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Rational design of reduced graphene oxide for superior performance of supercapacitor electrodes

S. Rasul^{1*}, A. Alazmi¹, K. Jaouen¹, M. N. Hedhili², P. M. F. J. Costa¹

Abstract

Strategies to synthesize reduced graphene oxide (rGO) abound but, in most studies, research teams select one particular oxidation-reduction method without providing a methodic reasoning for doing so. Herein, it is analyzed how diverse oxidation-reduction strategies commonly used can result in considerable performance differences of rGO for supercapacitor applications. Depending on the graphite oxidation method followed, the surface chemistry analysis of the products confirms that there is a marked disparity in the degree of oxidation and the nature of the oxygen functional groups present. Subsequent reduction of the oxidized graphite (using three different methods) showed that the maximum specific capacitance of rGOs produced from the classical Hummers' method was 128 F g^{-1} whereas an analogous material obtained from an improved Hummers' method reached $\sim 274 \text{ F g}^{-1}$ (both via an hydrothermal reduction route). Besides showing that the improved oxidation method results in superior capacitance performance, explained by the higher number of structural defects allied to a surface chemistry where residual hydroxyl and epoxy functional groups predominate, this study highlights the need to rationalize the oxidation-reduction strategies followed when investigating applications of rGO materials.

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1. Introduction

Electrochemical capacitors, also commonly called supercapacitors, store energy either within the electrochemical double-layer formed at the electrode/electrolyte interface (a.k.a. electrochemical double layer capacitors) or through fast surface-localized redox reactions (a.k.a. pseudo-capacitors) [1-4]. Carbon-based nanomaterials are excellent candidates to integrate the electrodes of supercapacitors due to their high surface area, good electrical conductivity, chemical stability and wide range of operating temperatures [5-8]. Among nanocarbons, graphene stands out as it exhibits exceptional electrical and thermal conductivities and mechanical strength. As a monolayer, graphene has a high specific surface area ($\sim 2675 \text{ m}^2 \text{ g}^{-1}$) which leads to a maximum theoretical capacitance of 550 F g^{-1} , thereby setting an upper limit for all carbon-based electrode materials [9, 10]. Still, considering the low mass loading and its accessible surface area, the areal capacitance of single-layer graphene is limited to $21 \text{ } \mu\text{F cm}^{-2}$ [9] which renders its device application impractical. This limitation has fueled the search for strategies to enhance the supercapacitor performance of graphene-based materials [11-13].

Much work has been carried out on reduced graphene oxide (rGO) to realize the mass production of graphene-based energy storage devices [14-17]. Among the most popular methods to synthesize rGO flakes is the Hummers' method [18] in which graphite is first oxidized in aqueous medium and subsequently reduced/exfoliated by utilizing, for instance, chemical [19-23], thermal [24], hydrothermal [25], electrochemical [26, 27] or microwave-assisted reduction means [28]. The flakes obtained via this or analogous methods are generally several tens of layers thick. Still, the dominant terminology refers to them as reduced "graphene" oxide. The use of the term graphene in rGO, as applied here, is therefore to be understood *sensu lato*.

It is known that the reduction of the graphite/graphene oxide (GO) by different oxidation-reduction routes bears a considerable effect on the structure and chemistry of the final product [29-33]. With the introduction of defects and assorted functional groups, it is plausible to state that a pronounced influence on the non-faradaic EDLC behavior of these materials should also be expected. While there are numerous studies available which describe the supercapacitor performance of rGO-based supercapacitors [4, 9, 11, 15, 29], we found that a systematic study describing how different oxidation-reduction strategies may influence the non-faradaic specific capacitance of these materials is missing. In our previous study [34], we synthesized GO by two of the most common synthesis methods, the classical Hummers' [18] and the improved Hummers' [35] methods, subsequently reducing them under thermal, chemical or hydrothermal conditions to obtain six different rGOs (see also tree sample scheme in Fig. 1a). Following up on that first study, here we analyze the complete set of GO and rGO products as we questioned how much influence the oxidation-reduction routes would have on the supercapacitor performance of these materials.

2. Experimental

As previously reported [34], graphite powder was oxidized to obtain GO using either the Hummers' method (HGO) or the so-called improved Hummers' method (IGO). This was followed by dividing each of the GO products into three parts which were then reduced using one of various treatments (thermal, chemical and hydrothermal). In the following, we keep to the notation introduced in [34] where, for instance, thermally reduced Hummer's graphene oxide (rHGO) in N_2 atmosphere is named rHGO/ N_2 .

The entire set of samples, from the initial graphite to the rGO, was structurally, chemically and electrochemically characterized. The powder X-ray diffraction (XRD)

analysis was performed on a diffractometer (Bruker D8 Advance) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology of the materials was characterized using an FEI NovaNano scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of $\sim 10^{-9}$ mbar. The survey and high-resolution XPS spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively. Samples were mounted in floating mode in order to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the aromatic sp^2 hybridized carbon (C=C) peak from the C 1s spectrum set at 284.4 eV.

For the electrochemical characterization, the working electrode was prepared by mixing the active material (5 mg) with 15 μl of Nafion (at 5 wt% in ethanol and water), in a solution of water and ethanol (1 ml, 50% v/v). The use of Nafion as a binder for carbon materials has been discussed previously in the literature [10, 36]. The mixture was then ultrasonicated for about 30 min until a fine, homogenous slurry was obtained. The slurry was drop-cast onto the glassy carbon electrode (5 mm diameter) and dried under an incandescent lamp for ~ 30 min. A three-electrode cell configuration was used in a BioLogic VMP3 electrochemical workstation to evaluate the electrochemical performance of the GO and rGO materials under cyclic voltammetry (CV) and galvanostatic charge-discharge conditions. A platinum (Pt) wire and a saturated calomel electrode (SCE) were employed as counter and reference electrode, respectively. All the electrochemical testing was carried out at room temperature using 1.0 M H_2SO_4 as an electrolyte.

3. Results and discussion

3.1 Materials characterization

To situate this study it is important to first clarify what distinguishes the HGO and IGO materials. The XRD spectra of these are shown in Fig. 1(b). The characteristic peak arising from the (002) basal plane appears at $2\theta = 11.5^\circ$ and 10.2° , for the HGO and IGO, respectively. The larger shift of the IGO (002) peak, relative to the initial graphite ($2\theta = 26.3^\circ$, see [34]), shows that its interlayer spacing is larger than in the HGO (estimated to be $7.7 \text{ \AA}$ and $8.6 \text{ \AA}$, for HGO and IGO, respectively). Since it is known that the interlayer spacing of these materials is directly proportional to their degree of oxidation [34], the XRD data confirms that the overall oxidation degree is higher in the IGO. The morphology of the HGO and IGO powders were characterized using SEM, as shown in Figs. 1 (c) and (d). The flake size of the initial graphite is $\sim 45 \mu\text{m}$ [34]. Upon oxidation the size of the flakes decreases, with the average size of the HGO particles being notably larger than that of the IGO ones. The SEM images indicate that both HGO and IGO form dense agglomerates containing layered structures. These aggregates exhibit a curved/wrinkled morphology which may be advantageous as it prevents the restacking of graphene sheets and results in the production of a mesoporous material. Moreover, the wrinkled nature of GO could help in the improved transport of electrolyte ions due to its mesoporous nature, hence enhancing the supercapacitor performance [31]. Further to this, the GOs were reduced by various treatments giving rise to products with different structural characteristics, as detailed in our previous study [34].

Figure 1: a) Sample tree diagram of GO and rGO products, b) XRD patterns of HGO and IGO (normalized), c) and d) SEM images of the HGO and IGO products.

3.2 Surface chemistry

As the activity of graphene-based supercapacitors is thought to be correlated with the presence of oxygen-containing functional groups [12, 26, 37], the surface chemistry of the initial graphite, GO and rGO products was studied in detail. Firstly, survey spectra for the graphite and the two GOs were acquired (Fig. SI 1a). As expected, the graphite shows an intense C 1s peak along with a small O 1s peak arising from atmospheric oxygen.

Figure 2: High-resolution C 1s XPS spectra of (a) HGO, (b) IGO, (c) rHGO/N₂, (d) rIGO/N₂, (e) rHGO/hydrazine, (f) rIGO/hydrazine, (g) rHGO/hydrothermal, (h) rIGO/hydrothermal.

This contrasts with the spectra of HGO and IGO, also displayed in Fig. SI 1a. These showed the existence of O 1s, C 1s and N 1s peaks located at ~532, 284 and 398 eV, respectively. Negligible amounts of S and Cl impurities were also observed. Next, as a reference, the high-resolution C 1s spectrum was recorded for the initial graphite powder (Fig. SI 1b). The spectrum shows an intense peak of C=C (sp^2 arrangement) located at 284.4 eV. The binding energy (BE) values for sp^2 bonding are commonly in the range of 284.4 eV to 284.6 eV for graphite and related materials (e.g. graphene oxide, reduced graphene oxide and multi walled carbon nanotubes) [38]. Besides the C=C peak, the C 1s spectrum deconvolution identified four other bands: sp^3 (285.3 eV), C-OH (286.4 eV), C=O (288.0 eV) and the $\pi-\pi^*$ satellite peak (290.8 eV). The observed BE difference of sp^2 to sp^3 (0.9 eV) matches previous reports for graphite and graphene (for diamond and carbon nanotubes the expected BE difference would be 0.8 eV and 1.3 eV, respectively) [39]. As regards the presence of vestigial peaks associated with C-OH and C=O, these can be attributed to residual surface oxidation of the initial graphite in result of prolonged exposure to atmospheric moisture (the powder was analyzed as-received from the vendor). With reference to the sp^2 bond BE, these carbon-oxygen groups are usually shifted by 1.4-2.4 eV for the hydroxyl (C-OH), 2.6-3.5 eV for the carbonyl (C=O) and 4.3-5.4 eV for the carboxyl (O-C=O) [39, 40]. It is relevant to note that the BE for an epoxy functional group is close to the hydroxyl BE, hence some band overlap of double- and single-bonded carbon-oxygen groups is expected. In the case here, the extent of this overlap is dependent on the synthesis method for the graphene oxide and subsequent reduction step [39, 41].

Referencing to the initial graphite C 1s peak, similar spectra were acquired and analyzed for the sets of GO and rGO products as shown in Fig. 2 (a-h). The overall

chemical character of the samples is summarized in Figs. 3a to 3c. In Fig. 2a, the HGO shows significant contribution from C with sp^2 -character which arises from the remnant graphitic carbon (even after the intensive oxidation process that took place using the classical Hummers' method). By contrast, for the IGO, the relative contribution of the sp^3 fraction increases greatly in result of the almost complete oxidation of the graphitic carbon (Fig. 2b), an observation corroborated by our XRD results (cf. Fig 1b). Similar sp^2/sp^3 ratio changes with oxidation degree were claimed by other groups [42]. The relative areal fraction of the C-OH peak was particularly high for both GOs, effectively dominating the C 1s spectrum of the IGO. As regards the contribution from the C=O and O-C=O peaks this was similar for both HGO and IGO but at a lower level than the C-OH fraction. Upon reduction, and independently of the method employed, the sp^3 C was converted to sp^2 C, as expected. Yet, we observed that the yield of this conversion differed. From Fig. 3a, it is possible to read that the maximum of sp^2 character for the set of rHGOs was achieved through the thermal reduction method, thereby implying the highest efficiency in the removal of oxygen-containing groups. In this respect, the trend observed was rHGO/hydrazine < rHGO/hydrothermal < rHGO/N₂. In the case of IGO, a similar trend was observed. As concerns the C-OH presence, it is higher in the rIGO/hydrothermal product followed by the rIGO/hydrazine and the rIGO/N₂. Notably, from the entire set of rGOs, only the rIGO/hydrazine was found to be significantly doped with nitrogen (3.7 at%). This presence of surface nitrogen in readable amounts bears some interesting interpretations. Firstly, it indicates that the most effective doping strategy for the initial graphite is achieved through the IGO approach (also confirmed by the higher yields of oxygen inclusion). We suspect that the absence of identifiable N in the rHGO/hydrazine is due to the detection limit. Secondly, N-doping will surely have a

non-negligible effect in the electrochemical behavior of the material, implying therefore that the specific capacitance of hydrazine reduced GOs should not be interpreted in light of just the presence of oxygen-containing functional groups.

Figure 3: The relevant components extracted from high resolution C 1s spectra (a) HGO, (b) IGO, (c) overall C, O and N contents (calculated from the survey spectra).

The C, O and N contents seen across the sets of GO and rGO products are summarized in Fig. 3c. The O quantification of HGO and IGO confirms the more extensive oxidation of the later (see XRD in Fig. 1b and previous analysis in [34]). However, when these materials are reduced - using the same method and under similar conditions, the oxygen moieties are equally eliminated, demonstrating that the final density of oxygen-containing groups is not dependent on the initial degree of oxidation (for instance, cf. C and O at% in rHGO/N₂ versus rIGO/N₂). Ultimately, our results imply that the yield of oxygen depletion is dominated by the reduction method employed which, for the present work, was N₂ > hydrothermal > hydrazine.

3.3 Electrochemical characterization

With the above surface chemistry analysis and the previous structural study [34], enough insight on the GOs and rGOs is gathered to study their electrochemical

behavior and potential use as electrode materials for supercapacitor applications. Accordingly, the HGO and IGO were tested by standard cyclic voltammetry (CV) and galvanostatic charge-discharge techniques. All the electrochemical performance tests were conducted in a three electrodes cell configuration. The specific capacitance was calculated from the charge-discharge profiles according to the following equation:

$$C_{sp} = (I \times \Delta t) / (\Delta V \times m)$$

Where C_{sp} is the specific capacitance (in $F\ g^{-1}$), I is the galvanostatic discharge current, Δt is the discharge time, ΔV is the potential window and m is the mass of the active material.

Fig. SI 2a shows the CV curves of the HGO and IGO in the potentials range of -0.1 - $0.9\ V$ vs. SCE at a scan rate of $100\ mV\ s^{-1}$ in $1.0\ M\ H_2SO_4$. The curves shown are typical of carbon materials. A comparison of the HGO and IGO CV curves points to a small difference in the double layer current within the potential window used. Next, these materials were tested under charge-discharge conditions at various current densities (Fig. SI 2b). The specific capacitance of HGO and IGO is similar at around $8\ F\ g^{-1}$, for a current density of $1\ A\ g^{-1}$, and decreases to about $1\ F\ g^{-1}$ at higher current densities ($50\ A\ g^{-1}$). As expected, the specific capacitance values are relatively low which, together with the observed decrease for higher current densities, can be attributed to the insulating nature of the GOs [37].

As concerns the CV profiles of the rHGO and rIGO sets, they were performed at a scan rate of $100\ mV\ s^{-1}$ in the potential range of -0.1 - $0.9\ V$ and are shown in Fig. 4a and 4b. All the CV curves show typical rectangular-like voltammograms. Particularly visible in the rIGO/hydrothermal product, the broad redox peak at $\sim 0.3\ V$ arises from the reversible reduction/oxidation of residual oxygen-containing functional groups (e.g. hydroxyl, carboxyl and epoxy) [31, 40, 43]. It may include the reversible

reduction/oxidation of quinone to hydroquinone which is well reported in literature [44]. This is also in agreement with XPS results where a significant amount of surface oxygen (~ 5%) is present on rIGO/hydro samples. This indicates that, in some cases, not only the EDLC but also the pseudocapacitance contributes to the total supercapacitor performance [31, 43, 44]. Taken together, the EDLC for the rGO follows a consistent trend, remarkably correlated with the reduction treatment: hydrothermal > hydrazine > N₂. Moreover, when the CV curves for the sets of rHGO and rIGO products are compared, the later show, generally, higher specific currents (especially in the case of the rHGO/hydrothermal versus rIGO/hydrothermal).

The galvanostatic charge-discharge profiles of the rGO, taken at current density of 1 A g⁻¹ in the potential range of -0.1- 0.9 V, are shown in Fig. 4c and 4d. The specific capacitance of rHGO/N₂, rHGO/hydrazine and rHGO/hydrothermal is 16, 85 and 128 F g⁻¹, respectively. For the rIGO samples, the specific capacitance for rIGO/N₂, rIGO/hydrazine and rIGO/hydrothermal is 14, 136 and 274 F g⁻¹, respectively. Clearly, the results imply that the reduction (cf. results within the same rGO set) and the oxidation (cf. results between the two rGO sets) treatments used have a significant effect on the specific capacitance of the rGO (exception made for the rGO/N₂ products showing similar behavior).

Figure 4: Cyclic voltammetric analysis of the sets of a) rHGO, b) rIGO materials; Charge/discharge behavior of c) rHGO and d) rIGO at current density of 1 A g^{-1} in $1.0 \text{ M H}_2\text{SO}_4$.

Figure 5: The specific capacitance performance vs current density for a) rHGO and b) rIGO in 1.0 M H₂SO₄.

To complement the above, the charge-discharge performance, taken at different current densities, for the sets of rHGO and rIGO electrodes is shown in Fig. 5a and 5b. For the rHGO products, the results indicate that the specific capacitance figures are relatively low at <150 F g⁻¹, irrespective of the current density used. Furthermore, the rHGO/hydrazine and rHGO/hydrothermal retain only 40% of the initial capacitance when cycled at higher rates, i.e. 100 A g⁻¹. Contrastingly, in the rIGO set, the capacitance figures are higher (exception to the rIGO/N₂, similar to the rHGO analogue) and the rIGO/hydrazine and rIGO/hydrothermal products show 70% and 60% capacity retention at higher charge-discharge rates, respectively. The fact that the rIGO/hydrazine shows the highest capacity retention could be attributed to the better electronic conductivity arising from the nitrogen doping, as confirmed in the previous XPS analysis [45].

Figure 6: Cyclic stability of rIGO/hydrothermal at 20 A g^{-1} .

A fundamental requirement for supercapacitor electrodes materials is to retain their specific capacitance up to several thousands of cycles. The cyclic stability of the rIGO/hydrothermal was tested, in three electrodes configuration, at the high current density of 20 A g^{-1} (Fig. 6a) along with comparatively lower current densities (2, 5 and 10 A g^{-1} , as shown in Fig. SI 3). The results demonstrate that the rIGO/hydrothermal maintains a very high specific capacitance ($>200 \text{ F g}^{-1}$) even after 2500 cycles at a considerably high current density rate. Note that during the first ~ 250 cycles, a gradual increase in capacitance was observed and subsequently, a stable cyclic behavior was observed for next 2250 cycles. We attributed this to the improved wettability and activation process of the electrode. As it is known, the improved wettability involves the continuous diffusion of the electrolyte ions into the rGO

porous structure/graphitic layers which will lead to a gradual increase in the effective charge storage sites of the carbon electrode and thus the specific capacitance [43].

4. Discussion

Our results incite a great deal of rationalization not only on the reduction treatment of the GOs, the focus of the large majority of the relevant literature, but also the starting oxidation step (often overlooked). It is advisable that, to design graphene—based electrodes bearing superior supercapacitor performance, one should consider the following points:

1. The initial degree of oxidation of the GO is critical as it will define the number of oxygen-containing functional groups and, afterwards, the density of structural defects in the structurally rearranged rGO.
2. The reduction treatment has a pronounced effect on the specific capacitance. Firstly, each treatment reduces the GOs in equal proportion, albeit via different mechanisms; hence, the oxygen functionalities in the rGO will differ qualitatively and quantitatively as a function of the reduction method (and the oxidation step, as per point 1). Each reduction treatment leads to different types and density of lattice defects. For example, during thermal reduction (N_2), the hydroxyl groups may desorb without altering the graphene structure (MD simulations in ref [40]). Contrastingly, the epoxy groups are more stable and distort the graphene lattice substantially on desorption. The ether and carbonyl components, the most thermodynamically stable oxygen-containing functional groups, can result from the thermal annealing between two nearby hydroxyl and epoxy groups [40]. Finally, one needs to observe for doping such as the presence of nitrogen inclusions, here illustrated in the rIGO/hydrazine. Supposedly, the nitrogen doping improves the electronic conductivity of rGO and hence its supercapacitor performance [45].

In this comparative study, the rIGO/hydrothermal is the best electrode material as it conjugates several of the above conditions. On one hand, the extensive oxidation provided by the IGO approach results in a material that has the right density and nature of functional groups. Thus, an incomplete oxidation step, as often seen in the literature, is not advisable for supercapacitor performance optimization. On the other hand, the hydrothermal reduction step is not harsh enough to entirely eliminate the oxygen groups while still being extensive to the point of inducing structural re-ordering of the carbon lattice. As observed above, complete absence of functional groups and too much lattice mending will reduce the supercapacitor performance drastically. Moreover, the type of remaining functional group matters. This is further compounded as some groups also refer to the need to control the pH levels of rGO derived from hydrothermal treatment [31]. In result of this, when compared to the performance reported for other carbon-based supercapacitor electrode materials such as activated carbon ($< 10 \text{ Wh kg}^{-1}$) [46], carbon nanotubes ($< 10 \text{ Wh kg}^{-1}$) [47], hydrazine-reduced GO (10 kW kg^{-1} at an energy density of 28.5 Wh kg^{-1}) [17] and other chemically reduced GOs ($< 10 \text{ Wh kg}^{-1}$) [48], our rIGO products consistently portray twice the specific energy ($>20 \text{ Wh kg}^{-1}$) at a power density of $\sim 50 \text{ kW kg}^{-1}$.

5. Conclusions

We have systematically probed the chemical, structural and supercapacitor performance of HGO and IGO and respective sets of rGO products obtained via thermal (in N_2), chemical (hydrazine) or hydrothermal means. Our results show that HGO and IGO have different degrees of oxidation, morphology and electrochemical response. When rGOs were utilized as electrode materials, the supercapacitor performance followed a trend dominated by the choice of reduction treatment,

hydrothermal > hydrazine > N₂. Moreover, the comparison of the supercapacitor performance of the rHGO and rIGO confirms that rIGO samples have, overall, higher specific capacitance. Our results demonstrate that the initial selection of the starting GO synthesis, when coupled to a judicious choice of the reduction treatment, can greatly influence the supercapacitive performance of these materials. Thus, we believe that this study will pave a path for better and more rational materials design strategies for graphene-based supercapacitor applications.

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Supporting information: Rational design of reduced graphene oxide for superior performance of supercapacitor electrodes

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Figure SI 1: a) Survey spectrum of Graphite (Sigma Aldrich, 325 mesh), HGO and IGO b) High-resolution C 1s XPS spectra of commercial graphite.

Figure SI 2: Cyclic voltammetric analysis and b) specific capacitance vs. number of cycles of HGO and IGO products in 1.0 M H₂SO₄.

Figure SI 3: Cyclic stability of rIGO/hydrothermal at various current densities in 1.0 M H₂SO₄.