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Femtosecond laser micromachining of polylactic acid/graphene composites for designing interdigitated microelectrodes for sensor applications

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ABSTRACT

There is an increasing interest in the last years towards electronic applications of graphene-based materials and devices fabricated from patterning techniques, with the ultimate goal of high performance and temporal resolution. Laser micromachining using femtosecond pulses is an attractive methodology to integrate graphene-based materials into functional devices as it allows changes to the focal volume with a submicrometer spatial resolution due to the efficient nonlinear nature of the absorption, yielding rapid prototyping for innovative applications. We present here the patterning of PLA-graphene films spin-coated on a glass substrate using a fs-laser at moderate pulse energies to fabricate interdigitated electrodes having a minimum spatial resolution of 5 μm. Raman spectroscopy of the PLA-graphene films indicated the presence of multilayered graphene fibers. Subsequently, the PLA-graphene films were micromachined using a femtosecond laser oscillator delivering 50-fs pulses and 800 nm, where the pulse energy and scanning speed was varied in order to determine the optimum irradiation parameters (16 nJ and 100 μm/s) to the fabrication of microstructures. The micromachined patterns were characterized by optical microscopy and submitted to electrical measurements in liquid samples, clearly distinguishing all tastes tested. Our results confirm the femtosecond laser micromachining technique as an interesting approach to efficiently pattern PLA-graphene filaments with high precision and minimal mechanical defects, allowing the easy fabrication of interdigitated structures and an alternative method to those produced by conventional photolithography.

1. Introduction

Graphene is a form of carbon with a particular two-dimensional hexagonal structure that has attracted scientific interest in recent years due to its unique optical [1,2], electronic [3] and mechanical properties [4]. Graphene-based materials have also been extensively investigated as potential materials to be applied in photodetectors [5], solar cells [6], sensors [7–9], polymer composites [10], and transparent electrodes [11]. In addition to its outstanding electrical properties, multilayer graphene has also been investigated in second harmonic generation optical processes [12], with considerable efforts recently employed to implement graphene or graphene-based composites in electronic devices [13,14].

Application of graphene-based materials in micro- and nanoelectronics often requires complex patterning methods [13–15] such as photolithography [16] and electron beam lithography [17]. In this direction, ultra-short laser patterning is an interesting methodology to structure graphene [18–20] once it provides intensities high enough to induce nonlinear optical processes in materials. As a consequence of such nonlinear interaction, ablation, phase transition or permanent structural changes can occur [21–23], clearly demonstrating that femtosecond lasers have created a new platform for processing materials with high precision fabrication at the micro- and nanoscale [24,25].

Femtosecond laser micromachining has been shown to be an important material's processing tool, capable of generating complex geometries with no need of photomasks and clean rooms, enabling the processing of materials in distinct atmospheres, as well as in a vacuum. Some advantages provided by femtosecond

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lasers micromachining are the efficient and high processing speed, limited thermal effects and damage to the substrate [26].

In this paper, we used femtosecond laser micromachining for patterning composite graphene films produced from conductive graphene/Polylactic acid (PLA) filaments. Graphene is well dispersed in PLA, which serves as a matrix material to improve the molding/extrusion [27]. At the same time, PLA is a biodegradable and biocompatible polymer, being, therefore, a good option for biosensor applications. Graphene has a strong bonding force with PLA [27], offering high conductivity and excellent mechanical properties to the polymeric material, which are interesting to design structures for applications in devices, electronics, and sensors. Raman spectroscopy was used to characterize both PLA-graphene pellets and films. By optical microscopy, we studied the influence of pulse energy and scanning speed on the produced features in order to determine the optimum irradiation parameters and the energy threshold for material removal. Later, two graphene patterns were laser fabricated - lines and interdigitated lines with width ranging from 5 to 40 μm - and finally, the electrical properties of both were characterized aiming applications of the graphene/PLA interdigitated lines as electrodes for an impedimetric sensor.

2. Experimental procedure

The PLA-graphene filament is a commercial composite material with polylactic acid (PLA) as the polymeric matrix and a dispersion of graphene fibers into it to provide improved mechanical and electrical properties. It was purchased from BlackMagic3D [28] as a filament, being composed of 90 wt% PLA and 10 wt% of graphene fibers [29,30].

Thin films were prepared by suspending the conductive graphene/Polylactic acid (PLA) filaments in chloroform to a final concentration of 50 mg mL^{-1}. Such suspension was spin-coated on a glass substrate at room temperature at 1200 rpm, providing 10 μm thick films. Raman spectroscopy was used to characterize the PLA-graphene films. The Raman spectra were obtained with a LabRAM micro Raman system, using a solid-state laser with a frequency of 532 nm (2.32 eV) and low power (~6 mW), to avoid thermal effects that could modify the graphene lattice.

The as-deposited films were micromachined using a Ti:Sapphire femtosecond laser oscillator, delivering 50-fs pulses centered at 800 nm with a repetition rate of 5 MHz. Micromachining was carried out by focusing the laser beam onto the sample surface with a microscope objective (0.65 NA). The position of the sample was controlled by means of an *xyz* translational stage that was moved at a constant speed, allowing the microfabrication of arbitrary geometries. The entire process was monitored using a CCD camera aligned to the microscope objective. The pulse energy and scanning speed were varied in the range of 8–28 nJ and 20–100 μm/s, respectively, in order to determine the optimum irradiation parameters for micromachining. To test the application of the PLA-graphene films as sensors, two graphene patterns were fabricated; lines with different widths and interdigitated lines. The x-y stage allows different geometries of the interdigitated lines enabling different electrode design as well as the pulse energy applied allows for distinct line separations.

The electrical properties of the micromachined PLA-graphene were measured with a Keithley 6487 Picoammeter scanning a DC voltage from −3 V to 3 V. The picoammeter was coupled to a probe station (Lab Assistant from SemiProbe) to better align the samples with the micro contacts.

As a proof of concept, two electronic-tongue (e-tongue) sensors were developed to distinguish three basic tastes, namely sweet, salt and bitter. Briefly, e-tongue devices are capacitive-based sensors designed to distinguish complex liquid systems. The device is established by integrating the sensing units, acting as the human papillae. The impedance of the system is measured and the response is analyzed to cluster similar behavior and distinguish different liquids. The micromachined electrodes were used as the sensing units as-prepared exploiting different interdigitated electrodes (IDEs) geometries to create the sensing units [31,32]. They were immersed in four different solutions viz. H_2O, 1 mM NaCl, 1 mM Sucrose, and 1 mM HCl, all of them prepared with deionized water. Electrical impedance measurements were carried out in a Solarton 1260A impedance analyzer coupled to a 1296 dielectric interface. Measurements were performed at room temperature using sinusoidal wave voltage with 50 mV amplitude, without dc bias, and in the frequency range 1 Hz–1 MHz. The impedance data acquisition started 5 min after the electrodes were left soaking in the prepared solutions in order to achieve the stabilization of the electrical double-layer at the electrode/electrolyte interface. All measurements were performed in triplicate with the electrodes washed in deionized water after each measurement, enabling the reuse of the same IDE in all liquid samples. The collected data were treated using Principal Component Analysis (PCA) [33], which allows a reduction in the dimensionality of the data without losing important information. The PCA plot shows the maximized variance of the samples allowing their discrimination at 1 mM.

3. Results and discussion

Fig. 1 displays the Raman spectra for the PLA-graphene filaments (black line) and spin-coated PLA-graphene films (gray line). Both spectra exhibit the characteristic D, G, D’ and 2D graphene peaks in the region between 1000 and 3000 cm^{-1}. The G-peak at ~1580 cm^{-1} corresponds to the E_{2g} phonon at the Brillouin zone center from carbon atoms vibrations [34,35]. The D-peak at ~1325 cm^{-1} is attributed to the breathing modes of six-atom rings, which requires a defect for its activation [36]. The D’ peak at ~1620 cm^{-1} is very common for this type of material and is related to the double resonance process [37]. The 2D peak is a second order overtone of a different plane vibration and can be used to determine the number of graphene layers [38], specifically the intensity ratio between the G (I_G) and 2D (I_{2D}) bands. From the data presented in Fig. 1 it was obtained I_{2D}/I_G ratios of 0.55 and 0.59 for the PLA-graphene filaments and PLA-graphene spin-coated film

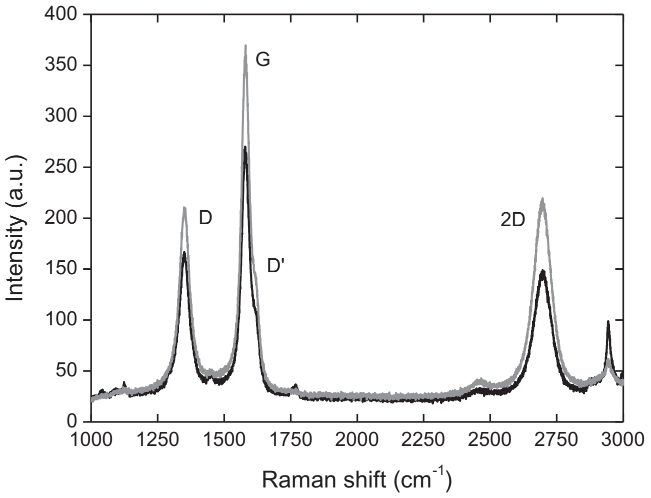

Fig. 1. Raman spectra for the PLA-graphene filaments (black line) and PLA-graphene spin-coated thin film (gray line) obtained with a laser excitation source at 532 nm (2.32 eV). The curves display the main Raman shift features of graphene, including the G, D, D’ and 2D peaks.