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GRAPHENE FOR ELECTRONIC DEVICES – SYNTHESIS AND CHARACTERIZATION

Mariana APOSTOL[1,2], Adrian ENACHE[1], Victor DICULESCU[1], Teddy TITE[1],
Melania ONEA[1], Ionut ENCULESCU[1],
Elena MATEI[1*], Ecaterina ANDRONESCU[2,3*]

In this paper, graphene was obtained on a copper substrate using the CVD method, and then it was transferred to various substrates such as glass and SiO_2/Si patterned with metallic interdigitated electrodes. The graphene thus obtained was characterized using Raman spectroscopy, scanning electron microscopy (SEM), current–voltage measurements, and electrochemical methods, in order to be used for sensing applications.

Keywords: graphene, chemical vapor deposition (CVD), Raman spectroscopy, electrochemical characterization.

1. Introduction

One important goal of the electronics industry is the development of new materials that are efficient in meeting high performance conditions while maintaining low energy consumption. For the fabrication of new complex components [1], it is necessary that the new generations of devices be based on novel materials with improved functionalities. These materials include those based on two-dimensional structures, e.g., graphene [2]. Graphene is a layer of carbon atoms arranged in a two-dimensional (2D) honeycomb structure in which carbon atoms are characterized by sp^2 hybridization [3]. For the first time, isolated and investigated in 2004, graphene has become a valuable and promising low-dimensional material aimed at developing applications in various fields. Graphene studies began early, in 1947, when the theory of a single atomic layer of carbon was explored by P.R. Wallace [4], continuing into the 1960s, when he studied graphene as a monolayer graphite on metal substrates. In 2004, Novoselov and Geim

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[1] National Institute of Material Physics, Atomistilor 405A, 077125, Magurele, Romania, e-mail: mariana.apostol@infim.ro, adrian.enache@infim.ro, victor.diculescu@infim.ro, teddy.tite@infim.ro, melania.onea@infim.ro, encu@infim.ro, elena.matei@infim.ro.

[2] Dept. of Science and Engineering of Oxide Materials and Nanomaterials, Faculty of Chemical Engineering and Biotechnologies, The National University of Science and Technology POLITEHNICA Bucharest, e-mail: mariana.apostol@infim.ro, ecaterina.andronescu@upb.ro

[3] Romanian Academy of Scientists, e-mail: ecaterina.andronescu@upb.ro

* Corresponding author: elena.matei@infim.ro;ecaterina.andronescu@upb.ro

separated the graphene monolayer using adhesive tape and pyrolytic graphite, further using it in experimental studies [5] work for which in 2010, they received the Nobel Prize [6]. In terms of specific properties, this 2D nanomaterial is very strong, with a breaking strength of about 200 times higher than steel [7] with thermal conductivity (5000 $Wm^{-1}K^{-1}$) higher than in metals such as Cu, good electronic mobility [8] high transparency [9], excellent thermal large specific surface area, biocompatibility and the possibility of surface functionalization, all of which deriving from its intrinsic structure [10]. Due to these properties, graphene has potential applications in almost any industrial field: electronics, telecommunications, materials industry, pharmaceuticals industry, and medicine [10,11]. For example, promising results have been obtained on devices based on graphene and used as transducers for recording the electrical activity of living cells for bioelectronics [12], as biosensors for the detection of cancer, and DNA hybridization with applications in medicine [13-15], as electrochemical sensors for the detection of dangerous ions [16] but also in the development of batteries and supercapacitors [17]. There are many chemical or physical methods of preparing graphene [18], but chemical vapor deposition (CVD) is the most efficient technique for large-area single-layer graphene synthesis on metal substrates. This technique is considered a relatively low-cost approach and produces a high-quality layer of graphene with a low number of defects, advantages which are necessary for developing applications at industrial-scale [19]. The process is based on the possibility of growing graphene on different substrates as copper, nickel, palladium, ruthenium, cobalt, iridium, and rhenium [20].

For numerous applications and devices which need the use of a high- quality material is necessary to employ well crystallized graphene with no contaminants or defects. Transferring graphene from the growth substrate to the one employed for a specific application is difficult. It is about dealing with a material that is one or few atoms thick, and the procedure is far from trivial. Therefore, both the synthesis and the transfer from the growth substrate to the necessary one represent important steps in developing advanced graphene devices. The aim of the present study was to describe an algorithm for the development of an appropriate active component for high-performance sensor applications, starting from the synthesis and transfer of graphene, and finishing with the characterization from the morpho-structural, electrical, and electrochemical point of view.

2. Materials and Methods

2.1 Materials

Copper foil (99.98 %) with a thickness of 25 µm (Merck, Germany) was used as a growth substrate. High-purity acetone and isopropyl alcohol (Merck, Germany) were employed to clean the substrates. In the transfer step, polymethyl methacrylate (950 PMMA A2 from KAYAKU Advanced Materials), KCl, and ammonium persulfate ($(NH_4)_2S_2O_8$) (Merck, Germany) were used. The electrolyte solutions of 0.1 M KCl ionic strength, as well as all necessary solutions, were prepared with analytical grade reagents and purified water from a Millipore Milli-Q system (conductivity $\leq$ 0.1 μS cm^{-1}). For electrical measurements and electrochemical analysis, interdigitated Au(100 nm)/Ti(10 nm) /SiO_2(50 nm)/Si electrodes made by photolithography were used.

2.2 Methods

2.2.1 Chemical vapor deposition

Graphene was obtained by employing a chemical vapor deposition (CVD) process using the AS-One Rapid Thermal Processor system from ANNEALSYS (Montpellier France), copper foil (99,98%) as catalytic substrate and methane (99,99% purity) as the carbon source.

2.2.2 Raman spectroscopy

The Raman spectra of the graphene/electrodes and graphene/glass were recorded at room temperature using a LabRam HR Evolution spectrometer from Horiba Jobin Yvon (Palaiseau, France), a He-Ne laser being employed for excitation with the wavelength of 633 nm.

2.2.3 Scanning Electron Microscopy (SEM)

For morphological analysis of the transferred graphene, a Gemini 500 field emission scanning electron microscope (FE-SEM) from Zeiss (Oberkochen, Germany) was used.

2.2.4 Electrical measurements (I-V)

The current–voltage characteristics of the graphene/electrode were measured at room temperature using a Keithley 2400, with the voltage difference between the electrodes being swept from -1V to +1V in steps of 0.5V.

2.2.5 Electrochemical analysis

Voltammetric experiments were performed using a computer-controlled Ivium potentiostat with IviumSoft version 2.219 (Ivium Technologies, Eindhoven, The Netherlands). Two types of electrochemical experiments were performed.

First, interdigitated Au/Ti /SiO_2/Si electrodes coated with a graphene layer were covered with 5 μL KCl of different concentrations or FBS (fetal bovine serum) solutions, and the potential applied between the electrodes varied toward positive and negative values at scan rate $v = 1$ mVs^{-1}.

The second experiment consisted of voltammetric measurements in a classical three electrode-configuration in a one-compartment electrochemical cell platform (ED-AIO-CELL-1x from Micrux, Spain). In this configuration, a graphene layer on a glass substrate was used as a working electrode, a Pt wire as a counter and an Ag/AgCl (3M KCl) as a reference electrode. Cyclic voltammograms were recorded using a scan rate of v = 100 mV s^{-1} with 2 mV step potential. For differential pulse voltammetry, the experimental parameters were pulse amplitude of 50 mV, pulse width of 100 ms, and scan rate of 5 mV s^{-1}.

3. Results

The workflow of graphene synthesis and transfer process is presented in Fig. 1. In the first step, the graphene was grown on a copper foil, further transferred on the substrate of interest, and finally characterized by Raman spectroscopy, scanning electron microscopy, electrical and electrochemical measurements.

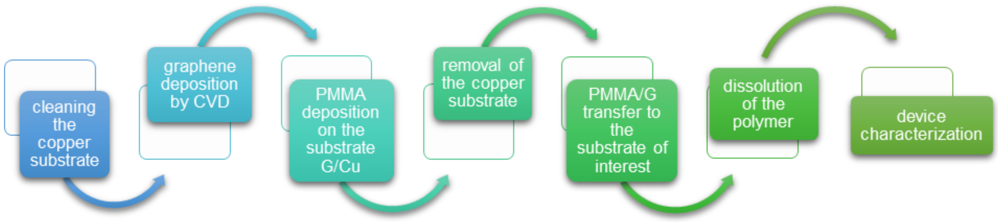

Fig. 1. Stages of growing-transferring graphene

3.1 Graphene preparation and transfer

A usual configuration set-up, as sketched in Fig. 2, employed for obtaining graphene by CVD, involves a tubular furnace that is used for achieving high temperatures, a quartz chamber, a vacuum control system, and flow regulators. In this study, graphene was grown on copper foil by CVD using the AS-One Rapid Thermal Processor system (ANNEALSYS) with full PC control of experimental/process parameters. Methane was used as a source of carbon. The first step was the cleaning of the Cu substrates. Copper foils of 2 x 2 cm^2 surface and 25 µm thickness were first ultrasonically cleaned for 15 min in acetone and isopropyl alcohol, respectively. The CVD process takes place in three stages. The first one is represented by a pretreatment of the catalyst substrate in a hydrogen atmosphere in order to reduce the native oxide, smooth the surface, and increase the size of the copper crystallites [21]. The second step is represented by the actual growth of graphene in a mixed gas atmosphere of CH_4 and H_2. The final step is represented by a rapid cooling in Ar medium. The conditions for the initial annealing step and for the growth of the graphene step are presented in Table 1.

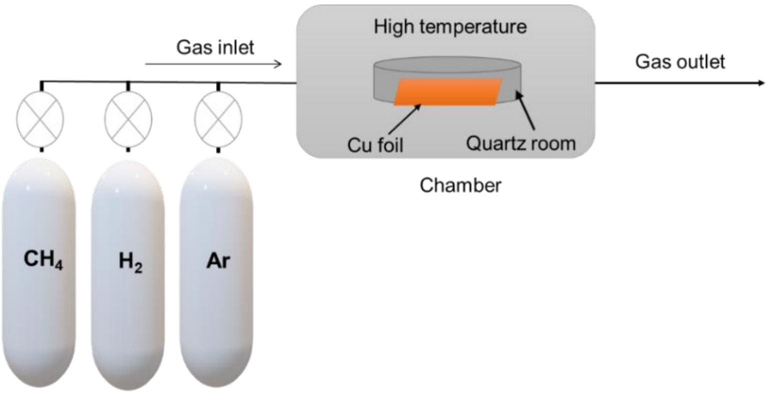

Fig. 2. Schematic representation of CVD process for graphene growth.

To achieve a functional electronic device based on a layer of graphene, a specific step is necessary in order to transfer the as-grown material onto the substrate of interest without inducing defects. There is great attention paid to this very important step because, as a consequence of the chosen transfer method, both defects such as wrinkles or cracks and impurities can be induced in the material, leading to a sharp decrease in the performance in comparison to the theoretical predictions. A transfer method that enables the manipulation of both single and multilayered graphene is based on a carrier polymer.

Table 1

Graphene growth conditions on Cu foil

Steps	Gas	Flow rate (sccm)	Pressure (mbar)	Time (minutes)	Temperature (°C)
Annealing	H_2	10	10	30	900
Graphene Growth	H_2:CH_4	8:24	10	15	900
Rapid cooling	Ar	-	until atm	-	240

Following the diagram in Fig. 1, after obtaining the graphene on copper (G/Cu) as described above, a PMMA layer was coated onto the surface G/Cu by spin-coating at 3000 rpm for 60 s. The PMMA layer was used as a sacrificial polymeric layer for the subsequent transfer step. Next, the PMMA/G/Cu sample was heated at 120°C for 2 minutes to strengthen the polymer.

Both electrochemical delamination and chemical methods can be used to remove the copper substrate [21]. In this study, the copper was removed chemically using a solution of 0.1 M ammonium persulfate, resulting in a PMMA/G layer floating on the surface of the etching solution. A few washes in DI water ensured the complete removal of the etching solution from the surface of the PMMA/G/substrate. The PMMA/G layer was further transferred to the sub-strate of interest.

Further, after the attachment of the PMMA/G layer at the substrate, the device was heated at 100°C to remove the water at the interface and ensure a better adhesion. Finally, the polymer film was removed by immersing the PMMA/G/substrate in acetone for several hours, then rinsing it with isopropanol and drying it under nitrogen flux.

An essential step in developing graphene-based devices is the functional characterization of the graphene samples produced and transferred on different substrates by this above-described procedure. In this study, graphene layers were transferred on glass and contacted with silver paste and on interdigitated Au/Ti/SiO_2/Si electrodes (Fig. 3).

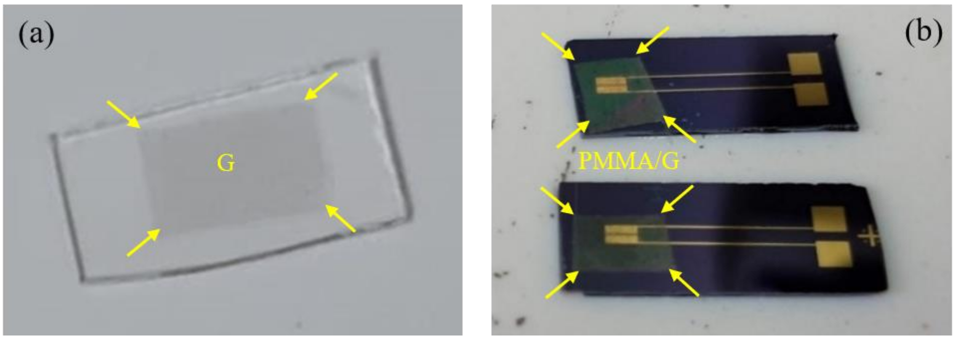

Fig. 3. Photographs of G/glass (a) and PMMA/G/interdigitated Au/Ti/SiO_2/Si electrodes (b).

3.2 Structural and morphological characterization

3.2.1 Raman spectroscopy

One of the most important methods of characterizing graphene is Raman spectroscopy. It is a vibrational technique that is very sensitive to the geometric structure and molecule bonding. Fig. 4 shows the Raman spectra for G/glass (a) and G/interdigitated Au/Ti/SiO_2/Si electrodes (b) collected with 633 nm excitation at room temperature.

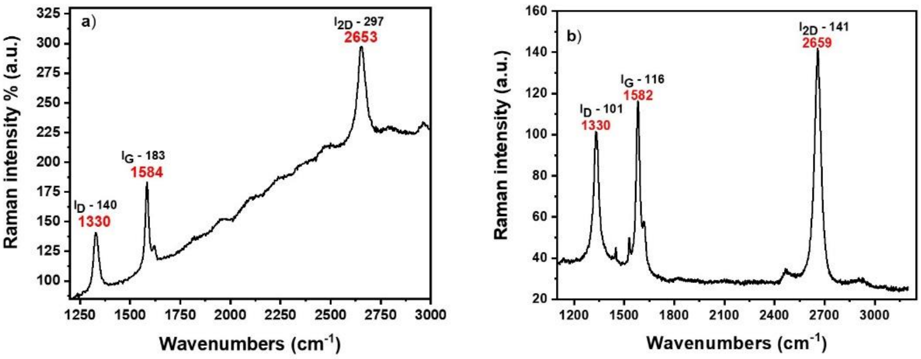

Fig. 4. Raman spectrum of G/glass (a) and G/interdigitated Au/Ti/SiO_2/Si electrodes (b).

The appearance of the D-band at 1330 cm^{-1} indicates that the material contains plane and edge defects. The maxima centered at 1582 and 2659 cm^{-1} are specific to graphene and assigned to the G and 2D bands, respectively. The graphene resulting from a CVD process is a mono or multi-layer film, usually a polycrystalline 2D material. According to the ratio of the intensities of the G and 2D bands it can be determined the number of graphene layers, so that if $I_{2D}/I_G > 2$, the graphene is a monolayer, while if $1 < I_{2D}/I_G < 2$, the graphene is a double-layer and if $I_{2D}/I_G < 1$ is a multi-layer [23]. The graphene obtained by the algorithm reported in this paper has two layers, according to the $I_{2D}/I_G = 1.2$.

The average crystallite size (L_a) of graphene can be calculated by using the equation (1) [24]:

$$L_a(\mathrm{nm}) = (2.4 \times 10^{-10})\lambda^4 \left(\frac{I_D}{I_G}\right)^{-1}, \tag{1}$$

where $\lambda = 633$ nm is the laser excitation. For the particular graphene layers being investigated in the present report, the $L_a = 33.54$ nm is a polycrystalline one.

3.3.2 Scanning Electron Microscopy (SEM)

Morphological analysis using scanning electron microscopy shows that the graphene is continuous and uniform and does not show any cracks (Fig. 5). Some wrinkles can be seen, most likely induced at the transfer stage. Some gray spots can also be observed on the transferred material, meaning that some multi-layer islands appear during the graphene growth process.

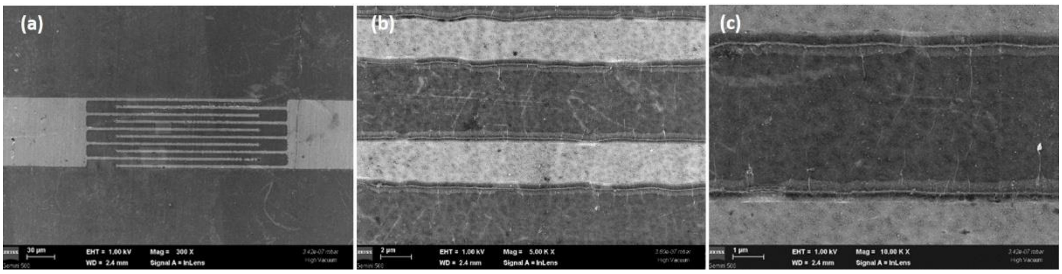

Fig. 5. SEM micrographs at different magnifications: a) 300 x, b) 5.00k x, and c)10.00k x, of the G/interdigitated Au/Ti/SiO_2/Si electrodes.

3.3 Electrical and electrochemical characterization

For the electrical characterization of the G/interdigitated Au/Ti/SiO_2/Si electrodes, a classical measurement of current-voltage (I-V) with two contacts was carried out. The I-V characteristic was recorded from -1V to +1V with a 0.5 V potential step. According to Fig. 6, the current varies linearly with the applied voltage for all the ranges, in agreement with an ohmic contact, while the calculated resistance value is 114 Ω. Such a low resistance for the graphene films, around a few hundred ohms, is consistent with the values reported in the literature [25].

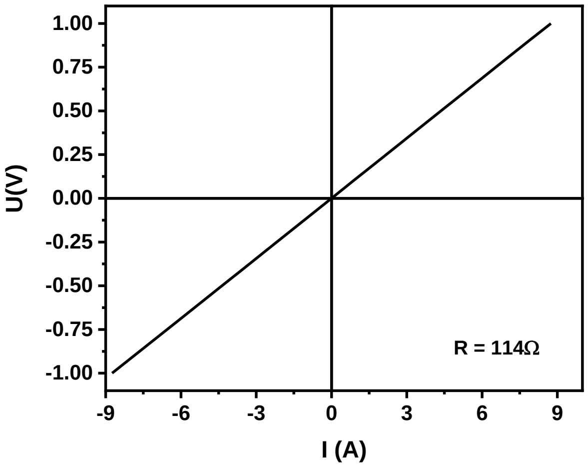

Fig. 6. I-V characteristics on G/interdigitated Au/Ti/SiO_2/Si electrodes.

Electrochemical measurements were performed in the same configuration as the electrical characterization. For this, one electrode was used as working and the other one as reference/counter while the current passing along the graphene layer was recorded function of the potential, which was scanned between -0.1 and +0.1 V, Fig. 7. In this configuration, the G/interdigitated Au/Ti/SiO_2/Si electrodes were covered within 5 µL solutions of different concentrations of KCl or with FBS and the resistance calculated for each solution showing the possibility of using such a kind of device for sensing applications, Fig. 7.

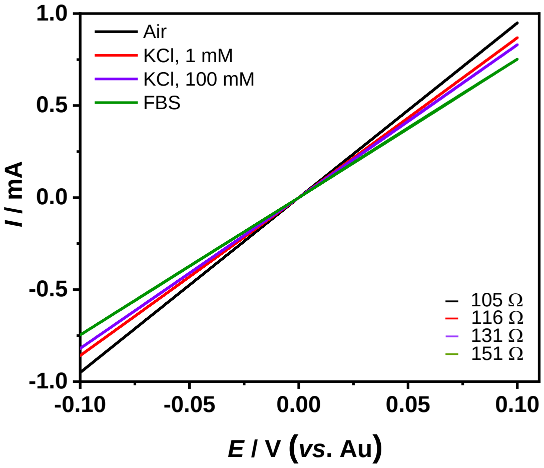

Fig. 7. The current recorded by scanning the potential applied between the G/interdigitated Au/Ti/SiO_2/Si electrodes coated with 5 µL solutions of KCl or FBS (fetal bovine serum).

In a new experiment, cyclic voltammograms were recorded between potential limits -0.7 ÷ +1.4 V (1st scan ▬) and 0.0 ÷ +1.4 V (2nd 🟥 and 3rd 🟦 scans) in 0.1 M KCl, in an three electrode system consisting of the G/glass as a working electrode, a platinum wire as the auxiliary electrode and an Ag/AgCl as reference. The voltammetric profile, as plotted in Fig. 8, shows a low capacitive current, indicating that such a graphene layer can be used as electrode material for electrochemical sensing applications. Moreover, on the cathodic region, from 0.0 V to -0.7 V, no oxygen reduction was observed, a fact which can be very useful in electrochemical systems where the removal of oxygen is not possible, e.g., the voltammetry of cell cultures.

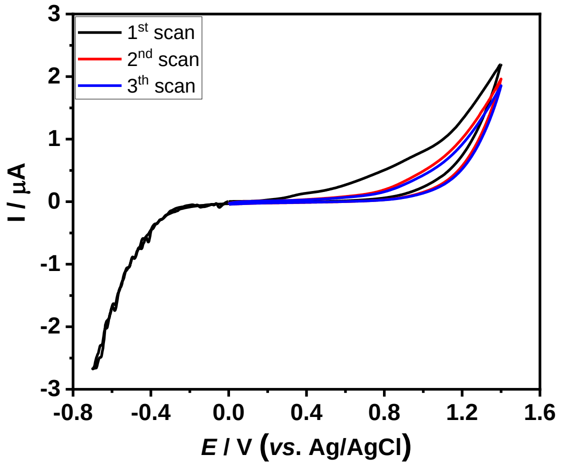

Fig. 8. Cyclic voltammograms at the G/glass electrode in 0.1 M KCl.

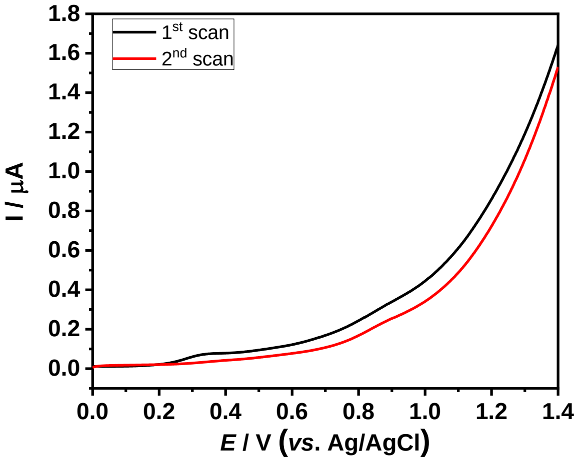

Fig. 9. Differential pulse voltammograms at the G/glass electrode in 0.1 M KCl.

Similar to cyclic voltammetry, the differential pulse voltammograms recorded at the G/glass electrode in 0.1 M KCl (Fig. 9) show a voltammetric profile specific to other carbon-based electrodes [26]. All these voltammetric results support the use of crystalline graphene as an electrode/transductor for (bio)sensing applications.

4. Conclusions

The present report deals with the growth and characterization of graphene for high-performance sensing devices. The bi-dimensional material was obtained by CVD on copper substrates and transferred by a chemical approach to both glass or systems of interdigitated Au/Ti/SiO_2/Si electrodes. In order to assess the quality of the material and its potential for applications, the graphene sheets were characterized by various methods after being transferred onto the chosen substrate. Structural, morphological, electrical, and electrochemical measurements were performed. The Raman scattering measurements show that a polycrystalline graphene with 2 layers and with a relatively high concentration of defects, evidenced by the high intensity of the D-band, was obtained. The microscopy measurements proved that a uniform graphene layer, without cracks but still presenting some wrinkles, was transferred. The material transferred onto metallic electrodes shows an ohmic contact and a low electrical resistance. The voltammetric profile indicates a low capacitive current, meaning that this graphene can be used as an electrode for electrochemical applications.

Based on these results, the approach presented is suited for the development of graphene-based devices, which can be the central component of electronic and electrochemical (bio)sensors allowing exploiting the unique physico-chemical properties of this material, especially its biocompatibility and the possibility of surface functionalization.

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