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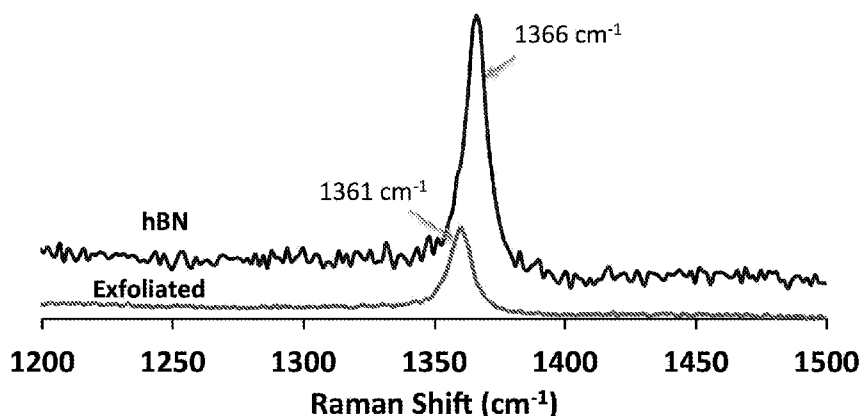


FIGURE 5

- (57) Abstract: This invention relates to a method of producing oxygenated inorganic two-dimensional materials which are suitable for suspending in aqueous media. In particular, it relates to an electrochemical method of making oxygenated nanoplatelets of hexagonal boron nitride and transition metal dichalcogenides.



Oxygenated 2-D materials

[0001] This invention relates to a method of producing oxygenated inorganic two-dimensional materials which are suitable for suspending in aqueous media. In particular, it relates to an electrochemical method of making oxygenated nanoplatelets of hexagonal boron nitride and transition metal dichalcogenides.

BACKGROUND

[0002] There is an increasing interest in the use of hexagonal boron nitride (hBN) and transition metal dichalcogenide (TMDC) nanoplatelets to replace traditionally used materials in many electronic, optoelectronic, energy storage and thermal management applications. For many of these applications, 2-D crystals that are able to form stable suspensions or inks are desirable. Changing the chemical properties of the hBN and TMDC by introducing chemically bonded functional groups to the surface or the edge of the nanoplatelets is also highly desired.

[0003] Despite the similarities to graphite, the large scale formation of oxygenated nanoplatelets of TMDC or hBN (i.e. analogues of graphene oxide (GO)) has not been achieved due to the inherent resistance of hBN and TMDCs to many of the oxidation processes traditionally used for preparing GO nanoplatelets. Oxygenated TMDCs have not, to the authors' knowledge, been described. Previous attempts to oxidise these materials have resulted in separation of the chalcogen and the transition metal and therefore with destruction of the molecular sheets. (unpublished work; see also Direct fabrication of thin layer MoS₂ field-effect nanoscale transistors by oxidation scanning probe lithography; Espinosa *et al.*; *Appl. Phys. Lett.*; **2015**, 106, 103503; A Raman Spectroscopic Study of MoS₂ and MoO₃: Applications to Tribological Systems; Windom *et al.*; *Tribology Letters*; **2011**; 42; 301-310). The preparation of oxygenated hBN has met with more success (Large Scale Thermal Exfoliation and Functionalization of Boron Nitride; Cui *et al.*; *Small*; **2014**, 12, 2352-2355.; Edge-Hydroxylated Boron Nitride Nanosheets as an Effective Additive to Improve the Thermal Response of Hydrogels; Xiao *et al.*; *Adv. Mater.*, **2015**, 27, 7196-7203). However, these approaches were not able to produce suspensions of oxygenated hBN in water which are stable for longer than a couple of days. Neither have usable concentrations of oxygenated hBN nanoplatelets been obtained.

[0004] Graphene oxide can be prepared from graphite by electrochemical processes which proceed via the intercalation of anionic species between the layers of graphene (GB2520496). The bonding between layers of layered compounds formed from more

than one element, such as hBN or TMDCs, are very different to that between graphene layers. For example, in the case of hBN, the bonding between neighbouring hBN layers is formed by so called 'lip-lip' interactions, which would be expected to be stronger than the weak Van der Waals forces operating between graphene layers. These stronger
5 interactions might be expected to impede the ability of anions to intercalate between the layers of such inorganic materials and/or ability of the intercalated layers to separate.

[0005] Furthermore, the electrochemical methods of preparing graphene oxide from graphite centre on the ability of graphite to conduct electricity. The graphite not only acts as the source of carbon sheets in the formation of graphene oxide but it also acts as the
10 anode in the electrochemical cell in which the graphene oxide is prepared. hBN and TMDCs are either non-conductive or are only poorly conductive and so cannot be used in the same way.

[0006] It is an aim of certain embodiments of this invention to provide a method of producing oxygenated nanoplatelets of materials, such as hBN or TMDCs, formed from
15 more than one element. It is an aim of certain embodiments of this invention to provide a method that is cheaper, more efficient or more readily scaled up than prior art methods.

[0007] It is an aim of certain embodiments of this invention to provide a method of producing hBN or TMDC nanoplatelets that are more oxygenated than prior art nanoplatelets.

20 [0008] It is an aim of certain embodiments of this invention to provide hBN or TMDC nanoplatelets that form stable suspensions in aqueous media. It is an aim of certain embodiments of this invention to provide hBN or TMDC nanoplatelets that form suspensions in aqueous media that are stable at higher concentrations than prior art nanoplatelets.

25 [0009] Certain embodiments of the invention satisfy some or all of the abovementioned aims.

BRIEF SUMMARY OF THE DISCLOSURE

[0010] In a first aspect of the invention is provided a method of producing oxygenated nanoplatelets of an inorganic material from a layered inorganic material in an
30 electrochemical cell, the layered inorganic material being formed of two or more elements that are not oxygen, the cell comprising:

an inert anode which is in contact with the layered inorganic material;

a cathode;

an electrolyte comprising a source of polyatomic anions;

wherein the method comprises:

passing a current through the cell to provide oxygenated nanoplatelets of the inorganic material.

5 **[0011]** The passage of the current through the cell causes the polyatomic anions to intercalate into the layered inorganic material and the resultant intercalated layered material to be exfoliated. The inorganic material also becomes oxygenated.

10 **[0012]** The inventor has found that, even though the inorganic layered materials are non-conductive or are poorly conductive, it is possible to exfoliate them by electrochemically inducing anionic intercalation into the layers simply by having the layered material in contact with an anode.

15 **[0013]** The oxygenated nanoplatelets made according to the methods of the invention are particularly hydrophilic (in contrast to nanoplatelets of the inorganic materials themselves) and are therefore capable of forming stable aqueous suspensions. The method of the invention has been shown to provide a stable suspension of oxygenated hBN with a concentration about 0.5 mg/mL. This concentration is almost twice that which has previously been reported for oxygenated hBN.

20 **[0014]** The cell may further comprise a reference electrode.

25 **[0015]** The method may also comprise collecting the oxygenated nanoplatelets of the layered inorganic material. It may be that the inert anode and the layered organic material are together contained within an enclosure comprising porous material. If this is the case, the step of collecting the nanoplatelets may comprise removing the enclosure comprising a porous material from the cell in such a way that the inorganic material in the membrane is retained in the enclosure. The method may comprise washing the inorganic material (either oxygenated nanoplatelets of the inorganic material or a mixture of oxygenated nanoplatelets of the inorganic material and layered inorganic material having polyatomic anions intercalated between the layers). Where the inorganic materials are retained in a porous material enclosure following collection from the cell, the washing step is preferably carried out with the inorganic materials still retained in the porous material enclosure. The washing step will typically be used to remove residual electrolyte.

30 **[0016]** The method may comprise suspending the nanoplatelets in an aqueous medium and subjecting the platelets to energy. The energy to which the suspension is subjected may be sonic energy. The sonic energy may be ultrasonic energy. It may be delivered

using a bath sonicator or a tip sonicator. Alternatively the energy may be a mechanical energy, e.g. shear force energy or grinding. Thus, the step of subjecting the suspension to energy could be achieved by sonicating the suspension. Alternative methods may include ball milling, roll milling, grinding, mechanical stirring or applying any other mechanical force. This sonication step may have the purpose of decreasing the flake size and/or thickness of the nanoplatelets or it may simply have the purpose of dispersing the nanoplatelets in the aqueous medium.

[0017] The method may comprise centrifuging the suspension, typically to remove bulk layered inorganic material, e.g. any which has been displaced during the production of the oxygenated platelets.

[0018] The process may be repeated in order to achieve more complete exfoliation or a higher level of oxidation.

[0019] It may be that the step of passing the current through the cell produces a mixture of oxygenated nanoplatelets of the inorganic material and layered inorganic material having polyatomic anions intercalated between the layers (which may or may not be oxygenated). In this case the method may further comprise:

collecting the resulting mixture of oxygenated nanoplatelets of the inorganic material and layered inorganic material having intercalated polyatomic anions;

suspending the mixture in an aqueous medium to form an aqueous suspension;

and

subjecting the suspension to energy to exfoliate the oxygenated layered inorganic material having intercalated polyatomic anions and to increase the amount of oxygenated nanoplatelets of the inorganic material in the suspension.

[0020] The energy to which the suspension is subjected may be sonic energy. The sonic energy may be ultrasonic energy. It may be delivered using a bath sonicator or a tip sonicator. Alternatively the energy may be a mechanical energy, e.g. shear force energy or grinding. Thus, the step of subjecting the suspension to energy could be achieved by sonicating the suspension. Alternative methods include ball milling, roll milling, grinding, mechanical stirring or applying any other mechanical force to exfoliate the intercalated layered inorganic materials further. The method may further comprise the step of washing the mixture of oxygenated nanoplatelets of the inorganic material and layered inorganic material having polyatomic anions intercalated between the layers. The method may comprise centrifuging the suspension to remove bulk inorganic material and/or any

remaining layered inorganic material having polyatomic anions intercalated between the layers.

[0021] The concentration of nanoplatelets in the final aqueous suspension may be within the range of 0.01 to 10 mg/mL, e.g. from 0.01 to 5 mg/mL. More typically, the concentration of nanoplatelets is within the range of 0.01 to 2 mg/mL. Even more typically, the concentration of nanoplatelets is within the range of 0.01 to 1 mg/mL. It may be that the concentration of the nanoplatelets is greater than 0.3 mg/mL or greater than 0.4 mg/mL.

[0022] The layered material is typically non-conductive or poorly conductive.

[0023] The layered material may be hexagonal boron nitride. Thus, the oxygenated nanoplatelets of the inorganic material may be oxygenated nanoplatelets of hexagonal boron nitride.

[0024] The layered material may be a transition metal dichalcogenide (e.g. MoS₂, WS₂, MoTe₂, MoSe₂ etc.). The layered material may be selected from MoS₂ and WS₂. The layered material may be MoS₂. The layered material may be WS₂. Thus, the oxygenated nanoplatelets of the inorganic material may be oxygenated nanoplatelets of a transition metal dichalcogenide (e.g. oxygenated nanoplatelets of MoS₂ or oxygenated nanoplatelets of WS₂).

[0025] The layered material may be a layered metal nitride (e.g. TiN), a layered metal boride, or a layered metal carbide, e.g. a binary layered metal carbide (sometimes called MAX phases).

[0026] The inert anode may be coated with the layered inorganic material. Preferably, the entire surface of the inert anode is coated with the layered inorganic material. The term 'entire surface' is intended to mean that any part of the surface of the anode which would otherwise be in contact with the electrolyte is coated with the layered inorganic material. The process is more efficient if no part of the surface of the anode is left in contact with the electrolyte. Electric current takes the path of least resistance and, as hBN and TMDCs are poor conductors, the electric current passed through the cell would by preference pass through any surface of the anode which is directly exposed to the electrolyte. The method of the invention still produces oxygenated nanoplatelets of inorganic materials if there are surfaces of the anode exposed to the electrolyte but the speed of the reaction and yields are typically lower.

[0027] The method may comprise the step of coating the inert anode with the layered inorganic material. This step will typically comprise forming a paste of the inorganic

material and coating the inert anode with the paste. The paste may be formed by suspending the layered material in a suitable solvent (e.g. N-methylpyrrolidone). The suspension of the layered inorganic material in the solvent may be sonicated. Typically this will be to disperse the inorganic material in the solvent rather than to decrease the size and/or thickness of the particles of layered inorganic material. It is within the bounds of this invention however that the sonication step does decrease the size and/or thickness of the particles of layered inorganic material.

[0028] It may be that the inert anode and the layered inorganic material are together contained within an enclosure comprising (or formed of) a porous material.

[0029] Any suitable porous material may be used, provided that it allows the electrolyte anions to access the anode and layered inorganic material in order to facilitate intercalation of electrolyte anions into the layered inorganic material. It must also have a pore size sufficiently small as to retain both the layered inorganic material and the exfoliated oxygenated nanoplatelets of the inorganic material in the vicinity of the anode. This both increases the efficiency of the intercalation/oxidation/exfoliation process, meaning that a larger proportion of the layered material is converted to oxygenated nanoplatelets, but also facilitates both collection of the nanoplatelets and cleaning of the cell, allowing it to be reused more rapidly afterwards. The pore size of the porous material will thus typically be smaller than the flake size of the desired oxygenated nanoplatelets.

[0030] The average pore size of the porous material may vary from 10 nm to 1 mm. Thus the average pore size may be at least 20 nm, at least 100 nm or at least 500 nm. The average pore size may at least 1 μm , at least 50 μm or at least 200 μm . The average pore size may be 500 μm or less or 250 μm or less. Typically, the porous filter has an average pore size of from 100 to 250 μm .

[0031] The porous material may comprise a porous woven material such as a woven cloth, e.g. a muslin cloth. Alternatively, the porous material may be a polymeric membrane or a plastic (such as wherein the electrode is provided encased in a plastic box). Preferred membranes are flexible (in order to maintain contact with the electrode as the electrode surface area changes during the reaction process). Thus, the porous material may include (a) a cellulose dialysis membrane (e.g., Spectra PorT, 25 nm pores); (b) polycarbonate membranes (c) muslin cloth or (d) a plastic box. The porous material may thus comprise a combination of one or more thereof.

[0032] An inert cathode is an electrode formed of an inert material. Thus, the inert anode may be any material which does not react in the electrochemical conditions of the method

of the invention. The inert anode may comprise or may be a material selected from platinum, iridium oxide, silver, glassy carbon, amorphous carbon, any amorphous conductive materials, hard graphite, a cermet or any conductive materials coated by any inert anode materials. The anode may be a conductive material (e.g. metal or carbon) coated with an inert material (e.g. platinum). The inert anode may be or may comprise any alloy provided that the potential applied across the cell is kept below the oxidation potential of the alloy. In particular embodiments, the inert anode is or comprises platinum. Thus, the inert anode may be platinum, e.g. a platinum wire or a platinum mesh.

[0033] The electrochemical cell may contain two electrodes (i.e. the anode and the cathode as defined above). The electrochemical cell may contain three electrodes. In the three-electrode system, the inert electrode and the bulk inorganic layered materials are subjected to anodic potential versus a reference electrode. Thus, the electrochemical cell may further comprise a reference electrode.

[0034] The cathode may consist of any suitable material known to those skilled in the art as it does not play a role in the oxygenation, other than to provide a counter electrode for the cations. For instance, the cathode may include a material selected from the groups consisting of transition metals, transition metal-containing alloys, transition metal-containing oxides, transition metal-containing ceramics and combinations thereof. Preferably, the cathode is made from an inert material. In embodiments, the cathode includes gold, silver, platinum or carbon, preferably gold, silver or platinum, more preferably platinum. Platinum mesh is particularly suitable. In embodiments, the cathode consists substantially of said gold, silver, platinum or carbon (i.e. wherein at least 90% by weight of the electrode consists of said gold, silver, platinum or carbon, for instance at least 95% by weight or 99% by weight). In embodiments, the cathode consists of said gold, silver, platinum or carbon. Suitably, said gold, silver, platinum or carbon is included at the surface of the electrode configured to contact the electrolyte, preferably wherein at least 10% by area of said electrode surface consists of said gold, silver, platinum or carbon, more preferably at least 80% by area. When the reaction at the cathode generates a gas, it is preferable to provide as large an electrode surface area as possible to prevent gas bubbles wetting it and/or disrupting the process at the anode. The cathode may also be placed in a membrane or molecule sieve to prevent undesired reactions in the electrolyte or interference with the process at the anode. The anode and the cathode could alternatively be placed in a two-compartment cell, wherein each compartment contains one electrode, and the compartments are connected through a channel.

[0035] The cathode may be an inert cathode which is in contact with the layered inorganic material. An inert cathode is an electrode formed of an inert material. Thus, the inert cathode may be any material which does not react in the electrochemical conditions of the method of the invention. Thus, the two working electrodes may be the same with the electrode which acts as the 'anode' and the electrode which acts as the 'cathode' alternating with the potential applied. The above embodiments described in relation to the inert anode may, therefore, apply equally to the inert cathode. As illustrative examples, it may be that the inert cathode is coated with the layered inorganic material, e.g. that the entire surface of the inert cathode is coated with the layered inorganic material. It may be that the inert cathode and the layered inorganic material are together contained within a porous material such as those described above in relation to the anode. It may be that the inert anode is or comprises platinum, e.g. is a platinum wire or a platinum mesh.

[0036] The electrolyte comprises a source of polyatomic anions. Thus, the electrolyte may comprise polyatomic anions. The term 'polyatomic anions' includes anions formed of two or more atoms. Said ions may be inorganic ions, i.e. non-organic ions. Said ions may comprise oxygen. Preferably the ions are non-organic ions containing oxygen. Non-organic ions are ions that do not comprise either carbon-carbon bonds or carbon-hydrogen bonds. The anions in a solvent may be constituent anions of said solvent and / or may be dissolved in said solvent (i.e. as anions in a solution). Preferably, said anions in a solvent are anions in a solution, more preferably anions in an aqueous solution. The polyatomic anions may be the conjugate base of a strong acid, e.g. nitrate ions, sulfate ions or phosphate ions. The source of said anions may be the acids of which the abovementioned anions are the conjugate bases. Thus the source of polyatomic anions may be nitric acid, phosphoric or sulfuric acid. Alternatively, the source of the anions is a salt. The polyatomic anions may be oxidising agents, e.g. anions selected from: permanganate, persulfate, percarbonate, dichromate, peroxide, periodate, perchlorate. The polyatomic anions may be hydroxide ions. The cationic counterions of the salt may be metal ions, e.g. ions of elements selected from the alkali metals and the alkali earth metals, e.g. potassium or sodium ions. The source of polyatomic anions is nitric acid or a nitrate salt. In certain particular embodiments, the source of polyatomic anions is nitric acid.

[0037] The concentration of the polyatomic anions in the electrolyte may be from 0.01 to 5 M. The concentration of the polyatomic anions may be from 0.05 to 1 M, e.g. from 0.1 to 0.3 M. The concentration of the polyatomic anions may be about 0.2 M. Thus, the concentration of the nitrate anions may be from 0.1 to 1 M. The concentration of nitrate

anions may be about 0.2 M. Thus, the concentration of nitric acid may be from 0.1 to 1 M. The concentration of nitric acid may be about 0.2 M.

[0038] Where the electrolyte is anions in an aqueous solution, the hydrogen ion concentration may be defined by pH. Thus, unless stated otherwise herein, an electrolyte of any suitable pH may be provided. Preferably, however, the pH of the electrolyte is >1 . The pH may be >2, and preferably >3 or >5. The pH may rise during the course of the electrochemical process as a result of removal of protons from the electrochemical system in the form of hydrogen gas. Preferably, the pH does not exceed 10. Thus in embodiments, the pH does not exceed 7. It may be that a neutral pH is used but, more preferably, the pH is maintained in a range from 2 to 5. Alkaline pHs (e.g. those above 7 or those above 10) are also tolerated.

[0039] Preferably, the electrolyte further comprises either non-ionic organic compounds or organic anions. Such species have been found to provide a more efficient exfoliation reaction when present, increasing yields and homogeneity of the product. Without wishing to be bound by theory, it is believed that these species contribute to the provision of a less oxidative environment and a more controlled oxidation/exfoliation reaction. It may be that they achieve this by being reduced at the cathode and thereby provide a reservoir of oxidisable species in the electrolyte which effectively 'buffer' the effects of excessive oxidative potential in the system by being oxidised in preference to the inorganic material. The non-ionic organic compounds or organic anions may thus be reducible species, e.g. those that comprise a heteroatom. Thus, the non-ionic organic compounds or organic anions may be oxygen containing organic compounds or organic anions. Examples of oxygen-containing non-ionic organic compounds include ketones (e.g. acetone), aldehydes, epoxides, carboxylic esters (e.g. methyl and ethyl acetate), alcohols (e.g. ethanol, methanol, isopropanol, t-butanol), carboxylic acids (e.g. acetic acid, propanoic acid). Examples of oxygen-containing organic anions include alkoxides and carboxylates .

[0040] It may be that the non-ionic organic compounds or organic anions are carboxylic acids or carboxylate.

[0041] A carboxylic acid may comprise one or more carboxylic acid groups per molecule. Typically, a carboxylic acid molecule comprises 1, 2 or 3 carboxylic acid functional groups. Where a carboxylic acid comprises more than 1 acid group, it may be that a single acid group is in the form of the deprotonated carboxylate salt and the rest remain protonated or it may be that more than one or all of the carboxylate groups are in the form of the deprotonated carboxylate salt. Typically, however, only one carboxylic acid group is in the form of a deprotonated carboxylate salt and the rest remain protonated. Typically the

carboxylic acid or carboxylate anion contains from 1 to 25 carbon atoms, e.g. from 1 to 8 or from 1 to 4 carbon atoms. The carboxylic acid or carboxylate may comprise other functional groups, e.g hydroxy groups or amine groups. More preferably, the carboxylic acid is acetic acid and/or citric acid or the carboxylate is the anion of acetic acid and/or citric acid. Preferably the electrolyte comprises a carboxylate. Thus, preferably the electrolyte comprises acetate and/or citrate ions. Other examples of carboxylates will be apparent to the skilled reader, such as including pentanoate, hexanoate, heptanoate, octanoate, nonanoate, decanoate, undecanoate, laurate, tridecylate, myristate, palmitate, margarate, stearate, arachidate, lactate, acrylate, succinate, acetoacetate, pyruvate, benzoate, salicylate, adipate, citrate, malate, carboxylate salts of amino acids, glycerate, glycolate and tartrate.

[0042] The carboxylate will typically have as a cationic counterion an alkali metal or an alkali earth metal. The carboxylate may be a sodium salt, a potassium salt or a lithium salt. Most preferably, the carboxylate may be a sodium salt. Thus, the electrolyte may comprise sodium acetate and/or sodium citrate. Most preferably, the electrolyte comprises both sodium acetate and sodium citrate.

[0043] Alternatively, the counterion may be an ammonium ion, e.g. a tetraalkyl or trialkyl ammonium ion.

[0044] It may be that the total concentration of non-ionic organic compounds or organic anions in the electrolyte is from 0.01 to 5 M, e.g. from 0.05 to 1 M. It may be that the total concentration of non-ionic organic compounds or organic anions in the electrolyte is from 0.1 to 0.7 M. It may be that the total concentration of non-ionic organic compounds or organic anions in the electrolyte is from 0.2 to 0.4 M. It may be that the total concentration of non-ionic organic compounds or organic anions in the electrolyte is about 0.3 M. Thus, it may be that the total concentration of sodium acetate and/or sodium citrate in the electrolyte is from 0.2 to 0.4 M. It may be that the total concentration of sodium acetate and/or sodium citrate in the electrolyte is about 0.3 M.

[0045] Particularly preferred aqueous electrolytes comprise nitric acid as the source of polyatomic anions and sodium acetate and/or sodium citrate as a source of organic anions. It may be that the electrolyte comprises nitric acid, sodium acetate and sodium citrate. It may be that the nitric acid has a concentration in the electrolyte of between 0.1 and 1 M and that the total concentration of sodium acetate and/or sodium citrate in the electrolyte is from 0.1 to 1 M. It may be that the nitric acid has a concentration in the electrolyte of between 0.1 and 0.5 M and that the total concentration of sodium acetate and/or sodium citrate in the electrolyte is from 0.1 to 0.7 M. It may be that the nitric acid

has a concentration in the electrolyte of between 0.1 and 0.3 M and that the total concentration of sodium acetate and/or sodium citrate in the electrolyte is from 0.2 to 0.4 M. It may be that the nitric acid has a concentration in the electrolyte of about 0.3 M, that the concentration of sodium acetate is about 0.2 M and that the concentration of sodium acetate is about 0.1 M.

[0046] The working potential of the cell will be at least that of the standard potential for intercalation. An overpotential may be used in order to increase the reaction rate and to drive the anions in between the layers of the inorganic material at the anode. An overpotential of 1 mV to 50 V may for instance be used against a suitable reference as known by those skilled in the art, e.g. from 1 mV to 10 V or from 1 mV to 5 V. In cells with only two terminals, and no reference electrode, a larger potential may be applied across the electrodes but a significant amount of the potential drop will occur over the cell resistance, rather than act as an overpotential at the electrodes. In these cases the potential applied may be up to 20V or 30V. Typically however an overpotential is not used in order to minimise the speed and extent of intercalation. The voltage applied across the electrodes may be cycled or swept. In one embodiment, both the electrodes comprise a non-carbon-based bulk 2D material in contact with an inert conductive material and the potential is swept so that electrodes change from positive to negative and vice versa. In this embodiment the cationic exfoliation would occur at both electrodes, depending on the polarity of the electrode during the voltage cycle. In some embodiments, alternating current can be used to allow for both fast intercalations and de-intercalations.

[0047] Typically, current is allowed to pass between the electrodes at a potential difference of from 1 to 10 V. Typically, the current is allowed to pass between the electrodes at a potential difference of less than 5V, such as at about 3 V. For instance, in embodiments, the bias voltage applied is less than 5 V.

[0048] The current density at the positive electrode will be controlled through a combination of the electrode's surface area and overpotential used. The method can also be carried out under current control. The current may be constant. The absolute current value will vary depending on the electrolyte resistance, size of electrodes and temperature, etc. and current may thus be varied by the skilled person depending on the reaction conditions. The current density may be at least 1 μA per cm^2 . Typically the current density is less than 15 A per cm^2 . Typically, the current density is in the range of 1 μA per cm^2 and 10 A per cm^2 .

[0049] The cell is operated at a temperature which allows for production of the desired material. The optimum operating temperature will vary with the nature of the electrolyte.

For instance, operating the cell near to the melting point and up to the boiling point of the electrolyte may be carried out in the present invention. The temperature within the electrochemical cell may in embodiments be at least -50°C , for example at least 0°C , or at least 10°C and is preferably at least 20°C . For example, the temperature within the

5 electrochemical cell may be room temperature. It may be that the temperature within the cell does not exceed 120°C or more preferably 50°C . Typically the temperature referred to above is the electrolyte temperature.

[0050] The electrochemical cell may be operated at any suitable pressure that allows for production of the desired oxygenated nanoplatelets, e.g. atmospheric pressure. The

10 electrochemical cell may be operated under any suitable gaseous atmosphere, e.g. under air.

[0051] The electrochemical process will be operated for a length of time adequate to provide the desired yield, level of oxygenation and thickness of the oxygenated nanoplatelets. The duration of the process typically refers to the length of time that a

15 current is passed between the electrodes in the presence of the intercalating anions prior to isolation of the oxygenated nanoplatelets. The current may be passed between the electrodes continuously or intermittently, typically continuously. In some embodiments, the length of time that a current is passed between the electrodes is greater than one minute, and preferably greater than one hour. Typically, the reaction duration is from 1 h to

20 72 h, e.g. from 5 h to 48 h or from 12 h to 36 h. The reaction duration may be about 24 h.

[0052] The method may be continuous.

[0053] Typically, the in-plane size of the oxygenated nanoplatelets produced is roughly the same or less than the size of the particles of the inorganic material used in the reaction. The size of the oxygenated nanoplatelets produced is typically from 10 nm to 10

25 mm.

[0054] The oxygenated nanoplatelets are typically either a single molecular layer thick or are few-layers thick. It may be that the oxygenated nanoplatelets are predominantly a single molecular layer thick. It may be that the oxygenated nanoplatelets are predominantly one or two molecular layers thick. It may be the oxygenated nanoplatelets

30 are predominantly few-layers thick.

[0055] It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the oxygenated nanoplatelets have a thickness of less than 50 nm. It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the oxygenated nanoplatelets have a

thickness of less than 10 nm. It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the oxygenated nanoplatelets have a thickness of less than 5 nm. It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the oxygenated nanoplatelets have a thickness of less than 3 nm.

[0056] The methods described herein are capable of producing high yields of oxygenated nanoplatelets. The yield of oxygenated nanoplatelets having a thickness of less than 50 nm may be greater than 10%, e.g. greater than 30% or greater than 50% or even greater than 80%. The yield of oxygenated nanoplatelets having a thickness of less than 10 nm may be greater than 10%, e.g. greater than 30% or greater than 50% or even greater than 80%. The yield of oxygenated nanoplatelets having a thickness of less than 5 nm may be greater than 10%, e.g. greater than 30% or greater than 50% or even greater than 80%.

[0057] Typically, the oxygenated nanoplatelets of the inorganic material comprise from 5% to 75% by weight oxygen. Thus, the oxygenated nanoplatelets of the inorganic material may comprise from 10% to 50% by weight oxygen.

[0058] In a second aspect of the invention is provided oxygenated nanoplatelets of an inorganic material prepared according to the method of the first aspect.

[0059] In a third aspect of the invention is provided a stable aqueous suspension of oxygenated nanoplatelets of hexagonal boron nitride in which the concentration of the nanoplatelets in the suspension is higher than or equal to 0.4 mg/mL.

[0060] In a fourth aspect of the invention is provided oxygenated nanoplatelets of a transition metal dichalcogenide. Said oxygenated nanoplatelets may be in the form of a stable aqueous suspension.

[0061] Where appropriate, the embodiments described above in relation to the first aspect of the invention apply equally to the third and fourth aspects of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0062] Embodiments of the invention are further described hereinafter with reference to the accompanying drawings, in which:

Figure 1 shows the suspension of oxygenated nanoplatelets of hBN made according to the methods of the invention after 2 weeks (right). hBN (left) is not dispersible in water.

Figure 2 shows an AFM image and height profile for an oxygenated nanoplatelet of hBN made according to the methods of the invention.

Figure 3 shows a SEM image for the oxygenated nanoplatelets of hBN made according to the methods of the invention.

5 Figure 4 shows the XRD pattern for bulk hBN and for the oxygenated nanoplatelets of hBN made according to the methods of the invention.

Figure 5 shows the Raman spectra of bulk hBN and of the oxygenated nanoplatelets of hBN made according to the methods of the invention.

10 Figure 6 shows the AFM image and height profile for an oxygenated nanoplatelet of MoS₂ made according to the methods of the invention.

Figure 7 shows the suspension of oxygenated nanoplatelets of WS₂ made according to the methods of the invention.

Figure 8 shows Raman spectra of bulk WS₂ (upper line) and of the oxygenated nanoplatelets of WS₂ made according to the methods of the invention (lower line).

15 Figure 9 shows the AFM image and height profile for an oxygenated nanoplatelet of WS₂ made according to the methods of the invention.

DETAILED DESCRIPTION

[0063] The term 'oxygenated' is intended to mean that the nanoplatelets of the inorganic material comprise greater than 5% by weight oxygen. Typically, the inorganic layered material used as a starting material in the methods of the invention would not comprise any oxygen or would contain less than 2% oxygen. This increased oxygen content provides the nanoplatelets with their preferential properties and in particular, their hydrophilicity. The oxygenation will typically be incorporated onto the nanoplatelet in the form of hydroxyl (-OH) groups but it is conceivable that it could be present in ketone-like groups (=O) or even epoxide-like groups (-O-). Where there is a source of carbon in the cell (e.g. where the electrolyte comprises non-ionic organic compounds or organic anions), the oxygen may be introduced onto the nanoplatelets in the form of carbonate or carboxyl groups. The oxygenation will be distributed between the constituent atoms of the inorganic material depending on the oxidation potential of said atoms, the proximity of said atoms to the surface or edge of the nanoplatelet, and other factors. In hBN, for example, the oxygen is believed to be associated more with the boron than with the nitrogen, with significantly more oxygen associated with the boron. In transition metal dichalcogenides,

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on the other hand, the oxygen is believed to be more evenly distributed, although it is more likely to be associated with chalcogens.

[0064] Throughout this specification, the term 'element' is intended to mean 'chemical element', i.e. an element selected from those in the periodic table.

5 **[0065]** Nanoplatelets are sheets or flakes of material that are less than 100 nm thick. They are formed of one or more layers of material. The dimensions of nanoplatelets are significantly greater in any direction (e.g. greater than 4 times or greater than 10 times or greater than 100 times) parallel to the planes of the layers than they are in the direction perpendicular to the planes of the layers.

10 **[0066]** The term 'layered inorganic material' refers to any material made up of (i.e. which is greater than 95% by weight formed from) two or more elements that are not oxygen. The material forms layered structures in which the bonding between atoms within the same layer is stronger than the bonding between atoms in different layers. Many examples of inorganic layered compounds have covalent bonds between the atoms within
15 the layers but van der Waals bonding between the layers. The term 'layered inorganic material' is not intended to encompass graphite or graphite oxide. Thus the oxygenated nanoplatelets formed in the methods of the invention are not graphene oxide (including reduced graphene oxide and partially oxidised graphene). The layered inorganic material may be formed of (i.e. which is greater than 95% by weight) two elements that are not
20 oxygen.

[0067] Many inorganic compounds exist in a number of allotropic forms, some of which are layered and some of which are not. For example boron nitride can exist in a layered graphite-like structure or as a diamond-like structure in which the boron and nitrogen atoms are tetrahedrally orientated. Examples of layered inorganic compounds to which
25 the present invention might be applied include: hexagonal boron nitride, transition metal dichalcogenides (TMDCs), Sb_2Te_3 , Bi_2Te_3 , layered metal nitrides (e.g. TiN), layered metal borides and layered metal carbides, e.g. binary layered metal carbides (sometimes called MAX phases).

[0068] TMDCs are structured such that each layer of the compound consists of three
30 atomic planes: a layer of transition metal atoms (for example Mo, Ta, W...) sandwiched between two layers of chalcogen atoms (for example S, Se or Te). Typically the chalcogen in the starting layered inorganic material will not be oxygen. Thus in one embodiment, the TMDC is a compound of one or more of Mo, Ta and W with one or more of S, Se and Te. There is strong covalent bonding between the atoms within each layer of

transition metal chalcogenide and predominantly weak Van der Waals bonding between adjacent layers. Exemplary TMDCs include NbSe₂, WS₂, MoS₂, TaS₂, PtTe₂, VTe₂.

[0069] The term 'few-layered' means nanoplatelets that are not a single molecular layer thick but that nevertheless are so thin that they exhibit different properties than the same compound when in the form of the bulk layered material. Not all of the properties of the compound will differ between a few-layered nanoplatelet and a bulk compound with a large number of layers but one or more properties are likely to be different. A more convenient definition would be that the term 'few layered' refers to a crystal that is from 2 to 9 molecular layers thick (e.g. 2 to 6 layers thick). A molecular layer is the minimum thickness chemically possible for that compound. In the case of boron-nitride one molecular layer is a single atom thick. In the case of the transition metal dichalcogenides (e.g. MoS₂ and WS₂), a molecular layer is three atoms thick (one transition metal atom and two chalcogen atoms). Thus, few-layer nanoplatelets are generally less than 50 nm thick, depending on the compound and are preferably less than 20 nm thick, e.g. less than 10 or 5 nm thick.

[0070] The term 'aqueous medium' can be understood to mean a liquid which contains water, e.g. which contains greater than 20% by volume water. The aqueous medium may contain more than 50% by volume water, e.g. more than 75% by volume water or more than 95% by volume water. The aqueous medium may also comprise solutes or suspended particles. The 'aqueous medium' may also comprise other solvents. It may therefore comprise organic solvents which may or may not be miscible with water. Where the aqueous medium comprises organic solvents, those solvents may be immiscible or sparingly miscible and the aqueous medium may be an emulsion. The aqueous medium may comprise solvents which are miscible with water, for example alcohols (e.g. methanol and ethanol). The aqueous medium may comprise additives which may be ionic, organic or amphiphilic. Examples of such additives include surfactants, viscosity modifiers, pH modifiers, ionicity modifiers, dispersants. The aqueous medium may be suitable for use as an ink. The aqueous medium may be substantially pure (e.g. greater than 98%) water. An 'aqueous suspension' is a suspension of a substance in an aqueous medium. e.g. substantially pure water. An 'aqueous solution' of a substance is that substance dissolved in an aqueous medium, e.g. substantially pure water.

[0071] A stable suspension is one in which the oxygenated nanoplatelets do not reaggregate after 2 days. Typically, the oxygenated nanoplatelets made according to the methods of the invention do not reaggregate after 7 days or even after 10 days. The stability of the suspension is dependent, at least in part, on the level of oxygenation on the

nanoplatelets. In general, higher levels of oxygenation on the nanoplatelets mean that aqueous suspensions of the nanoplatelets at higher concentration are stable.

[0072] Throughout the description and claims of this specification, the words “comprise” and “contain” and variations of them mean “including but not limited to”, and they are not intended to (and do not) exclude other moieties, additives, components, integers or steps. Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

[0073] Features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

[0074] The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

EXAMPLES

Methods and equipment

Characterisation of the oxygenated nanoplatelets:

[0075] Raman spectra were obtained using a Renishaw system 1000 spectrometer coupled to an Ar laser. The laser spot size was ~1-2 μm , and the power was about 1 mW when the laser was focused on the sample using an Olympus BH-1 microscope. Atomic force microscope (AFM) images were obtained using a Multimode Nanoscope V scanning probe microscopy (SPM) system (Veeco, USA) with Picoscan v5.3.3 software. Tapping mode was used to obtain the images under ambient conditions. The morphology of the

powder was also observed by SEM using a Carl Zeiss SUPRA SMT AG scanning electron microscope (LEO1525, Carl Zeiss, Oberkochen, Germany) with the accelerating voltage at 5kV. Samples for XRD were prepared by mixing the relevant powder with NaCl as a reference material. XRD analysis was conducted using a Philips X'PERT APD powder X-ray diffractometer ($\lambda = 1.54 \text{ \AA}$, CuK α radiation).

Example 1

[0076] hBN paste was formed by adding about 200mg of the powder (less than $2 \text{ }\mu\text{m}$) to 10 mL of N-methylpyrrolidone (NMP) and subjecting the mixture to mild sonication in an ultrasonic bath for 20 minutes. The paste was then dip-coated onto Pt mesh (25mm x 50mm) and dried under vacuum at $250 \text{ }^{\circ}\text{C}$ for 24 h. This step was repeated until all of the paste was deposited on the Pt mesh. The mesh was then folded and pressed manually into a pellet. The hBN-Pt pellet was wrapped with a hydrophilic polycarbonate membrane (200 nm Pore size) and then used as an anode in an electrochemical cell having a Pt mesh cathode and an aqueous electrolyte containing 0.2 M of sodium acetate trihydrate, 0.1 M sodium citrate, and 0.2 M nitric acid. A constant current of 100 mA was applied for 24 hours. The powder in the membrane was then washed with 2 L of water and the solid was separated from the liquid by centrifugation at 6000 rpm. The powder was then sonicated in an ultrasound bath (135 W) using sealed glass vials in water for 30 minutes to achieve the final suspension.

[0077] A white stable dispersion having a concentration $\sim 0.5 \text{ mg/mL}$ was produced. This concentration was almost twice that previously reported for oxygenated hBN. Atomic force microscopy (AFM) topographic images of the resultant nanoplatelets indicated a thickness of $\sim 1 \text{ nm}$ and a lateral size of $\sim 2 \text{ }\mu\text{m}$ was observed (Figure 2). The lateral size was further confirmed by the SEM image (Figure 3). The exfoliation was confirmed further by the XRD analysis (Figure 4), in which the intensity of the 002 peak at $2\theta \sim 26.5^{\circ}$, which characterizes the π - π stacking of the hBN sheets in the bulk gallery, had significantly decreased relative to the bulk hBN and the peak had clearly widened. Also, the diffraction peaks associated with H_3BO_3 were clearly visible, indicating the electrochemical treatment had led to the oxidation of the hBN nanoplatelets. Raman spectra of pristine hBN and oxygenated hBN nanoplatelets from water suspensions show differences in integrated intensity and the position of peaks: while the Raman spectrum of the commercial bulk hBN has a sharp band at 1366 cm^{-1} , the Raman spectrum of the water soluble oxygenated hBN nanoplatelets shows a less intense peak which has shifted to $\sim 1361 \text{ cm}^{-1}$.

Example 2

Example 1 was repeated using MoS₂ powder (Naturally occurring, 15 µm average size) in place of the hBN powder.

- 5 The concentration of the resultant water dispersion was measured to be 0.4 mg/mL. The exfoliation was confirmed by AFM, which showed nanoplatelets having a thickness below 2.5 nm (Figure 6).

Example 3

Example 1 was repeated using WS₂ powder (Sigma, less than 2 micron) in place of the hBN powder.

- 10 A light green solution having a concentration of 0.1 mg/mL was produced (see digital image in Figure 7). The exfoliation was first proved by Raman analysis. Generally there are two vibration modes of A_{1g} at ~ 420 cm⁻¹ and E_{2g}¹ at ~354 cm⁻¹, representing the out-of-plane W–S phonon mode and the in-plane W–S phonon mode, respectively. The ratio between the intensity of the two peaks E_{2g}¹/A_{1g} are in the range of 0.7 for the bulk sample.
- 15 This ratio increases as the number of layers decreases. From Figure 8, the ratio E_{2g}¹/A_{1g} was around 1.2, suggesting a successful exfoliation. That the exfoliation was a success was further confirmed by AFM analysis which showed nanoplatelets having a thickness of around 3 nm (figure 9).

CLAIMS

1. A method of producing oxygenated nanoplatelets of an inorganic material from a layered inorganic material in an electrochemical cell, the layered inorganic material being formed of two or more elements that are not oxygen;
- 5 the cell comprising:
 - an inert anode which is in contact with the layered inorganic material;
 - a cathode;
 - an electrolyte comprising a source of polyatomic anions;and wherein the method comprises:
 - 10 passing a current through the cell to produce oxygenated nanoplatelets of the inorganic material.
 2. A method according to claim 1, wherein the step of passing the current through the cell produces a mixture of oxygenated nanoplatelets of the inorganic material and layered inorganic material having polyatomic anions intercalated between the layers and the method further comprises:
 - 15 collecting the resulting mixture of oxygenated nanoplatelets of the inorganic material and layered inorganic material having intercalated polyatomic anions;
 - suspending the mixture in an aqueous medium to form a suspension; and
 - subjecting the suspension to energy to exfoliate the oxygenated layered inorganic material having intercalated polyatomic anions and to increase the amount of oxygenated nanoplatelets of the inorganic material in the suspension.
 3. A method of claim 1 or claim 2, wherein the layered inorganic material is hexagonal boron nitride.
 4. A method of claim 1 or claim 2, wherein the layered inorganic material is a transition metal dichalcogenide.
 - 25 5. A method of any one of claims 1 to 4, wherein the inert anode is coated with the layered inorganic material.
 6. A method of claim 5, wherein the entire surface of the inert anode is coated with the layered inorganic material.
 - 30 7. A method of any one of claims 1 to 6, wherein the inert anode and the layered inorganic material are together contained within a porous material.

8. A method of any one of claims 1 to 7, wherein the inert anode is or comprises platinum.
9. A method of any one of claims 1 to 8, wherein the electrochemical cell comprises a reference electrode.
- 5 10. A method of any one of claims 1 to 9, wherein the electrolyte is aqueous
11. A method of any one of claims 1 to 10, wherein the polyatomic anions comprise oxygen; optionally wherein the polyatomic anions are selected from nitrate, phosphate, sulfate, hydroxide, permanganate, dichromate, peroxide, percarbonate, persulfate, periodate and perchlorate.
- 10 12. A method of claim 11, wherein the source of polyatomic anions is nitric acid or a nitrate salt.
13. A method of claim 11 or claim 12, wherein the electrolyte further comprises either non-ionic organic compounds or organic anions
14. A method of claim 13, wherein the non-ionic organic compounds or organic anions
15 are carboxylic acids or carboxylate salts.
15. A method of claim 14, wherein the organic anions comprises carboxylate ions
16. A method of claim 15, wherein the carboxylate anions are citrate and/or acetate ions
17. A method of claim 16, wherein the electrolyte comprises sodium acetate and
20 sodium citrate.
18. Oxygenated nanoplatelets of an inorganic material prepared according to the method of any one of claims 1 to 17.
19. An aqueous suspension of oxygenated nanoplatelets of hexagonal boron nitride in which the concentration of the nanoplatelets in the suspension is higher than or equal to
25 0.4 mg/mL.
20. Oxygenated nanoplatelets of a transition metal dichalcogenide.

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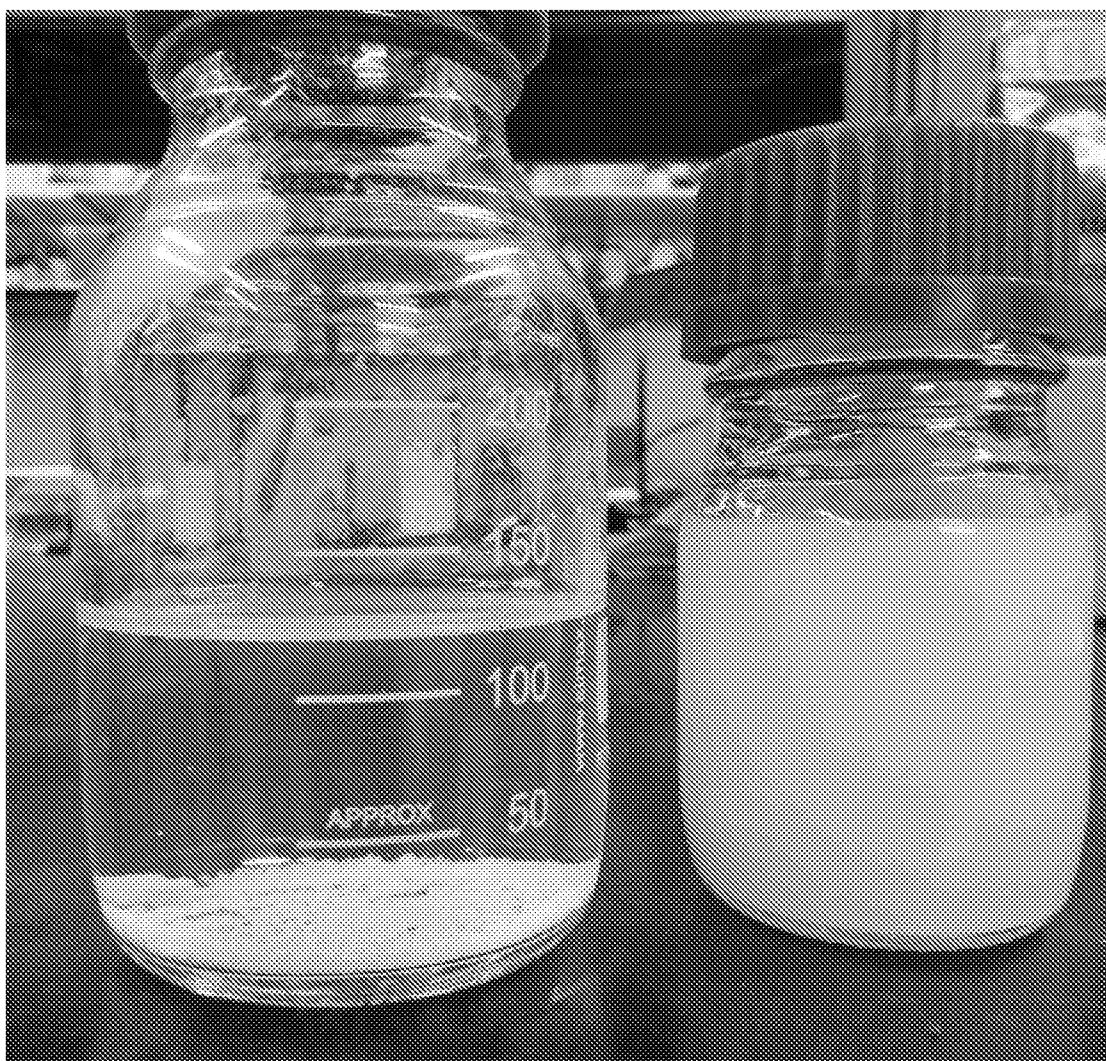


FIGURE 1

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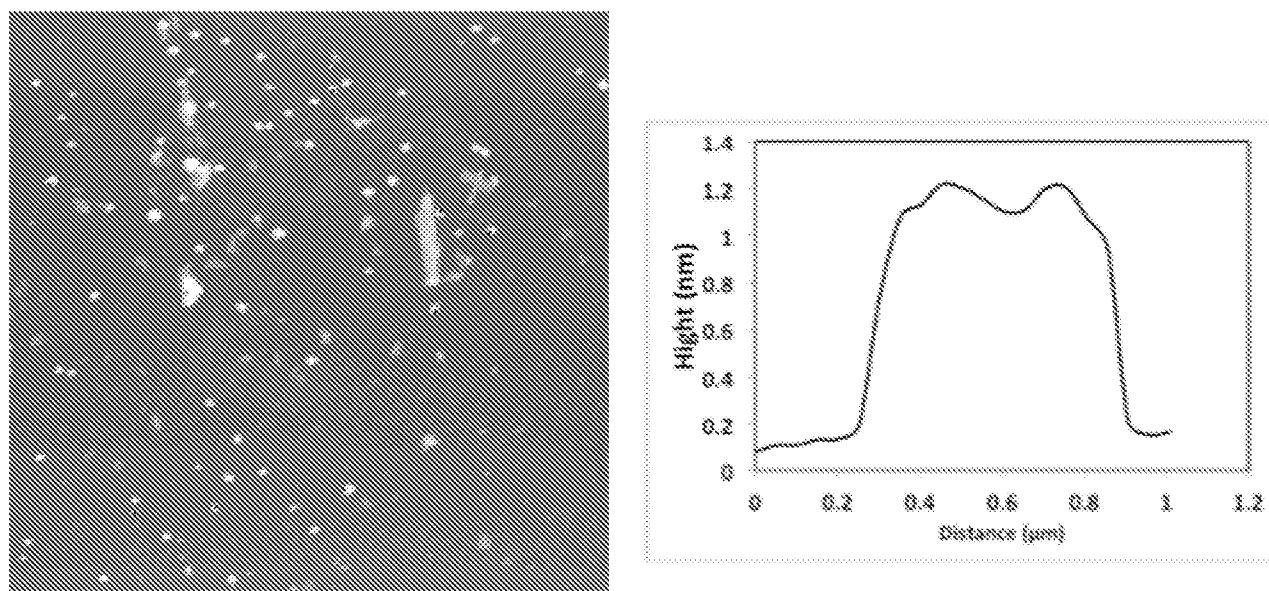


FIGURE 2

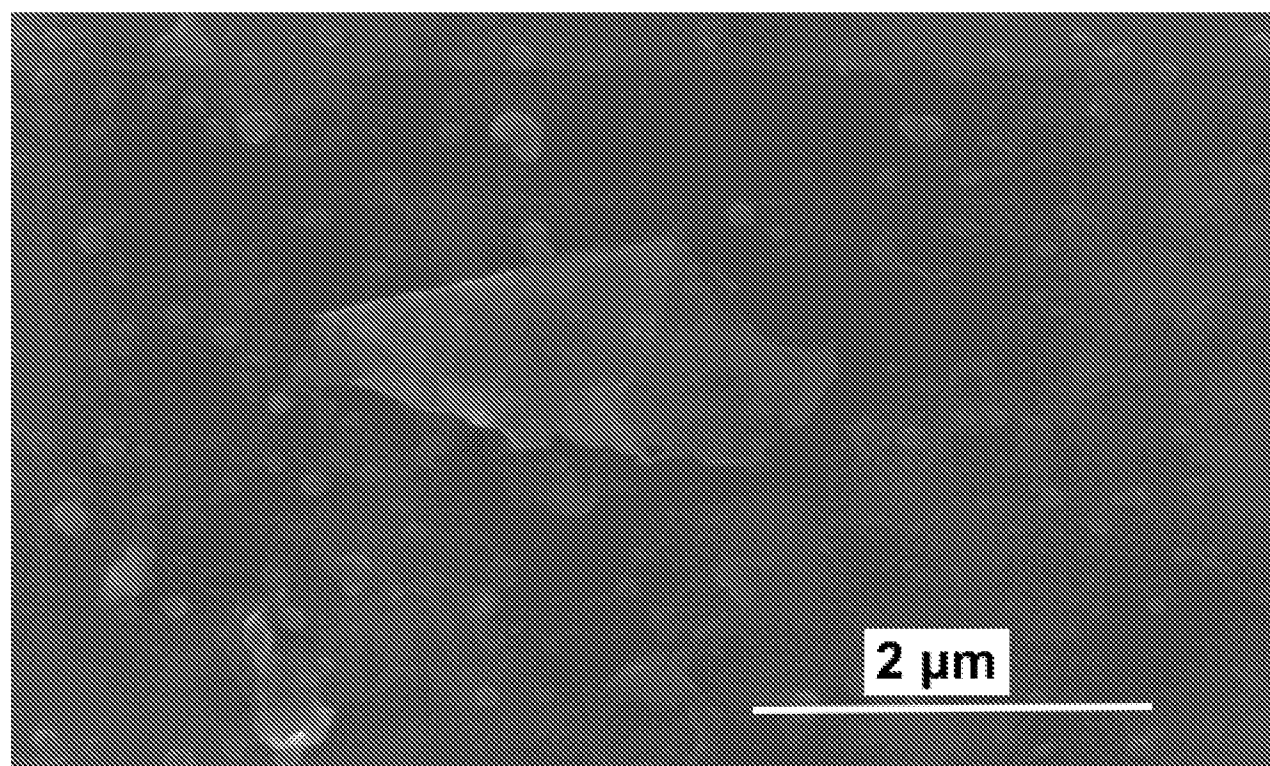


FIGURE 3

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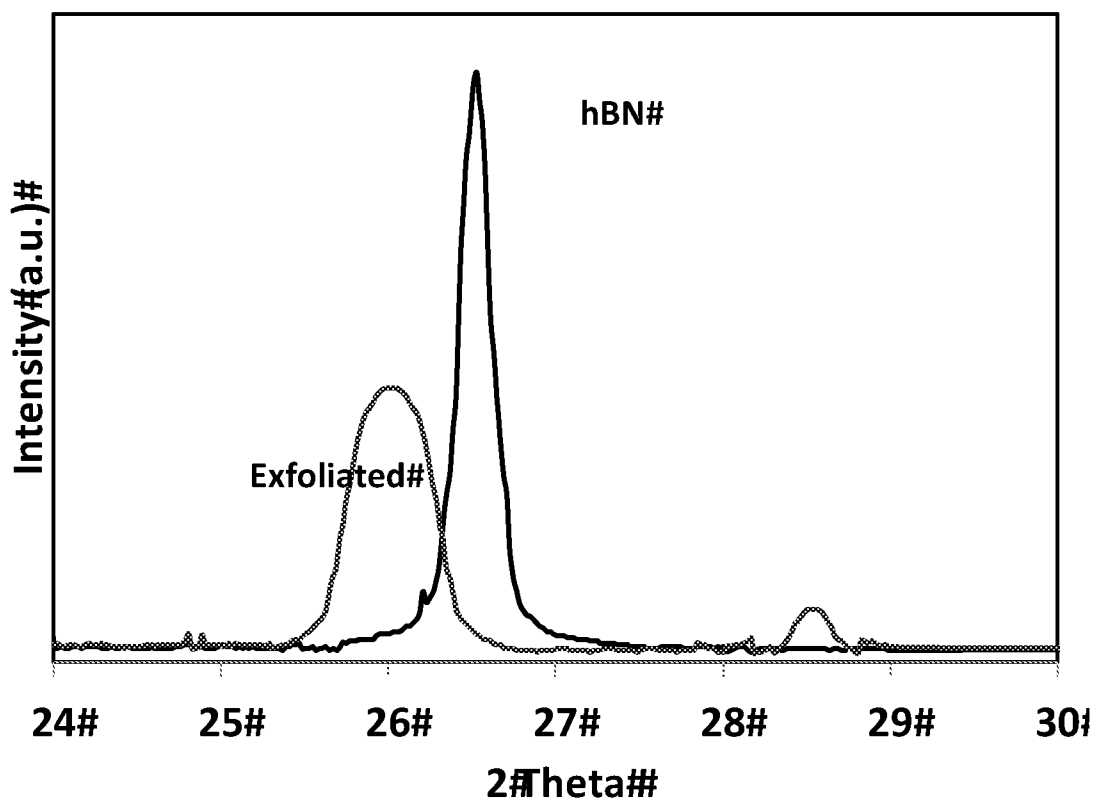


FIGURE 4

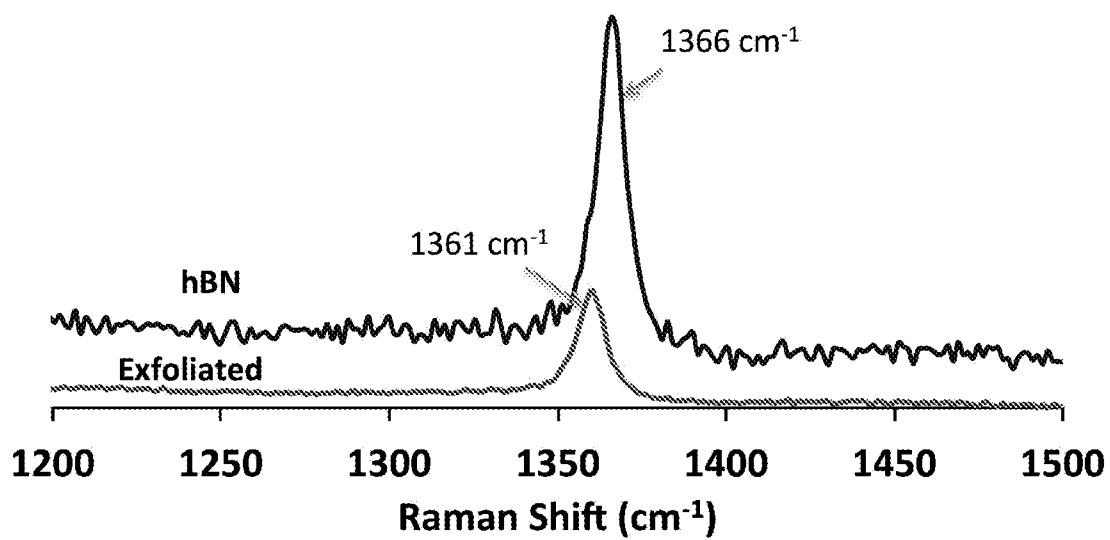


FIGURE 5

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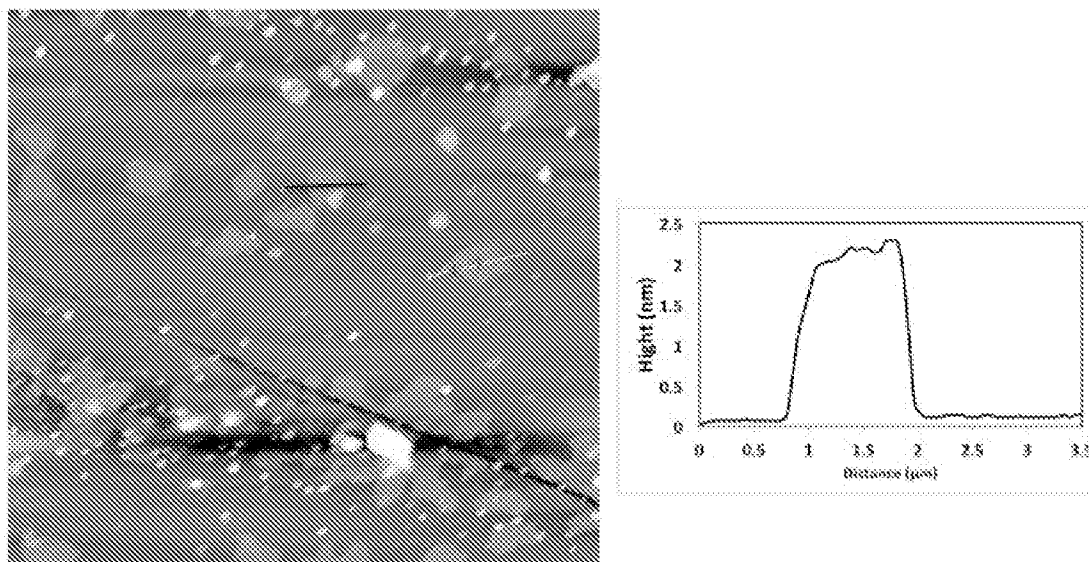


FIGURE 6

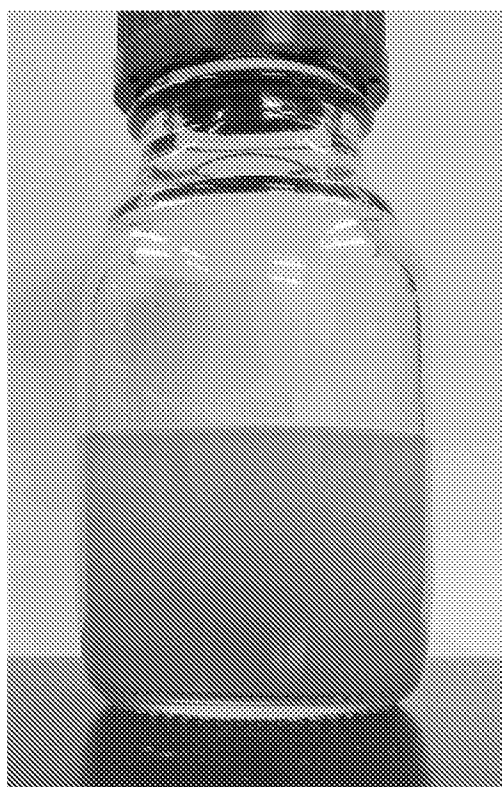


FIGURE 7

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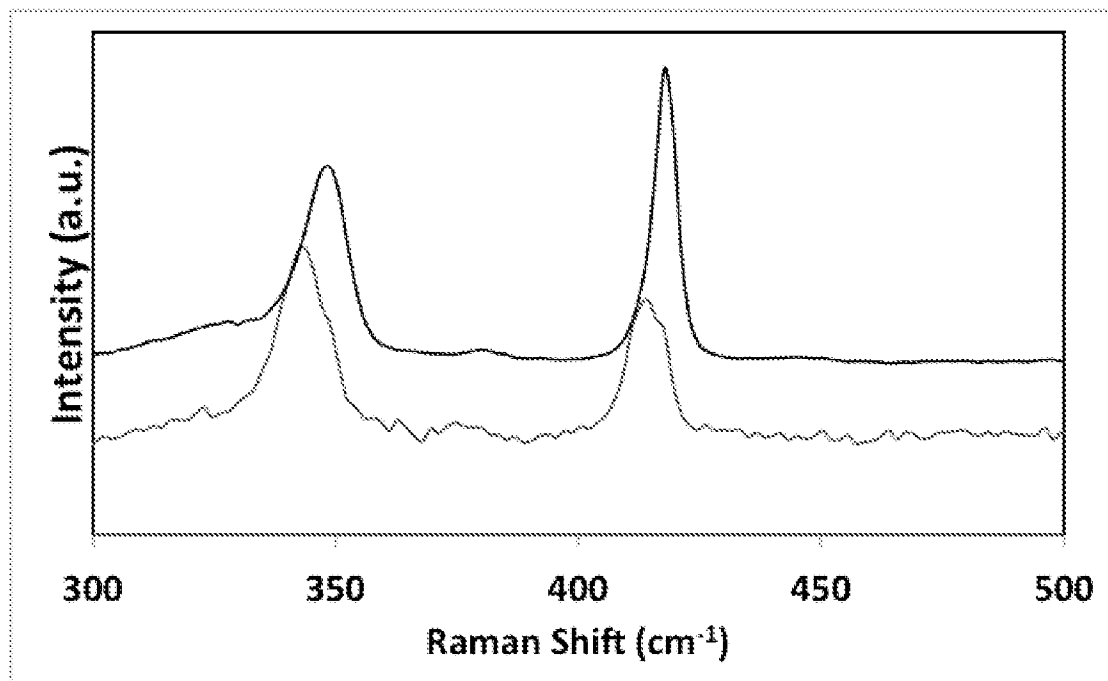


FIGURE 8

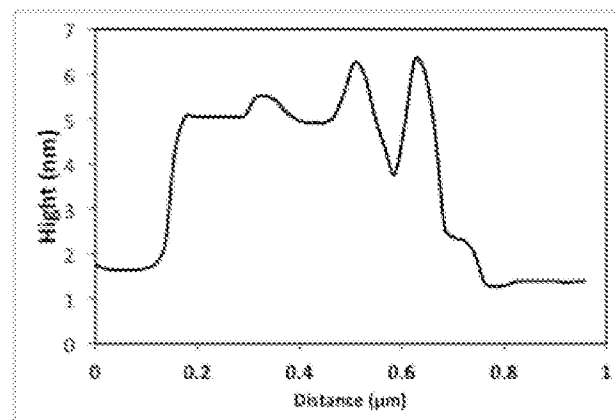


FIGURE 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/053768

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25B1/00
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)
C25B

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	page 5, line 28 - page 10, line 14; claims 1-13; examples 1-10 page 31, line 10 - page 38, line 3 -----	3,4
X	WO 2015/114357 A2 (UNIV MANCHESTER [GB]) 6 August 2015 (2015-08-06) abstract; claims 1, 3; figures 1-19; table 1 page 1, paragraph 0001 - page 3, paragraph 0018 page 13, paragraph 0070 - page 21, paragraph 0094 page 22, paragraph 0097 - page 25, paragraph 00109 page 33, paragraph 00135 - page 39, paragraph 00159 ----- -/--	18-20



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search

7 February 2017

Date of mailing of the international search report

16/02/2017

Name and mailing address of the ISA/

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Authorized officer

Cojuhovschi, Oana

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/053768

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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X	WO 2014/130687 A1 (UNIV CONNECTICUT [US]) 28 August 2014 (2014-08-28) abstract; figures 4-21 page 5, line 25 - page 14, line 5 page 19, line 26 - page 21, line 5 -----	18,19
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International application No

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