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. 14/189,501, filed on Feb. 25, 2014, now Pat. No. 9,107,312, which is a continuation 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.

(51) Int. Cl.
C09C 1/46 (2006.01)
C09D 11/037 (2014.01)
C09D 11/52 (2014.01)
C09D 17/02 (2006.01)
C09D 17/700 (2006.01)
C09D 7/12 (2006.01)
H05K 3/00 (2006.01)
C09D 11/102 (2014.01)
C08K 3/04 (2006.01)
B82Y 30/00 (2011.01)
B82Y 40/00 (2011.01)

(52) U.S. Cl.
CPC .......... C09D 11/037 (2013.01); C09D 11/102 (2013.01); C09D 11/52 (2013.01); C09D 17/02 (2013.01); C09D 17/700 (2013.01); H05K 1/092 (2013.01); H05K 3/0091 (2013.01); H05K 3/12 (2013.01); B82Y 30/00 (2013.01); B82Y 40/00 (2013.01); C01P 2004/02 (2013.01); C01P 2006/12 (2013.01); C01P 2006/40 (2013.01); C08K 3/04 (2013.01); H01L 29/24/0002 (2013.01); H05K 220/0323 (2013.01); Y10S 977/734 (2013.01); Y10S 977/847 (2013.01); Y10S 977/932 (2013.01)

(58) Field of Classification Search
CPC .......... H05K 3/0091; H05K 220/0323; H05K 1/092; Y10S 977/721; Y10S 977/742; Y10S 977/734; Y10S 977/847; Y10S 977/932; Y10S 977/842; C09D 11/52; C09D 11/037; C09D 11/102; C09D 17/700; C09D 17/1/02; C09D 7/1291; C08K 3/04; C09C 1/46; B82Y 40/00; B82Y 30/00; C01P 2004/02; C01P 2006/12; C01P 2006/40

See application file for complete search history.

References Cited

U.S. PATENT DOCUMENTS
7,763,187 B1 7/2010 Veedu et al.
8,105,376 B2 1/2012 Prud’Homme et al.
8,110,026 B2 2/2012 Prud’Homme et al.
8,110,524 B2 2/2012 Prud’Homme et al.
8,192,870 B2 6/2012 Aksay et al.
8,278,757 B2 10/2012 Crain et al.
2008/008822 A1 1/2008 Kowalski et al.

FOREIGN PATENT DOCUMENTS

OTHER PUBLICATIONS
Communication pursuant to Article 94(3) EPC dated May 28, 2014, in European Patent Application No. 09700241.5.

* cited by examiner
The present invention relates to printed electronic devices and methods for their manufacture.

FIELD OF THE INVENTION

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 circuits on a substrate and then applying 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., polyethylene), 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.

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 conductive pathway designed to achieve the desired electronic device. The pathway may be solid, mostly solid, in a liquid
or gel form, and the like. The ink may further optionally comprise a carrier other than a binder. When the ink has been applied to the substrate, all or part of the carrier may be removed to form the electrically conductive pathway. The binder may be cured or cross-linked after the ink has been applied to the substrate.

The printed electronic device formed from the application of the ink to the substrate may be optionally sintered or otherwise cured, which can result in the formation of direct bonds between the conducting particles and thus increase the number of conduction paths. In one embodiment of the invention, all or a portion of the device formed from the ink is not sintered and/or not otherwise cured.

To prepare the printed electronic device, the ink may be applied to the substrate using any suitable method, including, but not limited to, by syringe, spray coating, electrospray deposition, ink-jet printing, spin coating, thermal transfer (including laser transfer) methods, screen printing, rotary screen printing, gravure printing, capillary printing, offset printing, electrophotographic printing, ink-jet printing, laser printing, and the like.

The substrate may be any suitable material, including, for example, polymers, including thermoplastic and thermoset polymers; pulp products such as paper and cardboard (including coated and uncoated materials); synthetic papers; fabrics (including cloths) and textiles; metals; woods; glass and other minerals; silicon and other semiconductors; ceramics; laminates made from a variety of materials; and the like.

The substrate used in the present invention preferably have a surface area from about 300 to about 2630 m²/g, preferably from about 400 to about 2400 m²/g, more preferably from about 500 to about 2400 m²/g, and even more preferably from about 600 to about 2400 m²/g. A single graphite sheet has a maximum calculated surface area of 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 $A_{\text{max}}=298$ 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 m² 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/m³. The bulk density includes all values and subvalues therebetween, especially including 0.5, 1, 5, 10, 15, 20, 25, 30, 35 kg/m³.

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 75:1, or at least about 100:1, or at least about 200:1, 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, polyethylene dioxythiophene, polyaniline, polypyrrole, and the like. Examples of electrically conductive polymers include, but are not limited to, polyacetylene, polyethylene dioxythiophene, polyaniline, polypyrrole, and the like. 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.

Preferred binders are polymeric binders. Polymeric binders can be thermoplastic 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 can 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), polyethylene oxides with acetylene diols, ethylene oxide-propylene oxide copolymers, cellulose resins (such as cellulose, 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, polylefins, polystyrenes, olefin and styrene copolymers, epoxy resins, acrylate latex polymers, polyster acrylate oligomers and polymers, polyster diacrylate polymers, UV-curable resins, and polyamide, 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 Isopar® 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, diaeetone 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-pyrroldione, 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 anti-foamers, 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 Surlyn® and Dyno®), salts of carboxylic acids (including alkali metal and ammonium salts), and polysiloxanes.

Examples of grinding aids include stearates (such as Al, Ca, Mg, and Zn stearates) and acetylenic diols (such as those sold by Air Products under the trade names Surrlyn® and Dyno®).

Examples of adhesion promoters include titanium chelates and other titanium compounds such as titanium phosphate complexes (including butyl titanium phosphate), titanate esters, diisopropoxy titanium bis(ethyl-3-oxobutanoate),...
isopropoxy titanium acetylacetonate, 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 Phuronic® by BASF).

The inks are electrically conductive and preferably have a conductivity of at least about 10^{-3} S/cm. In one embodiment of the invention, when components of the printed electronic devices made from the inks are used as semiconductors, they preferably have a conductivity of about 10^{-3} S/cm to about 10^{-2} S/cm, or more preferably of about 10^{-2} S/cm to about 10^{-1} S/cm. In another embodiment of the invention, the inks preferably have a conductivity of at least about 10^{-1} S/cm or more preferably at least about 10^{-2} S/cm, or yet more preferably at least about 10^{-3} S/cm. The conductivity 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.). 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 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-linking, 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, including 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 planetary mixers, high pressure homogenizers, ball mills, attrition equipment, sandmills, and horizontal and vertical wet grinding mills, and the like.

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

After blending and/or grinding steps, additional components may be added to the inks, including, but not limited to, thickeners, 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 may take on a variety of forms. They may contain multiple layers of electronic components (e.g. circuits) and/or substrates. All or part of the printed layer(s) may be covered 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, transistors, 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; transistors; field-effect transistors; micromechanical systems (MEMS) devices; microwave circuits; antennas; indicators; chipless tags (e.g. for theft deterrence from stores, libraries, and the like); smart cards; sensors; liquid crystal displays (LCDs); signage; lighting; flat panel displays; flexible displays, including light-emitting diode, organic light-emitting diode, and polymer light-emitting diode displays; backplanes and frontplanes for displays; electroluminescent and OLED lighting; photovoltaic devices—backplanes; 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, calculators, 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 identification (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 RFID devices are for tracking shipping containers, products in stores, products in transit, and parts used in manufacturing processes; passports; 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 1

Graphite oxide is prepared from graphite by treatment with sulfuric acid, nitric acid, and potassium chlorate and then thermally exfoliated to form FGS according to the methods disclosed in Staudenmaier, L. Ber. Schenk. Chem. Ges. 1898, 31, 1481 and Schiepp, H. C. et al. J. Phys.

The inks are prepared as follows. A poly(ethylene oxide) (PEO) solution is prepared by mixing a sufficient amount of PEO with a 1:1 volume/volume mixture of ethanol and de-ionized water to produce a mixture containing 40 mg of PEO per mL of total solvent. After stirring overnight, a homogeneous PEO stock solution is obtained.

FGS is weighed and a sufficient amount of concentrated aqueous Pluronic® F127 (an ethylene oxide/propylene oxide copolymer surfactant supplied by BASF) solution (typically 2 mg/mL) is added to the FGS to yield a mixture having a 1:1 weight ratio of FGS and Pluronic F127. Sufficient de-ionized water is added to produce a suspension containing 1 mg FGS per mL of water. The resulting suspension is sonicated for 5 minutes with a duty cycle of 20 percent in an ice bath. 1 mL of the FGS suspension is then added to 3 mL of the PEO stock solution and the mixture is stirred for 3-5 minutes until homogeneous.

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 µm. The measured conductivity is about 12.4 S/m.

As described above for Example 2, the ink is formed into a film and its electrical conductivity is measured. The result is about 1.3x10^{-6} S/m.

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.

As described above for Example 2, the ink is formed into a film and its electrical conductivity is measured. The result is about 1.3x10^{-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.

The printed line has an electrical conductivity of about 19.6 S/m.

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. The printed line has an electrical conductivity of about 19.6 S/m.

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; 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 kept at 50°C on a hot plate until all of the solvent is evaporated to form films that are attached to the copper plates.

Copper tapes are attached parallel to each other on two ends of the film such that they cover the entire width of the film. The electrical conductivity of the film is measured across the copper tapes as described above for Example 1. The measured conductivity is about 12.4 S/m. 
to the finger nail—excellent; about 10 percent transfer—very good; about 20 percent transfer—good/very good; about 30 percent transfer—good; about 40 percent transfer—fair/good; about 50 percent transfer—fair; about 65 percent transfer—poor/fair; 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 rotor-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 1/16 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 electrical 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 (Surlynol 1041I, supplied by Air Products) (2.4 g), antifoaming agent (AF 204, supplied by Sigma) (0.2 g), and water (134.2 g). The mixture is ground in ball mill B at 693 rpm using 1/16 stainless steel balls as a grinding medium for 1.5 hours. The resulting dispersion is printed onto thermally stabilized PET, coated paper, and uncoated paper and the adhesion properties and electrical resistivity of the resulting printed films are measured. The results are given in Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="" /></td>
</tr>
</tbody>
</table>

**TABLE 1**

<table>
<thead>
<tr>
<th>Thermally stabilized PET</th>
<th>Coated Paper</th>
<th>Uncoated paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peel resistivity (O/sq.)</td>
<td>Resistivity (O/sq.)</td>
<td>Resistivity (O/sq.)</td>
</tr>
<tr>
<td>Example 4</td>
<td>Good</td>
<td>5-10</td>
</tr>
<tr>
<td>Example 5</td>
<td>Fair/good</td>
<td>10</td>
</tr>
</tbody>
</table>

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 polyanide 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 3000 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 acrylic acid, provided 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 polyamic acid (PAM) (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.

**TABLE 2**

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

The invention claimed is:

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

2. The printed electronic device of claim 1, wherein the electrically conductive ink is a gel.

3. The printed electronic device of claim 1, wherein the printed electronic device is selected from the group consisting of: a complete device, a sub-element of a device, and an electronic component.

4. The printed electronic device of claim 1, further comprising a material applied between the substrate and the electrically conductive ink, wherein the material is selected from the group consisting of: a semiconductor, a metal foil, and a dielectric material.

5. The printed electronic device of claim 1, wherein the single sheets of graphene have a carbon to oxygen ratio of at least about 100:1.

6. The printed electronic device of claim 1, wherein the electrically conductive ink further comprises a metal-coated...
material, and wherein the metal-coated material comprises one or more of: a particle, a powder, flakes, a foil, and a needle.

7. The printed electronic device of claim 1, wherein the electrically conductive ink further comprises a metal-coated material, and wherein the metal-coated material is selected from the group consisting of: glass fibers, glass beads, and a ceramic material.

8. The printed electronic device of claim 1, wherein the electrically conductive ink comprises a width of about 130 µm.

9. The printed electronic device of claim 1, wherein the electrically conductive ink comprises a thickness of about 300 µm.

10. A method of forming a printed electronic device, comprising:
    applying an electrically conductive ink to a substrate;
    wherein the electrically conductive ink is applied as a conductive pathway;
    wherein the electrically conductive ink comprises functionalized graphene sheets and at least one binder;
    wherein the functionalized graphene sheets completely comprise fully exfoliated single sheets of graphene; and wherein the functionalized graphene sheets comprise an X-ray or electron diffraction pattern that displays little or no signature corresponding to graphite or graphite oxide.

11. The method of forming a printed electronic device of claim 10, wherein the step of applying the electrically conductive ink comprising applying the electrically conductive ink as gel.

12. The method of forming a printed electronic device of claim 10, wherein the printed electronic device is selected from the group consisting of: a complete device, a subelement of a device, and an electronic component.

13. The method of forming a printed electronic device of claim 10, further comprising applying a material to the substrate prior to the step of applying the electrically conductive ink, wherein the material is selected from the group consisting of: a semiconductor, a metal foil, and a dielectric material.

14. The method of forming a printed electronic device of claim 10, wherein the single sheets of graphene comprise a carbon to oxygen ratio of at least about 100:1.

15. The method of forming a printed electronic device of claim 10, wherein the electrically conductive ink further comprises a metal-coated material, and wherein the metal-coated material comprises one or more of: a particle, a powder, flakes, a foil, and a needle.

16. The method of forming a printed electronic device of claim 10, wherein the electrically conductive ink further comprises a metal-coated material, and wherein the metal-coated material is selected from the group consisting of: glass fibers, glass beads, and a ceramic material.

17. The method of forming a printed electronic device of claim 10, wherein the step of applying the electrically conductive ink comprises applying the electrically conductive ink at a width of about 130 µm.

18. The method of forming a printed electronic device of claim 10, wherein the step of applying the electrically conductive ink comprises applying the electrically conductive ink at a thickness of about 300 nm.