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Challenges of Coating Textiles With Graphene

Different types of graphene for different textiles and applications

By Ana I. S. Neves*, Zakaria Saadi

College of Engineering, Mathematics and Physical Sciences, University of Exeter, EX4 5QF, UK

*Email: a.neves@exeter.ac.uk

Electronic textiles (e-textiles) hold the key for seamless integration of electronic devices for wearable applications. Compared to other flexible substrates, such as plastic films, textiles are, however, challenging substrates to work with due to their surface roughness. Researchers at the University of Exeter demonstrated that using different coating techniques as well as different types of graphene coatings is the key to overcome this challenge. The results of coating selected monofilament textile fibres and woven textiles with graphene are discussed here. These conductive textiles are fundamental components e-textiles, and some applications will be reviewed in this paper. That includes light-emitting devices, touch and position sensors, as well as temperature and humidity sensors. The possibility of triboelectric energy harvesting is also discussed as the next step to realise self-powered e-textiles.

1. Introduction

To make wearable technology more than simply portable, a seamless integration of individual electronic devices with textiles is paramount (1). Embedding traditional silicon-based electronic components and conventional metal electrodes onto textiles often results in cold, rigid, and heavy wearable devices. Comfort is particularly important in applications that require continuous use. For example, for remote healthcare monitoring, a bulky and uncomfortable device could deter the user from properly monitoring a vital parameter over time. If the sensor in question was imperceptibly integrated in a piece of clothing or in the patient's bedding, this would make continuous monitoring possible, increasing user engagement.

Our approach at the University of Exeter consists in building electronic devices directly on textile substrates. For that, all the components have to be lightweight and highly flexible, and whereas traditional hardware-type materials are not suitable due to their weight and rigidity, carbon-based materials, such as graphene, are a good alternative (2). Electrically conductive textiles are a fundamental component of any e-textiles. They are required for wiring, and they can also be the electrode at the base of in several applications. At Exeter we have explored different types of textile substrates, individual textile fibres (3,4) and woven fabrics (5) have been explored for this effect. By coating these substrates with graphene, the first of a growing family of two-dimensional materials, which is thin, lightweight and highly flexible (6), their otherwise insulating surfaces become conductive with no significant changes in mechanical properties which is important to preserve the comfort of the user.

However, the surface of textile substrates is very different from that of other substrates commonly used in flexible electronics, such as plastics, and even more so when compared to glass or silicon. Conventional multifilament textile fibres and their woven fabrics have inherently rough surfaces, which makes the adhesion of most materials very challenging without resorting to intermediate planarisation and adhesive layers. Moreover, additional layers can drastically change the thickness and the feel of a textile. This paper reviews some of the challenges in working with textile substrates and how a tailored approach of employing different types of graphene fabrication and transfer or deposition methods can be used to overcome some of those issues in making textiles electrically conductive. Another important matter is that the conductivity of these textiles is only as high as that of their graphene coating, which limits the scope of the applications. Different types of applications compatible with the properties of the different graphene-coated textiles are presented here.

2. Graphene(s)

Although graphene (specifically, single-layer graphene (SLG)) is defined as single layer of sp^2 carbon in a honeycomb structure, materials comprising more than one layer of graphene are also of interest, including few-layer graphene (FLG, ≤10 layers) (7), multi-layer graphene (MLG, >10 layers), and even ultra-thin graphite (UG, <100 layers). These graphene-based materials have different properties (electrical, mechanical, optical) depending on the fabrication and deposition methods, and are generally characterised ad hoc.

Out of the many graphene production routes (8), mainly two types of graphene were used for e-textile applications at Exeter: graphene grown by chemical vapour deposition (CVD, **Figure 1a**; and graphene films deposited from aqueous suspensions (**Figure 1b and c**). The former is a bottom-up technique in which a gaseous carbon source (e.g. methane) along with hydrogen at high temperatures

(≈1000°C) results in the growth of merging graphene domains to form a continuous film on a metal catalyst surface, usually copper or nickel. By tuning the growth parameters, it is possible to control the number of layers of graphene, from SLG to UG. The latter suspensions can be made using different types of graphene, themselves. This is achieved by directly exfoliating graphite (liquid-phase exfoliation of graphite, LEG) in water in the presence of a surfactant (9), or by mixing commercial graphene nanoplatelets (GNPs) in water. These GNPs can be obtained from different methods (10), some of which require oxidation of graphite and reduction to reduced graphene oxide, but are in general less hydrophobic than graphene powders, and therefore easier to disperse without a surfactant. Both these top-down methods, LEG and GNPs, start from graphite, an abundant material, therefore with reduced costs when compared with CVD, a technique that requires expensive metal substrates and high temperatures.

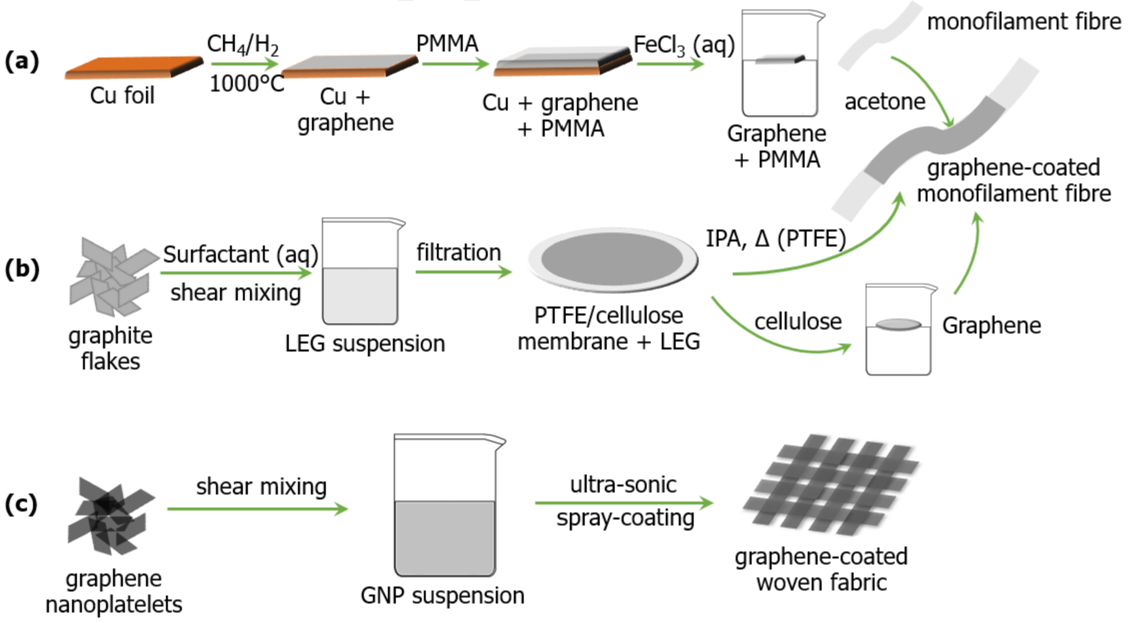

Fig. 1. Graphene production and transfer methods to coat monofilament textile fibras and woven fabrics: (a) CVD graphene growth and wet transfer; (b) shear exfoliation of graphite and vacuum filtration transfer; (c) GNP ultrasonic spray coating.

The fact graphene suspensions can be used with traditional coating methods, such as printing and casting, makes them ideally suitable for large-area applications (11). Nonetheless, CVD graphene has been demonstrated to have the potential for large-area and more control over the graphene structure and number of layers (12). We use wet-transfer methods for CVD graphene, specifically, etching the metallic growth substrate, copper or nickel, with a suitable etchant such as aqueous iron(III) chloride or ammonium persulfate. This is usually done with a carrier/protection layer, typically PMMA (poly(methyl methacrylate)), that can be easily removed after transfer (**Figure 1a**) (8), although for the thicker UG the same can be done without a supporting layer. The floating graphene is then collected with the target substrate. CVD graphene can conform to small variations in surface topography, but it will sever if the target substrate is not continuous.

As for the suspensions, we chose two main coating techniques. One uses vacuum filtration of fixed suspension volumes through membranes with selected pore size. The surfactant-stabilised graphene flakes in the suspension will cumulatively deposit on the membrane, forming a continuous FLG film of overlapping graphene flakes, making it possible to achieve some control over the average number of layers (**Figure 1b**). Depending on the membrane used, two different strategies can be employed to transfer these films onto the chosen substrate. With cellulose membranes, the film can be detached by slowly dipping it in water at a shallow angle, causing the graphene film to float. This film can subsequently be collected with the target substrate (13). If a PTFE (poly(tetrafluoroethylene)) membrane is used, the so-called isopropanol-assisted direct transfer (IDT) method can be used. The membrane is placed on top of the substrate, flooded with isopropanol, and placed in a hot plate. As the isopropanol evaporates, it forces the LEG film to detach from the membrane and transfer to the substrate (14).

The other technique used is ultrasonic spray-coating, an alternative to conventional air-pressure spraying techniques than uses ultrasonic frequencies to ensure no deposition occurs in the suspensions, while also controlling the drop formation. Whereas with IDT of LEG suspensions the surfactant is dissolved and therefore remains in the liquid after filtration, in spray coating all the dissolved surfactant molecules will precipitate with the graphene flakes as they are deposited in the substrate (**Figure 1c**). This results in the disruption of the percolation network of overlapping graphene flakes, and for this reason, spray-coating is more adequate for GNP suspensions than for LEG ones (5), as these are stable without surfactants.

Finally, it is important to highlight that the growth and transfer processes will affect the properties of the graphene coatings. CVD graphene is usually more conductive than LEG graphene, and also more transparent, which will greatly influence the type of applications they are suitable for. The transparency of CVD graphene generally depends on the number of layers (≈2.3% loss per layer (15)) and the way the layers stack (16). For a similar average number of layers, LEG will be less transparent due to the way individual flakes overlap, which will also result in a larger resistivity, usually in the range of the kΩ/sq for LEG, and of a few hundreds of Ω/sq for CVD. These values can be brought down through several approaches, namely chemical doping, to reach a few Ω/sq (17).

3. Graphene-coated textile fibres and their applications

Monofilament textile fibres have continuous and relatively smoother surfaces when compared with multifilament yarns. This makes them suitable for CVD graphene transfer. For this reason, extruded monofilament fibres of polypropylene (PP) and polylactic acid in a tape (flat) shape were used in our seminal work in this field (3). We have demonstrated that it is possible to coat these fibres with CVD graphene, rendering them conductive but still flexible. This was later extended to other polymers, polyethylene and nylon, tape- and cylindrically-shaped of different sizes (4). The best results were found with 2.4 mm wide PP fibres (**Figure 2a**), and therefore this was the platform chosen to take forward for e-textile applications. However, as shown in **Figure 2b and c**, the surface roughness of the PP is still high compared with conventional CVD graphene substrates such as silicon or poly(ethylene terephthalate) (PET). The vertical extrusion lines are particularly noticeable, but at this scale CVD graphene is still capable of conforming to the surface profile.

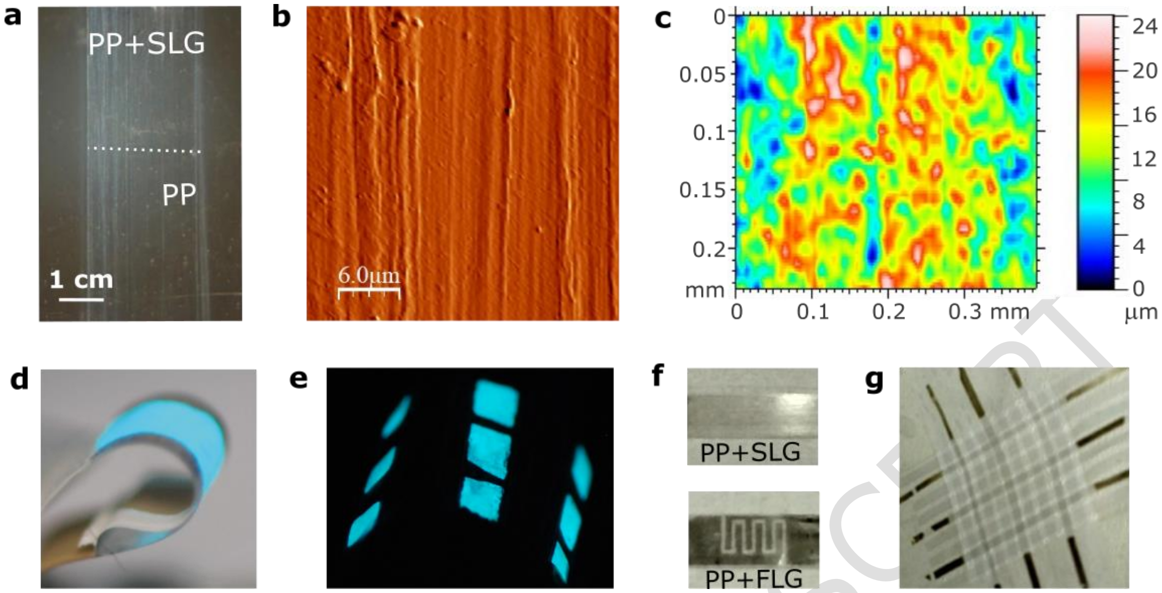

Fig. 2. (a) Tape-shaped monofilament PP fibres indistinguishably with (top) and without (bottom) SLG graphene coating (3); (b) AFM 30 × 30 µm image showing the vertical extrusion lines on a PP fibre (4); (c) non-contact optical surface analysis of a PP fibre with height profile (4). Application of graphene-coated PP fibres as: (d) single-fibre and (e) pixel-type electroluminescent devices (13); (f) single-fibre touch sensors with SLG (top) and FLG (bottom) (13) and (g) position sensors with SLG (13). Figures reproduced with permission from Springer Nature under a Creative Commons Attribution 4.0 International Licence (CC BY 4.0).

CVD graphene gives the lowest sheet resistance, 600 Ω/sq for PP coated with CVD SLG, decreasing to 200 Ω/sq for FLG (1-7 layers, average of 4). However, the more layers of graphene, the least transparent the coating will be, with FLG being at 77% transmittance compared with 97% for SLG, which added to the transparency of the fibres results in an overall electrode transmittance of *ca.* 90% and 70%, respectively (4). Transparent electrodes are required for example, for optoelectronic applications, such as photovoltaics and light-emitting devices. We selected FLG-coated PP for applications as alternating current electroluminescent (ACEL) devices (13), employing an emitting Cu-doped ZnS layer, an insulating $BaTiO_3$ layer, and a silver paste back electrode. Single-fibre devices (**Figure 2d**) and multi-fibre arrays that light up at the intersections to define pixels of different shapes (**Figure 2e**), were demonstrated in this work.

Most applications, however, do not require a transparent electrode or very high conductivity. We have demonstrated different types of sensors based on the same graphene-coated PP fibre platform. Capacitive touch sensors were shown with interdigitated electrodes patterned on graphene, with the sensing occurring when a finger shortens the electrodes, as can be seen in **Figure 2f** for the fairly transparent SLG and less transparent FLG (13). It was shown, however, that LEG can also be used for this purpose, which allows roll-to-roll fabrication and eliminates the need for specialised lithographic patterning techniques. Position sensitive fibre arrays were also demonstrated in the same work, comprising orthogonally intertwining conductive fibres separated by PMMA, with sensing points at the intersections (**Figure 2g**).

The same platform was used for temperature and humidity sensing. Whereas for light-emitting applications for example, require highly conductive electrodes, sensing relies on monitoring how the conductance or sheet resistance of the coating changes when subjected to different stimuli, and therefore they can still operate on more resistive coatings. Out of the different types of graphene used to coat PP fibres, the best performance in terms of temperature sensing was with trilayer graphene (TLG, 1-4 layers, average 3) (18). These resistive sensors have a negative thermal coefficient of resistance and have a linear response in the 30-45°C temperature range, making them suitable for human body temperature sensing, requiring operating voltages <1 V. Furthermore, these sensors prove to be robust to withstand repeated bending cycles and even to washing. Interestingly, the conductance of these graphene-coated PP fibres with different types of graphene was also shown to be sensitive to changes in ambient humidity (19), without the need of an additional sensing layer on top of graphene or lithographic steps, as previously demonstrated for LEG-coated PET (20).

4. Graphene-coated textile fabrics and their applications

The next step forward in e-textile applications of graphene is to use woven fabrics. Here, not only the material plays a key role in determining the properties of the surface, the type of weave or knit is also important, as is any finishing the fabric might have. In contrast to monofilament fibres, fabric surfaces are invariably discontinuous, which makes the use of CVD no longer viable for electrically conductive coatings. Films made from overlapping graphene flakes are a good alternative, as these small flakes can adopt the shape of the individual fibres they adhere to, while still being able to make a percolation network over a larger area. However, LEG coating via the IDT method is not appropriate for fabrics either, as the increased roughness compared with a sheet of PET or a monofilament PP fibre, also causes the film to crack during the transfer (**Figure 3a and 3b**). Other coating methods, such as dip-and-dry, with LEG suspensions also crack easily on the fabric surface (5).

At Exeter we found that, to coat textile fabrics with graphene aqueous suspensions, ultrasonic spray-coating is a viable alternative to other solution-based methods. The ultrasonic vibrations keep graphene dispersion homogeneous during the coating process, preventing agglomeration of flakes. The textile substrate being coated is placed on a hot plate at 100ºC to quicky dry as it is being coated. However, ultrasonic-spray coating is not appropriate for LEG obtained from graphite with a surfactant, which will inevitably precipitate in the hot substrate. These precipitates can cause disruption in conductive paths and separates the graphene flakes that are being deposited. For this reason, we have chosen to use GNPs, nowadays available at a reasonable cost, for the ultrasonic spray-coating of graphene on fabrics since GNPs form stable suspensions in water with no need for surfactants. **Figure 3c** shows the same nylon fabric as **Figure 3a**, with the fibres closely woven together, covered with a GNP film that is continuous overall, showing good coverage at the individual fibre level. The ultrasonic spray-coating process was employed on three different fabrics: nylon, polyamide and meta-aramid, with different weaving patterns (5). The lowest sheet resistance values of found were ca. 40 kΩ/sq, and they can withstand a large number of bending and compression cycles. Although, with no further treatment and optimisation, these materials are only suitable for applications that do not require highly conductive substrates, this method has the potential for scaling-up and is compatible with textile industry.

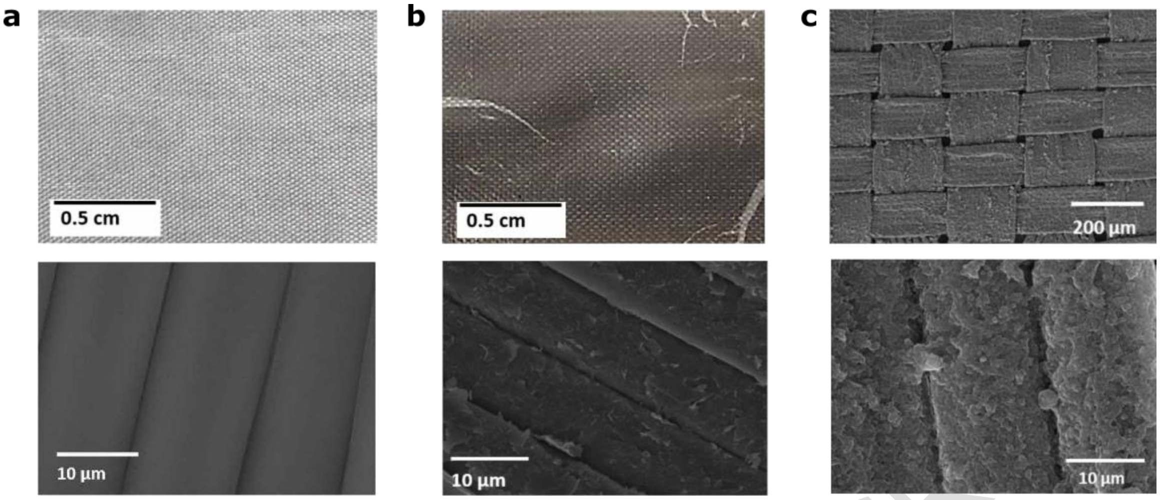

Fig. 3. Optical images (top) and SEM images (bottom) of: (a) nylon fabric; (b) same fabric coated with LEG via IDT, showing cracks and discontinuities from fibre to fibre. SEM images of the same nylon fabric coated with GNPs via ultrasonic spray coating (top) with details of continuous coverage at the individual fibre level (5). Figures reproduced with permission from IOP Science under a Creative Commons Attribution 4.0 International Licence (CC BY 4.0).

These graphene-coating techniques can be applied to integrate graphene electrodes for energy harvesting, namely combining it with PDMS (polydimethylsiloxane) in energy triboelectric nanogenerators (TENGs). The triboelectric effect is the conversion of mechanical energy into electrical energy by coupling triboelectrification whereby surface charges are exchanged between two different tribomaterials (usually dielectrics) with different charge polarities, and electrostatic induction. We have previously investigated a single-electrode TENG based on an IDT-transferred LEG film to a PET substrate, with a sheet resistance as low as 152.7 Ω/sq (14). PDMS, with its high electronegativity, is the active layer in this TENG device configuration. Opposite to the PDMS layer, a nitrile glove was used as another dielectric with neutral charge with the purpose of being positively charged during the triboelectrification process. Therefore, after contact-separation of the TENG device, this has produced an open-circuit voltage, V_{oc}, of 1.08 V and a short-circuit current, I_{sc}, of 0.25 μA. These values have been further enhanced by exposing PDMS trough fluorination using SF_6 plasma resulting in an increased V_{oc} of 4.69 V and I_{sc} of 0.65 μA. This pivotal work has allowed our research group to move on to exploring TENGs based on graphene electrodes, GNP-coated fabrics and CVD-coated PP fibres. Besides fluorination, several other approaches can improve the triboelectric performance of the PDMS layer, such as the use of charge-trapping layers and microstructuring. We have obtained promising results on textile TENG applications for self-powering e-textile devices, which we aim to report very soon.

5. Conclusions

The challenges in working with non-conventional substrates for electronics, such as flexible plastics and fabrics, may require a creative approach to translate established coating techniques. Here, we have reviewed our recent works on two very different types of textile substrates: monofilament textile fibres, and fully woven fabrics. Graphene provides a solution to tackling the inherent roughness of textile substrate, as it has been shown to conform to the surface. However, graphene obtained and/or transferred using different techniques has been shown to conform to the surface, resulting in a continuous conductive layer. With a smoother structure, monofilament PP fibres have been successfully coated with CVD graphene, which has proven to be suitable to cover continuous and reasonably flat surfaces. SEG transferred from vacuum filtration membranes is a good alternative at a decreased cost compared to CVD. This graphene-coated PP-fibre platform was then employed for different applications, such as electroluminescent devices, capacitive touch and position sensors, and resistive temperature and humidity sensors. These results open up the way for the miniaturisation of such devices to enable their full integration in textiles. For larger area and fully textile-integrated applications, ultrasonic spray coating of GNPs was found to be the best choice of graphene coating, with energy harvesting applications currently being explored. The examples reviewed here show that the issues posed by the roughness of textile substrates can be solved by adapting the coating material and method to the surface.

With a suitable wearable solution for power generation, small e-textile devices can be applied in several parts of the human body for vital sign-sensing, for example, or in other textiles in the household or healthcare environment, such as carpets, curtains, upholstery, or linens. We believe this is an important step towards applications in key developing technologies, including remote healthcare and home automation.

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The Author

	Ana I. S. Neves is a Senior Lecturer in Materials Engineering at the University of Exeter. Ana's research interests are in wearable applications of graphene-based materials, with a focus on sensing and energy harvesting. She has BSc, MSc and PhD in Chemistry from Instituto Superior Técnico, University of Lisbon. She was previously a Marie Skłodowska-Curie Individual Fellow and currently holds and EPSRC New Investigator Award.