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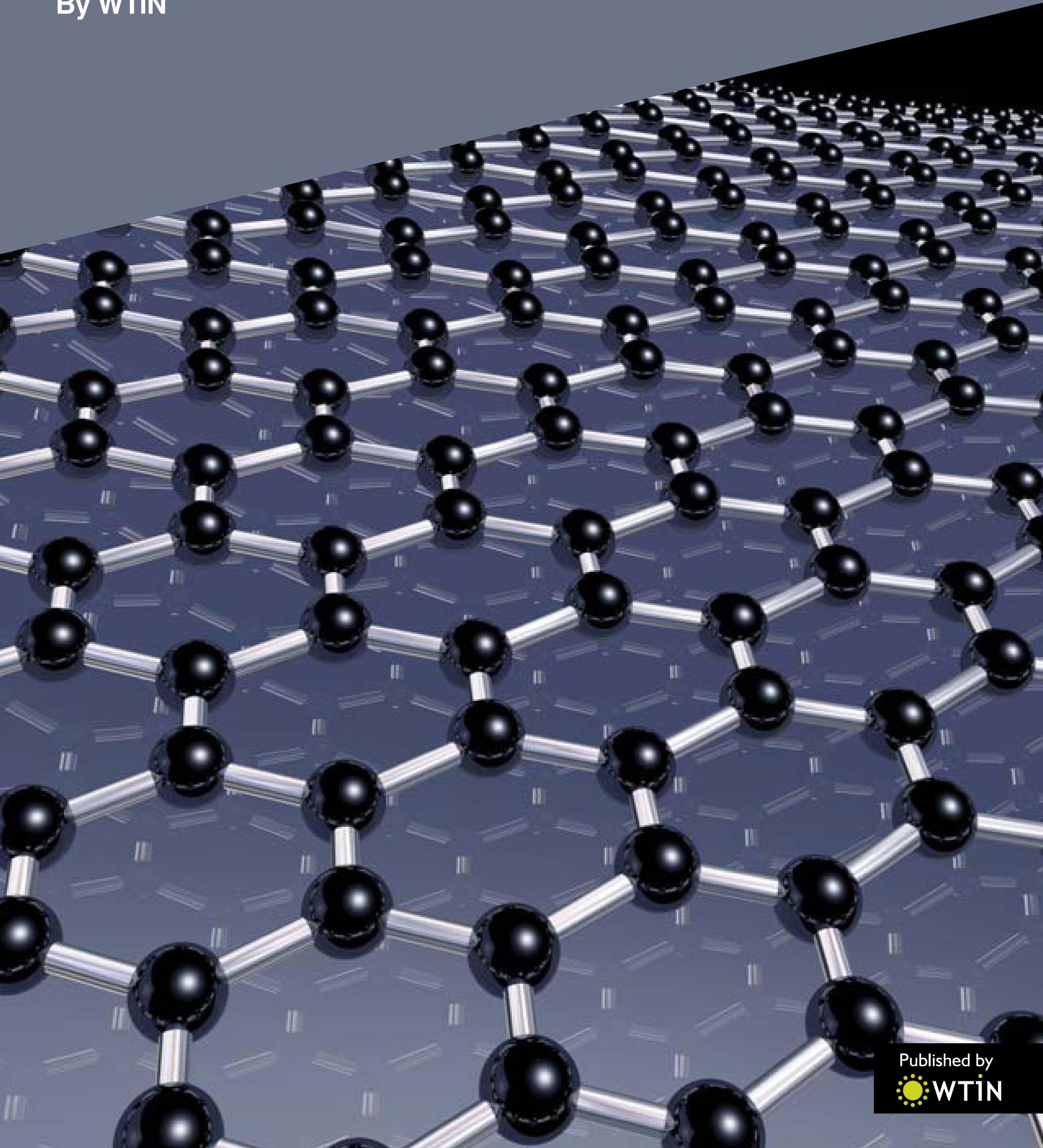
Graphene & its opportunities for the textile industry

By WTiN



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Executive Summary

Graphene is a single-atom-thick sheet of hexagonally arranged, bonded carbon atoms, either as a freestanding membrane or flake or adhered to a substrate. It has remarkable intrinsic properties such as very high tensile strength, excellent thermal and electrical conductivity, as well as high flexibility, elasticity and light weight, which can lead to unexpected advances. As it is thermally and electrically conductive, it has the potential to be used as a component in biosensors/bio-detectors and can also be used in wearable technology and areas such as patient care, sports and protective clothing.

In this report WTiN has provided information about graphene and its opportunities for the textile industry. The report begins with an introduction to graphene and its terminology and the graphene market. It then discusses graphene's properties and potential applications across different areas, and the challenges involved with this industry are addressed.

There are several different types of graphene products in the market which are produced in various ways. This can potentially make it difficult to supply a good quality of graphene that is suitable for a specific application. This report has therefore provided insights into different forms of graphene such as graphene film/membrane, graphene ink, graphene oxide (GO) and graphene flakes or nanoplatelets together with some information about their manufacturing routes. After that, we have compiled a comprehensive list of graphene suppliers for the textile industry and their types of products and services.

Due to the knowledge gap as to how graphene can be incorporated into textile products while adding suitable required functionalities, the next parts of this report have addressed approaches to incorporate graphene into textiles i.e. spinning graphene fibres (pure or composite) or graphene-enhanced fabrics through coating and printing techniques.

Finally, the last parts of this report will discuss real functionalities and performance that graphene can bring to technical textiles, including electrically conductive textiles and fire retardant, thermally conductive and UV protective fabrics. Moreover, this section will include new and commercialised textile developments and products using graphene, with a list of key players in this domain. This is by no means an exhaustive list, and new products are entering the market all the time, but it does provide an indication as to the types of products that are currently available commercially.

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Introduction

Textiles and fabrics have remained an essential piece of human life throughout the history, with natural fibres being the only raw materials back in the time, mainly from animals and vegetables, After that, synthetic polymeric fibres from petroleum were discovered towards the beginning of the 20th century to meet the rapidly increasing demand for fibres and to complement the limited availability of natural products. In the 21st century however, progression in textiles have been towards development of functional and smart textiles having particular properties including the electrical, thermal, optical, moisture and other technical behaviours. So far, different strategies have been employed to manufacture smart and conductive textiles for different purposes including integration of inorganic particles, metals, organic polymers and naturally derived materials into textiles at the fibre or fabric levels. However, the challenge is still remained to achieve lightweight, flexible, non-toxic, washable and yet high-performance smart textiles[1].

Graphene is a breakthrough 2D material in the 21st century and it is made of flat monolayer of carbon atoms, arranged in a honeycomb crystal lattice. Graphene is the basic building block of graphite and therefore a natural material and while it was discovered back in the 1940s, graphene sheet was physically isolated only in 2004 via a exfoliation method. This was globally recognized with a Nobel Prize in 2010. Graphene in its purest form has extraordinary electrical, thermal, optical and mechanical properties and it can promise a new generation of innovative devices including smart textiles.

Forms of carbon

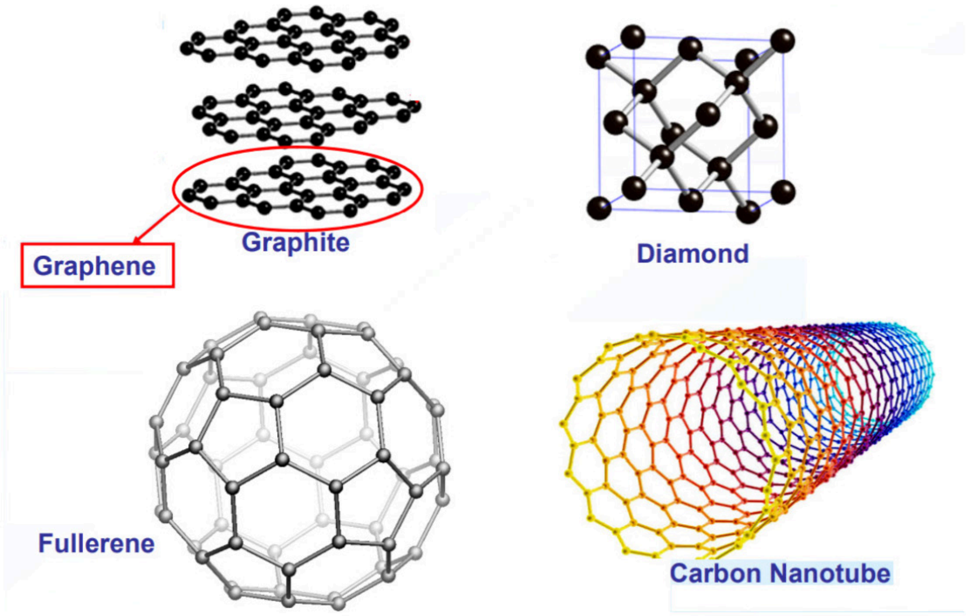
Carbon is one of the most remarkable elements among all chemical and it was one of the first which was known to human. It was known for years that carbon comes in two basic but interestingly different forms of materials; diamond and graphite, in which the atoms are arranged differently. The carbon atoms in diamond are arranged in a lattice form whereas in graphite they are arranged in a lamellar (layered or planer) structure[2].

Later on, the fullerene and carbon nanotube (CNT) in the 1990s and early 2000s, became the favourite research topic in materials science[3]. These are allotropes of carbon composed of flat sheets of carbon atoms arranged in a hexagonal pattern and when it comes in the form of hollow sphere or ellipsoid is called fullerene, whereas hollow cylindrical forms are known as nanotubes. Before discovery of graphene in the 21st century, there was always the debate on whether carbon could exist in two-dimension or not. Different forms of carbon are schematically shown in Figure 1.

Graphene terminology

Graphene was first discovered in 2004 by researchers from Manchester University, UK, when they succeeded in isolating a single layer of carbon atoms (graphene sheets) from a lump of bulk graphite with adhesive tape[5]. The development of this technique is called mechanical exfoliation of pristine graphene which won the Nobel Prize in Physics in 2010. Graphene in its purest form, is a single atomic layer of hexagonally arranged, bonded carbon atoms, which is either freely suspended or adhered to a substrate and is referred to as a 2D material. Graphene is also isolated bi- or tri-layer (two and three layers respectively), or multi-layer (more than three layers), and they display a range of different qualities as the number of layers increases, as well as becoming progressively cheaper as the layers multiply. A distinction is made

Figure 1. Different forms of carbon; graphite, diamond, fullerene, carbon nanotube and graphene[4]



between multi-layer graphene and graphite, when there are more than 10 layers of carbon, as even though the structure is the same, more numbers of layers result in different properties. To avoid confusion and issues, there is now an ISO document available (ISO 80004-13:2017) that defines "graphene is only one atomic layer of carbon up to only 10 layers of carbon" and it is more than that, it does not fit within graphene terminology.

Graphene and related materials have set to become a revolutionary material in different fields of science and engineering due to a combination of properties it has. The extraordinary properties such as high electron mobility, high thermal conductivity and mechanical properties of graphene makes it a key enabling technology to develop functional products in several areas of applications. These unique properties derive from its unique two-dimensional atomic morphology and electronic structure, generating new products that cannot (or may be difficult to) be obtained with current technologies or materials. There have been more than 10,000 patents granted to graphene-related technologies only in the first decade after discovery of it in 2004[3].

Achieving the new disruptive technologies and commercialising them based on graphene is conditional to reaching a variety of objectives and overcoming several challenges throughout the value chain, ranging from materials development and price to inclusion of it into components and systems.

Graphene properties

Graphene has many extraordinary properties. The unique plane structure and geometry of monolayer graphene contribute to its super properties. These remarkable properties of graphene provide infinite possibilities for many potential applications in many areas such as electronics, energy storage and conversion, biotechnology and especially improvement in composite fibre materials.

In this section, graphene properties will be explained, and they are categorised into mechanical, thermal, electrical, optical and chemical properties. It is important to consider that most of these properties and values are related to defect-free single layer graphene sheet. Defects in graphene for example can arise from the connection points between smaller flakes that have been stitched together and these defects can result in a weaker graphene with quite different properties[6].

Physical/mechanical properties

Graphene is the world's thinnest material and in fact the thickness of one single layer of graphene is around 0.34 nm and it is very lightweight with only 0.77 milligrams per sqm. Moreover, graphene is also one of the strongest materials and is stronger than both diamond and steel when they are compared in the same thickness. Graphene has a tensile strength (the maximum stress that a material can withstand while being stretched or pulled before failing or breaking) of over 1 Tpa and very high intrinsic strength (mechanical stiffness) of 125-130 GP.

Graphene has the highest surface area of all materials with 2630 m^2 g^{-1} surface area of a single graphene 2D sheet. Graphene sheets are flexible, and graphene is the most stretchable crystal which can be stretched up to 20% of its initial size without breakage. Moreover the small geometric pores in physical structure of graphene together with its thinness, makes graphene highly impermeable and suitable for filtration of any gas, ionic salts, and acids[7].

Electrical conductivity

Graphene at room temperature has the highest electrical current density which is one million times that of copper and the highest intrinsic electronic mobility (of charge carriers) equal to 2-2.5*10^5 cm^2 V^{-1} s^{-1} which is 100 times that of silicon. Graphene has the potential to be the fastest and most efficient conductor and to be used as a superconductor which can carry electricity with 100% efficiency.

Thermal conductivity

Graphene has superior thermal conductivity at room temperature when it is in the form of a single sheet membrane and thus is one of the most suitable materials for thermal management of different systems[8]. The in-plane thermal conductivity of graphene at room temperature is among the highest of any known material, about 2000–5000 W m^{-1} K^{-1} for freely suspended samples[8]. The upper end of this range is achieved for isotopically purified samples with large grains and it decreases significantly by introduction of any substrate, residue from sample fabrication and edges in smaller size graphene flakes.

For comparison, the thermal conductivity of natural diamond is ~2200 W m^{-1} K^{-1} at room temperature (that of isotopically purified diamond is 50% higher, or ~3300 W m^{-1} K^{-1}) and that of pyrolytic graphite is approximately 2000 W m^{-1} K^{-1} at room temperature[8,9].

Optical properties

Graphene in a single-layer sheet form has 97.7% optical transmittance which makes it very much transparent to the human eye. It has optical absorption of exactly 2.3% in the infrared limit (which is quite a lot for a 2D material), and when this property is combined with graphene's excellent electronic properties, it makes it suitable for very efficient photovoltaic, solar cells and transparent conductor applications.

Chemical properties

The above mentioned superior properties are characteristics of the graphene physical entity. Much less has been told about its chemical uniqueness. Physicists often refer to graphene as 'highly inert' material meaning that it does not readily react with other atoms, however this is not true. Graphene chemistry is unique not only by being made of carbon atoms, but their packing in a flat honeycomb structure which offers the forth valence electron on its own resulting in graphene having a flexible surface chemistry. This unique chemical structure of graphene facilitates many other functionalized derivatives, which provide a fertile research ground in many areas of applied science[10]. For example, graphene can be functionalised by various chemical groups, which can result in different materials such as graphene oxide (functionalized with oxygen and helium) or fluorinated graphene (functionalized with fluorine)[6].

Graphene Application

Having said that graphene has all of the above properties and graphene-associated patent filings are continued to increase. The growth has not been witnessed to be evenly spread across all the application areas. More than half the total number of patent applications involving graphene worldwide is related to electronics and optoelectronic application with the largest patent portfolio held by Samsung [11].

Researchers and product developers in the field of textiles are continuously integrating new materials to provide fabrics with new functionalities, and given graphene's properties, its incorporation on fabrics was a logical step. Many approaches have been developed to apply graphene in the field of textiles recently which has allowed the development of functional textiles with electroconductivity, thermal conductivity, antistatic, UV-protecting, photocatalytic abilities, antibacterial qualities and many other properties. The properties and their relevant potential applications are listed in Table 1 and the applications will be discussed in more details in the last part of this report.

Table 1. Graphene properties and relevant applications.

Graphene properties [12,13]	Relevant applications
Electrical properties • High electronic mobility ~ 2-2.5*10^5 cm^2 V^{-1} s^{-1} (at room-temperature) • high electric conductivity of ~106-108 Sm^{-1} • high ampacity of ~ 1–2 GA cm^{-2}	High speed electronic devices, computer chips, touchscreens, transistors, batteries, energy generation, supercapacitors, antennas **Textile specific application:** Smart textiles, biosensors, energy harvesting and storage, RFID, antistatic protection
Thermal properties • Thermal conductivity of ~ 2000–5000 W m^{-1} K^{-1} • High thermal stability	Heat sink, solar cells, electronics, thermal interface materials (TIM), energy storage **Textile specific application:** Thermal regulation, flame retardant, energy storage
Physical properties • High specific surface area of ~ 2630 m^2 g^{-1} of a single graphene sheet • Thickness of ~ 0.34 nm and weight of ~ 0.77 mg m^{-2} (one single layer of graphene) • High tensile strength (Young's modulus) of ~ 1-1.1 TPa • High intrinsic strength (mechanical stiffness) of ~ 125-130 GP • Optical transmittance of ~ 97.7-98 % • UV absorption at peak around 100-281 nm	Stretchable electrodes, pressure sensors, nanocomposites **Textile specific application:** Water, gas and acid filtration, sensitive gas sensors, fibrous composites, photovoltaic and solar cells, lightweight automotive textiles, protective textiles

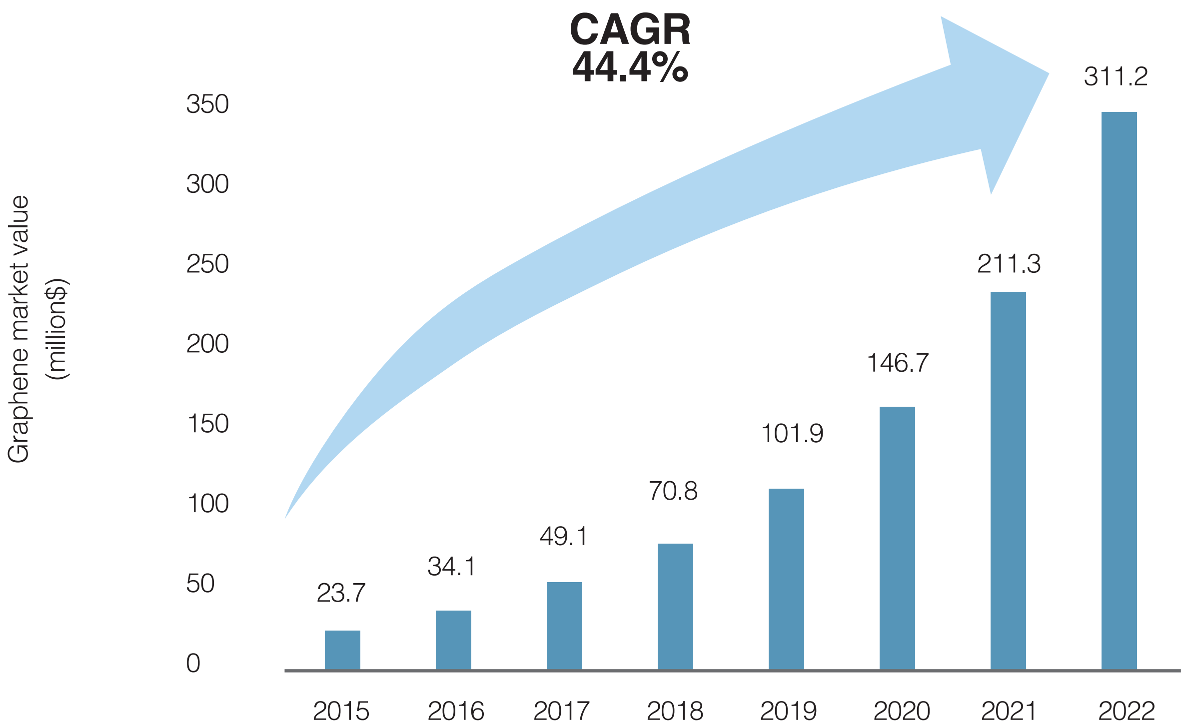
Graphene market

The Global Graphene market in 2015 was estimated for $23.7 million and it is anticipated to grow at a CAGR of 44.4% until 2022 and therefore it is expected to reach $311.2 million by 2022 (Figure 2)[14]. This growth is boosted initially by demands and applications with higher technology readiness levels such as electronics industry, graphene-based polymer composites, lithium-ion battery materials, development of graphene-based supercapacitors for battery less vehicles, replacement in silicon chips as well as application in energy conservation, water filtration and desalination.

Among different types of graphene product, the graphene nanoplatelets (GNP) commanded the graphene market followed by graphene-oxide (GO), and they have been estimated for about two-thirds of the overall market revenue in 2015, due to having lower price and yet wide range of application areas[14].

North America had dominated the graphene market in 2015 and it is expected to be the largest revenue-generating region during the forecast period due to growing energy sector. According to a report by Freedonia, the US will remain the leading global market for graphene through 2035, due to the growth in the fields of high-performance composites and energy storage devices, as well as by rising R&D projects in advanced electronics fields[15]. Moreover, Asia-Pacific is projected to be the fastest growing region over the forecast period and will remain the top regional consumer of graphene, owing to the driving factors such as presence of large graphite mines in China, growing electronics industries in countries such as China, Japan, India, and South Korea and ongoing research on graphene in this region[14,16].

Figure 2. Graphene market growth between 2015 and 2022[14].



The prospect for graphene is relied on cost reduction as currently producing high quality and defect free graphene products are at high cost. There are several companies who are producing graphene today but usually in small volumes and they usually use CVD based processes. However, there is a lot of research going into developing new ways to mass produce graphene in an affordable manner. Therefore, prices are expected to fall as manufacturing processes improve and production of high-quality graphene nanoplatelets and graphene oxide is scaled up by 2035. This can be achieved by semi-continuous processes (such as roll-to-roll methods) to make graphene film and following the expected cost drop, a more significant wave of commercialized graphene products is anticipated between 2020 and 2035[14,15].

Challenges with Graphene

Graphene has many potentials but there are still a lot of challenges to overcome.

Standards

One of the major challenges facing the graphene industry is the lack of standardization. The quality of graphene is very important when supplying it as the graphene which is produced through different processes may result in materials with different properties for eg better at heat conduction, but less suited for electronic conduction, etc. Therefore, for each specific project and application different quality of graphene might be required.

Currently the industry is lacking standard methods and protocols for fabrication or characterisation of graphene, however standardisation of graphene is a working progress and standardised characterisation methods for different graphene forms are being developed by different national and international bodies. The issues that need to be addressed is as follows;

- Terminology and nomenclature: standards for naming classes of graphene products.
- Metrology: standards for measurement and characterization efforts and result reporting.
- Performance: Graphene performance (strength, conductivity, etc.), reliability, quality, etc.
- Environmental, health and safety.

Several graphene standardization efforts are underway which are led by the world's leading standard institutes such as ANSI, ISO and the IEC. In October 2017, the NPL published the results of its work with ISO which can be regarded as the first graphene standard of its kind, ISO 80004-13:2017. In November 2017, the NGI and NPL collaborated to publish a "good practice guide" focusing on graphene metrology.

Cost

The graphene market is still at an early stage, so there are a lot of disorganisation with pricing, ordering, transport and handling. There is generally high cost involved in manufacturing of graphene and specially high-quality graphene sheets. But graphene flakes are no longer expensive at a point that would be prohibitive for a lot of industries. There are producers that can make platelets and flakes at a decent quality that can sell in bulk for US$50-100 per kilogramme, which is not considered a high cost, especially for niche markets and considering that in most applications small concentration of the graphene flakes is required[17].

Variation and uniformity

Currently there are many graphene materials available in the market and not all of them are equal. Therefore it is important to understand what material parameters such as graphene morphology and formulation/compounding technique and conditions is required depending on the final application level of results[18]. Moreover, it is also important to consider uniformity of the graphene materials within a batch and from batch-to-batch which is a key result of variation in manufacturing process, and this crucially necessitates working with a reliable supplier.

Safety

Another issue circling graphene is safety to human health. Like many other nanomaterial, the safety of graphene does not seem to be completely clarified, especially when it comes to inhalation (to lung) and exposure to skin. The risks should be assessed during the production, use and disposal of graphene-based materials and this needs to be particularly considered when using or handling graphene flakes or dry powders which are produced by thermal exfoliation of graphite[19].

However, there are studies conducted on research-grade and commercial graphene-based materials such as few-layer graphene GO and rGO that have shown graphene to be non-cytotoxic and non-genotoxic to human skin cells and murine lung cells and confirmed that graphene did not harm viability of these cells for up to 24-72h, depending on the concentration used (5-200 μg/ml). These studies can offer some reassurance regarding safety of graphene[19,20].

Furthermore, it is said that graphene in ink/paste form exposes lower level of risk to the consumers as in this form, graphene powder is contained within a polymeric matrix and it is not loosely available for inhalation. Similarly, graphene membranes also appear to pose minimal risk to the end consumer as they usually are laminated to a surface[17]. However, the two active parts in all graphene products, surfaces and edges, can still theoretically facilitate graphene attaching to biological molecules and adhering to cells[21]. Consequently, safety regulations just like other standardisations of graphene, must be developed to govern graphene manufacturing and use, hopefully in the near future.

Graphene types and manufacturing approaches

There are different routes for the production and synthesis of graphene that are successful to a certain extent. The original method used for graphene production (by Manchester University researchers) was via direct mechanical exfoliation of graphite with adhesive tape. This was a successful method for scientific purposes, but not suitable for industrial-scale uses.

There are several specific ways of producing graphene in a laboratory scale or at a commercial scale that can be categorised into two basic approaches. The first approach is 'top-down', which begins with a good-quality graphitic material (usually graphite) and via exfoliation (peeling), through mechanical, chemical, or electrochemical means, the number of carbon layers will be reduced and monolayer (or few-layer) graphene can be achieved. The second approach is a 'bottom-up' approach, which uses simpler molecules to produce a continuous film of graphene. This approach starts with a carbon source, eg in a gas form (usually methane) and by applying a high energy C and H, atoms will be disassociated and a layer of C atoms can be deposited on a substrate (usually metal or silicone)[6].

Types of graphene

There are two main types of graphene: graphene film (or membrane); and graphene flakes (or graphene nanoplatelets or nanopowder). In the market, there is also graphene-infused ink (or paste), in which graphene powder has been dispersed in a polymer or solvent. Moreover, due to the high cost and complex production of pure graphene, graphene oxide (GO) powder or ink (when the GO powder is dispersed in a liquid or paste) is also commonly available, as one of the derivatives of graphene. A summary of different types of graphene is found in Table 2.

Below, each of these graphene-based materials and their specific properties are explained in more detail:

Graphene film or membrane

Graphene monolayer film or membrane is a two-dimensional and very thin as well as fragile material. It usually requires a substrate to attach onto, and even on a substrate it is very challenging to have a defect-free monolayer film of graphene, as it is one-atomic layer thick. One should not contradict this with graphene being a super-strong material, even compared to the steel and diamond, as herein, the atomic scale of the material should not be forgotten, and graphene should be compared with the same atomic/thickness scale of other materials. Graphene film is not suitable to be applied

Table 2. Types of graphene, their manufacturing method and their suitability for textile application

Types of graphene	Manufacturing method	Suitability for textile application
Graphene film (or membrane)	Chemical vapour deposition (CVD)	Not suitable
Graphene powder (or graphene nanoplatelets or flakes)	Exfoliation of graphite through different chemical or mechanical processes	Suitable for dispersion in solution for spinning and coating
Graphene Oxide (GO) or reduced GO (rGO) powder	Oxidation of graphite (and deoxidation)	Suitable for dispersion in solution for spinning and coating (followed by a reduction process)
Graphene or GO ink/paste	Dispersion of graphene or GO in a solvent or polymeric paste	Suitable for spinning and coating formulation

on textile substrate as it cannot withstand the porosity and stretchability of textiles. It is mostly suited for higher technology applications of graphene such as electronic devices, computer chips, touchscreens, displays, transistors, etc.

Graphene monolayer film is usually made through chemical vapour deposition (CVD) method (bottom-up approach) and, in industry, it is commonly termed as CVD graphene. CVD uses hydrocarbon gas as a source and is capable of growing polycrystalline film of graphene deposited on a substrate that can be square meters in size. However, it has limitations, and achieving a good and uniform quality of graphene is challenging due to the presence of defects and voids that reduce film's structural stability and physical properties[22]. There are several companies that offer CVD-grown graphene, but a high-quality graphene film is usually very expensive due to the method being time-consuming and challenging.

Graphene flakes or powder

Because making graphene film is challenging, time-consuming, and therefore expensive, another route for the large-scale graphene production is the top-down approach to make graphene flakes or powder. They can be much cheaper but will not have the same properties as CVD film format of graphene.

The main method to produce graphene powder is to use a graphitic material, usually a good-quality graphite, as the base material, and through expansion and exfoliation processes graphite will be broken into very small pieces of graphene flakes. There are various technologies that different companies use to make graphene powders through, such as chemical processes, including liquid-phase exfoliation (LPE) method or using mechanical processes. For example, Directa Plus – one of the global graphene manufacturers – uses its own plasma super expansion technique to make graphene flakes[23].

The above-mentioned powder-formation processes cannot produce 100% monolayer graphene due to the randomness of the cleaving. In fact, a graphene powder product is a statistical distribution of graphene stacks of graphene layers. Moreover, lateral breaking also occurs – which produces a statistical distribution of platelets size and dimension.

Most of the known companies do not have the capability to produce graphene powder with only one atomic layer of carbon, and even if the majority of flakes are in less than 10 layers, the product has a good quality and it can be very expensive.

Graphene infused ink/paste

Apart from these two basic types of graphene, there is also graphene infused ink/paste available in the market, which is basically a polymeric matrix or a liquid base material within which graphene powder is dispersed. Graphene ink can be used to be coated or printed on different materials, and this expands the possibilities for applications of graphene for example in textiles or printed electronics.

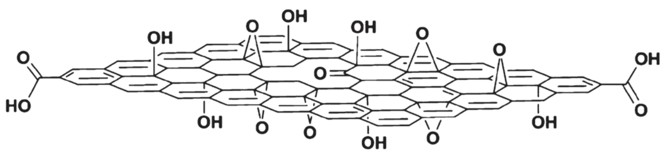
In the ink or paste form of graphene, the two main factors determining the quality and performance of the products are the concentration of graphene – which is added to the ink/paste – and how well the powders are dispersed in it. If the small pieces of powders are not well and stably dispersed, the graphene sheets will touch each other and stack on top of each other, and the ink will end up with dispersed graphite instead of graphene. Moreover, in terms of the amount of powders that defines the continuity of graphene sheets and their connections, different critical concentrations are needed for different applications and purposes. For example, for electrically conductive inks higher concentrations of graphene in inks might be needed and for adding mechanical strength or flexibility into a material, less concentration of ie as low as %0.01 might be sufficient.

Graphene oxide (GO)

As mentioned above, pure graphene manufacturing both in film or powder form is challenging and relatively hard and expensive to produce. Therefore, there are graphene derivatives such as graphene oxide (GO) commonly used for different application. GO is a sheet of graphene, laced with oxygen-containing groups (Figure 3) and it is commonly sold in powder form.

GO is usually produced through the powerful oxidation of graphite – which can be partially deoxidised to produce reduced graphene oxide (rGO). Not only is GO easier and cheaper to produce, but using GO is also easier as it is dispersible in water (and many other solvents). This is whereas, pure graphene has the low dispersibility in common organic and inorganic solvents but GO can easily be mixed with different polymers and solvents, and it can enhance the properties of composite materials such as tensile strength, elasticity, conductivity and more. However, GO has a high density of defects due to the nature of the oxidation process. Therefore, GO is an amorphous material and is not as good electrical and thermal conductor as crystalline graphene itself. When using graphene oxide, it is common to follow the method with performing a reduction process, using a reducing agent to convert non-conductive graphene oxide, to a conductive graphene. However, restoration might be only partial as there can be stubborn oxidised groups that can't be reduced.

Figure 3. Graphene oxide molecular structure



Supplying good-quality graphene

There are many companies globally supplying graphene products or 'claiming' to produce graphene. However, as mentioned in the manufacturing section, producing a good quality of graphene is a challenging process and therefore there is a large variation in its properties. There has been extensive research conducted by researchers from the National University of Singapore (NUS), which developed a systematic and reliable protocol to test graphene quality from 60 producers worldwide, using various microscopy and spectroscopy techniques[22].

It showed that there is hardly any high-quality graphene available from the current suppliers in the market, as defined by ISO, and most companies are producing graphite micro-platelets. The only ISO standard launched in 2017, classifies "graphene as a single layer of carbon atoms up to 10 well-defined stacked graphene layers. Graphene nanoplatelets should be between 1 and 3 nm thick and with lateral dimensions ranging from 100 nm to 100 μm." This can be a very likely reason for the slow development of graphene applications and is not a surprising result given that graphene is a nanomaterial and its characterisation depend on nanotechnology tools that are not readily available, or are too expensive, to ordinary producers and developers. Moreover, it is important to mention that different grades of graphene are required for different applications, and each particular application would require fine-tuning of the properties of the graphene material (with regards to thickness and size distributions). This necessitates the creation of stringent standards for graphene characterisation and production and is the only way forward to create a healthy and reliable worldwide graphene market. In the meantime, it is very important to choose a reliable supplier and characterise the supplied material by specialists in this field. Below, WTiN has compiled a comprehensive list of graphene suppliers for the textile industry and the types of products and services[22].

Global graphene manufacturers

Below, WTiN has compiled a rather comprehensive list of graphene suppliers for textile industry and their type of products and services.

Table 3. Global graphene manufacturers – in alphabetical order

Graphene manufacturer	Type of graphene	Applications	Further info
2DM Solutions www.2dmsolutions.com	Graphene powder nanoplatelets, formulations and masterbatches of graphene-impregnated polymers and coatings.	• Coatings for textiles, metals etc • Energy storage, paints, lubricants and 3D printing • Cement, concrete and advanced ceramics • Polymers • Water treatment • Photovoltaics	Based at the National University of Singapore. Manufactures high-quality graphene as an industrial additive. Offers technical support and R&D services.
Abalonyx www.abalonyx.no	Graphene oxide and graphene oxide derivatives.	• Energy storage • Medicine • Water treatment • Nanostructured, biomimetic materials	Founded in 2005, the Norwegian company ships the graphene oxide products in the form of aqueous paste and dry powder. Has developed a proprietary process for the production of graphene oxide.

Graphene manufacturer	Type of graphene	Applications	Further info
Adnano Technologies www.ad-nanotech.com	Carboxyl, hydroxl and amine functionalised graphene (1-4 layers), graphene dispersions, and customised grades and dispersions. Graphene oxide.	• Energy • Electronics •Automotive• • Structural composites • Flame retardants • Water purification	Based in India. Supplies high-quality graphene and carbon nanotubes and its forms in bulk quantity. Offers consultancy and analytical services.
Advanced Graphene Products (AGP) www.advanced grapheneproducts.com	Graphene flakes, graphene oxide in water dispersion, and graphene sheets (HSMG) – an alternative to standard CVD graphene.	• Not stated	AGP is a spin-off company from Lodz University of Technology, Poland. It is open for various forms of collaboration.
Applied Graphene Materials www.appliedgraphene materials.com	Nanoplatelets (powders/flakes) that don't require a substrate.	• Advanced composites and polymers • Supercapacitors and batteries • Functional fluids including oils and lubricants • Thermal management • Barriers and impermeable films • Display materials and packaging • Inks and 3D-printed materials	Based in Redcar, UK. Founded by Professor Karl Coleman in 2010. AGM works with commercial partners to develop applications for graphene. The company was formally known as Durham Graphene Science. Changed its name in 2013.
BT Corp (Bottom Up Technology Corporation) www.bt-corp.co	Graphene sheets under the name of BTGraph – 1-3 layered aggregates of sub-micron platelets.	• Transparent conductive film • Ballistic/fragment protection • Solar energy • Super capacitors • Touchscreens • Antibacterial paper • Biomaterials and tissue engineering	Based in India. Has CVD graphene equipment. Offers nano lab and manufacturing consultancies. Supports companies through BTCORP Innovation and Co-innovation Collaborative Networks.
China Carbon Graphite Group www.chinacarboninc. com	Single-layer graphene (film); graphene oxide; graphene nano argentum (powder)	Not specified, but CCG supplies all forms of graphene, so can be applied to many areas.	Headquartered in Shanghai. Has been a key player in China's graphite industry since 1986. Produces graphite, graphene and other carbon-based products. Partners with Hunan University.

Graphene manufacturer	Type of graphene	Applications	Further info
Directa-Plus www.directa-plus.com	Graphene-infused inks or paste marketed under G+	Current commercial applications: • Elastomers • Smart textiles • Water treatment • Polymer nanocomposites • Carbon fibre • 3D printing Near-term commercial applications: • Lubricants • Air treatment • Electronics • Catalytic converters • Energy • Soil treatment	Established in 2005, Directa-Plus utilises a patented technique called 'Plasma Super Expansion'. It produces graphene-based products at its factory in Milan, Italy. Has undertaken several industrial partnerships, mainly with textile-based companies.
Elcora Advanced Materials www.elcoracorp.com	EL-2D few-layer graphene (average of 2-4 layers) consisting of suspension or powder.	• Conductive coatings •Drag reduction • De-icing •Anti-fog • Filters • Supercapacitors • Lithium-ion batteries	Founded in 2011. A vertically-integrated graphite and graphene company. Produces graphene through its subsidiary Graphene Corp, located in Canada
First Graphene www.firstgraphite.com.au	Dispersed graphene (powders/flakes). Graphene sheets.	• Fire-retardant coating products •Concrete additives for increased strength • Super capacity batteries • Building materials • Wing manufacture	Australia's leading graphene company. First Graphene is currently engaging marketing personnel to develop sales outcomes. Recently announced the launch of its PureGRAPH product range offering larger lateral graphene sheet sizes.
GOGraphene www.go-graphene.com	Graphene oxide (powder, flakes and dispersions)	• Not stated	GOGraphene is a trading name of William Blythe Limited, an established inorganic speciality chemicals and advanced materials manufacturer based in Essex, UK. Offers an e-commerce service.

Graphene manufacturer	Type of graphene	Applications	Further info
Grafoid www.grafoid.com	Extracts few-layer graphene directly from graphite ore. Marketed as low cost. Traded under MesoGraf trade name	• Lithium-ion phosphate batteries • Polymers and plastics • Foam • Fuel cells • Solar panels and solar cells • Foils • Automotive and aerospace • Medical • Coatings and lubricants	Founded in 2011, Grafoid Inc is a graphene research, development and investment company that invests in, manages and develops markets for economically scalable graphene processes. The Grafoid Global Technology Centre is based in Kingston, Ontario. Described as a hub for joint venture. Grafoid partnered with Canadian company Focus Graphite – a global consolidator of natural flake graphite. Its subsidiary Graftprint3D produces metallic and polymer fine powders and graphene-enhanced polymer filaments for 3D printing materials.
Graphene Frontiers www.graphenefrontiers.com	CVD graphene	• Biosensors • Desalinisation • Electronics industries • Medical devices	Company began in 2010 and became a spin-out in 2011, under the University of Pennsylvania's UPstart programme. Positioned to mass-produce graphene on a commercial scale and at an economically viable cost. The process is able to transfer graphene to nearly any substrate.
Graphene Industries www.grapheneindustries.com	Graphene flakes (single, double, triple or >3-layer on 300 nm and 90 nm $SiO2$), membranes and devices.	• Hall bar geometries • Ultrasensitive gas sensors • Electron microscopy	Graphene Industries is a spin-out company incorporated in March 2007. Almost all production is carried out in the Manchester Centre for Mesoscience and Nanotechnology, UK. States on website that it is keen to discuss potential client requirements and provides samples tailored to particular applications.
Graphene Nanochem www.graphenenanochem.com	Graphene dispersions.	• Nanofluids • Rubber and polymers • Conductive inks	A nanotechnology commercialisation company with bases in London, Kuala Lumpur and Malaysia. Has the capability to manufacture various types of graphene nanomaterials but does not intend to be a volume supplier of graphene nanomaterials.
Graphene Square www.graphenesq.com	CVD graphene film, graphene oxide, quantum dot graphene	• Transparent conductive electrodes for flexible displays • Bio applications • Secondary batteries • Fuel cells • Barrier films • Conductive inks	Graphene Square Inc was launched in 2012 as a spin-off company from Professor Byung Hee Hong's research lab at Seoul National University, South Korea. Forecasts a net profit of US$100bn by 2020. Has the capability to offer customised graphene synthesis for large sizes. Can also transfer graphene onto customers' own substrates, chips and materials.
Graphenea www.graphenea.com	CVD films, graphene oxide, graphene field-effect transistors (GFETs)	• Bioelectronics • Photodetectors • Chemical sensors • Biosensors • Magnetic sensors	A technology company set up in 2010, Graphenea is one of Europe's main producers of graphene (based in Spain). It supplies special pricing for large-quantity orders. Offers an e-commerce service.

Graphene manufacturer	Type of graphene	Applications	Further info
Graphenest www.graphenest.com	Graphene nanoplatelets (powders, dispersions)	• Advanced composites • Functional inks	Based in Portugal. Develops multi-layer and few-layer graphene products. Graphenest is developing applications that are cost-prohibitive for the automotive, aerospace and packaging markets. Invites collaborative projects.
Graphensic AB www.graphensic.com	Electronic grade graphene and related products	Electronics and sensors	Located in Sweden. Founded in 2011. The first EU supplier of epitaxial graphene on silicon carbide. Graphensic developed a graphene-based resistance standard, the GRS. Offers a solution to perform precise calibrations of electrical resistance in terms of the Quantum Hall effect.
Graphitene www.graphitene.com	Graphene powder, dispersion, graphene-coated PET film, graphene oxide	• Energy generation and storage • Rubber and composites • Protective coatings	Graphitene is a second-generation nanomaterials company engaged in the research, development and sale of 'Graphitene'. Works with corporate partners to create custom graphene-based solutions. Has facilities in the UK, Norway and Estonia. Offers an e-commerce service.
Graphmatech www.graphmatech.com	Graphene nanocomposites (inc. thermal grease, 3D filament, conductive ink, polymer powder)	• Additives, coatings. Can even be 3D printed. See second table for commercial development involving Aros Graphene. •Thermal management •Self-lubricating mechanical parts •Energy storage •Electrical contacts	A Swedish materials technology startup company that invents, develops and sells novel graphene-based nanocomposites materials and services. Developed Aros Graphene in 2017 – a graphene hybrid material with a microstructure resulting in outstanding properties. Offers an e-commerce service.
Modern Synthesis Technology (MST) www.mstnano.com	Graphene nanopowder	•Composite materials •Masterbatches/additives •Lithium-ion batteries •Supercapacitors •Conductive polymers •Lightweight but strong plastics •Touch screens	Based in Latvia, MST is a graphene research and production company that emerged in 2016. Makes graphene suitable for a wide range of applications. Also provides other graphene materials based on carbon.

Graphene manufacturer	Type of graphene	Applications	Further info
Nanografen www.nanografen.com.tr	Graphene nanosheets. Portfolio includes functionalised graphene with different C/O ratio; graphene oxide; graphene from recycled carbon; graphene masterbatches.	• Energy • Aerospace • Automotive • Construction	Nanografen is an R&D and consulting company established in 2013 by scientists from Sabanci University Nanotechnology Research and Application Center and Inovent Company, Turkey. Produces high-quality graphene in high amounts and prepares graphene prototypes for several fields.
NanoXplore www.nanoxplore.ca	Graphene powder (GrapheneBlack) and hexo-G graphene-plastic masterbatch pellets and graphene-enhanced polymers	• Plastic piping • Automotive interiors • Protective sports equipment	Established in 2011, NanoXplore is headquartered in Quebec. It is a manufacturer and supplier of high- volume graphene powder for use in industrial markets.
Perpetuus Carbon www.perpetuusam.com	Graphene stacks with less than three atomic layers. The world's largest producer of purified and functionalised graphene.	• Various applications, including the automotive sector. See commercial development involving Gratomic Inc in next table.	Perpetuus operates a functionalised nanomaterial manufacturing facility in South Wales, employing the group's computer-controlled DBD Plasma Reactor.
Platonic Nanotech www.platonicnanotech.com	Graphene and graphene oxide powder	• Automotive • Electronics • Clothing and textiles • Food additives and packaging • Cosmetics • Household • Personal care/health • Sports equipment • Toys and children's goods	Based in India, Platonic Nanotech uses its proprietary 'bottom-up' process for the production of high-quality graphene. Also supplies carbon nanotubes. Offers an e-commerce service.
RD Graphene www.rd-graphene.com	3D graphene	• Biosensors • Energy • Flexible electronics • Wearables • Water treatment	Based in Scotland, UK. RD Graphene is in the process of developing and manufacturing graphene supercapacitors. Has developed graphene layer manufacturing processes that are currently patent pending. Invites collaboration opportunities.

Graphene manufacturer	Type of graphene	Applications	Further info
Stevens Institute of Technology www.stevens.edu	Graphene film based on graphene electrodes	• Sensors in wearable technology • The inkjet-printed graphene technology is the force behind startup company FlexTraPower, AKA Bonbouton. Referenced in second table.	Institute is based near New York City, US. To create the thin sheets of graphene electrodes, the researchers took ink containing tiny flakes of graphene oxide and placed it on a flexible substrate, using an inkjet printer. Then, to improve the conductivity of the electrodes, the graphene oxide was thermally reduced to graphene, or adjusted by adding nanoparticles of other materials to the ink.
Suzhou Graphene Nanotechnology Co Ltd www.graphenecn.com	Graphene powder and nanoplatelets, and graphene oxide	• Electrically and thermally conductive fillers • Additives for anti-corrosive coatings • Films or coatings for EMI shielding • Substrates for chemical and biochemical sensors	Established in China in 2012. Specialises in high-quality, thin-layer graphene. Properties, applications and packaging information available on website.
Ultrananotech www.ultrananotech.com	CVD graphene on substrates, graphene flakes, powders, pellets, filament, dispersion, foam, sheets.	• Composite materials • Conductive coatings • Solar cells • Supercapacitors • Multifunctional materials • Biosensors • 3D printing • EMI shielding	As well as graphene, Ultrananotech also supplies lab equipment and consultancy and patent services for both industrial and academic projects. Based in India. Can download product catalogue from website.

Graphene manufacturer	Type of graphene	Applications	Further info
Versarien www.versarien.com First subsidiary – 2-DTech www.2-dtech.com Second subsidiary – Cambridge Graphene www. cambridgegraphene. com	Graphene powder – marketed under Nanene (comprising mono, bi and few-layer graphene flakes) and Hexotene (nanoplatelet powder with large lateral dimensions). Graphene inks	Nanene: • Composites •Energy •Biomedical •Membranes •Coatings •Sensors •Electronics Hexotene: •Electronics •Ceramics, plastics and rubbers •Proton conductors, fuel cells, water electrolysis •Thermofluids and thermal management •High-performance inks for conductive applications •Graphene-enhanced composites •Supercapacitors and batteries •Flexible electronics •Antennas •Composites • Supercapacitors and batteries	Versarien was founded in 2010. Has formed partnerships to incorporate graphene into the apparel and aerospace sectors. See second table for details on Versarien's partnership with Bromley Technologies on a graphene-enhanced skeleton sled. 2-DTech is a spin-out from the University of Manchester, UK. Cambridge Graphene supplies proprietary graphene inks and undertakes development projects for customers.
Vorbeck Materials www.vorbeck.com	Based on single-atom thick functionalised graphene sheets.	• Antennas •RFID •Wearables •Battery development •Composites •Conductive inks	See second table for details on Vorbeck's partnership with MWV Packaging on a security sensor for packaging. Vorbeck is a leader in research, design, development and manufacturing of graphene. Born out of a Princeton Research Lab in the US. Has developed proprietary graphene material called Vor-x. The product line also includes Vor-ink and Vor-flex.
XFNANO Materials https://en.xfnano.com	CVD graphene, graphene powder, oxide, dispersion, nanoplatelets, flakes.	• Conductive films •Biological and medical applications •Flexible electrodes •Composite materials •Conductive coatings.	Founded in 2009, XFNANO Materials is described as an advanced nanomaterials and technical service provider. Based in China. Also sells CVD equipment. Offers an e-commerce service.
Xolve www.xolve.com	Graphene nanoplatelets	• Polymer composites • Energy storage materials	Based in the US, Xolve's platform has the capability of dissolving nanoparticles in stable solutions. The company is working with compounders, article manufacturers and OEM suppliers to improve composite material attributes.

Incorporation of graphene into textiles

The newest trend in textile material has been adding functionalities into it, and these functionalities can usually be achieved by adding additives both during the manufacturing of fibres or following the fibre/fabric manufacturing. After the discovery of graphene and given its extraordinary properties, the development & manufacture of graphene-incorporated textiles has become an emerging research topic. There have been many attempts in both academia and industry to do so by mostly coating or printing graphene ink onto a textile substrate and also many strategies have been developed as to how to incorporate graphene at the fibre level and during fibre manufacturing. Although the latter approach has been applied and attempted mostly at the research stage, and it is yet in its infancy in the textile industry. Below, different available strategies from the two mentioned approaches are discussed in more detail:

Graphene in fibre form

The manufacture of both neat graphene fibres and graphene composite fibre (a fibre made from both graphene and a polymeric material) is usually based on production methods such as wet spinning and dry-jet wet spinning of a precursor solution with or without coagulation bath as well as coating as spun polymer fibres with graphene[24]. Solution spinning, where a polymer is first dissolved into a solution using solvent and then graphene is dispersed into the solution, is an ideal approach for producing graphene composite fibres and can also be employed in approaches such as electrospinning[25].

Moreover, as manufacturing techniques such as melt spinning which requires a solid polymer to be softened by applying heat to a gel before fibre extrusion, is not an option for manufacturing neat graphene fibres due to the high-temperature stability of graphene. However, graphene-polymer composite fibres can be produced via the melt spinning method. In the following chapter, WTiN reports on the various methods of manufacture for fabricating graphene-based fibres.

Graphene-polymer composite spinning solution

When fabricating a graphene-polymer composite fibre, it is vital to make sure the graphene dispersed within the composite fibre has been dispersed homogeneously to ensure the graphene has an augmented reinforced surface area. This is because a large surface area is required in order to transfer graphene's many desired performance properties. It is common to apply non-covalent and covalent modifications to the composite solutions, to increase uniformity within the composite dispersions and tune the properties of graphene, accordingly, enhancing the fibre performance. Modification to the solution using non-covalent and covalent interactions can also adjust the carbon to oxygen atomic ratio, functional groups, electrical conductivity, and solubility in solvents[26]. It has been documented that when dispersing graphene in a polymer, the fabricated composite solutions can be dispersed in polar media, producing a stable suspension[27]. Moreover, research has found that when modifying graphene in a polymer, an advanced mechanical interlocking of the nanofiller-matrix interface is achieved, enhancing the transfer of performance properties from graphene to the composite fibre[28].

Solvent mixing is the easiest approach for the manufacture of graphene-polymer composite fibres, due to this method being the most simple to prepare homogeneous composite dispersions. This method also allows composite fibres to be manufactured using graphene oxide, which is advantageous as graphene oxide is easily dispersed in water and various polar organic solvents and can therefore produce well-dispersed composites. Following the manufacture of graphene oxide fibres, the graphene oxide can be easily converted to graphene through a simple reduction process in order to recover the sp2 carbon network of graphene[26].

For the in situ polymerisation method, chemically-modified graphene is blended with monomers or pre-polymers as well as solvent. Once parameters such as temperature and time are altered, the polymerisation reaction occurs. Composite fibres formed from in situ polymerisation can be manufactured by melt spinning, electrostatic spinning and wet spinning, among others; however, melt spinning is the most common method for this approach[26].

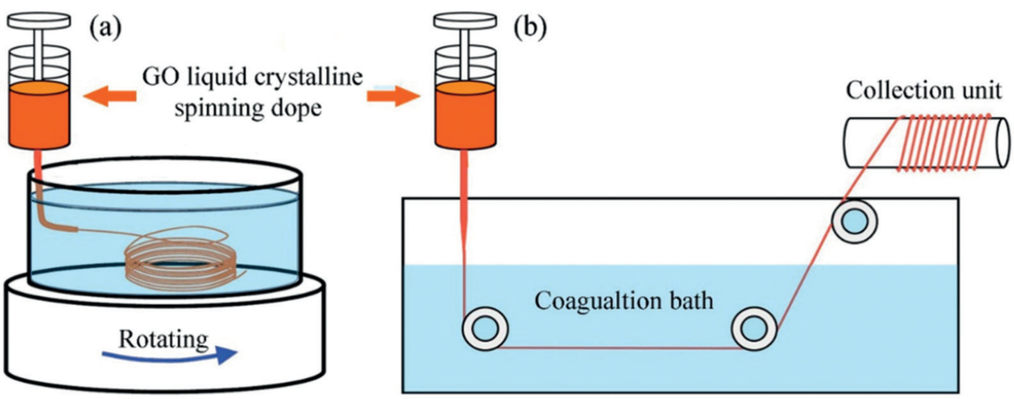
Forming a spinning solution by melt processing has much more commercial appeal in comparison to the solvent mixing and in situ polymerisation methods, as melt processing has more versatility and is more environmentally friendly due to the lack of solvent. Melt processing uses the approach of blending chemically-modified graphene directly into a melted polymer solution without the use of any solvent[26].

Wet spinning

Wet spinning is the most commonly used approach for manufacturing graphene fibres. For the wet spinning of graphene fibres, graphene oxide sheets are dissolved in an aqueous solution and interjected into a coagulation bath using a syringe. Graphene oxide fibres in a gel state are formed in the coagulation bath, then extracted and dried to form graphene oxide fibres. After subsequent chemical reduction, graphene oxide fibres can be manufactured for electrical conductivity performance. The speed at which the moving coagulation bath rotates (as seen in Figure 4a), as well as the speed at which the fibres are drawn onto the collection unit (as seen in Figure 4b), strongly influences the uniformity and continuity of the fibre formation[25].

Researchers from the Department of Polymer Science and Engineering of Zhejiang University, China, found the rotating method (Figure 4a) fabricated reduced graphene oxide fibres with the highest recorded strength of neat annealed graphene fibres with potential covalent cross-linking (420 MPa). This method was found to be very good for spinning small volumes of fibres. However, controlling the speed at which the fibres are moving, and therefore fibre uniformity, is limited with this method. The speed at which the fibres move is highly reliant on the force of friction amid the fibre surface and coagulant solution. In this method the speed at which the fibres move doesn't alter proportionally to the speed of the rotating coagulation bath. In contrast, an alternative method is shown in Figure 4 using a collection unit; this method

Figure 4: Wet spinning set-up showing graphene oxide fibres drawn by a rotating coagulation bath (a) and a collection unit (b).[2]



produces graphene oxide fibres with a constant drafting force and a regular movement speed. As a result, it offers advantages when manufacturing fibres with an accurate draw ratio while also offering the potential for scalability[29].

Further work from the Department of Polymer Science and Engineering of Zhejiang University, China, discovered aqueous graphene oxide liquid crystals with lamellar structures and employed the technique to distribute graphene oxide at a large concentration for the development of novel neat graphene microfilaments via the wet spinning method. The fabricated continuous microfibres were found to have a diameter ranging from 50–100 μ m, which could be modified by tailoring the nozzle size and drawing speed. Results found the fabricated fibres to have excellent mechanical strength and high conductivity. The researchers demonstrated the novel fibres could be knitted into complex patterns for application in wearable electronic textiles[30]. Although wet spinning is the most extensively researched method for the manufacture of neat graphene fibres, many composite graphene fibres with a variety of multifunctional properties have also been fabricated. This is mainly due to the liquid crystalline graphene oxide solution being a perfect host for many materials including metal nanowires, CNTs, and polymers[25].

Spinning solution for neat graphene fibres

A spinning solution is required for the fabrication of graphene oxide fibres via wet spinning. The mechanical properties and superior performance of graphene oxide fibres for this method, are highly dependent on the structural alignment and interactions of liquid crystals within the graphene oxide solution, as well as structural defects intrinsic to the graphene oxide sheets[31]. A huge challenge when spinning graphene into fibres is preventing the agglomeration of graphene particles. However, employing liquid crystalline graphene ensures agglomeration does not occur[26]. In wet spinning, the solution properties of the liquid crystalline graphene oxide are transferred to the macroscale fibres[31]. Graphene oxide spinning solution is stabilised in water by the mechanism of electrostatic repulsion[25].

Research from the Department of Polymer Science and Engineering of Zhejiang University, China, detailed the mechanism for when graphene oxide is dispersed in water for fibre spinning; the negatively charged graphene oxide sheets in the solution caused the zeta potential to reach −61 ± 5 mV[30]. However, it is believed the dispersed graphene oxide solution must have a zeta potential of lower than −30 mV to become stable[32]. The stabilisation of the solution is eliminated once the graphene oxide solution is injected into the coagulation bath; this is due to the nonsolvent, oppositely charged ions in the coagulation bath, proceeding in precipitation of the graphene oxide. The spinnability of the graphene oxide spinning solution is highly dependent on the lateral measurement of the graphene oxide sheets as well as the concentration of the spinning solution. It is only possible to spin gel state graphene oxide filaments when the spinning solution is completely in the nematic phase. Sheets of graphene oxide have an irregular shape and therefore, the lateral size measurement is taken from its nominal diameter, characterised as the diameter of an equal area circle. To enable the formation of a complete nematic phase the concentration of the spinning solution must be higher than the critical concentration, otherwise disconnected segments, collapsed ribbons, or separated particles will be fabricated.

It has been found that if the nominal diameter is 37 μm, the critical concentration would therefore be 0.75 mg mL^{-1} for graphene oxide fibre formation[25]; however, it is also possible to spin graphene oxide fibres when using a spinning solution with an increased concentration, as demonstrated by the work of the Department of Polymer Science and Engineering of Zhejiang University, China,[30] among others[6,7,35]. The viscosity of the graphene oxide spinning solution is also a determining factor for fibre spinnability[25]. Researchers from the School of Energy and Power Engineering, of the University of Shanghai for Science and Technology, China, suggested graphene oxide spinning solutions with a viscosity of 3 Pas or higher can be spun into continuous filaments[34]. While a group of researchers from Sichuan University, China, reported higher viscosities were experienced when larger graphene dispersions are employed, due to stronger interactions between the graphene sheets, and vice versa[35].

Coagulation bath

The coagulation bath can also have a high impact on the processing and properties of graphene-based fibres via wet spinning. When dispersing negatively charged graphene oxide in water, a stable dispersion is created. However, for fibre formation, the stabilisation of the spinning solution must be eradicated for the graphene oxide to precipitate, in order to form accumulation of the graphene oxide in a gel or dry state. The destabilisation of the graphene oxide spinning solution can be carried out using: a coagulation bath and methods including non-solvent precipitation; destabilisation by acid, base or salt solutions; counter-ion-neutralisation; crosslinking-induced aggregation; or low-temperature freeze-drying, among others.

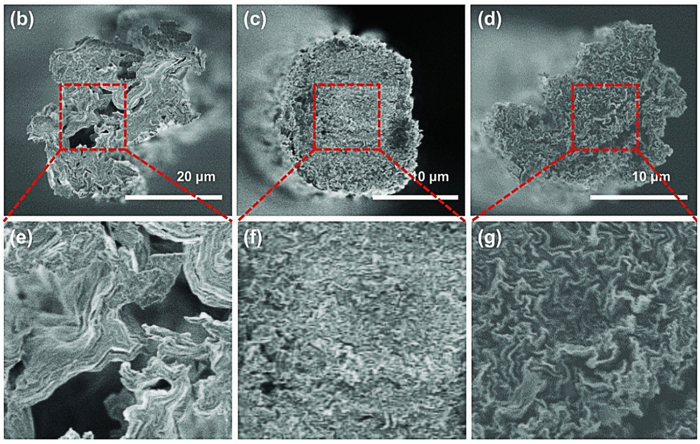
As the graphene oxide has an abundance of oxygen-containing polar groups, either polar solvents or ones which form a hydrogen bond with graphene oxide, such as H2O, DMF, acetonitrile (CH3CN), or tetrahydrofuran (THF), can be used to dissolve graphene oxide[25]. However, solvents without hydrogen bond-forming groups and no polarity can generate precipitation in graphene oxide sheets, as demonstrated by researchers from the Department of Chemistry at Rice University, US. It was reported that both graphene oxide and reduced graphene oxide fibres could be fabricated when employing an ethyl acetate bath, demonstrating that the acid, base and salt solutions offer added ions to the graphene oxide dissolution, eliminating the stabilisation of the graphene oxide solution, and causing the graphene oxide to precipitate[36,25]. As the graphene oxide spinning solution has a negative charge, polymers or ions which have an opposite charge and exhibit both hydrophilic and hydrophobic properties [33,37,34,38], as well as some divalent cations (Ca2+, Cu2+, Mg2+)[29,39], can each be selected as coagulants, meaning that a wide range of coagulants may be used for the wet spinning of graphene oxide fibres[25].

Fibre morphology and structure

During the fabrication of neat graphene oxide fibres via wet spinning, sheets of graphene oxide are aligned in consecutive layers, parallel to the fibre axis. Liquid from the wet spinning process is trapped between the layered sheets of graphene oxide during the formation of gel state fibres[25]. Subsequent to the wet spinning process, it is common for the gel state graphene oxide fibres to shrink by around one-tenth to one-third of their original size once dehydrated[29,40,41] – illustrating that a large volume of the gel state graphene oxide wet spun fibre is coagulant and/or remaining solvent[25]. As the liquid between the layers starts to evaporate during the fibre drying process, the sheets of graphene oxide buckle, filling empty spaces between the layers within the matrix, assisting the total liquid to be evaporated from the fibre[29,42,40]. It is for this reason that the surface morphology of dehydrated graphene oxide fibres is not smooth; instead the fibres have many creases and folds in a dentate morphology along the fibre length[25]. This type of surface morphology is seen in neat graphene fibres as well as reduced graphene oxide fibres and polymer modified graphene oxide fibres[43,44,45]. However, this wrinkled and creased morphology can have negative effects on the fibres mechanical strength and electrical/thermal conductivity properties.

Research by the Department of Materials Science from the Engineering Korea Advanced Institute of Science and Technology (KAIST) in the Republic of Korea, found a solution via incorporation of mussel-inspired adhesive polydopamine (PDA) which acts as an effective binder to improve the morphology of wetspun fibres. It was reported that when reinforcing the graphene wetspun fibres with PDA, the

Figure 5. Cross-sectional images of wet-spun b,e) PDA-free graphene fibres and c,f, d,g) improved morphology of PDA-graphene fibres[46].



mechanical strength was improved without sacrificing the electrical conductivity(figure 5)[46].

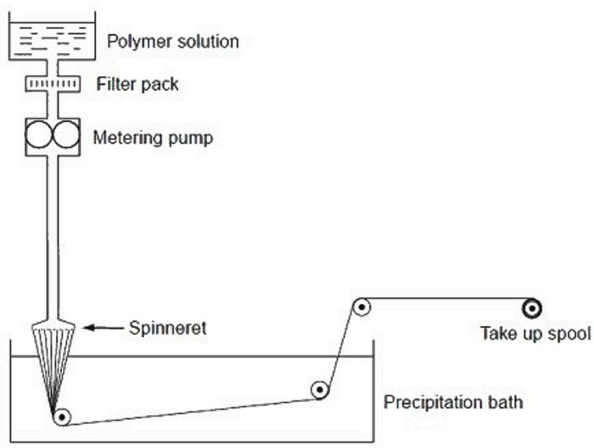
Moreover, it is possible to fabricate graphene oxide fibres with a variety of structures via wet spinning. Researchers from the Department of Polymer Science and Engineering of Zhejiang University, China, designed a method to fabricate graphene oxide and sodium carboxymethyl cellulose bicomponent microfibres via wet spinning. The core-sheath fibres were fabricated by simultaneously injecting both graphene oxide and sodium carboxymethyl cellulose into a coagulation bath, through both the inside and outer tunnels of a coaxial two-capillary spinneret. The sodium carboxymethyl cellulose sheath is ionically conductive, however, also electrically insulating, meaning that if this material is used for the sheath it will not produce a short circuit when multiple fibres are touching for application in woven smart textiles[47].

Hollow graphene fibres can also be formed using the same coaxial two-capillary spinneret. However, in this case, the graphene spinning solution is pushed through the outer tunnel while the coagulant is simultaneously pushed through the inner tunnel. This was demonstrated by researchers from the Department of Chemistry and Biochemistry, The Ohio State University, US, who fabricated continuous hollow graphene fibres with a necklace morphology[48]. Meanwhile, a group of researchers from the University of Wollongong, Australia, demonstrated the potential for the mass production of graphene microfibres via wet spinning by using a spinneret with multiple holes, fabricating 50 graphene oxide filaments in a single step [33,49]. And researchers from the Department of Polymer Science and Engineering from Zhejiang University, China, fabricated extremely porous graphene fibres and high specific surface area, by replacing the coagulation bath with liquid nitrogen to ensue multifunctional fibre properties[50].

Dry-jet wet spinning

Dry-jet wet spinning is very similar to wet spinning, however, in this method, the graphene oxide spinning solution is injected through an air gap while being subjected to heat and pressure prior to penetrating the coagulation bath. The fabricated fibres are subsequently washed and dried prior to being heat treated and drawn. This method can be used to avoid micro voids within the fibre matrix that can give the fibre adverse mechanical properties. The micro void fibre morphology is commonly seen in conventional wet spinning of graphene oxide fibres, due to the rapid evaporation of solvent from the fibre. The micro void morphology has been described in further detail in section 'Fibre morphology and structure (wet spinning)' [51,31]. When using the appropriate solvents (chlorosulfonic acid and diethyl ether), this

Figure 6: Schematic of the dry-jet wet spinning set up[51]



method can fabricate graphene oxide fibres with a smooth morphology and circular cross-sectional shape, which has not previously been possible by neither wet or dry spinning[25].

Researchers from the Department of Chemistry, Rice University, US, extruded a spinning solution of graphene oxide nanoribbons (GONRs) and chlorosulfonic acid for the fabrication of graphene oxide fibres via dry-jet wet spinning. The research demonstrated that fibres formed with an air gap of 12 cm between the tip of the injection and the coagulation bath had increased mechanical properties, when compared to fibres produced using a 2 cm air gap. The researchers found that when an air gap is included in the manufacturing process, the velocity gradient of the spinning solution from the tip of extrusion and the coagulation bath is reduced. Moreover, this approach fabricates a fibre with increased fibre alignment, due to the gravity aided stretching of the fibre. However, the study also demonstrated that an air gap which is too long can cause complications when drawing the fibres during spinning[52].

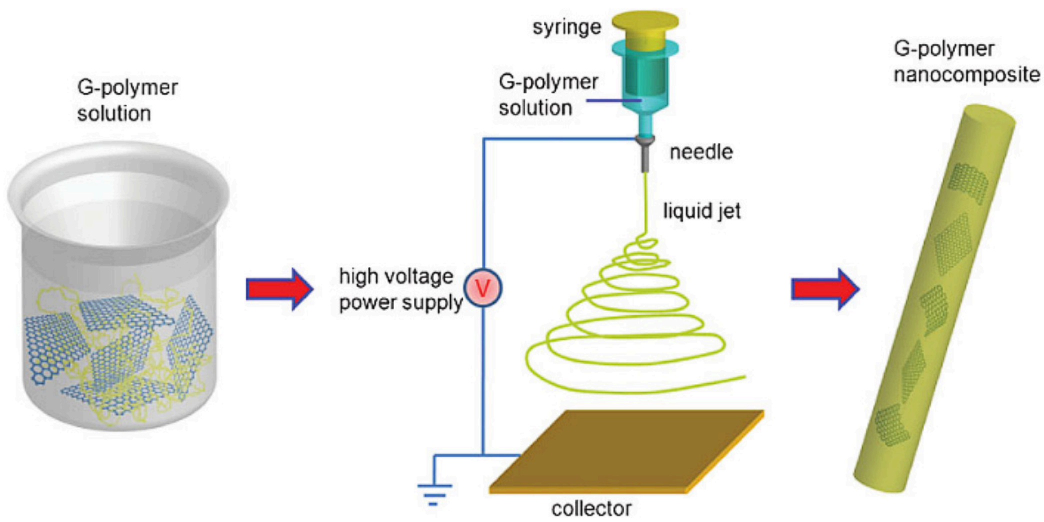
Electrospinning

Electrospinning uses an electric field to draw a graphene and polymer composite solution from the tip of a capillary to a collector. Voltage is applied to the solution, which causes a jet of the solution to be drawn towards a grounded collector. The fine jets dry to form composite graphene polymeric fibres, which can be collected on a web. As electrospinning requires the polymer to be dissolved in a solvent, it is not possible to spin neat graphene fibres via this method. However, electrospinning is well suited for the fabrication of graphene-polymer composite fibre. In fact, the process has been documented using graphene with a variety of polymers[53]. By choosing a suitable polymer and solvent system, nanofibres with diameters in the range of 40-2,000 nm (0.04-2 microns) can be made. Fibre diameters can be varied and controlled[53]. Traditional needle-based electrospinning faces challenges in quality control, such as the ability to produce the same fabric properties more than once, as well as issues with cost-effectiveness[54]. However, NanospiderTM equipment, from the company Elmarco, allows a high-volume production rate and uniformity of nanofibre webs, because the number and location of the jets are set up naturally in their ideal position after calculating the periodicity through an equation[55]. What is more, NanospiderTM equipment can produce material from almost all known polymers that are soluble in organic solvents and water, as well as polymer melts, which opens further commercial opportunities [55,56,57].

Melt spinning

It has become common to enhance fibre properties by combining graphene with another polymer, to form a composite material via melt blending. The melt spinning process which is more appealing to the industry, does not use any solvent, instead, polymer composite fibres are formed by melting polymer granules and subsequently blending the melt with graphene to form a composite spinning solution, which is then extruded via a spin head. The flow rate at which the molten spinning solution is extruded through the spin head is controlled by a metering pump. The spin head is required to filter any polymer chips that have not been melted prior to reaching the spin head. This step is included because unmelted polymer in an extruded fibre can cause weak points within the fibre. Once the fibres are extruded, the quench air is used to cool down the fibres as they emanate from the spin head. The speed at which the extruded fibres are wound can have a great impact on polymer alignment and therefore, the mechanical properties of the fibre. The melt spinning process has advantages over

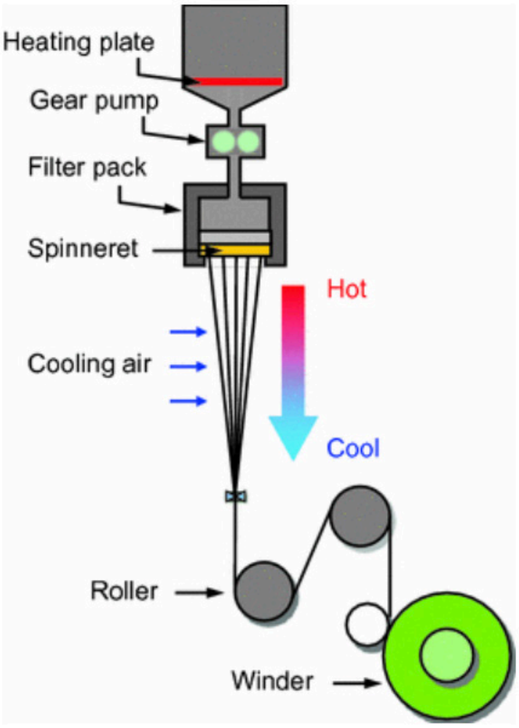
Figure 7: Schematic of the fabrication of graphene-polymer nanofibre composite via electrospinning. (G refers to graphene)[58]



other processes, as both fibres and monofilament yarns can be fabricated. It is also less expensive than other methods, produces fibres or filaments at a high speed, and no washing of the fibres is required as no solvent is used[51].

When fabricating graphene-polymer composites it is vital that the graphene sheets are homogeneously distributed in the chosen polymer melt. It is common for the graphene sheets to aggregate when in a composite due to attractive,

Figure 8: Illustration of a typical melt spinning process[59]



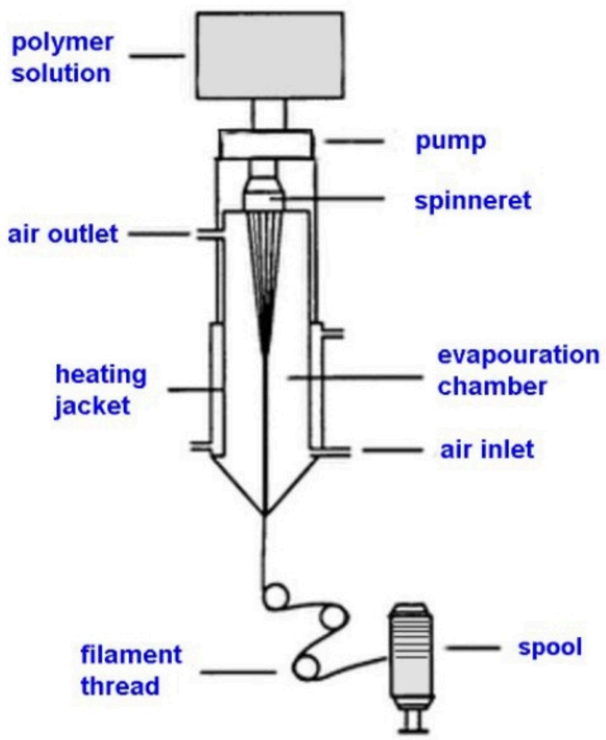
noncovalent interactions between the aromatic rings within the layers of graphene. However, surface attributes of the graphene sheets that are not compatible with a polymer matrix can also attribute to aggregation. Therefore, it is important to use chemical functionalisation to ensure graphene is dispersed in single sheets within a polymer melt, so to preserve the superior performance of single-sheet graphene when employed in a polymer composite. Researchers from the College of Materials Science and Engineering of Qingdao University, China, reported a method for the fabrication of nylon-6- (PA6-) graphene (NG) composite fibres via melt spinning. The mechanism of this method reduces the graphene oxide sheets to graphene by in situ polymerisation with concurrent thermal reduction. The researchers were able to homogenously disperse the graphene sheets in a caprolatam and 6-aminocaproic acid mixture due to the large amount of grafted PA6 arms on the graphene sheets (78 wt %). The fabricated graphene fibres that measured a metre in length and were manufactured via melt spinning were found to have a considerably increased tensile strength and Young's modulus, even when loading the polymer melt with only 0.1 wt % graphene[60].

Fibre manufacturing methods suitable for research purposes

Dry spinning

In the dry spinning method outlined in Figure 9, there is no coagulation bath. Alternatively, the graphene oxide spinning solution is extruded into a sealed tube and subjected to either heating or chemical reduction under increased temperature. Doing so removes the oxygen-containing groups and lowers the absolute zeta potential of the spinning solution, in order for the gel state fibres to precipitate, forming fibres due to electrostatic repulsion. The waste solvent from this process is often then collected and used again[25,51]. When spinning graphene oxide using this method, water is commonly used as the solvent. By further evaporating the solvent, a reduced graphene oxide fibre can be fabricated[25]. Fibres fabricated from dry spinning often have a high electrical conductivity without any need for additional treatment. Moreover, the dry spinning method allows for a variety of particles to be introduced to the graphene oxide spinning solution for the manufacture of composite fibres. However, the method involves sealing tube terminals and many hours of heating, meaning that this method is unsuitable for continuous fibre production.

Figure 9: Schematic of the dry spinning setup[51]



Electrophoretic assembly

The electrophoretic effect exists only in colloid solutions, as charged particles can be dragged and displaced when controlled by an electrical field. As a solution of graphene oxide dispersed in a solvent solution is considered a colloid, and due to graphene oxide particles being negatively charged, it is possible to spin graphene oxide fibres via the electrophoretic self-assembly approach[7]. This method uses a positively charged graphitic tip dipped into a graphene oxide and solvent solution. As a constant potential electric field is applied, the graphitic tip is drawn upwards and subsequently, a gel state graphene oxide fibre is formed at the tip of the graphitic electrode[25], as seen in Figure 10. By dehydrating the fibre and after thermal annealing, a reduced graphene oxide fibre with a smooth morphology and a circular cross-sectional shape can be fabricated. However, a disadvantage of the approach is that the moving speed of the graphitic tip is 0.1 mm/ min, therefore it is extremely slow and would take around one week to produce a fibre one metre in length[7].

Figure 10: A gel-state graphene fibre being formed as the graphitic tip is drawn up with an applied electric field[25]

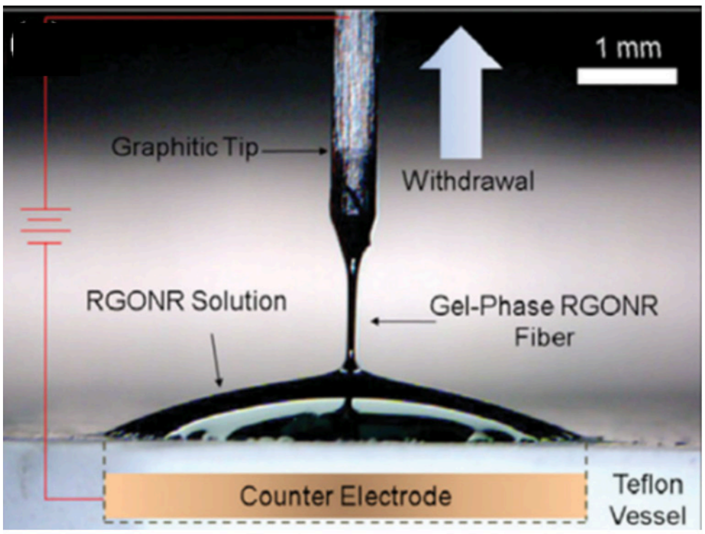


Table 4. Summary of graphene fibre/ yarn fabrication

Graphene fibre manufacture method	Neat graphene / graphene composite	Fibre formation with/ without solvent	Fibre morphology & properties	Suitable for continuous fibre production
Wet spinning	Neat graphene & graphene composite fibres	Solvent	• Micro voids • Wrinkled • Diameter ranging from 50–100 μ m	Suitable for mass production
Dry-jet wet spinning	Neat graphene & graphene composite fibres	Solvent	• Smooth • Circular cross section • Increased fibre alignment gives increased mechanical strength compared to wet spinning	Suitable for mass production
Melt spinning	Graphene composite	Without solvent	• Fibres and monofilament yarns can be produced • High tensile strength	Suitable for mass production
Electrospinning	Graphene composite	solvent	• Fibre diameter range of 40-2,000 nm • Specialist equipment can produce uniform fibre webs	Specialist equipment allows for high-volume production rate
Dry spinning	Neat graphene & graphene composite fibres	Solvent	• A high electrical conductivity without any need for additional treatment	Unsuitable for continuous fibre production
Electrophoretic assembly	Neat graphene	Solvent	• Smooth morphology and a circular cross-sectional shape	Extremely slow, not suitable for mass production
Film conversion	Neat graphene	With and without solvent	• Mechanically scrolled diameter range: 110 μm to 1.6 mm robust, flexible yarns/ fibres • Unzipping of carbon nanotubes diameter: 100 μ m • CVD: 20-50 μm diameter, with a typical electrical conductivity of ~1000 S/m • Unzipping carbon nanotubes can make only fibres a cm in length • Film conversion methods are not suitable for mass scale production	• Unzipping carbon nanotubes can make only fibres a cm in length • Film conversion methods are not suitable for mass scale production

Film conversion

Although conventional methods to form graphene fibres use a solution, it is also possible to convert graphene oxide from solid state or films into fibres. For this approach, free-standing and bendable graphene oxide films can be shrunk, bent and contorted into a fabricated graphene oxide fibre. To date, researchers have found two different methods to convert graphene oxide films into fibres: solvent evaporation and the unzipping of a carbon nanotube sheet. A group of researchers from the Research Center for Exotic

Nanocarbons of Shinshu University, Japan, fabricated graphene fibres by evaporating the solvent from graphene oxide dispersion to create a continuous graphene oxide film on a polytetrafluoroethylene (PTFE) plate substrate using layers of scotch tape to regulate the thickness of the film. Once the total solvent was evaporated, a stand-alone 800–1,200 cm2 graphene oxide film was produced. The researchers were then able to cut the film into lengths and twist each of the strips into a yarn[61].

The second approach was demonstrated by researchers from the Department of Materials Science and Engineering of the University of Texas, US, who employed the approach of unzipping carbon nanotube sheets to form graphene oxide fibres. The researchers chemically unzipped a constant and aligned sheet of carbon nanotubes using KMnO4 / H2SO4, therefore converting the carbon nanotube film into a graphene oxide nanorod film. The researchers found that once the graphene nanorod film was removed from the chemical solution, the film decreased in size forming a gel state fibre. And once the fibre had been dehydrated from all of the solvent in the solution, the dried fibre was fabricated. However, the researchers were not able to fabricate continuous fibres or fibres over a centimetre in size and therefore, this method is not considered practical[62].

As well as the above two methods, it is also possible to produce graphene fibres from a graphene film that has been fabricated in a chemical vapour deposition (CVD) chamber. A group of researchers from the Department of Mechanical Engineering, Tsinghua University, China, discovered graphene fibres could be formed by removing the synthesised graphene film from the substrate and placing it into an organic solvent with a low surface tension (22–25 mN m −1); the film forming a scroll shape. Once removed from the solvent the interfacial force between the graphene, air and solvent cause the scroll to shrink and transform into a fibre. Further evaporation of the solvent produced a graphene fibre with a monolithic morphology. The fabricated fibres were found to have a high electrical conductivity without any need for further treatment due to conductive graphene being used in place of graphene oxide[63,64].

Incorporating graphene post material manufacture

Although composite fibres have been commonly produced via the fabrication methods mentioned previously, these methods can consume a large amount of expensive raw material and sometimes, the described methods can attribute to the loss of flexibility and transparency. Therefore, coating the fibres, yarns or fabric with graphene can sometimes be more appropriate for some applications and is a simple, low cost and direct way to enhance fibre properties with low material waste[65,66]. In the following chapter, WTiN reports on the various methods of manufacture for fabricating graphene-based textiles via coating and printing, following material manufacture.

Pre-treatment

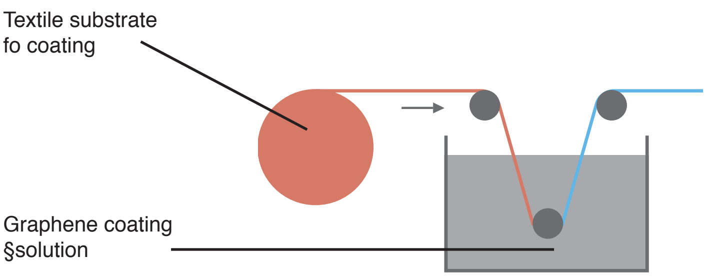
When graphene is coated directly onto a textile substrate, there can sometimes be little interaction between the graphene and the substrate. Once the substrate is dry and has experienced bending and folding, the graphene coating may be easily peeled away[67]. However, it is possible to achieve a stable adhered graphene coating, without any pre-treatment on the substrate surface, especially if the fibres are uniformly rough. Researchers have found that pre-treating the substrate surface can improve the electrical conductivity of the graphene coating, as well as the adhesion between the graphene and the substrate, producing textiles which are washable and functional[68,69].

Waterborne polyurethane (WPU) has been extensively used in research to enhance the adhesion of graphene coatings with a textile substrate, due to its attractive properties such as strong adhesion, high abrasion resistance, good compatibility and flexibility. Researchers from the School of Textiles and Clothing of Jiangnan University, China, found that by increasing the level of graphene oxide in the WPU composite coating paste via screen printing, the rubbing fastness was gradually decreased[67]. Extensive research has also been carried out to alter the surface roughness of textile substrates using oxygen plasma to improve the surface roughness and adhesion properties when coating graphene onto textiles. Using plasma is popular as this method can enhance the adhesion of graphene oxide deposits to a textile substrate by increasing the oxygen functional groups on the substrate, without changing the original properties of that substrate, while also being an eco-friendly approach[70]. Moreover, researchers from the Department of Organic and Nano Engineering of Hanyang University, Republic of Korea, took a different approach and pre-treated cotton fabric with a cationic agent to improve the adhesion between graphene oxide and the cotton substrate. Researchers found a 67.74% higher loading amount of graphene oxide on the cotton fabric which had been pre-treated with Bovine Serum Albumin as a cationic agent in comparison to the cotton fabric without any pre-treatment[71].

Dip coating (wet processing)

One approach for incorporating graphene into textiles is via the 'dip and dry' coating method, involving impregnation of graphene oxide to the fibres, yarns or fabrics after manufacture. The dip and dry method is simple, scalable as well as cost-effective and therefore, extensively used for research purposes. This method uses a high-speed pad dry unit which has the ability to commercially manufacture 150m per minute[68].

Figure 11: A schematic of the dip coating technique for the preparation of graphene-based fibres or fabrics[66]

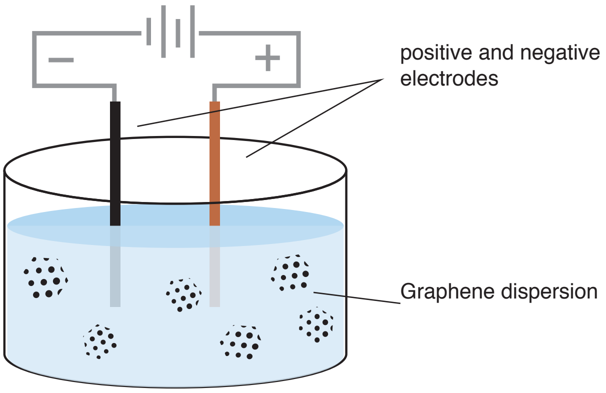


Graphene oxide is negatively charged and can therefore be dispersed homogeneously in aqueous solutions, forming a coating solution. However, when using graphene for this approach instead of graphene oxide, a dispersant is required to aid dispersion and stability because graphene does not have a charged surface and therefore, can often precipitate in aqueous solutions[24]. The dip and dry approach can be used for coating a layer of graphene on fibres, yarns or fabrics which are extremely porous with an intricate morphology of microfibrils, such as cellulosic materials[65].

The method entails dipping the fibres, yarns or fabric into the graphene solution bath at a constant speed, although a pre-treatment process could be required prior to dipping, dependent on the substrate. The material is subsequently soaked in the dispersion at room temperature for a designated amount of time (generally 30 minutes). The textile material is then pulled back up and out of the dispersion. As the material is pulled out of the solution a graphene film is deposited on the surface of the textiles – in this case the thickness of the coating is highly dependent on the speed at which the material is pulled out of the graphene solution; pulling the material slower creates a thinner layer of graphene coating, and vice versa. Once excess liquid from the process has been drained, the substrate is dried, and the solvent evaporates from the surface of the material, forming a thin graphene film on the surface of the substrate. It is common for the process to be repeated multiple times to ensure maximum adsorption of the graphene solution[72].

When using graphene oxide in the coating solution, it is common to follow the method by performing a reduction process, as detailed by Researchers from the Department of Textile Engineering of Islamic Azad University, Iran. In this study, the researchers subsequently immersed cotton fabric in a reducing agent to convert non-conductive graphene oxide – specifically brown cotton fabric to a conductive graphene black cotton fabric – as this process partially

Figure 12: A schematic drawing of the electrophoretic deposition (EPD) approach for the preparation of graphene-based coatings [66]



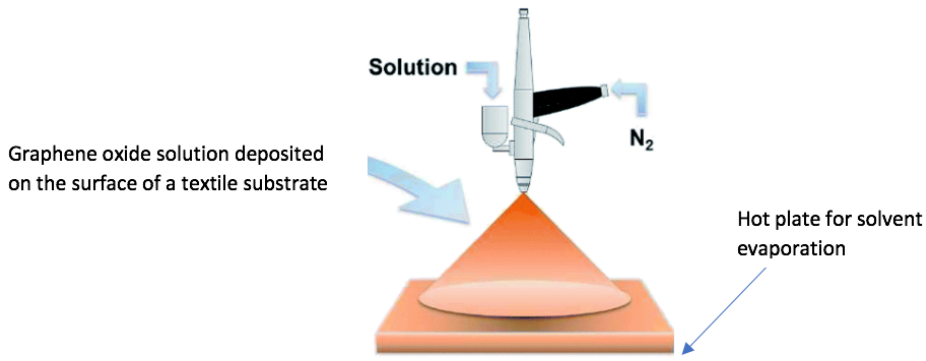
restores the sp2 structure[73]. However, restoration is often only partial as there can be stubborn oxidised groups which can't be reduced. The negatively charged graphene oxide interacts with the fabric's functional groups to further fix the graphene to the fabric surface[24]. The dip and dry approach has been found to have limitations because unless the graphene is entirely encapsulated within the pores of the material, the graphene can become easily lost from the material over its lifespan and therefore, can cause environmental concerns[65]. The quality of the coating is also often found to be inconsistent in comparison to other available methods such as spin coating[72].

Electrophoretic deposition (EPD) (wet processing)

The electrophoretic deposition (EPD) method is most commonly used to produce coatings and films, however, this method can also be employed to fabricate fibres, as detailed further in the 'Graphene in textiles' chapter. The EPD approach is a colloidal process which may be employed to any solid substrate as long as stable colloidal suspensions with particles that have a surface charge and are in the magnitude of <30 mm are used[74]. EPD coats graphene onto a textile substrate by using graphene oxide which is negatively charged, as well as a two-electrode cell including an electrode with a positive charge and one with a negative charge. Due to both the graphene oxide and the electrode having opposite charges, when an electric field is applied, the graphene oxide sheets in the dispersion adhere to the surface of the electrode via Vander Waals forces, forming a compact film of graphene oxide after drying[66], outlined in Figure 12. It is possible to apply the electric field in a direct electric current mode or in a modulated electric current mode. The electrophoretic deposition of graphene is highly dependent on the capacity for the graphene sheets to accumulate an electrical charge within the solvent, while the stability of the graphene suspension is also extremely important. It is most common to use graphene oxide as well as reduced graphene oxide for EPD, as these forms of graphene are the most easily dispersed. The solvents which have been used in research to disperse graphene oxide, reduced graphene oxide or modifed graphene flakes for this method include deionised water, isopropyl alcohol, ethanol, dimethylformamide, N-Methyl-2-pyrrolidone, and a mix of acetone/ethanol. However, it is common to use an aqueous solution as the solvent as it is low cost, and with water, a lower voltage can be used during the process, and it is also kinder to the environment. Plus, water has faster kinetics and aqueous suspensions are higher temperature applicable. That said, using water as a solvent can increase the possibility of side reactions to occur[74].

A common EPD setup uses two working counter electrodes combined with a power supply administering an electric field between both the electrodes. Typically, positively charged particles adhere to the cathode (cathodic EPD) and negatively charged particles adhere to the anode (anodic EPD). An advantage of this method is that EPD can produce coatings with a variety of microstructures by altering the parameters accordingly. Microstructures can range from extremely thin with only a single graphene sheet, or multilayer graphene that is hundreds of micrometres thick. It can also produce flat and homogeneous coatings, or those with a rough surface, as well as compact or interconnected porous

Figure 13: Mechanism of spray coating graphene onto a textile substrate[78]



coatings[75]. Researchers from the School of Materials Science and Engineering of Nanyang Technological University, Singapore, reported a density of 1.26 g cm-3 for EPD films which had been subsequently reduced[76]. It is common to see wrinkles on the surface of a graphene oxide coating formed via EPD, therefore, due to the highly wrinkled surface, graphene oxide films formed via this method can provide the advantage of a high surface area[75]. Other advantages of this method include a short deposition time, straightforward apparatus, low cost, and a large variety of substrate shapes can be coated[72]. It is common for side reactions to occur during EPD depending on the processing conditions; these side reactions can be viewed as either an advantage or destructive to the fabricated coating dependent on the final application. Side reactions can include reducing the graphene oxide during the process, electrochemical reaction of additives, dissolution of electrodes, and degradation of suspension media at high voltages[75].

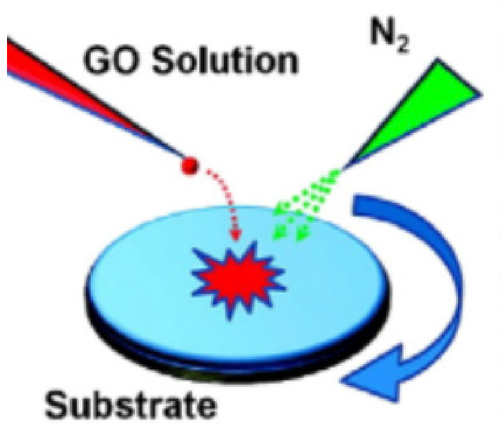
Solution spray coating (wet processing)

The solution spray coating method is a contact-free painting technique which entails dispersing graphene oxide or graphene oxide along with additives into a suitable solvent prior to spraying the solution onto the surface of any fibre or textile material substrate required for coating. The graphene-coated substrate is subsequently cured with heat to evaporate the solvent, leaving behind a deposit of graphene that conforms to the shape of the surface of the substrate[66], as demonstrated in Figure 13. This method uses an airbrush cup that is connected to a nitrogen tank providing the pressure required for spraying micron-size drops onto a textile substrate[66,26]. This solution spray coating approach can cover a large area quickly, is scalable, versatile, with low equipment costs and is extremely simple to carry out. It is particularly appropriate to use this method when low temperature processing is required. However, it is common to achieve a varied thickness across the coating due to the fast speed at which the solution is deposited. It is also challenging to ensure the graphene oxide or reduced graphene oxide sheets do not aggregate, crumple or wrinkle during the process[77].

Spin coating (wet processing)

Spin coating is a simple method which applies graphene oxide solution, generally made from a volatile solvent, to a flat substrate that is placed onto a spin rotator spinner which continuously rotates at high speed during application, displacing the graphene oxide solution to form a uniform layer of graphene oxide over the substrate until the necessary thickness is achieved; generally, 1–10 μm in thickness. The centrifugal force is the driving force which spreads the graphene oxide dispersion over the surface of the substrate to produce a thin film and controls the film thickness; however, the film thickness is also directly affected by the concentration of the graphene solution. The substrate is continuously spun until the total solvent has evaporated,

Figure 14: Spin coating technique for the deposition of graphene oxide onto a substrate[81]



leaving behind the graphene oxide deposit on the surface of the substrate[66,72,79].

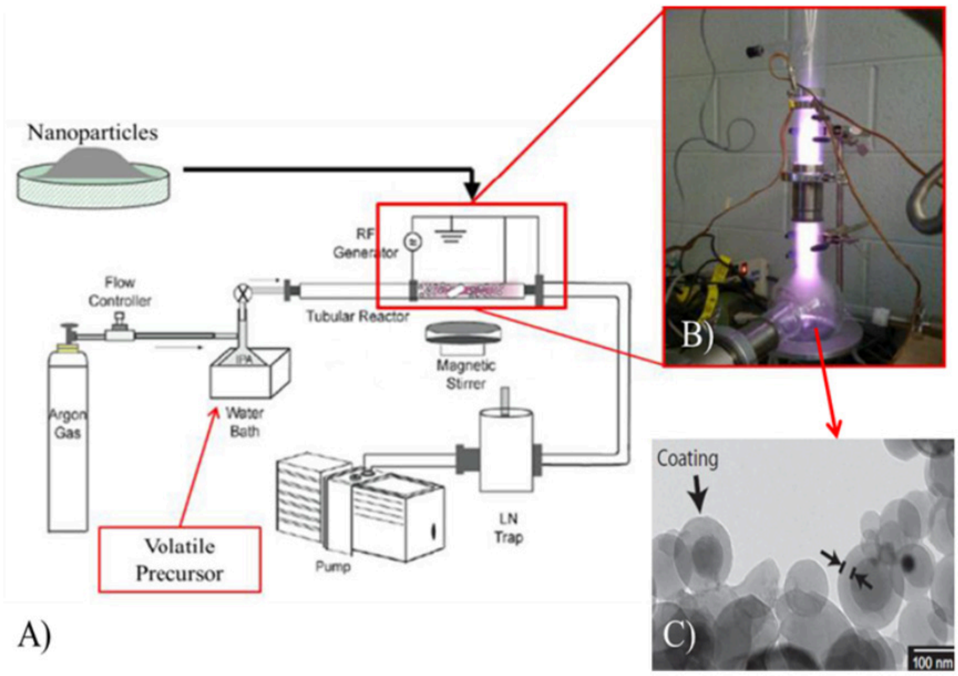
Additional treatments can also be employed to assist with the uniformity in the coating. For instance, researchers from the School of Information Science and Technology of Southwest Jiaotong University, China, used N2 gas to blow the graphene oxide solution in order to evaporate the water faster during the spin coating process [80]. The fabricated coating from the spin coating method is much denser and uniform in comparison to other coating methods such as the dip and dry coating method. However, limitations include: only being able to coat a flat surface; the shape and size of the substrate for coating is restricted to the size of the spin coating equipment; and not being able to coat a substrate with a complicated shape or uneven, complex structures with 3D features. This approach may also waste graphene ink, as the majority of the is thrown off the stage during spinning. Moreover, it is difficult to have a large throughput using spin coating because it is a batch process and therefore, it is not considered suitable for mass scale production[72].

Plasma-enhanced chemical vapour deposition (PECVD) (dry processing)

Chemical vapour deposition (CVD) can produce a solid coating from a volatile precursor vapour by chemical reaction, and this coating approach can be used for the synthesis of graphene sheets deposited directly onto a substrate. However, chemical vapour deposition is associated with extremely high temperatures during processing (as high as 1,150°C) and therefore, this approach is often used for coating metal and is not suitable for coating graphene directly onto a textile substrate without modification[82]. While it is possible to transfer a synthesised graphene film fabricated via CVD onto a textile substrate, this method brings disadvantages such as wrinkles, folds, cracks and unintentional doping, degrading the film quality[83].

The modified method named plasma-enhanced chemical vapour deposition (PECVD) is a quick one- step scalable approach that has the same aspects of CVD. However, the

Figure 15: Plasma-enhanced chemical vapour deposition (PECVD) reactor for depositing uniform coatings[84]



reactions are driven by electrical discharge, this approach allows lower temperatures to be applied to the substrate during the process, and therefore, it is possible to synthesise some textile substrates with graphene by using this method[85]. The PECVD approach inserts graphene nanoparticles into the PECVD chamber and then applies plasma in order to acutely break the organic precursor molecules into smaller nanoparticles, detailed in Figure 15A and B. The precursor molecules react with the solid graphene nanoparticles creating a coating around the graphene particles, as seen in Figure 15C, which can be deposited onto a textile substrate in the reaction chamber. The fabricated coating displays comparable physical properties to the chosen volatile precursor and therefore, by choosing a suitable precursor the properties of the coating can be adjusted[84]. This method allows the coating structure to be regulated at either the atomic or nanometre level[72], and the coating thickness can be adjusted by altering the residence time within the reactor[84]. This method has great potential for mass scale coating. Pure and dense graphene coating can be achieved, and parameters can be adjusted in order to manufacture coatings with a variety of surface morphologies, thicknesses and crystal structures. However, this approach has disadvantages such as safety hazards due to precursor gases, as well as a challenge in depositing composite materials, and large equipment costs[72].

Printing graphene onto textiles

Inkjet printing

The inkjet printing method has recently become the most common approach for printing graphene onto a textile substrate. Mainly because this method allows the graphene ink droplets to be deposited at chosen locations, without patterning the textiles prior to printing, while also being

Table 5. Summary of graphene coating methods for textile applications

Coating method	Microstructure	Disadvantages	Advantages	Throughput
Dip coating	• Thin graphene film on the surface of the substrate	• Pre-treatment required dependant on the substrate	• Simple, • Scalable • Cost-effective • Aqueous solution can be used • Can coat irregular and complex structures	• 150m/min • Suitable for mass production
Electrophoretic deposition (EPD)	• Range from: extremely thin (only a single graphene sheet) to multilayer (hundreds of micrometres thick) • Ranges from homogeneous to rough surface • Ranges from compact to interconnected and porous • Wrinkled surface	• Using water as a liquid medium in EPD may cause side reactions. (However, side reactions are sometimes seen as an advantage)	• Variety of substrate shapes can be coated • Straightforward apparatus • Low cost • High surface area due to wrinkled surface	• Short deposition time

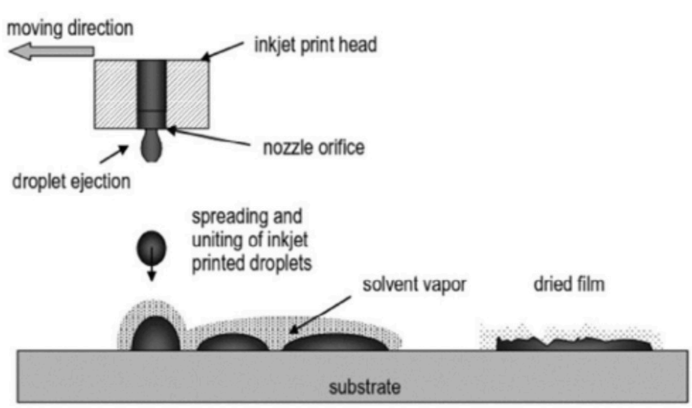
Solution spray coating	• Varied thickness • Thin films of graphene oxide conform to the shape of the substrate surface • Sprays micron-size drops	•Varied thickness •Often experience aggregation, crumpling or wrinkling of the graphene oxide sheets •Challenging to get a uniform film	• Fast • Scalable • Extremely simple to carry out • Large-area, high-throughput • Inexpensive • Industrially scalable process • Contact-free technique • Suitable for any substrate material • Suitable when low temperature processing is necessary • Low equipment cost • Versatile	• Suitable for mass production • Fast process time
Spin coating	• Dense and uniform layer of graphene oxide • Thickness ranges from 1 to 10 µm • Thin film	• Can coat only onto a flat surface • Shape and size of the substrate is restricted to the size of the equipment • Can't coat a substrate with a complicated shape • Wastes a large amount of ink • Batch process the method and so cannot be scaled up	• Accurate thickness control • High deposition uniformity • Fast process time • Low equipment cost • Reproducibility	• The batch process and restrictions on substrate size and shape means difficult to mass produce
Plasma-enhanced chemical vapour deposition (PECVD)	• Pure and dense graphene coating can be achieved • Variety of surface morphologies, thicknesses and crystal structures	• Safety hazards due to precursor gases • Challenge in depositing composite materials • Large equipment costs	• Allows application of lower temperatures which can be advantageous when coating a textile substrate	• Great potential for mass scale coating

cost-effective and enabling large-scale production. However, with a printing speed of 1.25–7000 mm s^{-1}, this approach has a low to medium throughput. The Inkjet printing method is simple to use while also resulting in little waste material, producing images with a resolution of approximately 2-12 μm and a film thickness ranging from 100–500nm [86,87].

The inkjet printing approach can be split into two principles: continuous inkjet and drop-on-demand methods. However, the continuous inkjet printing method recycles ink, unlike the drop-on-demand approach. The recycling of the ink can cause ink exposure to the atmosphere, in the process causing degradation. Additionally, the drop-on-demand approach does not waste as much material as the continuous inkjet method. Therefore, the drop-on-demand method is the common choice when printing expensive materials such as graphene or carbon nanotubes. Drop-on-demand printers can use both thermal and piezoelectric print heads, although thermal print heads are often less expensive and need less maintenance.

The piezoelectric print heads are the most commonly used print heads for printing graphene due to their versatility regarding the ink composition and their physical properties such as viscosity (ranging from 1–30cP) of solution and choice of solvent. A large variety of solvents such as water, oils, and organic solvents may be used with the piezoelectric print head, while the thermal print head is limited to using water as the solvent [87,86]. The drop-on-demand process often produces an extremely layered uniform microstructure, with a varied porosity[88].

Figure 16: Schematic illustration of inkjet printing[89]



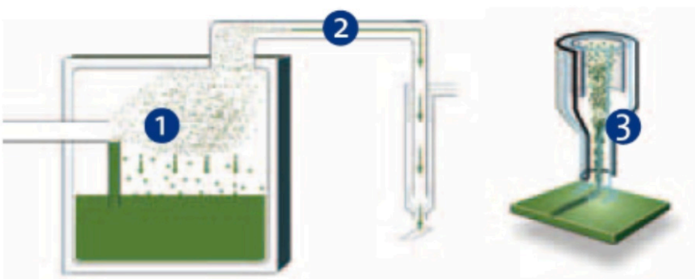
The three main mechanisms used in inkjet printing graphene are outlined in Figure 16; droplet ejection, droplet spreading, and droplet solidification. The printhead initially moves to the required position, where drops of the graphene ink are expelled from the nozzle onto the substrate. Upon contact with the substrate the ink spreads which joins the droplets together, forming a thin film of ink. As the solvent evaporates, the solid graphene deposits from the ink are left behind on the substrate surface and the volume of ink left on the substrate is significantly decreased. It is important that the graphene ink is well dispersed, to ensure the graphene particles do not agglomerate or cause the coffee ring effect. This effect can occur when there is a higher concentration of graphene at the perimeter of the droplet compared to the centre. Any agglomeration due to these effects could result in varied conductivity and complications in device operation [87]. Graphene inks used in inkjet printing are commonly formed via nanoplatelets that are produced by reduction or exfoliation of graphene oxide[88] and usually include graphene dispersed in a solvent, commonly with a surfactant. It is important that the sheets of graphene are less than a few hundred nanometres and that they do not agglomerate in the solvent. If the sheet size and agglomeration are not monitored, clogging of the nozzle can occur, which may cause disruptions to printing. Therefore, the choice of solvent is extremely important to ensure a homogeneously dispersed printing ink[87].

Inkjet printing has many advantages when printing graphene onto textiles, however, inkjet printing of graphene onto a textile substrate faces the challenge of printing a constant electrically conductive track onto a substrate which has an irregular and porous surface due to isotropic orientations of the fibres. Moreover, the morphology of a textile substrate is continually changing as the water molecules in the microclimate are exchanged – thereby making it a challenge to form a conductive track via inkjet inks with a low viscosity. Researchers from The National Graphene Institute of the University of Manchester, UK, have solved this problem by developing a nanoparticle-based pre-treatment, which can be printed via an inkjet printer onto specific substrate areas, prior to printing the graphene ink. The developed hydrophobic, breathable, pre-treatment layer enables conductive paths of inkjet printable graphene on a textile substrate[90].

Aerosol jet printing (AJP)

Aerosol jet printing has a very similar mechanism to inkjet printing, where digitally controlled graphene drops are deposited in precise locations[91]. However, this recently developed technology is specifically designed to print onto any non-flat, flexible or 3D substrate. As a result, this approach can deposit a film thickness ranging from 30-150nm of conductive graphene sheets onto a rough and porous textile substrate, without the same challenges experienced via inkjet printing of conductive graphene paths [92,86]. Moreover this approach eliminates the possibility of the coffee-ring formation which can commonly be experienced in inkjet printing of graphene[86] For aerosol jet printing, the ink is a dispersion of graphene sheets and solvent[92], with the capabilities to print ink that have viscosities ranging from 1–1000 cP[86]. The ink is placed into a tank which is subsequently atomised by either an ultrasonic or pneumatic process, shown in Figure 17.1. The aerosol of graphene ink formed during the process travels (Figure 17.2) towards the writing nozzle, where sheath gas drives the ink to be deposited onto a moving substrate, for deposition in the X-Y-Z planes, as outlined in Figure 17.3[92]. However, with a printing speed of 0.1–10 mm s^{-1}, Aerosol jet printing has a low throughput[86].

Figure 17: Illustration outlining the mechanism for aerosol jet printing[92]



Screen printing

Screen printing is a cheap, quick and simple method which has been commonly used to coat patterns onto textiles, wood, and glass. However, in recent years this technique has been used by researchers to apply graphene onto textiles, for the fabrication of electronic textile applications[93,87]. The screen printing approach is limited to producing prints with a resolution of approximately 40-100 μm and a thickness ranging from 14000–25000nm[87,86]. This method uses a mesh screen, commonly prepared by coating photochemically defined emulsion onto the mesh, using UV light to fix a patterned stencil in the emulsion. The fixing process creates open areas in the mesh, where graphene ink can be forced through the mesh openings using a squeegee to deposit graphene ink onto the substrate in the desired pattern[93].

Figure 18: Schematic illustration of screen printing[94]

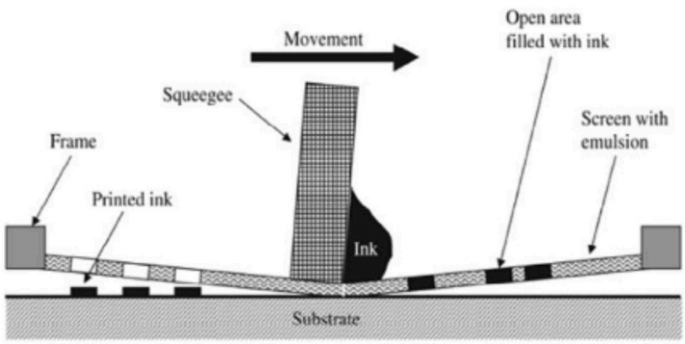
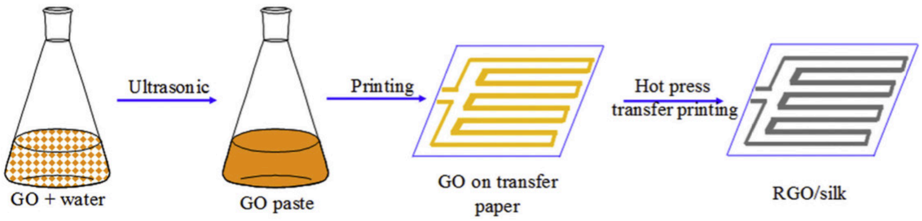


Figure 19: Schematic illustration of hot press transfer printing of GO on the surface of silk fabrics[95]



It is typical to experience a higher waste in material and a varied film thickness via screen printing, as this method is not an additive approach and therefore, there is less control over the parameters, in comparison to Inkjet printing and aerosol jet printing. However, screen printing is a much simpler process in comparison to the other mentioned processes. For depositing graphene onto textiles via screen printing, graphene nanoplatelets prepared either from reduction or exfoliation of graphene oxide are typically used for preparation of the printing solution. The graphene is uniformly dispersed, often via sonication in a solvent, which is generally water or a non-volatile organic compound. The graphene and solvent are then added to a binder, commonly waterborne polyurethane, to form the printing ink with a viscosity ranging from 30–12000cP. Due to the high pressure used when applying the ink to the substrate via the squeegee, the graphene is extremely stable on the substrate and therefore, it is not likely to wash or rub off[87,67,86]. It is possible to produce prints at a rate of 50–300 mm s^{-1} via screen printing, giving a medium to high throughput[86].

Transfer printing

For transfer printing, a single-layer film of graphene formed via chemical vapour deposition (CVD) is patterned onto an initial substrate, which is subsequently brought into contact with the final substrate requiring the coating. As the first substrate holding the graphene is peeled away from the final substrate, the graphene coating is transferred and remains on the final substrate due to shear stress. As the first and final substrates are pushed together and then pulled apart for the transfer of CVD graphene film, both the temperature and pressure must be highly regulated to ensure the graphene can be transferred without defects[87]. The heat used during the transfer process also converts graphene oxide to a reduced graphene oxide for use in a conductive application [95], as outlined in Figure 19. The transfer printing p rocess can be used to pattern graphene onto a textile substrate in resolutions of around 100 nm and below. This approach is a one-step process, which does not use any chemicals or solvents that can cause deterioration to the textile substrate. Therefore, this chemical and solvent-free method can be seen to have advantages for the printing of graphene onto textiles[87]. This method is straightforward, scalable, cost-effective and reproducible. However, the high pressure used in the method could lead to cracks and voids in the graphene film, the graphene can also be misaligned to the target substrate during transfer, therefore extra care must be taken[96].

Table 6. Summary of methods for printing graphene onto textiles

Printing method	Microstructure	Advantages	Disadvantages	Throughput
Inkjet printing	• Resolution of approximately 2-12 μm • Layered uniform microstructure • Varied porosity • Ink viscosity ranges from 1–30cP • Film thickness of 100–500nm	• Graphene deposited at chosen locations, without patterning the textiles prior to printing • Cost-effective • Suitable for large-scale production • Simple to use • Little wasted material • Versatility regarding viscosity of solution • Large variety of solvents may be used	• Clogging of the nozzle can occur • Challenge to form a conductive track without pre-treatment	• Suitable for large scale production • Low to medium throughput • Printing speed of 1.25–7000 mm s^{-1}
Aerosol jet printing (AJP)	• Resolutions of 10μm • Ink viscosities ranging from 1–1000 cP • Film thickness ranges from 30-150nm	• Can deposit conductive graphene onto rough and porous textiles without any pre-treatment • Eliminates the coffee-ring formation	• Nozzle clogging at high particle loading-Adjustment in solid phase leads to successful printing	• Low throughput • Printing speed of 0.1–10 mm s^{-1}
Screen printing	• Resolution of approximately 40 -100 μm • Ink viscosity ranging from 30–12000cP • Film thickness ranges from 14000 – 25000 nm	• Cheap • Fast process • Simple • Pressure applied to the ink makes the graphene is extremely stable - not likely to wash or rub off	• Higher waste in material compared to other methods • Varied film thickness • Less control over parameters compared to other methods	• Medium to high throughput • Printing speed of 50–300 mm s^{-1}
Transfer printing	• Resolutions of around 100 nm and below	• One-step process • Chemical and solvent-free method • Straightforward, • Scalable, • Cost-effective • Reproducible	• Stress to graphene leading to cracks and voids • Graphene transfer can be misaligned to the target substrate	• Time consuming process

Graphene applications in textiles

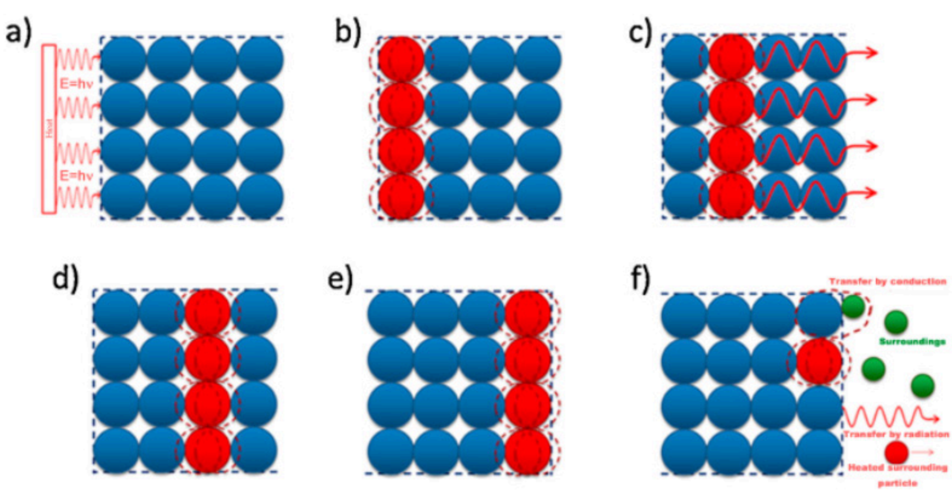
This part of the report will cover common functionalities and performance that graphene can bring into technical textiles, including electrically conductive textiles, fire retardant, thermally conductive, UV protective fabrics and etc. Moreover, graphene can be used in textiles applications in order to enable a higher operating temperature for the composite, attribute to antistatic properties, as well as adding increased strength to any composite[66].

To explain the mechanisms of these performances, we have compiled few of very recent developments examples from research institutes that focused on applying graphene in textiles and fibrous material to achieve such performances. Moreover, a list of examples of new and commercialised textile developments and products using graphene, with information about the relevant companies and partners are provided.

Thermally conductive applications

Graphene has the highest thermal conductivity out of all known materials, the thermal conductivity of single-layer graphene can be up to approximately 5000 W^{-1} K^{-1}. In comparison to copper, a material thought to be a good conductor, has a thermal conductivity of 400W m^{-1} K^{-1} at room temperature. The fast transfer of heat in graphene is attributed to the strong chemical bonds between the densely packed atoms within the lattice[97]. When some atoms in the graphene crystal lattice come into contact with a heat source, the heat flows from hot to cold[8]. Heat is spread from those atoms and passed to the surrounding atoms via vibrations, then again heat transfer spreads to the next neighbouring atoms and so on, resulting in an extremely quick thermal conduction[97]. The mechanism of heat transfer in crystalline materials in general and in graphene are shown in Figure 20 and Figure 21 respectively. However, research published in the MRS Bulletin published by Cambridge Core, reported that the thermal conductivity of graphene is significantly reduced when graphene is in contact with a substrate or enclosed in nanoribbons. The research detailed that the thermal conductivity of graphene supported by SiO_2 was measured as ~ 600 W m^{-1} K^{-1}[8]. Thermal conductivity of graphene has been applied to enhance various thermal regulation, flame retardant, smart textiles and energy storage applications.

Figure 20. The schematic of thermal conductance in a crystalline material [97]



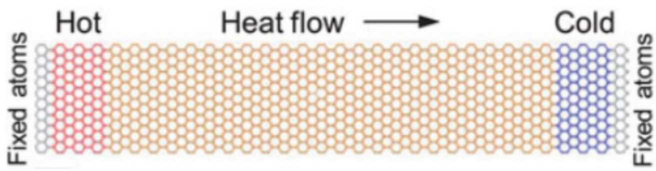
Batteries

For example, graphene has been used to regulate the temperature of batteries. A powerful battery can get very hot. If the speed at which heat is generated is quicker than it is dissipated, the battery becomes too hot and can stop working efficiently or catch fire. Therefore, it is important to regulate the heat of the battery pack via a thermal management system in order to increase the battery lifespan. Researchers from the Department of Mechanical Engineering of Wichita State University, US, found that integrating 8 wt % graphene nanoflake into polyacrylonitrile fibre battery separators improved the thermal conductivity from 3.5 to 8.5 $Wm^{-1} K^{-1}$. [98] Alternatively, it is common to use phase change materials for the thermal management of Lithium-ion batteries, however phase change materials have a very low thermal conductivity value in the range of 0.17 - 0.35 W mK^{-1} at room temperature and instead operate as a heat absorber. Researchers from the Department of Electrical Engineering and Materials Science, of the University of California, US, incorporated graphene to a hydrocarbon-based phase change material. Results found that by incorporating a hybrid phase change material with graphene fillers inside Li-ion battery pack leads to a higher thermal conductivity by more than two orders of magnitude, while maintaining the phase change materials latent heat storage ability[99].

Flame retardant applications

Improving the thermal stability and flame retardance of textile materials is critical for some applications where fire retardancy is required[100]. Research has discovered that graphene and its derivatives exhibit flame-retardant properties, attributing to an improved fire-retardant performance if used in textiles. Therefore, making graphene perfect as an environmentally-friendly fire retardant alternative at low loading for high temperature applications. Graphene has very high thermal conductivity and it can dissipate heat quickly and has extremely high thermal stability of 2126°C before degradation[101]. Therefore graphene has

Figure 21 Schematic illustrating the methodology for thermal transport in a graphene nanoribbon.[8]



advantageous properties over the majority of other polymers which are flammable and combustible, and burn quickly when in contact with a high release of heat, while also experience fast spreading of flames when coming in contact with fire, as well as releasing harmful smoke and toxic gasses[102].

Flame retardancy mechanism

For polymer materials to combust, heat, oxygen, fuel, and free radical reactions must be present. To inhibit combustion and give polymeric materials flame retardant properties, one or more of these key components must be disrupted. Graphene provides flame retardant properties via inhibiting heat and fuel, the mechanism used has three properties which work together simultaneously to inhibit combustion.

- Firstly, graphene has a two-dimensional layered microstructure in which encourages a continuous dense char to be formed concurrent to decomposition due to combustion. The newly formed char performs as a barrier preventing heat from being transferred therefore delaying thermal decomposition at elevated temperatures. The char creates a tortuous path, providing a larger pathway for the transfer of heat and mass from gaseous and condensed phases, advancing the thermal stability of the composite polymer[102].
- Secondly, graphene has a large specific surface area which enables adsorption of volatile organic compounds, while also preventing their release and diffusion, hindering flammability.
- Lastly, graphene has a huge number of reactive oxygen-

containing groups that are able to absorb heat and cool down a polymer substrate during combustion, as well as release gasses during combustion which reduce the oxygen concentration in the peripheral area of ignition.

Moreover, the strong interaction graphene has with polymer molecules allows graphene and the polymer to establish a three-dimensional network structure in the polymer matrix. Additionally, having high thermal conductivity properties mean that when graphene is used as a flame retardant on a polymer substrate, the graphene increases the viscosity of polymer at high heat, changing how the polymer would usually behave and preventing dripping and decomposition of the polymer material[102]. To summarise, using graphene in high temperature textile applications, graphene has been found to improve thermal stability[101], increase in the amount of char formed[103], supress smoke[66], limit the oxygen index value[104], improve the melt viscosity[105], achieve a lower peak heat release rate[100] as well as improving anti-dripping properties[105].

Pure graphene is extremely stable against ignition when subjected to a flame for only a few seconds. The area exposed to the flame will become red hot although the flame doesn't spread across the graphene and is quenched once the flame is removed. However, graphene oxide contains potassium salt impurities, therefore, when in contact with high temperatures, self-propagating combustion is triggered making graphene oxide extremely flammable[106]. Researchers from the College of Mechanics & Materials of Hohai University, China, investigated various degrees of oxidation with graphene as a fire-resistant material for polystyrene. The researchers reported a reduction in both thermal stability and peak of heat release rate when oxygen groups in reduced graphene oxide or graphene are increased. The researchers also found that the most efficient flame retardant contained 5 wt% of graphene when blended with polystyrene for fabrication of a composite material[107].

It has also been reported that when subjected to high temperatures, multi-layer graphene has increased thermal stability in comparison to single layer graphene[66]. A study by researchers from the Laboratory of Fire Science of the University of Science and Technology of China reported that when using graphene as an additive in a polymer matrix for fire resistance, the inclusion of graphene was found to delay the oxidation of the fabricated composite materials[105].

The Hohenstein Institute, Bönnigheim, Germany, tested the flame retardance of various graphene dispersions up to 7 wt.-% mixed with polyurethane, polyacrylate and polybutadiene as a binder and coated onto viscose fabric using the dip and dry technique. The reported results show that the graphene coated viscose has an afterburn time of 43 seconds and no reported afterglow time, in comparison to the viscose fabric that was not coated with graphene has a reported afterburn time of 69 seconds and an afterglow time of 85 seconds[108].

Electrical applications

Graphene has unique physical properties such as a uniquely high charge mobility (>200,000 cm2 V^{-1} S^{-1} for suspended graphene) and the ability to cleanly transport charge carriers applied by an electric field even at room temperature. This mechanism is named ballistic transport. When working together, these mentioned properties make graphene a perfect material to enhance properties in textiles, transforming the material to become electrically conductive or to improve existing conductivity [26]. The electrical conduction property of graphene has potential for use in smart textiles, biosensors, energy harvesting and storage, antistatic protection, transparent conducting electrodes, in photovoltaic cells, electrically conductive composite material applications.

For transportation of the electrical charge in graphene, the charge carriers can be adjusted from electron-like to hole-like by employing a gate voltage[109]. In order to reach optimum electrical conductivity, the concentration of graphene within a polymer matrix must be increased (dependent on how the graphene is introduced into the fibre or textile, while also dependent on the polymer type). In order to reach the optimum concentration for the conductive graphene within the matrix. Forming an infinite network of connected paths through the insulating polymer, producing a flow of electrical charge[26].

Researchers from the School of Textiles of Tianjin Polytechnic University, China, studied the impact of graphene concentration on the electrical conductivity of electrospun polyvinyl alcohol/sodium alginate/graphene nanofiber membranes. The researchers loaded the nanofibres with 0, 0.0375, 0.075, 0.25, 0.5, and 0.75 wt.% graphene concentration and results found that 0.075 wt.% of graphene loading is the critical conductive threshold in order for the graphene to be evenly distributed for optimal electrical conductivity[110]. Graphene based fibres are most commonly fabricated from graphene oxide due to the methods of fibre manufacture. However, this form of graphene is oxygenated and therefore, highly resistant to electrical charge. Consequently, a reduction treatment on the graphene oxide fibre is critical for the restoration of electrical conductivity[25].

A group of researchers from the Research Center for Exotic Nanocarbons of Shinshu University, Japan, fabricated a graphene oxide fibre via dry film scrolling and subsequent thermal annealing forming a graphene oxide fibre that is claimed to be has the highest electrical conductivity to date. The study also found that with an increase in annealing temperature from 300 °C to 2800 °C the conductivity was also found to increase from 6.4 to 416 S cm $^{-1}$[61]. Meanwhile, a study published by the College of Polymer Science and Engineering of Sichuan University, China, discovered that reduced graphene oxide wet spun fibres with a larger nominal diameter (30 µm) had a higher conductivity (52% higher) in comparison to fibres with a smaller dimension 5 µm. Moreover, the study also found that by improving the sheet alignment in the graphene oxide fibres, a higher electrical conductivity was found[35].

Wearable electronics

A study published by the Department of Polymer Science and Engineering from Zhejiang University, China, detailed the fabrication of reduced graphene oxide fibres doped with silver nanowires for application of a stretchable and electrically conductive fabric. The researchers used a prestraining-then-buckling approach to adhere the fabricated fibre to a Polydimethylsiloxane (PDMS) substrate. Results found the fabricated material to have a consistent electrical resistance after 50 cycles of stretching-relaxation at the tensile strain limit of 50%[40].

Researchers working for the centre for graphene science within the University of Exeter, UK, have developed a novel method for the fabrication of transparent, flexible and durable graphene enabled touch-sensors. The material manufacture involves coating and transferring single layer graphene grown by chemical vapour deposition and interdigitated electrodes that were also patterned onto the graphene coating using a micro-patterning technique onto polypropylene fibres. The graphene/ polypropylene electronic fibres were subsequently woven into a textile fabric. The method was shown to be compatible with the roll to roll approach, making this approach suitable for mass scale production. The researchers demonstrated that this method of fabrication, results in improved device performance in comparison graphene patterning via conventional lithography [111].

Photonics

Graphene based fibres have also been used for photoelectrode application. Researchers from the School of Chemistry of Beijing Institute of Technology, China, synthesized reduced graphene oxide and TiO_2 composite fibres via a hydrothermal process. The fabricated fibres were found to be photoresponsive, generating a photocurrent density of ca. 0.2 μA upon exposure to a 100 W light at room temperature[112].

Moreover, researchers from the School of Materials Science and Engineering of Nanyang Technological University in Singapore, fabricated flexible organic photovoltaic devices via transferring a chemically derived reduced graphene oxide film onto polyethylene terephthalate (PET) and using the reduced graphene oxide as transparent and conductive electrodes. The performance of the organic photovoltaic devices was found to depend on how well the charge can be transported through the reduced graphene oxide electrodes, when the optical transmission of reduced graphene oxide is above 65%. However, if the transmission of reduced graphene oxide was found to be below 65%, the performance of the organic photovoltaic devices is governed by the transparency of the reduced graphene oxide films [113].

UV blocking

UV (ultraviolet) radiation can cause harm to human health, being a catalyst to cause skin cancer and eye damage. As well as being destructive towards covalent bonds in organic materials, attributing to polymer deterioration, resulting in decreased polymer physical properties after UV exposure and so finding methods to ensure UV rays are blocked for certain applications is essential. Graphene is a noncatalytic and transparent material, and due to its very high surface area graphene oxide absorbs a large amount of UV light at low loading. Graphene has been found to have a UV absorption at peak around 100-281 nm, meaning graphene can efficiently absorb UV rays in this range which make graphene an excellent material for use in UV blocking applications. The UV shielding mechanism of graphene can be largely attributed to its unique 2D planar structure. The structure of graphene allows the majority of UV rays to be reflected, making graphene an excellent UV protector for the absorption of UV rays and blocking transmission through a fabric when used as a coating[114]. Many researchers have found graphene coatings to be highly durable, while they have also been found to continue to provide UV protection even after wash tests[24].

A team of researchers from the College of Textiles of Qingdao University, China, increased UV blocking properties of cotton fabric by dispersing graphene nanosheets as well as chitosan which was used as a dispersant aid, into a binding additive and then the mixture was coated onto the cotton fabric using the pad-dry-cure approach. Results found that even with a very low graphene loading (<1% wt) in the coating solution, adding the graphene to the cotton increased the UV blocking property up to 60 times higher than when compared with the cotton that had no coating. The researchers found that the coating was extremely durable and could be washed 10 times without seeing any change to the UV blocking properties[115]

A different team of researchers from the Textile Engineering Department of Amirkabir University of Technology, Iran, used the exhaustion and in-situ synthesis method to apply reduced graphene oxide and SnO_2 onto the surface of a PET fabric substrate in order to enhance UV blocking properties. The experimental results recorded the value of the UV protection factor to be enhanced around seven times (UPF of 216.9) when incorporating 0.2 wt% of reduced graphene oxide onto the material surface, in comparison to the UV protection factor of bare PET fabric which has a UPF value of around 33.5. The researchers found that the UV blocking mechanism of reduced graphene oxide could be enhanced when incorporating SnO2, due to the incorporation of SnO_2 particles increasing the range which UV rays can be absorbed[116].

Filtration

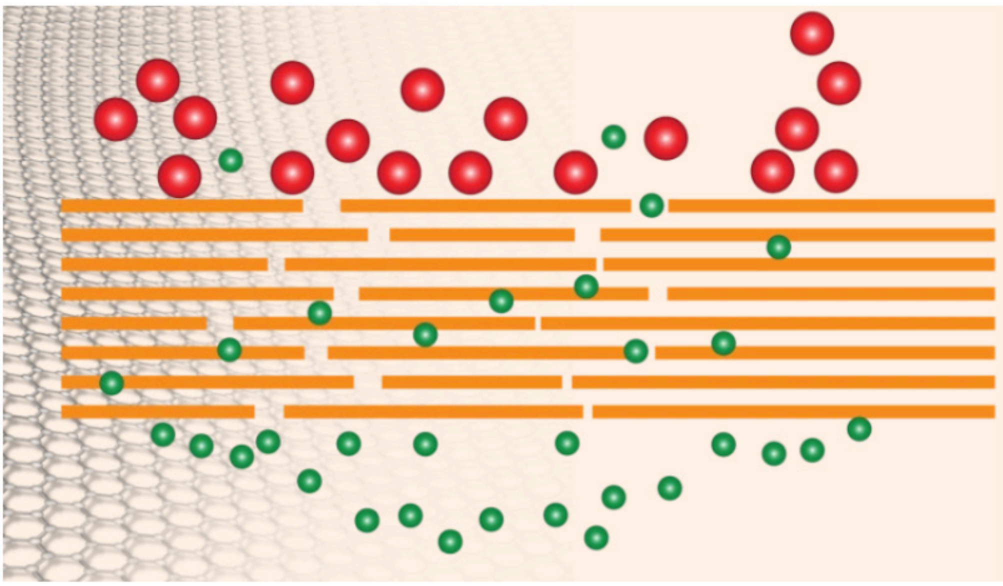
Graphene oxide membranes can be applied to form a barrier for high level filtration of liquid phase and gas phase separation[117]. The filtration capability of graphene oxide is attributed to the extremely defined nanoporous microstructure in graphene oxide sheets which can maximizes ion selectivity at a molecular level, further detailed in Figure 22. By controlling the pore sizes in the graphene membranes they can be applied to different filtration applications[118]. The pore sizes of graphene membranes can be adjusted to be smaller than the size of ions for application in water purification, as demonstrated in research published by the Department of Mechanical Engineering of MIT, USA[119,121].

Researchers from the National Graphene Institute at the University of Manchester, UK, recently demonstrated that a membrane made from multiple layers of graphene oxide can filter out sodium chloride from seawater more efficiently than any other existing method. This is because the pores in graphene can be precisely controlled, in order for graphene to act as a sieve with pores smaller than the molecules of salt. Preventing salt molecules from passing through the filter, while simultaneously allowing the water molecules to pass through the membrane, making seawater safe to drink for desalination applications[122]. Graphene filters also have an advantage in comparison to other existing filters, as once graphene filters come to the end of their life, they will no longer let any liquid pass through, giving a notification that the filter is no longer working. However in conventional filters it is impossible to tell if the filter is working adequately[123].

Composites

Graphene based materials are considered favourable materials to improve the properties of fibre reinforced composites, in a wide spectrum of polymer systems. Graphene based materials can provide high strength and stiffness, improved toughness and enhance impact and through-thickness properties[124]. Whilst providing improved mechanical strength, graphene is also uniquely light weight and therefore graphene has been commonly used in a wide range of applications such as aeronautical and

Figure 22: An illustration detailing the mechanism of molecular filtration of graphene (smaller molecules (in green) such as water having the ability to pass through the multiple layers of graphene oxide, forming a membrane (in orange), while the larger molecules (shown in red) such as salt are blocked due to their size[123].)



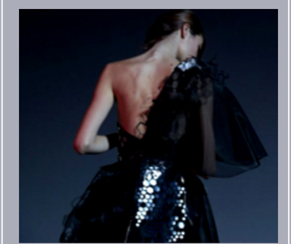
astronautical structures, automotive vehicles and sporting equipment[125] for the reduction of weight and improvement of mechanical properties[126].

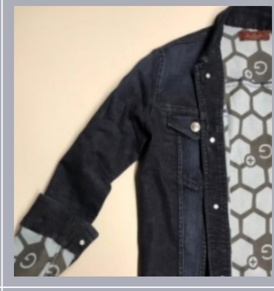
For example, researchers from the Department of Chemical Technologies of the Iranian Research Organization for Science and Technology (IROST), Iran, employed graphene oxide and functionalised graphene oxide for the reinforcement of carbon fibre and epoxy resin composites to enhance the mechanical properties. The study experimentally found that by incorporating 0.3 wt% of graphene oxide in the composites, a 22.5% gain in the tensile strength and a 23.3% advancement of Young's modulus was achieved. The researchers additionally found that the incorporation of functionalised graphene oxide could improve the dispersion of the graphene oxide within the polymer composite matrix, as well as the interfacial interaction between the polymer and the graphene oxide[125].

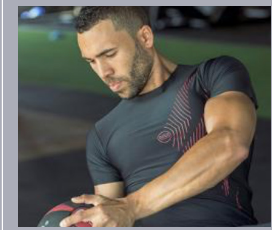
Commercialised examples of graphene in textiles

In this table, we have gathered a list of products and their targeted applications, some of the claims that have been made about the properties of these products and further details about the companies and their partners. This is by no means an exhaustive list, as new products are entering the market all the time, but it does provide an indication of the types of products that are available commercially

Table 7. Commercial applications of graphene in textile and composite products

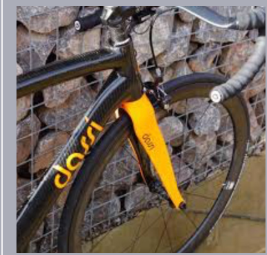
Company and partners	Product name/s and targeted application/s	Product description	Functions/ properties	Further details
Vollebak www.vollebak.com	**The Graphene Jacket** *Fashion and outdoor wear* 	The jacket is reversible with one side coated in graphene to make it conduct heat and electricity. Launched in 2018.	• Waterproof to 10,000 mm of liquid • Bacteriostatic • Durable • Enhanced strength	The company, based in London, worked with production partners in Italy and Portugal who had built Michael Phelps' swimsuit for the 2008 Beijing Olympics. Raw graphene was converted into graphene nanoplatelets and blended with polyurethane and nylon.
CuteCircuit www.cutecircuit.com **National Graphene Institute, University of Manchester** www.graphene.manchester.ac.uk	**The Intu Graphene Dress** *Fashion* 	A little black dress made from graphene which can change colour and design. Special graphene substrates (hexagonal crystal-like formations) incorporated into fabric design. Unveiled in Manchester in 2017.	• Senses the breathing of the wearer and illuminates parts of the dress through transparent conductive films in response to the captured biodata.	The Intu Graphene Dress was commissioned by Intu Trafford Centre to celebrate fashion innovation.

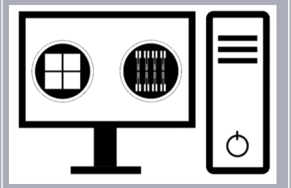
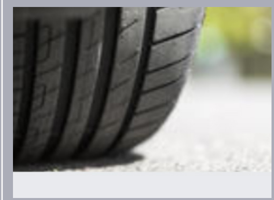
Company and partners	Product name/s and targeted application/s	Product description	Functions/ properties	Further details
Alfredo Grassi *www.grassi.it* **Directa Plus** *www.directa-plus.com*	**Directa Plus to supply G+ textiles to Alfredo Grassi (name yet to be announced)** *Protective clothing and workwear* 	Graphene-enhanced workwear using Directa Plus' G+ technology. Announcement initially made in 2017, followed by further news in 2018 that Directa-Plus had received a second order from Alfredo Grassi.	• Thermal regulation • Chemical-free • Heat dissipation • Energy harvesting • Antistatic • Bacteriostatic • Flame-retardant	Directa-Plus received the two orders following Grassi's successfully public tender to provide workwear incorporating G+ to an Italian government agency. The contract is expected to generate revenues for Directa Plus of approx. €0.6m over the next few months.
Arvind Limited *www.arvind.com* **Directa Plus** *www.directa-plus.com*	**Arvind Denim ft G+ (name yet to be announced)** *Fashion and outdoor wear* 	Denim fabrics incorporating G+ technology. Comprising a printed thermal circuit. Product development announced in May 2018.	• Thermal and electrical conductivity • Bacteriostatic • Heat dissipation • Energy harvesting • Data transmission • No odour effect	Based in India, Arvind says the collaboration with Directa Plus will further enhance its capabilities in innovation and research and accelerate its transformation into a technology-driven company.
Colmar www.colmar.it **Directa Plus** www.directa-plus.com	**Ski jacket collection including Technologic G+ jacket, Bormio G+ jacket and Guaina Zeno G+ jacket** *Sportswear* 	Ski jacket collections incorporating G+ technology. New collections announced in 2016, 2017 and 2018.	• Thermoregulation • Antistatic • Bacteriostatic • Quick-drying • Chemical-free	The hexagonal print in G+ transfers body heat from the hottest to the coldest parts, ensuring comfort and better blood circulation. The jacket has been worn by the French national ski team for multiple tournaments. Technologic G+ was selected as a Gold Winner in the 'Ski' category at ISPO Munich 2017.

Company and partners	Product name/s and targeted application/s	Product description	Functions/ properties	Further details
Deewear www.deewear.com **Directa Plus** www.directa-plus.com	**D-ONE** *Sportswear* 	Second-skin sportswear with high-performance technical layers that combine properties of G+ with the benefits of postural compress fabric, while offering superior comfort. Launched in 2017.	• Body heat preservation • Promotes health and hygiene • Ultra-thin and lightweight • Bacteriostatic • Anti-odour • Non-toxic • Aids circulation and postural support	The collection includes short sleeve T-shirts and leggings, which are available in 'basic' and 'advanced' versions, in different sizes and in a male or female fit. The internal side of the fabric, in direct contact with the skin, is printed with G+.
Eurojersey www.sensitivefabrics.it **Directa Plus** www.directa-plus.com	**G+ enhanced textiles (under Sensitive Fabrics brand)** *Sportswear, athleisure, underwear* 	High-quality warp-knit technical fabrics incorporating G+ technology. Collection unveiled at ISPO Munich 2018 and Première Vision 2018.	• Thermal regulation • Bacteriostatic	Eurojersey uses graphene in two forms: as a membrane bonded to one or two layers of Sensitive fabric, or as a printed pattern. The company's latest development is a Sensitive fabric printed with a layer of graphene in a honeycomb pattern.
Iterchimica www.iterchimica.it **Directa Plus** www.directa-plus.com	**Eco Pave** *Geotextiles, construction* 	Asphalt additive enhanced with G+ technology. Collaboration announced in 2017.	• Improves durability and sustainability of asphalt road surfaces	Due to the thermal management properties of G+, the asphalt is less susceptible to hardening and cracking in cold temperatures as well as to softening in warm temperatures. Beneficial for maintenance purposes such as repairing potholes.

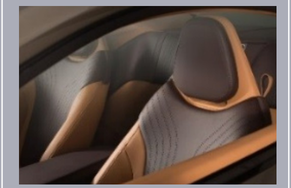
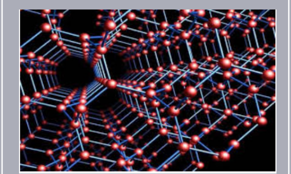
Company and partners	Product name/s and targeted application/s	Product description	Functions/ properties	Further details
Bioracer www.bioracer.com **Oakley** https://uk.oakley.com **Directa Plus** www.directa-plus.com	**G+ Graphene Aero Jersey** *Sportswear* 	Cycling garment incorporating G+ technology. Unveiled at Outdoor Friedrichshafen in 2018.	• Thermal regulation • Electrostatic • Bacteriostatic • Advanced moisture management • Anti-odour effect	The printed G+ planar thermal circuit distributes the heat generated by the body and dissipates it when required. This significantly improves comfort of the wearer and enables riders to use less energy to regulate their body temperature.
Vittoria www.vittoria.com **Directa Plus** www.directa-plus.com	**Qurano** *Sports gear* 	Bicycle wheels incorporating G+ technology	• Heat dissipation • Puncture reduction • Increased lateral stiffness • Weight reduction	The full-carbon wheel rims have been enhanced with graphene nanoplatelets provided by Directa Plus. Available in three different sizes.
Inov-8 (British subsidiary of Japanese company Descente Ltd) www.inov-8.com **National Graphene Institute, University of Manchester** www.graphene.manchester.ac.uk	**G-SERIES shoes** *Sportswear* 	The world's first-ever sports shoes to utilise graphene Launched in 2018.	• 50% harder wearing, stronger and more elastic • Tough grip	Patent-pending. The partners developed rubber outsoles for running and fitness shoes that in testing have withstood 1,000 miles. G-SERIES features three different shoe ranges.
Bromley Technologies Ltd www.bromleysports.com **Versarien** www.versarien.com	**Bromley X22 prototype sleds** *Sports gear* 	Graphene-enhanced carbon fibre composite skeleton sled Collaboration announced in 2016.	• Desirable structural properties • Drag reduction • Strength-to-weight ratio • Tougher impact properties	Technology was successful used by British Skeleton World Cup competitor Dominic Parsons at the Sochi Winter Olympic Games in 2014.

Company and partners	Product name/s and targeted application/s	Product description	Functions/ properties	Further details
MWV Packaging www.packaging-gateway.com **Vorbeck** www.vorbeck.com	**Natralock with Siren Technology** *Packaging/security* 	An anti-theft packaging solution. Launched in 2012.	• Allows exceptional security without interfering with product branding or deterring sales by requiring products to be placed behind a locked cabinet. • Provides three levels of security for retailers.	Product uses Vorbeck's graphene-based ink Vor-ink to enable an on-package alarm to protect the product from theft or tampering before purchase. It received the Product Development Award in Printed Electronics from IDTechEx in 2011.
Head www.head.com **Applied Graphene Materials (AGM**) www.appliedgraphenematerials.com	**Graphene XT** *Sports gear* 	Graphene-enhanced tennis racquets. Launched by British tennis player Andy Murray in 2015.	• Optimal weight distribution for a faster swing and more power • Generates more kinetic energy when player hits the ball • With less effort, more power is generated	The racquets are said to be up to 20% lighter than a conventional racquet and offer up to 30% higher mechanical strength compared to existing Head models. Graphene provided by AGM.
Head www.head.com **Applied Graphene Materials** www.appliedgraphenematerials.com	**Joy Series** *Sports gear* 	Graphene-enhanced skis for women. Launched in 2014.	• Lighter and more durable than standard skis providing more balance and control on the slopes.	The line includes several models. Graphene is used in the mid-section of the ski to allow heavier tip and tail of the ski to grip the snow. It is also used in Head's power boards.

Company and partners	Product name/s and targeted application/s	Product description	Functions/ properties	Further details
Dassi www.dassi.com	**The Dassi Interceptor in Graphene** *Sports and outdoor gear* 	Graphene-enhanced aero road bike. Follows the launch of Dassi's first-ever bike frame containing graphene in 2016.	• 30% lighter and twice as strong as regular carbon. • Unrivalled stiffness and weight • Aerodynamic • Customisable	Graphene was mixed with an epoxy resin developed by Dassi that was then electronically functionalised to disperse the graphene evenly within the resin. The carbon weave was then introduced into the resin mix, which in turn formed the graphene carbon material in a prepreg that can be used for laying up components.
Catlike www.catlike.es	**Mixino** *Sportswear* 	Graphene-enhanced cycling helmet Launched in 2014.	• Provides maximum protection with minimum weight.	Catlike incorporated graphene nanofibres into the manufacturing of cycling helmets. A new Mixino model was introduced in 2017 – the first cycling helmet to incorporate graphene nanofibres on its inner aramid skeleton. And in 2018, the company launched Mixino Evo – featuring internal mesh of aramid and graphene.
Catlike www.catlike.es	**Whisper Road** *Sportswear* 	The first cycling shoe that incorporates a sole infused with graphene. Launched in 2015.	• Extremely light • Boosts strength without adding weight.	The sole is super light and ergonomically curved to match the shape of the wearer's foot. The outside part of the Whisper Road incorporates Clarino microfibre, a material three times stronger than real leather with minimum weight, which dissipates heat in warm weather and retains it in cold weather.

Company and partners	Product name/s and targeted application/s	Product description	Functions/ properties	Further details
Biolin Scientific www.biolinscientific.com **ICN2 Nanobioelectronics and Biosensors Group** https://icn2.cat	**QSense GO sensor** *Security, medical devices, environment, electronics* 	A graphene oxide sensor Announced in 2016.	• Online measurement and monitoring of films • Enables interaction studies of graphene oxide with various substances	The developers used a quartz crystal microbalance containing patterned graphene, a system that measures mass variation. It is believed that the sensor could open the door to various applications with interest for diagnostics, safety/security and environmental monitoring.
Gratomic Inc https://gratomic.ca/ **Perpetuus Carbon Technologies Ltd** www.perpetuusam.com	**No brand name provided yet** *Automotive* 	Graphite-derived graphene and graphene hybrids for tyre elastomers Project announced in 2018.	• Improved handling fuel efficiency and braking efficiency • Reduction of air permeability • Lighter tyres • Lower rolling resistance, high impact and tensile properties • Potential for improved economy and superior performance	The joint venture takes the context of graphene nanoplatelets (multilayer graphene or graphene flakes) from Mined Bulk Graphite provided by Gratomic Inc. A material-enhancing component for mass-market commercial exploitation. The tyres can be produced by liberating surface modified flakes of nano-graphite, via PCT's patented plasma processing technology.

Company and partners	Product name/s and targeted application/s	Product description	Functions/ properties	Further details
Add North 3D www.addnorth.com **Graphmatech** www.graphmatech.com	**Aros Graphene-based filaments** *3D-printing* 	Aros Graphene-based filaments for 3D printing Announced in 2018.	• May grant ability to control the exact level of conductivity of the filament	The filaments may open up many different 3D-printing applications such as thermal management components, circuit boards and efficient electromagnetic and radio frequency shielding. Aros Graphene is a patented ionic graphene nanocomposite material developed by Graphmatech.
Haydale Graphene Industries www.haydale.com **National Graphene Institute, University of Manchester** www.graphene.manchester.ac.uk **Sheffield Advanced Manufacturing Research Centre** www.amrc.co.uk **University of Central Lancashire (UCLan)** www.uclan.ac.uk	**Juno** *Aerospace* 	The world's first graphene-skinned aeroplane (three-and-a-half metres) Unveiled by UCLan at Farnborough International Airshow in 2018.	• Advanced strength • Significant weight reduction • Reduced chance of ice build-up due to graphene's thermal conductivity allowing heat to spread throughout material • Electrical conductivity of graphene causes the energy of lightning strikes to be dispersed throughout the surface of the fuselage, preventing damage	The unmanned aerial vehicle (UAV) additionally features graphene-based batteries and 3D-printed components.

Company and partners	Product name/s and targeted application/s	Product description	Functions/ properties	Further details
Promethient www.thermavance.com	**Thermavance** *conductive heat transfer system* 	A graphene-enhanced seat warmer technology.	• User-friendly and can be activated by a smart phone app • Creates a heating or cooling effect • Can conduct heat to a higher extent than copper • Flexible • Light weight	The system uses conduction of heat as opposed to most other technologies that rely on transfer of heat through convection for the purpose of warming seats.
Graphene fibres/components for textiles				
Bonbouton (FlexTraPower) www.bonbouton.com	**Graphene sensors** 	Graphene sensors developed from inkjet-printable technology licensed from the Stevens Institute of Technology.	• Provide overall fitness feedback • Can prevent high risk wounds from developing • Can measure heart's electrical activity.	Bonbouton recently partnered with Liquid X Printed Metals to build temperature and pressure sensors directly on textiles using 3D printing techniques.
Shanghai Kyorene New Material Technology Co www.kyorene.net	**Graphene fibre** *Textiles* 	A graphene-enhanced fibre that has been used to produce clothes, sportswear and underwear.	• Antibacterial • Ultraviolet-proof • Anti-static • Heat preservation	The technology combines graphene with high polymer materials under room temperature.
Technow www.tech-now.ch	**Graphene Label** 	A soft and light graphene padding material comprised of graphene fibre, recycled polyester, polyester, cotton, nylon and rayon.	• High conductive capacities that regulate body temperature • Antibacterial • Electrostatic.	Can be used with virtually any fabric. Bonbouton recently partnered with Liquid X Printed Metals to build temperature and pressure sensors directly on textiles using 3D printing techniques.

Conclusion and outlook

It is said that graphene is a supernatural wonder material that is stronger than steel, or that it has superconductivity and all other sorts of extraordinary properties. One should bear in mind and consider the importance of atomic scale and that all these properties can be claimed when graphene is in its purest and defect-free form and comprises a one atomic layer membrane. However, lattice defects might be introduced during fabrication or transfer processes of graphene, or when graphene is produced in forms other than membrane i.e. powder or flakes, the level of performance and properties are compromised.

On the other hand, it is not envisioned that one atom thick graphene membrane will be used to cover a textile component such as fibres or fabrics, as stretching a textile material would probably be the limiting factor. Moreover, it is also important when incorporating graphene flakes into other materials such as textiles, that they are dispersed correctly in the matrix as otherwise researchers would end up with 'clumps of graphite' that would lose the two-dimensional aspect. With that being said, it is always advised not to have over-expectations of graphene and to consider the limitations and challenges.

Today, there are many graphene materials available in the market and not all of them are equal, and there are many companies globally supplying graphene products or 'claiming' to produce graphene. Moreover, producing a good quality of graphene is a challenging process and consequently, there is a large variation in its properties. Therefore, it is advised to understand what material parameters such as graphene morphology and formulation/ compounding technique and conditions are required depending on the final application level of results, and to consider that all the required and expected properties come down to the end-use application. Moreover, it is also important to consider uniformity of the graphene materials within a batch and from batch-to-batch, which is a key result of variation in the manufacturing process; this crucially necessitates supplying graphene from a reliable source.

In terms of bringing graphene into textile materials and products, there are two ways – one of which is using graphene-infused inks or paste which can be coated or printed on the outside of a textile material following textile manufacturing. The other way is to incorporate graphene at the fibre level by dispersing graphene powder in the spinning solution or melt, or by soaking fibres/yarns in a graphene solution following fibre manufacturing. There is no simple recipe as to which of these techniques are better or worse, as it again depends on the required performances of different applications. Likewise, there are lots of factors involved in learning the required graphene amount to be added into textiles, as it entirely depends on the level of functionality that is required, and it can be anything from as low as 0.01% to as high as 20-30% of graphene weight.

An additional challenge, but also an opportunity, might be that there are no off-the-shelf graphene enhanced textile products that one can supply. However, it has been noticed that there is quite a good number of graphene manufacturers who work closely with the textile industry, and they collaboratively work with a third-party textile manufacturer to deliver products for each application. Therefore, it is advised to work with a reliable supplier of graphene that can work with you towards the requirements of your R&D projects and can provide support during your developments.

Finally, it is worth mentioning that although thermal regulation has been the most common application of graphene in the textile and apparel industry, there is a much broader array of applications earmarked for textiles in the future. With smart textiles moving from being a niche market to a vital and prosperous field and the extraordinary electrical conductivity properties of graphene, novel and fascinating wearables and smart textile products are expected to be generated, taking advantage of graphene soon. This can include smart fabrics using graphene elements where the graphene-enhanced fibres and fabrics are the energy storage or energy generation devices or sensors that are integrated into the clothing itself. This is because the flexibility and light weight of graphene can help to solve the problem, we have currently with rigidity of electronics added onto textiles, and the fact that sensors in smart textiles can hardly be a part of the fabric at the moment. Moreover, there are a lot of research projects investigating the potential for producing neat graphene fibre or fabrics, which removes the need for a base fibre/ fabric substrate and can boost the flexibility and electrical conductivity of a garment.

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