Figure 23
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published: with international search report (Art. 21(3))
GRAPHENE CORE CONDUCTORS AND FABRICATION METHOD THEREFORE

Technical Field:

The technical field of the present invention is low resistance electrical conductors suitable for use in electrical cables and transmission lines, also electrical devices. In particular an application of the electrical conductors is in conductor bundles for electrical transmission lines, for example high power electrical transmission lines for use in electrical power grids.

Background of the Invention:

Electricity is one of the most important inventions that science has given to mankind. It is essential for the economic development of a country. Modern society is heavily dependent upon the use of electricity. Electricity is considered a very efficient way of energy consumption because it is weightless and easy to transport and distribute. The transport and distribution of electricity in most urban environments fully relies on an electric power grid consisting of transmission lines and the distribution network. The electric power transmission is the bulk transfer of electricity from power generation plants to electrical substations located near demand centres.

Electric resistance of transmission line materials causes the loss of electric energy during transmission. Temperature, spiralling, and skin effect are the main factors that affect the resistance of conductors used in transmission and distribution lines. The resistance of a conductor also increases with its temperature due to the phonon scattering. Changing temperature in electric transmission lines can also have a significant effect on power losses. Due to the structure of the transmission lines, current spiralling can also contribute to increases in conductor resistance. The skin effect increases the effective resistance of the electric power lines at higher alternating current frequencies.

Reduction in loses during transmission is desirable to enable any one or more performance improvements, such as improved efficiency, allow wider distribution, and improve power grid performance. There is a need for improved electrical transmission lines.
Summary of the Invention:

According to one aspect of the present invention there is provided an electrical conductor comprising a graphene core surrounded by a sheath, the graphene core comprising particulate graphene material compressed within the sheath.

In some embodiments the conductor is formed using a powder in tube process, wherein particulate graphene is placed in a tube comprising the sheath material and the tube drawn to thereby provide the graphene core and sheath. In an embodiment the graphene core and sheath structure form a wire. Other fabrication methods may also be used, for example utilising extrusion technologies including polymer extrusion or polymer coating/cladding/packaging technologies etc. to produce the graphene core and sheath conductor structure.

The particulate graphene powder can comprise graphene flakes.

The sheath can be formed of a metallic, polymer or other material. In some embodiments the sheath is formed of any one or more of: aluminium, copper, silver and gold.

Another aspect provides an electrical conductor comprising a plurality of electrical conductors as described above forming a cable.

Another aspect provides a multifilament conductor comprising a plurality of graphene core wires as described above.

Another aspect of the present invention provides an electrical power transmission line comprising a plurality of electrical conductors configured for transmission of high voltage alternating current electrical power; and at least one strengthening structure bundled with the electrical conductors to provide mechanical support to the power transmission line; wherein at least one electrical conductor comprises a graphene core composite conductor, each graphene core composite conductor comprising one or more electrical conductors comprising a graphene core of particulate graphene material compressed within the sheath.

In an embodiment of the electrical power transmission line each graphene core composite conductor comprises a plurality of electrically conductive wires, each wire comprising a graphene core compressed within a metallic sheath. For example, the plurality of electrically conductive wires can be further surrounded by a metal sheath. Each of the electrically conductive wires can be formed using a power-in-tube method for forming the wire comprising the graphene core.
According to another aspect of the present invention there is provided a method of producing an electrical conductor, the method comprising the steps of: providing particulate graphene material; placing the particulate graphene material into a hollow tube of drawable sheath material, and drawing the graphene filled tube to cause compression of the graphene material through deformation of the tube to provide an electrical conductor comprising a core of the particulate graphene material compressed within a sheath.

The step of drawing the graphene filled tube can comprise pulling the graphene filled tube through a series of drawing dies.

A method can further comprise a step of annealing the drawn graphene filled tube. The annealing step can be performed intermittently between drawing the graphene filled tube through the series of drawing dies.

In an embodiment of the method the graphene core electrical conductor is formed as a wire, and further comprising the step of forming a plurality of graphene core electrical conductor wires into a multifilament graphene core composite conductor. For example the plurality of graphene wires can be placed into a metal tube and drawn to provide the multifilament graphene core composite conductor.

An embodiment of the method further comprises a step of bundling one or more multifilament graphene core composite conductors into a transmission line cable.

Brief Description of the Drawings:

Figure 1 A flowchart of a process for fabrication a graphene metal composite conductor in accordance with an embodiment of the present invention.

Figure 2 Schematic illustration shows the procedure of monofilament and multifilament graphene/metal composite wire fabricated by powder-in-tube technique: (a) packing the graphene into the metal tubes; (b) drawing a monofilament wire; (c) insert the monofilament wires into another metal tube; (d) drawing a multifilament wire; (e) cross-section of a multifilament wire.

Figure 3a Shows a TEM image of as-received multilayered graphene flakes.

Figure 3b Shows a TEM image of monoatomic layered graphene exfoliated from the as-received multilayered graphene flakes.

Figure 4a shows the Tyndall Effect on as-received multilayered graphene flakes in ethanol.
Figure 4b shows the Tyndall Effect on which monoatomic layered graphene exfoliated from the as-received multilayered graphene flakes, well dispersed in ethanol.

Figure 5a and 5a show photographs demonstrating the densification of graphene packing density with centrifuging technology: (a) before, (b) after the densification.

Figure 6 Schematic illustration demonstrates the mechanism of electric conductivity enhancement induced by the formation of highly dense and well aligned graphene flakes; (a) mechanical force adds on the random distributed graphene flakes by the metal cladding in powder-in-tube processing; (b) texture formation of graphene flakes inside the drawn graphene/metal composite; (c) the principle of electric path ways established in the brick model.

Figure 7 Schematic illustration shows the structure of next generation high performance electric power grid transmission line made with the graphene/metal composite wires.

Figure 8a Represents the crystal structure of monolayer graphene, showing how an electron moves in a single atomic layered graphene sheet.

Figures 8b and 8c Illustrate the unit cell structure of single layer graphene.

Figure 9a Represents the crystal structure of bilayer graphene in a Bernal stacking configuration showing a top view.

Figure 9b Represents the crystal structure of bilayer graphene showing a side view, with electron hopping direction indicated by arrows.

Figure 9c and 9d Illustrate the unit cell structure of bi-layer graphene.

Figure 9e Schematic representation of how the electron moves in a bi-layer graphene sheet.

Figure 10a Illustrates a model configuration for conductance calculation for monolayer graphene.

Figure 10b Illustrates a model configuration for conductance calculation for bilayer graphene.

Figure 11a is a graph of the calculated conductance as a function of energy for monolayer graphene calculated for a 10 x 10 sheet of monolayer graphene in accordance with Figure 10a.
Figure 11b is a graph of the calculated conductance as a function of energy for bilayer graphene calculated for a 10 x 10 sheet of bilayer graphene in accordance with Figure 10b.

Figure 12 shows a representation of two overlapping sheets of monolayer graphene and the lead placement for modelling charge transfer between adjacent sheets of graphene.

Figures 13a to 13e are graphs of conductance for side contact graphene layers at different interlayer hopping energy.

Figures 14a and 14b are schematic illustrations of design parameters for the modelled interlayer electron transfer in bilayer graphene.

Figure 15a and 15b represent molecule structures used to model systems of graphene for investigating the geometric dependence of interlayer electronic couplings.

Figure 16 graphs scanning of dimer transfer integrals for the model graphene system of Figure 15a, having 3.6 Å intermolecular separation with a 180 degree in-plane rotation of one monomer scan of the change in electron transfer integrals (T.I.)

Figure 17 graphs scanning of dimer transfer integrals for the model graphene system of Figure 15b, having 3.6 Å intermolecular separation with a 180 degree in-plane rotation of one monomer scan of the change in T.I.

Figure 18 graphs scanning of dimer transfer integrals for the model graphene system of Figure 15a as a function of interlayer distances d at selected different in-plane rotation angles.

Figure 19 graphs scanning of dimer transfer integrals for the model graphene system of Figure 15b as a function of interlayer distances d at selected different in-plane rotation angles.

Figure 20 graphs Raman spectroscopy of the as-received and the as-annealed reduced graphene oxide (rGO).

Figure 21 graphs X-ray photoelectron spectroscopy (XPS) spectra of the as-received rGO and the as-annealed rGO.

Figures 22a and 22b graph AC current (50 Hz) dependence of (a) resistivity, and (b) temperature measured from pure Al wire and prototype Al/rGO composite wire, respectively.
Figure 23 is an image of a cross sectional the prototype Al/rGO composite wire.

Figures 24a and 24b graph AC current (50 Hz) dependence of (a) resistivity, and (b) temperature measured from prototype Al/rGO composite wire and Al/Al₂O₃ composite wire, respectively.

Detailed Description:

Aspects of the present invention provide an electrical conductor comprising a graphene core, transmission lines utilising the graphene core conductor, and methods for fabrication of the electrical conductor and transmission wires. Embodiments of the invention provide an electrical conductor comprising a graphene core surrounded by a sheath. The graphene core comprises particulate graphene material. The graphene material is compressed within the sheath. A preferred embodiment of the graphene core conductor provides an electrically conductive wire. Embodiments of the electrically conductive wire can be formed using a powder in tube process. The particulate graphene material is placed in a metallic tube and the tube drawn into a wire to thereby provide the graphene core and sheath.

Embodiments of the graphene core electrical conductor can be utilised in transmission line conductor bundles. Embodiments of graphene core wires can also be utilised in other devices and applications, for example transformers and electric motors.

Graphene is a single atomic layer of graphite, which is an abundant mineral. It is an allotrope of carbon that is made up of very tightly bonded carbon atoms organised into a hexagonal lattice. The atomic thin nature with unique sp² hybridisation enables graphene to achieve high performance in terms of electricity conduction, heat conduction, and strength. In particular, graphene is a zero-overlap semimetal with very high electrical conductivity. Each carbon atom has a total of 6 electrons with 2 in the inner shell and 4 in the outer shell. In bulk, these 4 outer shell electrons are available for chemical bonding, but in graphene, each atom is connected to 3 other carbon atoms in the two dimensional atomic layer, freeing 1 electron available in the third dimension for electronic conduction. These highly-mobile electrons are located above and below the graphene sheet. The linear Dirac dispersion at the K point in the band structure of graphene leads to zero effective mass of the electrons, thus avoiding phonon scattering and resulting in high electron mobility. Theoretical estimations indicate potential for embodiments having up to 200000 cm²/V-s at a carrier density of around 10¹² /cm² at room temperature. The corresponding resistivity of graphene
sheets has been reported as down to $10^8 \Omega \cdot \text{m}$, which is less than the resistivity of silver and it is the lowest otherwise known at room temperature.

Table 1 Resistivity and conductivity of various materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$\rho$ (Ω·m) at 20 °C</th>
<th>$\sigma$ (S/m) at 20 °C</th>
<th>Temperature coefficient (K$^{-1}$)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>$1.00 \times 10^{-8}$</td>
<td>$1.00 \times 10^8$</td>
<td>-0.0002</td>
<td>1.5 – 2.0</td>
</tr>
<tr>
<td>Silver</td>
<td>$1.59 \times 10^{-8}$</td>
<td>$6.30 \times 10^7$</td>
<td>0.0038</td>
<td>10.49</td>
</tr>
<tr>
<td>Copper</td>
<td>$1.68 \times 10^{-8}$</td>
<td>$5.96 \times 10^7$</td>
<td>0.003862</td>
<td>8.96</td>
</tr>
<tr>
<td>Gold</td>
<td>$2.44 \times 10^{-8}$</td>
<td>$4.10 \times 10^7$</td>
<td>0.0034</td>
<td>19.32</td>
</tr>
<tr>
<td>Aluminium</td>
<td>$2.65 \times 10^{-8}$</td>
<td>$3.77 \times 10^7$</td>
<td>0.00429</td>
<td>2.65</td>
</tr>
</tbody>
</table>

Table 1 lists the resistivity and conductivity of the most common used highly conductive materials. It shows the electric conductivity of graphene can be 37% higher than silver, more than 40% higher than copper, and 62% higher than aluminium. In particular, in some embodiments graphene can carry electrical current with densities up to 6 orders of magnitude higher than copper as a conductor of electricity. This demonstrates that graphene is a promising material for use in electrical conductors to potentially significantly reduce the loss of electric energy caused by the resistance of the transmission lines.

One known approach aiming to enhance electrical properties of materials added graphene or carbon nanotubes into copper or aluminium directly during the physical metallurgy process (e.g. melting and casting) to form materials that consist of a mixture of metal and graphene (or carbon nanotubes). However, it is almost impossible to form a metallic material with homogeneously dispersed graphene using known metallurgy processes, thus making it difficult to achieve enhancement of electrical conductance. In fact, this approach was found to be ineffective at improving electrical properties. It is believed that this is due to the graphene and/or carbon nanotubes forming inclusions (clusters) in the material, thus failing to enhance the electrical conductivity effectively. Further, inductance was a problem in transmission lines formed using this material, the inductance believed to be due to the cluster formations causing the conductors to have inconsistent structure.

Most of the graphene produced for industry applications is in a particulate or powder form, with the particles having flake shapes from several nanometres to hundreds of microns. The covalent nature of carbon bonds means the graphene flakes are extremely difficult to join together and shape to form products, particularly on a bulk scale.
The electrical current is transported in an atomic plane of graphene. However, fabricating and shaping a large scale graphene product is extremely difficult. The inventors have utilised recent advances in materials science and engineering to apply powder-in-tube technology to fabrication of electrical conductors incorporating graphene. "Powder-in-tube" is commonly used to fabricate ceramic based high temperature superconductors.

By using the powder-in-tube technique with graphene flakes, the inventors can produce a highly dense and well aligned graphene structure, thus significantly improving the electrical path way. This manufacturing method can be applied on a large scale.

The inventors envisage applying powder-in-tube fabrication methods to manufacture large scale graphene/metal composites for the application of high performance power grid transmission lines. Such transmission lines can enable significant reduction in electricity loss during transmission, by virtue of the graphene/metal composite conductors.

An example of the process for fabrication of electrical conductors in accordance to embodiments of the invention will now be discussed with reference to Figures 1 and 2. In a first step 110 particulate graphene is placed into a metal tube. For example, to fabricate electrical conductors in accordance with embodiments of the present invention, graphene flakes are packed into a metal tube, such as aluminium, copper and other metal or alloy tubes. In one embodiment the metal tube is an aluminium tube with outside diameter of 8 mm and inner diameter of 4 mm as shown in Figure 2(a). It should be noted that initial outer and inner diameters of the tube will vary between embodiments and may be chosen based on the operating parameters and specification for transmission lines. Subsequently the metal tube filled with graphene is drawn by pulling the material through a series of drawing dies with interval annealing to remove the strain caused by the cold work hardening. In this process the metal tube is drawn through first die 120 and if necessary 130 an annealing, heat treatment step performed 135, these steps 120 to 135 can be repeated each time using a smaller die 145. Each repetition of drawing 120 reduces the diameter of the tube, drawing the tube into a wire. This drawing also compresses the graphene within the tube providing a final wire structure having a graphene core compressed within the metallic sheath. The drawing and annealing steps end 140 once the desired wire thickness has been achieved, to provide a monofilament graphene core wire 150. For example, in one embodiment this process reduces the cross-section of the tube to a monofilament graphene/metal wire with an outside diameter of ~0.5 to 5 mm. In other embodiments wires may be produced having diameters of 0.1mm to around 10mm.

The ratio and rate of cross-section deformation can play an important role in determining the performance of the materials.
During the drawing processing, the random distributed graphene flakes are aligned along the interface between the graphene core and cladding. Each drawing step 120 compresses the graphene flakes within the tube. Figures 6a to 6c graphically illustrate alignment of graphene flakes by the drawing process. Initially the graphene flakes are packed into the tube randomly and as such will typically have no particular orientation. As mechanical compressive force $\sigma$ is applied during the drawing process, as shown in Figure 6a, this affects the random distribution of the graphene flakes and these begin to align as shown in Figure 6b. The higher extent of mechanical deformation through the drawing process leads to a higher density graphene core with better alignment of the graphene flakes, as shown in Figure 6c. Since the electric current only transmits along the graphene plane, such a textural structure of the graphene flakes substantially enhances the conductivity of the materials by improving the electrical current paths with the brick model as shown in Figure 6c. Therefore, the resistance of conductive wires made with the graphene/metal composite is lowered by the addition of the highly conductive graphene, thus reducing the loss of electric energy.

It should be appreciated that although the example discussed above uses a metallic tube that is drawn into the sheath, any suitable material may be used. In the example, an electrically conductive metal is used but other metals or metal alloys may also be used for the sheath material. However, the sheath material does not need to be metallic. As the graphene core is electrically conductive, the sheath material does not need to be electrically conductive. For embodiments formed using the above described powder in tube fabrication process, the selection of the tube/sheath material is constrained by mechanical properties required - for example choosing a material suitable for the drawing process and final conductor product - rather than electrical properties of the material. Other fabrication methods may also be used to produce the graphene core and sheath structure. Many alternatives exist for drawing, coating or cladding to produce the graphene core and sheath structure. For example extrusion technologies including polymer extrusion may be used. Alternatively, polymer coating/clADDING/pACKAGING technologies etc. may be used to produce the graphene core and sheath conductor structure. For example, a polymer can be used for coating or cladding to form the graphene core electric conductors. Alternative fabrication processes may also enable other types of materials (organic or inorganic) to be used to form a graphene core conductor, for example a ceramic sheath may be used. The choice of sheath materials may also take into consideration requirements for products produced incorporating the graphene core conductors, the requirement may be based on further processing techniques and well as end product requirements.
Embodiments of the graphene core conductor fabrication process can comprise graphene pre-processing and packing steps to improve the density of the particulate graphene inserted into the tube for drawing. For example, in an embodiment the graphene is received as multilayers graphene flakes. The as-received multilayered graphene flakes are exfoliated by a powerful sonication device with the power from 10 W to 16KW or higher with frequency from 10kHz to 50kHz or higher. Figures 3a and 3b show the bright field Transmission Electron Microscopy images of the as-received multilayered graphene flakes (Figure 3a) and the graphene flakes treated by the sonication technique (Figure 3b). The photographs of Figure 3a and 3b demonstrate that the as-received multilayered graphene flakes have been successfully exfoliated into the monoatomic layered graphene by using the sonication technique. The dispersion of the as-received multilayered graphene and the ultrasonic treated monoatomic layered graphene in ethanol can be simply determined with Tyndall Effects using laser as shown in Figures 4a and 4b. In general, the monoatomic layered graphene has a zero band-gap, possessing a much higher electric conductivity than that of the multilayered graphene. Thus the monoatomic layered graphene is preferred for fabrication of graphene core conductors in accordance with embodiments of the present invention.

In an embodiment graphene pre-processing can also include a densification process. The monoatomic layered graphene is first dried with a spray dryer and then packed into a rubber tube with a certain diameter. The rubber tubes are placed into plastic tubes, which are used in a centrifuging machine. The densification of the as-packed graphene is implemented using a centrifuging technique. For example, the packing density of the graphene can be reached to 0.65 g/cm$^3$ with the rotation speed of 10000 rpm for 2 mins. The centrifuged materials in the rubber tubes can be placed into a cold isostatic presser to further increase to the packing density. Subsequently a bar shape of graphene, which has very high density is inserted into the Al (or other cladding material) tube prior to the drawing process. In another embodiment, graphene powder can be packed directly into an aluminium tube ready for drawing. In such embodiments the powdered graphene may be placed in the tube and then densified using a centrifuge, compression, or other techniques to increase the packing density within the tube. A combination of densification techniques and processes may be used. In industry production, the graphene materials can be fed into the metal tubes in an automated process, for example filling Al tubes automatically by machines. The automated process may include one or more densification processing steps.

It should be appreciated that the proposed embodiments are suitable for large scale manufacture of electrical conductors using the proposed graphene powder in tube methodology. In accordance with this industrial application of the methodology it should be
appreciated that particulate graphene material produced in large quantities may vary in purity and structure. Although in theory using pristine graphene, having no defects or impurities, as the input material for manufacturing the graphene core wires should produce very high quality conductors, this is not currently practical for applications such as wires for transmission lines requiring high volume cost effective production to be an economic substitution for current transmission lines. Pristine graphene has been produced in highly controlled processes, but is not currently produced in large quantities. The current cost of pristine graphene is also prohibitive for use in large scale cost effective production processes. Although pristine graphene may be produced in a manner currently economically viable for used for some products, for example medical devices or lightweight sensors etc., it should be appreciated that large scale industrial wire production, for example for transmission lines, would be currently more cost effective if graphene materials of lower quality than pristine graphene are used. All known current industrial processes for large quantity production of graphene yield graphene having impurities and defects. Particle size and shape may vary for the individual sheets and flakes making up the particulate graphene material. Further, defects can also be present in the lattice structure. The nature and quantity of defects can be a consequence of the method used to produce the particulate graphene material. In embodiments of the present invention the process of compressing and drawing the graphene core wires causes close packing and alignment of the sheets and flakes of the graphene thereby improving charge transport characteristics. Improvement in charge transport characteristics can be achieved using this method even for particulate graphene material having defects and impurities, thus indicating suitability for commercial industrial production of graphene core conductors.

For example, in one known method for producing graphene is to chemically produce graphite oxide (and a number of different methods can be used), which is then dispersed in a basic solution to yield monomolecular sheets known as graphene oxide. The graphene oxide is then reduced to provide a graphene product. However, the reduce graphene oxide (rGO) has many chemical and structural defects. The quantity and type of defects vary greatly depending on the production methods used. Types of defects can include binding of oxygen within or to the graphene lattice structure (i.e. C-O, C-O-C, C=O and others). The variation in quantity and type of defects can affect the properties of the graphene material, for example it is known that the impurities in reduced graphene oxide cause the conductivity and charge motility of reduced graphene oxide to be significantly worse than that of pristine graphene. However, testing by the inventors has shown feasibility of embodiments prepared using reduced graphene oxide. For example, reduced graphene oxide should have more than 35% of C=C bonds. Demonstrating the potential feasibility of embodiments using
reduced graphene oxide despite such defects and impurities indicates potential feasibility of embodiments prepared using particulate graphene materials prepared using other manufacturing processes that include defects or impurities.

Some embodiments of the graphene core conductor fabrication method can also include graphene pre-processing steps to improve the characteristics of the input particulate graphene material to the powder in tube manufacturing process. In an embodiment heat treatment or annealing of the particulate graphene material may be performed before the packing and drawings steps to improve the quality of the materials. Annealing the reduce graphene oxide in a reduction atmosphere, such as hydrogen or nitrogen environments can remove the oxygen and other absorbed substances from the surface of the graphene, thus increasing the specific surface area of the materials. This processing can free electrons from the bonding of C-O, C-O-O, C=0, 0-C=0 etc. In turn this can increase the electron density. Therefore, annealing reduced graphene oxides may enhance the surface area of the particulate graphene (sheets and flakes) and improve the electrical conductivity.

In one example, reduced graphene oxide is the particulate graphene material in manufacturing graphene core wires using an embodiment of the powder in tube manufacturing technique. The reduced graphene oxide (rGO) can be heat treated to improve the properties of the particulate graphene material prior to input to the powder in tube manufacturing process. In an embodiment the particulate graphene material is annealed in a pre-processing step. Testing by the inventors has indicated that annealing can improve the specific surface area of rGO without any negative impact on the number of defects in the lattice structure. The improved surface area may be related to reduction in oxygen content and other impurities. The improved surface area may translate to improved conductance in the final graphene core wires produced.

Initial testing by the inventors performed surface analysis using Brunauer-Emmett-Teller (BET) surface analysis for measuring the specific surface area of reduced graphene oxide (rGO) comparing as produced rGO and the as produced rGO after an annealing process. In this example rGO was subject to annealing at 1000°C in an N₂ atmosphere for 1 hour. Table 2 shows the effect of heat treatment on the surface area of the reduce graphene oxide (rGO). The BET surface area of the as-received rGO is 404.36 m²/gram and this can be improved to 552.1 m²/gram by annealing the materials at 1000°C in N₂ atmosphere for 1 hour. It is believed that the improvement is related to the reduction of oxygen content and removal of other impurities.
Table 2. BET measurement of reduced graphene

<table>
<thead>
<tr>
<th>Material</th>
<th>State</th>
<th>Surface Area (m²/g)</th>
<th>Annealing Temperature (°C)</th>
<th>Time (min)</th>
<th>Annealing atmosphere</th>
<th>Baking temperature (°C)</th>
<th>Baking time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene</td>
<td>As-received</td>
<td>404.36</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>300</td>
<td>30</td>
</tr>
<tr>
<td>graphene</td>
<td>As-annealed</td>
<td>552.1</td>
<td>1000</td>
<td>60</td>
<td>N₂</td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

Therefore, before packing powder into the tube, rGO graphene may benefit from being thermally treated to reduce the oxygen content to the lowest level for enhancing the electron density of the materials.

Raman spectroscopy is an important part of graphene study. It is used to study the number of layers, quality of graphene, defects, doping and etc. in carbon-based materials. Figure 20 shows the Raman spectrum of the as-received 2010 and the as-treated 2020 rGO. Details of the positions and intensities in Figure 20 are tabulated in Table 3. The presence of the D- and G-bands is quite distinguishable in this figure. The D-band is known as the disorder band or the defect band it represents a ring breathing mode from sp² carbon rings whilst the G-band represents the in-plane vibrational mode involving the sp² hybridised carbon atoms that comprise the graphene sheet. The increase of I_D/I_G ratio suggests a decrease in the average size of sp² band or increase of defects.

Table 3. Raman spectroscopy of the reduced graphene sample at different states.

<table>
<thead>
<tr>
<th>State</th>
<th>Peaks</th>
<th>Intensity (cm⁻¹)</th>
<th>Raman shift (cm⁻¹)</th>
<th>FWHM (cm⁻¹)</th>
<th>I_D/I_G</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>D-band</td>
<td>5098.117</td>
<td>1344.691</td>
<td>120.021</td>
<td>1.158</td>
</tr>
<tr>
<td></td>
<td>G-band</td>
<td>4400.507</td>
<td>1584.643</td>
<td>83.922</td>
<td></td>
</tr>
<tr>
<td>Thermally annealed at 1000°C-1hr</td>
<td>D-band</td>
<td>5096.088</td>
<td>1344.75</td>
<td>118.38</td>
<td>1.159</td>
</tr>
<tr>
<td></td>
<td>G-band</td>
<td>4396.65</td>
<td>1584.73</td>
<td>83.46</td>
<td></td>
</tr>
</tbody>
</table>

It is interesting to note that the sample annealed at 1000°C for 1 hour in N₂ atmosphere has almost the same I_D/I_G ratio (see Table 3). This indicates that annealing at this temperature was effective to increase the surface area but did not result in creating more defects in the reduced graphene oxide lattice structure.
In general, the D-band would not appear in pristine graphene. Therefore, the appearance of D-band in both treated and non-treated rGO indicates the existence of chemical bonds and edges in the rGO sheets.

The X-ray photoelectron spectroscopy (XPS) spectra of the as-received 2010 and the as-annealed 2020 rGO are shown in Figure 21. C=C, C-C, C-O, C-O-C, C=O, and O=C=O characteristic peaks were observed at 284.5, 285, 286.4, 287.8, 289.2 and 290.85 eV, respectively. The percentage of C=C plus C-C bonds was increased from 63.86% to 78.67% by the annealing the materials at 1000°C for 1 hr in N₂ atmosphere. In other words, the intensity of oxygen-related functionalities (organic C-O, C-O-C, C=O and etc.) decreased substantially after reduction annealing. Table 4 tabulates the summary of the XPS results, including binding energy peak, and the atomic fraction of molecular bonding.

<table>
<thead>
<tr>
<th>Name</th>
<th>Peak BE</th>
<th>Atomic %</th>
<th>Bonding</th>
<th>Name</th>
<th>Peak BE</th>
<th>Atomic %</th>
<th>Bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s A</td>
<td>284.5</td>
<td>37.11</td>
<td>C=C</td>
<td>C1s A</td>
<td>284.5</td>
<td>52.34</td>
<td>C=C</td>
</tr>
<tr>
<td>C1s B</td>
<td>285</td>
<td>26.76</td>
<td>C-C</td>
<td>C1s B</td>
<td>285</td>
<td>26.33</td>
<td>C-C</td>
</tr>
<tr>
<td>C1s C</td>
<td>286.4</td>
<td>9.85</td>
<td>C-O</td>
<td>C1s C</td>
<td>286.4</td>
<td>8.13</td>
<td>C-O</td>
</tr>
<tr>
<td>C1s D</td>
<td>287.8</td>
<td>4.91</td>
<td>C-O-C</td>
<td>C1s D</td>
<td>287.8</td>
<td>2.76</td>
<td>C-O-C</td>
</tr>
<tr>
<td>C1s E</td>
<td>289.2</td>
<td>3.13</td>
<td>C=O</td>
<td>C1s E</td>
<td>289.2</td>
<td>1.18</td>
<td>C=O</td>
</tr>
<tr>
<td>C1s F</td>
<td>290.85</td>
<td>5.02</td>
<td>O-C=O</td>
<td>C1s F</td>
<td>290.82</td>
<td>5.63</td>
<td>O-C=O</td>
</tr>
<tr>
<td>N1sA</td>
<td>399.7</td>
<td>0.52</td>
<td>N-H</td>
<td>Sb3d5A</td>
<td>531.86</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>N1sB</td>
<td>401.89</td>
<td>0.26</td>
<td>Nitrate</td>
<td>O1sA</td>
<td>533.43</td>
<td>2.33</td>
<td>Organic C=O</td>
</tr>
<tr>
<td>O1sA</td>
<td>533.32</td>
<td>6.83</td>
<td>Organic C=O</td>
<td>O1sB</td>
<td>530.58</td>
<td>1.07</td>
<td>Organic C=O</td>
</tr>
<tr>
<td>O1sB</td>
<td>531.47</td>
<td>5.36</td>
<td>Organic C=O</td>
<td>S2p3A</td>
<td>163.81</td>
<td>0.17</td>
<td>Thiol, R-SH</td>
</tr>
<tr>
<td>S2p3A</td>
<td>168.41</td>
<td>0.25</td>
<td>Metal sulfate</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

The above discussion indicates that reduction annealing can be a useful pre-processing step to improve the properties of at least some types of particulate graphene materials prior to the powder in tube manufacturing process, potentially improving quality of the output graphene core wires. Annealing or other pre-processing steps may also be used. The pre-processing processes applied to the particulate graphene material may vary between embodiments. The pre-processing processes to apply may be chosen based on the types of defects and impurities present in the input, raw, particulate graphene material.

As discussed above, by compressing graphene flakes/sheets the charge transport behaviour of the graphene material can be improved. Embodiments of the present invention utilise this
property in combination with fabrication techniques utilising mechanical deformation to provide advantageous electrical conductors. To provide a better understanding of embodiments of the invention the following discussion describes charge transport behaviours between graphene layers. The inventors modelled the conductance in the graphene layers using open-sourced Kwant code. The calculations were performed applying an assumption that graphene behaves as a ballistic conductor. Further investigation on the effect of the structural geometry on the inter-layer charge hopping was performed using density functional theory. The modelled results indicate that interlayer charge hopping can significantly affect the overall conductance between the graphene sheets. The modelling and calculated results are discussed in further detail in the following paragraphs.

The conductance modelling method applied is based on a theory that since graphene has very high carrier mobility, it is possible to describe the electrical transport in graphene as ballistic conduction. To explain in more detail, the ballistic condition assumes that the electrons can travel almost without resistance and each electron does not interact with other electrons or defects within the graphene sheet. Furthermore, since the structure of graphene is a single atomic layer, the charge transport behaviour has to be described by the quantum theory. In a normal conductor, the conductance can be described by Ohm’s law: \( G = \sigma A/L \), where \( A \) is the area of the cross section of the conductor, \( L \) is the length of the conductor, and \( \sigma \) is its conductivity. However, as the cross-sectional area reaches atomic scale, as in the case of graphene, Ohm’s law ceases to apply and the conductance \( G \) has to be reformulated based on quantum-mechanical theory. A standard technique to calculate the conductance for nano-scaled device or material is the Landauer-Büttiker formalism

\[
G = \frac{e^2}{h} \sum_{nm} |S_{nm}|^2 \tag{Equation 1}
\]

Equation 1 describes the conductance as the sum of amplitude of transmission probability

\( |S_{nm}|^2 \) where \( S_{nm} \) is the scattering matrix. The scattering matrix \( S_{nm} \) describes behaviour of electrons when it is injected from a left-lead (n) to a right lead (m). Since the material is ballistic, it is not expected that there will be scattering inside the material, thus the scattering process occurs at the leads. In quantum theory, electrons can be described as travelling waves, the scattering process will result in incoming and out-going waves at the left-lead (n) and incoming and out-going waves on the right lead (m). The \( S_{nm} \) matrix relates to the incoming waves in left and right leads to the out-going waves on the left and right leads.

The Kwant software package for modelling quantum transport was used to calculate the conductance \( G \) for the single layer and bi-layer graphene, as well as side contact graphene.
It should be appreciated that although the KWANT software package was chosen by the inventors for modelling, other quantum transport simulation software may also have been used.

The following section describes the modelling as performed using KWANT. An example of the structure of monolayer graphene as used in the modelling is shown in Figure 8a. A unit-cell refers to the minimalist periodic repeated geometrical configuration and the number of atoms which are used to describe the crystal structure of a material. The unit-cell of graphene contains two Carbon atoms located at two different lattice positions. In graphene, there are two in-equivalent sub-lattices a and b. Figure 8b and 8c show the unit cell of single layer graphene. To perform the conductance calculation, the unit cells of a single layer graphene and of a bilayer graphene were expanded in the horizontal plane to simulate a graphene sheet, for the conductance calculation. The positions of sub-lattices a 810 and b 820 are shown in Figures 8b and 8c. Figure 8a shows schematically how an electron can move in a single layer graphene sheet. The nearest neighbouring hopping energy of $\beta_0 = 3.16$ eV was input in the Kwant program. Hopping energy refers to the energy of an electron when it moved from one carbon (C) atom to another C atom. The nearest hopping energy refers to the energy of an electron when it moves from sub-lattice a 810 to the closest sub-lattice b 820 as shown in Figure 8a. In the case of graphene, there are three closest sub-lattice b 820, 830, 840 surrounding one sub-lattice a 810. Conductance in a graphene sheet happens when an electron is injected from the left lead 850 and hops from a sub-lattice a to a sub-lattice b, or sub-lattice b to sub-lattice a until it reaches the right lead 860. The Kwant code calculates the overall transmission amplitude at the left and right lead to determine the overall conductance $G$ as shown in Equation 1.

Figures 9a and 9b represent crystal structure of bilayer graphene with Figure 9a representing a Bernal stacking geometry, and Figures 9c and 9d illustrate the unit cell structure of bilayer graphene. For the bilayer graphene structure, the unit-cell consists of 4 in-equivalent lattice sites $a_1$, $b_1$, 920, $a_2$ 930 and $b_2$ 940 within a Bernal stacking geometry as illustrated in Figure 9a. Bernal stacking refers to the geometry in which the $b_2$ 940 sub-lattice of one of the layer is located directly underneath the $a_1$ 910 sub-lattice of the other layer, while the $a_2$ 930 sub-lattice is located directly beneath the centre point of the layer composed of the $a_1$ 910 and $b_1$, 920 sub-lattices. Figure 9e shows schematically how an electron can move in a bilayer graphene sheet. The nearest neighbouring hopping energy 950 of $\beta_0 = 3.16$ eV was input in the Kwant program eV also input was the interlayer hopping energy 960 of $\gamma_1 = 0.4$ eV as shown in Figure 9e. The interlayer hopping energy $\gamma_1$ refers to how the electron moves from one C atom in one layer to the next C atom to the
next layer. In this context the nearest neighbour hopping energy is a measure of the kinetic energy required for electrons to travel within the same layer, and interlayer hopping energy is a measure of the kinetic energy required for an electron to move from one layer to the next. Here the interlayer hopping between the layers is only considered for \( a_1 \to a_2 \) and \( b_1 \to b_2 \). The hopping energies used in the leads are similar to those used in graphene mono-layer and bi-layer graphene.

Figures 10a and Figure 10b illustrate the modelled graphene sheets used for conductance calculation in the single layer, bilayer and side-contact graphene. The sheets were modelled by expanding the unit cells of the monolayer (Figures 8b, and 8c), and of the bilayer (9c and 9d) to form the monolayer sheet (Figure. 10a) and bilayer sheet (Figure. 10b). Conductance calculations were performed for sheets modelled having the unit cell expanded ten times in two perpendicular (\( x \) and \( y \)) horizontal directions (\( 10 \times 1 \, 0 \)). To calculate the conductance using the Kwant software program, the positions of the leads and the hopping positions need to be defined. The leads were attached to the zigzag edges (1 0 3 0, 1 0 3 5, and 1 0 4 0, 1 0 4 5 respectively) for the monolayer 1 0 1 0 in Figure 10a and bilayer 1 0 2 0 in Figure 10b. In single layer graphene 1 0 1 0, the leads are attached to the left 1 0 3 0 and right 1 0 3 5 side of the 1 0 \( \times 1 \, 0 \) unit cells of graphene sheet at the zigzag position edges. In the bilayer graphene 1 0 2 0, the leads 1 0 4 0, 1 0 4 5 are attached to both of the top and bottom layers on the left 1 0 4 5 and right 1 0 4 0 side with similar electron hopping as in the case of the bilayer region 1 0 2 0, i.e. \( a_1 \to b_1, a_2 \to b_2, b_1 \to a_1 \) and \( b_1 \to b_2 \) for both of the left and right lead.

Figure 12 illustrates a model for side contact graphene for modelling the charge transport between adjacent overlapping graphene sheets or flakes 1 2 1 0, 1 2 1 5 where there is some side contact or close proximity between the graphene sheets or flakes. The difference between side contact and bilayer graphene is for the bilayer graphene, electrons can move from the left side to right side within the same layer. For side-contact graphene layers, electrons cannot move from the left side to the right side in the same layer. Electrons now move from the left side of the bottom layer, then they jump to the top layer to reach the right side of top layer. For side contact graphene hopping in the leads 1 2 2 5, 1 2 2 0 is restricted to, \( a_1 \to b_1 \) for the left lead 1 2 2 5 and \( a_2 \to b_2 \) for the right lead 1 2 2 0. In this model, electrons are injected into one layer 1 2 1 5, and then hop from one layer to the next layer 1 2 1 0 to reach the lead 1 2 2 0 on the other side. The hopping in the bi-layer region 1 0 2 0 is still \( a_1 \to b_1, a_2 \to b_2, a_1 \to a_2 \) and \( b_1 \to b_2 \). The hopping energies used in the leads are similar to those used in graphene mono-layer and bi-layer graphene.
Simulated conductance results in single-layer graphene, bi-layer and overlapping layer (side contact) graphene

Figures 11a and 11b show the respective calculated conductance of monolayer $10:10$ (Figure 8a-d & Figure 10a) and bilayer 1020 graphene (Figure 9a-e & Figure 10b) as a function of energy, with $t=0$ indicating the Fermi level and increasing $t$ shows higher band occupancy and therefore higher conductance. As shown in Figures 11a and 11b, the monolayer $10:10$ and bilayer 1020 graphene shows constant conductance $1110$, $1130$ at the Fermi level ($t = 0$ eV). As the energy increases, step increases in conductance $1120$, $1140$ occur as more bands are filled. The conductance steps in bilayer graphene are twice as large as in monolayer graphene due to the coupling of the two layers.

However, when modelling conductance between two overlapping graphene sheets the conductance is dependent on how the electrons move between the layers, i.e. the value of $\gamma_1$ the interlayer hopping energy between the sheets. This model is illustrated in Figure 12, as two overlapped graphene sheets $12:10$ and $12:15$, with a lead attached to one sheet $1225$ and another electrode $1220$ attached to the other sheet at the opposite end, so a current transmission path $1230$, $1240$, $1250$ from one electrode $1225$ to the other $1220$, hopping $1240$ between the two sheets $12:15$, $12:10$. The calculations were performed using a model having two $10 \times 10$ graphene sheets $100\%$ overlapped using Bernal stacking configuration. It should be appreciated that the relative orientation between two independent graphene sheets or flakes can vary. Many different orientations may exist within a sample of graphene material. In practice, a Bernal stacking configuration, as used in the above modelling, may occur but is unlikely to be the only inter-particle orientation found in a real life sample of graphene particles. In practice partial overlapping of sheets is also anticipated. Further, graphene particles (sheets and flakes) will typically vary in size in practice. Thus, effects of particle distance and relative orientation on charge transport between particles need to be considered.

The inventors have modelled side by side contact transport between two graphene sheets, this modelling indicated that the interlayer electron hopping energy $\gamma_1$ plays an important role in determining the overall charge transport behaviour. To determine the role of the electron hopping energy $\gamma_1$ on the overall conductance from one graphene sheet to the other graphene sheet, the value of $\gamma_1$ was varied from $0$ to $0.4$ eV. A value of $0$ eV means that there is no conduction from the bottom layer to the top layer, while a value of $0.4$ eV represents the maximum conduction from the bottom layer to the top layer. The higher the value of $\gamma_1$ means that electron can easily hop between from one layer to the next so it has
high kinetic energy $\gamma_1$. In the case of bi-layer graphene with Bernal stacking, the maximum value of the kinetic energy $\gamma_1$ is 0.4 eV. In the modelling method for the side by side contact graphene sheets, the leads are attached only on the left of the bottom sheet and on the right of top graphene sheet, if there is no charge conduction between the top and bottom sheet ($t = 0$), the overall conductance would be zero. Figures 13a to e, graph the results of modelling conductance for side contact graphene layers for different values of $\gamma_1$, this model shows a high dependence between the interlayer hopping energy and overall conductance from one graphene sheet to the other. As there is more conduction between the sheets (higher $\gamma_1$), the conduction between the two layers increases as $\gamma_1$ reaches the maximum value of 0.4 eV, as illustrated in Figures 13a-e. The conductance increases from 0 to 1 as $\gamma_1$ increases from 0 to 0.4 eV. In a perfect bilayer graphene, the kinetic energy value of electrons $\gamma_1$ is 0.4 eV, which represents a perfect environment which would allow electrons to move easily from one layer to the next. When there is defect, it would be more difficult for electrons to move from one layer to the next, which would decrease the value of $\gamma_1$. Thus, by making it easier for electrons to travel from one sheet to the next using a method which optimizes the geometrical alignment between the layers can enhance current transmission from one side to the other side. The inventor's study is described in further detail below.

The effect of structural geometry on the interlayer charge hopping

As shown in Figures 13a-e, for the case of the side-contact transport between the two graphene sheets, the interlayer hopping energy plays an important role in determining the overall charge transport behaviour. Electron transfer integrals (T.I.) show whether there is charge transfer between layers and is an equivalent to hopping energy. The electron transfer integrals (T. I.s) between the layers were investigated using a DFT (discrete Fourier Transform) method. Two specific parameters were considered in the study as illustrated in Figures 14a and 14b: the interlayer distance $d$ and the relative rotational angle (twisting angle) $\alpha$ between the layers 1430, 1440 as shown in Figures 14a and b. Figure 14a and 14b are schematic illustrations of the design parameters investigated, in terms of their influences on the interlayer electron transfer integrals in bilayer discotic systems. One of the molecules, chosen to be investigated in the present study is shown in Figure 14b, which was selected as a structural model to represent graphene bi-layer. The design parameters investigated here include the interlayer stacking distance $d$ between two molecules, and the rotational angle $\alpha$ of one molecule with respect to the other.

Two different geometrical configurations for the bi-layer graphene were considered for a finite structure of graphene flakes, which contain either zigzag edges as illustrated in Figure
15a, or both armchair and zigzag edges as illustrated in Figure 15b. Figures 15a and 15b illustrate molecular structures used to represent model systems of graphene for investigating the geometric dependence of interlayer electronic couplings. Some initial calculations done with benzene and triphylene showed highly irregular angular (a) dependence on the coupling term, most likely due to the fact that the Generalized Gradient approximation (GGA) method failed to create the correct spin density distributions at the frontier orbitals for highly symmetrical molecules (i.e. unable to remove orbital degeneracies in the problem). Therefore, the above two polyaromatic molecules with lower group symmetries were chosen to represent graphene flakes. Both molecules can be regarded as (3x3) in size with 3 benzene rings along each edge. For the molecule of figure 14a, all four edges are of zigzag type, whereas for the molecule of Figure 14b, two edges are of zigzag type and the others are of armchair type. All edge carbons are capped with hydrogen atoms.

These different terminations of the graphene flakes can have strong influence on the interlayer charge hopping energy when the two graphene layers are twisted at different angle. For zigzag only graphene flakes, the charge transfer integral exhibits an oscillation between 0 and 180 degrees, this is demonstrated in Figures 16 and 17. Figure 16 shows scanning of dimer transfer integrals for the system of Figure 15a at 3.6 Å intermolecular separation with a 180 degree in-plane rotation of one monomer scan of the change in T.I. A perfect symmetrical pattern can be observed for this system due to the existence of inversion centre in the monomer. The scan was performed at 2 degree angle interval. Figure 17 shows scanning of dimer transfer integrals for the system of Figure 15b at 3.6 Å intermolecular separation with a 180 degree in-plane rotation of one monomer scan of the change in T.I. For this molecule that is lack of a rotational centre of symmetry, there is also a clear lack of symmetry in the pattern of T.I. scan with respect to the in-plane rotation angle.

Figures 16 and 17 show that the two layers exhibit strongest charge coupling when they are completely aligned (0 degrees), and then the charge coupling between layers decreases to a minimum value when the layers are 90 degree out of phase. The T.I. value then increases and reaches its maximum value at 180 degree. For configuration with mix-edges, the T.I. value decreases slowly as the twisting angle increases to 180 degree. As a result, this result demonstrates the importance of how the graphene layers are aligned with each other. Alignment between layers can strongly affect the overlapping of the wave function which can weaken the interlayer hopping energy, resulting in much weaker side-contact transport.

In addition to the rotational angles between the graphene layers, the role of the interlayer distance was also investigated for different rotational angles, which is demonstrated in Figures 18 and 19. Figure 18 shows scanning of dimer transfer integrals for the system of...
Figure 15a as a function of interlayer distances $d$ at a selected different in-plane rotation angles. Figure 19 shows scanning of dimer transfer integrals for the system of Figure 15b as a function of interlayer distances $d$ at a few different in-plane rotation angles. A trend can be observed for the zigzag termination in which it shows how maximum charge transfer integral for the shortest interlayer distance. This indicates that as the layers come closer together, the possibility for conductance between the layers increases, i.e. electrons can move from one layer to next. While for the mix armchair and zigzag terminations, the interlayer charge hopping increases at $d = 1.5 \text{ Å}$ and then decreases monotonically as the interlayer distance increases. Consequently, the overall results suggest that an optimal charge transport between the graphene layers is strongly dependent on the role of the interlayer distance and the rotational angle alignment between the layers so the interlayer hopping can reach its maximum energy similar to the transport in a perfect mono-layer graphene sheet.

Thus, it is advantageous for a manufacturing technique to encourage improved alignment between graphene particles, in particular in the layering of graphene sheets and flakes. Further, reduction in distance between graphene particles can also improve charge transport characteristics.

As discussed above the proposed powder in tube manufacturing technique encourages alignment and reduction of interlayer distance between graphene particles through the process of mechanical deformation. The drawing process combines a sideways (perpendicular) force with an elongating (parallel or aligned) force to elongate the powder in tube material, this combination of forces applied to the graphene particles encourages tight packing of the graphene particles. Flow effects of the drawing process encourage reorientation and alignment of graphene sheets, and the compression also forces reduction of interlayer distances. Thus, using a wire drawing technique can improve charge transfer properties of graphene materials, through improving alignment and density of the graphene sheets and flakes. Embodiments of the invention provide graphene core wires utilising powder in tube manufacturing techniques.

Prototype embodiments of graphene core wires were produced to perform some initial practical testing, and results of the prototype embodiment testing are provided below. These test results provide evidence indicating the potential of a powder in tube manufactured graphene core wire as a conductor for many applications. For prototype testing wires of pure Al, Al sheathed annealed reduced graphene oxide (rGO) composite, and also Al sheathed Al$_2$O$_3$ (Aluminium oxide) were drawn having outside diameters ranging from of 8 mm to 1 mm. The aluminium oxide core wires were produced using the same powder in tube
methodology and the graphene core wires to provide a wire having a non-conductive core (aluminium oxide being a known insulator) produced using the same technique for comparative analysis.

In order to understand the electrical transport in materials, wires of pure Al, Al sheathed rGO composite and also Al sheathed Al₂O₃ were drawn having outside diameter of φ8 mm to φ1 mm. Performance of these wires was measured for resistivity and temperature performance for 50Hz AC at varying amplitudes. AC measurements against the temperature were conducted using load currents of 2A, 5A, 8A, 10A, 12A, 15A, 18A, 20A, 22A, and 25A with a constant frequency of 50Hz and the corresponding temperature was carefully monitored using a thermocouple in accordance with the standard (ASTM B193).

Tables 5 and 6 tabulates the AC measurement results of the Al and Al sheathed rGO composite wires. Figure 22a shows the current versus resistance in Al 2210 and Al sheathed rGO composite 2220 wires in AC mode. The corresponding temperature rise versus current is also plotted for both Al 2210 and Al/rGO 2220 in Figure 22b. One can be seen that the resistivity of Al sheathed rGO composite wire 2220 is slightly better than that of Al wire 2210 at the lower currents but similar at high currents. The temperature response for the corresponding load current for both wires is similar. It should be noted that the cross section area of Al in the Al sheathed rGO composites is 10.8% less than that of the pure Al wires as shown in Figure 23. If the rGO core in the composite wire does not make any contribution to the electrical conduction, the resistivity of the composites should be 10.8% smaller than the resistivity of pure Al wires. Therefore, similar resistivity between the pure Al wires and the wires of Al sheathed rGO demonstrates that the rGO core contributes to the electrical conductance and its resistivity is similar to the resistivity of the pure Al. The electron density in rGO is much lower than that in the pristine graphene. In addition, the large amount of defects, such as organic C-O, C-O-C, C=0 and 0-C=0 etc. in rGO is also affect the electron mobility significantly. It is anticipated that the rGO has much lower electrical conductivity than the pristine graphene due to defects. Input particulate graphene material having less defects than the sample used in these presented test results may provide better conductivity than the current test results. However, the experimental results listed in Table 5 and plotted in Figures 22a and 22b evidence the feasibility of embodiments of this invention in the application of graphene enhanced performance of power transmission lines.

In order to verify the feasibility of graphene core conductors in accordance with embodiments of the invention graphene core wires were compared with wires prepared using the same method having non-conducting core material. For this test, pure alumina powder (99.9% Al₂O₃), which is an insulator with resistivity of 1x10⁶ Ω-m, was filled into the
Al tubes and drawn from $\phi 8\text{mm}$ to $\phi 1\text{mm}$ to form the Al sheathed $\text{Al}_2\text{O}_3$ composite wires for comparison. Figure 24a plots the measured resistivity of the Al sheathed $\text{Al}_2\text{O}_3$ 2410 and the one of Al sheathed rGO 2420. It should be appreciated that the aluminium sheath is conductive and so contributes to the overall conductivity of the wires. However, Figure 24b clearly shows better conductivity of the AL/rGO wires 2420 compared with the AL/ $\text{Al}_2\text{O}_3$, wires 2410 verifying the core of rGO makes significant contribution to the electrical conductance in Al sheathed rGO composites.

There is also significant potential to enhance electrical conductance by using high quality graphene instead of rGO in embodiments of graphene core wires. Further optimisation of fabrication parameters may also improve graphene core wire performance. Also in some embodiments the structure of the transmission lines may be optimised for utilising graphene core wires. The presented test results evidence the feasibility of this technology for electrical conductors and transmission lines.

<table>
<thead>
<tr>
<th>Table 5. Current vs. Resistivity and Temperature of Al and Al/rGO wires in AC mode (50Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Al</strong></td>
</tr>
<tr>
<td>Current (A)</td>
</tr>
<tr>
<td>2.094</td>
</tr>
<tr>
<td>5.068</td>
</tr>
<tr>
<td>8.06</td>
</tr>
<tr>
<td>10.06</td>
</tr>
<tr>
<td>12.04</td>
</tr>
<tr>
<td>15.2</td>
</tr>
<tr>
<td>17.98</td>
</tr>
<tr>
<td>20.08</td>
</tr>
<tr>
<td>24.84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 6. Current vs. Resistivity and Temperature of Al/$\text{Al}_2\text{O}_3$ and Al/rGO wires in AC (50Hz) mode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Al/$\text{Al}_2\text{O}_3$</strong></td>
</tr>
<tr>
<td>Current (A)</td>
</tr>
<tr>
<td>1.996</td>
</tr>
<tr>
<td>4.912</td>
</tr>
<tr>
<td>7.86</td>
</tr>
<tr>
<td>9.74</td>
</tr>
<tr>
<td>12.06</td>
</tr>
<tr>
<td>14.94</td>
</tr>
<tr>
<td>18.06</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>24.8</td>
</tr>
</tbody>
</table>
An application of the graphene core wires is in electrical devices and transmission lines. In some instances, such as for use in electrical motors or transformers the graphene core wire may be used directly in windings. Alternatively the, monofilament graphene core wires can be further processed to form multifilament wires 160. This further processing may simply comprise applying an insulating coating to one or more wires, alternatively further processing may comprise bundling, braiding, winding or wrapping multiple wires into a desired conductor or cable configuration. Multifilament wires may be formed from the graphene core wires using known fabrication techniques.

For application in transmission lines the monofilament graphene core wires are further processes to produce a multifilament wire as a basic component for the transmission lines 160. In this embodiment a plurality of monofilament graphene core wires are the arranged into either a round or hexagonal shape and then are inserted into another metal tube (as represented in Figure 2c for example this plurality of monofilament wires may comprise a stack of 7, 19, 37, 55, 61, 85, or higher numbers or other numbers of monofilament wires. This tube and plurality of monofilament wires are again drawn through a series of drawing dies, as represented in Figure 2d to form a multifilament graphene/metal composite wire, the representative cross section of the multifilament wire is shown in the Figure 2e. The multifilament wire can then be incorporated into a multi-wire transmission line bundle 170, which may comprise a plurality of conductive wires and additional wires or other structure having a primary purpose of providing mechanical support for the electrically conductive wires.

It should be appreciated that the techniques used for forming the initial monofilament graphene core wires, is based on known powder-in-tube techniques. After the initial monofilament wire fabrication, the subsequent multifilament wire and multi-wire transmission line bundles can also be fabricated using known techniques. Thus, embodiments of the present invention can enable improvements in transmission line performance without requiring significant change to manufacturing techniques or other transmission grid infrastructure. The electrical performance improvements being enabled by the graphene core wires.

The graphene core wires may also support other desirable transmission line performance characteristics. The thermal coefficient of graphene is two orders of magnitude lower than the listed metals in Table 1. Hence, it is envisaged that the effect on electrical resistance observed in the metallic conductors, including silver, copper and aluminium etc., caused by
significant temperature events may be reduced or avoided in transmission lines using graphene cores/filaments. In some cases, the increase of temperature may even result in slightly higher conductivity in transmission lines incorporating graphene core wires. This is because graphene has a negative thermal coefficient of -0.0002/K. The negative thermal coefficient is related to the increase of electron density with increasing the temperature, without influencing the electron mobility due to the zero effective mass of electrons in graphene. On the other hand, the high thermal conductivity of graphene can quickly dissipate heat generated due to electrical resistance. Therefore, the transmission line made with the graphene/metal composite may carry higher density of the electric current with reduced energy loss. Embodiments may also enable high performance with minimal performance impact due to temperature.

Further, compared to the other metallic conductors listed in Table 1, graphene presents the lowest density. Hence, using the graphene/metal composite for electric conductors can substantially reduce the total mechanical loading in the transmission lines. This can improve the mechanical properties of the transmission lines, for example reducing creeping problems.

Another advantage of the proposed graphene core and metallic sheath structure is that, regardless of the monofilament or multifilament graphene/metal composites, a substantial portion of the electric current passes through the higher conductive graphene filaments instead of copper (or other metal) cladding. This phenomenon minimises skin effects, which is the tendency for current density of an alternating current to be distributed having the greatest density nearest the surface of the conductor and decreasing towards the centre of the conductor, such effects manifest in increased resistance at high alternating current frequencies. This skin effect is mitigated by the concentration of current in the lower resistivity graphene core.

In an embodiment of this invention, mono-filament or multi-filament wires are used to fully replace currently used metal conductive wires, such as copper, and aluminium, to produce the next generation high performance electric power grid transmission lines. For example, known transmission line fabrication techniques include aluminium conductor steel reinforced (ACSR) and all-aluminium alloy conductor (AAAC) techniques bundling strengthening wires around conductive core wires, and composite core conductors such as ACCR and ACCC where the strengthening structure is a conductor core, for example carbon and glass fibre core, and the wires for carrying the electrical power are bundled around the supportive core
(as shown in the example photograph of Figure 7). In embodiments of the invention the electrically conductive wires (traditionally aluminium or copper) are replaced with the graphene core wires fabricated as discussed above. It is envisaged that the graphene/metal composite wires of the present invention can be incorporated into any known transmission line structure. For example, the photograph 700 of Figure 7 illustrates a structure where a plurality of conductive multifilament graphene/metal composite wires 710 are bundled around and supported by a strengthening core 720. Each of the multifilament wires 710 are fabricated as discussed above by drawing a plurality of graphene core fibres 730 in a metal casing 740.

Although the above described embodiment utilises graphene/metal composite conducting wires for all of the conductive wires in the transmission line bundle it is envisaged that hybrid structures may also be used, where a plurality of different types of wires are incorporated in the transmission line bundle.

Advantages of electric conductors made with the graphene/metal composites, can include reducing the resistance, limiting the temperature effects, and suppressing the skin effects. In some embodiments these advantages can increase the electric energy transmission efficiency of the transmission lines. For example, a 5% efficiency improvement can translate to significant cost and energy saving on a national scale. For example, the electrical energy consumption in China was 5500 TWh in 2015. 5% saving of this energy consumption is 275 TWh, which was slightly more than the total electrical energy consumption of Australia (248 TWh) in 2015.

Embodiments of the invention have the potential to increase the electrical conductivity of electric power grid transmission lines by up to 5% and possibly more in some embodiments by using highly conductive graphene to form graphene/metal composite wires for use as conductors in transmission line bundles. This translates to significant cost and energy saving on a national scale.

Embodiments of this invention utilize the unique electrical conductivity properties of graphene. The electrical current is transported in an atomic plane of graphene. However, fabricating and shaping a large scale graphene product is extremely difficult. The inventors have also proposed a wire fabrication method to overcome the difficulties of shaping graphene, to enable fabrication of graphene/metal composite high performance electric conductors. By using the powder-in-tube technique, we can produce the highly dense and
well aligned graphene structure, thus significantly improving the electrical pathway in large scale. Such conductors have a higher electrical conductivity than current electric wires.

The commercial applications are not only for the electric power transmission lines but also other devices including high performance transformers and electric motors.

It will be understood to persons skilled in the art of the invention that many modifications may be made without departing from the spirit and scope of the invention.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.
CLAIMS:

1. An electrical conductor comprising a graphene core surrounded by a sheath, the graphene core comprising particulate graphene material compressed within the sheath.

2. An electrical conductor as claimed in claim 1, the conductor being formed using a powder in tube process, wherein particulate graphene is placed in a tube comprising the sheath material and the tube drawn to thereby provide the graphene core and sheath.

3. An electrical conductor as claimed in claim 2 wherein the graphene core and sheath structure form a wire.

4. An electrical conductor as claimed in any one of the preceding claims wherein, the particulate graphene powder comprises graphene flakes.

5. An electrical conductor as claimed in any one of the preceding claims, wherein the sheath is formed of a metallic, polymer or other material.

6. An electrical conductor as claimed in claim 5 wherein the sheath is formed of any one or more of: aluminium, copper, silver and gold.

7. An electrical conductor comprising a plurality of electrical conductors as claimed in any one of claims 1 to 6 forming a cable.

8. A multifilament conductor comprising a plurality of graphene core wires as claimed in claim 3 or claim 6.

9. An electrical power transmission line comprising:

   a plurality of electrical conductors configured for transmission of high voltage alternating current electrical power; and

   at least one strengthening structure bundled with the electrical conductors to provide mechanical support to the power transmission line;

   wherein at least one electrical conductor comprises a graphene core composite conductor, each graphene core composite conductor comprising one or more electrical conductors comprising a graphene core of particulate graphene material compressed within the sheath.
10. An electrical power transmission line as claimed in claim 9 wherein each graphene core composite conductor comprises a plurality of electrically conductive wires, each wire comprising a graphene core compressed within a metallic sheath.

11. An electrical power transmission line as claimed in claim 10 wherein the plurality of electrically conductive wires are further surrounded by a metal sheath.

12. An electrical power transmission line as claimed in claim 10 or claim 11 wherein each of the electrically conductive wires are formed using a power-in-tube method for forming the wire comprising the graphene core.

13. A method of producing an electrical conductor, the method comprising the steps of:
   providing particulate graphene material;
   placing the particulate graphene material into a hollow tube of drawable sheath material, and
   drawing the graphene filled tube to cause compression of the graphene material through deformation of the tube to provide an electrical conductor comprising a core of the particulate graphene material compressed within a sheath.

14. A method as claimed in claim 13 wherein the step of drawing the graphene filled tube comprises pulling the graphene filled tube through a series of drawing dies.

15. A method as claimed in claim 14 further comprising a step of annealing the drawn graphene filled tube.

16. A method as claimed in claim 15 wherein the annealing is performed intermittently between drawing the graphene filled tube through the series of drawing dies.

17. A method as claimed in any one of claims 13 to 16 wherein the graphene core electrical conductor is formed as a wire, and further comprising the step of forming a plurality of graphene core electrical conductor wires into a multifilament graphene core composite conductor.

18. A method as claimed in claim 17 wherein the plurality of graphene wires are placed into a metal tube and drawn to provide the multifilament graphene core composite conductor.
19. A method as claimed in claim 15 or 18 further comprising a step of bundling one or more multifilament graphene core composite conductors into a transmission line cable.
Graphene powder inserted in tube

Tube drawn through die

Annealing required?

Annealing (heat treatment)

Further drawing?

Single filament wire

Multifilament wire forming

Transmission line bundle forming

Next drawing die

Figure 1
Figure 2

Figure 3a

Figure 3b
Figure 6

Direction of Current Flow
Figure 11a

Figure 11b
Figure 13b

Figure 13c
Figure 18

Figure 19
Figure 20

Figure 21
Figure 23

Figure 24a
Figure 24b
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

H01B 1/04 (2006.01)  H01B 1/18 (2006.01)  H01B 13/22 (2006.01)

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)

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

Electronic database consulted during the international search (name of database and, where practicable, search terms used)

EPODOC and WPIAP - CPC and IPC: H01B13/22, H01B1/04, H01B1/18. Keywords: graphene, power transmission, graphene core, compress, and the like keywords: TXTE (i.e. TXPEA, TXPEB, TXPEC, TXPEE, TXPEF, TXPEH, TXPEI, TXPEP, TXPES, TXPEPEA, TXPUSEOA, TXPUSEIA, TXPUSEA, TXPUSEB, TXPUSEA) - Keywords: graphene, particulate graphene, compress, sheath, metal sheath, anneal, power transmission, multi filament, and the like keywords; Google Scholar - Keywords: graphene, particulate, compress, sheath, tube, power transmission, and like keywords; Google Internet Search - Keywords: graphene, particulate, compress, sheath, tube, power transmission, and like keywords; Applicant(s)/Inventor(s) name searched in internal databases provided by IP Australia, AusPat and the Lens.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*  Citation of document, with indication, where appropriate, of the relevant passages  Relevant to claim No.

Documents are listed in the continuation of Box C

[X] Further documents are listed in the continuation of Box C  [X] See patent family annex

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed
  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  "&" document member of the same patent family

Date of the actual completion of the international search 30 June 2017

Date of mailing of the international search report 30 June 2017

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
Email address: pct@ipaustralia.gov.au

Authorised officer

Eugene Koh
AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No. 0262832580
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>GB 2487052 A (JOHN CLIFFORD COMPTON) 11 July 2012 whole document, in particular Abstract; Figure 5; page 4 paragraph 2, page 7 paragraph 2</td>
<td>1, 5</td>
</tr>
<tr>
<td>Y</td>
<td>whole document, in particular Abstract; Figure 5; page 1 paragraphs 1-3, page 4 paragraphs 2-7, page 7 paragraph 2</td>
<td>2-3, 7-8, 13-14, 17-18</td>
</tr>
<tr>
<td>A</td>
<td>whole document</td>
<td>4, 6, 9-12, 15-16, 19</td>
</tr>
<tr>
<td>X</td>
<td>CN 102592720 A (QINGWEN YU) 18 July 2012 whole document, in particular Abstract; paras. [0005], [0017], [0020]</td>
<td>1, 4-5, 9</td>
</tr>
<tr>
<td>Y</td>
<td>whole document, in particular Abstract; Fig. 1; paras. [0005], [0015], [0017], [0020]-[0021]</td>
<td>2-3, 7-8, 10-12</td>
</tr>
<tr>
<td>A</td>
<td>whole document</td>
<td>6, 13-19</td>
</tr>
<tr>
<td>X</td>
<td>CN 101483085 A (YIFANG YANG) 15 July 2009 whole document, in particular Abstract</td>
<td>1, 5-6</td>
</tr>
<tr>
<td>Y</td>
<td>whole document, in particular Abstract</td>
<td>2-3, 7-8, 10-12</td>
</tr>
<tr>
<td>A</td>
<td>whole document</td>
<td>4, 9, 13-19</td>
</tr>
<tr>
<td>Y</td>
<td>US 2014/0363677 A1 (HAMILTON SUNDSTRAND CORPORATION) 11 December 2014 whole document, in particular Abstract; Figs. 1, 5; paras. [0001]-[0002], [0017], [0023]</td>
<td>2-3, 7-8, 13-14, 17-18</td>
</tr>
<tr>
<td>A</td>
<td>whole document</td>
<td>1, 4-6, 9-12, 15-16, 19</td>
</tr>
<tr>
<td>A</td>
<td>CA 24232 15 A1 (SMITH, JACK B.) 20 September 2004 whole document</td>
<td>1-19</td>
</tr>
<tr>
<td>Box No. II</td>
<td>Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>--------------------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. ☑️ [ ] Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely: the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. ☑️ [ ] Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. ☑️ [ ] Claims Nos: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Box No. III</th>
<th>Observations where unity of invention is lacking (Continuation of item 3 of first sheet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This International Searching Authority found multiple inventions in this international application, as follows:</td>
<td></td>
</tr>
<tr>
<td>See Supplemental Box for Details</td>
<td></td>
</tr>
<tr>
<td>1. ☑️ [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.</td>
<td></td>
</tr>
<tr>
<td>2. ☑️ [ ] As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.</td>
<td></td>
</tr>
<tr>
<td>3. ☑️ [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:</td>
<td></td>
</tr>
<tr>
<td>4. ☑️ [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:</td>
<td></td>
</tr>
</tbody>
</table>

| Remark on Protest | ☑️ [ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee. |
|                   | ☑️ [ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation. |
|                   | ☑️ [ ] No protest accompanied the payment of additional search fees. |

Form PCT/ISA/210 (third sheet) (July 2009)
**Continuation of: Box III**

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 1-8 are directed to an electrical conductor. Specific to this group of claims is the feature of a graphene core comprising particulate graphene material compressed within a sheath.

- Claims 9-12 are directed to an electrical power transmission line. Specific to this group of claims is the feature of at least one strengthening structure bundled with the electrical conductors to provide mechanical support to the power transmission line.

- Claims 13-19 are directed to method of producing an electrical conductor. Specific to this group of claims is the feature of drawing the graphene filled tube to cause compression of the graphene material through deformation of the tube.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all of the claimed inventions and which provides a technical relationship among them is the feature of a graphene core comprising particulate graphene material compressed within a sheath.

However this feature does not make a contribution over the prior art because it is disclosed in each of the documents:

- GB 2487052 A (JOHN CLIFFORD COMPTON) 11 July 2012
- CN 102592720 A (QINGWEN YU) 18 July 2012
- CN 101483085 A (YIFANG YANG) 15 July 2009

Therefore in the light of this document this common feature cannot be a special technical feature. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied a posteriori.
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Publication Number</td>
<td>Publication Date</td>
</tr>
<tr>
<td>GB 2487052 A</td>
<td>11 July 2012</td>
</tr>
<tr>
<td>CN 102592720 A</td>
<td>18 July 2012</td>
</tr>
<tr>
<td>CN 101483085 A</td>
<td>15 July 2009</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>CA 24232 15 A1</td>
<td>20 September 2004</td>
</tr>
</tbody>
</table>

End of Annex