% nitrogen, 0 atomic % sulfur, and 13-22 atomic % oxygen. It is believed that the reduced graphene oxide in this sample was produced by a modified Hummer's and subsequent chemical reduction. For the sake of convenience, this material is referred to as "GRAPHENEA RGO" herein.

A second such reference material was obtained from Thomas Swan & Co. Ltd. (Rotary Way, Consett, County Durham, DH8 7ND, United Kingdom) under the trademark "ELICARB GRAPHENE." The datasheet for this material is available at http://www.thomas-swan.co.uk/advanced-materials/elicarb%C2%AE-graphene-products/elicarb%C2%AE-graphene. According to this datasheet, the graphene in this sample was produced by solvent exfoliation and particle size is in the 0.5 to 2.0 micrometer range. For the sake of convenience, this material is referred to as "ELICARB GRAPHENE" herein.

A third such reference material is expanded graphite (EG), produced by thermal expansion of conventional graphite intercalation compounds that are typically produced by chemical oxidation. One example expanded graphite is "L2136," a non-commercial material made available by Schunk Hoffmann Carbon Technologies AG (Au 62, 4823 Bad Goisern am Hallstättersee, Austria). The company does not disclose details about the manufacturing at the present time. For the sake of convenience, this material is referred to as "L2136" herein.

SUMMARY

Graphene and the production of graphene, including an apparatus and a method for expansion of graphite to graphene, are described herein.

In one aspect, the present disclosure refers to a composition comprising:

dehydrogenated graphite comprising a plurality of flakes having

at least one flake in 10 having a size in excess of 10 square micrometers,

an average thickness of 10 atomic layers or less, and

a defect density characteristic of at least 50% of μ-Raman spectra of the de-hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters having a D/G area ratio below 0.5, and wherein the composition is a composite and at least 30%, for example, at least 50% or at least 70% of sp3 hybridized carbon sites of the composition are one or more of:

a) functionalized with a non-hydrogen chemical group,

b) cross-linked with sp3 hybridized carbon sites of another flakes, or

c) otherwise chemically modified.

In another aspect, the present disclosure refers to a composition comprising:

dehydrogenated graphite comprising a plurality of flakes having

at least one flake in 10 having a size in excess of 10 square micrometers,

a coefficient of determination value of 2D single peak fitting of μ-Raman spectra of the de-hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters larger than 0.99 for more than 50 % of the spectra, and

a defect density characteristic of at least 50% of μ-Raman spectra of the de-hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters having a D/G area ratio below 0.5, and wherein the composition is a composite and at least 30%, for example, at least 50% or at least 70% of sp3 hybridized carbon sites of the composition are one or more of:

a) functionalized with a non-hydrogen chemical group,

b) cross-linked with sp3 hybridized carbon sites of another flakes, or

c) otherwise chemically modified.

In a further aspect, the present disclosure refers to an electrode comprising the composition disclosed herein.

In another aspect, the present disclosure refers to a battery or an electrochemical capacitor comprising the electrode disclosed herein, for example, wherein the battery is a lithium battery, a lithium-ion battery, a silicon anode battery, or a lithium sulfur battery.

In a further aspect, the present disclosure refers to a composition comprising:

hydrogenated graphite comprising a plurality of flakes having

at least one flake in 10 having a size in excess of 10 square micrometers,

an average thickness of 10 atomic layers or less, and

a defect density characteristic of μ-Raman spectra of the hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters and an excitation power below 2 mW at the focus of an 100X objective having an average D/G area ratio being between 0.2 and 4, wherein the majority of the defects are reversible hydrogenation of sp3-hybridized carbon sites away from the edges of the flakes, and wherein the composition is a composite and at least 5%, for example, at least 10%, of sp3 hybridized carbon sites of the composition are one or more of:

a) functionalized with a non-hydrogen chemical group,

b) cross-linked with sp3 hybridized carbon sites of another flakes, or

c) otherwise chemically modified.

In another aspect, the present disclosure refers to a composition comprising:

a reversibly hydrogenated graphite comprising a plurality of flakes having

at least one flake in 10 having a size in excess of 10 square micrometers,

a coefficient of determination value of 2D single peak fitting of μ-Raman spectra of the graphite after thermal treatment in inert atmosphere at 2 mbar and 800 °C, collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters, of larger than 0.99 for more than 50 % of the spectra, and

a defect density characteristic of μ-Raman spectra of the hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters and an excitation power below 2 mW at the focus of an 100X objective having an average D/G area ratio being between 0.2 and 4, wherein the majority of the defects are reversible hydrogenation of sp3-hybridized carbon sites away from the edges of the flakes, and wherein the composition is a composite and at least 5%, for example, at least 10%, of sp3 hybridized carbon sites of the composition are one or more of:

a) functionalized with a non-hydrogen chemical group,

b) cross-linked with sp3 hybridized carbon sites of another flakes, or

c) otherwise chemically modified.

In a further aspect, the present disclosure refers to an apparatus for the expansion of the graphite to graphene with at least one container provided for receiving an electrolyte, at least one anode and at least one cathode, characterized in that the cathode contains diamond or consists thereof.

In another aspect, the present disclosure refers to a method for the expansion of the graphite to graphene, wherein graphite particles and at least one electrolyte are introduced into at least one container and the graphite, through the application of an electrical voltage to at least one anode and at least one cathode is expanded,

characterized in that the cathode contains or consists of diamond and hydrogen is produced at the cathode.

The present disclosure provides a composition including dehydrogenated graphite comprising a plurality of flakes. The flakes have at least one flake in 10 having a size in excess of 10 square micrometers, an average thickness of 10 atomic layers or less, and a defect density

visible light, UV, or microwaves, wherein more that 50% of hydrogenated sp3 hybridized carbon sites are de-hydrogenated. The method can include a subsequent thermal treatment of the graphene flakes at a temperature from about 100°C to about 800°C, or from about 300°C to about 650°C, and for a period of from about 1 min to about 60 min, or from about 15 min to about 40 min. The graphene flakes can have an average surface area of more than 10 μm^2 or more than 50 μm^2 or of more than 100 μm^2.

The details of one or more implementations are set forth in the accompanying drawings and the description below. Other features, objects, and advantages will be apparent from the description and drawings, and from the claims.

DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic representation of an apparatus for the expansion of graphite.

FIG. 1a is a schematic representation of the hydrogenated graphite and graphene produced by the apparatus of FIG. 1 and the impact of various subsequent processing steps on that material.

FIGS. 2a, 2b are scanning electron micrographs of graphite after the electrochemical expansion.

FIG. 2c are scanning electron micrographs of ELICARB GRAPHENE.

FIG. 2d are scanning electron micrographs of GRAPHENEA RGO.

FIG. 3 is a Raman spectrum of graphite particles that had been expanded and thermally treated.

FIG. 4a is a spatially-resolved μ-Raman microscopy image of a graphene sample produced by the apparatus of FIG. 1.

FIG. 4b is a spatially-resolved μ-Raman microscopy image of a sample of GRAPHENEA RGO.

about 0.5 µm to about 20 to µm or from about 2 to about 5 µm. The diamond layer of the cathode 3 may optionally be doped using an n- or p-type dopant to reduce the electric resistance of the cathode. In some implementations, boron may be used as a dopant.

An anode 4 is also disposed in container 10. The anode has a shape and size that substantially occupies the entire base of the container 10. In this manner, a largely homogeneous electrical field is generated in container 10 and a large percentage of the container volume can be utilized in the production of the graphene.

In some implementations, anode 4 can include or be formed of a metal or an alloy. In some implementations, anode 4 may also include or be formed of diamond. The diamond may be mounted on a base body, as described with regard to the cathode, or implemented as free-standing diamond layer.

An optional separator 5 is also disposed in container 10. Separator 5 may include or be formed of, for example, polytetrafluoroethylene (PTFE), diamond, Al2O3 or other material. Separator 5 may include or be formed of a dielectric. Separator 5 can be provided with holes or with pores that, for example, have a diameter of less than 10 µm, less than 5 µm, less than 1 micrometer, or less than 0.5 µm. This allows the passage of electrolyte (for example, liquid water) and ions through separator 5 while preventing particles of graphite or graphene that are found within container 10 from coming into contact with anode 4.

In the illustrated implementation, separator 5 separates a cathode chamber 30 from an anode chamber 40. In other implementations, the separator 5 can be deposited directly on the anode 4 or fixed to the anode 4, for example, by adhesive bonding. Accordingly, anode chamber 40 can be omitted in some implementations.

In operation, at least one electrolyte is disposed in the container 10 between anode 4 and cathode 3. In some implementations, the electrolyte may be an aqueous electrolyte, and may optionally contain substances for increasing the electrical conductivity such as,

thickness of more than 10 atomic layers. As another example, in some implementations, 1% or more of layers 116 may have a thickness of more than 50 or even 100 atomic layers, for example, more than 5% or even more than 10% of the flakes may have a thickness of more than 50 or 100 atomic layers.

Nevertheless, the separated and dehydrogenated graphite layers 116 of sample 130 display graphene-like properties, including a high specific surface area, mechanical strength, and an absence of signatures of characteristic of AB-stacked layers, as well as graphene-like properties characteristic of sp2-hybridization of nearly all the carbon in dehydrogenated graphite layers 116. For example, chemical defects visible by Raman scattering are strongly reduced, optical transparency decreases, and the electron conductivity of graphite layers 116 is high. Moreover, individual dehydrogenated graphite layers 116 can be microscopically identified. These separated and dehydrogenated graphite layers 116 are often wrinkled and crumpled, which indicates that they are only few atomic layers thick.

As an end result, separated and dehydrogenated graphite layers 116 can be referred to as graphene in which many of the individual particles have a thickness of only 1 to 10 atomic layers and lateral dimensions that are inherited from the starting graphite material (often well in excess of 100 micrometers) are produced. In contrast with other techniques, the graphene includes a low number of layers (i.e., has a small thickness) and displays graphene-like properties rather than properties of bulk graphite. Indeed, the method is capable of producing relatively large graphene flakes with an average area of over 10 μm^2, more than 50 μm^2, or more than 100 μm^2. This method and apparatus thus allow high quality graphene to be produced in large quantities. The average surface area can be determined by transmission electron microscopy or scanning electron microscopy of a sample with a plurality of graphene flakes, wherein the size of the individual graphene flakes is determined by image analysis and statistical analysis.

crystal, i.e., the lateral structure of the graphite that is used as the starting material remains.

FIGS. 2b, 2c, 2d are scanning electron micrographs of samples that were dip-coated from dispersions onto polished, boron-doped conductive silicon <100> wafers. In particular, FIG. 2b shows graphene layers that were exfoliated from expanded graphite similar to that shown in FIG. 2a and dispersed in a solvent and then dip-coated onto the silicon substrate. The large lateral extent of graphene is clearly visible and, in this particular example, is more than 100 µm.

In contrast, FIG. 2c shows graphene obtained from a commercial ELICARB GRAPHENE dispersion. As shown, the graphene displays an average size of about 1 µm and no flakes with a diameter larger than 2 micrometers were observed.

FIG. 2d shows commercial GRAPHENEA RGO, dip -coated from a dispersion on a silicon substrate. As shown, individually-distinguishable flakes of the reduced graphene oxide display a diameter below 3 micrometers.

FIG. 3 is a Raman spectrum of graphite particles that had been expanded and thermally treated as described above with reference to FIG. 1 and illustrated in FIG. 1a. The symmetry and low full width half maximum of the 2D band indicates an expansion of the graphite to graphene flakes with a thickness of less than 10 atomic layers. The low relative intensity of the D band confirms desorption of hydrogen and a low number of structural defects in the graphene flake lattice.

FIGS. 4a, 4b, 4c, 4d are spatially-resolved µ-Raman microscopy images of different samples on a substrate. In particular, FIG. 4a is an image of a graphene sample produced by the electrochemical expansion of graphite to graphene using an approach consistent with the method described above. FIG. 4b is an image of a sample of GRAPHENEA RGO. FIG. 4c is an image of a sample of ELICARB GRAPHENE. FIG. 4d is an image of a sample of expanded graphite L2136.

WHAT IS CLAIMED IS:

1. A composition comprising:

dehydrogenated graphite comprising a plurality of flakes having

at least one flake in 10 having a size in excess of 10 square micrometers,

an average thickness of 10 atomic layers or less, and

a defect density characteristic of at least 50% of μ-Raman spectra of the de-hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters having a D/G area ratio below 0.5, and wherein the composition is a composite and at least 30%, for example, at least 50% or at least 70% of sp3 hybridized carbon sites of the composition are one or more of:

a) functionalized with a non-hydrogen chemical group,

b) cross-linked with sp3 hybridized carbon sites of another flakes, or

c) otherwise chemically modified.

2. A composition comprising:

dehydrogenated graphite comprising a plurality of flakes having

at least one flake in 10 having a size in excess of 10 square micrometers,

a coefficient of determination value of 2D single peak fitting of μ-Raman spectra of the de-hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters larger than 0.99 for more than 50 % of the spectra, and

a defect density characteristic of at least 50% of μ-Raman spectra of the de-hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters having a D/G area ratio below 0.5, and wherein the composition is a composite and at least 30%, for example, at least 50% or at least 70% of sp3 hybridized carbon sites of the composition are one or more of:

a) functionalized with a non-hydrogen chemical group,

b) cross-linked with sp3 hybridized carbon sites of another flakes, or

c) otherwise chemically modified.

3. The composition of either claim 1 or 2, wherein more than 60%, for example, more than 80%, or more than 85 % of μ-Raman spectra of the de-hydrogenated graphite have the coefficient of determination value larger than 0.99.

4. The composition of any one of claims 1 to 3, wherein more than 40%, for example, more than 50% or more than 65 % of the μ-Raman spectra of the de-hydrogenated graphite have the coefficient of determination value larger than 0.995.

5. The composition of any one of claims 1 to 4, wherein at least one flake in six has a size in excess of 10 square micrometers, for example, at least one flake in four.

6. The composition of any one of claims 1 to 5, wherein at least one flake in ten has a size in excess of 25 square micrometers, for example, at least two flakes in ten.

7. The composition of any one of claims 1 to 6, wherein the average thickness is seven atomic layers or less, for example, five atomic layers or less.

8. The composition of any one of claims 1 to 7, wherein the defect density is characteristic of at least 80% of the collected spectra having a D/G area ratio below 0.5, for example, at least 95% of the collected spectra having a D/G area ratio below 0.5.

9. The composition of any one of claims 1 to 8, wherein the defect density is characteristic of at least 50% of the collected spectra having a D/G area ratio below 0.2, for example, at least 70% of the collected spectra having a D/G area ratio below 0.2.

10. The composition of any one of claims 1 to 9, wherein the defect density is characteristic of at the average D/G area ratio being below 0.8, for example, below 0.5 or below 0.2.

11. The composition of any one of claims 1 to 10, wherein the composition is a particulate powder of dehydrogenated graphite flakes, for example, a black particulate powder of dehydrogenated graphite flakes.

12. The composition of any one of claims 1 to 11, wherein the plurality of the flakes of the dehydrogenated graphite are wrinkled, crumpled, or folded, for example, wherein the plurality of the flakes are assembled into a 3-dimensional structure.

13. The composition of any one of claims 1 to 12, wherein the full width half maximum of the G peak in μ-Raman spectra of the de-hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters is larger than 20 reciprocal centimeters, for example, larger than 25 reciprocal centimeters or larger than 30 reciprocal centimeters.

14. The composition of any one of claims 1 to 13, wherein the μ-Raman spectra of the de-hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters show a broad peak in the range between 1000 and 1800 reciprocal centimeters with a full width half maximum of more than 200 reciprocal centimeters, for example more than 400 reciprocal centimeters.

15. The composition of any one of claims 1 to 14, wherein more than 1%, for example, more than 5% or more than 10% of the flakes are of a thickness of more than 10 atomic layers.

16. The composition of any one of claims 1 to 15, wherein the composition is a composite, for example, wherein the composite further includes activated carbon or wherein the composite further includes a polymer.

17. An electrode comprising the composition of any one of claims 1 to 16.

18. A battery or an electrochemical capacitor comprising the electrode of claim 17, for example, wherein the battery is a lithium battery, a lithium-ion battery, a silicon anode battery, or a lithium sulfur battery.

19. A composition comprising:

hydrogenated graphite comprising a plurality of flakes having

at least one flake in 10 having a size in excess of 10 square micrometers,

an average thickness of 10 atomic layers or less, and

a defect density characteristic of μ-Raman spectra of the hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters and an excitation power below 2 mW at the focus of an 100X objective having an average D/G area ratio being between 0.2 and 4, wherein the majority of the defects are reversible hydrogenation of sp3-hybridized carbon sites away from the edges of the flakes, and wherein the composition is a composite and at least 5%, for example, at least 10%, of sp3 hybridized carbon sites of the composition are one or more of:

a) functionalized with a non-hydrogen chemical group,

b) cross-linked with sp3 hybridized carbon sites of another flakes, or

c) otherwise chemically modified.

20. A composition comprising:

a reversibly hydrogenated graphite comprising a plurality of flakes having

at least one flake in 10 having a size in excess of 10 square micrometers,

a coefficient of determination value of 2D single peak fitting of μ-Raman spectra of the graphite after thermal treatment in inert atmosphere at 2 mbar and 800 °C, collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters, of larger than 0.99 for more than 50 % of the spectra, and

a defect density characteristic of μ-Raman spectra of the hydrogenated graphite collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters and an excitation power below 2 mW at the focus of an 100X objective having an average D/G area ratio being between 0.2 and 4, wherein the majority of the defects are reversible hydrogenation of sp3-hybridized carbon sites away from the edges of the flakes, and wherein the composition is a composite and at least 5%, for example, at least 10%, of sp3 hybridized carbon sites of the composition are one or more of:

a) functionalized with a non-hydrogen chemical group,

b) cross-linked with sp3 hybridized carbon sites of another flakes, or

c) otherwise chemically modified.

21. The composition of either claim 19 or 20, wherein more than 60%, for example, more than 80%, or more than 85 % of μ-Raman spectra of the graphite have the coefficient of determination value larger than 0.99.

22. The composition of any one of claims 19 to 21, wherein more than 40%, for example, more than 50% or more than 65 % of the μ-Raman spectra of the graphite have the coefficient of determination value larger than 0.995.

23. The composition of claim 19 to 22, wherein at least one flake in six has a size in excess of 10 square micrometers, for example, at least one flake in four.

24. The composition of any of claims 19 to 23, wherein at least one flake in ten has a size in excess of 25 square micrometers, for example, at least two flakes in ten.

25. The composition of any of claims 19 to 24, wherein the average thickness is seven atomic layers or less, for example, five atomic layers or less.

26. The composition of any of claims 19 to 25, wherein the defect density is characteristic of at least 50% of the μ-Raman spectra collected at 532 nm excitation with a resolution better than 1.8 reciprocal centimeters and an excitation power below 2 mW at the focus of an 100X objective having a D/G area ratio above 0.5, for example, at least 80% or at least 95% of the collected spectra having a D/G area ratio above 0.5.

27. The composition of any of claims 19 to 26, wherein the defect density is characteristic of at least 50% of the collected spectra having a D/G area ratio above 0.8, for example, at least 60% or at least 90% of the collected spectra having a D/G area ratio above 0.8.

28. The composition of any of claims 19 to 27, wherein the defect density is characteristic of the average D/G area ratio being between 0.4 and 2, for example, between being 0.8 and 1.5.

29. The composition of any of claims 19 to 28, wherein at least 60%, for example, at least 75% of the defects are reversible hydrogenation of sp3-hybridized carbon sites away from the edges of the flakes.

30. An apparatus for the expansion of the graphite to graphene with at least one container provided for receiving an electrolyte, at least one anode and at least one cathode, characterized in that the cathode contains diamond or consists thereof.

31. The apparatus of claim 30, further comprising a separator which separates the anode from the cathode.

32. The apparatus according to claim 30 or 31, characterized in that the separator is in contact with the surface of the anode or that the separator is diamond and/or polytetrafluoroethylene and/or Al2O3 and/or ceramic and/or quartz and/or glass contains or consists thereof.

33. The apparatus according to one of claims 30 to 32, further comprising a drive means with which the separator, and optionally the anode, are rotatable.

34. The apparatus according to one of claims 30 to 33, characterized in that the separator, and optionally the anode are displaceably mounted, so that the distance between the cathode and the separator is changeable in operation of the apparatus.

35. The apparatus according to one of claims 30 to 34, further comprising an electric voltage supply set up to apply a DC voltage of from about 5 V to about 60 V between the anode and cathode, or from about 15 V to about 30 V, wherein the voltage is optionally pulsed.

36. The apparatus according to one of claims 30 to 35, further comprising a feed apparatus by which electrolyte and graphite particles can be fed as a dispersion into the at least one container and/or further comprising a discharge apparatus by which electrolyte and graphene flakes are dischargable from the at least one container as a dispersion.

37. A method for the expansion of the graphite to graphene, wherein graphite particles and at least one electrolyte are introduced into at least one container and the graphite, through the application of an electrical voltage to at least one anode and at least one cathode is expanded,

characterized in that the cathode contains or consists of diamond and hydrogen is produced at the cathode.

38. Method according to claim 37, characterized in that hydrogen is intercalated in the graphite particles and/or chemisorbed on the graphite particles, so that graphene flakes are exfoliated from the graphite particles.

39. Method according to any one of claims 37 or 38, characterized in that the anode is separated from the cathode by a separator.

40. Method according to claim 39, characterized in that the separator contains or consists of diamond and/or polytetrafluoroethylene and/or Al2O3 and/or ceramic and/or quartz and/or glass.

41. Method according to one of claims 37 to 40, characterized in that the separator, and optionally the anode are set into rotation and/or in that the separator,

and optionally the anode are shifted so that the distance between the cathode and the separator changes during operation of the apparatus.

42. Method according to any one of claims 37 to 41, characterized in that an electrical voltage from about 5 V to about 60 V, or an electrical voltage from about 10 V to about 50 V, or an electrical voltage from about 12 V to about 45 V, or an electric voltage from about 15 V to about 30 V is applied between the anode and cathode.

43. Method according to any one of claims 37 to 42, characterized in that graphite particles are supplied continuously to the container and/or that graphene flakes are removed continuously from the container.

44. Method according to any one of claims 37 to 43, further comprising the step of photo-treating the graphene flakes for dehydrogenation, for example, wherein the photo-treating including illuminating the graphene flakes with visible light, UV, or microwaves, wherein more that 50% of hydrogenated sp3 hybridized carbon sites are de-hydrogenated.

45. Method according to any one of claims 37 to 44, further comprising the step of: subsequent thermal treatment of the graphene flakes at a temperature from about 100°C to about 800°C, or from about 300°C to about 650°C, and for a period of from about 1 min to about 60 min, or from about 15 min to about 40 min.

46. Method according to one of claims 37 to 45, characterized in that the graphene flakes have an average surface area of more than 10 square micrometers or more than 50 square micrometers or of more than 100 square micrometers.