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(71) **Applicant** *(for all designated States except US)*: **N-BARO TECH CO., LTD** [KR/KR]; 974-1 Goryeon-ri, Ungchon-myeon, Ulju-gun, Ulsan 689-871 (KR).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **KWON, Young Jin** [KR/KR]; 282-1103, Hyundei Sungwoo 3 Cha Apt., 855 Sanghyeon-dong, Suji-gu, Yongin-si, Gyeonggi-do 448-130 (KR). **KIM, Jung Ho** [KR/KR]; 202-805, Woosung Apt., Sadang 2-dong, Dongjak-gu, Seoul 156-773 (KR). **GU, Ja Woon** [KR/KR]; 206-801, Okhyeon Jugong Apt., 478-1 Mugeo-dong, Nam-gu, Ulsan 680-808 (KR). **PARK, Won Hyung** [KR/KR]; 402, SeorinHeights, 431-11, Taehwa-dong, Jung-gu, Ulsan 681-819 (KR). **KIM, Su Bong** [KR/KR]; 101-1903, Halla Apt., Jwa 1-dong, Haeundae-gu, Busan 612-030 (KR). **SHIN, Cheol Min** [KR/KR]; 102-1411, Sinbok Hyundai Apt., Mugeo 2-dong, Nam-gu, Ulsan 680-763 (KR). **JI, Byoung Kyu** [KR/KR]; 89-2, Unhwa-ri, Onyang-eup, Ulju-gun, Ulsan 689-905 (KR). **KWON, Doo Hyo** [KR/KR]; 974-1, Goryeon-ri, Ungchon-myeon, Ulju-gun, Ulsan 689-871 (KR). **PARK, Sung Yeol** [KR/KR]; 103-1306, Namheung Apt., Bansong 2-dong, Haeundae-gu, Busan 612-731 (KR).

(74) **Agent**: **SHINSEGI PATENT LAW FIRM**; 3F., Yoong-Jun Bldg., 829-6 Yeoksam -dong, Gangnam-gu, Seoul 135-936 (KR).

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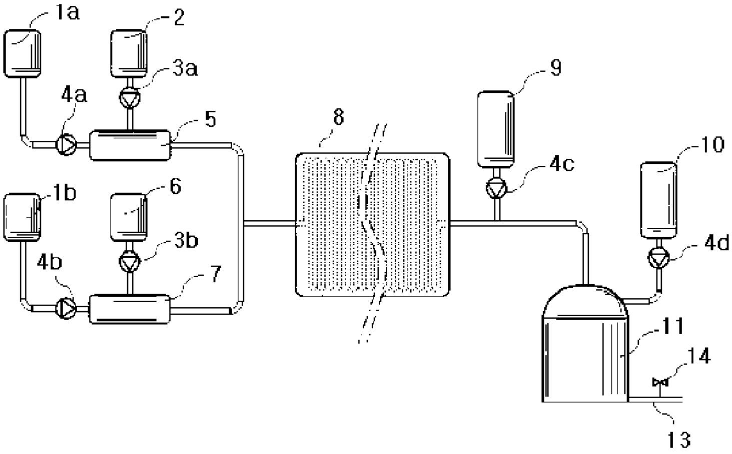
[Continued on next page]

(54) **Title**: A METHOD OF PRODUCING NANO-SIZE GRAPHENE-BASED MATERIAL AND AN EQUIPMENT FOR PRODUCING THE SAME

[Fig. 1]



(57) **Abstract**: The present invention is directed to a method of producing nano-size graphene-based material and an equipment for producing the same. The present invention provides a method of producing graphitic oxide by forcing graphite sulfuric slurry and $KMnO_4$ sulfuric solution into a lengthy micro-channel and by sustaining the mixture of the said graphite sulfuric slurry and the said $KMnO_4$ sulfuric solution in the said micro-channel at predetermined temperatures, by putting the said aqua solution of hydrogen peroxide to the reaction mixture to terminate oxidation, and by washing and drying the reaction mixture. The present invention provides a method of producing nano-size graphene-based material by exfoliating graphitic oxide by thermal shock in a vertical fluidized furnace. According to the present invention, graphitic oxide can be produced massively without risks of explosion by forcing all reagents as liquid phase continuously into a lengthy micro-channel surrounded and thermally controlled strictly by heat exchangers. Nano-size graphene-based material derived by exfoliating thus produced graphitic oxide can be imported into compositions and composites for various uses since it has physical characteristics comparable to carbon nanotube and dispersibility superior to carbon nanotube via residual functional groups.

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Description

Title of Invention: A METHOD OF PRODUCING NANO-SIZE GRAPHENE-BASED MATERIAL AND AN EQUIPMENT FOR PRODUCING THE SAME

Technical Field

[1] The present invention is directed to a method of producing nano-size graphene-based material and an equipment for producing the same. In addition, the present invention is directed to a method of producing graphitic oxide, intermediate for graphene-based material and equipment for producing graphitic oxide.

Background Art

[2] Graphene is single planar carbon material having honeycomb crystal lattice the structure of which is formed of carbons by sp^2 hybridization bonding and was discovered most recently among carbon nanostructures. The shape of graphene is the same as that of a single layer derived by fully severance between layers from graphite which is stacked layers of carbon honeycomb crystal lattice.

[3] In 2004, professor Andre Geim and et al from University of Manchester isolated graphene by peeling it off from graphite with Scotch tape and found excellent electric conductivity of the graphene so acquired by study of quantum hole effect. Thereafter, in 2008, James Hone and et al, researchers from university of Colombia confirmed the superior strength of graphene. In the same year, Alexander Balandin and et al, researchers from University of Riverside, California, measured the thermal conductivity of graphene as 5300pW/mpK, which is double that of carbon nano-tube.

[4] Longitudinal scission of carbon nanotube makes graphene structure and infinite enlargement of wall in carbon nanotube of single wall makes it similar to graphene. Therefore, the electronic, thermal and mechanical properties of graphene are expected to be comparable to those of carbon nano-tubes.

[5] For preparation of graphene, drawing method by mechanical exfoliation(repeated peeling) of graphite crystals by the above-mentioned Andre Geim, epitaxial growth on substrates , hydrazine reduction on graphitic oxide paper, chemical vapor deposition and cutting open of nanotubes in solution of potassium permanganate and sulfuric acid have been known but none of them go beyond laboratory preparation levels.

[6] On the other hand, the method of producing expanded graphite, the shape of which is worm-like or accordion-like, by adding thermal shock on graphite intercalated with acids or so on has been known since long before. Such worm-like expanded graphite is used as fillers or is rolled into sheets having anisotropic conductivity. Such expanded graphite resulting from loose bonding between layers of graphite is inferior to

graphene in physical properties and its particulate size is much bigger than graphene.

[7] Staudenmaier method wherein graphite flake is reacted with nitric acid and potassium perchlorinate for days has been known for preparing graphitic oxide. In addition, Hummers, in US patent No. 2798878, shortened the reaction time by using sulfuric acid, nitric acid and potassium permanganate as oxidants. The mixing of sulfuric acid, nitric acid and potassium permanganate together is exothermic reaction and may cause explosion at around 70°C or above. In these methods, Graphitic oxide is prepared by batch process in very small amount on each batch.

Disclosure of Invention

Technical Problem

[8] It is an object of the present invention to provide a method of producing massively and economically nano-sized material having structures and characteristics of graphene and an equipment for producing the same.

[9] It is another object of the present invention to provide a method of producing graphitic oxide, intermediate for graphene-based material mentioned above, and equipment for producing graphitic oxide.

Solution to Problem

[10] According to the present invention, there is provided a method of producing graphitic oxide comprising:

[11] 1) a step of preparing graphite sulfuric slurry by mixing graphite flake with sulfuric acid;

[12] 2) a step of preparing $KMnO_4$ sulfuric solution by dissolving $KMnO_4$ in sulfuric acid;

[13] 3) a step of preparing aqua solution of hydrogen peroxide;

[14] 4) a step of forcing the said graphite sulfuric slurry into a lengthy micro-channel having a beginning, a reacting portion and an outlet;

[15] 5) a step of forcing the said $KMnO_4$ sulfuric solution into the beginning of the said lengthy micro-channel;

[16] 6) a step of sustaining the mixture of the said graphite sulfuric slurry and the said $KMnO_4$ sulfuric solution in the said micro-channel at predetermined temperatures;

[17] 7) a step of putting the said aqua solution of hydrogen peroxide to the reaction mixture after the step 6);

[18] 8) a step of washing the reaction mixture after the step 7); and

[19] 9) a step of drying the reaction mixture after the step 8), wherein the step 1) to the step 6) are carried out continuously. At the step 7), the said aqua solution of hydrogen peroxide may be put into the said micro-channel in the vicinity of the outlet or into a separate mixing tank for mixing the said aqua solution of hydrogen peroxide with the reaction mixture.

[20] if necessary, the method of producing graphitic oxide may further comprises a step of filtering the reaction mixture after the step 6).

[21] According to the present invention, there is also provided a method of producing nano-size graphene-based material:

[22] 10) a step of pouring the graphitic oxide into a vertical fluidized furnace in reducing atmosphere;

[23] 11) a step of expanding the falling graphitic oxide by heating in the vertical fluidized furnace;

[24] 12) a step of collecting nano-size graphene-based material produced and carried on ascending flow near the ceiling of the vertical fluidized furnace;

[25] 13) a step of separating and storing the nano-size graphene-based material: and, if necessary,

[26] 14) a step of resupplying the furnace gas separated through the step 13) to the furnace with atmospheric gas.

[27] According to the present invention, there is also provided equipment for producing continuously graphitic oxide comprising:

[28] a supplying unit for graphite sulfuric slurry;

[29] a supplying unit for $KMnO_4$ sulfuric solution;

[30] a supplying unit for aqua solution of hydrogen peroxide;

[31] a micro-reactor including multiple micro-channel modules surrounded by heat-exchangers for constituting one lengthy micro-channel having a beginning connected to the said supplying unit for graphite sulfuric slurry and connected to the said supplying unit for $KMnO_4$ sulfuric solution , a reacting portion and an outlet;

[32] if necessary, a filtering unit for the reaction mixture connected to the micro-reactor;

[33] a mixing unit for mixing the reaction mixture with aqua solution of hydrogen peroxide connected to the micro-channel in the vicinity of its outlet;

[34] a washing unit connected to the mixing unit; and

[35] a drying unit connected to the washing unit;

[36] The mixing unit for mixing the reaction mixture with aqua solution of hydrogen peroxide may be incorporated as a part of the micro-channel or be built separately from the micro-channel. The reaction mixture discharged is washed and dried by a washing unit and a drying unit respectively to obtain final graphitic oxide. The said supplying unit for graphite sulfuric slurry and the said supplying unit for $KMnO_4$ sulfuric solution are connected together to the beginning of the micro-channel or connected apart to the beginning of the micro-channel. For example, the said supplying unit for $KMnO_4$ sulfuric solution is connected to a latter portion of the beginning of the micro-channel while the said supplying unit for graphite sulfuric slurry is connected to a former portion thereof.

[37] According to the present invention, there is also provided equipment for producing nano-size graphene-based material continuously comprising:

[38] a supplying unit for graphitic oxide;

[39] a vertical fluidized furnace having a lower inlet for taking in reducing atmospheric gas and an upper inlet connected to the supplying unit for the graphitic oxide;

[40] a collector with its inlet mounted under the ceiling of the vertical furnace for collecting produced nano-size graphene-based material; and, if necessary;

[41] a cyclone having an inlet connected to the collector, a storage for the nano-size graphene-based material and an outlet connected to the lower inlet of the vertical furnace to resupply separated atmospheric gas to the vertical furnace.

[42] Graphene is single planar carbon material having honeycomb crystal lattice. In the present invention, nano-size graphene-based material is defined as single and multiple layers of graphene having less than 100 nm thickness and not showing any distinct peaks more than traces in the range 2θ〉 2°. The nano-size graphene-based material has surface area 300~3000 m2/g and residual oxygen of less than 1.0 weight %. Graphite is stacked layers of graphene with the distance between layers 3.35Å apart showing a peak at 2θ=26.5 by XRD, while the graphitic oxide in this invention means fully oxidized graphite having functional groups including oxygen such as carboxyl group, hydroxyl or so and showing a peak at 2θ=10-15 by XRD due to loosening the distance between layers. By thermal shock, the graphitic oxide is converted to nano-size graphene-based material by separation between layers.

[43] The said graphite sulfuric slurry is prepared by dispersing graphite flake of generally 1 to 200㎛, preferably 5 to 50㎛ in size in concentrated sulfuric acid, preferably 97 weight % or more sulfuric acid, in the ratio of 1:10 to 1:100, preferably 1:30 to 1:50 based on graphite to sulfuric acid by weight. Graphite flake of too small size does not well form graphene by exfoliation since expanding pressure decreases as weight density gets lower, while graphite flake of too large size hinders mass mixing and mass transfer in the micro-channel. Since the oxidation reactivity becomes higher as the concentration of sulfuric acid increases, concentrated sulfuric acid of more than 97 weight % is desirable. Too high weight ratio of graphite to sulfuric acid hinders mass mixing and mass transfer in the micro-channel due to high viscosity, while too low weight ratio of graphite to sulfuric acid lowers reaction efficiency and increases the amount of exhausted sulfuric acid. The graphite sulfuric slurry is supplied in a predetermined exact amount by a dosing pump directly connected to the beginning of the micro-channel.

[44] The said $KMnO_4$ sulfuric solution is prepared by dissolving $KMnO_4$ powder in concentrated sulfuric acid, preferably 97 weight % or more sulfuric acid, in the ratio of typically 1:5 to 1:50, preferably 1:10 to 1:30 based on $KMnO_4$ to sulfuric acid by

weight. $KMnO_4$ is added safely and easily to the reaction mixture in the micro-channel as solution type. The said $KMnO_4$ sulfuric solution is supplied in a predetermined exact amount by another dosing pump directly connected to the beginning of the micro-channel.

[45] The concentration of the said aqua solution of hydrogen peroxide is not specially limited but generally 1 to 10 w%, preferably 2 to 7 w%. The weight ratio of graphite to aqua solution of hydrogen peroxide is not limited specifically, but is empirically in the ratio of 1:10 to 1:100, preferably 1:30 to 1:50 like the ratio of graphite to sulfuric acid in the graphite sulfuric slurry. The said aqua solution of hydrogen peroxide terminates the oxidation of graphite by reducing extra $KMnO_4$. Too much hydrogen peroxide causes higher washing and drying costs, while too little hydrogen peroxide does not terminate the oxidation reaction. Retention time for the reduction is within several tens of minutes after the said aqua solution of hydrogen peroxide is added.

[46] The reaction mixture in the micro-channel is maintained between 0℃ to 50℃, preferably 20℃ to 35℃ after the said $KMnO_4$ sulfuric solution is added to the said graphite sulfuric slurry. The efficiency of reaction is low at lower temperature, but danger of explosion exists above 70℃ exists. The micro-channel, especially a reacting portion thereof is strictly controlled within the range of the temperatures to prevent explosion caused by local overheating. The micro-channel is surrounded by heat-exchangers having cooling means.

[47] The micro-channel is 1㎛ to several tens of ㎜, preferably 1㎛ to several ㎜, most preferably 1㎛ to 1㎜ in inner diameter formed in anti-corrosive and anti-acidic material. Inner diameter of the micro-channel of less than several tens of mm is favorable to maintaining the reaction mixture within the range of temperatures to prevent explosion. In addition, less than several mm of inner diameter is favorable to efficiency of reaction due to thorough mixing. Accordingly, 1㎛ to 1㎜ of inner diameter is most preferable to promote reaction efficiency and to secure safe operation. The reaction mixture moves typically at the speed of several centimeters to several meters per second, preferably several centimeters to several tens of centimeters per second. The reaction mixture sustains in the micro-channel for several minutes to several hours preferably, for several minutes to two hours most preferably after $KMnO_4$ sulfuric solution is added to the graphite sulfuric slurry.

[48] The said graphite sulfuric slurry, the said $KMnO_4$ sulfuric solution and the said aqua solution of hydrogen peroxide are supplied in the strictly controlled amount into the micro-channel by corresponding dosing pumps. Especially, the said graphite sulfuric slurry and the said $KMnO_4$ sulfuric solution are desirably supplied in sufficient pressure and at sufficient speed to the micro-channel to cause turbulent flow in the channel.

[49] The reaction mixture is discharged from an outlet of the micro-reactor after the said aqua solution of hydrogen peroxide is added to reduce extra $KMnO_4$ and to terminate oxidation. The discharged reaction mixture is washed once or more by pure water or a little acidic water of pH=5~6 and dried below 200 ℃, preferably under vacuum within 48 hours at 80℃. The washing and the drying may be carried out continuously following the former procedures or separately.

[50] According to the present invention, graphitic oxide may be converted to nano-size graphene-based material through thermal shock using a vertical fluidized furnace. To elaborate, graphitic oxide washed and dried according to the present invention is poured into the vertical fluidized furnace with ascending flow formed inside by atmospheric gas. The heating in the furnace is achieved by ordinary heaters or by microwave. The ascending flow is generated by the blow pressure of atmospheric gas or convection current caused by heating. The atmospheric gas is produced by adding hydrogen gas to inert carrier gas such as nitrogen and argon. The temperature in the furnace is maintained at 500℃ to 1100℃. Falling graphitic oxide particles are expanded and split in a layer or layers, and split layers of graphene are floating carried by ascending flow and are picked at the inlet of the collector mounted under the ceiling of the furnace. If necessary, nano-size graphene-based material is separated by cyclone. Fred atmospheric gas by the cyclone may be fed back to the furnace.

Advantageous Effects of Invention

[51] According to the present invention, graphitic oxide can be produced massively without risks of explosion by forcing all reagents as liquid phase continuously into a lengthy micro-channel surrounded and thermally controlled strictly by heat exchangers. Nano-size graphene-based material derived by exfoliating thus produced graphitic oxide can be imported into compositions and composites for various uses since it has physical characteristics comparable to carbon nanotube and dispersibility superior to carbon nanotube via residual functional groups.

Brief Description of Drawings

[52] Figure1 is a schematic flow chart showing an embodiment for equipment of producing graphitic oxide according to the present invention.

[53] Figure2 is a partial disintegrated perspective view of the micro-reactor in the equipment shown in Figure 1.

[54] Figure3 is a schematic flow chart showing an embodiment for equipment of producing nano-size graphene-based material according to the present invention.

Best Mode for Carrying out the Invention

[55] Hereinafter, exemplary embodiments of the invention will be described in detail with reference to the accompanying drawings, but they should not be construed to limit the

scope of the present invention. Various alternatives or modifications would be possible while they would be within the scope of the present invention.

[56] Figure 1 and Figure 2 describe a method of producing graphitic oxide and an equipment for producing the same as embodiments of the present invention. A micro-reactor(8) consists of multiple micro-channel modules(8a, 8b, 8c, 8d, 8e, 8f, 8g) surrounded by heat-exchangers(17) to form one linked lengthy micro-channel of 1㎛ to several ㎜ in inner diameter. The linked micro-channel starts at the beginning, run through the multiple micro-channel modules (8a, 8b, 8c, 8d, 8e, 8f, 8g) and end at the outlet.

[57] Graphite sulfuric slurry is made by mixing, in a premixer(7), sulfuric acid supplied by a dosing pump(4b) for liquid and graphite flake supplied by a dosing pump(3b) for powder and is forced into the beginning of the micro-channel(20). $KMnO_4$ sulfuric solution is made by mixing, in a premixer(5), sulfuric acid supplied by a dosing pump(4a) for liquid and graphite flake supplied by a dosing pump(3a) for liquid and is forced into the beginning of the micro-channel(20).

[58] A micro-reactor(8) consists of multiple micro-channel modules(8a, 8b, 8c, 8d, 8e, 8f, 8g) surrounded by heat-exchangers(17) to control temperature strictly. Each micro-channel module has a channel(20), an entrance(18a) and exit(18b) and is connected to each other through the entrance(18a) and the exit(18b) to constitute one lengthy micro-channel(20). Each micro-channel plane(18) is inserted between two plain heat-exchangers having an entrance(19a) and an exit(19b) for cooling medium to constitute one micro-channel module(8c). Micro-channel modules(8a, 8b, 8c, 8d, 8e, 8f, 8g) are desirably stacked to spare space with insulations inserted between modules. In the vicinity of the beginning of the micro-channel, the temperature is desirably controlled at the lower portion of the region ranging 0℃ to 35℃ considering fluctuations of inflow and safe mixing rather than efficiency of reaction. In the latter part of the reacting portion in the micro-channel, the temperature is desirably controlled around 35℃ to maintain the reaction speed on a higher level.

[59] The graphite sulfuric slurry and the $KMnO_4$ sulfuric solution are mixed together in the micro-channel(20)and the reaction mixture is running in the channel for about 20 minutes. To the reaction mixture flowing into the hydrogen peroxide mixing tank(11) after dilution with pure water, 3 w% aqua solution of hydrogen peroxide is added to terminate the oxidation. Discharged reaction mixture from the hydrogen peroxide mixing tank(11) is washed and dried(not shown in the figures) to obtain graphitic oxide.

[60] Figure 3 describes one embodiment of the conversion from graphitic oxide to nano-size graphene-based material according to the present invention. By a supplier(23) graphitic oxide washed and dried according to the present invention is poured into the

vertical fluidized furnace(21) with inner temperature maintained at around 800℃. The falling graphitic oxide(24) in the furnace(21) is expanded and split in a layer or layers, and split layers of graphene are floating carried by ascending flow and are picked and absorbed at the inlet of the collector(25) mounted under the ceiling of the furnace(21). nano-size graphene-based material is separated by cyclone(26). Separated furnace gas through cyclone(26) is resupplied to the lower inlet of the furnace(21) with atmospheric gas supplied via a pipe(33) and a gas mixer(32) connected to the nitrogen tank(29) and the hydrogen tank(30). Isolated nano-size graphene-based material is collected at a storage(28) at the bottom of cyclone(26).

Industrial Applicability

[61] According to the present invention, graphitic oxide, intermediate for graphene-based material can be produced economically and massively. Also according to the present invention, the nano-size graphene-based material made by exfoliating thus produced graphitic oxide can be used in various fields such as polymeric composites, fillers, rechargeable batteries, transistors, super-capacitor, containers for storing hydrogen and bio-sensors utilizing electronic, thermal and mechanical properties and flexibility of graphene comparable to carbon nanotube, and high surface area and dispersibility superior to carbon nanotube.

Claims

[Claim 1] a method of producing graphitic oxide comprising:
1) a step of preparing graphite sulfuric slurry by mixing graphite flake with sulfuric acid;
2) a step of preparing $KMnO_4$ sulfuric solution by dissolving $KMnO_4$ in sulfuric acid;
3) a step of preparing aqua solution of hydrogen peroxide;
4) a step of forcing the said graphite sulfuric slurry into a lengthy micro-channel having a beginning, a reacting portion and an outlet;
5) a step of forcing the said $KMnO_4$ sulfuric solution into a beginning of the said lengthy micro-channel;
6) a step of sustaining the mixture of the said graphite sulfuric slurry and the said $KMnO_4$ sulfuric solution in the said micro-channel at predetermined temperatures;
7) a step of putting the said aqua solution of hydrogen peroxide to the reaction mixture after the step 6);
8) a step of washing the reaction mixture after the step 7); and
9) a step of drying the reaction mixture after the step 8), wherein the steps 1) to 6) are carried out continuously

[Claim 2] According to Claim1, the method of producing graphitic oxide further comprising a step of filtering the reaction mixture after the step 6)

[Claim 3] According to Claim1, the method of producing graphitic oxide wherein the step 7) is carried out for the reaction mixture discharged from the outlet of the said micro-channel by a separate mixing tank

[Claim 4] According to Claim1, the method of producing graphitic oxide wherein forcing the $KMnO_4$ sulfuric solution is latter than forcing the graphite sulfuric slurry at the beginning of the micro-channel

[Claim 5] According to Claim4, the method of producing graphitic oxide wherein the flaky size of the graphite is 1 to 200㎛ and the ratio of graphite to sulfuric acid by weight is 1:10 to 1:100 in the said graphite sulfuric slurry, the ratio of $KMnO_4$ to sulfuric acid by weight is 1:5 to 1:50 in the said $KMnO_4$ sulfuric solution, the concentration of the sulfuric acid is 97 weight % or more, the reaction mixture in the micro-channel is maintained between 0°C to 50°C, the micro-channel is 1㎛ to several tens ㎜ in inner diameter, and the reaction portion of the micro-channel is surrounded by heat-exchangers

[Claim 6] According to Claim5, the method of producing graphitic oxide wherein the flaky size of the graphite is 5 to 50㎛ and the ratio of graphite to sulfuric acid by weight is 1:30 to 1:50 in the said graphite sulfuric slurry, the ratio of $KMnO_4$ to sulfuric acid by weight is 1:10 to 1:30 in the said $KMnO_4$ sulfuric solution, the concentration of the sulfuric acid is 97 weight % or more, the concentration of the said aqua solution of hydrogen peroxide is 2 to 7 w% and the weight ratio of graphite to aqua solution of hydrogen peroxide is 1:30 to 1:50 based on hydrogen peroxide 3wt % aqua solution, the reaction mixture in the micro-channel is maintained between 20℃ to 35℃, the micro-channel is 1㎛ to 1㎜ in inner diameter, the reaction portion of the micro-channel has length corresponding several minutes to 2 hours of retention time, and the reaction mixture moves at the speed of several centimeters to several tens of centimeters per second in the micro-channel

[Claim 7] a method of producing nano-size graphene-based material comprising:

1) a step of preparing graphite sulfuric slurry by mixing graphite flake with sulfuric acid;

2) a step of preparing $KMnO_4$ sulfuric solution by dissolving $KMnO_4$ in sulfuric acid;

3) a step of preparing aqua solution of hydrogen peroxide;

4) a step of forcing the said graphite sulfuric slurry into a lengthy micro-channel having a beginning, a reacting portion and an outlet;

5) a step of forcing the said $KMnO_4$ sulfuric solution into a beginning of the said lengthy micro-channel;

6) a step of sustaining the mixture of the said graphite sulfuric slurry and the said $KMnO_4$ sulfuric solution in the said micro-channel at pre-determined temperatures;

7) a step of putting the said aqua solution of hydrogen peroxide to the reaction mixture after the step 6);

8) a step of washing the reaction mixture after the step 7);

9) a step of drying the reaction mixture after the step 8) to obtain graphitic oxide ;

10) a step of pouring the graphitic oxide obtained into a vertical fluidized furnace in reducing atmosphere;

11) a step of expanding the falling graphitic oxide in the vertical fluidized furnace;

12) a step of collecting nano-size graphene-based material produced and carried on ascending flow near the ceiling of the vertical fluidized

furnace; and

13) a step of separating and storing the nano-size graphene-based material, wherein the step 1) to the step 6) and the step 10) to the step 13) are carried out continuously

[Claim 8] According to Claim7, the method of producing nano-size graphene-based material wherein the nano-size graphene-based material is less than 100 nm thick, and has surface area 300~3000 m^2/g and residual oxygen of less than 1.0 weight %

[Claim 9] According to Claim8, the method of producing nano-size graphene-based material wherein the flaky size of the graphite is 1 to 200㎛ and the ratio of graphite to sulfuric acid by weight is 1:10 to 1:100 in the said graphite sulfuric slurry, the ratio of $KMnO_4$ to sulfuric acid by weight is 1:5 to 1:50 in the said $KMnO_4$ sulfuric solution, the concentration of the sulfuric acid is 97 weight % or more, the reaction mixture in the micro-channel is maintained between 0℃ to 50℃, the micro-channel is 1㎛ to several tens of ㎜ in inner diameter, and the reaction portion of the micro-channel is surrounded by heat-exchangers

[Claim 10] According to Claim9, the method of producing nano-size graphene-based material wherein the flaky size of the graphite is 5 to 50㎛ and the ratio of graphite to sulfuric acid by weight is 1:30 to 1:50 in the said graphite sulfuric slurry, the ratio of $KMnO_4$ to sulfuric acid by weight is 1:10 to 1:30 in the said $KMnO_4$ sulfuric solution, the concentration of the sulfuric acid is 97 weight % or more, the concentration of the said aqua solution of hydrogen peroxide is 2 to 7 w% and the weight ratio of graphite to aqua solution of hydrogen peroxide is 1:30 to 1:50 based on hydrogen peroxide 3wt % aqua solution, the reaction mixture in the micro-channel is maintained between 20℃ to 35℃, the micro-channel is 1㎛ to 1㎜ in inner diameter, the reaction portion of the micro-channel has length corresponding several minutes to 2 hours of retention time, and the reaction mixture moves at the speed of several centimeters to several tens of centimeters per second in the micro-channel

[Claim 11] equipment for producing continuously graphitic oxide comprising:

a supplying unit for graphite sulfuric slurry;

a supplying unit for $KMnO_4$ sulfuric solution;

a supplying unit for aqua solution of hydrogen peroxide;

a micro-reactor including multiple micro-channel modules surrounded by heat-exchangers for constituting one lengthy micro-channel having a

beginning connected to the said supplying unit for graphite sulfuric slurry and connected to the said supplying unit for $KMnO_4$ sulfuric solution , a reacting portion and an outlet;
a mixing unit for mixing the reaction mixture discharged from the outlet of the micro-channel with aqua solution of hydrogen peroxide;
a washing unit for the reaction mixture discharged from the mixing unit; and
a drying unit to obtain graphitic oxide

[Claim 12] According to Claim11, equipment for producing continuously graphitic oxide wherein the micro-channel is formed by linking micro-channel modules

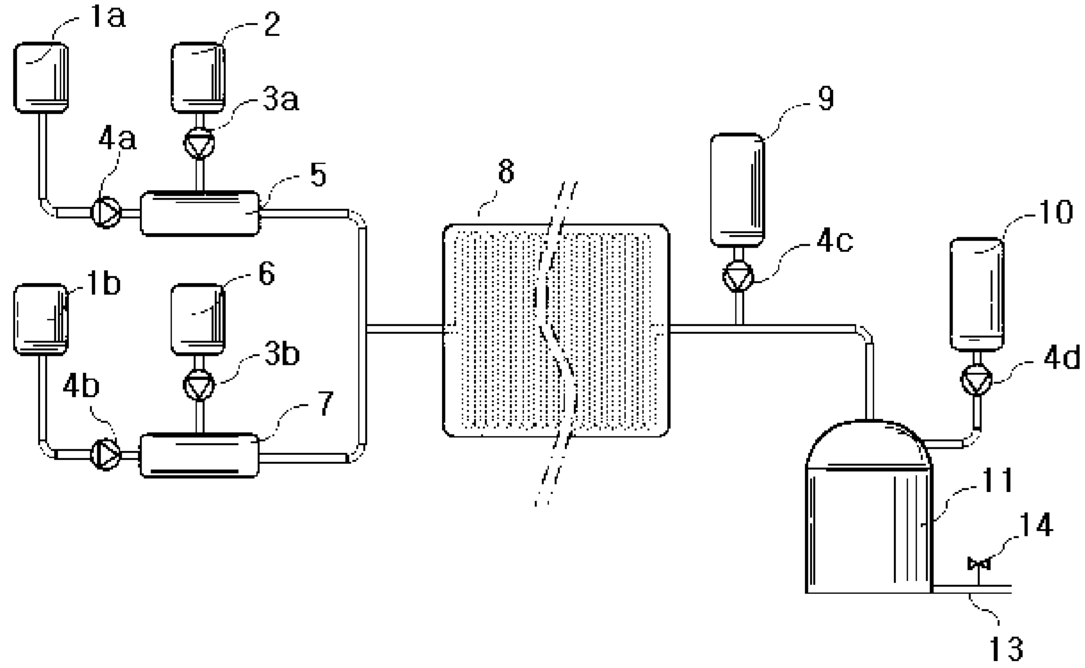
[Claim 13] According to Claim11, equipment for producing continuously graphitic oxide wherein the reaction portion of the micro-channel has length corresponding several minutes to 2 hours of retention time

[Claim 14] According to Claim11, equipment for producing continuously graphitic oxide wherein the mixing unit for mixing the reaction mixture with aqua solution of hydrogen peroxide may be incorporated as a part of the micro-channel

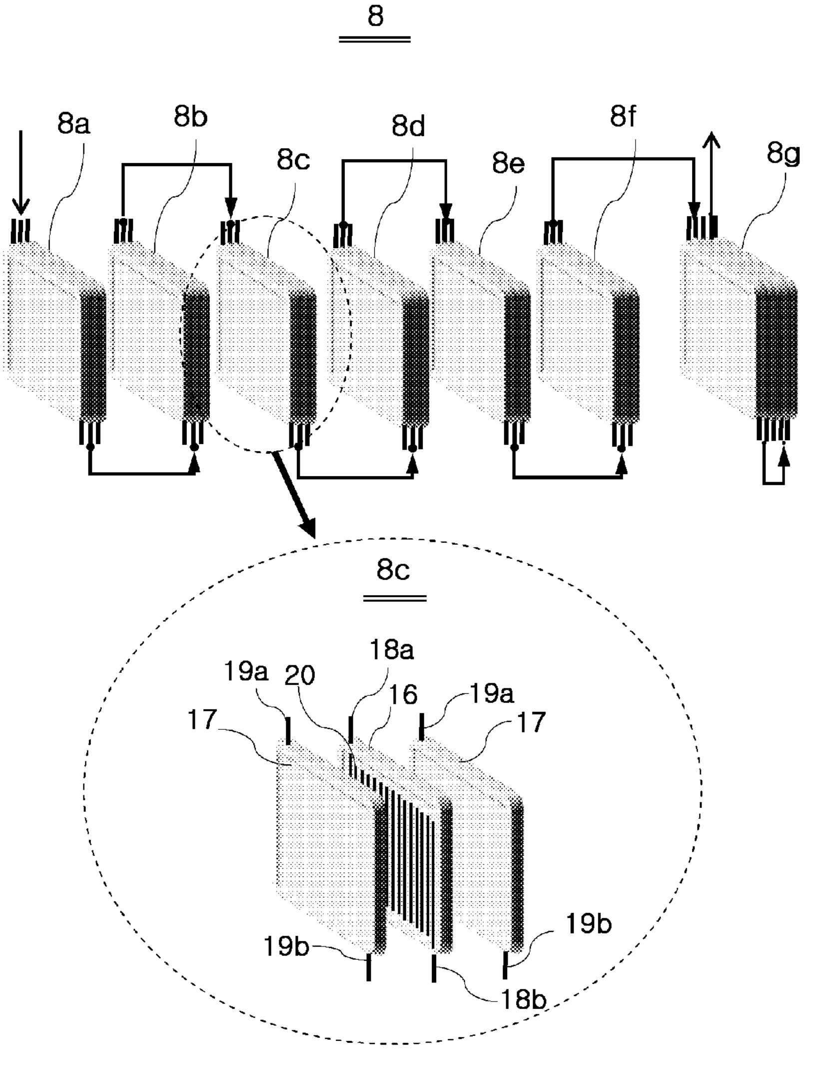
[Claim 15] equipment for producing continuously nano-size graphene-based material comprising:
a supplying unit for graphitic oxide;
a vertical fluidized furnace having an lower inlet for taking in reducing atmospheric gas and an upper inlet connected to the supplying unit for the graphitic oxide; and
a collector with its inlet mounted under the ceiling of the vertical furnace for collecting produced nano-size graphene-based material

[Claim 16] According to Claim 14, equipment for producing continuously nano-size graphene-based material further comprising a cyclone having an inlet connected to the collector, a storage for the nano-size graphene-based material separated and an outlet connected to the lower inlet of the vertical furnace to resupply separated atmospheric gas to the vertical furnace

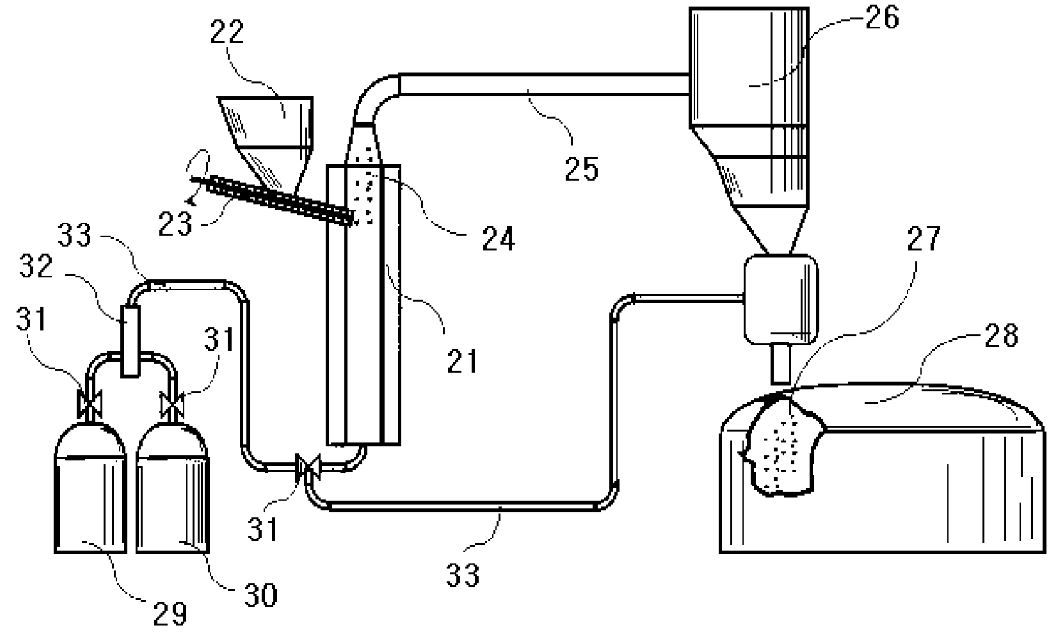
[Fig. 1]


1a
2
3a
4a
5
8
9
4c
10
1b
6
3b
4b
7
4d
11
14
13

[Fig. 2]


8
8a
8b
8c
8d
8e
8f
8g
8c
18a
19a
20
16
19a
17
17
19b
19b
18b

[Fig. 3]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2009/004465

A. CLASSIFICATION OF SUBJECT MATTER

C01B 31/04(2006.01)i, C01B 31/02(2006.01)i, B82B 3/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B 31/04; B05D 5/12; B82B 3/00; C01B 31/00; C08G 18/08; H01M 4/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: graphitic oxide, micro-channel, graphene, vertical fluidized furnace

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2001-256976 A (NICHIRIN CO., LTD.) 21 September 2001 See abstract, paragraphs 0031-0032.	1-6,11-14
A	US 2007-0092432 A1 (ROBERT PRUD`HOMME et al.) 26 April 2007 See abstract, paragraphs 0040-0095.	1-6,11-14
A	US 2006-0293443 A1 (ARNE REINHEIMER et al.) 28 December 2006 See abstract, paragraph 0037.	1-6,11-14
A	US 2008-0206124 A1 (JANG BOR Z. et al.) 28 August 2008 See abstract, paragraphs 0034-0055.	7-10,15-16
A	US 2009-0092747 A1 (ZHAMU ARUNA et al.) 09 April 2009 See abstract, paragraphs 0062-0081.	7-10,15-16
A	WO 2009-049375 A1 (UNIVERSITY OF WOLLONGONG et al.) 23 April 2009 See abstract; page 4, line 28-page 17, line 32.	7-10,15-16

☐ Further documents are listed in the continuation of Box C.　　☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 08 SEPTEMBER 2010 (08.09.2010)	Date of mailing of the international search report **08 SEPTEMBER 2010 (08.09.2010)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer LEE, Jin Hong Telephone No. 82-42-481-8649

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2009/004465

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

I. claims 1-6 and claims 11-14 are drawn to a method of producing graphitic oxide and an equipment for producing the same.

II. claims 7-10 and claims 15-16 are drawn to a method of producing nano-size graphene-based materials and an equipment for producing the same.

Since the above mentioned groups of claims do not share any of the technical features identified, a technically special relationship between the inventions does not exist.

Accordingly the claims do not relate to one invention or to a single inventive concept, a priori (PCT Rule 13.1).

1. ☒ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2009/004465

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		EP 2212248 A1	04.08.2010