Method of Forming a Self-assembled, Three-Dimensional Carbon Nanotube Network and Networks so Formed.

Technical Field

[001] This invention relates to a method of forming a self-assembled, three-dimensional carbon nanotube network and networks so formed.

Background

[002] Carbon nanotubes have been shown to exhibit extraordinary properties. The formation of carbon nanotubes "L", "T" and "Y" junctions has been studied for fabricating three-terminal nanoscale-systems. The functionality of carbon nanotubes as the building blocks for field-effect transistors, diodes, biochemical sensors and detectors has also been explored. However, carbon nanostructure assembly is difficult as the size proscribes direct tinkering or bonding. Current connecting methods for carbon nanotubes generally rely on sophisticated, high-cost, manual assembly. Known self-assembly processes require decoration of grown carbon nanotubes with catalyst particles. Both induce destruction of the nanotube structure, or pose a difficulty in controlling the nucleation sites for redeposition of carbon nanotubes.

[003] For large scale integration of carbon nanotubes in electronics or biological devices with high yield, well controlled growing sites, and relatively low production costs are required. The traditional assembly methods for carbon nanotubes cause mass production of carbon-nanotube-based devices to be difficult.

[004] Moreover, as the properties of carbon nanotubes are largely determined by their nanostructure, the occurrence of defects introduced by the traditional assembly methods can cause substantial degradation of their properties. Until the assembly method problems are overcome, carbon nanotube-based devices will remain in the research domain and will have limited commercial value.

[005] Therefore, new fabrication methodologies for, and new architectures of, carbon nanotubes are required for advancing the widespread application in materials and devices of carbon nanotubes.

[006] Assembly of carbon nanotubes that resemble a complex reticulation of a circuit structure would facilitate the fabrication of engineered, functional macroscale-systems from

nanoscale components. The development of carbon nanotube assembly methodologies would have potential applications in, for example, electronic devices, field-effect transistors, field emission sources, diodes, biosensors, gas sensors, chemical sensors, batteries, electrochemical devices, supercapacitors and actuators, gas and hydrogen storage, solar cell, photovoltaic devices, detectors and composites reinforced with carbon nanotubes.

Summary

[007] According to an exemplary aspect there is provided a method for forming self-assembled, three-dimensional carbon nanotube network, the method comprising: growing primary carbon nanotubes; and growing secondary carbon nanotubes, the secondary carbon nanotubes bridging and linking with the primary carbon nanotubes to form the self-assembled three dimensional carbon nanotube network.

[008] According to another exemplary aspect there is provided a method for forming self-assembled, three-dimensional carbon nanotube network, the method comprising: growing primary carbon nanotubes; and growing secondary carbon nanotubes, the primary carbon nanotubes being one of: aligned and non-aligned, and the secondary carbon nanotubes being the other of: aligned and non-aligned.

[009] According to yet another exemplary aspect there is provided a method for forming self-assembled, three-dimensional carbon nanotube network, the method comprising: growing primary carbon nanotubes; and growing secondary carbon nanotubes, the secondary carbon nanotubes growing from the primary carbon nanotubes.

[010] According to a further exemplary aspect there is provided a method for forming self-assembled, three-dimensional carbon nanotube network, the method comprising: placing spots of a catalyst on a substrate at locations where it is desired for primary carbon nanotubes to be grown, and growing the primary carbon nanotubes at those spots.

[011] According to a yet further exemplary aspect there is provided a method for forming self-assembled, three-dimensional carbon nanotube network, the method comprising: growing primary carbon nanotubes from a catalyst on a first substrate, retaining a portion of the catalyst at tips of the primary carbon nanotubes, placing the tips and the catalyst in contact with a layer of a carbon-containing material on a second substrate, and growing secondary carbon nanotubes from the tips of the primary carbon nanotubes.

[012] The secondary carbon nanotubes may bridge and link the primary carbon nanotubes. The secondary carbon nanotubes may be grown from the primary carbon nanotubes. The secondary carbon nanotubes may be grown in nanopores between the primary carbon nanotubes. Formation of the primary carbon nanotubes may be on a first substrate having a layer of a catalyst on the substrate. The layer of catalyst may be continuous or discontinuous. The primary carbon nanotubes may be grown only where the catalyst is located on the substrate. When the primary carbon nanotubes are grown, catalyst may be captured by tips of the primary carbon nanotubes. The secondary carbon nanotubes may grow from the tips of the primary carbon nanotubes. Before the secondary carbon nanotubes are grown, the tips of the primary carbon nanotubes may be applied to a second substrate having thereon a layer of or containing carbon. Before the tips of the primary carbon nanotubes are applied to the second substrate, the first substrate with the layer of catalyst and the primary carbon nanotubes may be rotated. The formation of the primary nanotubes may be at a first elevated temperature. Before the secondary carbon nanotubes are grown, the primary carbon nanotubes may be annealed at a second elevated temperature. The annealing may take place after the tips of the primary carbon nanotubes are applied to the layer of or containing carbon on the second substrate. Annealing may be for a predetermined period and the second elevated temperature is in the range 400 to 800 °C. During annealing, a reduced flow of a gas of or containing hydrogen is introduced. The predetermined period may be in the range 0.5 to 10 minutes. The secondary carbon nanotubes may be grown at a third elevated temperature.

[013] According to a further another aspect there is provided a self-assembled three-dimensional carbon nanotube network when formed by the above method.

[014] According to a semi-penultimate aspect, there is provided a self-assembled, three-dimensional carbon nanotube network comprising: a plurality of primary carbon nanotubes; and a further plurality of secondary carbon nanotubes, the secondary carbon nanotubes bridging and linking with the primary carbon nanotubes to form the self-assembled three dimensional carbon nanotube network.

[015] According to another semi-penultimate aspect there is provided a self-assembled, three-dimensional carbon nanotube network comprising: a plurality of primary carbon nanotubes; and a further plurality of secondary carbon nanotubes, the plurality of primary carbon nanotubes being one of: aligned and non-aligned, and the further plurality of secondary carbon nanotubes being the other of: aligned and non-aligned.

[016] According to a penultimate aspect there is provided a self-assembled, three-dimensional carbon nanotube network comprising: a plurality of primary carbon nanotubes; and a further plurality of secondary carbon nanotubes, the further plurality of secondary carbon nanotubes growing from the plurality of primary carbon nanotubes.

[017] The secondary carbon nanotubes may bridge and link the primary carbon nanotubes. The secondary carbon nanotubes may extend from the primary carbon nanotubes. The secondary carbon nanotubes may be in nanopores between the primary carbon nanotubes. The primary carbon nanotubes may be on a first substrate having a layer of a catalyst on the substrate. The layer of catalyst may be continuous or discontinuous. The primary carbon nanotubes may be only where the catalyst is located on the substrate. When the primary carbon nanotubes are grown, catalyst may be captured by tips of the primary carbon nanotubes. The secondary carbon nanotubes may extend from the tips of the primary carbon nanotubes.

[018] The primary carbon nanotubes may be arranged in closely-spaced pairs. Adjacent pairs of primary carbon nanotubes may be spaced apart such that there is at least one secondary carbon nanotube bridging and linking only the two primary carbon nanotubes of each pair. There may be no secondary carbon nanotubes bridging or linking primary carbon nanotubes of adjacent pairs.

[019] The self-assembled, three -dimensional carbon nanotube network may be used as a building block for at least one of: nanotube electronic devices, field-effect transistors, field emission sources, diodes, biosensors, gas sensors, chemical sensors, batteries, electrochemical devices, supercapacitors and actuators, gas and hydrogen storage, solar cells, photovoltaic devices, and detectors.

[020] The self-assembled, three -dimensional carbon nanotube network may be used as one of: a re-enforcement, and/or filler, in matrixes selected from the group consisting of: polymers, metals, alloys, ceramics, organics and inorganics, to form structural or functional composites.

[021] In each pair of primary carbon nanotubes, the primary carbon nanotubes may be used in a manner selected from: two electrodes, and one portion of the same electrode.

[022] The at least one secondary carbon nanotube may be used as a sensor element such that the self-assembled, three-dimensional carbon nanotube network is one of: a biosensor, a gas sensor, and a chemical sensor.

[023] The self-assembled, three-dimensional carbon nanotube network may be located between two substrates and may be used in a manner selected from: a supercapacitor material, a supercapacitor structure, an electron emission source, and a field emission source.

[024] Each pair of primary carbon nanotubes may be used as at least one portion of one of: the electrodes, the circuit, and the functional device, for batteries, solar cells, photovoltaic devices and detectors.

[025] After removal of the substrate, the self-assembled, three-dimensional carbon nanotube network may be transferred onto another substrate to form at least one selected from: electronic devices, field-effect transistors, field emission sources, diodes, biosensors, gas sensors, chemical sensors, batteries, electrochemical devices, supercapacitors and actuators, gas and hydrogen storage, solar cells, photovoltaic devices, and detectors.

[026] After removal of the substrate, the self-assembled, three-dimensional carbon nanotube network may be used as one of: a re-enforcement and filler, in at least one matrix selected from: polymers, metals, alloys, ceramics, organics and inorganics, to form composites.

[027] In each pair of primary carbon nanotubes one of the primary carbon nanotubes may be a source, and the other primary carbon nanotube may be a drain; and the secondary carbon nanotubes are a gate such that the pair of primary carbon nanotubes is a transistor.

[028] According to a final exemplary aspect there is provided a transistor comprising a source, a gate and a drain; wherein the source is a first primary carbon nanotube of a pair of primary carbon nanotubes, the drain is a second primary carbon nanotube of a pair of primary carbon nanotubes, and the gate is at least one secondary carbon nanotube bringing and linking the first primary carbon nanotube and the second primary carbon nanotube. The at least one secondary carbon nanotube may extend from a tip of at least one of the first and second primary carbon nanotubes.

Brief Description of the Drawings

[029] In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings.

[030] In the drawings:

Figure 1 is a series of schematic illustrations of the formation of a self-assembled, three-dimensional carbon nanotube network;

Figure 2 is two schematic illustrations of the catalyst layer on the substrate of the exemplary embodiment of Figure 1;

Figure 3 is a schematic illustration of the formation of the primary carbon nanotubes for the exemplary embodiment of Figure 2(b);

Figure 4 is an image of a three-dimensional carbon nanotube network formed by the exemplary embodiment of Figure 1;

Figure 5 is an image of a three-dimensional carbon nanotube network formed by the exemplary embodiment of Figure 1;

Figure 6 is a graph of the Raman spectroscopy of a three-dimensional carbon nanotube network formed by the exemplary embodiment of Figure 1; and

Figure 7 is two graphs of the current v voltage obtained from a three-dimensional carbon nanotube network formed by the exemplary embodiment of Figure 1 at temperatures of $20^{O}C$ and $100^{O}C$ respectively.

Detailed Description of the Exemplary Embodiments

[031] The exemplary embodiment provides a method for forming self-assembled, three-dimensional carbon nanotube network. The network may be a superlattice.

[032] As shown in Figures 1(a) and (b) and Figure 2, the method involves the growth of carbon nanotubes in two stages. In the first step of carbon nanotubes growth, a catalyst substrate or a wafer/substrate 100 is provided. The substrate 100 is of any known type suitable for formation of carbon nanotubes at temperatures in the range room temperature to 900 °C, preferably in the range 400 °C to 800 °C. The substrate 100 has applied thereto a catalyst layer 102 suitable for the formation of carbon nanotubes at temperatures in the range room temperature to 900 °C, preferably in the range 400 °C to 800 °C. As shown in Figure 2, the catalyst layer 102 may be substantially continuous over the substrate (Figure 2(a)) or may be discontinuous (Figure 2(b)).

[033] The substrate 100 with catalyst 102 is placed on a heating stage 104 in a carbon nanotube growth chamber (not shown). The catalyst 102 may include nickel, cobalt, iron, platinum,
palladium, and/or their alloys. The substrate 100 may be heated to a first room or elevated temperature in the range of, for example, room temperature to 900 °C, preferably in the range 400 °C to 800 °C. The carbon nanotube growth may be, for example, by arc-discharge, pyrolysis of hydrocarbons, chemical vapour deposition, laser vaporization of graphite targets, solar carbon vaporization, and electrolysis of carbon electrodes in molten ionic salts, and so forth. For the growth of carbon nanotubes growth over metal catalysts with pyrolysis of hydrocarbons, hydrocarbon species include methane, benzene, acetylene, naphthalene, ethylene, and so forth. A layer 106 of substantially aligned carbon nanotubes 108 is grown and obtained on the substrate 100. The carbon nanotubes 108 are primary carbon nanotubes. The layer 106 may be of non-aligned carbon nanotubes if required or desired.

[034] As shown in Figures 2(b) and Figure 3, when the catalyst 102 is discontinuous, the layer 106 of carbon nanotubes 108 is formed where the catalyst 102 is located on the substrate. Depending on the size of each "spot" 107 of catalyst 102, there will be at least one primary carbon nanotube 108 formed at the location of each spot 107. If the "spot" 107 is sufficiently small, there will be one carbon nanotube 108 formed for each "spot" 107. In this way, it is possible to exercise control over the size, location and spacing of the "spots" 107 of catalyst 102 to control the location and spacing of the carbon nanotubes 108.

[035] When the primary carbon nanotubes 108 are formed, there will be catalyst 102 at the tip 114 of each primary carbon nanotube 108 that is "captured" by the tip 114 during the formation of the primary carbon nanotube. That will be used during subsequent processing. The catalyst 102 may be captured at one or more of:

within the tip 114 of each primary carbon nanotube 108,

on the external surface of the tip 114 of each primary carbon nanotube 108, and

as a droplet over the tip 114 of each primary carbon nanotube 108.

The catalyst 102 is captured by the tips 114 when the tips 114 are first formed, and are continued to be held by the tips 114 during the growth of the primary carbon nanotubes 108. The tip 114 of each primary carbon nanotube 108 is that portion of the primary carbon nanotube 108 that is most remote from the substrate 100.

[036] The catalyst 102 may be solid and surface tension and/or physical holding may be used to hold the catalyst at the tips 114.

[037] A second substrate 110 is prepared and a layer 112 is deposited onto substrate 110. The layer 112 is of a material of or containing carbon such as, for example, amorphous carbon or any other material containing carbon suitable for forming secondary carbon nanotubes. The layer 112 is applied using for example, physical vapor deposition or chemical vapor deposition. The substrate 110 will subsequently be used for the formation of secondary carbon nanotubes.

[039] The substrate 110 with the layer 112 of or containing carbon is placed on the heating stage 104 in a carbon nanotube growth chamber (not shown). For the growth of secondary carbon nanotubes, the substrate 100 with layer 106 of primary carbon nanotubes 108 is upended or flipped such that the tips 114 of the primary carbon nanotubes 108, and the catalyst 102 held by the tips 114, are in contact with the layer 112 of or containing carbon and being on the second substrate 110.

[040] The primary carbon nanotubes 108 may be annealed for a predetermined period such as, for example 0.5 to 10 minutes at a second room or elevated temperatures in the range of, for example, room temperature to 900 °C, preferably 400 °C to 800 °C. During this annealing process, a reduced flow of a gas such as, for example, hydrogen or another gas containing hydrogen such as, for example, ammonia, is introduced.

[041] After annealing, the secondary carbon nanotubes 116 are grown in the nanopores 118 between the primary carbon nanotubes 108. Growth of the secondary carbon nanotubes may be by introducing a hydrocarbon gas such as, for example, methane, benzene, acetylene, naphthalene, or ethylene. This is preferably at a third room or elevated temperature that is more preferably the same as the second elevated temperature (although it may be different) and therefore may be in the range of, for example, room temperature to 900 °C, preferably 400 °C to 800 °C. Due to the presence of the catalyst 102 at the tips 114 of the primary carbon nanotubes 108 and the contact between the tips 114, the catalyst 102 and the layer 112, the secondary carbon nanotubes 116 grow from the primary carbon nanotubes 108 at the tips 114. The secondary carbon nanotubes 116 bridge and link the primary carbon nanotubes 108 to form a three-dimensional network 120 of carbon nanotubes 108, 116.

[042] In bridging and linking the primary carbon nanotubes 108, at least some of the secondary carbon nanotubes 116 grow from one primary carbon nanotube 108 and contact (both physically and electrically) a second primary carbon nanotube. This can be seen in Figures 4 and 5. In Figure 3, the primary carbon nanotubes 108 are arranged in closely-spaced pairs 130 that are spaced apart from adjacent pairs 130. By controlling the spacing between the primary carbon nanotubes 108 of each pair 130, and the spacing between adjacent pairs 130 of primary carbon nanotubes 108, the secondary carbon nanotubes will bridge and link only the two primary carbon nanotubes 108 of each pair 130, and will not bridge or link primary carbon nanotubes 108 of adjacent pairs 130.

[043] If required or desired, the formation of the secondary carbon nanotubes 116 may be repeated for tertiary carbon nanotubes, quaternary carbon nanotubes, and so forth, for more complex networks 120.

[044] The second substrate 110 is then removed to leave the network 120 and first substrate 100. The bonding of the primary carbon nanotubes 108 to the second substrate 110 is relatively low, thus facilitating its removal. The bonding of the primary carbon nanotubes 108 to the first substrate 100 is also relatively low and thus first substrate 100 may also be removed to leave the network 120. This may be in addition to or in place of the removal of the second substrate 110.

[045] Figures 4 and 5 respectively show a scanning electron microscope image and a transmission electron microscope image of a three-dimensional carbon nanotube network formed by the exemplary embodiment of Figures 1 to 3. The primary carbon nanotubes 108 and the secondary carbon nanotubes 116 can easily be seen. The secondary carbon nanotubes 116 are of a smaller diameter than the primary carbon nanotubes.

[046] Figure 6 is a graph of the Raman spectroscopy of a three-dimensional carbon nanotube network formed by the exemplary embodiment of Figure 1 and shows peaks at approximately 1,351 cm^{-1} and 1,590 cm^{-1}.

[047] Figure 7 is two graphs of the current versus voltage obtained from a three-dimensional carbon nanotube network formed by the exemplary embodiment of Figure 1 at temperatures of (a) 20^{o}C and (b) 100^{o}C. The results are compared with a composite having dispersed aligned carbon nanotubes. The graphs reveal that the conductivity of the three-dimensional carbon nanotube network according to the exemplary embodiment of

Figures 1 to 3 is higher than that of the composite having dispersed aligned carbon nanotubes at 20°C. At the higher temperature of 100°C, the composite having dispersed aligned carbon nanotubes has an increased but significantly non-linear conductivity relative to that of the three-dimensional carbon nanotube network formed by the exemplary embodiment of Figure 1.

[048] The three-dimensional carbon nanotube network can be used, for example, as a building block for nanotube electronic devices, field-effect transistors, field emission sources, diodes, biosensors, gas sensors, chemical sensors, batteries, electrochemical devices, supercapacitors and actuators, gas and hydrogen storage, solar cells, photovoltaic devices, detectors, and so forth; and as a re-enforcement or filler in various different matrixes such as, for example, polymers, metals, alloys, ceramics, organics and inorganics to form structural or functional composites.

[049] For the embodiment of Figure 3, in each pair 130, one of the primary carbon nanotubes 108 may be used as a source electrode, and the other as a drain electrode. The secondary carbon nanotube 116 may be used as a gate. In this way the pair 130 with the secondary carbon nanotubes is a transistor. Also for the embodiment of Figure 3, in each pair 130, the primary carbon nanotubes 108 may be used as two electrodes or one portion of the same electrode. The secondary carbon nanotube 116 may be used as an ultra-sensitive sensor element. In this way the pair 130 with the secondary carbon nanotubes 116 is a biosensor, gas sensor, or chemical sensor.

[050] For the embodiment of Figure 1, the three-dimensional network 120 of carbon nanotubes 108, 116 may be used as electron emission source or field emission source with the three-dimensional network 120 located or sandwiched between two substrates. Again for the embodiment of Figure 1, the three-dimensional network 120 of carbon nanotubes 108, 116 may be used as a supercapacitor material and structure, with the three-dimensional network 120 located or sandwiched between two substrates. Either or both of the substrates may be electrodes.

[051] For the embodiment of Figures 1 and 3, the three-dimensional network 120 of carbon nanotubes 108, 116 and the pair 130 may be used as the electrodes, circuit and/or functional device, or one portion of the electrode, circuit and/or functional device, for batteries, solar cells, photovoltaic devices and detectors. Again, for the embodiment of Figures 1 and 3, after removal of the substrate 100, the three-dimensional network 120 of

carbon nanotubes 108, 116 and the pair 130 may be transferred onto another rigid or flexible substrate to form antennas, electronic devices, field-effect transistors, field emission sources, diodes, biosensors, gas sensors, chemical sensors, batteries, electrochemical devices, supercapacitors and actuators, gas and hydrogen storage, solar cells, photovoltaic devices, detectors, and so forth.

[052] For the embodiment of Figure 1, the three-dimensional network 120 of carbon nanotubes 108, 116 may be removed from the substrate 100 and spun into yarn, fibre, rope or wire; or drawn into sheet or web; or woven into a textile using known techniques for spinning, drawing and/or weaving. The yarn/fibre/wire/sheet/web/textile may be used:

to form electronic devices, field-effect transistors, field emission sources, diodes, biosensors, gas sensors, chemical sensors, batteries, electrochemical devices, supercapacitors, actuators, and filaments;

for gas and hydrogen storage devices, solar cells, photovoltaic devices, detectors; and/or as

a re-enforcement or filler in various matrixes such as, for example, polymers, metals, alloys, ceramics, organics and inorganics to form structural or functional composites, and so forth.

[053] Finally, for the embodiment of Figure 1, after removal of the substrate 100, the three-dimensional network 120 of carbon nanotubes 108, 116 may be used as a re-enforcement or filler in various matrixes such as, for example, polymers, metals, alloys, ceramics, organics and inorganics to form structural or functional composites.

[054] Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations in details of design, construction and/or operation may be made without departing from the present invention.

The Claims:

1. A method for forming self-assembled, three-dimensional carbon nanotube network, the method comprising: growing primary carbon nanotubes; and growing secondary carbon nanotubes, the secondary carbon nanotubes bridging and linking with the primary carbon nanotubes to form the self-assembled three dimensional carbon nanotube network.
2. A method for forming self-assembled, three-dimensional carbon nanotube network, the method comprising: growing primary carbon nanotubes; and growing secondary carbon nanotubes, the primary carbon nanotubes being one of: aligned and non-aligned, and the secondary carbon nanotubes being the other of: aligned and non-aligned.
3. A method for forming self-assembled, three-dimensional carbon nanotube network, the method comprising: growing primary carbon nanotubes; and growing secondary carbon nanotubes, the secondary carbon nanotubes growing from the primary carbon nanotubes.
4. A method for forming self-assembled, three-dimensional carbon nanotubes network, the method comprising: placing spots of a catalyst on a substrate at locations where it is desired for primary carbon nanotubes to be grown, and growing the primary carbon nanotubes at those spots.
5. A method for forming self-assembled, three-dimensional carbon nanotube network, the method comprising: growing primary carbon nanotubes from a catalyst on a first substrate, retaining a portion of the catalyst at tips of the primary carbon nanotubes, placing the tips and the catalyst in contact with a layer of a carbon-containing material on a second substrate, and growing secondary carbon nanotubes from the tips of the primary carbon nanotubes.
6. A method as claimed in any one of claims 2 to 5, wherein the secondary carbon nanotubes bridge and link the primary carbon nanotubes.
7. A method as claimed in claim 2, claim 4 or claim 6 when dependent on claim 2 or claim 4, wherein the secondary carbon nanotubes are grown from the primary carbon nanotubes.
8. A method as claimed in any one of claims 1 to 7, wherein the secondary carbon nanotubes are grown in nanopores between the primary carbon nanotubes.
9. A method as claimed in any one of claims 1 to 4 or claims 6 to 8 when dependent on any one of claims 1 to 4, wherein formation of the primary carbon nanotubes is on a first substrate having a layer of a catalyst on the substrate.

10. A method as claimed in claim 9, wherein the layer of catalyst is selected from the group consisting of: continuous, and discontinuous.
11. A method as claimed in claim 9 or claim 10, wherein the primary carbon nanotubes are grown only where the catalyst is located on the substrate.
12. A method as claimed in any one of claims 9 to 11, wherein when the primary carbon nanotubes are grown, catalyst is captured by tips of the primary carbon nanotubes.
13. A method as claimed in claim 12, wherein the secondary carbon nanotubes grow from the tips of the primary carbon nanotubes.
14. A method as claimed in claim 12 or claim 13, wherein before the secondary carbon nanotubes are grown, the tips of the primary carbon nanotubes are applied to a second substrate having thereon a layer of or containing carbon.
15. A method as claimed in claim 14, wherein before the tips of the primary carbon nanotubes are applied to the second substrate, the first substrate with the layer of catalyst and the primary carbon nanotubes is rotated.
16. A method as claimed in any one of claims 1 to 15, wherein the formation of the primary nanotubes is at a first elevated temperature.
17. A method as claimed in any one of claims 1 to 16, wherein before the secondary carbon nanotubes are grown, the primary carbon nanotubes are annealed at a second elevated temperature.
18. A method as claimed in claim 17, wherein the annealing takes place after the tips of the primary carbon nanotubes are applied to the layer of or containing carbon on the second substrate.
19. A method as claimed in claim 17 or claim 18, wherein annealing is for a predetermined period and the second elevated temperature is in the range 400 to 800 °C.
20. A method as claimed in any one of claims 17 to 19, wherein during annealing, a reduced flow of a gas of or containing hydrogen is introduced.
21. A method as claimed in claim 19, wherein the predetermined period is in the range 0.5 to 10 minutes.
22. A method as claimed in any one of claims 1 to 21, wherein the secondary carbon nanotubes are grown at a third elevated temperature.
23. A self-assembled three-dimensional carbon nanotube network when formed by the method of any one of claims 1 to 22.
24. A self-assembled, three-dimensional carbon nanotube network comprising: a plurality of primary carbon nanotubes; and a further plurality of secondary carbon

nanotubes, the secondary carbon nanotubes bridging and linking with the primary carbon nanotubes to form the self-assembled three dimensional carbon nanotube network.

25. A self-assembled, three-dimensional carbon nanotube network comprising: a plurality of primary carbon nanotubes; and a further plurality of secondary carbon nanotubes, the plurality of primary carbon nanotubes being one of: aligned and non-aligned, and the further plurality of secondary carbon nanotubes being the other of: aligned and non-aligned.

26. A self-assembled, three-dimensional carbon nanotube network comprising: a plurality of primary carbon nanotubes; and a further plurality of secondary carbon nanotubes, the further plurality of secondary carbon nanotubes growing from the plurality of primary carbon nanotubes.

27. A self-assembled, three-dimensional carbon nanotube network as claimed in claim 25 or claim 26, wherein the secondary carbon nanotubes bridge and link the primary carbon nanotubes.

28. A self-assembled, three-dimensional carbon nanotube network as claimed in claim 26 or claim 27 when dependent on claim 26, wherein the secondary carbon nanotubes extend from the primary carbon nanotubes.

29. A self-assembled, three-dimensional carbon nanotube network as claimed in any one of claims 24 to 28, wherein the secondary carbon nanotubes are in nanopores between the primary carbon nanotubes.

30. A self-assembled, three-dimensional carbon nanotube network as claimed in claim any one of claims 24 to 29, wherein the primary carbon nanotubes are on a first substrate having a layer of a catalyst on the substrate.

31. A self-assembled, three-dimensional carbon nanotube network as claimed in claim 30, wherein the layer of catalyst is selected from the group consisting of: continuous, and discontinuous.

32. A self-assembled, three-dimensional carbon nanotube network as claimed in claim 30 or claim 31, wherein the primary carbon nanotubes are only where the catalyst is located on the substrate.

33. A self-assembled, three-dimensional carbon nanotube network as claimed in any one of claims 30 to 32, wherein when the primary carbon nanotubes are grown, catalyst is captured by tips of the primary carbon nanotubes.

34. A self-assembled, three-dimensional carbon nanotube network as claimed in claim 33, wherein the secondary carbon nanotubes extend from the tips of the primary carbon nanotubes.

35. A self-assembled, three-dimensional carbon nanotube network as claimed in any one of claims 24 to 34, wherein the primary carbon nanotubes are arranged in closely-spaced pairs; adjacent pairs of primary carbon nanotubes being spaced apart such that there is at least one secondary carbon nanotube bridging and linking only the two primary carbon nanotubes of each pair; there being no secondary carbon nanotubes bridging or linking primary carbon nanotubes of adjacent pairs.

36. A self-assembled, three-dimensional carbon nanotube network as claimed in any one of claims 24 to 35, wherein the self-assembled, three-dimensional carbon nanotube network is used as a building block for at least one selected from the group consisting of: nanotube electronic devices, field-effect transistors, field emission sources, diodes, biosensors, gas sensors, chemical sensors, batteries, electrochemical devices, supercapacitors and actuators, gas and hydrogen storage, solar cells, photovoltaic devices, and detectors.

37. A self-assembled, three-dimensional carbon nanotube network as claimed in any one of claims 24 to 35, wherein the self-assembled, three-dimensional carbon nanotube network is used as one of: a re-enforcement, and a filler, in matrixes selected from the group consisting of: polymers, metals, alloys, ceramics, organics and inorganics, to form structural or functional composites.

38. A self-assembled, three-dimensional carbon nanotube network as claimed in claim 35, wherein in each pair of primary carbon nanotubes, the primary carbon nanotubes are used in a manner selected from the group consisting of: two electrodes, and one portion of the same electrode.

39. A self-assembled, three-dimensional carbon nanotubes network as claimed in claim 38, wherein the at least one secondary carbon nanotube is used as a sensor element such that the self-assembled, three-dimensional carbon nanotube network is one of: a biosensor, a gas sensor, and a chemical sensor.

40. A self-assembled, three-dimensional carbon nanotubes network as claimed in any one of claims 30 to 39, wherein the self-assembled, three-dimensional carbon nanotube network is located between two substrates and is used in a manner selected from the group consisting of: a supercapacitor material, a supercapacitor structure, an electron emission source, and a field emission source.

41. A self-assembled, three-dimensional carbon nanotube network as claimed in any one of claims 35 to 40, wherein each pair of primary carbon nanotubes are used as at least one portion of one of: electrodes, circuit, and functional device, for batteries, solar cells, photovoltaic devices and detectors.

42. A self-assembled, three-dimensional carbon nanotube network as claimed in any one of claims 35 to 41, wherein, after removal of the substrate, the self-assembled, three-dimensional carbon nanotube network is transferred onto another substrate to form at least one selected from the group consisting of: antennas, electronic devices, field-effect transistors, field emission sources, diodes, biosensors, gas sensors, chemical sensors, batteries, electrochemical devices, supercapacitors and actuators, gas and hydrogen storage, solar cells, photovoltaic devices, and detectors.

43. A self-assembled, three-dimensional carbon nanotube network as claimed in any one of claims 24 to 42, wherein, after removal of the substrate, the self-assembled, three-dimensional carbon nanotube network is used as one of: a re-enforcement and a filler, in at least one matrix selected from the group consisting of: polymers, metals, alloys, ceramics, organics and inorganics, to form composites.

44. A self-assembled, three-dimensional carbon nanotube network as claimed in claim 35, wherein in each pair of primary carbon nanotubes one of the primary carbon nanotubes is a source, and the other primary carbon nanotube is a drain; and the secondary carbon nanotubes is a gate such that the pair of primary carbon nanotubes and the secondary carbon nanotube is a transistor.

45. A transistor comprising a source, a gate and a drain; wherein the source is a first primary carbon nanotube of a pair of primary carbon nanotubes, the drain is a second primary carbon nanotube of a pair of primary carbon nanotubes, and the gate is at least one secondary carbon nanotube bringing and linking the first primary carbon nanotube and the second primary carbon nanotube.

46. A transistor as claimed in claim 45, wherein the at least one secondary carbon nanotube extends from a tip of at least one of the first and second primary carbon nanotubes.

47. A method as claimed in any one of claims 1 to 22 further comprising forming the self-assembled, three-dimensional carbon nanotube network into at least one selected from the group consisting of: a yarn, a fibre, a rope, a wire, a sheet, a web, and a textile.

48. A method as claimed in claim 47, wherein the forming is by one of: spinning, drawing and weaving.

49. A self-assembled, three-dimensional carbon nanotube network as claimed in any one of claims 22 to 44, wherein the self-assembled, three-dimensional carbon nanotube network is formed into at least one selected from the group consisting of: a yarn, a fibre, a rope, a wire, a sheet, a web, and a textile.

50. A self-assembled, three-dimensional carbon nanotube network as claimed in claim 49, wherein the forming is by one of: spinning, drawing and weaving.

51. A yarn, fibre, rope, wire, sheet, web or textile formed by the method of claim 47 or claim 48.

52. A self-assembled, three-dimensional carbon nanotube network as claimed in claim 40 or any one of claims 41 to 44 when dependent on claim 40, wherein at least one of the two substrates is an electrode.