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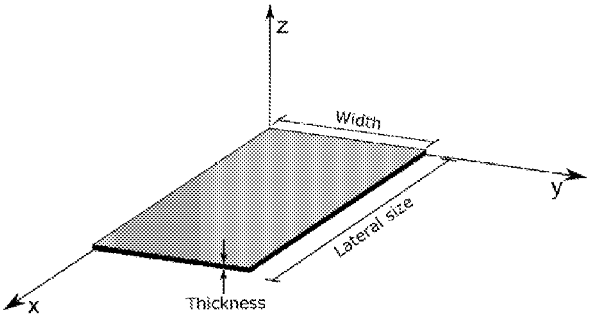
(54) **Title:** A METHOD FOR THE MANUFACTURE OF REDUCED GRAPHENE OXIDE FROM EXPANDED KISH GRAPHITE

Figure 1



(57) **Abstract:** The present invention relates to a method for the manufacture of reduced graphene oxide from kish graphite comprising: A. The provision of kish graphite, B. Optionally, a pre-treatment of kish graphite, C. The intercalation of kish graphite with a persulfate salt and an acid at room temperature to obtain intercalated kish graphite, D. The expansion of the intercalated kish graphite to obtain expanded kish graphite and E. An oxidation step of the expanded kish graphite to obtain graphene oxide and F. A reduction of graphene oxide into reduced graphene oxide.

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A method for the manufacture of reduced graphene oxide from expanded kish graphite

The present invention relates to a method for the manufacture of reduced graphene oxide from expanded Kish graphite. In particular, reduced 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.

It is known to produce reduced graphene oxide (rGO) by reducing graphene oxide (GO). Reduced graphene oxide is composed of one or a few layers of graphene sheets containing some oxygen functional groups. Thanks to its interesting properties such as a high thermal conductivity and a high electrical conductivity, reduced graphene oxide, being hydrophobic, has many applications.

For example, reduced Graphene Oxide can be produced by chemical process such as a reduction of graphene oxide using a reducing agent such as hydrazine, ascorbic acid, urea, NaOH or by mechanical process such as thermal reduction at high temperature in an inert atmosphere. However, rGO with low oxygen content, i.e lower than 10%, is very difficult to obtain. Indeed, chemical or mechanical processes usually provides rGO having more than 10% of oxygen groups. Some oxygens groups such as epoxy groups are very difficult to reduce with conventional methods. In addition, the obtained rGO contains lot of defects thus demonstrating very low electrical conductivity.

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

- the oxidation of Kish graphite with sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4) and sodium or potassium permanganate ($KMnO_4$) and
- the reduction of graphene oxide to obtain the reduced graphene oxide.

The patent application WO2018178845 discloses a method for the manufacture of reduced 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,

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,

iv. Optionally, the kish graphite is washed and dried,

C. An oxidation step of the pre-treated kish graphite obtained after step B) in order to obtain graphene oxide with an acid, sodium nitrate and an oxidizing agent and

D. A reduction of graphene oxide into reduced graphene oxide.

Nevertheless, when the oxidation step is performed with sodium nitrate ($NaNO_3$), toxic gases are produced leading to a polluting method. Moreover, the oxidation time is very long using (around 3 hours).

The patent application PCT/IB2019/052804 discloses a method for the manufacture of reduced 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 50µm being removed,

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

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,

iv. Optionally, the kish graphite is washed and dried,

C. An oxidation step of the pre-treated kish graphite in order to obtain graphene oxide with an acid, ammonium nitrate (NH_4NO_3) and an oxidizing agent and

D. A reduction of graphene oxide into reduced graphene oxide.

However, although the method using NH_4NO_3 is less polluting than the method using $NaNO_3$, there is a need to further provide an even less polluting method and to reduce the energy consumption.

Additionally, although the oxidation time is shorter using NH_4NO_3, i.e. 1hour and 30minutes, compared to the oxidation time of the method using $NaNO_3$, i.e. 3hours, there is still a need to reduce the oxidation time and therefore to improve the productivity of the synthesis of reduced graphene oxide.

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

This is achieved by providing a method for the manufacture of reduced graphene oxide from kish graphite comprising:

A. The provision of kish graphite,

B. Optionally, a pre-treatment of kish graphite,

C. The intercalation of kish graphite with a persulfate salt and an acid at room temperature to obtain intercalated kish graphite,

D. The expansion of the intercalated kish graphite at room temperature to obtain expanded kish graphite,

E. An oxidation step of the expanded kish graphite to obtain graphene oxide and

F. A reduction of graphene oxide into reduced graphene oxide.

The method according to the invention may also have the optional features listed below, considered individually or in combination:

- In step B), the pre-treatment of kish graphite comprises the following successive sub-steps:
  - A sieving step wherein the kish graphite is classified by size as follows:
    - Kish graphite having a size below 50µm,
    - Kish graphite having a size above or equal to 50µm,

    the fraction a) of kish graphite having a size below 50 µm being removed,
  - A flotation step with the fraction b) of kish graphite having a size above or equal to 50µm,
  - 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,
  - Optionally, the kish graphite is washed and dried,
- In step C), the ratio in weight of persulfate salt with respect to kish graphite is between 1 and 8,
- In step C), the ratio in weight of the acid with respect to kish graphite is between 2 and 8,
- In step C), the persulfate salt is chosen from: Sodium persulfate ($Na_2S_2O_8$), Ammonium persulfate ($(NH_4)_2S_2O_8$) and Potassium persulfate ($K_2S_2O_8$) or a mixture thereof,
- In step C), the acid is chosen from: H_2SO_4, HCl, HNO_3, H_3PO_4, $C_2H_2Cl_2O_2$ (dichloroacetic acid), HSO_2OH (alkylsulfonic acid) or a mixture thereof,

- In step D), the expansion is naturally performed by leaving the kish graphite, the persulfate salt and the acid at room temperature in an open vessel,
- Step E) comprises the following successive sub-steps:
    - The mixture of the expanded kish graphite with an acid, an oxidizing agent and optionally a salt,
    - The addition of a chemical element to stop the oxidation reaction,
    - the separation of graphite oxide from the mixture obtained in step E.ii),
    - The exfoliation of graphite oxide into graphene oxide,
- In step E.i), the salt is a nitrate salt chosen from: $NaNO_3$, NH_4NO_3, KNO_3, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Al(NO_3)_3$ or a mixture thereof,
- In step E.i), the acid is chosen from: H_2SO_4, HCl, HNO_3, H_3PO_4, $C_2H_2Cl_2O_2$ (dichloroacetic acid), HSO_2OH (alkylsulfonic acid) or a mixture thereof,
- In step E.i), the oxidizing agent is chosen from: potassium permanganate, H_2O_2, O_3, $H_2S_2O_8$, H_2SO_5, KNO_3, NaClO or a mixture thereof,
- In step E.ii), the chemical element used to stop the oxidation reaction is chosen from: an acid, non-deionized water, deionized water, H_2O_2 or a mixture thereof,
- When at least two chemical elements are chosen to stop the reaction, they are used successively or simultaneously,
- In step E.ii), the mixture obtained in step E.i) is gradually pumped into the chemical element used to stop the oxidation reaction,
- In step E.iii), the graphite oxide is separated by centrifugation, decantation, distillation or filtration,
- In step E.iv), the exfoliation is performed by using ultrasound, mechanical agitator, sieve shaker or thermal exfoliation,
- Step F) comprises the following sub-steps:

  - The reduction of GO into reduced graphene oxide (rGO), comprising one or a few layer(s) of graphene having between 10 and 25% by weight of oxygen functional groups, using a reducing agent and
  - Optionally, the reduction of rGO into microwave-reduced graphene oxide (MW-rGO), comprising one or a few layer(s) of graphene having less than 10% by weight of oxygen functional groups, by microwaving rGO under air atmosphere in presence of a catalyst,

- In step F.i), the reducing agent is chosen from: acid ascorbic; urea; hydrazine hydrate; alkaline solution such as NaOH or KOH; phenols such as gallic acid, tannin acid, dopamine or tea polyphenol; alcohols such as methyl alcohol, ethyl alcohol or isopropyl alcohol; glycine; sodium citrate or sodium borohydride,
- In step F.ii), the catalyst is chosen from: pristine graphene, graphene nanoplatelet(s), graphite or graphite nanoplatelets.

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,
- Reduced graphene oxide means graphene oxide that has been reduced. The reduced graphene oxide comprises one or a few layer(s) of graphene having some oxygen functional groups including ketone groups, carboxyl groups, epoxy groups and hydroxyl groups,
- Pristine graphene means that graphene is in its original condition, i.e. ideal, and does not have any defect.
- room temperature means between 0 and 45°C at atmospheric pressure.

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

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

A. The provision of kish graphite,
B. Optionally, a pre-treatment of kish graphite,
C. The intercalation of kish graphite with a persulfate salt and an acid at room temperature to obtain intercalated kish graphite,
D. The expansion of the intercalated kish graphite at room temperature to obtain expanded kish graphite,
E. An oxidation step of the expanded kish graphite to obtain graphene oxide and
F. A reduction of graphene oxide into reduced graphene oxide.

The method according to the present invention allows for the production of reduced graphene oxide having good quality. Moreover, the method including notably the intercalation at room temperature, the expansion at room temperature and the oxidation into graphene oxide, it is easy to implement at industrial scale and it is less polluting than methods of the prior art.

Without willing to be bound by any theory, it is believed that during the expansion, the persulfate salt acts like an oxidant to oxidize the edges of the kish graphite layers. Since the persulfate salt is an important oxygen donor, the intercalation gap between two kish graphite layers is further improved allowing the acid to enter more easily between the kish graphite layers. At the same time, a certain amount of persulfate salt can be dragged by the acid in the kish graphite interlayers. It is believed that the persulfate salt dragged in the interlayers will decompose and release O_2 gas causing an instantaneous pressure in the kish graphite interlayers making an exponential expansion of graphite at room temperature. The energy consumption is thus reduced and expanded kish graphite is easily obtained.

Moreover, it is believed that using expanded kish graphite according to the present invention significantly reduces the oxidation time compared to the methods for the manufacture of graphene oxide of the prior art. Indeed, it is believed that since there is a higher expansion volume, it is easier to oxidize the kish graphite layers since the gap between two kish graphite layers is higher using the persulfate salt and the acid. Thus, the oxidation time is significantly reduced and graphene oxide is easily obtained.

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 ironmaking plant, in a steelmaking plant, in the torpedo car and during ladle transfer.

Preferably, in step B), the pre-treatment of kish-graphite comprises 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,

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,

iv. Optionally, the kish graphite is washed and dried.

Without willing to be bound by any theory, it seems that when the kish graphite is pre-treated with the method according to the present invention, it allows for the production of reduced graphene oxide having improved quality since the pre-treated Kish graphite has a high purity. Indeed, the Kish graphite obtained after step B) has a purity of at least 90%. Moreover, the pre-treatment step B) is easy to implement at industrial scale and is more environmentally friendly than conventional methods.

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 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: hydrochloric acid, phosphoric acid, sulfuric acid, nitric acid or a mixture thereof.

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.

Once kish graphite has been provided and optionally pre-treated, it is intercalated with a persulfate salt and an acid at room temperature to obtain intercalated kish graphite (step C).

Preferably, in step C), the ratio in weight of persulfate salt with respect to kish graphite is between 1 and 8, more preferably between 1 and 6 and advantageously between 1 and 5. Indeed, without willing to be bound by any theory, it seems that the intercalation is further improved.

Preferably, in step C), the ratio in weight of the acid with respect to kish graphite is between 2 and 8, more preferably between 4 and 8. Indeed, if the ratio of the acid with respect to kish graphite is below 2, there is a risk that only a part of kish graphite is expanded. If the ratio of the acid with respect to kish graphite is above 8, there is a risk that the expansion occurs very slowly and that the volume expansion decreases. It is believed that the acid in excess prevent the persulfate salt from being dragged in the kish graphite interlayer. Therefore, it prevents the release of oxygen from the decomposition of the persulfate salt and thus the exponential expansion of kish graphite.

Preferably, in step C), the persulfate salt is chosen from the ones containing the peroxydisulfate anion $S_2O_8^{2-}$ More preferably, the persulfate salt is chosen from: Sodium persulfate ($Na_2S_2O_8$), Ammonium persulfate ($(NH_4)_2S_2O_8$) and Potassium persulfate ($K_2S_2O_8$) or a mixture thereof.

Preferably, in step C), the acid is a strong acid. More preferably, the acid is chosen from: H_2SO_4, HCl, HNO_3, H_3PO_4, $C_2H_2Cl_2O_2$ (dichloroacetic acid), HSO_2OH (alkylsulfonic acid) or a mixture thereof.

Preferably, in step C), kish graphite is first mixed with the acid and then the persulfate salt is added.

Preferably step C) lasts from 2 to 30 minutes.

Once kish graphite has been intercalated, it is expanded (step D).

Preferably, in step D), the expansion is naturally performed by leaving the kish graphite, the persulfate salt and the acid at room temperature in an open vessel. For example, the components are in an opened bowl, opened glassware, opened lab reactor or opened pilot reactor.

Preferably, step D) lasts from 2 to 60 minutes.

Once kish graphite has been expanded, it is oxidized to obtain graphene oxide (step E).

Preferably, step E) comprises the following successive sub-steps:

i. The mixture of the expanded kish graphite, an acid, an oxidizing agent and optionally a salt,
ii. The addition of a chemical element to stop the oxidation reaction,
iii. the separation of graphite oxide from the mixture obtained in step E.ii),
iv. The exfoliation of graphite oxide into graphene oxide.

Thanks to the expanded kish graphite, the oxidation time is significantly reduced compared to the oxidation steps of the prior art. Indeed, the oxidation time can be as short as 10 minutes compared to oxidation times of several hours for the oxidation steps of the prior art. Preferably the oxidation of the expanded kish graphite with an acid, an oxidizing agent and optionally a salt lasts from 5 to 15 minutes. Moreover, it seems that the oxidation of the expanded kish graphite without any salt, allows for an even shorter oxidation time. The ability to remove the salt from the oxidation step significantly limits pollution. Thus, preferably, the expanded kish graphite is mixed with an acid and an oxidizing agent, without any salt. In other words, the mixture of step E.i) preferably consists of kish graphite, acid and oxidizing agent.

Optionally, in step E.i), the salt is chosen from: $NaNO_3$, NH_4NO_3, KNO_3, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Al(NO_3)_3$ or a mixture thereof. Preferably the ratio in weight of salt with respect to the kish graphite is between 0.2 and 2.

Preferably, in step E.i), the acid is chosen from: H_2SO_4, HCl, HNO_3, H_3PO_4, $C_2H_2Cl_2O_2$ (dichloroacetic acid), HSO_2OH (alkylsulfonic acid) or a mixture thereof.

Preferably, in step E.i), 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. Preferably the ratio in weight of oxidizing agent with respect to kish graphite is between 2 and 10.

Then, advantageously in step E.ii), the chemical 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 chemical 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, hydrochloric acid 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 by this following reaction:

$$2KMnO_4 + H_2O_2 + 3H_2SO_4 = 2MnSO_4 + O_2 + K_2SO_4 + 4H_2O.$$

Without willing to be bound by any theory, it seems that when the chemical 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, the element used to stop the reaction is slowly added into the mixture obtained in step E.i). More preferably, the mixture obtained in step E.i) is gradually pumped into the element used to stop the oxidation reaction. For example, the mixture obtained in step E.i) is gradually pumped into deionized water to stop the reaction.

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

Optionally, the graphite oxide is washed. For example, the graphene 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: hydrochloric acid, phosphoric acid, sulfuric acid, nitride acid or a mixture thereof.

Optionally, the graphite oxide is dried, for example with air or at high temperature in the vacuum condition.

Preferably in step E.iv), the exfoliation is performed by using ultrasound, mechanical agitator, sieve shaker or thermal exfoliation. Preferably, the mixture obtained in step E.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 25% by weight of oxygen functional groups.

Then, in step F), graphene oxide is reduced into reduced graphene oxide.

Preferably, in step F.i), the reducing agent is chosen from: acid ascorbic; urea; hydrazine hydrate; alkaline solution such as NaOH or KOH; phenols such as gallic acid, tannin acid, dopamine or tea polyphenol; alcohols such as methyl alcohol, ethyl alcohol or isopropyl alcohol; glycine; sodium citrate or sodium borohydride. More preferably, the reducing agent is acid ascorbic since the ascorbic acid is more environmentally friendly.

After the reduction of GO into rGO, optionally rGO is washed. For example, rGO is washed with water. rGO can be dried, for example with air or by lyophilization.

Advantageously, in step F.i), the reduction is performed at a temperature between 50 and 120°C, more preferably between 90 and 100°C.

Preferably, in step F.i), the reduction is performed during less than 24 hours, more preferably during less than 15 hours and advantageously during 1 to 10 hours.

By applying the method according to the present invention, reduced graphene oxide (rGO), comprising one or a few layer(s) of graphene having between 10 and 25% by weight of oxygen functional groups is obtained.

Optionally, in step F.ii), rGO is further reduced into microwave-reduced graphene oxide (MW-rGO).

Preferably, in step F.ii), the catalyst is chosen from: pristine graphene, graphene nanoplatelet(s), graphite or graphite nanoplatelets. More preferably, the catalyst is pristine graphene. Without willing to be bound by any theory, it is believed that pristine graphene can better absorb the electromagnetic field in the form of microwaves due to the nature, the form and the properties of pristine graphene. Indeed, pristine graphene, being conductive, is a single layer of Graphite consisting of carbons bonded together in a hexagonal honeycomb lattice. It is an allotrope of carbon in the structure of a plane of sp^2 bonded atoms with which microwaves are attracted and can easily be absorbed.

Preferably, in step F.ii), the ratio in weight of rGO with respect to the catalyst is as follows: $50 \leq \frac{amount\ of\ rGO}{amount\ of\ catalyst} \leq 150$. Advantageously, the ratio in weight of rGO with respect to the catalyst is as follows: $75 \leq \frac{amount\ of\ rGO}{amount\ of\ catalyst} \leq 125$. Without willing to be bound by any theory, it is believed that when the ratio in weight of rGO with respect to the catalyst is as above, the reduction of rGO into MW- rGO is further improved. Indeed, this above ratio leads to MW-rGO having even less oxygen groups.

Preferably, in step F.ii), the microwave frequency is between 300MHz and 100GHz, preferably between 1 and 5GHz and for example, of 2.45GHz.

Preferably, step F.ii) is performed with a microwave frequency heating device. Preferably, it is a microwave oven.

Advantageously, the microwave has a power between 100W and 100KW, more preferably between 100 and 2000KW.

Preferably, in step F.ii), the microwaving is performed during at least 2 seconds. Indeed, without willing to be bound by any theory, it is believed that when the microwaving is performed during at least 2 seconds, the reduction into MW-rGO is further improved.

Optionally, Microwave-reduced graphene oxide (MW-rGO) comprising one or a few layer(s) of graphene having less than 10% by weight, more preferably less than 7%, by weight of oxygen functional groups is obtained.

Figure 1 illustrates an example of one layer of reduced 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 reduced 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.

Preferably, reduced graphene oxide is deposited on metallic substrates to improve some properties such as corrosion resistance of metallic substrates.

In another preferred embodiment, reduced graphene oxide is used as cooling reagent. Indeed, reduced 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 can be used to cool down a metallic substrate.

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

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

Examples:

Trials 1 to 4 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.

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 with a ratio in weight acid / kish graphite of 0.5. Trials were then washed with deionized water and dried in air at 90º C. The purity of the kish graphite was of 95%.

After, the kish graphite was intercalated at 25 or 35°C for 5 minutes with ammonium persulfate and sulfuric acid with different ratios. The mixture was then left in an open vessel for 5 minutes to let the kish graphite expand. The obtained material is called expanded Kish Graphite.

Trials 1 to 4 were mixed at room temperature with sulfuric acid and $KMnO_4$ and optionally ammonium nitrate. The mixture contained 1 part by weight of expanded kish Graphite, 3.5 parts by weight of $KMnO_4$, 100 parts by weight of sulfuric acid and optionally 0.5 part by weight of ammonium nitrate. After the oxidation, the mixtures were gradually pumped into deionized water. H_2O_2 in aqueous solution was added until there was no more gas production 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. It was then 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.

L-ascorbic acid were mixed in water with graphene oxide of Trials 1 to 4. The reaction mixtures were agitated at 90°C to reduce the graphene oxide sheets. Trials were then washed and dried to obtain reduced graphene oxide powder.

Then, for Trials 2 and 3, rGO was disposed in a microwave oven (800W) under air atmosphere during 2 seconds. A catalyst being Pristine Graphene was added. rGO was reduced into MW-rGO by microwaving.

Graphene oxide and reduced graphene oxide were analyzed by scanning electron microscopy (SEM), X ray diffraction spectroscopy (XRD), Transmission electron microscopy (TEM), LECO analysis and Raman spectroscopy.

Trials 5 and 6 correspond respectively to Trial 1 of WO2018178845 and Trial 1 of PCT/IB2019/052805. Table 1 shows the results obtained.

The method of Trials 1 to 4 is more environmental-friendly than comparative Trials. Moreover, the oxidation time with the method of Trials 1 to 4 is significantly lowered compared to the methods of the prior art illustrated with Trials 5 and 6.

Trials 3 and 4 with the intercalation and expansion steps performed at 35°C confirmed that ambient temperature or 25°C (Trials 1 and 2) is enough to obtain graphene oxide comprising a high percentage of oxygen groups and correspondingly a reduced graphene oxide of high quality.

Trials 2 and 4 with oxidation times of 1 hour confirmed that oxidation times longer than respectively 10 minutes (Trial 1) and 30 minutes (Trial 3) do not improve any further the quality of the graphene oxide. In other words, extremely short oxidation times are enough to sufficiently oxidize the expanded kish graphite. This significantly reduces the energy consumption.

Trials 1 also confirmed that expanded kish graphite can be oxidized without salt even faster than with salt (Trial 3)). The ability to remove the salt from the oxidation step significantly limits pollution.

Trials 2 and 3 also confirmed that microwaving successfully reduces further the reduced graphene oxide, allowing to reach percentages of oxygen groups below 10%.

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Method		Trial 1 *	Trial 2*	Trial 3*	Trial 4*	Trial 5 (Trial 1 of WO2018178845)	Trial 6 (Trial 1 of PCT/IB2019/052804)
Origin of Kish graphite		Steelmaking plant	Steelmaking plant	Steelmaking plant	Steelmaking plant	Steelmaking plant	Steelmaking plant
Pre-treatment of Kish graphite Sieving step		Done	Done	Done	Done	Done	Done
Intercalation	Compounds	$(NH_4)_2S_2O_8$ and H_2SO_4, 25°C	$(NH_4)_2S_2O_8$ and H_2SO_4, 25°C	$(NH_4)_2S_2O_8$ and H_2SO_4, 35°C	$(NH_4)_2S_2O_8$ and H_2SO_4, 35°C	-	-
	Ratio in weight of persulfate salt / kish graphite	3	3	3	3	-	-
	Ratio in weight of acid / kish graphite	6	6	6	6	-	-
Expansion		Static, 25°C	Static, 25°C	Static, 35°C	Static, 35°C	-	-
Oxidation step	Mixture	Done with H_2SO_4, $KMnO_4$	Done with H_2SO_4, $KMnO_4$	Done with H_2SO_4, $KMnO_4$ and NH_4NO_3	Done with H_2SO_4, $KMnO_4$ and NH_4NO_3	Done with H_2SO_4 and $NaNO_3$	Done with H_2SO_4 and NH_4NO_3
	Oxidation time	10minutes	1h	30minutes	1h	3h	1h30min
	Element to stop the reaction	Water followed by H_2O_2	Water followed by H_2O_2	Water followed by H_2O_2	Water followed by H_2O_2	Water followed by H_2O_2	Water followed by H_2O_2
	Exfoliation	Ultrasound	Ultrasound	Ultrasound	Ultrasound	Ultrasound	Ultrasound
Graphene oxide		GO comprising 43% of oxygen groups, average Lateral size up to 100µm, purity of 99.8 %	GO comprising 46% of oxygen groups, average Lateral size up to 100µm, purity of 99.9 %	GO comprising 47% of oxygen groups, average Lateral size up to 100µm, purity of 99.7%	GO comprising 45% of oxygen groups, average Lateral size up to 70µm, purity of 99.8%	GO comprising 40% of oxygen groups, Lateral size from 20 to 35 µm, purity of 99.5%	GO comprising 49% of oxygen groups, average Lateral size from 10 to 20 µm, purity of 99,5 %
Reduction step		Done with acid ascorbic during 3 hours	Done with acid ascorbic during 3 hours	Done with acid ascorbic during 3 hours	Done with acid ascorbic during 3 hours	Done with acid ascorbic during 3 hours	Done with acid ascorbic during 3 hours
		-	microwaved, catalyst pristine graphene, Ratio $\frac{amount\ of\ rGO}{amount\ of\ catalyst} = 100$	microwaved, catalyst pristine graphene, Ratio $\frac{amount\ of\ rGO}{amount\ of\ catalyst} = 100$	-	-	-

Reduced graphene oxide	Reduced Graphene oxide having an average Lateral size about 40µm, 21% of oxygen groups, purity of 99.5%	Reduced Graphene oxide having an average Lateral size about 40µm, 4% of oxygen groups, purity of 99.5%	Reduced Graphene oxide having an average Lateral size about 40µm, 4% of oxygen groups, purity of 99.5%	Reduced Graphene oxide having an average Lateral size about 40µm, 21% of oxygen groups, purity of 99.5%	Reduced Graphene oxide having an average Lateral size from 20 to 30µm with purity of 99.5% and an average thickness of 1-6nm	Reduced Graphene oxide comprising 17% of oxygen groups and having an average Lateral size from 15 to 30 µm 99,5 % and an average thickness of 1-6 nm

* according to the present invention

CLAIMS

1. Method for the manufacture of reduced graphene oxide from kish graphite comprising:
   - A. The provision of kish graphite,
   - B. Optionally, a pre-treatment of kish graphite,
   - C. The intercalation of kish graphite with a persulfate salt and an acid at room temperature to obtain intercalated kish graphite,
   - D. The expansion of the intercalated kish graphite at room temperature to obtain expanded kish graphite,
   - E. An oxidation step of the expanded kish graphite to obtain graphene oxide and
   - F. A reduction of graphene oxide into reduced graphene oxide.

2. Method according to claim 1, wherein in step B), the pre-treatment of kish graphite comprises 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,
   - 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,

    iv. Optionally, the kish graphite is washed and dried.

3. Method according to any one of claims 1 or 2, wherein in step C), the ratio in weight of persulfate salt with respect to kish graphite is between 1 and 8.

4. Method according to any one of claims 1 to 3, wherein in step C), the ratio in weight of the acid with respect to kish graphite is between 2 and 8.

5. Method according to any one of claims 1 to 4, wherein in step C), the persulfate salt is chosen from: Sodium persulfate ($Na_2S_2O_8$), Ammonium persulfate ($(NH_4)_2S_2O_8$) and Potassium persulfate ($K_2S_2O_8$) or a mixture thereof.

6. Method according to any one of claims 1 to 5, wherein in step C), the acid is chosen from: H_2SO_4, HCl, HNO_3, H_3PO_4, $C_2H_2Cl_2O_2$ (dichloroacetic acid), HSO_2OH (alkylsulfonic acid) or a mixture thereof.

7. Method according to any one of claims 1 to 6, wherein in step D), the expansion is naturally performed by leaving the kish graphite, the persulfate salt and the acid at room temperature in an open vessel.

8. Method according to any one of claims 1 to 7, wherein step E) comprises the following successive sub-steps:
    i. The mixture of the expanded kish graphite with an acid, an oxidizing agent and optionally a salt,
    ii. The addition of a chemical element to stop the oxidation reaction,
    iii. the separation of graphite oxide from the mixture obtained in step E.ii),
    iv. The exfoliation of graphite oxide into graphene oxide.

9. Method according to claim 8, wherein in step E.i), the salt is a nitrate salt chosen from: $NaNO_3$, NH_4NO_3, KNO_3, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Al(NO_3)_3$ or a mixture thereof.

10. Method according to any one of claims 8 or 9, wherein in step E.i), the acid is chosen from: H_2SO_4, HCl, HNO_3, H_3PO_4, $C_2H_2Cl_2O_2$ (dichloroacetic acid), HSO_2OH (alkylsulfonic acid) or a mixture thereof.

11. Method according to any one of claims 8 to 10, wherein in step E.i), the oxidizing agent is chosen from: potassium permanganate, H_2O_2, O_3, $H_2S_2O_8$, H_2SO_5, KNO_3, NaClO or a mixture thereof.

12. Method according to any one of claims 8 to 11, wherein in step E.ii), the chemical element used to stop the oxidation reaction is chosen from: an acid, non-deionized water, deionized water, H_2O_2 or a mixture thereof.

13. Method according to claim 12, wherein when at least two chemical elements are chosen to stop the reaction, they are used successively or simultaneously.

14. Method according to any one of claims 8 to 13, wherein in step E.ii), the mixture obtained in step E.i) is gradually pumped into the chemical element used to stop the oxidation reaction.

15. Method according to any one of claims 8 to 14, wherein in step E.iii), the graphite oxide is separated by centrifugation, decantation, distillation or filtration.

16. Method according to anyone of claims 8 to 15, wherein in step E.iv), the exfoliation is performed by using ultrasound, mechanical agitator, sieve shaker or thermal exfoliation.

17. Method according to any one of claims 1 to 16, wherein step F) comprises the following sub-steps:

i. The reduction of GO into reduced graphene oxide (rGO), comprising one or a few layer(s) of graphene having between 10 and 25% by weight of oxygen functional groups, using a reducing agent and

ii. Optionally, the reduction of rGO into microwave-reduced graphene oxide (MW-rGO), comprising one or a few layer(s) of graphene having less than 10% by weight of oxygen functional groups, by microwaving rGO under air atmosphere in presence of a catalyst.

18. Method according to claim 17, wherein in step F.i), the reducing agent is chosen from: acid ascorbic; urea; hydrazine hydrate; alkaline solution such as NaOH or KOH; phenols such as gallic acid, tannin acid, dopamine or tea polyphenol; alcohols such as methyl alcohol, ethyl alcohol or isopropyl alcohol; glycine; sodium citrate or sodium borohydride.

19. Method according to any one of claims 17 or 18, wherein in step F.ii), the catalyst is chosen from: pristine graphene, graphene nanoplatelet(s), graphite or graphite nanoplatelets.

Figure 1

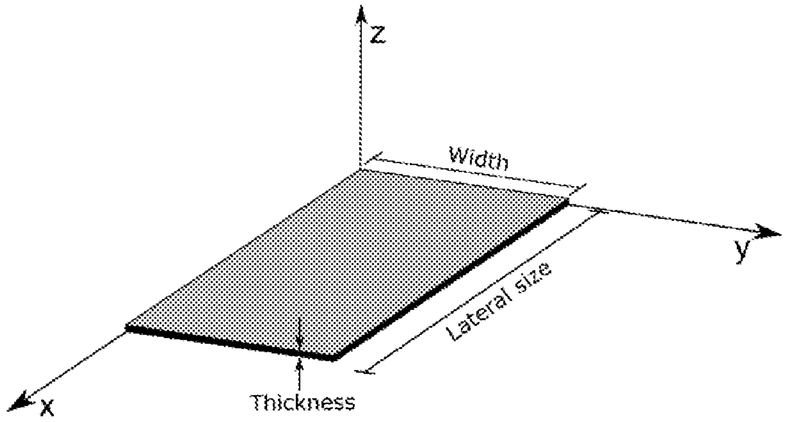
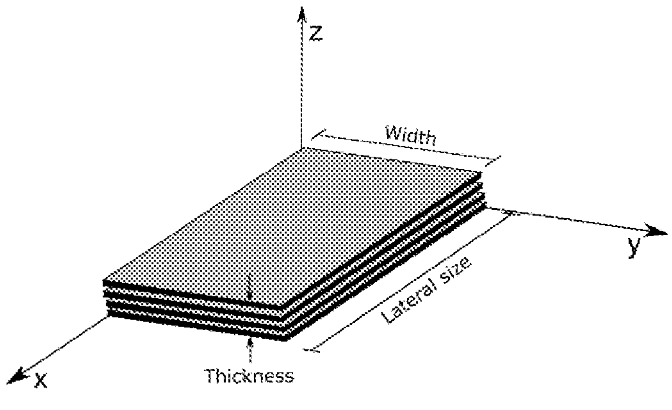


Figure 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2020/054459

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

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A	WO 2018/178845 A1 (ARCELORMITTAL [LU]) 4 October 2018 (2018-10-04) cited in the application page 3, line 24 - page 8, line 12 -----	1-19
A	JUNG-CHUL AN ET AL: "Preparation of Kish graphite-based graphene nanoplatelets by GIC (graphite intercalation compound) via process", JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY, vol. 26, 1 June 2015 (2015-06-01), pages 55-60, XP055549211, KOREA ISSN: 1226-086X, DOI: 10.1016/j.jiec.2014.12.016 "Experimental" ----- -/--	1-19

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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

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Date of the actual completion of the international search 13 July 2020	Date of mailing of the international search report 21/07/2020
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Corrias, M

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 2017/027731 A1 (METOXS PTE LTD [SG]; JALBOUT ABRAHAM [US]) 16 February 2017 (2017-02-16) paragraphs [0023] - [0034]; claims 1-20 -----	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2020/054459

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