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Flexible transparent sensors from reduced graphene oxide micro-stripes fabricated by convective self-assembly

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ABSTRACT

Reduced graphene oxide (rGO) currently represents an attractive alternative material for graphene and its already well-known electronics applications. Due to its liquid phase processing it can be produced inexpensively on large scale, but its deposition into films/patterns of defined geometry on solid substrates remains challenging. In this work, rGO micro-stripes with controlled morphology are prepared on polyethylene terephthalate substrates by Stop&Go Convective Self-Assembly. This method allows the deposition of regular arrays of rGO stripes by independently adjusting the stripe geometry and array period in an inexpensive, clean and fast way, and without any lithographic patterning. The as-obtained rGO stripes are highly transparent, flexible and good electrical conductors, properties which are of great value for future electronic devices. We exploit these properties for fabricating for the first time a bi-functional strain and humidity sensor which is optically transparent.

1. Introduction

The bidimensional hexagonal structure of sp^2 hybridized carbon atoms in graphene renders a unique combination of mechanical, optical and electrical properties that could be harnessed in the fields of optoelectronics and sensing [1–4]. The high mobility, optical transparency and flexibility of this wonder material have been exploited in devices such as field-effect transistors (FET), organic light emitting diodes (OLED), solar cells and even touch screens [5–8]. Furthermore, graphene has the potential to be a surpassing alternative to the presently dominating indium tin oxide (ITO) as a transparent conductor, since the price of Indium is rising and graphene is also flexible [3,9].

To this end, the large scale synthesis and production of graphene is still a challenge to overcome. A promising approach is the growth via chemical vapor deposition (CVD) on substrates, by which graphene with few defects can be obtained on large areas. While CVD graphene is of high quality, in most cases it requires a nontrivial transfer step from the catalytic conductive substrate (Ni, Cu, Pt etc.) onto the desired substrate [4]. This induces numerous defects and contaminants in graphene's atomic structure and also adds to the already high manufacturing costs [10,11]. If certain geometries/patterns are required, additional lithographic steps need to be employed, which make use of resists and etchants, and can induce further contamination. An alternative to graphene is graphene oxide (GO) and its reduced form (rGO) obtained by the widely known Hummers chemical exfoliation of graphite [12,13]. Despite being obtained only as defective micro and nano sized flakes, GO and rGO have the advantage of liquid phase processing and large scale production at low costs. Previously, GO/rGO films (including patterned ones) have been fabricated by spin or drop casting, vacuum-filtration procedures and even ink-jet printing of high-concentration GO/rGO suspensions [14,15]. Using these techniques, numerous electronic devices have already been demonstrated. Many of these applications highlight the sensing properties of graphene, exploiting its high surface area and high sensitivity to the surrounding environment [16]. Graphene based sensors for temperature [17,18], pressure [19,20], gas and vapor [21,22] and even for pH [23] were developed.

Several reports on graphene strain sensors were recently published, showing its great potential for such applications. Using

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mechanically cleaved, CVD-made or liquid suspended graphene, the developed strain sensors had gauge factors (g) ranging from 1.9 to 11.4 [1]. Zhao et al. increased g to 300 using nanographene films, thus by far exceeding the performances of the conventional metal film gauges [1,2]. While these are promising results, most of the protocols involve patterning by e-beam lithography and CVD [1,3,4]. Not only is this expensive and time consuming (ultra-high vacuum, high temperatures), but also the resists involved in the processing often contaminate the sensors [5,6].

A technique not yet utilized, to our knowledge, in the production of GO/rGO films is convective self-assembly (CSA), sometimes known also as evaporation-induced self-assembly. Generally, large area uniform or patterned films from suspensions of colloidal nanoparticles and microparticles were produced by CSA [30]. Here, the possibilities of the CSA technique in the deposition of rGO from suspensions are explored. We report on the controlled fabrication of periodic arrays of rGO micro-stripes on flexible transparent substrates from low concentration aqueous suspensions of rGO flakes by CSA, in conditions of ambient pressure and temperature, without using any lithography and in a time effective manner. The morphological, optical and electrical properties of these rGO stripes are investigated. Their potential for electronics applications is demonstrated by their capacity to work both as sensitive strain sensors and as humidity sensors.

2. Experimental

2.1. rGO flake elaboration

For the synthesis of rGO flakes in water the widely known Hummers modified method was employed [7]. Graphite flakes (325 mesh, 99.9995%) were mixed with concentrated H_2SO_4, KNO_3 and $KMnO_4$ to be oxidized for prolonged periods of time. Ultrapure water and H_2O_2 were added to finish the reaction. The graphite oxide obtained after several washing procedures (with HCl and water), was exfoliated to single layered and few layered graphene oxide by ultrasounds. Finally, GO was reduced to rGO chemically with hydrazine hydrate (24–26%) under microwave radiation in an Anton Paar Monowave 300 system [8]. No additional surfactants are needed to stabilize the rGO suspension. The spectroscopic and microscopic characterizations of GO and rGO are presented in the Supplementary Data.

2.2. rGO micro-stripe fabrication

In this work, rGO micro-stripes were fabricated using Stop&Go Convective Self Assembly (Stop&Go CSA) [9] on 175 μm thick polyethylene terephthalate (PET) foils. The customized CSA setup consists of a supporting glass slide placed at a small angle (20–25°) in the proximity of a substrate (~200 μm distance). The substrate is fixed on an aluminum plate which can be translated automatically with a speed v via a software-regulated actuator. The temperature of the plate is controlled by water circulation; during sample preparation it was maintained at 25 °C. A droplet of aqueous suspension of rGO flakes (0.05 mg ml^{-1}) was pipetted in the cusp between the glass slide and the substrate to form a linear meniscus that is horizontally translated across the moving substrate.

2.3. Characterizations

Optical microscopy images were recorded with a conventional microscope in reflection configuration. AFM topographical analyses of the samples were performed on a Witec Alpha 300 RA atomic force microscope, operating in tapping mode. The surface morphology of the samples was investigated by scanning electron microscopy (SEM) with a dual beam FEI QUANTA 3D FEG microscope at 5 kV accelerating voltage. A Witec Alpha 300 RA confocal Raman microscope was employed to perform the Raman measurements either on the as-prepared samples or in liquid phase with the rGO suspension held in a quartz cell. The excitation radiation (532 nm Nd-Yag laser line) was focused by a 100× or 20× objective for the solid and liquid phase respectively. The fitting of the Raman spectra was made with a combination of Lorentz and Bano-Wigner-Fano profiles recommended for carbon structures [10].

Optical transmission spectra were recorded through an Axio Observer Z1 Zeiss microscope in transmission configuration using a halogen lamp as a white light source. The transmitted radiation was collected through a 10× (0.45 NA) objective and guided by an optical fiber (100 μm diameter) to an Ocean Optics USB4000 spectrometer. The sample area from which light is collected approximates to a disc having a diameter of 15 μm (see Supplementary Data for details concerning the evaluation of this area). Transmission spectra are thus performed on individual rGO stripes. In case that transmission spectra are recorded on strips narrower than 15 μm, the spectra displayed were corrected by taking into account the unoccupied area. All the spectra were corrected with a baseline recorded on bare PET substrate.

Electrical measurements were performed in a two-probe configuration with a Keithley 6487 picoamperemeter, after contact gold electrodes (50 nm thick, separated by ~80 μm) were deposited by thermal evaporation (Prevac system) across a number of 25 rGO micro-stripes. The resistivity was estimated by considering the cross-section of the stripes from AFM measurements and the length of the stripes.

To estimate the carrier mobility in the rGO stripes, field effect transistors (FET) were fabricated by depositing rGO stripes on doped silicon wafers with 300 nm thick SiO_2; the source and drain electrodes were deposited by thermal evaporation and the Si substrate acted as a back-gate electrode. The drain-source current (I_{DS}) was recorded as a function of gate-source voltage (V_{GS}) while the drain-source voltage (V_{DS}) was maintained at 0.5 V. The linear region of the characteristic transfer curve was used to estimate the electron and hole mobility, similar to other works [11,12]. The transfer characteristic curve and details regarding the calculations are given in Supplementary Data.

Uniaxial strain and cycling tests were performed using a Deben micro tensile stage. The strain applied on the samples was measured by acquiring optical microscopy images of the substrate. A Keithley 6430 sourcemeter was used for the electrical measurements; the applied voltage was 0.5 V. This setup was placed in a climate chamber in order to control the temperature and the relative humidity. The strain sensitivity of the rGO stripes was studied at a temperature of 25 °C and a relative humidity of 45%. The humidity sensitivity of the unstrained rGO stripes was quantified by varying the relative humidity in the climate chamber.

3. Results and discussions

3.1. rGO stripes of controlled morphology

Generally, during a standard CSA process the so called *stick-slip* behavior is observed [9,13]. Gold nanoparticle wire patterns on polyethylene terephthalate (PET) substrate were obtained by regulating the substrate temperature and the translation speed of the meniscus line, but the width and wire spacing could not be controlled independently [9]. To allow precise control over the morphology and spacing of the deposited stripes, an improved CSA variant was developed, namely Stop&Go CSA [9]. In this variant, the morphology control is achieved by willingly triggering the stick/