Graphene coated fabrics by ultrasonic spray coating for wearable electronics and smart textiles

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Graphene coated fabrics by ultrasonic spray coating for wearable electronics and smart textiles

Kavya Sreeja Sadanandan[1], Agnes Bacon[1], Dong-Wook Shin[1], Saad F. R. Alkhalifa[1,2], Saverio Russo[1], Monica F. Craciun[1], Ana I. S. Neves[1]

[1]Centre for Graphene Science, College of Engineering, Mathematics and Physical Sciences, University of Exeter, EX4 4QF, Exeter, United Kingdom
[2]University of Duhok, Duhok, 42001, Kurdistan Region, Iraq

E-mail: m.f.craciun@exeter.ac.uk, a.neves@exeter.ac.uk

Abstract. The seamless incorporation of electronics in textiles have the potential to enable various applications ranging from sensors for the internet of things to personalised medicine and human-machine interfacing. Graphene electronic textiles are a current focus for the research community due to the exceptional electrical and optical properties combined with the high flexibility of this material, which makes it the most effective strategy to achieve ultimate mechanical robustness of electronic devices for textile integrated electronics. An efficient way to create electronic textiles is to fabricate devices directly on the fabric. This can be done by coating the textile fabric with graphene to make it conductive. Here we discuss successful and efficient methods for coating graphene nanoplatelets (GNPs) on textile substrates of nylon, polyester and meta-aramid using ultrasonic spray coating technique. These coatings are characterised by scanning electron microscopy, contact angle and electrical conductivity measurements in order to identify the optimal textile electrode. Our study provides the foundation for the large-area fabrication of graphene electronic textiles.

Keywords: Graphene nanoplatelets (GNPs), ultrasonic spray coat, textiles, electrode

1. Introduction

Textile-based electronics is an emerging technology that will play a strategic role in various areas ranging from the internet of things to remote health monitoring, medical therapies and human-machine interfacing. To enable such advances, there are still many challenges to overcome. One of the critical challenges is the seamless incorporation of electronics in textiles that will preserve their softness and comfort. Within this area, a key feature is the realisation of electrically conductive coatings on textile that conform to the irregular and coarse structures of the textile fabrics. The use of ultrathin 2D materials, with only few-atom thickness, resulting in extreme flexibility and high fracture strengths, constitutes one of the strategies to achieve this aim. Graphene is a current focus for the research on conductive textiles due to its outstanding mechanical[1], electrical[2] and optical properties[3]. The biocompatibility[4] and large-scale graphene processibility[5] further facilitate applications for textile electronics. This includes textile based energy harvesting and storage devices such as solar cells, nanogenerators and supercapacitors, as well as various type of sensors and actuators using graphene as their electrodes or active materials.

The difficulty of directly integrating graphene onto textiles lies in achieving the required conductivity following a cost-effective and scalable way. Methods for producing graphene include micromechanical exfoliation or cleavage of graphite, liquid-phase exfoliation (LPE) of graphite, chemical vapour deposition (CVD), synthesis on silicon carbide (SiC) substrate and by reducing graphene oxide (GO) to obtain reduced grephene oxide, rGO[6]. The quality, quantity and suitability of graphene produced differs for each of these methods and the best route is typically chosen based on the properties desired. For example, micromechanical exfoliation, where graphite is exfoliated to graphene by mechanical forces, produces graphene with the highest quality in terms of carrier mobility and crystalline structure. However, apart from its use in fundamental research studies, this method is time-consuming and is not scalable for large-area applications. CVD method includes the thermal catalytic growth of graphene on a metal substrate and has emerged as one of the most competitive growth methods for securing the industrial exploitation of graphene, due to its compatibility with Si and roll-to-roll technologies. However, this method is costly considering the high temperatures (∼1000 °C), pure metal substrate and the transfer methods available thereafter. LPE is one of the lowest cost, easy manufacture and industrially scalable methods for the production of few-layer graphene (FLG) with reasonable quality. It allows the separation of graphite into graphene layers in a liquid medium to produce FLG dispersions, stabilised by a surfactant[7, 8, 9] or solvents[10]. Recent progress in LPE made by using high-shear blending has significantly improved the quality of graphene and the volume-time dependency of exfoliating graphene in water, allowing for the production of more than 100 litres per hour of defect-free graphene solution[9]. However, electrically insulting surfactants need to be removed after the deposition of the film in order to render the film electrically conductive[11], while organic solvents

are not environmental friendly. Preparation of rGO requires a series of reactions involving oxidation of graphite, conversion to few-layer graphene oxide and finishing with its reduction to produce reduced graphene oxide. The use of strong agents during the reactions leaves rGO with potentially less quality compared to other methods of production but it is potentially one of the lowest cost methods to follow.

Various approaches have been explored so far towards fabricating conductive graphene textiles. One approach is the incorporation of graphene in textile fibres[12, 13, 14, 15] as a conductive substrate which can be used either as wiring for devices or to fabricate the devices directly on them. Such textile electrodes have been used in sensors[16], light emitting devices[17], photovoltaic cells[18], as flexible high capacity electrodes for batteries[19] and supercapacitors[20, 21]. A second approach is needed for creating conductive textile fabrics without compromising the properties of the fabric. The works so far on integrating graphene in fabric include semi-flexible devices attached to the fabric by using planarisation layers[22], inkjet printing[23, 21] dip coating process[13, 14], brush coating[24], screen printing[25, 15] and spray coating[26, 27, 28, 29, 30, 31, 32, 33, 34, 35]

Spray coating of graphene on textile fabrics is emerging as one of the more promising techniques to overcome the limitations of the irregular and coarse structures of textile fabrics[27]. Beyond textiles, spray coating of graphene on glass, quartz and plastic substrates has also gain considerable interest in academia[36, 34] and industry[37] as it is a mature thin film fabrication technique, scalable to large areas. Various spray techniques involving air pressure for the atomisation such as hand-held air sprayer, air brush, pneumatic spray nozzles are currently being explored for the deposition of graphene and various types of graphene composites on textiles[26, 27, 32, 28, 31, 38, 30, 34, 29]. Air pressure methods are inexpensive and allow high throughput, however precise deposition control is limited. The ultrasonic spray technique where the atomisation is caused by ultrasonic frequencies is an alternative method that can be used to obtain a more homogeneous dispersion and to improve film uniformity. In this method, the droplet size can be controlled precisely through the ultrasonic drop formation creating a narrow distribution of drop sizes, comparable or smaller than those obtained by inkjet printing. Ultrasonic spray coating has been explored so far for various classes of materials such as organic solar cells[39, 40], the light emitting layer in polymer OLEDs[41] and perovskites solar cells[42].

In this study, we explore the use of different types of solution processed graphene materials for coating textile fabrics for their potential application as an electrode in fabricating wearable devices. FLG obtained from LPE by high shear mixing of graphite and commercial graphene nanoplatelets (GNPs) are used here to produce water based graphene suspensions which do not require surfactants, are stable as well as environmentally friendly since they do not require organic solvents. Different methods of coating using these two types of suspensions are analysed for their coverage, adhesion and electrical conductivity on different textile substrates. The ultrasonic spray coating method is studied extensively considering their application to large scale

coating as well as their reproducibility. Specifically, water based graphene suspension has been sprayed on various textile substrates using an ultrasonic spray coater for the fabrication of conductive textile electrodes. These comprise heat resistant meta-aramid and the more commonly used nylon and polyester. Ultrasonic spray coating using a suspension of GNPs was found to be the best method and best precursor suspension for the fabrication of conductive textile electrodes. These are characterised by Raman spectroscopy, scanning electron microscopy, energy dispersive spectroscopy and conductivity measurements to identify the optimal conductive textile electrode. This study paves the way towards the large scale fabrication of 2D devices on fabrics for wearable electronics.

2. Experimental methods

Textile fabrics of meta-aramid (F-00910-Z01), nylon (G-60287-Q10) and polyester (M-09305-A01) used here for the studies are provided by Heathcoat Fabrics Ltd. These substrates are used as provided and after ultraviolet-ozone (UVO) variable time surface treatments with an Ossila UV-Ozone cleaner. Scanning electronic microscopy (SEM) was performed in a TESCAN VEGA3 microscope on samples coated with a thin conductive layer of chromium, at an accelerating voltage of 20 kV and working distance of 15 mm. Electron dispersive spectroscopy (X-Max EDS, Oxford Instruments) connected to the SEM were used for elemental analysis at the same operating conditions. The sheet resistance of each graphene coated fabric was measured using the van der Pauw method to obtain an average resistance value for the coating. The thickness of the coatings was measured with a Taylor Hobson TalyScan 150 non-contact scanning instrument, at a speed of 200 μm/s and a spacing of 1 μm along x and 5 μm along y axes.

Figure 1 shows the optical and scanning electron microscopy of the fabrics before any treatment of coating, from the optical images of the fabric weaves, and down to individual fibre level. Figure 1(a) shows the meta-aramid fabric with comparatively well-spaced weaving. Figures 1(b) and 1(c) show nylon and polyester, respectively, with their denser weaving pattern on 1 mm and individual fibres on a 10 μm scale bar. It can be seen from the figure that nylon has a tightly packed weaving pattern, a flatter surface while the meta-aramid fabric has a high surface roughness of visible scale created by its thicker and loosely bound yarns.

2.1. Graphene suspensions

Two different type of water based graphene suspensions were used. The first one was prepared by shear exfoliation of graphite flakes (Sigma-Aldrich) in the presence of sodium cholate (Sigma-Aldrich), as described previously[11]. This results in an aqueous suspension of FLG stabilised by the surfactant. The second was prepared by suspending commercially available GNPs (Cheap Tubes, Inc), based on a method we previously

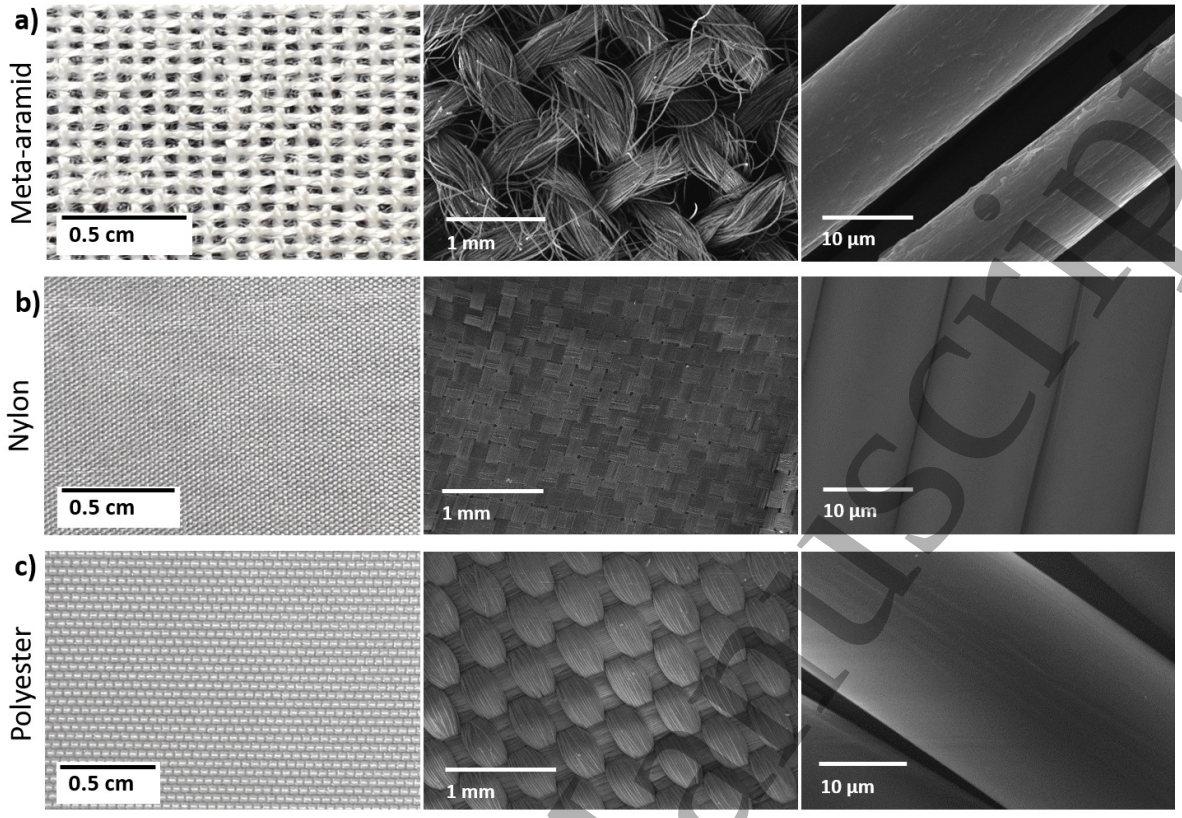

Figure 1. Optical and scanning electron microscopy images of fabrics in rows with (a) meta-aramid, (b) nylon and (c) polyester showing their weaving pattern on an optical scale to individual fibres on a micrometer scale.

described[43]. According to the manufacturer, these GNPs are chemically exfoliated from natural graphite. These GNPs have an oxygen content of ca. 13.5%, as shown by the SEM-EDS chacterisation (supplementary Figure S1). 0.8 grams of this GNPs were dispersed in 1 litre of de-ionised water using the same Silverson L5 high shear mixer at 5000 rpm for 120 minutes. These GNPs do not require a surfactant to be stably dispersed since they have a residual oxygen content of ca. 13.5% from the manufacturing, and these residual oxygen-containing groups makes them less hydrophobic than those of FLG, which are obtained from direct exfoliation of pristine graphite.

2.2. Graphene coating methods

In order to identify the best method to coat the textiles with graphene, different coating methods were tested. Firstly we used the FLG suspension to coat nylon substrates by dip and dry cycles, membrane filtration followed by dip coating[11], and ultrasonic spray coating. Figure 2 schematically describes these three methods and summarises the corresponding results.

As the name suggests, the dip and dry method consists in dipping the nylon substrate in the FLG suspension and drying it on a hotplate. The cycle was repeated

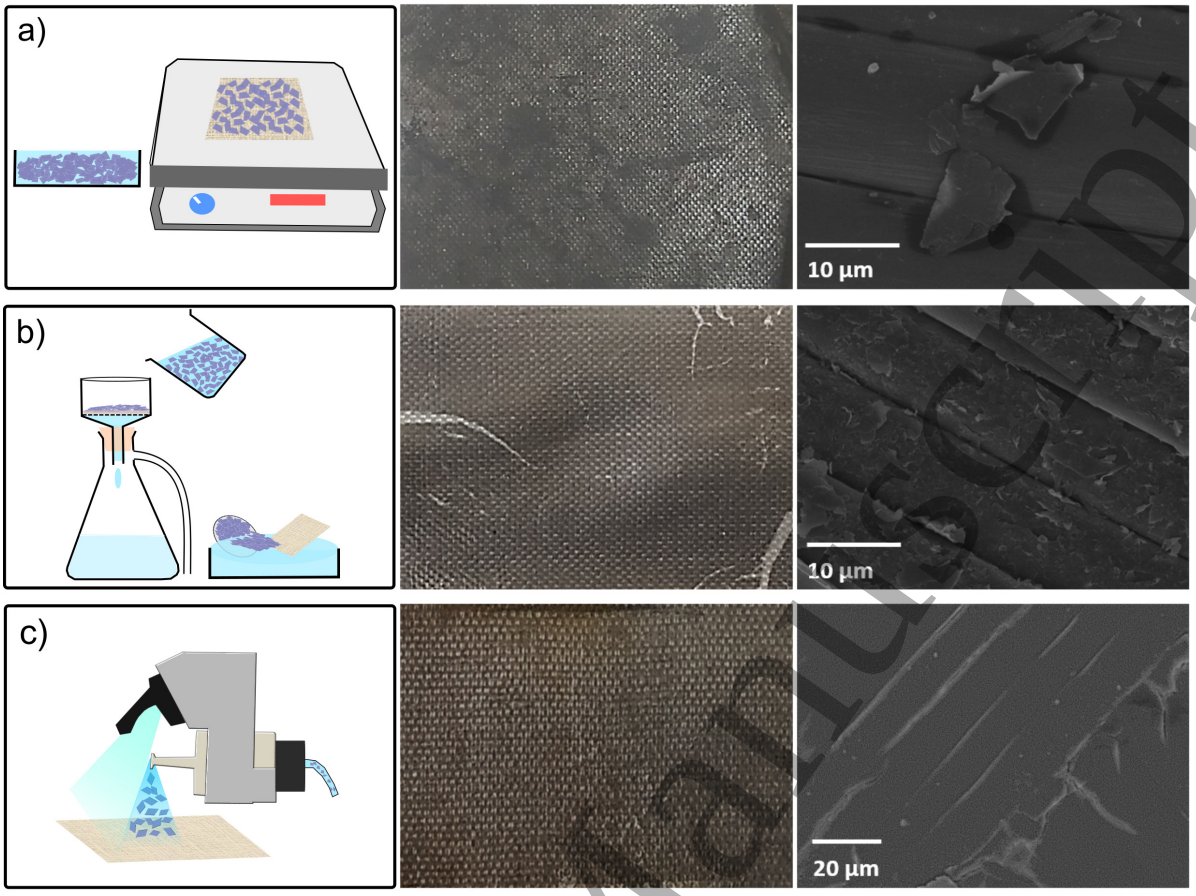

Figure 2. Different methods of coating done on nylon fabric with liquid phase exfoliated few-layer graphene suspension: (a) dip and dry cycles; (b) membrane dip coating; and (c) ultrasonic spray coating. The first column depicts each method, the second column shows an optical image of the coated sample, and the third column shows the scanning electron microscopy images of the coated surfaces.

10 times until there was a visible amount of FLG flakes coated on the fabric (Figure 2a). The second method consisted of passing 60 ml of FLG suspension through a PTFE membrane (Millipore) in a vacuum filtration setup. The film formed over the filter membrane is released carefully on a water surface by dipping it at a shallow angle with respect to the surface. The released film can be then scooped with the nylon fabric (Figure 2b). The final method of ultrasonic spray coating is an automated way of spraying graphene suspension onto the substrate (Figure 2c) and it is explained in detail in the next section. As it can be seen in Figure 2, dip and dry cycles can only leave a small amount of FLG flakes onto the fabric. The surface coverage is improved using the membrane dip coating, but with visible cracks to the film, which inevitably result in high resistance. Ultrasonic spraying of graphene suspension formed an even film over the fabric covering the whole fibres providing a uniformly coated surface. However, FLG suspensions contain a considerable amount of the surfactant, sodium cholate, which precipitates as the coated fabric dries. The surfactant residue prevents good overlapping

between flakes and breaks the percolation network necessary for electrical conduction. It was then deemed necessary to use a different source of graphene flakes which was stable enough in suspension to allow for spray coating, but without the need for a surfactant.

2.3. Ultrasonic spray coating of GNPs suspension on textile

A SONO-TEK ExactaCoat ultrasonic spray coater (supplementary Figure S2) was used. This emerging technology makes use of an ultrasonic nozzle to spray the loaded suspension onto a substrate, and it is suitable to coat large areas without any need for fillers or stabilisers. It is combined with an ultrasonic syringe to keep an evenly dispersed suspension during the process, not allowing the flakes/particles in the suspension to settle down. The suspension is loaded into the syringe, and it gets sonicated while being pumped into the nozzle. The ultrasonic vibration created in the nozzle oscillates the suspension inside to form capillary waves. Reaching the atomising surface (tip) of the nozzle, these waves acquires an amplitude large enough to detach from the surface, forming the spray (Figure 3 and supplementary Figure S3). The droplet size is controlled by the frequency of ultrasonic vibration as they follow an inverse linear proportionality. We used an impact ultrasonic spray shaping nozzle of 48 kHz frequency. The spray is then directed onto the substrate by a jet air deflection provided by a supply of compressed air gas. The gas supply merely helps in shaping the spray and does not involve in pushing the suspension like a conventional pressure spray. The fabric substrates were kept on a hot plate set to 120° C to quickly evaporate the water present.

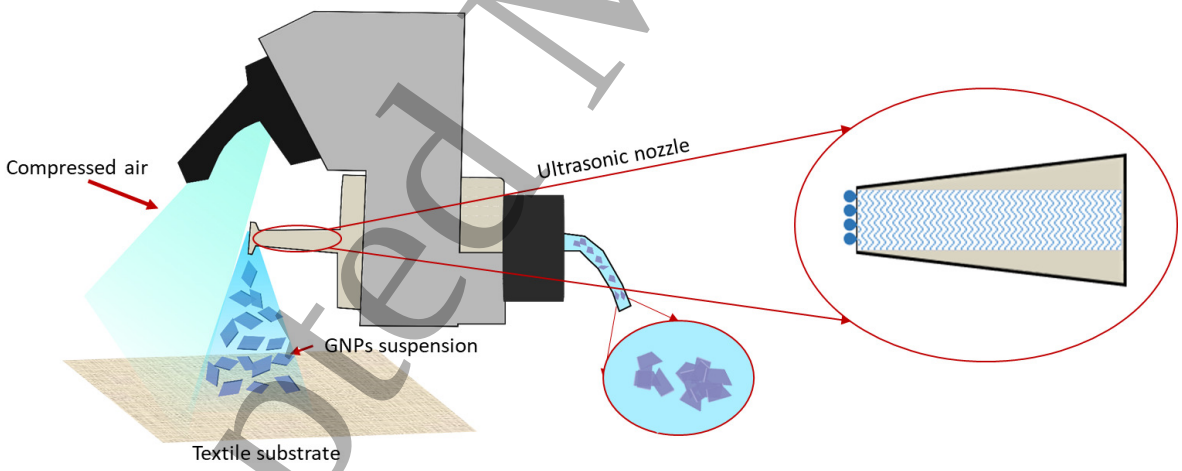

Figure 3. Schematic depiction of the ultrasonic nozzle of the ExactaCoat. The ultrasonic vibration inside the nozzle tube causes the suspension to move as capillary waves. Upon reaching the tip of the nozzle, the droplet acquires a large enough amplitude to detach itself. The droplets are collected and directed onto the hotplate beneath by the jet air deflector equipped above the nozzle. Vibrations also help in breaking down any clusters present in the suspension to produce a better dispersed suspension.

A square-shaped mask was kept over the substrate to obtain a uniform coating

with strict boundaries on the substrate (supplementary Figure S4) and to create a suitable shape for the sheet resistance and thickness measurements. Three sequential coating cycles were employed to coat the fabrics. For the van der Pauw method of sheet resistance measurement, silver ink contacts are placed on the four corners of the square shaped coating to connect the voltage and current probes (shown in supplementary Figure S5) to a Keithley source meter. Resistance measurements are made by passing current through the adjacent probes and measuring the voltage at the other ends. Sample is rotated periodically and measured at each configuration to arrive at an average sheet resistance value using the van der Pauw formula.

Ultrasonic spray coating has been used recently to form transparent conductive films of rGO and single-walled carbon nanotubes (SWCNT) composites with low surface roughness[44]. They have also been increasingly studied in the production of various types of solar cells[45, 40, 46] and organic light emitting devices[47] replacing its traditional time consuming and costly steps of fabrication. However to the best of our knowledge, this is the first time this system has been used to coat textile fabrics with graphene nanoplatelets suspension. Choosing an ultrasonic spray coating over regular pressure spraying has the advantages of more control over the flow of material thus reducing the wastage of chemicals. It provides a narrow droplet size distribution for a uniform coating and helps to acquire reproducible results as it is an automated process. Most importantly it has the potential, when integrated in electronic textile application, to not change the texture or feel of the fabric as the process is quite similar to dyeing fabric and can be scaled up easily.

3. Results and discussions

3.1. Characterisation of GNPs suspension

As detailed in a previous study, the estimated number of graphene layers in these GNPs suspensions is 10-14 per flake, determined by Raman mapping[43]. The ratio of intensities of D peak to G peak were also analysed and indicate that there are no significant defects introduced to the basal plane of these GNPs. To ascertain the thickness of each ultrasonic-coating cycle performed, sequential measurements were done with a non-contact scanning instrument. This was performed on a PET (polyethylene terephthalate) sheet coated with 3 cumulative spray-coating cycles to avoid the noise from the rough topographies of the fabrics. The results are shown in supplementary Figure S6, and indicate a thickness of ca. 50 μm per cycle.

3.2. GNPs coated textiles

The conductive textiles coated with GNPs by ultrasonic spray coating were analysed under a scanning electron microscope to study the morphology of GNPs on each fabric surface. Figure 4 shows meta-aramid, nylon and polyester fabrics coated with graphene flakes, showing how the coating covers the fabric with good and uniform adhesion down

to the fibre level. This is in striking contrast with what was observed when FLG suspensions were used to coat nylon using the same method.

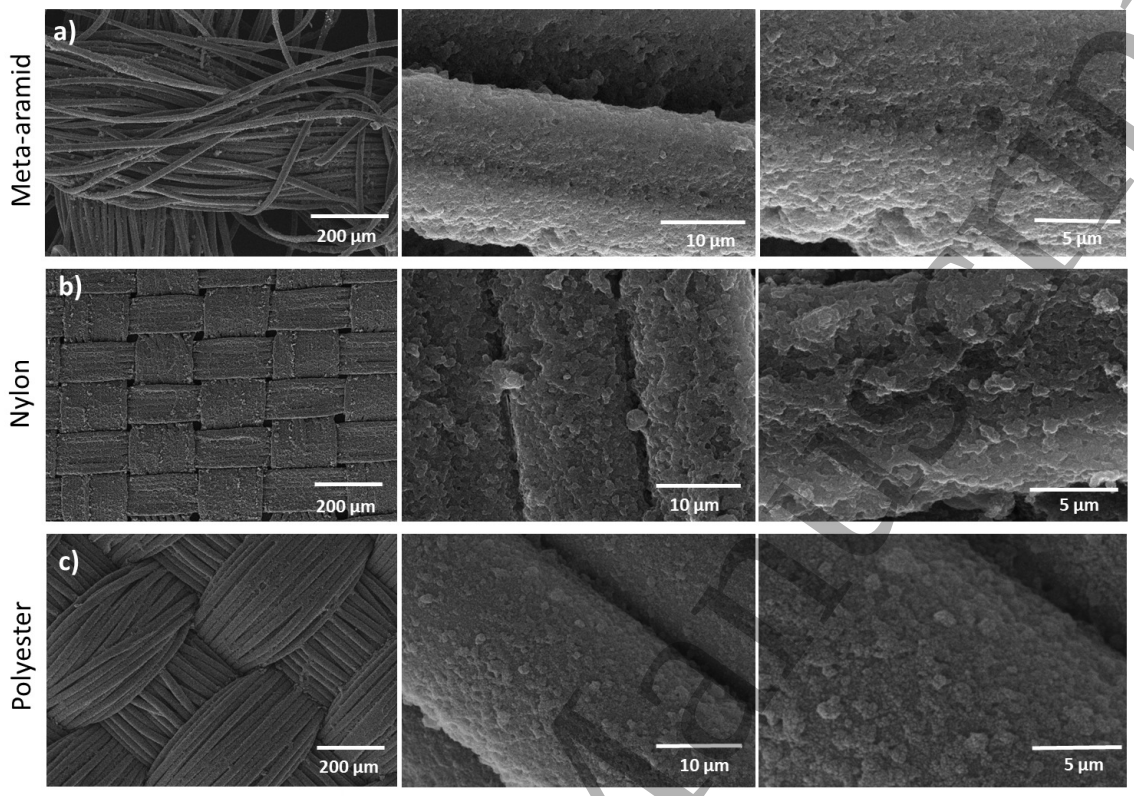

Figure 4. Scanning electron microscopy images of graphene nanoplatelets (GNPs) suspension spray coated on (a) meta-aramid (b) nylon and (c) polyester fabric showing the flakes adhered onto the individual fibres of each fabric under three different low to high magnifications.

Although the GNPs coating is visually clear on the fabric (supplementary Figure S4), Raman spectroscopy is done before and after the coating to attest to the GNPs coverage on the fabric (supplementary Figure S7).

Spray coating of fibres/fabrics has been reported, starting with a graphene oxide suspension and later reducing it to restore its conductive properties by thermal or chemical reduction procedures[26]. However, a final reduction step often results in damaging the coating and/or the substrate. Our proposed method skips all those steps, avoiding the additional damage. This also helps with the flexibility of the sample since a film like coating over the fabric might be more prone to cracks while bending, cutting off possible conductive channels.

To assess if the adhesion of graphene to fabrics can be further improved, a contact angle goniometer was used to monitor the effect of UVO surface treatment of the fabrics. The purpose of the UVO treatment was to make the surface of the fabrics more hydrophilic. The change in contact angle between a water droplet and the surface of the substrate was then recorded against increasing UVO exposure time of the substrate

(supplementary Figure S8). As the GNPs were produced by chemical exfoliation, the residual oxygen-containing groups present in the material not only play an important part in stabilising the suspensions, it also assists the interaction of the GNPs with the UVO-treated hydrophilic textile substrate obtained. Figure 5a shows how the contact angle of the fabric with a water droplet (dyed in green for illustrative purposes, on meta-aramid, inset of Figure 5a), changes for each fabric before and after coating with GNPs, and before and after UVO treatment. For all fabrics, a 5-minute UVO treatment resulted in much smaller contact angles, corresponding to improved wettability. The improvement was such that in the case of nylon the droplet completely disappeared against the fabric. The GNP coating on each fabric also contributes to improved hydrophilicity, which might be useful if more layers are to be added to the surface of the graphene coated fabrics, when used as electrodes for different purposes.

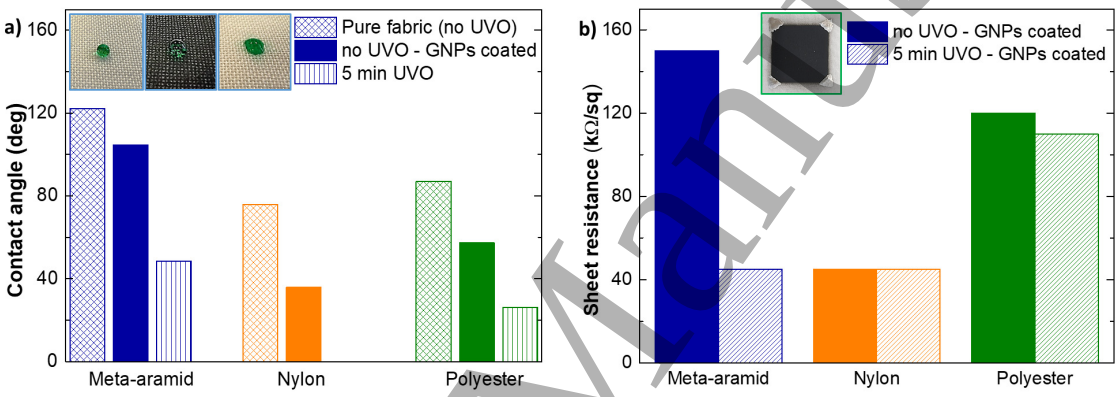

Figure 5. (a) Changes in contact angle for untreated and un-coated fabrics, GNPs coated fabrics, and fabrics after a 5-minute UVO treatment. Inset photos show a green-coloured water droplet on an untreated meta-aramid fabric, same fabric after GNPs coating and after 5 minutes of UVO treatment, respectively. (b) Sheet resistance of GNPs coated fabrics with no UVO treatment and after the 5 minute UVO treatment. Inset photos shows GNPs coated polyester with 4 van der Pauw contacts.

Sheet resistance values were determined for GNPs coated fabrics with and without UVO treatment. The lowest values achieved are shown in Figure 5b, with a photo of the coated fabrics with four silver electrodes for the van der Pauw method of measurement. While nylon had same sheet resistance of 45 kΩ/sq before and after the UVO treatment, polyester and meta-aramid showed a decrease in sheet resistance, with the latter by an order of magnitude to the value, reaching the same as nylon after the UVO treatment. The change in the sheet resistance of polyester was very small. While all fabrics seem to respond in similar ways to the 5 minutes UVO treatment, with a significant decrease in contact angle because of the increase in wettability that comes from the generation of additional oxygen-containing groups at its surface, this does not translate to a comparable decrease in sheet resistance, which seems to indicate that the surface morphology of the fabrics is the dominant parameter. Nylon is the least rough fabric,

with small individual fibres in the fabric, so this calendered morphology is already optimal for a uniform almost purely two-dimensional coating. Polyester has a larger surface roughness, but with the individual fibres still very close together in the fabric, although with larger variations between bundles, so the coating quality does not seem to improve significantly with increased wettability, same as with nylon, although generally less conductive. In meta-aramid, on the other hand, the fibrils are much less organised and oriented, with several layers being exposed in a more three-dimensional fashion. With a larger exposed surface, the increase in wettability seems to more noticeably influence the resulting coating quality, which results in a decrease of the sheet resistance when the coating is applied after the UVO treatment.

3.3. Stress and strain cycles

As these conductive textiles are expected to be used as electrodes on wearable devices, it is important to have consistent behaviour under stress and strain in order to have a long-term usage without significant degradation. A series of bending and compression cycles were performed on these textile electrodes to study their response to varying amounts of stress and strain. This includes measuring the sheet resistance after bend and compressed positions of the textile electrodes at different diameters (<14 mm) repeated upto 2000 times to compare the response to the value at the point of zero bending/compression, i.e its flat position (supplementary Figure S9). Nylon and polyester fabrics without any UVO exposure (pure fabrics) had more or less the same behaviour under compression (Figure 6a), and bending (Figure 6c). Nylon fabric with just 5 minutes of UVO exposure had a high and varying sheet resistance compared to its point of no bending/compression (shown in supplementary Figure S10) indicating damage to its calendered fibres. While the meta-aramid fabric had a varied response based on the UVO treatment time, ranging from 0, 5 to 15 minutes. Prolonged UVO exposure of 15 minutes has an adverse effect on the fabric compared to 5 minutes of exposure as seen in Figure 6b and 6d for compression and bending, respectively.

Even though in some cases the resistance varies from certain points of bending/compression by an order of magnitude, the behaviour of all three fabrics remained almost consistent throughout in various bending/compression diameters (Figure 6e and 6f) on an increased number of trials up to 2000 cycles. This might be the result of flakes initially moving around while bending/compressing the fabric and settling to give a consistent value there onwards. This would be minimised by a mechanical treatment post-spray-coating and by encapsulation to protect the coating and preserve its properties. In devices with a layered structure, such as nanogenerators or solar cells, the graphene electrode on the fabric would be immediately protected by the adjacent layer, which will eliminate the need to individually encapsulate the conductive layer.

Though the range of sheet resistance for our GNPs coated conductive fabrics are useful towards fabrication of wearable sensors and nanogenerators, for some other

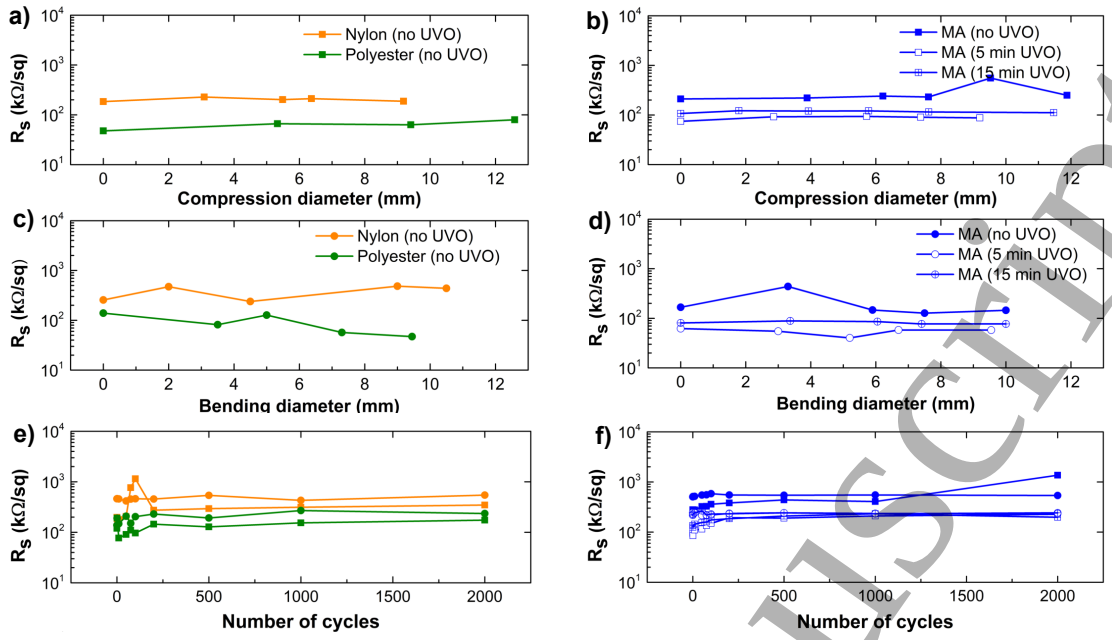

Figure 6. Sheet resistance of nylon (in orange), polyester (in green) and meta-aramid (in blue) to varying degrees of stress and strain cycles: (a) and (b) in compression; (c) and (d) in bending; and (e) and (f) over 2000 bending (circles) and compression (squares) cycles. Solid, hollow and cross fillings on each symbol indicate no UVO, 5 minutes UVO and 15 minutes UVO treatment on fabrics prior to their GNPs coating respectively.

applications it still remains quite high. However, there are several strategies to decrease it further, such as increasing the thickness of the GNP coating. Here, this can be achieved by spraying the GNPs more than 3 times or by using a GNP suspension of higher concentration. Using a highly concentrated GNPs suspension (1.7 grams/litre) to spray coat the fabrics resulted in sheet resistance value as low as 4.5 kΩ/sq for 5-minute UVO-treated polyester. However, there is a limit to this approach of increasing the thickness to decrease sheet resistance. On the one hand, suspensions of increased concentration are not as stable over the spray-coating process time, with GNPs deposition at the bottom as the suspension is being drawn into the ultrasonic spray system. On the other hand, whether we apply more cycles of coating or use a more concentrated suspension, there is a point where the coatings become fragile and easily crack under bending/compression. A further reduction in sheet resistance could possibly obtained with the addition of dopants to the suspension, such as metal nanoparticles.

4. Summary

The first step towards the realisation of truly wearable textile-base electronics is to have a conductive textiles as electrodes. Here we have shown a simple, low-cost, efficient, and highly scalable method of ultrasonic spray coating for coating three types of textile fabrics, meta-aramid, polyester and nylon, with a water based graphene nanoplatelets

suspension. These textile electrodes show a sheet resistance as low as 4.5 kΩ/sq without any intentional doping or required additives for improved adhesion. A simple ultraviolet ozone treatment can improve the adhesion of the conductive coating. This can be utilised in sensors or energy-harvesting wearable technologies, including solar cells, nanogenerators, supercapacitors and thermoelectric devices.

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