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A low voltage, flexible, graphene-based electrothermal heater for wearable electronics and localized heating applications

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Abstract

Recent years have seen a rapid increase in the level of sophistication in modern day devices which has given rise to the demand for better performance in all of their components, one of which is the heating element. Two excellent approaches to this need would be to improve the materials from which these Joule's heating elements are made and the other to design improved heater geometries for best temperature distribution. In this paper, we discuss a high performance electrothermal heater prepared from laser reduced graphene oxide (LrGO) deposited on Polyethylene Terephthalate (PET) flexible Substrate. The surface morphology and structural properties of the prepared LrGO films were investigated by means of Scanning Electron Microcopy (SEM), X-Ray Diffraction (XRD) and Raman Spectroscopy (RS). Electrothermal (ET) responses of the fabricated electrothermal heaters to different driving DC voltages were studied by Infrared thermal Imagery. An electrothermal heater with a low Sheet resistance of ~ 52 Ω/sq was fabricated and it can attained a steady state temperature of up to 135 °C in only 10 seconds when a low voltage of 9 V was applied. A finite Element model (FEM) was prepared for this heater which agreed well with the experimental results. Power consumption for this heater is as low as 0.389 W/cm^2, making it a suitable candidate for energy-saving applications such as wearable electronic.

Keywords: Flexible Electronics; Photothermal Reduction; Graphene Oxide, Wearable, Low Voltage; Electrothermal heaters

1. Introduction

Electrothermal heating commonly referred to as joule heating is the transduction of electrical energy into heat energy. This physical phenomenon finds its place in a wide range of electronic applications[1,2]. With the rapid advancements in modern technology, it has become more pertinent to find cheaper ways to prepare flexible heaters for wearable applications. Up until now, we only find in the market, the traditional heating materials such as Ferro-Chromium based alloys, nichrome, molybdenum disilicide glass, carbon fiber and etched foils which all suffer major setbacks such as heavy weight and/or low heating efficiency along with low flexibility[3–5]. Fairly recently, indium tin oxide films have been introduced into the market[6]. These films are

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highly transparent and conductive but suffer low flexibility and could potentially become very expensive as the base materials, Tin and Indium, come from non-renewable reserves.

For wearable applications such as hot jackets and hot packs, features such as electrical safety, flexibility, high transduction efficiency, light weight and low cost are highly needed and none of the aforementioned heating materials satisfy all these conditions[6]. This has sparked great research attention in this area as the technical applications for this heating phenomenon are endless.

In attempt to meet these needs, metal nanostructured heaters were proposed but these heaters adhere very poorly to flexible polymer substrates and their performance tend to degrade with time due to oxidation of the particle junctions. Nanostructures from more inert metals such as Silver and Gold were proposed[5]. However, the high cost of these heaters makes them unfavorable for casual use. Heaters have also been prepared based on carbon nanotubes (CNTs) [7,8]. Although CNT films have excellent transduction efficiencies in high concentrations, they exhibit poor adhesion to flexible substrates[6]. Stretchable heater have also been prepared from nanocomposites between conductive polymers such PEDOT:PSS and waterborne poly-urethane (WPU) with reduced graphene oxide. These heaters showed great bendability, stretchability and high steady state temperatures but require longer response time due to inferior conductivity in comparison to graphene and CNT[9]. Low-cost heaters have been prepared by direct laser induction of Polyimide sheets but this heater need very long response time and have relatively low conductivity[10]. Nano composites of GO and silver nanoparticles have been prepared by laser reduction. This films showed great transduction efficiencies but used large concentration of the silver nanoparticles rendering them expensive. [4]

Laser scribing presents a facile, low-cost method for the preparation RGO based flexible thin films. Therefore, in our attempts to fill the gap still present in the research, we demonstrate a simple laser reduction technique to produce low-cost, flexible and highly efficient electrothermal heating elements from graphene oxide films prepared by Hummer's method. We also built a FEM which gave a close approximation of the electrothermal behavior observed in the LrGO heater and can thus be extended to study the behavior LrGO in high end applications such as defoggers and wearable electronics

2. Method

Graphite Oxide flakes were prepared using the modified Hummer method from graphite powder according to the procedure in our previous work.[11,12]. A few layer GO solution with concentration of 4mg/ml was prepared by dissolving graphite oxide flakes in distilled water by bath sonication for 1 hr followed by mild sonication with a probe ultrasonication device for another 2 h. A minute amount non-exfoliated graphite oxide was removed from solution by centrifugation at 3000 rpm for 30 minutes. The GO solution (0.254 ml/cm2) was drop casted on plasma-treated PET. An adhesive tape was used to select the PET exposed area, and GO film was allowed to dry under ambient conditions for 48 hrs.

The laser reduction process for GO films was performed by subjecting the as-prepared films to same amount of CO2 laser energy with a 10.6μm wavelength (Universal laser system, VLS 2.30). An area of 30 × 20 mm2 was scanned into the GO film to produce a LrGO) Film. LrGO electrothermal heater with final effective area of 20 × 20 mm2 was obtained by applying copper conducting tape and silver paste at the edges of the reduced area, as shown in Fig. 1b. The terminals of a DC power supply were attached to the two copper terminals of the LrGO heater and variable DC voltages were applied across these terminals. The temperature measurements were recorded on the NEC TH9260 Infrared camera and temperature changes against time were recorded.

A 3D Finite Element Analysis was used to study the electrothermal behavior of the LrGO film. Acommercial FE simulation tool used to build a 3D model of the heater as seen in Fig. 2b where the effective heating area of the film was 20mm by 20mm with a thickness of 50 μm laid upon of PET substrate of thickness 100 μm. 5 mm copper strips were used as electrical connect and for the sake of simplicity a 4-node square element was used for the numerical modeling of every section. The density of the mesh was later increased to enhance accuracy of the results. We assumed anisotropic behavior in the thermal and electrical behavior of the LrGO film because of the expectation of randomness in the orientation of the GO sheets during deposition and a further increase in this randomness during laser reduction. The material properties of LrGO and PET used can be seen in Table 1 of the supplementary document. For air convection coefficient we used 120 W/mK, and to mimic experimental conditions, we loaded the electrical circuit with an internal resistance of 1.5 Ω. The unpatterned FEM was validated with experimental data. The study will be extended to a patterned film as shown in Fig 2f and other applications. The analysis was repeated and the results are as presented in the Fig. 2e

3. Results and Discussion

3.1 Structural Characterization

In attempts to understand the microstructure of the prepared GO and LrGO thin films, XRD analyses were conducted with the Shimadzu labX 6100, RS with the Senterra II, and SEM images were obtained with the JEOL JSM 6010-LV for morphological studies.

The typical sheet-like morphology of GO can be observed from the SEM micrograph of GO film shown in Fig. 1a. This planar structure is maintained even after performing laser reduction process as seen clearly from Fig 1b, which is a key factor contributing positively to the conductivity of the film. Fig. 1c shows the magnified image of the laser scribed surface of the LrGO film. Despite the smooth appearance of the film in Fig. 1f Graphene sheets can still be noticed flaking off the film alongside cracks and voids in Fig 1c which are detrimental to the conductivity of the film.

The Raman shift in Fig. 1d shows the typical drop in overall intensity after laser reduction was observed. The bond stretch at 1330.5 represents vibration coming from the defects in the crystal lattice typically known as the D band. The stretch observed at 1578 cm-1 represents vibrations from the sp^2 C-C bond locked in the hexagonal Carbon ring, and typically known and the G band. We also observe the second order resonation of the D and G bands indicated as the D+G band. After laser reduction, I_D/I_G ratio increased from 0.94 to 0.98, along with reduction in the widths of all the bands. As previously discovered, the increase in the ID/IG ratio indicates an increase in the disordering of the graphitic structures due to the removal of oxygen functional groups without the restoration of sp^2 domains [13]. Also, the 2D band at 2860 cm^{-1} appears and it signifies a reduction in lattice defects with respect to GO despite the increase in the I_D/I_G ratio[14]. These obtained results would explain the sharp increase in conductivity of the due to laser reduction since as the removal of a great majority of the oxygen groups is a closely followed by the restoration of some of sp^2 domains which do not all need to be locked in a complete hexagonal ring in order to contribute to the intensity of the G-Band [16].

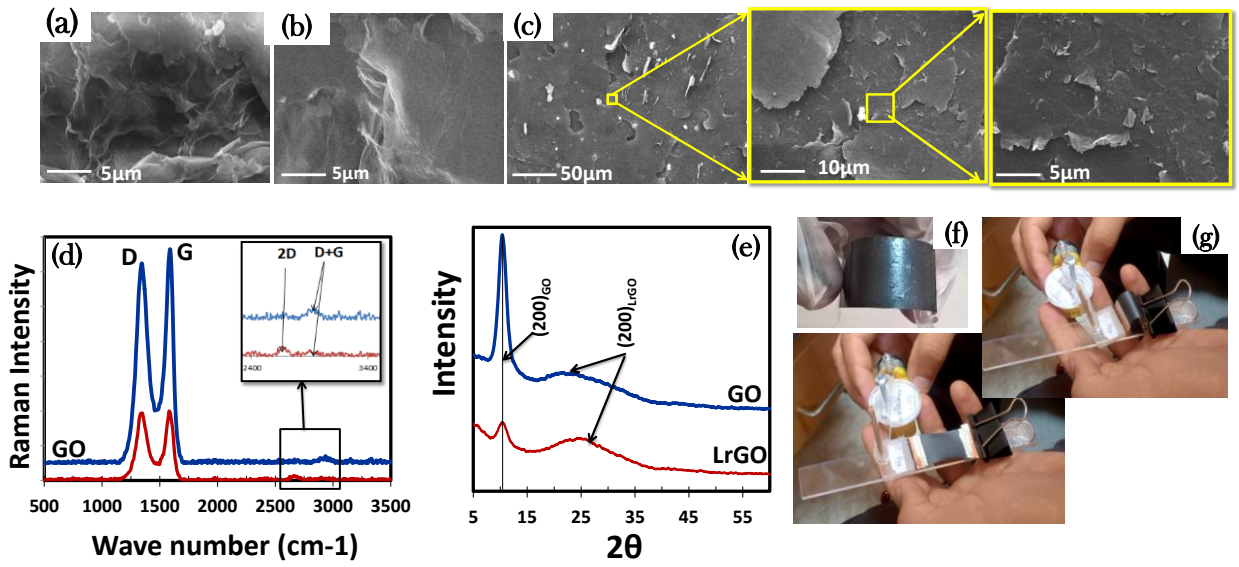

Fig.1. Structural Analysis of GO and LrGO:(a) SEM Images of GO, (b) SEM Images of LrGO Flakes, (c)SEM images of the Laser Scribed Surface (d) Raman Shifts of GO and LrGO, (e) XRD pattern of GO and LrGO (f) Image of LrGO film (g) Flexibility test set up

In the XRD plot in Fig. 1 e we observed one major peak at a position of 9.6º in the GO pattern which corresponds to the (002) plane. The interlayer spacing of GO, d, was calculated using Bragg's law ($2d\sin\Theta = n\lambda$) to be 0.9213 nm. After laser reduction however we observe the (001) peak at the 2θ angle of 16.6º and the (002) the 22.38º. From this, the interlayer distance of LrGO was calculated to be 0.392 nm. This drop in interlayer distance is attributed to loss of complex oxygen functional groups between the layers of the GO.[17] However, this is still 12% larger than that of graphite, implying that even after laser reduction, some oxygen groups are left between the sheets. This agrees well with observations in the FT-IR spectra in previous works which

reveal that the epoxy groups persist on even after laser reduction[16, 19]. The widening of the (001) peak after laser reduction is indicative of comparatively longer range order in the sp^2 domain with respect to GO.[20]

3.2 Electrical Characterization of the LrGO film

The FEM showed a good Voltage distribution (Fig. 2g) across the heater which is important for good electrothermal behavior. The oxygen groups introduced between graphite layers during Chemical exfoliation make GO electrically insulating[21,22]. After laser reduction, a large drop in sheet resistance was recorded to stand at 52Ω/sq. The thickness of GO and LrGO were measured under SEM which gave 12 µm and 58 µm, respectively. The volume expansion may be attributed to photothermal nature of the reduction mechanism associated with Long wavelength lasers such as the 10.6 µm CO_2 laser[18,23]. The conductivity of LrGO was calculated to be 332 S/m. This volume expansion caused by the CO_2 Laser beam makes it difficult for very high conductivities to be achieved since the film is abounding in with micrometer-scale pores, cracks, and inter-sheet voids[23]. Much higher conductivities have already been achieved with shorter wavelength laser such as the diode laser (532 nm) with which 3600 S/m conductivity was achieved[24], Femtosecond laser (790 nm) – 2.56 x104 S/m[25] and the KrF excimer laser (248 nm) – 1.8 x 104 S/m[26], because a more efficient photochemical reduction takes place with shorter wavelengths.

We demonstrate however, a facile, tunable method by which flexible heaters could be prepared at very low start-up and running costs, with a commercial CO^2 laser engraving machine.

3.3 Electrothermal Measurements

In the FEM, when potential difference of 9V was applied across the copper terminals, the simulated output was a good temperature distribution and quick ET response of about 13 seconds. The heater returned to room temperature very rapidly when the voltage was removed. The FEM agreed well with the experimental results as seen in Fig. 2d and can thus be used for further analysis for commercial applications such as defoggers and hot clothes. Fig. 2e equally reveals a great progression in the temperature distribution from the time the voltage is applied until 5 s after the potential difference is switched off.

During Joule heating the Temperature rise (ΔT) is directly proportional to the electrical power consumed , P which is related to driving voltage V and Resistance R by $P=V^2/R$. [6] Film preparation was optimized to achieve the lowest possible resistance so as to achieve maximum temperature rise at desired driving voltages.

A direct current was applied to the copper terminals of the heaters and thermal responses to different driving voltages were recorded. When a specific voltage was applied, we observed a rapid temperature rise of the entire film until it reached a saturation temperature after 10 s. This temperature was held steady until the applied voltage was removed whence the temperature drops rapidly to the room temperature. An increase in steady state temperature was observed as driving voltage was increased(Fig 2a). This great performance owes partly to fact that the low sheet resistance of the LrGO film allowed for a higher transduction efficiency of electrical energy to Joule Heat[3], and the high thermal conductivity of the LrGO allows for very quick distribution of the generated heat.

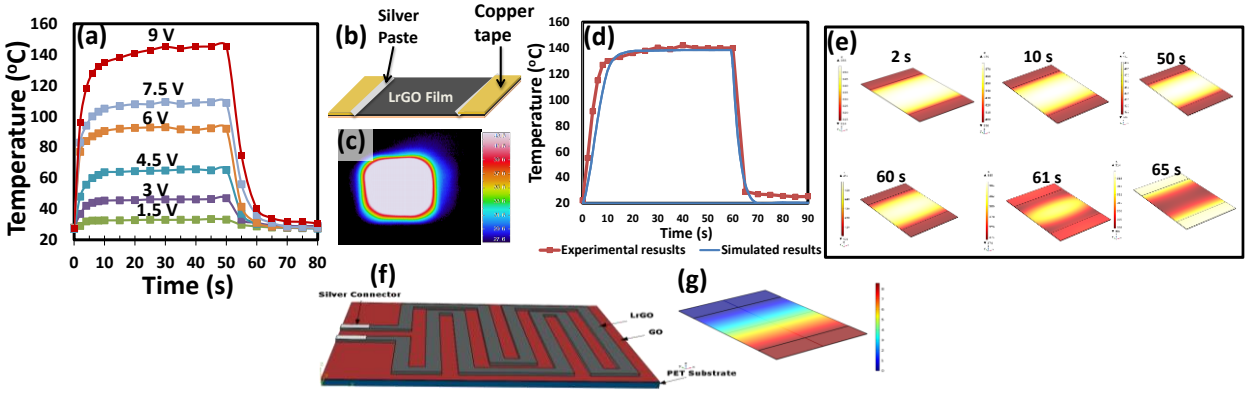

Fig 2. Electrothermal Analysis Result(a) Electrothermal response to different voltages, (b) Heater Schematic (c) Thermal Image of film at 9 V applied voltage(d) Validation of FEM with Experimental Data (e) Progression of temperature distribution with time in FEM (f) Heater Schematic with rectangular Pattern (g) Voltage distribution at 60 s in FEM

The thermal images in Fig. 2c reveal an excellent temperature distribution across the film with over 95% of the film at over 90% of the steady state temperature. This great performance can be explained by the good uniformity in the prepared film and the also the high thermal conductivity of the Graphene sheets in the LrGO film.

The film was deposited on a flexible PET substrate and good adhesion to the substrate was achieved giving the film excellent bendability (Fig 1g). thus making it suitable for flexible applications like hot jackets and hot pack for the treatment of arthritis where low voltages are needed but transparency is not. At only 3V of driving voltage steady state temperature of 45℃ was reached making our heater good enough for low energy hot clothing. For the treatment of Arthritis temperature of about 41 to77oC needed to be maintained for long periods and hurting joints of a patient to provide pain relief and comfort during thermotherapy[27,28]. The LrGO heater can do the job with less than 5 V of driving voltage. This will allow for power savings needed for long term portable use without the need for a battery recharge. Even better performance can be achieved by doping the GO film with elements such as Nitrogen, Sulfur and Boron[29], or preparing nanocomposite films with Silver[4] of gold Nano particles. We intend to explore these avenues in future work. One limitation to this study would be the low glass transition temperature of the PET substrate used (60-85 ℃). This renders this LrGO film heater only suitable for applications with working temperatures below 60℃. This can however be overcome by finding solutions to do the GO deposition and reduction on more thermally stable substrates like Polyimide and PDMS despite the adhesion problems they pose. We hope to achieve this in subsequent studies.

4. Conclusion

In the course of this study, we demonstrated that low-cost flexible thin film graphene based heaters can be fabricated on PET substrate via facile techniques like drop casting and laser reduction. A low sheet resistance of 52 Ω/sq. was achieved thin the 10.6 μm CO2 Laser despite the effect of volume expansion which enable us to achieve a thermal response of up to 135 ℃ at only 9V driving Voltage. This heater is suitable for wearable applications such as hot clothing and hot packs in which safety, flexibility, thermal stability and power savings is needed.

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