ABSTRACT
Granules of graphene oxide may be produced from a dispersion of nanoscale graphene oxide sheets by a spray drying method. Such granules have a three-dimensional corrugated morphology. The complexity of the corrugations, and the size distribution of the granules can be varied through selection of the spray-drying equipment used, and variation of the composition of the dispersion and the spray-drying parameters. Structural modifiers may be included in the graphene oxide dispersion to control the ultimate morphology of the granules. The granules of graphene oxide may be thermally reduced at a moderate temperature of 220°C to increase the granules’ electrical conductivity. The reduced granules may be used to fabricate electrodes for supercapacitors. The power and energy density of such an electrode material is comparable to those of conventional/commercial activated carbon-based electrodes.
FIG. 7

Power Density ($\log_{10}(\text{kWh/kg})$)

Energy Density ($\log_{10}(\text{Wh/kg})$)
GRANULES OF GRAPHENE OXIDE BY SPRAY DRYING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of U.S. Provisional Patent Application No. 61/754,223, filed on Jan. 18, 2013, the disclosure of which is incorporated by reference herein.

FIELD OF THE INVENTION

[0002] The present invention relates to granules of graphene oxide and methods of making same, and, more specifically, to granules of graphene oxide useful for fabricating electrical components.

BACKGROUND OF THE INVENTION

[0003] Graphene has recently received significant attention due to its many attractive properties, including chemical and electrochemical stability; electrical conductivity; and high theoretical surface area (e.g., 2630 m²/g). This theoretical surface area compares well to those of: carbon nanotubes (CNT) (e.g., 1315 m²/g); and is commercially available activated carbon (typically, 500 m²/g). A common method of producing CNT is chemical vapor deposition (CVD), which has remained quite expensive despite several decades of research and development. In contrast, graphene can be prepared by a number of diverse routes, ranging from CVD to mechanical cleavage of graphite. In particular, thermal-chemical exfoliation of graphite powder has rapidly become a cost-effective method for large-scale production of graphene and graphene oxide nanosheets. With this method, the price of graphene and graphene oxide sheets is projected to be $50/kg over next several years. This projected price is comparable to that of electronic grades of activated carbon.

[0004] Graphene oxide nanosheets may be regarded as being graphene nanosheets with various functional groups, such as carboxylic acid and phenolic hydroxyl groups, attached to the edges or basal plane. Graphene oxide can be reduced to graphene. Aqueous dispersions of graphene oxide nanosheets are colloidal stable, a state generally attributed to electrostatic interactions resulting from the ionization of these functional groups. Due to the presence of oxidized functional groups, graphene oxide nanosheets are surface active. Graphene oxide can be easily reduced by thermal reduction, chemical reduction, or flash reduction to obtain reduced graphene oxide, a material that is comparable to graphene.

[0005] In the majority of current research and practical applications, the processing of graphene oxide nanosheets is based on filtration of graphene oxide dispersion through a membrane filter. Concerns raised by such filtration-based methods include:

[0006] (1) stacking of graphene oxide nanosheets due to van der Waals force, which renders a portion of the surface area inaccessible, thereby adversely affecting the electrochemical or electrical properties (e.g., capacitance) of the graphene oxide devices;
[0007] (2) re-stacking of graphene oxide nanosheets during application, such as, for example, in supercapacitors where irreversible loss of capacity during cycling occurs, and is likely due to re-stacking of nanosheets during charging and discharging operation; and

SUMMARY OF THE INVENTION

[0008] (3) environmental, safety and health (ESH) concerns associated with both the processing and the application of graphene oxide, since the material is cytotoxic in its nanoscale form.

[0009] In an embodiment of the present invention, granules comprising graphene nanosheets have a corrugated morphology with substantially greater surface area and longer ion pathways than non-corrugated granules of comparable size. In some embodiments, the granules include a structural modifier that modifies the morphology of the granules, and increases the degree and complexity of the corrugations. In some embodiments, the granules include reduced graphene oxide. In some embodiments, the granules are primarily reduced graphene oxide. In some embodiments, the granules are components of electrodes for capacitors.

[0010] In an embodiment of a method of the present invention, an aqueous dispersion of graphene oxide nanosheets is spray-dried to form granules of graphene oxide. In some embodiments, the aqueous suspension also includes structural modifiers that modify the morphology of the granules. In some embodiments, the structural modifier is a salt having volatile components (e.g., ammonium bicarbonate). In some embodiments, the graphene oxide granules are reduced so as to modify their electrical properties. In some embodiments, the reduced graphene oxide granules are combined with a binder to form an electrode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] For a more complete understanding of the present invention, reference is made to the following detailed description of an exemplary embodiment considered in conjunction with the accompanying drawings, in which:

[0012] FIG. 1 is a scanning electron microscopy image of granules of graphene oxide prepared without a structural modifier according to a method of the present invention;
[0013] FIG. 2 is a second scanning electron microscopy image of granules of graphene oxide prepared without a structural modifier according to a method of the present invention;
[0014] FIG. 3 is a third scanning electron microscopy image of granules of graphene oxide prepared with a structural modifier according to a method of the present invention;
[0015] FIG. 4 is a fourth scanning electron microscopy image of granules of graphene oxide prepared with a structural modifier according to a method of the present invention;
[0016] FIG. 5 is a graph of the cyclic voltammetry response of an electrode prepared from thermally reduced granules of graphene oxide according to an embodiment of the present invention;
[0017] FIG. 6 is a plot of the specific capacitance of the electrode tested to produce the data of FIG. 5 against the number of charge/discharge cycles to which the electrode was subjected; and
[0018] FIG. 7 is a Ragone plot of power density against energy density for the electrode of FIGS. 5 and 6.

DETAILED DESCRIPTION OF THE INVENTION

[0019] The present invention includes a method of making granules of graphene oxide having a three-dimensional corrugated morphology, which includes a step of spray drying a graphene oxide dispersion. In some embodiments of the
invention, a suitable graphene oxide dispersion is prepared by dispersing graphite oxide solid into a solvent under ultrasonic conditions to form a stable dispersion of single molecular layers of graphene oxide. In some embodiments of the invention, the nanosheets of graphene oxide have a thickness of one to a few molecular layers and lateral dimensions of about 100 nm to about 1000 nm (1 μm). In other embodiments of the present invention, graphene oxide dispersions prepared by other means, or having graphene oxide sheets with other thicknesses or other nanoscale or microscale lateral dimensions may be used.

In an embodiment of a method of the present invention, a graphene oxide dispersion is spray dried using, for example, a commercial spray dryer to produce graphene oxide granules having dimensions in the range of about 1 μm to about 20 μm. In some embodiments of the invention, spray-dried granules of graphene oxide have a three-dimensional corrugated morphology. In some embodiments of the invention, the three-dimensional corrugated morphology of the granules is tailored by adjusting the parameters of the spray drying process, the method and conditions for atomizing the graphene oxide dispersion, or by including a structural modifier. For the purpose of the present disclosure, a structural modifier is a physical or chemical additive to the graphene oxide solution which affects the morphology of the granules produced during the spray drying process.

In an embodiment of the present invention, the graphene oxide granules are thermally reduced at moderate temperatures (e.g., a temperature of about 220°C) in an inert environment or in air to increase the electrical conductivity of the granules. In an embodiment of the present invention, the granules are used in electrical components (e.g., supercapacitors). The power and energy density of electrodes fabricated from thermally-reduced granules of graphene oxide may be comparable to those of activated carbon-based electrodes prepared using commercially-available activated carbon. Embodiments of the present invention provide an effective, robust, scalable, and safe method for processing graphene oxide into a form (i.e., corrugated granules) which not only retains the nanoscale properties of graphene oxide nanosheets, but which also presents minimal ESH issues compared to graphene nanotechnologies in the prior art.

In an embodiment of the present invention, granules of graphene oxide are prepared from a graphene oxide dispersion using a spray dryer (e.g., BUCHI Mini Spray Dryer B-290, BUCHI Corporation, New Castle, Del.). A suitable graphene oxide may be prepared from a commercially-available source, or prepared using known techniques. In an embodiment of the invention, solid graphene oxide, synthesized using a modified Hummers method, is obtained from a commercial source (e.g., Cheap Tubess, Inc., Brattleboro, Vt.). To prepare the dispersion of graphene oxide nanosheets, the graphite oxide solid is dispersed in de-ionized water using a pulsed ultrasonic probe. The dispersed graphene oxide nanosheets are typically single-layered or a few layers thick and have micron or sub-micron lateral dimensions in the range of about 100 nm to about 1000 nm. The graphene oxide nanosheet dispersions are colloidal stable at various concentrations. An exemplary graphene oxide dispersion, prepared at a concentration of 5 mg/ml by the aforesaid method, was found to be stable for months, mostly likely due to the presence of various oxidized functional groups (e.g., carboxylic acid and phenolic hydroxyl groups) formed at the edges or basal plane of the nanosheets by the strong oxidants used to synthesize the graphene oxide.

In the following exemplary embodiments, granules of graphene oxide were produced from a graphene oxide dispersion (5 mg/ml) by spray drying (i.e., atomizing the dispersion to produce droplets, and drying the droplets in a gas stream). The droplets were produced using a pneumatic nozzle having a diameter of about 1 mm at a gas pressure of 50 psi and a graphene oxide dispersion feeding rate of 2.74 mL/min. The droplets produced had a size distribution in the range of about 10 μm to about 100 μm. The droplets were dried inside the spray dryer, forming granules of graphene oxide from the dispersed graphene oxide sheets. The inlet temperature of the spray dryer was higher than the boiling temperature of water (e.g., about 120°C). The aspirator in the spray dryer was set at 100%. Air was used as the drying gas, but other gas or gas mixtures may be used. The granules of graphene oxide were separated from the gas flow by a cyclone separator, and collected in an electrically-grounded container. FIGS. 1 and 2 present examples of graphene oxide granules produced by the aforesaid method. The granules generally have dimensions in the range of about 1 μm to about 2 μm. The granules have a corrugated three-dimensional morphology. A typical surface area of a granule formed by the foregoing process was about 394 m²/g as measured by BET analysis.

The three-dimensional morphology of graphene oxide granules (e.g., graphene oxide granules 10, 12, 14, 16, 18) prepared by the method of the present invention can be varied by adjusting the parameters of the spray-drying process. Parameters which may be varied include, but are not limited to: the type of atomizer and conditions of atomization; the conditions of the spray drying step, such as inlet temperature and the feed rate of the graphene oxide dispersion and/or the drying gas; and the use of structural modifiers in the graphene oxide dispersion to modify the three-dimensional morphology of the granules. Structural modifiers for controlling the morphology of the graphene oxide granules may include salts having volatile or non-volatile components, nanoparticles of various substances, and carbon nanotubes. Such structural modifiers, as well as others, may modify the nanoscale structure of the granules.

In an exemplary embodiment of the present invention, ammonium bicarbonate (NH₄HCO₃) was added to the graphene oxide dispersion to serve as a structural modifier during the spray drying. Dissolving a high concentration (5 mg/ml) of NH₄HCO₃ into the graphene oxide dispersion did not noticeably affect the stability of the dispersion. A graphene oxide dispersion with NH₄HCO₃, having both components at concentrations of 5 mg/ml, was spray dried under the conditions previously described. FIGS. 3 and 4 show that the resulting granules (e.g., granules 20, 22, 24, 26) are more highly corrugated than the granules of FIGS. 1 and 2, which were produced without NH₄HCO₃. Due to the low decomposition temperature of NH₄HCO₃, the structural modifier decomposes during the spray drying process and does not contaminate the granules of graphene oxide.

The graphene oxide granules having corrugated three-dimensional morphologies have various potential applications, which include, but are not limited to, energy storage, water desalination, catalysis, sorption of oil or solvents, or as additives to polymeric or ceramic materials. Such granules have also been demonstrated to have applications as an electrode material of supercapacitors for energy storage. A
complex corrugation provides a greater surface area to the granules, as well as long ion pathways which, for capacitors, provide a high current density.

[0027] To demonstrate the electrical properties of the graphene oxide granules of the present invention, granules prepared without a structural modifier were reduced at 220°C under a helium atmosphere for 12 hours. The color of the granules changed to black after the reduction, suggesting the transformation of graphene oxide to graphene. After reduction, the granules have similar morphologies to those of the spray-dried granules before reduction. The reduced granules of graphene oxide were then mixed with a polytetrafluoroethylene (PTFE) aqueous dispersion (10 wt %) and pressed at a pressure of 10 MPa to the surface of a titanium (Ti) foil having a thickness of 100 μm. Titanium was selected as the current collector due to its compatibility with the chosen sulfuric acid (H₂SO₄) electrolyte. PTFE served as a binder for the granules, at a concentration of about 5 wt % relative to the weight of the granules. Two such electrodes were prepared and soaked in 1M H₂SO₄ electrolyte. The electrodes were then inserted into a polyethylene-based pouch using a Celgard 3401 membrane (Celgard, LLC, Charlotte, N.C.) as a separator to form a capacitor. The packaged capacitor was clamped for cyclic voltammetry and constant current charge/discharge measurements using a multifunction MACCOR Model 4304 desktop automated test system (MACCOR, Inc., Tulsa, Okla.).

[0028] FIG. 5 is a cyclic voltammetry (CV) plot of the capacitor at different voltage scan rates, varied from 0.02 V/s to 0.5 V/s. CV is a standardized electrochemical characterization test for supercapacitor electrodes. The reduced graphene oxide granule-based capacitor exhibited fairly rectangular CV curves characteristic of a pure double-layer capacitance device. The specific capacitance of the capacitor ranged from 0 about 40 F/g to about 78 F/g with respect to the reduction of the scan rate from 0.5 V/s to 0.02 V/s, respectively. The specific capacitance of 78 F/g compared favorably with the gravimetric capacitance of 72 F/g of activated carbon powder (Norit DL-C-30, Cabot Corporation, Boston, Mass.). The activated carbon powder capacitor was tested as a control material prepared in the same manner as described above, but using activated carbon powder in place of the reduced spray-dried granules of the present invention. Moreover, the measured capacitances of the granule-based capacitor were of the same order of magnitude as other graphene-based capacitor prepared by conventional powder-based methods without any pseudo-capacitive contributions.

[0029] FIG. 6 is a plot of the specific capacitance of the granule-based capacitor against the number of charge/discharge cycles to which the granule-based capacitor was subjected at 0.1 V/s. The capacitor retained 83% of its initial capacitance after 1000 cycles.

[0030] FIG. 7 is a Ragone plot of energy density and power density for the granule-based capacitor. Although both the power density and energy density for the granule-based capacitor are lower than for some activated carbon capacitors, the performance of the granule-based electrodes may be optimized through routine modifications to the methods of preparing the granules and the electrode.

[0031] The performance of the exemplary granule-based capacitor is within the range of performance which may be achieved with activated carbon capacitor. The electrochemical performance of the graphene oxide capacitor demonstrates the significance of the scalable processing method for preparing graphene oxide granules from graphene oxide according to methods of the present invention. For supercapacitor applications, the power and energy density of the electrodes produced from the graphene oxide granules can be improved upon by further tailoring the factors that affect the three-dimensional morphology of the granules. Such factors may include the spray drying equipment used, spray-drying process parameters, and the use of structural modifiers in the graphene oxide dispersion.

[0032] It will be understood that the embodiments described herein are merely exemplary and that a person skilled in the art may make many variations thereof and modifications thereto without departing from the spirit and scope of the invention. All such variations and modifications are intended to be included within the scope of the invention, which is described in the appended claims.

1. An artifact, comprising granules, each granule including a plurality of graphene oxide nanosheets having lateral dimensions in the range of about 100 nm to about 1000 nm, said granules having corrugated morphologies.

2. A method of preparing granules of graphene oxide having corrugated morphologies, said method comprising the steps of:

   - dispersing graphite oxide and a structural modifier in an aqueous medium, thereby forming an aqueous dispersion;
   - atomizing the dispersion, thereby forming a spray of droplets of the dispersion; and
   - drying the droplets of the dispersion, thereby forming granules including a plurality of graphene oxide nanosheets.