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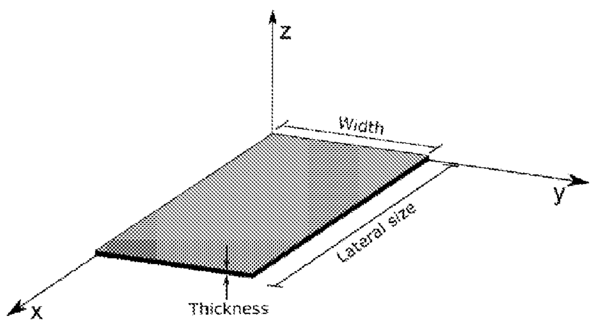
(54) **Title:** A METHOD FOR THE MANUFACTURE OF GRAPHENE OXIDE FROM KISH GRAPHITE

Figure 1



(57) **Abstract:** The present invention relates to a method for the manufacture of graphene oxide from Kish graphite comprising the pretreatment of kish graphite and the oxidation of pre-treated kish graphite into graphene oxide, the graphene oxide obtained with at least 45% by weight of oxygen functional groups and the use of the graphene oxide.

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A method for the manufacture of graphene oxide from Kish graphite

The present invention relates to a method for the manufacture of graphene oxide from Kish graphite. In particular, graphene oxide will have applications in metal industries including steel, aluminum, stainless steel, copper, iron, copper alloys, titanium, cobalt, metal composite, nickel industries, for example as coating or as a cooling reagent.

Kish graphite is a byproduct generated in the steelmaking process, especially during the blast furnace process or iron making process. Indeed, Kish graphite is usually produced on the free surface of molten iron during its cooling. It comes from molten iron at 1300–1500°C, which is cooled at a cooling rate between 0.40°C/min and 25°C/h when transported in the torpedo car or at higher cooling rates during the ladle transfer. An extensive tonnage of Kish graphite is produced annually in a steel plant.

Since Kish graphite comprises a high amount of carbon, usually above 50% by weight, it is a good candidate to produce graphene based materials. Usually, Graphene based materials include: graphene, graphene oxide, reduced graphene oxide or nanographite.

Graphene oxide is composed of one or few layers of graphene sheets containing oxygen functional groups. Thanks to its interesting properties such as a high thermal conductivity and a high electrical conductivity, graphene oxide has many applications as mentioned above. Moreover, the presence of oxygen functional groups make it hydrophilic and therefore it can be easily dispersed in water.

Usually, graphene oxide is synthesized based on Hummer Method comprising the following steps:

- the creation of a mixture of Kish graphite, sodium nitrate ($NaNO_3$) and sulfuric acid (H_2SO_4),
- the addition of sodium or potassium permanganate (KMnO4as oxidizing agent to oxidize graphite into graphite oxide and
- the mechanical exfoliation of graphite oxide into monolayer or a few layers of graphene oxide.

The patent KR101109961 discloses a method of manufacturing graphene, comprising:

- a step of pretreating Kish graphite,
- a step of manufacturing graphite oxide by oxidizing the pretreated Kish graphite with an acid solution;
- a step of manufacturing graphene oxide by exfoliating the graphite oxide and
- a step of manufacturing reduced graphene oxide by reducing the graphene oxide with a reducing agent.

In this Korean patent, the pre-treatment of Kish graphite comprises: a flushing process, a process of purification using a chemical pretreatment composition and a mechanical separation process (separation by size). After the process of purification, the purified Kish graphite is separated by size, the Kish graphite having a particle size of 40 mesh or less, i.e. 420μm or less, is kept for the manufacture of graphene oxide.

However, the pretreatment of Kish graphite comprises 2 steps using a chemical composition: the flushing step and the process of purification step. In the Example of KR101109961, the flushing step is performed with an aqueous solution comprising water, hydrochloric acid and nitric acid. Then, the process of purification is performed with a pretreatment composition comprising a chelating agent, an iron oxide remover, a surfactant, an anionic and nonionic polymer dispersant and distilled water. At industrial scale, two chemical treatments are difficult to manage since a lot of chemical waste has to be treated and the stability of such composition is difficult to control.

Moreover, the pretreatment composition needs a long time preparation. The productivity is therefore slowed. Additionally, the pre-treatment of Kish graphite including the process of purification using the pretreatment composition is not environmentally friendly.

Finally, the oxidation of the pretreated Kish graphite is performed with sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4) and potassium permanganate (KMnO4). Nevertheless, the use of sodium nitrate results in the formation of toxic gases such as NO_2, N_2O_4, and NH_3 which are not environmentally friendly.

The purpose of the invention is to provide a less polluting method for the manufacture of graphene oxide from Kish graphite compared to the conventional methods. Additionally, the object is to provide an industrial method to obtain graphene oxide having good quality in the shortest time possible.

This is achieved by providing a method according to claim 1. The method can also comprise any characteristics of claims 2 to 12 taken alone or in combination.

The invention also covers Graphene oxide according to claim 13.

The invention also covers the use of graphene oxide obtainable for the deposition on a metallic substrate according to claim 14.

Finally, the invention covers the use of graphene oxide as a cooling reagent according to claim 15.

The following terms are defined:

- Graphene oxide means one or a few layer(s) of graphene comprising oxygen functional groups including ketone groups, carboxyl groups, epoxy groups and hydroxyl groups and
- A flotation step means a process for selectively separating Kish graphite which is hydrophobic material from hydrophilic materials.

Other characteristics and advantages of the invention will become apparent from the following detailed description of the invention.

To illustrate the invention, various embodiments and trials of non-limiting examples will be described, particularly with reference to the following Figures:

Figure 1 illustrates an example of one layer of graphene oxide according to the present invention.

Figure 2 illustrates an example of a few layers of graphene oxide according to the present invention.

The invention relates to a method for the manufacture of graphene oxide from kish graphite comprising:

A. The provision of kish graphite,
B. A pre-treatment step of said kish graphite comprising the following successive sub-steps:
    i. A sieving step wherein the kish graphite is classified by size as follows:
        a) Kish graphite having a size below 50μm,
        b) Kish graphite having a size above or equal to 50μm,

the fraction a) of kish graphite having a size below 50 µm being removed,

ii. A flotation step with the fraction b) of kish graphite having a size above or equal to 50µm and

iii. An acid leaching step wherein an acid is added so that the ratio in weight (acid amount)/(kish graphite amount) is between 0.25 and 1.0,

C. An oxidation step of the pre-treated kish-graphite obtained after step B) in order to obtain graphene oxide comprising the following successive sub-steps:

i. The preparation of a mixture comprising the pre-treated kish-graphite, an acid and ammonium nitrate (NH_4NO_3), the mixture being kept at a temperature below 5°C,

ii. The addition of an oxidizing agent into the mixture obtained in step C.i),

iii. After the targeted level of oxidation is reached, the addition of an element to stop the oxidation reaction,

iv. the separation of graphite oxide from the mixture obtained in step C.iii) and

v. The exfoliation of graphite into graphene oxide.

Without willing to be bound by any theory, it seems that the method according to the present invention allows for the production of graphene oxide having good quality from high purity pre-treated Kish graphite. Indeed, the Kish graphite obtained after step B) has a purity of at least 90%. Moreover, the method including the pre-treatment of kish graphite and the oxidation into graphene oxide is easy to implement at industrial scale and is less polluting than methods of the prior art, in particular the one using $NaNO_3$. Indeed, on the one hand, it is believed that no toxic gases produced during the oxidation are N_2, O_2 and H_2O with NH_4NO_3 instead of toxic gases with $NaNO_3$. On the other hand, the amount of gases produced with NH_4NO_3 is higher than the one produced with $NaNO_3$. Thus, more gases are intercalated between the kish graphite layers so that during the oxidation step C.ii),

$KMnO_4$ can easily navigate between the kish graphite layers and oxidize them. It results in a significant reduction of the oxidation time compared to NaNO3.

Preferably, in step A), the Kish graphite is a residue of the steelmaking process. For example, it can be found in a blast furnace plant, in an iron making plant, in the torpedo car and during ladle transfer.

In step B.i), the sieving step can be performed with a sieving machine.

After the sieving, the fraction a) of Kish graphite having a size below 50 µm is removed. Indeed, without willing to bound by any theory, it is believed that the kish graphite having a size below 50µm contains a very small quantity of graphite, for example less than 10%.

Preferably in step B.ii), the flotation step is performed with a flotation reagent in an aqueous solution. For example, the flotation reagent is a frother selected from among: methyl isobutyl carbinol (MIBC), pine oil, polyglycols, xylenol, S-benzyl-S'-n-butyl trithiocarbonate, S,S'-dimethyl trithiocarbonate and S-ethyl-S'-methyl trithiocarbonate. Advantageously, the flotation step is performed using a flotation device.

Preferably, in step B.i), the fraction a) of kish graphite having a size below 55 µm is removed and in step B.ii), the fraction b) of kish graphite has a size above or equal to 55µm. More preferably, in step B.i), the fraction a) of kish graphite having a size below 60 µm is removed and wherein in step B.ii), the fraction b) of kish graphite has a size above or equal to 60µm.

Preferably, in steps B.i) and B.ii), the fraction b) of kish graphite has a size below or equal to 300 µm, any fraction of kish graphite having a size above 300 µm being removed before step B.ii).

More preferably in steps B.i) and B.ii), the fraction b) of kish graphite has a size below or equal to 275 µm, any fraction of kish graphite having a size above 275 µm being removed before step B.ii).

Advantageously, in steps B.i) and B.ii), the fraction b) of kish graphite has a size below or equal to 250 µm, any fraction of kish graphite having a size above 250 µm being removed before step B.ii).

In step B.iii), the (acid amount)/(kish graphite amount) ratio in weight is between 0.25 and 1.0, advantageously between 0.25 and 0.9, more preferably between 0.25 and 0.8. For example, the (acid amount)/(kish graphite amount) ratio in weight is between 0.4 and 1.0, between 0.4 and 0.9 or between 0.4 and 1. Indeed, without willing to be bound by any theory, it seems that if the (acid amount)/(kish graphite amount) ratio is below the range of the present invention, there is a risk that the kish graphite comprises a lot of impurities. Moreover, it is believed that if the (acid amount)/(kish graphite amount) ratio is above the range of the present invention, there is a risk that a huge amount of chemical waste is generated.

Preferably, in step B.iii), the acid is selected among the following elements: chloride acid, phosphoric acid, sulfuric acid, nitric acid or a mixture thereof.

Then, optionally, the kish graphite is washed and dried.

The pre-treated Kish graphite obtained after step B) of the method according to the present invention has a size above or equal to 50µm. The pre-treated Kish graphite has a high purity, i.e. at least of 90%. Moreover, the degree of crystallinity is improved compared to conventional methods allowing higher thermal and electrical conductivities and therefore higher quality.

In step C.i), the pre-treated kish graphite is mixed with an acid and ammonium nitrate (NH_4NO_3). Preferably in step C.i), the acid is selected among the following elements: chloride acid, phosphoric acid, sulfuric acid, nitric acid or a mixture thereof. In a preferred embodiment, the mixture comprises the pre-treated kish-graphite, sulfuric acid and ammonium nitrate.

Preferably in step C.ii), the oxidizing agent is chosen from: potassium permanganate ($KMnO_4$), H_2O_2, O_3, $H_2S_2O_8$, H_2SO_5, KNO_3, NaClO or a mixture thereof. In a preferred embodiment, the oxidizing agent is potassium permanganate.

Then, advantageously in step C.iii), the element used to stop the oxidation reaction is chosen from: an acid, non-deionized water, deionized water, H_2O_2 or a mixture thereof.

In a preferred embodiment, when at least two elements are used to stop the reaction, they are used successively or simultaneously. Preferably, deionized water is used to stop the reaction and then H_2O_2 is used to eliminate the rest of the oxidizing agent. In another preferred embodiment, H_2O_2 is used to stop the reaction and eliminate the rest of the oxidizing agent. In another preferred embodiment, H_2O_2 is used to stop the reaction by this following reaction:

$$2KMnO_4 + 3H_2O_2 = 2MnO_2 + 3O_2 + 2KOH + 2H_2O.$$

Then, to eliminate MnO_2, an acid can be used. For example, HCl is added to the mixture so that the following reaction happens:

$$MnO_2 + 2HCl = MnCl_2 \text{ (soluble in water)} + H_2O.$$

Without willing to be bound by any theory, it seems that when the element to stop the reaction is added into the mixture, there is a risk that this addition is too exothermic resulting in explosion or splashing. Thus, preferably in step C.iii), the element used to stop the reaction is slowly added into the mixture obtained in step C.ii). More preferably, the mixture obtained in step C.ii) is gradually pumped into the element used to stop the oxidation reaction. For example, the mixture obtained in step C.ii) is gradually pumped into deionized water to stop the reaction.

In step C.iv), graphite oxide is separated from the mixture obtained in step C.iii). Preferably, the graphite oxide is separated by centrifugation, by decantation or filtration.

Then, optionally, graphite oxide is washed. For example, graphite oxide is washed with an element chosen from among: deionized water, non-deionized water, an acid or a mixture thereof. For example, the acid is selected among the following elements: chloride acid, phosphoric acid, sulfuric acid, nitride acid or a mixture thereof.

After, the graphite oxide can be dried, for example with air or at high temperature in the vacuum condition.

Preferably in step C.v), the exfoliation is performed by using ultrasound or thermal exfoliation. Preferably, the mixture obtained in step C.iii) is exfoliated into one or a few layers of graphene oxide.

By applying the method according to the present invention, Graphene oxide comprising at least 45% by weight of oxygen functional groups and having an average lateral size between 5 and 50µm, preferably between 10 and 40µm and more preferably between 10 and 30 µm comprising at least one layer sheet is obtained.

Figure 1 illustrates an example of one layer of graphene oxide according to the present invention. The lateral size means the highest length of the layer through the X axis, the thickness means the height of the layer through the Z axis and the width of the nanoplatelet is illustrated through the Y axis.

Figure 2 illustrates an example of a few layers of graphene oxide according to the present invention. The lateral size means the highest length of the layer through the X axis, the thickness means the height of the layer through the Z axis and the width of the nanoplatelet is illustrated through the Y axis.

The obtained graphene oxide has good quality since it is produced from the pre-treated Kish graphite of the present invention. The percentage of oxygen functionalities is high. Thus, the graphene oxide is easy dispersible in water and other organic solvents.

Preferably, graphene oxide is deposited on metallic substrate steel to improve some properties such as corrosion resistance of a metallic substrate.

In another preferred embodiment, graphene oxide is used as cooling reagent. Indeed, graphene oxide can be added to a cooling fluid. Preferably, the cooling fluid can be chosen from among: water, ethylene glycol, ethanol, oil, methanol, silicone, propylene glycol, alkylated aromatics, liquid Ga, liquid In, liquid Sn, potassium formate and a mixture thereof. In this embodiment, the cooling fluid be used to cool down a metallic substrate.

For example, the metallic substrate is selected from among: aluminum, stainless steel, copper, iron, copper alloys, titanium, cobalt, metal composite, nickel.

The invention will now be explained in trials carried out for information only. They are not limiting.

Examples:

Trials 1, 2 and 3 were prepared by providing Kish graphite from steelmaking plant. Then, Kish graphite was sieved to be classified by size as follows:

a) Kish graphite having a size below < 63µm and
b) Kish graphite having a size above or equal to 63µm.

The fraction a) of Kish graphite having a size below 63 µm was removed.

For Trials 1 and 2, a flotation step with the fraction b) of Kish graphite having a size above or equal to 63µm was performed. The flotation step was performed with a Humboldt Wedag flotation machine with MIBC as frother. The following conditions were applied:

- Cell volume (l): 2,
- Rotor speed (rpm): 2000,
- Solid concentration (%): 5-10,
- Frother, type: MIBC,
- Frother, addition (g/T): 40,
- Conditioning time (s): 10 and
- Water conditions: natural pH, room-temperature.

All Trials were then leached with the hydrochloric acid in aqueous solution. Trials were then washed with deionized water and dried in air at 90º C.

After, Trial 1 was mixed with ammonium nitrate and sulfuric acid while Trials 2 and 3 were mixed with sodium nitrate and sulfuric acid in an ice-bath. Potassium permanganate was slowly added into Trials 1 to 3. Then, mixtures were transferred into water bath and kept at 35°C to oxidize the Kish graphite.

After the oxidation, Trials were gradually pumped into deionized water.

For Trial 1, the heat was removed and H_2O_2 in aqueous solution was added until there was no gas producing. MnO_2 was produced. Then, HCl was added to the mixture to eliminate MnO_2.

For Trials 2 and 3, After stopping the oxidation reaction, the heat was removed and H_2O_2 in aqueous solution was added until there was no gas producing and mixtures were stirred to eliminate the rest of H_2O_2.

Then, for all Trials, Graphite oxide was separated from the mixture by decantation. They were exfoliated using ultrasound in order to obtain one or two layer(s) of graphene oxide. Finally, graphene oxide was separated from the mixture by centrifugation, washed with water and dried with air to obtain graphene oxide powder. Table 1 shows the results obtained.

Method		Trial 1 *	Trial 2	Trial 3
Origin of Kish graphite		Steelmaking plant	Steelmaking plant	Steelmaking plant
Pre-treatment of Kish graphite	Sieving step	Done, Kish graphite having a size above or equal to 63µm kept	Done, Kish graphite having a size above or equal to 63µm kept	Done, Kish graphite having a size above or equal to 63µm kept
	Flotation step	Done	Done	Not done
	Acid leaching step	Done with HCl, (the acid amount)/(kish graphite amount) ratio in weight is of 0.78	Done with HCl, (the acid amount)/(kish graphite amount) ratio in weight is of 0.78	Done with HCl, (the acid amount)/(kish graphite amount) ratio in weight is of 1.26
Pre-treated kish graphite purity		95%	95%	74.9%
Oxidation step	preparation of the mixture	Done with H_2SO_4 and NH_4NO_3	Done with H_2SO_4 and $NaNO_3$	Done with H_2SO_4 and $NaNO_3$
	Gases produced	N_2, O_2 and H_2O	NO_2, N_2O_4 and NH_3	NO_2, N_2O_4 and NH_3
	Addition of an oxidizing agent	$KMnO_4$	$KMnO_4$	$KMnO_4$
	Oxidation time	1h30min	3hours	3hours
	Element to stop the reaction	Water followed by H_2O_2	Water followed by H_2O_2	Water followed by H_2O_2
	Exfoliation	Ultrasound	Ultrasound	Ultrasound
Product obtained		Graphene oxide comprising 49% of oxygen groups and having an average Lateral size from 10 to 20 µm with purity of 99,5 %	Graphene oxide comprising 40% of oxygen groups and having an average Lateral size from 20 to 35 µm with purity of 99.5%	Graphene oxide comprising 30% of oxygen groups and having an average lateral size from 20 to 35 µm with purity of 99.0%

* according to the present invention

The method of Trial 1 is more environmentally friendly than the method used for Trials 2 and 3. Moreover, the oxidation time with the method of Trial 1 is divided by two. Finally, the graphene oxide obtained with Trial 1 has a high quality comprises more oxygen functional groups compared to Trials 2 and 3.

CLAIMS

1. Method for the manufacture of graphene oxide from kish graphite comprising:
   A. The provision of kish graphite,
   B. A pre-treatment step of said kish graphite comprising the following successive sub-steps:
      i. A sieving step wherein the kish graphite is classified by size as follows:
         a) Kish graphite having a size below 50μm,
         b) Kish graphite having a size above or equal to 50μm,

      the fraction a) of kish graphite having a size below 50 μm being removed,
      ii. A flotation step with the fraction b) of kish graphite having a size above or equal to 50μm and
      iii. An acid leaching step wherein an acid is added so that the ratio in weight (acid amount)/(kish graphite amount) is between 0.25 and 1.0,
   C. An oxidation step of the pre-treated kish-graphite obtained after step B) in order to obtain graphene oxide comprising the following successive sub-steps:
      i. The preparation of a mixture comprising the pre-treated kish-graphite, an acid and ammonium nitrate (NH_4NO_3), the mixture being kept at a temperature below 5°C,
      ii. The addition of an oxidizing agent into the mixture obtained in step C.i),
      iii. After the targeted level of oxidation is reached, the addition of an element to stop the oxidation reaction,

iv. Optionally, the separation of graphite oxide from the mixture obtained in step C.iii) and

v. The exfoliation of graphite oxide into graphene oxide.

2. Method according to claim 1, wherein in step B.i), the fraction a) of kish graphite having a size below 55 µm is removed and in step B.ii), the fraction b) of kish graphite has a size above or equal to 55µm.

3. Method according to claim 2, wherein in steps B.i) and B.ii), the fraction b) of kish graphite has a size below or equal to 300 µm, any fraction of kish graphite having a size above 300 µm being removed before step B.ii)

4. Method according to anyone of claims 1 to 3, wherein in step B.iii), the acid amount/kish graphite amount ratio in weight is between 0.25 and 0.9.

5. Method according to anyone of claims 1 to 4, wherein in step B.iii), the acid is selected among the following elements: chloride acid, phosphoric acid, sulfuric acid, nitric acid or a mixture thereof.

6. Method according to anyone of claims 1 to 5, wherein in step C.ii), the oxidizing agent is chosen from: potassium permanganate (KMnO4), H_2O_2, O_3, $H_2S_2O_8$, H_2SO_5, KNO_3, NaClO or a mixture thereof.

7. Method according to anyone of claims 1 to 6, wherein in step C.iii), the element used to stop the oxidation reaction is chosen from: an acid, non-deionized water, deionized water, H_2O_2 or a mixture thereof.

8. Method according to claim 7, wherein when at least two elements are chosen to stop the reaction, they are used successively or simultaneously.

9. Method according to anyone of claims 1 to 8, wherein in step C.iii), the mixture obtained in step C.ii) is gradually pumped into the element used to stop the oxidation reaction.

10. Method according to anyone of claims 1 to 9, wherein in step C.vii), the exfoliation is performed by using ultrasound or thermal exfoliation.

11. Method according to anyone of claims 1 to 10, wherein in step C.iv), the graphite oxide is separated by centrifugation, by decantation or filtration.

12. Method according to anyone of claims 1 to 11, wherein in step C.i), the acid is selected among the following elements: chloride acid, phosphoric acid, sulfuric acid, nitric acid or a mixture thereof.

13. Graphene oxide comprising at least 45% by weight of oxygen functional groups and having an average lateral size between 5 and 50µm comprising at least one layer sheet obtainable from the method according to anyone of the claims 1 to 12.

14. Use of graphene oxide obtainable from the method according to anyone of claims 1 to 12 or according to claim 13 for the deposition on a metallic substrate.

15. Use of graphene oxide obtainable from the method according to anyone of the claims 1 to 12 or according to claim 13 as a cooling reagent.

Figure 1

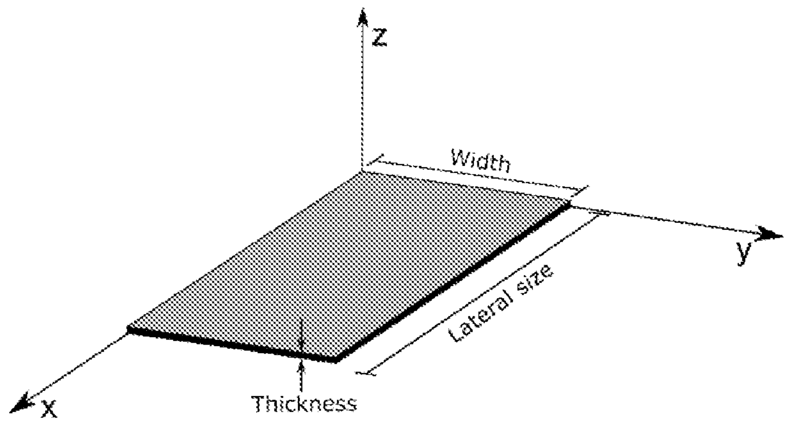
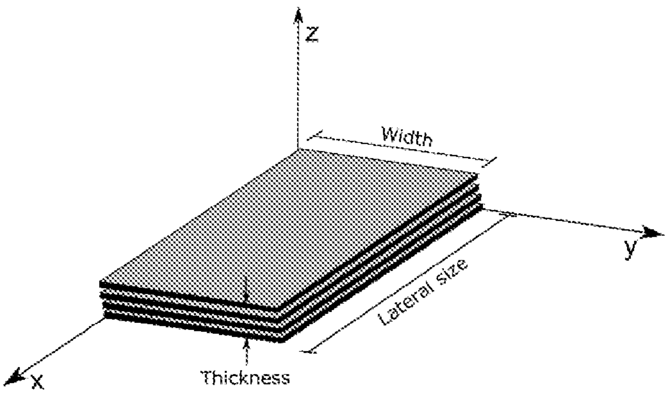


Figure 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/053415

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B32/23 C01B32/184 C01B32/194
ADD.

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

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2017/027731 A1 (METOXS PTE LTD [SG]; JALBOUT ABRAHAM [US]) 16 February 2017 (2017-02-16) paragraphs [0018] - [0037]; claims 1-20	1-15
X	JIANGUO SONG ET AL: "Preparation and Characterization of Graphene Oxide", JOURNAL OF NANOMATERIALS, vol. 2014, 1 January 2014 (2014-01-01), pages 1-6, XP055557522, US ISSN: 1687-4110, DOI: 10.1155/2014/276143 "Experiment and methods", " Results and discussion"; figure 1; table 1	13,14

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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Date of the actual completion of the international search	Date of mailing of the international search report
19 February 2019	25/02/2019

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/053415

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RANJBARZADEH RAMIN ET AL: "Empirical analysis of heat transfer and friction factor of water/graphene oxide nanofluid flow in turbulent regime through an isothermal pipe", APPLIED THERMAL ENGINEERING, PERGAMON, OXFORD, GB, vol. 126, 27 July 2017 (2017-07-27), pages 538-547, XP085198090, ISSN: 1359-4311, DOI: 10.1016/J.APPLTHERMALENG.2017.07.189 "Experimental approach"	15
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