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(54) Title: ELECTROSPUN COMPOSITE NANOFIBER COMPRISING GRAPHENE NANORIBBON OR GRAPHENE OXIDE NANORIBBON, METHODS FOR PRODUCING SAME, AND APPLICATIONS OF SAME

(57) Abstract: Disclosed herein is a method, of forming a nanofiber that includes: providing a fluid comprising a polymer or a ceramic precursor; providing a fluid comprising at least one functionalized or non-functionalized carbon allotrope, chosen from a graphene nanoribbon or a graphene oxide nanoribbon, dispersed therein; electrospinning the fluid through an opening; wherein the fluid comprising a polymer and the fluid comprising at least one functionalized or non-functionalized carbon allotrope are the same or different. Further disclosed herein is a nanofiber material made with the above method. Further disclosed herein are applications of the material.



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**ELECTROSPUN COMPOSITE NANOFIBER COMPRISING GRAPHENE
NANORIBBON OR GRAPHENE OXIDE
NANORIBBON, METHODS FOR PRODUCING SAME, AND APPLICATIONS
OF SAME**

CROSS-REFERENCE

[01] This application claims the benefit of U.S. Provisional Application No. 61/911,847, filed on December 4, 2013 and entitled “Nanostructured Carbon, Methods for Producing Same, and Applications of Same,” which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[02] The present application for patent is in the field of nanostructured carbon materials. More specifically, the present application discloses nanostructured carbon fibers, the method of producing them and uses thereof.

BACKGROUND

[03] Nanotechnology is an emerging field that uses the principles of science and engineering to fabricate materials or structures of dimensions in the nanometer scale. Nanoscale materials can display unusual and unique property profiles as compared to macromaterials. Physical, chemical and biological properties such as shape, orientation, surface chemistry, topology and reactivity exhibited by these materials may originate from their small dimensions. These material properties can translate into unusual electrical, optical, magnetic, mechanical, thermal and biological properties for these materials.

[04] Some nanostructures or nanoscale materials currently under investigation include quantum dots and wires, nanoscale self-assembled materials and thin films, nanocrystals, nanotubes, nanowires, nanorods, nanofoams, nanospheres, nanoplatelets, nanoribbons, nanofibers, and aerogels. Among these nanostructures, nanofibers form one of the most extensively investigated areas. The word nanofiber refers to fibrous structures usually made of carbon, organic polymers or organometallic polymers with diameter less than one micrometer. Nanofibers can be fabricated using various processing techniques such as drawing, self assembly, template synthesis, phase separation, dry spinning, and electrospinning.

[05] Attempts have been made to produce graphene composite nanofibers. For example, in U.S. Patent No. 8,519,045, Jang et al. disclose a “graphene composite nanofiber..., characterized in that graphenes are dispersed to a surface and/or inside of a nanofiber.” “[T]he

nanofiber has a diameter of 1-1000 nm...” However, the low graphene concentrations and other deficiencies of Jang may not be suitable to produce nanofibers having the desired electrical and mechanical characteristics for applications such as battery electrodes and reinforced plastics. Moreover, exfoliated graphene, such as utilized by Jang, yields fragments having a wide dispersity and poorly controlled shape.

[06] Therefore, there remains a need for a nanofiber having increased graphene loading, improved graphene distribution uniformity and improved property control. Further, there remains a need for a process of making nanofibers having improved manufacturing rates, increased graphene loading, improved graphene and/or nanofiber uniformity, improved performance characteristics, and/or improved property control. Still further, there remains a need for articles of manufacture that comprise graphene nanofibers having increased graphene loading, improved graphene uniformity, improved performance characteristics, and improved property control. These needs as well as others are addressed in the present application.

SUMMARY

[07] Provided herein are nanostructured carbon structures, processes for manufacturing such structures and uses of the same. In specific embodiments, provided herein are nanofibers comprising a matrix material (e.g., polymer or carbon), with carbon allotrope (graphene nanoribbons) embedded therein. In specific embodiments, provided herein are carbon-silicon composite nanofibers comprising a matrix material (e.g., polymer or carbon), with carbon allotrope embedded therein. In more specific embodiments, provided herein are carbon-silicon composite nanofibers comprising a carbon matrix, with carbon allotrope (graphene nanoribbons) and silicon nanoparticles embedded therein. In certain specific embodiments, the nanofiber matrix is carbon, such as carbonized polymer. In various embodiments, all or part of the graphene nanoribbons (GNRs) are embedded in the matrix.

[08] For example, in some instances, provided herein are processes of forming a nanomaterial (e.g., a composite nanofiber), the process comprising:

- a. providing one or more fluid, the one or more fluid(s) comprising (i) a polymer or ceramic precursor and (ii) at least one carbon allotrope, chosen from a graphene nanoribbon or a graphene oxide nanoribbon; and
- b. electrospinning the fluid(s) to form a nanomaterial.

[09] In some embodiments, a first fluid comprising polymer or ceramic precursor is provided and a second fluid comprising carbon allotrope dispersed therein is provided and the first and

second fluids are combined prior to electrospinning. In certain embodiments, the one or more fluid(s) comprise polymer (e.g., and the nanomaterial is a composite nanofiber comprising a polymer matrix and graphene nanoribbons embedded therein). In some embodiments, the one or more fluid(s) comprise polymer and the process further comprises carbonizing the polymer after electrospinning (e.g., and the nanomaterial is a composite nanofiber comprising a carbon matrix – e.g., comprising amorphous carbon – with graphene nanoribbons embedded therein). In specific embodiments, the one or more fluids comprise polymer, graphene nanoribbons, and silicon nanoparticles (e.g., and the nanomaterial is a composite nanofiber comprising a carbon or polymer matrix – e.g., depending on whether or not the polymer is carbonized – with graphene nanoribbons and silicon nanoparticles embedded in the matrix). In various embodiments, the graphene nanoribbons utilized herein comprise, e.g., substituted or unsubstituted graphene nanoribbons, graphene oxide nanoribbons, and/or reduced graphene oxide nanoribbons.

[10] Also, provided herein are such nanomaterials, included those produced by or able to be produced by such manufacturing processes and devices incorporating such nanomaterials, such as lithium ion and/or lithium air (oxygen) batteries and parts thereof. Other embodiments are described in throughout this specification and in the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[11] **Figure 1** illustrates an embodiment of the method of forming a nanofiber using (optionally, gas assisted) electrospinning.

[12] **Figure 2** illustrates scanning electron micrograph (SEM) and transmission electron micrograph (TEM) images of (a) conventional electrospinning and (b) gas assisted electrospinning.

[13] **Figure 3** illustrates an embodiment of a lithium-air or lithium oxygen battery that comprises a film made from the nanofibers as disclosed herein.

[14] **Figure 4** illustrates various charge and discharge curves for batteries similar to that illustrated in **Figure 3**, employing films made from nanofibers comprising different graphene nanoribbons as described herein.

[15] **Figure 5** illustrates the battery capacities of various lithium ion batteries after repeated cycling for batteries fabricated as described herein.

[16] **Figure 6** illustrates various charge and discharge curves for lithium-air batteries.

[17] **Figure 7** illustrates a schematic of a supercapacitor that employs the electrospun

nanofibers, comprising graphene nanoribbons as disclosed herein.

[18] **Figure 8** illustrates a comparison of specific capacitance of various carbon materials including graphene nanoribbons in the electric double layer supercapacitor application.

[19] **Figure 9** illustrates a schematic of the fabrication of a nanofiber film using nanofibers comprising graphene nanoribbons as disclosed herein. In this illustration, multiple electrospinning nozzles similar to those in **Figure 1** are used.

[20] **Figure 10** illustrates structural representations of the armchair and zigzag graphene nanoribbon configurations.

[21] **Figure 11** (panel A) illustrates a TEM image of MWCNT; (panel B) a TEM image of exemplary graphene nanoribbons; a low (panel C) and a high (panel D) magnification SEM image of exemplary GNR/Si-C nanofibers; (panel E) a TEM image of exemplary GNR/Si-C nanofibers; and (panel F) an SEM image of an anode using exemplary GNR/Si-C nanofibers.

[22] **Figure 12** illustrates CV of a lithium ion half cell with an anode comprising GNR (panel A) or Si-C nanofibers or GNR/Si-C nanofibers (panel B); a long-term CV of a lithium ion half cell with an anode comprising GNR/Si-C nanofibers (panel C); and Nyquist plots of Si-C nanofibers and GNR/Si-C nanofibers (panel D).

[23] **Figure 13** illustrates (panel A) initial charge/discharge curves of exemplary GNR/Si-C fiber anodes and similar Si-C fiber anodes in lithium ion half cells; (panel B) initial charge/discharge curves for exemplary GNR/Si-C fiber anodes in half cells at variable current rates; (panel C) the rate capability of a half cell having an exemplary GNR/Si-C nanofiber containing anode.

[24] **Figure 14** illustrates the capacity of a lithium ion half cell comprising exemplary GNR/Si-C fibers over 100 cycles.

DETAILED DESCRIPTION

Exemplary Embodiments Illustrated by Drawings

[25] **Figure 1** illustrates an embodiment of the method of forming a nanofiber *via* electrospinning, optionally, gas assisted (e.g., coaxially gas assisted). A reservoir, **101**, of a fluid comprising a polymer and an at least one functionalized or non-functionalized carbon allotrope, chosen from a graphene nanoribbon or a (reduced or unreduced) graphene oxide nanoribbon, dispersed therein is dispensed into a pump such as syringe pump, at least one functionalized or

non-functionalized carbon allotrope, chosen from a graphene nanoribbon or a (reduced or unreduced) graphene oxide nanoribbon, dispersed therein is placed into a pump, such as a syringe pump, **102**. Optionally, a high speed gas such as air, is streamed into the pump nozzle, **103**, to produce effects associated with gas assisted deposition. A variable high voltage source, **104**, is electrically connected to the pump nozzle or spinneret, **105**. The nanofiber, **108** and **109**, thus produced is deposited onto a substrate, **106**, to form a matted film, **107**.

[26] **Figure 2** illustrates scanning electron micrograph (SEM) and transmission electron micrograph (TEM) images of **(a)** conventional electrospinning and **(b)** gas assisted electrospinning. Conventional electrospinning yields the matted film in the SEM, **201**. The TEMs, **202** and **203**, show the level of definition that may be obtained thereby. The SEM, **204**, illustrates a film comprising well defined electrospun nanofibers. The TEM, **205**, illustrates the well defined dispersion and orientation of carbon allotrope that may be obtained by electrospinning.

[27] **Figure 3** illustrates an embodiment of a lithium-air or lithium oxygen battery that comprises a film made from the nanofibers as disclosed herein. Elemental lithium, **301**, is used to form the battery cathode, in contact with an electrolyte, **302**, comprising a lithium salt. In this embodiment, the cathode, **303**, is formed from a mat of electrospun nanofibers comprising a polymer and a functionalized or non-functionalized graphene nanoribbon. Not shown are optional catalysts for breaking Li-O and O-O bonds at specific energies. Further not shown are optional compatible interface membranes, e.g., that may be useful for separations. Oxygen molecules, **304**, diffuse through the electrospun nanofiber mat to carry out the REDOX chemistry of the battery.

[28] **Figure 4** compares charge and discharge curves for lithium ion batteries described infra in **Examples 22-23**. In particular, **Figure 4(a)** illustrates charge **402** and discharge **401** cycles for a lithium ion battery made with nanofibers containing silicon nanoparticles but no carbon nanoribbons and **Figure 4(b)** illustrates charge **404** and discharge **403** cycles for a lithium ion battery made with nanofibers containing silicon nanoparticles and functionalized carbon nanoribbons.

[29] **Figure 5** illustrates the battery capacities of various lithium ion batteries after repeated cycling for batteries fabricated as described infra in **Examples 22-25**. Shown are battery capacity curves for batteries containing nanofibers having no graphene nanoribbons **501**, nanofibers having functionalized graphene nanoribbons **502**, nanofibers having unfunctionalized

graphene nanoribbons **503**, and nanofibers having exfoliated graphene nanoribbons **504**.

[30] **Figure 6** illustrates various charge and discharge curves for lithium-air batteries similar to that illustrated in **Figure 3**, employing films made from nanofibers comprising different graphene nanoribbons as described herein. In **Figure 6(a)**, charging (upper curves) and discharging curves (lower curves) illustrate the battery capacity. The curves **601** and **605**, represent charging and discharging cycles, respectively for a battery made with graphene nanoribbons in a Nafion matrix, wherein the graphene nanoribbons were produced by reductive opening of multiwalled carbon nanotubes with sodium-potassium alloy and functionalized with hexadecyl groups. As **605** shows, the charge capacity of the battery, thus obtained, is approximately 2,200 mA h/g_{carbon}. The curves **602** and **606**, represent charging and discharging cycles, respectively for a battery made with graphene nanoribbons in a Nafion matrix, wherein the graphene nanoribbons were produced by reductive opening of multiwalled carbon nanotubes with sodium-potassium alloy but were not functionalized. As **606** shows, the charge capacity of the battery, thus obtained, is approximately 4,000 mA h/g_{carbon}. The curves **603** and **607**, represent charging and discharging cycles, respectively for a battery made with graphene nanoribbons in a Nafion matrix, wherein the graphene nanoribbons were produced by exfoliation of the functionalized graphene nanoribbons used in **601** and **605** above.. As **607** shows, the charge capacity of the battery, thus obtained, is approximately 2,950 mA h/g_{carbon}. The curves **604** and **608**, represent charging and discharging cycles, respectively for a battery made with graphene nanoribbons in a Nafion matrix, wherein the graphene nanoribbons were produced by exfoliation of the unfunctionalized graphene nanoribbons used in **602** and **606** above. As **608** shows, the charge capacity of the battery, thus obtained, is approximately 3,200 mA h/g_{carbon}.

[31] In **Figure 6(b)**, charging (upper curves) and discharging curves (lower curves) illustrate the battery capacity. The curves **609** and **613**, represent charging and discharging cycles, respectively for a battery made with gas assisted electrospun nanofibers, wherein the selected graphene nanoribbon used in the electrospun nanofiber was produced by reductive opening of multiwalled carbon nanotubes with sodium-potassium alloy and functionalized with hexadecyl groups. As **613** shows, the charge capacity of the battery, thus obtained, is approximately 1,800 mA h/g_{carbon}. The curves **610** and **614**, represent charging and discharging cycles, respectively for a battery made with gas assisted electrospun nanofibers, wherein the selected graphene nanoribbon used in the electrospun nanofiber was produced by reductive opening of multiwalled carbon nanotubes with sodium-potassium alloy but were not functionalized. As **614** shows, the

charge capacity of the battery, thus obtained, is approximately 4,000 mA h/g_{carbon}. The curves **611** and **615**, represent charging and discharging cycles, respectively for a battery made with gas assisted electrospun nanofibers, wherein the selected graphene nanoribbon used in the electrospun nanofiber was produced by exfoliation of the graphene nanoribbons used in **609** and **613**. As **615** shows, the charge capacity of the battery, thus obtained, is approximately 6,500 mA h/g_{carbon}. The curves **612** and **616**, represent charging and discharging cycles, respectively for a battery made with gas assisted electrospun nanofibers, wherein the selected graphene nanoribbon used in the electrospun nanofiber was produced by exfoliation of the graphene nanoribbons used in **602** and **606**. As **616** shows, the charge capacity of the battery, thus obtained, is approximately 4,900 mA h/g_{carbon}.

[32] **Figure 7** illustrates a schematic of a supercapacitor that employs the electrospun nanofibers, comprising graphene nanoribbons as disclosed herein. In the Figure, **701** represents a line to the electrode, **702**. Similarly, **703** represents a line to the electrode, **704**. An optional porous separator, **705**, separates the two portions of the capacitor. In this embodiment, the mesoporous regions **506** and **508** comprise mats of electrospun nanofibers comprising graphene nanoribbons infused with a solid or fluid electrolyte; a closeup of which is illustrated schematically as **707** and **709**.

[33] **Figure 8** illustrates a comparison of specific capacitance of various carbon materials including graphene nanoribbons in the supercapacitor application. Specific capacitances in F/g_{carbon} are shown for scan rates from 4 mV/sec to 50 mV/sec. The curves **801** - **804**, represent specific capacitances, respectively for an electric double layer supercapacitor made with gas assisted electrospun nanofibers, comprising selected graphene nanoribbons, as shown in **Figure 7**, supra. As **801-804** show, the specific capacitances, thus obtained, are approximately 32 F/g_{carbon}, (@ 4 mV/sec), 42 F/g_{carbon}, (@ 10mV/sec), 78 F/g_{carbon}, (@ 4 mV/sec), and 72 F/g_{carbon}, (@ 4 mV/sec), respectively. These were tested against gas assisted electrospun nanofiber mats having commercially available carbon materials, Vulcan XC-72, available from Cabot Corporation of Boston, MA, and Super-P conductive carbon black, available from TimCal Graphite and Carbon of Bodio Switzerland. Curves **805** and **806** show specific capacitances of 22 F/g_{carbon}, (@ 4 mV/sec), and 15 F/g_{carbon}, (@ 4 mV/sec), respectively.

[34] **Figure 9** illustrates a schematic of the fabrication of a nanofiber film using nanofibers comprising graphene nanoribbons as disclosed herein. In this illustration, multiple electrospinning nozzles similar to those in **Figure 1** are used. An array of electrified nozzles, **1001**, supplied with the same or different fluids comprising graphene nanoribbons and one or

more binder polymers. A gas jet, at **1002**, provides for gas assisted electrospinning from each of the arrayed nozzles. Electrospun nanofibers, **1003**, are deposited on a flexible substrate **1004**. In this way roll to roll coating may be accomplished. Not shown are concentric and random arrays. These can be implemented in similar fashion to the array shown.

[35] **Figure 10** illustrates structural representations of the armchair and zigzag graphene nanoribbon configurations, either form of which is optionally present in the embodiments described herein.

[36] **Figure 11** (panel A) illustrates a TEM image of MWCNT having a diameter of about 100 nm. Such MWCNT, larger diameter, or smaller diameter variants are optionally utilized to prepare GNRs described and utilized in the embodiments provided herein. **Figure 11** (panel B) illustrates a TEM image of exemplary graphene nanoribbons (unzipped MWCNT, such as illustrated in panel A) having a width of about 200 nm. **Figure 11** also illustrates a low and a high magnification SEM image (panels C and D, respectively) and TEM image (panel E) of exemplary GNR/Si-C nanofibers prepared or provided herein. Further, even after grinding of the nanofibers in preparation of an anode material, the composites retain their fiber morphology as illustrated in the SEM image of **Figure 11** (panel F).

[37] **Figure 12** (panel A) illustrates cyclic voltammogram (CV) of an exemplary lithium ion half cell with an anode comprising GNR alone **1201**. In certain embodiments, the current density of GNR/Si-C nanofibers **1203** is increased by about 20% when compared to Si-C nanofibers **1202** (i.e., nanofibers lacking GNR inclusions), as illustrated in **Figure 12** (panel B). **Figure 12** (panel C) illustrate exemplary long term cyclic voltammograms (CVs) of half cells comprising an exemplary GNR/Si-C containing anode, with the 50th cycle represented by **1204** and the 300th cycle represented by **1205**. In some embodiments, any lithium ion battery cells or anodes provided herein retain at least 60%, at least 70%, at least 80% or at least 90% initial capacity after 25, 50, 100, 200, or 300 cycles. **Figure 12** (panel D) illustrates exemplary Nyquist plots of GNR/Si-C nanofiber anodes **1207** versus Si-C nanofiber anodes **1206**, demonstrating exemplary improved performance of fibers having GNR inclusions.

[38] **Figure 13** (panel A) illustrates initial charge/discharge curves of exemplary GNR/Si-C fiber anodes **1302** and similar Si-C fiber anodes **1301** in lithium ion half cells, the GNR containing fibers exhibiting higher capacities than Si-C fibers, even when silicon content is held constant. **Figure 13** (panel B) illustrates initial charge/discharge curves for exemplary GNR/Si-C fiber anodes in half cells at variable current rates. **Figure 13** (panel C) illustrates the rate

capability of a half cell having an exemplary GNR/Si-C nanofiber containing anode. In some instances, any nanofibers or anodes provided herein have initial charge/discharge capacities of at least 750 mAh/g (per gram active anode material), at least 850 mAh/g (per gram active anode material), at least 1,000 mAh/g, at least 1,200 mAh/g, at least 1,500 mAh/g, at least 2,000 mAh/g, or any other suitable capacity at any suitable rate, such as 0.1C, 0.5C, 1C, 2C, or the like.

[39] **Figure 14** illustrates the capacity of a lithium ion half cell comprising exemplary GNR/Si-C fibers over 100 cycles. The capacity retention of cells having anodes with GNR/Si-C fibers was about 93.7% after 100 cycles (calculated from a 100th discharge capacity of 1,464 mAh/g versus a 1st discharge capacity of 1,563 mAh/g) whereas cells having anodes with Si-C fibers were observed to have about 60% retention after 100 cycles.

Detailed Description of General Exemplary Embodiments

[40] As used herein, the conjunction “and” is intended to be inclusive and the conjunction “or” is not intended to be exclusive unless otherwise indicated or required by the context. For example, the phrase “or, alternatively” is intended to be exclusive. The articles “a” and “the” as used herein are understood to encompass the plural as well as the singular unless otherwise indicated or required by the context. As used herein, the term “copolymer” is understood to comprise two or more monomer repeat units and a “polymer” may be a homopolymer, or a copolymer. As used herein, when the prefix, “(meth)acryl” is used, “acryl” or “methacryl” are intended. For example, (meth)acrylate may represent an acrylate or a methacrylate. As used herein, the adjective, “exemplary” is intended to mean illustrative of a characteristic, without expressing preference. As used herein, the term “monomer repeat unit” or, simply, “monomer,” is used to describe the unreacted monomer or the reacted unit within the polymer. “Graphene nanoribbons,” as defined herein, refer to, for example, single or multi layers of graphene that have been obtained by unzipping of Carbon NanoTubes (CNT), such as Multi Walled Carbon NanoTubes (MWCNT). Aspect ratio is understood to be the ratio of two lengths expressed as the longer divided by the shorter. In addition, reference to an embodiment or characteristic of a graphene nanoribbon provided in the description herein shall be understood to include individual reference to graphene nanoribbons, as well as functionalized and non-functionalized variants thereof, graphene oxide nanoribbons, and reduced graphene oxide nanoribbons. Reference to a graphene nanoribbons herein, without reference to its functionalized or non-functionalized variant, shall be understood to include both variants.

[41] Disclosed herein is a method, of forming a nanofiber comprising: (a) providing a fluid comprising a polymer; (b) providing a fluid comprising at least one functionalized or non-functionalized carbon allotrope, the carbon allotrope chosen from a graphene nanoribbon or a graphene oxide nanoribbon, dispersed therein; and electrospinning the fluid through an opening, such as a nozzle, by applying a high voltage to the nozzle and pumping the combined fluid or fluids through the nozzle. Exemplary voltages may be between 1kV and 100 kV. Further exemplary voltages may be between 5kV and 50 kV. Still further exemplary voltages may be between 10 kV and 30 kV. In one embodiment, the fluid comprising a polymer and the fluid comprising at least one functionalized or non-functionalized carbon allotrope may be the same fluid. In another embodiment, the fluid comprising a polymer and the fluid comprising at least one functionalized or non-functionalized carbon allotrope are different fluids. To form the composite, the fluids are combined either *ex situ* or *in situ*, prior to use. A further embodiment is the application of a high-speed circumferentially uniform gas flow at the nozzle (or co-axial gas assisted electrospinning) to improve nanofiber definition and dispersion of additives such as functionalized or unfunctionalized graphene nanoribbons, (reduced or unreduced) graphene oxide nanoribbons, semiconductor nanoparticles, nanorods or the like.

[42] In certain embodiments, following electrospinning a nanofiber comprising a polymer matrix with graphene nanoribbon (functionalized or non-functionalized) or graphene oxide nanoribbon (reduced or non-reduced) embedded therein, a process provided herein further comprises thermally treating such nanofiber. In certain embodiments, the thermal treatment is a low temperature treatment (e.g., about 100 C to about 300 C, such as about 200 C) (such as to stabilize the polymer component), a high temperature treatment (such as to carbonize the polymer component) (e.g., about 500 C to about 2000 C, about 700 C to about 1500 C, about 800 C to about 1200 C, or the like), or a combination thereof. In specific embodiments, the thermal treatment is utilized to produce a nanofiber comprising a carbon (e.g., amorphous carbon) matrix comprising graphene nanoribbon (functionalized or non-functionalized) or graphene oxide nanoribbon (reduced or non-reduced) embedded therein.

[43] In some embodiments, the nanofiber comprises a polymer matrix with graphene nanoribbon – or graphene oxide nanoribbon or reduced graphene oxide nanoribbon - (functionalized or non-functionalized) embedded therein. In other embodiments, the nanofiber comprises a carbon matrix (e.g., amorphous carbon) with graphene nanoribbon – or graphene oxide nanoribbon or reduced graphene oxide nanoribbon - (functionalized or non-functionalized) embedded therein.

[44] Further disclosed herein is a nanofiber comprising: (a) a polymer; and (b) at least one functionalized or non-functionalized carbon allotrope, chosen from a graphene nanoribbon or a (reduced or unreduced) graphene oxide nanoribbon; wherein the weight ratio of the functionalized or non-functionalized carbon allotrope to the polymer present in the nanofiber(s) may be from about 1% to about 90% of the carbon nanofiber composition. In specific embodiments, the weight ratio of the functionalized or non-functionalized carbon allotrope to the polymer present in the nanofiber(s) is greater than 5% (e.g., about 6 wt. % to about 90 wt. %). Further, the weight ratio of the functionalized or non-functionalized carbon allotrope to the polymer may be 1% to 10%. Still further, the weight ratio of the functionalized or non-functionalized carbon allotrope to the polymer may be 2% to 20%. Still further, the weight ratio of the functionalized or non-functionalized carbon allotrope to the polymer may be 6% to 20%. Still further, the weight ratio of the functionalized or non-functionalized carbon allotrope to the polymer may be 6% to 50%. Still further, the weight ratio of the functionalized or non-functionalized carbon allotrope to the polymer may be 20% to 90%.

[45] Various methods for making graphene nanoribbons are known, including, for example, adhesive tape exfoliation of individual graphene layers cut to size from graphite, chemical-based exfoliation of graphene layers cut to size from graphite, and chemical vapor deposition processes. Such methods provide on the order of picogram quantities of graphene nanoribbons. Recently, larger quantities of functionalized and non functionalized graphene nanoribbons and graphene oxide nanoribbons have been obtained by Tour et al, as disclosed in WIPO Patent Application WO/2013/040356, U.S. Patent Application No. 20120197051 and U.S. Patent Application No. 2012/0129736.

[46] Graphene nanoribbons provided herein are prepared according to any suitable method. In specific instances, carbon nanotubes (multiwalled carbon nanotubes) are exposed to metal source, such as an alkali metal source in the absence of a solvent, whereupon the carbon nanotubes are opened longitudinally (e.g., opened or unzipped carbon nanotubes, which are optionally subjected to subsequent or concurrent functionalization). Further reaction with various electrophiles, whether dissolved in solvent or introduced neat, yield functionalized graphene nanoribbons. Alkali metals include lithium, sodium, potassium, rubidium and cesium. Reaction conditions may be such that the alkali metals are in a molten state, in the solid state, or in a vapor state or combinations hereof. Further embodiments include exposing the carbon nanotubes to liquid sodium-potassium alloy or alkali metals dissolved in liquid ammonia before introducing electrophiles. Alkali metals may further be introduced in a vapor state. Further,

combinations of metals may be used, either as eutectics, melts, cooled melts or simple mixtures.

[47] In various embodiments, suitable aprotic solvents include, without limitation, diethyl ether, tetrahydrofuran, 1,4-dioxane, glyme, 1,2-dimethoxyethane, diglyme, tetraglyme, dipropylene glycol dimethylether, dipropylene glycol dialkyl ethers, 1,2-dimethoxypropane, amines, N,N,N',N'-tetramethylethylenediamine, triethylamine, 1,4-diazabicyclo[2.2.2] octane, trialkylamines, dialkylarylamines, alkyl diarylamines, dimethylformamide, combinations including any of the foregoing or combinations thereof.

[48] Quenching any reactive species may be accomplished by exposing the opened carbon nanotubes to various protic solvents. Suitable protic solvents may include, without limitation, formic acid, n-butanol, isopropanol, n-propanol, ethanol, methanol, acetic acid, water, mineral acids in water or other protic or aprotic solvents, including hydrochloric acid, sulfuric acid, or phosphoric acid, sulfonic acids such as toluene sulfonic acid, camphorsulfonic acid, trifluoromethane sulfonic acid, or perfluorobutane sulfonic acid, amines such as ammonia, diethyl amine, dialkylamines, monoalkylamines, diarylamines, monoarylamines, monoalkylmonoarylamines, combinations including any of the foregoing or combinations thereof.

[49] Moreover, various electrophiles may be utilized to form functionalized graphene nanoribbons. In some embodiments, the electrophiles may include at least one of water, alcohols, organic halides, alkenes, alkyl halides, acyl halides, allylic halides, benzyl halides, benzylic halides, alkenyl halides, aryl halides, alkynyl halides, fluoralkyl halides, perfluoroalkyl halides, aldehydes, ketones, methyl vinyl ketones, esters, sulfonate esters, acids, acid chlorides, carboxylic acids, carboxylic esters, carboxylic acid chlorides, carboxylic acid anhydrides, carbonyl bearing compounds, enones, nitriles, carbon dioxide, halogens, monomers, vinyl monomers, ring-opening monomers, isoprenes, butadienes, styrenes, acrylonitriles, methyl vinyl ketones, methacrylates, 1,4-dimethoxy-2-vinylbenzene, methyl methacrylate, alkyl acrylates, alkyl methacrylates, trimethylsilyl chlorides, tert-butyldimethylsilyl chlorides, triphenylsilyl chlorides, epoxides, carbon dioxide, carbon disulfide, tert-butanol, 2-methylpropene, bromine, chlorine, iodine, fluorine, and combinations thereof.

[50] In various embodiments, the electrophiles may be associated with transition metal catalysts, such as palladium-containing systems, nickel-containing systems, or iron-containing systems. In some embodiments, the electrophiles may not be associated with transition metal catalysts.

[51] In some embodiments, the electrophile may include one or more monomers, such as olefins, vinyl monomers, styrenes, isoprenes, butadienes, acrylonitriles, methyl vinyl ketones, alkyl acrylates, alkyl methacrylates, ring opening monomers, epoxides, and combinations thereof. In some embodiments, the monomers may polymerize upon addition to graphene nanoribbons, thereby forming polymer-functionalized graphene nanoribbons.

[52] Suitable electrophiles for treating reductively opened carbon nanotubes may be monomers, such as those capable of anionic polymerization, or molecules having electrophilic functional groups. These include, without limitation, water, alcohols, organic halides, alkenes, alkynes, alkyl halides, acyl halides, allylic halides, benzyl halides, benzylic halide, alkenyl halides, aryl halides, alkynyl halides, fluoralkyl halides, perfluoroalkyl halides, aldehydes, ketones, methyl vinyl ketones, esters, sulfonate esters, phosphonate esters, acids, acid chlorides, carboxylic acids, carboxylic esters, carboxylic acid chlorides, carboxylic acid anhydrides, carbonyl bearing compounds, enones, nitriles, carbon dioxide, halogens, monomers, vinyl monomers, ring-opening monomers, isoprenes, butadienes, styrenes, acrylonitriles, methyl vinyl ketones, (meth)acrylates, 1,4-dimethoxy-2-vinylbenzene, methyl (meth)acrylate, alkyl (meth)acrylates, trialkylsilyl chlorides, tert-butyldimethylsilyl chlorides, triphenylsilyl chlorides, epoxides, carbon dioxide, carbon disulfide, tert-butanol, 2-methylpropene, bromine, chlorine, iodine, fluorine, or combinations thereof.

[53] Accordingly, functionalization of graphene nanoribbons may include polymer chains, bound small molecules or functional groups. Functionalized sites, may include, without limitation, polystyrene, polyisoprene, polybutadiene, poly(meth)acrylonitrile, polymethyl vinyl ketone, poly alkyl acrylate, poly alkyl(meth)acrylate, a polyol, an alkyl group, an acyl group, an allylic group, a benzyl group, a benzylic group, an alkenyl group, an aryl group, an alkynyl group, an aldehyde, a ketone, an ester, a sulfonate, a phosphonate, a halide, a carboxyl group, a carbonyl group, a halogen, or combinations thereof. In some embodiments, such as in certain instances of graphene oxide and reduced graphene oxide, the graphene nanoribbons are functionalized with oxygen (including, e.g., oxygen containing groups), such as oxo (e.g., an =O bond formed with one graphene carbon, or a >O ring forming oxygen formed with two graphene carbons), hydroxyl, carboxylic acid, ester (e.g., -COOR, wherein R is a C1-C6 alkyl), carboxylate (e.g., RCOO-, wherein R is a C1-C6 alkyl), or the like. In some instances, graphene oxide is highly functionalized with oxygen groups, whereas reduced graphene oxide is less functionalized and, in some instances, has defects in the graphene structure (e.g., due to radical formation during the reduction process).

[54] Further in brief, graphene oxide nanoribbons may be produced by exposing carbon nanotubes to an oxidizing agent such as potassium permanganate in sulfuric acid. The oxidizing agent may also include protective agents such as trifluoroacetic acid, ortho phosphoric acid and boric acid or any reagent convertible to these acids under the reaction conditions such as corresponding salts or anhydrides. The reaction mixture is then filtered, centrifuged or a combination thereof to obtain the solid product. In addition, separation by either or both of the foregoing methods may be promoted by flocculation.

[55] Highly oxidized graphene nanoribbons, obtained as described supra, may be reduced using methods similar to those described supra to form graphene nanoribbons having carboxylic acid groups substituted on the edges.

[56] Functionalized graphene nanoribbons may be reduced to form non-functionalized graphene nanoribbons. For example, edge terminating hydroxyl groups may be reacted with toluene sulfonyl chloride to form the ester, followed by reduction with lithium aluminum hydride sodium borohydride or other suitable hydride compound. In certain cases, the functionalized graphene nanoribbons may be hydrogenated using hydrogen and a suitable catalyst such as platinum.

[57] Electrospinning of nanofibers may be accomplished by the method set forth by Joo et al. in U.S. Patent Application No. 20130040140. In brief, the apparatus comprises a first conduit suitable for providing a fluid comprising polymers and other additives such as functionalized or unfunctionalized graphene nanoribbons or graphene oxide nanoribbons, and a second conduit suitable for providing a gas stream. The first and second conduits may be tubes. Further, the first conduit may surround the second conduit or vice versa (e.g., concentric and/or coaxially aligned tubes, such as to provide coaxial gas-assisted electrospinning of the fluid). The gas stream may be a high velocity gas stream and may be heated. Further, the heated gas stream may maintain a high temperature at the end of the first conduit providing a jet of fluid. The fluid may comprise a polymer melt or may comprise a solvent (e.g., organic solvent and/or water). The solvent may have low volatility or high volatility. In certain circumstances, the heated gas stream may enhance solvent evaporation. In other circumstances, the gas stream may be cooled. In some circumstances, the cooled gas stream may suppress solvent evaporation and/or premature solidification using a gas refrigerated to room temperature or below, cooled by Joule-Thompson cooling, or infused with a solvent suitable for inhibiting evaporation or substitution for the existing solvent. Gases may include, without limitation, air, water vapor, nitrogen, oxygen, helium, neon, argon xenon or combinations thereof. In certain circumstances gaseous organic

molecules may be used. These include, without limitation, methane, ethane, propane, methylamine, gaseous halocarbons or combinations thereof. In certain circumstances, the high velocity gas may comprise a vapor of a solvent or reagent such as a crosslinking reagent. Gases may require elevated temperature to remain stable in the gaseous state. In certain embodiments, use of gas-assisted electrospinning improves nanofiber production rates as well as improves nanoinclusion dispersion and non-aggregation in resultant nanofibers. In certain embodiments, such improved dispersion/reduced aggregation provides nanofibers with improved and more uniform performance characteristics, such as mechanical properties, electrical/electronic conductivity, and the like.

[58] Polymers may include any suitable molecular weight or composition capable of producing a liquid state in a melt, in solution or otherwise dispersed in a solvent or a diluent. While the final nanofiber may comprise a heavily crosslinked polymer, selection of a precursor having no or fewer crosslinks may allow a solution or melt to form and electrospinning to proceed. Suitable polymers may include polyesters, polycarbonates, polyolefins, poly(meth)acrylates, polyethers, polyamides, polyimides, acryl polymers, polyurethanes, polymers produced by condensation polymerization such as phenolic novolak polymers, formaldehyde adducts such as urea formaldehyde polymers, butadiene nased polymers, or random or block copolymers of any of the foregoing. In particular, polymers may include, without limitation from poly(vinylidene fluoride), poly(vinylidene fluoride-co-trifluoroethylene), poly(vinylidene fluoride-co-hexafluoropropylene), poly(vinylidene fluoride), poly(vinylidene fluoride-co – vinylidene chloride), poly(vinylidene fluoride), poly(vinylidene fluoride-co-trichloroethylene), poly(meth)acrylonitrile, poly((meth)acrylonitrile-co-methyl methacrylate), poly (meth)acrylic acid, poly methyl (meth)acrylate, polyvinyl chloride, poly(vinylidenechloride- co-methyl (meth)acrylate), polyethylene, polypropylene, nylon 12, nylon-4,6, nylon 5, nylon 7, nylon 9, aramid, polybenzimidazole, polyvinyl alcohol, poly vinyl acetate, poly(vinyl alcohol – co – vinyl acetate), cellulose, cellulose acetate, cellulose acetate butyrate, polyvinyl pyrrolidone, poly(bis-(2-(2-methoxy-ethoxyethoxy)) phosphazene, poly(ethylene imide), poly(ethylene succinate), poly(ethylene sulphide), poly(oxymethyleneoligo-oxyethylene), poly(propylene oxide), poly(vinyl acetate), polyaniline, poly(ethylene terephthalate), poly(hydroxy butyrate), poly(ethylene oxide), SBS copolymer, poly(lactic acid), polypeptide and protein, phenolic resins, epoxy resin, polycarbonate resin, nafion, coal-tar pitch petroleum pitch or combinations thereof. Polymers used in the nanofibers described herein may be in melt state or dispersed in a solution, sol, or suspension.

[59] Suitable for producing dispersions and solutions for the fluids described herein include water, glycol ether acetates, esters, α -hydroxy esters, α -alkoxy esters alcohols, ketones, amids, imines, ethers, ether esters, ether alcohols and the like. Specifically, solvents may include, without limitation, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate (PGMEA), ethyl-3-ethoxypropionate, methyl-3-methoxypropionate, butyl acetate, amyl acetate, cyclohexyl acetate, 3-methoxybutyl acetate, 3-ethoxyethyl propionate, 3-ethoxymethyl propionate, 3-methoxymethyl propionate, methyl acetoacetate, ethyl acetoacetate, methyl pyruvate, ethyl pyruvate, propylene glycol monomethyl ether propionate, propylene glycol monoethyl ether propionate, methyl ethyl ketone, methyl amyl ketone, cyclohexanone, cyclopentanone, diacetone alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, 3-methyl-3-methoxybutanol, N-methylpyrrolidone, dimethylsulfoxide, γ -butyrolactone, propylene glycol methyl ether acetate, propylene glycol ethyl ether acetate, propylene glycol propyl ether acetate, methyl lactate, ethyl lactate, propyl lactate, butanone, 2-pentanone, 2-hexanone, 2-heptanone, and tetramethylene sulfone. The solvents may be used alone or as mixtures.

[60] Suspension of the electropinning precursor components may be promoted by adding one or more anionic, cationic or nonionic or amphoteric surfactants.

[61] Nonionic surfactants include, without limitation, compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Nonlimiting examples include polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 16 carbon atoms, in either a straight chain or branched chain configuration, with from about 4 to 25 moles of ethylene oxide per mole of alkyl phenol. Further non limiting examples include the water-soluble condensation products of aliphatic alcohols containing from 8 to 20 carbon atoms, in either straight chain or branched configuration, with an average of from 1 to 25 moles of ethylene oxide per mole of alcohol. Further non limiting examples include the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms with from about 2 to 10 moles of ethylene oxide per mole of alcohol; and condensation products of propylene glycol with ethylene oxide. Still further non limiting examples include the condensation products of alcohols having an

alkyl group containing from about 12 to 15 carbon atoms with an average of about 3 moles of ethylene oxide per mole of alcohol. Further contemplated are mixtures of any of the foregoing.

[62] Cationic surfactants include alkyl quaternary ammonium salts, benzylalkylammonium salts, pyridinium salts, and imidazolinium salts. Examples include, without limitation, ditallowalkyldimethyl (or diethyl or dihydroxyethyl) ammonium chloride (or other halide), ditallowalkyldimethylammonium methyl sulfate, dihexadecylalkyl (C16) dimethyl (or diethyl, or dihydroxyethyl) ammonium chloride, dioctodecyl- alkyl (C18)dimethylammonium chloride, dieicosylalkyl(C20) dimethylammonium chloride, methyl (I) tallowalkyl amido ethyl (2) tallowalkyl imidazolinium methyl sulfate (commercially available as Varisoft 475 from Ashland Chemical Company), or mixtures of those surfactants. Further non limiting examples of cationic surfactants include ditallowalkyldimethylammonium methyl sulfate, methyl (I) tallowalkyl amido ethyl (2) tallowalkyl imidazolinium methyl sulfate, and mixtures of those surfactants.

[63] Amphoteric surfactants are those which contain both an acidic and a basic hydrophilic group. These ionic functions may be based on the anionic groups such as carboxylates, sulfonates, phosphonates, and the like as well as cationic groups such as those discussed above. In addition, ether or hydroxyl groups may also be present to enhance the hydrophilicity of the surfactant molecule. Exemplary amphoteric surfactants include, without limitation, betaine derivatives, such as, for example, alkylamidopropyl betaine, alkyl dimethyl betaine, bishydroxyethyl betaine, alkylamido propyl betaine, lauryl betaine, and the like, glycine derivatives, such as, for example, cocoamphocarboxy glycinate, lauroamphocarboxy glycinate, caprylamphocarboxy glycinate, oleoamphocarboxy glycinate, oleoamphopolycarboxy glycinate, N-alkyl glycinate, and the like, imino derivatives, such as, for example, cocoiminodipropionate, octyliminodipropionate, and the like, imidazoline derivatives, such as, for example, coconut imidazoline, and the like, lecithin derivatives, and aminocarboxylic acids.

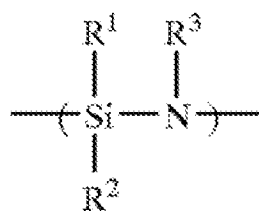
[64] Non limiting exemplary anionic surfactants may be carboxylates, sulfates, sulfonates, phosphates, phosphonates, and the like and may include, without limitation, sodium or ammonium alkylsulfonates such as sodium dodecylsulfonate, sodium or ammonium alkylsulfates such as sodium hexadecyl-1 -sulfate, and sodium alkylbenzenesulfonates such as sodium or ammonium dodecylbenzenesulfonate. Further non limiting examples include, fluorinated surfactants such as perfluorooctan sulfonates (PFOS) or perfluorooctanoic acid salts (PFOA), and the like.

[65] Among the foregoing, certain polymers may provide properties suitable for forming

devices. For example, polymers comprising vinylidene fluoride repeat units and other polymers such as the odd nylons may exhibit ferroelectric, piezoelectric and electrostrictive properties. Such materials may be suitable for use in acoustic sensors, actuators and artificial muscles when used as composites with the functionalized or non-functionalized carbon allotropes described herein. Such composites, when formed as nanofibers, films comprising nanofiber mats, or spun yarns comprising electrospun nanofibers may induce an electric current or charged state when bent or flexed or undergo electrostriction or contraction upon the application of a voltage.

[66] In addition to organic polymers, the polymer matrix may further comprise silicon oxides made with ceramic precursors. Suitable ceramic precursor materials include materials which are capable of reacting with oxygen and/or moisture at low temperature, optionally including in the presence of a catalyst, such as, for example, perhydropolysilazane (PHPS) or organopolysilazanes to provide ceramic materials with reduced temperature curing. The polysilazanes can react with oxygen and moisture from air in the presence of a catalyst, such as an amine or metal catalyst to form dense silicon dioxide films at room temperature. Examples of perhydropolysilazanes useful in the current disclosure are described in US4,397,828, US4,840,778, US4,720,532, US6329487, US4,312,970, US4,395,460, US4,788,309 US No. 8,084,186 included here by reference for the perhydropolysilazanes and organopolysilazanes described therein.

[67] Suitable polysilazanes of the current disclosure may comprise a structure having a structural unit represented by the general formula:



wherein R^1 , R^2 and R^3 are each independently a hydrogen atom, or a substituted or unsubstituted, branched or unbranched hydrocarbon group. In one embodiment of the polysilazane at least one of R^1 and R^2 represents a hydrogen atom. The hydrocarbon group may be substituted with halogens such as chlorine, bromine and fluorine, an alkoxy group, an alkoxycarbonyl group, a silyl group or an amino group. Any of R^1 , R^2 and R^3 may be a silicon containing group such as, for example, a siloxane, an organosiloxane, a silsesquioxane, an organosilsesquioxane, a POSS group (e.g., comprising one or more of the structural units:

RSiO_{1.5}, wherein R is, e.g., a hydrocarbon), a silane, an organosilane, or other silicon containing substituents. The hydrocarbon group includes an aliphatic hydrocarbon group and an aromatic hydrocarbon group, and the aliphatic hydrocarbon group may include a chain hydrocarbon group and a cyclic hydrocarbon group. Examples of the hydrocarbon group include an alkyl group, an alkenyl group, a cycloalkyl group, a cycloalkenyl group, an aryl group, and an arylalkyl group. The number of carbon atoms in these hydrocarbon atoms is not limited, but is usually 20 or less, and preferably 10 or less. In the present invention, preferred is an alkyl group having 1 to 8 carbon atoms, and particularly 1 to 4 carbon atoms. In the hydrocarbon group-containing silyl group, a preferable hydrocarbon group is an alkyl group having 1 to 20 carbon atoms, and particularly 1 to 6 carbon atoms. The number of hydrocarbon atoms to be combined with Si is within a range from 1 to 3. In the hydrocarbon containing amino group and hydrocarbonoxy group, the number of carbon atoms in the hydrocarbon group is within a range from 1 to 3.

[68] The polysilazane having a silazane structure represented by the general formula (1) in a molecular chain may be a polysilazane having a chain, cyclic or crosslinked structure, or a mixture thereof. The number-average molecular weight is within a range from 100 to 100,000, and preferably from 300 to 10,000. Such a polysilazane includes conventional perhydropolysilazane, organopolysilazane, and a modified compound thereof.

[69] The polysilazanes may be produced by any method known in the art. One method, for example, is to react a dihalosilane represented by the general formula SiR¹R²X₂ (X=F, Cl, Br, or I and R¹ and R² are described above) with a base in an inert atmosphere to form a dihalosilane adduct and then reacting the dihalosilane adduct with ammonia or R³-NH₂ (R³ being described above) at approximately 40° C. to 80° C. The reaction time and reaction pressure are not particularly limited.

[70] The polymer materials useful in the current disclosure may be polyamide resins, aramid resins, m-aramid resin, polyalkylene oxides, polyolefins, polyethylenes, polypropylenes, polyethyleneterephthalates, polyurethanes, rosin ester resins, acrylic resins, polyacrylate resins, polyacrylamides, polyvinyl alcohols, polyvinyl acetates, polyvinyl ethers, polyvinylpyrrolidones, polyvinylpyridines, polyisoprenes, polylactic acids, polyvinyl butyral resins, polyesters, phenolic resins, polyimides, vinyl resins, ethylene vinyl acetate resins, polystyrene/acrylates, cellulose ethers, hydroxyethyl cellulose, ethyl cellulose, cellulose nitrate resins, polymaleic anhydrides, acetal polymers, polystyrene/butadienes, polystyrene/methacrylates, aldehyde resins, polyacrylonitriles, cellulosic polymers, polyketone

resins, polyfluorinated resins, polyvinylidene fluoride resins, polyvinyl chlorides, polybenzimidazoles, poly vinyl acetates, polyethylene imides, polyethylene succinates, polyethylene sulphides, polyisocyanates, SBS copolymers, polylactic acid, polyglycolic acid, polypeptides, proteins, epoxy resins, polycarbonate resins, coal-tar pitch petroleum pitch and combinations thereof.

[71] As noted supra, the polymer may be provided in a solution that comprises a (e.g., volatile) solvent. Moreover, the high velocity gas stream may comprise a solvent vapor. The hardened nanofibers may comprise hollow portions along the nanofiber axis, wherein the hardened nanofibers have a diameter in the range of 500 nm to 10 μm . The gas stream velocity may be greater than about 1 m/s, greater than about 10 m/s, or in the range of 1 m/s to 300 m/s. The gas stream temperature may be greater than 313K, or in the range of 313-523 K.

[72] In a reverse configuration where the inner channel is used for a gas stream, the resulting fibers can be made to possess a hollow structure along the fiber axis. The controlled gas runs through the inner channel of a spinneret, while a molten polymer passes through the outer channel. In some instances, the inner gas stream prevents the outer melt jet from collapsing, resulting in fibers that possess a hollow structure along the fiber axis.

[73] Nano-and microfibers produced as described herein may have a diameter of 500 nm to 10 μm . The diameter of the hollow nanofiber may be about 50 nm, about 60 nm, about 70 nm, about 80 nm, about 90 nm, about 100 nm, about 150 nm, about 200 nm, about 250 nm, about 300 nm, about 350 nm, about 400 nm, about 450 nm, about 500 nm, about 550 nm, about 600 nm, about 650 nm, about 700 nm, about 750 nm, about 800 nm, about 850 nm, about 900 nm, about 950 nm, about 1 μm , about 2 μm , about 3 μm , about 4 μm , about 5 μm , about 6 μm , about 7 μm , about 8 μm , about 9 μm , about 10 μm , about 20 μm , or about 30 μm . In certain embodiments, the hollow nano- and microfibers have a diameter of about 1 μm to about 10 μm . In some embodiments, the nano- and microfibers have a diameter of about 2 μm to about 30 μm .

[74] A gas assisted electrospinning apparatus may comprise a spinneret having two or more channels of gas jet devices. One of the advantages of the present invention is that gas assisted electrospinning allows the close packing of spinnerets, thereby enabling nanofibers to be deposited substantially faster and with more control over their orientation and mix. In some embodiments, the gas assisted electrospinning apparatus comprises more liquid polymer channels than gas stream channels. In other embodiments, the gas assisted electrospinning apparatus comprises more gas stream channels than liquid polymer channels.

[75] Within the spinning apparatus, the liquid polymer may surround the high velocity gas. In other embodiments, the high velocity gas may surround or envelope the liquid polymer. Moreover, the high velocity gas may be heated, or, alternatively, cooled, or, alternatively, at room temperature.

[76] In certain circumstances the process for making a nano- or microfiber may comprise injecting a charged liquid polymer into a high velocity gas stream. In some circumstances, the charged liquid polymer forms a jet. In certain circumstances, the liquid polymer is a neat polymer melt or a polymer solution. In some circumstances, the high velocity gas stream surrounds the charged liquid polymer. In some circumstances, the high velocity gas stream is heated. In some circumstances, the high velocity gas stream is confined within a guide channel. In some embodiments, the guide channel guides the nanofiber jet to a desired location on a collector plate.

[77] In any gas-assisted electrospinning apparatus or process described herein, the first nozzle end and the second nozzle end may be located on the same end of the longitudinal axis, in the same axial position along the longitudinal axis, or, offset along the longitudinal axis. The first nozzle end may be closer to the supply end than the second nozzle end or vice versa. Moreover, the first nozzle end and the second nozzle end may be offset from each other by about 0.1 μm , by about 0.2 μm , by about 0.5 μm , by about 0.8 μm , by about 1.0 μm , by about 1.5 μm , by about 2.0 μm , by about 2.5 μm , by about 3.0 μm , by about 3.5 μm , by about 4.0 μm , by about 4.5 μm , by about 5.0 μm , by about 5.5 μm , by about 6 μm , by about 7 μm , by about 8 μm , by about 9 μm , by about 10 μm , by about 15 μm , or by about 20 μm . The first nozzle and the second nozzle may be offset from each other by less than 0.1 μm , by less than 0.2 μm , by less than 0.5 μm , by less than 0.8 μm , by less than 1.0 μm , by less than 1.5 μm , by less than 2.0 μm , by less than 2.5 μm , by less than 3.0 μm , by less than 3.5 μm , by less than 4.0 μm , by less than 4.5 μm , by less than 5.0 μm , by less than 5.5 μm , by less than 6 μm , by less than 7 μm , by less than 8 μm , by less than 9 μm , by less than 10 μm , by less than 15 μm , by less than 20 μm , by 20 μm , or by more than 20 μm .

[78] In any gas-assisted electrospinning apparatus or process described herein, the gas stream may comprise air. The gas stream may consist essentially of air. The gas stream may comprise an inert gas. The gas stream may consist essentially of an inert gas. Inert gasses may include, but are not limited to, nitrogen, helium, argon, neon, other noble gases, or carbon dioxide. The gas stream may comprise the vapor of a solvent. The gas stream may comprise the vapors of a

reagent. The gas stream may comprise a nebulized solvent or reagent. The solvent or reagent may affect the surface characteristics of the product nanofiber. The solvent or reagent may add functionality to the product nanofiber. The solvent or reagent may cause in-situ cross-linking of the liquid polymer jet and/or the hardened nanofiber. The solvent or reagent may change the morphology of the product fiber. The solvent or reagent may change the surface morphology of the product fiber. Solvents or reagents in the gas stream may be used to tune the morphology of the product fiber. The solvent or reagent may coat the liquid polymer jet and/or the hardened nanofiber. The solvent or reagent may provide for doping of the liquid polymer jet and/or the hardened nanofiber. A fiber may be cross-linked by the solvent or reagent in the gas stream.

[79] In any gas-assisted electrospinning apparatus or process described herein, the gas stream velocity may be in the range of 0.01 m/s to 350 m/s. The gas stream velocity may be about 0.01 m/s, about 0.02 m/s, about 0.05 m/s, about 0.1 m/s, about 0.2 m/s, about 0.5 m/s, about 1.0 m/s, about 2.0 m/s, about 5.0 m/s, about 10 m/s, about 15 m/s, about 20 m/s, about 25 m/s, about 30 m/s, about 35 m/s, about 40 m/s, about 45 m/s, about 50 m/s, about 75 m/s, about 100 m/s, about 150 m/s, about 200 m/s, about 250 m/s, about 300 m/s, or about 350 m/s. The gas stream velocity may be between 100 m/s and 350 m/s. The gas stream velocity may be greater than 0.01 m/s, greater than 0.02 m/s, greater than 0.05 m/s, greater than 0.1 m/s, greater than 0.2 m/s, greater than 0.5 m/s, greater than 1.0 m/s, greater than 2.0 m/s, greater than 5.0 m/s, greater than 10 m/s, greater than 15 m/s, greater than 20 m/s, greater than 25 m/s, greater than 30 m/s, greater than 35 m/s, greater than 40 m/s, greater than 45 m/s, greater than 50 m/s, greater than 75 m/s, greater than 100 m/s, greater than 150 m/s, greater than 200 m/s, greater than 250 m/s, greater than 300 m/s, or greater than 350 m/s. The gas stream velocity may be less than 0.01 m/s, less than 0.02 m/s, less than 0.05 m/s, less than 0.1 m/s, less than 0.2 m/s, less than 0.5 m/s, less than 1.0 m/s, less than 2.0 m/s, less than 5.0 m/s, less than 10 m/s, less than 15 m/s, less than 20 m/s, less than 25 m/s, less than 30 m/s, less than 35 m/s, less than 40 m/s, less than 45 m/s, less than 50 m/s, less than 75 m/s, less than 100 m/s, less than 150 m/s, less than 200 m/s, less than 250 m/s, less than 300 m/s, or less than 350 m/s. The gas stream velocity may be between 100 m/s and 350 m/s. The gas stream velocity may be between 200 m/s and 300 m/s. The gas stream velocity May be between 250 m/s and 350 m/s. The gas stream velocity May be between 1 m/s and 100 m/s. The gas stream velocity may be between 5 m/s and 50 m/s.

[80] In any gas-assisted electrospinning apparatus or process described herein, the gas stream temperature may be in the range of 313K to 523K. The gas stream temperature may be above 243K, above 253K, above 263K, above 273K, above 283K, above 293K, above 303K, above

313K, above 323K, above 333K, above 343K, above 353K, above 363K, above 373K, above 383K, above 393K, above 403K, above 413K, above 423K, above 433K, above 443K, above 453K, above 463K, above 473K, above 483K, above 493K, above 503K, above 513K, above 523K, above 533K, above 543K, above 553K, above 563K, above 573K, above 623K, above 673K, above 723K, or above 773K. The gas stream temperature may be below 243K, below 253K, below 263K, below 273K, below 283K, below 293K, below 303K, below 313K, below 323K, below 333K, below 343K, below 353K, below 363K, below 373K, below 383K, below 393K, below 403K, below 413K, below 423K, below 433K, below 443K, below 453K, below 463K, below 473K, below 483K, below 493K, below 503K, below 513K, below 523K, below 533K, below 543K, below 553K, below 563K, below 573K, below 623K, below 673K, below 723K, or below 773K. The gas stream temperature may be between 473 k and 673K. The gas stream temperature may be between 373K and 573K. The gas stream temperature may be between 323K and 473K. The gas stream temperature may be between 243K and 293K. Further, the gas stream temperature may be at room temperature.

[81] Nanofibers, produced as described supra, may be produced by several nozzles at once. The nozzles may be arrayed as shown in **Figure 7**, or in a concentric or random array or an array having any other convenient shape. In one embodiment, individual nozzles, each fitted with a fluid inlet and a gas inlet may be arrayed in the desired pattern. In another embodiment, a filter membrane may be used to extrude the fibers through the pores while an electric field is applied between a conducting face and ground. The conducting face may be on the upstream or downstream side as long as the voltage polarity is adjusted accordingly. Circumferentially symmetrical gas flow may be accomplished within a sleeve on the downstream side of the filter.

[82] Nanofibers from one of the multi-nozzle configurations above may be deposited on a porous or continuous substrate to form a dense or sparse mat or, alternatively, a plurality of nanofibers may be spun to form a yarn. A free standing film, comprising a mat of nanofibers may be made by depositing one or more fibers on a substrate coated with poly tetrafluoroethylene or graphite and then teased from the surface, sometimes under water or other liquid. In another embodiment, a free standing film may be formed on the surface of a fluid such as water or an incompatible organic solvent and then lifted off.

[83] Substrates may comprise polymers such as, without limitation, polyethylene terephthalate, polycarbonates, polyesters, polyimides, polyurethanes, polyamides, poly (meth)acrylates, polyvinyl chloride, polyethylene, polypropylene and combinations thereof. Other substrates include electronic materials and semiconductors such as silicon, silicon dioxide,

silicon nitride, silicon oxynitride, zinc oxide, titanium dioxide, titanium nitride, perovskites such as lead zirconate titanate and the like.

[84] The nanofibers, described herein, may further include nanostructured materials such as metal nanoparticles such as gold, silver or platinum nanoparticles, nanorods such as silver nanorods, or zinc oxide nanorods, or other structured nanomaterials such as silicon, germanium, zinc oxide, zinc sulfide, zinc selenide, zinc telluride, gallium phosphide, gallium arsenide, gallium antimonide, gallium nitride, indium nitride, indium phosphide, indium arsenide, indium antimonide, aluminum nitride, copper(I) oxide copper (II) oxide, iridium oxide, or combinations thereof. Such materials may be selected for their respective band gaps (for a given combination of size and work function) while others may be selected for their exciton binding energies. For example, undoped zinc oxide exhibits an exciton bunding energy of about 59 meV, Cu_2O exhibits an exciton bunding energy of about 97 meV, and hexagonal GaN exhibits an exciton bunding energy of about 23 meV. In this way, in applications where recombination is an issue, the electronic properties of transparent conductive materials and matrix materials in batteries, and solar cells can be adjusted as desired. Nanostructures (e.g., nanoparticles) have any suitable dimensions, such as a length, width, or diameter of about 1 nm to about 1000 nm, such as about 20 nm to about 100 nm.

[85] After they are formed as individual fibers, matts, yarns or other structures or coatings, the nanofibers may be heat treated at temperatures sufficient to decompose or otherwise remove some or all of the the polymer matrix. Without intending to be bound by theory, various polymer degradation mechanisms may be in operation. For example, in one embodiment, the applied temperature may be sufficiently above the ceiling temperature of the polymer so that the rate of depolymerization exceeds the rate of re-polymerization and the monomer repeat units of the matrix polymer are allowed to evaporate; thus resulting in polymer loss. In another embodiment, the matrix polymer may undergo thermal elimination reactions, resulting in the evaporation of some or all of the remaining polymer fragments. In another embodiment, the polymer may be degraded by the addition of addition reactions such as hydrogen addition, In yet another embodiment, the polymer may undergo oxidative degradation, resulting in a loss of some or all of the polymer mass. In yet another embodiment, the polymer may undergo oxidative decomposition resulting in mass loss and in the formation of nonvolatile char. In yet another embodiment, the polymer matrix may be biologically degraded. In another embodiment, the polymer matrix may be photolytically degraded. In another embodiment, the polymer matrix may be degraded by galvanic action. In still another embodiment, the polymer

matrix may be degraded by the action of halogens or pseudo halogen compounds. In still another embodiment, the polymer matrix may be degraded by plasma or reactive ion etch chemistries. Thermal degradation may obtain at temperatures from about 65° C to about 1500° C, from about 300° C to about 1000° C, from 400° C to about 950° C or from about 600° C to about 900° C. Plasma or reactive ion degradation may obtain in plasmas having halogen species such as halogen radicals, positively charged halogen species, or halogen containing molecules. Moreover, the application of bias voltages may accelerate ionic species and introduce a sputtering component to polymer degradation.

[86] The structure of the graphene nanoribbon may be tailored to yield desired electronic properties. First, longitudinally cleaving multi-walled nanotubes will yield carbon nanoribbons with a wider distribution of widths than if single walled nanotubes are cleaved. Further, when a perfect nanoribbon is of the zig-zag type, its band structure is consistent with that of a conducting material, regardless of aspect ratio. When a perfect nanoribbon is of the armchair type, its conductivity varies based on its aspect ratio because of quantum confinement effects. Quantum-confinement effects and inter-edge superexchange interactions may be tuned by varying the ribbon width. The configuration of the nanoribbon depends on the carbon nanotube selected to be opened. For example, if a carbon nanotube is cut straight along the outer atoms of a row of hexagons, one produces a zigzag edge. On the other hand, if a carbon nanotube is cut along a 30° angle through the middle of the hexagons and one obtains scalloped edges, known as "armchair" edges. Between these two extremes are a variety of chiral vectors describing edges stepped on the nanoscale. Accordingly, choosing the proper pitch and diameter or simply the diameter of a conductive nanotube, may be used to adjust the electronic properties of the resulting graphene nanoribbon. Graphene nanoribbons described herein comprise zig-zag type graphene nanoribbons, armchair nanoribbons, or combinations thereof. **Figure 10** illustrates structural representations of the armchair and zigzag configurations.

[87] Graphene nanoribbons are understood to have aspect ratios greater than 10:1, greater than 15:1, greater than 30:1, greater than 40:1, greater than 50:1, greater than 100:1 or greater than 200:1. In another embodiment, graphene nanoribbons are understood to have aspect ratios between 50:1 and 200,000,000:1. In another embodiment, graphene nanoribbons are understood to have aspect ratios between 500:1 and 200,000,000:1. In another embodiment, graphene nanoribbons are understood to have aspect ratios between 5,000:1 and 200,000,000:1. In another embodiment, graphene nanoribbons are understood to have aspect ratios between 50,000:1 and 200,000,000:1. In another embodiment, graphene nanoribbons are understood to

have aspect ratios between 500,000:1 and 200,000,000:1. Any suitable width (or diameter) of a nanoribbon is optionally utilized. In some instances, graphene nanoribbons with larger width GNRs are optionally prepared from larger MWCNTs and smaller width GNRs are prepared from narrower width GNRs. In some instances, GNR widths are optionally about 5 nm to about 500 nm, such as about 10 nm to about 250 nm, e.g., about 20 nm or about 200 nm.

[88] The nanofibers of this invention may be employed in various electromechanical devices. In a hypothetical example, a mat of nanofibers comprising ferroelectric or piezoelectric polymers and graphene nanoribbons is configured to function as an acoustic sensor, in which flexion of the mat by acoustically induced motion produces a voltage between two electrodes on either side of the mat or on interdigitated electrodes impressed on the mat, wherein the alternating digits are connected to a separate electrode for sensing. In a further hypothetical example, the polymer exhibits electrostrictive properties such as with polyvinylidene fluoride-co-trichloroethylene, a nanofiber composite comprising that polymer and graphene nanoribbons is deposited as a mat, as described above, or spun as a yarn. Electrical charges applied to the resulting structure produce contraction; such that an actuator or artificial muscle is formed.

[89] Nanofibers provided herein may be utilized in a number of applications. In some embodiments, such nanofibers are utilized in battery applications, such as lithium battery applications (e.g., lithium ion batteries or lithium air batteries). In some embodiments, the battery is a lithium air battery. In some embodiments, the lithium battery comprises a first electrode, a second electrode, and an electrolyte. In some embodiments, the first electrode comprises a nanofiber or plurality of nanofibers comprising a graphene nanoribbon embedded therein. In specific embodiments, the nanofiber(s) comprise a carbon matrix (e.g., carbonized polymer of a nanofiber described herein) with graphene nanoribbon (e.g., functionalized or nonfunctionalized) embedded therein.

[90] In some embodiments, the lithium battery is a lithium air (oxygen) battery and the first electrode is a cathode and the second electrode is an anode. In specific embodiments, the cathode comprises a nanofiber or plurality of nanofibers comprising graphene nanoribbon embedded therein (i.e., in the nanofiber(s)). In specific embodiments, the nanofibers comprise a carbon matrix, the graphene nanoribbon(s) embedded therein. In some embodiments, the anode comprises lithium metal.

[91] In certain embodiments, the lithium battery is a lithium ion battery and the first electrode

is an anode and the second electrode is a cathode. In specific embodiments, the anode comprises nanofiber(s) comprising a carbon-silicon composite, with graphene nanoribbon(s) (e.g., functionalized or nonfunctionalized) embedded in the nanofiber(s). In certain embodiments, the nanofiber comprises a carbon matrix (e.g., carbonized polymer), silicon nanoparticles and graphene nanoribbons. In specific embodiments, the silicon nanoparticles and graphene nanoribbons are embedded in the carbon matrix (e.g., wherein the silicon nanoparticles and/or graphene nanoribbons are substantially non-aggregated and/or well dispersed in the nanofiber matrix). In some embodiments, less than 70%, less than 50%, less than 30%, less than 25%, less than 20%, less than 10% (e.g., by number or by weight) of the nanoparticles and/or nanoribbons are aggregated in the carbon matrix. Illustrations of aggregated and non-aggregated nano-inclusions are illustrated, for example, in PCT/US2013/028165, published as WO 2013/130712, entitled Silicon Nanocomposite Nanofibers, which is incorporated herein for such disclosure.

[92] In some embodiments, nanofibers comprising carbon (i.e., non-GNR carbon, e.g., amorphous carbon or carbonized polymer), silicon (e.g., silicon nanoparticles), and GNR (e.g., functionalized or nonfunctionalized graphene nanoribbon or graphene oxide nanoribbons) comprise about 0.5 wt % to about 20 wt % GNR, about 30 wt % to about 90 wt % silicon (e.g., silicon nanoparticles), and about 5 wt % to about 70 wt % carbon (i.e., non-GNR carbon). In specific embodiments, such nanofibers comprise about 1 wt % to about 10 wt % GNR, about 50 wt % to about 80 wt % silicon (e.g., silicon nanoparticles), and about 10 wt % to about 50 wt % carbon (i.e., non-GNR carbon).

[93] For lithium ion battery applications, the cathode may comprise any suitable cathode material including, by way of non-limiting example, LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (wherein x , y and z are 0-1 and the sum of x , y , and z is 0.8-1.2, 1, or about 1), or the like.

[94] For lithium (e.g., ion or air (oxygen)) battery applications, the electrolyte may be chosen from a range of lithium salts in protic nonprotic electrolytes. For example, non-aqueous organic solvents, such as N-methyl acetamide, acetonitrile, acetals, ketals, esters, carbonates, sulfones, sulfites, sulfolanes, aliphatic ethers, cyclic ethers, glymes, polyethers, phosphate esters, siloxanes, dioxolanes, N-alkylpyrrolidones, substituted forms of the foregoing, and blends thereof may be used. Fluorinated derivatives of the foregoing are also useful as liquid electrolyte solvents. Protic solvents include water and various alcohols.

[95] Examples of useful solid polymer electrolytes include, but are not limited to, those

comprising one or more polymers selected from the group consisting of polyethers, polyethylene oxides, polypropylene oxides, polyimides, polyphosphazenes, polyacrylonitriles, polysiloxanes, derivatives of the foregoing, copolymers of the foregoing, crosslinked and network structures of the foregoing, and blends of the foregoing.

[96] In addition to electrolyte solvents, gelling agents, and polymers as known in the art for forming non-aqueous electrolytes, the non-aqueous electrolyte may further comprise one or more ionic electrolyte salts, also as known in the art, to increase the ionic conductivity.

[97] Examples of ionic electrolyte salts for use in the electrolytes of the present invention include, without limitation, LiSCN, LiBr, LiI, LiClO₄, LiAsF₆, lithium trifluoromethane sulfonate, lithium methane sulfonate, LiBF₄, LiB(Ph)₄, LiPF₆, LiC(SO₂CF₃)₃, and LiN(SO₂CF₃)₂, LiMoO₄, and the like. Other electrolyte salts include lithium polysulfides (Li₂S_x), and lithium salts of organic ionic polysulfides (LiS_xR)_n, where x is an integer from 1 to 20, n is an integer from 1 to 3, and R is an organic group, and those disclosed in U.S. Pat. No. 5,538,812 to Lee et al.

[98] The electrochemical cells, disclosed herein, may further comprise a separator interposed between the cathode and anode. The separator may be a solid non-conductive or insulative material which separates or insulates the anode and the cathode from each other preventing short circuiting, and which permits the transport of ions between the anode and the cathode. Such materials include, without limitation, polyethylene, ultra high molecular weight polyethylene, polytetrafluoroethylene, polypropylene, polyvinyl chloride, polyvinylidene fluoride and copolymers thereof, other fluoropolymers, polyamides such as Nylon-66, polyurethanes, polyacrylonitrile, aramid, polyethylene terephthalate, polyimide, poly(methyl(meth)acrylate, copolymers having the monomer repeat units of the foregoing or combinations of the foregoing. Separators may be made of polymer materials having thicknesses from 10 nm to 200 μm. Separators may comprise filter membranes made from the foregoing polymers or any other suitable material, having filter pore sizes of from 10 nm to 200 μm. Separators may also comprise ceramic materials and clays, especially nanoclays and nanoceramics. In addition, separators may comprise polyacrylonitrile / nanoclay (PAN/NC) separators.

[99] A further variety of separator materials are known. Examples of suitable solid porous separator materials include, but are not limited to, polyolefins, such as, for example, polyethylenes and polypropylenes, glass fiber filter papers, and ceramic materials. Further examples of separators and separator materials suitable for use in this invention are those

comprising a microporous xerogel layer, for example, a microporous pseudo-boehmite layer, which may be provided either as a free standing film or by a direct coating application on one of the electrodes, as described in U.S. patent application Ser. No. 08/995,089, now U.S. Pat. No. 6,153,337, and U.S. patent application Ser. No. 09/215,112 by Carlson et al. Solid electrolytes and gel electrolytes may also function as a separator in addition to their electrolyte.

[100] The pores of the separator may be partially or substantially filled with electrolyte solution. Separators may be supplied as porous free standing films which are interleaved with the anodes and the cathodes during the fabrication of cells. Alternatively, the porous separator layer may be applied directly to the surface of one of the electrodes, for example, as described in PCT Publication No. WO 99/33125 to Carlson et al. and in U.S. Pat. No. 5,194,341 to Bagley et al.

[101] Further, a variety of catalysts may be used to facilitate breakage of the O-O and Li-O bonds. Such catalysts may include, without limitation gold, silver, platinum, palladium, manganese, cobalt, rubidium, oxides thereof and combinations thereof.

[102] For applications involving electrical double layer (supercapacitor) devices, electrolytes include, without limitation, the electrolytes listed above for the lithium (e.g., ion or air (oxygen)) battery application and further include mineral acids such as sulfuric acid, hydrochloric acid, phosphoric acid and the like and further include lithium perchlorate, KOH. Matrix materials for gel-type electrolytes include, without limitation, polyurethane, polyvinylalcohol, poly(acrylonitrile), and poly(acrylonitrile), polyethylene oxide – co – propylene oxide.

[103] Further, the nanofibers disclosed herein may be used as separation materials for removing impurities from waste streams, chemical reaction vessels and for removing volatile organic compounds from airborne exhaust. In this application, a nanofiber may be electrospun as described above but with an increased loading of graphene nanoribbons in the polymer matrix. Exemplary graphene nanoribbon loadings (weight ratio) are from 10% - 90%. Further exemplary graphene nanoribbon loadings are from 20% - 60%. Further exemplary graphene nanoribbon loadings are from 30% - 50%. Suitable polymers include, without limitation, curable materials and resins having epoxy, melamine, methylol urethane and acryl. Crosslink density may be adjusted to control diffusion into the nanofiber. In one embodiment, the nanofibers are collected on a porous substrate and cured, to produce an insoluble material with controllable permeability.

EXAMPLES

Example 1. In this example, the synthesis of non-functionalized graphene nanoribbons (GNRs) is described. 0.5 g of multi-walled carbon nanotubes (MWCNTs) were dispersed in 175 mL of anhydrous and degassed 1,2-dimethoxyethane. Thereafter, 0.3 g of sodium/potassium alloy was added to the mixture under a dry nitrogen atmosphere. The reaction mixture was sonicated using probe sonication (QSonica) for 2 minutes. This was followed by stirring under nitrogen at room temperature for a day. After 24 hours, an excess molar amount of methanol was added. The formed graphene nanoribbons were then washed and isolated by filtration and the product was then dried *in vacuo* for 24 hours at 100° C.

[104] **Example 2.** In this example, a method is provided for exfoliating and improving the electrical conductivity of the graphene nanoribbons from **Example 1**. The non-functionalized graphene nanoribbons obtained from **Example 1** were dispersed in chlorosulfonic acid and sonicated for 24 hours at room temperature. The product was then recovered by filtration, washed repeatedly with deionized water to neutral pH and then dried.

[105] **Example 3.** In this example, a protocol is provided for preparing functionalized graphene nanoribbons. Unzipping of MWCNTs was done as in **Example 1**, except that before the addition of alcohol to quench the unzipping process, 3.1 g of 1-iodohexadecane was added to the flask under a blanket of argon or nitrogen. The reaction was allowed to proceed for 24 hours. Then the same work up & recovery procedure as in **Example 1** was done to obtain the product except that the product was dried at 50° C *in vacuo*. Optionally, the functionalized sample can be subjected to Soxhlet extraction using any cyclic aliphatic hydrocarbon solvent for 24 hours. The product was ready for use after 24 hours of drying in a vacuum oven at 50° C.

[106] **Example 4.** In this example, a method is provided for exfoliating the functionalized graphene nanoribbons from **Example 3**. The functionalized graphene nanoribbons obtained from **Example 3** were dispersed in chlorosulfonic acid and sonicated for 24 hours at room temperature. The product was then recovered by filtration and washed repeatedly with deionized water to neutral pH and then dried.

[107] **Example 5.** In this example, a method is provided for preparing Graphene oxide nanoribbons (GONRs). **(a)** To a 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (360:40 mL) in a reaction flask were added 3.0 g of MWCNTs and KMnO₄, 15.0 g, 5 wt equiv. The reaction was then stirred at room temperature for 2 h. At the end of this period, the reaction mixture was poured onto ice (~400 mL) with 30% H₂O₂, 3 mL for 5 wt. equiv. The resulting mixture was then filtered suspended in dionized water and centrifuged at 4000 rpm for 1 h. The supernatant

was decanted and the remaining solid dried *in vacuo* overnight at room temperature. **(b)** Same as **Example 5 (a)** except that 6 g, 2 wt. equiv. of KMnO_4 were used.

Example 6. In this example, a protocol is provided for making reduced graphene oxide nanoribbons (r-GONRs). (a) GONRs from **Examples 5 (a)** and **(b)** were placed in a small glass container, preheated to 190° C under a blanket of nitrogen. The sample was held at that temperature for 30 min and then removed. (b) Alternatively, a sample from **Examples 5 (a)** or, alternatively, **(b)** was placed in a glass container preheated to 480° C and held at that temperature for 30 min. The products appeared highly expanded in volume (>2times).

[108] **Example 7.** In this example, a protocol is provided for making nanostructured carbon fibers using graphene nanoribbons. Polylactic acid chips, 5 g, (PLA, MW 186 kDa) (Cargill Dow) were charged into a vial along with the graphene nanoribbons of **Example 1**, 0.1 g, heated to 240° C under nitrogen and agitated to disperse the GNRs in the polymer melt. The resulting melt was loaded into a glass syringe and heated up to 220-240° C. The molten mixture was then pumped into the inner channel of the spinneret, while hot air gas was passed through the outer channel. The gas was heated to 210° C, and its velocity at the nozzle was 300 m/s. The distance between the nozzle and collection plate was kept at about 9 cm and a melt flow rate of about 10 $\mu\text{l}/\text{min}$ was maintained. A charge of +20 kV was maintained at the collector. The process settings are summarized in Table 1.

Table 1	
PLA / GNR Melt Electrospinning Process Settings	
Inner (melt) nozzle	4.13×10^{-4} m ID, 7.18×10^{-4} m OD
Outer (air) nozzle	1.194×10^{-3} m ID
Melt flow rate	0.01 ml/min
Air velocity at nozzle	300 m/s
Melt temperature at nozzle	483 K
Air temperature at nozzle	483 K
Applied potential	0 V (nozzle), 20 kV (collector)
Nozzle to collector distance	9 cm

[109] **Example 8.** In this example, a protocol is provided for making nanostructured carbon fibers using functionalized graphene nanoribbons. The same protocol as **Example 6** is used except that the functionalized graphene nanoribbons of **Example 2** were mixed with the polymer.

[110] **Example 9.** In this example, a protocol is provided for making nanostructured carbon fibers using graphene oxide nanoribbons. The same protocol as **Example 6** was used except that the graphene oxide nanoribbons of **Example 4** were mixed with the polymer.

[111] **Example 10.** In this example, a protocol is provided for making nanostructured carbon fibers using reduced graphene oxide nanoribbons. The same protocol as **Example 6** was used except that the graphene oxide nanoribbons of **Example 5** were mixed with the polymer.

[112] **Example 11.** In this hypothetical example, a protocol is provided for making nanostructured carbon fibers using graphene nanoribbons and polyvinyl alcohol. The same protocol as **Example 6** is used except that the polymer is polyvinyl alcohol (130 kDa).

[113] **Example 12.** In this example, a protocol is provided for making nanostructured carbon fibers using graphene nanoribbons. A precursor is prepared by combining 1.0 g polyvinyl alcohol (PVA, 79 kDa, 88% hydrolyzed), with 9.0 g water. The first composition was heated to 95° C for at least 8 hours. A second composition was prepared by combining 1 g water, 0.5 g acetic acid, 3 drops Triton X-100 surfactant (Sigma Aldrich Chemical Company), and tin acetate. The second composition was mixed for at least 4 hours. The first and second compositions were combined and mixed for at least 2 hours to form a fluid stock. The fluid stock was electrospun in a coaxial gas assisted manner, using a flow rate of 0.005 to 0.02 mL/min, a voltage of 10-20 kV and a tip to collector distance of 10-20 cm. Electrospinning of the fluid stock prepares an as-spun precursor nanofiber, which was subsequently thermally treated at a temperature of 500° C - 1000° C in air.

[114] **Example 13.** In this example, a protocol was provided for making a nanostructured nanofiber composite from a precursor. 1.0 g PVA (88% hydrolyzed, 78 kDa) was combined with 9.0 g water and, 0.02 g of the GNRs from **Example 1**, and heated at 95° C for 8 hours. Silicon nanoparticles, 1.0 g, (SiNPs, purchased from Silicon and Amorphous Materials, Inc., 20-30 nm (actual average size about 50 nm)) were added to the polymer solution and sonicated at room temperature for 4 hours, and then heated and mixed at 50° C for an additional 4 hours. The fluid stock was gas-assisted electrospun from a needle apparatus having an inner nozzle and an outer nozzle coaxially aligned, the inner nozzle providing the precursor, the outer nozzle providing dry air. The fluid stock was provided at a flow rate of 0.01 ml/min, the voltage used was 20 kV, the needle apparatus tip to collector distance was 15 cm. Additional details may be found in Table 2. The nanofibers were then treated with heat under Argon: at 900° C (using a heat and cool rate of 2° C/minute).

Table 2

PVA / SiNPs / (optional) GNRs Electrospinning Process Settings	
Inner (precursor) nozzle	4.13×10^{-4} m ID, 7.18×10^{-4} m OD
Outer (air) nozzle	1.194×10^{-3} m ID
Flow rate	0.01 ml/min
Air velocity at nozzle	300 m/s
Nozzle to collector distance	15 cm
Temperature (nominal)	300 K
Applied potential	0 V (nozzle), 20 kV (collector)

[115] **Example 14.** Similar to **Example 12**, except that no GNRs are added to the precursor before electrospinning.

[116] **Example 15.** Similar to **Example 12**, except that GNRs from **Example 2**, 0.015 g, was added to the precursor before electrospinning.

[117] **Example 16.** Similar to **Example 12**, except that GNRs from **Example 3**, 0.015 g, was added to the precursor before electrospinning.

[118] **Example 17.** Similar to **Example 12**, except that GNRs from **Example 4**, 0.015 g, was added to the precursor before electrospinning.

[119] **Example 18.** Similar to **Example 12**, except that GNRs from **Example 5**, 0.015 g, was added to the precursor before electrospinning.

[120] **Example 19.** Similar to **Example 12**, except that GNRs from **Example 6**, 0.015 g, was added to the precursor before electrospinning.

[121] **Example 20.** Similar to **Example 12**, except that GNRs from **Example 1**, 0.012 g, and mesoporous zinc oxide, 0.003g were added to the precursor before electrospinning.

[122] **Example 21.** Similar to **Example 12**, except that GNRs from **Example 1**, 0.003g, and carbon granules (Super C 65) 0.012g were added to the precursor before electrospinning.

[123] **Example 22.** In this example, a protocol is provided for making a lithium ion battery using a nanostructured nanofiber composite from as a negative electrode. Coin cell-typed Li-ion batteries were fabricated by using various nanofibers. The present example uses the nanofibers from **Example 14**. The nanofibers were combined with poly(acrylic acid) (PAA, Mw=3,000,000) in a weight ratio of 85:15 in 1-Methyl-2-pyrrolidinone (NMP, Aldrich). The slurry was deposited on a current collector, having approximately 9 μm of thickness (Cu foil,

MTI). The coated substrate was dried in the vacuum oven at 80° C to remove the NMP solvent; thus forming the working electrode.

[124] For fabricating the half cells, Li metal was used as a counter electrode and polyethylene, having approximately 25 μm of thickness was utilized as a separator between working electrode and counter electrode. The mass of working electrode was 3-4 mg/cm^2 . The coin cell-typed Li-ion batteries were assembled in Ar-filled glove box with 1 mole of LiPF_6 dissolved in ethylene carbonate and fluoroethylene carbonate (50:50 w/w) as the electrolyte. Reference is made to **Figure 4(a)**, showing charging, **402**, and discharging, **401**, curves for the battery of this example.

[125] The cut off voltage during the galvanostatic tests was 0.01 - 2.0 V for anode and 2.5 - 4.2 V by using battery charge/discharge cyclers (available from MTI). The cyclic performance of half-cells was carried out. Reference is made to **Figure 5**, curve **501**, showing battery capacity over many cycles. Full cells are prepared in a similar manner, and comprise nanofibers as anode and stock LiCoO_2 as cathode. The cut off voltage during the galvanostatic tests was 2.5 - 4.5 V. The impedance measurements for all battery cells were performed from 1 Hz to 10 kHz frequency under potentiostatic mode at open circuit voltages of the cells.

[126] **Example 23.** Similar to **Example 22** except that the nanofibers from **Example 16** are used. Reference is made to **Figure 4(b)**, showing charging, **404**, and discharging, **403**, curves for the battery of this example. Further reference is made to **Figure 5**, curve 502, showing battery capacity over many cycles.

[127] **Example 24.** Similar to **Example 22** except that the nanofibers from **Example 15** are used. Reference is made to **Figure 5**, curve 504, showing battery capacity over many cycles.

[128] **Example 25.** Similar to **Example 22** except that the nanofibers from **Example 13** are used. Reference is made to **Figure 5**, curve 504, showing battery capacity over many cycles.

[129] **Example 26.** Similar to **Example 22** except that the nanofibers from **Example 20** are used.

[130] **Example 27.** Similar to **Example 22** except that the nanofibers from **Example 21** are used.

[131] **Example 28.** GNRs (e.g., having an average observed width of about 200 nm) of 12 mg/mL concentration were dispersed into aqueous 10 wt% PVA solution for 12 hours and Pro-sonicator (from Qsonicator) was used to disperse GNRs into the solution. 10 wt % Si NPs

purchased from MTI were blended into the PVA/GNR mixture with probe-sonication for 6 hours. The prepared fluid stock was electrospun with a voltage of 10 kV at a rate of 5 mL/min toward a copper foil collector that was 12 cm from the electrospinning nozzle. The PVA/GNR/Si NP composite nanofibers were collected and thermally treated at 200 C under air, followed by thermal treatment at 900 C under argon for 5 hours to produce GNR/Si-C nanofibers (GNR and Si NP embedded in a carbon matrix). **Figure 11** illustrates a low and a high magnification SEM image (panels C and D, respectively) and TEM image (panel E) of the GNR/Si-C fibers, which present a one-dimensional structure. The high magnification SEM and the TEM images illustrate well-distributed Si NP and GNR in a carbon matrix (carbonized PVA). Based on thermal gravimetric analysis (TGA), it is estimated that the fibers comprise about 5 wt % GNR, about 72 wt % Si NP, and about 23 wt % non-GNR carbon (carbonized PVA).

[132] The GNR/Si-C nanofibers were blended with Super C (Timcal) and poly(acrylic acid) (MW=3,000,000, Aldrich) in a weight ratio of 60:20:20 to manufacture lithium ion battery anodes. Half-cells were prepared using a lithium metal counter electrode and a polyethylene separator (in a 2032 coin cell). Full cells were prepared using lithium metal oxide materials (e.g., $\text{LiMn}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{O}_2$). 1M lithium hexafluorophosphate and dimethylene carbonate and fluoroethylene carbonate were combined to form the electrolyte. Cells were tested under galvanostatic charge/discharge process under a cut off voltage window from 0.01 to 1.5 V vs. Li/Li⁺. Full cells were cut off by a specific capacity of 1 mAh in charge process and cut off by a voltage of 2.5 V.

[133] For comparison purposes, similar nanofibers and cells were prepared lacking GNRs. In addition, similar cells were prepared using GNRs alone or MWCNTs alone. For illustrative purposes, **Figure 11** (panel B) shows a TEM image of exemplary graphene nanoribbons (unzipped CNT) having a width of about 200 nm, compared to a TEM image of MWCNT having a diameter of about 100 nm (panel A).

[134] **Figure 12** (panel A) illustrates cyclic voltammogram (CV) of a half cell comprising GNR anode from 0 to 1.5 V versus Li/Li⁺. The GNR cell exhibited typical carbon behavior, reacting with lithium ions by being lithiated at about 0.01 V vs. Li/Li⁺ and delithiated at around 0.2 V vs Li/Li⁺. While the current density of the GNR anode is decreased compared to MWCNT anodes, the current density of GNR/Si-C nanofibers is increased by about 20% when compared to Si-C nanofibers (i.e., nanofibers lacking GNR inclusions), as illustrated in **Figure 12** (panel B). **Figure 12** (panel C) illustrate long term cyclic voltammograms (CVs) of half cells

comprising the GNR/Si-C containing anode. The CVs, run at a scan rate of 10 mV/s, the cells show stability to 350 cycles. In addition, as illustrated by the Nyquist plots of **Figure 12** (panel D), nanofibers comprising GNR inclusion have improved charge transport compared to those nanofibers lacking GNR inclusions.

[135] **Figure 13** (panel A) illustrates initial charge/discharge curves of Si-C fiber anodes **1301** and GNR/Si-C fiber anodes **1302** in half cells. As can be seen, GNR-Si/C fibers exhibit higher capacities than Si-C fibers when silicon content is held constant. **Figure 13** (panel B) illustrates initial charge/discharge curves for GNR/Si-C fiber anodes in half cells at variable current rates. **Figure 13** (panel C) illustrates the rate capability of a half cell having a GNR/Si-C fiber anode. The fibers demonstrated outstanding initial charge/discharge capacities from slow to fast current rates, without dramatic capacity losses with increasing C rates, with initial charge/discharge capacities of about 2,300 mAh/g at 0.1 C, about 1,500 mAh/g at C, and about 860 mAh/g at 2C and the stability demonstrated. Indeed, the capacity at 1C was observed to be about three times greater than the capacity previously reported by Kim et al, *ChemElectroChem* 1:220-226 (2014) for Si-C fibers lacking GNR inclusions.

[136] Inclusion of GNR structures in the anode fibers were also observed to improve battery cycle life performance. **Figure 14** illustrates the capacity over 100 cycles. The (charge and discharge) capacity retention of cells having anodes with GNR/Si-C fibers **1402** was about 93.7% after 100 cycles (calculated from a 100th discharge capacity of 1,464 mAh/g versus a 1st discharge capacity of 1,563 mAh/g) whereas cells having anodes with Si-C fibers **1401** were observed to have about 60% retention after 100 cycles.

[137] Similar processes were utilized to produce MWCNT/Si-C fibers according to the processes described above, with MWCNT having diameters of about 100 nm (e.g., as illustrated in **Figure 11**). However, such composites resulted in poor quality fibers, with MWCNTs that were not incorporated into the Si-C fibers and high concentrations of aggregated carbon nanotubes observed. Such MWCNT composites provided much lower reversible capacities than of GNR/Si-C fibers.

[138] Similar processes were utilized to produce GNR/Si-C fibers where the GNR had a much smaller average width (e.g., prepared by unzipping MWCNT with a diameter of about 10 nm). Additionally, similar processes were utilized to produce MWCNT/Si-C fibers with the MWCNT having an average diameter of about 10 nm. Resultant MWCNT/Si-C fibers had a poor capacity retention of about 75% whereas the smaller sized GNR composite fibers had good cycle

retention of about 90% during half-cell cycling.

[139] Full cell performance was also measured using GNR/Si-C fiber anodes and Li-NMC. The full cell was tested at about 0.3C through cut-off capacity by 1 mAh in charge process and cut-off voltage by 2.5 V in discharge process. Cycling was performed for 25 cycles without fading. The gravimetric capacity normalized by active mass of anode was about 1,440 mAh/g.anode. The energy density of the full cell was about 475 Wh/kg, calculated from the absolute capacity of 1 mAh multiplying 3.8 V, followed by dividing total electrode mass of both anode and cathode. The energy density was at least about three times greater than other full cell batteries using CNT-Si fibers in the anode or reported graphite anode cells.

[140] **Example 29.** The following provides a protocol for constructing a Li-air battery. Cathodes were prepared by mixing a catalyst ink from Nafion (DE2020, ion-power) and the graphene nanoribbons from **Example 3** in a weight ratio of 0.5/1 in isopropanol. The ink was coated on a Celgard (2500) separator via casting. The lithium-air battery assembly was carried out in an argon-filled glovebox. Lithium foil was first put at a bottom current collector made of stainless steel and covered by two layers of the above described separators, followed by the cathode and current collector mesh. On top of each layer was added 15 μ L of a 1M solution of LiCF_3SO_3 in tetraethylene glycol dimethyl ether (tetraglyme). After being sealed in the glove box, the cell was purged with oxygen saturated with tetraglyme vapor for 10 min. Reference is made to **Figure 6(a)**, curves **601** and **605**, which shows charge and discharge curves for a lithium ion battery using the above graphene nanoribbons.

[141] A similar cell was constructed as above, except that the cathode was formed by producing a mat of nanofibers on the Celgard (2500) separator substrate as described in **Example 16**. The fibers incorporated the GNRs from **Example 3**. Reference is made to **Figure 6(b)**, curves **609** and **613**, which shows charge and discharge curves for a lithium ion battery using the above nanofibers.

[142] **Example 30.** As in **Example 29** but with graphene nanoribbons from **Example 1** for the first battery and with the cathode formed from a mat of nanofibers from **Example 13** for the second battery. For the first battery, reference is made to curves **602** and **606** of **Figure 6(a)**. For the second battery, reference is made to curves **610** and **614** of **Figure 6(b)**.

[143] **Example 31.** As in **Example 29** but with graphene nanoribbons from **Example 4** for the first battery and with the cathode formed from a mat of nanofibers from **Example 17** for the second battery. For the first battery, reference is made to curves **603** and **607** of **Figure 6(a)**.

For the second battery, reference is made to curves **611** and **615** of **Figure 6(b)**.

[144] **Example 32.** As in **Example 29** but with graphene nanoribbons from **Example 2** for the first battery and with the cathode formed from a mat of nanofibers from **Example 15** for the second battery. For the first battery, reference is made to curves **604** and **608** of **Figure 6(a)**. For the second battery, reference is made to curves **612** and **616** of **Figure 6(b)**.

[145] **Example 33.** The following provides a protocol for constructing an electric double layer supercapacitor. Working electrodes were prepared by mixing an ink from Nafion (DE2020, ion-power) and VULCAN[®] XC-72 (surface area: 218 m²/g, mesopore: 60%), available from Cabot Corporation in a weight ratio of 1/3 in isopropanol and sonicated until dispersed. The ink was coated on stainless steel electrodes via electrospinning and allowed to dry. Electrochemical measurements were done in a three-electrode MTI-BST8 electrochemical workstation in which a platinum wire was used as the counter electrode and Ag/AgCl was used as the reference electrode in 3 mol/L H₂SO₄. A plot of specific capacitance (F/g_{carbon}) vs. Scan Rate (mV/sec) may be seen in **Figure 8**, curve **805**.

[146] **Example 34.** Similar to **Example 33** except that Super P (surface area: 60 m²/g, no mesopores) available from TimCal Ltd. Was used as the carbon source. A plot of specific capacitance (F/g_{carbon}) vs. Scan Rate (mV/sec) may be seen in **Figure 8**, curve **806**.

[147] **Example 35.** Similar to **Example 33** except that the electrodes were prepared by forming a mat of nanofibers as described in **Example 16**, using graphene nanoribbons prepared as in **Example 3**. A plot of specific capacitance (F/g_{carbon}) vs. Scan Rate (mV/sec) may be seen in **Figure 8**, curve **801**.

[148] **Example 36.** Similar to **Example 33** except that the electrodes were prepared by forming a mat of nanofibers as described in **Example 13**, using graphene nanoribbons prepared as in **Example 1**. A plot of specific capacitance (F/g_{carbon}) vs. Scan Rate (mV/sec) may be seen in **Figure 8**, curve **801**.

[149] **Example 37.** Similar to **Example 33** except that the electrodes were prepared by forming a mat of nanofibers as described in **Example 17**, using graphene nanoribbons prepared as in **Example 4**. A plot of specific capacitance (F/g_{carbon}) vs. Scan Rate (mV/sec) may be seen in **Figure 8**, curve **803**.

[150] **Example 38.** Similar to **Example 33** except that the electrodes were prepared by forming a mat of nanofibers as described in **Example 15**, using graphene nanoribbons prepared as in **Example 2**. A plot of specific capacitance (F/g_{carbon}) vs. Scan Rate (mV/sec) may be seen

in **Figure 8**, curve **804**.

[151] Although the present invention has been shown and described with reference to particular examples, various changes and modifications which are obvious to persons skilled in the art to which the invention pertains are deemed to lie within the spirit, scope and contemplation of the subject matter set forth in the appended claims.

What is claimed is:

1. A method, of forming a composite nanofiber comprising:
 - a. providing a fluid comprising a polymer or ceramic precursor;
 - b. providing a fluid comprising at least one carbon allotrope, chosen from a graphene nanoribbon or a graphene oxide nanoribbon, dispersed therein;
 - c. electrospinning the fluid(s) to form the composite nanofiber;
 wherein the fluid comprising a polymer or ceramic precursor and the fluid comprising at least carbon allotrope are the same or different;
 wherein the at least one carbon allotrope is a graphene nanoribbon or a reduced or unreduced graphene oxide nanoribbon.
2. The method of Claim 1, wherein the electrospinning is gas assisted.
3. The method of Claim 1, wherein the fluid comprising a polymer and the fluid comprising at least carbon allotrope are the same and wherein the weight ratio of the functionalized or non-functionalized carbon allotrope to polymer is greater than a lower limit chosen from 1%, 2%, 6%, 10% or 20% and wherein the weight ratio is less than 90%.
4. The method of Claim 1, wherein the at least carbon allotrope is derived from at least one multi-walled carbon nanotube.
5. The method of Claim 4, wherein the carbon allotrope is produced by exposing the at least one multi-walled carbon nanotube to at least one alkali metal and then exposed to an electrophile chosen from water, alcohols, organic halides, alkenes, alkynes, alkyl halides, acyl halides, allylic halides, benzyl halides, benzylic halide, alkenyl halides, aryl halides, alkynyl halides, fluoralkyl halides, perfluoroalkyl halides, aldehydes, ketones, methyl vinyl ketones, esters, sulfonate esters, phosphonate esters, acids, acid chlorides, carboxylic acids, carboxylic esters, carboxylic acid chlorides, carboxylic acid anhydrides, carbonyl bearing compounds, enones, nitriles, carbon dioxide, halogens, monomers, vinyl monomers, ring-opening monomers, isoprenes, butadienes, styrenes, acrylonitriles, methyl vinyl ketones, (meth)acrylates, 1,4-dimethoxy-2-vinylbenzene, methyl (meth)acrylate, alkyl (meth)acrylates, trialkylsilyl chlorides, tert-butyl dimethylsilyl chlorides, triphenylsilyl chlorides, epoxides, carbon dioxide, carbon disulfide, tert-butanol, 2-methylpropene, bromine, chlorine, iodine, fluorine, or combinations thereof; or wherein the carbon allotrope is substituted by at least one substituent chosen from polystyrene, polyisoprene, polybutadiene, poly(meth)acrylonitrile, polymethyl vinyl ketone, poly alkyl acrylate, poly

alkyl(meth)acrylate, a polyol, an alkyl group, an acyl group, an allylic group, a benzyl group, a benzylic group, an alkenyl group, an aryl group, an alkynyl group, an aldehyde, a ketone, an ester, a sulfonate, a phosphonate, a halide, a carboxyl group, a carbonyl group, a halogen, or a combination thereof.

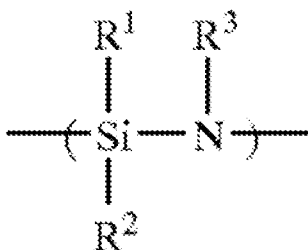
6. The method of Claim 1, further comprising:

- d. heating the composite nanofiber at a temperature sufficient to decompose or evaporate the polymer in an atmosphere comprising a gas chosen from air, oxygen, helium, neon, argon or krypton.

7. The method of Claim 1, further comprising:

- d. heating the composite nanofiber at a temperature greater than 400° C in an atmosphere comprising a gas chosen from air, oxygen, helium, neon, argon or krypton.

8. The method of Claim 1, wherein the polymer is chosen from poly(vinylidene fluoride), poly(vinylidene fluoride-co-trifluoroethylene), poly(vinylidene fluoride-co-hexafluoropropylene), poly(vinylidene fluoride), poly(vinylidene fluoride-co-vinylidene chloride), poly(vinylidene fluoride), poly(vinylidene fluoride-co-trichloroethylene), poly(meth)acrylonitrile, poly((meth)acrylonitrile-co-methyl methacrylate), poly(meth)acrylic acid, poly methyl (meth)acrylate, polyvinyl chloride, poly(vinylidenechloride-co-methyl (meth)acrylate), polyethylene, polypropylene, nylon 12, nylon-4,6, nylon 5, nylon 7, nylon 9, aramid, polybenzimidazole, polyvinyl alcohol, poly vinyl acetate, poly(vinyl alcohol – co – vinyl acetate), cellulose, cellulose acetate, cellulose acetate butyrate, polyvinyl pyrrolidone, poly(bis-(2-(2-methoxy-ethoxyethoxy))) phosphazene, poly(ethylene imide), poly(ethylene succinate), poly(ethylene sulphide), poly(oxymethyleneoligo-oxyethylene), poly(propylene oxide), poly(vinyl acetate), polyaniline, poly(ethylene terephthalate), poly(hydroxy butyrate), poly(ethylene oxide), SBS copolymer, poly(lactic acid), polypeptide and protein, phenolic resins, epoxy resin, polycarbonate resin, nafion, coal-tar pitch petroleum pitch or combinations thereof.
9. The method of Claim 1, wherein the ceramic precursor comprises a structural unit represented by the general formula:



(I)

wherein R^1 , R_2 and R^3 are each independently a hydrogen atom, or a substituted or unsubstituted, branched or unbranched hydrocarbon group.

10. A method of forming a composite of nanofibers comprising:

- a. deploying the method of Claim 1 one or a plurality of times according to a generally linear, generally concentric or generally random array;
- b. collecting one or more nanofibers produced thereby (i) on the substrate to form a mat; or (ii) as a spun yarn.

11. A nanofiber comprising:

- a. carbon, a ceramic, a polymer or a ceramic precursor (e.g., the nanofiber comprising a matrix, the matrix comprising carbon, a polymer, a ceramic, or a ceramic precursor); and,
- b. at least one carbon allotrope, the carbon allotrope chosen from a functionalized or non-functionalized graphene nanoribbon or a graphene oxide nanoribbon;
wherein the carbon allotrope is from about 1 weight % to about 90 weight % of the nanofiber.

12. The nanofiber of Claim 11, further comprising a nanostructured semiconductor; said semiconductor chosen from silicon, germanium, zinc oxide, zinc sulfide, zinc selenide, zinc telluride, gallium phosphide, gallium arsenide, gallium antimonide, gallium nitride, indium nitride, indium phosphide, indium arsenide, indium antimonide, aluminum nitride, copper(I) oxide or combinations thereof.

13. The nanofiber of Claim 11, wherein the functionalized or non-functionalized carbon allotrope comprises a graphene nanoribbon having structure chosen from an armchair structure or a zig-zag structure.

14. The nanofiber of Claim 11, wherein the at least one functionalized or non-functionalized carbon allotrope is derived from a multi-walled carbon nanotube.

15. The nanofiber of Claim 11, wherein the functionalized carbon allotrope is substituted by at least one substituent chosen from polystyrene, polyisoprene, polybutadiene, poly(meth)acrylonitrile, polymethyl vinyl ketone, poly alkyl acrylate, poly alkyl(meth)acrylate, a polyol, an alkyl group, an acyl group, an allylic group, a benzyl group, a benzylic group, an alkenyl group, an aryl group, an alkynyl group, an aldehyde, a ketone, an ester, a sulfonate, a phosphonate, a halide, a carboxyl group, a carbonyl group, a halogen, or combinations thereof.
16. The nanofiber of Claim 11, wherein the weight ratio of the functionalized or non-functionalized carbon allotrope to polymer is greater than a lower limit chosen from 1%, 2%, 6%, 10% or 20% and wherein the weight ratio is less than 90%.
17. The nanofiber of Claim 11, wherein the polymer is chosen from poly(vinylidene fluoride), poly(vinylidene fluoride-co-trifluoroethylene), poly(vinylidene fluoride-co-hexafluoropropylene), poly(vinylidene fluoride), poly(vinylidene fluoride-co-vinylidene chloride), poly(vinylidene fluoride), poly(vinylidene fluoride-co-trichloroethylene), poly(meth)acrylonitrile, poly((meth)acrylonitrile-co-methyl methacrylate), poly (meth)acrylic acid, poly methyl (meth)acrylate, polyvinyl chloride, poly(vinylidenechloride- co-methyl (meth)acrylate), polyethylene, polypropylene, nylon 12, nylon-4,6, nylon 5, nylon 7, nylon 9, aramid, polybenzimidazole, polyvinyl alcohol, poly vinyl acetate, poly(vinyl alcohol – co – vinyl acetate), cellulose, cellulose acetate, cellulose acetate butyrate, polyvinyl pyrrolidone, poly(bis-(2-(2-methoxy-ethoxyethoxy)) phosphazene, poly(ethylene imide), poly(ethylene succinate), poly(ethylene sulphide), poly(oxymethyleneoligo- oxyethylene), poly(propylene oxide), poly(vinyl acetate), polyaniline, poly(ethylene terephthalate), poly(hydroxy butyrate), poly(ethylene oxide), SBS copolymer, poly (lactic acid), polypeptide and protein, phenolic resins, epoxy resin, polycarbonate resin, nafion, coal-tar pitch petroleum pitch or combinations thereof.
18. A film disposed on a substrate, comprising one or more of the nanofibers of Claim 11.
19. A yarn comprising one or more of the nanofibers of Claim 11, wherein the nanofibers are formed and then twisted.
20. An electronic device comprising the film of Claim 18; and a semiconductor material.
21. An electromechanical device comprising:
 - a. a yarn comprising one or more of the nanofibers of Claim 11, wherein the nanofibers are formed and then twisted; or, alternatively, a mat, comprising one or more of the nanofibers of Claim 11;

- b. two or more electrodes for applying or sensing a voltage;
wherein the polymer comprises a ferroelectric or piezoelectric polymer.
22. The electromechanical device of Claim 21, wherein the ferroelectric or piezoelectric polymer is chosen from poly(vinylidene fluoride), poly(vinylidene fluoride-co-trifluoroethylene), poly(vinylidene fluoride-co-hexafluoropropylene), poly(vinylidene fluoride), poly(vinylidene fluoride-co-vinylidene chloride), poly(vinylidene fluoride), poly(vinylidene fluoride-co-trichloroethylene), nylon 5, nylon 7, nylon 9, or combinations thereof.
23. A lithium battery (e.g., a lithium ion battery or a lithium air battery), comprising:
- a. an electrolyte; and
 - b. a film, comprising one or more of the nanofibers of Claim 11;
wherein the carbon allotrope is a functionalized or non-functionalized graphene nanoribbon.
24. The Lithium battery of Claim 23, wherein the film further comprises a catalyst, said catalyst comprising gold, silver, platinum, palladium, manganese, cobalt, rubidium, oxides thereof or combinations thereof.
25. The lithium battery of Claim 23, wherein the nanofibers further comprise a nanostructured semiconductor; said semiconductor chosen from silicon, germanium, zinc oxide, zinc sulfide, zinc selenide, zinc telluride, gallium phosphide, gallium arsenide, gallium antimonide, gallium nitride, indium nitride, indium phosphide, indium arsenide, indium antimonide, aluminum nitride, copper(I) oxide or combinations thereof.
26. The Lithium battery of Claim 23, wherein the nanofibers further comprise zinc oxide nanofibers.
27. An electrochemical double layer device, comprising:
- a. a first metal electrode, having a first coating, comprising the film of Claim 18 disposed thereon;
 - b. a second metal electrode, having a second coating, comprising the film of Claim 18 disposed thereon;
 - c. an electrolyte; and
 - d. a separator.
28. A device for removing contaminants from a fluid, comprising: a porous substrate having the film of Claim 18 disposed thereon.
29. An electronic device comprising: a conducting substrate; and the film of Claim 18 disposed thereon; wherein the conducting substrate comprises at least one metal chosen

from lithium, calcium, strontium, molybdenum, steel, copper, gold, platinum, palladium, cobalt, rhodium, iridium, nickel, manganese, chromium, vanadium, niobium or oxidized forms thereof.

30. A nanofiber comprising:

- a. carbon (e.g., non-GNR carbon, such as amorphous carbon) or polymer;
- b. silicon; and
- c. graphene nanoribbons, the graphene nanoribbons being about 1 weight % to about 90 weight % of the nanofiber.

31. A carbon-silicon composite nanofiber comprising graphene nanoribbons embedded in a nanofiber matrix.

32. The nanofiber of either one of claims 30 or 31, comprising silicon nanoparticles embedded in a nanofiber matrix comprising carbon.

33. The nanofiber of either one of claims 30 or 31, comprising silicon nanoparticles embedded in a nanofiber matrix comprising polymer.

34. The nanofiber of any one of claims 30-33, wherein the nanofiber comprises about 1 wt % to about 20 wt % graphene nanoribbons and about 50 wt % to about 95 wt % silicon nanoparticles.

35. An electrode comprising a plurality of nanofibers of any one of claims 30-34.

36. A lithium ion battery comprising a cathode, an anode, and a separator, the anode comprising a plurality of nanofibers of any one of claims 30-34.

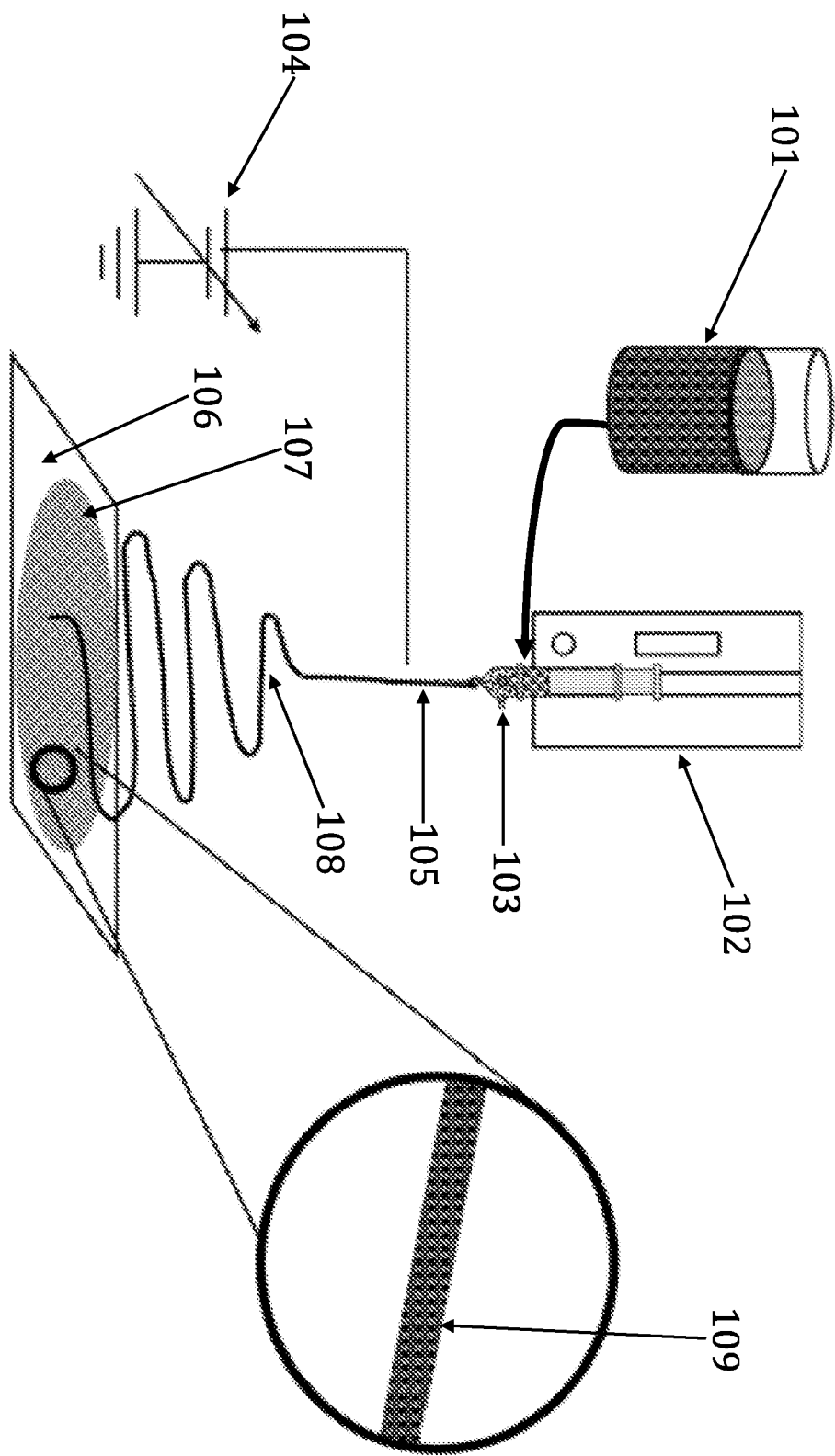


Figure 1

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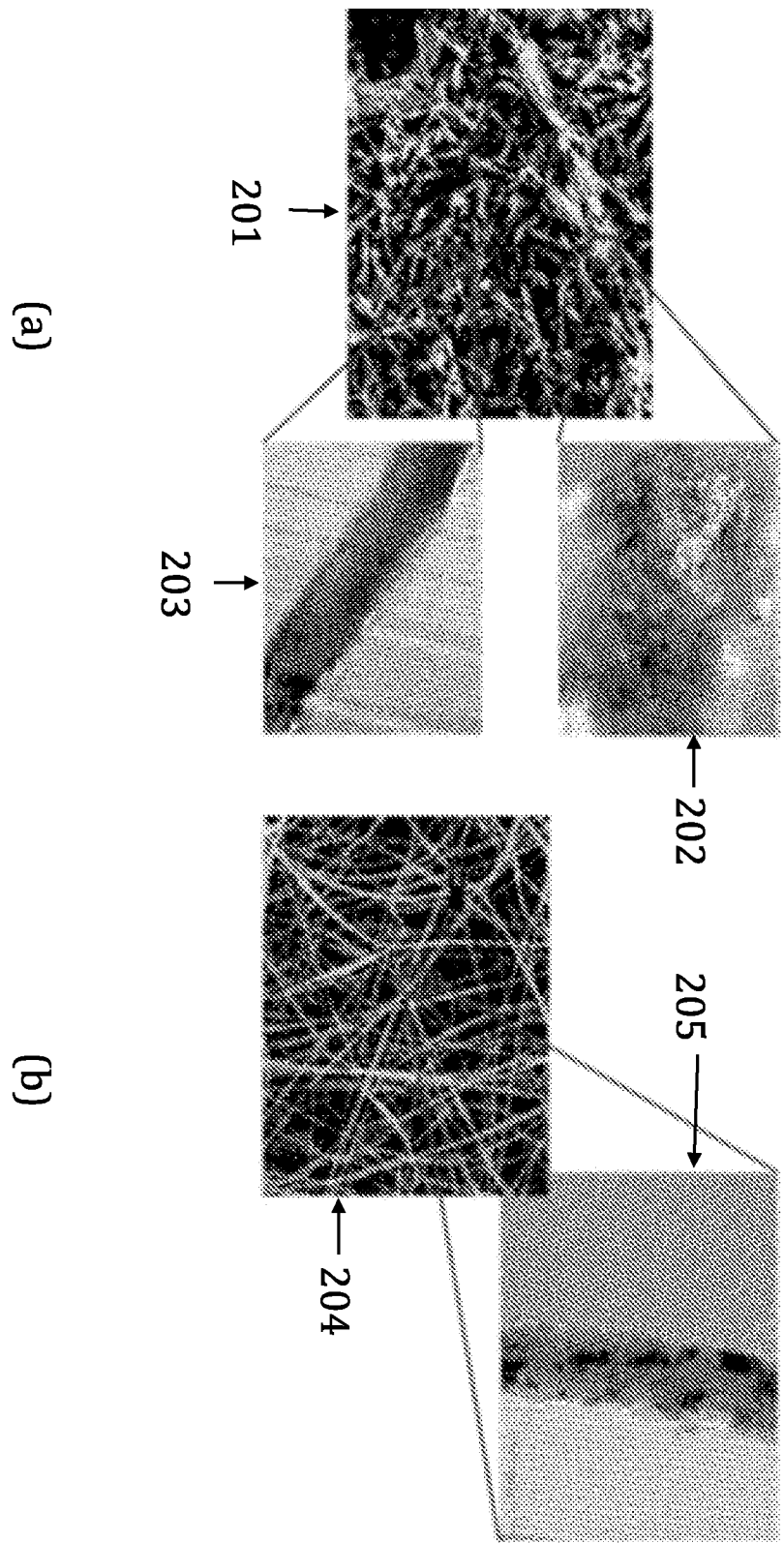


Figure 2

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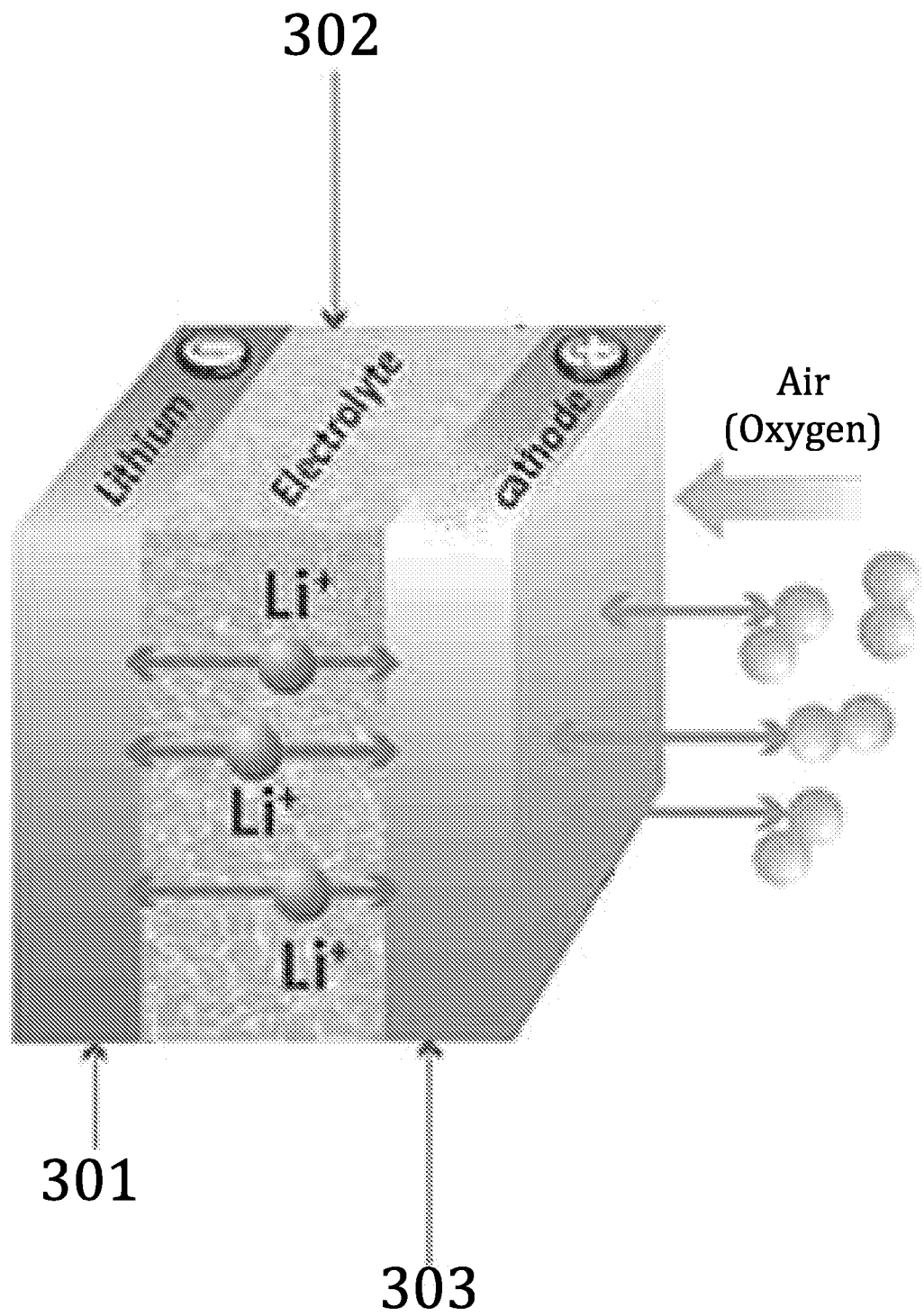
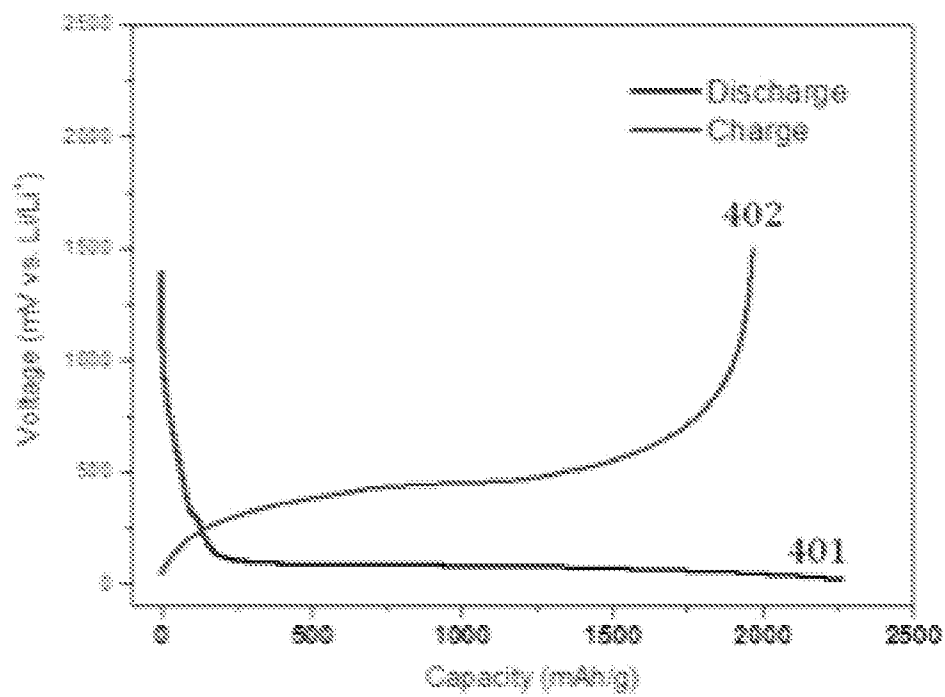
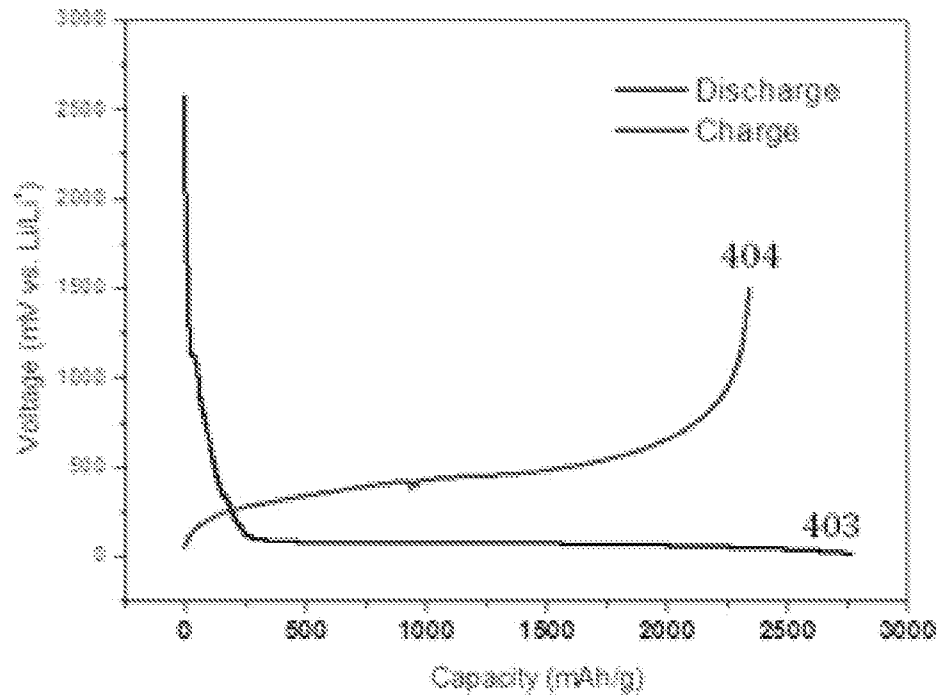


Figure 3

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(a)



(b)

Figure 4

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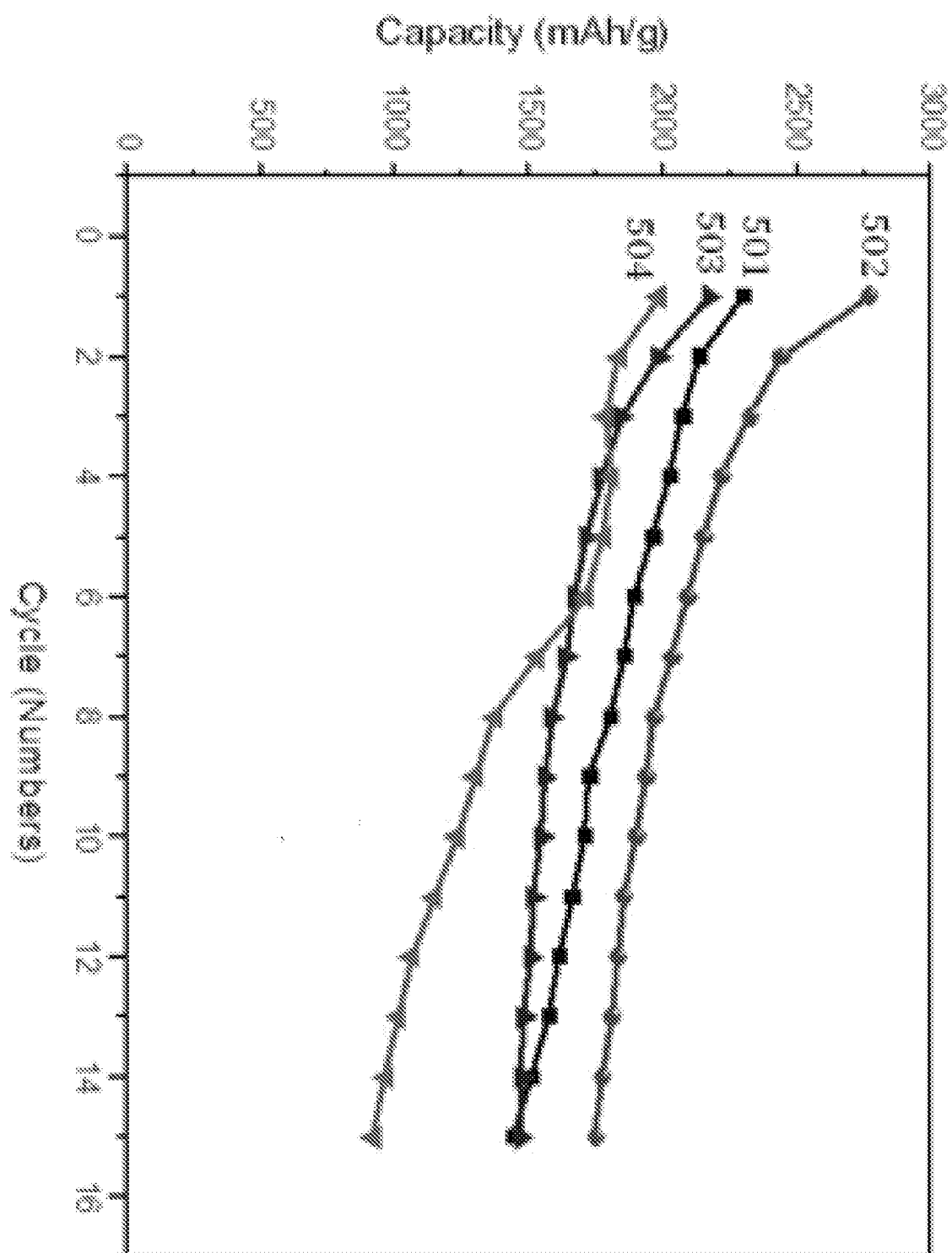
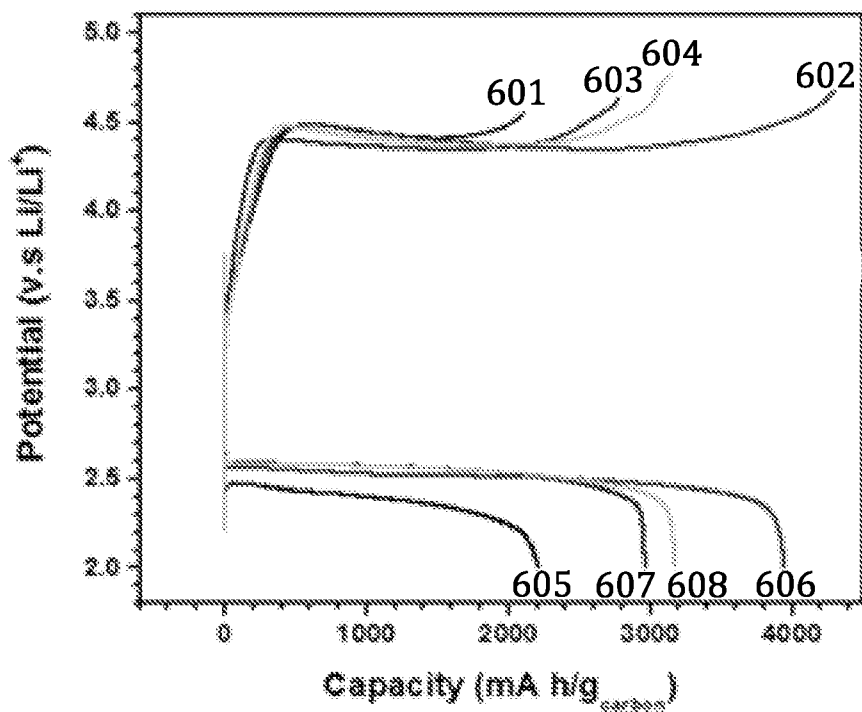
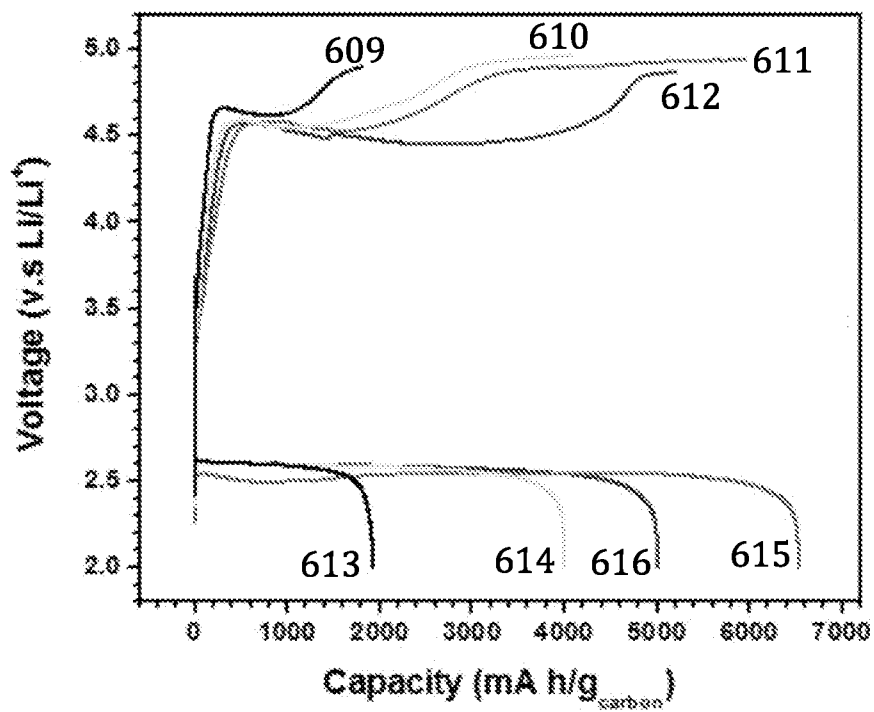


Figure 5

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(a)



(b)

Figure 6

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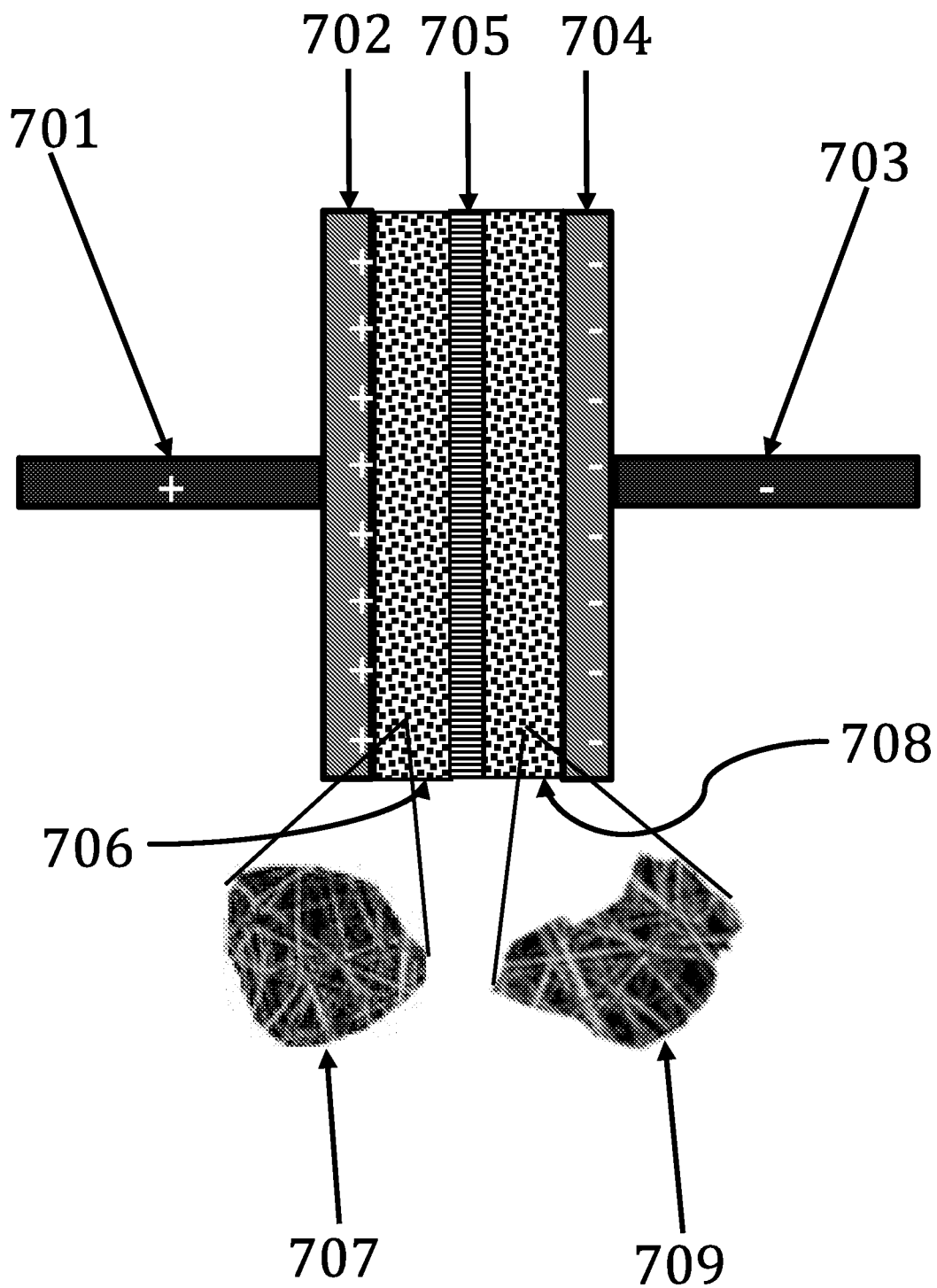


Figure 7

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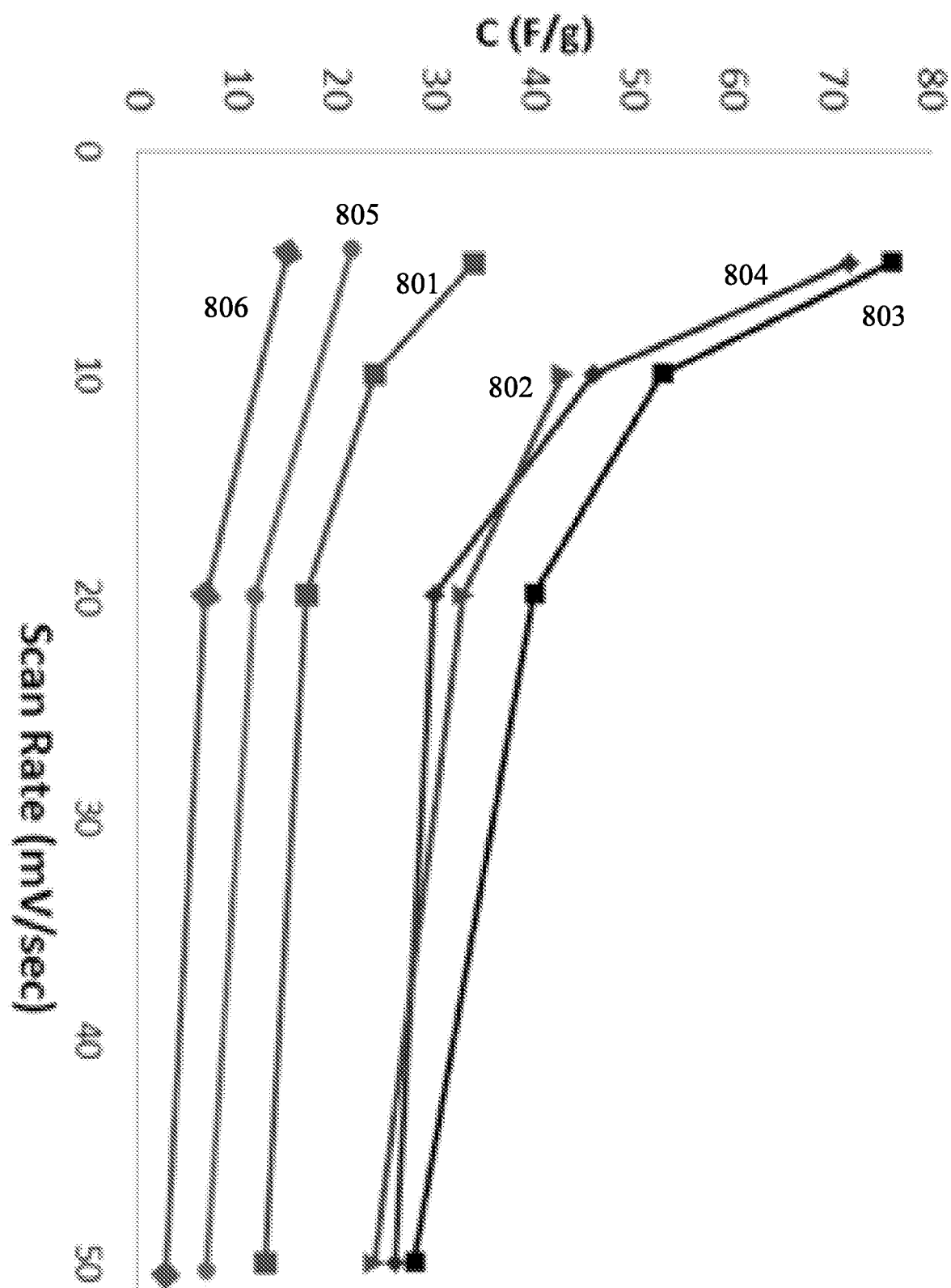


Figure 8

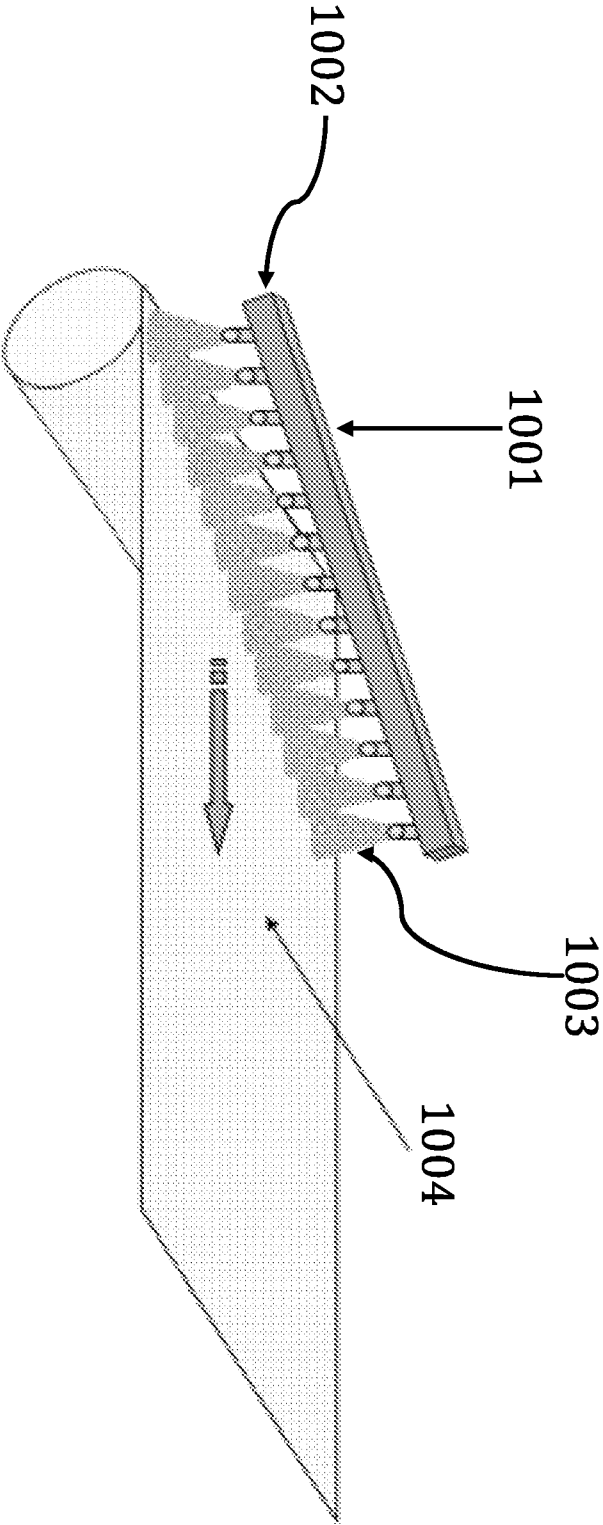


Figure 9

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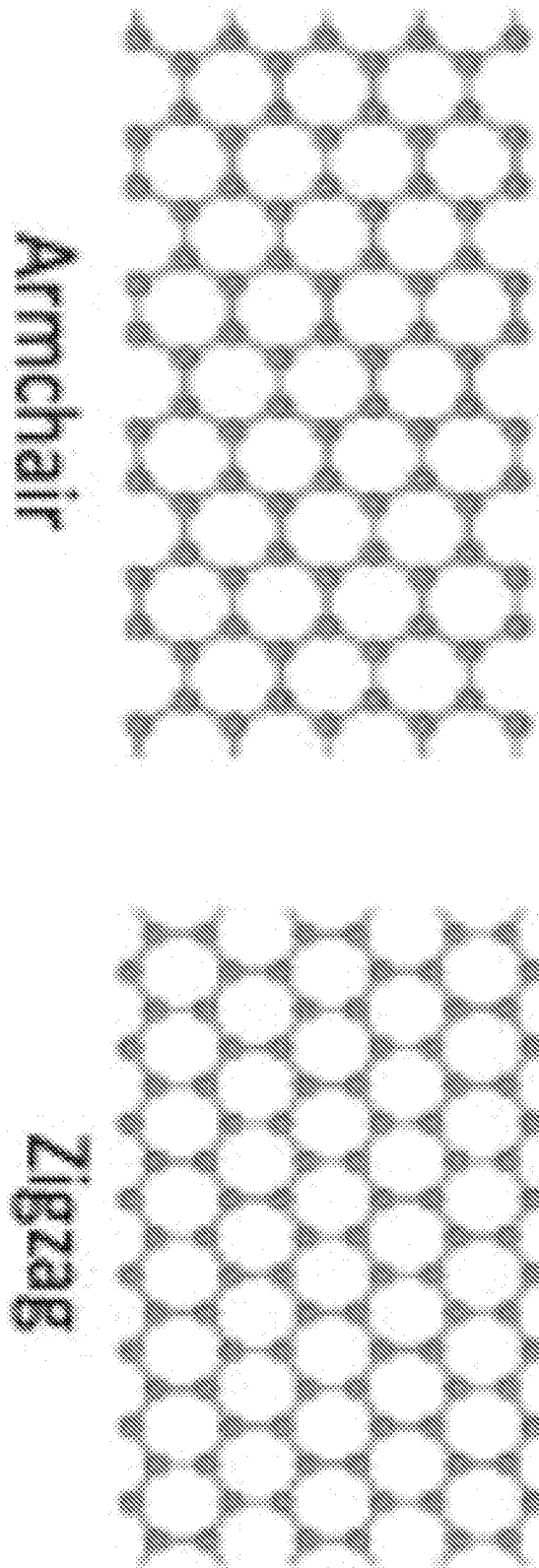


Figure 10

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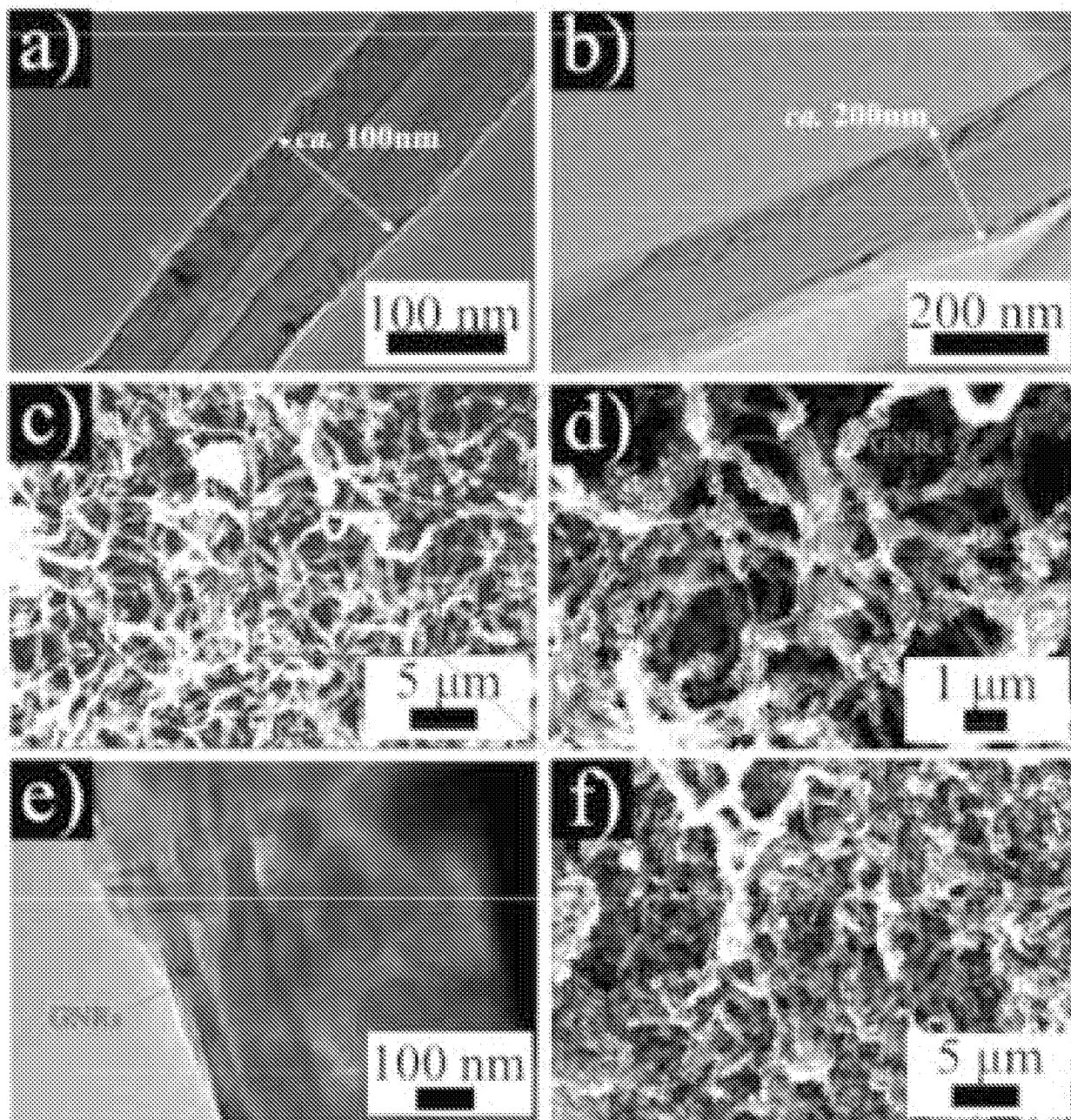


Figure 11

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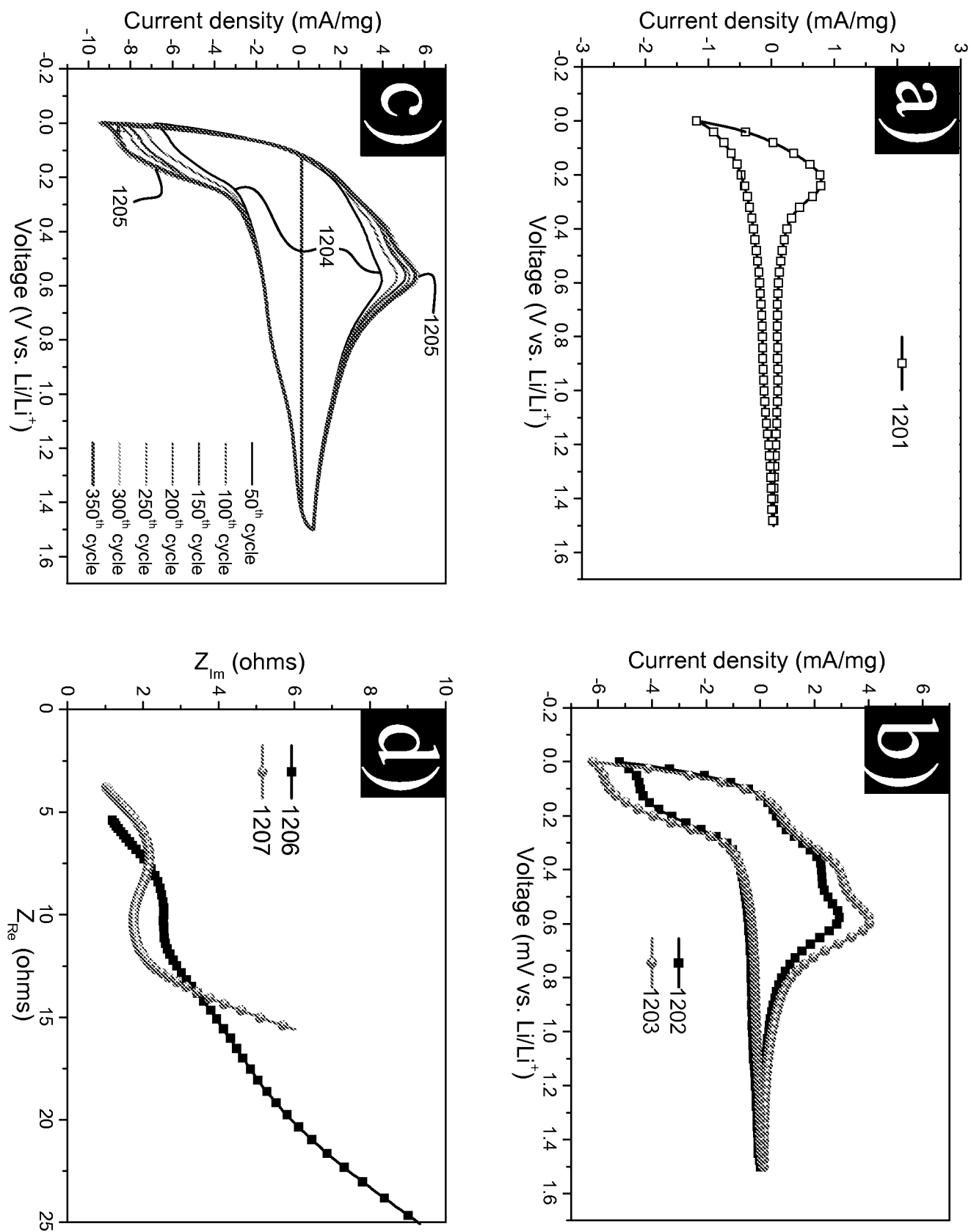


Figure 12

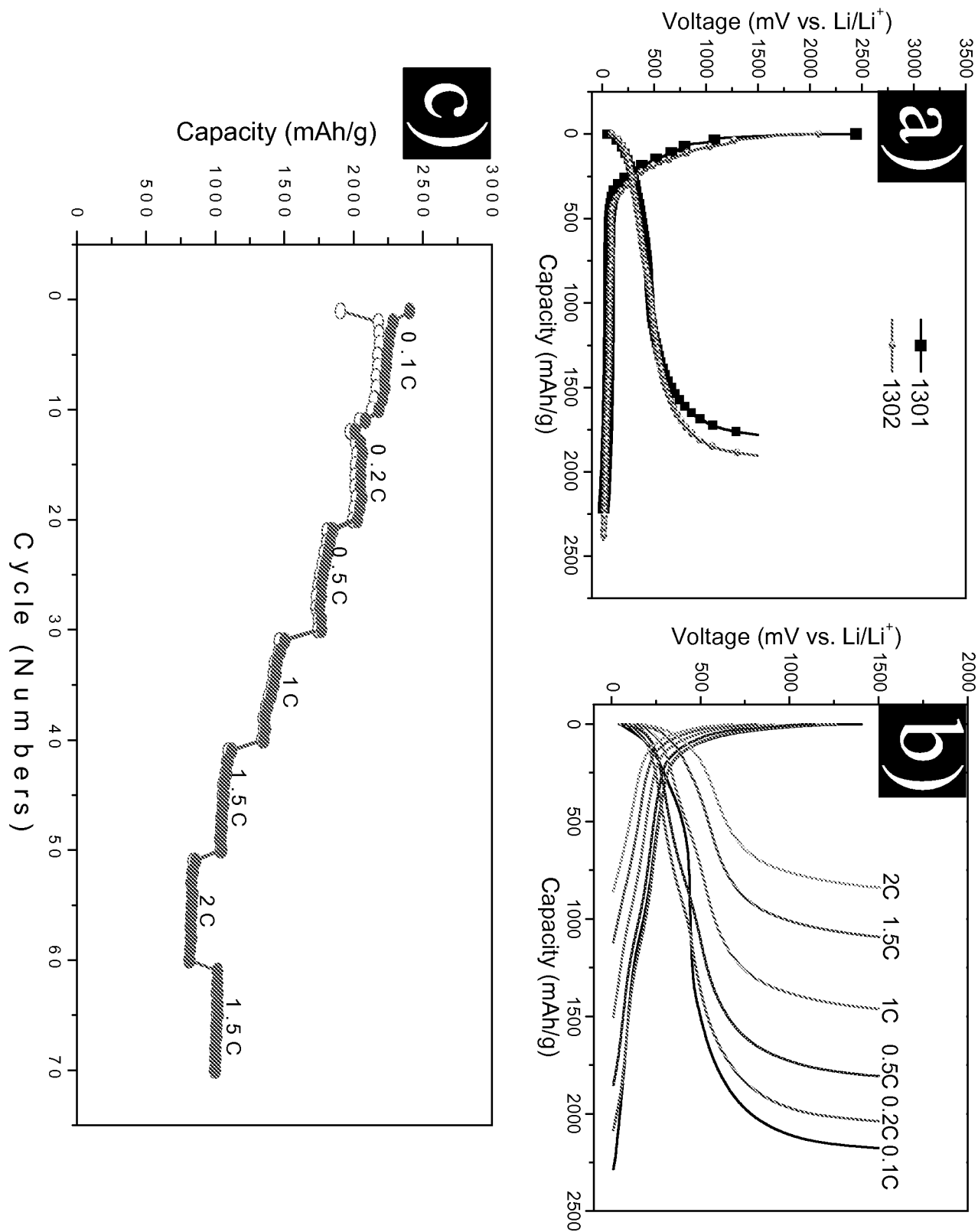


Figure 13

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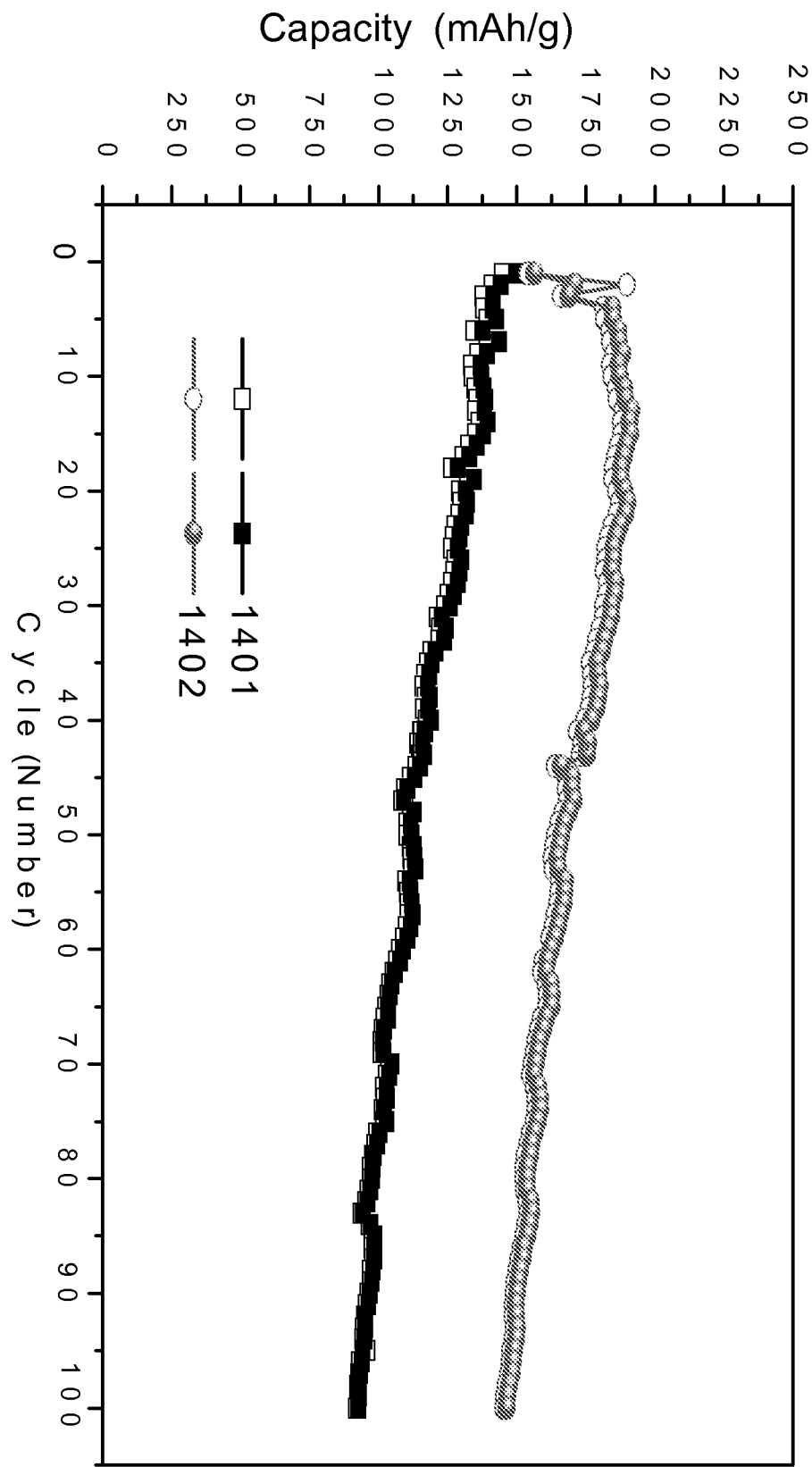


Figure 14

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/068343

A. CLASSIFICATION OF SUBJECT MATTER

INV. D01D5/00 D01D5/14 C01B31/04 H01M4/86 H01G11/36
H01M4/62 H01M10/052 D01F1/09 D01F1/10 B82Y30/00

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)

D01D C01B C04B H01M H01G D01F B82Y

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)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HIDETOSHI MATSUMOTO ET AL: "Electrospun Composite Nanofiber Yarns Containing Oriented Graphene Nanoribbons", ACS APPLIED MATERIALS & INTERFACES, vol. 5, no. 13, 13 June 2013 (2013-06-13), pages 6225-6231, XP055170887, ISSN: 1944-8244, DOI: 10.1021/am401161b	1-8, 10-29
Y	page 6226, column 1 - page 6230, column 2; figures 1,2,3,6,9 ----- -/--	30-36



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

23 February 2015

Date of mailing of the international search report

27/02/2015

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/068343

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	XIANG ZHANG ET AL: "Electrospun TiO ₂ -Graphene Composite Nanofibers as a Highly Durable Insertion Anode for Lithium Ion Batteries", JOURNAL OF PHYSICAL CHEMISTRY C, vol. 116, no. 28, 28 June 2012 (2012-06-28), pages 14780-14788, XP055170924, ISSN: 1932-7447, DOI: 10.1021/jp302574g	1-3, 6-13, 15-29
Y	the whole document -----	30-36
X	US 2012/315815 A1 (FONG HAO [US] ET AL) 13 December 2012 (2012-12-13) abstract; figures 4a, 4b paragraphs [0004], [0062], [0069], [0071] - [0080] -----	11,13, 16,18, 20,21, 27,28
Y	WO 2013/130712 A1 (UNIV CORNELL [US]) 6 September 2013 (2013-09-06) cited in the application the whole document -----	30-36

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/068343

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012315815	A1	13-12-2012	NONE

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			EP 2820710 A1 07-01-2015
			KR 20140137399 A 02-12-2014
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			TW 201348536 A 01-12-2013
			WO 2013130690 A1 06-09-2013
			WO 2013130712 A1 06-09-2013
