Printed electronic device comprising a substrate onto at least one surface of which has been applied a layer of an electrically conductive ink comprising functionalized graphene sheets and at least one binder. A method of preparing printed electronic devices is further disclosed.
Related U.S. Application Data

continuation of application No. 14/751,418, filed on Jun. 26, 2015, now Pat. No. 9,504,150, which is a continuation of application No. 14/189,501, filed on Feb. 25, 2014, now Pat. No. 9,107,312, which is a division of application No. 13/603,818, filed on Sep. 5, 2012, now Pat. No. 8,697,485, which is a division of application No. 12/866,079, filed as application No. PCT/US2009/030570 on Jan. 9, 2009, now Pat. No. 8,278,757.

(60) Provisional application No. 61/026,273, filed on Feb. 5, 2008.

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\[ H05K 3/00 \] (2006.01)
\[ C09D 11/102 \] (2014.01)
\[ C09D 17/102 \] (2006.01)
\[ C09D 17/000 \] (2006.01)
\[ C09D 7/40 \] (2018.01)
\[ C08K 3/01 \] (2006.01)
\[ B82Y 3/000 \] (2011.01)
\[ B82Y 3/400 \] (2011.01)

(52) U.S. Cl.
CPC .......... \[ C09D 11/037 \] (2013.01); \[ C09D 11/102 \] (2013.01); \[ C09D 11/52 \] (2013.01); \[ C09D 17/102 \] (2013.01); \[ C09D 17/000 \] (2013.01); \[ H05K 1/092 \] (2013.01); \[ H05K 3/0091 \] (2013.01); \[ H05K 3/12 \] (2013.01); \[ B82Y 3/000 \] (2013.01); \[ B82Y 3/400 \] (2013.01); \[ C09D 2006/04 \] (2013.01); \[ C09K 3/000 \] (2013.01); \[ H01J 292/4000 \] (2013.01); \[ H05K 2201/0323 \] (2013.01); \[ Y10S 977/734 \] (2013.01); \[ Y10S 977/847 \] (2013.01); \[ Y10S 977/932 \] (2013.01)

Field of Classification Search

See application file for complete search history.

References Cited

U.S. PATENT DOCUMENTS


FOREIGN PATENT DOCUMENTS


OTHER PUBLICATIONS


Communication pursuant to Article 94(3) EPC dated May 28, 2014, in European Patent Application No. 09 709 241.5.


* cited by examiner
1 PRINTED ELECTRONICS

CROSS-REFERENCE TO RELATED APPLICATIONS


This invention was made with Government support under Grant No. CMS-0609049, awarded by the National Science Foundation, and under Grant No. NCC1-02037, awarded by NASA. The Government has certain rights in the invention.

FIELD OF THE INVENTION

The present invention relates to printed electronic devices and methods for their manufacture.

BACKGROUND

Printed electronics are increasingly finding uses in a great variety of applications, including portable electronics, signage, lighting, product identification, packaging flexible electronic devices (such as those that can be rolled or bent), photovoltaic devices, medical and diagnostic devices, antennas (including RFID antennas), displays, sensors, thin-film batteries, electrodes and myriad others. Printed electronics have a variety of advantages over electronics made using other methods, including subtractive methods. Printing can be faster than normal subtractive methods (such as etching) and can generate less waste and involve the use of fewer hazardous chemicals than in such methods. The resulting electronics can be more facilely used in flexible devices, such as displays, that are designed to be rolled, twisted, bent, or subjected to other distortions during use.

Printed electronics are typically made by printing the electronic circuit or other component or device on a substrate using an electrically conductive metal-based ink. The inks typically contain silver particles, and occasionally copper particles, other metallic particles, and/or conductive polymers. However, conductive polymers alone are generally not sufficiently electrically conductive. Furthermore, the resulting printed metallic circuits are usually insufficiently electrically conductive to be effective in most applications, including in devices in which the circuits are regularly stressed by bending and/or stretching during use. The printed substrates must therefore often be heated at elevated temperatures to sinter the conductive metal particles in order to achieve the desired levels of electrical conductivity. The temperatures used in sintering processes frequently limit the substrates that can be selected for the preparation of the electronics. For example, while it would be desirable to use inexpensive materials such as paper, polyolefins (e.g., polypropylene), and the like as substrates for printed electronics in many applications, the sintering temperatures often required are too high to be used with paper.

Furthermore, silver is costly and other, non-precious, metals can form oxides upon exposure to the environment that can render the material insufficiently conductive for the application. Additionally, the use of metal-based inks can add weight to the resulting device, and the aforementioned sintering process can add one or more additional steps, time, and complexity to the fabrication process. It would thus be desirable to obtain printed electronic devices using inks that do not contain costly precious metals, that are lighter weight, and that do not require sintering to become sufficiently electrically conductive, and that could therefore be used on a wider variety of substrate materials, including paper and polyolefins such as polyethylene.


SUMMARY OF THE INVENTION

Disclosed and claimed herein is a printed electronic device, comprising a substrate comprising at least one surface, wherein a layer of an electrically conductive ink has been applied to a portion of the surface, and wherein the ink comprises functionalized graphene sheets and at least one binder. Further disclosed and claimed herein is a method for forming the printed electronic device.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an optical microscope image of electrically conductive lines printed from an ink comprising functionalized graphene sheets embedded into poly(ethylene oxide).

DESCRIPTION

As used herein, the term “electrically conductive ink” encompasses materials comprising electrically conductive materials suspended and/or dissolved in a liquid, as well as pastes and materials in substantially solid form containing little or no liquids. Electrically conductive inks may be free-flowing, viscous, solid, powdery, and the like. The term “ink” is used to refer to an ink in a form that is suitable for application to a substrate, as well as the material after it is applied to a substrate both before and after any post-application treatments (such as evaporation, cross-linking, curing etc.).

The printed electronic devices (also referred to herein as “printed electronics”) of the present invention may be in the form of complete devices, parts or sub elements of devices, electronic components, and the like. They comprise a substrate onto at least one surface of which has been applied a layer of an electrically conductive ink comprising high surface area functionalized graphene sheets and at least one binder.

The printed electronics are prepared by applying the ink to a substrate in a pattern comprising an electrically con-
fluorinated ethylene propylene (FEP), polytetrafluoroethylene (PTFE), and polyethylene terephthalate (PET). The high surface area functionalized graphene sheets, which are also referred to herein as "FGS", are graphene sheets having a surface area of from about 300 to about 2630 m²/g. In some embodiments of the present invention, the FGS primarily, almost completely, or completely comprise fully exfoliated single sheets of graphene (often referred to as "graphene"), while in other embodiments, they may comprise partially exfoliated graphene sheets, in which two or more sheets of graphene have not been exfoliated from each other. The FGS may comprise mixtures of fully and partially exfoliated graphene sheets.

One method of obtaining graphene sheets is from graphite and/or graphite oxide (also known as graphitic acid or graphene oxide). Graphite may be treated with oxidizing and intercalating agents and exfoliated. Graphite may also be treated with intercalating agents and electrochemically oxidized and exfoliated. Graphene sheets may be formed by ultrasonically exfoliating suspensions of graphite and/or graphite oxide in a liquid. Exfoliated graphite oxide dispersions or suspensions can be subsequently reduced to graphene sheets. Graphene sheets may also be formed by mechanical treatment (such as grinding or milling) to exfoliate graphite or graphite oxide (which would subsequently be reduced to graphene sheets).

Reduction of graphite oxide to graphene may be by means of chemical reduction using hydrogen gas or other reducing agents. Examples of useful chemical reducing agents include, but are not limited to, hydrazines (such as hydrazine, N,N-dimethylhydrazine, etc.), sodium borohydride, hydroquinone, and the like. For example, a dispersion of exfoliated graphite oxide in a carrier (such as water, organic solvents, or a mixture of solvents) can be made using any suitable method (such as ultrasonication and/or mechanical grinding or milling) and reduced to graphene sheets.

In a preferred method, graphite is oxidized to graphite oxide, which is then thermally exfoliated to form high surface area FGS that are in the form of thermally exfoliated graphite oxide, as described in US 2007/0092432, the disclosure of which is hereby incorporated herein by reference. The thus-forming thermally exfoliated graphite oxide may display little or no signature corresponding to graphene or graphite oxide in its X-ray or electron diffraction patterns.

Graphite oxide may be produced by any method known in the art, such as by a process that involves oxidation of graphite using one or more chemical oxidizing agents and, optionally, intercalating agents such as sulfuric acid. Examples of oxidizing agents include nitric acid, sodium and potassium nitrates, perchlorates, hydrogen peroxide, sodium and potassium permanganates, phosphorus pentoxide, bisulfites, and the like. Preferred oxidants include KClO₃, HNO₃, and KClO₄; KMnO₄ and/or NaMnO₄; KMnO₃ and NaNO₃; K₂SO₄ and P₂O₅, and KMnO₄ and HNO₃; and HNO₃. A preferred intercalation agent includes sulfuric acid. Graphite may also be treated with intercalating agents and electrochemically oxidized.

Exfoliation, including the exfoliation of graphite oxide is preferably carried out at temperatures of at least 220°C or more, preferably at temperatures of from 220 to 3000°C. The FGS used in the present invention preferably have a surface area of from about 300 to about 2630 m²/g, or more preferably from about 350 to about 2400 m²/g, or still more preferably from about 400 to about 2400 m²/g, or yet more preferably from about 500 to about 2400 m²/g. In another preferred embodiment, the surface area is about 1100 m²/g. A single graphene sheet has a maximum calculated surface area of about 2630 m²/g. The surface area includes all values and subvalues therebetween, especially including 400, 500, 600, 700, 800, 900, 100, 110, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2100, 2200, 2300, 2400, and 2500 m²/g.

Surface area can be measured using either the nitrogen adsorption/BET method or, preferably, a methylene blue (MB) dye method.

The dye method is carried out as follows: A known amount of FGS is added to a flask. At least 1.5 g of MB are then added to the flask per gram of FGS. Ethanol is added to the flask and the mixture is ultrasonicated for about fifteen minutes. The ethanol is then evaporated and a known quantity of water is added to the flask to re-dissolve the free MB. The undissolved material is allowed to settle, preferably by centrifuging the sample. The concentration of MB in solution is determined using a UV-vis spectrophotometer by measuring the absorption at λ_{max}=298 nm relative to that of standard concentrations.
The difference between the amount of MB that was initially added and the amount present in solution as determined by UV-vis spectrophotometry is assumed to be the amount of MB that has been adsorbed onto the surface of the FGS. The surface area of the FGS are then calculated using a value of 2.54 m$^2$ of surface covered per one mg of MB adsorbed.

The FGS preferably have a bulk density of from about 40 to about 0.1 kg/m$^3$. The bulk density includes all values and subvalues therebetween, especially including 0.5, 1, 5, 10, 15, 20, 25, 30, 35 kg/m$^3$.

The FGS typically have an overall carbon to oxygen molar ratio (C:O ratio), as determined by elemental analysis of at least about 1:1, or more preferably, at least about 3:2. Examples of carbon to oxygen ratios include about 3:2 to about 85:15; about 3:2 to about 20:1; about 3:2 to about 30:1; about 3:2 to about 40:1; about 3:2 to about 60:1; about 3:2 to about 80:1; about 3:2 to about 100:1; about 3:2 to about 200:1; about 3:2 to about 500:1; about 3:2 to about 1000:1; about 3:2 to greater than 1000:1; about 10:1 to about 30:1; about 80:1 to about 100:1; about 20:1 to about 100:1; about 20:1 to about 500:1; about 20:1 to about 1000:1. In some embodiments of the invention, the carbon to oxygen ratio is at least about 10:1, or at least about 20:1, or at least about 35:1, or at least about 50:1, or at least about 100:1, or at least about 200:1, or at least about 300:1, or at least about 400:1, or at least about 500:1, or at least about 750:1, or at least about 1000:1.

The carbon to oxygen ratio also includes all values and subvalues between these ranges.

The inks used in the present invention may optionally contain additional electrically conductive components other than the functionalized graphene sheets, such as metals (including metal alloys), conductive metal oxides, polymers, carbonaceous materials other than the high surface area functionalized graphene sheets, and metal-coated materials. These components can take a variety of forms, including particles, powders, flakes, foils, needles, etc.

Examples of metals include, but are not limited to silver, copper, aluminum, platinum, palladium, nickel, chromium, gold, bronze, and the like. Examples of metal oxides include antimony tin oxide and indium tin oxide and materials such as fillers coated with metal oxides. Metal and metal-oxide coated materials include, but are not limited to metal coated carbon and graphite fibers, metal coated glass fibers, metal coated glass beads, metal coated ceramic materials (such as beads), and the like. These materials can be coated with a variety of metals, including nickel.

Examples of electrically conductive polymers include, but are not limited to, polyacetylene, polypolyethylene dioxythiophene, polyaniline, polypyrrole, and the like.

Examples of carbonaceous materials other than the high surface area functionalized graphene sheets include, but are not limited to, carbon black, graphite, carbon nanotubes, vapor-grown carbon nanofibers, carbon fibers, metal coated carbon fibers.

Preferred binders are polymeric binders. Polymeric binders can be thermoplastics or thermosets and may be elastomers. Binders may also comprise monomers that can be polymerized before, during, or after the application of the ink to the substrate. Polymeric binders may be cross-linked or otherwise cured after the ink has been applied to the substrate. Examples of preferred polymeric binders include polyethylenes such as poly(ethylene oxide) (also known as poly[ethylene glycol]), poly(propylene oxide) (also known as poly[propylene glycol]), ethylene oxide/propylene oxide copolymers, cellulose resins (such as ethyl cellulose, ethyl hydroxyethyl cellulose, carboxymethyl cellulose, cellulose acetate, cellulose acetate propionates, and cellulose acetate butyrates), and poly(vinyl butyral), polyvinyl alcohol and its derivatives, ethylene/vinyl acetate polymers, acrylic polymers and copolymers, styrene/acrylic copolymers, styrene/maleic anhydride copolymers, isobutylene/maleic anhydride copolymers, vinyl acetate/ethylene copolymers, ethylene/ acrylic acid copolymers, polyolefins, polystyrenes, olefin and styrene copolymers, epoxy resins, acrylic latex polymers, polyester acrylate oligomers and polymers, polyester diacrylate polymers, UV-curable resins, and polyamides, including polyamide polymers and copolymers (i.e., polyamides having at least two different repeat units) having melting points between about 120 and 255°C (such as those sold under the trade names Macromelt by Henkel and Versamid by Cognis).

The inks may optionally comprise one or more carriers in which some or all of the components are dissolved, suspended, or otherwise dispersed or carried. Examples of suitable carriers include, but are not limited to, water, distilled or synthetic isoparaffinic hydrocarbons (such as Isoper© and Norpar© (both manufactured by Exxon) and Dowanol© (manufactured by Dow)), citrus terpenes and mixtures containing citrus terpenes (such as Purogen, Electron, and Postiron (all manufactured by Purogen)), limonene, aliphatic petroleum distillates, alcohols (such as methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, sec-butanol, tert-butanol, diacetone alcohol, butyl glycol, and the like), ketones (such as acetone, methyl ethyl ketone, cyclohexanone, i-butyl ketone, 2,6,8-trimethyl-4-nonanone and the like), esters (such as methyl acetate, ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, carbitol acetate, and the like), glycol ethers (such as propylene glycol monomethyl ether and other propylene glycol ethers, ethylene glycol monobutyl ether and other ethylene glycol ethers, ethylene and propylene glycol ether acetates), N-methyl-2-pyrrolidone, and mixtures of two or more of the foregoing and mixtures of one or more of the foregoing with other carriers. Preferred solvents include low- or non-VOC solvents, non-hazardous air pollution solvents, and non-halogenated solvents.

The inks may optionally comprise one or more additional additives, such as dispersion aids (including surfactants, emulsifiers, and wetting aids), adhesion promoters, thickening agents (including clays), defoamers and antifoamers, biocides, additional fillers, flow enhancers, stabilizers, cross-linking and curing agents, and the like. In one embodiment of the present invention, the surfactant is at least one ethylene oxide/propylene oxide copolymer.

The inks may also optionally comprise one or more prepolymers, oligomers, photo-initiators, and additional additives to allow for curing by UV, electron beam, or infra-red radiation.

Examples of dispersing aids include glycol ethers (such as poly(ethylene oxide)), block copolymers derived from ethylene oxide and propylene oxide (such as those sold under the trade name Pluronic© by BASF), acetylenic diols (such as 2,5,8,11-tetramethyl-6-dodecyn-5,8-diol ethoxylate and others sold by Air Products under the trade names Surfynol© and Dynol©), salts of carboxylic acids (including alkali metal and ammonium salts), and polysiloxanes.

Examples of grinding aids include stearates (such as Al, Cu, Mg, and Zn stearates) and acetylenic diols (such as those sold by Air Products under the trade names Surfynol© and Dynol©).

Examples of adhesion promoters include titanium chelates and other titanium compounds such as titanium phos-
phate complexes (including butyl titanium phosphate), titan-
ate esters, disopropoxy titanium bis(ethyl-3-oxobutanoate),
isoproxy titanium acetylactonate, and others sold by
Johnson-Matthey Catalysts under the trade name Vertec.

Examples of thickening agents include glycol ethers (such
as poly(ethylene oxide), block copolymers derived from
ethylene oxide and propylene oxide (such as those sold
under the trade name Pluronic® by BASF).

The inks are electrically conductive and preferably have
a conductivity of at least about \(10^{-8}\) S/cm. In one embodi-
ment of the invention, when components of the printed
electronic devices made from the inks are used as semicon-
ductors, they preferably have a conductivity of about \(10^{-8}\)
S/cm to about \(10^{-7}\) S/cm or preferably of about \(10^{-7}\)
S/cm to about \(10^{-6}\) S/cm. In another embodiment of the
invention, the inks preferably have a conductivity of at least
about \(10^{-6}\) S/cm, or more preferably at least about \(10^{-5}\) S/cm,
or yet more preferably at least about \(10^{-4}\) S/cm. The conduc-
tivities of the inks are determined after they have been
applied to the substrate and subjected to any post-application
treatments (such drying, curing, cross-linking, etc.).

The FGS are preferably present in the ink in at least about
0.01 weight percent based on the total weight of the ink. In
one embodiment of the invention, the FGS are preferably
present in the ink in at least about 0.01 weight percent, or
more preferably in at least about 0.05 weight percent, or yet
more preferably in at least about 0.1 weight percent, or still
more preferably in at least about 0.5 weight percent, or even
more preferably in at least about 1 weight percent, where the
weight percentages are based on the total weight of the ink
after it has been applied to the substrate and subjected to any
post-application treatments (such drying, curing, cross-link-
ing, etc.). However, as will be appreciated by those skilled
in the art, the amount of FGS present in the inks can be
selected based on the desired electrical conductivity and the
particular binders and other optional components chosen.

The inks preferably contain a sufficient amount of FGS
such that they have electrical conductivities that are greater
than those of the corresponding materials containing each
component of the ink in question except for the FGS.

The inks may be made using any suitable method, includ-
ing wet or dry methods and batch, semi-continuous, and
continuous methods.

For example, components of the inks, such as two or more
of the functionalized graphene sheets, binders, carriers,
and/or other components may be blended by using suitable
mixing, dispersing, and/or compounding techniques and
apparatus, including ultrasonic devices, high-shear mixers,
two-roll mills, three-roll mills, cryogenic grinding crushers,
extruders, kneaders, double planetary mixers, triple plan-
etary mixers, high pressure homogenizers, ball mills, attri-
 tion equipment, sandmills, and horizontal and vertical wet
grinding mills, and the like.

The resulting blends may be further processed using wet
dry grinding technologies. The technologies can be con-
tinuous or discontinuous. Examples include ball mills, attri-
tion equipment, sandmills, and horizontal and vertical wet
grinding mills. Suitable materials for use as grinding media
include metals, carbon steel, stainless steel, ceramics, sta-
bilized ceramic media (such as yttrium stabilized zirconium
oxide), PTFE, glass, tungsten carbide, and the like.

After blending and/or grinding steps, additional compo-
nents may be added to the inks, including, but not limited to,
thickening viscosity modifiers, and the like. The inks may
also be diluted by the addition of more carrier.

After they have been printed on a substrate, the inks may
be cured using any suitable technique, including drying and
oven-drying (in air or another inert or reactive atmosphere),
UV curing, IR curing, microwave curing or drying, and the
like.

The printed electronic devices of the present invention
take on a variety of forms. They may contain multiple
layers of electronic components (e.g. circuits) and/or sub-
strates. All or part of the printed layer(s) may be covered or
coated with another material such as a cover coat, varnish,
cover layer, cover films, dielectric coatings, electrolytes and
other electrically conductive materials, and the like. There
may also be one or more materials between the substrate and
printed circuits. Layers may include semiconductors, metal
foils, and dielectric materials.

The printed electronics may further comprise additional
components, such as processors, memory chips, other
microchips, batteries, resistors, diodes, capacitors, transis-
tors, and the like.

The printed electronic devices may take on a wide variety
of forms and be used in a large array of applications.

Examples include but are not limited to: passive and active
devices and components; electrical and electronic circuitry,
integrated circuits; flexible printed circuit boards; transis-
tors; field-effect transistors; microelectromechanical sys-
tems (MEMS) devices; microwave circuits; antennas; indi-
cators; chipless tags (e.g. for theft deterrence from stores,
libraries, and the like); smart cards; sensors; liquid crystal
display lines (LCDs); signage; lighting; flat panel displays;
flexible displays, including light-emitting diode, organic
light-emitting diode, and polymer light-emitting diode dis-
plays; backplanes and frontplanes for displays; electrolumi-
nescent and OLED lighting; photovoltaic devices—back-
planes; product identifying chips and devices; batteries,
including thin film batteries; electrodes; indicators; printed
circuits in portable electronic devices (for example, cellular
telephones, computers, personal digital assistants, global
positioning system devices, music players, games, calcula-
tors, and the like); electronic connections made through
hinges or other movable/bendable junctions in electronic
devices such as cellular telephones, portable computers,
folding keyboards, and the like); wearable electronics; and
circuits in vehicles, medical devices, diagnostic devices,
instruments, and the like.

Preferred electronic devices are radiofrequency identifi-
cation (RFID) devices and/or components thereof and/or
radiofrequency communication device. Examples include,
but are not limited to, RFID tags, chips, and antennas. The
RFID devices may be ultrahigh frequency RFID devices,
which typically operate at frequencies in the range of about
868 to about 928 MHz. Examples of uses for RFIDs are for
tracking shipping containers, products in stores, products in
transit, and parts used in manufacturing processes; pass-
ports; barcode replacement applications; inventory control
applications; pet identification; livestock control; contactless
smart cards; automobile key fobs; and the like.

EXAMPLES

General Details for Examples 1-3 and Comparative Example

Graphite oxide is prepared from graphite by treatment
with sulfuric acid, nitric acid, and potassium chloride and
then thermally exfoliated to form FGS according to the
Chem. B. 2006, 110, 8535-8539 (and its Supporting Infor-
mation) and McAllister, M. J. et al. Chem. Materials 2007
19 4396-4404.
Example 1

An ink is prepared as described above using PEO having a molecular weight of 4,000,000. The ink is printed electrohydrodynamically onto a glass substrate using the method disclosed in WO 2007/053621. The printing is done at a flow rate of 0.5 mL/hr under a 2200 kV potential difference between electrodes that are 7.2 mm apart. The width of the lines is about 140 µm and the thickness is about 300 nm. The printed line has an electrical conductivity of about 19.6 S/m.

Example 2

An ink is prepared as described above using PEO having a molecular weight of 4,000,000. The ink is printed electrohydrodynamically onto a glass substrate using the method disclosed in WO 2007/053621. The printing is done at a flow rate of 0.5 mL/hr under a 2200 kV potential difference between electrodes that are 7.2 mm apart. The width of the lines is about 130 µm.

Comparative Example 1

An ink is prepared as described above substituting carbon black (supplied by Cabot Corp.) for the FGS and using PEO having a molecular weight of 300,000. The ink is printed electrohydrodynamically onto a glass substrate using the method disclosed in WO 2007/053621. The printing is done at a flow rate of 0.5 mL/hr under a 2200 kV potential difference between electrodes that are 7.2 mm apart. The width of the lines is about 130 µm.

Example 3

An ink is prepared as described above using PEO having a molecular weight of 4,000,000. The ink is printed electrohydrodynamically onto a glass substrate using the method disclosed in WO 2007/053621. The printing is done at a flow rate of 0.5 mL/hr under a 2200 kV potential difference between electrodes that are 7.2 mm apart. The width of the lines is about 140 µm and the thickness is about 300 nm. The printed line has an electrical conductivity of about 19.6 S/m.

General Details for Examples 4-14:

Preparation of Test Samples

The inks in the form of liquid dispersions are printed onto a substrate using a doctor blade and then dried in air in an oven at 125°C. to form a film. Testing is done on the printed films.

Electrical Conductivity

The point-to-point resistivity (in ohms) of the films is measured using a standard multimeter across contact points consisting of two spots of silver paste having a diameter of about 0.3 mm that are applied to the surface of the film about 1 inch apart. The resistance across these points is also measured using a standard multimeter and the reading is divided by 10 to calculate the resistivity in ohms/square. Results given as a single number are an average of several measurements and results given as a range of figures indicate the high and low readings from several measurements.

Peel Resistance

A fingernail is drawn back and forth across the surface of the film five times. The surface of the film where it was scratched and the tip of the nail are examined and the scratch resistance of the film is assessed as follows: excellent is no noticeable transfer of the film surface to the nail; very good is minimal transfer and no noticeable indentation on the surface of the film; good is some indentation of the film surface; fair is removal of a substantial portion of the film; and poor is where the substrate is visible. In some cases no cohesive film adhered to the substrate is formed.

Scratch Resistance

A fingernail is drawn across the surface of the film. The film and tip of the nail are visually inspected. The scratch resistance is graded as follows: no transfer of film material to the fingernail=excellent; about 10 percent transfer=very good; about 20 percent transfer=good; about 30 percent transfer=fair; about 40 percent transfer=fair/good; about 50 percent transfer=fair/very good; about 65 percent transfer=poor; about 85 percent transfer=poor; and about 100 percent transfer (the substrate is fully visible and very little to no printed material remains)=very poor.
Ink Preparation Methods

Ball mill A: An Eiger Mini 250 Type M250-VSE-TEFV horizontal grinding mill

Ball mill B: A vertical stainless steel vertical grinding mill having four stainless steel arms situated 90° away from each other. The mill is driven by a compressed air motor and has a bottom discharge valve.

High shear mixer: A homogenizer having a roto-stator overhead stirrer.

Ingredients used in the Formulations:

Electron and Positron are citrus terpene-based solvents supplied by Ecolink, Tucker Ga.

Example 4

A 4.9 weight percent aqueous solution of poly(ethylene oxide) (PEO) having an average molecular weight of 600, 000 (236.2 g) is combined with FGS having a C-O ratio of approximately 100:1 (2.4 g), ethylene oxide/propylene oxide copolymer surfactant (Pluronic F127, supplied by BASF) (2.4 g), antifoaming agent (AF 204, supplied by Sigma) (0.3 g), and water (50 g). The mixture is ground in ball mill B at 650 rpm using %60 stainless steel balls as a grinding medium for 6 hours. The resulting dispersion is printed onto thermally stabilized PET, coated paper, and uncoated paper and the adhesion properties and electrically resistivity of the resulting printed films are measured. The results are given in Table 1.

Example 5

A 10.8 weight percent aqueous solution of poly(ethylene oxide) (PEO) having an average molecular weight of 600, 000 (110.8 g) is combined with FGS having a C-O ratio of approximately 100:1 (2.4 g), surfactant (Surfynol 104H, supplied by Air Products) (2.4 g), antifoaming agent (AF 204, supplied by Sigma) (0.3 g), and water (134.2 g). The mixture is ground in ball mill B at 693 rpm using %60 stainless steel balls as a grinding medium for 6 hours. The resulting dispersion is printed onto thermally stabilized PET, coated paper, and uncoated paper and the adhesion properties and electrically resistivity of the resulting printed films are measured. The results are given in Table 1.

TABLE 1

<table>
<thead>
<tr>
<th>Additive</th>
<th>Peel resistance</th>
<th>Resistivity (Ω/sq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 6</td>
<td>none</td>
<td>Excellent</td>
</tr>
<tr>
<td>Example 7</td>
<td>BYK</td>
<td>Very good</td>
</tr>
<tr>
<td>Example 8</td>
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<td>Excellent</td>
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<td>Example 9</td>
<td>PANI</td>
<td>Excellent</td>
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<tr>
<td>Example 10</td>
<td>BYK</td>
<td>Excellent</td>
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<tr>
<td>Example 11</td>
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<td>Excellent</td>
</tr>
<tr>
<td>Example 12</td>
<td>PANI</td>
<td>Good</td>
</tr>
</tbody>
</table>

The invention claimed is:

1. A combination, comprising:
   - an electronic device comprising a hinge or a bendable junction;
   - a printed electronic device traversing the hinge or the bendable junction, the printed electronic device comprising:
     - an electronic conductive ink applied to the surface and comprising functionalized graphene sheets and a binder; and
     - wherein the functionalized graphene sheets completely comprise fully exfoliated single sheets of graphene; and
   - comprise at least one of an X-ray or electron diffraction pattern that displays little or no signature corresponding to graphite or graphite oxide.

Examples 6-12

In the case of Examples 6-10, a 20 weight percent solution of polyamide binder (Versamid 750, supplied by Cognis) in isopropyl alcohol (200 g) is combined with FGS having a C-O ratio of approximately 100:1 (10 g) and additional isopropyl alcohol (40 g). In the case of Examples 18 and 19, a 20 weight percent solution of polyamide binder (Versamid 750, supplied by Cognis) in isopropyl alcohol (70 g) is combined with FGS having a C-O ratio of approximately 100:1 (6 g) and additional isopropyl alcohol (124 g).

In all cases, the resulting suspensions are ground for 1.5 hours at 100°F in ball mill A at 5000 rpm for 1.5 hours using 0.3 mm 5% yttrium stabilized zirconium oxide as the grinding medium. In the cases of Examples 7 and 10, BYK-ES80 (an alkylammonium salt of an unsaturated acidic carboxylic acid ester supplied by BYK USA, Wallingford, Conn.) (0.2 g) is added to 10 g of the resulting dispersion. In the cases of Examples 9 and 12, a 10 weight percent solution of polyaniline (PANI) (Panipol F, supplied by Panipol Oy, Porvoo, Finland) in chloroform (2 g) is added to 10 g of the resulting dispersion. After each of these additives is added, the resulting mixture is blended for about a minute in the high shear mixer. In each case the resulting dispersion is printed onto thermally stabilized PET and the adhesion properties and electrical resistivity of the printed films are measured. The results are given in Table 2.
6. The combination of claim 1, wherein the electrically conductive ink further comprises a metal-coated material comprising one or more of a glass fiber, a glass bead, and a ceramic material.

7. The combination of claim 1, wherein the functionalized graphene sheets comprise a molar carbon-to-oxygen molar ratio of at least 100:1.

8. The combination of claim 1, wherein the printed electronic further comprises a material positioned over the electrically conductive ink; and the material comprises one or more of a dielectric coating or an electrolyte.

9. The combination of claim 1, wherein the printed electronic device further comprises a material positioned between the electrically conductive ink and the substrate; and the material comprises one or more of a semiconductor, a metal foil, and a dielectric material.

10. The combination of claim 1, wherein the printed electronic device is in the form of a printed circuit board.

11. The combination of claim 1, wherein the printed electronic device is in the form of a transistor.

12. The combination of claim 1, wherein the printed electronic device is in the form of a field-effect transistor.

13. The combination of claim 1, wherein the printed electronic device is in the form of a microelectromechanical system device.

14. A method to fabricate a combination, comprising: exfoliating graphite to form functionalized graphene sheets, the functionalized graphene sheets completely consisting of fully exfoliated single sheets; and forming at least one of an X-ray or electron diffraction pattern that displays little or no signature corresponding to graphite or graphite oxide; forming an electrically conductive ink by combining the functionalized graphene sheets and a binder; printing the electrically conductive ink on to a surface of a substrate thereby forming a printed electronic device, the electrically conductive ink is printed as a conductive pathway; and applying the printed electronic device to one of a hinge or a bendable junction of an electronic device, the printed electronic device traversing the hinge or the bendable junction of the electronic device.

15. The method of claim 14, wherein the printed electronic device is one of a complete device, a sub-element of a device, and an electronic component.

16. The method of claim 14, further comprising applying a material between the substrate and the electrically conductive ink, the material comprising one or more of a semiconductor, a metal foil, and a dielectric material.

17. The method of claim 14, further comprising applying a material between the substrate and the electrically conductive ink, the material comprising one or more of a semiconductor, a metal foil, and a dielectric material.

18. The method of claim 14, further comprising applying a material on to the electrically conductive ink, the material comprising one or more of an dielectric coating or an electrolyte.

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