



US 20170066923A1

(19) **United States**

(12) **Patent Application Publication**  
**HARDMAN et al.**

(10) **Pub. No.: US 2017/0066923 A1**

(43) **Pub. Date: Mar. 9, 2017**

(54) **CIRCULAR FEW LAYER GRAPHENE**

**Publication Classification**

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(51) **Int. Cl.**  
**C09C 1/52** (2006.01)  
**H01B 1/04** (2006.01)  
**C01B 31/04** (2006.01)

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(52) **U.S. Cl.**  
CPC ..... **C09C 1/52** (2013.01); **C01B 31/0438**  
(2013.01); **H01B 1/04** (2013.01); **C01B**  
**2204/04** (2013.01); **C01B 2204/32** (2013.01);  
**C01P 2004/24** (2013.01); **C01P 2004/61**  
(2013.01)

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(21) Appl. No.: **15/259,884**

(57) **ABSTRACT**

(22) Filed: **Sep. 8, 2016**

**Related U.S. Application Data**

(60) Provisional application No. 62/215,854, filed on Sep.  
9, 2015.

Disk shaped fine carbon particles. A fine carbon particle  
having a diameter of less than 3 microns and a height of less  
than 0.05 micron substantially in disk form are described.  
Admixtures with other fine particles are also described.

Fig. 1

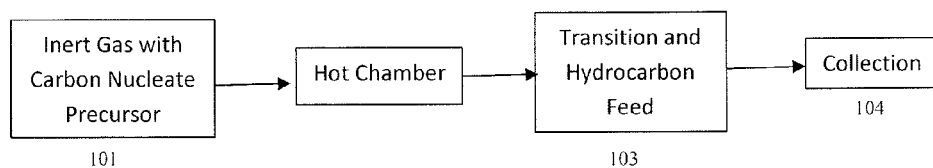


Fig. 2

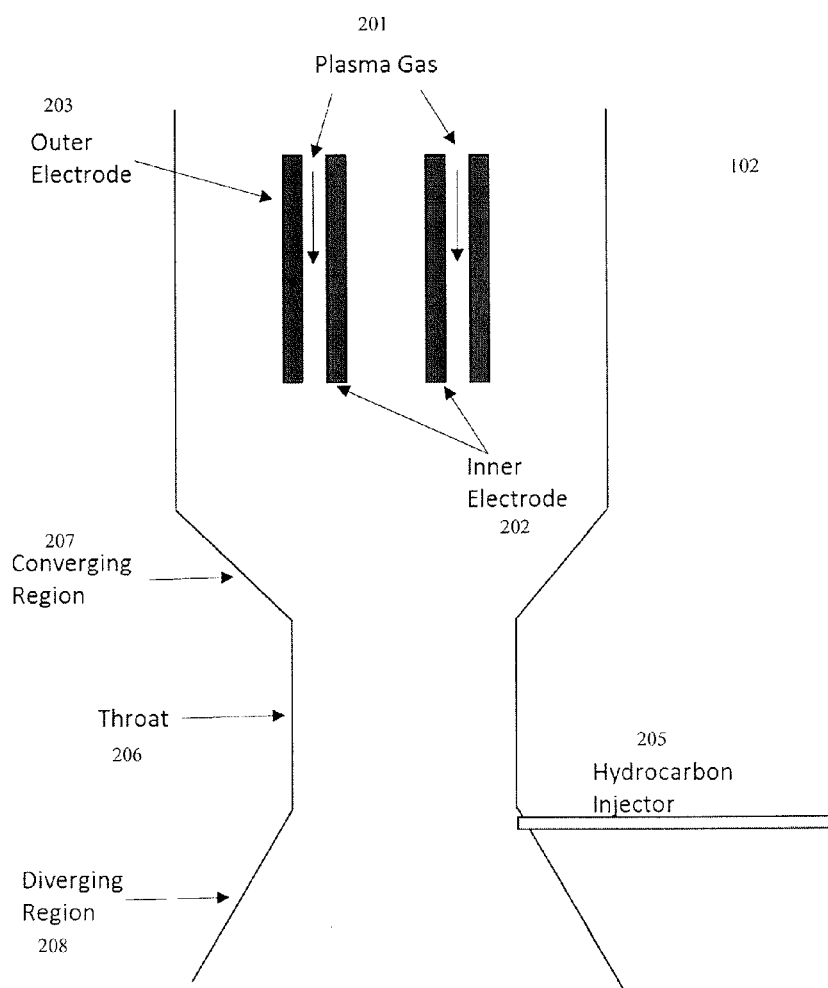


Fig. 3

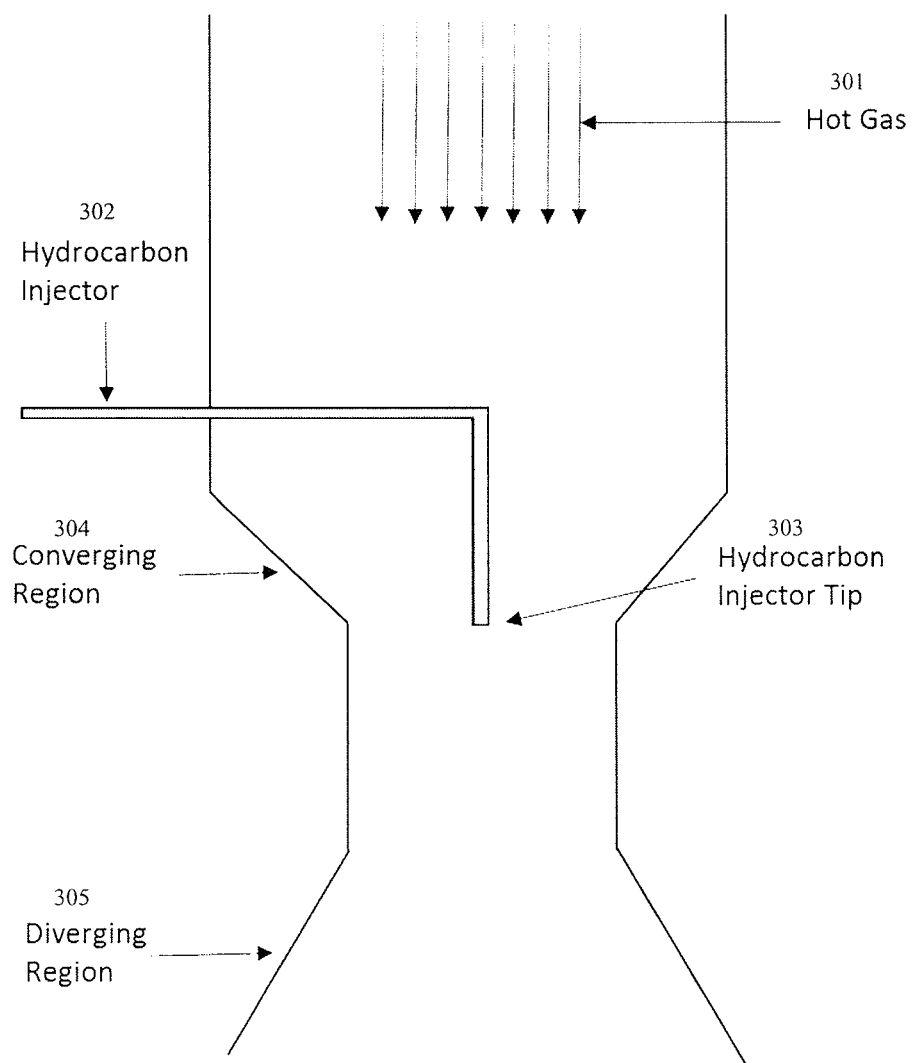


Fig. 4

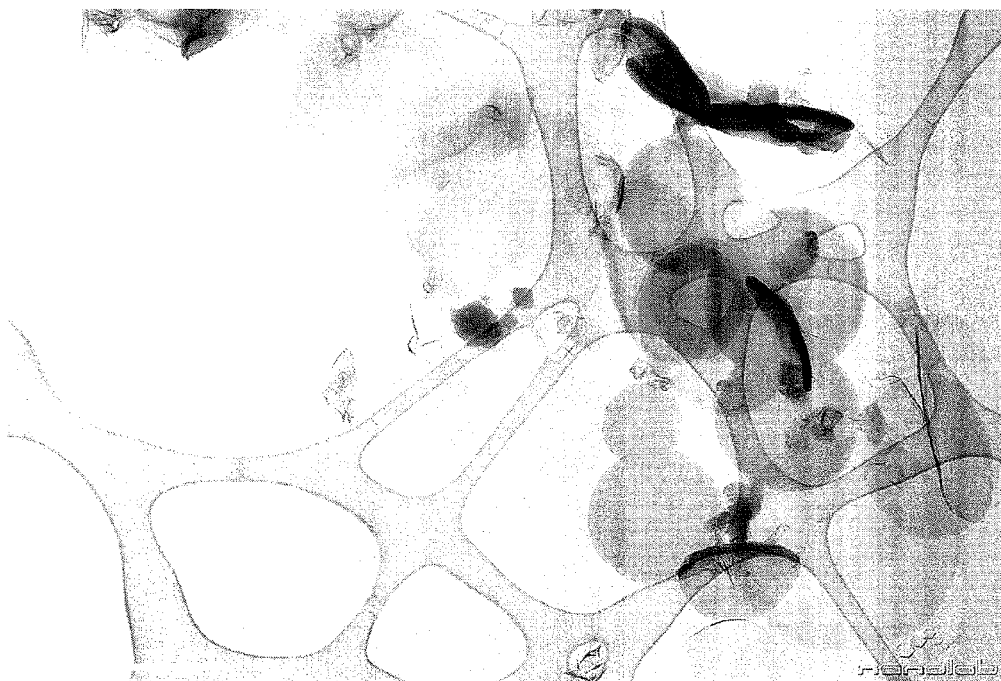


Fig. 5



**CIRCULAR FEW LAYER GRAPHENE****CROSS REFERENCE TO RELATED APPLICATIONS**

**[0001]** The instant application claims priority to U.S. Provisional Application No. 62/215,854, filed Sep. 9, 2015, the disclosure of which is incorporated by reference herein in its entirety.

**TECHNICAL FIELD**

**[0002]** The field of art to which this invention generally pertains is methods and apparatus for making use of electrical energy to affect chemical changes.

**BACKGROUND**

**[0003]** There are many processes that can be used and have been used over the years to produce carbon black. The energy sources used to produce such carbon blacks over the years have, in large part, been closely connected to the raw materials used to convert hydrocarbon containing materials into carbon black. Residual refinery oils and natural gas have long been a resource for the production of carbon black. Energy sources have evolved over time in chemical processes such as carbon black production from simple flame, to oil furnace, to plasma, to name a few. As in all manufacturing, there is a constant search for more efficient and effective ways to produce such products, and to produce new and improved products. Varying flow rates and other conditions of energy sources, varying flow rates and other conditions of raw materials, increasing speed of production, increasing yields, reducing manufacturing equipment wear characteristics, etc. have all been, and continue to be, part of this search over the years.

**[0004]** The embodiments described herein meet the challenges described above, and additionally attain more efficient and effective manufacturing process.

**BRIEF SUMMARY**

**[0005]** Fine carbon particles are described including a fine carbon particle having a diameter of less than 3 microns and a height of less than 0.05 micron, substantially in disk form.

**[0006]** Additional embodiments include: the particle described above where the disk includes a circumference and a diameter, and wherein the circumference is 95% to 105% of 3.1415 times the diameter; an admixture of fine carbon particles including the disks described above present in an amount of at least 1% by weight; the admixture described above where the disks are present in an amount of at least 10% by weight; the particle described above where the diameter/height aspect ratio is at least 4; the particle described above where the aspect ratio is at least 10 but less than 200; the particle described above where the aspect ratio is between 4 and 150; the particle described above made by two distinct injection regions of carbonaceous feedstock; the particle described above made by a gas phase process using natural gas; an admixture of spherical and/or ellipsoidal fine carbon particles including at least 1% by weight of the particles described above.

**[0007]** These and additional embodiments are further described below.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**[0008]** FIG. 1 demonstrates a flow chart of a process described herein.

**[0009]** FIGS. 2 and 3 depict various apparatus for carrying out processes described herein.

**[0010]** FIGS. 4 and 5 show typical Transmission Electron Micrograph (TEM) images of carbon nanoparticle produced by processes herein.

**DETAILED DESCRIPTION**

**[0011]** The particulars shown herein are by way of example and for purposes of illustrative discussion of the various embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description making apparent to those skilled in the art how the several forms of the invention may be embodied in practice.

**[0012]** The present invention will now be described by reference to more detailed embodiments. This invention may, however, be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art.

**[0013]** Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. The terminology used in the description of the invention herein is for describing particular embodiments only and is not intended to be limiting of the invention. As used in the description of the invention and the appended claims, the singular forms "a," "an," and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. All publications, patent applications, patents, and other references mentioned herein are expressly incorporated by reference in their entirety.

**[0014]** Unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should be construed in light of the number of significant digits and ordinary rounding approaches.

**[0015]** Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Every numerical range given throughout this specification will include every nar-

rower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein.

**[0016]** Additional advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

**[0017]** Few Layer Graphenes (FLG) are an emerging class of materials with a variety of applications including batteries, polymer composites, elastomers, and conductive inks just to name a few. There has been little penetration of FLGs into mainstream applications due to the high cost of FLG production. There have not been any reports of circular few layer graphene disks in the literature. Few layer graphenes are comprised of particles that possess two or more layers of graphene and have a shape that is best described as flat or substantially flat. A fine particle is described as a particle that has at least one dimension that is less than 100 nm (nanometers). Spherical or ellipsoidal particle can mean singular particles and can also mean a plurality of particles that are stuck together in a fashion analogous to that of a bunch of grapes or aciniform. Carbon black is an example of this type of fine carbon particle.

**[0018]** U.S. Pat. No. 8,486,364 describes a process to make graphene flakes from the gas phase utilizing a plasma torch with a natural gas feed. However, the particles that are generated are flake-like and do not have any circular nature. Other patents in the FLG area describe methods to chemically intercalate graphite and then exfoliate the graphite through the use of rapid heating. These methods also differ significantly from the method described herein and introduce surface defects at the graphene surface due to oxidation from chemical intercalation or due to oxidation during the rapid heating process.

**[0019]** FIG. 1 shows a non-limiting example of process steps utilized to make circular few layer graphene disks via gas phase process. The first step (101) is the loading of a hydrocarbon into an inert gas (nitrogen, hydrogen, argon, etc.). The second step which can optionally be simultaneous with the first step is the heating (102) of this gas mixture to at least 2400° C. At this point, a transition can optionally be present where the reactor walls converge (207) to a narrow throat (206) and then diverge (208) to a larger cavity. This is known as a transition. The next step or occurring simultaneously with the transition is the addition (103) of a second hydrocarbon source. The second feedstock allows for the growth of disks with virtually perfect circular edges at the nano-domain size regime. And finally, the thus-formed disks are collected (104).

**[0020]** FIG. 2 shows a schematic representation of an embodiment of a typical apparatus described herein. Plasma gas (201) such as oxygen, nitrogen, argon, helium, air, hydrogen, carbon monoxide, hydrocarbon (e.g. methane, ethane, unsaturated) etc. (used alone or in mixtures of two or more) is injected into an annulus created by two electrodes that are positioned in the upper chamber in a concentric fashion. Plasma forming electrodes are arranged with an inner (202) and outer (203) electrode and a sufficiently large voltage is applied between the two electrodes. Electrodes are typically made of copper, tungsten, graphite, molybdenum, silver etc. The thus-formed plasma then enters into the

reaction zone where it reacts/interacts with a hydrocarbon feedstock that is fed at the hydrocarbon injector (205) to generate a carbon black product. The walls of the vessel can withstand the plasma forming temperatures (refractory, cooled etc.), with graphite being the preferred material of construction. And the hydrocarbon injector(s) can be located anywhere on a plane at or near the throat or further downstream of the throat in the diverging region of the reactor. The hydrocarbon injector tips are arranged concentrically around the injection plane and there can be at least 6 injectors and up to 18 tips of this sort, or even a continuous slot, as non-limiting examples.

**[0021]** FIG. 3 shows another embodiment of the apparatus described herein. Hot gas (301) is generated in the upper portion of the reactor either through the use of three or more AC electrodes, through the use of concentric DC electrodes as shown in FIG. 2 or through the use of a resistive or inductive heater, more detail of which can be found in commonly assigned, copending U.S. Patent Application Ser. No. 62/209,017, filed Aug. 24, 2015, the disclosure of which is herein incorporated by reference. The hot gas is comprised of at least 50% hydrogen by volume that is at least 2400° C. The hydrocarbon injector (302) can be cooled and enters from the side of the reactor and then turns into an axial position in regard to hot gas flow. The hydrocarbon injector tip (303) can be one opening or a plurality of openings that can inject hydrocarbons in clockwise or counter clockwise flow patterns to optimize mixing. Optionally, there are converging regions (304) leading to a narrowing of the reactor and then diverging regions (305) downstream of the converging region.

**[0022]** In the past, plasma generator designs have not been able to meet the power, corrosion resistance, and continuous operation requirements to produce carbon black because of such things as the insufficient unit power of their basic components and the tendency of these components to decay when exposed to hydrogen plasma, resulting in lost reactor time, increased capital costs, and uneconomically produced carbon black, among other things. For more details concerning methods of heating hydrocarbons rapidly to form carbon nanoparticles and hydrogen please see the following commonly assigned, copending U.S. patent applications, the disclosures of which are herein incorporated by reference: Ser. No. 62/111,317, Carbon Black Combustible Gas Separation; Ser. No. 14/591,541, Use Of Feedstock In Carbon Black Plasma Process; Ser. No. 14/601,761, Plasma Gas Throat Assembly And Method; Ser. No. 14/601,793, Plasma Reactor; Ser. No. 62/198,431, DC Plasma Torch Electrical Power Design Method And Apparatus; Ser. No. 14/591,528, Integration Of Plasma And Hydrogen Process With Combined Cycle Power Plant, Simple Cycle Power Plant, And Steam Reformer; Ser. No. 62/202,498, Method Of Making Carbon Black; Ser. No. 14/610,299, Plasma Torch Design; Ser. No. 14/591,476, System For High Temperature Chemical Processing; Ser. No. 62/198,486, Method Of Making Carbon Black Including Thermal Transfer Gas; Ser. No. 62/111,341, Regenerative Cooling Method And Apparatus.

**[0023]** FIGS. 4 and 5 are Transmission Electron Micrographs (TEM) of typical carbon nanoparticles prepared by the processes described herein. The circular few layer graphene disks can clearly be seen in the micrograph and the thickness can be approximated based on the transparency of the disks in the micrograph of FIG. 4.

**[0024]** Acceptable hydrocarbon feedstock includes any chemical with formula  $C_nH_x$  or  $C_nH_xO_y$ , where  $n$  is an integer, and  $x$  is between 1 and  $2n+2$ , and  $y$  is between 0 and  $n$ . For example simple hydrocarbons such as: methane, ethane, propane, butane, etc. can be used, as well as aromatic feedstock such as benzene, toluene, methyl naphthalene, pyrolysis fuel oil, coal tar, coal, heavy oil, oil, bio-oil, bio-diesel, other biologically derived hydrocarbons, or the like. Also, unsaturated hydrocarbon feedstocks can also be used, such as: ethylene, acetylene, butadiene, styrene and the like. Oxygenated hydrocarbons such as; ethanol, methanol, propanol, phenol, ether, and similar are also acceptable feedstocks. These examples are provided as non-limiting examples of acceptable hydrocarbon feedstocks which can further be combined and/or mixed with other acceptable components for manufacture. Hydrocarbon feedstock referred to herein, means that the majority of the feedstock is hydrocarbon in nature. A preferred hydrocarbon feedstock for this process is natural gas.

**[0025]** The dimensions of the disk can be defined by the diameter of the circle (D) and the height (H) of the disk. The parameter of D/H is defined herein as the aspect ratio. For extremely thin disks, the aspect ratio can be quite high. Where parity or near parity of D and H is reached, this type of object can also be described as a cylinder. For flat jagged flakes, ellipsoids, and other non-circular shapes, the diameter can be taken to be the shortest dimension in the flat plane of the particle.

**[0026]** FIG. 1 shows one method to make circular few layer graphene. Another method that can be employed is the slow mixing of hydrocarbon into a hot effluent stream of gas. In one such example, the effluent hot stream is mainly hydrogen and the hydrocarbon precursor is natural gas. The natural gas slowly mixes into the hot gas such that the majority of the natural gas at the boundary layer is very close to the temperature of the hot gas. The hot gas can be from 2400° C. to 3400° C. in temperature. At these temperatures six membered carbon rings are favored over five membered carbon rings and therefore more planar particles are formed. In this way, the formation of carbon black which is comprised of spherical particles, for instance, can be avoided. As the remainder of the natural gas is mixed into the effluent hot gas stream, carbon growth can occur at the edges of the planar structure. The high energy sites will react first, which will afford the lowest energy configuration, which in this case is a circular few layer graphene disk. In this way, the process can either consist of one injection point or two injection points.

**[0027]** One layer of graphene possesses 2630 m<sup>2</sup>/g (square meters per gram) of surface area. Two layers of graphene possess half of 2630 m<sup>2</sup>/g or 1315 m<sup>2</sup>/g. This relationship holds for many hundreds of thousands of layers as the space between the sheets of stacked graphene are not accessible through nitrogen based BET (Brunauer-Emmett-Teller) surface area as described in ASTM D-6556-10.

#### EXAMPLE 1

##### Manufacture of FLG Particle as Shown in FIG. 4

**[0028]** Samples were prepared as described in FIG. 2. The power output of the DC electrodes was 860 kW (kilowatts). Hydrogen plasma gas was generated at 3200° C. in the

presence of 2.5% by volume methane. The hot gas impregnated with carbon was then mixed with natural gas for a final reaction temperature of 2600° C. assuming full mixing and conversion of methane to circular few layer graphene disks and hydrogen. The natural gas flow was 25 kg/hr (kilograms/hour) through 18 injectors spaced in a circular pattern around a central axis. Based upon the TEM, there are only 10-20 sheets present. This corresponds to a surface area of 130 to 260 m<sup>2</sup>/g. The average diameter of the disks corresponds to approximately 500 nm and the average thickness is 5 nm. This gives an aspect ratio of 100.

#### EXAMPLE 2

##### Manufacture of FLG Particles as Shown in FIG. 5

**[0029]** Samples were prepared as described in FIG. 3. The power output of the DC electrodes was 750 kW. Hydrogen plasma gas was generated at 2600° C. in the presence of 2.5% by volume methane. The hot gas impregnated with carbon was then mixed with natural gas for a final reaction temperature of 1700° C. assuming full mixing and conversion of methane to circular few layer graphene disks and hydrogen. The natural gas flow was 75 kg/hr through one central injector. The nitrogen surface area of this sample is 18 m<sup>2</sup>/g. The corresponding thickness is approximately 50 nm. The average diameter of the disks as measured by SEM is 1000 nm. This corresponds to an aspect ratio of 20.

**[0030]** Thus, the scope of the invention shall include all modifications and variations that may fall within the scope of the attached claims. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

What is claimed is:

1. A fine carbon particle having a diameter of less than 3 microns and a height of less than 0.05 micron, substantially in disk form.
2. The particle of claim 1 wherein the disk includes a circumference and a diameter, and wherein the circumference is 95% to 105% of 3.1415 times the diameter.
3. An admixture of fine carbon particles including the disks of claim 3 present in an amount of at least 1% by weight.
4. The admixture of claim 3, wherein the disks are present in an amount of at least 10% by weight.
5. The particle of claim 1 wherein the diameter/height aspect ratio is at least 4.
6. The particle of claim 5 wherein the aspect ratio is at least 10 but less than 200.
7. The particle of claim 5 wherein the aspect ratio is between 4 and 150.
8. The particle of claim 1 made by two distinct injection regions of carbonaceous feedstock.
9. The particle of claim 1 made by a gas phase process using natural gas.
10. An admixture of spherical and/or ellipsoidal fine carbon particles including at least 1% by weight of the particles of claim 1.

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