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The impact of graphene oxide nanosheet lateral dimensions on the electrochemical performance of nanoporous graphene-based electrodes

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ABSTRACT

Electrodes based on nanoporous reduced graphene oxide (rGO) have been developed as the interfacing component in different designs of neural implants in a variety of therapeutic and monitoring applications. The starting graphene oxide (GO) nanosheets lateral dimensions influenced the staking order, roughness and thickness of the derived rGO films, including the formation of nanochannels. Apart from the morphological differences observed, the GO lateral dimension also impacted on the film conductivity, and on the overall electrochemical performance of the rGO electrodes. While electrodes fabricated from nano-scale GO sheets (us-GO) only showed diffusion-limited impedance in the high frequency regime, the electrical response of electrodes from micron-scale GO sheets (L-GO) was limited by diffusion in the whole frequency range due to a less disordered nanoporous film. At 1 kHz, us-GO electrodes, due to their larger capacitance, presented a higher charge injection limit ($Q_{inj,l}$) than L-GO electrodes. Due to the higher conductivity of L-GO, electrodes exhibited half the ohmic drop (*IR*) of electrodes made of us-GO. This work highlights the importance of GO nanosheet engineering to optimize the performance of rGO electrodes in terms of $Q_{inj,l}$ and *IR*, two key figures of merit in neuroelectronic applications.

1. Introduction

Electronic and electrochemical devices based on graphene-related materials, like reduced graphene oxide (rGO), have raised significant interest for their use in different applications, especially in energy [1] and biomedicine. [2,3] The nanoporous nature of rGO thin electrodes leads to outstanding electrochemical performance in terms of areal capacitance, reaching values in the order of 100 mF/cm², [4] notably exceeding that of single layer graphene (2μ F/cm²) [5] while preserving, to a large extent, other properties of single layer graphene, such as high conductivity, [6] flexibility, [7,8] biocompatibility [9,10] and chemical and electrochemical stability. [11] This unique combination makes rGO electrodes a promising candidate for neural interfacing technologies, as we recently demonstrated to achieve monitoring and neuromodulation of activity in the central and peripheral nervous systems. [12]

The nanoporous structure of the rGO electrodes [13] can be achieved by means of bottom-up preparation methods, e.g. vacuum filtration, as graphene oxide (GO) dispersions are able to form nanosheet networks, [14] resulting in free-standiang GO films with nanometric size channels. The preparation of GO nanosheets of different lateral dimensions can be controlled by ultrasonication of the GO dispersions. [15] It has been hypothesized that GO nanosheet dimension impacts on various downstream parameters such as morphology, conductivity and porosity of the GO films. [16] It has been described that a wide range of GO film morphologies, from highly porous to closely-packed films, can be obtained depending on the starting GO nanosheet lateral dimensions, as a result of the GO filtering process. [14] Large nanosheets are expected to provide well-ordered laminar stacking, with minimal void space between GO layers. In contrast, small nanosheets tend to induce more torturous channel formation with randomly stacked materials,

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triggering the formation of a highly porous film structure. [17,18] Jiang et al. reported thermodynamic models showing that smaller GO nanosheet dimensions can lead to an increase in the ratio of interfacial atoms, resulting in more chemically active surfaces. [19] Finally, the pore dimension has been directly related to the conductivity of the film, [20] as it determines ionic transport resistance. [17,21] It has been reported that rGO films prepared from large GO nanosheets present higher electrical conductivity due to the lower inter-sheet contact resistance. [22]

In this work, we explore the effect of GO nanosheet characteristics on the performance of the derived rGO electrode technology. Considering their potential use in neural interfaces, we particularly focus on assessing the electrochemical performance of rGO electrodes in a relatively high frequency range, typically from 1 kHz to 10 kHz, where the impact of the GO nanosheet lateral dimension has not been systematically studied. GO nanosheets of different lateral sizes were prepared to interrogate the influence of the final rGO morphology on the electrochemical performance of rGO electrodes. Besides expected differences in the magnitude of the electrode impedance, our results reveal a different frequency response of the impedance for electrodes prepared with GO of different dimensions. Furthermore, the charge injection capability is evaluated as a function of the frequency, for both types of rGO electrodes, highlighting the importance of materials engineering and devoted characterization towards the optimization of nanoporous rGO electrodes for a target application.

2. Experimental methods

2.1. GO nanosheet suspension

Biological-grade us-GO and L-GO nanosheets dispersed in water, were produced in-house by the modified Hummers' method as previously reported [23] using graphite flakes(Graflake 9580), obtained from Nacional Grafite Ltd. (Brazil), as a starting material, and fully characterized as described (Table S1). [15] The structural and morphological properties for the us-GO and L-GO nanosheets were determined by atomic force microscopy (AFM), scanning electron microscopy (SEM) and optical microscopy.

2.2. Electrode fabrication

GO electrodes were prepared by filtering 40 mL of us-GO or L-GO suspensionin a vacuum filtering system through a nanopore inorganic anodisc membrane (Whatman Anopore Inorganic Membranes, Cyvita) with a diameter of 47 mm and a pore size of $0.02 \,\mu$ m, to form GO thin films. After 16 h filtering, GO films were peeled off from the anopore membrane and transferred to an Au substrate by wet transfer method (MilliQ water). The Au substrate was based on Si/SiO₂ wafers (1 × 1 cm²) with a deposition of Ti/Au (10/100 nm) using an electron beam deposition system (e-beam). A self-assembly monolayer (SAM) based on hydrazide-PEG-thiol (Interchim) was deposited on the substrate by



Fig. 1. rGO electrode fabrication and morphological characterization of ultrasmall (us-GO) and large GO (L-GO) nanosheets. a. Schematic representation of the fabrication steps resulting in the rGO electrodes, depicting the starting GO nanosheet material of different lateral dimensions; the GO film assembly by vacuum filtration; the GO film transfer and HT reduction to form rGO films; and the final rGO electrode encapsulation with PDMS. b. SEM and optical images of us-GO and L-GO. Histograms (bottom), representing 269 individual sheets of us-GO and 267 individual sheets of L-GO, using a Gaussian single peak fitting (solid line). c. Height AFM images of us-GO and L-GO. Cross-section analysis (bottom) along the indicated dashed white lines. Z scale bar from 0 to 5 nm.

immersion of the Au substrate in hydrazide-PEG-thiol diluted in EtOH (12 mg/4 mL) during 16 h. Afterwards, the Au substrate was dried with nitrogen, and the GO film was transferred by wet transfer method, and hydrothermally (HT) reduced using a commercial autoclave, during 3 h at 134 °C and 2 bar. Encapsulation of the rGO electrodes after HT reduction was performed with polydimethylsiloxane (PDMS) films with an open hole, from 1.2 to 1.5 mm of diameter, to avoid the contact of the Ti/Au layer with the solution (Fig. 1a).

2.3. Optical microscope

Optical images of GO nanosheets were acquired with a Nikon Eclipse LV100 microscope in transmittance mode at a magnification of $50\times$. Only micrometre-sized nanosheets were visible under the optical microscope, which resulted in the recording of images of L-GO, and non-detected nanosheets for the us-GO. The L-GO nanosheets images were analyzed with ImageJ (version 1.8.0).

2.4. X-ray diffraction (XRD)

XRD measurements were conducted using a PANanalytical X'Pert Pro diffractometer, coupled with a ceramic X-ray tube of Cu K α radiation ($\lambda = 1.540598$ Å) working in ambient conditions. The interlayer distance ($d_{(hkl)}$) was calculated from Bragg's law, $\lambda = 2d_{(hkl)}sin(\theta)$, where λ is 1.540598 Å, θ is the registered diffraction angle. [24] XRD peaks were fitted by Gaussian amplitude curves to the extract the full width of the half maximum (FWHM) of the (001) and (002) peaks, corresponding to GO and rGO, respectively.

2.5. Scanning electron microscope (SEM)

GO nanosheets SEM images were recorded with a Magellan 400 L field emission scanning electron microscope (Oxford Instruments) equipped with an Everhart-Thornley secondary electrons detector, using an acceleration voltage of 20 kV and a beam current of 0.1 nA. The GO sample was deposited on an Ultrathin C on Lacey C grid (Ted Pella), any excess of material was removed and dried overnight at room temperature. The lateral dimension distribution was analyzed using ImageJ. FEI Quanta 650F ESEM microscope was used to measure the rGO electrode cross-sectional thickness. Samples were prepared by cutting the rGO electrode with a diamond tip. The measurements were performed with an accelerating voltage of 10 kV. The thickness of rGO were analysed using ImageJ.

2.6. Profilometer

The GO/rGO film thickness were measured using a stylus profilometer instrument (KLA Tencor Inc., Alphastep D500) with a 2 μ m of diamond tip stylus. The measurements were performed in a vertical measurement range of 100 nm with a force of 0.03 mg to avoid damage to the GO/rGO film.

2.7. Electrical conductivity

Electrical conductivity measurements were performed in air using a Keithley 2400 sourcemeter in a two-point configuration. The samples measured consisted of rGO films of 3 mm of diameter deposited on a SiO2/Ti/Au substrate (1 \times 1 cm).

2.8. Atomic force microscope (AFM)

AFM images of GO nanosheets were acquired in an Asylum MFP-3D atomic force microscope (Oxford instruments) operating in standard air-tapping mode. Silicon probes (Ted Pella) with a resonance frequency of 300 kHz and a nominal force of 40 N/m were used. Samples were

prepared by covering a freshly cleaved mica surface (Ted Pella) with 20 μ L of poly-L-lysine 0.01 % solution (Sigma-Aldrich). After washing with water, 20 μ L of GO suspension (100 μ g/mL) was drop-casted and washed again with water. The images of rGO electrodes were acquired using silicon probes with a resonance frequency of 150 kHz and a nominal force of 5 N/m. AFM height images were processed using Gwyddion software (version 2.57).

2.9. Electrochemical characterization

A three-electrode configuration was used for the electrochemical characterization, with a Pt wire counter electrode (CE), an Ag/AgCl reference electrode (RE), and the rGO electrodes as the working electrodes (WE). A SP-200 Biologic potentiostat was used to perform the measurements. PBS 150 mM was used as working solution (10 mM PBS, 137 mM NaCl and 3 mM KCl) prepared by tablets (Sigma Aldrich) diluted in MilliQ water. Electrochemical activation of rGO electrodes was performed by cyclic voltammetry (CV) applying a scan rate (ν) of 0.05 V/s in a potential window from -0.9 to 0.8 V, vs Ag/AgCl, during 100 cycles. [4] The areal capacitance (C_A) was obtained from the CV following:

$$C_A = \frac{1}{2A\nu(V_2 - V_1)} \int_{V_1}^{V_2} I(V) dV$$
⁽¹⁾

where *A* is the geometric area of the electrode in cm^2 , V_1 and V_2 are the extremes of the potential window. [25]

Potentiostatic electrochemical impedance spectroscopy (PEIS) was performed at 0.2 V, vs Ag/AgCl, with an amplitude of 10 mV and in a frequency range from 10 kHz to 10 mHz. The complex capacitance was calculated from the PEIS following:

$$C'(\omega) = -\frac{Z'(\omega)}{\omega |Z(\omega)|^2}$$
(2)

$$C''(\omega) = -\frac{Z'(\omega)}{\omega |Z(\omega)|^2}$$
(3)

where $C(\omega)$ is the real capacitance in mF, $C(\omega)$ is the imaginary capacitance in mF, |Z(w)| is the modulus of the impedance in Ω , $Z'(\omega)$ is the real impedance in Ω , $Z''(\omega)$ is the imaginary impedance in Ω , and ω is the angular frequency in rad/s.

Biphasic current pulses were applied to evaluate the integral capacitance (C^{int}) working at high frequency, and the maximum chargeinjection limit ($Q_{inj,l.}$). A symmetric current cathodic/anodic (I_a , I_c) was applied by fast chronopotentiometry, with a symmetric cathodal and anodal pulse widths ($t_c = t_a$), and at different frequency (0.2, 0.4, 0.8, 1.6 and 3.2 ms), to evaluate the C^{int} of the electrodes working at high frequency, applying a charge of 0.04 mC/cm². To evaluate the $Q_{inj,l.}$ biphasic pulses with the same pulse width of 1 ms were applied, with different $Q_{inj, \sim} 0.2$, 0.4 and 0.6 mC/cm². The biphasic pulses were performed with an interpulse delay of 1 ms. See Supplementary Information for C^{int} and $Q_{ini, l}$ calculation.

2.10. Data Availability

All relevant data obtained to evaluate the main findings of the paper are openly available in CORA repository: https://doi.org/10.34810 /data1823. All other raw data are available from the corresponding author upon reasonable request.

3. Results

3.1. Fabrication of nanoporous rGO electrodes

GO nanosheet suspensions of two different lateral dimension ranges

were used as starting materials in the fabrication process, as shown in Fig. 1a (see also Supplementary Information for more details). The starting GO nanosheet suspensions are prepared as previously reported, [15] consisting of either GO nanosheets with nanometer-scale lateral dimension (ultrasmall GO; us-GO) or GO nanosheets with micrometre-scale lateral dimensions (large GO, L-GO). Fig. 1b depicts SEM of us-GO and optical microscopy images of L-GO, evidencing the difference in lateral dimensions of the two types of GO nanosheets. Fig. 1c shows representative height AFM images of us-GO and L-GO nanosheets deposited on cleaved mica substrates. From the analysis of SEM and optical microscopy images, the corresponding histograms of the lateral dimension (bottom of Fig. 1b) indicate that us-GO sheet population is almost entirely below 100 nm, while the L-GO population is in the few micrometre range. In the corresponding AFM cross-sections (bottom of

Fig. 1c), the thickness of both GO types is identical, approximately \sim 1.2 nm, typical of single/double-layer GO sheets. [26] Thorough physicochemical characterization of the GO suspensions used in this study has been performed and is shown in Table S1.

From the above GO nanosheet suspensions, micrometre-thick GO films were prepared using the vacuum filtration technique. [27] Depending on the volume and concentration of the GO suspension, the GO film thickness could be controlled. Throughout this work a volume of 40 mL of the GO nanosheet dispersions (concentration 0.15 mg/mL) was filtered to assemble the GO films with a thickness in the range of 1.5 μ m. For the subsequent fabrication of the rGO electrodes, GO films of 4 mm diameter were transferred (wet method) onto rigid Si/SiO₂//Ti/Au substrates. Then, the electrodes were HT reduced at 134 °C for 180 min to form rGO films. As previously reported, this reduction method



Fig. 2. Morphological characterization of GO and rGO films prepared from GO nanosheets suspension of different lateral dimensions. a. XRD spectra of GO films prepared from us-GO and L-GO nanosheet suspension. b. XRD spectra of rGO films, including spectral fitting with two Gaussian functions. c. SEM cross-sectional images of us-rGO and L-rGO films. d. AFM topographic images $(20 \times 20 \ \mu\text{m})$ of us-rGO and L-rGO films; Z scale bar from 0 to 450 nm. e. Current-voltage curves used to calculate the conductivity of the rGO films. f. Schematic representation of impact of the GO nanosheet lateral dimension on the structure of the GO films obtained by the vacuum filtering process, indicating that the use of smaller nanosheets (us-GO) leads to a more disordered film. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

promoted the formation of small pores in the ensuing films due to the evolution of gaseous species (H_2O and CO_2). [28] After HT reduction, an encapsulation step was performed using a PDMS film, resulting in the final rGO electrodes with an exposed area of 1.5 mm of diameter, approximately (Fig. 1a).

3.2. Influence of the nanosheet dimensions on the structural properties of GO film`

Once the GO nanosheets were filtered, GO films were characterized before and after HT reduction by means of XRD. Fig. 2a shows the XRD patterns of us-GO and L-GO electrodes. Both spectra show the typical feature of GO films, the diffraction peak (2θ) characteristic of the (001)plane centred at $\sim 10^{\circ}$, [29] slightly broaden due to the expansion of the graphite lattice because of the introduction of oxygenated functional groups. The spectra also show the characteristic peak of the Au substrate, at $2\theta \sim 38^\circ$. As GO presents a laminar structure, by using Bragg's equation, it is possible to calculate the interlayer distance $(d_{(001)})$ between adjacent GO nanosheets, [30] leading to 8.2 and 8.0 Å for us-GO and L-GO films, respectively, already revealing a slightly more compact structure of L-GO. Moreover, the full-width-half-maximum of the (001) peak (FWHM(001)) can provide information about the crystallinity of the GO films, [31] in particular about the stacking disorder resulting from GO film assembly. The FWHM_{(001)} is 2.50 \pm 0.01 $^{\circ}$ and 1.56 \pm 0.02 $^{\circ},$ for us-GO and L-GO films, respectively. These results indicate a higher stacking disorder for the us-GO film, in agreement with previously reported studies that observe that smaller GO nanosheets present larger amount of exposed edges, resulting in more randomly stacking graphene laminates. [18] We thus conclude that the observed differences have their origin in the effect of the GO nanosheet lateral dimension on the filtering process, and next we evaluate if they are maintained after the reduction process.

Fig. 2b shows the XRD spectra of us-rGO and L-rGO films. In the case of rGO, two characteristic diffraction peaks are observed (in addition to that of the Au substrate), at $2\theta \sim \! 19^\circ$ and $\sim 24^\circ\!,$ the latter one close to the graphite characteristic diffraction plane (002) at $2\theta \sim 26.5^{\circ}$. [32] After reduction, the $d_{(002)}$ is significantly reduced, for both us-rGO and L-rGO films, down to 3.7 Å, due to the removal of oxygenated groups (but without fully recovering the graphitic structure). The measured $\text{FWHM}_{(002)}$ are 5.94 \pm 0.04 and 5.17 \pm 0.03 for us-rGO and L-rGO, respectively, revealing larger disorder for the us-rGO films, confirming that the difference in the stacking of the GO film is kept after reduction. The presence of the second peak at $\sim 19^{\circ}$ has been previously attributed to stacking inhomogeneities due to remaining oxygen-related functional groups or stacking corrugations during film assembly. [32] The contribution of this peak is, as expected, more prominent for the L-rGO films as corrugation is more likely to happen in nanosheets of larger lateral dimensions. [17]

Fig. 2c presents SEM cross-section images of us-rGO and L-rGO films, revealing differences in thickness and roughness. For the same concentration of filtered material, thicknesses of about 2.2 and 1.7 μ m, are measured (using a profilometer) for us-rGO and L-rGO, respectively. The larger thickness of the us-rGO electrode is attributed to the random distribution of us-GO nanosheets, also observed in the previous XRD analysis. Moreover, the rougher surface observed in the SEM image of us-rGO topography reveals that, despite the total height of the 20 \times 20 μ m images is larger for the L-rGO films, due to its higher nanosheet corrugation, the roughness in a small area (1 \times 1 μ m) is larger for us-rGO. The statistic rms is 7.5 \pm 1.7 and 4.9 \pm 1.4 nm for us-rGO and L-rGO, respectively. Height profiles are provided in the Supplementary Information.

Finally, the resistivity of us-rGO and L-rGO films is calculated from current-voltage experiments, presented in Fig. 2e. Different lateral dimensions lead to a difference in the rGO film conductivity. The calculated resistivity is 170 \pm 25 and 43 \pm 4 Ω -cm for us-rGO and L-rGO,

respectively. The higher conductivity shown by the L-rGO film, compared to us-rGO, can be attributed to the denser packed structure of the L-rGO, which is reported to present a lower contribution of the intersheet resistance. [14]

As schematically represented in Fig. 2f, we have confirmed the impact that the GO nanosheet lateral dimension has on the stacking process, where larger nanosheets lead to a more ordered and compact film with higher conductivity. Next, we will study the impact of such film different structure and conductivity on the electrochemical performance of the rGO electrodes.

3.3. Frequency response of rGO electrodes: the role of diffusion-limited ion transport

After fabrication, the electrodes are electrochemically activated following the previously reported CV activation protocol for nanoporous rGO electrodes. This activation is shown to promote the ionic diffusion through the material nanopores, increasing the specific capacitance and decreasing the impedance, leading to an enhancement of the electrochemical performance. [4] The assessment of the electrochemical performance of the us-rGO and L-rGO electrodes is performed by means of CV and PEIS (see Fig. S2 for the characterization of bare Au electrodes). Fig. 3a shows the recorded CVs for us-rGO and L-rGO electrodes, at a scan rate of 0.2 V/s. At this ν , the us-rGO electrode exhibits better charge storage capability than the L-rGO electrode, as evidenced by the higher C_A , calculated from the integration of the CVs (Eq. (1)), [25] 62.1 and 55 mF/cm² for us-rGO and L-rGO, respectively. We have previously explained the shape of the CVs considering the pseudocapacitive response of nanoporous rGO electrodes, characterized by the contribution of a cationic electro-adsorption process (in the cathodic bias regime) and of a protonation/deprotonation process (redox peak around 0.1 V vs Ag/AgCl). [4] Fig. 3b shows the scan rate-normalized CVs for the us-rGO electrode conducted at different ν (data for L-rGO electrode can be found in Fig. S3a). The graph represents the current density (j), considering the geometric area of the electrode, normalized by the ν , i.e. j/ν . In the case of a purely capacitive electrode, j/ν , which can be assigned to a differential capacitance, should be independent of the ν . [33] However, this is not observed in Fig. 3b; instead, it shows a decrease of the differential capacitance with the scan rate.

To compare the dependence of the CVs on the scan rate for both usrGO and L-rGO electrodes, Fig. 3c depicts C_A as a function of ν , ranging between 0.05 V/s and 0.5 V/s. Fig. 3c reveals a significant decrease of CA with increasing ν , for both types of rGO electrodes, a phenomenon which is observed in non-ideal capacitors or in electrodes in which transport is governed by diffusion. [34] Moreover, the CA is higher for us-rGO electrodes, consistent with the results in Fig. 3a, specially at higher ν . A common analysis applied to CVs and used to assess the impact of diffusive transport in electrodes consists in plotting the anodic or cathodic current, at a fixed potential, as a function of ν . Fig. S3b is a loglog representation of the anodic current (at 0.2 V vs Ag/AgCl, corresponding to the open circuit voltage) as a function of ν . The observed linear dependence in the log-log representation confirms the power law relation between the current and the scan rate, $I \sim \nu^{b}$. According to the fitting parameter *b*, two extreme cases can be differentiated: i) $b \sim 1$ is characteristic of a diffusion-independent process or a pure capacitive process, ii) $b \sim 0.5$ corresponds to a process controlled by semi-infinitediffusion. [35,36] In the case of the rGO electrodes b value is 0.82 and 0.70 for us-rGO and L-rGO electrodes, respectively. It suggests that, in the frequency range corresponding to the evaluated ν , the response of both types of electrodes can be described by an intermediate scenario, being the us-rGO electrode slightly closer to the pure capacitive behaviour.

To explore the role of the nanosheet lateral dimension on the performance of rGO electrodes, in particular to assess the role of diffusion, a PEIS study is conducted. Fig. 4a presents the Bode plots for us-rGO and L-rGO electrodes, obtained at different bias potentials (vs the reference



Fig. 3. Cyclic voltammetry characterization and scan rate dependence, in PBS 150 mM. a. CVs of us-rGO and L-rGO electrodes measured at 0.2 V/s. b. CVs of us-rGO at different ν (0.05, 0.1, 0.2, and 0.5 V/s). *j* normalized by the ν , representing a differential capacitance. c. C_A as a function of the ν for us-rGO and L-rGO.



Fig. 4. Electrochemical impedance spectroscopy characterization of us-rGO and L-rGO electrodes. a. Bode plot representation of the impedance measured for different DC bias potentials, from 0.8 to -0.9 V in steps of 0.2 V vs Ag/AgCl. Grey lines in the phase diagram represents the frequency region (0.5–1.5 Hz) where the phase cross -45° . b. Frequency dependence of the *C* of the us-rGO electrode. c. Nyquist plot representation of the impedance measurements. Insets zoom-in the high frequency range (above 1 Hz). Solid dark lines in the insets represents the different slopes for n = 0.87 and n = 0.5, respectively. d. Schematic representation of the ionic diffusion process for us-rGO and L-rGO electrodes, blue arrows represent the ionic diffusion path through the nanochannels. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electrode). In general, the Bode plots are consistent with an electrode response in which the high frequency regime is dominated by resistive contributions and the very low frequency by capacitive contributions. In an ideal capacitive regime, the phase of the impedance reaches -90° ; however, for non-ideal capacitors, as is the case of electrodes described by an inhomogeneous electrode/electrolyte interface, the phase of the impedance does not reach -90° . [37,38] In the very low frequency regime, i.e. < 1 Hz, significant differences between the two types of

electrodes are visible. In the case of the us-rGO electrodes, the phase of the impedance approaches -80° , consistent with the expected response of a non-ideal capacitor. For the L-rGO electrodes, on the other hand, the phase at very low frequency remains at -45° , indicating a diffusion-limited electrode response.

To compare PEIS results with the C_A magnitude and ν response obtained from CV (see Fig. 3c), we use the real part of the complex capacitance (*C*), which is a good approximation in the low frequency

regime. [35] Fig. 4b presents *C* as a function of frequency for the us-rGO electrode (data for the L-rGO electrode can be found in Fig. S3c). The magnitude of *C* is compatible with the value of C_A , which is obtained at low ν , corresponding to frequencies <1 Hz. At very low frequency, *C* shows a clear bias dependence, being almost constant for negative polarizations and decreasing for positive polarizations. We have previously discussed this bias-dependence in terms of a pseudocapacitive response with the characteristic frequency dependence. [39] The potential dependence of *C* is in good agreement with the asymmetry observed in the CV, which shows an increase of the differential capacitance at negative polarization. This can be explained by a cationic electro-adsorption/desorption process, [4] occurring at potentials below -0.2 V (vs Ag/AgCl), at which the *C* reaches the maximum value.

For both, us-rGO and L-rGO electrodes, the Bode plots in Fig. 4a suggest the presence of an intermediate frequency regime (1 Hz–100 Hz), connecting the capacitive and the resistive responses. In order to better visualize this, Fig. 4c shows a Nyquist representation of the impedance data. In the case of an ideal capacitor, the Nyquist plot should show a vertical line. In this ideal scenario, the electrochemical system can be described as a circuit based on a series resistance and a double layer capacitance (R_s - C_{dl}). [40] For non-ideal capacitive electrodes, however, the Nyquist plot should be a tilted line, in which the deviation from a vertical line represents the deviation from the ideality. [37,38] In the case of an electrode response limited by diffusion, the slope of this line should be 1.

Due to the non-ideal behaviour of rGO electrodes, the electrical circuit cannot be described as a R_s - C_{dl} system, and C_{dl} is typically replaced by a constant phase element (CPE), with an impedance described by $Z_{CPE} = 1/Y_0(j\omega)^n$, where ω is the angular frequency, j is the imaginary number, n is the exponent related with the ideality of the system (ideality factor, see Supplementary Information for more details), and Y_0 is a parameter that can be directly assign to a capacitance when n is equal to 1. In Fig. 4c, the Nyquist spectra of the us-rGO electrode is characteristic of porous electrodes, [41] revealing a transition between two well differentiated regimes. Below 8 Hz, approximately, the response of the us-rGO electrode shows a straight capacitive line related with the CPE [41] which is consistent with that of a nonideal capacitor (the line with the highest slope in the inset of Fig. 4c corresponds to a non-ideality factor of n = 0.87). Above 8 Hz the response of the us-rGO electrode is limited by diffusion, displaying a 45° line (the line with the lowest slope represents a non-ideality factor n =0.5). On the other hand, Fig. 4c confirms that the L-rGO electrode mostly exhibits a response characteristic of a diffusion-limited electrode in all the frequency regime. The difference in the electrochemical performance of both types of electrodes can be explained by their different structure, as depicted in Fig. 4d. The more compact and less disordered stacking of the L-rGO film impedes ion transport, resulting in the diffusion-limited response of the L-rGO electrode at all frequencies. In the case of the us-rGO electrode, with a more disordered nanoporous structure, the diffusion limitation is only observed above a breakpoint frequency of 8 Hz.

Finally, in the very high frequency region, the electrodes are eventually dominated by a resistive component (as confirmed by the phase of the impedance spectra shown in Fig. 4a), which can be the combined contribution of the electrolyte and the electrode resistance. As observed in the insets of the Nyquist plots in Fig. 4c, the L-rGO electrode exhibits a lower impedance (resistive in nature), which we attribute to the higher conductivity of the L-rGO film (see Fig. 2e). [42]

3.4. Charge injection limit and ohmic drop as a function of nanosheet size

As mentioned in the introduction, rGO electrodes are used in neural interfaces for neuronal recording and stimulation. [12] For this application, the electrodes must show a good electrochemical performance, mostly in terms of high capacitance and low impedance at relatively high frequencies, between 1 kHz and 10 kHz. In order to evaluate the

capacitance of the electrodes at high frequency, where impedance spectroscopy is dominated by the resistive components, a fast chronopotentiometry pulse study is conducted. Fig. S5 shows the characteristic electrode polarization (*E*) measured as a function of time, in response to biphasic current pulses. From this graph we can calculate the voltage drop (ΔE), which includes information about the ohmic drop (*IR*) and the polarization potential (ΔE_p) resulting from the charging of the electrode/electrolyte interface. Thus, the biphasic pulses could be used to calculate the C^{int} of the electrode working at high frequency, as well as the charge injection limit ($Q_{inj,l}$) of the electrode (see Supplementary Information for more details.). [43] The *IR*, which depends on the applied current (*I*), is the voltage that drops at the resistive component of the electrode/electrolyte interface (*R*). [44] It is a key parameter to consider in neuromodulation applications, since it can limit the energy efficiency of implantable neural interfaces. [45]

Fig. 5a shows curves of E vs time for different pulse widths, corresponding to frequencies between 312 Hz and 5 kHz. For all the experiments, the same anodic and cathodic charge is injected ($Q_{inj} = 0.04 \text{ mC}/$ cm^2). The equilibrium potential (E_{ipp}) is equal for all investigated pulse widths, which is an indication of the absence of irreversible reactions. [43] It is also noted that *IR* increases as the pulse width decreases, which is expected since a larger current is applied for shorter pulses to deliver the same charge. From these measurements, by the integration of ΔE after subtraction of IR, the C^{int} could be calculated for each pulse width (see Supplementary Information). [46] Fig. 5b shows the cathodic and anodic integral capacitance (C_{cat}^{int} and C_{an}^{int}) as a function of the pulse frequency for the us-rGO and L-rGO electrodes, revealing their frequency dependence. At the highest measured frequency (5 kHz), the capacitance is below 1 mF/cm², orders of magnitude below the capacitance measured from PEIS at very low frequencies (see Fig. 4b). The frequency dependence shown in Fig. 5b is typical of porous electrodes, where the electrical response of the electrode is governed by ion diffusion. [41] Moreover, by comparing both type of electrodes, it is observed that at the lowest tested frequency C^{int} is larger for the us-rGO electrode, as previously observed in the CV measurements (conducted at low frequency < 5 Hz), since the diffusion through the nanopores is more accessible in us-rGO than in L-rGO. However, such difference decreases as frequency increases, and both electrodes show the same C^{int} at the maximum frequency analysed.

The Q_{inj,l} is an important figure of merit of electrodes for applications in neural interfaces, [44] and is defined as the maximum charge that can be injected within the safe electrochemical potential window of the electrode (-0.9 V to 0.8 V vs Ag/AgCl for rGO electrodes). For this application, the Qinj is typically delivered at frequencies between 1 kHz and 10 kHz, as mentioned above. To investigate the effect of the GO nanosheet lateral dimension on Qinj, l, in Fig. 5c E vs time is represented for us-rGO and L-rGO electrodes in response to symmetric biphasic current pulses (1 ms pulse width and 1 ms interphase time) injecting different charge (0.4 and 0.6 mC·cm⁻²). To evaluate $Q_{ini,b}$ Fig. 5e depicts the anodic (E_a) and cathodic (E_c) electrode polarization as a function of the Q_{inj} . From this representation, the $Q_{inj,l}$ can be extrapolated for the two types of electrodes. For us-rGO electrodes the cathodic and anodic $Q_{ini,l}$ are 1.6 \pm 0.1 and 0.9 \pm 0.07 mC/cm², respectively, and for L-rGO electrodes 1.2 \pm 0.1 and 0.8 \pm 0.07 mC/cm². The resulting higher $Q_{ini,l}$ of the us-rGO electrode with respect to L-rGO electrode is consistent with its higher C^{int} (0.95 \pm 0.04 and 0.71 \pm 0.02 mF/cm², cathodic and anodic, respectively) compared to that of the L-rGO electrode (0.63 \pm 0.02 and 0.56 \pm 0.05 mF/cm², cathodic and anodic, respectively). Again, such difference is attributed to the different porous structure of the film, being the us-rGO film a more disordered material which facilitates ion diffusion through the bulk of its porous structure. Finally, we compare the IR for the two different types of rGO electrodes, as it is another relevant performance metric in neuromodulation applications. Fig. 5d depicts the IR as a function of Q_{ini}, revealing that the L-rGO electrode has nearly half the IR of the us-rGO electrode, which results



Fig. 5. Chronopotentiometry study of us-rGO and L-rGO electrodes. a. Pulse width study (3.2, 1.6, 0.8 and 0.4 ms) applying the same Q_{inj} (0.04 mC/cm²). b. C^{int} (calculated from panel a) as a function of the pulse frequency. Solid symbols represent C_{cat}^{int} , and empty symbols represent C_{an}^{int} . c. Q_{inj} , study (0.4 and 0.6 mC/cm²) with the same pulse width (1 ms). d. Statistical cathodic and anodic electrode polarization as a function of Q_{inj} , used to extrapolate the $Q_{inj,l}$. Black solid lines represent the potential window between -0.9 V and 0.8 V vs Ag/AgCl. e. Statistical *IR* as a function of Q_{inj} . Solid lines represent the average of the measurement and dashed lines the standard deviation of the measurements.

from the higher conductivity of the L-rGO electrode (see Fig. 2e).

4. Conclusions

In this study, we investigated the effect of GO nanosheet lateral dimension on the properties of nanoporous rGO electrodes (prepared by vacuum filtration of GO and HT reduced) and evaluated its impact on the electrochemical performance. Our findings reveal differences in terms of structure, morphology and electrical conductivity for micrometre-thick films prepared from ultrasmall GO and large GO nanosheets. The L-GO nanosheets results in more ordered, conductive and slightly thinner films compared to the ones prepared from us-GO nanosheets.

The observed structural and electrical differences have a significant impact on the electrochemical performance of the rGO electrodes. The better stacked and less disordered L-rGO films display an electrochemical response limited by diffusion in the investigated frequency range (from 0.1 Hz to 10 kHz). In contrast, us-rGO electrodes exhibit a pseudocapacitive response in the low frequency regime (below 8 Hz), which is due to the diffusion-enhancement enabled by the more disordered bulk structure of the porous electrode. This distinctive behaviour is clearly observed in the potential-dependent frequency response of the impedance, which is notably different for both materials.

We have also investigated the effect of the GO nanosheet lateral dimension on the capability of the electrodes to inject charge at high frequency, which is an important figure of merit for neurotechnology applications of rGO electrodes. From chronopotentiometry, we found that us-rGO electrodes show a slightly higher charge injection limit than L-rGO electrodes; however, this difference decreases at shorter pulse widths (i.e, higher frequencies), when ion transport becomes severely impeded. Finally, we observe a significant lower ohmic drop for the L- rGO electrodes, which can be understood due to their higher conductivity. This is a key parameter to consider when designing implantable neural interfaces; in order to reduce the size of the implant and its power consumption, electrode materials with low *IR* are particularly important.

Our work contributes to comprehend the interplay between the GO nanosheet size and the electrochemical performance of rGO electrodes. With special attention on figure of merits relevant for the specific case of neural interface applications, where interest is on the high frequency range, our study offers guidelines for tailoring the design of rGO technology.

CRediT authorship contribution statement

María del Pilar Bernicola: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Miquel Madrid-Gimeno: Investigation, Formal analysis. Nerea Murillo-Cremaes: Methodology. Tommaso Battisti: Methodology. Neus Lozano: Writing – review & editing, Methodology, Investigation. Kostas Kostarelos: Writing – review & editing, Project administration. Jose A. Garrido: Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. Elena del Corro: Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: J. A.G. and K.K. declare that they hold interest in INBRAIN Neuroelectronics which has licensed technology described in this paper. All other authors declare no competing interests. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.diamond.2024.111722.

Data availability

Data will be made available on request.

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