

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
8 March 2012 (08.03.2012)

PCT

(10) International Publication Number  
**WO 2012/031037 A1**

(51) International Patent Classification:  
**B05D 5/12** (2006.01)

(21) International Application Number:  
PCT/US2011/050084

(22) International Filing Date:  
31 August 2011 (31.08.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
61/379,713 2 September 2010 (02.09.2010) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))



WO 2012/031037 A1

(54) Title: METAL SUBSTRATES HAVING CARBON NANOTUBES GROWN THEREON AND PROCESSES FOR PRODUCTION THEREOF

(57) Abstract: Processes for growing carbon nanotubes on metal substrates are described herein. The processes include depositing a catalyst precursor on a metal substrate, optionally depositing a non-catalytic material on the metal substrate, and after depositing the catalyst precursor and the optional non-catalytic material, exposing the metal substrate to carbon nanotube growth conditions so as to grow carbon nanotubes thereon. The carbon nanotube growth conditions convert the catalyst precursor into a catalyst that is operable for growing carbon nanotubes. The metal substrate can remain stationary or be transported while the carbon nanotubes are being grown. Metal substrates having carbon nanotubes grown thereon are also described.

METAL SUBSTRATES HAVING CARBON NANOTUBES GROWN THEREON  
AND PROCESSES FOR PRODUCTION THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority under 35 U.S.C. § 119 from United States Provisional Patent Application serial number 61/379,713, filed September 2, 2010, which is incorporated herein by reference in its entirety. This application is also related to United States Patent Applications 13/042,397, filed March 7, 2011, and 12/611,073, filed November 2, 2009, each of which is also incorporated herein by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR  
DEVELOPMENT

[0002] Not applicable.

FIELD OF THE INVENTION

[0003] The present invention generally relates to carbon nanotubes, and, more specifically, to carbon nanotube growth.

BACKGROUND

[0004] Carbon nanotubes have been proposed to have utility in a number of applications due to their large effective surface area, mechanical strength, and thermal and electrical conductivity. Many of these applications are particularly well suited for carbon nanotubes grown on metal substrates.

[0005] In order to synthesize carbon nanotubes, a catalyst is generally needed to mediate carbon nanotube growth. Most often the catalyst is a metal nanoparticle, particularly a zero-valent transition metal nanoparticle. A number of processes for synthesizing carbon nanotubes are known in the art including, for example, micro-cavity, thermal- or plasma-enhanced chemical vapor deposition (CVD) techniques, laser

ablation, arc discharge, flame synthesis, and high pressure carbon monoxide (HiPCO) techniques. Generally, such processes for synthesizing carbon nanotubes involve generating reactive gas phase carbon species under conditions suitable for carbon nanotube growth.

**[0006]** Synthesis of carbon nanotubes on solid substrates can be carried out using many of these techniques. Oftentimes, the solid substrate can be a refractory substance such as, for example, silicon dioxide or aluminum oxide. However, it is considered very difficult in the art to grow carbon nanotubes on metal substrates. There are several reasons for this difficulty. First, some metals have melting points that are in the temperature range at which carbon nanotubes typically form (*e.g.*, about 550°C to about 800°C), thereby rendering the metal substrate susceptible to thermal damage. Aluminum is an illustrative example of such a metal substrate (m.p. = 660°C). Damage can include, for example, melting, cracking, warping, pitting and thinning, particularly in thin metal substrates. Even in a metal substrate having a melting point in excess of the carbon nanotube growth temperature, extended exposure to carbon nanotube growth conditions can compromise the metal substrate's structural integrity by forming similar types of thermal damage. Furthermore, interactions between the metal catalyst and the metal substrate can severely limit the diffusion of atomic carbon into the metal catalyst, thereby significantly inhibiting or prohibiting carbon nanotube growth.

**[0007]** In view of the foregoing, reliable processes for growing carbon nanotubes on metal substrates would be of substantial benefit in the art. The present disclosure satisfies this need and provides related advantages as well.

## SUMMARY

**[0008]** In some embodiments, carbon nanotube growth processes described herein include depositing a catalyst precursor on a metal substrate, depositing a non-catalytic material on the metal substrate, and after depositing the catalyst precursor and the non-catalytic material, exposing the metal substrate to carbon nanotube growth conditions so as to grow carbon nanotubes thereon. The carbon nanotube growth conditions convert the catalyst precursor into a catalyst that is operable for growing carbon nanotubes.

[0009] In some embodiments, carbon nanotube growth processes described herein include depositing a catalyst precursor on a metal substrate that has a melting point of about 800°C or less, and after depositing the catalyst precursor, exposing the metal substrate to carbon nanotube growth conditions so as to grow carbon nanotubes thereon. The carbon nanotube growth conditions convert the catalyst precursor into a catalyst that is operable for growing carbon nanotubes.

[0010] In some embodiments, carbon nanotube growth processes described herein include depositing a catalyst precursor on a metal substrate; depositing a non-catalytic material on the metal substrate; after depositing the catalyst precursor and the non-catalytic material, exposing the metal substrate to carbon nanotube growth conditions so as to grow carbon nanotubes thereon; and transporting the metal substrate while the carbon nanotubes are being grown. The non-catalytic material is deposited prior to, after or concurrently with the catalyst precursor. The carbon nanotube growth conditions convert the catalyst precursor into a catalyst that is operable for growing carbon nanotubes.

[0011] In some embodiments, metal substrates having carbon nanotubes grown thereon by the present carbon nanotube growth processes are described herein.

[0012] The foregoing has outlined rather broadly the features of the present disclosure in order that the detailed description that follows can be better understood. Additional features and advantages of the disclosure will be described hereinafter, which form the subject of the claims.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0013] For a more complete understanding of the present disclosure, and the advantages thereof, reference is now made to the following descriptions to be taken in conjunction with the accompanying drawings describing specific embodiments of the disclosure, wherein:

[0014] FIGURES 1A and 1B show illustrative SEM images of carbon nanotubes grown on a copper substrate using a palladium catalyst under static chemical vapor deposition conditions for 5 minutes at a temperature of 750°C;

[0015] FIGURE 2 shows an illustrative SEM image of carbon nanotubes grown on a copper substrate using a palladium catalyst under continuous chemical vapor deposition conditions at a temperature of 750°C and a linespeed of 1 ft/min, which is equivalent to 1 minute of carbon nanotube growth time;

[0016] FIGURES 3A and 3B show illustrative SEM images of carbon nanotubes grown on a copper substrate using an iron nanoparticle catalyst under static chemical vapor deposition conditions for 5 minutes at a temperature of 750°C, where the iron nanoparticle catalyst was deposited over a layer of non-catalytic Accuglass T-11 Spin-On Glass;

[0017] FIGURES 4A and 4B show illustrative SEM images of carbon nanotubes and carbon nanofibers grown on a copper substrate using an iron nanoparticle catalyst under static chemical vapor deposition conditions for 30 minutes at a temperature of 750°C, where the iron nanoparticle catalyst was deposited under a layer of non-catalytic Accuglass T-11 Spin-On Glass;

[0018] FIGURES 5A and 5B show illustrative SEM images of carbon nanotubes grown on a stainless steel wire mesh substrate using an iron nanoparticle catalyst under continuous chemical vapor deposition conditions at a temperature of 800°C and a linespeed of 2 ft/min, which is equivalent to 30 seconds of carbon nanotube growth time, where the iron nanoparticle catalyst was deposited under a layer of non-catalytic Accuglass T-11 Spin-On Glass;

[0019] FIGURES 6A and 6B show illustrative SEM images of carbon nanotubes grown on a copper substrate using an iron nitrate catalyst precursor under static chemical vapor deposition conditions for 5 minutes at a temperature of 750°C, where the iron nitrate catalyst precursor was deposited concurrently with a non-catalytic aluminum nitrate material;

[0020] FIGURES 7A and 7B show illustrative SEM images of carbon nanotubes grown on an aluminum substrate using an iron nitrate catalyst precursor under static chemical vapor deposition conditions for 1 minute at a temperature of 750°C, where the iron nitrate catalyst precursor was deposited concurrently with a non-catalytic aluminum nitrate material;

[0021] FIGURES 8A and 8B show illustrative SEM images of carbon nanotubes grown on an aluminum substrate using an iron nitrate catalyst precursor under static chemical vapor deposition conditions for 1 minute at a temperature of 580°C, where the iron nitrate catalyst precursor was deposited concurrently with a non-catalytic aluminum nitrate material;

[0022] FIGURES 9A and 9B show illustrative SEM image of carbon nanotubes grown on an aluminum substrate using an iron nitrate catalyst precursor under continuous chemical vapor deposition conditions at a temperature of 750°C and a linespeed of 1 ft/min, which is equivalent to 1 minute of carbon nanotube growth time, where the iron nitrate catalyst precursor was deposited concurrently with a non-catalytic aluminum nitrate material;

[0023] FIGURE 10 shows an illustrative SEM image of carbon nanotubes grown on an aluminum substrate using iron nitrate catalyst precursor under continuous chemical vapor deposition conditions for 10 minutes at a temperature of 550°C; and

[0024] FIGURES 11A and 11B show illustrative SEM images of carbon nanotubes grown on an aluminum substrate using an iron acetate/cobalt acetate catalyst precursor under continuous chemical vapor deposition conditions for 10 minutes at a temperature of 550°C.

#### DETAILED DESCRIPTION

[0025] The present disclosure is directed, in part, to processes for growing carbon nanotubes on metal substrates. The present disclosure is also directed, in part, to metal substrates having carbon nanotubes grown thereon that are produced by the present carbon nanotube growth processes.

[0026] Carbon nanotubes have demonstrated utility in a number of applications that take advantage of their unique structure and properties including, for example, large surface area, mechanical strength, electrical conductivity, and thermal conductivity. When grown on a metal substrate, carbon nanotubes and the metal substrate form a composite architecture that advantageously allows the beneficial properties of the carbon nanotubes to be imparted to the metal substrate. However, growth of carbon nanotubes on metal substrates has proved particularly difficult in the art.

[0027] As a non-limiting example of the benefits that can be conveyed to a metal substrate by carbon nanotubes, the mechanical properties of a metal substrate can be improved by growing carbon nanotubes thereon. Such metal substrates can be particularly useful for structural applications due to their improved fracture toughness and fatigue resistance, for example. Metals including, for example, copper, nickel, platinum, silver, gold, and aluminum have a face centered cubic (fcc) atomic structure that is particularly susceptible to fatigue failure. Growth of carbon nanotubes on these metals, in particular, or other metals having an fcc atomic structure can markedly improve their mechanical strength by preventing fatigue cracks from propagating, thereby increasing the number of stress cycles that the metal can undergo before experiencing fatigue failure.

[0028] Another non-limiting example of the benefits that carbon nanotubes can convey to a metal substrate is an enhancement of the metal substrate's electrical properties. For example, metal films used as current collectors in batteries can exhibit improved current collection properties when carbon nanotubes are grown thereon. Metal substrates containing carbon nanotubes grown thereon can also be used as electrodes in supercapacitors and other electrical devices. Not only do the carbon nanotubes improve the electrical conductivity of the electrodes, but they also increase the overall electrode surface area and further increase its efficiency.

[0029] In some embodiments, the carbon nanotube growth processes described herein can be conducted in a substantially continuous manner with the metal substrate being transported while carbon nanotubes are being grown thereon. Given the benefit of the present disclosure, one having ordinary skill in the art will recognize the advantages

of transporting a metal substrate during carbon nanotube growth, particularly a metal substrate having a melting point of about 800°C or less. Among the many advantages of such carbon nanotube growth processes are 1) limiting thermal damage (*e.g.*, melting) to metal substrates by minimizing exposure time to high temperature conditions, and 2) enabling the high throughput growth of sufficiently large quantities of carbon nanotubes for commercial applications. In some embodiments, the metal substrate can be transported in a zero- or low tension condition such that undue stress is not placed on the metal substrate during transport, which could lead to metal fatigue. In spite of the foregoing advantages of such carbon nanotube growth processes, it should also be understood that the present carbon nanotube growth processes can be conducted in a batchwise (static) manner in alternative embodiments.

**[0030]** In some embodiments, carbon nanotubes grown on a metal substrate can be chemically or mechanically adhered to the metal substrate. Carbon nanotubes grown on a metal substrate by the present processes (*i.e.*, infused carbon nanotubes) can be more strongly adhered to the metal substrate than would pre-synthesized carbon nanotubes held in place by simple van der Waals physisorption interactions. Hence, the present metal substrates having carbon nanotubes grown thereon are distinguished from metal substrates having had pre-formed carbon nanotubes deposited thereon (*e.g.*, from a carbon nanotube solution or suspension). In some embodiments, the carbon nanotubes can be directly bonded to the metal substrate (*e.g.*, by a covalent bond). In other embodiments, the carbon nanotubes can be indirectly bonded to the metal substrate via a catalytic material used to mediate the carbon nanotubes' synthesis and/or via a non-catalytic material deposited on the metal substrate.

**[0031]** As used herein, the term "catalyst" refers to a substance that is operable to form carbon nanotubes when exposed to carbon nanotube growth conditions.

**[0032]** As used herein, the term "catalytic material" refers to catalysts and catalyst precursors. As used herein, the term "catalyst precursor" refers to a substance that can be transformed into a catalyst under appropriate conditions, particularly carbon nanotube growth conditions.

[0033] As used herein, the term “nanoparticle” refers to particles having a diameter between about 0.1 nm and about 100 nm in equivalent spherical diameter, although nanoparticles need not necessarily be spherical in shape. As used herein, the term “catalytic nanoparticle” refers to a nanoparticle that possesses catalytic activity for mediating carbon nanotube growth.

[0034] As used herein, the term “transition metal” refers to any element or alloy of elements in the d-block of the periodic table (Groups 3 through 12), and the term “transition metal salt” refers to any transition metal compound such as, for example, transition metal oxides, nitrates, chlorides, bromides, iodides, fluorides, acetates, citrates, carbides, nitrides, and the like. Illustrative transition metals that can form catalytic nanoparticles suitable for synthesizing carbon nanotubes include, for example, Ni, Fe, Co, Mo, Cu, Pt, Au, Ag, alloys thereof, salts thereof, and mixtures thereof.

[0035] As used herein, the terms “spoolable lengths” or “spoolable dimensions” equivalently refer to a material that has at least one dimension that is not limited in length, thereby allowing the material to be stored on a spool or mandrel, for example, in a reel-to-reel process. A material of “spoolable lengths” or “spoolable dimensions” has at least one dimension that allows the growth of carbon nanotubes thereon while the material is being transported. However, a material of spoolable lengths can also have carbon nanotubes grown thereon in a batchwise manner, if desired.

[0036] As used herein, the term “carbon nanotube growth conditions” refers to any process that is capable of growing carbon nanotubes in the presence of a suitable catalyst. Generally, carbon nanotube growth conditions generate a reactive carbon species, oftentimes by the pyrolysis of an organic compound.

[0037] As used herein, the terms “convey” and “conveying” will be understood to be synonymous with the terms “moving” and/or “transporting”.

[0038] In various embodiments, carbon nanotube growth processes described herein can include depositing a catalyst precursor on a metal substrate, depositing a non-catalytic material on the metal substrate, and exposing the metal substrate to carbon nanotube growth conditions after depositing the catalyst precursor, so as to grow carbon

nanotubes thereon. When exposed to the carbon nanotube growth conditions, the catalyst precursor can be converted into a catalyst that is operable for growing carbon nanotubes.

**[0039]** In other various embodiments, carbon nanotube growth processes described herein can include depositing a catalyst precursor on a metal substrate that has a melting point of about 800°C or less, and after depositing the catalyst precursor, exposing the metal substrate to carbon nanotube growth conditions so as to grow carbon nanotubes thereon. When exposed to the carbon nanotube growth conditions, the catalyst precursor can be converted into a catalyst that is operable for growing carbon nanotubes.

**[0040]** In still other various embodiments, carbon nanotube growth processes described herein can include depositing a catalyst precursor on a metal substrate; depositing a non-catalytic material on the metal substrate; after depositing the catalyst precursor and the non-catalytic material, exposing the metal substrate to carbon nanotube growth conditions so as to grow carbon nanotubes thereon; and transporting the metal substrate while the carbon nanotubes are being grown. The non-catalytic material can be deposited prior to, after or concurrently with the catalyst precursor. When exposed to the carbon nanotube growth conditions, the catalyst precursor can be converted into a catalyst that is operable for growing carbon nanotubes.

**[0041]** The form of the metal substrate can vary without limitation in the present embodiments. However, in some embodiments, the form of the metal substrate can be compatible with the metal substrate being transported during carbon nanotube growth (*e.g.*, in a reel-to-reel process). A suitable metal substrate form that can be transported during carbon nanotube growth includes, for example, metal fibers or various metal fiber forms that are made from metal fibers. In some embodiments, the metal substrate can be in non-limiting forms such as, for example, metal fibers, metal filaments, metal wires, metal rovings, metal yarns, metal fiber tows, metal tapes, metal ribbons, metal wire meshes, metal tubes, metal films, metal braids, woven metal fabrics, non-woven metal fabrics, metal fiber plies, and metal fiber mats. Higher order forms such as, for example, woven and non-woven metal fabrics, metal fiber plies, and metal wire meshes can be formed from lower order metal substrates such as, for example, metal fibers, metal filaments, and metal fiber tows. That is, metal fibers, metal filaments, or metal fiber tows

can have carbon nanotubes grown thereon, with formation of the higher order forms taking place thereafter. In other embodiments, such higher order forms can be preformed with growth of carbon nanotubes thereon taking place thereafter. As used herein, the foregoing metal substrates will be collectively referred to as metal fibers.

**[0042]** Filaments include high aspect ratio fibers having diameters generally ranging in size between about 1  $\mu\text{m}$  and about 100  $\mu\text{m}$ . Rovings include soft strands of fiber that have been twisted, attenuated and freed of foreign matter.

**[0043]** Yarns include closely associated bundles of twisted filaments, wherein each filament diameter in the yarn is relatively uniform. Yarns have varying weights described by their 'tex,' (expressed as weight in grams per 1000 linear meters), or 'denier' (expressed as weight in pounds per 10,000 yards). For yarns, a typical tex range is usually between about 200 and about 2000.

**[0044]** Fiber braids represent rope-like structures of densely packed fibers. Such rope-like structures can be assembled from yarns, for example. Braided structures can include a hollow portion. Alternately, a braided structure can be assembled about another core material.

**[0045]** Fiber tows include associated bundles of untwisted filaments. As in yarns, filament diameter in a fiber tow is generally uniform. Fiber tows also have varying weights and a tex range that is usually between about 200 and about 2000. In addition, fiber tows are frequently characterized by the number of thousands of filaments in the fiber tow, such as, for example, a 12K tow, a 24K tow, a 48K tow, and the like.

**[0046]** Tapes are fiber materials that can be assembled as weaves or as non-woven flattened fiber tows, for example. Tapes can vary in width and are generally two-sided structures similar to a ribbon. In the various embodiments described herein, carbon nanotubes can be grown on a tape on one or both sides of the tape. In addition, carbon nanotubes of different types, diameters or lengths can be grown on each side of a tape, which can be advantageous in certain applications.

[0047] In some embodiments, fiber materials can be organized into fabric or sheet-like structures. These include, for example, woven fabrics, non-woven fiber mats, meshes and fiber plies, in addition to the tapes described above.

[0048] The types of carbon nanotubes grown on the metal substrates can generally vary without limitation. In various embodiments, the carbon nanotubes grown on the metal substrates can be, for example, any of a number of cylindrically-shaped allotropes of carbon of the fullerene family including single-wall carbon nanotubes, double-wall carbon nanotubes, multi-wall carbon nanotubes, and any combination thereof. One of ordinary skill in the art will recognize that the types of carbon nanotubes grown on the metal substrate can be varied by adjusting the carbon nanotube growth conditions. In some embodiments, the carbon nanotubes can be capped with a fullerene-like structure. That is, the carbon nanotubes have closed ends in such embodiments. However, in other embodiments, the carbon nanotubes can remain open-ended. In some embodiments, closed carbon nanotube ends can be opened through treatment with an appropriate oxidizing agent (*e.g.*, HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>). In some embodiments, the carbon nanotubes can encapsulate other materials after being grown on the metal substrate. In some embodiments, the carbon nanotubes can be covalently functionalized after being grown on the metal substrate. In some embodiments, a plasma process can be used to promote functionalization of the carbon nanotubes.

[0049] Carbon nanotubes can be metallic, semimetallic or semiconducting depending on their chirality. An established system of nomenclature for designating a carbon nanotube's chirality is recognized by those having ordinary skill in the art and is distinguished by a double index (n,m), where n and m are integers that describe the cut and wrapping of hexagonal graphite when formed into a tubular structure. In various embodiments, carbon nanotubes grown on metal substrates according to the present embodiments can be of any specified chirality or mixture of chiral forms.

[0050] In addition to chirality, a carbon nanotube's diameter also influences its electrical conductivity and the related property of thermal conductivity. In the synthesis of carbon nanotubes, a carbon nanotube's diameter can be controlled by using catalytic nanoparticles of a given size. Typically, a carbon nanotube's diameter is approximately

that of the catalytic nanoparticle that catalyzes its formation. Therefore, a carbon nanotube's properties can be controlled in one respect by adjusting the size of the catalytic nanoparticle used for its synthesis, for example. By way of non-limiting example, catalytic nanoparticles having a diameter of about 1 nm to about 5 nm can be used to grow predominantly single-wall carbon nanotubes. Larger catalytic nanoparticles can be used to prepare predominantly multi-wall carbon nanotubes, which have larger diameters because of their multiple nanotube layers. Mixtures of single-wall and multi-wall carbon nanotubes can also be grown by using larger catalytic nanoparticles in the carbon nanotube synthesis. Catalytic nanoparticles of a desired size can also be purchased from various commercial sources, or they can be prepared *in situ* from a catalyst precursor according to the present embodiments.

**[0051]** In various embodiments herein, the diameter of the carbon nanotubes grown on a metal substrate can range between about 1 nm and about 500 nm. In some embodiments, the diameter of the carbon nanotubes can range between about 1 nm and about 10 nm. In other embodiments, the diameter of the carbon nanotubes can range between about 1 nm and about 30 nm, or between about 5 nm and about 30 nm, or between about 15 nm and about 30 nm. In some embodiments, the diameter of the carbon nanotubes can range between about 10 nm and about 50 nm or between about 50 nm and about 100 nm. In other embodiments, the diameter of the carbon nanotubes can range between about 100 nm and about 300 nm or between about 300 nm and about 500 nm. Generally, larger carbon nanotubes can be formed at higher loadings of the catalytic material, where nanoparticle agglomeration can lead to larger carbon nanotube diameters. At lower loadings of the catalytic material, the carbon nanotubes diameters can be less sensitive to agglomeration effects, and the carbon nanotube diameters generally can range between about 1 nm and about 50 nm, for example.

**[0052]** In some embodiments, an average length of the carbon nanotubes grown on the metal substrate can be between about 1  $\mu\text{m}$  and about 1000  $\mu\text{m}$ , including all values and subranges therebetween. In some embodiments, an average length of the carbon nanotubes can be less than about 1  $\mu\text{m}$ , including about 0.5  $\mu\text{m}$ , for example. In some embodiments, an average length of the carbon nanotubes can be between about 1

μm and about 10 μm, including all values and subranges therebetween. In still other embodiments, an average length of the carbon nanotubes can be greater than about 500 μm. Generally, higher loadings of the catalytic material in the present embodiments can favor greater carbon nanotube growth rates and longer carbon nanotubes.

**[0053]** In some embodiments, the carbon nanotubes grown on the metal substrate can be present as individual carbon nanotubes. That is, the carbon nanotubes can be present in a substantially non-bundled state. In some embodiments, the carbon nanotubes grown on the metal substrate can be present as a carbon nanostructure containing interlinked carbon nanotubes. In such embodiments, substantially non-bundled carbon nanotubes can be present as an interlinked network of carbon nanotubes. In some embodiments, the interlinked network can contain carbon nanotubes that branch in a dendrimeric fashion from other carbon nanotubes. In some embodiments, the interlinked network can also contain carbon nanotubes that bridge between carbon nanotubes. In some embodiments, the interlinked network can also contain carbon nanotubes that have at least a portion of their sidewalls shared with other carbon nanotubes.

**[0054]** In some embodiments, graphene or other carbon nanomaterials can be grown on a metal substrate by appropriate modifications to the growth conditions. Such modifications will be evident to one having ordinary skill in the art. It should be recognized that any embodiment herein referencing carbon nanotubes can also utilize graphene or other carbon nanomaterials while still residing within the spirit and scope of the present disclosure.

**[0055]** In various embodiments, the catalytic material of the present processes can be a catalyst or a catalyst precursor. That is, the catalytic material can be an active catalyst that can directly catalyze the formation of carbon nanotubes in some embodiments. For example, the catalytic material can be catalytic nanoparticles (*e.g.*, transition metal nanoparticles or lanthanide metal nanoparticles) that can directly catalyze the formation of carbon nanotubes without further transformation being needed. In other embodiments, the catalytic material can be a catalyst precursor that is initially catalytically inactive but can be converted through one or more chemical transformations into an active catalyst. Such conversion to an active catalyst can occur prior to and/or

during exposure of the metal substrate to carbon nanotube growth conditions. According to some embodiments, a catalyst precursor can be converted into an active catalyst without exposure to a discrete reduction step (*e.g.*, H<sub>2</sub>) prior to being exposed to suitable carbon nanotube growth conditions. In some embodiments, the catalyst precursor can attain an intermediate catalyst state (*e.g.*, a metal oxide) prior to being converted into an active catalyst upon exposure to suitable carbon nanotube growth conditions. For example, a transition metal salt can be converted into a transition metal oxide that is converted into an active catalyst upon exposure to carbon nanotube growth conditions.

**[0056]** In various embodiments, the catalytic material can be a transition metal, a transition metal alloy, a transition metal salt, or a combination thereof. In some embodiments, the catalytic material can be in the form of catalytic nanoparticles. In other embodiments, the catalytic material can be in the form of a catalyst precursor. In some embodiments, the catalyst precursor can be a transition metal salt or a combination of transition metal salts such as, for example, a transition metal nitrate, a transition metal acetate, a transition metal citrate, a transition metal chloride, a transition metal fluoride, a transition metal bromide, a transition metal iodide, or hydrates thereof. In some embodiments, such transition metal salts can be transformed into a transition metal oxide upon heating, with conversion to an active catalyst taking place as described in further detail hereinafter. In alternative embodiments, transition metal carbides, transition metal nitrides, or transition metal oxides can be used as the catalytic material. Illustrative transition metal salts that can be suitable for practicing the present processes include, for example, iron (II) nitrate, iron (III) nitrate, cobalt (II) nitrate, nickel (II) nitrate, copper (II) nitrate, iron (II) acetate, iron (III) acetate, cobalt (II) acetate, nickel (II) acetate, copper (II) acetate, iron (II) citrate, iron (III) citrate, iron (III) ammonium citrate, cobalt (II) citrate, nickel (II) citrate, copper (II) citrate, iron (II) chloride, iron (III) chloride, cobalt (II) chloride, nickel (II) chloride, copper (II) chloride, hydrates thereof, and combinations thereof. In alternative embodiments, the catalytic material can include substances such as, for example, FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and combinations thereof, any of which can be in the form of nanoparticles. In still further embodiments, lanthanide metal salts, their hydrates, and combinations thereof can be used as a catalyst precursor.

[0057] In embodiments in which an intermediate catalyst state has been formed from a catalyst precursor, the intermediate catalyst state can be converted into an active catalyst (*e.g.*, catalytic nanoparticles) without a separate catalyst activation step being conducted prior to exposure of the metal substrate to carbon nanotube growth conditions. In contrast, it has been conventional in the art to activate carbon nanotube catalysts with hydrogen in a separate step before proceeding with carbon nanotube growth. In the present embodiments, formation of an active catalyst can take place upon exposure of the intermediate catalyst state to carbon nanotube growth conditions. For example, during the synthesis of carbon nanotubes, pyrolysis of acetylene in a carbon nanotube growth reactor results in the formation of hydrogen gas and atomic carbon. The hydrogen gas can react with a transition metal oxide or like intermediate catalyst state to produce zero-valent transition metal catalytic nanoparticles. Formation of a metal carbide thereafter and ensuing diffusion of carbon into the catalyst particles can result in the formation of carbon nanotubes on a metal substrate.

[0058] In some embodiments, a non-catalytic material can also be used in the present processes in conjunction with the catalytic material. Although carbon nanotubes can be grown on metal substrates according to the present processes even without a non-catalytic material being present, use of a non-catalytic material in conjunction with the catalytic material can result in improved carbon nanotube growth rates and better carbon nanotube coverage. Without being bound by theory or mechanism, it is believed that the non-catalytic material can limit interactions of the catalytic material with the metal substrate that can otherwise inhibit carbon nanotube growth. Further, it is also believed that the non-catalytic material can facilitate the dissociation of a catalyst precursor into an active catalyst and promote the anchoring of carbon nanotubes to the metal substrate. In addition, the non-catalytic material can act as a thermal barrier to protect the surface of the metal substrate and shield it from thermal damage, including melting, during carbon nanotube growth.

[0059] In some embodiments, the use of a non-catalytic material in conjunction with a catalyst precursor can enable the growth of carbon nanotubes on a metal substrate without a separate operation being used to convert the catalyst precursor into an active

catalyst suitable for carbon nanotube growth. That is, in some embodiments, a catalyst precursor can be used in conjunction with a non-catalytic material to directly grow carbon nanotubes on a metal substrate upon exposure to carbon nanotube growth conditions. In some embodiments, formation of an active catalyst from a catalyst precursor can involve the formation of an intermediate catalyst state (*e.g.*, a transition metal oxide). In some embodiments, the intermediate catalyst state can be formed by heating the catalyst precursor to its decomposition temperature such that a metal oxide (*e.g.*, a transition metal oxide) is formed. In some embodiments, the present processes can include forming catalytic nanoparticles from a catalyst precursor while the metal substrate is being exposed to carbon nanotube growth conditions, optionally while the metal substrate is being transported. In alternative embodiments, the present processes can include forming catalytic nanoparticles from a catalyst precursor or intermediate catalyst state prior to exposing the metal substrate to carbon nanotube growth conditions. For example, a separate catalyst activation step can be conducted, if desired, such as by exposing the catalyst precursor or intermediate catalyst state to hydrogen. In some embodiments, the catalyst precursor or intermediate catalyst state can be deposited or formed on the metal substrate, and the metal substrate can then be stored for later use. That is, the metal substrate can be loaded with a catalyst precursor or intermediate catalyst state and then exposed to carbon nanotube growth conditions at a later time.

**[0060]** Non-catalytic materials that can be suitable for practicing the present processes are generally substances that are inert to carbon nanotube growth conditions. As described above, such non-catalytic materials can be further operable to stabilize the catalytic material, thereby facilitating carbon nanotube growth. In some embodiments, the non-catalytic material can be an aluminum-containing compound, a silicon-containing compound, or a combination thereof. Illustrative aluminum-containing compounds can include aluminum salts (*e.g.*, aluminum nitrate, aluminum acetate and/or aluminum isopropoxide) or hydrates thereof. Illustrative silicon-containing compounds can include glasses and like silicon dioxide formulations, silicates and silanes. In some embodiments, an alkoxy silane, an alumoxane, alumina nanoparticles, spin on glass, or glass nanoparticles can be used as the non-catalytic material.

**[0061]** When a non-catalytic material is used in the present processes, the catalytic material can be deposited prior to, after, or concurrently with the catalytic material. In some embodiments, the catalytic material can be deposited prior to the non-catalytic material. That is, in such embodiments, the catalytic material can be deposited between the metal substrate and the non-catalytic material. In other embodiments, the catalytic material can be deposited after the non-catalytic material. That is, in such embodiments, the non-catalytic material can be deposited between the metal substrate and the catalytic material. In still other embodiments, the catalytic material can be deposited concurrently with the non-catalytic material. Regardless of the deposition sequence, the combination of the catalytic material and the non-catalytic material form a catalyst coating on the metal substrate. In some embodiments, the catalyst coating can have a thickness ranging between about 5 nm and about 1  $\mu\text{m}$ . In other embodiments, the catalyst coating can have a thickness ranging between about 10 nm and about 100 nm or between about 10 nm and about 50 nm.

**[0062]** In some embodiments, the catalytic material and the non-catalytic material can be deposited by a technique or combination of techniques such as, for example, spray coating, dip coating, roller coating, or a like solution-based deposition technique. In some embodiments, the catalytic material and the non-catalytic material can be deposited from at least one solution. In some embodiments, the catalytic material can be deposited from a first solution, and the non-catalytic material can be deposited from a second solution. In such embodiments, the catalytic material can be deposited prior to or after the non-catalytic material. In other embodiments, the catalytic material and the non-catalytic material can be deposited concurrently from the same solution. In some embodiments, the at least one solution can contain water as a solvent.

**[0063]** In some embodiments, the catalytic material and the non-catalytic material can each have a concentration in the at least one solution ranging between about 0.1 mM and about 1.0 M. In other embodiments, the catalytic material and the non-catalytic material can each have a concentration in the at least one solution ranging between about 0.1 mM and about 50 mM, or between about 10 mM and about 100 mM, or between about 50 mM and about 1.0 M. When the catalytic material and the non-catalytic

material are in the same solution, the referenced concentration ranges refer to the concentration of each component in the solution, rather than the overall solution concentration. Solution concentrations ranging between about 10 mM and about 100 mM for each component can typically be most reliable for mediating carbon nanotube growth on a metal substrate, although this range can vary based on the identities of the metal substrate, the catalytic material and the non-catalytic material, and the deposition process and deposition rate.

**[0064]** The solvent(s) used in the at least one solution can generally vary without limitation, provided that they effectively solubilize or disperse the catalytic material and the non-catalytic material, if present. Particularly suitable solvents can include, for example, water, alcohols (*e.g.*, methanol, ethanol, or isopropanol), esters (*e.g.*, methyl acetate or ethyl acetate), ketones (*e.g.*, acetone or butanone), and mixtures thereof. In some embodiments, a small amount of a co-solvent can be added to achieve solubility of a transition metal salt in a solvent in which the salt is otherwise not sufficiently soluble. Illustrative examples of such co-solvents can include, for example, glyme, diglyme, triglyme, dimethylformamide, and dimethylsulfoxide. Generally, solvents having a relatively low boiling point are preferred such that the solvent can be easily removed prior to exposure of the metal substrate to the carbon nanotube growth conditions. Ready removal of the solvent can facilitate the formation of a homogenous coating of the catalytic material. In higher boiling point solvents or those that tend to pond on the surface of the metal substrate, a non-uniform distribution of the catalytic material can occur, thereby leading to poor carbon nanotube growth and coverage.

**[0065]** Although inclusion of a non-catalytic material is generally advantageous in the present processes, there can be an upper limit in the amount of non-catalytic material above which carbon nanotube growth becomes infeasible. This can be particularly true when the non-catalytic material is deposited after or concurrently with the catalytic material. Such a limit does not necessarily apply when the non-catalytic material is deposited prior to the catalytic material. If too much non-catalytic material is included, the non-catalytic material can excessively overcoat the catalytic material, thereby inhibiting diffusion of a carbon feedstock gas into the catalytic material and

blocking carbon nanotube growth. In some embodiments, a molar ratio of the non-catalytic material to the catalytic material can be at most about 6:1. In other embodiments, a molar ratio of the non-catalytic material to the catalytic material can be at most about 2:1.

**[0066]** Metal substrates of the present processes can generally vary without limitation, provided that they are not substantially damaged by the carbon nanotube growth conditions. In various embodiments, carbon nanotube growth conditions of the present disclosure can involve a temperature ranging between about 550°C and about 800°C to permit rapid carbon nanotube growth rates of up to about 8.3 μm/sec or more. Further details of carbon nanotube growth conditions and reactors for carbon nanotube growth are set forth hereinbelow. According to the present embodiments, even low melting metal substrates (*e.g.*, metal substrates having melting points of less than about 800°C) can be substantially undamaged during brief exposure times to the carbon nanotube growth conditions. The non-catalytic material used in some embodiments of the present processes can protect the metal substrate from thermal exposure, thereby permitting brief exposure of the metal substrate to temperatures above its melting point to take place. Further, transporting the metal substrate during carbon nanotube growth under high temperature conditions can additionally limit the exposure time to temperatures at or above the metal substrate's melting point, which can also minimize the amount of thermal damage. It should be noted that thermal damage can still occur even in metal substrates having a melting point in excess of the carbon nanotube growth temperature, and the present processes can likewise be advantageous for these types of metal substrates.

**[0067]** In some embodiments, metal substrates of the present processes can have a melting point of about 800°C or less. Illustrative metal substrates having a melting point about 800°C or less that can be used in conjunction with the present processes include, for example, aluminum (m.p. = 660°C), aluminum alloys (m.p. = 480°C – 660°C), magnesium (m.p. = 650°C), zinc (m.p. = 420°C), lead (m.p. = 327°C), tin (m.p. = 232°C) and lead-antimony alloys (m.p. = 250°C – 420°C).

**[0068]** After deposition of the catalytic material, a chemical vapor deposition (CVD)-based process or other process for growing carbon nanotubes can be used to grow carbon nanotubes on the metal substrate. Illustrative processes for carbon nanotube synthesis include, for example, micro-cavity, thermal or plasma-enhanced CVD techniques, laser ablation, arc discharge, flame synthesis and high pressure carbon monoxide (HiPCO) synthesis, all of which are known to one having ordinary skill in the art. In some embodiments, the CVD-based growth process can be plasma-enhanced. In some embodiments, the process for growing carbon nanotubes can take place continuously with the metal substrate being conveyed in a continuous manner through a reactor while being exposed to carbon nanotube growth conditions.

**[0069]** In the embodiments described herein, carbon nanotube growth can take place in a continuous (*i.e.*, moving metal substrate) manner or under batchwise (*i.e.*, static metal substrate) conditions. In non-limiting embodiments, growth of carbon nanotubes can take place in reactors that are adapted for continuous carbon nanotube growth. Illustrative reactors having such features are described in commonly owned United States Patent application 12/611,073, filed November 2, 2009, and United States Patent 7,261,779, each of which is incorporated herein by reference in its entirety. Although the above reactors are designed for continuously conveying a substrate through the reactor for exposure to carbon nanotube growth conditions, the reactors can also be operated in a batchwise mode with the substrate remaining stationary, if desired. Further details of an illustrative carbon nanotube reactor and certain process details for growing carbon nanotubes are set forth hereinafter. It should be noted that the processes described herein are not tied to a particular carbon nanotube reactor, and any suitable reactor known to one of ordinary skill in the art can be utilized in the present processes.

**[0070]** Carbon nanotube growth can be based on a chemical vapor deposition (CVD) process that occurs at elevated temperatures. The specific temperature is a function of catalyst choice, but can typically be in a range of about 500°C to about 1000°C. In some embodiments, the temperature can be in a range of about 550°C to about 800°C. In various embodiments, the temperature can influence the carbon nanotube growth rate and/or the carbon nanotube diameters obtained.

[0071] In various embodiments, carbon nanotube growth can take place by a CVD-based process, which can be plasma-enhanced. The CVD process can be promoted by a carbon-containing feedstock gas such as, for example, acetylene, ethylene, and/or methane. The carbon nanotube synthesis processes generally use an inert gas (*e.g.*, nitrogen, argon, and/or helium) as a primary carrier gas in conjunction with the carbon-containing feedstock gas. The carbon-containing feedstock gas is typically provided in a range from between about 0.1% to about 50% of the total mixture. In some embodiments, the carbon-containing feedstock gas can range between about 0.1% and about 10% of the total mixture. A substantially inert environment for CVD growth can be prepared by removal of moisture and oxygen from the growth chamber.

[0072] A strong plasma-creating electric field can optionally be employed to affect the direction of carbon nanotube growth. A plasma can be generated by providing an electric field during the growth process. By properly adjusting the geometry of the plasma spray and electric field, vertically aligned carbon nanotubes (*i.e.*, perpendicular to the metal surface) can be synthesized. Under certain conditions, even in the absence of a plasma, closely-spaced carbon nanotubes can maintain a substantially vertical growth direction resulting in a dense array of carbon nanotubes resembling a carpet or forest.

[0073] In some embodiments, acetylene gas can be ionized to create a jet of cold carbon plasma for carbon nanotube synthesis. The carbon plasma is directed toward the metal substrate. Thus, in some embodiments, processes for synthesizing carbon nanotubes on a metal substrate include (a) forming a carbon plasma; and (b) directing the carbon plasma onto the catalytic material disposed on the metal substrate. In some embodiments, a metal substrate can be actively heated to between about 550°C and about 800°C to facilitate carbon nanotube synthesis. To initiate the growth of carbon nanotubes, two or more gases are bled into the reactor: an inert carrier gas (*e.g.*, argon, helium, or nitrogen) and a carbon-containing feedstock gas (*e.g.*, acetylene, ethylene, ethane or methane).

[0074] In some embodiments, carbon nanotube growth can take place in a special rectangular reactor designed for continuous synthesis and growth of carbon nanotubes on fiber materials. Such a reactor is described in commonly-owned, co-pending patent

application 12/611,073, incorporated by reference hereinabove. This reactor utilizes atmospheric pressure growth of carbon nanotubes, which facilitates its incorporation in a continuous carbon nanotube growth process. In addition, the reactor can be operated in a batchwise manner with the metal substrate being held stationary, if desired. More conventional reactors for static carbon nanotube growth can also be used. In some embodiments, carbon nanotubes can be grown via a CVD process at atmospheric pressure and an elevated temperature in the range of about 550°C and about 800°C in a multi-zone reactor. The fact that the carbon nanotube synthesis occurs at atmospheric pressure is one factor that facilitates the incorporation of the reactor into a continuous processing line for carbon nanotube growth on the metal substrate. Another advantage consistent with in-line continuous processing using such a multi-zone reactor is that carbon nanotube growth occurs in seconds, as opposed to minutes (or longer), as in other procedures and apparatus configurations typical in the art.

[0075] Carbon nanotube synthesis reactors designed in accordance with the above embodiments can include the following features:

[0076] Rectangular Configured Synthesis Reactors: The cross-section of a typical carbon nanotube synthesis reactor known in the art is circular. There are a number of reasons for this including, for example, historical reasons (*e.g.*, cylindrical reactors are often used in laboratories) and convenience (*e.g.*, flow dynamics are easy to model in cylindrical reactors, heater systems readily accept circular tubes (*e.g.*, quartz, *etc.*), and ease of manufacturing. Departing from the cylindrical convention, the present disclosure provides a carbon nanotube synthesis reactor having a rectangular cross section. The reasons for the departure include at least the following:

[0077] **1) Inefficient Use of Reactor Volume.** Since many metal substrates that are to be processed by the reactor are relatively planar (*e.g.*, flat tapes, sheet-like forms, or spread tows or rovings), a circular cross-section is an inefficient use of the reactor volume. This inefficiency results in several drawbacks for cylindrical carbon nanotube synthesis reactors including, for example, a) maintaining a sufficient system purge; increased reactor volume requires increased gas flow rates to maintain the same level of gas purge, resulting in inefficiencies for high volume production of carbon nanotubes in

an open environment; b) increased carbon-containing feedstock gas flow rates; the relative increase in inert gas flow for system purge, as per a) above, requires increased carbon-containing feedstock gas flow rates. Consider that the volume of an illustrative 12K glass fiber roving is approximately 2000 times less than the total volume of a synthesis reactor having a rectangular cross-section. In an equivalent cylindrical reactor (*i.e.*, a cylindrical reactor that has a width that accommodates the same planarized glass fiber material as the rectangular cross-section reactor), the volume of the glass fiber material is approximately 17,500 times less than the volume of the reactor. Although gas deposition processes, such as CVD, are typically governed by pressure and temperature alone, volume can have a significant impact on the efficiency of deposition. With a rectangular reactor there is a still excess volume, and this excess volume facilitates unwanted reactions. However, a cylindrical reactor has about eight times that volume available for facilitating unwanted reactions. Due to the greater opportunity for competing reactions to occur, the desired reactions effectively occur more slowly in a cylindrical reactor. Such a slow down in carbon nanotube growth, can be problematic for the development of continuous growth processes. Another benefit of a rectangular reactor configuration is that the reactor volume can be decreased further still by using a small height for the rectangular chamber to make the volume ratio better and the reactions even more efficient. In some embodiments disclosed herein, the total volume of a rectangular synthesis reactor is no more than about 3000 times greater than the total volume of a metal substrate being passed through the synthesis reactor. In some further embodiments, the total volume of the rectangular synthesis reactor is no more than about 4000 times greater than the total volume of the metal substrate being passed through the synthesis reactor. In some still further embodiments, the total volume of the rectangular synthesis reactor is less than about 10,000 times greater than the total volume of the metal substrate being passed through the synthesis reactor. Additionally, it is notable that when using a cylindrical reactor, more carbon-containing feedstock gas is required to provide the same flow percent as compared to reactors having a rectangular cross section. It should be appreciated that in some other embodiments, the synthesis reactor has a cross-section that is described by polygonal forms that are not rectangular, but are relatively similar thereto and provide a similar reduction in reactor volume relative to a reactor

having a circular cross section; and c) problematic temperature distribution; when a relatively small-diameter reactor is used, the temperature gradient from the center of the chamber to the walls thereof is minimal, but with increased reactor size, such as would be used for commercial-scale production, such temperature gradients increase. Temperature gradients result in product quality variations across the metal substrate (*i.e.*, product quality varies as a function of radial position). This problem is substantially avoided when using a reactor having a rectangular cross-section. In particular, when a planar substrate is used, reactor height can be maintained constant as the size of the substrate scales upward. Temperature gradients between the top and bottom of the reactor are essentially negligible and, as a consequence, thermal issues and the product-quality variations that result are avoided.

**[0078]**        **2) Gas introduction.** Because tubular furnaces are normally employed in the art, typical carbon nanotube synthesis reactors introduce gas at one end and draw it through the reactor to the other end. In some embodiments disclosed herein, gas can be introduced at the center of the reactor or within a target growth zone, symmetrically, either through the sides or through the top and bottom plates of the reactor. This improves the overall carbon nanotube growth rate because the incoming feedstock gas is continuously replenishing at the hottest portion of the system, which is where carbon nanotube growth is most active.

**[0079]**        Zoning. Chambers that provide a relatively cool purge zone extend from both ends of the rectangular synthesis reactor. It has been determined that if a hot gas were to mix with the external environment (*i.e.*, outside of the rectangular reactor), there would be increased degradation of the metal substrate. The cool purge zones provide a buffer between the internal system and external environments. Carbon nanotube synthesis reactor configurations known in the art typically require that the substrate is carefully (and slowly) cooled. The cool purge zone at the exit of the present rectangular carbon nanotube growth reactor achieves the cooling in a short period of time, as favorable for continuous in-line processing.

**[0080]**        Non-contact, hot-walled, metallic reactor. In some embodiments, a metallic hot-walled reactor (*e.g.*, stainless steel) is employed. Use of this type of reactor

can appear counterintuitive because metal, and stainless steel in particular, is more susceptible to carbon deposition (*i.e.*, soot and by-product formation). Thus, most carbon nanotube synthesis reactors are made from quartz because there is less carbon deposited, quartz is easier to clean, and quartz facilitates sample observation. However, it has been observed that the increased soot and carbon deposition on stainless steel results in more consistent, efficient, faster, and stable carbon nanotube growth. Without being bound by theory it has been indicated that, in conjunction with atmospheric operation, the CVD process occurring in the reactor is diffusion limited. That is, the carbon nanotube-forming catalyst is “overfed;” too much carbon is available in the reactor system due to its relatively higher partial pressure (than if the reactor was operating under partial vacuum). As a consequence, in an open system — especially a clean one — too much carbon can adhere to the particles of carbon nanotube-forming catalyst, compromising their ability to synthesize carbon nanotubes. In some embodiments, the rectangular reactor is intentionally run when the reactor is “dirty,” that is with soot deposited on the metallic reactor walls. Once carbon deposits to a monolayer on the walls of the reactor, carbon will readily deposit over itself. Since some of the available carbon is “withdrawn” due to this mechanism, the remaining carbon feedstock, in the form of radicals, reacts with the carbon nanotube-forming catalyst at a rate that does not poison the catalyst. Existing systems run “cleanly” which, if they were open for continuous processing, would produce a much lower yield of carbon nanotubes at reduced growth rates.

**[0081]** Although it is generally beneficial to perform carbon nanotube synthesis “dirty” as described above, certain portions of the apparatus (*e.g.*, gas manifolds and inlets) can nonetheless negatively impact the carbon nanotube growth process when soot creates blockages. In order to combat this problem, such areas of the carbon nanotube growth reaction chamber can be protected with soot inhibiting coatings such as, for example, silica, alumina, or MgO. In practice, these portions of the apparatus can be dip-coated in these soot inhibiting coatings. Metals such as INVAR (a nickel-steel alloy commercially available from ArcelorMittal) can be used with these coatings as INVAR has a similar CTE (coefficient of thermal expansion) ensuring proper adhesion of the

coating at higher temperatures, preventing the soot from significantly building up in critical zones.

**[0082]**        Combined Catalyst Reduction and Carbon Nanotube Synthesis. In the carbon nanotube synthesis reactor disclosed herein, both catalyst reduction and carbon nanotube growth can occur within the reactor. In a typical process known in the art, a reduction step typically takes 1 – 12 hours to perform. Both operations can occur in a reactor in accordance with the present disclosure due, at least in part, to the fact that carbon-containing feedstock gas is introduced at the center of the reactor, not the end as would be typical in the art using cylindrical reactors. The reduction process occurs as the metal substrate enters the heated zone. By this point, the gas has had time to react with the walls and cool off prior to reducing the catalyst (via hydrogen radical interactions). It is this transition region where the reduction can occur. At the hottest isothermal zone in the system, carbon nanotube growth occurs, with the greatest growth rate occurring proximal to the gas inlets near the center of the reactor.

**[0083]**        It is understood that modifications which do not substantially affect the activity of the various embodiments of this invention are also included within the definition of the invention provided herein. Accordingly, the following Examples are intended to illustrate but not limit the present invention.

**[0084]**        EXAMPLE 1: Carbon Nanotube Growth Under Static CVD Conditions at 750°C on a Copper Substrate Using a Palladium Catalyst. For this example, a palladium dispersion in water at a concentration of 0.5 wt% was used to deposit the catalytic material. In this case, a non-catalytic material was not deposited on the copper substrate. The 0.5 wt% palladium dispersion was applied to an electroplated copper foil substrate by a dip coating process to form a thin liquid layer. The substrate was then dried for 5 minutes with a heat gun at 600°F. Carbon nanotubes were grown under carbon nanotube growth conditions using the reactor described above, with the exception that the reactor was run with the substrate held stationary, rather than being continuously conveyed through the reactor. Under static growth conditions using this catalyst system, carbon nanotubes ranging from 5 nm to 30 nm in diameter and from 0.1 μm to 300 μm in length were obtained, depending on the growth temperature and the residence time in the

reactor. Carbon nanotube growth conducted under static chemical vapor deposition conditions for 5 minutes at a temperature of 750°C produced carbon nanotubes of about 3 µm in length that ranged from 18 nm to 25 nm in diameter. FIGURES 1A and 1B show illustrative SEM images of carbon nanotubes grown on a copper substrate using a palladium catalyst under static chemical vapor deposition conditions for 5 minutes at a temperature of 750°C. FIGURE 1A is at 11,000x magnification, and FIGURE 1B is at 80,000x magnification.

[0085] EXAMPLE 2: Carbon Nanotube Growth Under Continuous CVD Conditions at 750°C on a Copper Substrate Using a Palladium Catalyst. The carbon nanotube growth of EXAMPLE 1 was repeated with the exception that the copper substrate was conveyed through the reactor at a processing speed of 1 ft/min during its exposure time to the carbon nanotube growth conditions. Under continuous carbon nanotube growth conditions, carbon nanotubes having lengths up to 23 µm and a 15 nm average diameter were obtained. FIGURE 2 shows an illustrative SEM image of carbon nanotubes grown on a copper substrate using a palladium catalyst under continuous chemical vapor deposition conditions at a temperature of 750°C and a linespeed of 1 ft/min, which is equivalent to 1 minute of carbon nanotube growth time. In FIGURE 2, the magnification is 3,000x. Thus, significantly longer carbon nanotubes were obtained under continuous carbon nanotube growth conditions than were obtained when the reactor was run in a static manner.

[0086] EXAMPLE 3: Carbon Nanotube Growth Under Static CVD Conditions at 750°C on a Copper Substrate Using an Iron Catalyst and a Non-Catalytic Material. The carbon nanotube growth of EXAMPLE 1 was repeated, except a non-catalytic material was deposited on the metal substrate and an iron nanoparticle catalyst was substituted for palladium. A 4 vol% solution of Accuglass T-11 Spin-On Glass (Honeywell International, Inc., Morristown, New Jersey) in isopropanol was applied to an electroplated copper foil metal substrate via a dip coating process. The copper substrate was thereafter dried for 5 seconds at 600°F using a heat gun. A catalyst solution of 0.09 wt% iron nanoparticles (8 nm diameter) in hexane solvent was applied by a dip coating process, and the copper substrate was dried for 5 seconds using a stream of compressed

air. Under static growth conditions using this catalyst system, carbon nanotubes ranging from 5 nm to 15 nm in diameter and from 0.1  $\mu\text{m}$  to 100  $\mu\text{m}$  in length were obtained, depending on the growth temperature and the residence time in the reactor. Carbon nanotube growth conducted under static chemical vapor deposition conditions for 5 minutes at a temperature of 750°C produced carbon nanotubes of about 3  $\mu\text{m}$  in length that ranged from 8 nm to 15 nm in diameter. FIGURES 3A and 3B show illustrative SEM images of carbon nanotubes grown on a copper substrate using an iron nanoparticle catalyst under static chemical vapor deposition conditions for 5 minutes at a temperature of 750°C, where the iron nanoparticle catalyst was deposited over a layer of non-catalytic Accuglass T-11 Spin-On Glass. FIGURE 3A is at 2,500x magnification, and FIGURE 3B is at 120,000x magnification.

**[0087]** EXAMPLE 4: Carbon Nanotube Growth Under Static CVD Conditions at 750°C on a Copper Substrate Using an Iron Catalyst and a Non-Catalytic Material. The carbon nanotube growth of EXAMPLE 3 was repeated with the exception that the order of addition of the non-catalytic material and the iron nanoparticle catalyst were reversed. That is, the iron nanoparticle catalyst solution was deposited on the metal substrate by dip coating, and the non-catalytic material was added by dip coating thereafter. In this case, the concentration of the iron nanoparticle catalyst solution was 0.9 wt%, and the concentration of Accuglass T-11 Spin-On Glass in isopropanol was 1 vol%. Even when the catalyst was applied under the non-catalytic material, the iron nanoparticles were still able to mediate carbon nanotube growth. Carbon nanotube growth conducted under static chemical vapor deposition conditions for 30 minutes at a temperature of 750°C produced carbon nanotubes and carbon nanofibers of about 50  $\mu\text{m}$  in length that ranged from 150 nm to 300 nm in diameter. FIGURES 4A and 4B show illustrative SEM images of carbon nanotubes and carbon nanofibers grown on a copper substrate using an iron nanoparticle catalyst under static chemical vapor deposition conditions for 30 minutes at a temperature of 750°C, where the iron nanoparticle catalyst was deposited under a layer of non-catalytic Accuglass T-11 Spin-On Glass. FIGURE 4A is at 110x magnification, and FIGURE 4B is at 9,000x magnification. In this case, the increase in carbon nanotube and carbon nanofiber diameter can primarily be attributed to the larger concentration of iron nanoparticles used as well as a longer growth time.

**[0088]** EXAMPLE 5: Carbon Nanotube Growth Under Continuous CVD Conditions at 800°C on a Stainless Steel Wire Mesh Substrate Using an Iron Catalyst and a Non-Catalytic Material. The carbon nanotube growth of EXAMPLE 4 was repeated with the exception that a stainless steel wire mesh substrate was conveyed through the reactor at a processing speed of 2 ft/min during its exposure time to the carbon nanotube growth conditions at a temperature of 800°C. In this case, the concentration of the iron nanoparticle catalyst solution was 0.027 wt%, and the concentration of Accuglass T-11 Spin-On Glass in isopropanol was 2.5 vol%. Under continuous carbon nanotube growth conditions, carbon nanotubes having lengths up to about 50 µm and a 15 nm average diameter were obtained. FIGURES 5A and 5B show illustrative SEM images of carbon nanotubes grown on a stainless steel wire mesh substrate using an iron nanoparticle catalyst under continuous chemical vapor deposition conditions at a temperature of 800°C and a linespeed of 2 ft/min, which is equivalent to 30 seconds of carbon nanotube growth time, where the iron nanoparticle catalyst was deposited under a layer of non-catalytic Accuglass T-11 Spin-On Glass. FIGURE 5A is at 300x magnification, and FIGURE 5B is at 20,000x magnification.

**[0089]** EXAMPLE 6: Carbon Nanotube Growth Under Static CVD Conditions at 750°C on a Copper Substrate Using an Iron Nitrate Catalyst Precursor and a Non-Catalytic Material. The carbon nanotube growth of EXAMPLE 3 was repeated with the exception that iron nitrate nonahydrate was substituted as a catalyst precursor and aluminum nitrate nonahydrate was substituted as the non-catalytic material. Further, the iron nitrate nonahydrate and the aluminum nitrate nonahydrate were added concurrently. That is, the iron nitrate nonahydrate catalyst precursor and the aluminum nitrate nonahydrate non-catalytic material were combined into a single solution and deposited on the copper substrate concurrently by dip coating. In this case, the concentration of the iron nitrate catalyst solution was 60 mM in isopropanol, and the concentration of aluminum nitrate in the same solution was also 60 mM. Even when the catalyst precursor was applied concurrently with the non-catalytic material, the iron catalyst was still able to mediate carbon nanotube growth. Carbon nanotube growth conducted under static chemical vapor deposition conditions for 5 minutes at a temperature of 750°C produced carbon nanotubes of up to about 75 µm in length that ranged from 15 nm to 25 nm in

diameter. FIGURES 6A and 6B show illustrative SEM images of carbon nanotubes grown on a copper substrate using an iron nitrate catalyst precursor under static chemical vapor deposition conditions for 5 minutes at a temperature of 750°C, where the iron nitrate catalyst precursor was deposited concurrently with a non-catalytic aluminum nitrate material. FIGURE 6A is at 1,800x magnification, and FIGURE 6B is at 100,000x magnification.

**[0090]** EXAMPLE 7: Carbon Nanotube Growth Under Static CVD Conditions at 750°C on an Aluminum Substrate Using an Iron Nitrate Catalyst Precursor and a Non-Catalytic Material. A solution of 60 mM iron (III) nitrate nonahydrate and 60 mM aluminum nitrate nonahydrate was prepared in 50% isopropyl alcohol/50% water. The solution was then applied to an aluminum substrate via a dip coating process, and the solvent was removed with a heat gun (600°F). Thereafter, carbon nanotube growth was conducted at 750°C under static CVD conditions for 1 minute to produce carbon nanotubes having a length of ~35 μm and diameters ranging between 18 nm and 25 nm. FIGURES 7A and 7B show illustrative SEM images of carbon nanotubes grown on an aluminum substrate using an iron nitrate catalyst precursor under static chemical vapor deposition conditions for 1 minute at a temperature of 750°C, where the iron nitrate catalyst precursor was deposited concurrently with a non-catalytic aluminum nitrate material. When the carbon nanotube growth was repeated at 650°C, 600°C and 580°C, progressively shorter carbon nanotubes were observed for similar growth times (~3 μm, ~1.5 μm and ~0.5 μm, respectively). At 550°C, no carbon nanotube growth occurred. FIGURES 8A AND 8B show illustrative SEM images of carbon nanotubes grown on an aluminum substrate using an iron nitrate catalyst precursor under static chemical vapor deposition conditions for 1 minute at a temperature of 580°C, where the iron nitrate catalyst precursor was deposited concurrently with a non-catalytic aluminum nitrate material.

**[0091]** EXAMPLE 8: Carbon Nanotube Growth Under Continuous CVD Conditions at 750°C on an Aluminum Substrate Using an Iron Nitrate Catalyst Precursor and a Non-Catalytic Material. The carbon nanotube growth of EXAMPLE 7 was repeated at 750°C, with the exception that the metal substrate was transported through a

continuous CVD carbon nanotube growth reactor at a linespeed of 1 ft/min. Under these conditions, carbon nanotubes between 10 nm and 16 nm in diameter were achieved. FIGURES 9A and 9B show illustrative SEM images of carbon nanotubes grown on an aluminum substrate using an iron nitrate catalyst precursor under continuous chemical vapor deposition conditions at a temperature of 750°C and a linespeed of 1 ft/min, which is equivalent to 1 minute of carbon nanotube growth time. As shown in FIGURE 9A, a more uniform coverage of longer carbon nanotubes was produced under continuous CVD conditions, compared to the static growth of EXAMPLE 7. Further, less substrate damage was observed.

**[0092]** EXAMPLE 9: Carbon Nanotube Growth Under Static CVD Conditions at 550°C on an Aluminum Substrate Using an Iron Nitrate Catalyst Precursor Without a Non-Catalytic Material. A solution of 7.5 mM iron (III) nitrate nonahydrate was prepared in methanol. The solution was applied to an aluminum substrate via a dip coating process, and then air dried to remove the solvent. Thereafter, carbon nanotube growth was conducted at 550°C under static CVD conditions for 10 minutes to produce carbon nanotubes having a length of ~1 μm and diameters ranging between 5 nm and 10 nm. FIGURE 10 shows an illustrative SEM image of carbon nanotubes grown on an aluminum substrate using an iron nitrate catalyst precursor under static chemical vapor deposition conditions for 10 minutes at a temperature of 550°C. As shown in FIGURE 10, a fairly uniform coverage of carbon nanotubes was produced when using methanol as the solvent.

**[0093]** EXAMPLE 10: Carbon Nanotube Growth Under Static CVD Conditions at 550°C on an Aluminum Substrate Using an Iron Acetate/Cobalt Acetate Catalyst Precursor. A solution of 1.4 mM iron (II) acetate and 1.3 mM cobalt (II) acetate was prepared in 1 vol% ethylene glycol/99 vol% ethanol. The solution was applied to an aluminum substrate via a dip coating process, and then air dried to remove the solvent. Thereafter, carbon nanotube growth was conducted at 550°C under static CVD conditions for 10 minutes to produce carbon nanotubes having a length of ~2 μm and diameters ranging between 10 nm and 20 nm. FIGURES 11A and 11B show illustrative SEM images of carbon nanotubes grown on an aluminum substrate using an iron acetate/

cobalt acetate catalyst precursor under static chemical vapor deposition conditions for 10 minutes at a temperature of 550°C. As shown in FIGURE 11A, a fairly uniform coverage of carbon nanotubes was produced when using ethylene glycol/ethanol as the solvent.

[0094] Although the invention has been described with reference to the disclosed embodiments, those of ordinary skill in the art will readily appreciate that these embodiments are only illustrative of the invention. It should be understood that various modifications can be made without departing from the spirit of the invention. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present invention. While compositions and methods are described in terms of “comprising,” “containing,” or “including” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and operations. All numbers and ranges disclosed above can vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any subrange falling within the broader range is specifically disclosed. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. If there is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

## CLAIMS

What is claimed is the following:

1. A carbon nanotube growth process comprising:
  - depositing a catalyst precursor on a metal substrate;
  - depositing a non-catalytic material on the metal substrate; and
  - after depositing the catalyst precursor and the non-catalytic material, exposing the metal substrate to carbon nanotube growth conditions so as to grow carbon nanotubes thereon;wherein the carbon nanotube growth conditions convert the catalyst precursor into a catalyst that is operable for growing carbon nanotubes.
2. The carbon nanotube growth process of claim 1, further comprising:
  - transporting the metal substrate while the carbon nanotubes are being grown.
3. The carbon nanotube growth process of claim 1, wherein the catalyst precursor is deposited prior to the non-catalytic material.
4. The carbon nanotube growth process of claim 1, wherein the catalyst precursor is deposited after the non-catalytic material.
5. The carbon nanotube growth process of claim 1, wherein the catalyst precursor is deposited concurrently with the non-catalytic material.
6. The carbon nanotube growth process of claim 1, wherein the catalyst precursor comprises a transition metal salt selected from the group consisting of a transition metal nitrate, a transition metal acetate, a transition metal citrate, a transition metal chloride, hydrates thereof, and combinations thereof.
7. The carbon nanotube growth process of claim 6, wherein the transition metal salt is selected from the group consisting of iron (II) nitrate, iron (III) nitrate, cobalt (II) nitrate, nickel (II) nitrate, copper (II) nitrate, iron (II) acetate, iron (III) acetate, cobalt (II) acetate, nickel (II) acetate, copper (II) acetate, iron (II) citrate,

iron (III) citrate, iron (III) ammonium citrate, cobalt (II) citrate, nickel (II) citrate, copper (II) citrate, iron (II) chloride, iron (III) chloride, cobalt (II) chloride, nickel (II) chloride, copper (II) chloride, hydrates thereof, and combinations thereof.

8. The carbon nanotube growth process of claim 1, wherein the catalyst precursor is selected from the group consisting of FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and combinations thereof.
9. The carbon nanotube growth process of claim 1, wherein the non-catalytic material is selected from the group consisting of an aluminum salt or a hydrate thereof, a glass, a silicate, a silane, and combinations thereof.
10. The carbon nanotube growth process of claim 9, wherein the aluminum salt is selected from the group consisting of aluminum nitrate, aluminum acetate, hydrates thereof, and combinations thereof.
11. The carbon nanotube growth process of claim 1, wherein the catalyst precursor and the non-catalytic material are each deposited from at least one solution.
12. The carbon nanotube growth process of claim 11, wherein the at least one solution comprises water as a solvent.
13. The carbon nanotube growth process of claim 11, wherein the catalyst precursor and the non-catalytic material each have a concentration ranging between about 0.1 mM and about 1.0 M in the at least one solution.
14. The carbon nanotube growth process of claim 11, wherein the catalyst precursor and the non-catalytic material each have a concentration ranging between about 50 mM and about 1.0 M in the at least one solution.
15. The carbon nanotube growth process of claim 11, wherein the catalyst precursor and the non-catalytic material are each deposited by a technique selected from the group consisting of spray coating, dip coating, roller coating, and combinations thereof.

16. The carbon nanotube growth process of claim 11, wherein a molar ratio of the non-catalytic material to the catalyst precursor is at most about 6:1.
17. The carbon nanotube growth process of claim 11, wherein a molar ratio of the non-catalytic material to the catalyst precursor is at most about 2:1.
18. The carbon nanotube growth process of claim 1, wherein the catalyst precursor and the non-catalytic material comprise a catalyst coating on the metal substrate having a thickness ranging between about 5 nm and about 1  $\mu\text{m}$ .
19. A carbon nanotube growth process comprising:
  - depositing a catalyst precursor on a metal substrate;
  - wherein the metal substrate has a melting point of about 800°C or less; and
  - after depositing the catalyst precursor, exposing the metal substrate to carbon nanotube growth conditions so as to grow carbon nanotubes thereon;
  - wherein the carbon nanotube growth conditions convert the catalyst precursor into a catalyst that is operable for growing carbon nanotubes.
20. The carbon nanotube growth process of claim 19, further comprising:
  - transporting the metal substrate while the carbon nanotubes are being grown.
21. The carbon nanotube growth process of claim 19, further comprising:
  - depositing a non-catalytic material on the metal substrate prior to exposing the metal substrate to carbon nanotube growth conditions.
22. The carbon nanotube growth process of claim 21, wherein the catalyst precursor is deposited prior to the non-catalytic material.
23. The carbon nanotube growth process of claim 21, wherein the catalyst precursor is deposited after the non-catalytic material.
24. The carbon nanotube growth process of claim 21, wherein the catalyst precursor is deposited concurrently with the catalytic material.

25. The carbon nanotube growth process of claim 21, wherein the catalyst precursor and the non-catalytic material are each deposited from at least one solution.
26. The carbon nanotube growth process of claim 25, wherein the at least one solution comprises water as a solvent.
27. The carbon nanotube growth process of claim 25, wherein a molar ratio of the non-catalytic material to the catalyst precursor is at most about 6:1.
28. The carbon nanotube growth process of claim 25, wherein a molar ratio of the non-catalytic material to the catalyst precursor is at most about 2:1.
29. The carbon nanotube growth process of claim 25, wherein the catalyst precursor and the non-catalytic material are each deposited by a technique selected from the group consisting of spray coating, dip coating, roller coating, and combinations thereof.
30. The carbon nanotube growth process of claim 21, wherein the non-catalytic material is selected from the group consisting of an aluminum salt or a hydrate thereof, a glass, a silicate, a silane, and combinations thereof.
31. The carbon nanotube growth process of claim 30, wherein the aluminum salt is selected from the group consisting of aluminum nitrate, aluminum acetate, hydrates thereof, and combinations thereof.
32. The carbon nanotube growth process of claim 19, wherein the catalyst precursor comprises a transition metal salt selected from the group consisting of a transition metal nitrate, a transition metal acetate, a transition metal citrate, a transition metal chloride, hydrates thereof, and combinations thereof.
33. The carbon nanotube growth process of claim 32, wherein the transition metal salt is selected from the group consisting of iron (II) nitrate, iron (III) nitrate, cobalt (II) nitrate, nickel (II) nitrate, copper (II) nitrate, iron (II) acetate, iron (III) acetate, cobalt (II) acetate, nickel (II) acetate, copper (II) acetate, iron (II) citrate, iron (III) citrate, iron (III) ammonium citrate, cobalt (II) citrate, nickel (II) citrate,

copper (II) citrate, iron (II) chloride, iron (III) chloride, cobalt (II) chloride, nickel (II) chloride, copper (II) chloride, hydrates thereof, and combinations thereof.

34. The carbon nanotube growth process of claim 19, wherein the metal substrate is selected from the group consisting of aluminum, aluminum alloys, magnesium, zinc, and lead-antimony alloys.
35. A carbon nanotube growth process comprising:  
depositing a catalyst precursor on a metal substrate;  
depositing a non-catalytic material on the metal substrate;  
wherein the non-catalytic material is deposited prior to, after, or concurrently with the catalyst precursor;  
after depositing the catalyst precursor and the non-catalytic material, exposing the metal substrate to carbon nanotube growth conditions so as to grow carbon nanotubes thereon;  
wherein the carbon nanotube growth conditions convert the catalyst precursor into a catalyst that is operable for growing carbon nanotubes;  
and  
transporting the metal substrate while the carbon nanotubes are being grown.
36. The carbon nanotube growth process of claim 35, wherein the metal substrate has a melting point of about 800°C or less.
37. A metal substrate having carbon nanotubes grown thereon prepared by the carbon nanotube growth process of claim 35.

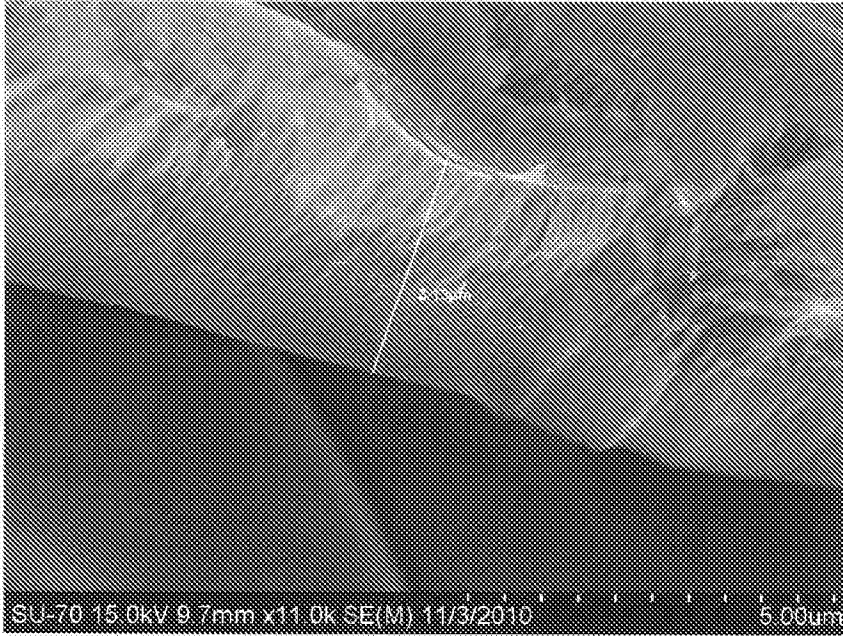


FIGURE 1A

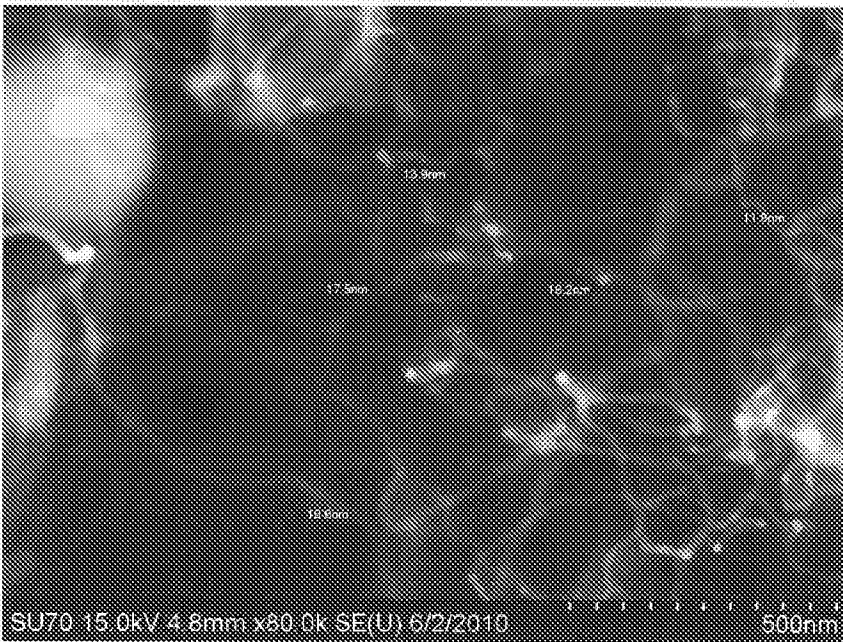


FIGURE 1B

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FIGURE 2

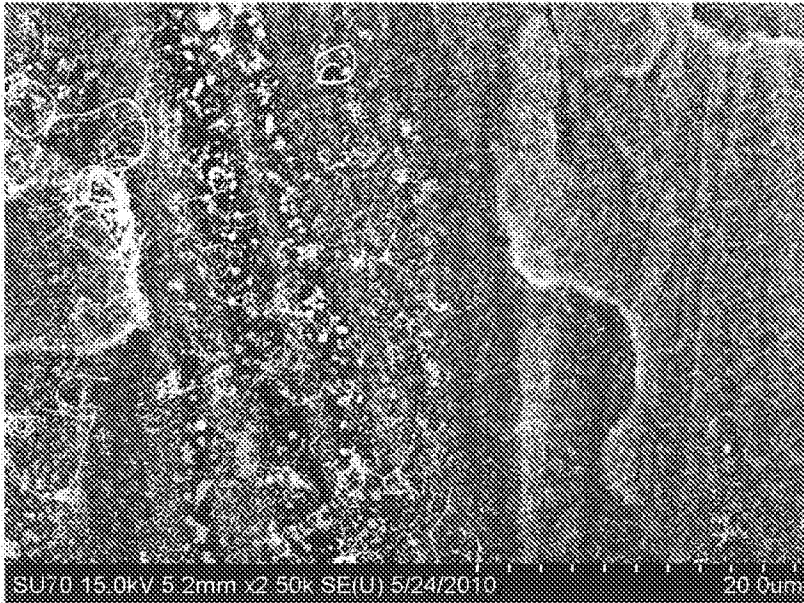


FIGURE 3A

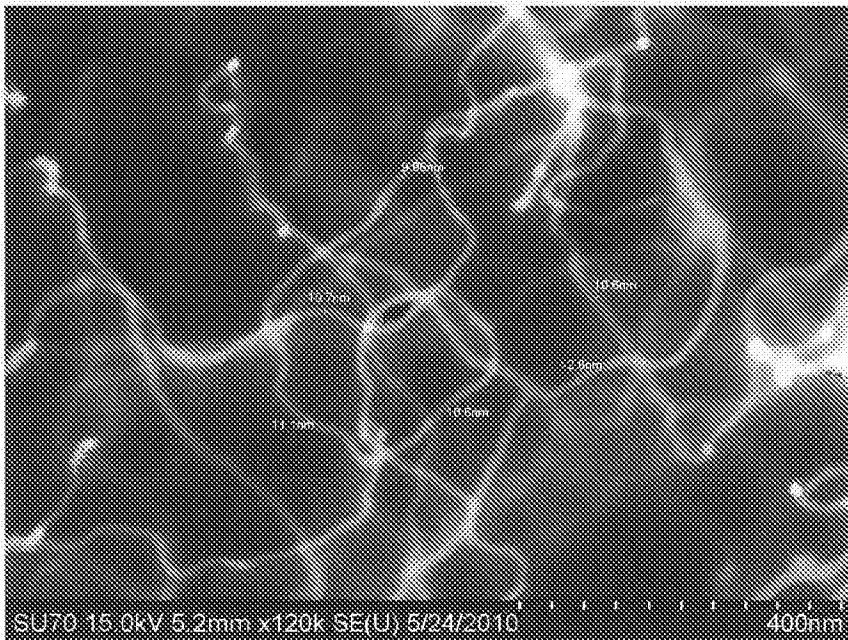


FIGURE 3B



FIGURE 4A

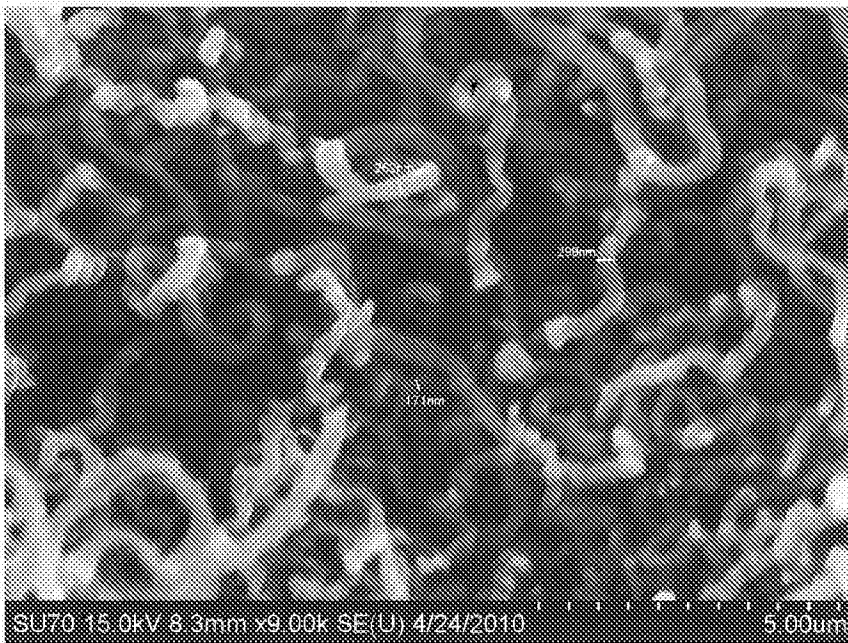


FIGURE 4B

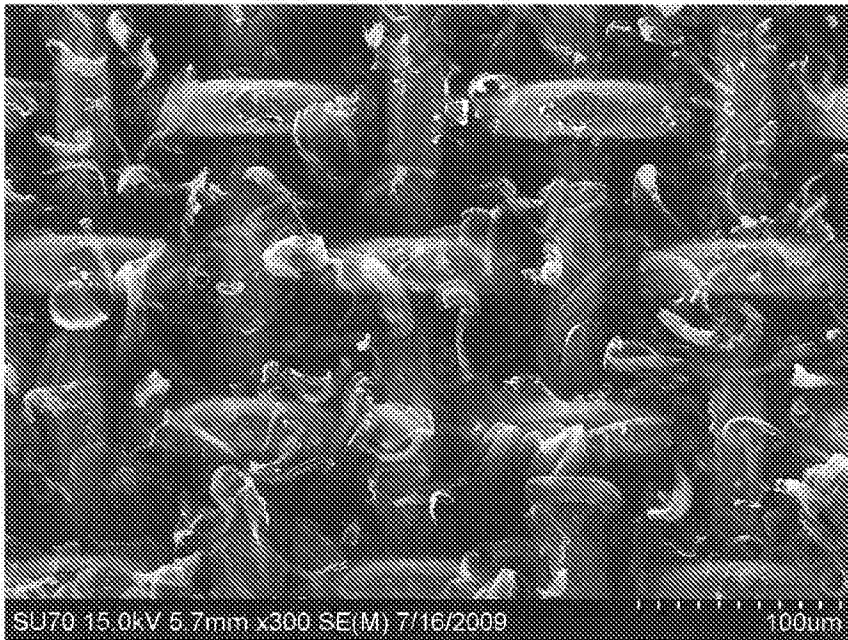


FIGURE 5A

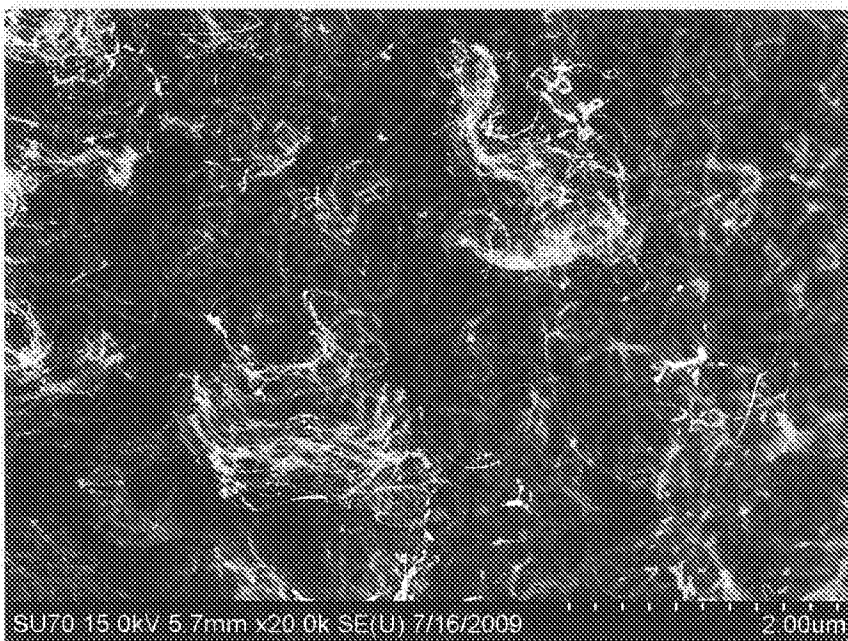


FIGURE 5B

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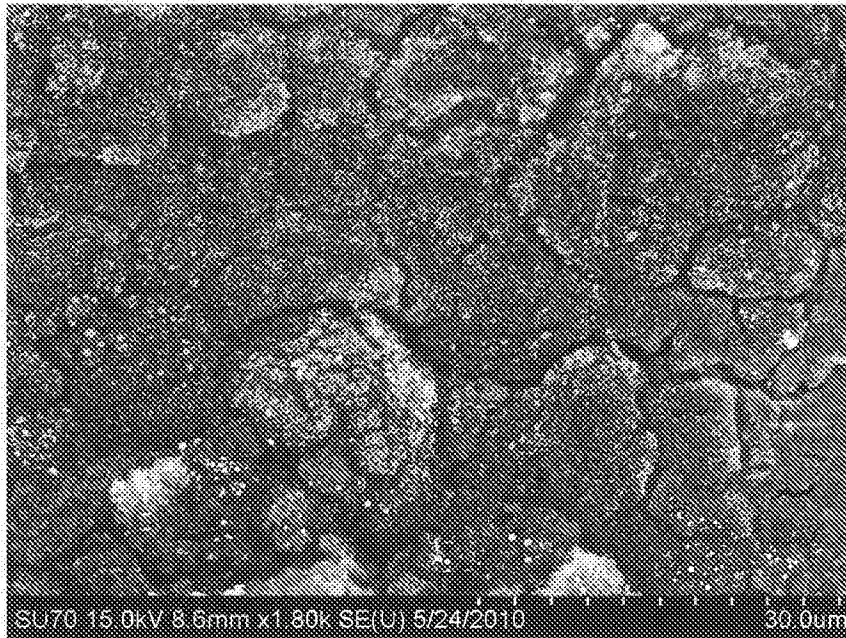


FIGURE 6A

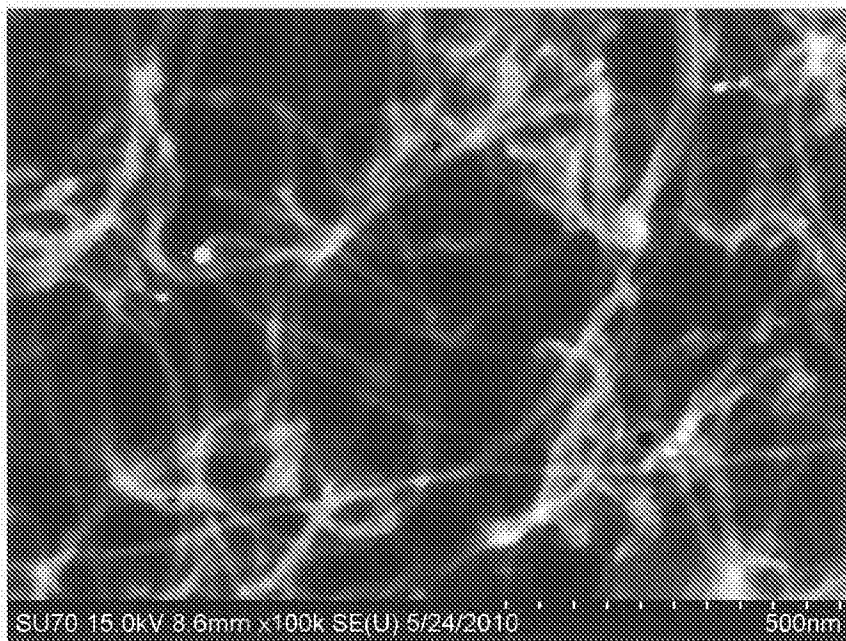


FIGURE 6B

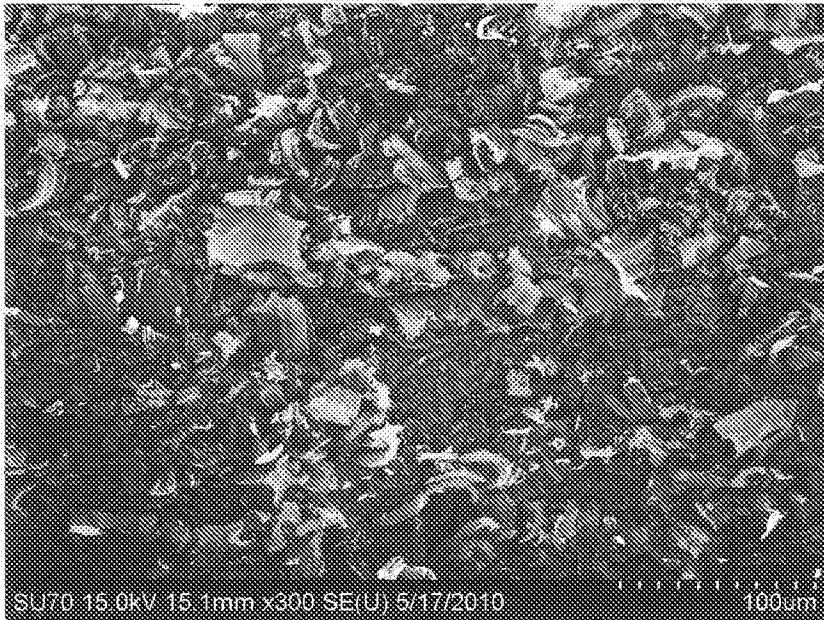


FIGURE 7A



FIGURE 7B

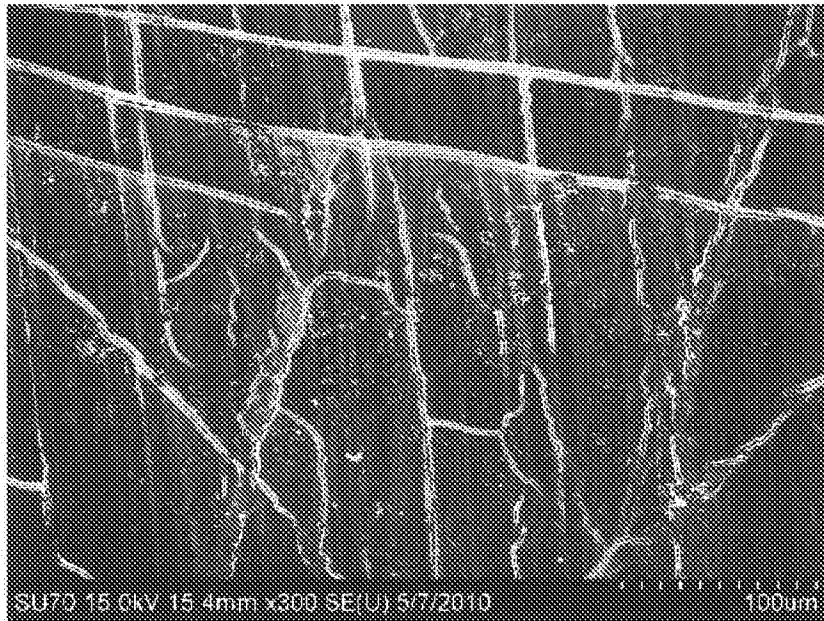


FIGURE 8A



FIGURE 8B

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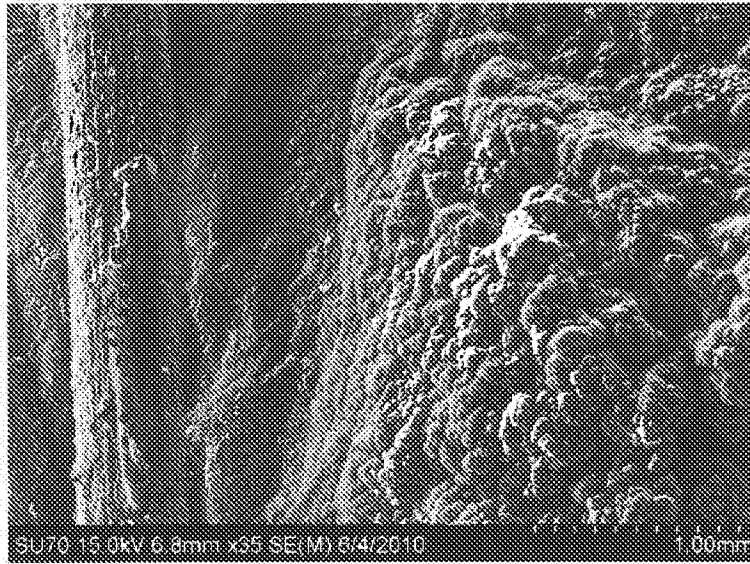


FIGURE 9A

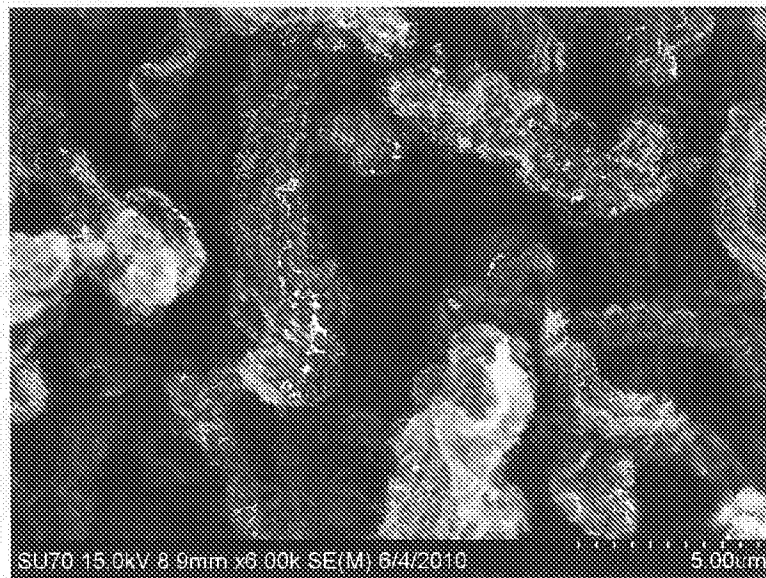


FIGURE 9B

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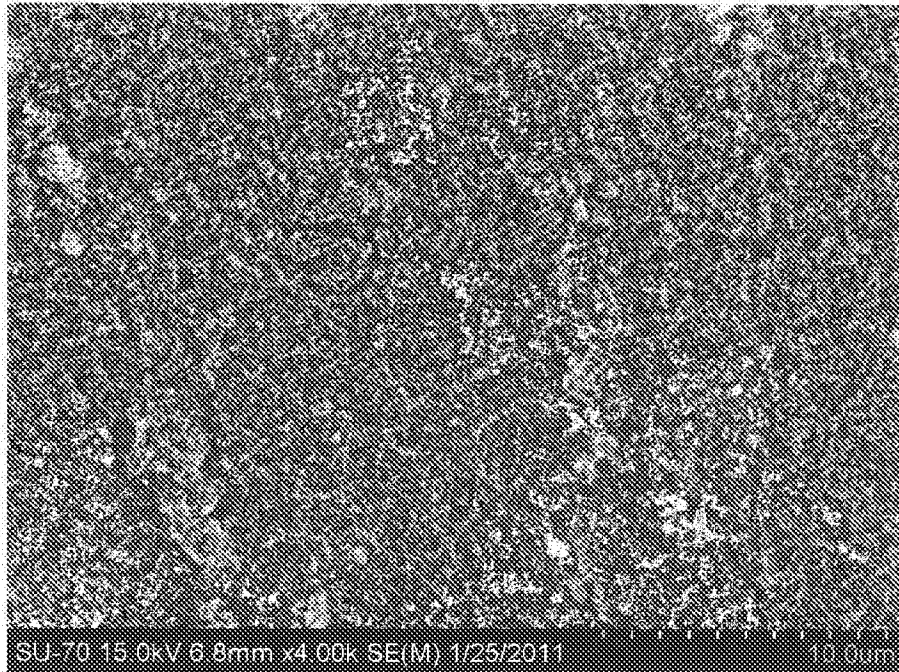


FIGURE 10

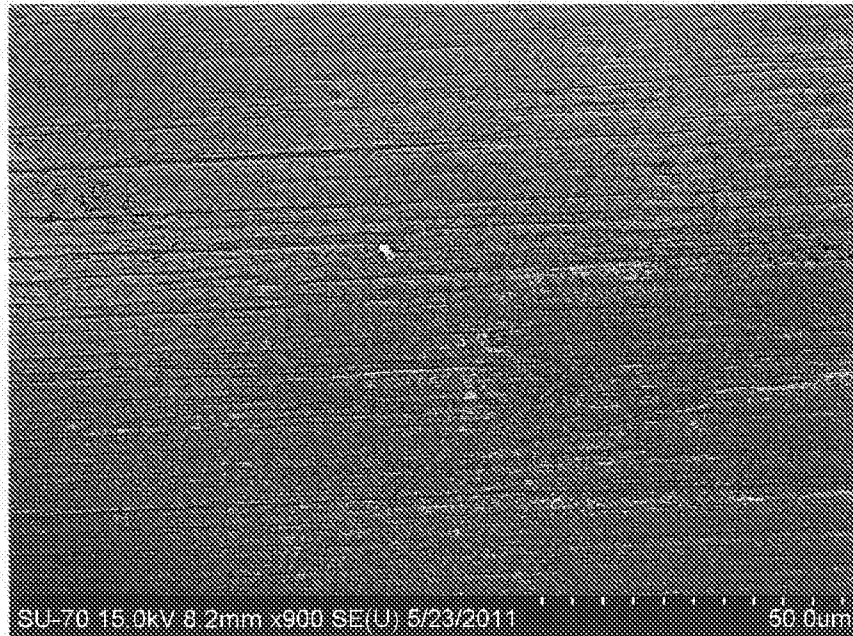


FIGURE 11A

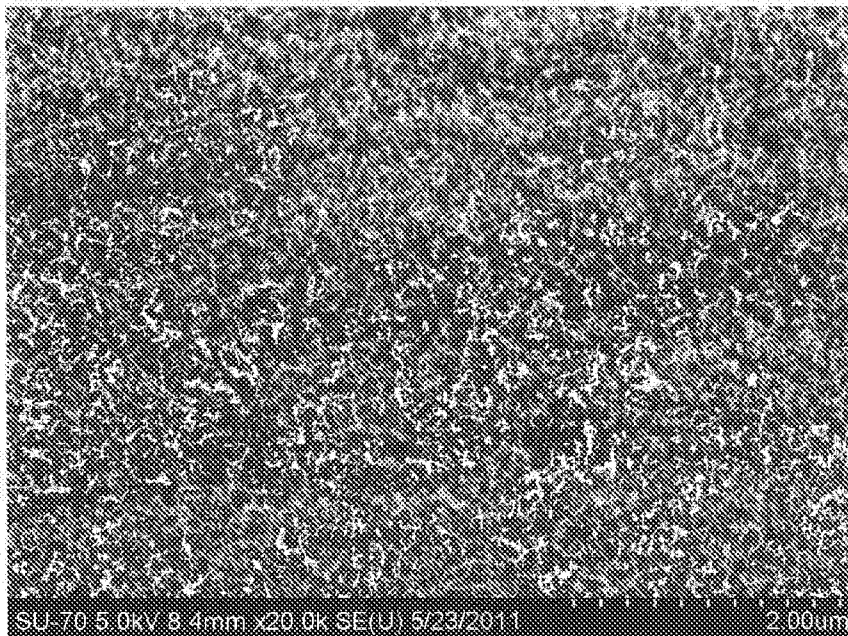


FIGURE 11B

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 11/50084

<p>A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - B05D 5/12 (2011.01) USPC - 427/113 According to International Patent Classification (IPC) or to both national classification and IPC</p>																																
<p>B. FIELDS SEARCHED</p> <p>Minimum documentation searched (classification system followed by classification symbols) IPC(8) - B05D 5/12 (2011.01) USPC - 427/113</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched IPC(8) - B05D 5/12 (2011.01) USPC - 427/113,249.2,248.1,404,406; 423/447.1; 502/416,102,103</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PubWEST (USPT,PGPB,EPAB,JPAB); Google, Google Patent Search terms used: Carbon nanotubes catalyst non-catalyst metal substrate foil base precursor copper aluminum silver gold nickel platinum cnt</p>																																
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>US 2007/0020167 A1 (Han et al.) 25 January 2007 (25.01.2005), entire document, especially para [0019], [0048], [0049], [0034], [0053], [0031], [0032]</td> <td>1-34</td> </tr> <tr> <td>Y</td> <td>US 6,967,013 B2 (Someya et al.) 22 November 2005 (22.11.2005), entire document, especially col 2, ln 59-61; col 2, ln 22-30; col 2, ln 22-30; col 8, ln 17-23; col 4, ln 42-49; claim 8</td> <td>1-37</td> </tr> <tr> <td>Y</td> <td>US 2007/0092431 A1 (Resasco et al.) 26 April 2007 (26.04.2007), para [0032], [0089]; claim 1, 6</td> <td>2, 5, 9, 10, 20, 24, 35-37</td> </tr> <tr> <td>Y</td> <td>US 2009/0072222 A1 (Radisic et al.) 19 March 2009 (19.03.2009), para [0029]</td> <td>11, 12, 25-29</td> </tr> <tr> <td>Y</td> <td>US 2005/0112052 A1 (Gu et al.) 26 May 2005 (26.05.2005), para [0015], [0016]</td> <td>30-31</td> </tr> <tr> <td>A</td> <td>US 2009/0099016 A1 (Carruthers et al.) 16 April 2009 (16.04.2009), entire document</td> <td>1-37</td> </tr> <tr> <td>A</td> <td>US 2007/0259128 A1 (Parsapour) 08 November 2007 (08.11.2007), entire document</td> <td>1-37</td> </tr> <tr> <td>A</td> <td>US 2004/0184981 A1 (Liu et al.) 23 September 2004 (23.09.2004), entire document</td> <td>1-37</td> </tr> <tr> <td>A</td> <td>Zhang et al. "Integration and characterization of aligned carbon nanotubes on metal/silicon substrates and effects of water." Applied Surface Science 255 (2009) 5003-5008, entire document</td> <td>1-37</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	US 2007/0020167 A1 (Han et al.) 25 January 2007 (25.01.2005), entire document, especially para [0019], [0048], [0049], [0034], [0053], [0031], [0032]	1-34	Y	US 6,967,013 B2 (Someya et al.) 22 November 2005 (22.11.2005), entire document, especially col 2, ln 59-61; col 2, ln 22-30; col 2, ln 22-30; col 8, ln 17-23; col 4, ln 42-49; claim 8	1-37	Y	US 2007/0092431 A1 (Resasco et al.) 26 April 2007 (26.04.2007), para [0032], [0089]; claim 1, 6	2, 5, 9, 10, 20, 24, 35-37	Y	US 2009/0072222 A1 (Radisic et al.) 19 March 2009 (19.03.2009), para [0029]	11, 12, 25-29	Y	US 2005/0112052 A1 (Gu et al.) 26 May 2005 (26.05.2005), para [0015], [0016]	30-31	A	US 2009/0099016 A1 (Carruthers et al.) 16 April 2009 (16.04.2009), entire document	1-37	A	US 2007/0259128 A1 (Parsapour) 08 November 2007 (08.11.2007), entire document	1-37	A	US 2004/0184981 A1 (Liu et al.) 23 September 2004 (23.09.2004), entire document	1-37	A	Zhang et al. "Integration and characterization of aligned carbon nanotubes on metal/silicon substrates and effects of water." Applied Surface Science 255 (2009) 5003-5008, entire document	1-37
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<p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td>"&amp;" document member of the same patent family</td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	"P" document published prior to the international filing date but later than the priority date claimed																					
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<p>Date of the actual completion of the international search 06 January 2012 (06.01.2012)</p>		<p>Date of mailing of the international search report <b>24 JAN 2012</b></p>																														
<p>Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201</p>		<p>Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774</p>																														