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(54) Title: GRAPHENE-BASED SENSOR

(57) Abstract: The present invention relates to a textile-based sensor which incorporates graphene into the fibre. The graphene is incorporated by a dyeing process in which a liquid composition containing the graphene is contacted with the fibre. The present invention thus also relates to a process for the preparation of a graphene-based yarn and the use of the resulting yarn in a variety of sensing applications. The graphene-based yarns of the invention may be derived from naturally occurring materials such as cotton or may be based on synthetic materials such as polyester, nylon, viscose, etc., or may be a blend of natural and synthetic materials. The present invention also relates to a screen-printed textile or a porous material, such as paper, printed on its surface with a 2D material such as graphene. This printed textile (fabric) has the 2D material incorporated by a screen-printing process in which a liquid or paste composition containing the 2D material is contacted with the textile or paper substrate. The present invention thus also relates to a process for the preparation of a graphene-or other 2D material-printed substrate and the use of the resulting printed substrate in a variety of applications such as wearable technology. The textiles of the invention may be derived from naturally occurring materials such as cotton or may be based on synthetic materials such as polyester, nylon, viscose, etc., or may be a blend of natural and synthetic materials.

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Graphene-based Sensor

Introduction

The present invention relates to a textile-based sensor which incorporates graphene into the fibre. The graphene is incorporated by a dyeing process in which a liquid composition containing the graphene is contacted with the fibre. The present invention thus also relates to a process for the preparation of a graphene-based yarn and the use of the resulting yarn in a variety of sensing applications. The graphene-based yarns of the invention may be derived from naturally occurring materials such as cotton or may be based on synthetic materials such as polyester, nylon, viscose, etc., or may be a blend of natural and synthetic materials.

Background of the Invention

The sensing applications of the present invention depend on the electronic properties of graphene and its ability to conduct electricity. Graphene is a two-dimensional allotrope of carbon in which a planar sheet of SP^2 hybridised carbon atoms is arranged in a honeycomb pattern of tessellated hexagons. Essentially graphene is a single layer of graphite though the term graphene is frequently used to describe materials having up to ten atomic layers, i.e. sheets of carbon. Graphene is a semi-metal with a high room temperature charge carrier mobility. It is stable in ambient conditions and its electronic properties can be controlled through application of an electric field as with traditional silicone transistors (K S Novoselov, A K Geim, S V Morozov, D Jiang, Y Zhang, S V Dubonos, I V Grigorieva and A A Firsov, “Electric Field Effect in Atomically Thin Carbon Films”, Science, vol. 306, no. 5696, pp. 666-669, **2004**). Individual atomic planes of graphite, i.e. graphene can be extracted from various bulk crystals by a variety of methods. The electrical conductivity of graphene stands out amongst materials since it is millions of times larger than that of copper and the material has a very high thermal conductivity.

The advent of graphene and subsequent discovery of its multitude of superior properties has led to the identification of many other two-dimensional crystals through both chemical modification of graphene to produce graphene derivatives and from the exfoliation of other layered compounds. Other two-dimensional materials which have been isolated include $NbSe_2$, bismuth, strontium, calcium, copper oxide (BSCCO), h-BN, WS_2 and MoS_2. These materials are also stable and can exhibit complimentary electronic properties to graphene, such as being insulators, semiconductors or superconductors.

Sheets of such two-dimensional materials are frequently referred to as nanosheets. These nanosheets of inorganic two-dimensional materials can be used either alone or in combination with other such materials to form ultra-thin electronic devices with a range of interesting properties. For example, BN and MoS_2 have been used in conjunction with graphene to form quantum tunnelling transistor heterostructures (WO 2012/127245) while MoS_2 and WS_2 have been used in conjunction with graphene to form photovoltaic heterostructures (WO 2013/140181). Graphene has also been incorporated in verticle heterostructures in combination with an insulating material such as BN and a semiconductor material such as TMDC to produce LEDs having a very high quantum efficiency and/or which are capable of emitting a broader range of visible radiation (PCT/GB2015/051784).

Numerous methods are available for the production of graphene and other 2D materials. The literature describes an enormous variety of methods for obtaining 2D materials. Liquid-phase exfoliation is a scalable approach for the production of nanosheets of two-dimensional crystals, based on exfoliation of their bulk counterparts via chemical wet dispersion followed by ultra-sonication. This technique offers many advantages in terms of cost reduction, scalability and compatibility with any substrate, including cheap and flexible substrates. Currently this process generally uses organic solvents such as N-methylpyrrolidone (NMP) and N,N-dimethylformamide (DMF) although these materials are toxic and have high boiling points.

Conductive yarns have been described previously. For example, US 6,497,951 describes electrically conductive yarns which provide a resistance which is variable with temperature. These conductive elements have been used as heating elements in textiles such as knit or woven fabrics. The electrically conductive elements were incorporated into the textile and electricity is passed through the conductive elements to allow heating. In this document, distinct electrical conductors are intermixed with a thermal expansive low conductive matrix which is then used to encapsulate the yarn core. The conductive material and yarn core is itself encapsulated within an insulator layer such that the arrangement is effectively a circular laminate structure similar to the cross section of onion rings with the yarn at its centre.

US 6,713,733 also describes a flexible heater made from electrically conductive threads or fibres as the heating media. The conductive fibres are encapsulated by negative temperature coefficient material which is able to form temperature sensing heating cables. The heater may contain continuous positive temperature coefficient temperature sensors to precisely control the temperature in the heater. The temperature sensors are made of electrically conductive fibres, metal wires or fibre optical filaments. These fibres are

intended to be incorporated into a material such as an electric heating blanket. The threads or fibres may contain carbon or graphite. The negative temperature coefficient sensing means is disclosed as being a polymeric material.

Kahng et al describe the strain and temperature response of multi-walled carbon nanotube yarns on a stainless steel test beam. This is a NASA conference paper and can be accessed from a Technical Report Server. The following link has all the information about publication date and the conference details for the Khang article: http://ntrs.nasa.gov/search.jsp?R=20080040160. In this disclosure, carbon nanotube yarns of approximately 10 nm diameter were drawn from a carbon nanotube forest on a silicon substrate and twisted to produce a single yarn. The strain was then tested for the resulting yarn by electrical measurements. The authors noted that the glass transition temperature of the base composite material needed to be improved to higher values in order to have any suitability for practical use.

Numerous processes are described for treating fibres such as cellulosic fibres to impart a variety of performance characteristics such as shrinkage resistance. This may involve treating the fabric with a chemical composition. In the case of a cross-linkable polymer such as cellulose, the fabric may then be heated to bring about cross-linking of the cellulose polymer molecules within the textile. For example, US 4,820,307 describes catalysts for the rapid esterification and cross-linking of fibrous cellulose in textile using polycarboxylic acids. The cross-linking process is effected by reacting a polycarboxylic acid, such as citric acid, at elevated temperatures in the presence of catalysts which are acidic or weakly basic salts. This process normally involves elevated temperatures of over 150ºC, however.

There are two types of products used to colour textile materials: dyes and pigments. Dyes are water-soluble compounds and can be divided into a number of different classes such as direct, reactive, sulphur-based, indigo, basic or acidic. The benefit of using a dye is that it penetrates the fibre itself. However, using dyes requires additional rinsing steps, which result in highly polluted water with residual dyes and the process also suffers the disadvantage that it requires considerable amounts of water and energy as well as taking a long time. In contrast, pigments are chemically inert and are not soluble in water or in most of the usual solvents used in a colouring process. Consequently, pigments cannot penetrate into the fibre itself in the same manner as a dye can but these remain on the surface of the fibre.

In an alternative process US 5,447,537 describes a polymerisation cross-linking treatment of cellulose-containing fabrics using unsaturated monomers having at least two carboxyl groups. The process utilises potassium persulfate as a free radical initiator and sodium

hypophosphite as the esterification catalyst. US 2016/0047087 describes a novel pigment dyeing method for textile materials.

Yun – Advanced Materials, 2013 discloses nylon, cotton and polyester yarns coated with uniform rGO. The yarn is first functionalised by dipping it into bovine serum albumin to form positive charges on the surface. This is an expensive reagent and is unsuited to large scale manufacture. The functionalised yarn is dipped into an aqueous GO solution where the negatively charged GO particles attach themselves uniformly to the surface of the yarn using a dyeing technique. The GO is reduced using HI in a low temperature vapour reduction step after attaching it to the yarn. The yarns disclosed within are shown to be electrically conductive but there is no discussion of thermal conductivity.

Shateri-Khalilabad – Carbohydrate Polymers, 2013 discloses GO nanosheets deposited onto cotton textiles through dipping and drying. The GO is then reduced to form rGO fabrics. Cotton fabric is dipped into a 0.05% GO dispersion, soaked for 30 mins and dried for 30 mins at 90°C. These fabrics were then reduced using $NaBH_4$, hydrazine, ascorbic acid, $Na_2S_2O_4$ and NaOH. This is a two-step process which also requires a number of washing steps. There is a discussion of electrical conductivity but not thermal conductivity. One significant difference between this document and the present invention resides in the reduction of graphene oxide in the present invention before applying to the yarn.

Fugetsu et al, ScienceDirect, 2010 discusses adding GO to acrylic yarns using a dyeing approach. The fabrics consist of polyarylate yarns and were soaked in a 0.3% GO solution at pH of 2.13 (liquor ration 100:1) at ~ 23°C. The fabrics were dried and then immersed in a solution of 0.5% sodium hydrosulfate for 30 mins at 90°C to reduce the graphene oxide. The fabrics are then air dried. The fabrics are described as being electrically conductive but there is no discussion of the use as a temperature sensor. There is also a significant difference between this document and the present invention in that the GO is added to a fabric sheet rather than a yarn. The dyeing time is lengthy and it is unlikely that the process could be commercially feasible.

CN103966844 discloses the formation of conductive graphene fibres. Various textiles are listed as possible fibre materials, including nylon, cotton and polyester. The method of preparing the fibres includes the following steps: modifying the textile surface with a silane coupling agent. This process therefore requires an additional functionalisation step for the yarn before it is dyed. A graphene oxide dispersion is prepared using Hummers method and the GO is reduced before adding to the fibre with hydrazine hydrate. The rGO concentration is 5% in the dispersion. The fibre is then soaked into the rGO dispersion to coat it with the rGO. The document outlines that the fibres show good electrical conductivity and exemplifies the preparation of a cotton fibre graphene composite material.

CN103046151 discloses a different method to the present invention but and involves the formation of a regenerated cellulose fibre which is treated with reduced graphene oxide. The method of making the fibre includes the steps: mixing together a graphene oxide dispersion made by the Hummers method and a solution of regenerated cellulose fibres and spinning the solution to give and intermediate graphene oxide cellulose fibre blend. The cellulose fibre is then regenerated and the graphene oxide is reduced using hydrazine hydrate. There is no disclosure of how well the graphene oxide is adhered to the cellulose fibres in this process.

None of the above prior art documents appear to disclose the use of a graphene based yarn as a temperature sensor.

It is an aim of the invention to provide a process for incorporating a 2D material such as reduced graphene oxide or a graphene derivative or another 2D material into a yarn in order to produce a yarn which is capable of conducting electricity. It is also an aim to produce a yarn whose electrical conductivity can be influenced by environmental factors such as, but not limited to, one or more of temperature, humidity, strain, and light. A further aim is to provide a reliable, repeatable, economical process for preparing a yarn incorporating a 2D material. Ideally, the resulting yarn should be durable in the sense that the 2D material is securely bound to the yarn so that it cannot be displaced by mechanical wear and tear. The yarn should also be resistant to washing with detergents. A further aim is therefore to provide a process which allows retention of the 2D material in the yarn over an extended period of time. This means that the initial properties of the yarn will not change substantially over time or degrade. Another aim is to produce a 2D material-containing yarn which can be incorporated into a garment or another textile material such as bedding and other linen products. A further aim is to provide a yarn which has uniform characteristics so that it can be used in a sensor. Another aim is to provide a yarn that can be used in a variety of sensor applications. It is also an aim of the invention to provide a sensor incorporating a yarn which includes a conducting and / or a semi-conducting yarn made according to the invention. Another aim is to provide a process which is relatively simple and convenient to scale up and is suitable for commercial manufacture. The further aim is to employ readily available and relatively inexpensive components in the process. A further aim is to provide a process which does not require lengthy processing steps, such as washing or a pre-functionalisation step. Ideally, the process the invention should be completed within a relatively short time frame.

The present invention satisfies some or all of the above aims.

According to the present invention, there is provided a process for preparing a yarn incorporating a two-dimensional material, the process comprising the steps of:

(a) providing a liquid composition comprising a two-dimensional material selected from a conducting 2D material and a semi-conducting 2D material;

(b) contacting the yarn with the liquid composition for a period of time; and

(c) drying the yarn.

In a second aspect of the present invention there is provided a yarn incorporating a 2D material. This 2D material-containing yarn is prepared according to the above process.

In certain cases, the two-dimensional material containing yarn of the present invention is physically distinct from equivalent materials produced in accordance with prior art methods because of the processing method. This is due to the intimate binding between the 2D material and the yarn.

The 2D material of the invention can be thought of being chemically inert with respect to the liquid composition used to apply it to the yarn. In this respect it is similar to a pigment used to dye a conventional textile. As mentioned above, pigments used for colouring textiles are chemically inert and are not soluble in water or in most of the usual solvents used in a colouring process. The incorporation of a 2D material such as graphene into a fibre can thus be considered to be analogous to the incorporation of a pigment into a fibre. The use of pigments involves a need for binders, generally of the thermoplastic elastomer type, and the use of fixing agents in order to ensure that the pigment remains associated with a yarn, i.e. the colour does not leach. Similar considerations apply to 2D materials since these do not penetrate the bulk of the yarn itself but may be thought of as being absorbed onto the surface of the yarn.

The 2D material may be retained in place either by electrostatic forces, hydrogen bonds or direct covalent bonding. In the context of the present invention, the term “incorporating” when describing a yarn incorporating a 2D material such as graphene means that the 2D material is associated with the yarn in the same way that a pigment can be thought of as being associated with a yarn; in other words, the 2D material is absorbed onto the yarn and is intimately bound to the yarn but does not form part of its bulk structure.

In the process of the present invention, a binder may be included in the liquid composition when preparing the yarn in order to effect efficient binding between the yarn and the 2D material. An alternative way of achieving the same result is to have a pre-treatment step for the yarn before it is contacted with the liquid composition containing the 2D material. The pre-treatment step may be chemical activation using a solution containing an activating agent or the pre-treatment step may be a surface treatment of the yarn such as a plasma treatment. Normally only one pre-treatment step would be needed although it is

possible that more than one pre-treatment step could be used and this could be a mixture of chemical activation and surface activation.

Plasma surface modification of polymeric material is well known and has been extensively investigated. Plasma is considered to be a partially ionized gas containing ions, electrons, and neutral particles produced by interaction of electromagnetic field with gas under appropriate pressure. The interaction of plasma with the surface of polymeric films changes their chemical and physical properties. It is the consequence of different processes such as oxidation, degradation, cross linking, and structural changes, which may occur in a thin superficial layer. An important feature of plasma treatment is that it affects only the surface of a material subjected to treatment, and a very thin near-surface layer with a thickness varying from 100 Å to several micrometers. The bulk of the polymer remains intact under these conditions, retaining the mechanical, physicochemical, and electro-physical properties of the original material. The treatment of polymers by different types of plasma (microwave, radio frequency, corona discharge) is often applied for modification of dyeability and printability, and water repellency. Plasma treatment on fibre and polymer surfaces results in the formation of new functional groups such as -OH, -C=O, -COOH which affect the fabric's wettability. Plasma treatment does not require the use of any solvent and the treatment can be effected in a short time. Plasma treatments have been widely used in the treatment of textiles and polymer fibres and the skilled person will appreciate how to pre-treat the yarns of the present invention using this technique.

This pre-treatment “activates” the yarn so that it is able to bind strongly with the 2D material. It is also possible to include both a pre-treatment step for the yarn and also a binder in the liquid composition. The liquid composition containing the 2D material may be referred to as an ink; certainly, in the case of reduced graphene oxide products which can be used are known as “graphene inks”.

In the case of non-cellulosic fibres, binders or polymers help to cross-link the 2-D material such as reduced graphene oxide onto textiles in the same manner as pigment printing. Thus, any binder or cross-linking agent that find utility in conventional textile printing processes for binding pigment to textile yarns can be used as a binder in the process of the present invention. Acrylic polymers (such as butadiene acrylates) will operate as suitable cross-linking agents; they perform the same function for pigment with fibres used in clothing products etc. The same is true of polyamides which can also function as cross-linkers.

An alternative method for activating the yarn relates to a pre-treatment by plasma treatment (surface modification) of textiles. This type of pre-treatment improves

absorbency of the 2-D material to the yarn. In other words, this improves the binding of the 2-D material to the yarn.

This intimate binding between the yarn and the 2D material results in novel physical properties for the yarn according to the invention. Thus, whilst it is the case that carbon products have been incorporated into yarns, such as those described above in the prior art section, it is nevertheless the case that the yarn produced according to the process of the present invention is physically distinct. In this regard, one very interesting property of the yarns of the present invention resides in the negative temperature coefficient of the yarn. In addition, the yarn is very sensitive to relatively small changes in environmental factors such as temperature and strain. This means that the yarn is suitable for making a sensor which has a good degree of accuracy and a high resolution.

The strong binding of the 2-D material to the yarn means that the yarn is also stable over a period of time so that the performance is reliable and repeatable. It also means that the yarn can be worn and washed over an extended period of time without degrading the properties. This has significant benefits when producing wearable technology such as gowns or jackets to be worn by patients or athletes or other users of wearable technology incorporating sensing devices.

The liquid compositions which contain the 2-D material may be aqueous compositions or may be formed from one or more non-aqueous solvents. Aqueous compositions are preferred. Aqueous compositions may include a small amount, for example up to 20%, of a non-aqueous solvent.

The liquid compositions which contain the 2D material, amongst other things, that are used in the preparation of the yarn by the process of the invention may be a commercially-available formulation containing the 2D material.

Bespoke liquid compositions may also be used as inks in the process of the present invention. For example, it is also possible to produce inks containing 2D materials following exfoliation of the nanosheets from suitable two-dimensional material precursors, i.e. from bulk crystals. These materials are frequently referred to as 2-D inks and such inks may be suitable for inkjet printing. We have found that, in certain cases, 2-D inks may also be used for dyeing yarns in order to produce yarns of the present invention. In order to be suitable, the ink needs to meet a number of performance criteria. For example, the viscosity of the ink must normally be in the range of around from 2 to 30 cPs. The surface tension should normally be in the range of 20 to 50 mN/M. The ink should also have a low rate of evaporation at ambient temperature in order to avoid any processing difficulties.

A bespoke liquid composition containing 2-D material may be prepared by the process described below. In this process,an ink formulation comprising a plurality of nanosheets of an inorganic material dispersed in an aqueous vehicle is prepared, the process comprising:

a) providing a source of the inorganic material (e.g. one or more multi-layered bulk particles of the inorganic material) in a first aqueous medium comprising a stabiliser;

b) subjecting the source of the inorganic material in the first aqueous medium to energy (e.g. sonic energy) to break up or exfoliate the source of the inorganic material to obtain an aqueous dispersion of nanosheets of the inorganic material in the first aqueous medium;

c) if the aqueous dispersion obtained in step b) above comprises some remaining source material that has not been converted into dispersed nanosheets, the method optionally further comprises the step of separating any residual source material from the dispersion;

d) optionally separating the dispersed nanosheets from the aqueous medium following step b) or step c) above and then redispersing the nanosheets in a further aqueous medium;

e) optionally separating the dispersed nanosheets from the aqueous medium following step d) above and then redispersing the nanosheets in a further aqueous medium one or more times;

f) separating the nanosheets from the aqueous medium in the dispersion formed in any one of steps (b), (c) (d) and (e) above; and

g) re-dispersing the nanosheets collected in step (f) in an aqueous vehicle comprising a surface tension modifier and a viscosity modifier to form the ink formulation.

The commercial liquid formulation i.e. the commercial ink which forms the basis for the liquid composition used in the process the invention, or the bespoke liquid composition which may also be used, may then be supplemented by the addition of a binder as necessary.

A bespoke ink formulation can be prepared as described above and this ink formulation may then comprise a plurality of nanosheets of an inorganic material in an aqueous vehicle,

wherein the nanosheets are associated with a stabiliser that renders the nanosheets dispersible within the aqueous vehicle and the aqueous vehicle further comprises at least one surface tension modifier and at least one viscosity modifier;

and wherein the mass ratio of inorganic material to stabilizer present in the formulation is greater than 3:1. Such an ink formulation will advantageously possess low levels of

stabiliser in the aqueous vehicle. The reason for this is that any excess stabiliser (e.g. in the liquid composition which may be an aqueous composition) may be detrimental because it could affect the mechanical and/or the electrical properties of the eventual yarn. It is therefore desirable to have liquid formulations in which the amount of excess stabiliser is as low as possible. Suitable stabilisers are known in the art.

The 2D material represents from 0.5% by weight to 25% by weight of the liquid composition, and more preferably from 1% to 15% or from 1 to 10% by weight of the liquid composition. In a most preferred embodiment, the liquid composition contains from 2% to 8% by weight of the 2D material. For reference, 1 weight percent of the 2D material in the liquid composition (dispersion) of the 2D material means 10mg/ml of the 2D material is present in the dispersion.

The liquid composition may comprise a binder. The reason for this is that commercial formulations may or may not contain the necessary binder already and/or the yarn may or may not have been pre-treated. If the yarn has been pre-treated before contact with the liquid formulation then a binder may be unnecessary. Normally it is preferable to include a binder in the liquid composition.

2-D materials which otherwise would have no affinity for fibres, can be fixed on to fibers in order to produce the yarns of the present invention using a variety of binding agents or binders. The choice of binder depends upon the properties required in the binding film (softness, elasticity, plasticity, solvent stability etc.). Binders are normally prepared by the copolymerization of different monomers and usually unsaturated monomers such as vinyl chloride, dichloroethene, acrylic acid, acrylonitrile, acrylic acid esters & ethers etc. are used. A commonly used binder in the pigment printing process is based on styrenebutadiene, styrene acrylate or vinyl acetate-acrylate co- polymer and such a binder can be used in the process of the present invention. The choice of binder will always depend upon the final fastness requirement for the 2-D material (which will ultimately affect the durability of the ultimate textile product). We have found that binders used in textile pigment printing are suitable binders for use in the present invention.

Binders are normally thus polymeric materials such as PVA and the like. PVA is a preferred binder. PSS and PVP may also be used. The binder may be a single material or maybe a mixture of materials such as PVA in combination with another polymer.

The binder represents from 0.5% by weight to 15% by weight of the liquid composition, and more preferably from 1% to 10% by weight of the liquid composition. In a most preferred embodiment, the liquid composition contains from 2% to 8% by weight of the binder. For reference, 1 weight percent of the binder in the liquid composition (dispersion) means that 10mg/ml of the binder is present in the dispersion.

The liquid composition used in the process of the invention may also include additional components such as one or more of stabilisers, dispersants, surfactants, antioxidants. The commercial ink formulation or the bespoke formulation may therefore be supplemented with one or more of these additional components as necessary.

Not all 2D materials serve as conductors of electricity. Only those 2D materials which are capable of conducting electricity can be used in the sensor application of the invention.

Reduced graphene oxide (rGO) contains a number of OH groups which are able to react with OH groups in cellulose fibre and this assists in the binding to the yarn. A cross-linking agent and/or binding agent can assist in this process. Other fibres such as viscose can be used in the invention by utilising an additive such as a cross/linker and/or binder and/or by pre-treatment of the yarn as discussed above. The analogy for this process may once again be found in the textile industry where colouring agents are bound to fibres.

Reduction of graphene oxide may also be achieved chemically or electrolytically. However, it is preferred that the method of reduction of graphene oxide is chemical i.e. using a chemical reducing agent in solution. Chemical reducing agents can be organic or inorganic, with organic reducing agents being preferred.

GO can be chemically reduced using a solution of a commercially available organic reducing agent. Ascorbic acid or hydrazine are commonly used examples of suitable reducing agents. Hydroiodic acid may also be used as a reducing agent. The reducing agent is dispersed in solution with various polymers such as PSS/PVA/PEDOT.PSS/PVP. The polymer may or may not be present; when present in solution the polymer is a conductive polymer. In some embodiments, it is preferable that the organic reducing agent is not hydrazine or a hydrazine-based compounds because these may be toxic. Ascorbic acid is a preferred reducing agent because it is safe, environmentally friendly and has low toxicity, whilst still being an effective[MnK1] reducing agent.

The resulting rGO dispersions are then washed in deionised water to remove residuals and the rGO powder is then dispersed in water at desired concentrations in order to formulate inks.

The process of the invention is effectively an in situ chemical reduction to produce rGO and then coating the textile yarn with rGO followed by drying. This provides a convenient one-pot type of process.

Whilst reduced graphene oxide (rGO) is the preferred 2D material for incorporation into a yarn, other conductive or semiconductor 2D materials may be used. Molybdenum disulphide (MoS_2) and tungsten disulphide (WS_2) are two such materials. The 2-D material may thus be any conductive or semi-conducting material. Reduced graphene oxide (rGO)

is preferred as the 2-D material. Reduced graphene oxide is a good 2-D material because it contains a number of hydroxyl and epoxy oxide functional groups and this facilitates binding to the yarn. This is especially true when the yarn is a material such as cellulose which has its own polar functional groups such as hydroxyl. In one embodiment, the 2-D material is not pristine graphene. Semiconducting 2D materials which are preferred thus specifically include MoS_2 and WS_2.

The liquid formulation comprises a plurality of flakes or nanoparticles (the two terms are used interchangeably in this context) dispersed throughout the liquid. In the preferred embodiment, the material is rGO which may be thought of as partially oxygenated graphene flakes. The individual flakes of 2-D material (such as rGO) may be a single atomic layer thick. However, it is possible to use flakes or nano particles of 2-D material which individually have from 2 to 10 atomic layers thick in the liquid composition. In practice, there will be a distribution of flakes throughout the solution which have different atomic or molecular thicknesses. On average, the flakes will be from 1 to 10 or from 2 to 10 layers in thickness in the liquid composition. As discussed below, in the case of certain 2-D materials the term “layer” may refer to a single atomic layer or a molecular layer may be, for example three atomic layers.

It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the 2-D material flakes have a diameter of less than 10 μm. It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the 2-D material flakes have a diameter of greater than 50 nm. It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the 2-D material flakes have a diameter of less than 5 μm. It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the 2-D material flakes have a diameter of greater than 100 nm. It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the 2-D material flakes have a diameter of less than 2 μm. It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the 2-D material flakes have a diameter of greater than 200 nm.

It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the 2-D material has a thickness of from 1 to 10 atomic layers or molecular layers as appropriate. In this regard, the reader’s attention is drawn to the fact that 2-D materials such as graphene are defined in terms of their individual atomic layers whereas 2-D materials such as MoS_2 and the like have a single layer which actually comprises three atomic layers and these are frequently referred to as molecular layers.

Thus in the case of a material such as MoS_2 the term "single layer" refers to a single molecular layer. It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the 2-D material has a thickness of from 1 to 5 atomic layers or molecular layers. Thus, it may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the 2-D material has a thickness of from 1 to 3 atomic or molecular layers. It may be that greater than 50% by weight (e.g. greater than 75% by weight, greater than 90% or greater than 98%) of the 2-D material has a thickness of from 2 to 5 atomic or molecular layers.

In the case in which yarns of produced where more than one 2D material is present, such as the light sensor described below, subsequent dyeing steps may be utilised to introduce different 2D materials to the yarn. Normally this would be in adjacent sections of the yarn so that there might be a region of yarn containing one 2-D material which is then in contact with a neighbouring region of yarn containing a different 2-D material. In this way, it is possible to create a yarn containing two or more regions of 2-D material in which any two neighbouring regions are based on different 2-D material.

A third aspect of the present invention provides the use of a two-dimensional material-containing yarn as a sensor. The yarn is produced according to the process of the present invention. As described above, the yarn produced according to the process of the invention and has unusual characteristic that it has a negative temperature coefficient when it incorporates reduced graphene oxide, i.e. as the temperature increases the resistance decreases. The fact that this yarn prepared in accordance with the present invention is distinguished from similar yarns arises as a result of this negative temperature coefficient in this instance.

The comparative example discussed below shows a similar yarn also incorporating graphene which has a positive temperature coefficient, i.e. as the temperature increases the resistance increases. Thus an important feature of the yarn of the present invention is the negative temperature coefficient.

The two-dimensional material containing yarn of the present invention is conductive and the negative temperature coefficient enables the yarn to be used in temperature sensing applications. However, the conductivity of the yarn is also influenced by other environmental factors such as strain, humidity, pressure, the chemical composition of the atmosphere around it, pH and concentration. Thus, the yarn may be used as a temperature sensor, a strain sensor, a humidity sensor, a pH sensor, a pressure sensor, a gas sensor or a concentration sensor. Other applications taking advantage of the change in conductivity of the yarn in response to environmental conditions may also become apparent.

The changes of the environmental properties to which the yarn of the present invention is able to respond can be detected both by wire i.e. as part of a hard-wired sensor circuit and wirelessly using appropriate RFID technology.

A sensor prepared from a yarn according to the present invention may include an electrical circuit; and a yarn produced according to the process of the invention described above. The yarn will be in electrical contact with the electrical circuit, optionally wherein an insulator of less than 100 μm thickness is present between the electrical circuit and the yarn, wherein the yarn is effective to alter the electrical properties of the circuit in response to environmental changes experienced by the yarn. Electrical contact in this context thus also includes the situation in which there is a thin insulation layer between the electrical circuit and yarn since the circuit will still be operable when a thin insulating layer is present. For the purposes of this aspect and others relating to the sensor, the sensor may be constructed with the electrical circuit being in direct electrical contact (i.e. electrical contact) with the yarn or it may be constructed using a thin insulation layer between the sensor and the yarn. The electrical insulator, when present, is usually less than 100 μm thick.

Any textile material may be used in the production of the yarn of the invention. The yarn may thus be based on natural fibres, on synthetic fibres, or on a blend of the two. Preferably the yarn is a natural fibre or a natural fibre blended with one or more other materials which can be natural or synthetic. Cotton is particularly preferred as a substrate for the two-dimensional material when forming the two-dimensional material containing yarn. However, cotton may be blended with polyester and/or viscose and/or polyamide according to the particular application. Silk may also be used as the natural fibre. Cellulose, wool, hemp and jute are also natural fibres that may be used in the production of the yarn of the invention. Polyester, polycotton, nylon and viscose are synthetic fibres that may be used in the production of the yarn of the invention.

One of the more interesting potential applications of the yarn of the invention is in wearable technology. The ability to incorporate a temperature and/or humidity sensor into a smart textile has numerous potential benefits in health and medical care applications. The temperature and/or humidity sensor yarns of the invention are intended for incorporation into smart textile products. This might include wearable garments such as underwear or shirts or in bed linen. These textiles will then be able to continuously monitor vital functions of patients. For example, a humidity sensor might be used to measure sweating or incontinence and a temperature sensor might be used to measure the temperature of a patient, or indeed the presence or absence of a patient in a bed.

One benefit of the yarns of the present invention, when incorporated into textile products, is expected to be the ability to be used in garments which, once soiled, can then be washed and reused without any major loss of performance. To date this has been a major problem in the prior art and the materials of the present invention represent a major step forwards in this area.

The two-dimensional material containing yarn of the present invention may be hard-wired to a suitable circuit for the purposes of providing a sensor output. Alternatively, it may be included as part of a radio frequency temperature sensor so that wireless interrogation and output from the sensor can be achieved.

The step of contacting the yarn with the liquid composition may be a method of dyeing. Any conventional method may be used for dyeing the yarn. Methods of particular interest include the pad mangle technique. In this process, the yarn is passed over a roller and into a bath containing a liquid composition of the 2D material and then fed under a submerged roller before exiting the bath and being fed between a pair of rollers which operate as a mangle. The yarn is maintained in a slight state of tension. This process is a continuous process. The process for producing the yarn of the present invention may be continuous or it may be a batch process. Thus, in another variant, the exhaust dyeing technique involves submerging a yarn, cone or hank or a yarn in some other form in a vessel containing a liquid composition comprising the two-dimensional material. In this technique, typically 10 ml of solution is used for each 1 g of yarn. Since this is a batch process it is often convenient to rotate or agitate the vessel, particularly if there is more than one cone or hank in the batch in order to mix the solution. The yarn is dipped, i.e. submerged in the solution in freeform or on a cone etc. and left for a period of time. The length of time only needs to be sufficient to wet the yarn with the liquid composition and may be as little as about 5 seconds or as long as 4 hours, or from 5 seconds to 60 minutes, and preferably, from 5 seconds to 30 minutes.

Another method of dyeing the yarn is dip coating. In this method the yarn is dropped or dipped into a vessel containing a liquid solution of the 2D material.

The liquid composition of the 2D material is normally aqueous based. However, the composition may include additional solvents and may include a mixture of solvents but not water, or it may be a solvent other than water. For practical purposes, an aqueous medium is preferred because this has a number of handling, environmental and cost advantages. The liquid composition may contain a number of further additives. For example, the composition may include a surfactant and/or a disbursement. The solution may also contain a cross-linking agent in order to facilitate binding between the 2D material and the fibre. The liquid composition may also contain a binder. It is important

that the 2D material binds to the fibre and the presence of a cross-linker and/or binder assists in this process. The cross-linker and/or binder serves to coat the yarn and facilitate binding of the 2D material to the yarn. However this material itself does not conduct.

In another aspect of the invention there is provided a yarn incorporating two or more 2D materials. In another aspect of the invention there is provided the use of a yarn containing two or more different two-dimensional materials. Thus, in one arrangement it is possible to have a section of yarn which includes a conductive material such as reduced graphene oxide adhered to the yarn followed by a discrete section in which a semiconducting 2D material is adhered to the yarn and which is in electrical contact with the region containing the conductive material and then an adjacent section in which another (the same or different) conducting two-dimensional material is adhered to the yarn so as to form a linear series of conducting material/semiconducting material/conducting material in linear sequence. This is analogous to a semiconductor material in a solid state device being sandwiched between two layers of conductive material. In this aspect of the invention, the yarn can then act as a light sensor. When the yarn is exposed to light in the region of the semiconductor electrons are promoted into the conduction band and cause a current to flow and this current can then be measured. The yarn can thus operate as a photodetector.

The 2D material may be prepared by any conventional means. The Hummers method is one convenient way of preparing 2D material.

As discussed above, any conventional ink containing the may be used in preparing the liquid composition for the process of the present invention.

There are a number of important considerations when preparing a fibre for incorporation of a 2-D material. For example, in the case of a cotton fibre, the cotton fibres provide higher polarity, hydrogen-bonding and wettability in their natural form. In addition, untreated cotton fibres are extremely hydrophilic due to the presence of abundant hydroxyl groups in their cellulosic molecules. Therefore, residual hydroxyl groups of rGO possibly form strong hydrogen bond with cellulosic fibres containing hydroxyl groups. The presence of polymers such as PSS/PVP/PVA in the liquid medium i.e. the liquid composition used to introduce the 2-D material to the yarn helps to form uniform rGO dispersion and hence uniform coating on the yarn as demonstrated in below SEM images.

As cotton contains abundant amount of hydroxyl groups it may form strong hydrogen bonding with residual OH groups in rGO. Another important effect is the formation of polymer (binders) film around the graphene flake (or other 2-D material), which make the rGO (or other 2-D material) stable in water and also enable them to cross-link with textile

fibres/fabric/yarn. This would be the main mode of binding for other fibres which do not have hydroxyl groups or other polar groups.

The invention is also illustrated by the following Figures in which:

Figure 1 shows SEM images of reduced graphene oxide coated yarn produced according to the process of the invention;

Figure 2 shows the temperature sensing properties of the yarn of Figure 1 ability and illustrates the Resistance Vs Temp (C) characteristics for the yarn; and

Figure 3 demonstrates the performance of a reduced graphene oxide coated yarn according to the invention as a strain sensor and illustrates strain sensor cyclability.

Figure 4 is a photograph of the graphene ink used in the process;

Figure 5 shows the yarn being dipped into the graphene ink for the purposes of producing a comparative yarn;

Figure 6 shows the comparative yarn being dried;

Figure 7 shows the comparative yarn fixed to a sheet of paper using conductive epoxy resin;

Figure 8 shows a photograph of the resulting yarn under magnification;

Figure 9 is a graph of resistance against temperature for the comparative yarn and indicates a positive temperature coefficient. It also indicates the non-linear nature of the relationship between temperature and resistance.

Example 1: Graphene-based textile sensors

Yarn Preparation

100% cotton yarn was scoured (NaOH) and bleached (H_2O_2) at 110°C for 30 minutes. Scouring removes the natural impurities (such as oil, fat and waxes) and unwanted materials from fibre spinning process (such as spinning oil). In addition it increases the absorbency of fibres and hence provides better pick up of colours (during dyeing/printing) and chemicals (during finishing). Bleaching (H_2O_2) removes natural colouring matters from the fibre and make it ready for subsequent colouration process.

Note: although only cotton yarn was used in this experiment, it is envisaged that other yarns could be used and these results will be applicable to other yarn types such as polyester, polycotton, nylon, viscose, wool etc.

Synthesis of GO and chemical reduction

The graphene oxide (GO) was synthesized using modified Hummers method. Briefly the oxidation of graphite to graphite oxide is accomplished by treating graphite with a water-free mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate. The mixture was cooled in ice and $KMnO_4$ was added over 70 mins. The mixture was then allowed to warm to room temperature (with stirring) and then left to stir for 7 days. The mixture became thicker with time, and after about 3 days, stirring became impossible. The dark mixture was then slowly dispersed into 550 ml 5 wt.% H2SO4 in water (approx 1 hour) and stirred for a further 3 hours. Hydrogen peroxide (15 g, 30 vol) was added over 5 mins with considerable effervescence; the mixture turned into a yellow/gold glittery suspension and was stirred for a further 2 hours. The mixture was then further diluted with 500 ml of 3 wt.% H_2SO_4/0.5 wt.% H_2O_2 and left to stir overnight. The mixture was then centrifuged at 8,000 rpm for 20 mins, which resulted in the separation of the mixture into two roughly equal portions, together with a small quantity of very dark coloured pellet (which was discarded). One of the portions was a clear supernatant liquid (which was decanted and discarded) the other being a thick dark yellow viscous liquid. The viscous liquid was then dispersed with vigorous shaking (5-10 mins) into a further 500 ml of 3 wt.% H_2SO_4/0.5 wt.% H_2O_2. This washing procedure was repeated several times, during which the viscous fraction became progressively less glittery and progressively darker, such that by the 4th washing no glitter was visible. The mixture was then washed with pure water (500 ml), 1M HCL and concentrated via centrifugation (discarding the colorless supernatant) until the supernatant was neutral (pH 7) (5 washing cycles). This gave a dark browny-orange viscous liquid (aGO) which can be used directly as an aqueous suspension of GO or can have the remaining water removed via high speed centrifugation and vacuum drying.

The GO was chemically reduced using Ascorbic acid or hydrazine in various polymers such as PSS/PVA/PEDOT.PSS/PVP. The resulting rGO dispersions were washed in deionised water several times in order to remove residuals. Finally, rGO powders were dispersed in water at desired concentrations in order to formulate inks.

In one example, the liquid composition i.e. the inks were exfoliated in the process discussed above. Briefly, the inks may contain rGO (5 mg/mL to 10 mg/mL) in water and polymers/ binder (cross-linkers) concentration in a ratio of (1:5 to 1:10) (rGO:Polymers). The polymers/binder/ stabiliser used may be one or more as follows:PVP (Polyvinylpyrrolidone) 10 K to 100 K Mw; PDADMAC (Polydiallyldimethylammonium chloride) 200K Mw; PEDO:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate); PSS (polystyrene sulfonate).

The inks are in liquid form (in aqueous medium) but we envisage using them in the form of thicker pastes as well. The would have a slightly higher viscosity than water. In addition to or in place of water, other regular solvents (NMP/IPA etc) which are used for graphene can also be used in these formulations.

A very effective formulation can be produced from rGO/PEDOT:PSS because it incorporates a conductive polymer (PEDOT:PSS). Alternatively, rGO/PSS, which does not have a conductive polymer, is very good because it benefits from a very stable dispersion and thus creates a uniform coating on the yarn (possibly PSS acts as binder and serves to improve cross-linking with the fibre).

Yarn Coating

There are several techniques which can be used to coat textile yarn with graphene dispersions/ink as described above. These are pad mangle, exhaust dyeing technique and dip-coating. In this experiment exhaust dyeing method was used, where 2 gm of yarn was taken in a bath containing 1:10 (Materials: Liquor) rGO dispersions. The temperature of the bath was gradually increased (2°C/min) to 60°C and run for 1 hour. After that, the samples were dried at 100 C for 10 minutes. This process was repeated for 5 times in order to reduce the electrical resistivity of the coated yarn.

The number of coating cycles and drying/curing temperature has been optimised for various inks.

In an alternative procedure, the textile yarn could be coated with GO similarly and then reduced with ascorbic acid or hydrazine.

Device Fabrication and Characterisations

Graphene coated yarn has been investigated for various electronic textiles application such as various sensors (strain sensors, temperature sensors, humidity sensors, capacitive sensors, pH sensors, glucose sensors, gas sensors etc), supercapacitors and heating elements. These coated yarns can be knitted or woven into different fabric structures so as to increase the sensitivity of the device.

The graph in Figure 2 (Temperature Sensors: Resistance Vs Temp (C)) demonstrates the change of resistance with increased temperature (temperature sensors). The graphene coated yarn demonstrates very high sensitivity to the temperature. These coated yarns/patch could also potentially be connected to wireless device to record the data and transfer to a mobile app.

Example 2 - Comparative Example - Graphene Yarn and Yarn Sensor Testing

A graphene-containing yarn was prepared as a comparative example. The yarn was prepared by dipping a sample of yarn in a commercially available graphene conductive ink from China. The ink was manufactured by 'Changzhou Xichen Material Technology'. The yarn we used consists of 50% cotton and 50% polyester (black), the diameter is 0.3mm. In order to prepare the graphene coated yarn, the yarn was simply dipped into the graphene ink and fully covered by the ink for a period of several minutes. After that, the yarn was dried under 100℃ for approx. 1 hour.

The final graphene coated comparison yarn was fixed by conductive epoxy on paper. The results of the test of the comparative yarn are shown in Table 1 below. The DC resistance of the sample under different temperature was been measured and the results are given in Table 1 and also shown in Figure 9.

Temperature (℃)	Resistance (kΩ)	Changing rate (%)
30	2.175	
40	2.185	0.46
50	2.196	0.50
60	2.241	2.05

Table 1. Comparative Yarn Test Results

As it can be seen in Figure 9, that the change of resistance is not as sensitive as the yarn is prepared according to the present invention. Furthermore, although the resistance does change with temperature it both demonstrates a positive temperature coefficient and is not linear. The change rate is broadly proportional to temperature but it would not be suitable to prepare a reliable sensor.

The present invention also relates to a screen-printed textile or a porous material, such as paper, printed on its surface with a 2D material such as graphene. This printed textile (fabric) has the 2D material incorporated by a screen-printing process in which a liquid or paste composition containing the 2D material is contacted with the textile or paper substrate. The present invention thus also relates to a process for the preparation of a graphene- or other 2D material-printed substrate and the use of the resulting printed substrate in a variety of applications such as wearable technology. The textiles of the invention may be derived from naturally occurring materials such as cotton or may be based on synthetic materials such as polyester, nylon, viscose, etc., or may be a blend of natural and synthetic materials.

Another feature of these materials is that they can be used for screen printing 2-D materials onto textiles, and other porous substrates such as paper, in order to provide conductive materials.

According to another aspect of the present invention, there is provided an electrically conductive material comprising:

a porous substrate material, preferably a textile;

optionally a hydrophobic surface coating covering at least a portion of a surface of the porous substrate material; and

an electrically conductive track or film disposed on the hydrophobic surface coating;

wherein: the electrically conductive track or film comprises a conductive 2D material, preferably one or more of: graphene, reduced graphene oxide, a graphene derivative obtained by chemical modification of graphene or graphene oxide.

Chemical modification of graphene or graphene oxide can be achieved by using one or more of an acid, an oxidizing agent, a reducing agent and a halogenating agent to

introduce one or more different functional groups. For example, a halogenating agent reviews to introduce fluorine or chlorine.

According to a further aspect of the present invention, there is provided a process for forming an electrically conductive material, the process comprising:

(i) providing a porous substrate material, preferably a textile;

(ii) optionally, applying a hydrophobic coating to the substrate:

(iii) screen printing a paste formulation onto at least a portion of a surface of the porous substrate material to form a film or track on at least part of the surface thereby forming a printed substrate; and

(iv) drying the printed substrate,

wherein the paste composition comprises a conductive 2D material (preferably graphene, reduced graphene oxide, or a graphene derivative) and a thickener, and wherein the viscosity of the paste is at least 1Pa.

In a further aspect, the present invention provides an electrically conductive material obtainable by, obtained by, or directly obtained by any process of the present invention defined herein. Thus the invention may relate to a screen-printed electrode. This electrode will be printed on a fabric (textile) substrate or it may be printed on another porous substrate such as paper. It is also possible that printing could be effected on a non-porous substrate using the compositions of the invention.

According to a further aspect of the present invention, there is provided an electronic circuit or device comprising an electrically conductive material of the present invention.

According to a further aspect of the present invention, there is provided a textile or garment comprising an electrically conductive material of the present invention.

The term “graphene derivative” includes graphene oxide, reduced graphene oxide, partially oxidised graphene, hydrogenated graphene (graphane), fluorinated graphene and any other functionalised graphene material, including graphene functionalised with oxygen or nitrogen containing groups. The graphene derivative may be oxygenated graphene and may encompass any graphene like material that comprises more than 1% oxygen by weight, 5% or more oxygen by weight, e.g. 10% or more, or 20% or more oxygen by weight, or even 25% or more oxygen by weight. Thus, the term ‘oxygenated graphene’ may refer to graphene oxide, reduced graphene oxide, partially oxidised graphene etc.

Where the oxygenated graphene is reduced graphene oxide or partially oxidised graphene, the oxygen level may be lower than in graphene oxide. For example, the amount of oxygen in the oxygenated graphene may be less than 20% oxygen by weight, less than 10% oxygen by weight or less than 5% oxygen by weight, for example 1% to 10% oxygen by weight, 1% to 5% oxygen by weight. The oxygenated graphene may comprise 1%, 2%, 3%, 4% or 5% oxygen by weight or any subrange within those values.

Various other thickening agents apart from acrylate polymers can also be used. Thus a range of natural and synthetic rheology modifiers (with shear thinning property) can be used to make viscous screen printing pastes such as one or more of: carboxymethylcellulose (CMC), sodium alginate, gum Arabic, PVP360K, PVP higher K (PVP is polyvinylpyrrolidone), PEO (Polyethylene Oxide), and PEPO (polyether polyol). The thickening agent may be used alone or in combination.

The viscosity of the paste (>1Pa) is the key parameter to make screen printing paste as it helps to hold the shape of the design (pattern). Therefore a rheology modifier i.e. thickener is always needed for screen printing.

Other components may be added as needed to the paste. For example the same polymers / monomer which were mentioned above in relation to yarn sensors for improving adhesion can also be added to the screen printing paste to enable better adhesion with the textile substrates. For example, acrylates can be added to help to cross-link in the fabric in the same way as described for the yarn.

The rGO dispersion used in the screen printing paste can be an aqueous dispersion. Thus the same aqueous dispersions were used as were used in treating the yarn as described above. Thus compositions may contain the same components but, in the case of the paste, the viscosity was modified using 1-1.5 wt.% commercially available acrylic thickener or another thickening agent as outlined above. Although, in our experiments we used aqueous dispersions, other solvents can also be used (as mentioned in the context of dyeing the yarns).

The 2D materials used can include those listed in relation to the yarn. However, for this screen printing application the 2D material should be a conductive 2D material. GO, pristine graphene, graphene nanoplatelets, and functionalised graphene can all be used. The viscosity is modified to make screen printing inks to be used for similar applications.

A variety of substrates can be used. We used textiles. However, we also screen printed sensors onto PEN /PEL (electronic paper/photo paper[MnK2])/ substrates and these worked well. Silicon wafer may also be used as a substrate.

The textile material (fabric) does not require any surface pre-treatment as the thickening agents help to hold the pattern on rough and porous textiles surface. However, these dispersions can be modified as inkjet inks and can be printed using a surface pre-treatments (same way disclosed in for example PCT/GB2015/052309 and the contents of that document relative to suitable compositions for inks are incorporated herein by reference). However, a hydrophobic pre-treatment step would help to make it more continuous and increase the conductivity so this is an optional step.

The hydrophobic surface that is formed on the substrate by the application of the hydrophobic surface coating is a surface that has an equilibrium contact angle of water against air, at 25 °C, of greater than 60° and less than or equal to 175°.

The hydrophobic surface coating may include hydrophobic materials as well as superhydrophobic materials (i.e. materials that provide a hydrophobic surface having an equilibrium contact angle of greater than 150°).

The hydrophobic surface coating may comprise any suitable hydrophobic material or a mixture of such materials. Suitably, the hydrophobic material is a hydrophobic polymer.

In an embodiment, the hydrophobic surface coating comprises particles (e.g. microparticles) formed from a hydrophobic polymeric material.

In another embodiment, the hydrophobic surface coating comprises a curable material that can be cured in order to harden the hydrophobic surface coating. Suitable curable materials are well known in the art. In a particular embodiment, the curable material is a UV-curable material (or lacquer). It will be understood that curing such UV curable materials may then be cured by exposure to UV radiation following application to the substrate surface.

Any suitable hydrophobic polymer, or oligomer in the case of a UV curable material, may be used. Examples of suitable hydrophobic polymers include styrene, (meth)acrylate, acrylate, ester, olefin, vinyl ester, vinyl pyrrolidone, vinylpyridine based polymers and any appropriate copolymers. The skilled person will appreciate copolymers suitable for use. The suitable hydrophobic polymer may be cross-linked through suitable covalent or non-covalent interactions, typically triggered by heat or actinic radiation.

In an embodiment, the hydrophobic polymeric material is a polystyrene based polymer. In a specific embodiment, the hydrophobic polymeric material is a polystyrene based co-polymer comprising styrene, divinylbenzene and hydroxyl methacrylate.

In an embodiment, the hydrophobic surface coating forms a hydrophobic surface on the porous substrate material having an equilibrium contact angle of water against air, at 25 °C, of greater than or equal to 90° and less than or equal to 175°. In a further embodiment, the hydrophobic coating forms a hydrophobic surface on the porous substrate material having an equilibrium contact angle of water against air, at 25 °C, of greater than or equal to 90° and less than or equal to 165°. In a further embodiment, the hydrophobic coating forms a hydrophobic surface on the porous substrate material having an equilibrium contact angle of water against air, at 25 °C, of greater than or equal to 90° and less than or equal to 145°. In a further embodiment, the hydrophobic coating forms a hydrophobic surface on the porous substrate material having an equilibrium contact angle of water against air, at 25 °C, of greater than or equal to 90° and less than or equal to 135°. In a further embodiment, the hydrophobic coating forms a hydrophobic surface on the porous substrate material having an equilibrium contact angle of water against air, at 25 °C, of greater than or equal to 100° and less than or equal to 125°.

The screen printing technique is a conventional screen printing process employing the novel materials of the invention to produce novel products which have conductive portions thereon.

For inkjet printing there are few key parameter we need to maintain (depending on inkjet printhead) such as: viscosity (2-30 cPs) for the printer (a Dimatix Material printer), surface tension 25-50 mN/m, particle size (up to 5 microns) depending on the nozzle diameter. However there are no such requirements for screen printing except that a higher viscosity (>1 Pa) is needed. The viscosity should preferably be less than 100Pa and more preferably less than 10Pa.

The benefits of this screen printing process is that the textile can be printed at higher speed and that it is suitable for large scale production. It is particularly suitable for graphene and graphene derivatives (to print large graphene flakes and this in turn provides better conductivity).

Example 3: Screen printed graphene inks onto textiles (fabrics) / Flexible substrates

rGO dispersions were mixed with acrylate-based synthetic thickening agent (viscosity modifier) to make screen printing paste. These pastes were printed onto textile fabric using screen printing technique. The printed fabric was dried at 100 C for 10 minutes and cured (thermally fixed/ crosslinked) at 150 C for 5 minutes. GO pastes were made similarly, however it was reduced back to rGO after printing using ascorbic acid or other reduction techniques.

Various applications for the sensors of the present invention have been tested and proof of concept has been established for types of sensors including: Capacitive sensors, moisture, humidity, temp etc.

It is envisaged that the materials of the present invention will find uses in ECG/EMG/EOG devices, conformal electronics and even supercapacitors. The yarns of the invention are also expected to find utility as graphene-based flexible textile heating elements.

The present invention can thus be used to prepare a yarn which has a range of possible applications. The yarns of the invention have a number of benefits relative to conventional yarns and/or sensing devices which are as follows:

- Faster T response time
- More sensitive
- More durable
- Flexible etc
- Washable
- Less heating (reduced carbon footprint)
- Environmental friendly/ (biodegradable) – graphene aspect.
- Cheaper

Claims

1. A process for preparing a yarn incorporating a two-dimensional material, the process comprising the steps of:

(d) providing a liquid composition comprising a two-dimensional material selected from a conducting 2D material and a semi-conducting 2D material;

(e) contacting the yarn with the liquid composition for a period of time; and

(f) drying the yarn.

2. A process according to claim 1, wherein the liquid composition includes a binder.

3. A process according to claim 1 or 2, wherein the binder is prepared by the copolymerization of different monomers and preferably unsaturated monomers such as vinyl chloride, dichloroethene, acrylic acid, acrylonitrile, acrylic acid esters and ethers.

4. A process according to claim 1 or 2, wherein the binder is PVA or PSS.

5. A process according to any preceding claim, wherein the liquid composition may also include additional components such as one or more of stabilisers, dispersants, surfactants, antioxidants.

6. A process according to any preceding claim, wherein the process includes a pre-treatment step for the yarn before it is contacted with the liquid composition containing the 2D material.

7. A process as claimed in claim 6, wherein the pre-treatment step may be chemical activation using a solution containing an activating agent or the pre-treatment step may be a surface treatment of the yarn such as a plasma treatment.

8. A process as claimed in any preceding claim, wherein the liquid composition which contain the 2-D material is an aqueous composition.

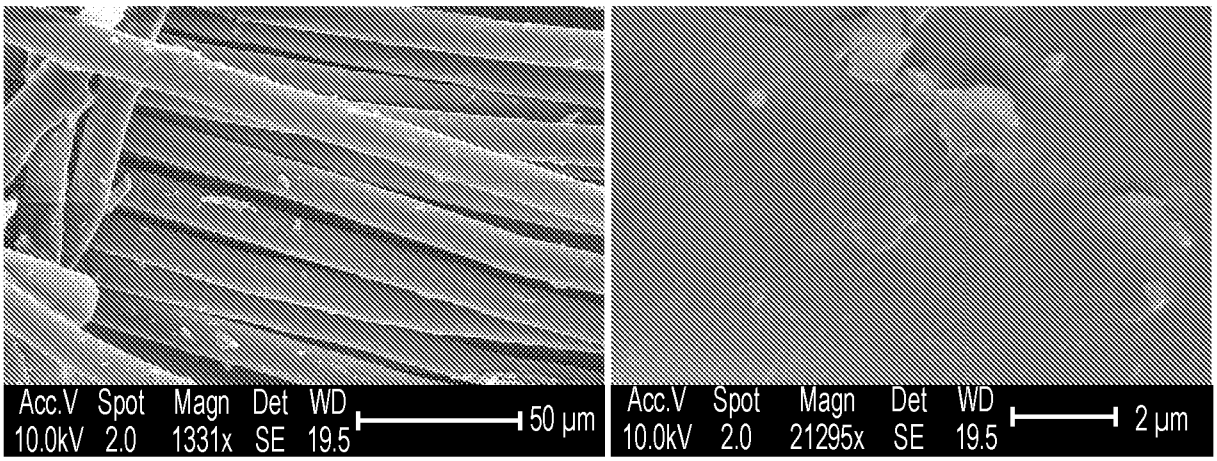
9. A process as claimed in any preceding claim, wherein the 2D material is a material which is capable of conducting electricity, and preferably is rGO.

10. A process as claimed in any preceding claim wherein the 2D material represents from 0.5% by weight to 25% by weight of the liquid composition, and more preferably from 1% to 10% by weight of the liquid composition.

11. A process as claimed in any preceding claim wherein the 2-D material is in the form of flakes and the flakes have an average of up to 10 layers.

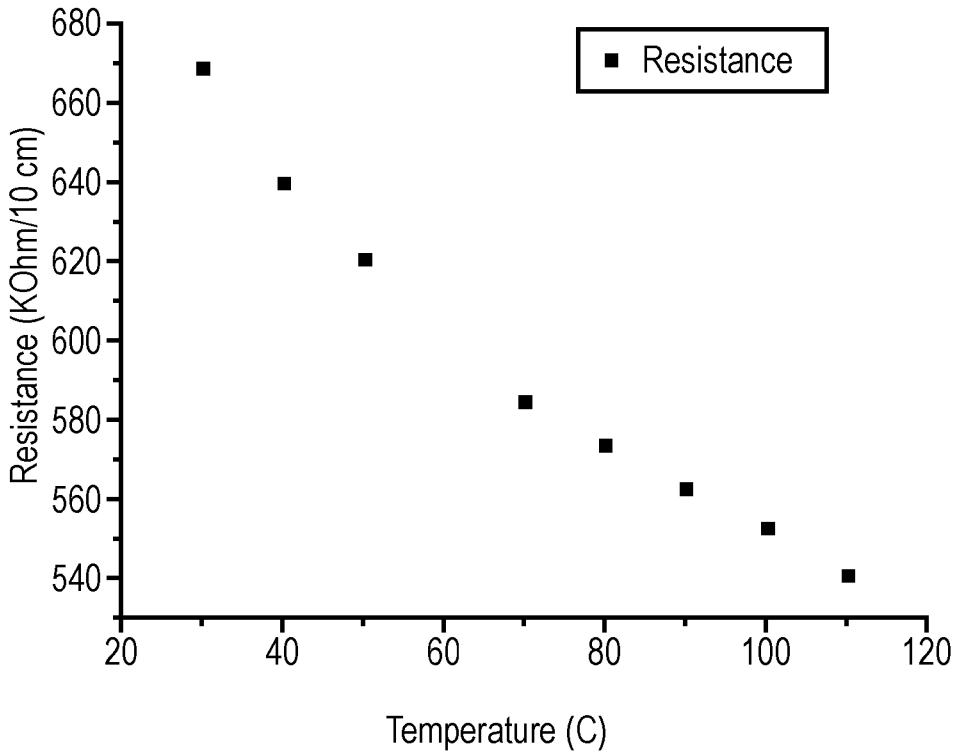
12. A process as claimed in any preceding claim wherein the yarn is a natural fibre, preferably the yarn is cotton.

13. A yarn incorporating a 2D material prepared by the process of any of claims 1 to 12.
14. The use of a two-dimensional material-containing yarn prepared according to any of claims 1 to 12 as a sensor, preferably as a temperature sensor.



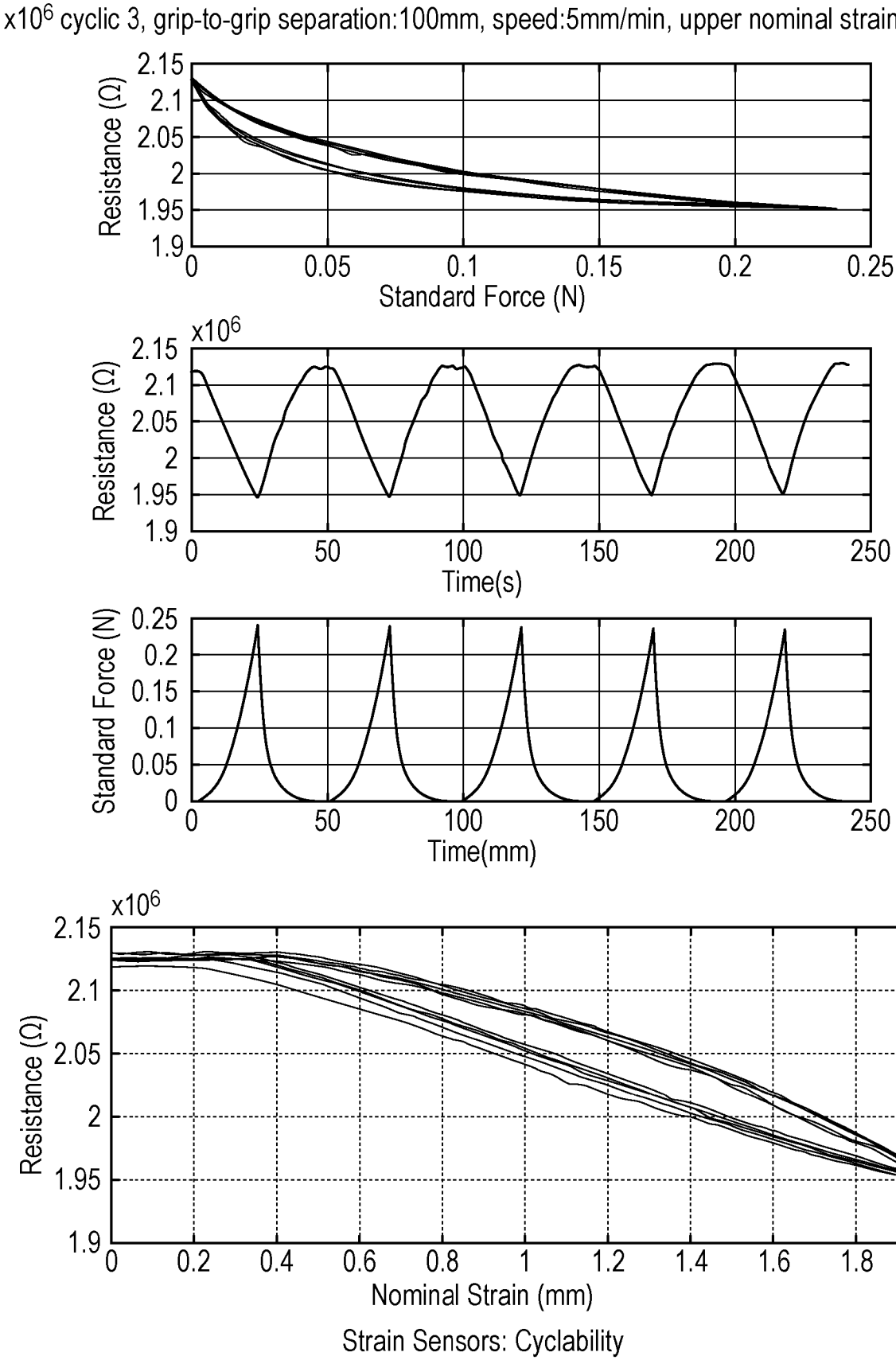
SEM images of graphene coated yarn

FIG. 1



Temperature Sensors: Resistance Vs Temp (C)

FIG. 2

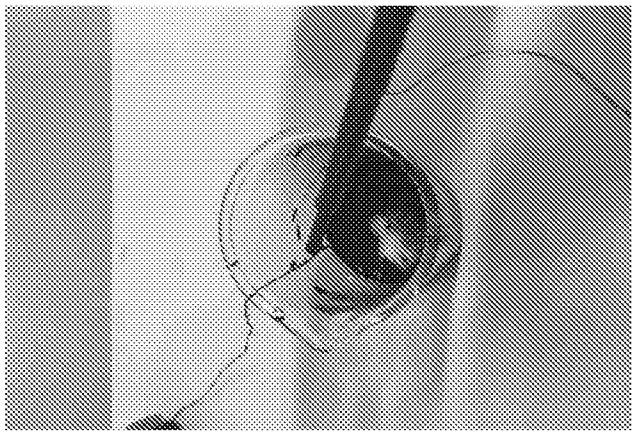


Strain Sensors: Cyclability

FIG. 3

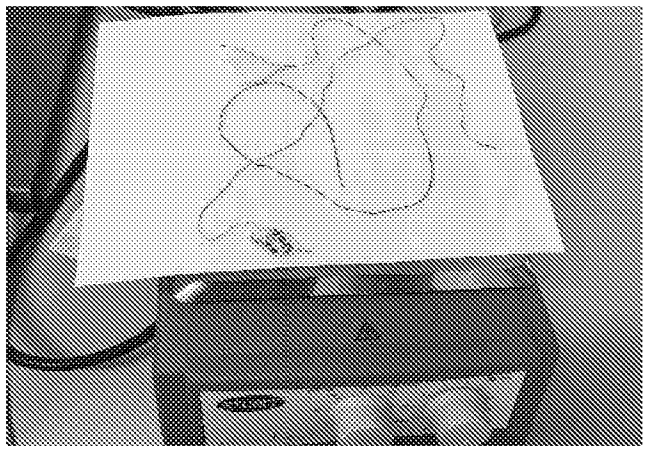
Graphene ink from China for comparative example

FIG. 4



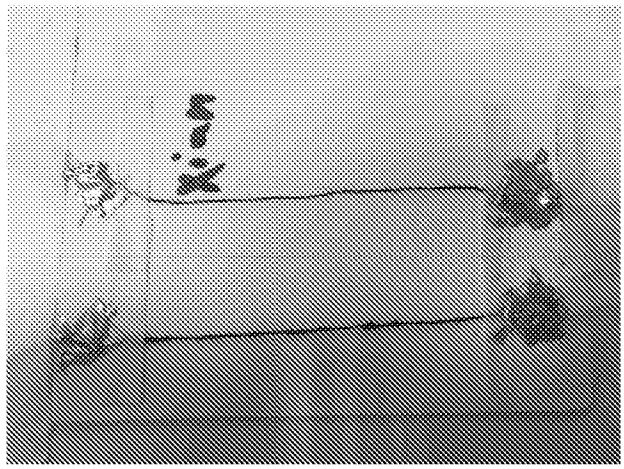
Graphene ink dipping of comparative yarn sample

FIG. 5



Graphene ink drying of comparative yarn sample

FIG. 6



Comparative Yarn Sample

FIG. 7

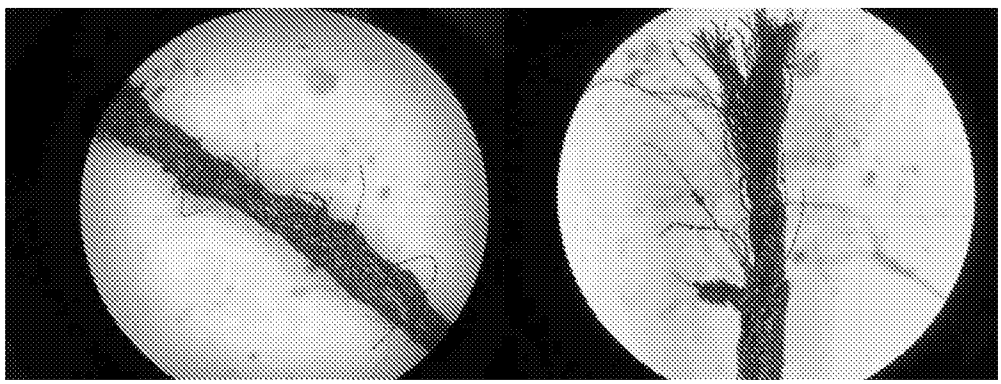
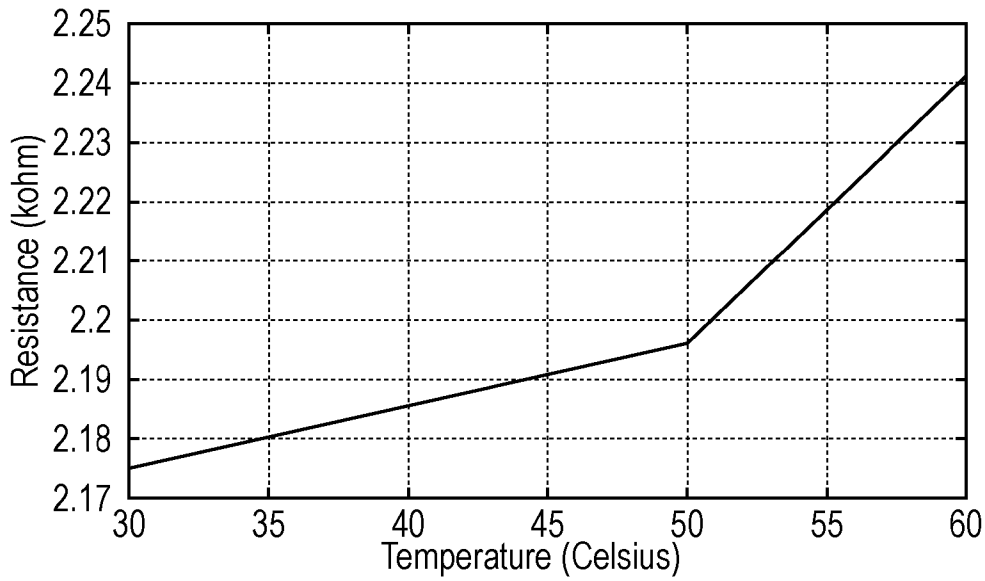


Photo of the Comparative Yarn Sample

FIG. 8



Comparative Yarn Sample Test Results

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2017/051777

A. CLASSIFICATION OF SUBJECT MATTER
INV. D06M11/74
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D06M D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JUNG JIN PARK ET AL: "Highly Stretchable and Wearable Graphene Strain Sensors with Controllable Sensitivity for Human Motion Monitoring", ACS APPL.MATER.INTERFACES, vol. 7, no. 11, 25 March 2015 (2015-03-25) , pages 6317-6324, XP055330479, ISSN: 1944-8244, DOI: 10.1021/acsami.5b00695 Results and Discussion; page 6319, column 1st Experimantal Section; page 6322, column 2nd ----- -/--	1,2,4, 6-9, 12-14

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 August 2017	06/09/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Rella, Giulia

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHAO CHEN ET AL: "Reduced graphene oxide and polypyrrole/reduced graphene oxide composite coated stretchable fabric electrodes for supercapacitor application", ELECTROCHIMICA ACTA, vol. 172, 15 May 2015 (2015-05-15), pages 12-19, XP029169522, ISSN: 0013-4686, DOI: 10.1016/J.ELECTACTA.2015.05.019 Preparation of rGO coated fabrics; page 13 page 16, column 2nd	1,6-9, 11,13
X	KR 101 597 176 B1 (PINE CO LTD [KR]) 24 February 2016 (2016-02-24) WPI abstract Example 1 claims 1-4	1-3,12, 13
X	KR 101 561 207 B1 (DACCCARBON [KR]) 20 October 2015 (2015-10-20) claims 1, 2, 5, 7, 8	1-4,10, 13
X	CN 104 882 613 A (INST METAL RES CHINESE ACAD SC) 2 September 2015 (2015-09-02) WPI abstract paragraph [0022]	1,5,8, 10,12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2017/051777

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 101597176 B1	24-02-2016	NONE	
KR 101561207 B1	20-10-2015	NONE	
CN 104882613 A	02-09-2015	NONE	