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Housseinou Ba, Christophe Sutter, Vasiliki Papaefthimiou, Spyridon Zafeiratos, Armel Bahouka, et al.. Foldable flexible electronics based on few-layer graphene coated on paper composites. *Carbon*, 2020, 167, pp.169-180. 10.1016/j.carbon.2020.05.012 . hal-03064446

HAL Id: hal-03064446

<https://hal.science/hal-03064446>

Submitted on 29 Apr 2024

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Foldable Flexible Electronics based on Few-Layer Graphene Coated on Paper Composites

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Keywords: Few-layer graphene, conductive paper, lightweight composites, flexible electronics

Abstract

In this work, we describe an eco-friendly and cost-efficient method for the production of highly dispersed few-layer graphene solution using karaya gum as bio-inspired exfoliating agent. The as-synthesized graphene aqueous solution can be easily applied on paper sheet through dip- or brush-coating thanks to the binding properties of the gum and to the functional groups on the paper surface with the graphene sheets. The as-synthesized composites display high mechanical strength and high electrical conductivity for numerous downstream applications. Electronic circuits can be designed on such graphene-paper composites either by controlling the graphene deposit or by post-laser etching with high lateral resolution. The laser beam can also be used to create local graphitization or partial etching of the conductive line in order to generate conductive areas with different resistance. The designed smart graphene paper was experimentally tested in different electronic applications, such as lightweight conductive circuit, as well as flexible keyboard which can be directly linked to a computer, thus opening up a new route for the development of daily life connected objects.

1. Introduction

Paper is inexpensive, lightweight, biodegradable displaying hierarchical fibres porous structure along with an easy surface wettability, due to the presence of oxygenated functional groups. These characteristics render it a prime candidate substrate for being coated with different materials and generate final composites with improved physical properties in many application fields. Among them, electronic circuits paper-based composites have received an ever increasing scientific interest for numerous potential applications such as lightweight displays, transistor, sensors, batteries and supercapacitors, photovoltaics, and radio frequency identification tags [1–12]. The conductive circuit is deposited onto the paper surface through a number of different methods including printing [13] and mechanical selective transfer [14,15] processes. For electronic applications of high interest is to find new easy scale up methods combined with high precision patterning of the complete electronic circuit, with direct integrated components displaying various resistance values which could significantly reduced the production time. Such electronic circuits should also have a low production cost, in order to be integrated in the market share of standard uses, i.e. multiple and lightweight/flexible electronic circuits for transportation and domestic devices. Entire carbon-based electronic circuits also represent an environmental alternative for the reduction of metal components which call for tedious recycling process.

Graphene, a two-dimensional conducting material constituting by carbon atoms arranged in a hexagonal lattice [16], has been intensively investigated over the last decade in several domains ranging from electronic applications, to gas sensors and 2D catalytic supports [17–22]. This is mostly linked to the extraordinary physical properties of graphene such as high electrical conductivity, lightweight, high percolation threshold, high mechanical and chemical stability along with flexibility and easy functionalization.[23–28] Despite the numerous methods proposed so far, a simple and easily scalable deposition process for large

scale applications is still lacking. It has been recently reported that few-layer graphene (FLG), containing between 2 to 20 graphene layers, can be efficiently produced through aqueous exfoliation of graphite-based materials with a relatively high FLG concentration up to 100 g. L⁻¹ [29,30-34]. Such aqueous solution dispersed FLG can be further processed for producing lightweight graphene@substrate composites with high electrical conductivity and mechanical resistance for potential applications in the field of flexible electronic field or as conductive polymer composites [29, 30-34]. The synthesis was carried out in almost exclusively water medium, i.e. 98%, and under room temperature which significantly reduces the problem of toxicity linked with the use of organic media or high temperature processes and also to the overall cost of the process. During the deposition and drying step steam represents the most important gaseous compound which also improves the cost-efficiency of the process for post-process gaseous treatment. In addition, it is worthy to note that the exfoliating agent used can be partly recycled for at least three exfoliations which also contribute to the reduction cost and amount of this later.

The combination of good electrical conductivity of graphene and robust mechanical stability of the paper host matrix renders it an ideal candidate for flexible electronics application. The development of paper-based flexible electronic devices needs a precise control of the electrical contacts with high lateral resolution. The possibility to control the local resistance of the device is also an advantage since a complete electronic circuit, i.e. resistance with various levels or other electronic components can be produced in a single pass. Such a control is not straightforward when using traditional techniques as for example printing or transfer due to the uniform deposit of the graphene-based material on the coated surface. Laser patterning has recently been reported by Zang et al. for the synthesis of molybdenum carbide-graphene paper composites for different applications [35]. It is expected

that such high lateral patterning technique could be beneficial for the design and production of lightweight and flexible paper-based electronic circuits with all the advantages cited above.

The present report deals with the fabrication of lightweight, high electrical conductivity and flexible foldable electronic devices based on paper coated with a thin film of few-layer graphene (FLG), using either paint brush or direct dipping depositing methods from an aqueous FLG solution followed by laser patterning and local graphitization. The binding properties of the karaya gum exfoliating agent combined with the anchor sites for the FLG on the paper substrate assures the strong adhesion at the interface, while the stacking is also favoured by van der Waals forces during the drying process. Electronic circuits of different forms and of various integrated resistances can be easily obtained by performing laser etching of the FLG film at different depth or by local graphitization in order to control the local resistance of the different components. The scale up process developed in this work is extremely simple, since is based on a standard industrial setup for cloth fabrication through dipping and drying. Finally, industrial laser patterning would allow easy production of large amounts of the composites for subsequent applications.

2. Results and discussion

2.1 FLG@Paper synthesis and properties

The paper used in the present work is consisted by a commercial ones produced by Navigator Universal and the characteristics of the paper are summarized in Table S1 (Supporting Information). The FLG@paper substrate was obtained by dip-coating of the paper inside the aqueous solution of FLG or through brush coating, followed by drying for 30 minutes at 130°C for removing water and increases the percolation of the different FLG sheets. The coating process was repeated several times (with a FLG concentration of 5 g/L) in order to ensure a homogeneous coverage of the paper filamentous by the graphene film. The as-

synthesized composite displays a shiny grey colour due to the presence of a homogeneous layer of FLG on its surface. Digital photos of the paper cross-section, before and after FLG brush coating, are presented in Fig. 1a and b. The FLG is present as a thin and homogeneous micrometric layer covering the paper surface as shown in Fig. 1b and the SEM image of Fig. 1c. It is worthy to note that the paper sheet thickness was slightly decreased, from $75 \pm 5 \mu\text{m}$ to $70 \pm 5 \mu\text{m}$, after wet coating by the graphene solution followed by a drying step at 130°C . Such result could be explained by the shrinkage of the paper filamentous upon drying due to the existence of strong van der Waals forces which reduce the distance between the different filamentous upon drying [36]. Similar results have already been reported during macroscopic shape carbon-based materials synthesis [37–40]. The conductivity of the FLG/paper composites as a function of the coating, followed by an intermediate thermal treatment at 130°C for 30 minutes between each coating cycle, is presented in Fig. 1d and confirms a significant increase of the electrical conductivity with increasing the coating cycles, and consequently the FLG concentration in the composite. As shown in the digital photos in Fig. 1e and f, the FLG@paper annealed at high temperature exhibits better stability as compared to the un-coated one. SEM analysis indicates the formation of cracks inside the paper matrix which eventually lead to a complete loss of its mechanical strength (Fig. 1e). On the other hand, for the FLG coated paper the continuous FLG layer covering the paper surface prevents the formation of cracks and increase the mechanical stability of the composite (Fig. 1f).

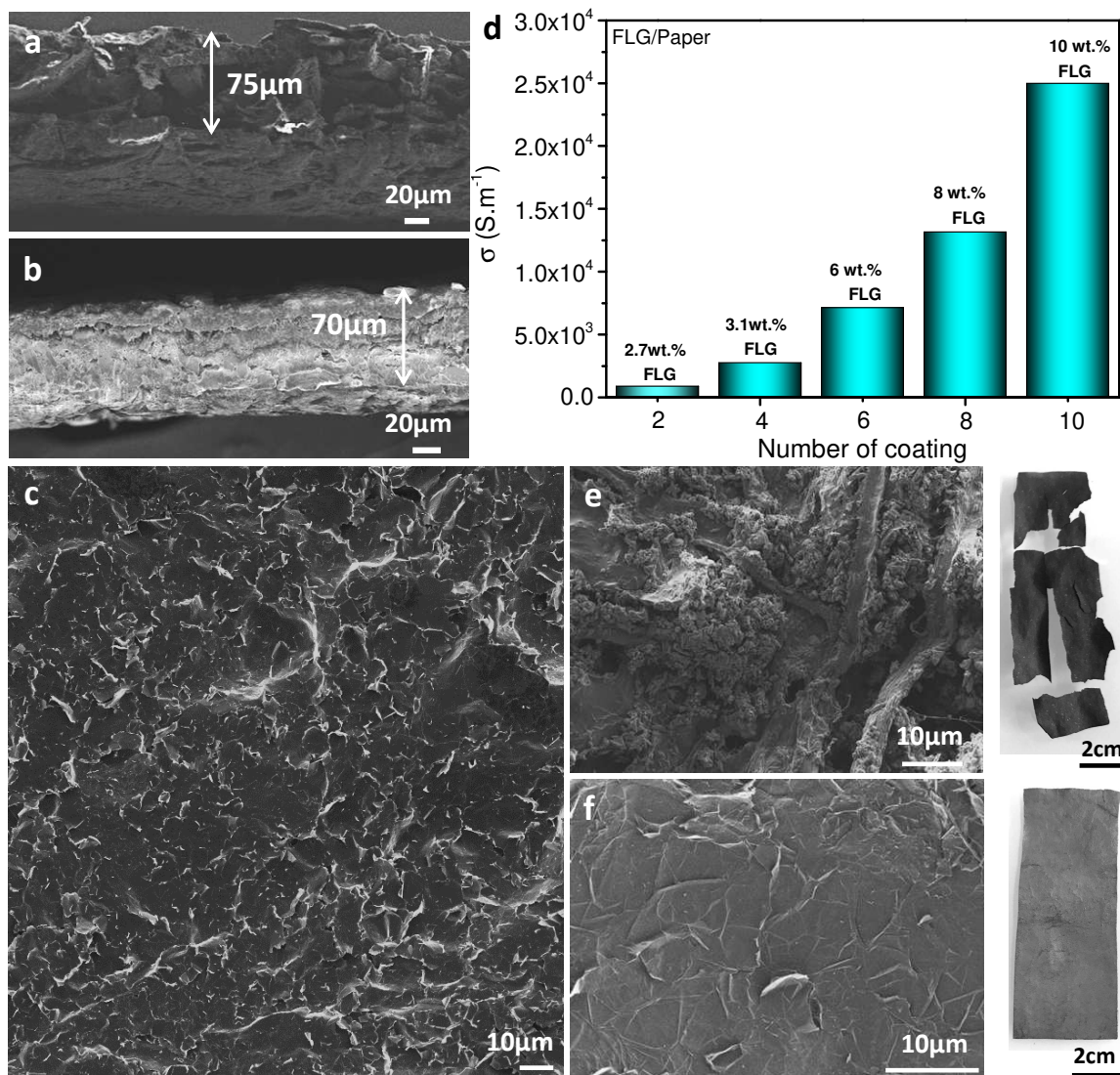


Figure 1. (a, b) Digital photos of the paper cross-section before and after FLG coating. (c) SEM micrograph of the FLG@paper composite evidences the homogeneous coverage of the paper surface by a thin layer of FLG making the electrical contact. (d) Conductance values of the FLG@paper composites as a function of the FLG coating cycles and FLG concentration. (e, f) SEM micrographs of the pristine paper and FLG@paper composite after annealing at 700°C in helium for 1 h. Inset: Digital photos showing the gross morphology and the mechanical resistance of the two materials after the annealing process which confirms the high mechanical stability of the FLG@paper composite.

It is expected that the 2D morphology of the FLG and the strong van der Waals forces play the role of healing structure for preventing cracks formation within the composite upon annealing process. **Indeed, the wrapping of the 2D FLG around the paper sheet filamentous**

could participate in the increase of the cellulose filamentous strength which could prevent cracks upon heat annealing. The wrapping of the FLG around filamentous can be clearly seen in a FLG@cotton cloth filamentous (Fig. 5c and f) as such phenomenon is not easy mapped in the FLG@paper sheet due to the presence of some FLG on the paper surface which mask the analysis and also to the very dense stacking of the filamentous in the paper sheet. One can see that on the uncoated paper sheet a large part of the structure was collapsed and only few filamentous remain which are neither dense nor strong enough to maintain the whole matrix. During the wetting/drying process the sheets of the FLG tend to approach each other via the forces of van der Waals and therefore contribute to reinforcing the mechanical strength of the final composite.

Raman spectroscopy was used to investigate the structure and the quality of the synthesized material. The Raman spectra show two typical D and G bands at 1345 cm^{-1} and 1590 cm^{-1} , respectively. The D band is attributed to the disordered sp^3 hybridized carbon, while the G band is associated with the crystallized graphitic sp^2 [41,42]. The composites display a relatively low I_D/I_G ratio which confirms the high graphitization of the pristine exfoliated FLG used in the present work. The weak intensity of the D-band observed in all analyzed samples confirms the effectiveness of the exfoliation process, which does not increase the density of structural defects [38]. The 2D Raman peak ($\sim 2690\text{ cm}^{-1}$) is characteristic of the stacked number of graphene layers indicates the presence of graphene with less than 10 stacking layers.[43]

The nature and concentration of the chemical species present on the surface of different samples were also analyzed by XPS and the results are presented in Fig. 2b and c. The main surface components determined in the XPS survey spectra of the FLG and FLG@paper are C, O and N (Fig. 2b). Traces of Cl, Si, S and Ca were also present in the XPS spectrum of the composite which could be issued from the FLG solution, i.e. impurities in water and chemical components issued from the exfoliant compound. The % surface content

of the different elements calculated assuming a homogeneous distribution arrangement model is given in Table 1.

Table 1. Atomic surface ratios of the different elements measured by XPS on the exfoliated FLG and FLG/Paper composites after oven drying at 130°C.

Sample	N (at. %)	C (at. %)	O (at. %)	S (at. %)	Si (at. %)	Cl (at. %)	Ca (at. %)
FLG	2.1	93.6	4.3	0	0	0	0
FLG@paper	7.3	78.7	12.4	0.4	0.4	0.3	0.4

High resolution XPS C1s, N1s and O1s spectra, normalized to the same height, are displayed in Fig. 2c and S2. All C1s peaks were deconvoluted in 5 components, (sp^2 C and sp^3 C/C-OH, C-OR, C=O and COO) and a $\pi-\pi^*$ transition loss peak [39,40]. From this analysis it is evident that the oxidized C species increase in the FLG@paper sample due to the thermal treatment at 130°C in air after the coating step and also from the deposited aqueous solution.

The influence of the FLG coating layer on the thermal stability of the paper sheet substrate was investigated by thermogravimetric analysis (TGA). The TGA results obtained on the uncoated and FLG (6 wt. %) @paper composite is presented in Fig. 2d and e. The FLG coating leads to a slight improvement of the thermal stability of the composite as compared to the pristine paper, according to the shift of the TGA peaks to higher temperatures. Such results could be attributed to the presence of the FLG layer on the composite surface which forms a barrier and protects the underneath paper against combustion.

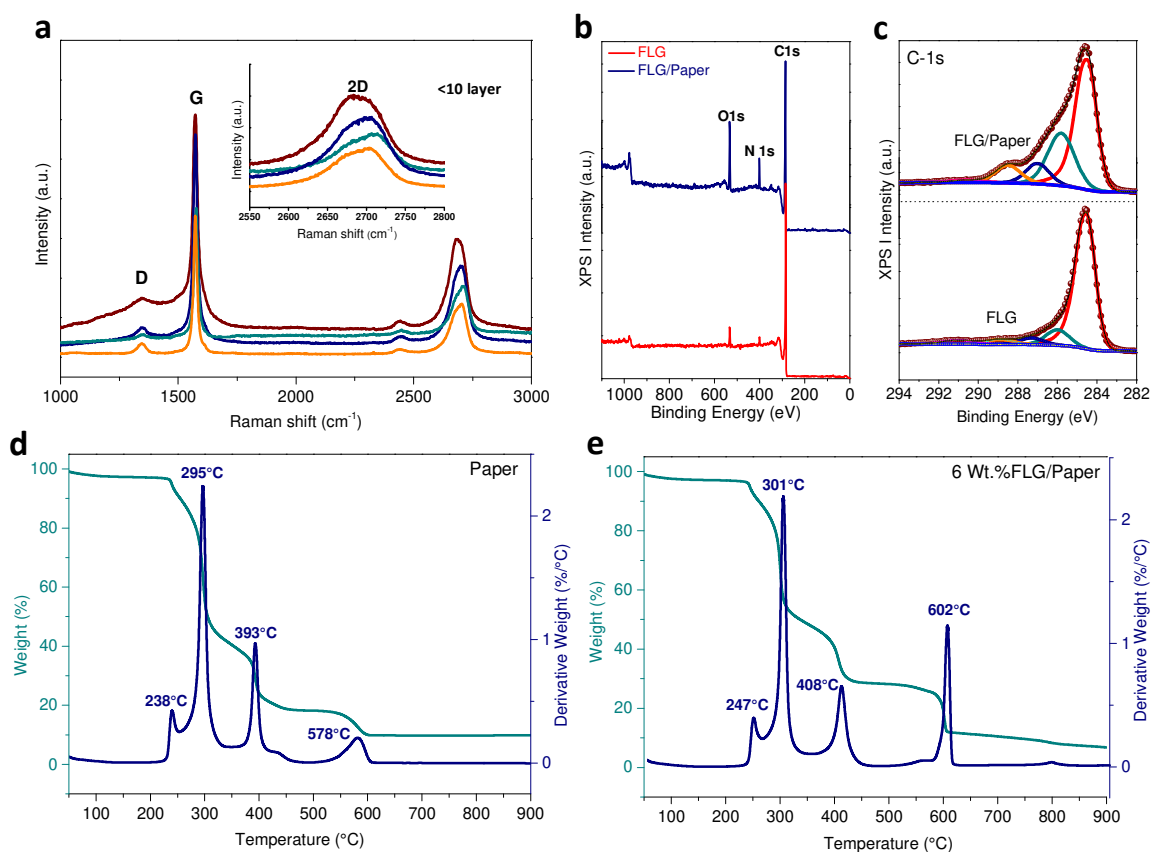


Figure 2. (a) Raman spectra of FLG and the corresponding 2D high-resolution peaks collected on different sample areas. (b, c) XPS survey and C1s high resolution spectra of pristine paper and FLG@paper composite. (d, e) TGA curves recorded on the pristine paper and FLG@paper composite.

For lightweight/flexible composites the mechanical adhesion of the conductive layer on the host matrix is highly important in order to prevent electrical conductivity loss during the handling or manipulating of the composite. Evaluation of the electrical conductivity of the FLG@paper composite, before and after crumbling, shows that the system displays almost no electrical conductivity deterioration after the crumbling process (Fig. 3a). **Indeed, the electrical conductivity measurements on the fresh FLG@paper composite and the same after crumbling display no significant change, i.e. 851 S. m^{-1} instead of 846 S. m^{-1} .** Such results could be attributed to the strong adhesion properties of the FLG coating onto the paper matrix which exclude crack formation inside the composite and preventing the interruption of the

electrical conductivity paths. The continuous electrical path of the FLG layer could also at the origin of such high resistance as electrical conductivity path remains unchanged from one side to another one even if some local cracks can be formed during the crumbling step. Such result is in good agreement with that reported on the mechanical resistance of the FLG@paper after high temperature annealing where the FLG coating layer prevents the formation of cracks inside the composite structure.

Paper can be damaged upon wetting or long sojourn in water, due to the swelling of the cellulose fibres or to the possible detachment of the FLG layer from the paper surface if the adhesion is not strong enough. In order to evaluate the mechanical adhesion of the FLG layer on the paper substrate the composite was immersed in deionized water for two days and the electrical conductivity measurements of the composite, before and after immersion, was used as a measure of the mechanical adhesion of the FLG layer on the paper (Fig. 3b and c). The electrical conductance is slightly decreased after the immersion step, i.e. 1.0×10^4 to 0.8×10^4 S. m⁻¹. The recovered FLG@paper composite also shows no weight loss after the test, confirming the high adhesion of the FLG on the paper surface. Mechanical adhesion of the FLG layer on the paper surface is also investigated by submitting the composite to a sonication in a mixture of ethanol:water (50:50) for 5 minutes. According to the results no weight loss was observed after the sonication treatment which confirms the high mechanical adhesion of the FLG layer on the paper surface. Such high adhesion could be explained by several facts: (i) surface chemical interactions between the oxygenated groups on the exfoliated FLG, generated during the exfoliation process through local energetic micro-bubbles and the water medium, and those present on the paper fibres host matrix, (ii) the van der Waals forces generated during the drying step which induces the shrinkage of the FLG film on the paper fibre matrix.

The FLG coating layer on the FLG@paper (Figure 3d(i)) can be also protected by applying a thin layer of polyurethane on the composite surface to produce a highly flexible and hydrophobic conductor for operating under harsh outdoor conditions (Fig. 3d(ii)). In another preparation the FLG@paper composite was contacted on both sides with copper electrodes followed by brush coating of a thin layer of polyurethane on the surface of the composite (Figure 3d(iii)). The application of the polyurethane layer not only enhances the mechanical resistance of the system for repeated folding and transport but also insulates the top-most surface against moisture (surrounded in white in Fig. 3d(iii)) of the device while the conductivity of the underneath FLG layer is retained (red square in Fig. 3d(iii)). The composite can be folded or scrolled for transportation (Fig. 3d(iv) and (v)) without any visible damages while the electrical conductivity is retained. Polyurethane can be also replaced by other flexible materials with higher temperature resistance depending to the downstream applications.

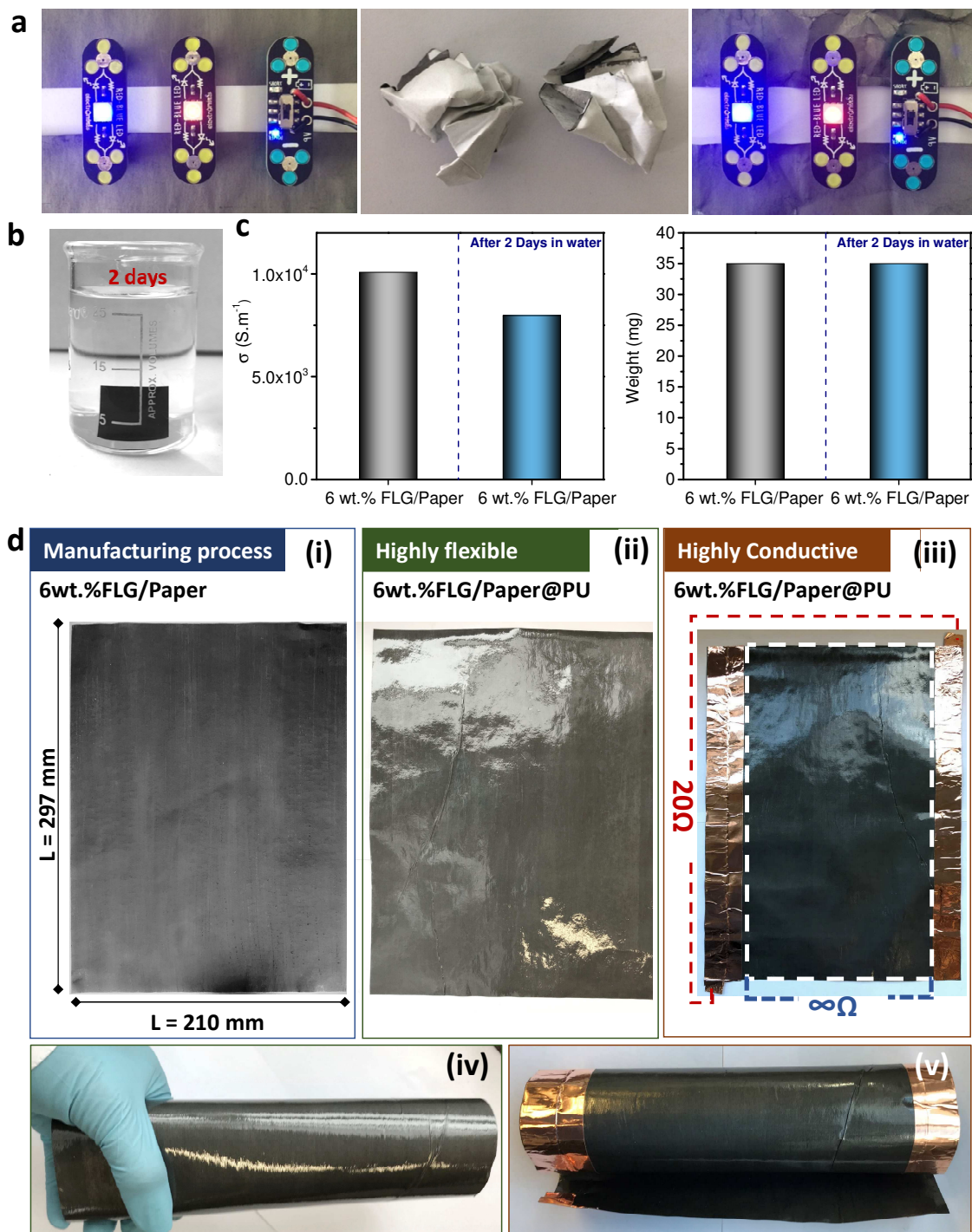


Figure 3. (a) Resistance towards crumbling of the FLG@paper composite synthesized by brush coating process (2 layers). (b and c) Digital photo of the FLG@paper immersed in distilled water for 48 h and the electrical conductivity values and weight change of the FLG@paper composite before and after immersion in water for 48 h followed by a drying step at 130°C. (d) Digital photos of (i) the as-synthesized FLG@paper (oven dried at 130 °C), (ii, iii) the corresponding flexible and foldable FLG@paper composite with a protective polyurethane layer and patterned copper electrodes on the top for easy handling and transport, (iv, v) evidence of the high flexibility of the FLG@paper and FLG@paper after polyurethane coating and electrodes patterning.

Mechanical/Electrical Degradation test of FLG@paper composites

Flexible electronic devices are frequently subjected to handling and transport which could influence their electrical properties through the formation of creases which block the conduction pathway. The mechanical/electrical fatigue tests of two FLG@paper composites synthesized by dip and brush coating were evaluated by repeated folding of the composites under different angles as depicted in Fig. 4a. The results clearly evidence the extremely high retention of the electrical conductivity of the composite synthesized by dip coating method (Fig. 4b). On the other hand, in case of the composite synthesized by brush coating method, the repeated folding at $+180^\circ$ leads to a progressive loss of the electrical conductivity (Fig. 4b). The same results are also observed for $+180^\circ$ folding kept at different duration and confirm the high mechanical resistance of the composite made by dip-coating process (Fig. 4c).

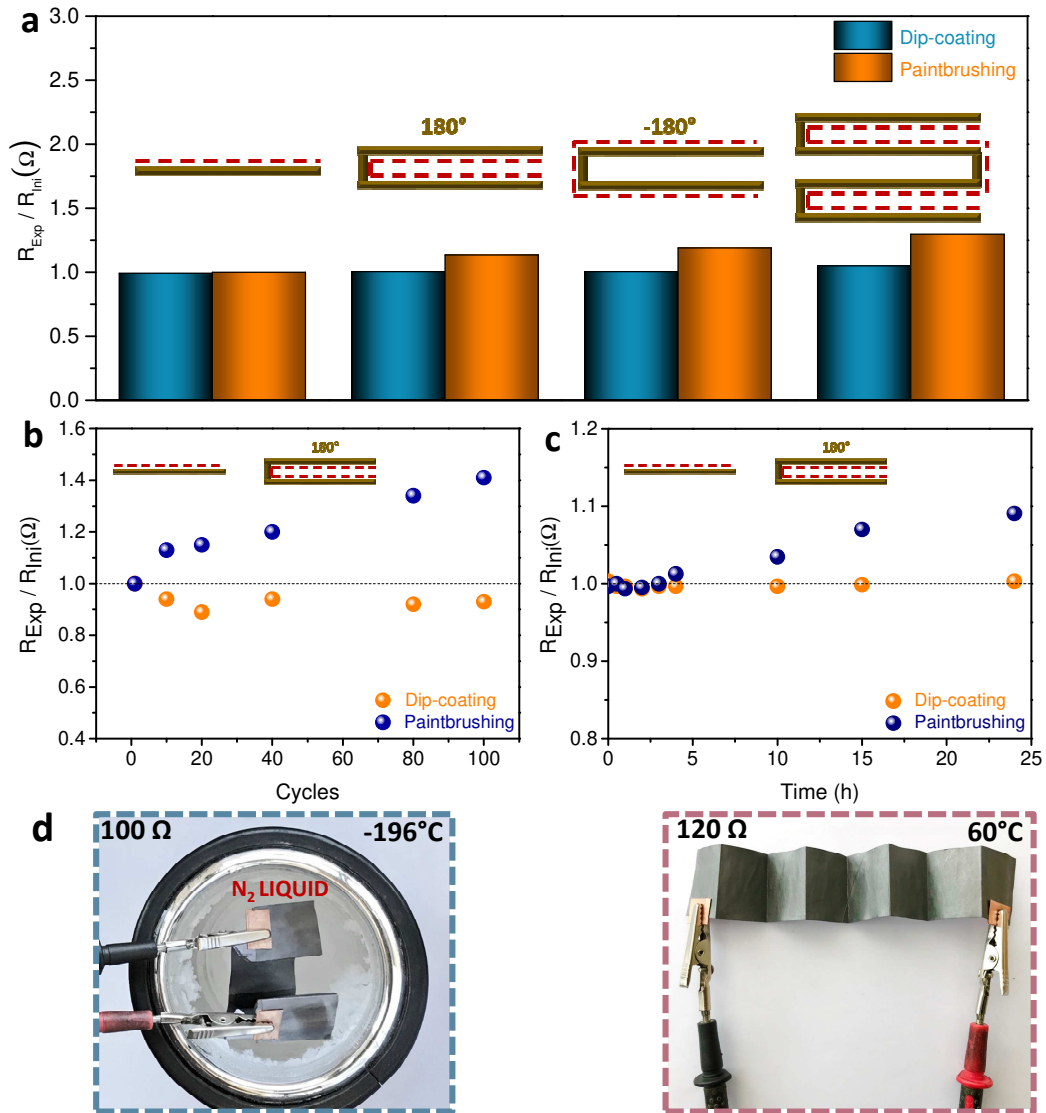


Figure 4. (a) Influence of the folding angle on the electrical conductivity of the FLG@paper composites synthesized by dip coating and brush coating after 20 cycles, (b) as a function of folding cycles and (c) times under stress at $+180^\circ$. (d) Digital photos showing the high resistance of the FLG@paper composite under different exposure temperature ranged from -196°C to $+60^\circ\text{C}$.

Such results could be explained by the fact that by dip coating, the whole surface of the cellulose filamentous of the paper sheet, both outer and inner part, was covered with a homogeneous layer of FLG which displays a higher resistance towards cracks after repeated folding. In the case of brush coating, the coating is only at the surface and thus displays a lower mechanical adhesion since creases can be formed after repeated folding leading to a

gradual loss of the electrical conductivity. Similar results have also been reported by Adam et al. [13] for tin and zinc printed on paper sheet, similar to the brush coating method presented above, where complete loss of electrical conductivity was observed after only ten folding cycles. The results obtained here are of great interest for the downstream applications, since the coating method should be adapted to provide a final composite with the highest possible mechanical resistance. The composite achieved by dip-coating process has also been subjected to a temperature variation test ranging from 60°C to -196°C, in order to evaluate its mechanical stability behaviour under different temperature conditions. According to the results recorded in Fig. 4d the macroscopic structure and the resistance value of the FLG@paper composite remain unchanged after successive immersion at N₂ liquid temperature and heating up to 60°C which confirms the extremely stability of the as-synthesized composite.

It is worthy to note that SEM analysis indicates that the FLG topmost layer remains similar regardless the coating method (Fig. 5a and b). However, one should expected that in the composite prepared by dip-coating method the inner part of the paper matrix could be better infiltrated with the FLG leading to a higher resistance toward mechanical solicitation. The densely packing of the cellulose fibres in the paper sheet as well as the large coverage of the fibres by the FLG film render the SEM observation less straightforward in this case. In order to overcome such technical problem another composite using cotton cloth has been synthesized. The fibres in the cotton cloth are more separate from each other and thus, one can easily check out the wrapping of the FLG layer around the fibre (Fig. 5c). According to the results one can confirm the high adhesion of the FLG film on an individual cotton cloth fibre through dip-coating process.

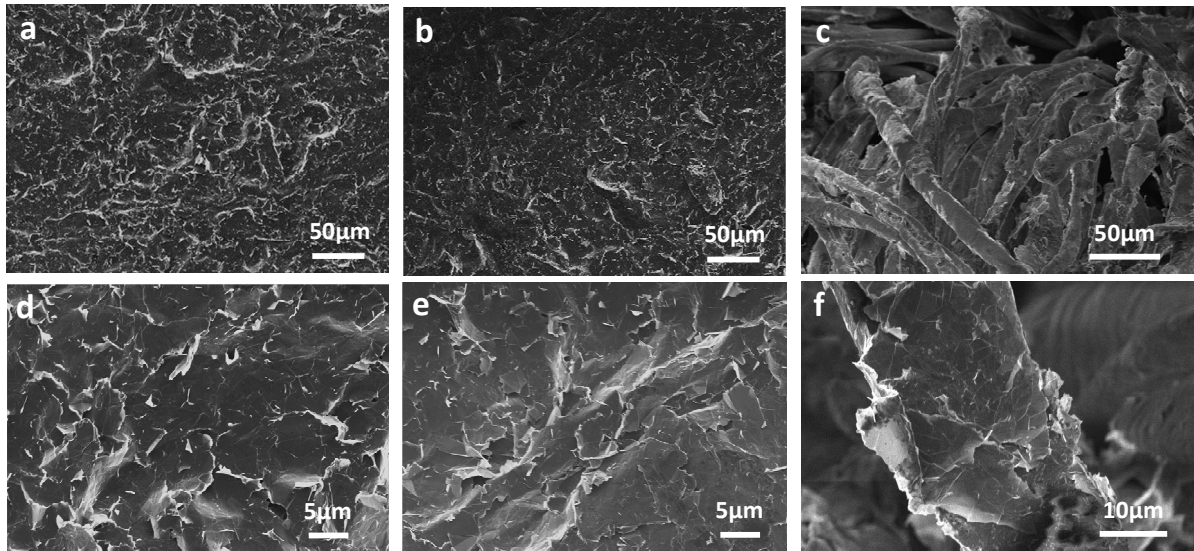


Figure 5. Representative SEM micrographs of the FLG@paper composites prepared by (a, d) brush-coating and (b, e) dip-coating. (c, f) SEM micrograph of a FLG@cotton cloth prepared by dip-coating displaying the high wrapping behaviour of the FLG layer around the host fibre.

2.2 Potential Applications of the FLG@paper Composites as Flexible Electronic Platform

2.2.1 Flexible circuits through laser patterning

Complete electronic circuits containing different components, i.e. resistances with various values, impedances, etc., can also be generated from the FLG@paper composites by laser patterning/graphitization process in a single step. Fig. 6 shows the different types of electronic circuits made by laser patterning from the FLG coated paper sheet. The laser patterning/etching process allows one to groove the FLG at different depth and thus, to control the resistance of the final composite at different points of the circuit. Examples of laser etching with different depths, by adjusting the power and time of etching, leading to the formation of FLG@paper surfaces with different resistance values, are displayed in Fig. 6a. The laser beam can also be used to perform local graphitization of the deposited FLG film in order to improve its electrical conductivity. The laser etching can be also tuned to produce

electronic circuits with various sizes as presented in Fig. 6b. According to the results presented before, the laser etching process could be efficiently used to produce flexible electronic circuits with different connecting paths and various resistances for numerous downstream applications (Fig. 6c). Examples of two planar resistances which can be directly integrated inside the whole electronic circuit are presented in the right part of Fig. 6c. Fig. 6d shows two laser-designed circuits, corresponding to an interdigital electrode and a temperature sensor. It is clearly evidenced that the current flow is efficiently carried by the graphene tracks acting as an interconnector between the battery and the red LED light bulb. Additionally, the high-resolution optical images of the laser patterned FLG@paper (Fig. 6e) allows one to engineer well-defined pathway and edge for the different compounds of the flexible electrical circuit for downstream applications. It is worthy to note that such composites could also be prepared by replacing paper sheet by other flexible polymers as laser patterning can be conducted on any type of substrates and not only paper sheet.

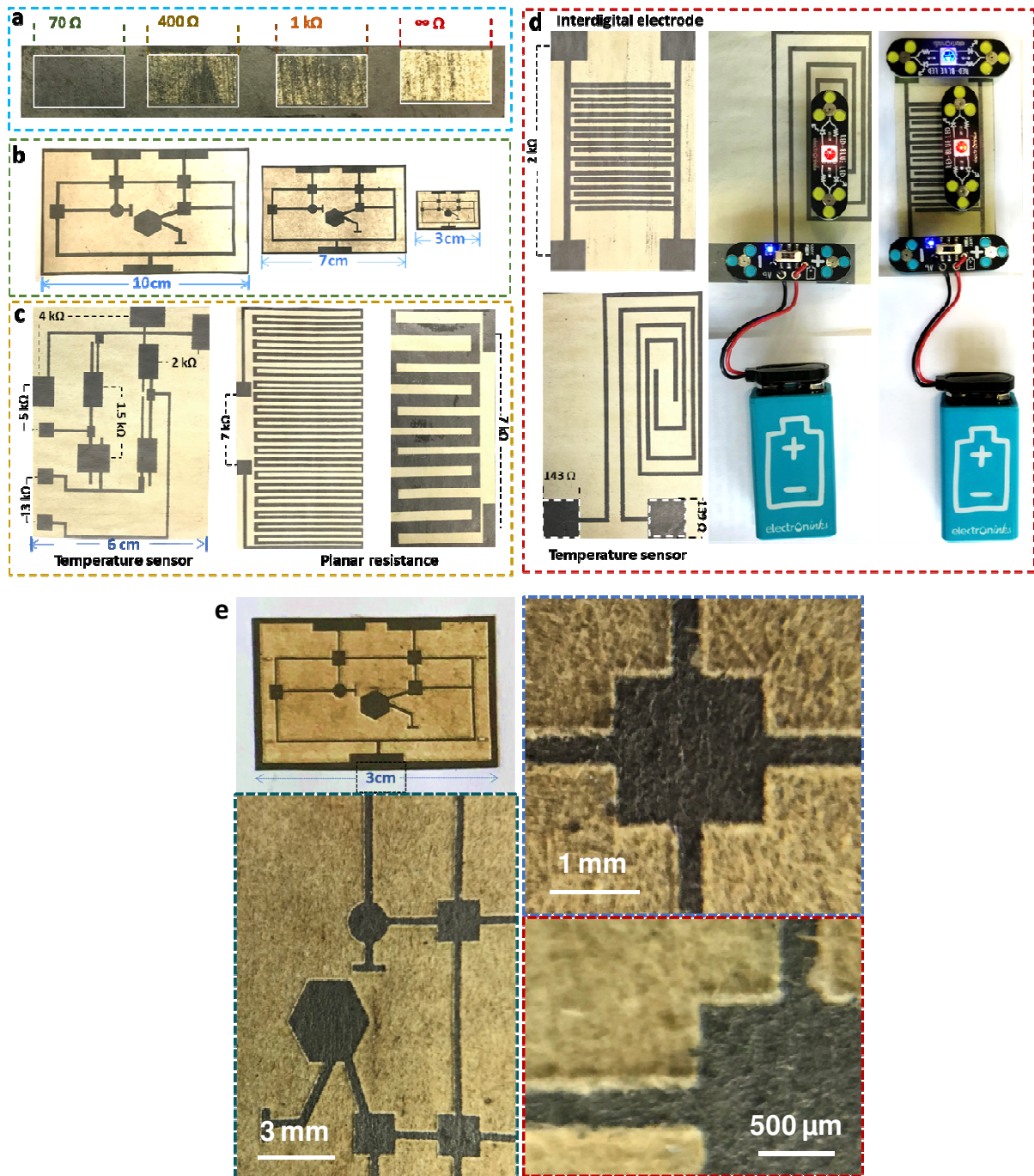


Figure 6. (a) Optical photos of the FLG@paper with different FLG layer thickness as a function of laser etching depth. (b) Electronic circuits on paper sheet after laser etching with different sizes. (c) Left: Electronic circuit with integrated resistances displaying different resistance values produced by laser etching at different thicknesses. Right: Examples of resistances with different values which can be directly integrated inside the electronic circuit by laser patterning. (d) Digital photos of interdigital electrode and sensor and examples of conductivity. (e) Digital photos evidencing the relatively high lateral resolution of the laser patterning process.

It is worthy to note that the electrical conductivity of the different patterned circuits presented in Fig. 6 remains relatively low taken into account the high resistance values reported, i.e. 70Ω as a lower limit. Such results are explained by the fact that the samples used for laser patterning were prepared by brush-coating with only two layers. For future applications one can imagine to use samples with thicker FLG layer in order to improve the electrical conductivity before laser patterning. Another way to increase the electrical conductivity of the final circuits could be to increase the duration of the local laser graphitization process in order to improve the conductivity.

2.2.2 Flexible keyboard

The as-synthesized FLG@paper with patterned circuit produced by brush coating was used to build up a flexible and lightweight paper-based computer keyboard as shown in Fig. 7. The system is composed of two distinct elements, an electronic module of rapid Arduino module and the flexible keyboard itself consisted of FLG film deposited on a **thicker** paper sheet host matrix. The soft keyboard consists of a matrix of crossed conductive strips deposited by brush coating process, using a pattern, from an aqueous solution of FLG followed by a thermal treatment at 130°C , one horizontal strip per line and one vertical strip per column. Each conductive strip is connected to a digital input of the Arduino module, where inputs are by default at a potential of 5 V. When the keypad is pressed, the corresponding conductor strips are connected to the 0 V of the system consisting of a two-sided conductive graphene paper interposed within the flexible keyboard and connected to the 0V of the system. Consequently, the Arduino micro-controller module, which embeds the necessary code for decoding the keys actuated by the user and continuously scans the state of the various conductive strips, decodes the position of the key which has been pressed by the user and returns the character corresponding to the computer via USB port (Fig. 7 and Fig. S5 and S6, supporting information). **In this present state the keyboard can be rolled without any**

damage to the different graphene patterning strips. The keyboard can be operated under slight bending due to the intrinsic characteristics of the as-prepared system, i.e. graphene strips coated on a thick host paper sheet and the use of uncoated paper sheet as insulator gap (blue strips in Fig. 7b). However, it is expected that such prototype can be optimized by replacing the insulator gap of uncoated paper sheets by a thinner one or even by a polymer ones which could provide more flexibility to the system. It is worthy to note that in our recent work the FLG film with high anchorage forces can be directly deposited onto polyethylene sheet with higher flexibility and resistance towards bending or manipulating [32].

2.2.3 Flexible capacitor

In a different application, the FLG@paper was used as capacitor for electricity storage. The conductive paper composite was synthesized by the dip coating approach of highly dispersed graphene solution on paper substrate. The electronic component consists of two graphene electrode papers which are separated by a polarizable plastic insulator. The device and value obtained from an auto-ranging digital multimeter are presented in Fig. S4 (supporting information). Finally, the FLG@paper can be also used as flexible multi-contacts device for connecting different systems from a single electricity source. In this case, the paper circuit was synthesized through a dip coating method in order to provide the highest mechanical resistance to the device against repeated folding. The flexible connector could be useful for mobile applications with lightweight and low size which facilitates the transport.

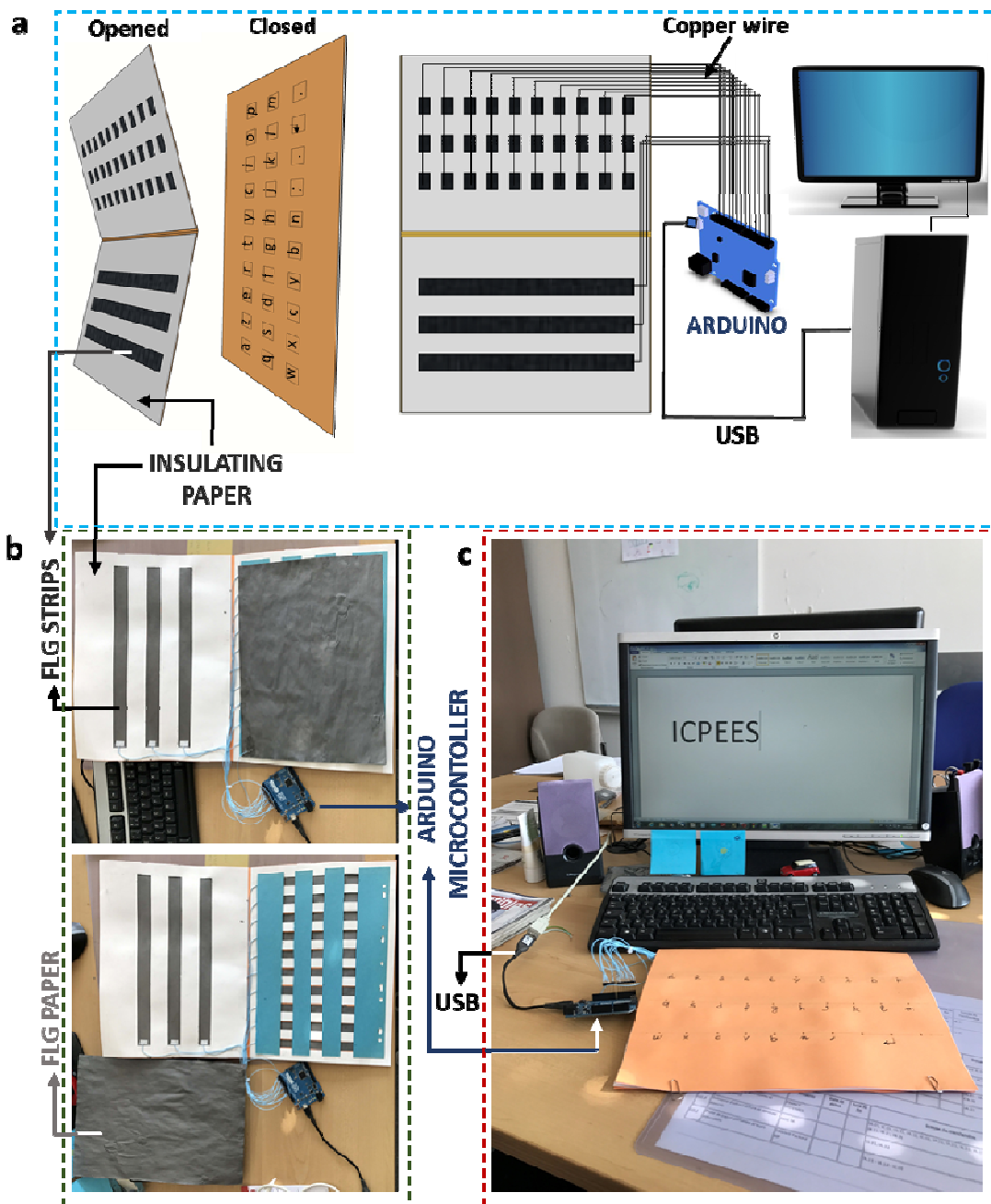


Figure 7. 3D illustration and optical picture of the different components of the flexible, lightweight and foldable keyboard based on FLG@paper composites.

3. Conclusion

In this report, we describe a straightforward and easy to scale-up approach to produce flexible conductive composites through a few-layer graphene coating, i.e. FLG@paper, by simple dip-coating or brush coating processes followed by low temperature thermal treatment. The as-synthesized lightweight and flexible FLG@paper conductive composites display extremely high mechanical resistance against folding or crumbling thanks to the strong interaction between the FLG coating layer and the cellulose filamentous of the substrate. Complete electronic circuits with integrated components, displaying various resistances by selective etching/graphitization of the FLG layer, can be produced from the FLG@paper composites through local and controlled laser etching process. This process allows one to produce flexible and lightweight electronic circuits with various sizes and functionalities for downstream applications such as electrical connectors/circuits or sensors. The synthesis is simple and does not require high-tech process and could open a new era for the development of low cost, lightweight, metal-free and flexible electronic circuits based on graphene coated on commercial paper sheet. Additional research based on the use of the same coating technique for preparing conductive polymer composites with extremely low conductive material is ongoing and confirms the high potential of the process.

4. Materials and Methods

4.1. Few-layer graphene synthesis

Long been notorious for its outstanding nutritional and pharmaceutical interest the Karaya gum obtained from *Sterculia urens* is used as green exfoliation agent to synthesize few-layer graphene from expanded graphite in aqueous solution in the present work (Fig. S1a, supporting information). Karaya gum is a highly water-soluble and complex polysaccharide also called hydrocolloids, consisting of galactopyranose (~ 44%), arabinopyranose, arabinofuranose (~ 25%), rhamnopyranose (~14%), glucuropyranosyl uronic acid (~ 15.5%)

and 4-*O* methyl glucopyranosyl uronic acid (~ 1.5%) and a small amount (~ 2%) of protein, which can be summarized into aromatic rings linked to oxygen functional groups [44, 45]. During the exfoliation process the hydrophobic polypeptide chains of the gum will adsorb on the graphene surface by van der Waals interactions (in particular through π - π interaction), and the branched oxygen groups which are present in the gum will serve as a binder to ensure a good dispersion of the mechanically exfoliated graphene sheets in the aqueous solution.

For the experiments an amount of 5 g of expanded graphite starting raw material and $y = 0.5$ g of natural exfoliating agent, also acting as emulsifying system, were added in a recipient filled with distilled water (500 mL). The mixture was subjected to probe ultra-sonication process assisted with mechanical stirring during 2 h at room temperature through external cooling device.

Different concentrations of FLG in the solution, ranged from 0.1 to 30g/L, can be achieved depending to the downstream application. It is worthy to note that higher FLG concentration, i.e. 100 g/L, could also be obtained by changing the surfactant as reported in ref. 32. The nanostructures and morphologies of the as-synthesized product were investigated by SEM and TEM. The SEM and TEM micrographs clearly show the presence of highly dispersed few-layer graphene with micrometers size and a graphene sheet stacking number less than 10 (Fig. S1b to d, Supporting information). The number of graphene sheets stacking layer was also analyzed by Raman.

4.2. FLG@paper composites synthesis

The synthesis was carried out by two methods: (i) dip coating: the paper sheet was immersed into an aqueous solution of dispersed FLG (5 g/L) followed by an oven dried at 130°C for 30 min. Cellulose paper is composed of polysaccharide formed by glucose chains linked by glycosidic bonds β 1- 4 [46]. The interaction between cellulose and FLG could thus occur

naturally by covalent bonding between the π - π bonds of the aromatic groups and thanks to the self-adhesive properties of the gum which acts as a glue, resulting an improved adhesion [47]. Additional binding could also be formed between the oxygenated functional groups presence on both surfaces as well.

The characteristics of the paper sheet used in the present work are summarized in Table S1 (SI).

The impregnation was repeated several times until a desirable resistance value was obtained (Fig. S3a, supporting information); (ii) brush coating: the paper sheet was coated with a FLG solution (5 g/L) by a brush followed by an oven drying at 130°C for 30 min. The impregnation was repeated several times until a desirable resistance value was obtained (Fig. S3b, Supporting information). The as-synthesized FLG@paper composite was finally heat treated in air at 200°C for 1 h in order to desorb all the moisture. All kinds of paper can be used in the process.

4.3. Characterization techniques

The scanning electron microscopy (SEM) was carried out on a Zeiss 2600F with a resolution of 5 nm. The sample was deposited onto a double face graphite tape in order to avoid charging effect during the analysis. Thermal stability was determined using a TG analyzer (Thermo) with a heating rate of 10°C/min from room temperature to 900°C in O₂ (20%)-He environment. The X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultrahigh vacuum (UHV) spectrometer equipped with a VSW Class WA hemispherical electron analyzer. A monochromated Al K α X-ray source (1486.6 eV) was used as incident radiation. Survey and high-resolution spectra were recorded in constant pass energy mode (90 and 44 eV, respectively). The CASA XPS program with a Gaussian-Lorentzian mix function and Shirley background subtraction was employed to deconvolute the XP spectra. The Raman spectra were recorded using LabRAM ARAMIS Horiba Raman spectrometer equipment.

Spectra were recorded over the range of 500 - 4000 cm^{-1} at the laser excitation wavelength of 532 nm. The sample was deposited on glass substrate by dip-coating of its suspension and carefully dried before measurement.

The electrical resistance was monitored by four-point probing method using a Potentiostat Bio-Logic SP300 (Grenoble, France) or by using directly a Fluke auto-ranging digital multimeter.

4.4 Laser patterning and graphitization

The graphene based electronic circuit was designed using a CO_2 laser operating in continuous mode (QCW) at laser excitation wavelength of 10.6 μm with a 100 μm beam trace. The cleaning and track creation parameters differ according to the circuits. The drawn circuits (Fig. S7, supporting information) are converted into **computer-aided manufacturing (CAM)** and recharged in the laser device. **The circuit drawing was made by the software COREL DRAW. Lines were defined as minimum line and the space between each line is set to be 0.018 mm oriented at zero degree (parallel to the horizontal line) and the definition was set at 1200 dpi. During the laser patterning a cross jet air was set at 45° with respect to the scanning direction before the laser spot to remove the graphene dust and to avoid re-deposition of such dust. The spot at the focus point has a diameter of 100 μm . The scanning speeds are relatively fast ranging from 50 mm/s to 350 mm/s and a power output between 1 and 10 W was used as at power higher than 10 W some damages were observed on the paper..**

For the graphitization process the same power, i.e. 1-10 W, was used with a frequency of 5 kHz. The process was aimed to provide enough energy, which was converted into heat, to the graphene layer, i.e. local graphitization, while preserving the paper's integrity underneath. In the graphitization process the energy efficiency was determined by tracking the value of linear energy (E_L), which was obtained by dividing the power by the scan speed, and is expressed as J/mm. The graphitization process was carried at E_L ranged between 0.03 and 0.12 J/mm.

Acknowledgement

The SEM analysis was carried out at the facilities of ICPEES (UMR7515 and UMR7504 CNRS-University of Strasbourg). TEM experiments were carried out at the IPCMS facilities and Dr. Walid Baaziz and Prof. Ovidiu Ersen (UMR 7504) are gratefully acknowledged. We would like also to thank Jean-Michel Duchazaubeneix of MELIAD (<https://www.meliad-sas.com/fr/entreprise>) for help during the laser patterning process.

Conflict id Interest

The authors declare no conflict of interest

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Graphical abstract

