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Step-by-step surface potential tuning of patterned graphene by polyelectrolyte coating

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ABSTRACT

The fine control of the interfacial properties of functionalized graphene is a key point for its applications, especially in biosensing devices. We have here used an *in-house* developed technique to fabricate microsized patterned graphene via laser ablation and then we have functionalized the interface with poly-D-lysine, a biocompatible polyelectrolyte normally used as a promoter for cell adhesion. Scanning Kelvin probe microscopy shows that a surface potential contrast appears at the patterned regions, with ablated regions of silicon substrate exhibiting higher surface potential than the surrounding background, whereas both levels have negative values. By subsequent coating with the poly-D-lysine it is possible to change stepwise the surface potential levels, while keeping the contrast at the patterned regions constant, up to neutralizing the initial negative values. With further dipping in a polyelectrolyte solution of opposite sign, such as polystyrene sulfonate, it is then possible to decrease the surface potential shifting it again back to negative values. The starting substrate chosen for graphene transfer allows deciding the sign of the surface potential contrast between two adjacent regions of the pattern.

1. Introduction

The use of single or few layers graphene for the fabrication of biosensing devices is appealing, given the peculiar properties of this material (transparency, conductivity, robustness) [1]. The fabrication of devices requires the capability of controlled patterning of the surfaces by selective coating with graphene. Further, functionalization of graphene with organic or biological compounds forming a hybrid material [2, 3] is another task attracting the interest of the community, since it opens the way to selectively impart specific properties to the patterned graphene, allowing for controlled tuning of the surface and its selective interaction with the environment. It has been shown that organic molecules grown on graphene may adopt preferred orientation compared to the case of substrates such as e.g. silicon, also due to residuals of poly-methylmetacrylate (PMMA) after transfer of graphene to the final substrate of use [4–6]. In the recent past, we have developed and applied a reliable method for patterning large area graphene by UV single-shot laser ablation [7, 8]. By properly tuning the laser fluence, single layer graphene (SLG) can be selectively removed from micrometric areas of silicon or glass substrate, giving rise to a patterned surface alternating graphene regions with ablated (substrate) regions, in a geometry of choice [7]. This procedure is quick and straightforward when compared to other lithography-based patterning methods. In our previous studies, we have used the fabricated patterned interfaces as substrate for cell seeding. First we investigated adhesion of neurons, after proper uniform functionalization with a cell-adhesive molecule [7]; in that case, in spite of the chemical homogeneity of the substrate after the coating, geometrically ordered functional neural network could be obtained, where neurons preferentially adhered and/or migrated onto the graphene areas, avoiding the ablated ones. In a subsequent work [8], where Chinese hamster ovary cells were cultured, in parallel with single cell adhesion experiments, we also measured a very high adhesion of a silicon nitride probe onto coated graphene as compared to the ablated (i.e. glass substrate) regions.

Intrigued by these observations, and with the aim of gaining more insight on the physico-chemical properties of the patterned (and coated) substrates, we focus here our attention onto the surface potential (SP). Actually, many molecular recognition mechanisms of cells are based on electrostatics [9, 10]. The possibility to tune and to control the SP of the interface could be very important in view of the development of biosensors, since it would provide a method to gain access or to prevent the binding of selected biomolecules. To this purpose, we

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have used scanning Kelvin probe microscopy (SKPM) to measure the SP of our patterned graphene. The surfaces have been functionalized by coating with charged polyelectrolytes, and the layer deposition has been monitored via both SKPM and Raman spectroscopy. The polyelectrolytes of choice were the positively charged poly-D-lysine (PDL), one of the most commonly used cell-adhesion molecules [11] and the negatively charged poly(sodium-4styrene sulfonate) (PSS), a well characterized molecules frequently used in layer-by-layer assemblies [12, 13].

2. Materials and methods

2.1. SLG transfer

SLG grown by chemical vapor deposition on copper (Cu) was purchased from 2D Tech (UK). SLG on SiO_2 was a commercial product purchased from Graphene Supermarket. According to the manufacturer, SLG was transferred on SiO_2 by wet etching procedure and SiO_2 was 285 nm thick. A PMMA solution (MicroChem, 950,000 MW, 9–6 wt% in anisole) was spin-coated (Sawatec SM-180-BT spinner) on SLG/Cu foils at 3000 rpm for 45 s and then the SLG on the opposite side of the Cu foil was removed by 100 W oxygen plasma (180 s), followed by drying at room temperature for 12 h. The Cu was wet-etched using 0.2 M Ammonium persulphate solution in a Petri dish and the PMMA/SLG stack was floated on the surface of the solution. The stack of PMMA/SLG was carefully rinsed in ultrapure water (Millipore, 18 MΩcm) to remove the traces of the Cu etchant, and was scooped on the target substrate (1 cm × 1 cm Si). The transferred SLG substrate was annealed in air at 180 °C for 3 h to obtain a firm adhesion to the glass coverslip and washed with acetone to remove any trace of organic contaminants. All the solvents were purchased from Sigma Aldrich. The quality of the SLG transfer was monitored by Raman spectroscopy.

2.2. Laser patterning of graphene

Exploiting the absorption peak of SLG in the deep UV at 4.6 eV, ablation patterning of the transferred SLG was carried out by a KrF excimer laser with 248 nm wavelength. The Si\SLG surface was patterned in its central area with an array of ablated squares with 40 μm side and 40 μm gap, each obtained by exposure to a single pulse at a laser fluence of 0.5 J/cm^2.

2.3. Raman characterization

Raman spectra have been collected with Horiba Jobin Yvon LabRAM HR800 at ambient conditions. A 632.8 nm excitation line in backscattering geometry through a 50× objective lens was used to excite the SLG on Si.

2.4. Polyelectrolyte coating

PDL (Sigma-Aldrich, MW 30.000–70.000) was dissolved in ultrapure water in a concentration of 0.1 g/L; PSS (Sigma-Aldrich, MW 70.000) was used at a 0.2 g/L concentration in ultrapure water. For each dipping step, the sample was immersed in the polyelectrolyte solution for 20 min and subsequently rinsed for 2 min in ultrapure water for 3 times. After wetting the substrates were dried under gentle Nitrogen flow.

2.5. SKPM

The measurements were carried out on an atomic force microscope MFP-3D (Asylum Research, CA, USA), acquiring images at maximum scan size of 90 μm, with 256^2 pixels, at a (single) line scan frequency of 0.2 Hz. A MESP probe (Bruker, MA, USA) was used, with nominal properties as follows: cantilever resonance frequency of ~75 kHz and

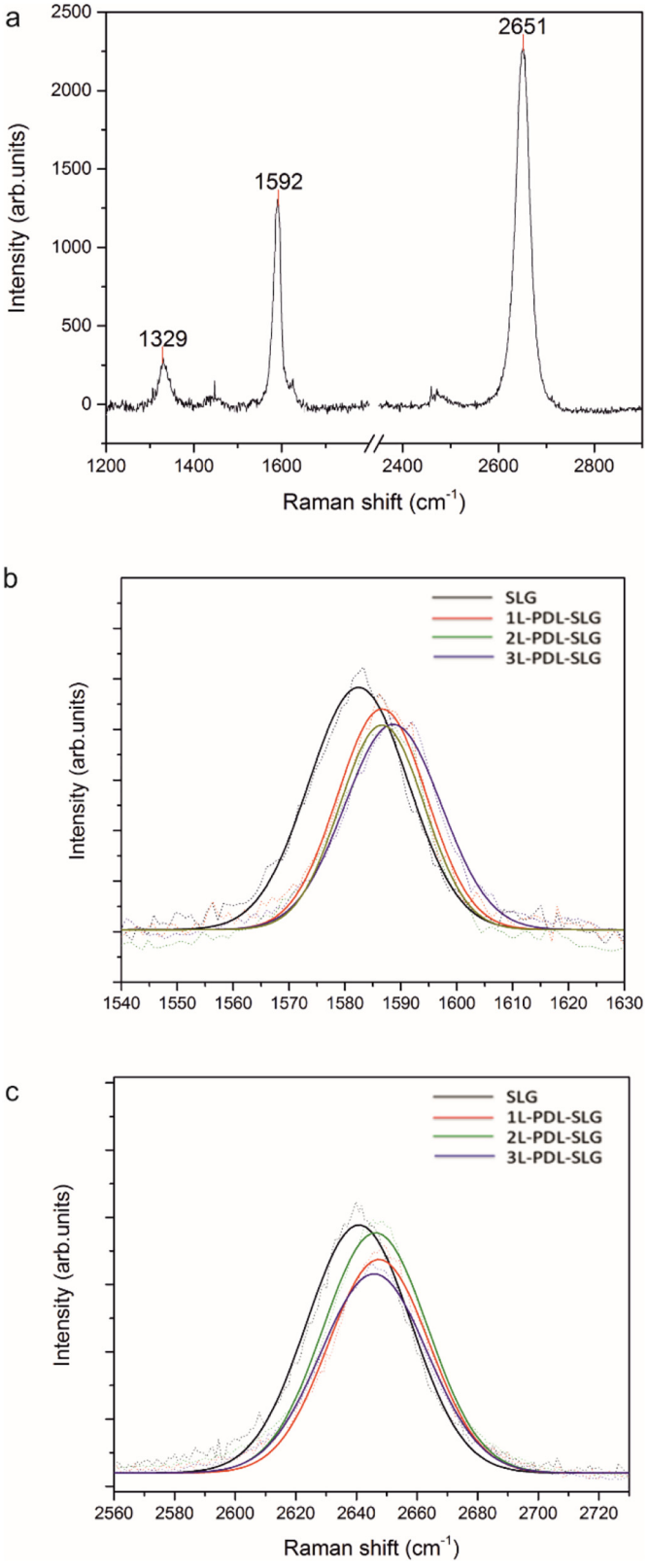

Fig. 1. typical Raman spectrum of SLG transferred onto Si substrate. G-band located at ~1590 cm^{-1} is due to the in plane vibration of sp2 carbon atoms, the 2D located at ~2650 cm^{-1} are visible. The D band at ~1300 cm^{-1} indicates the presence of some defects/impurities (a) G-band Raman peak of bare SLG (black, dotted) and of PDL coated SLG after different dipping cycles (colors, dotted). A progressive shift towards higher wave number is observable (b). 2D-band Raman peak of bare SLG (black, dotted) and of PDL coated SLG after different dipping cycles (colors, dotted). A progressive shift towards higher wave number is observable (c).