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# Hydrothermal synthesis of a graphene-based composite enabling the fabrication of a current collector-free microsupercapacitor with improved energy storage performance

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## Abstract

Herein, the development and the characterization of an all-solid state symmetrical and current collector-free microsupercapacitor based on a new reduced graphene oxide-polydopamine (rGO-PDA) composite are reported. The rGO-PDA composite is synthesized by a facile, eco-friendly and scalable hydrothermal approach in the presence of dopamine which can not only contribute to the oxygen functional groups removal from graphene oxide but also polymerize onto the rGO sheets reducing their restacking and improving the wettability of the electrode. The optimized rGO-PDA composite material exhibits excellent capacitance and cycling stability as well as an improved rate capability compared to the pristine rGO in  $\text{Na}_2\text{SO}_4$  solution. This performance enhancement can be linked to the higher transfer kinetic and lower transfer resistance values of the ions involved in the charge storage process of rGO-PDA, as determined by *ac*-electrogravimetry. Furthermore, an all-solid-state microsupercapacitor was prepared employing the optimized rGO-PDA composite as electrode material. Interdigitated electrodes were obtained thanks to a  $\text{CO}_2$  laser and a  $\text{Na}_2\text{SO}_4$ /PVA hydrogel was employed, no current collector was used. This device achieves a noteworthy energy density of  $6.2\text{mWh}\cdot\text{cm}^{-3}$  at a power density of  $0.22\text{W}\cdot\text{cm}^{-3}$ . Moreover, it exhibits exceptional cycling stability, retaining 104% of its initial capacity even after undergoing 10,000 cycles at  $2\text{V}\cdot\text{s}^{-1}$ .

## Introduction

Micro-scale energy storage devices have become notably essential in the development of portable and wearable electronic devices [1-5]. Among the various micro-scale energy storage devices, micro-supercapacitors and micro-batteries have gained significant attention owing to their unique properties and potential applications. While micro-batteries have been the traditional choice for energy storage in microelectronics, microsupercapacitors have emerged as a promising alternative due to their higher power density, faster charge and discharge rates, and longer cycle life [6-8]. For instance, microsupercapacitors have been shown to possess significant promise in powering wearable electronics, such as smartwatches and fitness trackers, due to their high-power density and fast charging capabilities [9, 10].

Graphene, a two-dimensional material, has emerged as a promising material for microsupercapacitors. Owing to its high surface area, excellent electrical conductivity, and mechanical strength, graphene-based microsupercapacitors offer several advantages including high power density, long cycle life, and the potential for easy integration into microelectronic devices. As a result, graphene-based microsupercapacitors have attracted significant research interest and hold great promise for a wide range of applications [11-13].

For the synthesis of graphene, several methods have been developed comprising chemical vapor deposition, liquid-phase exfoliation, and reduction of graphene oxide (GO) [14-17]. Among these methods, the hydrothermal reduction of GO has emerged as a promising approach for the synthesis of graphene due to its advantages over other methods. Hydrothermal reduction of GO offers several advantages, such as low cost, ease of production, scalability, and the potential for tailoring the properties of the resulting graphene [18, 19]. In recent years, there has been growing interest in using green reducing agents to replace toxic and harmful reducing agents in the hydrothermal reduction process. Among the reductors, dopamine (DA), a natural catecholamine neurotransmitter, has shown great potential as a green reducing agent for

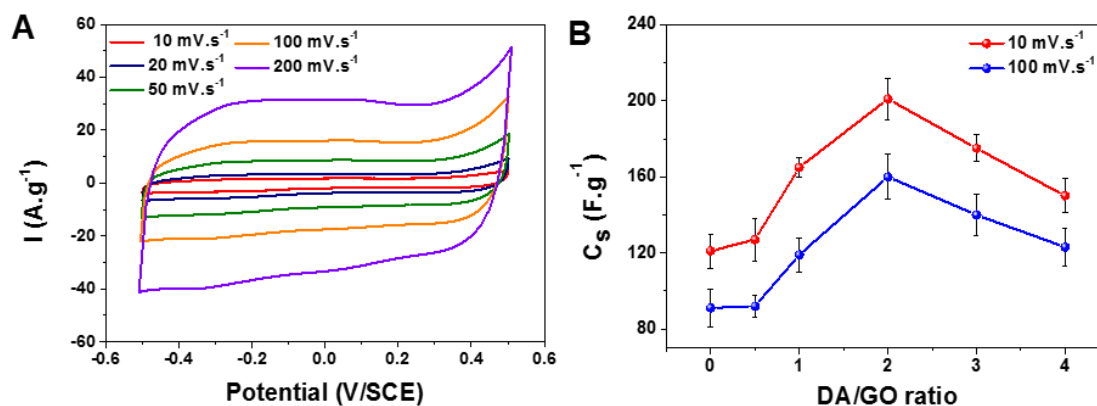
reducing GO. It has been demonstrated that in a solution synthesis involving the dopamine and GO, dopamine can not only remove oxygen functional groups from graphene oxide but also self-polymerize on the rGO sheets which reduces the restacking of the graphene sheets and improves the wettability of the electrode due to the presence of the nitrogen in PDA [20-24]. Here, we present a cost-effective and environmentally friendly approach for large-scale production of reduced graphene oxide (rGO) using the hydrothermal method, leveraging the multifunctional properties of polydopamine (PDA). The optimized composite material, rGO-PDA, exhibits improved volumetric and gravimetric capacitances, superior cycling stability and enhanced transfer kinetics as well as low transfer resistance for the species involved in the charge balance process compared to pristine rGO. Finally, a current collector free solid-state interdigitated microsupercapacitor was successfully fabricated using the optimized composite through laser cutting and tests with a gel electrolyte interface presented remarkable charge storage performance.

## Results and Discussion

### Optimization of the rGO-PDA composite

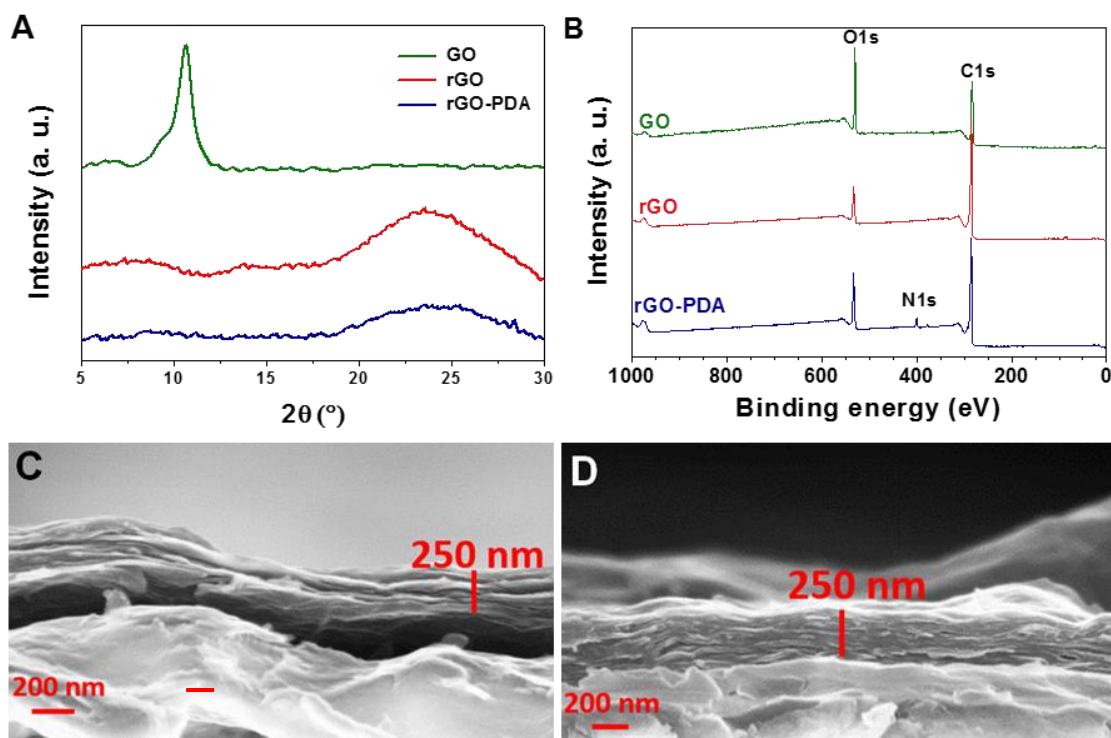
After the hydrothermal treatment of the GO suspension containing dopamine, a black powder was obtained by vacuum filtration (**Figure S1**). Various rGO-PDA composites were prepared (see Experimental Section). In order to obtain an rGO-PDA composite material with optimized capacitance, the influence of the initial DA/GO ratio (**Table S1**) on the electrochemical response of the final product was investigated. **Figure S2** shows the voltammograms of the various materials tested (DA/GO mass ratio: 0.5 to 4). A quasi-rectangular signal is observed for all these electrodes (**Figure S2** and **1A**). From these voltammograms, the gravimetric capacitances ( $C_g$  in  $F \cdot g^{-1}$ ) at two scan rates (10 and 100  $mV \cdot s^{-1}$ ) were calculated, they are shown in **Figure 1B**. From this figure, it is clear that the rGO-PDA composite obtained with an initial

DA/GO ratio of 2 has the highest gravimetric capacitance ( $208 \text{ F}\cdot\text{g}^{-1}$  at  $10 \text{ mV}\cdot\text{s}^{-1}$ ) and is therefore considered to be the optimized composite. Its electrochemical response is shown in **Figure 1A**.



**Figure 1:** (A) Cyclic voltammograms of the optimized rGO-PDA prepared with a DA/GO ratio of 2, in 0.5 M  $\text{Na}_2\text{SO}_4$  at different scan rates. (B) Gravimetric capacitance at two scan rates ( $10$  and  $100 \text{ mV}\cdot\text{s}^{-1}$ ) of the rGO-PDA composite film obtained with different dopamine/GO mass ratios.

### Morphological and compositional analyses of rGO-PDA composite



**Figure 2:** (A) Diffractograms of GO, rGO and optimized rGO-PDA films (DA/GO mass ratio = 2). (B) XPS survey spectra from GO, rGO, and optimized rGO-PDA films. SEM micrographs of the cross-section of (C) rGO and (D) rGO-PDA films on Au/quartz.

**Figure 2A** shows the XRD patterns of the three samples GO, rGO and optimized rGO-PDA deposited on a glass substrate. The pattern of GO shows the (001) diffraction peak at  $2\theta = 10.5^\circ$  (corresponding to a d-spacing of 0.842 nm), which is in good agreement with the literature values [25, 26]. After hydrothermal treatment, this characteristic peak is no longer detected. This result shows that for both samples, rGO and rGO-PDA, the graphene oxide has been successfully reduced by the hydrothermal method. For both samples a new broad peak appears around  $2\theta = 23^\circ$ .

The chemical composition of GO, rGO, and rGO-PDA films deposited on gold-coated mica was determined by XPS. **Figure 2B** shows the XPS survey spectra obtained for these samples and **Table S2** shows the chemical composition in atomic % of their surface. For the optimal rGO-PDA composite (DA/GO = 2), PDA nitrogen is detected around a binding energy of 400

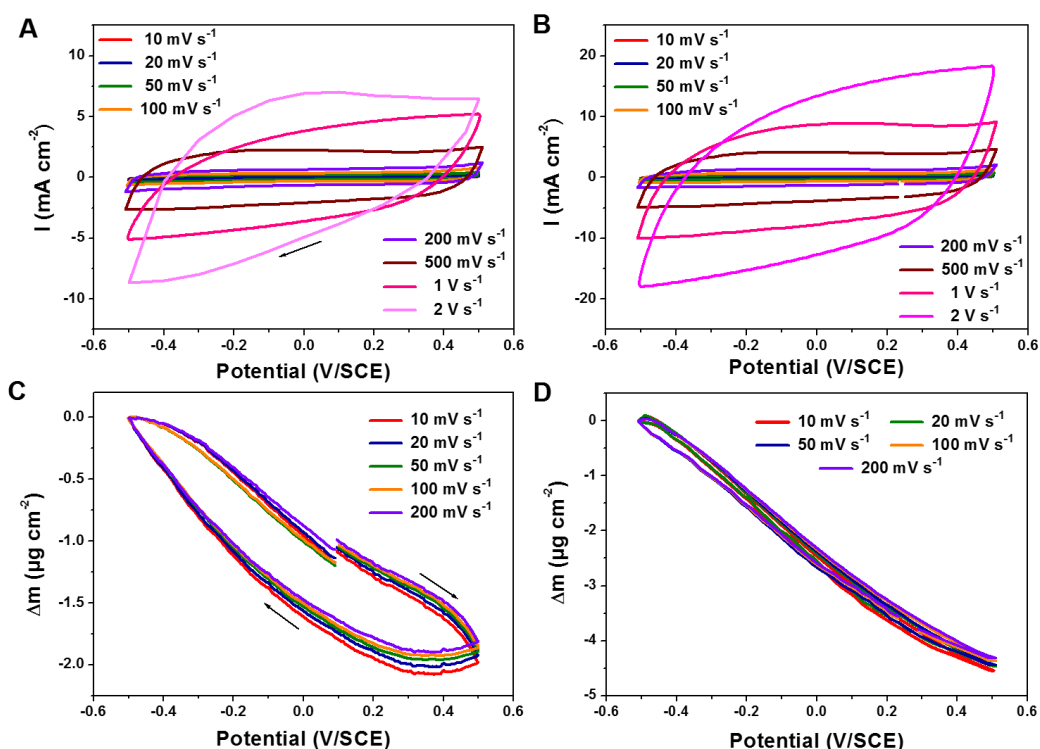
eV (**Figure 2B**). The atomic N/C ratio for the rGO-PDA composite is 0.053 whereas it is 0.123 for the PDA (theoretical value: 0.125 based on the DA formula  $C_8H_{11}NO_2$ ) (**Table S2**) [27]. The low N/C ratio confirms that this material is a composite of rGO and PDA.

In order to determine the density of rGO and rGO-PDA, films were first formed by drop casting on a quartz electrode to determine their mass. Thanks to nanogram sensitivity of QCM, the mass loading of the electrodes was estimated to be 7.8  $\mu\text{g}$  for rGO and 8.5  $\mu\text{g}$  for rGO-PDA film. The thickness of rGO and rGO-PDA films were then estimated from the SEM observations (**Figure 2C** and **2D**) allowing us to calculate their volume (the geometric area of the two films being 0.2  $\text{cm}^2$ ). The density of the rGO-PDA composite was estimated to be 1.69  $\text{g}\cdot\text{cm}^{-3}$  and those of the rGO to be 1.55  $\text{g}\cdot\text{cm}^{-3}$ . The slight difference in densities observed between the two films could be explained by the presence of PDA between the rGO sheets.

#### Electrogravimetric behavior of rGO and rGO-PDA in 0.5 M $\text{Na}_2\text{SO}_4$

**Figure 3** shows the current-mass voltammograms of rGO and rGO-PDA films, as a function of potential, obtained at different scan rates from 10 to 2000  $\text{mV}\cdot\text{s}^{-1}$  for cyclic voltammetry and from 10 to 200  $\text{mV}\cdot\text{s}^{-1}$  for mass/potential curves.



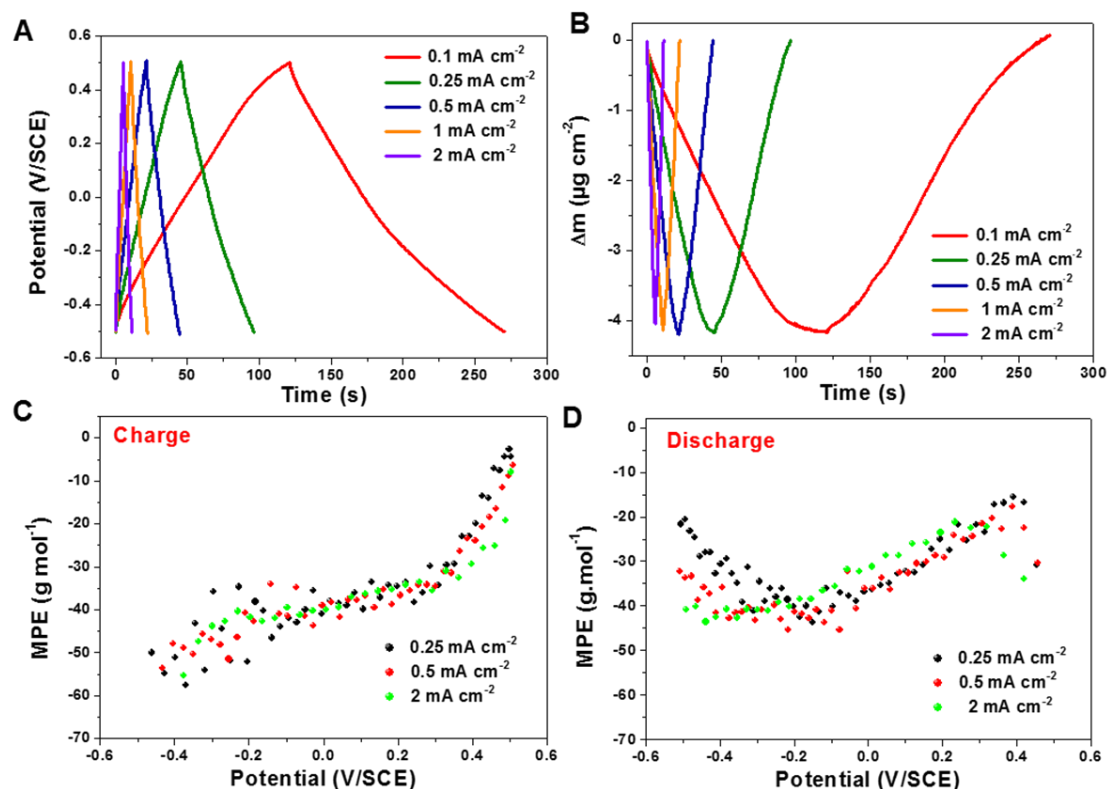


**Figure 3:** Voltammograms for (A) rGO and (B) rGO-PDA and mass variation *versus* potential for (C) rGO and (D) rGO-PDA at various potential scan rates, in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution.

**Figure S3, 4A** and **4B** show the galvanostatic charge-discharge curves for these two films at different current densities and the associated mass changes. It is clearly seen that for both films, the mass decreases during charging (**Figure S3B** and **4B**) (or anodic sweep of potential for potentiodynamic cycling) (**Figure 3C** and **3D**) and increases during discharging (**Figure S3A** and **4B**) (or cathodic sweep of potential for potentiodynamic cycling (**Figure 3C** and **4D**)). These results indicate that the electroneutrality of rGO and rGO-PDA is mainly maintained by the participation of cations.

Since both rGO and rGO-PDA electrodes have almost the same mass loading, the high discharge times (151 s for rGO-PDA *versus* only 80 s for rGO at a current density of 0.1 mA·cm<sup>-2</sup>) observed during charge-discharge cycles for the rGO-PDA composite compared to the rGO (**Figure 4A** and **S3A**) may indicate a larger surface area developed for the charge storage process for the composite electrode. In addition, the absence of hysteresis in the mass response

of the rGO-PDA composite electrode in contrast to the rGO (**Figure 4B** and **S3B**) indicates that electroadsorption and electrodesorption of the species involved in the charge compensation process occur at very similar rates.



**Figure 4:** (A) Potential variation with time and (B) mass variation with time, related to galvanostatic charge/discharge of the optimized rGO-PDA at different current densities in 0.5 M Na<sub>2</sub>SO<sub>4</sub>. MPE function calculated from the of the QCM-CDG response at different current densities during (C) charge and (D) discharge for the rGO-PDA composite.

From the EQCM measurements, an interesting function, the mass per electron (MPE),  $Fdm/dq$ , can be calculated. This value allows to estimate the average molar mass of the ions involved in the charge compensation process within the electrode. If solely one species is involved, the MPE corresponds to its molar mass. The  $Fdm/dq$  function of the rGO-PDA composite upon charging and discharging for three current densities (0.25, 0.5, and 2 mA.cm<sup>-2</sup>) was calculated (from the QCM-GCD response (**Figure 4A** and **4B**)). **Figure 4C** and **4D** show the calculated

MPE values as a function of the imposed potential. For the three current densities, the  $Fdm/dq$  curves have a similar shape. The variation of the MPE with potential and its deviation from 23  $\text{g}\cdot\text{mol}^{-1}$  (corresponding to a bare  $\text{Na}^+$ ) can be explained by the participation of more than one species in the charge compensation process. *Ac*-electrogravimetry remains the only gravimetric technique that can identify the number and nature of species participating directly or indirectly in the charge compensation process.

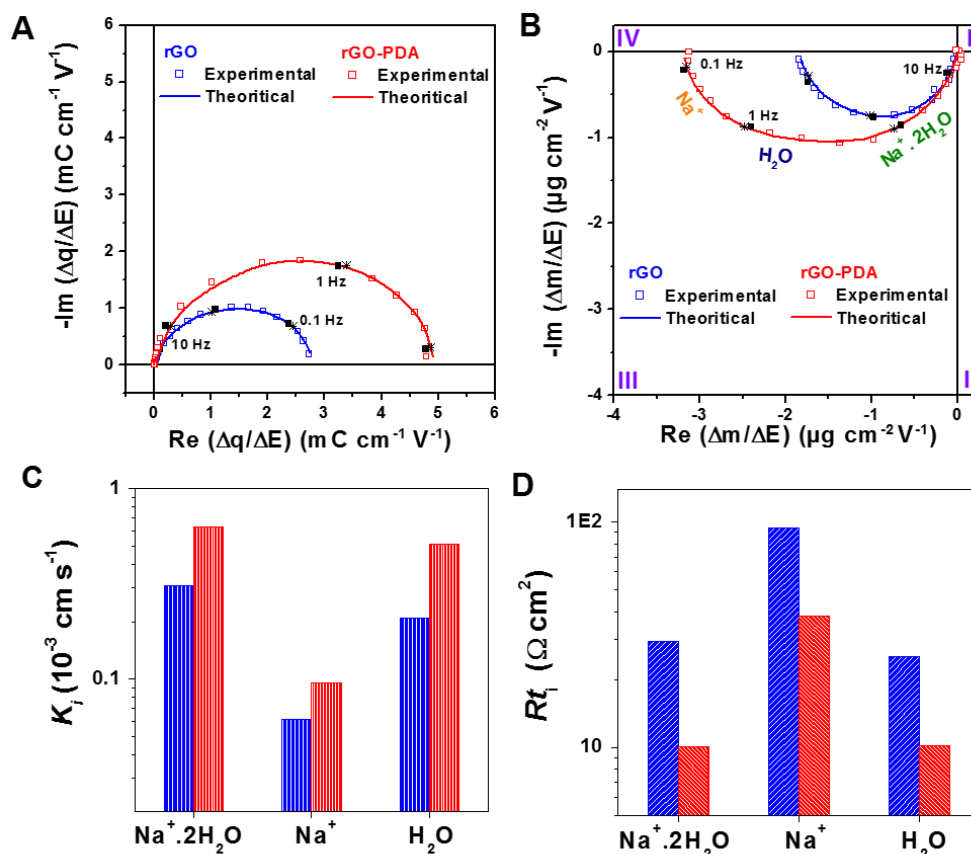
### Ac-electrogravimetry

In order to find out the species involved in the charge compensation process and to have information on their transfer kinetics at the electrolyte/electrode interface, *ac*-electrogravimetry measurements were performed at several potentials over the range of -0.5 to 0.5 V/SCE. **Figure 5A** shows the charge/potential transfer function,  $\Delta q/\Delta E(\omega)$ , of rGO and rGO-PDA at a potential of -0.3 V/SCE. This transfer function can reveal the contribution of charged species involved in the charge compensation process. The charge/potential transfer function curves,  $\Delta q/\Delta E(\omega)$ , of the two electrodes (**Figure 5A**) show a depressed loop, which can be attributed to the participation of more than one charged species with fairly close ion transfer constants at the interface. It is important to note that the  $\Delta q/\Delta(\omega)$  loop diameter is larger for rGO-PDA, indicating that more ions are involved in the charge compensation of the composite electrode (knowing that both films have similar mass). This result is very consistent with the current densities achieved by cyclic voltammetry between these two electrodes (**Figure 3**).

The experimental charge/potential transfer function data,  $\Delta q/\Delta(\omega)$ , were fitted with the theoretical function given by **Equation S2**. Good agreement was obtained between the theoretical and experimental curves by taking into account the involvement of two ionic species. Two parameters, related to kinetics of interfacial transfer and inverse of the transfer resistance

( $K_i$  and  $G_i = \frac{1}{F \times R t_i}$ ) for each of these two species were obtained by this fitting process, and

are reported in **Table S3**.



**Figure 5:** Experimental and theoretical transfer functions of rGO (blue) and rGO-PDA (red) electrodes at a potential of  $-0.3$  V vs. SCE: (A)  $\Delta q/\Delta E(\omega)$  and (B)  $\Delta m/\Delta E(\omega)$ , in  $0.5$  M  $\text{Na}_2\text{SO}_4$  solution. (C)  $K_i$  and (D)  $R t_i$  of ions and water molecule at  $-0.3$  V vs. SCE for rGO (blue) and rGO-PDA (red).

The  $\Delta q/\Delta E(\omega)$  transfer function provides information on the contribution of charged species but does not allow for their identification. For this, simultaneously measured electrogravimetric transfer function,  $\Delta m/\Delta(\omega)$ , was analyzed to identify both charged and neutral (solvent) species. For both films (rGO and rGO-PDA), the electrogravimetric responses,  $\Delta m/\Delta(\omega)$ , are in the third

quadrant, consistent with the transfer of cationic species or cationic species with solvent (**Figure 5B**). The two parameters,  $K_i$  and  $G_i$ , for the two ionic species previously obtained from **Equation S2 (Table S3)** were used for fitting the electrogravimetric transfer function,  $\Delta m/\Delta(\omega)$ , (**Equation S3**). The additional parameters,  $K_i$  and  $G_i$  for the free solvent molecules as well as the molar mass ( $M_i$ ) of each species were estimated after fitting.

The process of fitting the experimental  $\Delta m/\Delta(\omega)$  curves reveals the participation of two cations:  $\text{Na}^+ \cdot 2\text{H}_2\text{O}$  at high frequencies and  $\text{Na}^+$  at low frequencies. Free  $\text{H}_2\text{O}$  molecules were detected at intermediate frequencies. The transfer order of the two cations as well as the participation of free water is consistent with *ac*-electrogravimetry measurements previously performed on carbon materials in similar electrolytes [28-31].

The interfacial transfer constants,  $K_i$ , of the different species involved in the charge compensation process as a function of the applied potential for rGO and rGO-PDA are shown in **Figure S4**. From this figure, it is clear that the three exchanged species transfer faster at the composite electrode interface, rGO-PDA, compared to that at the rGO. As an example, the interfacial transfer kinetics of  $\text{Na}^+ \cdot 2\text{H}_2\text{O}$  cation is twice faster at the rGO-PDA interface compared to rGO (**Figure 5C**). This finding underlines faster charge-discharge kinetics for the rGO-PDA composite. In addition, this composite shows lower transfer resistance,  $Rt_i$ , compared to the rGO electrode whatever the species (**Figure 5D**).

### Correlation between EQCM and *ac*-electrogravimetry results

To validate our assumption concerning the involvement of three species in the charge storage process in rGO and rGO-PDA, we used a methodology that takes advantage of the complementarity between EQCM and *ac*-electrogravimetry. [28, 32]

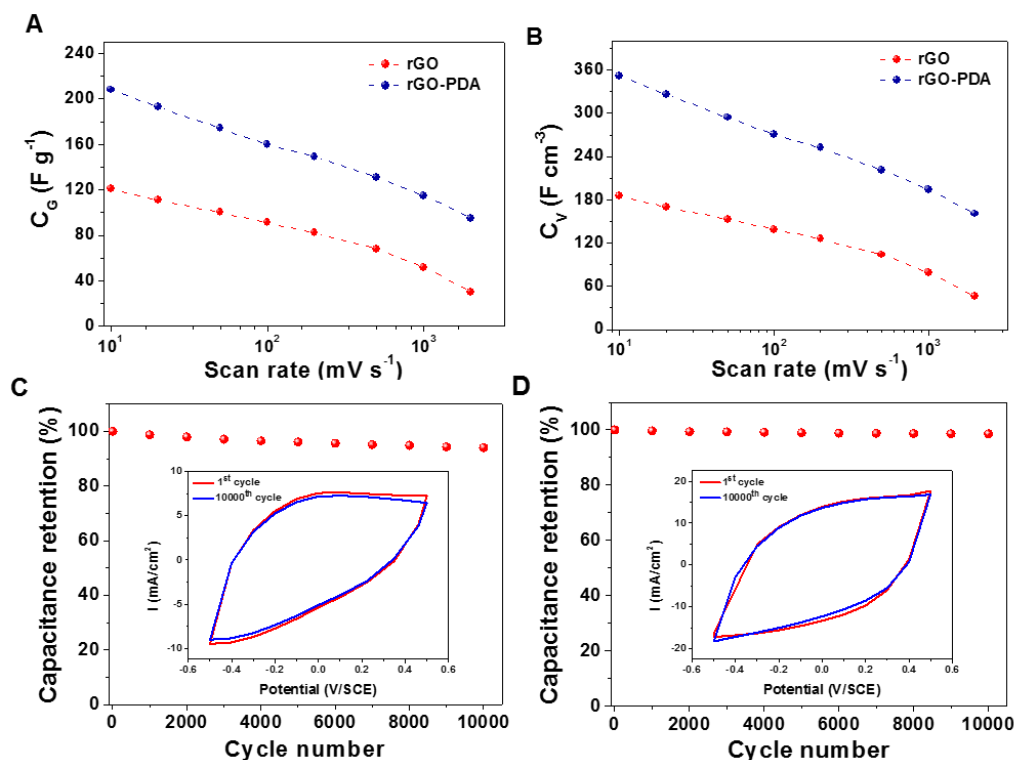
Using the parameters  $K_i$  (**Figure S4**) and  $G_i$  obtained by fitting the experimental transfer functions, the relative concentration variation,  $C_i - C_0$ , of the species, identified by exploitation

of the *ac*-electrogravimetry data, as a function of the applied potential can be estimated. This quantity is calculated by the low-frequency integration of **Equation S4** and shown in **Equation 5**. **Figure S5A** and **S5B** show the variations of the relative concentration,  $C_i-C_0$ , of the three species identified for rGO and rGO-PDA films ( $\text{Na}^+ \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  and  $\text{Na}^+$ ) as a function of the potential. For both films, the free solvent ( $\text{H}_2\text{O}$ ) shows the largest concentration variation in the potential range of -0.5 to 0.5 V/SCE.

From the relative concentration variations (**Figure S5A** and **S5B**), the mass variations of each species ( $\Delta m_i$ ) as a function of the potential can be calculated by considering the molar mass of each (**Figure S5C** and **S5D**). Reconstruction of the global mass change can be performed by adding the contributions of the individual mass changes (**Figure S6**). A good agreement is obtained between the mass measured with conventional EQCM at  $10 \text{ mV} \cdot \text{s}^{-1}$  and the mass reconstructed from *ac*-electrogravimetry in the potential range studied for both rGO and rGO-PDA films. This result confirms the participation of the three species in the charge storage process *ie.*  $\text{Na}^+ \cdot \text{H}_2\text{O}$ ,  $\text{Na}^+$  and  $\text{H}_2\text{O}$ .

### Evaluation of the charge storage performance of the rGO-PDA composite

The capacitances were calculated from the cyclic voltammograms depicted in **Figure 3**. **Figure 6A** and **6B** show the gravimetric and volumetric capacitances as a function of scan rate, for rGO and rGO-PDA, respectively. From these figures it is obvious that the rGO-PDA composite has higher gravimetric capacitances and voltammetric capacitances than the rGO. At a scan rate of  $10 \text{ mV} \cdot \text{s}^{-1}$ , rGO-PDA has a volume capacitance of  $351 \text{ F} \cdot \text{cm}^{-3}$  and a gravimetric capacitance of  $208 \text{ F} \cdot \text{g}^{-1}$  compared to only  $185 \text{ F} \cdot \text{cm}^{-3}$  and  $121 \text{ F} \cdot \text{g}^{-1}$  for rGO which is higher than those reported for carbon-based electrodes for EDLCs [33-36].



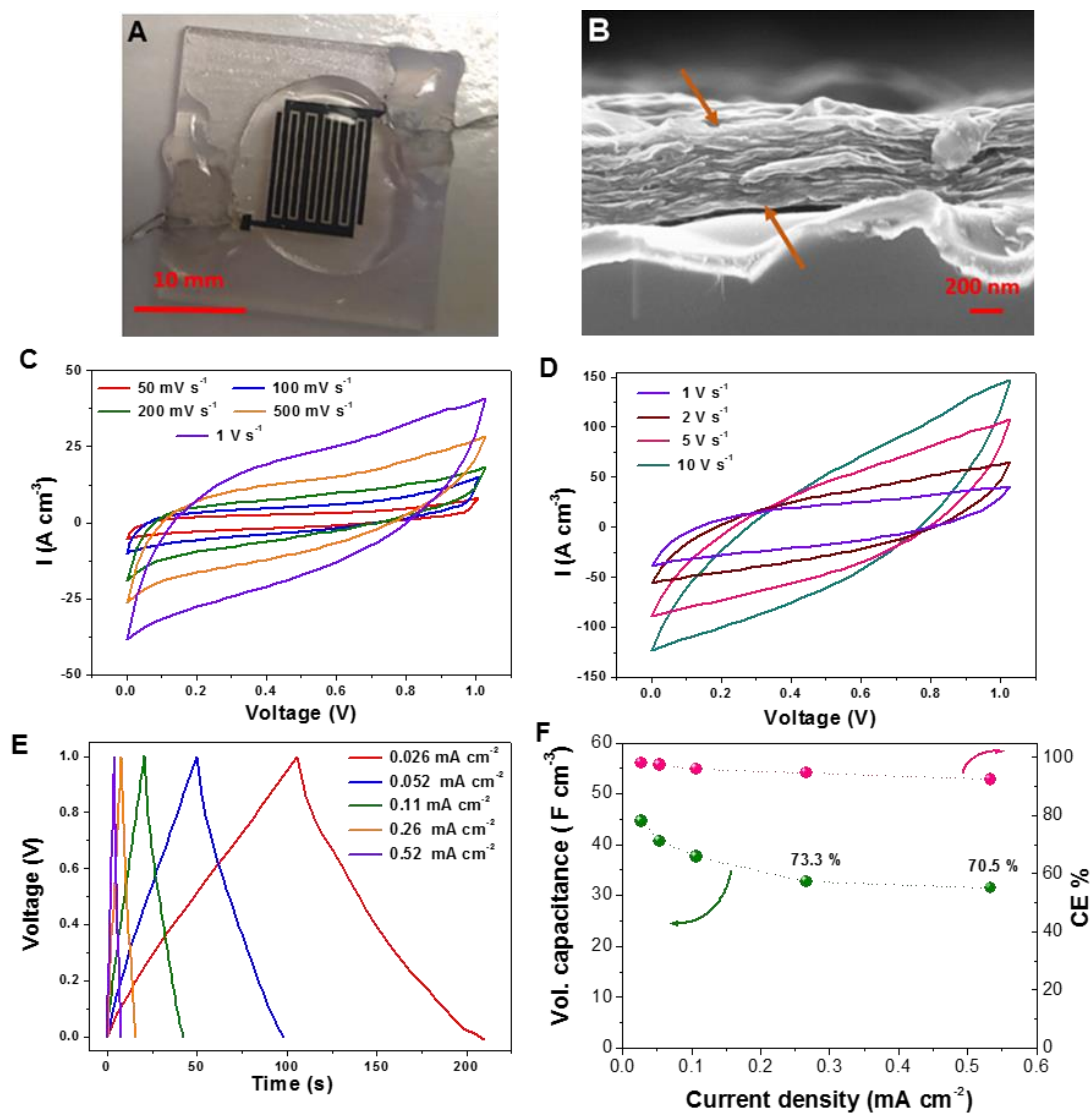
**Figure 6:** Variation of (A) gravimetric and (B) volumetric capacitance of rGO and rGO-PDA as a function of the potential scan rate. Cycling stability of (C) rGO and (D) rGO-PDA at a scan rate of  $2 \text{ V} \cdot \text{s}^{-1}$  in  $0.5 \text{ M Na}_2\text{SO}_4$ .

The rGO-PDA composite also exhibits better capacitance retention as the scan rate increases. Indeed, rGO-PDA has a capacitance of  $208 \text{ F} \cdot \text{g}^{-1}$  at  $10 \text{ mV} \cdot \text{s}^{-1}$  and  $95 \text{ F} \cdot \text{g}^{-1}$  at  $2000 \text{ mV} \cdot \text{s}^{-1}$  (i.e., 45% retention) while rGO has a capacitance of  $121 \text{ F} \cdot \text{g}^{-1}$  at  $10 \text{ mV} \cdot \text{s}^{-1}$  and  $30 \text{ F} \cdot \text{g}^{-1}$  at  $2000 \text{ mV} \cdot \text{s}^{-1}$ , corresponding to 45% and 25% capacitance retention, respectively. These results which indicate faster charge/discharge kinetics for the composite electrode are in good agreement with the lower time constant of rGO-PDA compared to the pristine rGO (**Figure S7** and **Table S4**). The cycling stability of both rGO and rGO-PDA films was studied by cyclic voltammetry at a scan rate of  $2 \text{ V} \cdot \text{s}^{-1}$  (**Figure 6C** and **6D**). The composite electrode shows excellent cycling stability. Indeed, the rGO-PDA whose initial capacitance is  $155 \text{ F} \cdot \text{g}^{-1}$ , stabilizes at  $152 \text{ F} \cdot \text{g}^{-1}$  after 10,000 cycles, i.e. a decrease of 1.5 % and thus a capacitance retention of 98.5 % against only 94 % for the rGO.

### Microsupercapacitor based on rGO-PDA composite electrodes

Figure 7A depicts a digital image of the rGO-PDA MSC fabricated on a Plexiglas substrate. This MSC is composed of 12 (2 x 6) interdigital fingers. Each interdigital finger has a width of around 500  $\mu\text{m}$ . The global surface area covered by the interdigital electrodes is 75  $\text{mm}^2$ . The inter-electrode interdigital spacing has been set at 200  $\mu\text{m}$ . It's worth mentioning that no residual material resulting from the etching is observed within the interfinger space, guaranteeing the absence of short circuits in the microdevice (an ohmmeter was also used for verification purposes). A SEM image of the cross-section of an interdigital finger composed of rGO-PDA is presented in **Figure 7B**. It can be clearly seen that the rGO-PDA film deposited on the Plexiglass substrate is 600 nm thick. The electrochemical behavior of the rGO-PDA MSC, without current collector, was first evaluated by cyclic voltammetry and galvanostatic charge-discharge using a gel electrolyte ( $\text{Na}_2\text{SO}_4/\text{PVA}$ ) (**Figure 7C** and **7D**). The voltammograms of this MSC at different scan rates are plotted in **Figure 7C** and **7D**. It can be clearly noticed a deviation from the voltammograms obtained in the three-electrode configuration (**Figure 3B**). This can be attributed to an increase in the resistance of the micro-device due to the absence of a current collector and the gel electrolyte.

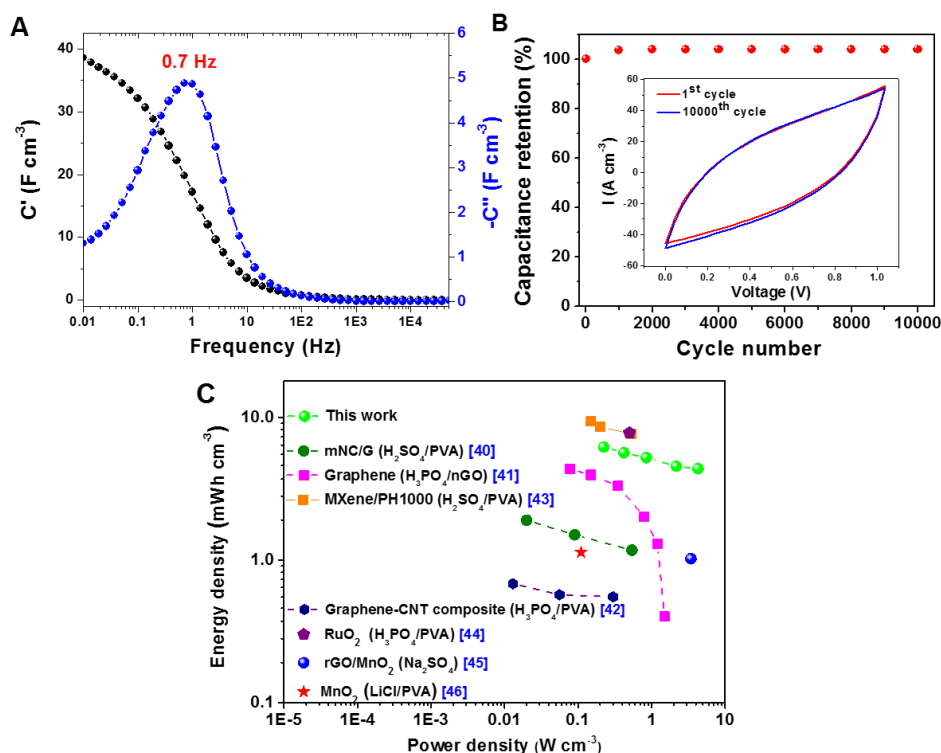




**Figure 7:** A) Digital photography of the rGO-PDA MSC fabricated on a Plexiglas substrate. B) SEM micrograph of the cross-section of an interdigitated rGO-PDA finger. C, D) CV curves of rGO-PDA MSC at different scan rates, from  $0.05 \text{ V}\cdot\text{s}^{-1}$  to  $10 \text{ V}\cdot\text{s}^{-1}$ . E) GCD curves recorded at various current densities. F) Volumetric capacitance (left axis) and coulombic efficiency (right axis) of rGO-PDA MSC calculated from GCD curves *versus* applied current density.

**Figure 7E** shows the GCD curves of rGO-PDA based MSC. A triangular shape, characteristic of supercapacitors, is observed for all the tested current densities. The volumetric capacitances and the coulombic efficiency (CE) calculated from the charge-discharge curves are shown in

**Figure 7F.** At a current density of  $0.026 \text{ mA}\cdot\text{cm}^{-2}$ , even without a current collector, the rGO-PDA MSC exhibits a coulombic efficiency of 98% and a volumetric capacitance of  $45 \text{ F}\cdot\text{cm}^{-3}$ .



**Figure 8:** A) Bode plot of the volumetric capacitance of rGO-PDA MSC, determined at 0.3 V. B) Cycling stability of the rGO-PDA MSC at a scan rate of  $2 \text{ V}\cdot\text{s}^{-1}$ . C) Ragone plot of rGO-PDA MSC (light green scatters) in comparison with some recent studies.

The complex capacitance as a function of frequency was calculated from the electrochemical impedance spectroscopy measurements performed at 0.3 V, it is plotted in **Figure 8A**. The evolution of the imaginary capacitance  $C''(\omega)$  shows a maximum at a characteristic frequency ( $f_0$ ) of 0.7 Hz which corresponds to a relaxation constant  $\tau_0$  of 1.43 s. The evolution of the real capacitance  $C'(\omega)$  of the microdevice as a function of frequency (**Figure 8A**) shows a maximum capacitance of  $39 \text{ F}\cdot\text{cm}^{-3}$  at low frequencies. This value, corresponding to the real capacitance of the microdevice, is in good agreement with the values obtained by galvanostatic charge-discharge at low current densities (**Figure 7F**).

The long-term cycling property of the rGO-PDA based MSC was evaluated by repeated CV cycles at a sweep rate of  $2000 \text{ mV}\cdot\text{s}^{-1}$  within an operating voltage from 0 to 1 V. The rGO-PDA MSC exhibits a capacitance retention of 104% after undergoing 10,000 cycles (**Figure 8B**), the slight increase of the capacitance at the beginning of the cycling can be attributed to the activation of the composite material due to the continuous ion diffusion within the pores of the electrode material [34, 37].

Energy density and power density are crucial parameters for assessing the performance of energy storage devices. The volumetric energy and power density of the rGO-PDA MSC, calculated from the GCD profiles, are presented in the Ragone plot shown in **Figure 8C**. The rGO-PDA MSC demonstrates an impressive volumetric energy density of  $6.20 \text{ mWh}\cdot\text{cm}^{-3}$  at a power density of  $0.22 \text{ W}\cdot\text{cm}^{-3}$ . Even at a higher power density of  $4.30 \text{ W}\cdot\text{cm}^{-3}$ , this MSC still maintains a substantial energy density of  $4.33 \text{ mWh}\cdot\text{cm}^{-3}$ . These values exceed the performances of all-solid microsupercapacitors (with hydrogel electrolyte) reported in the literature in recent years, based on carbon materials [38-40]. Furthermore, in comparison to MSCs based on alternative material classes such as MXene [41]  $\text{RuO}_2$  [42], rGO- $\text{MnO}_x$  [43] et  $\text{MnO}_2$  [44], the rGO-PDA MSC developed in this work exhibits comparable energy densities.

## Conclusions

In summary, an innovative and eco-friendly hydrothermal approach was developed to prepare a composite electrode based on rGO and PDA for large scale synthesis of electroactive material. The hydrothermal reduction of GO was characterized by X-ray diffraction and the presence of PDA was confirmed by XPS. The positive effect of PDA on the electrochemical performance of the rGO-PDA composite was demonstrated by the various electrogravimetric (EQCM and *ac*-electrogravimetry) and electrochemical (CV, GCD, EIS) characterization techniques. For both rGO and optimized rGO-PDA electrodes, the same species are involved in the charge

compensation process. However, the kinetic constants corresponding to the interfacial transfer of the active species are greater for rGO-PDA than for rGO. This rapid charge transfer at the rGO-PDA/electrolyte interface results in fast charge/discharge kinetics (low relaxation time  $\tau_0$ ) and therefore better rate capability. The rGO-PDA composite material also showed good cycling stability due to the presence of the PDA between the rGO sheets, which reduces agglomeration of the rGO sheets. The results obtained for the optimized composite, in NaSO<sub>4</sub> solution and in a three-electrode configuration, motivated us to create symmetrical all-solid-state and current collector-free interdigitated micro-supercapacitors (MSCs) using a laser engraving technique, with rGO-PDA as the active material. The MSC based on rGO-PDA demonstrated exceptional cycling stability, retaining 104% of its capacity after 10,000 cycles at 2 V·s<sup>-1</sup>, and good rate capability without current collector. Moreover, it achieved a notable energy density of 6.20 mWh·cm<sup>-3</sup> at a power density of 0.22 W·cm<sup>-3</sup>. These results outperform or are comparable to the most recently reported MSCs based on graphene or other materials.

## Experimental Section

### Materials

Dopamine (DA) hydrochloride, potassium phosphate monobasic (KH<sub>2</sub>PO<sub>4</sub>), potassium phosphate dibasic (K<sub>2</sub>HPO<sub>4</sub>), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and GO suspension (4 mg·mL<sup>-1</sup>, dispersion in H<sub>2</sub>O) were purchased from Sigma Aldrich. The GO suspension was diluted with water to reach a concentration of 1 mg·mL<sup>-1</sup> of GO. All solutions were prepared with double distilled water (18.2 MΩ·cm, Purelab flex ELGA, water purification system). Phosphate buffered saline solution (PBS) with a pH of 7.2 was prepared by mixing 0.1 M of KH<sub>2</sub>PO<sub>4</sub> and 0.1 M of K<sub>2</sub>HPO<sub>4</sub>.

### Hydrothermal synthesis of rGO-PDA powder and electrode formation

In 4 mL of GO suspension (at  $1 \text{ mg}\cdot\text{mL}^{-1}$ ), 66.7 mg  $\text{K}_2\text{HPO}_4$ , 54.4 mg  $\text{KH}_2\text{PO}_4$  (0.2 M PBS pH 7.2) and different amounts of dopamine (2, 4, 8, 12 and 16 mg) were solubilized. After 30 minutes in an ultrasonic bath, the suspension was transferred to a Teflon autoclave (6 mL volume) and heated to  $160^\circ\text{C}$  for 8 h. For the reference rGO, the hydrothermal reaction was performed in the same way but in the absence of dopamine. After the hydrothermal treatment, a black powder was obtained by vacuum filtration, it was rinsed several times with ethanol and then bidistilled water (**Figure S1**). Then, the obtained powders were suspended in bidistilled water ( $1 \text{ mg/mL}$ ) to prepare the ink used to deposit the rGO and rGO-PDA films. The ink was homogenized by an ultrasonic probe which, unlike a conventional ultrasonic bath, allows for pulses of power to break up the aggregates more easily. In order to avoid too much heating, the agitation by the ultrasonic probe was carried out while keeping the sample (ink) in an ice bath. For the electrogravimetric and electrochemical characterizations,  $6 \mu\text{L}$  of the rGO-PDA (or rGO) suspension ( $1 \text{ mg}\cdot\text{mL}^{-1}$ ) were deposited on the gold electrode of the quartz resonator (AWS-Sensors, Spain) ( $0.2 \text{ cm}^2$ ). The rGO-PDA film was obtained after a drying step at  $70^\circ\text{C}$  in an oven for 40 min. The mass of the films deposited on the quartz electrode was estimated from the frequency variation of the latter (without and with film) in air via the Sauerbrey equation [45].

### Electrochemical and electrogravimetric characterizations

The electrochemical and electrogravimetric characterizations were performed using a standard three-electrode configuration and an Autolab potentiostat (Metrohm, France). The gold electrode ( $0.5 \text{ cm}$  in diameter,  $0.2 \text{ cm}^2$ ) on a quartz ( $1.4 \text{ cm}$  in diameter) (modified with rGO or rGO-PDA) was used as the working electrode, a saturated calomel electrode (SCE) and a platinum grid were used as reference electrode and counter electrode, respectively.

For the EQCM experiments, we used a lab-made QCM coupled with an Autolab potentiostat (PGSTAT12). Under the gravimetric regime, the mass variation,  $\Delta m$ , was obtained from  $\Delta f$  by using of the Sauerbrey equation ( $\Delta f = -k_s \times \Delta m$ ), where  $k_s$  is the experimental mass sensitivity constant which has a value of  $16.3 \text{ Hz} \cdot \text{cm}^2 \cdot \text{g}^{-1}$  for 9 MHz AT-cut QCM [46].

The applicability of the Sauerbrey equation (verification of the gravimetric regime) on the rGO and rGO-PDA films was verified by using electroacoustic measurements [34, 47].

For *ac*-electrogravimetry measurements [48], we employed a four-channel frequency response analyzer (FRA, Solartron 1254) and a lab-built potentiostat. The coated quartz electrode was polarized at a given potential and a sinusoidal small amplitude potential perturbation (20 mV) was applied. The frequency range of the measurements extended from 63 kHz and 10 mHz. The working electrode mass change,  $\Delta m$ , was measured at the same time as the *ac* response,  $\Delta I$ , of the electrochemical system.

### **Morphological and compositional characterizations**

For SEM observations, a field emission gun scanning electron microscope (FEG-SEM) (Ultra55, Zeiss) operating at 5 kV was used. An Omicron Argus X-ray photoelectron spectrometer with monochromatized Al K $\alpha$  excitation (1486.6 eV) was used for XPS analyses. For the acquisition of the survey and high-resolution spectra, the band-pass energy was fixed at 100 and 20 eV, respectively. The determination of the XPS peak area was done after subtraction of the background calculated using Shirley's method. The element peak intensities were corrected by the Scofield factors. XPS spectrum processing was performed using Casa XPS software (Casa Software Ltd., UK). For the XPS analyses, the films were deposited on a gold-coated mica substrate. XRD was recorded with a Philips PANalytical X'Pert Pro diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). The films were deposited on a glass substrate.

### **Preparation of the rGO-PDA microsupercapacitor (MSC)**

A microsupercapacitor (MSC) using the optimized rGO-PDA composite as the electrode material was produced on a Plexiglass substrate. Initially, a 2 cm square was etched on the Plexiglass substrate using a CO<sub>2</sub> laser cutter (Trotec SP500). Then a rGO-PDA film was deposited onto the Plexiglass substrate by drop-casting of 0.2 mL of the rGO-PDA suspension (at 1 mg·mL<sup>-1</sup>). Finally, using the CO<sub>2</sub> laser, the undesired material areas (interdigitated finger spacing) were removed according to an image prepared through the Trotec JobControl® software. The laser parameters, power, scan rate and pulse duration, were set to 35 W and 35 cm·s<sup>-1</sup> and 1.25 ms, respectively.

### **Preparation of the Na<sub>2</sub>SO<sub>4</sub>/PVA gel electrolyte**

The Na<sub>2</sub>SO<sub>4</sub>/PVA gel electrolyte was prepared by adding 0.25 g of Na<sub>2</sub>SO<sub>4</sub> and 0.25 g of PVA into 2.5 mL of distilled water and heated to 80 °C under vigorous stirring until the solution turned transparent. Na<sub>2</sub>SO<sub>4</sub>/PVA gel electrolyte was subsequently drop-casted onto the interdigitated patterns and solidified overnight.

### **Electrochemical characterizations of the all-solid-state device**

Cyclic Voltammetry (CV), Galvanostatic Charge/Discharge (GCD), and Electrochemical Impedance Spectroscopy (EIS) were performed using an Autolab potentiostat, at room temperature. CV was recorded at various potential scan rates, between 100 and 10,000 mV·s<sup>-1</sup> in the 0–1 V range. GCD was done at different current densities in the range 0.026 – 0.52 mA·cm<sup>-2</sup>. EIS spectra were recorded at a potential of 0.3 V in the frequency range of 10 mHz –50 kHz with an amplitude of 10 mV.

### ***Supporting Information***

Supporting information is available online. 1. rGO-polydopamine composite preparation and characterizations (Figure S1 and S2, Table S1 and S2); 2. EQCM characterization of rGO (Figure S3); 3. *Ac*-electrogravimetry (Figure S4-S6, Table S3); 4. EIS characterization of rGO and rGO-PDA (Figure S7, Table S4); 5. Microsupercapacitor characterization (Figure S8 and S9); 6. References [48, 49].

## Keywords

Composite, graphene, hydrothermal synthesis, microsupercapacitor, polydopamine.

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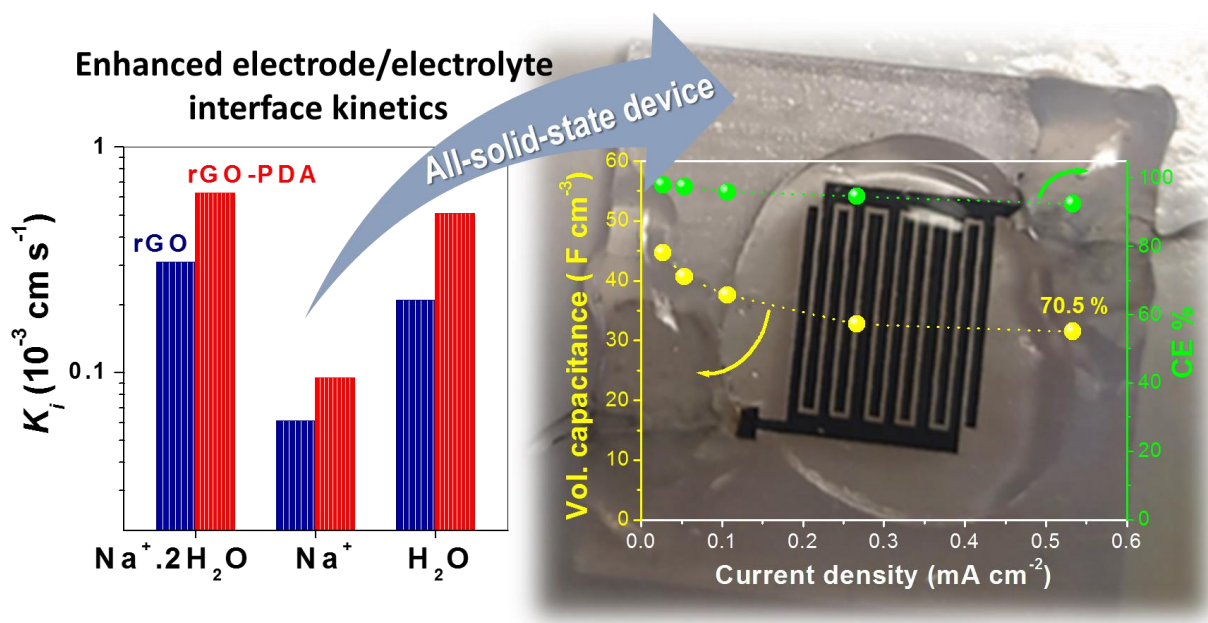
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A new reduced graphene oxide-polydopamine (rGO-PDA) material was obtained by an hydrothermal treatment of an aqueous solution containing GO and dopamine. The optimised rGO-PDA composite reveals superior transfer ion kinetics at the electrode/electrolyte interface compared to pristine rGO, probed by advanced electrogravimetry. A current collector-free device composed of interdigitated rGO-PDA electrodes was tested using a  $\text{Na}_2\text{SO}_4/\text{PVA}$  hydrogel electrolyte. It achieves remarkable energy and power densities with exceptional cycle stability.