin, chitosan and polyvinyl alcohol.

[0132] Examples of inorganic host compounds include intercalation compounds, zeolites and Hofmann type complexes.

[0133] The antibody is not particularly limited as long as it undergoes an antigen-antibody reaction with a specific antigen; it may be a polyclonal antibody or monoclonal antibody, and further examples include IgG, IgM, IgE, Fab', Fab, F(ab')₂ of IgG, and avidin.

[0134] The antigen is not particularly limited and can be appropriately selected according to the identity of antibody; examples include plasma proteins, tumor markers, apoproteins, virus antigens, autoantibodies, coagulation/fibrinolysis factor, hormones, drugs in blood, HLA antigens and biotin.

[0135] Examples of plasma proteins include immunoglobulins (IgG, IgA, IgM, IgD, and IgE), complementary components (C3, C4, C5, and C1q), CRP, α_1 -antitrypsin, α_1 -microglobulin, β_2 -microglobulin, haptoglobin, transferrin, ceruloplasmin and ferritin.

[0136] Examples of tumor markers include α -fetoprotein (AFP), carcinoembryonic antigen (CEA), CA 19-9, CA125, CA 15-3, SCC antigen, prostate gland acid phosphatase (PAP), PIVKA-II, γ -seminoprotein, TPA, Elastase I, nerve specific enolase (NSE) and immunosuppression acidic protein (IAP).

[0137] Examples of apoproteins are apo A-I, apo A-II, apo B, apo C-II, apo C-III and apo E.

[0138] Examples of virus antigens include hepatitis B virus (HBV) antigens, hepatitis C virus (HCV) antigens, HTLV-I, HIV, rabies virus, influenza virus and rubella virus.

[0139] Examples of HCV antigens include HCVc100-3 recombinant antigen, pHCV-31 recombinant antigen and pHCV-34 recombinant antigen, and mixtures thereof can be used suitably. Examples of HIV antigens include virus surface antigens such as HIV-I env.gp41 recombinant antigen, HIV-I env.gp120 recombinant antigen, HIV-I gag.p24 recombinant antigen and HIV-II env.p36 recombinant antigen.

[0140] Pathogens other than viruses are MRSA, ASO, toxoplasma, mycoplasma, and STD, for example.

[0141] Examples of autoantibodies include anti-mitochondrion antibody, anti-siloglobulin antibody, antinuclear antibody, rheumatism factor, anti-mitochondrion antibody and myelin antibody.

[0142] Examples of coagulation/fibrinolysis factors include fibrinogen, fibrin decomposed products (FDP), plasminogen, α_2 -plasmin inhibitor, Antithrombin III, β -thromboglobulin, Factor VIII, Protein C and Protein S.

[0143] Examples of hormones include pituitary hormones (LH, FSH, GH, ACTH, TSH, and prolactin), thyroid hormones (T₃, T₄, and siloglobulin), calcitonin, parathyroid hormone (PTH), adenocorticotrophic hormones (aldosterone, cortisol), gonad hormone (hCG, estrogen, testosterone, hPL), and pancreatic and gastrointestinal hormones (insulin, C-peptide, glucagon, gastrin). Other examples include renin, Angiotensin I, Angiotensin II, enkephalin and erythropoietin.

[0144] Examples of drugs in blood are antiepileptics such as carbamazepine, primidone and valproic acid; circulatory organ disease drugs such as digoxin, quinidine, digitoxin and theophylline; and antibiotics such as gentamycin, kanamycin and streptomycin.

[0145] Suitable examples of the foregoing proteins include proteins with low molecular weight ranging from about 6,000 to 13,000, which have high affinity to heavy metals, in particular zinc, cadmium, copper and mercury. These proteins are present in the liver, kidney and other organs or tissues of the animal, and have recently been shown to reside also in microorganisms. They have a high content of cysteine and contain a distribution of amino acids with almost no aromatic residues. In addition, they are important substances which detoxify cadmium and mercury in the body and also participate in the storage and distribution of trace metals indispensable to the living body, such as zinc and copper.

[0146] Examples of such heavy metals include alkyl mercury compounds (R—Hg), mercury (Hg) or compounds thereof, cadmium (Cd) or compounds thereof, lead (Pb) or compounds thereof, hexavalent chromium (Cr₆⁺), copper (Cu) or compounds thereof, zinc (Zn) or compounds thereof, cyan, arsenic, selenium, manganese, nickel, iron, zinc, selenium, and tin.

[0147] According to the process of the present invention for producing a carbon nanotube chain, it is possible to produce the carbon nanotube chain efficiently.

[0148] The carbon nanotube chain of the present invention consists of the foregoing carbon nanotubes that are regularly spaced and have both adsorption capability and releasing capability. For this reason, the carbon nanotube chain of the present invention can be readily designed and handled, and can be applicable to a wide range of fields. For example, the carbon nanotube chain of the present invention is capable of detection of various types of targets including disease-causing substances, biological substances and toxic substances, and of being suitably applicable to various fields including sensors such as target detectors, biosensors, and gas sensors.

(Target Detector)

[0149] The target detector of the present invention comprises the carbon nanotube chain of the present invention and a holder and, where necessary, further comprises additional member(s) appropriately selected.

[0150] The carbon nanotube chain preferably comprises a capturing portion capable of capturing a detection target.

[0151] The capturing portion is not particularly limited as long as it is capable of capturing a detection target, and can be appropriately selected depending on the intended purpose; however, the capturing portion is preferably formed of the foregoing target capturing body, and the carbon nanotube chain and the target capturing body are preferably held together by chemical bonding.

[0152] Note that details of the carbon nanotube chain, detection target, and target capturing body are the same as those described above.

[0153] The material, shape, structure, size, thickness, etc., of the holder are not particularly limited and can be appropriately determined as long as the holder can be held and operated by hand, with the carbon nanotube chain(s) immobilized to its surface. For example, a metallic plate made for instance of aluminum, an acrylic plate made for instance of plastic can be used, both of which are 10 cm by 1 cm and 1 cm thick, for example.

[0154] The position at which the carbon nanotube chain is immobilized to the holder is not particularly limited and can be appropriately determined depending on the intended purpose; for example, the support of the carbon nanotube chain is immobilized to the top end surface of the holder in such a way that carbon nanotubes are oriented in a direction substantially orthogonal to the length of the holder. In this case, the number of the carbon nanotube chains to be immobilized to the holder is not particularly limited; one or more of the carbon nanotube chains may be immobilized, depending on the intended purpose. When two or more of the carbon nanotube chains are used, different substances (e.g., detection targets to be described later) can act on the carbon nanotube chains, whereby simultaneous analysis of these substances (detection targets) is made possible.

[0155] The method of immobilizing the carbon nanotube chain to the holder is not particularly limited and can be appropriately determined depending on the intended purpose; for example, the carbon nanotube chain can be immobilized to the holder with an adhesive, which may be purchased ready-made or may be prepared as needed. Examples of the adhesive include two-component epoxy adhesives.

[0156] The method of target detection by means of the carbon nanotube chain bearing the target capturing body is not particularly limited and can be appropriately determined depending on the intended purpose; for example, detection methods that involve ELISA, vibration or viscosity measurement sensor, hybridization probe, or the like can be used.

[0157] Upon detection by ELISA, antibody, for example, corresponds to the target capturing body bound to the carbon nanotube in the target detector. A fluorescent-labeled target substance is captured by the antibody, excited by irradiation with a laser beam followed by emission of light, and identified by measuring the intensity of the light.

[0158] Upon detection using the vibration or viscosity measurement sensor, the support and carbon nanotubes chemically bonded or fixed to the electrodes of a quartz crystal oscillator or a surface acoustic wave (SAW) device, for example, correspond to the target capturing body. When a target substance is allowed to act on the target capturing body, the target substance is specifically bonded to the

capturing portion of the target capturing body to thereby causes a change in the weight or viscosity of the target capturing body. This change is detected and converted into frequency change by the quartz crystal oscillator or surface acoustic wave device. Thus, the presence of the target substance can be determined by detecting this frequency change with a frequency counter.

[0159] Moreover, the target substance in a sample can be quantified (concentration can be determined) from the calibration curve of that target substance, which is previously obtained by preparing samples containing different concentrations of the target substance.

[0160] Note that the quartz crystal oscillator refers to a thin quartz plate having metallic electrodes formed on its both sides by vapor deposition, wherein vibration of given frequency is generated by inverse piezoelectric effect after applying alternating voltage across the electrodes. For example, a quartz crystal oscillator (9 MHz, AT-cut) with silver-deposited electrodes can be used.

[0161] The surface acoustic wave (SAW) device refers to a solid article with a pair of comb-shaped electrodes formed on its surface; it converts an electric signal into a surface acoustic wave (an acoustic or supersonic wave that propagates on the solid surface), transmits it to the counter electrode, and outputs it as an electric signal again. With this SAW device, it is possible to obtain a signal of specific frequency in response to stimulation. For example, ferroelectrics that offer piezoelectric effect, such as lithium tantalate and lithium niobate, quartz, and thin films of zinc oxide can be used as the materials of the SAW device.

[0162] Upon detection by means of hybridization probe, a single-stranded DNA obtained by chemical denaturation corresponds to the target capturing body. By allowing a labeled DNA probe to act on, or hybridize to, the target capturing body, detection of a specific DNA sequence is made possible that is complementary (i.e., A (adenine) for T (thymine), and G (guanine) for C (cytosine)) to the DNA probe. The hybridization detection method allows systematic analysis of activation (expression) of multiple genes responsible for cancers, immunological diseases, etc.

[0163] Since the target detector of the present invention comprises the carbon nanotube chain of the present invention, various substances can be reacted with and adsorbed to the carbon nanotubes, and various targets can be adsorbed to or released from the carbon nanotubes. In addition, since the carbon nanotube chain is fixed to the holder, it is possible to ensure a high degree of ease of use by allowing the holder to be held by hand. Furthermore, if the number of the carbon nanotube chain to be fixed is 1, the carbon nanotube chain can be partitioned into multiple regions so that different substances can be bound to the terminals of the carbon nanotubes of different regions. If the number of the carbon nanotube chain to be fixed is 2 or more, it is possible to allow different substances to bind to different chains. An example for the former case is as follows: when a carbon nanotube chain is partitioned into two regions for use as a sensor for detecting particular pollutants in wastewater, target capturing bodies capable of capturing heavy metals are specifically bound to the carbon nanotubes in one of the two regions, and target capturing bodies capable of capturing cyan are specifically bound to the carbon nanotubes in the other region, whereby two different pollutants can be detected at the same

time. Alternatively, it is also possible to achieve simultaneous detection of two different pollutants by using two carbon nanotube chains—one having carbon nanotubes to which target capturing bodies capable of capturing heavy metals are bound, and one having carbon nanotubes to which target capturing bodies capable of capturing cyan are bound.

[0164] The target detector of the present invention is capable of high-sensitivity detection, and qualitative and quantitative analysis, of various types of targets including disease-causing substances, biological substances and toxic substances, and can be suitably used in various fields including sensors such as biosensors and gas sensors.

(Target Detection Method)

[0165] The target detection method of the present invention uses the target detector of the present invention described above and causes the target detector to act on a sample containing the detection target, and where necessary, further includes additional step(s) appropriately selected.

[0166] The target detector is the target detector of the present invention, and the detection target is the same as that described above.

[0167] When a sample containing the detection target is allowed to act on the target detector, the detection target is captured by the target capturing body of the target detector.

[0168] The method of causing the target detector to act on sample is not particularly limited and can be appropriately determined depending on the intended purpose; for example, a method of immersing the target detector having the target capturing body in the sample can be used.

[0169] Note that when the target detector comprises the plurality of carbon nanotube chains, it is possible to achieve simultaneous analysis of multiple detection targets by immobilizing different types of target capturing bodies to each carbon nanotube chain.

[0170] The method of target detection by means of the carbon nanotube chain bearing the target capturing body is not particularly limited and can be appropriately determined depending on the intended purpose; for example, detection methods that involve ELISA, vibration or viscosity measurement sensor, hybridization probe, or the like can be used.

[0171] Upon detection using ELISA, antibody, for example, corresponds to the target capturing body bound to the carbon nanotube in the target detector. A fluorescent-labeled target substance is captured by the antibody, excited by irradiation with a laser beam followed by emission of light, and identified by measuring the intensity of the light.

[0172] Upon detection using the vibration or viscosity measurement sensor, the support and carbon nanotubes chemically bonded or fixed to the electrodes of a quartz crystal oscillator or a surface acoustic wave (SAW) device, for example, correspond to the target capturing body. When a target substance is allowed to act on the target capturing body, the target substance is specifically bonded to the capturing portion of the target capturing body to thereby causes a change in the weight or viscosity of the target capturing body. This change is detected and converted into frequency change by the quartz crystal oscillator or surface acoustic wave device. Thus, the presence of the target

substance can be determined by detecting this frequency change with a frequency counter.

[0173] Moreover, the target substance in a sample can be quantified (concentration can be determined) from the calibration curve of that target substance, which is previously obtained by preparing samples containing different concentrations of the target substance.

[0174] Note that the quartz crystal oscillator refers to a thin quartz plate having metallic electrodes formed on its both sides by vapor deposition, wherein vibration of given frequency is generated by inverse piezoelectric effect after applying alternating voltage across the electrodes. For example, a quartz crystal oscillator (9 MHz, AT-cut) with silver-deposited electrodes can be used.

[0175] The surface acoustic wave (SAW) device refers to a solid article with a pair of comb-shaped electrodes on its surface; it converts an electric signal into a surface acoustic wave (an acoustic or supersonic wave that propagates on the solid surface), transmits it to the counter electrode, and outputs it as an electric signal again. With this SAW device, it is possible to obtain a signal of specific frequency in response to stimulation. For example, ferroelectrics that offer piezoelectric effect, such as lithium tantalate and lithium niobate, quartz, and thin films of zinc oxide can be used as the materials of the SAW device.

[0176] Upon detection by means of hybridization probe, a single-stranded DNA obtained by chemical denaturation corresponds to the target capturing body. By allowing a labeled DNA probe to act on, or hybridize to, the target capturing body, detection of a specific DNA sequence is made possible that is complementary (i.e., A (adenine) for T (thymine), and G (guanine) for C (cytosine)) to the DNA probe. The hybridization detection method allows systematic analysis of activation (expression) of multiple genes responsible for cancers, immunological diseases, etc.

[0177] With the target detection method of the present invention, it is possible to achieve efficient, high-precision detection, and qualitative and quantitative analysis of various targets contained in sample. For example, analysis or screening of enzymes, coenzymes, enzyme substrates, enzyme inhibitors, clathrate compounds, metals, antibodies, antigens, proteins, microorganisms, viruses, cell debris, metabolites, nucleic acids, hormones, hormone receptors, lectins, sugars, physiologically active substances and physiologically active substance receptors, allergens, blood proteins, tissue proteins, nucleic substances, virus particles, neurotransmitters, heptanes, parasites, endocrine-disturbing chemicals, chemical species or derivatives thereof, and gaseous components can be realized. Thus, the target detection method of the present invention can be suitably used for development of medicine, disease diagnosis, sensing of target substances, biological molecules and gases, etc.

EXAMPLES

[0178] Hereinafter, the present invention will be described with reference to Examples, which however shall not be construed as limiting the scope of the present invention.

(Nanohole Structure Formation Experiment)

[0179] A mold with a pattern of lines and spaces (pitch=150 nm) was pressed against an aluminum layer to be

anodized for forming nanoholes (alumina pores) therein, thereby imprinting the pattern of lines (concaves or grooves) and spaces (convexes or lands) to the aluminum layer surface. In this way, as shown in FIG. 2A, a pattern of alternating grooves and linear lands (i.e., a pattern of regularly spaced grooves) was formed. Subsequently, the aluminum layer was anodized at 60V in diluted oxalic acid, resulting in the self-organization of nanoholes (alumina pores) formed only in the grooves along their length (in other words, nanohole rows were formed), as shown in FIG. 2B.

Example 1

—Preparation of Carbon Nanotube Chain—

<Nanohole Structure Formation Step>

[0180] As shown in FIG. 3A, using an EB mask writer (ELS7000, manufactured by ELIONIX CO., LTD.), an EB resist was applied over a SiC substrate and lines were written to produce a pattern of concaves and convexes (lines and spaces), followed by etching treatment to obtain a SiC mold 50. Note that the interval (pitch) between adjacent concave lines (grooves) in the pattern was 150 nm, the depth of the grooves was 100 nm, and the ratio of the width of the convex or land to the width of the concave or groove, (convex width/concave width), was 1:1.

[0181] As shown in FIG. 3B, Nb was vacuum-deposited onto a silicon substrate 52 by sputtering to a thickness of 50 nm so as to form an electrode layer that is identical to that described above, and aluminum was vacuum-deposited onto the electrode layer to a thickness of 350 nm by sputtering of an aluminum sputtering target so as to form a metallic layer 54 identical to that described above. The SiC mold 50 was then pressed against the metallic layer 54 so that the pattern on the surface of the SiC mold 50 is imprinted onto the surface of the metallic layer 54. As shown in FIG. 2A, it resulted in the formation of a pattern of concaves and convexes on the surface of the metallic layer 54. It should be noted that the SiC mold 50 was pressed against the metallic layer 54 at a pressure of 3,000 kg/cm² using a hydraulic pressing machine.

[0182] The metallic layer 54 having the foregoing pattern imprinted thereto was then anodized at 60V in a diluted oxalic acid bath. As shown in FIGS. 2B and 3C, it resulted in the production of a nanohole structure 58 in which a number of nanoholes (alumina nanoholes, or alumina pores) 56 are formed only in the grooves in such a way that they orient in a direction substantially perpendicular to the surface of the metallic layer 54. Note that the interval between adjacent nanoholes 56 in the grooves was about 150 nm, the thickness of the metallic layer 54 (i.e., the depth or length of each nanohole 56) was 300 nm, and the opening diameter of each nanohole 56 was 50 nm.

<Carbon Nanotube Formation Step>

[0183] Using propylene gas as a carbon source gas from which carbon nanotubes are formed and using nitrogen as a carrier gas, carbon was deposited by CVD both on the outer surface of the nanohole (alumina nanohole) structure 58 and in the nanoholes 56. More specifically, the silicon substrate 52 having the nanoholes 56 was placed into a quartz reaction tube, which was then heated to 800° C. in 2 hours under nitrogen flow. Thereafter, 1.2% propylene and nitrogen gas

(carrier gas) were introduced into the reaction tube, followed by CVD at 800° C. for 2 hours. Subsequently, propylene supply was stopped, and the reaction tube was cooled to room temperature under nitrogen flow.

[0184] Following the step described above, as shown in FIG. 3D, a carbon layer 60 was deposited over the surface of the nanohole structure 58 and carbon nanotubes 62 were formed in the nanoholes 56 of the nanohole structure 58. The average length of the carbon nanotubes was 300 nm.

<Carbon Removal Step>

[0185] The nanohole structure 58 having the carbon layer 60 deposited on its surface was placed on a turn table for polishing, a wrapping tape with an abrasive coating (particle size=3 μm) was pressed against the nanohole structure 58, and the turn table was rotated while supplying coolant water for surface polishing. In this way, as shown in FIG. 3E, the carbon layers 60 deposited on surfaces of the lands 64 between the grooves (i.e., both the carbon layer deposited on the top surface of the lands 64 of the metallic layer 64 and the carbon layer deposited to the side surfaces of the lands 64) were removed.

<Metallic Layer Dissolving Step>

[0186] Next, the nanohole structure 58 from which the carbon layers 60 deposited on the surfaces of the lands 64 between grooves had been removed was subjected to hydrothermal treatment with NaOH (condition: 10M NaOH, autoclave at 150° C.) to dissolve away the metallic layer (alumina layer) 54, and neutralized by diluted hydrochloric acid. As a consequence, as shown in FIG. 3F, it resulted in the formation of a linear carbon nanotube chain 68 according to the present invention, which consists of a row of carbon nanotubes 62 that are at one end bonded to a linear article 66 in such a way that they are oriented in a direction substantially perpendicular to the surface of the linear article 66.

Example 2

—Preparation of Carbon Nanotube Chain—

[0187] A carbon nanotube chain of Example 2 was prepared as in Example 1 except that the following carbon removal step was adopted.

<Carbon Removal Step>

[0188] The nanohole structure 58 having the carbon layer 60 deposited on its surface, obtained by the foregoing carbon nanotube formation step, was set to an oxygen ion beam system, wherein the ion source adopted in the system was a 20 kv ECR (Electron Cyclotron Resonance) source placed so that the incident angle of an ion beam was 45° with respect to the sample holder. As shown in FIG. 4, the nanohole structure 58 was then irradiated with a 500 eV oxygen ion beam 70 to remove the carbon layers 60 deposited on the surfaces of the lands 64 between the grooves, i.e., both the carbon layer deposited on the top surface of the lands 64 of the metallic layer 54 and the carbon layer deposited to the side surfaces of the lands 64 (see FIG. 3E).

[0189] Subsequently, as in Example 1, the metallic layer dissolving step was performed to provide a linear carbon nanotube chain 68 according to the present invention, which consists of a row of carbon nanotubes 62 that are at one end bonded to a linear article 66 in such a way that they are

oriented in a direction substantially perpendicular to the surface of the linear article **66** (see FIG. 3F).

Example 3

—Preparation of Carbon Nanotube Chain—

[0190] A carbon nanotube chain of Example 3 was prepared as in Example 1 except that the following carbon removal step was adopted.

<Carbon Removal Step>

[0191] The nanohole structure **58** having the carbon layer **60** deposited on its surface, obtained by the foregoing carbon nanotube formation step, was set to an ion milling system (ME-1001, manufactured by Veeco Instruments). The nanohole structure **58** was then irradiated with an argon ion beam at an incident angle of 30° under the condition that the acceleration voltage was 50V and current density was 20 mA/cm², to remove the carbon layers **60** deposited on the surfaces of the lands **64** between the grooves, i.e., both the carbon layer deposited on the top surface of the lands **64** of the metallic layer **64** and the carbon layer deposited to the sides of the lands **64**.

[0192] Subsequently, as in Example 1, the metallic layer dissolving step was performed to provide a linear carbon nanotube chain **68** according to the present invention, which consists of a row of carbon nanotubes **62** that are at one end bonded to a linear article **66** in such a way that they are oriented in a direction substantially perpendicular to the surface of the linear article **66** (see FIG. 3F).

Example 4

—Preparation of Carbon Nanotube Chain—

[0193] A carbon nanotube chain of Example 4 was prepared as in Example 1 except that the following nanohole structure formation step was adopted.

<Nanohole Structure Formation Step>

[0194] Using an EB mask writer (ELS7000, manufactured by ELIONIX CO., LTD.), lines were written on the resist layer of 40 nm thickness that had been formed on a glass substrate by spin coating, to thereby produce a pattern of concaves and convexes (lines and spaces). Note that the interval (pitch) between adjacent concave lines (grooves) in the pattern was 60 nm, the depth of the grooves was 50 nm, and the ratio of the width of the convex or land to the width of the concave or groove, (convex width/concave width), was 1:1. A Ni layer was then formed on the pattern of concaves and convexes by sputtering, and while using the Ni layer as an electrode, the Ni layer was thickened to 0.3 mm by electroforming in a nickel sulfamate bath. The Ni layer was then polished to produce a Ni mold.

[0195] Nb was then vacuum-deposited onto a silicon substrate by sputtering to a thickness of 50 nm so as to form an electrode layer that is identical to that described above, and aluminum was vacuum-deposited onto the electrode layer to a thickness of 350 nm by sputtering of an aluminum sputtering target so as to form a metallic layer identical to that described above. The Ni mold was then pressed against the metallic layer so that the pattern on the surface of the Ni mold is imprinted onto the surface of the metallic layer. It resulted in the formation of a pattern of concaves and

convexes on the surface of the metallic layer. It should be noted that the Ni mold was pressed against the metallic layer at a pressure of 3,000 kg/cm² using a hydraulic pressing machine.

[0196] The metallic layer having the foregoing pattern imprinted thereto was then anodized at 18V in a diluted sulfuric acid bath. As shown in FIG. 5, it resulted in the production of a nanohole structure in which a number of nanotubes (alumina nanoholes, or alumina pores) as through holes are formed only in the grooves in such a way that they orient in a direction substantially perpendicular to the surface of the metallic layer. Note that the interval between adjacent nanoholes in the grooves was significantly small (about 45 nm), the thickness of the metallic layer (i.e., the depth or length of each nanohole) was 350 nm, and the opening diameter of each nanohole was 20 nm.

[0197] Subsequently, as in Example 1, the carbon nanotube formation step, carbon removal step, and metallic layer dissolving step were performed to provide a linear carbon nanotube chain **68** according to the present invention, which consists of a row of carbon nanotubes **62** that are at one end bonded to a linear article **66** in such a way that they are oriented in a direction substantially perpendicular to the surface of the linear article **66** (see FIG. 3F).

Example 5

—Preparation of Carbon Nanotube Chain—

[0198] During EB exposure as did in the nanohole structure formation of Example 1, the exposure dose was changed at a given frequency, whereby a pattern of concaves and convexes was obtained in which the width of each concave (groove) was changed at 100 nm intervals as shown in FIG. 1A. Thereafter, a Ni mold was fabricated as in Example 3. A carbon nanotube chain of Example 5 was then prepared as in Example 1 except that anodization was conducted at 40V in diluted sulfuric acid. The carbon nanotube chain had a structure like that shown in FIG. 1B, and it was confirmed that nanoholes (alumina pores) were regularly spaced at intervals corresponding to those for areas of the groove that have a large width.

Example 6

—Preparation of Target Detector—

[0199] As the holder described above, bar-shaped acrylic plates made of plastic that are 10 cm by 1 cm and 1 cm thick were prepared, and a 1cm linear article **66** of the carbon nanotube chain **68** of each of Examples 1 to 5 was immobilized to the top end surface of the holder **82** with an adhesive (Aronalfa™, produced by Toa Gosei) in such a way that the carbon nanotubes **62** are oriented in a direction substantially orthogonal to the length of the holder **82**. In this way target detectors **80** like that shown in FIG. 6 were prepared.

[0200] In the target detectors **80** that have the carbon nanotube chains prepared in Examples 1 to 3, carbon nanotubes are spaced at 150 nm intervals in each carbon nanotube chain; thus, the number of carbon nanotubes in each carbon nanotube chain is 67,000. In the target detector **80** that has the carbon nanotube chains prepared in Example 4, carbon nanotubes are spaced at 45 nm intervals in each carbon nanotube chain; thus, the number of carbon nanotubes in

each carbon nanotube chain is 222,000. In the target detector **80** that has the carbon nanotube chains prepared in Example 5, carbon nanotubes are spaced at 100 nm intervals in each carbon nanotube chain; thus, the number of carbon nanotubes in each carbon nanotube chain is 100,000.

—Evaluation of Adsorption Capability of Target Detector—

[0201] Detection of an endocrine-disturbing chemical was conducted by adsorbing it to a target detector prepared below.

[0202] As shown in FIG. 6, a target detector **80** was prepared by immobilizing **100** carbon nanotube chains **68** of Example 5, each having a linear article of 2 cm long and carbon nanotubes spaced at 100 nm intervals, to the holder **82**. As shown in FIG. 7A, the carbon nanotube chains **68** of the target detector **80** were immersed in a solution containing bisphenol A, an endocrine-disturbing chemical, at a concentration of 1 ng/ml. As shown in FIG. 7B, the target detector **80** was then taken out of the bisphenol A containing-solution and immersed in methanol solution, releasing the adsorbed ingredients in the solution. Analysis of the solution by high-performance liquid chromatography revealed the presence of bisphenol A. It was also established that quantitative analysis is also possible since the intensity of a detection signal is substantially proportional to concentration.

[0203] It was established from the results shown above that detection of bisphenol A is possible even in trace concentrations, i.e., the target detector having the carbon nanotube chains has a adsorption capability to bisphenol A and thus can be applicable to the adsorption detection technique that utilizes a selective adsorption capability. It should be noted that the target detector described above offered a similar adsorption capability to 4-n-nonylphenol, 4-tert-octylphenol, dioxin, etc.

Example 7

—Detection of Target—

[0204] Detection of α -fetoprotein (AFP) was conducted using a target detector having chemically-modified carbon nanotubes.

[0205] The carbon nanotube chains **68** of the target detector **80** of Example 6, wherein 100 carbon nanotube chains **68** of Example 5, each having a linear article of 2 cm long and carbon nanotubes spaced at 100 nm intervals, are immobilized to the holder **82** (see FIG. 6), were first immersed in concentrated nitric acid solution, and heated at 800° C. for 3 hours to introduce a carboxylic group ($-\text{COOH}$) to the carbon nanotubes **62**. The carbon nanotubes **62** were then modified with streptavidin, followed by immobilization of biotinylated anti-AFP antibody thereto. An AFP-containing sample and a $\text{Ru}(\text{bpy})_3^{2+}$ -labeled anti-AFP antibody were then allowed to act on the carbon nanotubes **62**, followed by detection of AFP by electrochemiluminescence using $\text{Ru}(\text{bpy})_3^{2+}$. The detection limit of AFP was as low as 10 ng/ml and quantitative detection was possible. It was therefore established that this target detector can be applicable to analysis of biomacromolecules that entails chemical modification.

[0206] According to the present invention, it is possible to solve the foregoing conventional problems and to provide a

carbon nanotube chain consisting of a row of carbon nanotubes of 1 μm or less in length, the carbon nanotube chain being suitably used for instance as a target detector or sensor; an efficient production process for the carbon nanotube chain; a target detector which is capable of high-sensitivity detection, and qualitative and quantitative analysis, of various types of targets including disease-causing substances, biological substances and toxic substances by using the carbon nanotube chain, and which can be suitably used as a biosensor and gas sensor; and a target detection method capable of easy, high-sensitivity detection of targets by using the target detector.

[0207] The carbon nanotube chain of the present invention is capable of detection of various types of targets including disease-causing substances, biological substances and toxic substances, and of being suitably applicable to various fields including sensors such as target detectors, biosensors, and gas sensors.

[0208] The target detector of the present invention is also capable of detection of various types of targets including disease-causing substances, biological substances and toxic substances, and of being suitably applicable to various fields including sensors such as target detectors, biosensors, and gas sensors.

[0209] The process of the present invention for producing a carbon nanotube chain can be used for the production of the carbon nanotube chain of the present invention.

[0210] The target detection method of the present invention is capable of easy, high-sensitivity detection of targets.

What is claimed is:

1. A carbon nanotube chain comprising:

a support; and

a plurality of carbon nanotubes bonded at one end to a surface of the support,

wherein the plurality of carbon nanotubes is oriented in a direction substantially orthogonal to the surface of the support.

2. The carbon nanotube chain according to claim 1, wherein the support is a linear article and the carbon nanotubes are aligned in a row.

3. The carbon nanotube chain according to claim 1, wherein the end of each of the carbon nanotubes bonded to the support is opened, and the other end thereof is closed.

4. The carbon nanotube chain according to claim 1, wherein the carbon nanotubes are identical in at least any one of length, thickness, and outer diameter.

5. The carbon nanotube chain according to claim 1, wherein the average length of the carbon nanotubes is 1 μm or less.

6. The carbon nanotube chain according to claim 1, wherein the support is made of carbon.

7. The carbon nanotube chain according to claim 1, wherein the carbon nanotubes are covered with a functional material.

8. The carbon nanotube chain according to claim 1, wherein the carbon nanotube chain is used for capturing a detection target.

9. The carbon nanotube chain according to claim 1, wherein the carbon nanotube chain comprises a target capturing body which comprises a binding portion capable of

being bound to the carbon nanotube and a target capturing portion capable of capturing a detection target.

10. The carbon nanotube chain according to claim 9, wherein the carbon nanotube and the target capturing body are held together by chemical bonding.

11. A target detector comprising:

a carbon nanotube chain; and

a holder;

wherein the carbon nanotube chain comprises a capturing portion capable of capturing a detection target, and

wherein the carbon nanotube chain comprises a support and a plurality of carbon nanotubes bonded at one end to a surface of the support, wherein the plurality of carbon nanotubes is oriented in a direction substantially orthogonal to the surface of the support.

12. The target detector according to claim 11, wherein the capturing portion is formed of a target capturing body which comprises a binding portion capable of being bound to the carbon nanotube and a target capturing portion capable of capturing a detection target.

13. A process for producing a carbon nanotube chain, comprising:

forming grooves in a metallic layer;

performing a nanohole formation treatment to form a nanohole structure in which a row of nanoholes is formed in each of the grooves, the nanoholes being oriented in a direction substantially orthogonal to a surface of the metallic layer;

forming a carbon nanotube in each of the nanoholes,

removing carbon deposited on surfaces of lands of the metallic layer between the grooves; and

dissolving away the metallic layer,

wherein the carbon nanotube chain comprises a support and a plurality of carbon nanotubes bonded at one end to a surface of the support, wherein the plurality of carbon nanotubes is oriented in a direction substantially orthogonal to the surface of the support.

14. The process for producing a carbon nanotube chain according to claim 13, wherein the metallic layer is made of aluminum.

15. The process for producing a carbon nanotube chain according to claim 13, wherein the width of each of the grooves is changed at regular intervals along the length thereof.

16. The process for producing a carbon nanotube chain according to claim 13, wherein the nanohole formation treatment is anodization.

17. The process for producing a carbon nanotube chain according to claim 13, wherein the carbon nanotubes are formed by chemical vapor deposition (CVD).

18. The process for producing a carbon nanotube chain according to claim 13, wherein removal carbon deposited on surfaces of the lands of the metallic layer is performed by at least one of wrapping and chemical mechanical polishing (CMP).

19. The process for producing a carbon nanotube chain according to claim 13, wherein removal of carbon deposited on the side surfaces of the lands of the metallic layer is performed by application of one of an ion beam and electron beam thereto at angles with respect to the length and height of the lands.

20. A target detection method comprising:

causing a target detector to act on a sample containing a detection target,

wherein the target detector comprises a carbon nanotube chain and a holder,

wherein the carbon nanotube chain comprises a support and a plurality of carbon nanotubes bonded at one end to a surface of the support, wherein the plurality of carbon nanotubes is oriented in a direction substantially orthogonal to the surface of the support, and

wherein the carbon nanotube chain comprises a capturing portion capable of capturing the detection target.

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