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Cotton Fabrics Coated with Few-Layer Graphene as Highly Responsive Surface Heaters and Integrated Lightweight Electronic-Textile Circuits

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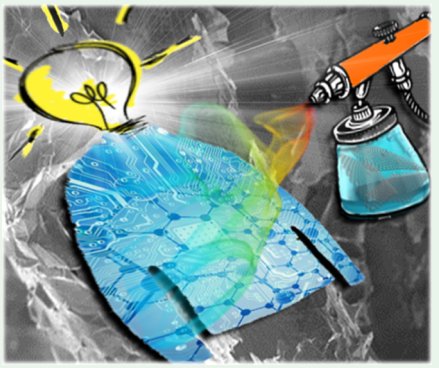
ABSTRACT: In this work, we describe an eco-friendly and cost-efficient method for the production of highly dispersed few-layer graphene solutions using karaya gum as a bioinspired exfoliating agent. The as-synthesized graphene aqueous solutions can be easily applied on a cotton cloth through dip- or brush-coating, thanks to the interaction between the graphene sheets decorated with the gum and the functional groups on the cotton cloth host substrate surface. The as-prepared fabric composites display high mechanical stability, anchorage, and high electrical conductivity that make them excellent candidates within a relatively high number of technological applications. The study mainly focuses on the potentialities of cotton fabric composites as planar heating devices or electronic-textile (e-textile) circuits prepared by postlaser treatment. By means of a laser beam, local graphitization or partial etching of the graphene conductive lines can be achieved to generate conductive areas with different resistances, which can act as flexible and integrated electronic circuits. Besides lightweight conductive circuits, the graphene-coated cotton fabrics were experimentally tested for other technological applications, that is, as flexible metal-free markers or for IR shielding or as nonflammable barriers for the protection of sensitive devices or to prevent flame spreading. This technology allows one to open a new route toward the development of daily life connected and flexible e-textile devices of added value with low carbon footprint impact.



KEYWORDS: *few-layer graphene, cotton cloth, e-textiles, laser patterning, composite*

1. INTRODUCTION

Electronic textiles (e-textiles) represent a novel type of high-tech products resulting from the integration of complex electronic structures and common textiles. They can find applications in several areas ranging from the production of biomedical,[1−3] sensing[4] and power generation, or energy storage devices[5−8] to addressable wiring devices for everyday needs.[9] Different technologies have been developed until now for the production of e-textiles, and they can include embroidering, knitting, weaving, spinning, braiding, coating, printing, and chemical treatment.[10] Depending on their downstream applications (i.e., wearable displays, portable power systems, high-performance sportswear, or health-monitoring devices),[11−13] e-textiles should maintain key properties such as high flexibility and stretchability, lightweight, and high resistance toward leaching upon their washing. The fabrication of e-textiles relies on the homogeneous coating of a textile support by an efficient layer of a conductive material which confers electrical conductivity to the composite. Cotton cloth is a flexible and hierarchical porous support made of natural cotton fibers, which displays a relatively high thermal resistance and can be used as a macroscopic host matrix for the deposition of a conductive layer. Other advantages of the cotton fabric are due to its economic processability and mechanical and flexible properties.[14−16] The cotton cloth also displays numerous functional groups such as hydroxyl and carbonyl functionalities on its surface, which provide anchorage sites for linking with the deposited conductive graphene layer, hence improving the final mechanical strength of the coated composite.[17] According to a recent review article on e-textiles and their application areas,[18] there is still a lot of room available for improving this technology, especially regarding the large scale-up production of these composites. Recently, Novosolov and co-workers described an interesting technique for the scalable production of e-textiles based on the pad-dry deposit of a thin layer of reduced graphene oxide (rGO) on the surface of a host

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matrix.[19] The potential manufacturing rate of e-textiles by this technique was estimated to be ≈150 m/min using the already existing industrial production method. In addition, their electrical conductivity was made variable as a function of the number of depositing cycles, hence varying the number of rGO layers deposited on the textile fibers. However, the use of rGO can face with some technical limitations, especially because of the tedious and less than trivial synthesis of both GO and rGO materials. The use of hydrocolloids for the production of exfoliated graphene and few-layer graphene (FLG) sheets has received growing interest compared to that of organic solvents, especially because of their reduced environmental impact.[20,21]

Graphene and FLG are two-dimensional (2D) conductors with a high effective surface area as well as chemical stability along with high mechanical strength and flexibility. These unique properties have made it possible to employ them in a number of high-technological applications during the past decades.[22−28] Graphene and related materials were also extensively investigated as transparent heaters[29−32] in place of metal nanowires. However, for graphene suspended in liquid media, classically produced through the liquid-phase exfoliation (LPE) process, aggregation or restacking phenomena rapidly occur because of high van der Waals attraction forces between single or few graphene layers, which render its processability rather hard if not impossible.[33−35] Such a problem is not encountered with graphene produced through chemical vapor deposition, followed by transfer to the host substrate. Anyway, the high surface energy of the graphene sheets confers them a high tendency to wrap foreign structures upon contact, followed by a drying step. This property is of high interest for the preparation of graphene/macroscopic composites with potential applications in the field of detection or electrically conductive devices.

This property has prompted us to combine FLG sheets with a macroscopic host support such as a cotton fabric to provide composite materials with potential applications in several technological areas such as electronics, health care, wearable cloths, sensors, and heating and power storage devices.[13,36−38] As far as industrial applications of these composites are concerned, they should be produced on a large scale under green conditions and with the lowest costs in order to reduce the problems linked with the postsynthesis purification paths. In addition, the conductive coating layer should not imply health and security issues during its fabrication as well as during the composite processing. This is the case of cotton fabrics functionalized with carbon nanotubes (CNTs). For the latter, health and safety issues linked to their ultimate use[39−41] remain a matter of debate within the scientific community.

In this work, we describe the straightforward production of e-textiles from a commercial cotton matrix by its coating with an aqueous suspension of FLG sheets. The FLG synthesis was carried out in a water medium, that is, 98%, containing a biocompatible exfoliant and under room temperature (rt), which significantly reduces the environmental impact and the overall cost of the process. In general, LPE of raw graphite to produce graphene or FLG sheets is generally based on the use of various organic solvents such as *N*,*N*-dimethylformamide, *ortho*-dichlorobenzene, 1-methyl-2-pyrrolidone, benzyl benzoate, acetophenone, benzonitrile, dimethyl sulfoxide, or dioxane.[42] All these solvents are toxic and expensive and generally possess high boiling points, and thus, their large-scale use raises important environmental concerns. All these solvents need special handling precautions during the exfoliation procedure, and liquid or gaseous phases resulting from the processing method need to be treated as they cannot be released as such in the environment. Accordingly, LPE in a water medium significantly reduces the environmental impact of the process, while the lack of postsynthesis treatment of volatile organic compounds contributes to the reduction of the process costs. During the deposition and drying steps, only steam was released. This feature simplifies significantly the postprocess gaseous treatment compared to that encountered with organic solvents. As a result, LPE in the water medium, with or without additives, represents an interesting alternative to the production of graphene-based materials for different downstream applications.[43,44] The as-prepared composites have been successfully applied as low-energy-consuming and fast heat on/off switchable heaters as well as flexible textile-based composites to produce electronic circuits through laser patterning paths. They displayed a highly flexible behavior together with an extremely high electrical conductivity and durability against repeated bending or scrolling treatments. This latter feature is expected to reduce significantly all main issues related to material loss/alteration upon use, hence limiting any accidental breathing of hazardous particles from potential end users. The effect of FLG sheet concentration in the aqueous medium has also been investigated with respect to the electrical conductivity of produced e-textiles, and the results obtained on optimized samples have been thoroughly discussed. Laser patterning of e-textiles has also been applied either to generate integrated electronic circuits with a high lateral resolution or to prepare electronic tracks featured by variable electrical resistance for replacing metal compounds and plastics usually used nowadays which pose problems for the environment both in terms of production and in terms of waste disposal. The laser patterning of e-textiles for the production of electronic circuits of variable dimensions and featured by e-tracks with different resistances has only few precedents in the literature, especially for the manufacture of flexible and lightweight metal-free electronic circuits. Indeed, e-textiles are generally produced in the form of a single and homogeneous composite showing a similar resistance throughout the whole sample. Finally, FLG-coated cotton cloths have been successfully used as efficient flame retardants or flame barriers suitable for preventing fire spreading.

2. MATERIALS AND METHODS

2.1. FLG Synthesis. Karaya gum obtained from *Sterculia urens* was employed as a green exfoliating agent to synthesize FLG sheets from expanded graphite (EG) in aqueous solution. Karaya gum is a highly water-soluble polysaccharide also known as a highly charged (ionic) hydrocolloid, and it consists of galactopyranose (∼44%), arabinopyranose/arabinofuranose (∼25%), rhamnopyranose (∼14%), glucuropyranosyl uronic acid (∼15.5%) together with 4-*O*-methyl glucuropyranosyl uronic acid (∼1.5%), and a small amount (∼2%) of proteins, which can be summarized into aromatic rings linked to oxygen functional groups.[45,46] Its exfoliation power is basically ascribed to the ability of the hydrophobic polypeptide chains of the gum to be adsorbed at the graphene surface through van der Waals interactions ($\pi-\pi$ stacking interactions mainly), while branched hydrophilic O-containing moieties ensure a good dispersion of the mechanically exfoliated graphene sheets in the aqueous medium.

For exfoliation experiments, an amount of 5 g of EG (as a starting raw material) and 0.5 g of karaya gum (as both a natural emulsifying agent and stabilizing agent) were added to 500 mL of distilled water. The exfoliation process was carried out in a Branson digital sonifier (SFX550 model made by Emerson Co., featuring with a nominal power of 400 W at 20 kHz and equipped with a 1/2″ disruptor horn)

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operating at a power of 40 W (10% of the nominal power) at rt for 2 h. The mixture was continuously stirred (300 rpm) while maintaining its temperature constant at rt by means of an external cooling device. During the sonication process, cavitation micrometer bubbles are formed in the liquid phase. The bubble collapse induced by cavitation releases intense local energy, that is, a temperature of 5000 °C and a local pressure exceeding several hundred atmospheres,[47] which break down the loosely connected EG to yield graphene and FLG or ultrathin graphite flakes. The as-formed graphite-based materials were stabilized through surface interaction by the karaya gum, thus forming stable suspensions in the liquid medium.

Different concentrations of FLG in the aqueous suspension (from 2 to 10 g/L) were used depending on the composite downstream application. The nanostructures and morphologies of the as-synthesized products were investigated by scanning electron microscopy and transmission electron microscopy (SEM and TEM). SEM and TEM micrographs clearly showed the presence of highly dispersed micrometer-sized FLG sheets generally formed by less than 20 stacked layers. The number of stacked graphene sheets and the nature of the surface functional groups were also analyzed by Raman spectroscopy and X-ray photoelectron (XP) spectroscopy (XPS).

2.2. Synthesis of FLG-Coated Cotton Cloth Composites (FLG@CC). The synthesis of FLG-coated cotton cloth composites (FLG@CC) was accomplished through two methodologies: paint brushing and dip coating. With the former method, the FLG water solution was deposited on the cotton cloth using a paint brush; hence, FLG sheets (5 g/L) were deposited on the painted material face only. With the latter method (dip coating), the cotton cloth was soaked with an aqueous solution of dispersed FLG (5 g/L), and hence, its whole matrix was coated by FLG. Regardless of the method used, the FLG deposit step can be repeated at will to get composites with variable FLG loading. After each application, samples were heated to dryness in an oven at different temperatures, 100−200 °C, for 30 min to desorb all moisture and to strengthen the wrapping of the host substrate by an FLG layer.

The cotton cloth was purchased from IKEA Inc., and its composition was in line with that of traditional cotton cloths:[48] cellulose (94%), proteins/pectins (2%), minerals (1%), waxes/organics (1.5%), and others (1%). Different types of cotton cloths can be used (in principle) for the preparation of the relative composites. It is formed by linear chains of thousands of $\beta(1-4)$-linked D-glucose units,[49] and the interaction with FLG sheets naturally occurs (covalently) because of the adhesive properties of the exfoliating agent available at the surface of FLG sheets (karaya gum). The gum acts as a hydrophilic glue and ensures excellent adhesion at the graphene coating.[50] Additional binding could also be formed between the bonding from the oxygenated functional groups present on both surfaces as well.

2.3. Characterization Techniques. SEM was carried out on a ZEISS 2600F with a resolution of 5 nm. Samples were deposited onto a double-face graphite tape in order to avoid charging effects throughout the analysis. TEM was carried out on a JEOL 2100F working at an accelerated voltage of 200kV, equipped with a probe corrector for spherical aberrations and with a point-to-point resolution of 0.2 nm. To prevent restacking phenomena of FLG, the suspension did not undergo any intermediate drying process, but it follows the following sample preparation method: 1 mL of the FLG aqueous suspension was diluted with 5 mL of ethanol, and the suspension was subjected to sonication for 5 min. Afterward, a drop of the suspension was cast on a copper grid covered with a holey carbon membrane for TEM observation and evaporated to dryness in air. XPS measurements were carried out using an ultrahigh vacuum spectrometer equipped with a VSW Class WA hemispherical electron analyzer. A monochromatic Al Kα X-ray source (1486.6 eV) was used as the incident radiation. Survey and high-resolution spectra were recorded in the constant pass energy mode (90 and 44 eV, respectively). The CasaXPS 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. The spectra were recorded in the range of 500−4000 cm^{-1} using the laser excitation wavelength of 532 nm. Samples were deposited on a glass substrate by dip coating and carefully dried before each measurement.

The electrical resistance was measured by a four-point probing method using a potentiostat Bio-Logic SP300 (Grenoble, France) or directly using a Fluke autoranging digital multimeter.

The water contact angle measurements were conducted using a Krüss drop shape analyzer (DSA25).

2.4. Laser Patterning of FLG Composites and Graphitization. Electronic circuits were designed using a CO_2 laser (Epilog Mini, 40 W) operating in a quasi-continuous mode at the laser excitation wavelength of 10.6 μm with a 100 μm beam trace. The cleaning and track creation parameters differ from circuit to circuit. All circuits are computer-drawn (CAM) using CorelDRAW as the software, and files are charged in the laser device. Lines were defined as the minimum, and the space between each line was set to 0.018 mm oriented at 0° (parallel to the horizontal line) at 1200 dpi as the resolution. During the laser patterning, the cross-jet air was set at 45° with respect to the scanning direction and before the laser spot to remove all graphene dusts and avoid their redeposition. The spot at the focus point had a diameter of 100 μm. The scanning speeds were relatively fast (from 50 to 350 mm/s), and the power output was between 1 and 10 W maximum. Power outputs higher than 10 W were found to damage the textiles.

For the graphitization process, the same laser output power, that is, 1−10 W, was used at a frequency of 5 kHz. The process was used to heat graphene deposits to induce local graphitization phenomena while preserving the underneath textile integrity. In the graphitization process, the energy efficiency (expressed as J/mm) was determined by tracking the value of linear energy (E_L), which was obtained by dividing the power by the scan speed. The graphitization process was carried out at an E_L between 0.03 and 0.12 J/mm.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Properties of FLG@CC. EG was used as a precursor for the FLG synthesis. Figure 1A (left) displays a digital photo of EG on the top of an aqueous solution

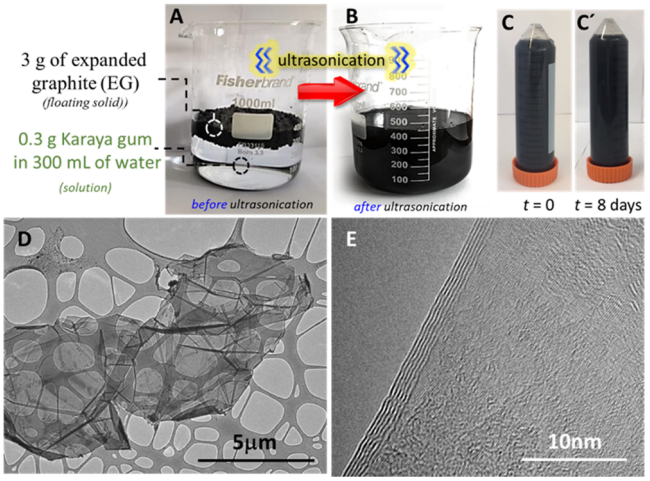

Figure 1. Process sketch for the EG exfoliation. Digital images of a batch of EG (3 g) as a floating solid in a water medium containing 0.1 wt % of karaya gum as a surfactant before (A) and after (B) the ultrasonication treatment (exfoliation process) for 2 h. (C,C′) FLG solutions (10 g/L) at different settling times: t = 0 and t = 8 days, respectively. None of these homogeneous FLG dispersions show any appreciable formation of deposits. (D,E) Representative TEM micrographs of FLG after the exfoliation process at different magnifications.

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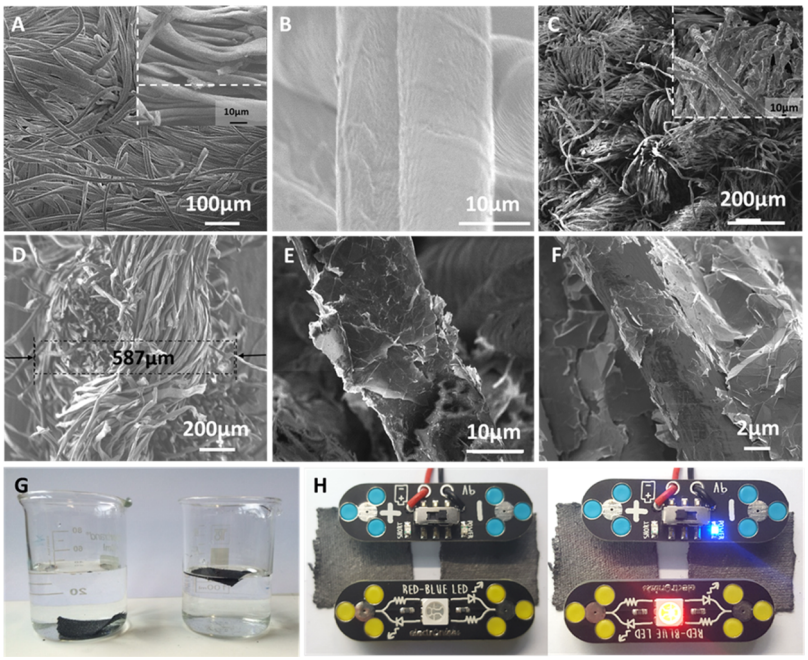

Figure 2. Representative SEM micrographs: (A,B) pristine cotton cloth showing the fibrous structure of the substrate with a smooth surface, (C,D) FLG@CC through dip and brush coating, (E,F) high-magnification view of the FLG@CC through dip and brush coating. (G) Digital photo showing the hydrophilic character of the FLG@cotton cloth treated at a low temperature (130 °C) and the same after treatment at 200 °C with a hydrophobic character. (H) Electrical conductivity of the FLG@cotton cloth assessed by a remote electrical supply device: left: off-mode, right: on-mode.

containing 0.1 wt % of karaya gum as an exfoliating agent (see the Materials and Methods section). Figure 1A (right) illustrates the same sample after treatment with a probe sonicator operated at 10 W and rt for 2 h. This latter picture accounts for the generation of highly and homogeneously dispersed graphite sheets in the water solution.

TEM micrographs of the as-obtained suspension are shown in Figure 1B,C and confirm the high exfoliation efficiency of the adopted protocol to give FLG sheets only, featured by less than 20 layers and a thickness < 10 nm. TEM analysis also shows the generation of relatively large graphene sheets (up to several square micrometers) that make them highly attractive materials for coating applications.

Indeed, the combination of large dimensions and low thicknesses allows graphene sheets to stack and even wrap around microfilaments of a given hosting matrix, hence ensuring improved mechanical stability to the final composites (*vide infra*). The high-resolution TEM micrograph (Figure 1C) illustrates a representative FLG sample obtained under our exfoliation protocol that consists of six, highly crystalline graphene layers (according to the side view). Some wavy structures observed on the FLG surface are attributed to the presence of adsorbed compounds (i.e., the exfoliating agent or residues rising from the sample preparation for the TEM analysis). Looking at the relatively large distribution of FLG sheets in terms of sizes and thickness, materials should be properly named ultrathin graphite flakes in accord with the classification proposed by Bøggild[51] and based on the work of Castro Neto *et al.*[52] carried out on graphene samples produced from 60 different producers. However, it is important to stress that the quality of graphene used depends on its ultimate application as each application needs graphene samples with different physical characteristics. The high stability of exfoliated FLG sheets is finally confirmed by only negligible material residues settling down from the aqueous suspensions upon standing the samples per several days (Figure 1D).

As shown in Figure 2, SEM analysis of the cotton fabric at different magnifications has revealed a woven structure made of entangled microfilaments of a smooth surface. SEM micrographs of the cotton textile after brush or dip coating with an FLG solution are presented in Figure 2C,D. These latter figures reveal that cotton fibers are homogeneously coated with a thin layer of FLG and the pristine morphology of the textile is almost entirely preserved at least at low magnifications. SEM micrographs at higher magnifications of FLG@CC (Figure 2E,F) highlight a complete coating of the fibers by highly wrapped and shrunk FLG sheets that form a rough and interconnected graphene network all around the cellulose fibers, thus conferring an excellent electrical conductivity to the composite (*vide infra*). However, not all FLG sheets are completely wrapped around the fabric microfilaments, but some of them remain only loosely attached to those coating the microfilaments. We thought that the latter ensures a highly interconnected and conductive network all over the extension of the matrix in its downstream application, that is, metal-free and lightweight electrical textiles. The wrapping of the fabric microfilaments by a homogeneous layer of FLG sheets is not trivial because of the high entanglement of filaments in the host fabrics.

The SEM micrographs evidence the high wrapping of the FLG sheets around the cellulose fibers, indicating the high interaction between the two materials. The roughness of the FLG-coated cellulose fiber can also make the composite highly attractive for filtering applications. Indeed, the higher the roughness of the entangled fibers, the higher their interactions with exogenous particles, and hence, the higher the material filtration efficiency. The highly efficient coating of FLG sheets around cotton fibers can be ascribed to the generation of

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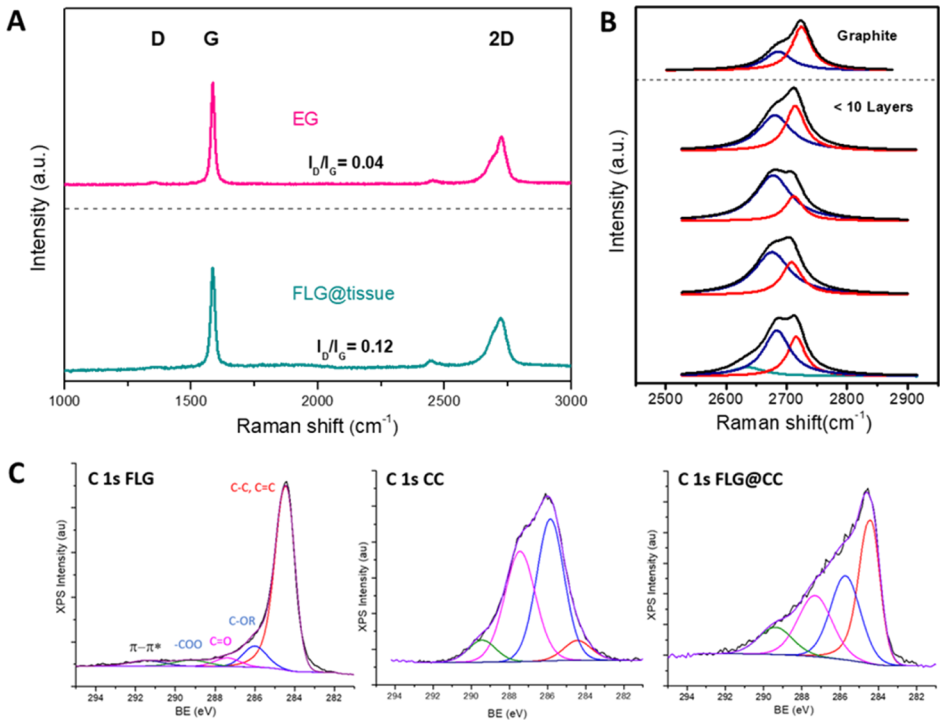

Figure 3. (A) Raman spectra of pristine EG and FLG@CC. (B) Raman spectra of exfoliated FLG showing the presence of FLG with different graphene layers. (C) Deconvoluted C 1s XPS spectra recorded on FLG, the pristine cotton cloth, and the FLG@cotton cloth showing the presence of different C−O functional groups on the sample surface.

strong H-bond interactions during the material drying between the functional groups of the fabric and those of the gum available on the FLG surface.[17,53] The drying procedure allows FLG sheets to shrink around the cotton fibrils. Notably, the temperature applied during the drying step of the composite can change dramatically its surface properties. Although a drying treatment at 130 °C produces a material with a hydrophilic surface character, temperatures of 200 °C render it essentially hydrophobic in nature (Figure 2G, left vs right).

Digital photos of water drops at the surface of the different FLG@CC samples (Figure S1, after coating and thermal treatment at two different temperatures) highlight the influence of the postthermal treatment on the hydrophobicity of the composites. Accordingly, a 3 wt % FLG@CC sample treated at 100 °C absorbs water as soon as drops meet its surface (Figure S1A). On the other hand, a 3 wt % FLG@CC sample treated at a temperature ≥200 °C highlights its improved hydrophobic character as water forms almost round-shaped drops with an average contact angle of about 130° (Figure S1B). This experiment unveiled how properties of the composites change from hydrophilic to hydrophobic upon a simple material heat treatment at relatively moderate temperatures. According to Wang *et al.*,[54] the surface energy of the composites falls in the range of 29 ± 5 $mJ{\cdot}m^{-2}$. Thus, it can be stated that the thermal treatment of FLG@CC composites reduces the wettability and decreases their interfacial adhesion with liquids. Such a result is of high interest because it demonstrates that an appropriate thermal treatment of FLG@CC samples allows to control their wettability, a feature that is crucial in the area of e-textiles. Moreover, it should also be noticed that the hydrophobicity of samples depends significantly on the textural properties of the host matrix, that is, the diameter and density of the filaments as well as the way in which they are interwoven. Unfortunately, this feature is more challenging to be evaluated. Such a behavior can be reasonably attributed to the occurrence of dehydration/condensation processes between functionalities on cotton fibers and those of the gum on the exfoliated FLG sheets. Such a treatment that can be formally regarded as a more complete removal of moisture trapped between graphene sheets, increasing remarkably the graphene adhesion to the hosting matrix. This is a fundamental feature that improves the mechanical flexibility of the composites. According to SEM analysis, FLG@CC retains the mechanical flexibility of the pristine cotton fibers without any appreciable morphology alteration after repeated folding (Figure S2). Finally, a preliminary assessment of the electrical conductivity of FLG@CC was verified using a remote electrical device as shown in Figure 2H.

The Raman spectra of EG and FLG@CC are shown in Figure 3A and demonstrate how the graphitic degree of EG is almost entirely retained after the material exfoliation and FLG coating of the cotton fabric. Figure 3B finally accounts for the 2D Raman component of EG and exfoliated FLG sheets made of a different number of graphene layers. It should be stressed that coatings consist of several FLG sheets stacked one on another, which form a deposit with an average thickness in the range of few tens to hundred nanometers regardless of the coating process used: paint brushing or dip coating. In addition, such coating procedures generate films with poorer physical properties compared to those of a pure graphene sheet because of the presence of defects and irregular stacking of FLG sheets with randomized dimensions and thicknesses. In spite of this, composites prepared with the presented method hold physical properties that are required for their target application. A related work has been recently reported by Novoselov and co-workers for the development of a deicing setup obtained by coating several FLG sheets onto glass-roving fibers through a dip-dry-cure technique.[55] Similar to our e-

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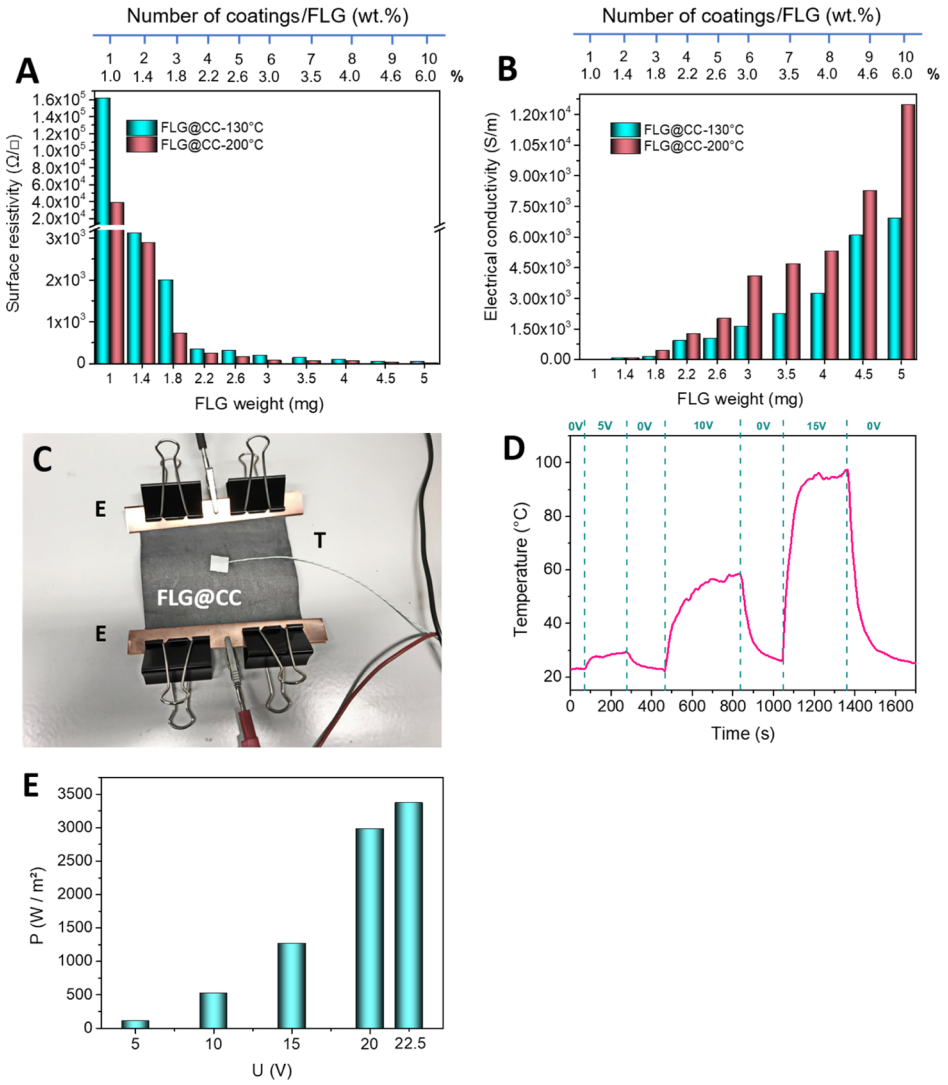

Figure 4. (A) Surface resistivity and (B) electrical conductivity as a function of coating cycles, FLG loading, and heat treatment temperature. (C) Digital photo of the device consisting a FLG@cotton cloth (13 cm × 13 cm) for thermal property measurements: T, planar thermocouple for temperature recording; E, copper electrodes; FLG@CC, cotton cloth coated with 4 wt % of FLG after temperature treatment at 200 °C for 1 h. (D) Responsive surface temperature as a function of the applied voltage. (E) Specific power generated as a function of the applied voltage.

textiles, the coating presented by these authors consisted of several FLG sheets staked one on another to generate a relatively thick electrical conductive film on the glass-roving fibers. It can be inferred that for applications such as surface heaters or electronic circuits for daily-life use, the most important issue does not rely on the production of high-quality graphene sheets but rather on the possibility to generate stable FLG sheet suspensions in the largest and simplest possible way. Catching this target opens the way to the cheap and large-scale production of metal-free, electrically conductive composites. Finally, a coating technique based on the use of FLG sheets similar to that described in the present work deserves a note. In a very recent contribution, Palmieri and Papi have successfully employed FLG sheets as coating materials for the production of personal protective equipment (medical devices) or facemasks to minimize the risk of virus transmission.[56]

XPS results of the pristine cotton fabric are presented in Figures 3C, S3, and S4 and confirm the presence of a large amount of hydroxyl and carbonyl groups on the surface, which confers to the substrate a hydrophilic character. On the other hand, the oxygenated functional group concentration is relatively small in the FLG sample after the exfoliation process according to the survey spectrum, while a large amount of such groups is detected on the cotton fabric surface (Figure S3). Oxygen decreased, while carbon increased on FLG@cotton cloth, which is in good agreement with the surface coating process. The area and position of these components are given in Table S1. Some small amounts of nitrogen and calcium were also observed on the FLG@cotton cloth XPS survey spectrum, which could be attributed to some impurities, issued from the different preparation steps, which were subsequently deposited onto the sample. However, such impurities are expected neither to play a crucial role nor to have any influence on the applications which will be investigated after. The non-deconvoluted C 1s XPS spectra of the different samples are presented in Figure S4 and confirm the large concentration of oxygenated functional groups on the pristine cotton cloth and almost the absence of such groups on the FLG. The C/O surface atomic ratios were calculated from the areas of the XPS peaks and were properly corrected taking into account the atomic sensitivity factors of each element: C/O_{FLG} = 37.3, C/O_{CC} = 2.2, and $C/O_{FLG@CC}$ = 4. All C 1s XPS peaks were

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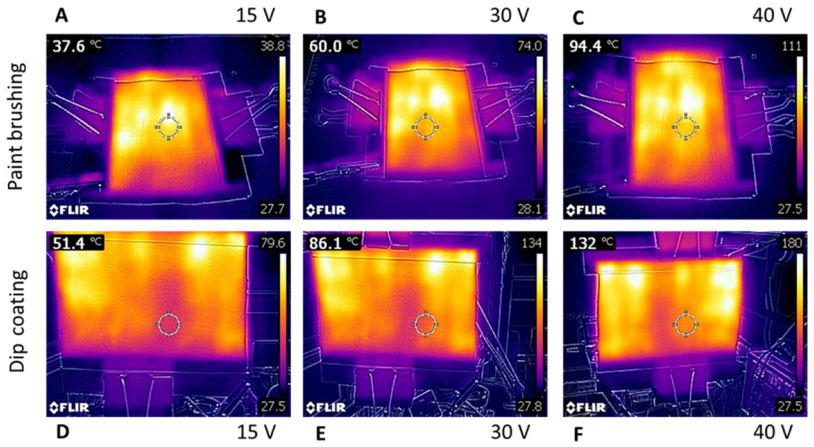

Figure 5. (A–C) Surface temperature measured using a FLIR camera of the FLG@cotton fabric (15 cm × 15 cm) composite, with an FLG loading of 2 wt %, made by paint brushing on one side of the host matrix under different applied voltages. (D–F) Surface temperature measurement using a FLIR camera of FLG@CC made through the dip-coating (both sides) process, which significantly increases the FLG deposit, with an FLG loading of 4.5 wt %, as well as the electrical conductivity, leading to a significant improvement of the surface temperature under the same applied voltage.

analyzed in four components at ca. 284.4 eV (sp^2 C/sp^3 C) and higher-binding-energy (BE) components that correspond to C–OR or C–N, C═O, and O–C═O and a π–π^* transition loss peak at ca. 291 eV (Figure 3C).[57,58] The area and position of these components are given in Table S1. The O 1s peaks were analyzed in two components, that is, a high-BE component corresponding to singly bonded oxygen in carbonyls and esters and a low-BE component attributed to singly bonded oxygen in alcohols, ethers, and epoxies (Figure S5).

The anchorage stability of the FLG@CC composite was also evaluated by immersing the sample in a mixture of ethanol/water (20:80 v/v %), followed by a sonication step for 30 min at rt. The digital photos of the samples before and after sonication are displayed in Figure S6 and confirm the complete retention of FLG in the composite as no trace of any FLG was found in the supernatant solution.

3.2. Electrical Conductivity Measurements of FLG@CC e-Textiles. The surface resistivity (in Ω/□) and electrical conductivity (S/m) of the FLG@CC e-textile after heat treatment at 130 °C for 15 min for each deposition were measured using a four-point probe, and the results are shown in Figure 4A,B. From these data, it can be inferred that a relatively small amount of FLG in the composite (3 wt %) confers the material with a low surface resistivity and a relatively high electrical conductivity (1500 S m^{-1}) that reaches values up to 7000 S m^{-1} for a 6 wt % of the FLG deposit. This electrical conductivity trend is attributed to the good percolation of the FLG sheets within the cotton matrix, a behavior similar to that previously observed in the case of CNT-based composites.[59−61] The increased electrical conductivity of FLG@CC follows the number of coating cycles to which the hosting matrix undergoes, and it is directly attributed to the improvement of FLG sheet percolation. Noteworthily, the overall electrical conductivity of FLG@CC improves as a function of the temperature of the sample drying treatment. For instance, the electrical conductivity of a 6 wt % FLG-coated cotton cloth increases from 7000 to 13,000 S m^{-1} by drying the sample at 200 °C instead of 100 °C. The FLG loading and drying temperature of the composite tune appreciably the ultimate material electrical conductivity. Such a remarkable improvement of electrical conductivity upon the increase of the drying temperature can be explained (as above) by improved FLG sheet self-adhesion and the shrink around the cotton fibers as well as the desorption of moisture or adsorbed compounds on its surface. Indeed, the reduction of moisture trapped between graphene sheets reinforces the van der Waals contributions, hence improving the graphene interlayer connection. Anyway, high-temperature (≥300 °C) treatments should be somehow avoided as they can alter the mechanical resistance of the composite, except for specific applications as a flame-retardant composite (see below). Hence, a compromise between drying temperature, electrical conductivity, and physical properties of the final material is mandatory to be fixed. The possibility of tuning the electrical conductivity of the FLG@CC composites by varying their (thermal) drying treatment represents an interesting tool for modulating the material chemicophysical properties and hence their ultimate technological applications. It should be stressed that such a kind of control is not available for classical metal conductors or conducting polymeric films so far.

The electrical resistance of graphene coatings translates into rapid material heating upon the application of an external potential. Accordingly, the temperature of FLG@CC was monitored using a planar thermocouple applied directly at the surface of the composite (Figure 4C). The results shown in Figure 4D show the high-temperature response of FLG@CC in terms of heating upon the application of an external potential and cooling at the open circuit. In a model experiment, 15 V dc power supply triggers rapid heating of the composite up to 95 °C within 100 s, followed by an even more rapid cooling process when the power supply is switched off. The temperature at the maximum remains relatively stable, which could be due to the 2D structure of the heater with a high heat response. The specific power (W/m^2) calculated as a function of the applied voltage is shown in Figure 4E. Devices featured by such a rapid surface heating/cooling response can find applications in several technological fields such as heated seats or lightweight/high-performance heated surfaces. At odds with traditional bulk heating, surface heating allows to get a homogeneous temperature all over the material surface with a reduced energy impact. Moreover, the generally large surface area and low thickness of the heating phase allow one to reach rapidly the steady-state temperature. These features prompted

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us to explore our FLG@CC composites as highly on/off-responsive surface heaters. The large surface area and low thickness of the heating devices also provide a rapid steady-state temperature.

3.3. Synthesis of FLG@CC e-Textiles as High On/Off-Responsive Surface Heaters. For model e-textiles to be applied as surface heater devices, cotton cloths (225 cm^2, 15 cm × 15 cm) were coated with 2 and 4.5 wt % FLG aqueous solution by paint brushing or dip coating before being dried at 130 °C for 1 h. Afterward, all e-textiles were decorated with two copper electrodes located on opposite sides and a thin layer of Teflon was applied to their external surfaces (on the regions between the two copper electrodes). Teflon coating was used to confer a higher mechanical resistance to the composites. It allowed one to prevent the electrical conductivity loss caused by any accidental heater surface wetting and also for the security of the device. Finally, all e-textiles were heated by means of an external dc power supply.

According to the results, all heated e-textiles reach a steady-state temperature within a few tens of seconds. The target temperature value is a function of the external applied potential (V), and it is constantly maintained till the power supply varies or it is switched off. As shown in Figure 5A−C, for FLG@CC prepared by paint brushing (one single face is FLG- coated with an FLG loading of 2 wt %), the maximum temperature reached by the composite is 94 °C at an applied potential of 40 V dc.

On the other hand, the e-textile prepared by dip coating (both cotton faces are FLG-coated with an overall FLG loading of 4.5 wt %) (Figure 5D−F) reaches a stable surface temperature of about 50 °C already at an applied voltage of 15 V and quickly rises up to 130 °C for an applied potential of 40 V. In addition, a higher FLG loading reduces significantly the time needed to heat the composite to its maximum temperature. While the paint-brushed FLG@CC requires about 30 s to reach 94 °C (an applied potential of 40 V), the double-face-coated FLG@CC reaches 132 °C in less than 20 s. The higher the FLG loading, the higher the surface temperature reached by the composite (for a given applied potential) and the shortest the time needed to get it. Accordingly, the whole matrix-coated e-textile by dip coating can reach higher temperatures in a faster way than its single-face-coated counterpart when the same external potential is applied. Whatever is the method used for the preparation of the e-textile (paint brushing vs dip coating), the surface temperature is remarkably stable and it remains unchanged even after several on/off switching runs, hence indicating that no surface heater deterioration takes place appreciably upon use.

Overall, it is apparent that e-textiles prepared by the dip-coating method provide more homogeneously coated cotton fibers, thus ensuring improved heating efficiency to the composites.

Figure S8 shows an FLG@CC composite with 8 wt % loading by the dip-coating process which displayed a surface temperature of 83 °C under an applied voltage of 22 V. The technique also allows us to produce FLG@CC with variable dimensions depending on the downstream applications. An example of an FLG@CC composite with a dimension of 0.56 m × 0.36 m × 0.0005 m is shown in Figure S9.

3.4. FLG@CC e-Textiles as Metal-Free Thermal Markers. Invisible and flexible markers can find use in several applications both in civil and in military areas. We have shown how the FLG@CC fabric can be used as a thermal marker with a high responsive time at a low energy input. One main advantage of the FLG@CC fabric as a thermal marker is the absence of any metal component. This feature makes our marker highly attractive, sustainable, and safe while preventing any interaction with other detection systems.

Figure 6 illustrates the application of an FLG@CC e-textile as a thermal marker. In this experiment, a series of parallel

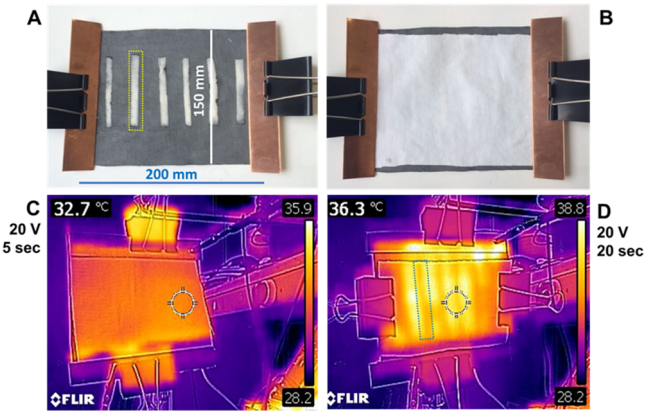

Figure 6. (A) Digital photo of the FLG/resin/CC fabric with a series of uncoated parallel strips, (B) digital photo of the assembly consisting of an FLG/resin/CC fabric and an uncoated CC fabric on the top, playing the role of a mask, and (C,D) corresponding thermal images of the marker as a function of the heating duration under an applied voltage of 20 V. The uncoated area is marked in a box for the sake of clarity.

strips were applied on the conductive fabric (Figure 6A) and a second plain textile with no FLG deposits was used to mask the e-textile surface (Figure 6B). The application of a potential (20 V) to the e-textile led to rapid heating of the hidden surface. The process was followed using a FLIR thermal camera that revealed the underneath fingerprint of the strip-decorated e-textile (Figure 6C,D). Such a technology can also allow the targeted heating of specific areas of the e-textile by playing with patterning of its electrically conductive deposits or by applying different potentials to separate conductive inlets. This will allow the display of messages or images which can be thermally mapped using an IR detector.

It can be inferred that the moderate production costs of FLG@CC fabrics along with the light weight, flexibility, and their rapid thermal response to the applied potentials can make this class of composites highly attractive as thermal markers in several technological areas such as on-site or individual thermal markers in applications nowadays. On a different perspective, an FLG-coated matrix can also be employed to preserve the heat of a body or hot object, hence reducing heat (energy) dispersion to the surrounding environment. To this aim, our FLG paint-brushing technology was successfully applied to a lab nitrile rubber glove (FLG@glove) to simplify the experiment. FLG@glove was straightforwardly prepared by coating the lab glove with a 5 g/L FLG aqueous suspension, followed by thermal stabilization of FLG deposits in an oven at 80 °C for 15 min. The FLG loading measured by weighing the glove before and after FLG coating was amounted to 0.8 wt %. Digital photos of the FLG-coated and uncoated gloves are shown in Figure 7A. The corresponding FLIR thermal images of a coated and uncoated glove are shown in Figure 7B, where

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Figure 7. (A) Digital and (B) FLIR images of the uncoated and FLG-coated gloves, followed by a thermal treatment at 80 °C for 15 min. The experiments were carried out at an ambient temperature of 26 °C. The heat radiation can be clearly visualized on the FLG-coated glove which displays an orange thermal color (left) instead of a bright-yellow color for the uncoated one (right). (C) FLIR image of FLG@glove and (D) uncoated glove with almost 4 °C difference in terms of heat radiation.

it is evident how the FLG coating reduces the body heat loss through IR radiation.

Indeed, FLG@glove displays a lower surface temperature (30.6 °C) (Figure 7C) with a color closest to orange compared to the temperature measured on the plain one (34.3 °C) (Figure 7D) featuring with a color closest to bright yellow. Similar to other literature precedents,[62−64] the FLG surface coating of wearable garments reduces the body heat dissipation (via IR radiation) to the external environment and allows the body to be maintained under thermal comfort conditions. In addition, such equipment can be used to reduce the IR detectable level of radiating hot bodies or objects.

3.5. FLG@CC e-Circuits Prepared by Laser Ablation/Graphitization. Our methodology for the preparation of thin and homogeneous FLG coating of cotton cloths has also been employed in combination with a surface ablation technique for the preparation of e-circuits through laser patterning[65,66] of the graphene deposit. Such a technique allows one to generate electrically conductive tracks with high lateral precision for the cheap production of highly flexible and versatile circuit boards or smart e-textiles. The laser patterning/etching allows one to groove, with an extremely high processing rate (see the Materials and Methods section), the FLG deposit at different depths, thus controlling and modulating the track electrical resistance without damaging the host cotton matrix. In addition, it is worthy to note that using the laser technique, the patterns could be prepared with high lateral precision as well as with a high production speed in order to cope with industrial development and use.

In a model experiment, an FLG@CC was prepared by paint-brushing one face of a cotton cloth (ca. 16 cm^2) with an FLG aqueous solution (5 g/L). The graphene deposit was repeated twice, and FLG@CC was dried in an oven at 130 °C for 2 h after each deposit. The FLG loading of the as-prepared composite was 1.3 wt %, and its surface showed a mean electrical resistance of 50 Ω (Figure 8A). A laser was used to selectively remove a part of the FLG deposit, hence creating e-textile areas with a high lateral resolution and variable electrical resistance. Figure 8B illustrates an example where complete FLG removal was accomplished locally by laser ablation without damaging the cotton matrix underneath. As illustrated in the figure, the laser-treated areas present a virtually infinite electrical resistance. Similar to our previous report on graphene-coated paper sheets,[65] the laser beam can also be used to drive heat locally on the FLG deposits. This approach does not aim at removing FLG layers but is used to increase their graphitization degree through laser surface irradiation, hence changing their ultimate electrical conductivity. By this way, the areas at the FLG@CC surface featured by variable

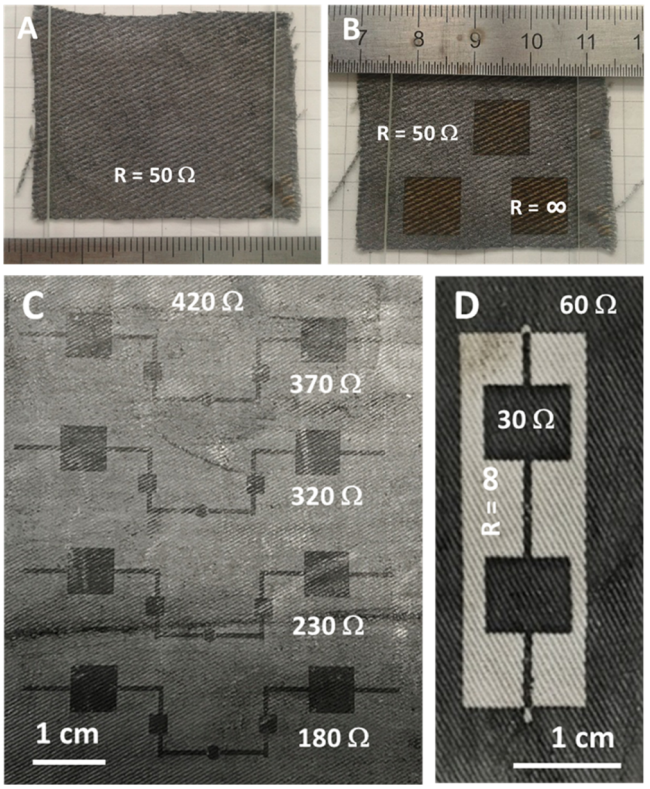

Figure 8. (A) Pristine FLG/cotton composite with an average surface resistance of 50 ± 5 Ω. (B) Same FLG/cotton composite with three square areas which were etched by laser ablation showing an infinite resistance value compared to that of the untreated area. (C) Digital photo of different connectors with reducing resistance produced on FLG@CC after laser patterning and graphitization with different durations. (D) Digital photo of the same FLG@CC after patterning and local graphitization for modifying the resistance of the different areas with a high lateral resolution.

electrical resistances (from 420 down to 180 Ω) have been created (Figure 8C). As shown in Figure 8C, the higher the graphitization degree, the lower the local electrical resistance of the treated e-textile area and the darker its color.

Figure 8D illustrates the combination of the two laser treatments: laser etching (to increase the resistance of the area) and graphitization (to decrease the resistance of the area). By adjusting the output laser power, different electrical connection paths featured by variable electrical resistances can be generated, thus giving rise to real flexible electronic circuits with a high lateral resolution. In addition, all laser treatments can be accomplished while preserving the whole integrity of the cotton matrix underneath.

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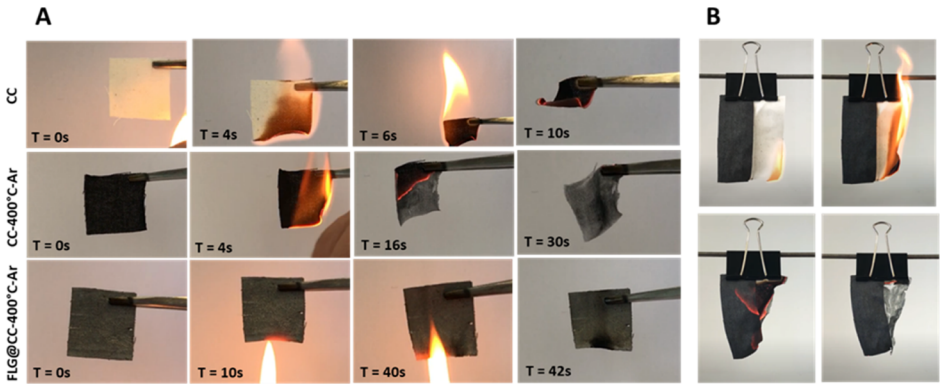

Figure 9. (A) Digital photos of the combustion behavior of the different materials in contact with a direct flame. CC: pristine cotton cloth without any treatment; CC-400°C-Ar: cotton cloth after heat treatment under argon flow at 400 °C for 1 h; FLG@CC-400°C-Ar: cotton cloth after heat treatment under argon at 400 °C for 1 h, followed by two dip-coating impregnations in an aqueous solution of FLG and oven drying at 150 °C for 30 min after each impregnation. (B) Example of the inflammable character of FLG@CC-400°C-Ar compared to that of the pristine uncoated cotton cloth stapled alongside, which steadily burns within a few seconds after contacting with a flame.

3.6. FLG@CC as Flame-Retardant e-Textiles. FLG coating of cotton cloths was finally investigated to prevent the material ignition and combustion upon its direct exposure to open flames. To this aim, FLG@CC was prepared by dip coating as follows: the cotton matrix was preliminarily treated under an inert atmosphere (Ar) at 400 °C for 1 h to remove as much as possible the oxygenated functional groups from the fiber matrix before being soaked in a 5 g/L FLG aqueous suspension and dried in an oven at 200 °C for 30 min.

The procedure was repeated twice to get a homogeneous coating of the cotton fibers with a final FLG loading close to 3 wt %. The as-prepared dark-gray composite was exposed to an open flame, and the results are shown in Figure 9A. According to this digital sequence, the plain cotton matrix was almost entirely burned within a few seconds (10 s). The same after heat treatment under argon at 400 °C for 1 h (CC-400°C-Ar) displays a slower combustion, mostly through the smoldering mode, and becomes completely consumed after 30 s. The smoldering combustion of the sample could be explained by the absence of oxygenated functional groups which constituted the cellulose fibers after heat treatment at 400 °C. However, the remaining cotton fibers still display high affinity with oxygen and thus get consumed with time because of their low thermal stability, being totally consumed after 30 s since their contact with a direct flame. On the other hand, FLG@CC-400°C-Ar showed important flame-retardant properties, maintaining its original shape almost unaltered even after prolonged contact (40 s) with an open flame. Despite the observed glowing of the region directly in contact with the flame (due to heat absorption by FLG deposits), no material combustion took place. This flame-retardant behavior can be ascribed to the homogeneous FLG coating of cotton fibers that prevents oxygen diffusion through the textile matrix, hence conferring the composite with an extremely high oxidation resistance. These results can be attributed to the complete coverage of the cotton cloth fibers by a layer of FLG with high oxidation resistance that prevents oxygen diffusion to the inner fibers, resulting in a barrier for the flammable diffusion process.

In another experiment, the FLG@CC-400°C-Ar sample was stapled with an untreated/uncoated CC sample (Figure 9B). The CC sample was put in contact with a flame, and a series of snapshots were taken as a function of time to highlight the inflammable character of the graphene-coated cotton cloth. FLG@CC-400°C-Ar displays significant glowing, but no combustion occurred, which confirms the high flame resistance of the composite. It is thus expected that such FLG@CC can be efficiently used as a lightweight and flexible flame barrier retardant or even a flame inhibitor for the protection of fragile structures or to protect people from flame, that is, firemen or military applications. The easy preparation method also renders FLG@CC a cost-effective material for such challenging applications.

Another example of the high flame resistance of the FLG@CC-400°C-Ar composite is shown in Figure S10. In such an example, FLG@CC-400°C-Ar was used as an uninflammable hosting device for melting metal, that is, stain. The preformed FLG@CC composite can thus be used as a mold for making a controlled shaped metal with a low melting point.

4. CONCLUSIONS

Flexible composites consisting of an FLG-decorated cotton fabric with high stability and tunable electrical conductivity for use as flexible surface heaters have been synthesized. The composites displayed a high thermal response and stability against the heating and shutdown processes and confirmed their high potential for the targeted applications in the field of e-textiles. The excellent electrical and thermal properties as well as the high degree of entanglement of FLG provide a fast response, stability, and a high surface temperature even at low input power (small applied voltage). The as-synthesized composite could also be efficiently used as a metal-free thermal marker for stationary or mobile sources in both civilian and military applications. Complete flexible electronic circuits with various resistance values and connectivities can be made on one-side-coated FLG@cotton cloth using laser patterning and local graphitization without damaging the cotton cloth host substrate underneath. The low-cost production and the high performance observed render the FLG@CC fabric composite competitive compared to those using silver or metal nanoparticles available in the market. The obtained results demonstrate that thin-layer-coated FLG on a cotton cloth could be a promising candidate for low-cost wearable, flexible, and stretchable heaters under low applied voltages. These composites can be further used in other applications such as lightweight/high-performance metal-free IR reflectors to reduce the heat loss through IR radiation to the ambient

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environment. Finally, the coating of a thermally treated cotton cloth with a graphene layer also effectively prevents the burning of the composite even after prolonged contact with a flame, which renders such a composite highly interesting for being used as a flame barrier to protect sensitive structures or people from flame propagation. Work is ongoing to investigate the use of such composites as dual-surface materials, that is, hydrophilic cotton fibers coated with a graphene layer as heat absorbers, for the water desalination process, or as graphene-coated polymer fibers, with a highly rough surface and long-term stability, to be used as electrical filters with a high heat on/off triggering system for trapping and for inactivating living matter such as viruses or bacteria.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.0c01861.

Digital photos and contact angle of the water droplet on the surface of the FLG@CC composites after coating, followed by different thermal treatments; digital and SEM images of the FLG@CC composites after the repeated folding process; XPS survey spectra of pristine FLG, the CC, and theFLG@CC composite; XPS C 1s spectra of FLG, the CC, and FLG@CC; high-resolution XPS O 1s spectra of FLG, the CC, and FLG@CC; digital photos of the FLG@CC composite immersed inside a mixture of ethanol/water (20:80 v/v %) and the same after sonication for 30 min; thermal behavior of FLG@CC (8 wt % loading) under different applied voltages; digital photo of the FLG@CC composites with large dimensions produced through the dip-coating process with an FLG aqueous solution of 10 g L^{-1}; experiments evidencing the high oxidative resistance of the FLG@CC composites; and area and position of C 1s peak components of the three samples (PDF)

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Author Contributions

H.B.: conceptualization, investigation, writing—original draft and editing, and visualization. L.T.-P.: investigation. V.P.: investigation and editing. C.S.: conceptualization and investigation. S.P.: investigation. A.B.: investigation and writing—original draft. Y.L.: investigation. L.N.-D.: conceptualization. G.G.: conceptualization and writing—original draft. C.P.-H.: conceptualization, supervision, writing—original draft and editing, and project administration.

Notes

The authors declare no competing financial interest.

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