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(54) **SELECTIVE FUNCTIONALIZATION OF CARBON NANOTUBES BASED UPON DISTANCE TRAVELED**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 1058 days.

This patent is subject to a terminal disclaimer.

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(63) Continuation-in-part of application No. 10/320,698, filed on Dec. 13, 2002, now Pat. No. 7,276,266.

(51) **Int. Cl.**
H05H 1/24 (2006.01)

(52) **U.S. Cl.** **427/535**; 427/569; 427/575; 427/576; 427/294; 427/903

(58) **Field of Classification Search** 427/533, 427/535, 538, 562, 569, 575, 576, 585, 255.24, 427/255.26, 294, 903
See application file for complete search history.

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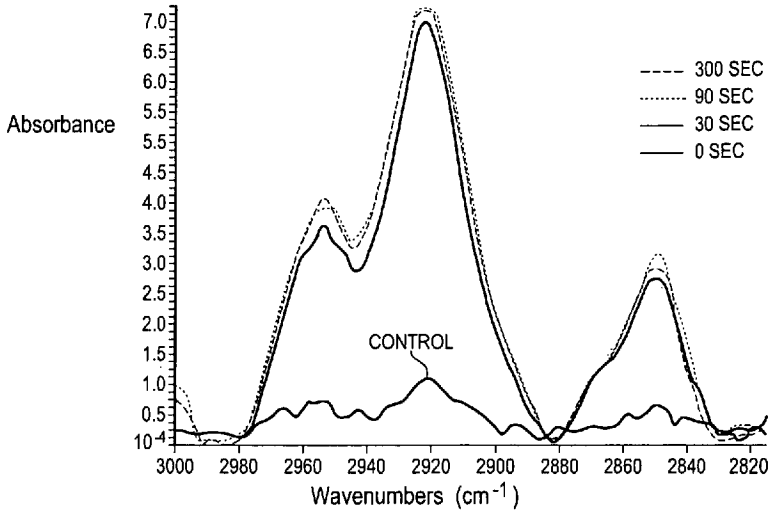
(57) **ABSTRACT**

Method and system for functionalizing a collection of carbon nanotubes (CNTs). A selected precursor gas (e.g., H_2 or NH_3 or NF_3 or F_2 or CF_4 or C_nH_m) is irradiated to provide a cold plasma of selected target particles, such as atomic H or F, in a first chamber. The target particles are directed toward an array of CNTs located in a second chamber while suppressing transport of ultraviolet radiation to the second chamber. A CNT array is functionalized with the target particles, at or below room temperature, to a point of saturation, in an exposure time interval no longer than about 30 sec. The predominant species that are deposited on the CNT array vary with the distance d measured along a path from the precursor gas to the CNT array; two or three different predominant species can be deposited on a CNT array for distances d=d1 and d=d2>d1 and d=d3>d2.

33 Claims, 5 Drawing Sheets



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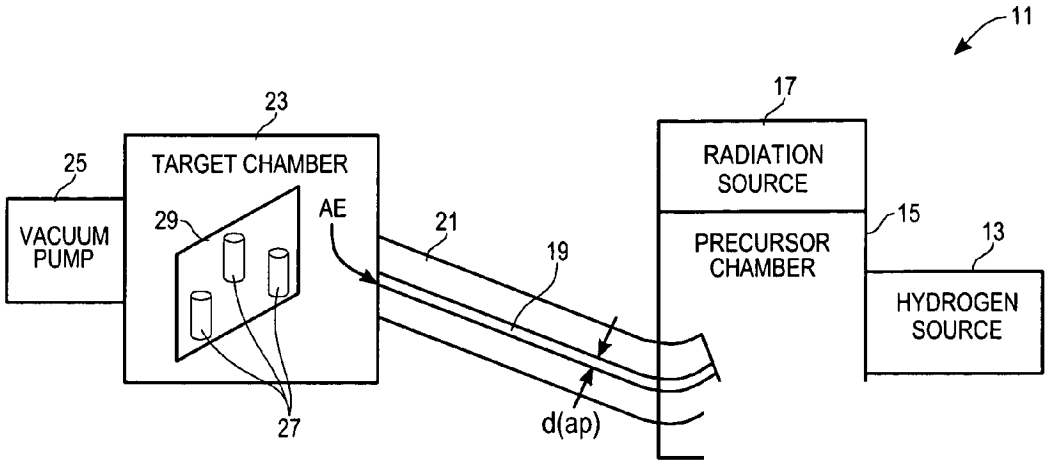
11
23
TARGET CHAMBER
25
VACUUM PUMP
29
AE
21
19
27
d(ap)
17
RADIATION SOURCE
PRECURSOR CHAMBER
15
13
HYDROGEN SOURCE

Fig. 1

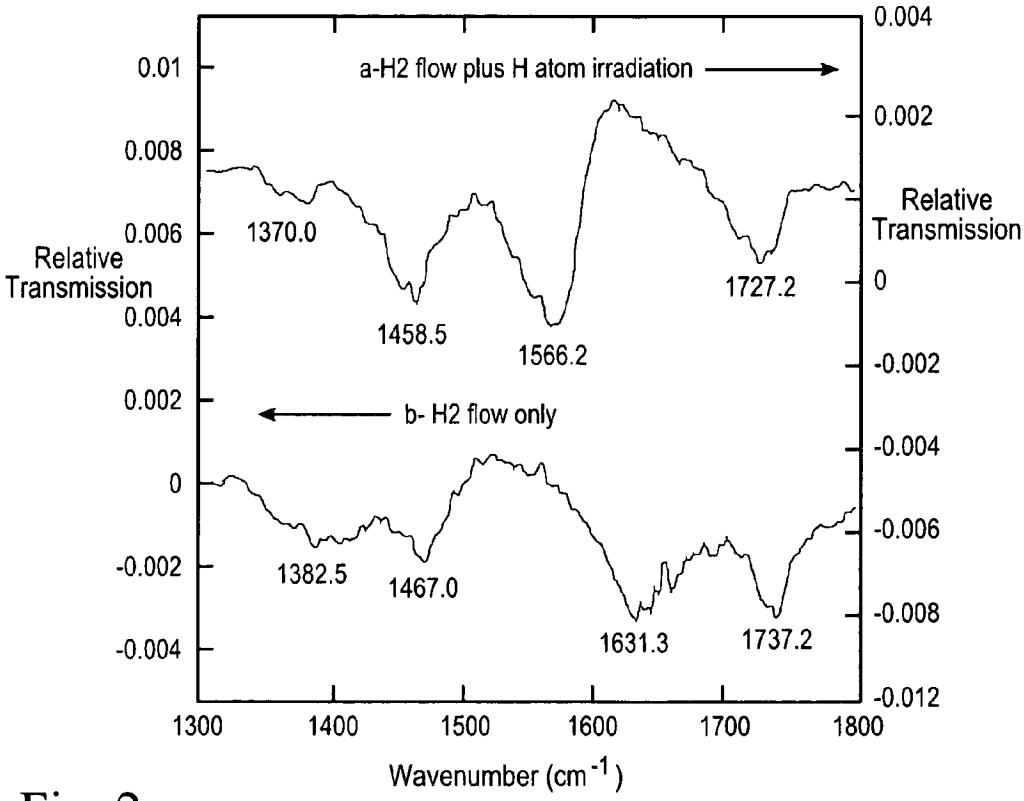
a-H2 flow plus H atom irradiation
b- H2 flow only
Relative Transmission
Relative Transmission
1370.0
1458.5
1566.2
1727.2
1382.5
1467.0
1631.3
1737.2
0.01
0.008
0.006
0.004
0.002
0
-0.002
-0.004
0.004
0.002
0
-0.002
-0.004
-0.006
-0.008
-0.012
1300
1400
1500
1600
1700
1800
Wavenumber (cm-1)

Fig. 2

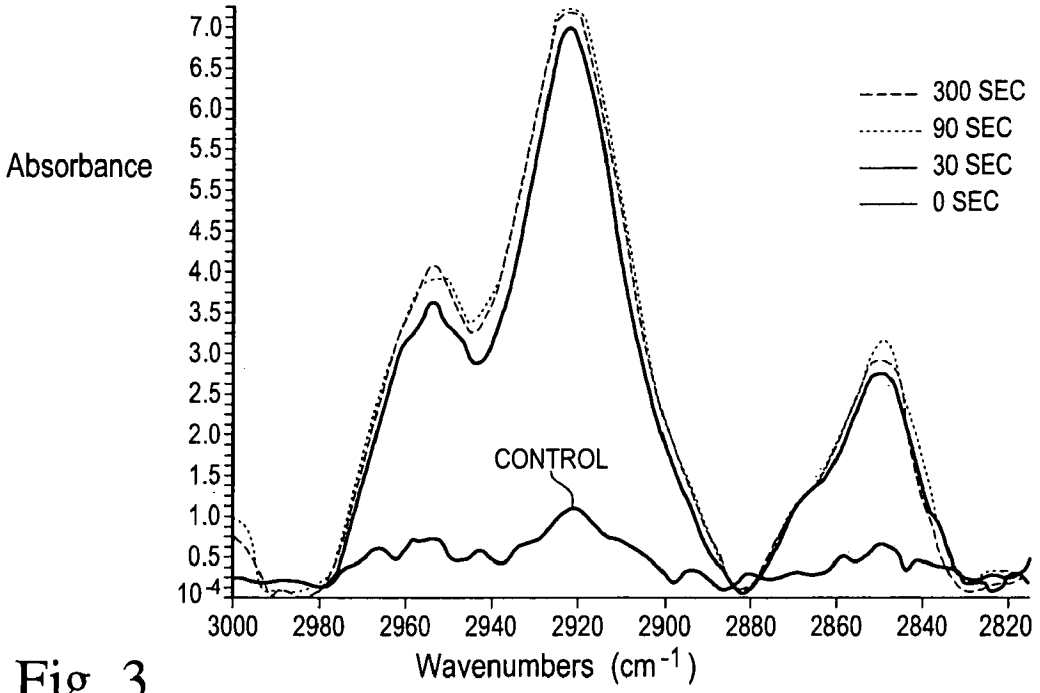
Absorbance
7.0
6.5
6.0
5.5
5.5
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
10-4
300 SEC
90 SEC
30 SEC
0 SEC
CONTROL
3000
2980
2960
2940
2920
2900
2880
2860
2840
2820
Wavenumbers (cm-1)

Fig. 3

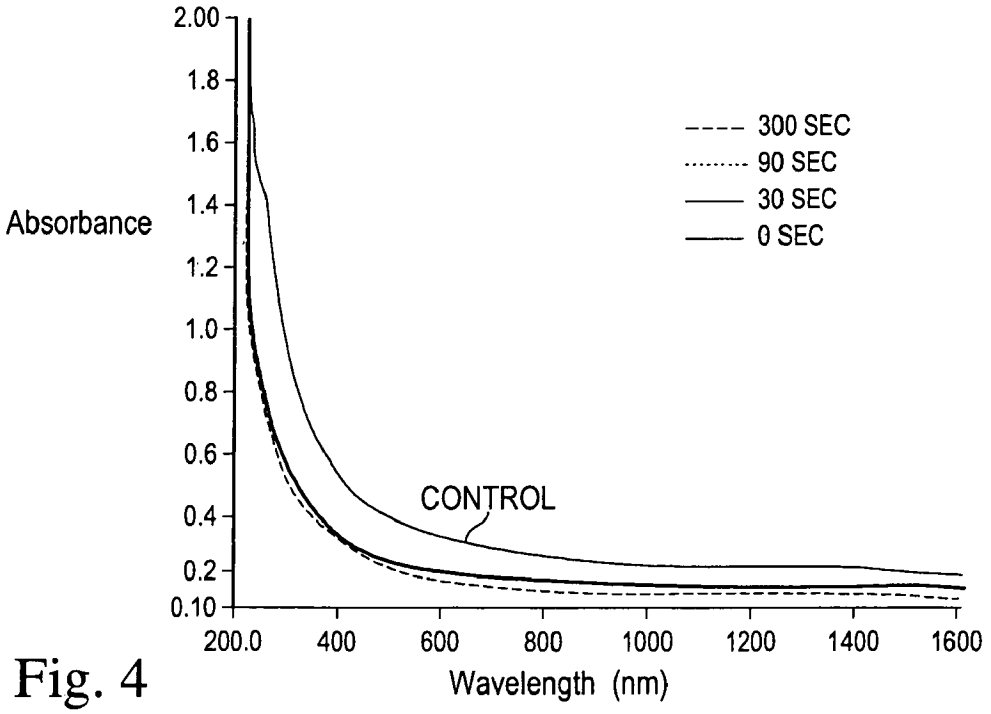
Absorbance
2.00
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.10
300 SEC
90 SEC
30 SEC
0 SEC
CONTROL
200.0
400
600
800
1000
1200
1400
1600
Wavelength (nm)

Fig. 4

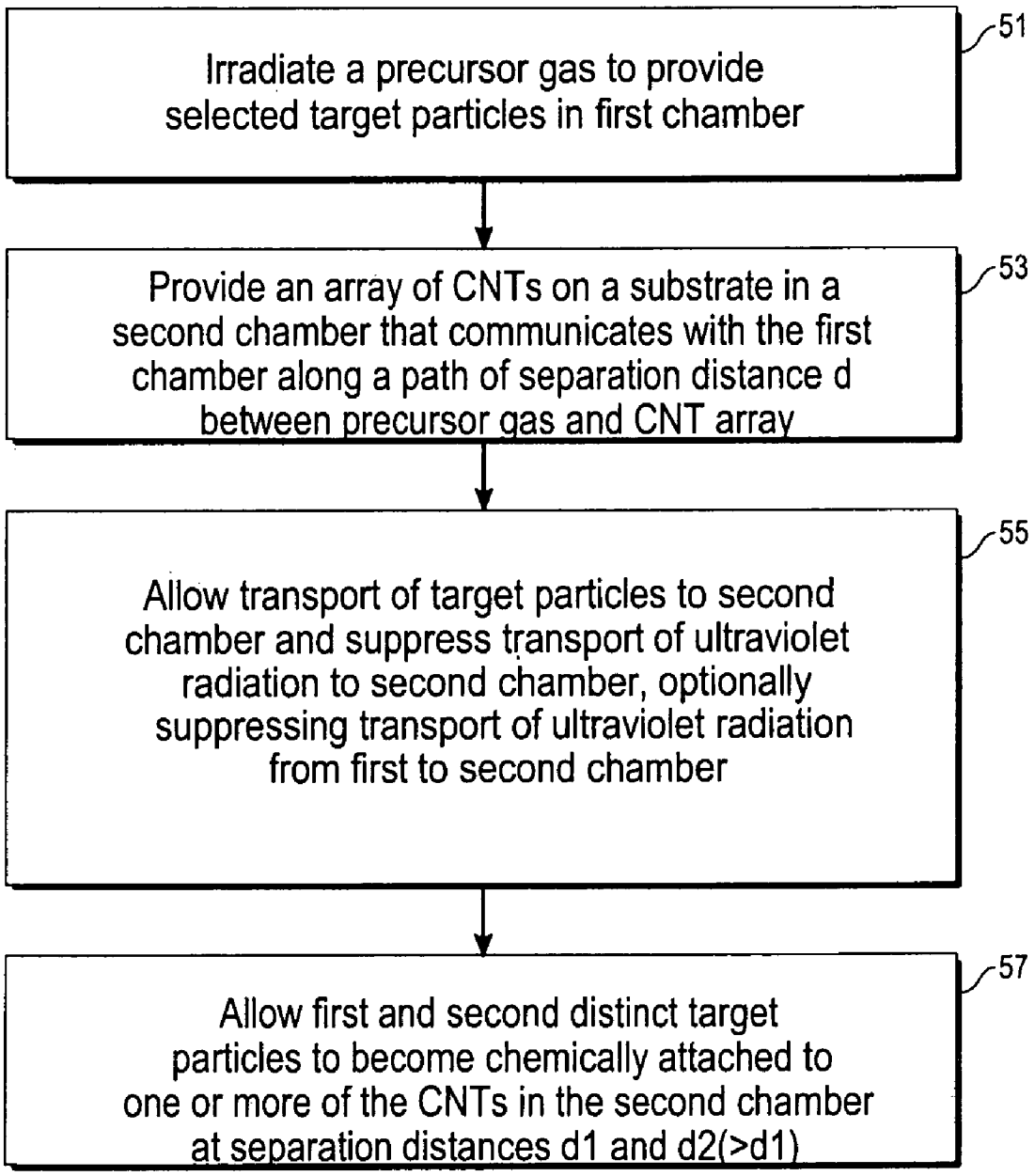
Irradiate a precursor gas to provide selected target particles in first chamber
51
Provide an array of CNTs on a substrate in a second chamber that communicates with the first chamber along a path of separation distance d between precursor gas and CNT array
53
Allow transport of target particles to second chamber and suppress transport of ultraviolet radiation to second chamber, optionally suppressing transport of ultraviolet radiation from first to second chamber
55
Allow first and second distinct target particles to become chemically attached to one or more of the CNTs in the second chamber at separation distances d1 and d2(>d1)
57

Fig. 5

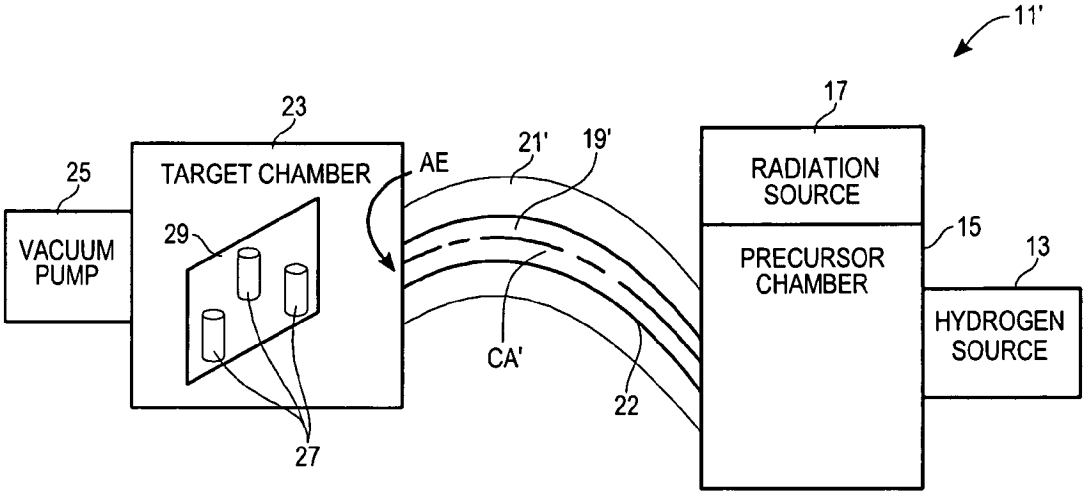
11'
23
TARGET CHAMBER
25
VACUUM PUMP
29
AE
21'
19'
17
RADIATION SOURCE
PRECURSOR CHAMBER
15
13
HYDROGEN SOURCE
CA'
22
27

Fig. 6

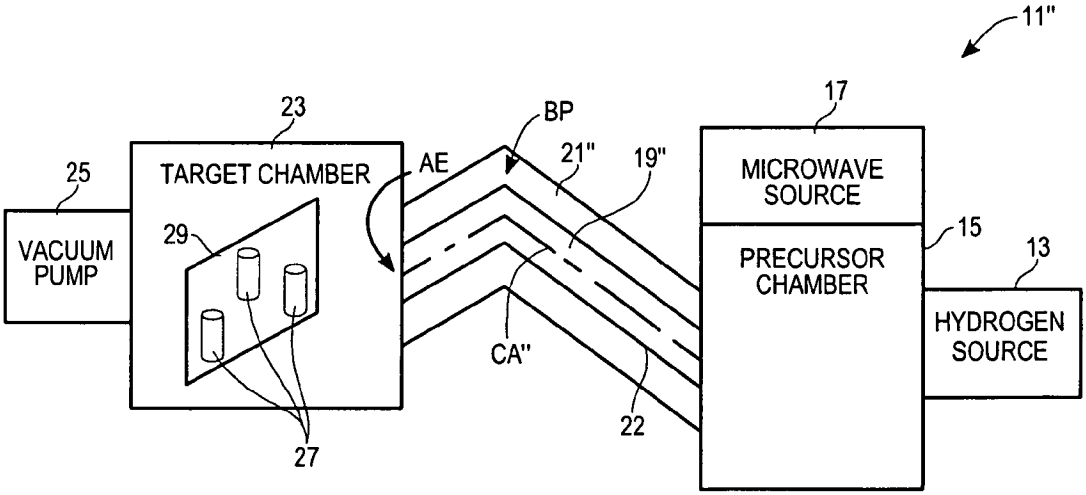
11"
23
TARGET CHAMBER
25
VACUUM PUMP
29
AE
BP
21"
19"
17
MICROWAVE SOURCE
PRECURSOR CHAMBER
15
13
HYDROGEN SOURCE
CA"
22
27

Fig. 7

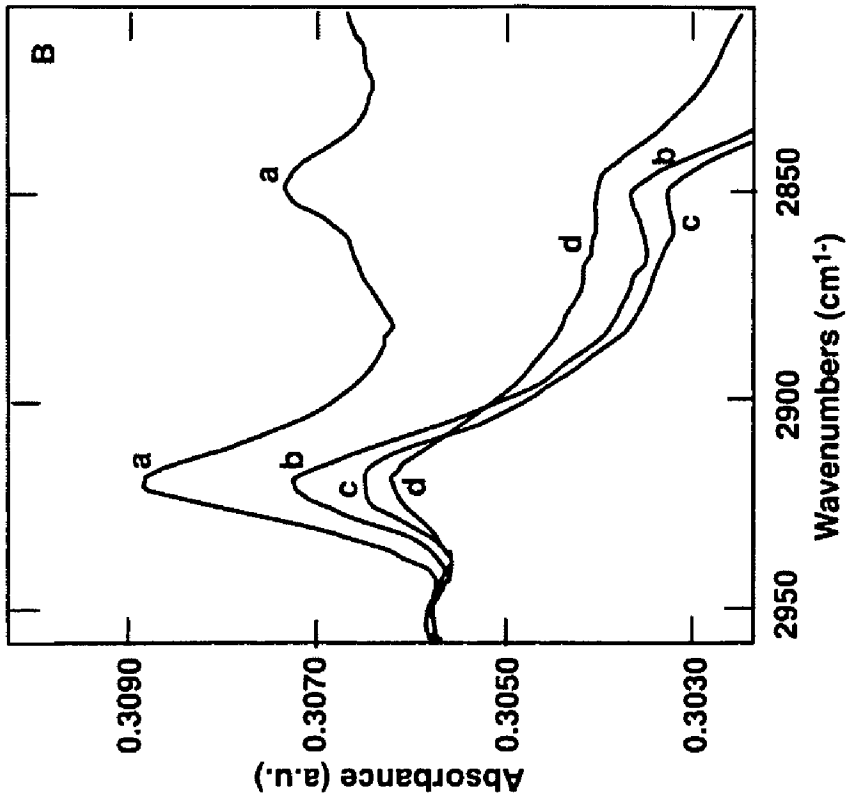
B
Absorbance (a.u.)
0.3090
0.3070
0.3050
0.3030
Wavenumbers (cm^{1-})
2950
2900
2850
a
b
c
d

Fig. 8B

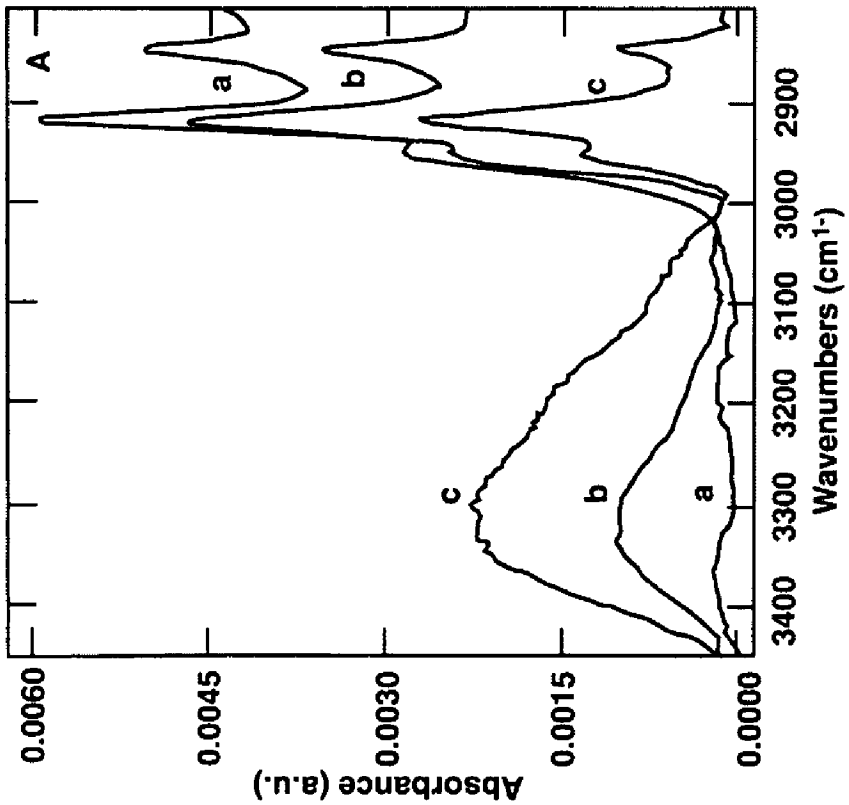
A
Absorbance (a.u.)
0.0060
0.0045
0.0030
0.0015
0.0000
Wavenumbers (cm^{1-})
3400
3300
3200
3100
3000
2900
a
b
c

Fig. 8A

SELECTIVE FUNCTIONALIZATION OF CARBON NANOTUBES BASED UPON DISTANCE TRAVELED

This application is a continuation-in-part of application Ser. No. 10/320,698, filed Dec. 13, 2002 now U.S. Pat. No. 7,276,266.

FIELD OF THE INVENTION

This invention is related to addition of functional groups to collections of carbon nanotubes.

BACKGROUND OF THE INVENTION

Carbon nanotubes (CNTs) have attracted much attention, due to their extraordinary mechanical properties and their unique electronic properties. A CNT is topologically equivalent to a two-dimensional graphite sheet rolled into a cylinder, with a cylinder diameter as small as 0.7 nanometers (nm) and with a cylinder length up to several microns (μm). A CNT can be single walled (SW) or multiple walled (MW) and can also be fabricated as a nanofiber or other CNT structure. A CNT can be characterized by its chiral vector components (n,m), which helps determine tube diameter, electronic properties and other properties. Depending upon the chirality (n-m divisible by 3 or otherwise), a CNT can be conducting (metal-like) or semiconducting.

CNTs are being studied for applications in high strength/low weight composites, membranes, mechanical filters, body armor, space suits, electronics, nano-electro-mechanical systems, heat exchange systems, radiators, chemical sensors, physical sensors, actuators, data storage, computers and other applications. In some of these applications, chemical functionalization (addition of one or more specified chemical groups to a basic structure) may be necessary to alter the CNT properties for particular applications. For example, functionalization of the CNT tip or the side walls with suitable probe molecules can provide chemical sensors that recognize certain target species and ignore all others. Development of functional composites may require functionalization of a collection of CNTs to allow the tubes to be dispersed more easily in a host matrix.

An ideal functionalization process should be clean, produce relatively little residue for disposal, should be efficient, selective, and reasonably fast, should be scalable to large scale production, should not require use of complex apparatus to produce the target species or attach the species to the CNTs, and should not require complex chemical processing.

The CNT functionalization process reported in the literature use wet chemical procedures and work with liquids or vapors, to which the CNTs are exposed. An example is use of hot flowing fluorine to attach fluorine atoms to CNTs, as reported by E. T. Michelson et al Chem. Phys. Lett. vol 296 (1998) 188. Large quantities of wet chemicals are often required, with most of the chemicals becoming residues that must be disposed of under hazardous substance guidelines. Recycling of the chemicals used is seldom an option.

What is needed is a CNT functionalization process that is "dry" produces relatively little residue for clean-up, is flexible enough to be used for large numbers of chemical functional groups, is reasonably selective, is scalable, and does not

require use of complex apparatus or complex processing to achieve functionalization of a collection of CNTs.

SUMMARY OF THE INVENTION

These needs are met by the present invention, which provides a selective, scalable approach, not involving "wet" chemistry, for functionalization of a collection of CNTs with any of a large class of elements and compounds, including hydrogen, the alkali metals, selected hydrocarbons, selected organic species, and the halogens. Taking hydrogen as an example of a target species, atomic hydrogen is produced by applying a glow discharge to a molecular hydrogen source to provide a cold plasma, and using a strong pressure differential to direct the atomic hydrogen thus produced toward the CNTs. Atomic hydrogen that is not received by the CNTs can be allowed to recombine and can be recovered for another glow discharge cycle.

When a given target molecule, such as NH_3 or CF_4, is provided as a source for functionalization, the predominant species present will depend, in part, on the distance of separation d between the source and the collection of CNTs that serve as the target. For example, where N_2 is the target molecule, at a distance d=1 cm, the predominant molecular components appear to be C═N and C═N; and at a distance d=2.5 cm, the predominant molecular components appear to be C—$(NH)_2$ and/or C═NH_2. For a distance d≧7 cm in certain situations, little or no functionalization is present, in part because the molecular sub-components provided by the breakup of N_2 have recombined and are no longer available to react with the CNT target.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. **1**, **6** and **7** illustrate systems for practicing the invention.

FIG. **2** graphically illustrates FTIR spectra of non-functionalized CNTs. and CNTs functionalized according to the invention.

FIG. **3** graphically illustrates saturation of CNT functionalization, using hydrogen, at various times.

FIG. **4** graphically illustrates absorption of the samples from FIG. **3** in portions of the ultraviolet, visible and infrared spectrum.

FIG. **5** is a flow chart of a procedure for practicing the invention.

FIGS. **8**A and **8**B are graphs illustrating FTIR spectra for target molecules deposited on a CNT array located at a distance of 2.5 cm from a precursor gas (N_2).

DESCRIPTION OF PREFERRED MODES OF THE INVENTION

FIG. **1** illustrates a system **11** for practicing the invention to provide hydrogen as the species for functionalization of the CNTs. The system **11** includes a precursor source **13** that feeds hydrogen (e.g., molecular hydrogen, with a purity of 99.9999 percent or better) to a partially evacuated precursor chamber **15**. Molecular hydrogen in the precursor chamber **15** is irradiated by a microwave source or other suitable radiation source **17**, for example, a McCarroll cavity operating at 2.45 GHz and powered by an Opthos microwave generator. The radiation source **17** provides sufficient radiant energy to produce a cold plasma, in which the free electrons, with typical temperatures T_e≈a few electron volts (1 eV corresponds to T=11,604 K), are much hotter than the resulting partially ionized gas, which has typical temperatures T_g≈350-1000 K.

This discharge produces electrons by ionization and radicals, especially atomic hydrogen as a precursor particle, by dissociation.

Part of the atomic hydrogen thus produced is received in an aperture **19** in a plug **21** of Teflon or other suitable material having an outer diameter of 5-25 mm, where the aperture **19** has a selected diameter (e.g., d(ap)≈1 mm), has a selected length (e.g., 5-25 mm, or greater if desired), and connects the precursor chamber **15** with a target chamber **23** that contains a collection of CNTs **27**, assembled in an array on a substrate **29**, such as CaF_2. The substrate **29** is located adjacent to an aperture exit AE of the aperture **19**, is oriented substantially perpendicular to the particle flow direction within the aperture at the aperture exit, and coated with purified CNTs. At appropriate time intervals, the substrate **29** can be removed from the target chamber **23** to harvest the functionalized CNTs and can be replaced by another substrate including non-functionalized CNTs. Purity of the CNTs used here is monitored using transmission electron microscopy, which verifies that troublesome substances, such as Fe nano-particle, are removed by the purification process (described in Khare et al, Nano Lett. vol. 2 (2002) pp. 73-77, incorporated by reference herein).

The precursor chamber **15** and the target chamber **23** are maintained at pressures of 100-1000 μm Hg and 1-10 μm Hg (optionally including an inert carrier gas, such as including N_2, Ne or Ar), respectively, so that a large pressure ratio (100:1 to 500:1) exists between the two chambers. This large pressure ratio will encourage most of the atomic hydrogen produced in the precursor chamber **15** to move relatively quickly into and along the aperture **19** and to collide, react with and functionalize the CNTs **27**. This functionalization process has been performed at room temperature and at temperatures down to liquid nitrogen temperatures.

FIG. **2** shows FTIR spectra for wavenumbers ν'=1300-1800 cm^{-1}, illustrating relative transmission for a CNT array (i) exposed to H_2 plus atomic H produced by a glow discharge and (ii) exposed to only H_2 (no discharge). C—H bending modes at wavenumbers of about ν'=1370 cm^{-1} and ν'=1459 cm^{-1} are manifest in the infrared spectrum curve, as expected from other experimental data. Two other spectral features occur at ν'=1566 cm^{-1} and ν'=1727 cm^{-1}, which may correspond to C—C vibration in unfunctionalized CNTs and to C═C or C═O vibration in any carbonyl groups that are present. CNTs are known to absorb O atoms and CH_m molecules easily, even at very low pressures, and O atoms and/or CH_m molecules may be present as trace impurities in the hydrogen. The intensities of the extrema in the discharge curve did not change for exposure time intervals of between one and seven hours.

This approach provides substantially complete hydrogen functionalization of an assembly of CNTs, in a time interval as small as 30 sec. This is shown in FIG. **3**, which is a graph illustrating variation of infrared absorbance in CNT samples exposed to atomic hydrogen for a selected infrared region (ν'=2820-3000 cm^{-1}) of the spectrum corresponding to C—H stretching bonds in CH_m (m=2, 3).

The CNT samples were exposed for time intervals of 0 sec (control specimen), 30 sec, 90 sec and 300 sec. The absorption values for 30, 90 and 300 sec are substantially the same and are a factor of about 6 higher than the corresponding values for the control specimen, indicating that the hydrogen functionalization of CNTs saturates in an exposure time interval no greater than 30 sec. The absorption differences between the exposure time intervals Δt=30, 90 and 300 sec in FIG. **3** are very small, but each of these absorption levels is much greater than the corresponding absorption value for the control sample level. Further experiments indicate that the hydrogen functionalization of CNTs saturates in a time interval that may be less than 30 sec. Chemisorption of atomic hydrogen onto CNT side walls is a slightly exothermic process, with an estimated energy of about 26 kcal/mole.

FIG. **3** graphically illustrates the FTIR spectra obtained for a control sample (0 sec) and samples exposed for time intervals Δt=30, 90 and 300 sec. The band at ν'=2924 cm^{-1} (corresponding to a wavelength λ=3.4 μm) arises from C—H stretching bonds and is in reasonable agreement with a computer-modeled value of about ν'=2900 cm^{-1}. The unmodified SWCNTs do not have any infrared (IR) modes near ν'=2900 cm^{-1}, although a small background level of C—H stretching mode is present in the control sample, as shown. As the SWCNTs are exposed to the H atoms, hydrogen functionalization of the nanotubes rapidly saturates, as indicated in the preceding. Subsidiary features at wavenumbers ν'=2955 cm^{-1}, ν'=2871 cm^{-1}, ν'=2863 cm^{-1}, and ν'=2854 cm^{-1} are typical of C—H stretching modes in CH_m groups, which are present in small amounts in H_2 gas, even after liquid nitrogen trapping. Methane (CH_4) is known to be easily absorbed onto SWCNTs, and this may contribute to the background manifested by the control sample. Exposure of identical samples of SWCNTs to H_2 molecules (no discharge present, but with trace amounts of hydrocarbon impurities) under identical conditions for identical time intervals produced the same peaks, but at peak intensities several orders of magnitude smaller. Therefore, the absorption results in FIG. **3** can be attributed to functionalization of SWCNTs with atomic hydrogen, exposed to the plasma.

Experiments to demonstrate substantial functionalization of single wall CNTs (SWCNTs) with atomic hydrogen have been performed. Molecular hydrogen gas (H_2, 99.9999 percent purity) was passed through a liquid nitrogen trap to eliminate water and hydrocarbon impurities, with an H_2 pressure of about 500 μm Hg in the precursor chamber **15**. The pressure in the CNT chamber **23** was about 1 μm Hg. The H_2 precursor gas was irradiated, and a beam of H particles was directed along a central axis CA (FIGS. **6**, **7**) of the aperture **19** toward an array of SWCNTs on the substrate **29** in the CNT chamber **23**. The SWCNTs were produced by the HiPCO process and were purified, as described in the Khare et al article, op cit. The approach extends to other procedures, in addition to HiPCO, for producing SWCNTs and MWCNTs.

Before functionalization with H, the SWCNTs were baked in a vacuum for 30 minutes at a temperature T=810° C. to remove hydrocarbon impurities. A Thermo Nicolet Nexus 670 Fourier transform infrared (FTIR) spectrometer at 4 cm^{-1} resolution and a Perkin Elmer UV-VIS-NIR spectrometer (model Lambda 900) were used to analyze control (non-functionalized) and functionalized SWCNT samples.

Recombination of atomic hydrogen to produce molecular hydrogen, as well as other reactions, will also produce ultraviolet radiation within the precursor chamber **15**, and such radiation is known to break C—H bonds in hydrogenated structures such as hydrogenated CNTs. For this reason, the aperture **19** in the plug **21** is aligned with an initial and/or final aperture segment that is curvilinear (referred to herein as "off-axis alignment"), or is otherwise configured so that little or no uv radiation is received by the target chamber **23** from the precursor chamber **15**.

Recent theoretical studies by Bauschlicher et al, reported in Nano Lett. vol. 1 (2001) pp. 223 and in Nano Lett. vol. 2 (2002) p. 337, indicate that the maximum hydrogen coverage on the outside of a CNT is about 50 percent, due to sp^3 hybridization. Ultraviolet absorption, arising from $\pi \rightarrow \pi^*$

excitations in a CNT covered with H atoms, are expected to be reduced to about half the absorption values found for "bare" CNTs with no H atoms present. FIG. **4** shows UV-VIS-NIR absorption data for the same samples as shown in FIGS. **2** and **3**. The spectra are featureless for CNTs having varying diameters and bandgaps. The decrease in UV absorption intensity is consistent with decrease in the fraction of C—C n bonds present, as would be expected. These UV-VIS-NIR data are consistent with the IR results of FIG. **3** and supports the hypothesis that the SWCNT data, shown in FIG. **3**, indicate substantial functionalization of these CNTs with atomic hydrogen.

This approach uses a glow discharge or cold plasma irradiation of the precursor molecules (here, H_2) to provide functionalization of CNTs. The procedure is a clean, low temperature process that requires a relatively small amount of precursor gas (here, H_2) and uses relatively high efficiency plasma production. A cold plasma process can be used for production of single species atomic halogens, beginning with a precursor gas such as F_2, Cl_2, Br_2 or I_2. A cold plasma process can be used for production of single species atomic alkali metals (single valence), such as Li, Na, K, Rb and Cs. A cold plasma process can also be used for production of low atomic weight hydrocarbons, such as C_nH_{2n}, C_n—H_{2n+1}, and C_nH_{2n+2} (n=1, 2, 3) and for organic species such as dichlorocarbene (H_2CCl_2), although the species selectivity here will not be high. The precursor gas can be irradiated using dc, radiofrequency, microwave, or inductive or electron cyclotron resonance (ECR) discharges.

Multiple wall CNTs can also be functionalized using the approaches disclosed here, although it is likely that the outer or exposed layer(s) of CNTs in the initial structure will be the primary sites for such functionalization.

FIG. **5** is a flow chart illustrating a procedure for practicing the invention. In step **51**, a selected precursor gas is irradiated to provide selected target particles in a first chamber. In step **53**, a collection of CNTs on a selected substrate is provided in a second chamber that is in fluid communication with the first chamber, where one or more selected locations on the substrate are located at a distance d, measured along a path from the precursor gas in the first chamber to the selected location on the substrate in the second chamber. The distance d lies in a selected range, for example, 1 cm≦d≦7 cm, which may vary with the density of the precursor gas and/or with the density of residual gas, if any, in the second chamber. In step **55**, transport of target particles from the first chamber to the second chamber is allowed; optionally, the first chamber-to-second chamber communication mechanism is configured to suppress transport of ultraviolet radiation from the first chamber to the second chamber. In step **57**, first and second distinct species of target particles are allowed to become chemically attached to one or more CNTs within the second chamber at respective distances d**1** and d**2**, where d**1**<d**2** and d**1** and d**2** are within the selected range for d.

Another method of suppressing transport of uv radiation from the precursor chamber **15** to the target chamber **23** is illustrated in FIG. **6**. An elongated aperture **19'** in a plug **21'** is provided with a curvilinear central axis CA' having substantial curvature, rather than with the linear or straight axis illustrated in FIG. **1**, so that no radiation, and more particularly no uv. radiation, can travel in a single straight line in moving from the precursor chamber **15** to the target chamber **23**. Optionally, where the aperture axis is linear or curvilinear, part or all of the interior or side walls of the aperture **19'** are lined with a substance **22** that absorbs uv radiation and that, in response to such absorption, either (i) does not emit radiation or (ii) emits only radiation at infrared or lower energies that do not cause C—H or C—C bond breakage in CNTs or functionalized CNTs.

Another method of suppressing transport of uv radiation from the precursor chamber **15** to the target chamber **23** is illustrated in FIG. **7**. An elongated aperture **19"** is provided with a central axis CA" that includes two or more linear (or curvilinear) segments that are joined together at one or more bend points BP, at each of which the directions of the two contiguous segments are substantially different. With this configuration, no radiation (ultraviolet or otherwise) can travel in a single straight line in moving from the precursor chamber **15** to the target chamber **23**. Again, part or all of the interior or side walls of the aperture **19"** are lined with a substance **22** that absorbs uv radiation and that, in response to such absorption, either (i) does not emit radiation or (ii) emits only radiation at infrared or lower energies that do not cause C—H or C—C bond breakage in CNTs or functionalized CNTs.

In experiments performed using N_2 as the precursor gas, where the distance d**1** was arranged to be about 1 cm, the predominant species of target molecule deposited on the CNTs were bands characteristic of C═N and C═N; and where the distance d**2** was about 2.5 cm, the predominant species of target molecules deposited including molecules containing C—NH_2 and/or C═N. Residual hydrogen is believed to be responsible for appearance of H in the C—NH_2. For distances d at least equal to 7 cm, no deposits arising from the precursor gas could be detected, possibly due to recombination. The precursor gas was present at a pressure in a range of 300-550 mTorr, and a microwave discharge was used to create target molecules in the first chamber. FIGS. **8**A and **8**B are graphs illustrating FTIR spectra for target molecules deposited on a CNT array located at a distance of 2.5 cm from a precursor gas (here, N_2).

In experiments using NH_3 as the precursor gas, at precursor chamber pressures of about 180 mTorr, N—H stretching modes, at 3183~3343 cm^{-1}, N—H_2 bending modes and C═N modes at 1668-1670 cm^{-1}, and C═N modes, at 1560-1584 cm^{-1}, are observed for separation distance d=1 cm, but no C═N modes are observed.

In experiments using CF_4 as the precursor gas, with estimated bond energies of 2.1-5.4 eV for CF_4, CCl_4, CBr_4, CI_4, and CAt_4, at precursor chamber pressures in a range 500-1000 mTorr, the observed target molecules deposited on the CNTs were CF_x (x=0.5-2 plus x=4). At a distance d**1**=1 cm, the CNT array was merely etched by the activated precursor gas, through chemical reactions after about 300 sec of discharge. At distances d at least equal to 7 cm, species C—F and CF_4 were detected (at 1282 cm^{-1}). Initially observed (residual) C—H band intensities decreased with increasing time, likely due to displacement of the H component with plasma species.

This approach can also be applied to functionalize a nanostructure using a halogen, such as F, Cl, Br, I or At or a mixture thereof, beginning with F_2, Cl_2, Br_2, I_2, or At_2, with estimated bond energies of 1.5-2.0 eV, to form activated or excited initial products such as F*, Cl*, Br* I* or At* that will react and combine with C in a CNT array. Again, the predominant reaction product(s), such as C—F or C—Cl, at a given CNT array location will vary with the separation distance, d≈d**1** or d≈d**2** or d≈d**3** (d**1**<d**2**<d**3**) between the location where the precursor is activated and the CNT array location. Where a mixture of functionalizing halogens, such as C—F and C—Br, is desired in a functionalized CNT array, one or more precursors, drawn from the inter-halogen group F—Cl, F—Br, F—I, F—At, Cl—Br, Cl—I, Cl—At, Br—I, Br—At

or I—At, with estimated bond energies of 1.8-2.5 eV, can be provided as part or all of the precursor gas in the chamber **15**. The radiation energies needed for production of the activated or excited initial products (e.g., F*, Cl*, Br*, I* or At*) are estimated to be somewhat lower than, but of the same order of magnitude as. the energies needed to produce C═N or C—$(NH_x)_{2-x}$. Use of a halide (HF, HCl, HBr HI or HAt as a precursor gas will produce one or more of a first group of reaction products, such as CH_w (w=1, 2, 3, 4), at one separation distance d**1**, a second group, such as CN_x (x=1, 2, 3), at a second separation distance d**2**, and a third group, such as C—$(N—H_y)_{2-y}$ (y=1, 2), at a third separation distance d**3**. This last approach is useful if more than one of these three groups of reaction products is needed for one, two or more applications.

This approach can also be used to functionalize a nanostructure using a precursor having a structure similar to NH_3, such as NF_3, NCl_3, NBr_3, NI_3 or NAt_3. Where, for example, NF_3 is used, N—F stretching modes, N—F_2 bending modes and C═N modes will likely appear for a suitable small separation distance, such as d=1 cm, but no C═N modes are likely to be observed. Where the separation distance d is 7 cm or larger, N+N recombination occurs, and only F atoms, but no N atoms, remain for functionalization of the CNT array at these distances. This will also occur where NCl_3, NBr_3, NI_3 or NAt_3 is provided as the precursor gas.

*In general, it is preferable to provide separate CNT arrays at two or more different separation distances d corresponding to different desired dominant functionalization species. If two different functionalization species are to be provided, at the same distance or at different distances d, this can be achieved by either of at least two approaches: (i) locate first and second CNT arrays at first and second different distances, d=d**1** and d=d**2**, respectively, in a single target chamber and (ii) locate first and second CNT arrays at first and second different distances, d=d**1** and d=d**2**, respectively, in first and second target chambers.

What is claimed is:

1. A method for functionalizing a collection of carbon nanotubes (CNTs), the method comprising:

irradiating a precursor gas to provide selected first target particles that contain N in a first chamber having a first selected sub-Torr chamber pressure p**1**;

providing a collection of first target CNTs on a substrate in a second chamber having a second selected sub-Torr pressure p**2**, where p**2** is not more than about 0.01·p**1**;

providing a particle communication mechanism that allows transport of at least a portion of the first target particles from the first chamber to the second chamber;

allowing at least one first target particle to react with and become chemically attached to at least one first target CNT in the second chamber; and

choosing a distance of transport d, of the at least one first target particle that is irradiated in the first chamber to at least one first target CNT in the second chamber, to lie in a first transport distance range, d<d**1**, where d**1** is selected to increase a likelihood that the reaction product of the at least one first target particle and the at least one first target CNT will be one of a group of one or more target reaction products that differs from the first target CNT.

2. The method of claim **1**, further comprising choosing said first target particle and said first target CNT so that said reaction products include at least one of C═N, C═N, C—NH_2, C—NH and C—$(NH)_2$.

3. The method of claim **1**, further comprising choosing said first target particles to include at least one of NH_3 and N_2.

4. The method of claim **1**, further comprising configuring said particle communication mechanism so that transport of ultraviolet radiation from said first chamber to said second chamber is suppressed or eliminated.

5. The method of claim **4**, wherein said transport of said ultraviolet radiation from said first chamber to said second chamber is suppressed by providing an elongated aperture, having an aperture central axis and an aperture side wall and connecting said first and second chambers, further comprising arranging the aperture according to at least one of the following: (i) the aperture central axis is aligned off-axis so that little or no ultraviolet radiation that is produced within said first chamber can move in a single straight line from said first chamber to said second chamber, (ii) the aperture central axis is curvilinear, and is provided with sufficient curvature so that substantially no ultraviolet radiation that is produced within said first chamber can move in a single straight line from said first chamber to said second chamber, and (iii) the aperture central axis has at least one bend point at which a direction of the central axis changes abruptly so that substantially no ultraviolet radiation that is produced within said first chamber can move in a single straight line from said first chamber to said second chamber.

6. The method of claim **5**, further comprising providing at least a portion of said aperture side wall with a chemical substance (i) that absorbs said ultraviolet radiation and emits no radiation in response thereto or (ii) that absorbs said ultraviolet radiation and, in response thereto, emits radiation having an emitted energy that is lower than required to cause a bond breakage in at least one of a C—C bond and a C—H bond.

7. The method of claim **1**, further comprising choosing said first target particles from a group of target particle species consisting of H, Li, Na, K, Rb, Cs, F, Cl, Br, I, At, dichlorocarbene, C_nH_{2n}, C_nH_{2n+1} and C_nH_{2n+2}, with n=1, 2 and 3.

8. The method of claim **1**, wherein said step of irradiating said precursor gas comprises irradiating said precursor gas with at least one of a dc source, a radiofrequency source, a microwave source and an induction source of radiation to provide a cold plasma.

9. The method of claim **1**, further comprising choosing said pressure p**2** in a range 1 μm Hg≦p**2**≦10 μm Hg.

10. The method of claim **1**, further comprising allowing said at least one first target particle to become chemically attached to said at least one first target CNT in said second chamber in an exposure time interval no longer than about 30 sec.

11. The method of claim **1**, further comprising allowing said at least one first target particle to become chemically attached to said at least one first target CNT at a temperature in said second chamber that is no greater than about room temperature.

12. The method of claim **1**, further comprising choosing said distance d**1** to be about 1 cm.

13. The method of claim **1**, further comprising:

allowing at least a second target particle to react with and become chemically attached to at least a second target CNT in said second chamber,

where a distance of transport d' of the second target particle that is irradiated in said first chamber to the second target CNT in said second chamber is chosen to lie in a second transport distance range, d**1**<d'<d**2**, where the value d**2** is selected to increase a likelihood that a second reaction product of the second target particle and the second target CNT will be one of a group of at least one target reaction products that differs from said first target CNT and from said first reaction product.

14. The method of claim **13**, further comprising choosing said pressure p**1** in a range 100 μm Hg≦p**1**≦1000 μm Hg.

15. The method of claim **14**, further comprising choosing said distance d**1** to be about 1 cm and choosing said distance d**2** to be about 7 cm.

16. The method of claim **13**, further comprising choosing said distance d**1** to be about 1 cm and choosing said distance d**2** to be about 2.5 cm.

17. A method for functionalizing a collection of carbon nanotubes (CNTs), the method comprising:

irradiating a precursor gas to provide selected first target particles that contain at least one of F, Cl, Br, I and At in a first chamber having a first selected sub-Torr chamber pressure p**1**;

providing a collection of first target CNTs on a substrate in a second chamber having a second selected sub-Torr pressure p**2**, where p**2** is not more than about 0.01·p**1**;

providing a particle communication mechanism that allows transport of at least a portion of the first target particles from the first chamber to the second chamber;

allowing at least one first target particle to become chemically attached to at least one first target CNT in the second chamber; and

choosing a distance of transport d, of the at least one first target particle that is irradiated in the first chamber to a first target CNT in the second chamber, to lie in a first transport distance range, d<d**1**, where d**1** is selected to increase a likelihood that the reaction product of the first target particle and the first target CNT will be one of a group of at least one target reaction products that differs from the first target CNT.

18. The method of claim **17**, further comprising choosing said first target CNT so that said reaction products include at least one of C—F_2, C—Cl_2, C—Br_2, C—I_2, and C—At_2.

19. The method of claim **17**, further comprising choosing said first target particles to include at least one of C—F_4, C—Cl_4, C—Br_4, C—I_4, and C—At_4.

20. The method of claim **17**, further comprising configuring said particle communication mechanism so that transport of ultraviolet radiation from said first chamber to said second chamber is suppressed or eliminated.

21. The method of claim **20**, wherein said transport of said ultraviolet radiation from said first chamber to said second chamber is suppressed by providing an elongated aperture, having an aperture central axis and an aperture side wall and connecting said first and second chambers, further comprising arranging the aperture according to at least one of the following: (i) the aperture central axis is aligned off-axis so that little or no ultraviolet radiation that is produced within said first chamber can move in a single straight line from said first chamber to said second chamber, (ii) the aperture central axis is curvilinear, and is provided with sufficient curvature so that substantially no ultraviolet radiation that is produced within said first chamber can move in a single straight line from said first chamber to said second chamber, and (iii) the aperture central axis has at least one bend point at which a direction of the central axis changes abruptly so that substantially no ultraviolet radiation that is produced within said first chamber can move in a single straight line from said first chamber to said second chamber.

22. The method of claim **20**, further comprising providing at least a portion of said aperture side wall with a chemical substance (i) that absorbs said ultraviolet radiation and emits no radiation in response thereto or (ii) that absorbs said ultraviolet radiation and, in response thereto, emits radiation having an emitted energy that is lower than required to cause a bond breakage in at least one of a C—C bond, a C—F bond, a C—Cl bond, a C—Br bond, a C—I bond and a C—At bond.

23. The method of claim **17**, further comprising:

allowing at least a second target particle to react with and become chemically attached to at least a second target CNT in said second chamber,

where a distance of transport d' of the second target particle that is irradiated in said first chamber to the second target CNT in said second chamber is chosen to lie in a second transport distance range, d**1**<d'<d**2**, where the value d**2** is selected to increase a likelihood that a second reaction product of the second target particle and the second target CNT will be one of a group of at least one target reaction products that differs from said first target CNT and from said first reaction product.

24. The method of claim **23**, further comprising choosing said distance d**1** to be about 1 cm and choosing said distance d**2** to be about 2.5 cm.

25. The method of claim **23**, further comprising choosing said distance d**1** to be about 1 cm and choosing said distance d**2** to be about 7 cm.

26. A method for functionalizing a collection of carbon nanotubes (CNTs), the method comprising:

irradiating a precursor gas to provide selected first target particles that contain at least one of NF_x, NCl_x, NBr_x, NI_x, and NAt_x (x=1, 2, 3) in a first chamber having a first selected sub-Torr chamber pressure p**1**;

providing a collection of CNTs on a substrate in a second chamber having a second selected sub-Torr pressure p**2**, where p**2** is not more than about 0.01·p**1**;

providing a particle communication mechanism that allows transport of at least a portion of the first target particles from the first chamber to the second chamber;

allowing at least one of the first target particles to become chemically attached to at least one of the first target CNT in the second chamber; and

choosing a distance of transport d, of the at least one first target particle that is irradiated in the first chamber to a first target CNT in the second chamber, to lie in a first transport distance range, d<d**1**, where d**1** is selected to increase a likelihood that the reaction product of the first target particle and the first target CNT will be one of a group of at least one target reaction products that differs from the first target CNT.

27. The method of claim **26**, further comprising choosing at least one of said first target particle and said first target CNT so that said reaction products include at least one of CF_a (a=1, 2, 3), CCl_b (b=1, 2, 3), CBr_c (c=1, 2, 3), CI_d (d=1, 2, 3) and CAt_e (e=1, 2, 3).

28. The method of claim **27**, further comprising configuring said particle communication mechanism so that transport of ultraviolet radiation from said first chamber to said second chamber is suppressed or eliminated.

29. The method of claim **28**, wherein said transport of said ultraviolet radiation from said first chamber to said second chamber is suppressed by providing an elongated aperture, having an aperture central axis and an aperture side wall and connecting said first and second chambers, further comprising arranging the aperture according to at least one of the following: (i) the aperture central axis is aligned off-axis so that little or no ultraviolet radiation that is produced within said first chamber can move in a single straight line from said first chamber to said second chamber, (ii) the aperture central axis is curvilinear, and is provided with sufficient curvature so that substantially no ultraviolet radiation that is produced within said first chamber can move in a single straight line from said first chamber to said second chamber, and (iii) the

aperture central axis has at least one bend point at which a direction of the central axis changes abruptly so that substantially no ultraviolet radiation that is produced within said first chamber can move in a single straight line from said first chamber to said second chamber.

30. The method of claim **29**, further comprising providing at least a portion of said aperture side wall with a chemical substance (i) that absorbs said ultraviolet radiation and emits no radiation in response thereto or (ii) that absorbs said ultraviolet radiation and, in response thereto, emits radiation having an emitted energy that is lower than required to cause a bond breakage in at least one of a C—C bond, a C—F bond, a C—Cl bond, a C—Br bond, a C—I bond and a C—At bond.

31. The method of claim **26**, further comprising:

allowing at least a second target particle to react with and become chemically attached to at least a second target CNT in said second chamber,

where a distance of transport d' of the second target particle that is irradiated in said first chamber to the second target CNT in said second chamber is chosen to lie in a second transport distance range, $d1<d'<d2$, where the value d**2** is selected to increase a likelihood that a second reaction product of the second target particle and the second target CNT will be one of a group of at least one target reaction products that differs from said first target CNT and from said first reaction product.

32. The method of claim **31**, further comprising choosing said distance d**1** to be about 1 cm and choosing said distance d**2** to be about 2.5 cm.

33. The method of claim **32**, further comprising choosing said distance d**1** to be about 1 cm and choosing said distance d**2** to be about 7 cm.

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