



- (51) International Patent Classification:
C01B 31/04 (2006.01) *C25B 1/00* (2006.01)
- (21) International Application Number:
PCT/GB2016/050792
- (22) International Filing Date:
22 March 2016 (22.03.2016)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
1505304.4 27 March 2015 (27.03.2015) GB
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- (81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to the identity of the inventor (Rule 4.17(i))*
- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

- *with international search report (Art. 21(3))*

- (54) Title: PRODUCTION OF FUNCTIONALIZED GRAPHENE

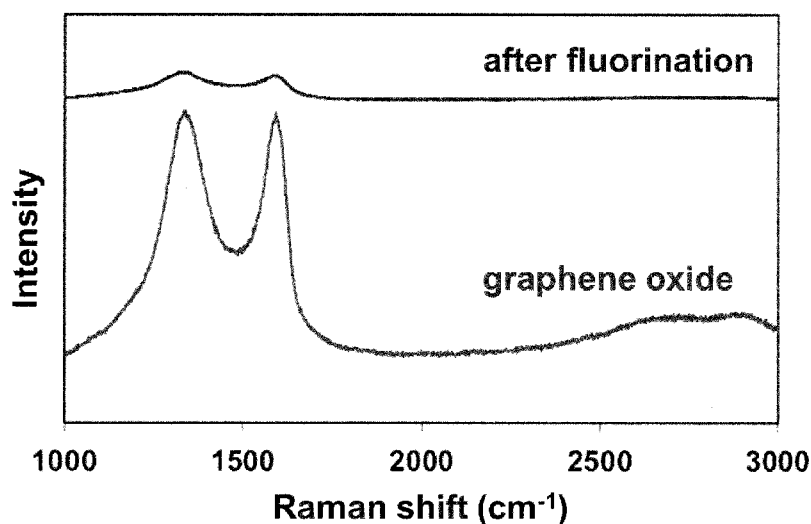


Figure 7

- (57) Abstract: The present invention relates to a process for the production of halographene and related halogenated graphite nanoplatelet structures.



Production of Functionalized Graphene

This application claims priority from GB 1505304.4 filed 27 March 2015, which is
5 incorporated by reference for all purposes.

Field of invention

The present invention relates to a process for the production of halographene and related
halogenated graphite nanoplatelet structures.

Background

Graphene is an atomically thick, two dimensional sheet composed of sp^2 carbons in a
honeycomb structure. It can be viewed as the building block for all the other graphitic
carbon allotropes. Graphite (3-D) for example includes many layers of graphene stacked on
15 top of each other, with an interlayer spacing of $\sim 3.4 \text{ \AA}$ and carbon nanotubes are graphene
tubes.

Single-layer graphene is one of the strongest materials ever measured, with a tensile
strength of $\sim 130 \text{ GPa}$ and possesses a modulus of $\sim 1 \text{ TPa}$. Graphene's theoretical surface
20 area is $\sim 2630 \text{ m}^2/\text{g}$ and the layers are gas impermeable. It has very high thermal (5000
 W/mK) and electrical conductivities (up to 6000 S/cm).

There many potential applications for graphene, including but not limited to:

- (a) an additive for mechanical, electrical, thermal, barrier and fire resistant properties
25 of a polymer;
- (b) an active component of an electrode for enhancing surface area and conductivity
for applications such as fuel cells, super-capacitors and lithium ion batteries;
- (c) a conductive, transparent coating for the replacement of indium tin oxide (such as
used in touch-screen technologies); and
- 30 (d) a component in electronics.

Graphene was first reported in 2004, following its isolation by Professor Geim's group at the
University of Manchester. Graphene research since then has increased rapidly. This
research has extended to functionalised graphene and the advantageous properties various
35 functionalized graphene products exhibit.

Fluorographene (FG) is such a functionalized graphene. It may also be referred to as perfluorographene and graphene fluoride. It is a transparent fluorinated carbon nanomaterial, and is regarded as one of the important candidate materials for advanced technological applications because of its distinctive magnetic, electrical and electronic properties. These include

- (a) a high negative magneto resistance (a factor of 40 at the field of 9 T),
- (b) a wide optical bandgap (3.8 eV), and
- (c) a strong insulating behaviour (room-temperature resistance larger than 10 GU).

Fully-fluorinated graphene has a fluorine atom bound to each carbon atom. Its theoretical chemical formula is $(CF)_n$. Of course, it will be appreciated that defects and edge states will result in local variation of this theoretical formula.

Fluorographene, in its most stable state, has a chair-type conformation, similar to graphane.

A number of methods have been used previously to synthesize fluorographene. For example, graphene has been synthesized by heating graphene in fluorine containing atmosphere such as XeF_2 , CF_4 , F_2 etc gases at high temperature.¹⁻³ Laser irradiation has also been reported selectively to fluoridize graphene covered by fluoropolymers.⁴

Fluorographene can be also produced in reasonable quantities via solution-based mechanical exfoliation of graphite fluoride in organic solvents.⁵⁻⁶ Chemical exfoliation of fluorinated graphite has also been utilized for the preparation of fluorographene, followed by ultrasonication in a liquid-phase environment. However, these methods are complicated, often use atmospheres of highly toxic gases, and give only low yield and / or poor fluorination.

CN104445154 describes a method of producing what it describes to be fluorinated graphene by arc discharge.

In Nanoscale, 2014, 6, p6065 Jankovsky et al. describe bromination of graphite oxide using bromine or hydrobromic acid under reflux in an autoclave at elevated temperature and pressure. They describe the product as brominated graphene.

Summary of invention

The present inventors have conceived a new process for producing halogenated graphene and related halogenated graphene nanoplatelet structures from graphene and / or graphite platelets and / or graphene oxide using redox processes. The process of the invention is

carried out in an electrochemical cell. The process does not require the forcing high temperature and / or pressure conditions of the chemical methods of the prior art, and is therefore safer and more energy efficient. The process of the invention is easily implemented (typically single step) and can be used to produce large quantities of material, which is typically of very high quality. As described herein, the source of halogen may be a halide salt, which minimises the use of potentially toxic gaseous starting materials. Through selection of appropriate conditions, little or no toxic halogen gas is produced as a by-product.

In a first aspect, the present invention provides process for producing halogenated graphene and / or halogenated graphite nanoplatelet structures having a thickness of less than 100 nm, the process comprising electrochemical reaction of graphite platelets and / or graphene and / or graphene oxide in an electrochemical cell, wherein the cell includes:

(a) a negative electrode comprising said graphite platelets and / or graphene and / or graphene oxide;

(b) a positive electrode; and

(c) an electrolyte comprising halide ions and / or elemental halogen;

wherein the process includes the step of passing a current between the electrodes.

Preferably, the process produces halogenated graphene. More preferably, the process produces more halogenated graphene by total surface area and /or by weight than halogenated graphite nanoplatelet structures. More preferably, the process produces substantially only halogenated graphene.

As used herein, graphene and halogenated graphene refer to single layer and "few layer (halogenated) graphene", which is typically 2 to 10 (halogenated) graphene layers thick. The properties of the material, particularly the electronic properties, are a function of the number of layers.

Suitably, the starting material, which may be graphite platelets and / or graphene and / or graphene oxide, is provided an outer coating of a negative electrode. For example, the starting material may be applied as a paste and then dried. The thickness of such a coating may vary. For example, the inventors have shown that a 2 mm thickness works in the processes described herein. Accordingly, the thickness may be any suitable thickness. For example, and not by way of limitation, the thickness may be from 1 μ m to 1 cm. It will be appreciated that thicker layers may produce more material but may require longer reaction times.

Suitably, the starting material is provided on a conductive rod. Together, they form the anode. For example, the starting material may be provided deposited onto a glassy carbon rod. Glassy carbon (also referred to as glass-like carbon and vitreous carbon) is known in the art as an electrode material.

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However, it will be appreciated that the anode may comprise only starting material, which may, for example, be pre-formed in a mould.

Without wishing to be bound by any particular theory, the inventors believe that, during the step of passing a current between the electrodes halide ions migrate to the anode, where they are reduced to generate a halogen atom. This halogen atom adsorbs to the surface of the graphene and / or graphite nanoplatelet structures, where it undergoes a reaction to form a covalent bond.

Where the starting material is graphene oxide, the loss of oxygen and halogenation at thought to occur at least partially contemporaneously. Without wishing to be bound to any particular theory, the inventors speculate that the process is dependent on the oxygen functionality present. Some direct replacement of oxygen-containing groups is thought to occur, along with ring opening of epoxide moieties (if present). The inventors also speculate that reaction between the oxygen-containing groups and the halogen may occur to generate, for example, hypofluorite and hypochlorite moieties.

In some embodiments the starting material is graphite platelets. In some embodiments the starting material is graphene. In some embodiments, the starting material is graphene oxide. The graphene oxide may be single or few layer graphene oxide, or "bulk" graphene oxide (i.e. many layers stacked).

The electrolyte itself may be a halide salt. Mixtures of salts may be used. Mixtures of salts may be eutectic mixtures.

The electrolyte may be molten halide salt. The electrolyte may be halide salt in solution. For example, it may be dissolved in an organic solvent, for example, *N*-methylpyrrolidine, dimethylsulfide, dimethylsulfoxide, dimethylformamide, or dissolved in an ionic liquid.

For example, for fluoride salts the salt may be potassium hydrogen fluoride, hydrogen fluoride, potassium hydrogen fluoride, lithium fluoride, caesium fluoride, sodium fluoride, calcium fluoride, magnesium fluoride, imidazolium fluoroborate, or an ammonium fluoride.

For example, for bromide salts the salt may be lithium bromide, sodium bromide, potassium bromide, caesium bromide, calcium bromide, or magnesium bromide.

- 5 The electrolyte may be an ionic liquid. In other words, the ionic liquid may be the source of halogen, for example, fluorine or bromine.

Ionic liquids are known in the art. Fluorine-containing ionic liquids are known in the art and include 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][NTf₂]), tetrabutylphosphonium tetrafluoroborate, radecyl(trihexyl)phosphonium hexafluorophosphate, tetradecyl(trihexyl)phosphonium tetrafluoroborate, etradecyl(trihexyl)phosphonium hexafluorophosphate, trimethylsulfonium bis(trifluorosulfonimide)tetradecyl (trihexyl)phosphonium tetrafluoroborate, 15 tetrabutylphosphonium tetrafluoroborate, and 1-butyl-2-methylpyridinium hexafluorophosphate.

Bromine-containing ionic liquids are known in the art and include tetrabutylphosphonium bromide, tetradecyl(trihexyl)phosphonium bromide, 1-butyl-2,3-dimethylimidazolium bromide, 20 1-butyl-3-methylimidazolium bromide, 1-decyl-3-methylimidazolium bromide.

It will be appreciated that, for chlorination and iodination, the corresponding salts and ionic liquids may be used.

- 25 A preferred ionic liquid is 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]).

Suitably, the concentration is about 0.5 M halide salt in organic solvent or ionic liquid.

- 30 The electrolyte may be an ionic liquid through which a halogen gas is passed during the step of applying a current. In this case, the halogen gas may react at the cathode to produce halide ions, which may then transfer to the anode to undergo the desired redox process.

- 35 The halogenated graphene and / or halogenated graphite nanoplatelet structures may be fluorinated, chlorinated, brominated or iodinated. In some embodiments it is / they are fluorinated or brominated. In some preferred embodiments it is / they are fluorinated.

Accordingly, the process may be a process for producing fluorographene and / or fluorographite nanoplatelet structures having a thickness of less than 100 nm, wherein the electrolyte comprises fluoride and / or F_2 . Suitably, the electrolyte may be potassium hydrogen fluoride or a fluoride salt, for example, sodium fluoride, dissolved in an ionic liquid, for example an ionic liquid as listed above. A preferred electrolyte is NaF dissolved in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]).

The electrolyte comprising F_2 may be generated by passing F_2 gas through an electrolyte. As described above, during application of a potential difference between the electrodes (the step of passing current), this F_2 is thought to be reduced at the cathode to generate fluoride ions.

In some embodiments, the process is a process for producing bromographene and / or bromographite nanoplatelet structures having a thickness of less than 100 nm, wherein the electrolyte comprises bromide and / or Br_2 . Accordingly, the electrolyte may be, by way of example and not by way of limitation, sodium bromide, lithium bromide, potassium bromide, or mixtures thereof. The electrolyte may also be an ionic liquid containing a suitable halogen source such as a bromonium (Br^+) ion.

Analogous to as described above for fluorine, electrolyte comprising Cl_2 may be generated by passing Cl_2 gas through an electrolyte the electrolyte comprising Br_2 may be generated by passing Br_2 gas through an electrolyte.

The degree of bromination obtained by methods of the invention is desirable. Halogenated graphene derivatives may be interesting for a variety of applications owing to their physical and chemical properties. For example, even low level halogenation may provide materials having desirable electronic properties useful in electronic devices.

Few methods have thus far been reported, and typically display only low bromination with high oxygen content and / or unwanted hydrogenation.

Advantageously, as described herein, the methods of the invention can begin with graphene (rather than graphene oxide) and do not disturb the morphology of the starting material – that is, graphenic character is preserved.

Accordingly, in a further aspect the present invention relates to brominated graphene and to brominated graphite nanostructures (both of which of course may be partially brominated).

Thus, in a further aspect, the present invention may provide brominated graphene and / or brominated graphite nanostructures having a bromine content of greater than 5 at.%, preferably greater than 7 at.%, more preferably greater than 9 at.%. Exemplified herein is bromographene having a bromine content of about 10 at.%.

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Suitably, the brominated graphene and / or brominated graphite nanostructures that are substantially free of other functionalization. For example, it may be preferred that the material produced is substantially free of graphene oxide and brominated graphene oxide (i.e. wherein less than 10% by weight, such as less than 5% by weight, preferably less than 2%, more preferably less than 1% by weight of the material produced is graphene oxide). For example, the oxygen content may be less than 20 at.%, less than 15at.%, less than 10at.%, less than 5at.% or even less than 2at%.

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In a further aspect of the invention is provided halogenated graphene and / or halogenated graphene nanoplatelet structures prepared according to a process as described in any of the above aspects and embodiments. In a further aspect, the invention provides a composition including halogenated graphene and / or halogenated graphite nanoplatelet structures prepared according to a process as described in any of the above aspects and embodiments. In a still further aspect is provided an article including said composition or said halogenated graphene and / or halogenated graphite nanoplatelet structures prepared according to a process as described in any of the above aspects and embodiments, or, optionally, a derivative of said composition or halogenated graphene and / or halogenated graphite nanoplatelet structures.

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25 Detailed Description

Definitions

Graphene, graphene oxide and graphite nanoplatelet structures – layers, thickness, and defects

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The process of the present invention produces halogenated graphene and / or halogenated graphite nanoplatelet structures having a thickness of less than 100 nm. In embodiments, the process produces halogenated graphene or halogenated graphite nanoplatelet structures having a thickness of less than 100 nm. In embodiments, the process produces halogenated graphene and halogenated graphite nanoplatelet structures having a thickness of less than 100 nm. In embodiments, the process of the present invention produces halogenated graphene. In embodiments, the process produces halogenated graphite

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nanoplatelet structures having a thickness of less than 100 nm. The process of the present invention may for example produce halogenated graphene or a combination of halogenated graphene and halogenated graphite nanoplatelet structures having a thickness of less than 100 nm.

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As used herein, graphene, graphene oxide, and halogenated graphene refer to single layer “monolayer” and “few layer” materials. “Few layer” means typically 2 to 10 layers thick. The properties of the material, particularly the electronic properties, are a function of the number of layers. The number of layers may be determined by SEM imagery. The graphenic nature of a structure may be determined spectroscopically.

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The graphite nanoplatelet structures (starting material) and halogenated graphite nanoplatelet structures have a thickness of less than 100 nm. In embodiments, the graphite nanoplatelet structures (starting material) and / or halogenated graphite nanoplatelet structures are ≤ 90 nm thick, such as ≤ 80 , ≤ 70 , ≤ 60 , ≤ 50 , ≤ 40 , ≤ 30 or ≤ 20 nm thick, preferably ≤ 10 nm thick and more preferably ≤ 1 nm thick.

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In embodiments, the process produces more halogenated graphene by surface area than halogenated graphite nanoplatelet structures having a thickness of less than 100 nm, preferably wherein substantially all material produced by the process is halogenated graphene by surface area (wherein at least 90%, preferably at least 95%, more preferably at least 98%, e.g. at least 99% of the material produced by the process is halogenated graphene by surface area), such as wherein all material produced by the process is halogenated graphene. In embodiments, the process produces more halogenated graphene by weight than halogenated graphite nanoplatelet structures having a thickness of less than 100 nm, preferably wherein substantially all material produced by the process is halogenated graphene by weight (wherein at least 90%, preferably at least 95%, more preferably at least 98%, e.g. at least 99% of the material produced by the process is graphene by weight), such as wherein all material produced by the process is halogenated graphene.

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The honeycomb of carbon atoms in graphene is typically a uniform polyhexagonal structure. The skilled person will understand however that graphene may include one or more amorphous regions (i.e. regions of amorphous graphene), such as wherein the carbon atoms do not form uniform hexagons. For instance, graphene may include Stone-Wales defects wherein one or more rings of carbon atoms contains other than six carbons in number (i.e. where the number of carbons in a single ring is other than six carbons in number), such as rings of carbon atoms independently selected from five (e.g. pentagonal),

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seven (heptagonal), eight (octagonal), nine (nonagonal) and ten (decagonal) carbon atoms, particularly one or more of five (e.g. pentagonal), seven (heptagonal), and eight (octagonal) carbon atoms, more particularly one or more of five (e.g. pentagonal) and seven (heptagonal) carbon atoms. It will be appreciated that such amorphous regions will be halogenated to produce regions having halogenated carbon rings containing more and / or carbon atoms than six. Typically, the material produced by the present process is substantially free of amorphous halogenated graphene. For instance, the material may contain less than 10% by weight, for example less than 5% by weight, preferably less than 2% by weight, more preferably less than 1% by weight of amorphous halogenated graphene. In embodiments, the material produced by the present process does not include amorphous halogenated graphene. It will be appreciated that the degree of amorphous halogenated graphene will typically be determined by the morphology starting material.

Halogenated graphene and halogenated graphite nanoplatelet structures – extent of halogenation

The process of the present invention provides a desirable extent of halogenation.

Fully-halogenated graphene has the theoretical chemical formula $(CX)_n$, wherein X represents a halogen. For example, fully-fluorinated graphene has the theoretical chemical formula $(CF)_n$, that is, a 1:1 ratio of carbon : fluorine. Of course, it will be appreciated that defects and edge states will result in local variation of this theoretical formula. For example, at holes and edges carbon atoms may bear more than one fluorine atom, leading to $>CF_2$ and $-CF_3$ positions.

It will be appreciated that halogenated, as used herein, refers to 2D and nanoplatelet materials having less than 100% halogenation (i.e. not fully fluorinated) in addition to fully halogenated material. For example, the halogenated graphene and halogenated graphite nanoplatelet structures may have at least 10 at.% X, more preferably at least 20 at.% X, more preferably at least 25 at.% X, more preferably at least 30 at.% X, more preferably at least 35 at.% X, more preferably at least 40 at.% X. In embodiments, the halogenated graphene and halogenated graphite nanoplatelet structures may be substantially fully-halogenated. For example, they have at least 45 at.% X, at least 47 at.% X, or even about 50 at.% X. In each case, X is a halogen, for example, F, Cl, Br, or I, preferably F or Br, more preferably, F.

It will be appreciated that halogenated, as used herein, refers to 2D and nanoplatelet materials having less than 100% halogenation (i.e. not fully halogenated) in addition to fully

halogenated material. For example, the halogenated graphene and halogenated graphite nanoplatelet structures may have a halogen:carbon ratio of $\geq 0.2:1$, more preferably $\geq 0.3:1$, more preferably $\geq 0.4:1$, more preferably $\geq 0.5:1$, more preferably $\geq 0.6:1$, more preferably $\geq 0.7:1$, more preferably $\geq 0.8:1$.

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In embodiments, the halogenated graphene and halogenated graphite nanoplatelet structures may be substantially fully-halogenated. For example, they have a halogen:carbon ratio of $\geq 0.9:1$, more preferably $\geq 0.95:1$, or even about 1:1.

10 It will be appreciated that, because halogen species can intercalate between the layers of few layer graphene, the maximum theoretical value is 50 at.% even for multilayer graphene.

The present invention provides, in some embodiments, halogenated graphene and halogenated graphite nanoplatelet structures that are substantially fully-halogenated. For
15 example, Example 1 details the production of halogenated graphene having 51 at.% F content. This slightly greater than theoretical maximum value may be attributed to experimental error and / or additional fluorination at edges and holes. Certain halogen atoms may also bond to other halogen atoms, slightly increasing the halogen content. For example, the inventors have observed a small amount bromine-bromine attachment in the
20 bromographene materials and methods described herein.

Small amounts of other functionalization may be present. "Other functionalization" as used herein refers to bonds to atoms other than to the desired halogen (for example, to oxygen and other atoms/functional groups).

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Suitably, the process produces halogenated graphene and / or halogenated graphite nanostructures that are substantially free of other functionalization. For example, it may be preferred that the material produced is substantially free of graphene oxide and halogenated graphene oxide (i.e. wherein less than 10% by weight, such as less than 5% by weight,
30 preferably less than 2%, more preferably less than 1% by weight of the material produced is graphene oxide).

For example, the halogenated graphene and / or halogenated graphite nanostructures may include carbon-boron bonds.

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Suitable conditions*Potential difference*

During the step of passing a current through the cell, a potential difference (PD) is applied between the anode and cathode. This is referred to as the voltage. Suitable voltage may be in the region of 1-5 V, more preferably 2-4 V, more preferably, 2.5-3.5 V. A preferred voltage is 3.0 V. A reference electrode may be used to enable better control of the process. When measuring the potential with reference to the reference electrode, the discharge potential may be lower than 1 V.

During the processes described herein, halogen atoms are thought to be generated at the anode. Preferably, these adsorb onto the surface of the graphene and / or graphite nanoplatelet structures to undergo the desired covalent bond formation. However, the present inventors observe that, if the potential difference is higher than necessary for this desired reaction, halogen atoms may combine to generate halogen gas, which bubbles away as a by-product. Through appropriate selection of the (PD) applied, the unwanted generation of halogen gas at the anode may be minimised. It will be appreciated that exhaust gases from the reaction may be scrubbed, as it known in the art.

Suitably, the process is not carried out at substantially elevated pressure. For example, the process may be carried out at atmospheric pressure, or slightly above (for example, under a positive pressure argon flow). For example, the pressure may be less than 2.0 atm, less than 1.5 atm, less than 1.2 atm. Using elevated pressures may improve the solubility of the halogen in the electrolyte.

The positive electrode

The positive electrode is the electrode held at the more positive potential of the negative and positive two electrodes. The positive electrode may consist of any suitable electrode material known to those skilled in the art.

The positive electrode may thus be selected independently from any of the embodiments described herein for the negative electrode. The positive electrode may be identical or different in substance to the negative electrode, typically different. Where the positive electrode is identical in substance to the negative electrode, the electrodes will differ only in terms of their relative electrical potential. For instance, the positive electrode 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 positive electrode is made from an inert material. In embodiments, the positive electrode is formed from stainless steel.

Reference electrode

5 A reference electrode (or pseudo-reference electrode) may also be used, in addition to the negative and positive electrodes. The reference electrode may be any suitable material, such as Ag/AgCl, Ag/AgBF₄. The use of a reference electrode may assist control of the potential distribution of the system. In turn this can lead to improved reproducibility and minimise the generation of halogen gas at the anode.

Operating temperature

10 The electrochemical cell may be operated at any suitable temperature that allows for production of the desired graphene / graphite nanoplatelet structures. The optimum operating temperature will depend on the nature of the electrolyte and / or the form of carbon oxide used (as well as its solubility in the electrolyte medium).

20 The temperature within the electrochemical cell may thus be at least 10°C, preferably at least 20 °C. For instance, the temperature within the electrochemical cell may be cell room temperature. In some embodiments, the temperature within the electrochemical cell is at least 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C or 100 °C. In the case of molten salts, the temperature within the cell may for example be up to 1500 °C. In some embodiments, the temperature within the cell does not exceed 1000 °C, 900 °C, 800 °C or 700 °C, preferably the cell operating temperature does not exceed 650 °C, 600 °C, 550 °C, 500 °C, 450 °C, 400 °C, 350 °C, 300 °C, 250 °C, 200 °C, 150 °C or more preferably 120 °C. In other
25 embodiments, the temperature within the cell does not exceed 110 °C, more preferably the temperature within the cell does not exceed 100 °C, 90 °C, 80 °C, 70 °C, 60 °C or more preferably 50 °C.

Operating pressure

30 The electrochemical cell may be operated at any suitable pressure that allows for production of the desired halogenated graphene / graphite nanoplatelet structures. The optimum operating pressure will depend on the nature of the electrolyte. Typically, the cell is operated at or above atmospheric pressure. The cell may for example be operated at pressures greater than atmospheric pressure, which would have the advantage of increasing
35 halogen gas solubility in the electrolyte.

Operating atmosphere

The electrochemical cell may be operated under any suitable gaseous atmosphere. For example, the electrochemical cell in processes of the invention may be operated under an anhydrous atmosphere and / or an inert atmosphere. Suitably, the cell may be operated under nitrogen and / or argon. However, the electrochemical cell may also be operated under air, CO₂, helium or even a mixture of such gases. In some embodiments, the atmosphere may comprise a halogen gas: either a pure halogen gas or a halogen gas in a carrier gas, for example, fluorine in helium, argon or neon.

Duration of reaction

The electrochemical process may be operated for a length of time adequate to provide a desirable degree of halogenation of the graphene and / or graphite nanoplatelet structures. The duration of the process typically refers to the length of time that a current is passed between the electrodes during the current passing step of the process. The current may be passed between the electrodes continuously or intermittently, typically continuously. Intermittent current may include switching polarity between two identical electrodes.

In some embodiments, the length of time that a current is passed between the electrodes in the current passing step is greater than 10 min, 20 min, 30 min, 40 min, 50 min preferably greater than one hour. Typically, the reaction duration from 1 h to 72 h, such as from 1 h to 48 h, for instance 1 h to 24 h. In further embodiments, the length of time that a current is passed between the electrodes in the current passing step is from 1 h to 10 h, 1 h to 5 h or 1 h to 4 h. Typically the length of time is about 3 h.

Additional process steps

In some embodiments, the process includes an initial step of forming a deposit of graphene and /or graphene oxide and /or graphite nanoplatelet structures onto a suitable material for use as an electrode. For example, the process may include an initial step of forming a deposit of graphene and /or graphene oxide and /or graphite nanoplatelet structures onto glassy carbon, for example, onto a glassy carbon rod.

In some embodiments, the process further includes the step of isolating the halogenated graphene / halogenated graphite nanoplatelet structures.

Where the halogenated graphene / graphite nanoplatelet structures are suspended in the electrolyte or have fallen to the floor of the electrochemical cell, isolation of the halogenated

graphene / graphite nanoplatelet structures can be achieved by separation from the electrolyte according to a number of separation techniques, including:

(a) filtering;

(b) using centrifugal forces to precipitate / accumulate the halogenated graphene or halogenated graphite nanoplatelet structures; and

(c) collecting the halogenated graphene or halogenated graphite nanoplatelet structures at the interface of two immiscible solvents.

In some embodiments the halogenated graphene / graphite nanoplatelet structures are isolated by filtration. For example, the halogenated graphene / graphite nanoplatelet structures may be isolated by filtration using a fine membrane material, such as Anopore™ inorganic membrane (i.e. Anodisc™ which is commercially available from GE Healthcare).

In some embodiments, the halogenated graphene and / or halogenated graphite nanoplatelet structures having a thickness of less than 100 nm are obtained as a deposit (e.g. coat) on the negative electrode. Isolation may be performed by mechanical removal of the deposit from the electrode surface, such as by mechanical abrasion or by ultrasonication. In some cases, halogenated graphene and / or halogenated graphite nanoplatelet may be collected from the electrolyte by leaching out the electrolyte and filtration.

The process may include the further step of manipulating the halogenated graphene / graphite nanoplatelet structures either prior to isolation (such as in the electrochemical cell), or after isolation from the electrochemical cell. For example, the halogenated graphene / graphite nanoplatelet structures may be washed to remove contaminants prior to or following isolation, for instance to remove residual electrolyte from the product surface. In embodiments, the process includes the step of forming and / or shaping the halogenated graphene / graphite nanoplatelet structures prior to, or following, isolation, such as forming and / or shaping the halogenated graphene into an article. In embodiments, the process includes the step of incorporating the halogenated graphene and / or halogenated graphite nanoplatelet structures into an article.

In some embodiments, the halogenated graphene / graphite nanoplatelet structures are subject to exfoliation, such as by using ultrasonic energy and / or other techniques known to those skilled in the art to decrease the flake size and number of graphene layers. Exfoliation by sonication for instance may be performed after the electrochemical reaction has completed and / or during the electrochemical reaction.

Suitably, the present processes include a pre-electrolysis step to purify the electrolyte prior to passing a current between the electrodes. This pre-electrolysis step may include passing a current through the electrolyte between two additional electrodes before the electrochemical halogenation reaction has commenced. The additional electrodes may be formed of any suitable conducting material, such as platinum.

Typically, the process of the present invention does not include irradiating an electrode surface.

The skilled person will understand that the above embodiments are described by way of example only. Other embodiments falling within the scope of the claims will be apparent to the skilled reader. It will be appreciated that the features specified in each aspect and embodiment may be combined with other specified features in other embodiments, to provide further embodiments.

Brief Description of the Drawings

Figure 1 shows high resolution scans of the XPS C1s peak of the starting material (A) and product (B) of example 1.

Figure 2 shows an XPS scan of the product of example 1.

Figure 3 shows overlaid Raman spectra of the starting material and product of example 1.

Figure 4 shows overlaid FTIR spectra of the starting material and product of example 1.

Figure 5 shows SEM images of the product of example 1.

Figure 6 shows a high resolution scan of the XPS C1s peak of the product of example 2.

Figure 7 shows overlaid FTIR spectra of the starting material and product of example 2.

Figure 8 shows overlaid Raman spectra of the starting material and product of example 2.

Figure 9 shows a high resolution scan of the XPS C1s peak of the product of example 3.

Figure 10 shows an XPS scan of the product of example 4.

Figure 11 shows XPS scans of the product of example 5.

Experimental Analysis

Raman Spectroscopy

Raman spectroscopy was conducted using a Renishaw RM Mkl system 1000 with 633 nm HeNe laser (at power <mW) as the excitation source; and Renishaw inVia Raman microscope equipped with 532 nm and 633 nm excitation sources. Flakes of the material to be analysed were deposited on an oxide-covered silicon wafer.

The Raman signatures for a halographene sample (after halogenation) are different to that of the graphene starting materials. Raman techniques can therefore be used to determine the presence of C-X defects that interrupt π -conjugation as the halogenation increases.

5 XPS

XPS spectroscopy can be used to determine the elemental compositions of both the starting materials and halogenated products, and to determine the nature of the chemical bonds present. XPS spectroscopy was conducted using a Kratos Axis Ultra X-ray photoelectron spectrometer equipped with an aluminium/magnesium dual anode and a monochromated aluminium X-ray source.

Fourier Transformation InfraRed

Fourier-transform infrared (FTIR) spectroscopy was performed at room temperature using a Varian 3100 FTIR spectrometer. The samples were ground with KBr and then pressed into disks. These data are used to detect functionality in the halogenated products.

Examples

Example 1 – production of fluorographene from graphene powder

Graphene powder (100 mg, prepared via the method described in WO2013/132261, which is herein incorporated by reference in its entirety) was mixed with 10 ml *N*-methylpyrrolidine (NMP) and sonicated for 15 minutes to prepare a paste. The paste was then cast onto a glassy carbon rod and dried under vacuum at 100 °C. The resultant graphene-coated glassy carbon was then used as an anode in an electrochemical cell with potassium hydrogen fluoride molten salt as electrolyte and a stainless steel rod (3 mm diameter) as a cathode. The cell was placed at the bottom of stainless steel air-tight molten salt reactor and the experiment was conducted under a flow of argon. The cell was heated to 270 °C and a potential of 3 V was applied for 3 hours. The anode was then removed from the molten salt and then allowed to cool to room temperature under argon. The sample was then washed with water to remove the salt residues.

The colour of the graphene powder changed from black to light grey. XPS spectroscopy was employed to determine the elemental composition in the graphene starting material and produced fluorographene nanosheets (**Figures 1 and 2**). While the C 1s peak for graphene showed only one single peak associated with the C=C and C-C bond on graphene (**Figure 1A**), the C 1s of the fluorinated product is deconvoluted to several symmetrical peaks (**Figure 1B**). In addition to the peaks for the two carbon bond, there are three peaks at

289.0, 291.0, 292.0 eV assigned to covalent C–F, C–F₂, C–F₃ bonds, respectively. The total fluorine content was 51% indicating complete fluorination of the graphene flakes.

Comparison of the Raman spectra of the starting material and product also confirms fluorination (**Figure 3**). While the starting graphene material exhibits the characteristics of multilayer graphene with a G band at 1580 cm⁻¹ and a 2D band at 2670 cm⁻¹, the intensity of the peaks after fluorination has significantly reduced and the 2D band disappeared. These changes are typical evidence of the increase in C-F defects that interrupt π -conjugation as the degree of fluorination increases.

According to the FTIR measurements, the initial graphene had almost no functional groups attached to its surface as can be concluded from the featureless spectrum. After fluorination, there are two peaks located at 1212 cm⁻¹ and 1084 cm⁻¹ can be ascribed to the stretching vibration of the C–F covalent bonds and the semi-ionic stretching vibration of C–F bonds, respectively (**Figure 4**).

The sheet quality of the product of example 1 can be observed in the SEM pictures shown in **Figure 5**.

Example 2 - production of fluorographene from graphene oxide

In this example, graphene oxide prepared via hummer process was used as a precursor for graphene instead of multilayer graphene. The fluorination time was limited to 1 hour only. All other conditions were the same.

The XPS results showed that the oxygen content decreased from 34% to 2%, while the product has 28% fluorine. High resolution scans for C1 peaks showed two major peaks associated to the C–C bond at 284.8 eV and the C–F bond at 298 eV. There are also some minor peaks for the residual oxygen functional groups centred at ~ 285.7 and 287 eV, as well as for the C–F₂ at ~ 291 eV. (**Figure 6**).

The Raman spectrum before fluorination showed typical features of graphene oxide: a wide intense band at ~1580 cm⁻¹ (G band) due to the E_{2g} vibration mode that originates from graphitic sp²-hybridized carbon, and another intense band at 1333 cm⁻¹ (the D Band) generated by the A_{1g}-symmetric vibration mode in the disordered structure and/or the edge planes of graphite. After fluorination, the intensity of the bands significantly decreased to a wave-like bands (**Figure 7**). The presence of the band in the G position indicates that the graphitic structure is preserved.

By way of comparison, Example 1 was fully fluorinated. The ideal Raman spectra is therefore featureless with respect graphenic qualities and the peaks (including the G band) should disappear (or at least significantly diminish). Example 2 is partially fluorinated, which mean the graphitic nature is still detectable. These data therefore confirm that the fluorination process doesn't convert the graphene/ GO to amorphous materials; i.e. the graphenic nature of the material is preserved.

FTIR spectra of the graphene oxide starting material and fluorinated product were compared (Figure 8). The typical characteristic peaks of GO can be observed:

- (1) C=O stretching vibration appears at 1746 cm^{-1} ,
- (2) the O-H the stretching and deformation vibration appears at 3420 cm^{-1} and 1395 cm^{-1} respectively,
- (3) Aromatic C=C stretching vibration at 1625 cm^{-1} ,
- (4) epoxy C-O stretching vibration at 1220 cm^{-1} , and
- (5) the alkoxy C-O stretching vibration at 1053 cm^{-1} .

After electro-fluorination the intensity of the peaks for oxygen functional groups significantly decreased and the two peaks characterising the F-C stretching at 1212 cm^{-1} and 1084 cm^{-1} became dominate, confirming that the oxygen functional groups have been replaced by fluorine-based functionality.

Example 3 - production of fluorographene from graphene oxide

The process was as described for example 2, save that 0.5 M sodium fluoride dissolved in 1-methyl-3-butylimidazolium tetrafluoroborate [BMIm][BF₄] was used as the electrolyte.

The elemental analysis calculated from the XPS results showed 12 at.% fluorine, 8 at.% oxygen, and 2.5 at% boron.

This example demonstrates the feasibility of using salts dissolves in ionic liquids for the production of fluorographene and fluorinated graphite nanoplatelet structures.

Example 4 - production of fluorographene from graphene oxide

The process was as described for example 1, save that the electrolysis was conducted for 10 minutes only. The fluorine content of the resultant sample was 1.5 at% only (Figure 10).

This example demonstrates that the extent of fluorination is, in part, a function of reaction duration.

Example 5 – production of bromographene from graphene powder

- 5 Similar to example 1, but the electrolyte was a eutectic mixture of LiBr-KBr, the operating temperature was 400 °C and the applied voltage was 3.5 V.

10 High resolution XPS analysis (**Figure 11**) of the Br 3d showed two clear peaks: the peak at ~70.8 eV corresponds to the Br-C bond, while the peak at higher value (~72 eV) is likely caused by some contamination of 72.6 eV and higher values for BrO³⁻. Interestingly the peak at ~68 eV previously reported for the contamination Br was not observed in the current work.

15 The C 1s peak also confirmed the Br-C bond. The peak can be fitted into two components at 284.6, corresponding to C 1s of sp² hybridized carbon, and another peak at higher value for the Br-C bond. After considering the relevant atomic sensitivity factors, semi-quantitative analysis of the higher resolution data indicated a composition of 10.2 atom% Br in the sample.

- 20 This example demonstrates that the methods of the invention are applicable to bromographene, and provides partially-brominated graphene having a useful degree of bromination. To date, methods for the production of brominated graphene have yielded only low Br-content, and / or have had a high oxygen content.

25

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Claims

1. A process for producing halogenated graphene and / or halogenated graphite
5 nanoplatelet structures having a thickness of less than 100 nm, the process comprising
electrochemical reaction of graphite platelets and / or graphene and / or graphene oxide in
an electrochemical cell, wherein the cell includes:
- (a) a negative electrode comprising said graphite platelets and / or graphene and / or
graphene oxide;
- 10 (b) a positive electrode; and
- (c) an electrolyte comprising halide ions and / or elemental halogen;
- wherein the process includes the step of passing a current between the electrodes.
2. The process of claim 1, wherein the graphite platelets and / or graphene and / or
15 graphene oxide is / are deposited on a glassy carbon rod.
3. The process of any preceding claim, wherein the process is for producing
fluorographene and / or fluorographite nanoplatelet structures having a thickness of less
than 100 nm, wherein the electrolyte comprises fluoride and / or F_2 .
- 20 4. The process of claim 3, wherein the electrolyte is molten potassium hydrogen fluoride.
5. The process of claim 3, wherein the electrolyte is a fluoride salt dissolved in an organic
solvent or an ionic liquid; or wherein the electrolyte is a fluorine-containing ionic liquid.
- 25 6. The process of claim 3, wherein the electrolyte comprising F_2 is generated by passing F_2
gas through an electrolyte.
7. The process of claim 1 or claim 2, wherein the process is for producing bromographene
30 and / or bromographite nanoplatelet structures having a thickness of less than 100 nm,
wherein the electrolyte comprises bromide and / or Br_2 .
8. The process of claim 7, wherein the electrolyte is a eutectic mixture of lithium bromide
and potassium bromide.
- 35 9. The process of claim 7, wherein the electrolyte comprising Br_2 is generated by passing
 Br_2 gas through an electrolyte.

10. Brominated graphene and / or brominated graphite nanostructures having a bromine content of greater than 5 at.%, optionally greater than 7 at.%, optionally greater than 9 at.%.

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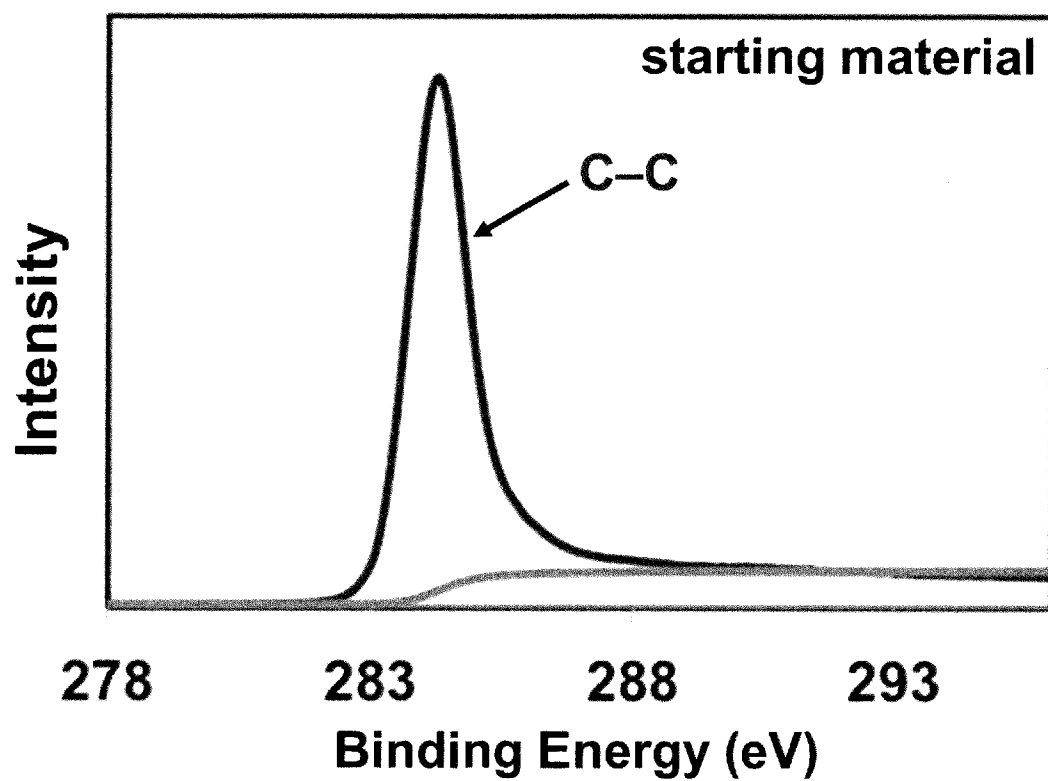


Figure 1a

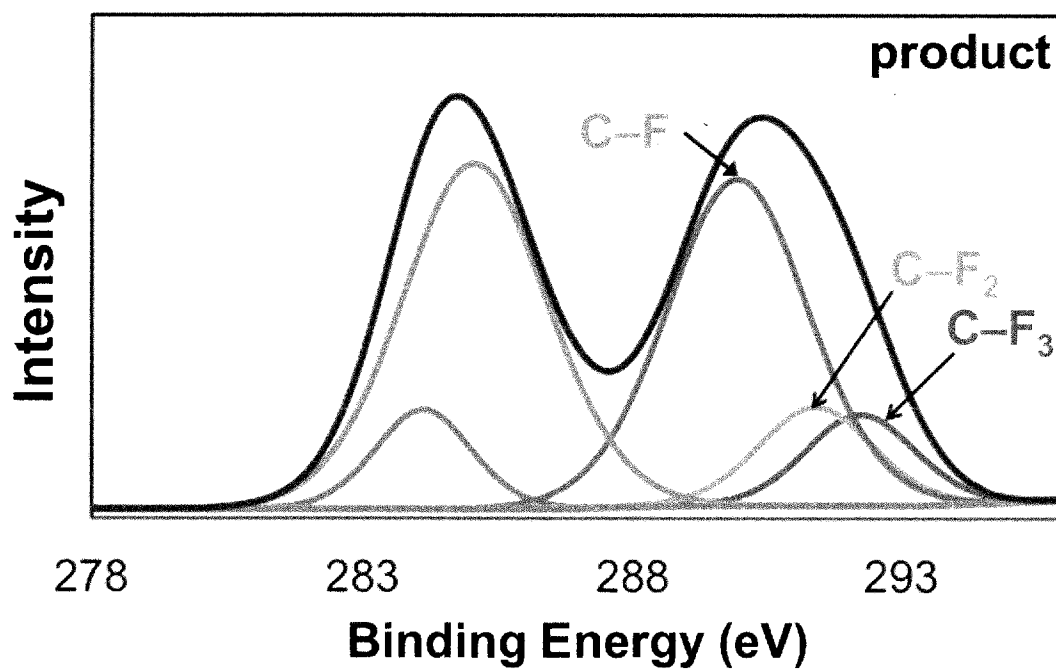


Figure 1b

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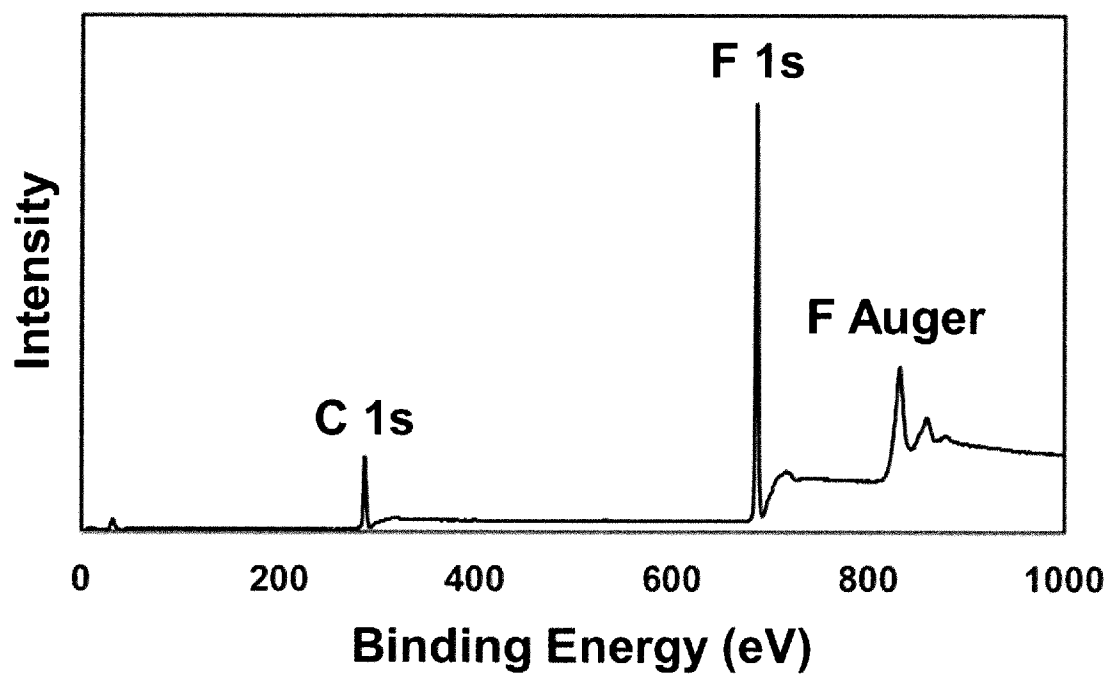


Figure 2

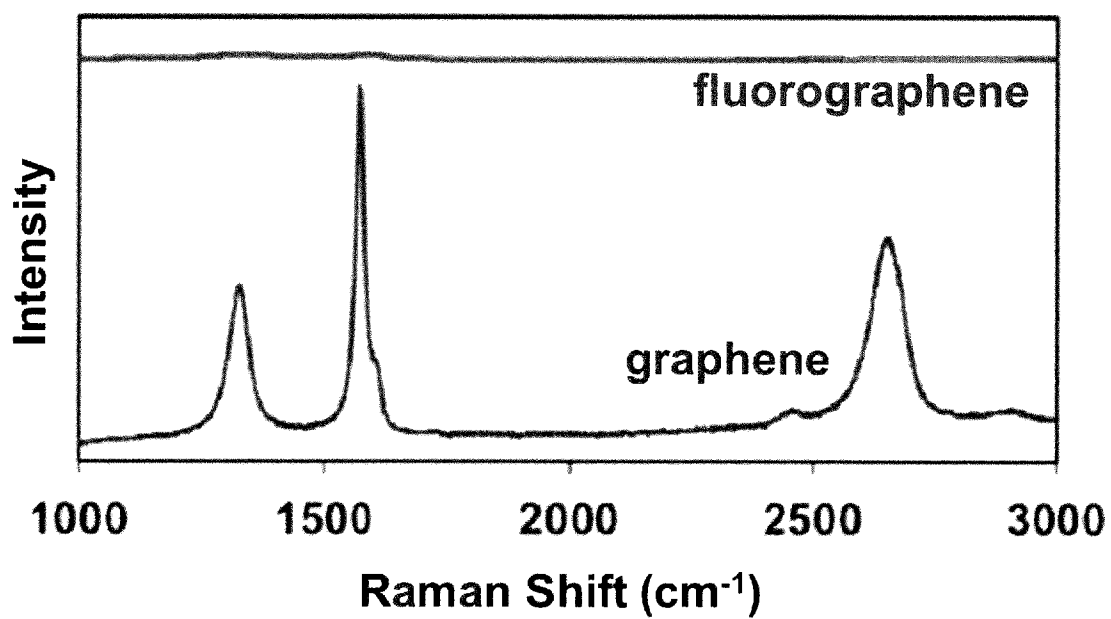


Figure 3

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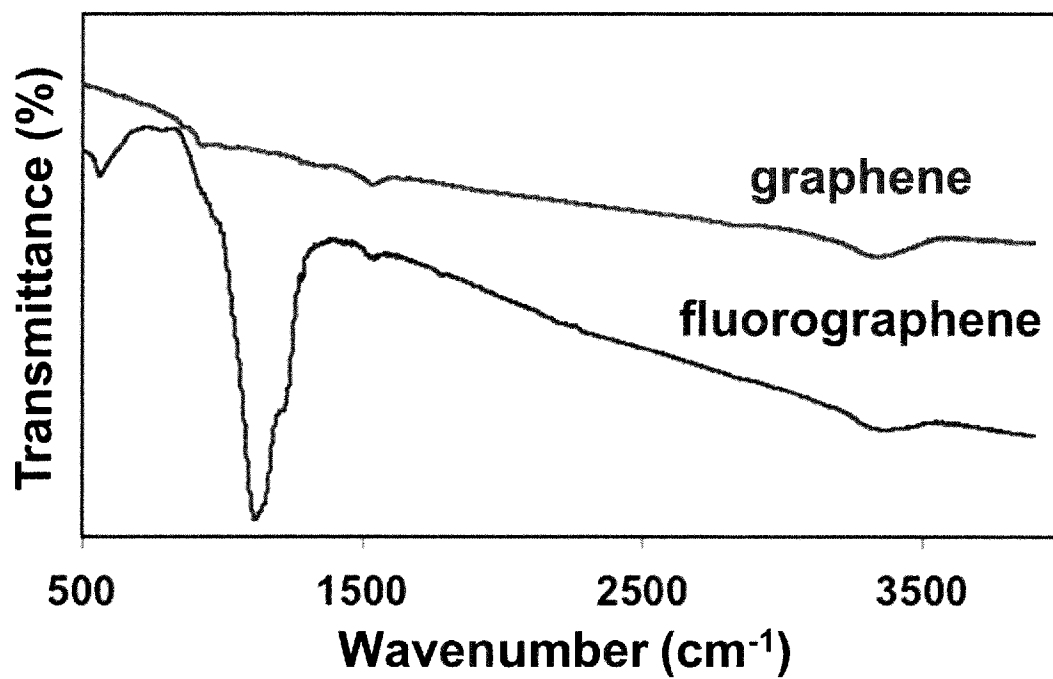


Figure 4

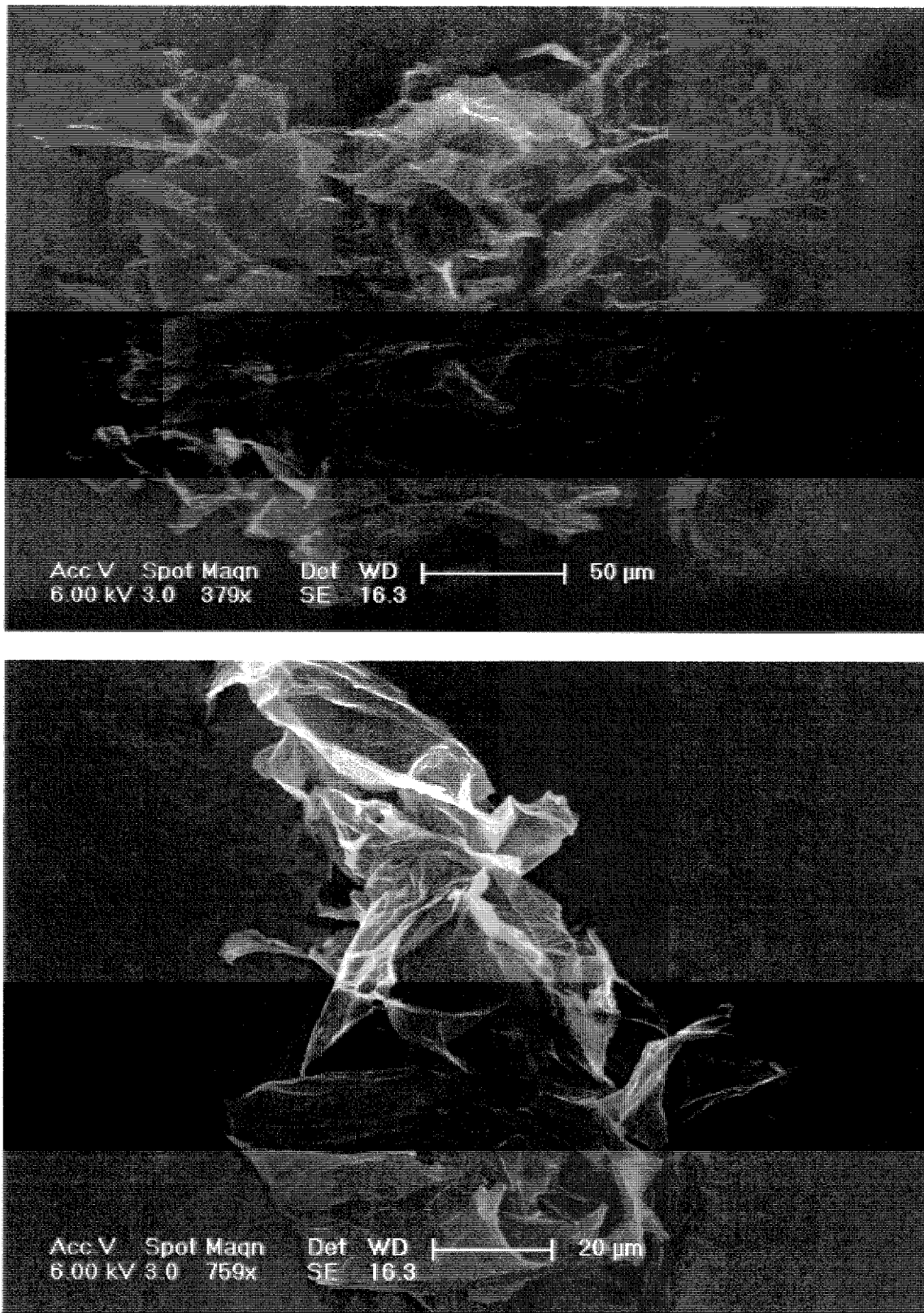


Figure 5

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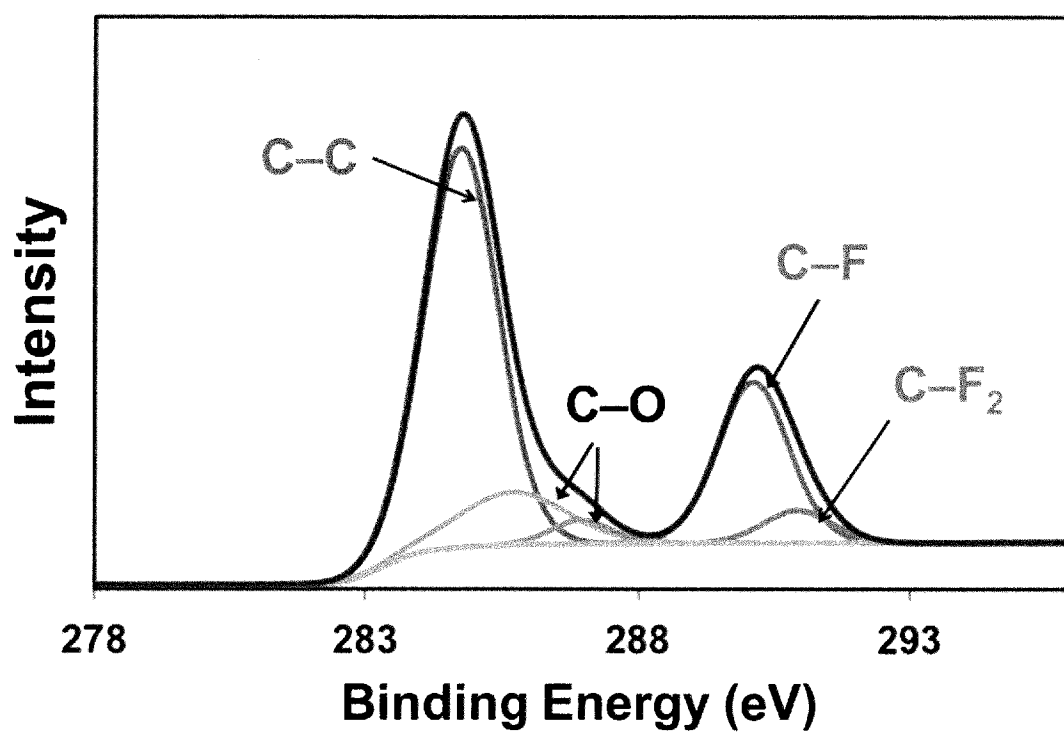


Figure 6

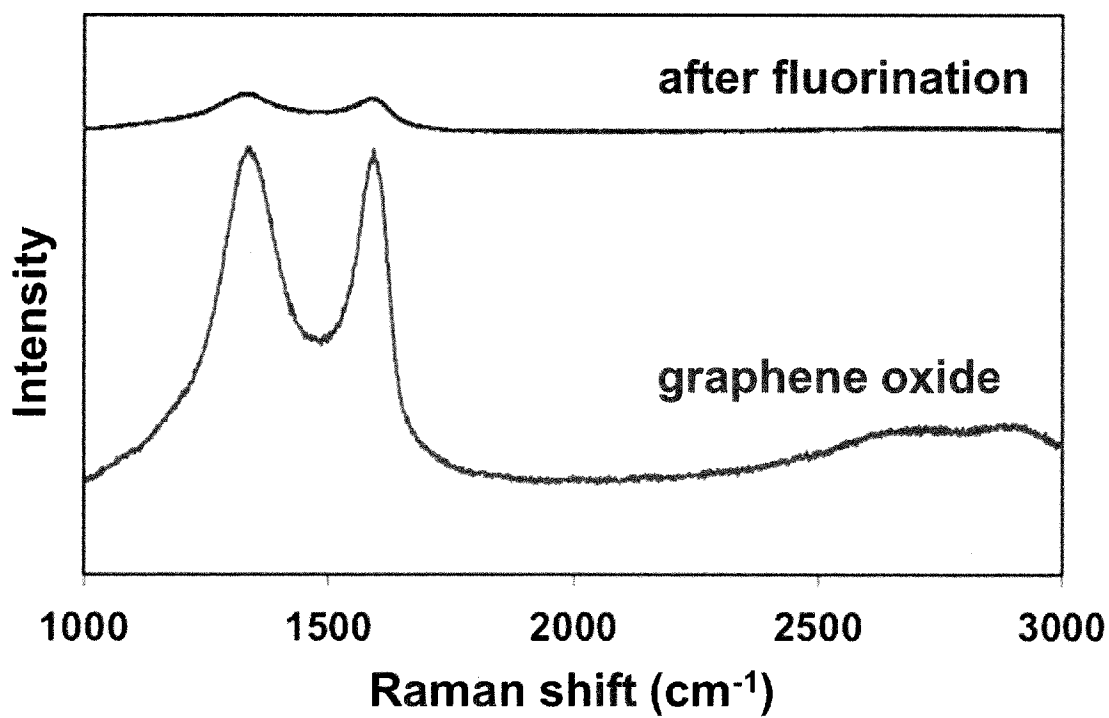


Figure 7

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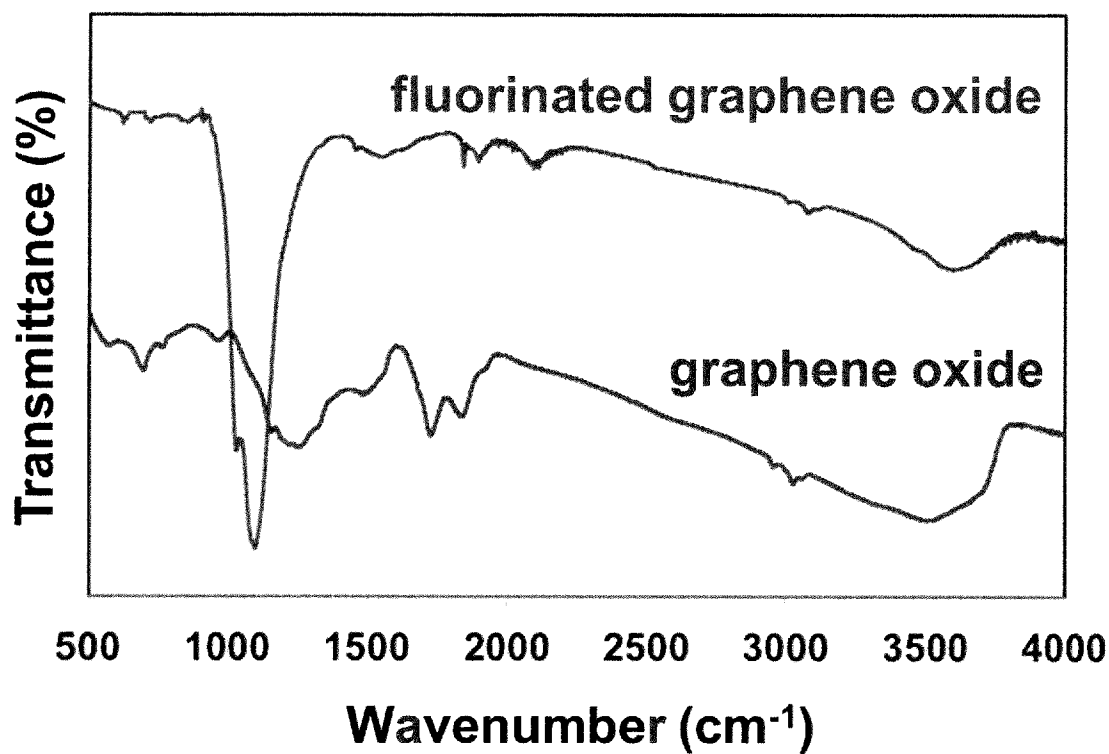


Figure 8

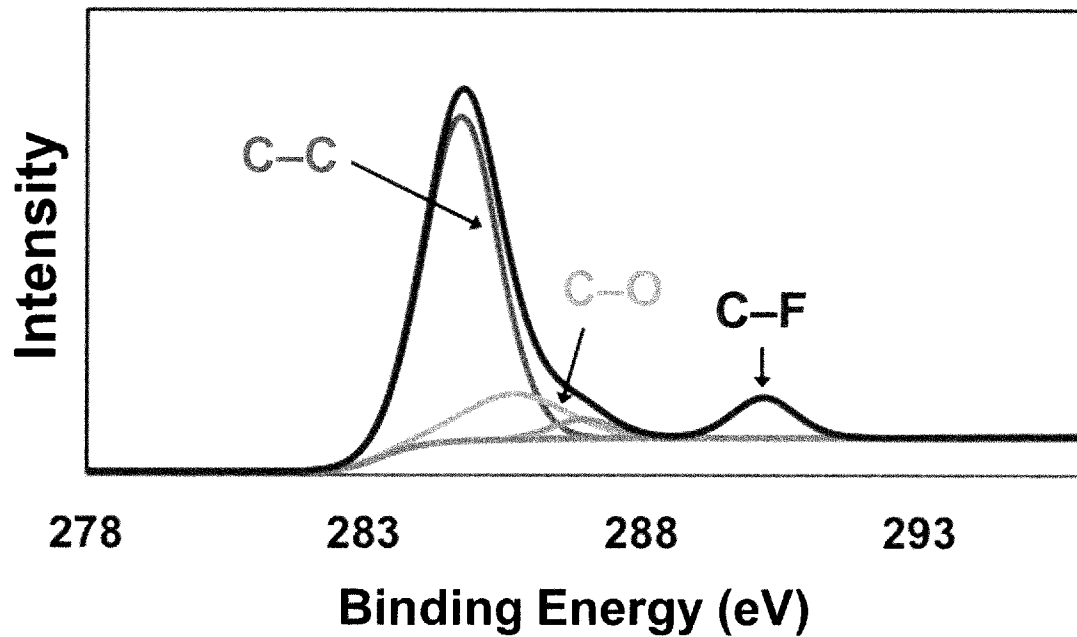


Figure 9

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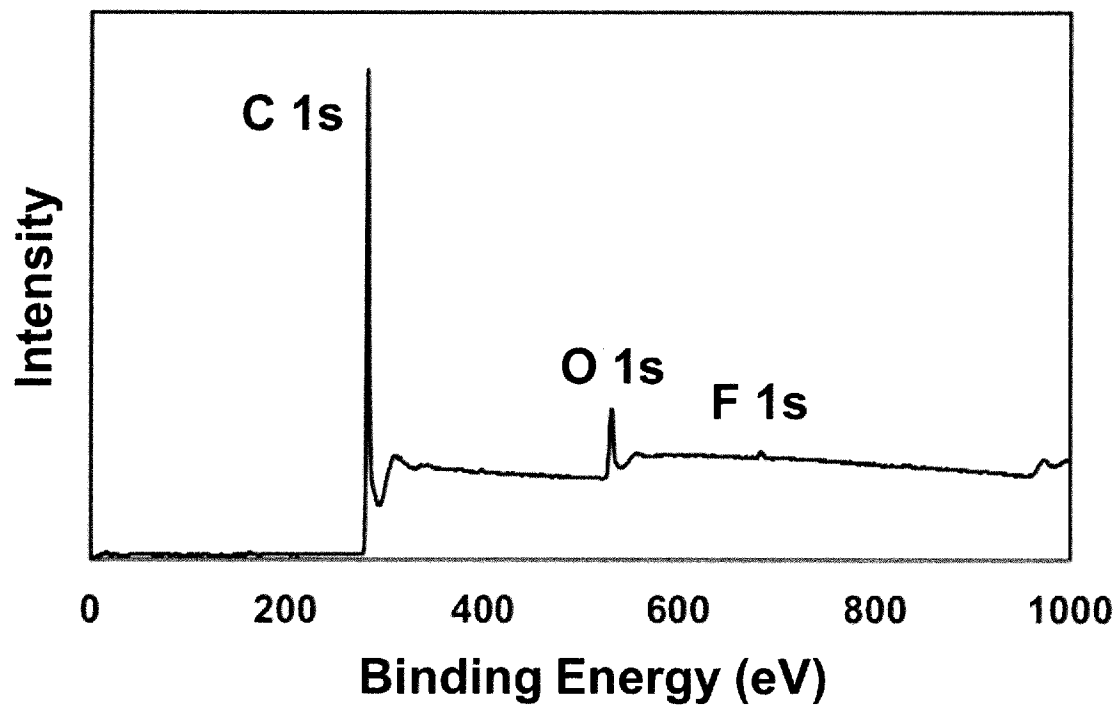


Figure 10

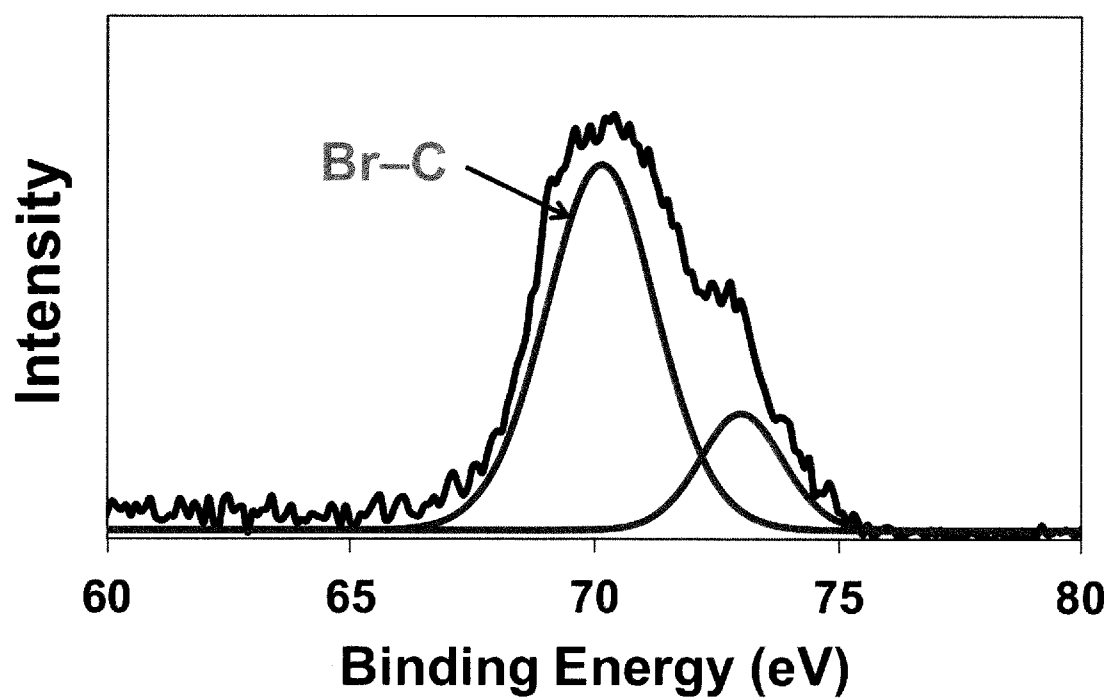
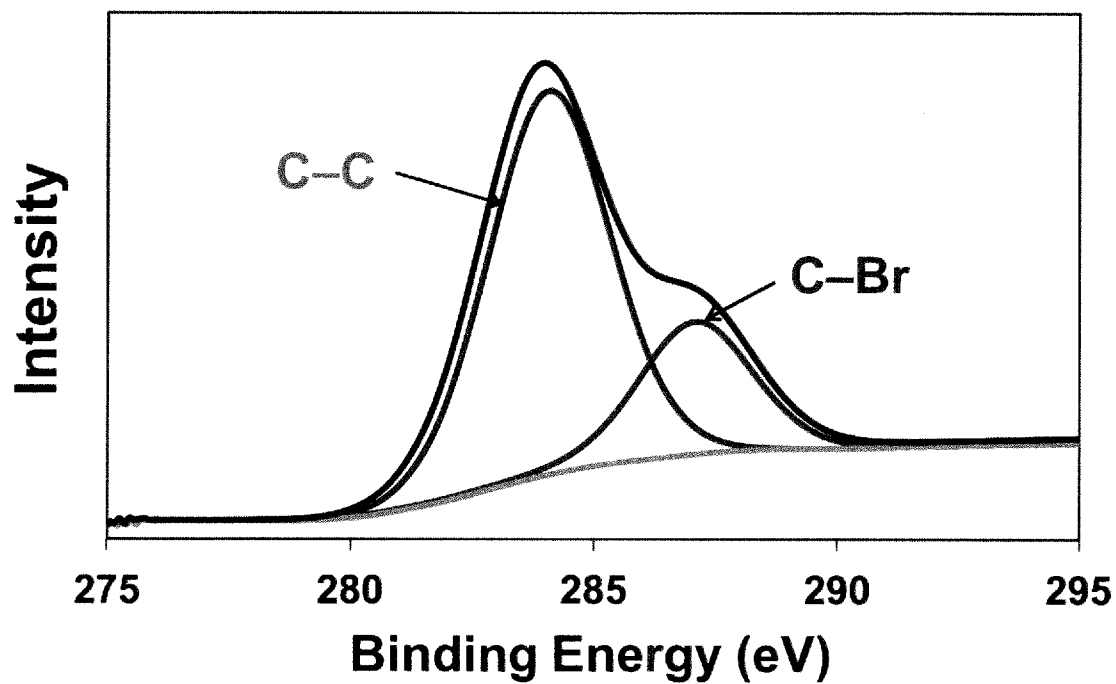


Figure 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/050792

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B31/04 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)
C01B 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, CHEM ABS Data, INSPEC, COMPENDEX

C. 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 2013/132261 A1 (UNIV MANCHESTER [GB]) 12 September 2013 (2013-09-12) claims 1-18 ----- -/--	1,3



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

13 June 2016

Date of mailing of the international search report

21/06/2016

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2016/050792

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2016/050792

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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Information on patent family members

International application No

PCT/GB2016/050792

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