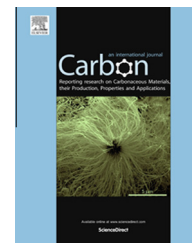


Available at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/carbon](http://www.elsevier.com/locate/carbon)

# Large area graphene and graphene oxide patterning and nanographene fabrication by one-step lithography



Esteban Climent-Pascual<sup>a</sup>, Miguel García-Vélez<sup>b</sup>, Ángel Luis Álvarez<sup>b</sup>, Carmen Coya<sup>b,\*</sup>, Carmen Munuera<sup>a</sup>, Xavier Díez-Betriu<sup>a</sup>, Mar García-Hernández<sup>a</sup>, Alicia de Andrés<sup>a,\*</sup>

<sup>a</sup> Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, Madrid 28049, Spain

<sup>b</sup> Escuela Técnica Superior de Ingeniería de Telecomunicación (ETSIT), Universidad Rey Juan Carlos, 28933 Madrid, Spain

## ARTICLE INFO

### Article history:

Received 10 December 2014

Accepted 2 April 2015

Available online 10 April 2015

## ABSTRACT

A cheap and green technology based on electro-erosion, performed at room conditions and scalable to large area ( $\text{cm}^2$ ) is demonstrated for structuring graphene and graphene oxide films on any substrate. This one-step technique based on electrical discharges produced by a direct current voltage source competes favorably with laser patterning. The threshold voltage for complete graphene elimination as determined by Raman mapping is around 20 V. At low relative humidity conditions (30%) the transformation to graphene oxide is also detected for operating voltages above 40 V, the oxidation being probably mediated by the residual adsorbed water at the surface. We also show the close correlation of atomic force microscopy (AFM) phase images with the modified graphene characteristics while AFM topographic images are dominated by extrinsic aspects. The use of a spring probe relaxes the requirement of precision for the tip-sample distance and sample flatness to around  $10\ \mu\text{m}$  which is very convenient for large scale applications. Furthermore, this technique allows the formation of high quality nanographene, with size around 18 nm, and graphene micro-ribbon lattices in a very fast way and very well defined edges, with dimensions down to  $1\ \mu\text{m}$  width and mm length, very promising for terahertz graphene plasmonic applications.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Large area low-cost patterning is a challenging problem in graphene research. Patterning of graphene and graphene oxide (GO) films is currently performed with different techniques depending on the application and the required scale. In some cases the objective is obtaining the architectures required for the fabrication of devices. The scales of the

features and of the overall patterned areas vary enormously, from submicrometer scales, in some electronics applications as sensors, transducers or biological chips [1], to areas of square centimeters or meters for displays, touch screens, OLEDs, photovoltaics or electrodes for batteries and super-capacitors [2,3]. Another type of applications require tailoring graphene as quantum dots or nanoribbons with controlled shape and size with the fundamental objective to modify

\* Corresponding authors.

E-mail addresses: [carmen.coya@urjc.es](mailto:carmen.coya@urjc.es) (C. Coya), [ada@icmm.csic.es](mailto:ada@icmm.csic.es) (A. de Andrés).

<http://dx.doi.org/10.1016/j.carbon.2015.04.018>

0008-6223/© 2015 Elsevier Ltd. All rights reserved.

the properties, for example to induce a gap in the electronic structure [4], to functionalize the edges or to create a new periodicity required in graphene plasmonic applications [5].

Among the different technologies, one-step techniques have important technological benefits and are being extensively studied. The mechanism in one-step patterning is mainly related to breaking C–C bonds either directly or through chemical reactions. Electron or ion beams allow patterning graphene and related materials to the smallest scales but are limited to small patterned areas and the high involved energies produce unwanted defects such as amorphisation [6]. Nanoscale patterning with atomic force microscopy (AFM) is mediated by localized oxidation of graphene by adsorbed water layers following the same chemical reactions proposed for tunneling microscopy, STM, in graphite more than 20 years ago [1,7] (see also reviews [6,8] and included references). Nevertheless the observation of a different behavior in ultra high vacuum led to propose a different mechanism based in the sublimation of carbon from graphite [9]. But in general, humidity dependent electrochemical processes are proposed for any AFM patterning including the reduction of graphene oxide films [10]. The use of other adsorbed molecules was proposed to lower the imprint size down to 3 nm [11]. Recently a correlation between the work function of graphene oxide and relative humidity has been demonstrated [12]. On the other hand the use of the AFM tip as knife, without applied voltage, is not effective for graphene on SiO<sub>2</sub>/Si because its tendency to fold [13]. Complex systems to increase the patterned area are being developed as an array of five nano-tips allowing scales up to 500  $\mu\text{m}$  [14], but the approaching mechanism based in force-feedback is too slow and ultimately prevents their applications at mm scales. While the nano-size of the patterned areas prevents their Raman characterization, oxidation of submicron islands on graphite with AFM has been evidenced by Raman [15]. Many aspects of the mechanisms, as the relevance of the sign of the applied voltage with apparently contradictory results [16–18], are still under discussion.

In order to reach the length scales required for large area applications or when the nanoscale is not necessary and cost is an issue, other alternatives are required. There is an intensive effort on the use of lasers of different energies, from the infrared to the ultraviolet, and different time scales, from continuous to femto-second lasers [19] to pattern graphene and graphene oxide materials [20–22]. Lasers are being used either to induce the partial reduction of graphene oxide films providing paths of increased conductivity and particularly well suited for applications in batteries and supercapacitors [2,3], or to eliminate graphene [23,24]. Recently, a soft lithography-based approach has been used over square millimeter areas [25]. In these cases the resolution of the patterned features is in the micron range.

In the present work we demonstrate a one-step method that allows patterning of graphene, and GO or reduced GO (rGO) in room conditions at speeds of tens mm/s, similar to those used by conventional printers, so theoretically scalable to dimensions of cm  $\times$  cm. It operates through different mechanisms based on the electrical erosion concept, which uses low continuous voltages and has been recently proven as a successful patterning technique for different conductive

materials as ITO, Al:ZnO or metals [26]. By tuning the voltage and pressure of the tip it is possible to remove graphene, GO or rGO as well as to oxidize graphene. We also study the potential of this procedure to modify graphene in a novel way to obtain high quality nanographene and micro-ribbons. We demonstrate that it is an efficient large-area and cost-effective patterning procedure for electronic device development.

## 2. Experimental

### 2.1. The samples

The arc-erosion technique has been applied to graphene, graphene oxide and reduced graphene oxide thin films. Commercial CVD graphene transferred onto 1 cm  $\times$  1 cm p-doped Si substrates with a 90 nm SiO<sub>2</sub> layer (Graphene Supermarket) has been used as-received. These samples have single layer graphene with a considerably large number of double and multi-graphene islands with diameters in the range from 1 to 2 micron dispersed over the surface (Supp. Info Fig. S2). Topographic atomic force microscopy (AFM) images of the as-received samples (Supp. Info Fig. S3) show a relatively rough surface with a rms value of 1.8 nm. Graphene wrinkles, characteristic of CVD grown graphene, are observed in the 2  $\times$  2  $\mu\text{m}^2$  image, presenting a non-uniform height due to the local adsorption of adsorbates (most probably PPMA residues from the transfer process) along them. These adsorbates are present all over the graphene surface and are better resolved in the high resolution images, where a discontinuous layer of  $\sim$ 2 nm in height covers most of the graphene surface.

The graphene oxide (GO) films were deposited on Si and on glass by spin coating and some were reduced in hydrazine and annealed at 300  $^{\circ}\text{C}$  for 2 h, we will refer to these films as rGO, as described in. The thickness of the GO is within 4–10 nm, which correspond to 4–10 layers [27] these films are almost 100% transparent in the VIS-IR range and highly resistive. The thickness of the rGO films decreases during the reduction process about 30% for the same number of layers reaching sheet resistances as low as 3 k $\Omega$  with transmittance about 85% @ 550 nm [27].

### 2.2. The electroerosion set-up

Electro-erosion is performed using a tip-to-plane electrode configuration, suitable to affect local regions of the order of the tip diameter (20–30  $\mu\text{m}$ ). The tip is driven by means of a purpose-built machine, PC controlled using a software routine. It handles independent Z and XY piezo-positioners (38  $\mu\text{m}$  trip with 0.05 nm resolution, and 100  $\mu\text{m}$  trip/0.4 nm resolution for the vertical and horizontal axes respectively), coupled to electromechanical micro-steppers of 10 cm trip, 0.1  $\mu\text{m}$  resolution and 1  $\mu\text{m}$  reproducibility (a schema of the set-up is presented in the Supporting information file, Fig. S1). Commercial spring-tips (beryllium copper) by Harwin Inc., are used to damp the contact between tip and sample, with a spring constant of 300 N/m  $\pm$  20%. We used truncated cone-shaped probes with 60 $^{\circ}$  apex angle, and

Download English Version:

<https://daneshyari.com/en/article/1413335>

Download Persian Version:

<https://daneshyari.com/article/1413335>

[Daneshyari.com](https://daneshyari.com)