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(54) **GROWTH OF SINGLE-WALLED CARBON NANOTUBES**

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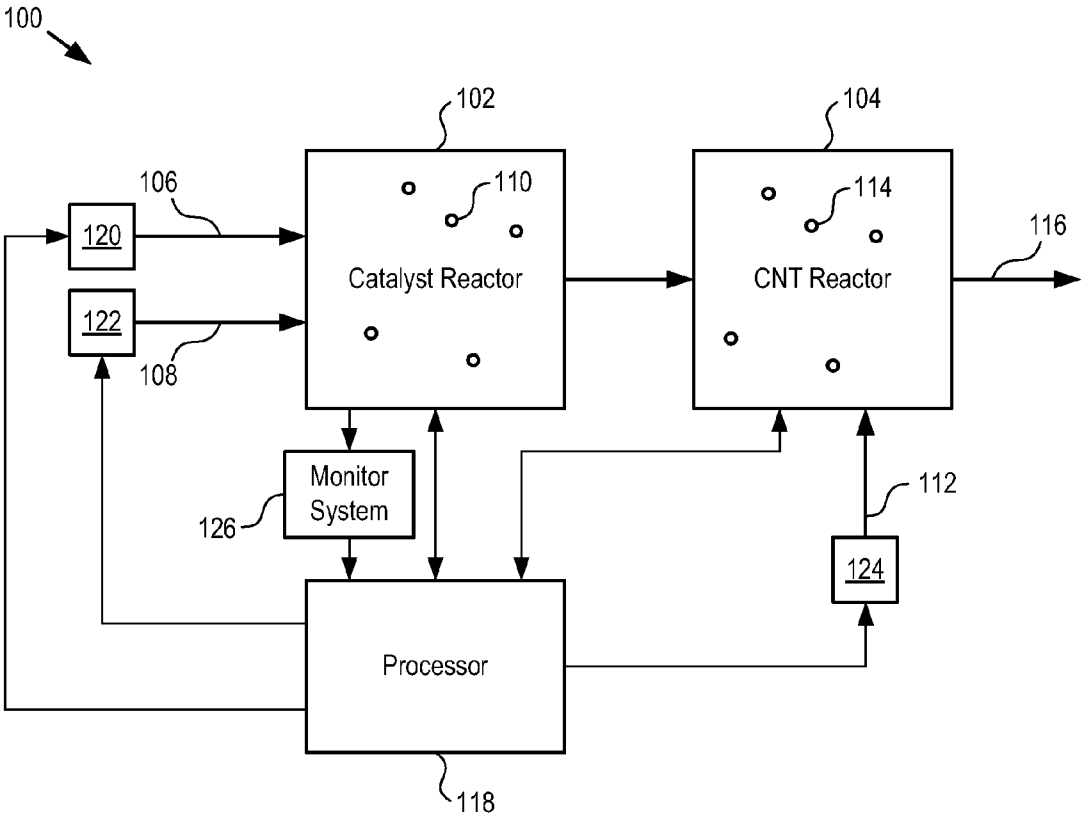
(57) **ABSTRACT**

A method for synthesizing carbon nanotubes having a narrow distribution of diameter and/or chirality is presented. The method comprises providing catalyst particles to a reactor for synthesizing the carbon nanotubes, wherein the catalyst particles are characterized by a narrow distribution of catalyst-particle diameters and a narrow distribution of catalyst-particle compositions. Preferably, the catalyst particles are characterized by a mean catalyst-particle diameter of 2.6 nm or less and a composition of Ni_xFe_{1-x}, wherein x is less than or equal to 0.5.



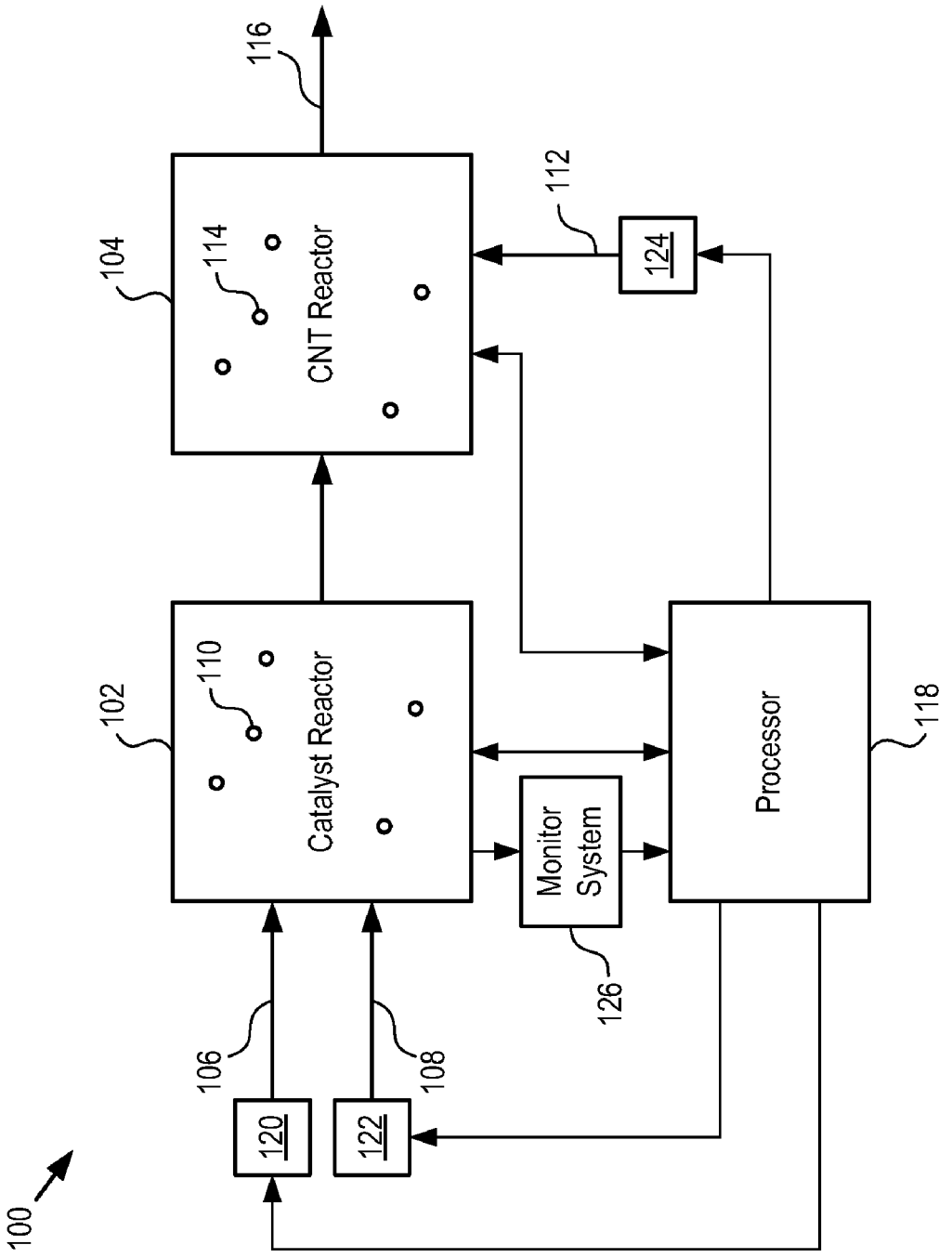

100
102
104
106
108
110
112
114
116
118
120
122
124
126
Catalyst Reactor
CNT Reactor
Monitor System
Processor

FIG. 1

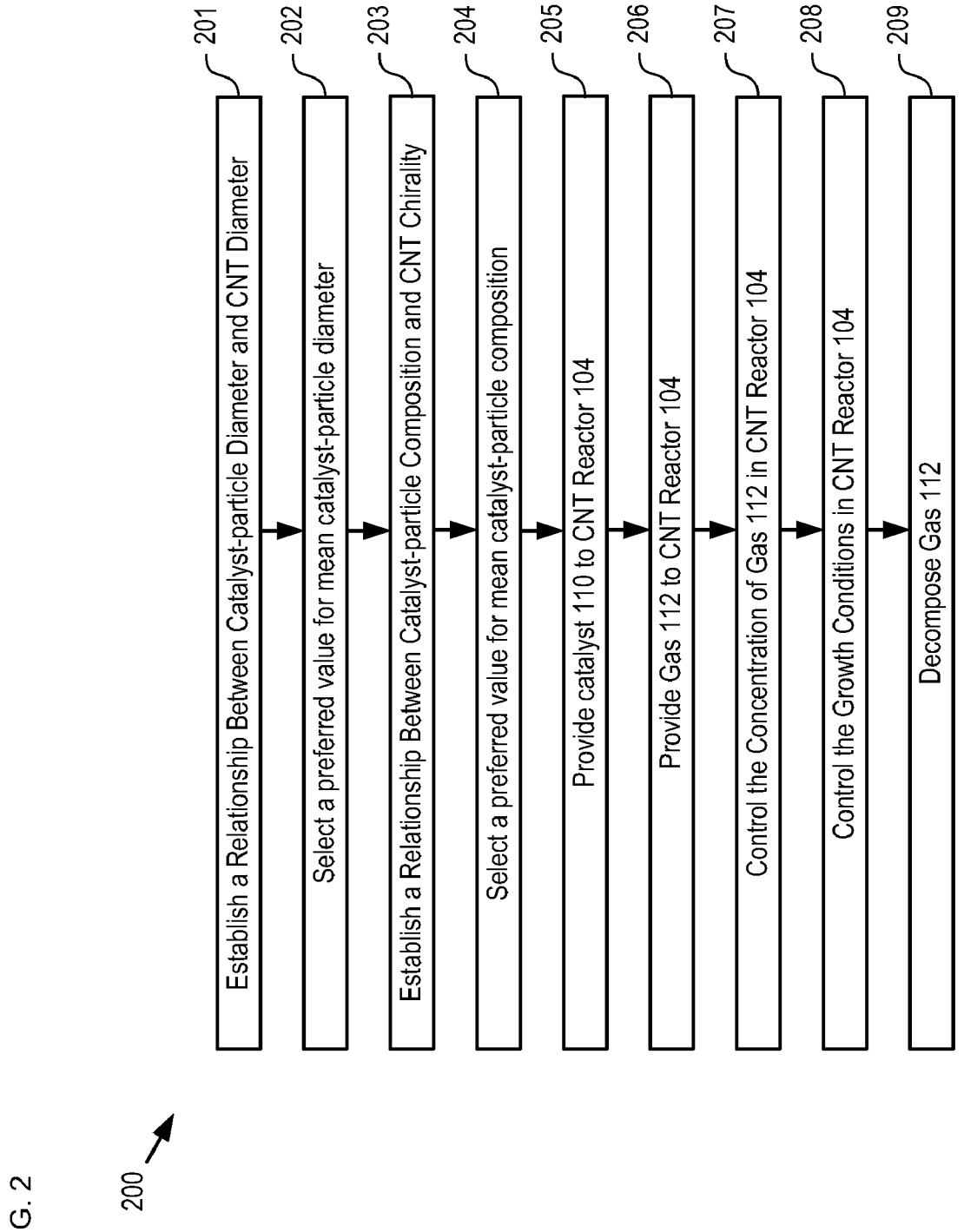

200
201
Establish a Relationship Between Catalyst-particle Diameter and CNT Diameter
202
Select a preferred value for mean catalyst-particle diameter
203
Establish a Relationship Between Catalyst-particle Composition and CNT Chirality
204
Select a preferred value for mean catalyst-particle composition
205
Provide catalyst 110 to CNT Reactor 104
206
Provide Gas 112 to CNT Reactor 104
207
Control the Concentration of Gas 112 in CNT Reactor 104
208
Control the Growth Conditions in CNT Reactor 104
209
Decompose Gas 112

FIG. 2

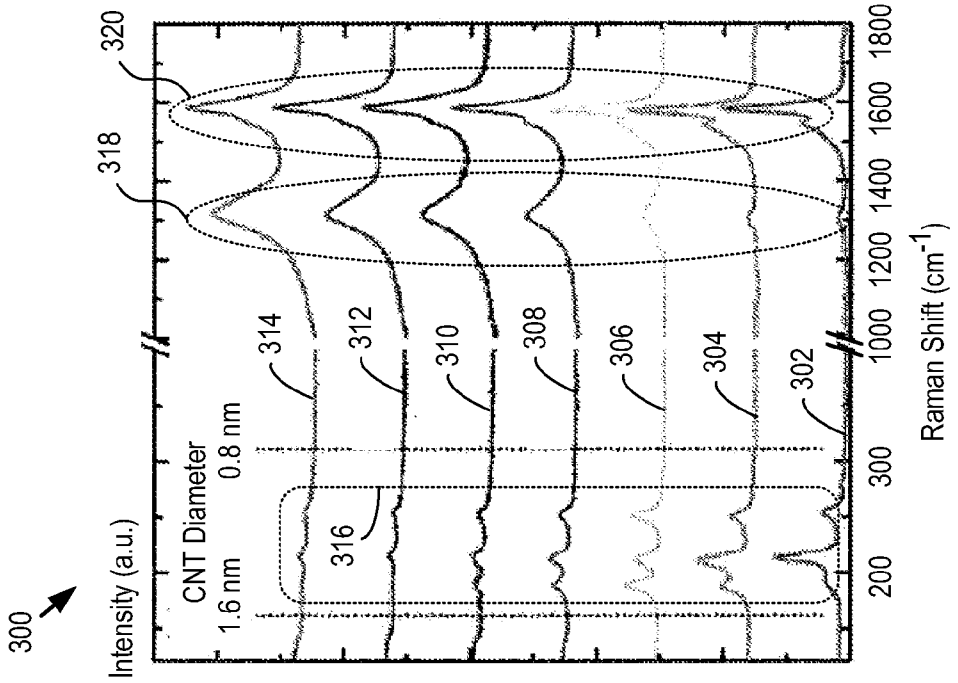

300
Intensity (a.u.)
CNT Diameter
1.6 nm
0.8 nm
316
314
312
310
308
306
304
302
318
320
200
300
1000
1200
1400
1600
1800
Raman Shift (cm-1)

FIG. 3

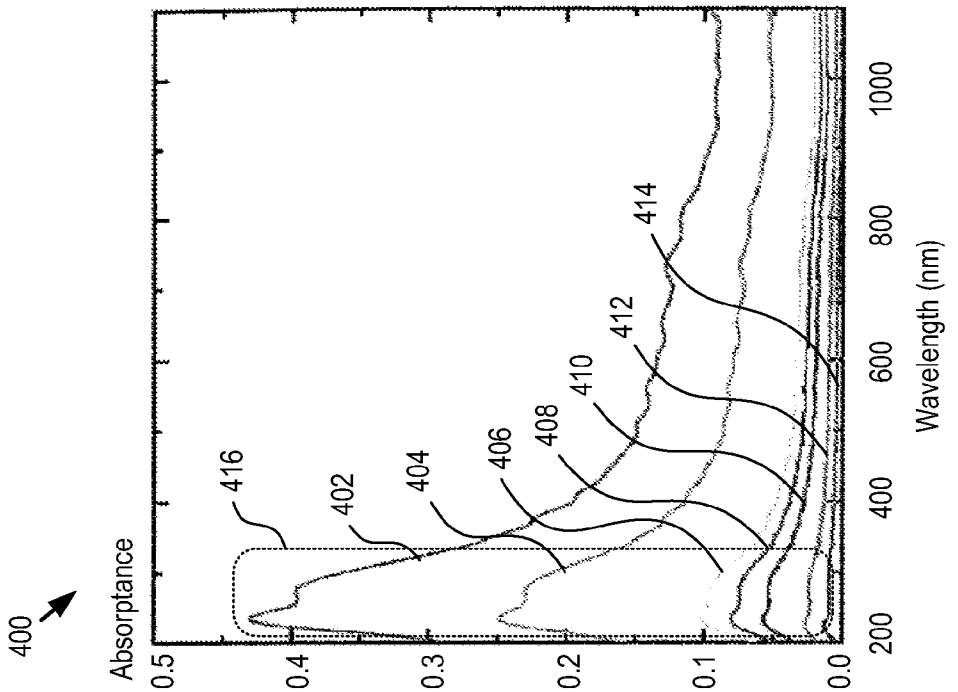

400
Absorptance
0.5
0.4
0.3
0.2
0.1
0.0
416
402
404
406
408
410
412
414
200
400
600
800
1000
Wavelength (nm)

FIG. 4

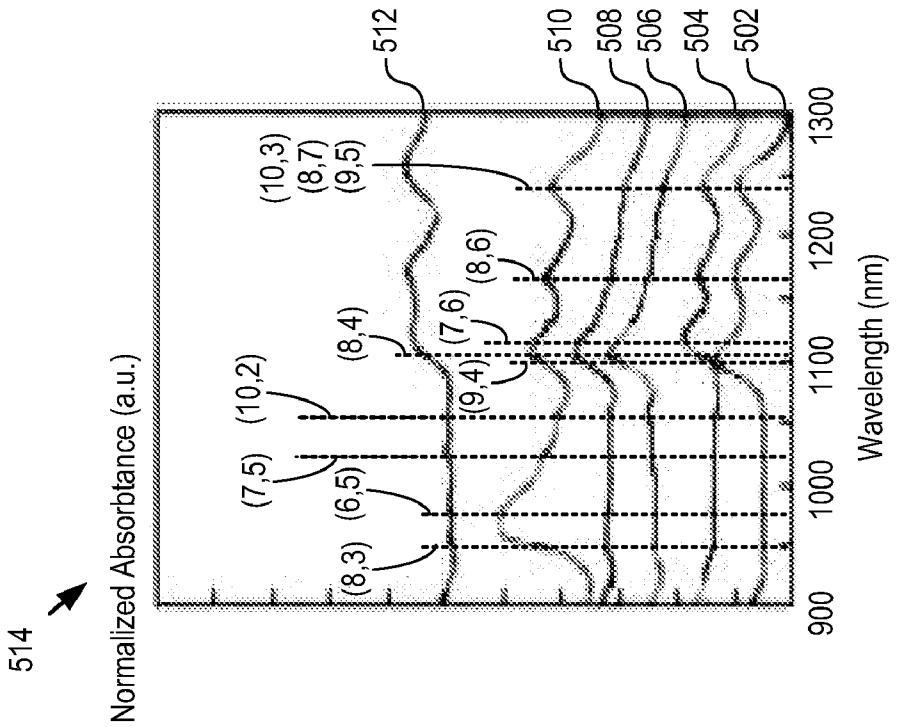

514
Normalized Absorbtance (a.u.)
(10,3)
(8,7)
(9,5)
(10,2)
(8,4)
(7,6)
(8,6)
(9,4)
(7,5)
(6,5)
(8,3)
512
510
508
506
504
502
900
1000
1100
1200
1300
Wavelength (nm)

FIG. 5B

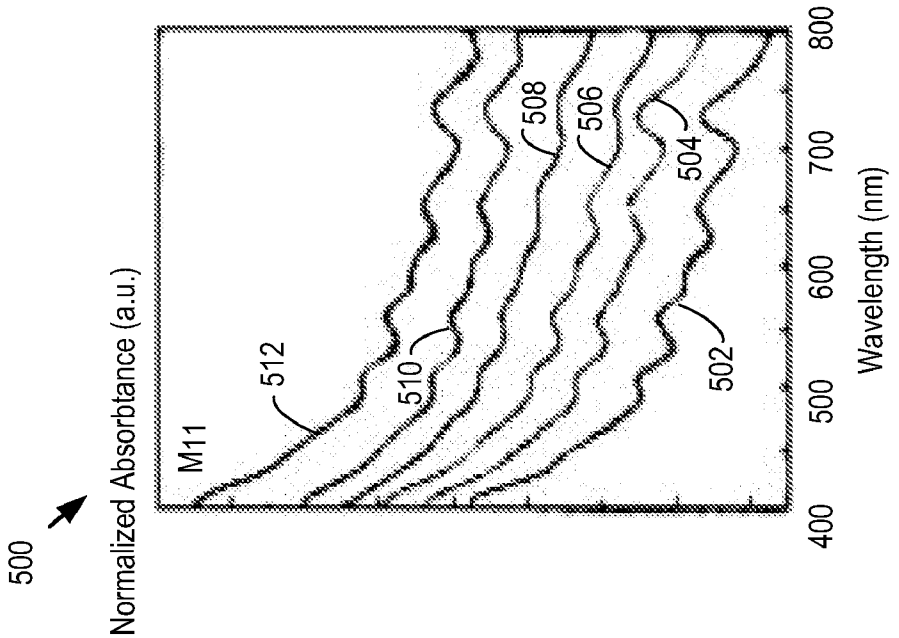

500
Normalized Absorbtance (a.u.)
M11
512
510
508
506
504
502
400
500
600
700
800
Wavelength (nm)

FIG. 5A

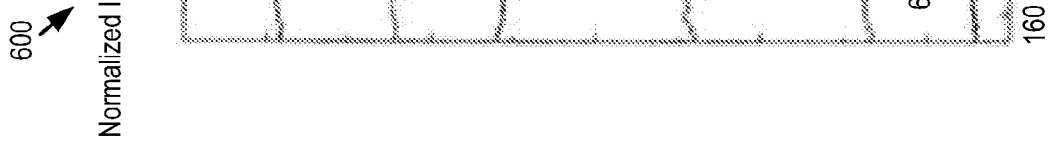


FIG. 6A

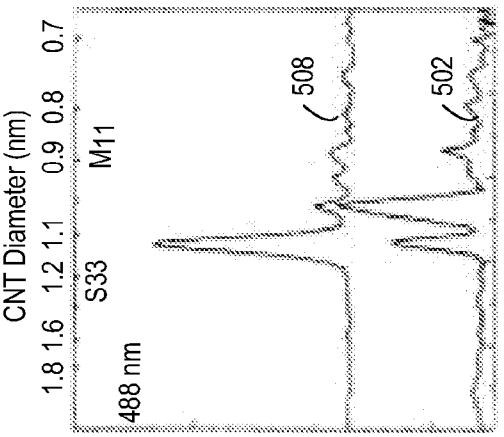


FIG. 6B

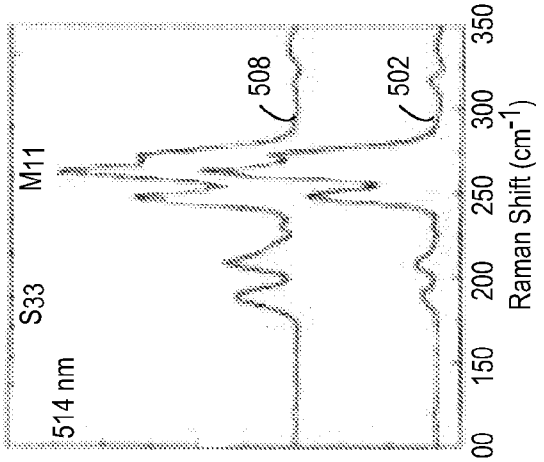


FIG. 6C

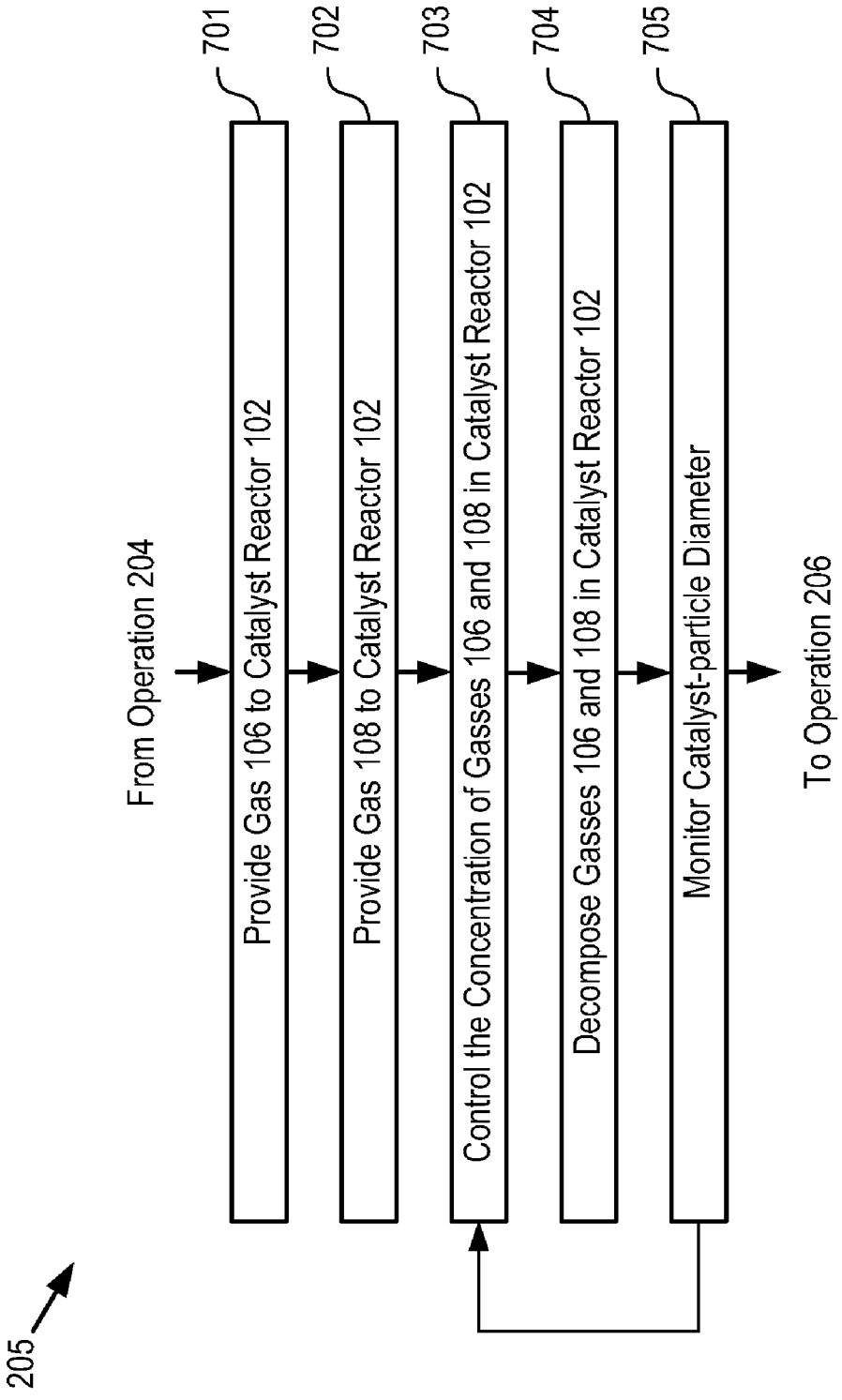

205
From Operation 204
701
Provide Gas 106 to Catalyst Reactor 102
702
Provide Gas 108 to Catalyst Reactor 102
703
Control the Concentration of Gasses 106 and 108 in Catalyst Reactor 102
704
Decompose Gasses 106 and 108 in Catalyst Reactor 102
705
Monitor Catalyst-particle Diameter
To Operation 206

FIG. 7

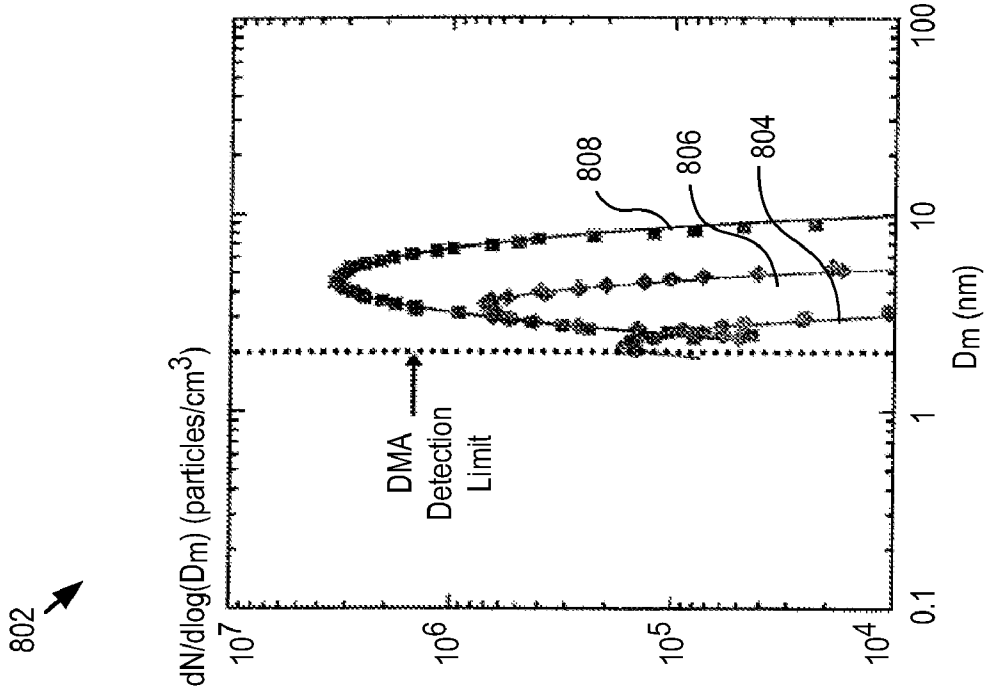

802
dN/dlog(Dm) (particles/cm3)
10^7
10^6
10^5
10^4
0.1
1
10
100
Dm (nm)
DMA
Detection
Limit
808
806
804

FIG. 8B

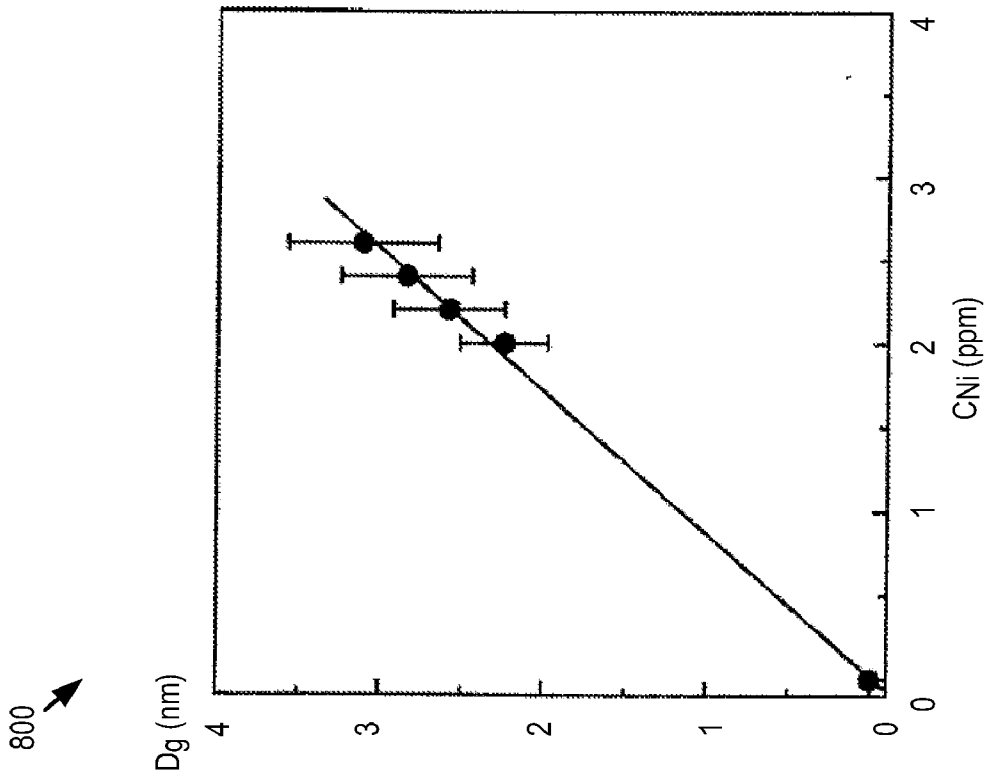

800
Dg (nm)
0
1
2
3
4
0
1
2
3
4
CNi (ppm)

FIG. 8A

GROWTH OF SINGLE-WALLED CARBON NANOTUBES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application Ser. No. 61/264,969, filed Nov. 30, 2009, entitled "Chiral-selective Growth of Single-walled Carbon Nanotubes," which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to material synthesis in general, and, more particularly, to the synthesis of carbon nanotubes.

BACKGROUND OF THE INVENTION

[0003] A carbon nanotube (CNT) is a one-carbon-atom-thick layer of graphite (i.e., a graphene sheet) rolled into a seamless, closed cylinder. Typical CNT diameters are a few nanometers (nm) or less but they can have lengths that are in the millimeter range or larger.

[0004] Carbon nanotubes exhibit unique physical, electrical, and chemical properties that offer the potential for revolutionary impact in a broad range of diverse applications areas, such as electronics, materials, medicine, law enforcement, architecture, national defense, and fashion. These properties depend on the physical characteristics of the carbon nanotube, such as the number of walls (i.e., single-wall, double-wall, etc.), diameter, and chirality (i.e., the way the graphene sheet is wrapped about itself). For example, depending upon its structure, a CNT can behave like a metal, such as gold or aluminum, or like a semiconductor, such as silicon or gallium arsenide.

[0005] Carbon nanotubes are synthesized in a number of ways, including arc discharge formation, laser ablation, and chemical vapor deposition. Unfortunately, it has proven difficult to selectively produce large volumes of CNTs having uniform material characteristics in a cost-effective manner. This has proven to be a barrier to their use in many applications—particularly those wherein a specific chirality is desired.

[0006] In order to isolate particular types of CNTs, high-volume, non-selective synthesis has been coupled with post-synthesis sorting techniques. Several sorting approaches have been demonstrated, the most promising of which is based on density-based centrifugation of a slurry of disparate carbon nanotubes. This approach is still too expensive for consideration in large-scale systems, however.

[0007] A method for synthesizing carbon nanotubes having improved purity would represent a significant advance in the state-of-the-art in nanotechnology.

SUMMARY OF THE INVENTION

[0008] The present invention enables the substantially selective synthesis of carbon nanotubes characterized by a desired diameter and chirality without some of the costs and/or limitations of the prior art. Embodiments of the present invention are well suited for synthesizing carbon nanotubes characterized by a narrow distribution of carbon-nanotube diameter and/or narrow distribution of carbon-nanotube chirality.

[0009] The present invention substantially decouples the influence of catalyst-particle size and catalyst-particle composition on carbon nanotube chirality and size. Some embodiments of the present invention comprise selection of a first preferred value for catalyst-particle diameter based on a relationship between catalyst-particle diameter and carbon-nanotube diameter. Carbon nanotubes are then synthesized in the presence of catalyst particles having a mean catalyst-particle diameter substantially equal to this first preferred value. Some embodiments of the present invention further comprise selection of a second preferred value for catalyst-particle composition based on a relationship between catalyst-particle composition and carbon-nanotube chirality. Carbon nanotubes are then synthesized in the presence of catalyst particles characterized by the second preferred value for catalyst-particle composition as well as the first preferred value for catalyst-particle diameter.

[0010] In some embodiments, catalyst particles having a mean diameter of 2.6 nm or less are provided to a reactor for synthesizing carbon nanotubes. In some embodiments, the mean diameter of the catalyst particles is substantially equal to 2.2 nm. In some embodiments, the catalyst particles are synthesized in a catalyst reactor prior to being provided to the reactor for synthesizing carbon nanotubes.

[0011] In some embodiments, nickel-iron catalyst particles having a composition of Ni_xFe_{1-x}, wherein x is less than or equal to 0.5 are provided to the reactor for synthesizing carbon nanotubes. In some embodiments, the composition of the catalyst particles is substantially $Ni_{0.27}Fe_{0.73}$. In some embodiments, the catalyst particles are synthesized in a catalyst reactor prior to being provided to the reactor for synthesizing carbon nanotubes.

[0012] In some embodiments, the present invention comprises selection of a catalyst reactor having a reactor volume that is less than one nanoliter. Restricting reactor volume to less than one nanoliter enables growth of catalyst particle populations characterized by a narrow distribution of catalyst-particle diameters that are less than 5 nm.

[0013] An embodiment of the present invention comprises a method for synthesizing carbon nanotubes, wherein a first relationship exists between a first property of a first catalyst particle comprising a first metal and a second property of a first carbon nanotube synthesized via the first catalyst particle, the method comprising: selecting a first preferred value for the first property based on the first relationship; providing a plurality of catalyst particles to a first reaction chamber, each of the plurality of catalyst particles being characterized by the first property having a value substantially equal to the first preferred value; controlling the concentration of a first gas in the first reaction chamber, the first gas comprising carbon; and controlling the temperature of the first reaction chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. **1** depicts a schematic diagram of a continuous-flow, gas-phase carbon nanotube reactor system in accordance with an illustrative embodiment of the present invention.

[0015] FIG. **2** depicts operations of a method for synthesizing carbon nanotubes in accordance with the illustrative embodiment of the present invention.

[0016] FIG. **3** depicts Raman spectra for carbon nanotube samples grown via catalyst particles having different catalyst-particle diameters in accordance with the illustrative embodiment of the present invention.

[0017] FIG. **4** depicts absorption spectra for carbon nanotube samples grown via catalyst particles having different mean diameters in accordance with the illustrative embodiment of the present invention.

[0018] FIGS. **5**A and **5**B depict absorption spectra for carbon nanotube samples grown with different growth conditions in accordance with the illustrative embodiment of the present invention.

[0019] FIGS. **6**A-**6**C depict the RBM regions of Raman spectra for carbon nanotube samples synthesized with compositionally tuned catalyst particles in accordance with the illustrative embodiment of the present invention.

[0020] FIG. **7** depicts sub-operations suitable for providing catalyst particles to CNT reactor **104** in accordance with the illustrative embodiment of the present invention.

[0021] FIG. **8**A displays a plot of synthesized catalyst-particle diameters with respect to metalocene concentration in accordance with the illustrative embodiment of the present invention.

[0022] FIG. **8**B displays a plot of distributions of catalyst-particle diameters synthesized in different metalocene concentrations in accordance with the illustrative embodiment of the present invention.

DETAILED DESCRIPTION

[0023] FIG. **1** depicts a schematic diagram of a continuous-flow, gas-phase carbon nanotube reactor system in accordance with an illustrative embodiment of the present invention. System **100** comprises catalyst reactor **102**, CNT reactor **104**, gas inlets **106**, **108**, and **112**, and outlet **116**. System **100** synthesizes carbon nanotubes **114** by decomposing gas **112** in CNT reactor **104**. The synthesis of carbon nanotubes **114** occurs via the presence of catalyst particles **110** in the CNT reactor.

[0024] FIG. **2** depicts operations of a method for synthesizing carbon nanotubes in accordance with the illustrative embodiment of the present invention. It is an aspect of the present invention that carbon nanotubes having a set of desired material properties can be selectively synthesized by selecting and controlling the size and/or composition of the catalyst particles used to enable the synthesis. Method **200** begins with operation **201**, wherein a relationship between catalyst-particle diameter and carbon-nanotube diameter is established.

[0025] FIG. **3** depicts Raman spectra for carbon nanotube samples grown via catalyst particles having different catalyst-particle diameters in accordance with the illustrative embodiment of the present invention. Plot **300** shows the intensity spectra for carbon nanotube samples **302**, **304**, **306**, **308**, **310**, **312**, and **314**, grown via catalyst particles having mean catalyst-particle diameters of 2.2, 2.5, 2.6, 2.7, 2.8, 2.9, and 3.1 nm, respectively. The spectra for each of carbon nanotube samples **302**, **304**, **306**, **308**, **310**, **312**, and **314** is normalized with respect to G-band (1545 cm^{-1}) intensity peak **320**.

[0026] Several characteristics of the grown nanotubes are inferred from the data shown in plot **300**. First, the spectra clearly exhibit radial breathing-mode (RBM) peaks **316** in the range of 120-250 cm^{-1}. These peaks are characteristic of single- or double-wall carbon nanotubes. The intensity of peaks **316** for samples **302** through **314** increases as the catalyst-particle diameter decreases, which indicates a higher percentage of single-wall and double-wall carbon nanotubes in the carbon nanotube samples grown via smaller diameter catalysts.

[0027] Second, one skilled in the art will recognize that the diameter and chirality of bundled sign- or double-walled carbon nanotubes is determined from the position of the RBM peaks using the relationship $\omega_{RBM}=234/d+10$, wherein ω_{RMB} is the RMB frequency and d is the nanotube diameter. From plot **300**, it is evident that peaks **316** of carbon nanotube sample **302** (i.e., grown via catalyst particles having a mean particle-diameter of 2.2 nm) appear at 192, 214, and 254 cm^{-1}. This corresponds to a carbon-nanotube diameter within the range of 0.8-1.6 nm. One skilled in the art will recognize that carbon-nanotube diameter is indicative of the number of walls in a carbon nanotube and that a carbon-nanotube diameter less than 1.6 nm indicates a single-wall carbon nanotube.

[0028] Third, peaks **320** exhibit splitting that becomes more pronounced as the diameter of the catalyst particle decreases. Such splitting is due to zone folding of the phonon dispersion in single-wall carbon nanotubes. This demonstrates that the purity of single-wall carbon nanotubes increases with decreasing catalyst-particle diameter.

[0029] Fourth, peaks **318** increase in intensity with particle diameter. The increased intensity is associated with increasing disorders or amorphous carbon in multi-walled carbon nanotubes, which suggests a decrease in the purity of single-wall carbon nanotubes with increasing catalyst-particle diameter.

[0030] FIG. **4** depicts absorption spectra for carbon nanotube samples grown via catalyst particles having different mean diameters in accordance with the illustrative embodiment of the present invention. Plot **400** shows the absorption spectra for carbon nanotube samples **402**, **404**, **406**, **408**, **410**, **412**, and **414**, grown via catalyst particles having mean catalyst-particle diameters of 2.2, 2.5, 2.6, 2.7, 2.8, 2.9, and 3.1 nm, respectively.

[0031] Peaks **416** arise from surface excitation of single-wall carbon nanotubes. Plot **400** shows that peaks **416** decrease in intensity with increasing catalyst-particle diameter. This decrease is due to that fact that the fraction of single-wall carbon nanotubes is decreasing with increasing catalyst-particle diameter.

[0032] In contrast, peaks **316** of the spectra for carbon nanotube samples **304** through **314** (i.e., for catalyst particles of increasing diameter) show an increasing ratio of the intensity of the peaks at 192-212 cm^{-1}. This confirms that the use of these catalyst particles leads to the formation of carbon nanotubes having larger diameters (i.e., multi-wall carbon nanotubes).

[0033] At operation **202**, a preferred value for catalyst-particle diameter of catalyst particles **110** is selected based on the relationship between catalyst-particle diameter and carbon-nanotube diameter and wall number established in operation **201**. Based on this relationship, it is an aspect of the present invention that the preferred value for mean catalyst-particle diameter for catalyst particles **110** is selected as a diameter of less than 2.5 nm. In some embodiments, the preferred value for mean catalyst-particle diameter for catalyst particles **110** is selected as approximately 2.2 nm. In some embodiments, the preferred value for mean catalyst-particle diameter for catalyst particles **110** is selected as less than 2.2 nm. By choosing a preferred value for catalyst-particle diameter of <2.5 nm, the present invention enables

substantially selective synthesis of carbon nanotubes having diameters less than approximately 1.6 nm (i.e., single-wall carbon nanotubes).

[0034] At operation **203**, a relationship between catalyst-particle composition and carbon-nanotube chirality is established. It is an aspect of the present invention that carbon-nanotube diameter and carbon-nanotube chirality are constrained by the size and composition of the catalyst particle that enables its synthesis. The present invention, therefore, decouples the provision of catalyst particles having a specific diameter from the provision of catalyst particles having a specific composition. This decoupling is accomplished by enabling separate control over catalyst-particle diameter and catalyst-particle composition.

[0035] FIGS. **5**A and **5**B depict absorption spectra for carbon nanotube samples grown with different growth conditions in accordance with the illustrative embodiment of the present invention. Each of plots **500** and **514** comprises absorption spectra for carbon nanotubes samples **502**, **504**, **506**, **508**, **510**, and **512**. Carbon nanotube sample **502** was grown via catalyst particles having a composition of pure nickel, at a growth temperature of 600° C. Carbon nanotube sample **504** was grown via catalyst particles having a composition of $Ni_{0.67}Fe_{0.33}$, at a growth temperature of 600° C. Carbon nanotube sample **506** was grown via catalyst particles having a composition of $Ni_{0.5}Fe_{0.5}$, at a growth temperature of 600° C. Carbon nanotube sample **508** was grown via catalyst particles having a composition of $Ni_{0.27}Fe_{0.73}$, at a growth temperature of 600° C. Carbon nanotube sample **510** was grown via catalyst particles having a composition of $Ni_{0.27}Fe_{0.73}$, at a growth temperature of 700° C. Carbon nanotube sample **512** was grown via catalyst particles having a composition of pure iron, at a growth temperature of 700° C. Each carbon nanotube sample was synthesized via catalyst particles having a mean catalyst-particle diameter of 2 nm. The spectra for each of carbon nanotube samples **502**, **504**, **506**, **508**, **510**, and **512** is normalized with respect to the sample intensity at 587 nm and offset from one another for clarity.

[0036] Plots **500** and **514** illustrate that the composition of the catalyst particles used significantly affects the chirality of the synthesized carbon nanotubes. For example, spectra for carbon nanotube samples **502** through **510** show a decrease in the M_{11} peak intensities as iron content is increased in samples grown at 600° C. The decrease in the M_{11} peak intensity indicates a depletion of metallic nanotubes in the synthesized samples.

[0037] The chirality (i.e., the manner in which the graphene sheet of a carbon nanotube is wrapped) is represented by a pair of indices (n,m), referred to as the "chiral vector" of the carbon nanotube. The integers n and m denote the number of unit vectors along two directions in the crystal lattice of graphene.

[0038] As seen in plots **500** and **514**, the simultaneous shift in the S_{11} region from (9,4) carbon nanotubes in sample **502** to (7,6) carbon nanotubes in sample **504** to (8,4) carbon nanotubes in sample **510** further demonstrates improvement in the growth selectivity of semiconductor-type carbon nanotubes with increasing iron content in the catalyst particles.

[0039] FIGS. **6**A-**6**C depict the RBM regions of Raman spectra for carbon nanotube samples synthesized with compositionally tuned catalyst particles in accordance with the illustrative embodiment of the present invention.

[0040] Plot **600** shows peaks **606** and **608** (located at approximately 280 and 300 cm^{1}, respectively) for the absorption spectra for carbon nanotube samples **502** through **512**. Peaks **606** and **608** are stronger in the spectra for carbon nanotube samples grown via catalyst particles having an iron content of 50% or more. Further, peaks **602** and **604** (located at approximately 195 and 215 cm^{-1}, respectively) are significantly suppressed in the spectrum for carbon nanotube sample **508** (grown via nickel-iron catalyst particles having a composition of $Ni_{0.27}Fe_{0.73}$, at a growth temperature of 600° C.).

[0041] Peaks **602** and **604** correspond to larger-diameter metallic-type carbon nanotubes. Peaks **606** and **608** correspond to smaller semiconductor-type carbon nanotubes. As a result, plot **600** demonstrates a relationship between the iron content in Ni_xFe_{1-x} catalyst particles and chirality of carbon nanotubes synthesized via those catalyst particles. Specifically, plot **600** shows that more selective growth of semiconductor-type carbon nanotubes occurs when Ni_xFe_{1-x} catalyst particles have an iron content of 50% or more. Further, plot **600** suggests that the highest selectivity for semiconductor-type carbon nanotubes occurs when the catalyst particles have the formula $Ni_{0.27}Fe_{0.73}$.

[0042] Plots **610** and **612** show RBM spectra for samples **502** and **508**, wherein the spectra are taken at excitation wavelengths of 488 and 514 nm, respectively. Plots **610** and **612** demonstrate that the fraction of semiconductor-type carbon nanotubes is higher in sample **508** (catalyst particles having the formula $Ni_{0.27}Fe_{0.73}$) than for sample **502** (catalyst particles of pure nickel).

[0043] At operation **204**, a preferred value for catalyst-particle composition for catalyst particles **110** is selected based on the relationship between catalyst-particle composition and carbon-nanotube chirality established in operation **203**. Based on this relationship, it is an aspect of the present invention that the preferred catalyst-particle composition for catalyst particles **110** is selected as Ni_xFe_{1-x}, wherein x is less than or equal to 0.5. In some embodiments, the preferred composition for catalyst-particles **110** is $Ni_{0.27}Fe_{0.73}$. By choosing a preferred composition for catalyst-particles **110** of Ni_xFe_{1-x}, wherein x is less than or equal to 0.5 (preferably 0.27), the present invention enables substantially selective synthesis of semiconductor-type carbon nanotubes.

[0044] At operation **205**, catalyst particles **110** are introduced into CNT reactor **104**. Catalyst particles **110** are characterized by a narrow size distribution centered on a diameter of approximately 2.2 nm. In some embodiments, catalyst particles **110** have a diameter that is less than or equal to 2.5 nm.

[0045] CNT reactor **104** is a conventional steady-state continuous-flow reactor furnace. In some embodiments, CNT reactor is a reactor other than a continuous flow reactor furnace, such as a high-vacuum growth chamber, etc.

[0046] CNT reactor **104** provides values for the temperature and pressure in the reactor to processor **118**. Processor **118** maintains the temperature of CNT reactor **104** as approximately 600° C. The pressure of CNT reactor **104** is maintained as substantially atmospheric pressure. One skilled in the art will recognize that the values for temperature and pressure in CNT reactor **104** are matters of process design and that in some embodiments of the present invention they can be other than 600° C. and atmospheric pressure, respectively.

[0047] Processor **118** is a conventional processor suitable for receiving pressure and temperature information from each of catalyst reactor **102** and CNT reactor **104**, controlling the pressure and temperature of each of catalyst reactor **102** and CNT reactor **104**, and controlling the flow of gasses **106**, **108**, and **112** via mass flow controllers **120**, **122**, and **124**.

[0048] Catalyst particles **110** are nanometer-scale, substantially spherical particles comprising nickel and iron. Catalyst particles **110** are substantially uniform in diameter and composition in accordance with the present invention. Each of catalyst particles **110** has a diameter that is less than approximately 2.5 nm. In some embodiments, each of catalyst particles **110** has a diameter of approximately 2.2 nm. In some embodiments, catalyst particles **110** comprise a metal that is other than either nickel or iron. Suitable metals for use in catalyst particles **110** include, without limitation, cobalt, ruthenium, and molybdenum. In such alternative embodiments, however, catalyst-particle size and catalyst-particle composition are independently controlled.

[0049] FIG. **7** depicts sub-operations suitable for providing catalyst particles to CNT reactor **104** in accordance with the illustrative embodiment of the present invention. Operation **205** begins with sub-operation **701**, wherein gas **106** is provided to catalyst reactor **102**.

[0050] Catalyst reactor **102** is an atmospheric microplasma reactor that is suitable for decomposing metallic precursor gas by electron impact ionization. In some embodiments of the present invention, metallic precursor gasses are decomposed in another non-thermal reaction. In some embodiments of the present invention, metallic precursor gasses are decomposed in another plasma reaction.

[0051] The volume of catalyst reactor **102** is approximately 1 nanoliter. In some embodiments, the volume of catalyst reactor **102** is less than 1 nanoliter. It is an aspect of the present invention that limiting the volume of the catalyst reactor to 1 nanoliter or less enables the growth of catalyst particles have catalyst-particle diameters less than 5 nm, wherein the catalyst particles have narrow size distribution.

[0052] Gas **106** is a metallic precursor gas that contains nickel. Suitable precursor gasses include, without limitation, nickelocene, ferrocene, and the like.

[0053] In the illustrative embodiment, gas **106** is provided by sublimation of packed solid nickelocene powder at room temperature with a flow of argon (Ar) gas. This flow of gas was than diluted with additional Ar gas and provided to mass flow controller **120**.

[0054] FIG. **8**A displays a plot of synthesized catalyst-particle diameters with respect to metalocene concentration in accordance with the illustrative embodiment of the present invention. Plot **800** shows data points for catalyst-particle diameters for nickel catalyst particles formed in a microplasma reactor with nickelocene concentrations of 2.0, 2.2, 2.4, and 2.6 ppm. It can be inferred from plot **800** that limiting the concentration of metalocene in catalyst reactor **102** to less than 2.6 ppm enables formation of catalyst particles having diameters of 2.5 nm or less. It can be further inferred that a linear relationship exists between the nickelocene concentration and nickel catalyst particle size, at least for concentration levels between 2.0 and 2.6 ppm.

[0055] Table 1 below provides a summary of catalyst-particle diameters for catalyst particles synthesized in different metalocene concentrations. Specifically, Table 1 provides measurement data for pure nickel catalyst particles formed in a microplasma reactor at different concentrations of nickelocene.

Metalocene Concentration (ppm)	Catalyst-particle Diameter (nm)	Standard Deviation
2.0	2.2	1.13
2.2	2.6	1.13
2.4	2.8	1.15
2.6	3.1	1.16
5.2	4.7	1.22

[0056] It should be noted that the standard deviation for catalyst-particle diameter increases with increasing nickelocene concentration. As a result, by limiting metalocene concentration to 2.6 ppm or less, catalyst particles can be synthesized with narrow size distributions.

[0057] The narrowing of catalyst-particle diameter distribution with decreasing catalyst-particle diameter can be seen pictorially in FIG. **8**B, which displays a plot of distributions of catalyst-particle diameters synthesized in different metalocene concentrations in accordance with the illustrative embodiment of the present invention. Plot **802** shows measured catalyst-particles diameters for nickel catalyst particle samples **804**, **806**, and **808**, which were synthesized in a microplasma reactor with nickelocene concentrations of 2.0, 2.6, and 5.2 ppm, respectively. It can be clearly seen from plot **802** that the size distribution for catalyst particle sample **804** is narrower than the size distribution of catalyst particle sample **806**, which is narrower than the size distribution of catalyst particle sample **808**. Plot **802**, therefore, supports the inference from plot **800** that catalyst diameter distribution becomes narrower as metalocene concentration decreases.

[0058] At sub-operation **702**, gas **108** is provided to catalyst reactor **102**. In some embodiments, gas **108** comprises ferrocene.

[0059] At sub-operation **703**, processor **118** controls mass flow controllers **120** and **122** to maintain a total metalocene concentration in catalyst reactor **102** within the range of approximately 2.0 parts-per-million (ppm) to approximately 2.6 ppm. In some embodiments, the concentration of gas **106** in catalyst reactor **102** is controlled as 2.2 ppm.

[0060] The ratio of nickel to iron in a catalyst particle corresponds well to the relative concentrations of their respective metal precursors (i.e., gasses **106** and **108**) in catalyst reactor **102**. In the illustrative embodiment, therefore, processor **118** controls each of mass flow controllers **120** and **122** to maintain a ratio of nickelocene to ferrocene in catalyst particles **110** of approximately 27:73. In some embodiments, the ratio of nickelocene to ferrocene maintained at or below 1:1 to ensure a composition for catalyst particles **110** of Ni_xFe_{1-x}, wherein x is less than or equal to 0.5.

[0061] At sub-operation **704**, gasses **106** and **108** are decomposed in catalyst reactor **102** to synthesize catalyst particles **110**.

[0062] At sub-operation **705**, monitor system **126** monitors catalyst-particle diameter for catalyst particles **110** in real time. Monitor system **126** comprises a cylindrical differential mobility analyzer (DMA) and an ultrafine condensation particle counter (CPC). Monitor system **126** samples catalyst particles **110** by enabling some of the catalyst particles to enter a bipolar charger. In the bipolar charger, the catalyst

particles acquire a single positive or negative charge. The charged particles are then directed into the DMA. By adjusting the voltage applied by the DMA, particles having a specific narrow electrical mobility are transmitted and counted. This count is then provided to processor **118**, which controls growth conditions in catalyst reactor **102** and the flow rates of gasses **106** and **108** (i.e., concentrations of gasses **106** and **108**) to maintain the selected value for catalyst-particle diameter.

[0063] Returning now to FIG. **2**, at operation **206**, gas **112** is provided to CNT reactor **104**. Gas **112** comprises acetylene (C_2H_2). In some embodiments, gas **112** comprises a different carbon-containing gas. Gasses suitable for use in gas **112** include, without limitation, carbon monoxide, methane, pentane, octane, and the like. In some embodiments, a second gas, such as hydrogen, is also provided to CNT reactor **104**.

[0064] At operation **207**, mass flow controller **124** controls the flow rate of gas **112**, which determines its concentration in CNT reactor **104**. Processor **118** controls mass flow controller **120**.

[0065] At operation **208**, processor **118** controls the carbon nanotube growth conditions within CNT reactor **104**. Typical growth conditions controlled by processor **118** include growth temperature, reactor pressure, residence time of catalyst particles in the reactor, and the like. In the illustrative embodiment, the growth temperature in CNT reactor **104** is controlled to maintain 600° C.; however, it will be clear to one skilled in the art, after reading this specification, how to specify, make, and use alternative embodiments of the present invention wherein the temperature of CNT reactor **104** is maintained at a different growth temperature.

[0066] At operation **209**, gas **112** is decomposed in CNT reactor **104**, in the presence of catalyst particles **110**, to synthesize carbon nanotubes **114**, which are then provided at outlet **116**.

[0067] It is to be understood that the disclosure teaches just one example of the illustrative embodiment and that many variations of the invention can easily be devised by those skilled in the art after reading this disclosure and that the scope of the present invention is to be determined by the following claims.

1. A method for synthesizing carbon nanotubes, wherein a first relationship exists between a first property of a first catalyst particle comprising a first metal and a second property of a first carbon nanotube synthesized via the first catalyst particle, the method comprising:
- selecting a first preferred value for the first property based on the first relationship;
- providing a plurality of catalyst particles to a first reaction chamber, each of the plurality of catalyst particles being characterized by the first property having a value substantially equal to the first preferred value;
- controlling the concentration of a first gas in the first reaction chamber, the first gas comprising carbon; and
- controlling the temperature of the first reaction chamber.

2. The method of claim **1** further comprising selecting the first property as catalyst-particle diameter.

3. The method of claim **2** wherein the first preferred value is selected as a catalyst-particle diameter that is less than 2.5 nanometers.

4. The method of claim **1** further comprising selecting the first property as catalyst-particle composition.

5. The method of claim **4** wherein the first preferred value is selected as a catalyst-particle composition having the formula $M1_xM2_{1-x}$, wherein M1 is the first metal and M2 is a second metal, and wherein x is less than or equal to 0.5.

6. The method of claim **5** wherein the first preferred value is selected such that the first metal is nickel and the second metal is iron, and x is substantially equal to 0.27.

7. The method of claim **1** further comprising selecting the second property as carbon-nanotube diameter.

8. The method of claim **1** further comprising selecting the second property as the number of carbon-nanotube walls.

9. The method of claim **1** further comprising selecting the second property as carbon-nanotube chirality.

10. The method of claim **1** further comprising synthesizing the plurality of catalyst particles, wherein the plurality of catalyst particles is synthesized by operations comprising:
- providing a second gas to a second reaction chamber, wherein the second gas comprises a first metal precursor comprising the first metal;
- controlling the concentration of the second gas in the second reaction chamber; and
- decomposing the second gas.

11. The method of claim **10** wherein the concentration of the second gas in the second reaction chamber is controlled to be less than 2.1 parts-per-million.

12. The method of claim **10** wherein synthesizing the plurality of catalyst particles further comprises:
- providing a third gas to the second reaction chamber, wherein the third gas comprises a second metal precursor;
- controlling the concentration of the third gas in the second reaction chamber; and
- decomposing the third gas.

13. The method of claim **10** further comprising providing the second reaction chamber, wherein the second reaction chamber has a volume that is less than or equal to approximately 1 nanoliter.

14. The method of claim **10**, wherein a second relationship exists between the concentration of the second gas in the second chamber and catalyst-particle diameter, and wherein synthesizing the plurality of catalyst particles further comprises controlling the concentration of the second gas based on the second relationship.

15. The method of claim **10** wherein the concentration of the second gas is controlled by operations comprising:
- monitoring the mean catalyst-particle diameter;
- providing a first signal that is based on the monitored mean catalyst-particle diameter; and
- providing the first signal to a controller, wherein the controller controls a flow of the second gas into the second chamber based on the first signal.

16. A method for synthesizing carbon nanotubes, wherein a first relationship exists between catalyst-particle diameter and a first physical property of a carbon nanotube synthesized via the catalyst particle, and wherein a second relationship exists between a ratio of a first metal and a second metal in a catalyst particle and the chirality of a carbon nanotube synthesized via the catalyst particle, the method comprising:
- selecting a first preferred value for the catalyst-particle diameter based on the first relationship;
- selecting a second preferred value for the ratio based on the second relationship;
- providing a plurality of catalyst particles to a first reaction chamber, wherein the plurality of catalyst particles is characterized by a mean catalyst-particle diameter that is substantially equal to the first preferred value, and

wherein the plurality of catalyst particles is further characterized by a mean ratio of the first metal and second metal that is substantially equal to the second preferred value;

controlling the concentration of a first gas in the first reaction chamber, wherein the first gas comprises carbon; and

controlling the temperature of the first reaction chamber.

17. The method of claim **16** further comprising selecting the first physical property as carbon-nanotube diameter.

18. The method of claim **16** further comprising selecting the first physical property as the number of carbon-nanotube walls.

19. The method of claim **16** further comprising:

synthesizing the plurality of catalyst particles in a second reaction chamber; and

conveying the plurality of catalyst particles from the second reaction chamber to the first reaction chamber.

20. The method of claim **19** wherein the plurality of catalyst particles is synthesized by operations comprising:

providing a second gas to the second reaction chamber, wherein the second gas comprises a first metal precursor that comprises the first metal;

controlling the concentration of the second gas in the second reaction chamber;

providing a third gas to the second reaction chamber, wherein the third gas comprises a second metal precursor that comprises the second metal;

controlling the concentration of the third gas in the second reaction chamber; and

decomposing the second gas and the third gas.

21. The method of claim **19** further comprising providing the second reaction chamber, wherein the second reaction chamber has a volume that is less than or equal to approximately 1 nanoliter.

22. The method of claim **16**, wherein a third relationship exists between the first metal, the second metal, and the catalyst-particle crystal structure, and wherein a fourth relationship exists between catalyst-particle crystal structure and carbon-nanotube chirality, and wherein the method further comprises:

selecting a preferred carbon-nanotube chirality;

selecting a preferred catalyst-particle crystal structure based on the preferred carbon-nanotube chirality and the fourth relationship; and

selecting each of the first metal and the second metal based on the preferred catalyst-particle crystal structure and the third relationship.

23. The method of claim **22** wherein the preferred catalyst-particle crystal structure is selected based on the lattice structure of carbon nanotubes characterized by the preferred carbon-nanotube chirality.

24. A method comprising:

controlling the concentration of a first gas in a first reaction chamber, wherein the first gas comprises a first metal precursor comprising nickel, and wherein the first concentration is controlled to be less than 2.5 ppm;

decomposing the first gas; and

synthesizing a plurality of catalyst particles in the first reaction chamber.

25. The method of claim **24** wherein the concentration of the first gas is controlled such that the plurality of catalyst particles is characterized by a mean catalyst-particle diameter of less than 2.5 nanometers.

26. The method of claim **24** further comprising:

controlling the concentration of a second gas in the first reaction chamber, wherein the second gas comprises a second metal precursor comprising iron;

controlling the combined concentration of the first gas and second gas in the first reaction chamber to a concentration within the range of approximately 2.0 ppm and approximately 2.6 ppm; and

decomposing the second gas.

27. The method of claim **26** wherein the concentration of the first gas and the concentration of the second gas are controlled such that the plurality of catalyst particles is characterized by a mean catalyst-particle diameter of less than 2.5 nanometers.

28. The method of claim **26** wherein the concentration of the first gas and the concentration of the second gas are controlled such that the plurality of catalyst particles is characterized by a catalyst-particle composition having the formula Ni_xFe_{1-x}, and wherein x is less than or equal to 0.5.

29. The method of claim **28** wherein the concentration of the first gas and the concentration of the second gas are controlled such that x is substantially equal to 0.27.

30. The method of claim **26** further comprising:

providing the plurality of catalyst particles to a second reaction chamber;

controlling the concentration of a third gas in the second reaction chamber, wherein the third gas comprises carbon;

controlling the temperature of the second reaction chamber; and

synthesizing a plurality of carbon nanotubes in the second reaction chamber.

31. The method of claim **24** further comprising providing the first reaction chamber, wherein the first reaction chamber has a volume that is less than or equal to approximately 1 nanoliter.

32. The method of claim **24**, wherein the method further comprises:

providing the plurality of catalyst particles to a second reaction chamber;

controlling the concentration of a second gas in the second reaction chamber, wherein the second gas comprises carbon;

controlling the temperature of the second reaction chamber; and

synthesizing a plurality of carbon nanotubes in the second reaction chamber.

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