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(54) Title: CRYSTALLINE GRAPHITE NANOFIBERS AND A PROCESS FOR PRODUCING SAME

(57) **Abrégé/Abstract:**

A carbon nanofiber having substantially graphite sheets that are substantially parallel to the longitudinal axis of the nanofiber and a produce for producing same. The carbon nanofibers are produced by contacting an iron, or an iron:copper bimetallic, or an iron:nickel bimetallic bulk catalyst with a mixture of carbon monoxide and hydrogen at temperatures from about 625 °C to about 725 °C for an effective amount of time.



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(54) Title: CRYSTALLINE GRAPHITE NANOFIBERS AND A PROCESS FOR PRODUCING SAME

(57) Abstract: A carbon nanofiber having substantially graphite sheets that are substantially parallel to the longitudinal axis of the nanofiber and a produce for producing same. The carbon nanofibers are produced by contacting an iron, or an iron:copper bimetallic, or an iron:nickel bimetallic bulk catalyst with a mixture of carbon monoxide and hydrogen at temperatures from about 625 °C to about 725 °C for an effective amount of time.

CRYSTALLINE GRAPHITE NANOFIBERS AND A PROCESS FOR PRODUCING SAME

5 Cross-Reference to Related Applications

[0001]

This application is a continuation-in-part of USSN 09/659,441 filed September 8, 2000.

10 Background of the Invention

Field of the Invention

[0002]

This invention relates to a process for producing substantially crystalline graphitic carbon nanofibers comprised of graphite sheets. The graphite sheets
15 are substantially parallel to the longitudinal axis of the carbon nanofiber. These carbon nanofibers are produced by contacting a bulk iron, or an iron:copper bimetallic, or an iron:nickel bimetallic catalyst with a mixture of carbon monoxide and hydrogen at temperatures from about 625°C to about 725°C for an effective amount of time.

20 Description of Related Art

[0003]

Nanostructure materials, particularly carbon nanostructure materials, are quickly gaining importance for various potential commercial applications. Such applications include their use to store molecular hydrogen, to serve as
25 catalyst supports, as reinforcing components for polymeric composites, and for use in various types of batteries. Carbon nanostructure materials are generally prepared from the decomposition of carbon-containing gases over selected catalytic metal surfaces at temperatures ranging from about 500°C to about 1,200°C.

30

[0004]

U.S. Patent Nos. 5,149,584 and 5,618,875 to Baker et al. teach carbon nanofibers as reinforcing components in polymer reinforced composites. The carbon nanofibers can either be used as is, or as part of a carbon-carbon
5 structure comprised of carbon fibers having carbon nanofibers grown therefrom. The examples in these patents show the preparation of various carbon nanostructures by the decomposition of a mixture of ethylene and hydrogen in the presence of metal catalysts, such as iron, nickel, a nickel:copper alloy, an iron:copper alloy, etc.

10 [0005]

Also, U.S. Patent No. 5,413,866 to Baker et al. teaches carbon nanostructures characterized as having a shape that is selected from the group consisting of branched, spiral, and helical. These carbon nanostructures are taught as being prepared by depositing a catalyst containing at least one Group
15 IB metal and at least one other metal, on a suitable refractory support, then subjecting the catalyst-treated support to a carbon-containing gas at a temperature from the decomposition temperature of the carbon-containing gas to the deactivation temperature of the catalyst.

[0006]

20 U.S. Patent No. 5,458,784 also to Baker et al. teaches the use of the carbon nanostructures of U.S. Patent No. 5,413,866 for removing contaminants from aqueous and gaseous streams; and U.S. Patent No. 5,653,951 to Rodriguez et al. discloses and claims that molecular hydrogen can be stored in layered carbon nanostructure materials having specific distances between layers. The
25 examples in these patents teach the aforementioned preparation methods, as well as the decomposition of a mixture of carbon monoxide and hydrogen in the presence of an iron powder catalyst at 600°C. All of the above referenced US patents are incorporated herein by reference.

[0007]

While various carbon nanostructures and their uses are taught in the art, there is still a need for improvements before such nanostructure materials can reach their full commercial and technical potential. For example, while the art
5 broadly discloses carbon nanostructures having crystallinities from about 5 to 95%, it has heretofore not been possible to produce carbon nanostructures with crystallinities greater than about 95%.

Summary of the Invention

10 [0008]

In accordance with the present invention, there is provided substantially crystalline graphitic carbon nanofibers comprised of graphite sheets that are substantially parallel to the longitudinal axis of the nanofibers, wherein the distance between the graphite sheets is from about 0.335 nm to about 0.67 nm,
15 and having a crystallinity greater than about 95%.

[0009]

In a preferred embodiment, the distance between the graphite sheets is from about 0.335 and 0.40 nm.

[0010]

20 Also in accordance with the present invention, there is provided a process for producing substantially crystalline graphitic carbon nanofibers which process comprises reacting a mixture of CO/H₂ in the presence of a bulk powder catalyst comprised of iron, iron:copper bimetallic, or iron:nickel bimetallic for an effective amount of time at a temperature from about 625°C to
25 about 725°C.

[0011]

In a preferred embodiment, the catalyst is an iron:copper bimetallic catalyst wherein the ratio of iron to copper is from about 1:99 to about 99:1 and

the ratio of CO to H₂ is from about 95:5 to about 5:95, preferably from about 80:20 to about 20:80.

Brief Description of the Drawings

[0012]

- 5 Figure 1a is a representation of a platelet carbon nanofiber, which is comprised of substantially graphite sheets that are substantially perpendicular to the longitudinal axis, or growth axis, of the nanofiber.

[0013]

- 10 Figure 1b is a representation of a cylindrical carbon nanostructure that is comprised of continuous carbon sheets and is in the form of tube within a tube within a tube and having a substantially hollow center.

[0014]

- 15 Figure 1c is a representation of a ribbon carbon nanofiber of the present invention that is comprised of graphitic sheets that are substantially parallel to the longitudinal axis of the nanofiber.

[0015]

- 20 Figure 1d is a representation of a faceted tubular carbon nanofiber of the present invention and is comprised of continuous sheets of graphitic carbon but having multifaceted flat faces. The graphitic sheets are also substantially parallel to the longitudinal axis of the nanofiber.

[0016]

- 25 Figure 1e is a representation of a herringbone carbon nanofiber wherein the graphitic platelets or sheets are at an angle to the longitudinal axis of the nanofiber.

Detailed Description of the Invention

[0017]

The carbon nanofibers of the present invention possess novel structures in which graphite sheets, constituting the nanostructure, are aligned in a direction that is substantially parallel to the growth axis (longitudinal axis) of the nanofiber. The carbon nanofibers are sometimes referred to herein as “ribbon” nanofibers and multifaceted tubular nanofibers. The carbon nanostructures of the present invention are distinguished from the so-called “fibrils” or cylindrical carbon nanostructures. The terms “carbon nanofibers” and “carbon nanostructures” are sometimes used interchangeably herein. The graphite sheets that compose the nanostructures of the present invention are either discontinuous sheets or faceted flat-faced tubular structures. On the other hand, cylindrical carbon nanostructures, or “fibrils” are composed of continuous circular graphite sheets and can be represented by tube within a tube structure having a substantially hollow center. In addition, the carbon nanofibers of the present invention have a unique set of properties, that includes: (i) a nitrogen surface area from about 40 to 300 m²/g; (ii) an electrical resistivity of 0.4 ohm•cm to 0.1 ohm•cm; (iii) a crystallinity from about 95% to 100%; and (iv) a spacing between adjacent graphite sheets of 0.335 nm to about 1.1 nm, preferably from about 0.335 nm to about 0.67 nm, and more preferably from about 0.335 to about 0.40 nm.

[0018]

The catalysts used to prepare the carbon nanofibers of the present invention are bulk metals in powder form wherein the metal is selected from the group consisting of iron, iron:copper bimetallics, and iron:nickel bimetallics. It is well established that the ferromagnetic metals, iron, cobalt, and nickel, are active catalysts for the growth of carbon nanofibers during decomposition of certain hydrocarbons or carbon monoxide. Efforts are now

being directed at modifying the catalytic behavior of these metals, with respect to nanofiber growth, by introducing other metals and non-metals into the system. In this respect, copper is an enigma, appearing to be relatively inert towards carbon deposition during the CO/H₂ reaction. Thus, it is unexpected
5 that Fe or the combination of Cu or Ni with Fe has such a dramatic effect on carbon nanofiber growth in the CO/H₂ system in the temperature range of about 625°C to about 725°C. Preferably from about 650°C to about 725°C, and more preferably from about 670°C to about 725°C. Iron:copper catalysts are preferred for preparing the carbon nanostructures of the present invention.

10 [0019]

The average powder particle size of the metal catalyst will range from about 0.25 nanometers to about 5 micrometer, preferably from about 1 nanometers to about 3 micrometer and more preferably from about 2.5 nanometers to about 1 micrometer. When the catalyst is a bimetallic catalyst,
15 the ratio of the two metals can be any effective ratio that will produce substantially crystalline carbon nanofibers in which the graphite sheets are substantially parallel to the longitudinal axis of the nanofiber, at temperatures from about 625°C to about 725°C in the presence of a mixture of CO/H₂. The ratio of iron to either copper or nickel will typically be from about 1:99 to
20 about 99:1, preferably from about 5:95 to about 95:5, more preferably from about 3:7 to about 7:3; and most preferably from about 6:4 to about 7:3. The bimetallic catalyst can be prepared by any suitable technique. One preferred technique is by co-precipitation of aqueous solutions containing soluble salts of the two metals. Preferred salts include the nitrates, sulfates, and chlorides of
25 iron, copper, and nickel particularly the nitrates. The resulting precipitates are dried and calcined to convert the salts to the mixed metal oxides. The calcined metal powders are then reduced at an effective temperature and for an effective time.

[0020]

The catalyst powders used in the present invention are preferably prepared by the co-precipitation of aqueous solutions containing appropriate amounts of iron, nickel and copper nitrates using ammonium bicarbonate. The precipitates were dried overnight at about 110°C before being calcined in air at 400°C to convert the carbonates into mixed metal oxides. The calcined powders are then reduced in hydrogen for 20 hours at 400°C. Following this treatment the reduced catalyst is cooled to room temperature in a helium environment before being passivated in a 2% oxygen/helium mixture for 1 hour at about room temperature (24°C).

[0021]

It is known that carbon nanostructures can be prepared by reacting a catalyst in a heating zone with the vapor of a suitable carbon-containing compound. While the art teaches a wide variety of carbon-containing compounds as being suitable, the inventors hereof have found that only a mixture of CO and H₂ will yield carbon nanofibers with unexpected high crystallinities in the unique structures of nanofibers of the present invention in the temperature range of about 625°C to about 725°C. That is, crystallinities greater than about 95%, preferably greater than 97% more preferably greater than 98%, and most preferably substantially 100%.

[0022]

After the nanofibers are grown, it may be desirable to treat them with an aqueous solution of an inorganic acid, such as a mineral acid, to remove any excess catalyst particles. Non-limiting examples of suitable mineral acids include sulfuric acid, nitric acid, and hydrochloric acid. Preferred is hydrochloric acid.

[0023]

It is within the scope of this invention to increase the spacing between the graphite sheets by any suitable means, such as by intercalation. Intercalation involves incorporating an appropriate intercalation compound
5 between platelets. Intercalation compounds suitable for graphite structures are comprehensively discussed in Applications of Graphite Intercalation Compounds, by M.Inagaki, Journal of Material Research, Vol 4, No.6, Nov/Dec 1989, which is incorporated herein by reference. The preferred intercalation compounds for use with the nanofibers of the present invention are alkali and
10 alkaline-earth metals. The limit to which the spacing of the graphite sheets will be increased for purposes of the present invention will be that point wherein the carbon nanofibers no longer can be characterized as graphitic. That is, the spacing can become so large that the carbon now has properties different than those of graphite. In most cases the electro-conductivity is enhanced. It is
15 important for the practice of the present invention that the carbon nanofibers maintain the basal plane structure representative of graphite.

[0024]

A major advantage of the graphite nanofibers of the present invention over other graphitic materials is their flexibility with regard to modification of
20 surface chemistry. For example, the carbon nanostructures of the present invention contain a substantial number of edge sites, which are also referred to as edge regions. The edge regions of the nanostructures of the present invention can be made either basic (introduction of NH_4^+ groups) or acidic (addition of COOH^- groups) by use of appropriate methods. Furthermore, the
25 presence of oxygenated groups (hydroxyl, peroxide, ether, keto or aldehyde) that are neither acidic nor basic in nature can impart polarity to the graphite structure. These groups in turn can react with organic compounds to house unique structures for separations. Polar groups will promote the interaction of carbon edge atoms with other polar groups such as water. As a consequence,

the interaction of graphitic materials with aqueous solutions can be greatly enhanced due to the presence of acid, basic or neutral functionality.

[0025]

The distribution of polar groups in active carbon (non-graphitic) occurs in a random fashion, whereas the graphitic nanofibers of the present invention, such sites are located at the edges of the graphene layers. Addition of oxygenated groups can be achieved by selected oxidation treatments including treatment with peroxides, nitric acid, potassium permanganate, etc. Functionality can also be incorporated by electrochemical oxidation, at for example 2.3 volts for various periods of time. The nature of the groups will be dependent upon the oxidation time and the voltage. Polar sites can also be eliminated by reduction, out-gassing in vacuum at 1000°C or treatment in hydrazine at about 35°C. Following this procedure, the graphite nanofiber will become hydrophobic. Theodoridou and coworkers, (Met. 14, 125 (1986)), demonstrated that very efficient surface oxidation of carbon fibers can be achieved by d.c. oxidation or repetitive anodic oxidation and cathodic reduction of the material in acidic, alkaline or neutral aqueous media. It was believed that this method had the advantage over other procedures in that thick layers of surface oxides could be produced without damaging the fiber structure. These workers also capitalized on the conductive properties of graphitized carbon fibers to introduce various noble metals onto such materials via the use of electrochemical procedures. The possibility of controlling the functionality of the graphite surface could have a direct impact on both the chemistry of the supported metal particles and their morphological characteristics.

25 [0026]

The present invention will be illustrated in more detail with reference to the following examples, which should not be construed to be limiting in scope of the present invention.

[0027]

Gas flow reactor experiments were carried out in a horizontal quartz tube (40 mm i.d. and 90 cm long) contained in a Lindberg tube furnace, at temperatures over the range of about 450°C to 700°C. Gas flow rates to the reactor were regulated by MKS mass flow controllers. In a typical experiment, 50 mg of given catalyst powder was dispersed in a substantially uniform manner along the base of a ceramic boat, which was subsequently placed at the center of the reactor tube. After reduction of the sample at 600°C for 2 hours, the system was flushed with helium and brought to the desired temperature level before being reacted with in the CO/H₂ mixture for a period of 2 hours. The total amount of solid carbon formed in any given experiment was determined at the completion of the reaction by weight difference. The composition of the gas phase was measured at regular intervals by taking samples of the inlet and outlet streams, which were then analyzed by gas chromatography using a 30m megabore (CS-Q) capillary column in a Varian 3400 GC unit. Carbon and hydrogen atom balances, in combination with the relative concentrations of the respective components, were applied to obtain the various product yields. In order to obtain reproducible carbon deposition data it was necessary to follow an identical protocol for each experiment.

[0028]

The structural details of the carbon materials resulting from the interaction of the CO/H₂ mixtures with the various powdered bimetallic catalysts were examined in a JEOL 2000 EX II transmission electron microscope that was fitted with a high resolution pole piece capable of providing a lattice resolution of 0.18 nm. Temperature programmed oxidation studies (TPO) of the various carbon materials were carried out in a Cahn 2000 microbalance in the presence of a CO₂/Ar (1:1) mixture at a heating rate of 5°/min. The degree of crystallization of a given type of carbon nanostructure was determined from a comparison of the oxidation profile of two standard

materials, amorphous carbon and single crystal graphite when treated under the same conditions.

Example 1

[0029]

5 In the first set of experiments selected Fe:Cu catalysts were heated in the presence of a CO/H₂ (4:1) mixture at temperatures ranging from 450°C to 700°C. Table I below shows the number of grams of carbon nanofibers per weight of catalyst produced after a period of 2 hours at each temperature. In each case the optimum yield of carbon nanofibers was generated at temperatures between 550°C and 600°C.
10 The most active catalysts were those that contained a larger fraction of iron than copper.

Table I

Effect of Temperature on the amount of Carbon Nanofibers (grams/grams of Catalyst) from the Decomposition of CO/H₂ over selected Fe:Cu
15 **Powders**

Temperature (°C)	Fe:Cu (1:9)	Fe:Cu (3:7)	Fe:Cu (7:3)
450	1.10	1.15	1.31
500	2.55	4.15	10.83
20 525	4.48		
550	6.14	9.81	12.02
600	7.86	10.15	11.55
625	5.07		
650	3.72	4.21	4.40
25 700	1.24	1.15	1.31

Example 2

[0030]

A second series of experiments was carried out at 550°C under
30 conditions where selected Fe:Cu catalysts were heated in CO/H₂ mixtures in which the percent of H₂ was progressively increased. The data presented in Table II below shows that the number of grams of carbon nanofibers per weight of catalyst produced after 2.5 hours reached a maximum for each system when the reactant gas contained between 20 to 50% of hydrogen.

35

Table II

Effect of Percent H₂ in the CO/H₂ reactant mixture on the amount of Carbon Nanofibers (grams/grams of Catalyst) formed over Fe:Cu Catalysts at 550°C

5		Catalyst	20 % H₂	50 % H₂	80 % H₂
		Pure Fe	17.53	16.86	14.16
		Fe-Cu (7:3)	16.63	17.23	12.96
		Fe-Cu (5:5)	16.41	15.74	12.14
10		Fe-Cu (3:7)	13.78	13.71	12.51
		Fe-Cu (1:9)	8.7	10.41	10.79

Example 3**[0031]**

15 Another set of experiments was performed at 600°C under conditions where selected Fe:Cu catalysts were heated in CO/H₂ mixtures in which the percent of H₂ was progressively increased. The data presented in Table III below shows that in this case the number of grams of carbon nanofibers per weight of catalyst produced after 2.5 hours reached a maximum for each
20 system when the reactant gas contained 20% of hydrogen.

Table III

Effect of Percent H₂ in the CO/H₂ reactant mixture on the amount of Carbon Nanofibers (grams/grams of Catalyst) formed over Fe:Cu Catalysts at 600°C

25		Catalyst	20% H₂	33% H₂	50% H₂	67% H₂	80% H₂
		Fe-Cu (1:9)	7.86	7.37	7.11	5.26	3.96
		Fe-Cu (3:7)	10.15	8.91	7.44	6.35	4.05
30		Fe-Cu (7:3)	11.85	9.33	8.99	4.77	3.23

Example 4**[0032]**

In a set of experiments carried out at 600°C for 2 hours it was found that
35 the number of grams of carbon nanofibers per weight of catalyst produced after

2.5 hours with a CO/H₂ mixture was dependent upon the percentage of copper in the Fe:Cu bimetallic catalyst. It can be seen from Table IV below that as the fraction of copper exceeds 40% there is a gradual decrease in carbon nanofiber yield. It can also be seen that a catalyst containing pure copper does not
5 produce carbon nanofibers.

Table IV

The effect of catalyst composition on carbon nanofiber formation from the Fe-Cu catalyzed decomposition of CO/H₂ (4:1) after 1.0 hours at 600°C

10

% Copper in catalyst		Grams of carbon nanofibers/grams catalyst
	0	8.8
	30	11.65
15	50	11.60
	70	10.25
	80	9.10
	90	7.35
	95	4.70
20	100	0

Example 5

[0033]

25

In a further set of experiments the overall degree of crystallinity of the carbon nanofibers produced from the interaction of selected Fe:Cu catalysts with a CO/H₂ (4:1) mixture at 600°C for 2.0 hours was determined from temperature programmed oxidation of the nanofibers in CO₂. The characteristics of the controlled gasification of carbonaceous solids in CO₂ provides a sensitive method of determining the structural perfection of such
30 materials. The data shown in Table V below indicates that the degree of crystallinity of carbon nanofibers generated from an Fe-Cu (7:3) catalyst is significantly higher than that of the same type of nanofibers grown under identical reaction conditions on a pure iron catalyst.

Table V

**Percent reactivity of carbon nanofibers
in CO₂ as a function of reaction temperatures**

Carbon Material	805°C	900°C	950°C	1000°C	1050°C
Nanofibers from Fe	29.1%	52.0%	72.8%	86.2%	100.0%
Nanofibers from Fe-Cu (7:3)	5.2%	12.8%	30.6%	57.0%	100.0%

Example 6**[0034]**

In a series of characterization studies performed in a high resolution transmission electron microscope, small sections of carbon nanofibers grown from the decomposition of CO/H₂ mixtures at 600°C over various metal and bimetallic catalyst systems were examined and representative micrographs taken of each sample. A compilation of the observations made from inspection of several micrographs from each sample is given in Table VI below. Also included for comparison purposes are corresponding data for nanofibers grown from the interaction of the same series of catalysts with C₂H₄/H₂ at 600°C.

Table VI

Comparison of structural features of carbon nanofibers from the decomposition of CO/H₂ (4:1) and C₂H₄/H₂ (4:1) over various metal and bimetallic catalysts at 600°C

	<u>Catalyst</u>	Nanofiber Structure	
		<u>C₂H₄/H₂</u>	<u>CO/H₂</u>
5			
10	Fe	No nanofiber growth	Platelet
	Ni	Straight amorphous nanofibers	No nanofiber growth
15	Co	Straight amorphous nanofibers	No nanofiber growth
	Fe-Ni	Straight coiled & branched "herring-bone"	Faceted Tubular/Ribbon
20	Ni-Cu	Straight coiled & branched "herring-bone"	No nanofiber growth
	Co-Cu	Amorphous straight, Coiled & branched	No nanofiber growth
25	Fe-Cu	Straight coiled & branched "herring-bone"	Platelet

[0035]

30 A carbon nanofiber having graphite sheets at an angle to the longitudinal axis of the nanofiber is referred to as a "herringbone structure".

Example 7

[0036]

35 In another series of characterization studies, performed in a high resolution transmission electron microscope, samples of carbon nanofibers grown from the decomposition of CO/H₂ mixtures over a powdered iron catalyst at temperatures over the range 550 to 670°C were examined. The data

presented in Table VII below indicates that there is a very narrow temperature window, 600 to 625°C, where the structures of the nanofibers are produced exclusively in the form of platelet structures. Below this temperature the solid carbon product is found to consist of a mixture of herring-bone and platelet conformations, whereas at temperatures of 650°C there is a tendency for the structures to acquire a faceted tubular or ribbon arrangement, which becomes the only form at 670°C.

Table VII

Characteristics of carbon nanofibers produced from the iron catalyzed decomposition of a CO/H₂ (4:1) mixture as a function of reaction temperature

	<u>Catalyst</u>	<u>Temperature (°C)</u>	<u>Nanofiber Structure</u>
15	Fe	550	Herring-bone & Platelet
	Fe	580	Herring-bone & Platelet
	Fe	600	Platelet
	Fe	625	Platelet
	Fe	650	Platelet & Faceted Tubular/Ribbon
20	Fe	670	Faceted Tubular/Ribbon

Example 8

[0037]

In another series of characterization studies, performed in a high resolution transmission electron microscope, samples of carbon nanofibers grown from the decomposition of CO/H₂ mixtures over a powdered iron-copper (7:3) catalyst at temperatures over the range 550 to 670°C were examined. The observations from these experiments are presented in Table VIII below.

30

Table VIII

Characteristics of carbon nanofibers produced from the iron-copper (7:3) catalyzed decomposition of a CO/H₂ (4:1) mixture as a function of reaction temperature

5	<u>Catalyst</u>	<u>Temperature (°C)</u>	<u>Nanofiber Structure</u>
	Fe-Cu (7:3)	550	Herring-bone & Platelet
	Fe-Cu (7:3)	575	Platelet
	Fe-Cu (7:3)	600	Platelet
10	Fe-Cu (7:3)	625	Platelet
	Fe-Cu (7:3)	650	Platelet & Faceted Tubular/Ribbon
	Fe-Cu (7:3)	670	Faceted Tubular

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What is Claimed is:

1. A substantially crystalline graphitic carbon nanofiber comprised of substantially graphite sheets that are substantially parallel to the longitudinal axis of the nanofibers, wherein the distance between graphite sheets is from about 0.335 nm to about 0.67 nm, and having a crystallinity greater than about 95%.
2. The nanofiber of claim 1 wherein said substantially graphite sheets are separate and non-continuous sheets.
3. The nanofiber of claim 1 which is characterized as having continuous substantially graphite sheets forming a non-cylindrical multifaceted tubular structure.
4. The nanofiber of the claim 1 wherein the distance between the graphite sheets is from about 0.335 and 0.40 nm.
5. The nanofiber of claim 1 wherein at least a portion of the edge regions of the nanofiber contain a functional group selected from the group consisting of basic groups, acidic groups, and oxygenated groups.
6. The nanofiber of claim 5 wherein the functional group is a basic group that is a NH_4^+ group.
7. The nanofiber of claim 5 wherein the functional group is an acid group which is a COOH^- group.
8. The nanofiber of claim 5 wherein the functional group is an oxygenated group selected from the group consisting of hydroxyl, peroxide, ether, keto, and aldehyde.
9. A substantially crystalline graphitic carbon nanofiber comprised of substantially graphite discontinuous sheets that are substantially parallel to the longitudinal axis of the nanofibers, wherein the distance between

- graphite sheets is from about 0.335 nm to about 0.67 nm, and having a crystallinity greater than about 95%.
10. The nanofiber of the claim 9 wherein the distance between the graphite sheets is from about 0.335 and 0.40 nm.
 11. The nanofiber of claim 9 wherein at least a portion of the edge regions of the nanofiber contain a functional group selected from the group consisting of basic groups, acidic groups, and oxygenated groups.
 12. The nanofiber of claim 11 wherein the functional group is a basic group that is a NH_4^+ group.
 13. The nanofiber of claim 11 wherein the functional group is an acid group which is a COOH^- group.
 14. The nanofiber of claim 11 wherein the functional group is an oxygenated group selected from the group consisting of hydroxyl, peroxide, ether, keto, and aldehyde.
 15. A substantially crystalline graphitic carbon nanofiber comprised of continuous substantially graphite sheets that are substantially parallel to the longitudinal axis of the nanofibers and which has a substantially non-cylindrical multifaceted tubular structure, wherein the distance between graphite sheets is from about 0.335 nm to about 0.67 nm, and having a crystallinity greater than about 95%.
 16. The nanofiber of the claim 15 wherein the distance between the graphite sheets is from about 0.335 and 0.40 nm.
 17. The nanofiber of claim 15 wherein at least a portion of the edge regions of the nanofiber contain a functional group selected from the group consisting of basic groups, acidic groups, and oxygenated groups.

18. The nanofiber of claim 17 wherein the functional group is a basic group that is a NH_4^+ group.
19. The nanofiber of claim 17 wherein the functional group is an acid group which is a COOH^- group.
20. The nanofiber of claim 17 wherein the functional group is an oxygenated group selected from the group consisting of hydroxyl, peroxide, ether, keto, and aldehyde.
21. A process for producing a substantially crystalline graphitic nanofiber wherein at least a portion of which are comprised of graphite sheets that are substantially parallel to the longitudinal axis of the nanofiber, which process comprises reacting a mixture of CO/H_2 in the presence of a catalyst selected from the group consisting of Fe, Fe:Cu bimetallic, and Fe:Ni bimetallic powder catalysts for an effective amount of time at a temperature from about 625°C to about 725°C .
22. The process of claim 21 wherein said nanofibers are characterized as having separate and non-continuous substantially graphite sheets.
23. The process of claim 21 wherein said nanofibers are characterized as having continuous substantially graphite sheets forming a non-cylindrical multifaceted tubular structure.
24. The process of claim 21 wherein the catalyst is an Fe:Cu bimetallic wherein the ratio of Fe to Cu is from about 1:99 to about 99:1.
25. The process of claim 24 wherein the ratio of Fe to Cu is from about 3:7 to about 7:3
26. The process of claim 21 wherein the catalyst is an Fe:Ni bimetallic wherein the ratio of Fe to Ni is from about 1:99 to about 99:1.

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27. The process of claim 26 wherein the ratio of Fe to Ni is from about 3:7 to about 7:3.
28. The process of claim 21 wherein the ratio of CO to H₂ is from about 95:5 to about 5:95.
29. The process of claim 28 wherein the ratio of CO to H₂ is from about 80:20 to about 20:80.
30. The process of claim 25 wherein the ratio of CO to H₂ is from about 80:20 to about 20:80.
31. The process of claim 21 wherein the crystallinity of the nanofiber is greater than about 98%.
32. The process of claim 25 wherein the crystallinity of the nanofiber is greater than about 98%.
33. The process of claim 21 wherein the particle size of the bimetallic powder is from about 0.25 nanometer to about 5 micrometer.
34. The process of claim 33 wherein the particle size of the bimetallic powder is from about 2.5 nanometers to about 1 micrometer.
35. A process for producing a substantially crystalline graphite nanofibers comprised of graphite sheets that are substantially perpendicular to the longitudinal axis of the nanofibers, which process comprises reacting a mixture of CO/H₂ in the presence of a Fe:Cu bimetallic catalyst in powder form for an effective amount of time at a temperature from 575°C to 625°C.
36. The process of claim 35 wherein the ratio of Fe to Cu is from about 1:9 to about 9:1.

[illegible]

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Schematic Rendition of Various Types of Graphite Nanofibers

