Postprint published in [Energy Storage Materials](#)

[Volume 25](#), March 2020, Pages 740-749

Towards high-efficient microsupercapacitors based on reduced graphene oxide with
optimized reduction degree

Vanesa Rodriguez-Mata, Javier Hernández-Ferrer, Clara Carrera, Ana M. Benito,
Wolfgang K. Maser, Enrique García-Bordejé*,

Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, E-50018 Zaragoza,
Spain, jegarcia@icb.csic.es

Acknowledgements

Financial support from Spanish Ministry MINECO (project ENE2016-79282-C5-1-R),
Gobierno de Aragón (Grupo Reconocido DGA T03_17R), and associated EU Regional
Development Funds are gratefully acknowledged.

* Corresponding author: Tel.: +34 976733977; fax.: +34 976733318 *E-mail address:* jegarcia@icb.csic.es

Keywords

supercapacitor; reduced graphene oxide; aerogel; reduction degree; porous structure

Abstract

Reduced graphene oxide aerogels synthesized using different times of hydrothermal treatment have been tested as raw material to prepare electrochemical supercapacitors. The gravimetric electrochemical capacitance measured using 1M Na₂SO₄ as electrolyte was maximized for aerogels that underwent 45 min of hydrothermal treatment. The aerogels synthesized for longer durations of hydrothermal treatment exhibited higher electrical conductivity but the gravimetric capacitance drops dramatically due to an increasing resistance to diffusion of the electrolyte ions. The impeded diffusion is boosted by the intensified crosslinking between graphene sheets, which narrows the pores between them in the prepared electrode. The rGO aerogel attained for 45 min of hydrothermal treatment provided a high gravimetric capacitance of 400 F g⁻¹ and 100 F g⁻¹ at 50 A g⁻¹ for three-electrode and two electrodes configuration, respectively, as well as good cyclic stability, competing with other similar carbon materials. Activation pretreatments or adding a second component (glucose, dopamine, Mn, Fe, CNT) did not provide significant change of capacitance respect to pristine rGO aerogel.

1. Introduction

Electric energy storage has emerged as an enabling technology for the widespread utilization of intermittent energy production from renewable energy sources. Moreover, the development of compact and miniaturized electronic devices demands for energy storage microsystems. Li-ion batteries have the drawback that they are dangerous due to

the presence of lithium, they can overheat and the lifecycle is limited because undergo redox reaction. Supercapacitors (SCs) are evolving as rechargeable micro energy storage systems because of the fast charge-discharge cycles, high power density and stable performance, recyclability, high efficiency, low internal resistance and wide temperature operating range [1]. The main drawback is that the gravimetric energy density is one order of magnitude lower than conventional batteries [2]. The electrodes of commercial supercapacitors are mainly based on activated carbon, with capacitances between 40 and 160 F/g in liquid electrolyte and with low charging-discharging velocities of about 10 A/g. In these devices, the performance depends on the pore distribution of the activated carbon, requiring a material with accurately controlled porosity [3, 4]. From the point of view of the devices, besides a high specific capacitance, the carbon materials should exhibit a high volumetric and gravimetric energy density, must be able to work with electrolytes of high voltage, and meet a balance between porosity and density [5]. In theory, the capacitance of carbon materials will achieve a maximum for electrodes with pore sizes approaching that of the ions in the electrolyte. Compared to activated carbon (AC), which possess high micro- and mesoporosity, ideally graphene sheets presents mainly external surface area, which enables superior diffusion rate specially for large molecule electrolytes such as ionic liquid (IL). In addition, the large pores allows the loading with redox-active materials like metal oxides without blocking the pores. Graphene-based materials have been investigated for supercapacitors due to their high surface, light weight, high electrical conductivity, fast charge/discharge rate and excellent mechanical, chemical and electrochemical stability [6]. Some studies have reported gravimetric and areal energy densities of graphene-based devices similar to those of Li batteries [5, 7-9]. A single sheet of graphene shows a double layer capacitance per surface area of $\sim 21 \mu\text{F}/\text{cm}^2$ [10].

If all the surface of graphene is fully accessible to electrolytes, graphene-based SCs could achieve a specific capacitance up to ~550 F/g leading to high energy density[11]. However, graphene papers exhibit only modest power densities and rate capabilities due to the limited porous structure and the tendency of graphene layers to restack by π - π interaction. Many efforts have been focused in preventing graphene from restacking. For instance, several spacers such as CNTs [12] or diamines [13] have been used to avoid restacking, reaching high capacitances up to 318 F/g. In this line, 3D graphene-based electrodes such as graphene foams or aerogels have been investigated to tune material porosity, showing good rate capability [14]. Single layer graphene or nanomesh graphene have been prepared by chemical vapour deposition on templates such as zeolite [15] or porous MgO [16] resulting in specific capacitance of 233 F/g with 5000 cycles and 255 F/g, respectively. Using graphene hydrogels modified with 2-aminianthraquinone led to specific capacitances about 258 F/g [17]. 3D Graphene aerogels prepared by hydrothermal treatment of GO dispersions have been used as SCs due to its excellent porous percolation network [18-22]. Graphene aerogels porous structure and surface chemistry can vary significantly depending on the preparation conditions such as time of hydrothermal treatment and drying method. In [23] it was found that the drying method had an effect on pore size and capacitive performance but a long hydrothermal treatment time was kept constant in all cases. To the best of our knowledge, there is no systematic study about the effect of different hydrothermal treatment times/reduction degrees on its electrical capacitive performance. In particular, graphene aerogel synthesised using short hydrothermal treatment times (45 min) has not been tested as supercapacitors. Previously, we prepared graphene aerogels by hydrothermal reduction and investigated the effect of pH and hydrothermal treatment time on the reduction degree and porous structure [24]. Herein, we evaluated the

capacitive performance of rGO aerogels synthesised by hydrothermal method. A relationship between the degree of reduction and porous structure of the aerogels prepared after different hydrothermal treatment times and the capacitive performance has been found. A short time of hydrothermal reduction (45 minutes) is crucial to achieve very high capacitance values. The best materials were also tested in the two electrode assembly exhibiting high power and energy density. This paves the way to promising supercapacitors based on rGO with optimized reduction degree and porous structure.

2. Experimental

Materials

GO dispersion was purchased from Graphenea (4 mg/mL). CNT were NC7000 purchased from Nanocyl. High surface area activated carbon (Norit SX Ultra Cat 8020-1) was gently supplied by CABOT.

Aerogel synthesis

The synthesis steps and nomenclature for the different carbon aerogels whose electrochemical behaviour was analysed is compiled in Scheme 1 and explained in detail in Table S1. Graphene aerogels were synthesized by hydrothermal treatment of GO dispersions. To this end, 10 ml of a 2 mg/mL GO aqueous dispersions (Graphenea) with or without (A) the addition of 200 μ L of NH_3 was introduced in a 50 ml Teflon-lined autoclave at 180 $^{\circ}\text{C}$ for a certain time (from 45 min to 18 h). This process produces a monolithic hydrogel, which takes the shape of the container inside the autoclave. The hydrogel attained was then frozen by immersing the vial containing the hydrogel within liquid N_2 . Alternatively, the freezing was performed directionally from

the bottom to the top by placing the hydrogel in a support frozen with liquid N₂, leading to aerogels with unidirectional channels. For more details about the preparation see [25]. The solidified hydrogel is then transferred into a freeze-drying vessel (Telstar Cryodos) under vacuum (less than 0.3 mBar) and freeze-dried for 48 h to obtain the aerogel. The aerogels are named as GA followed by time of hydrothermal treatment.

Scheme 1. Diagram of the preparation steps and nomenclature of the samples

Characterisation of materials

Surface areas were determined by N₂ adsorption at 77 K (BET) using a Micromeritics ASAP 2020 apparatus, after outgassing for 4 h at 423 K. Alternatively, it was also determined by CO₂ adsorption (Dubinin–Radushkevich) at 273 K up to 1 Bar in the same apparatus, after outgassing under the same conditions. The density of the cylindrical aerogel (ρ_c) in g cm⁻³ was calculated as weight (w) of the cylinder divided by the volume (V_c), which was calculated as:

$$V_c = \pi \frac{D^2}{4} L \quad \text{eq. 1}$$

The diameter of cylinder (D) and the length of cylinder (L) in cm were measured with a micrometer gauge.

The total pore volume (V_{TOT}) was calculated as

$$V_{TOT} = V_c - \frac{w}{\rho_g} \quad \text{eq. 2}$$

where w is the weight of the cylinder and ρ_g is the density of rGO sheets which was assumed to be 1.06 g cm^{-3} , as reported for graphene.[26]

C,H,S elemental analysis was carried out by combustion in a ThermoFlash 1112 elemental analyzer equipped with a thermal conductivity detector. Oxygen analysis was done by direct assay which involves pyrolysis of the sample at 1070°C in a nickel/carbon bed under a known He flow. The outlet flow, after passing a separation column, ends in a TCD detector. The oxygen content of sample is quantified on the basis of CO analyzed.

SEM analysis was carried out with a SEM EDX Hitachi S-3400N microscope with variable pressure up to 270 Pa and with an EDX Röntec XFlash de Si(Li) analyzer. The samples were sputtered with gold previously to measurements. The images were obtained from the secondary electron signal.

X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer in configuration theta-theta using nickel-filtered $\text{CuK } \alpha$ radiation (wave length= $1.54 \text{ \AA}$), a graphite monochromatic source and scintillation detector. 2θ angles from 3 to 80° were scanned with a length step of 0.05 and an accumulation time of 3 s . To apply the Scherrer equation we used the software BRUKER-AXS TOPAS and a shape factor of 0.89 . The (002) peak was fitted to a asymmetric split pseudo-Voigt

function taking into account the distortion of the equipment but neglecting any lattice distortion.

Raman characterisation was performed on a Horiba Jobin Yvon, LabRAM HR UV-VIS NIR. Raman spectra were recorded with an Ar-ion laser beam at an exciting radiation wavelength of 532 nm. The subtraction of the baseline and the fitting of the peaks were performed with Origin pro 8.5 software according to previous work.[27]

DC electrical conductivity (σ) was measured by a two point probe using a Keithley 4200 instrument provided with four source measurement units and a preamplifier. The cylindrical rGO aerogels were pressed between two copper contact plates in each circular side of the cylinder. Bulk resistivity (ρ , in $\Omega \cdot m$) was calculated applying the expression:

$$\rho = \frac{SV}{LI} \quad \text{eq. 3}$$

where S/L is a geometrical factor, *i.e.* S is the surface of the circular side of the cylindrical aerogel and L is the height of the cylinder; V is the potential between the central probes and I is the current intensity circulating between the outer probes. The electrical conductivity (σ in S/m) is calculated as the reciprocal of the resistivity.

Electrochemical testing

For testing in three-electrode configuration, the electrode was prepared according to the following protocol. The aerogel was ground in an agate mortar. 2 mg of the ground aerogel is mixed with 10 mL 2-propanol and 100 μL Nafion. Subsequently, it is treated in ultrasound until obtaining a stable dispersion. On the cleaned glassy carbon electrode (3 mm diam.), 40 μL of the dispersion is added in droplets of 2 μL letting drying between additions. At the end, 8 μg of aerogel samples have been added and the

electrode is allowed to dry overnight. Three electrodes of each material were prepared to check reproducibility, and the capacitance values are an average of the three values.

The prepared electrodes were tested electrochemically in a three electrode assembly by cyclic voltammetry at room temperature using a Metrohm Autolab potentiostat. The reference electrode was Ag/AgCl and a Pt mesh was used as counter-electrode. 75 mL of 1M sodium sulphate solution was used as electrolyte with a 100 ml Metrohm cell, which is large enough to prevent any mass transfer resistance.

The experiments were carried out in N₂ atmosphere. The electrode is introduced in the electrolyte and it is checked that no gas bubble is formed on the electrode. An initial cyclic voltammetry was carried out at scan rates of 100 mV/s and 10 complete cycles, from -0.5 V up to 1 V. After this initial step, cyclic voltammograms were recorded at scan rates of 5, 10, 20, 50, 100, 200 and 500 mV/s. The stability was tested during 2000 CV cycles at 100 mV/s. In order to calculate the capacitance using cyclic voltammetry curves, the integral of the curve was measured, and then capacitance was calculated according to equation 4

$$C = \frac{\bar{I}}{v} = \frac{\int_{E_1}^{E_2} I(E) dE}{(E_2 - E_1)v} \rightarrow C(F/g) = \frac{(|\int_{-0.5}^{1.0} I_{anodic}(E) dE| + |\int_{1.0}^{-0.5} I_{cathodic}(E) dE|)/2}{1.5 \cdot v (V/s) \cdot 8 \cdot 10^{-6} (g)} \quad \text{eq. 4}$$

In the charge-discharge method, a chronopotentiometry is carried out, *i.e.* a constant intensity is applied of 50 A/g, positive in the charge and negative in the discharge and the potential is measured. Being the intensity constant, I, the specific capacitance can be calculated directly applying equation 5, where Δt is the time of charge or discharge in each cycle and ΔE is the difference of potential in one charge or discharge.

$$C = \frac{I \cdot \Delta t}{\Delta E} \rightarrow C(F/g) = \frac{400 \cdot 10^{-6} (A) \cdot \Delta t (s)}{\Delta E (V) \cdot 8 \cdot 10^{-6} (g)} \quad \text{eq. 5}$$

Electrochemical Impedance Spectroscopy (EIS) measurements were carried out at 0.25 V (vs. Ag/AgCl), in a frequency range from 10⁵ to 0.01 Hz, in order to gain insight in

the processes that occurs during the charge-discharge of the graphene aerogels, GA45 and GA2h.

Supercapacitors were prepared for testing in two-electrode configuration. The supercapacitors consist of two electrodes, a separating membrane and an aqueous electrolyte. For the preparation, we followed the steps illustrated in Figure S1.[28] Two pieces of aluminum paper 1cm wide are glued to scotch paper as illustrated in Figure S1 a. On each piece of aluminum paper, 8 μg of aerogel is deposited from an aqueous dispersion as that used for the electrochemical characterization of the glassy carbon electrodes in three-electrode configuration. The Nafion was necessary to improve the adhesion to aluminum paper in a controlled area. Subsequently, the area of the sample is wetted with a solution of the electrolyte (Na_2SO_4 1M) and a polycarbonate filter squared-shaped paper of 1.2 cm side over one of the electrodes is glued to the scotch tape at the borders. The two electrodes are overlapped so that each electrode is pointing to one different direction, as illustrated in Figure S1 c. Finally, the two electrodes are sealed with scotch tape, creating a compartment preventing liquid loses or air entrance. Subsequently, the two electrode device was tested in charge-discharge cycles carried out from 0-1.5 V under constant current of 50 A/g.

3. Results and discussion

3.1. rGO aerogels tested in 3-electrode configuration

The preparation of rGO aerogels was carried out under basic media (pH=11) adding NH_3 or under acidic media (pH=3) without NH_3 addition (Scheme 1). Table S1 of Supplementary material explains in detail the different electrode materials and the nomenclature. In brief, the rGO aerogels are denoted as GA followed by the time of hydrothermal treatment and _A, standing for acidic when the synthesis is carried out in

absence of NH_3 . As standard the synthesis is carried out in basic conditions, *i.e.* NH_3 addition, and _A is absent in the sample name. In a previous study,[24] it was found that basic pH provided aerogels with larger macroporosity. Figure 1a shows the specific capacitances measured using 1M Na_2SO_4 as electrolyte of electrodes prepared from rGO aerogels attained for different times of hydrothermal treatment, namely 35 min, 45 min, 2h and 18 h. The values of electrochemical capacitance exhibits a maximum for aerogels that underwent 45 min of hydrothermal treatment (GA45 or GA45_A), regardless the pH value used in the preparation. Accordingly, the capacitance is very sensitive to the variation of the time of hydrothermal treatment but the pH of the medium has insignificant impact on the capacitance. This time-dependent capacitance is systematically reproduced for several preparations and for both pH values. The aerogels mentioned heretofore are attained directly after freeze drying without any additional treatment, but if the aerogel is annealed in inert atmosphere at 800 °C (GA45_800), the capacitance decays dramatically. XRD diffraction (Figure S3) indicates that there is negligible increase of stacking during hydrothermal treatment since the interlayer distance remains constant. However, the annealing at 800 °C produces the increase of rGO sheet stacking as indicated by the shifting of the (002) peak to values closer to graphite and the increase of crystal size due to aggregation of graphene sheets in direction perpendicular to the plane (002). Figure 1b compares the capacitance of optimum graphene aerogel (GA45) with other reference carbon materials such a high surface area activated carbon (AC, Norit SX), carbon nanotubes (CNT, nanocyl) and electrochemically reduced graphene oxide (ERGO). This later one is derived from the same starting GO as that used for aerogels, but electrochemically reduced after being deposited on the electrode. The aerogel GA45 exhibited significantly higher capacitance than all these reference materials. In Figure 1b, the capacitances of aerogels with

different structural features are also compared. These different structures resulted by applying different drying conditions to the hydrogel attained after 45 min of hydrothermal treatment. The drying conditions were namely: (i) freeze drying after ice templating of unidirectional pores by directional freezing in liquid N₂ at -196 °C (GA45_U); (ii) freeze-drying after freezing at -18 °C in a refrigerator (GA45_C); (iii) drying at room temperature without previous freezing (GA45_NL). The change of the structure from foam-like pores (GA45) to unidirectional pores (GA45_U) does not supply significant difference in terms of capacitance. In contrast, the capacitance is reduced when freezing in a freezer (-18 °C) instead of using liquid N₂ (-196 °C) and it is substantially reduced when it is dried at room temperature (GA45_NL) instead of using freeze drying. When drying in a freezer the freezing is slower than in liquid N₂ and the rGO sheets have more time for re-arranging and stacking. When drying at room temperature, the 3D porous structure is completely destroyed and the aerogel volume shrinks dramatically due to the intensive stacking of the sheets and macroporosity collapse. GA45_NL has capacitance values comparable to GA18 and GA18A suggesting that the reason of the decreased capacitance can be the intensive sheet crosslinking in both cases. In contrast to this work, it was reported that the room temperature drying led to higher capacitance than freeze drying due to a reduction of macropores [23] but they only applied long hydrothermal treatment time and they used the aerogel without grinding to prepare the electrode. Herein, the aerogels were ground, removing the macropores for all the materials.

Composite materials were prepared expecting to increase the capacitance by different approaches aimed to either increasing the conductivity when adding CNT (CACNT45, GACNTOX45), or adding supplementary faradaic pseudocapacitance (GA45Fe, GA45_Mn) or rising the active surface area (GAGLU45_800, GAK45, GA45_K_800,

GA45_CO2). None of these approaches succeeded in increasing the capacitance with respect to pristine GA45 (Figure 1c).

The rectangular shape of cyclic voltammograms (Figure 1d) is characteristic of supercapacitors. The stability was tested during 2000 CV cycles, showing excellent cyclic stability with a 87% capacity retention (Figure S2 of Supplementary information).

Figure 1. Performance of carbon materials in 3-electrode configuration at a scan rate of 100 mV/s in 1M sodium sulfate electrolyte: (a) gravimetric capacitance calculated from cyclic voltammetry curve of graphene aerogels prepared for different times of hydrothermal treatment under basic and acid pH (_A) and after an additional heat treatment in inert gas; (b) Comparison of specific capacitance between graphene aerogels prepared using 45 min of hydrothermal treatment and

some reference materials and different drying methods; (c) specific capacitance of graphene aerogels with additives or after treatments during hydrothermal synthesis (*in-situ*) and post-synthesis (*ex-situ*); (d) cyclic voltammograms at 100 mV/s of the best performing materials either untreated or treated with additives. The error bars corresponds to the standard deviation of 3 different electrodes prepared with the same material.

To unravel the reasons of the significant impact of the hydrothermal treatment time on the gravimetric capacitance, the aerogels prepared at different hydrothermal treatment times were thoroughly characterised. The macroscopic dimensions of the aerogel shrink with the time of hydrothermal treatment (Figure S4 of Supplementary material). The shrinking is correlated with an apparent bending graphene sheets and smaller separation between them as observed in SEM images (Figure 2 and Figure S5 for aerogels prepared at basic and acid pH, respectively). This suggests an intensification of the crosslinking between rGO sheets as hydrothermal treatment proceeds. The crystal size determined by applying the Scherrer equation to XRD results (Figure S3 and Table S2) decreases from 14.1 nm in GO to 1.6 after 45 min of hydrothermal treatment and later to 1.4 for 18 h. This seems to indicate that the size of graphitic domains decreases upon hydrothermal treatment. The interplanar distance also decreases sharply from GO to GA45min, but then does not vary for longer hydrothermal treatment time suggesting that the sheets do not stack further for longer durations of hydrothermal treatment. However, it is worth mentioning that this does not guarantees that they do no restack in the prepared electrode. Raman spectroscopy is commonly used to assess the defects of carbon materials. The ratio between the intensity of characteristic bands D and G (I_D/I_G) is usually taken as a measure of the density of defects [29, 30]. In our case (Figure S6 of

Supplementary material), the I_D/I_G decreases from GO to GA45 which can be attributed to the creation of more ordered graphitic domains and then increases for further hydrothermal treatment time, which may be attributed to the increase of defects. A possible explanation is that the increased folding of rGO sheets as hydrothermal treatment proceeds creates cracks within them.

Figure 2. Representative SEM images at two magnifications of aerogels attained at different times of hydrothermal treatment illustrating the increasing proximity and intensification of crosslinking/aggregation between rGO sheets: (a) GA35; (b) GA45; (c) GA2h; (d) GA18h.

The electrochemical capacitance of active carbons is usually defined by the effective surface area accessible to the ions, which may differ considerably from that determined

by gas physisorption because the gases have molecular sizes much smaller than those of the ions used as electrolytes in supercapacitor operating with most common electrolyte ions. Notwithstanding, we also characterised the surface area by N_2 and CO_2 physisorption (Table 1). Activated carbon SX Norit exhibits an adsorption isotherm of type I corresponding to a microporous material (Figure S7 a) leading to the highest surface area and micropore volume among tested samples. The adsorption isotherms of CNT (NC7000) and graphene aerogels are of type-IV with a hysteresis loop (Figure S7 of Supplementary material). These isotherms show little uptake at low relative pressures ($P/P_0 < 0.1$), indicating low micropore volume. The hysteresis loop and upward trend at high relative pressures ($P/P_0 > 0.95$) may originate from the presence of meso-macropores as those observed by SEM.[31] CNT contains the highest mesopore volume and negligible micropore volume. The Surface area of graphene aerogels determined by N_2 physisorption is relatively low (between 50-174 m^2g^{-1}). Larger surface areas are obtained when using CO_2 as the absorbate. This is attributed to the presence of narrow micropores (<0.7 nm), also called “ultramicropores”, in which the diffusion of N_2 at 77 K is kinetically hindered [32]. In spite of the fact that SX Norit has much larger surface area than rGO aerogels, the former one exhibited lower gravimetric capacitance. This is consistent with [33] that states that surface area is a valid descriptor of capacitance for comparing activated carbons but not for graphene. They explain that in the case of graphene type-materials the electrochemical surface area is larger than that estimated by gas adsorption because a voltage-driven mechanism may facilitate the access of electrolyte ions to spaces between carbon layers. Regarding the evolution with time of textural parameters, it is difficult to derive general conclusions because the textural parameters are very similar and the differences are in the range of uncertainty. The main conclusion that can be derived from surface area measurements is that the maximum of

specific capacitance for 45 min is not correlated to higher surface area value. The increase of surface area and pore volume, mainly in the mesopore range, suggest that pores are due to the space between graphene sheets, which get closer as the hydrothermal treatment proceeds. N₂ physisorption does not supply information regarding macropores. An indication of the amount of macropores is the apparent total pore volume (V_{TOT}) calculated from the volume of the cylindrical aerogel as explained in the experimental section. V_{TOT} is the only textural parameter that is the highest for 45 min of hydrothermal treatment time, both for acidic and basic media. V_{TOT} decreases as hydrothermal treatment proceeds because of the intensification of the crosslinking between rGO sheets by van der Waals forces or H-bonds between the graphene nanosheets as shown above.

Table 1. Textural parameters measured by N₂ and CO₂ physisorption

Carbon sample	N ₂ adsorption				CO ₂ adsorption	Total pore Volume ^c	Areal capacitance ^d
	Surface area (S_{N_2})	Pore volume (V_p)	Micropore volume ^a (V_{mic})	Mesopore volume ^a (V_{mes})	Surface area ^b (S_{CO_2})	V_{TOT}	
	m ² g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	m ² g ⁻¹	cm ³ g ⁻¹	F m ⁻²
SX Norit	949	0.77	0.32	0.45	581	n.d	0.19
CNT	230	1.12	0.01	1.11		n.d	0.07
GA35	50	0.13	0.01	0.12	255	n.d.	3.99
GA45	133	0.19	0.06	0.13	313	130	2.91
GA2h	98	0.26	0.02	0.24	234	104	2.86
GA18h	173	0.48	0.03	0.45	165	71	0.97
GA45_A	113	0.33	0.02	0.31	212	149	3.21
GA2h_A	174	0.42	0.03	0.39	265	84	1.69

GA18h_A	171	0.42	0.04	0.38	301	54	0.95
GACNTOX	208	0.70	0.03	0.65	210	n.d	1.96

^a V_{mic} calculated by the t-plot method and V_{mes} calculated by subtracting micropore volume (V_{mic}) from total pore volume (V_p).

^b calculated using the Duvinin-Raduschkevich method

^c including macropores. n.d.= not determined because it does not contains macropores

^d Relative to Surface Area (S_{N2})

It is important to note that the macroscopic structure is destroyed to prepare the electrode, *i.e.* the aerogel is ground, graphene sheets are redispersed and drop-casted on the electrode. SEM image of Figure S8b shows that the macropores disappear upon drop-casting. Therefore, the architecture of the macropores (50 nm to microns), which could be important for supercapacitor device fabrication,[23] does not play any role on the values of capacitance attained here. Therefore, the differences in capacitances found here are due to aspects intrinsic to the sheets such as the degree of reduction (oxygenated surface groups contents) affecting the degree of sheet stacking or crosslinking upon electrode preparation. This degree of crosslinking/aggregation may have a definitive influence on the accessibility of the electrolyte and electrical conductivity. To shed some light into the reduction degree of aerogels after different times of hydrothermal treatment, we analysed the degree of reduction by measuring the oxygen content by elemental analysis and XPS (Table 2).

Table 2. Elemental analysis and XPS quantification for aerogels prepared at different hydrothermal treatment times and unidirectional freeze drying

sample	hydrothermal		elemental analysis		XPS	
	treatment	time	O/C (at%)	N/C (at%)	C/O	N/C
	(min)				(at.	(at%)
Norit SX	0		11.74	0	13.5	0.4
GA35	35		27.0	10.9	6.2	5.6
GA45	45		14.9	10.6	11.2	6.5
GA2h	120		13.5	10.1	12.0	6.9
GA18h	1080		13.0	10.3	12.5	6.3
GA45_A	45		23.7	1.5	7.2	0.9
GA2h_A	120		20.2	0.8	8	0.5
GA18h_A	1080		19.6	0.8	8.1	0.5

The oxygen content decreases dramatically from sample GA35 to GA45 will probably increase the intrinsic electrical conductivity, explaining the increase of gravimetric capacitance after 45 min of hydrothermal treatment time. Nevertheless, the gravimetric capacitance decreases dramatically for hydrothermal durations longer than 45 min despite the slight decrease of oxygen content. In fact, the electrical conductivity of aerogels increases slightly from 45 to 2h and is larger for aerogels prepared adding NH_3 (Figure 3a). The increasing electrical conductivity is correlated with lower oxygen content but it can be also due to an increased crosslinking between rGO sheets. However, the conductivity is not a descriptor of capacitance values, GA45 exhibiting the highest capacitance and lowest conductivity. Comparing aerogels prepared under acidic and basic media, neither the two-fold lower oxygen content nor the presence of a 6-7 % nitrogen of the latter lead to differences in gravimetric capacitances. Therefore, neither electrical conductivity nor pseudocapacitance due to surface chemistry (oxygen

or nitrogen content) seem to explain the highest gravimetric capacitance for GA45 and its significant decay for GA2h.

The different crosslinking degree found in the characterisation may affect the ion diffusion properties in the dropcasted electrode. The transport properties were investigated by electrochemical impedance spectroscopy (EIS). Both GA45 and GA2h electrodes show similar features in the impedance spectrum at low frequencies (Figure 3b), exhibiting a non-ideal capacitor behavior, with a final phase of *ca.* 78° (0.01 Hz), with the difference that the GA2h material has higher impedance modulus than GA45, which is consistent with the higher capacitance obtained by cyclic voltammetry and galvanostatic methods for the latter material. At higher frequencies, more differences arise, with a hump appearing in the phase Bode plot (Figure 3b) for the GA2h aerogel that cannot be seen in the GA45 min case. This frequency region of the impedance spectra is commonly related to diffusion phenomena, which shows that there is also a significant difference in the diffusion regime inside the pores, that is, changes in pore shape and/or size. Therefore, GA45 exhibits either shorter ion transport distance or offer faster ion transport channels than GA2h. The impedance spectrum for GA45 is accurately fitted by the equivalent circuit explained in [34] consisting of a resistance (R_s , mostly due to the solution) and two constant phase elements in series (Figure S9). One possesses an exponent of *ca.* 0.5, and describes diffusion phenomena inside the porous structure of the electrode (Q_{diff}), while the other, with an exponent close to 1, represents the double-layer capacitance (Q_{dl}). Obtained values are shown in Table 3. The fitting shows that the access to the pores is mainly governed by linear semi-infinite diffusion, which reveals a quite high value of pore diameter. On the contrary, in the case of GA2h material, an additional resistance, in parallel with the diffusion impedance R_{diff} (see Figure S9 and Table 3), must be added in order to fit the spectrum, this reveals that,

in some pores, the access of ions is not controlled by a linear semi-infinite diffusion, or a constant thickness diffusion, but by an activated process (namely ion desolvation, or interaction with the pore walls). Furthermore, admittance values in this latter case are almost half the value of the obtained for GA45, which is consistent with the rest of electrochemical measurements, as well as with the physical-chemical characterization.

Table 3. Parameters obtained by model fitting

	GA45	GA2h
Rs/ohm	16.8	17.1
$Q_{\text{diff}}, Y0/ \text{ohm}^{-1} \cdot \text{s}^N$	$1.84 \cdot 10^{-3}$	$7.74 \cdot 10^{-4}$
Q_{diff}, N	0.423	0.487
$R_{\text{diff}}/\text{ohm}$	-	675
$Q_{\text{dl}}, Y0/ \text{ohm}^{-1} \cdot \text{s}^N$	$6.46 \cdot 10^{-4}$	$7.74 \cdot 10^{-4}$
Q_{dl}, N	0.9	0.883
Chi-square	$6.5127 \cdot 10^{-3}$	$8.323 \cdot 10^{-3}$

Figure 3. Comparison of axial electrical conductivity of aerogels for different times of hydrothermal treatment (GA35 was not possible to measure since the aerogel was not formed yet). Electrochemical impedance spectroscopy (EIS) properties of aerogels prepared for 45 min and 2h of hydrothermal treatment: (b) Bode phase plot; (c) Bode modulus plot; (d) Nyquist plot. Experimental conditions 1M Na_2SO_4 , 0.25 V vs. Ag/AgCl.

3.2. Best-performing rGO aerogels tested in 2-electrode configuration device

Figure 4. Galvanostatic charge-discharge (GCD) curves for 2-electrode devices from 0-1.5 V: (a) GCD cycle at different currents with GA45; (b) GCD cycle for selected materials at 50 A g⁻¹; (c) 10 GCD cycles; (d) Ragone diagram putting into perspective the home-made supercapacitors.

Galvanostatic charge discharge (GCD) curves (voltage vs. time) were performed in two electrode home-made assembly. The GCD curves at different current (25-200 A/g) (Figure 4a) and that for the different materials at constant $I=50 \text{ A g}^{-1}$ (Figure 4b) display a triangular shape, indicating a good electrochemical reversibility. 10 GCD cycles were performed (Figure 4c) showing a good cyclic stability as confirmed before by 2000 cyclic voltammograms.

With the specific capacitance of the 2-electrode devices, it is possible to calculate the density of energy and power, which are two typical parameters to classify the supercapacitors. To calculate these values, we used the following equations:

$$E_{\text{grav-electrode}}(\text{Wh/g}) = C \cdot 0.5 \cdot (\Delta U)^2 / 3600 \quad \text{Eq 3}$$

$$E_{\text{grav-device}}(\text{Wh/g}) = f \cdot 0.25 \cdot E_{\text{grav-electrode}} \quad \text{Eq 4}$$

$$P_{\text{grav-device}}(\text{W/L}) = 3600 \cdot E_{\text{grav-device}} / \Delta t_{\text{discharge}} \quad \text{Eq 5}$$

where, C is the specific capacitance of the electrode in F g^{-1} , ΔU is the charge-discharge potential in V, f is a non-dimensional factor corresponding to the fraction of volume of the electrodes, and $\Delta t_{\text{discharge}}$ is the time of discharge of the device for ΔU .

The values of gravimetric capacitance and gravimetric energy and power densities of the best performing materials are compiled in Table 4. Theoretically, the values of capacitance measured in a 2-electrode device must be 4 times lower than those measured in a 3-electrode configuration. This is because the 2-electrode device consists of two supercapacitors in series so that the total capacitance will be half and it contains the double of mass since there are two working electrodes. The gravimetric capacitances of the electrodes prepared with additives (Mn) and activation treatments with KOH (GAK45) are smaller than pure rGO aerogel. Adding CNT, the capacitance is slightly higher but this small increase does not justify additional preparation steps and the use of CNT.

The selected materials have been plotted in the Ragone diagram (Figure 4d). They are located in the range of gravimetric power density typical for supercapacitors, between 2 and 5 kW kg^{-1} , while the gravimetric energy density is superior, close to 9 W h kg^{-1} , making the materials very promising for further device developments.

Table 4. Specific capacitance of 3 and 2 electrodes calculated from the charge-discharge curve at 50 A g⁻¹ of selected materials and energy and power gravimetric density of the devices in 2 electrodes configuration

Material of electrode	Specific capacitance (F/g)		$\Delta t_{\text{discharge}}$ (s)	$E_{\text{grav-device}}$ (Wh/kg)	$P_{\text{grav-device}}$ (kW/kg)
	3-electrode	2 electrodes			
GA_45B	387.9	104.4	6.03	8.16	4.87
GA_45U	389.2	93.4	5.37	6.57	4.41
GACNTOX45	409.2	109.7	6.46	8.57	4.77
GA45_Mn	359.1	89.7	5.12	5.26	3.70
GAK45	311.8	61.8	4.03	2.41	2.15

Table 5 compiles a list of selected supercapacitors in the literature based on graphene aerogels prepared from GO reduction and some of the best carbon-based supercapacitors. The rGO aerogels prepared here have gravimetric capacitances (around 100 F g⁻¹ at 50 A g⁻¹ in two-electrode configuration) comparable or superior to other graphene aerogels reported in the literature (Table 4). Compared to the best performing non-redox SCs carbon materials, gravimetric capacitance of our graphene aerogel is similar to that of ordered mesoporous carbons,[35] although still slightly lower than some carbon microcapsules or activated carbons.[36] The good performance of graphene aerogel materials can be attributed to its open structure which facilitates diffusion and swapping of ions during charging and discharging. In the literature,[37, 38] improved diffusion is claimed as the reason of enhanced capacitance for carbon materials with hierarchical porous structure or for the absence of bottleneck pores,[37, 38] as it is the case of the present rGO aerogel.

Table 5. Electrochemical performance of rGO graphene aerogels prepared from GO reduction in the literature

Refere nce	Descripción	Electrolyte	Confi gurati on of electr odes	Electroc hemical capacita nce/perfo rmance
[39]	GO reduced with hidrazine	Aqueous KOH	3	135 F/g
[40]	Graphene hydrogel by hydrothermal GO treatment	5M KOH	3	160 F/g
[19]	GO hydrogel crosslinked with EDA	2 M KOH	3	231 F/g
[20]	GA on Ni foam	6 M KOH	3	366 F/g at 2A/g
[41]	CO ₂ activated GA	1 M H ₂ SO ₄	3	278.5 F/g
[42]	GA-SiO ₂ composite with hierarchical structure	1 M H ₂ SO ₄	3	226 F/g
[21]	Graphene hydrogel reduced with hydrazine	5 M KOH	2	222 F/g
[43]	GA of nanographene	5 M KOH		101.5 F/g
[44]	Nitrogen plasma treated graphene	6 M KOH	2	280 F/g
[22]	GA activated with KOH	Organic and ionic liquid	2	70 Wh/kg
[18]	Hydrothermal synthesis of GA doped with N using organic amine	5 M KOH	2	205 W/g a 185 A/g
[35]	Ordered mesoporous carbon	0.5 M H ₂ SO ₄	2	150 F/g (at 1 A/g)
[36]	Carbon microcapsules	KOH and Li ₂ SO ₄	2	270 F/g (at 0.1 A/g)

Conclusions

Graphene aerogel prepared by hydrothermal treatment of GO dispersion is a 3D porous carbon material that has received recently high attention for several applications

including for supercapacitors. However, to the best of our knowledge the effect of the hydrothermal treatment time and reduction degree on the capacitive performance is elusive in the literature. In this work, reduced graphene oxide (rGO) aerogels with increasing degree of reduction/crosslinking have been produced from graphene oxide (GO) dispersion exposed to rising durations of hydrothermal treatment. As the hydrothermal treatment proceeds, the space between corrugated graphene sheets become narrower and the connections between them intensify. The specific gravimetric and areal capacitance measured using 1M Na₂SO₄ as electrolyte is maximized for the electrodes prepared from graphene aerogels that underwent a hydrothermal treatment time of 45 min. This rGO aerogel provides very high gravimetric capacitances of 400 F g⁻¹ and 100 F g⁻¹ at 50 A g⁻¹ for three-electrode and two electrodes configuration, respectively, and good cyclic stability. The specific capacitance rivals that of high-surface area activated carbon, CNT, electrochemically reduced graphene and other similar carbon materials in the literature. The maximum capacitance found at 45 min of hydrothermal treatment is a trade-off between increased reduction degree/electrical conductivity and the degree of interaction/crosslinking between the sheets. Both parameters increase as the hydrothermal treatment proceeds, but they produce opposite effect on capacitance. While the former is beneficial for the capacitance, the latter is detrimental for the diffusion and accessibility of the electrolyte ions. The presence of a few oxygenated groups avoids the stacking of rGO sheets in the prepared electrode favouring the diffusion of the electrolyte. Different strategies have been attempted here to modify the rGO aerogel such as preparing hybrids with CNT, dopamine, glucose, Fe or Mn and activating with KOH or CO₂. Some of these materials afforded similar performance as unmodified rGO aerogel, but none of them surpasses its performance, rendering additional preparation steps redundant. Therefore, the hydrothermal reduction

of GO to produce rGO aerogels is very promising method for the preparation of supercapacitors based on pure carbon material.

Reference List

- [1] L. Zhang, X. Hu, Z. Wang, F. Sun, D.G. Dorrell, A review of supercapacitor modeling, estimation, and applications: A control/management perspective, *Renewable Sustainable Energy Rev.*, 81 (2018) 1868-1878.
- [2] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nat. Mater.*, 7 (2008) 845.
- [3] M. Enterría, F.J. Martín-Jimeno, F. Suárez-García, J.I. Paredes, M.F.R. Pereira, J.I. Martins, A. Martínez-Alonso, J.M.D. Tascón, J.L. Figueiredo, Effect of nanostructure on the supercapacitor performance of activated carbon xerogels obtained from hydrothermally carbonized glucose-graphene oxide hybrids, *Carbon*, 105 (2016) 474-483.
- [4] Y. Xu, G. Shi, X. Duan, Self-Assembled Three-Dimensional Graphene Macrostructures: Synthesis and Applications in Supercapacitors, *Acc. Chem. Res.*, 48 (2015) 1666-1675.
- [5] H. Li, Y. Tao, X. Zheng, J. Luo, F. Kang, H.-M. Cheng, Q.-H. Yang, Ultra-thick graphene bulk supercapacitor electrodes for compact energy storage, *Ener. Environ. Sci.*, 9 (2016) 3135-3142.
- [6] L. Huang, D. Santiago, P. Loyselle, L. Dai, Graphene-Based Nanomaterials for Flexible and Wearable Supercapacitors, *Small*, 0 (2018) 1800879.
- [7] M.F. El-Kady, R.B. Kaner, Scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage, *Nat. Commun.*, 4 (2013) 1475.
- [8] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna, P. Simon, Ultrahigh-power micrometre-sized supercapacitors based on onion-like carbon, *Nat. Nanotech.*, 5 (2010) 651.
- [9] X. Yang, C. Cheng, Y. Wang, L. Qiu, D. Li, Liquid-Mediated Dense Integration of Graphene Materials for Compact Capacitive Energy Storage, *Science*, 341 (2013) 534-537.
- [10] J. Xia, F. Chen, J. Li, N. Tao, Measurement of the quantum capacitance of graphene, *Nat. Nanotech.*, 4 (2009) 505.
- [11] J. Chen, C. Li, G. Shi, Graphene Materials for Electrochemical Capacitors, *J. Phys. Chem. Lett.*, 4 (2013) 1244-1253.
- [12] Y. Wang, Y. Wu, Y. Huang, F. Zhang, X. Yang, Y. Ma, Y. Chen, Preventing Graphene Sheets from Restacking for High-Capacitance Performance, *J. Phys. Chem. C*, 115 (2011) 23192-23197.
- [13] H. Banda, S. Périé, B. Daffos, P.-L. Taberna, L. Dubois, O. Crosnier, P. Simon, D. Lee, G. De Paëpe, F. Duclairoir, Sparsely Pillared Graphene Materials for High-Performance Supercapacitors: Improving Ion Transport and Storage Capacity, *ACS Nano*, (2019).
- [14] C. Li, G. Shi, Functional Gels Based on Chemically Modified Graphenes, *Adv. Mater.*, 26 (2014) 3992-4012.
- [15] Y. Wang, H. Sun, R. Zhang, S. Yu, J. Kong, Large scale templated synthesis of single-layered graphene with a high electrical capacitance, *Carbon*, 53 (2013) 245-251.
- [16] G. Ning, Z. Fan, G. Wang, J. Gao, W. Qian, F. Wei, Gram-scale synthesis of nanomesh graphene with high surface area and its application in supercapacitor electrodes, *Chem. Commun.*, 47 (2011) 5976-5978.
- [17] X. Yang, J. Zhu, L. Qiu, D. Li, Bioinspired Effective Prevention of Restacking in Multilayered Graphene Films: Towards the Next Generation of High-Performance Supercapacitors, *Adv. Mater.*, 23 (2011) 2833-2838.
- [18] P. Chen, J.-J. Yang, S.-S. Li, Z. Wang, T.-Y. Xiao, Y.-H. Qian, S.-H. Yu, Hydrothermal synthesis of macroscopic nitrogen-doped graphene hydrogels for ultrafast supercapacitor, *Nano Energy*, 2 (2013) 249-256.

- [19] V.H. Luan, H.N. Tien, L.T. Hoa, N.T.M. Hien, E.-S. Oh, J. Chung, E.J. Kim, W.M. Choi, B.-S. Kong, S.H. Hur, Synthesis of a highly conductive and large surface area graphene oxide hydrogel and its use in a supercapacitor, *J. Mater. Chem. A*, 1 (2013) 208-211.
- [20] S. Ye, J. Feng, P. Wu, Deposition of Three-Dimensional Graphene Aerogel on Nickel Foam as a Binder-Free Supercapacitor Electrode, *ACS Appl. Mater. Interf.*, 5 (2013) 7122-7129.
- [21] L. Zhang, G. Shi, Preparation of Highly Conductive Graphene Hydrogels for Fabricating Supercapacitors with High Rate Capability, *J. Phys. Chem. C*, 115 (2011) 17206-17212.
- [22] Y. Zhu, S. Murali, M.D. Stoller, K.J. Ganesh, W. Cai, P.J. Ferreira, A. Pirkle, R.M. Wallace, K.A. Cychoz, M. Thommes, D. Su, E.A. Stach, R.S. Ruoff, Carbon-Based Supercapacitors Produced by Activation of Graphene, *Science*, 332 (2011) 1537-1541.
- [23] Y. Tao, X. Xie, W. Lv, D.-M. Tang, D. Kong, Z. Huang, H. Nishihara, T. Ishii, B. Li, D. Golberg, F. Kang, T. Kyotani, Q.-H. Yang, Towards ultrahigh volumetric capacitance: graphene derived highly dense but porous carbons for supercapacitors, *Sci. Rep.*, 3 (2013) 2975.
- [24] E. García-Bordejé, S. Víctor-Román, O. Sanahuja-Parejo, A.M. Benito, W.K. Maser, Control of the microstructure and surface chemistry of graphene aerogels via pH and time manipulation by a hydrothermal method, *Nanoscale*, 10 (2018) 3526-3539.
- [25] V. Rodríguez-Mata, J.M. González-Domínguez, A.M. Benito, W.K. Maser, E. García-Bordejé, Reduced Graphene Oxide Aerogels with Controlled Continuous Microchannels for Environmental Remediation, *ACS Appl. Nano Mater.*, 2 (2019) 1210-1222.
- [26] M.A. Rafiee, J. Rafiee, Z. Wang, H. Song, Z.-Z. Yu, N. Koratkar, Enhanced Mechanical Properties of Nanocomposites at Low Graphene Content, *ACS Nano*, 3 (2009) 3884-3890.
- [27] L. Roldán, A.M. Benito, E. García-Bordejé, Self-assembled graphene aerogel and nanodiamond hybrids as high performance catalysts in oxidative propane dehydrogenation, *J. Mater. Chem. A*, 3 (2015) 24379-24388.
- [28] P. Jiménez-Manero, Ph. D. Thesis, University of Zaragoza, <http://digital.csic.es/handle/10261/33993>, (2011).
- [29] M.S. Dresselhaus, A. Jorio, A.G.S. Filho, R. Saito, Defect characterization in graphene and carbon nanotubes using Raman spectroscopy, *Philos. Trans. R. Soc. London, Ser. A*, 368 (2010) 5355-5377.
- [30] F. Tuinstra, J.L. Koenig, Raman Spectrum of Graphite, *J. Chem. Phys.*, 53 (1970) 1126-1130.
- [31] X. Yang, X. Zhuang, Y. Huang, J. Jiang, H. Tian, D. Wu, F. Zhang, Y. Mai, X. Feng, Nitrogen-enriched hierarchically porous carbon materials fabricated by graphene aerogel templated Schiff-base chemistry for high performance electrochemical capacitors, *Polym. Chem.*, 6 (2015) 1088-1095.
- [32] D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano, Usefulness of CO₂ adsorption at 273 K for the characterization of porous carbons, *Carbon*, 42 (2004) 1233-1242.
- [33] B. Lobato, L. Suárez, L. Guardia, T.A. Centeno, Capacitance and surface of carbons in supercapacitors, *Carbon*, 122 (2017) 434-445.
- [34] P. Taberna, P. Simon, Electrochemical Techniques, in: F. Béguin, E. Frąckowiak (Eds.) *Supercapacitors* 2013.
- [35] T. Lin, I.-W. Chen, F. Liu, C. Yang, H. Bi, F. Xu, F. Huang, Nitrogen-doped mesoporous carbon of extraordinary capacitance for electrochemical energy storage, *Science*, 350 (2015) 1508-1513.
- [36] M. Sevilla, A.B. Fuertes, A Green Approach to High-Performance Supercapacitor Electrodes: The Chemical Activation of Hydrochar with Potassium Bicarbonate, *ChemSusChem*, 9 (2016) 1880-1888.
- [37] S. Herou, M.C. Ribadeneyra, R. Madhu, V. Araullo-Peters, A. Jensen, P. Schlee, M. Titirici, Ordered mesoporous carbons from lignin: a new class of biobased electrodes for supercapacitors, *Green Chem.*, 21 (2019) 550-559.
- [38] J. Pampel, T.-P. Fellerger, Opening of Bottleneck Pores for the Improvement of Nitrogen Doped Carbon Electrocatalysts, *Adv. Ener. Mater.*, 6 (2016) 1502389.

- [39] M.D. Stoller, S. Park, Y. Zhu, J. An, R.S. Ruoff, Graphene-Based Ultracapacitors, *Nano Lett.*, 8 (2008) 3498-3502.
- [40] Y. Xu, K. Sheng, C. Li, G. Shi, Self-Assembled Graphene Hydrogel via a One-Step Hydrothermal Process, *ACS Nano*, 4 (2010) 4324-4330.
- [41] S. Yun, S.-O. Kang, S. Park, H.S. Park, CO₂-activated, hierarchical trimodal porous graphene frameworks for ultrahigh and ultrafast capacitive behavior, *Nanoscale*, 6 (2014) 5296-5302.
- [42] Z.-S. Wu, Y. Sun, Y.-Z. Tan, S. Yang, X. Feng, K. Müllen, Three-Dimensional Graphene-Based Macro- and Mesoporous Frameworks for High-Performance Electrochemical Capacitive Energy Storage, *J. Am. Chem. Soc.*, 134 (2012) 19532-19535.
- [43] A. Kudo, P.G. Campbell, J. Biener, Nanographene Aerogels: Size Effect of the Precursor Graphene Oxide on Gelation Process and Electrochemical Properties, *ChemNanoMat*, 4 (2017) 338-342.
- [44] H.M. Jeong, J.W. Lee, W.H. Shin, Y.J. Choi, H.J. Shin, J.K. Kang, J.W. Choi, Nitrogen-Doped Graphene for High-Performance Ultracapacitors and the Importance of Nitrogen-Doped Sites at Basal Planes, *Nano Lett.*, 11 (2011) 2472-2477.