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(54) **METHOD OF EXFOLIATING AND FUNCTIONALIZING GRAPHITE ANODE**

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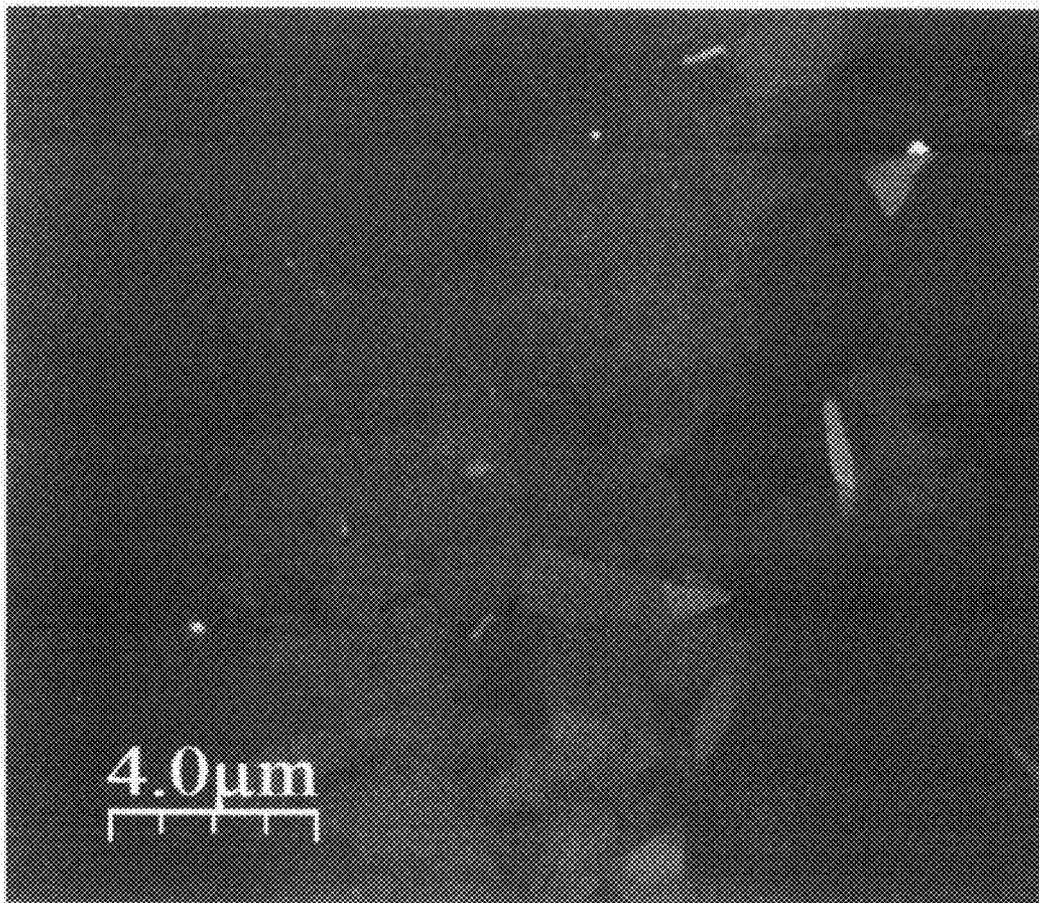
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(57) **ABSTRACT**

A. providing an electrochemical cell with a first graphitic electrode and a second conductive electrode, wherein the first graphitic electrode is made of any one of HOPG, natural graphite, and synthetic graphite, the first graphitic electrode is held at a most positive potential, and the second conductive electrode is conductive, wherein a current passes through the electrochemical cell; B. providing an electrolyte of a solvent in the electrochemical cell, wherein the electrolyte has specific oxygen containing salts and base. Thereby, the graphitic electrode is functionalized and exfoliated by applying a voltage between the two electrodes thus producing graphene oxide.

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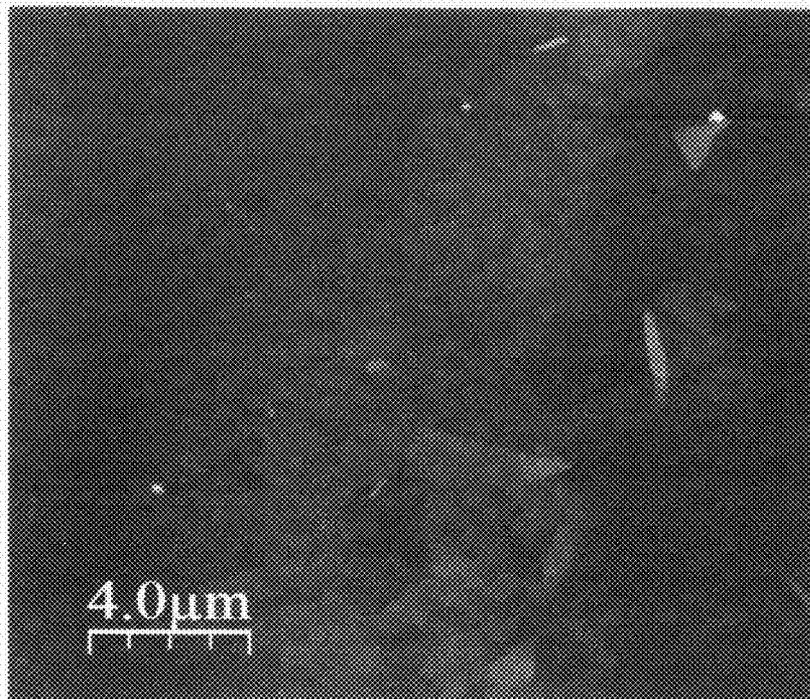


FIG. 1

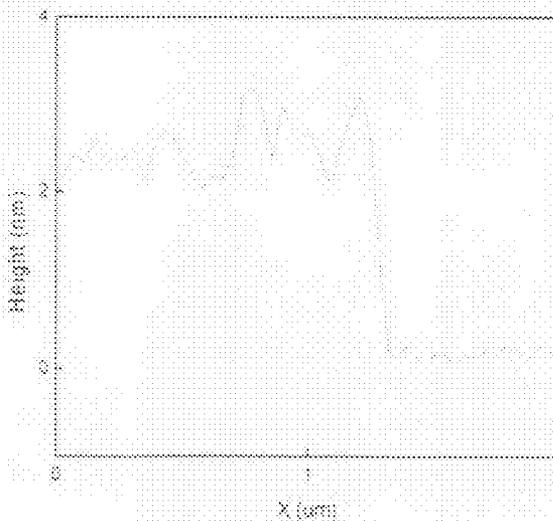


FIG. 2

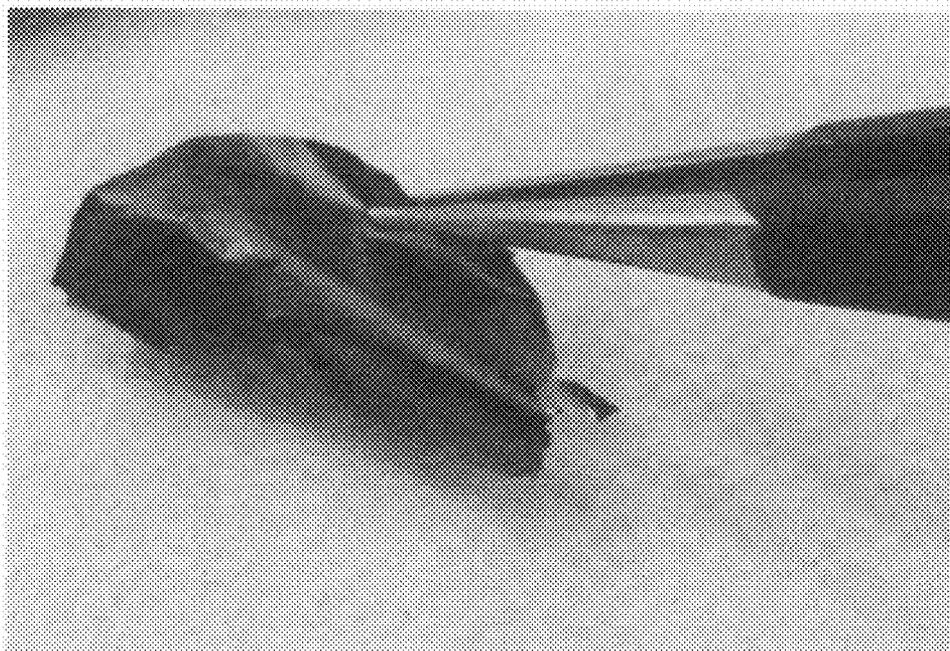


FIG. 3

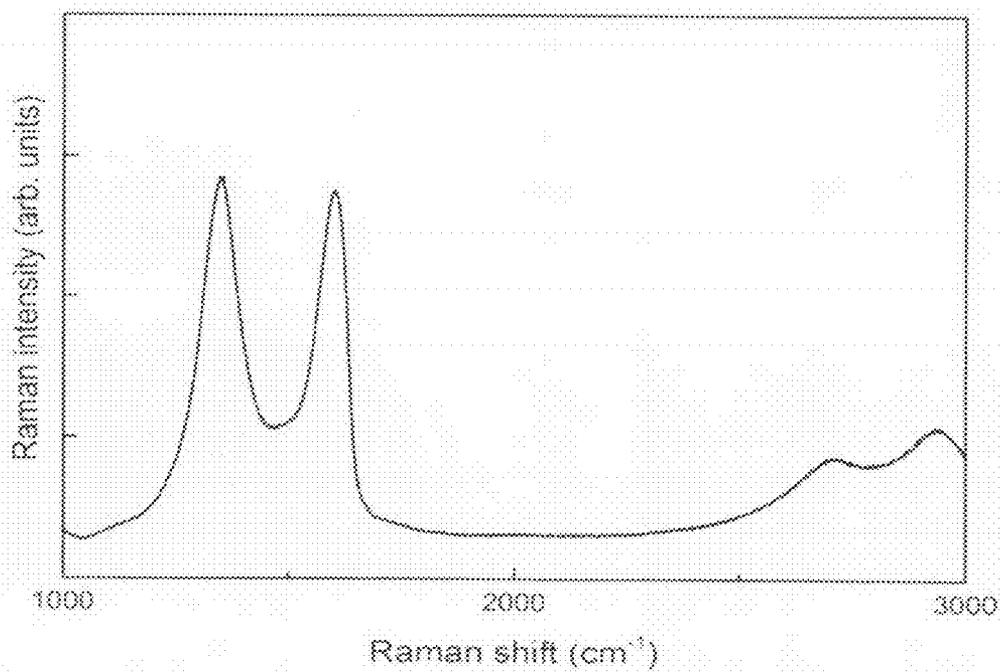


FIG. 4

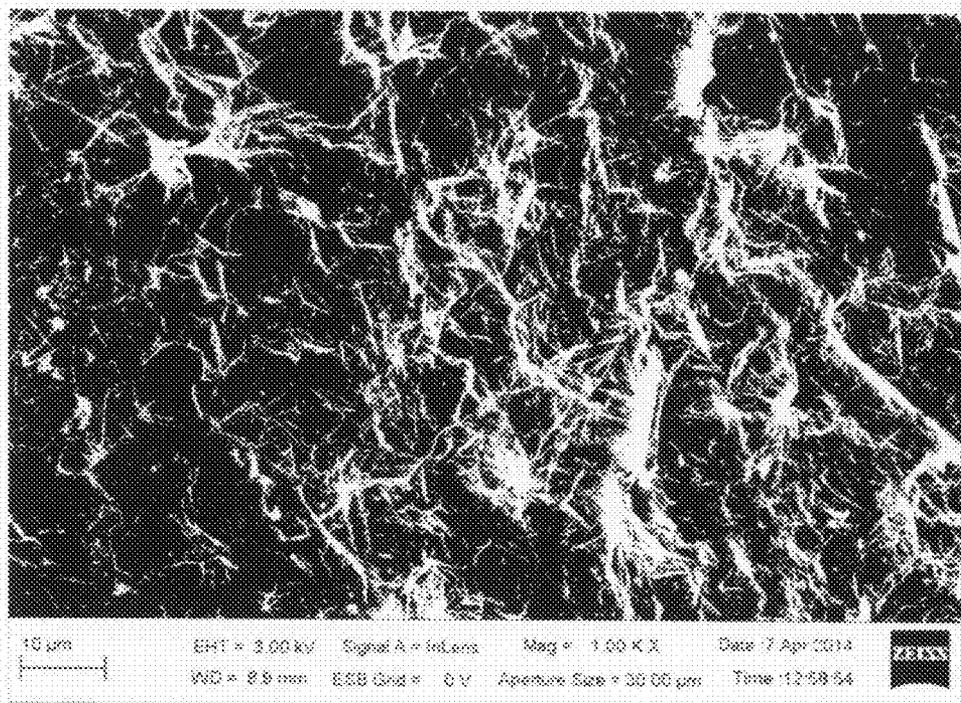


FIG. 5

METHOD OF EXFOLIATING AND FUNCTIONALIZING GRAPHITE ANODE

FIELD OF THE INVENTION

[0001] The present invention relates to a method of exfoliating and functionalizing a graphite anode.

BACKGROUND OF THE INVENTION

[0002] Graphene materials have been at the center of large focus in the recent years because of graphene's exceptional properties. Graphene has a unique range of properties, ranging from record electrical conductivity, thermal conductivity, mechanical stability and others. As a result, a variety of applications are envisaged in the coming years.

[0003] However, pristine graphene are difficult to process since they are not dispersed in solvents routinely used by industry making it difficult for the widespread adoption. As such, graphene oxide is routinely used as a substitute for this. Graphene oxide is graphene which has been functionalized through epoxy, carboxyl and hydroxyl groups. Graphene oxide flakes are readily dispersed in variety of organic solvents and even water due to the electrostatic interaction between the aforementioned groups and the water. Graphene oxide is also an interesting system in its own accord. Laminates of graphene oxide prepared by means of vacuum filtration of GO dispersions are impermeable to anything other than water molecules or very few selected ions.

[0004] Graphite oxide is traditionally prepared through a chemical reaction between an oxidizing agent and strong acids as initially proposed by W. S. Hummers and R. E. Offeman in 1958. They used a combination of sulfuric acid, potassium permanganate and other chemicals. The technique, routinely named as Hummer's method has undergone several modifications since but they main theme of using strong acid and oxidizing agents has not been changed. Graphite oxide can be converted into single-layer graphene oxide by sonication graphite oxide using either a tip sonicator or placing a suspension of graphite oxide in a solvent in an ultrasonic bath.

[0005] The material prepared by the above methodology technique is unfavorable for scale-up as there is a large amount of acidic waste and manganese-containing waste. For reference, for 5 grams of graphene oxide produced using this technique, several liters of water are required in order to remove the acidic sulfuric acid from the final product the reaction and return the pH back to neutral. As the process scales into the kilograms, several tones are required for the washing part of the existing terms making such scale-up impractical. This is the problem that the current invention is addressing.

[0006] The present invention has arisen to mitigate and/or obviate the afore-described disadvantages.

SUMMARY OF THE INVENTION

[0007] The primary objective of the present invention is to provide a method of exfoliating and functionalizing a graphite anode which produces large amounts of graphene oxide or partially oxidized graphene without the need of either using strong acids, at the same time without requiring sonication steps. To achieve this, the exfoliation and oxidation of the graphitic anode happens in an electrochemical cell comprising of an electrolyte containing an oxygen containing salt and a strong base. The use of such salts and base in the present

invention is both non-obvious and the complete opposite of the traditional Hummers methods for preparing graphite oxide.

[0008] To obtain above objectives, a method of producing graphene oxide in an electrochemical cell contains steps of:

[0009] A. providing an electrochemical cell with a first graphitic electrode and a second conductive electrode, wherein the first graphitic electrode is made of any one of HOPG, natural graphite, and synthetic graphite, the first graphitic electrode is held at a most positive potential, and the second electrode is conductive.

[0010] B. providing an electrolyte of a solvent in the electrochemical cell, wherein the electrolyte has specific oxygen containing salt along with a base to produce graphene oxide in the electrochemical cell.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] These and other features, aspects, and advantages of the present invention will become better understood with regard to the following description, appended claims, and accompanying drawings where:

[0012] FIG. 1 is an optical image of a material on an oxidized silicon substrate of a method of producing a graphene oxide in an electrochemical cell according to a preferred embodiment of the present invention.

[0013] FIG. 2 is a diagram showing the height profile of graphene oxide flakes measured by Atomic Force Microscopy. The height corresponds to 1 layer of graphene oxide.

[0014] FIG. 3 is a diagram showing the material of the method of producing the graphene oxide in the electrochemical cell being then pushed through appropriate membranes to prepare free-standing GO papers according to the preferred embodiment of the present invention.

[0015] FIG. 4 is a diagram view showing Raman spectrum of a material of a method of producing graphene oxide in an electrochemical cell according to another preferred embodiment of the present invention.

[0016] FIG. 5 is a diagram showing the permeation of water and isopropanol through free-standing graphene oxide membranes.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The present invention will be described with reference to illustrative embodiments. For this reason, numerous modifications can be made to these embodiments and the results will still come within the scope of the invention. No limitations with respect to the specific embodiments described herein are intended or should be inferred.

[0018] With reference to FIGS. 1 to 5, a method of producing graphene oxide in an electrochemical cell according to a preferred embodiment of the present invention comprises steps of:

[0019] A. providing an electrochemical cell with a first graphitic electrode and a second conductive electrode, wherein the first graphitic electrode is made of any one of HOPG, natural graphite, and synthetic graphite, the first graphitic electrode is held at a most positive potential, and the second conductive electrode is conductive

[0020] B. providing an electrolyte of a solvent in the electrochemical cell, wherein the electrolyte has specific oxygen to produce graphene oxide in the electrochemical cell.

[0021] Regarding electrodes of the electrochemical cell, the first graphitic electrode is a graphitic material. In one

embodiment, high-quality crystalline may be used, in other embodiment partially exfoliated graphite may be used. In some embodiments, graphite already intercalated with salts may be used.

[0022] In some embodiments, the first graphitic electrode is contained within a plastic mesh. This facilitates the exfoliated and oxidized particles to remain in proximity of the first graphitic electrode and in close electrical contact with it for both further exfoliation and oxidation.

[0023] The second conductive electrode can be any material known in those skilled in the art as it does not play an important role in the process. Graphite, stainless steel or any conductive material polymer that is compatible with the solvents, electrolyte may be used. In one embodiment, both the first electrode and the second conductive electrode are graphitic and their voltage are alternated between the first graphitic electrode and a second graphite electrode resulting in oxidation and exfoliation of both the first and second graphitic electrodes. As for the electrolyte, it consists of ions in a solvent. The ions result from oxygen-containing anions. Preferable are nitrate, perchlorate, sulfate, persulfate and phosphate anions. Nitrites, Sulfites, chlorites and phosphites may also be used in one embodiment, the electrolyte may contain a single oxygen-containing atom and in another embodiment it may contain a combination of two or more.

[0024] The counterions (i.e., cations) play no important role in the process and can be selected from a variety of elements including, but not limited to, lithium, sodium, potassium, ammonium, magnesium, copper, lead, cadmium, strontium, nitronium, silver caesium, barium, aluminium and others.

[0025] The base can be the hydroxides of the alkali and alkaline earth metals, which include but is not limited to sodium hydroxide, calcium hydroxide. Other examples of bases include, but not limited to, members of the Arrhenius bases e.g. tetrabutylammonium hydroxide, cesium hydroxide, strontium hydroxide, barium hydroxide. The base is selected such that it is compatible with the solvent and electrode materials.

[0026] In some embodiment the concentration of the oxygen-containing salts may be 1 mM, 0.1M, 0.2M or 0.5M, whereas the maximum concentration may be 2M, or 5M. In some embodiments, the concentration of the strong base may be 1 mM, 0.1M, 0.2M or 0.5M, whereas the maximum concentration may be 2M, or 2M. In some embodiment, the concentration of the electrolyte exceed the saturation limit of the solvent.

[0027] The solvent which can be used include any organic solvent or other solvent in which the electrolyte salts and base are highly soluble. Favorable solvent include but are not limited to: water or organic solvents, including but not limited to acetone, isopropanol, DMSO and others.

[0028] In addition, a working potential of the electrochemical cell will be that requiring the oxidation and exfoliation of the first graphitic electrode. In one embodiment, where a reference is included in the electrochemical cell, the voltage is adjusted slightly above this potential. In another embodiment, where the electrochemical cell only comprises by a single electrode an overpotential is applied which may be 10V, 15V, 20V or 30V. The voltage may be kept constant or may be swapped to facilitate exfoliation at both electrodes.

[0029] The electrochemical cell is operated at a temperature which achieves the correct level of oxidation and exfoliation. In one embodiment, the electrochemical cell tempera-

ture is adjusted to allow for maximum exfoliation and of the first graphitic electrode. In another embodiment, the temperature is increased to allow the more kinetic ions to cause increased oxidation in the first graphitic electrode. The electrochemical cell may be operated at a temperature range of at least 10 C, preferable at least 20 C. The operating temperature may be 30 C, 40 C, 50 C, 60 C, 70 C, 80 C, 90 C or 100 C. Higher or lower operating temperatures may be used. The optimum operating temperature depends on the combination of salt and base used in the process and on the solvent used to suspend them. The higher temperatures facilitate higher concentrations of oxygen-containing salts and base.

[0030] Preferably, the electrolyte is not consumed during the process and may be recycled and used in further electrochemical runs. In such embodiments the electrolyte is recovered by means of filtration, at the interface of two immiscible liquids, by centrifugation or by techniques known by those skilled in the art.

[0031] Thereby, analysis of the graphene material produced by the process is routinely conducted by means of Raman spectroscopy.

[0032] Raman spectroscopy of graphite has been performed for more than 40 years and it recently has been extended to single-layer graphene, its few-layer counterparts and to graphene oxide and few-layer graphene oxide.

[0033] The Raman spectrum of all graphitic materials such as graphite, graphene and carbon nanotubes is characterized by two main peaks: The D peak which is located at around 1350 cm^{-1} . This is a first order Raman peak which lies far from the Γ point of the Brillouin zone and as such require defects (or sp^3 material) within the basal plane of the graphite for its activation. The G peak is located at around the 1580 cm^{-1} and is associated with the stretching of all sp^2 rings and chains and corresponds to a phonon at the Γ point of the Brillouin zone. The 2D peak is an overtone, i.e. the second order of the D peak and is activated through a double-resonant process. In pristine graphene the width, and not the position, of the 2D peak can be used to unambiguously prove layer thickness. The position may vary due to factors such doping or strain. For pristine graphene, the D peak is absent as there are no defects. The G and 2D peaks are both sharp and the ratio of their intensity (hereby denoted $I(G/2D)$) is 1:4, that is, the intensity of the 2D is nearly four times as intense as the G peak.

[0034] For graphene oxide the situation markedly changes. The introduction of epoxy, carboxyl and hydroxyl sp^3 -bonded functional groups on the surface of graphene's basal planes means that the Raman spectrum is different. The D and G peak become much broader and the intensity of the 2D peaks falls well-below that of the G and D peaks. New combination modes are also visible which are attributed to G+D and peaks.

[0035] Although there is no strict requirement for defining graphene oxide, the material referred to as graphene oxide must be analogous to the material produced by the traditional Hummer's method and behave in a similar manner. The most important requirement for this is the water-dispersibility and high oxygen content due to the functionalization with the functional groups. This is vital since it makes the material easy to process on an industrial level.

[0036] The produced graphene oxide material was also characterized by atomic force microscopy in tapping mode as well as by optical microscopy to determine contrast levels. The former technique gives height thickness measurements to

prove atomically thin layer thickness while the latter can also provide quantitative information from the optical contrast the flakes provides when dispersion is drop-casted on a silicon substrate with a carefully chosen oxide layer. The term “graphene oxide” is typically referred to when the graphene oxide flake is around 1 nm thickness but we refer to “graphene oxide” as an umbrella term for both monolayer and few-layer (few nanometer thickness) graphene oxide flakes. The thickness of the flakes produced may vary from 1 nm to 100 nm, but preferentially will be less than 100 nm, more preferentially less than 50 nm and more preferentially under 10 nm.

[0037] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms “a”, “an” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms “comprises” and/or “comprising,” when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

[0038] The corresponding structures, materials, acts, and equivalents of all means or step plus function elements in the claims below are intended to include any structure, material, or act for performing the function in combination with other claimed elements as specifically claimed. The description of the present invention has been presented for purposes of illustration and description, but is not intended to be exhaustive or limited to the invention in the form disclosed. Many modifications and variations will be apparent to those of ordinary skill in the art without departing from the scope and spirit of the invention. The embodiment was chosen and described in order to best explain the principles of the invention and the practical application, and to enable others of ordinary skill in the art to understand the invention for various embodiments with various modifications as are suited to the particular use contemplated.

[0039] Without further elaboration, it is believed that the above description has adequately enabled the present invention. The following examples are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever. The publications cited herein are hereby incorporated by reference in their entirety.

[0040] In example 1, a nitrate salt (cation: sodium) was used in water with the base being potassium hydroxide. The solution was stirred for approximately 10 minutes to dissolve the salt and base in the water. Subsequently two graphite rods were inserted as electrodes. A voltage of 10V was applied between the two electrodes. After about 10 seconds, the first graphitic electrode visibly started to exfoliate with the product having a characteristic brown color associated with graphene oxide. The process was stopped after 30 minutes and 0.1 grams of powder was recovered after filtration. The powder was suspended by gently shaking in water, and 1 mL was drop-casted onto a Si:SiO₂ substrate for further characterization. The optical image of the material on the oxidized silicon substrate is shown in FIG. 1. The Raman spectrum of the material is shown in FIG. 2.

[0041] To determine oxygen content a graphene oxide paper was prepared by suspending the powder in water and mildly sonicating for 10 minutes. The material was then pushed through appropriate membranes to prepare free-standing GO papers as illustrated in FIG. 3. It should be noted

that the material had the characteristic mechanical strength and flexibility of GO paper. The SEM of the GO paper shows characteristics ripples and folds associated with GO paper and individual flakes are not readily observable. The oxygen content was determined to be 30%.

[0042] In example 2, a sulfate salt was used in water with the base being sodium hydroxide. The process run for 1 hour and 0.3 grams of material was recovered after filtration. The Raman spectrum of the material is presented in FIG. 4.

[0043] It is to be noted that, the Raman spectrum is characterized by two broad peaks centered around 1350 cm⁻¹ and 1580 cm⁻¹, the D and G peaks, respectively. The second-order peaks, the 2D are heavily quenched as the functionalization of graphene's basal plane results in the suppression of the double-resonant process. This is an indication of preparation of graphene oxide.

[0044] The material was then mixed with water and shaken. Small amounts of graphene oxide dispersion was then drop-casted on a silicon wafer covered with 290 nm oxide. Tapping mode AFM reveals that the flakes have thickness of 1 nm indicating a single atomic layer of graphene oxide as shown in FIG. 2.

[0045] In order to further testament to the quality of the graphene oxide membranes prepared in this manner, the graphene oxide membrane was tested by x-ray diffraction. The usual graphite peak near 2θ was less prominent and sharp than graphite and a peak emerged near 11θ, which is evidence of graphene oxide formation.

[0046] The membranes were also tested for permeation of water and other organic solvents. It was found that water permeates at a fast unimpeded rate, while isopropanol, is completely blocked. This in agreement with literature stating that such graphene oxide membranes allow permeation of water but block all other species including helium.

[0047] In example 3, a perchlorate salt was used in water (cation: lithium) with the base being tetramethylammonium hydroxide.

[0048] All of the features disclosed in this specification may be combined in any combination. Each feature disclosed in this specification may be replaced by an alternative feature serving the same, equivalent, or similar purpose.

[0049] Thus, unless expressly stated otherwise, each feature disclosed is only an example of a generic series of equivalent or similar features.

[0050] From the above description, one skilled in the art can easily ascertain the essential characteristics of the present invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Thus, other embodiments are also within the scope of the following claims.

What is claimed is:

1. A method of producing graphene oxide in an electrochemical cell comprising steps of:
 - A. providing an electrochemical cell with a first graphitic electrode and a second conductive electrode, wherein the first graphitic electrode is made of any one of HOPG, natural graphite, synthetic graphite and partially exfoliated graphite the first graphitic electrode is held at a most positive potential, and the second electrode is conductive;
 - B. providing an electrolyte in the electrochemical cell comprising a solvent, wherein the electrolyte contains spe-

cific oxygen containing salts and a strong base facilitating exfoliation and oxidation of the graphite electrode..

2. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the graphitic electrode is pretreated by any one of sonication, ultrasound, and chemical.

3. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the second conductive electrode is a conductive polymer or a metal.

4. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the solvent is water.

5. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the solvent is an organic solvent.

6. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the solvent is a mixture between water and an organic solvent.

7. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 5, wherein the solvent is any one of acetone, isopropanol, ethanol and methanol.

8. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the electrolyte consists of salts where in an anionic part is any one of sulfate, nitrate and chlorate.

9. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the electrolyte consists any one of persulfate, perchlorate, and perphosphate.

10. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 9, wherein the cationic part of the salt is selected from sodium, potassium, and ammonium.

11. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 10, wherein the cationic part of the salt is selected from sodium, potassium, and ammonium.

12. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the electrolyte further consists of an Arrhenius base.

13. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 12, wherein the base is any one of potassium hydroxide, sodium hydroxide, and tetraethylammonium hydroxide.

14. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the electrolyte is recovered by i) filtration, ii) interface of two immiscible liquid, and iii) centrifugation.

15. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the graphene oxide is used to prepare water-dispersible suspensions.

16. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the graphene oxide is used to prepare freestanding graphene oxide membranes.

17. The method of producing the graphene oxide in the electrochemical cell as claimed in claim 1, wherein the graphene oxide is used to prepare composite materials.

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