Accepted Manuscript

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PII: S0277-5387(16)30141-3
DOI: <http://dx.doi.org/10.1016/j.poly.2016.04.044>
Reference: POLY 11972

To appear in: *Polyhedron*

Received Date: 2 March 2016
Accepted Date: 30 April 2016

Please cite this article as: A. Alazmi, S. Rasul, S.P. Patole, P.M.F. Costa, Comparative study of synthesis and reduction methods for graphene oxide, *Polyhedron* (2016), doi: <http://dx.doi.org/10.1016/j.poly.2016.04.044>

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Comparative study of synthesis and reduction methods for graphene oxide

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Abstract

Graphene oxide (GO) and reduced graphene oxide (rGO) have congregated much interest as promising active materials for a variety of applications such as electrodes for supercapacitors. Yet, partially given the absence of comparative studies in synthesis methodologies, a lack of understanding persists on how to best tailor these materials. In this work, the effect of using different graphene oxidation-reduction strategies in the structure and chemistry of rGOs is systematically discussed. Two of the most popular oxidation routes in the literature were used to obtain GO. Subsequently, two sets of rGO powders were synthesised employing three different reduction routes, totalling six separate products. It is shown that the extension of the structural rearrangement in rGOs is not just dependent on the reduction step but also on the approach followed for the initial graphite oxidation.

Keywords

Synthesis; Chemical Exfoliation; Graphite oxidation; Reduced graphene oxide; Graphene.

Introduction

Graphene is a remarkable two-dimensional material¹ which has been receiving tremendous attention from academics and industrialists alike². Amongst its many potential applications are supercapacitors³, conductive coatings composites⁴, catalysis⁵ and flat panel displays⁶. While the latter requires large-area films, other applications such as supercapacitors are better realised via particulates (or “flakes”)⁷. With respect to this, tailoring of the graphene’s shape, structure and chemistry is highly desirable. The challenge of a cost-effective mass production method of application-specific graphene flakes remains quite present, however. To this end, much work has been carried out on the synthesis of rGO. One of the most popular chemical methods to obtain rGO is to first oxidize graphite flakes in aqueous medium and subsequently reduce them. For both steps, a myriad of approaches have been reported with the most common being oxidation via the classical Hummer’s method (or an adaptation of this)^{1, 8} followed by a reduction step resorting to heat⁹ or chemical reactions¹⁰. Although it has been recognised that the use of different oxidation-reduction routes has a considerable effect on the final rGO properties¹, comparative studies on this issue have been lacking. This is particularly important if one is to understand by which means each approach influences the final structure and chemistry of the rGO flakes and to which extent can we control/tailor this. On the other hand, different reduction methods will have an important effect on the surface’s chemical structure of rGO. For instance, as regards energy-related applications, several studies in the literature have delved on the supercapacitance performance of rGO-based electrodes synthesized either by the classical Hummers’ method¹¹ or an adaption of this^{8b}. Still, these authors do not justify their rGO synthesis approach or analyze systematically what is the best oxidation-reduction synthesis strategy for such applications. In this comparative study, we describe how using common methodologies for rGO synthesis affects the final product’s oxidation degree, structure and chemical signature.

Materials and methods

Synthesis of graphene oxide

Graphite powder (Sigma-Aldrich, particle-size <45 μm or Alfa Aesar, <50 μm) was first oxidized using one of two commonly used chemical processes: the Hummers' method ¹² or the so-called Improved-Hummers' method ^{8b} (with additional KMnO_4). Note that the two graphite powders are equivalent as they have similar particle size and XRD patterns (Fig. S1). For the classical Hummers' synthesis, 3 g of graphite powder (Sigma-Aldrich) and 1.5 g of NaNO_3 (Fisher Scientific, 99%) were mixed with 75 mL of concentrated H_2SO_4 (Sigma Aldrich, 99%). The reaction was cooled to <5 $^\circ\text{C}$ in an ice bath and stirred for 2 h. 9 g of KMnO_4 (Acros, 99%) was added in small portions, to maintain the reaction temperature below 20 $^\circ\text{C}$, and constantly stirred for another hour. Then, the suspension was warmed to room temperature, by removing the cooling bath, at which time deionized water (100 mL) was slowly added (caution: the reaction is highly exothermic and evolution of gas was noticed). An oil bath was used to keep the reaction temperature constant at 90 $^\circ\text{C}$. Subsequently, 300 mL of deionized water was added and the mixture was continuously stirred for another hour and a half. An extra 1 L of deionized water was poured into the mixture followed by the slow addition of 30 mL H_2O_2 (Sigma Aldrich, 30%). This action turned the colour of the mixture from dark brown to yellow and was accompanied by the release of heat. After cooling to room temperature, the product was diluted with deionized water to a total volume of 2 L. Finally, the suspension was repeatedly washed with water and centrifuged (Hettich U320, 9000 rpm, 10 min) until the pH was nearly neutral. At this point, the suspension was vacuum dried in the centrifuge tubes (60 $^\circ\text{C}$, 12 hours) and the resulting powder collected.

For the Improved-Hummers' synthesis, 3 g of graphite powder (Alfa Aesar) was added to a mixture of 360 mL H_2SO_4 (Sigma Aldrich, 99%) and 40 mL H_3PO_4 (Sigma Aldrich, 85 wt.%). This was followed by the slow addition of 18 g of KMnO_4 (Acros, 99%), taking care that the reaction temperature was maintained at <20 $^\circ\text{C}$. Then, the resulting suspension was heated, in an oil bath, to 50 $^\circ\text{C}$ and stirred for 12 hours. The colour of the mixture turned from black to mud-brown. The reaction was allowed to cool to room temperature and treated with 400 mL of cold deionised water plus 3 mL of H_2O_2 (Sigma Aldrich, 30%). The product was washed and dried using the same procedures described above.

The GO products prepared by the classical and improved Hummers' methods are hereafter designated as HGO and IGO, respectively.

Thermal reduction

A sample of HGO or IGO, typically in the order of 400 mg, was thermally reduced for 2 hours in a horizontal tube furnace under N₂ atmosphere at 900 °C (heating rate of 5 °C min⁻¹). The thermally reduced GO is hereafter designated as rHGO/N₂ or rIGO/N₂^{9b}.

Chemical reduction

The chemically-induced reduction of HGO (or IGO) was carried out by loading 100 mg of the GO powder into a 500 mL round-bottom flask and then disperse it in 100 mL of deionised water. This yielded a brown slurry that, upon stirring for 12 hours, became clear. 1 mL of a hydrazine hydrate solution (NH₂NH₂·H₂O, Sigma Aldrich, 25%) was then added and the mixture heated in an oil bath at 100 °C. A water-cooled condenser was fitted to the flask and the reaction allowed to proceed for 24 h, after which a black solid had precipitated. The chemically reduced GO is hereafter designated as rHGO/hydrazine or rIGO/hydrazine¹³.

Hydrothermal reduction

100 mg of HGO (or IGO) powder was dispersed in 40 mL of deionized water and stirred for 24 hours to form an aqueous dispersion. Then, the mixture was transferred to a 50 mL Teflon-lined autoclave and kept in an oven at 180 °C for 24 hours. The product was collected, washed several times with deionized water and dried at 50 °C for 24 hours. The hydrothermally reduced GO is hereafter designated as rHGO/hydrothermal or rIGO/hydrothermal¹⁴.

Characterization

The Fourier transform infrared (FTIR) spectral analysis was carried out on a Thermo Scientific spectrometer (Nicolet iS10) and performed in transmission mode using KBr pellets. Raman spectra were obtained with a WITec Alpha300RA spectrometer using an excitation wavelength of 488 nm. Thermogravimetric analysis (TGA) data was recorded on a Netzsch TG209-F1 instrument at a heating rate of 10 °C min⁻¹ in N₂. Thermogravimetric analysis with mass spectrometry (TGA-MS) was carried out in a Netzsch TG209-F1 coupled to a QMS 403 C

Aëolos using a He flow with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. 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 samples was observed with scanning electron microscopy (SEM) (FEI Quanta 600, 4 kV) and the structure of the flakes studied with transmission electron microscopy (TEM) (FEI Tecnai BioTwin, 120 kV).

Results and discussion

A. Sample Tree

The two methods we selected for the oxidation step, just as for the subsequent reductions, are the most common procedures referred to by other teams. The first oxidation method is the Hummers' method (KMnO_4 , NaNO_3 , H_2SO_4), which is the most common approach used for producing GO. The second method is the Improved-Hummers' method (KMnO_4 , 9:1 $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$). In this regard, Tour et al. have demonstrated that preparing GO in 9:1 $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ while excluding NaNO_3 clearly improves the efficiency of the oxidation process and subsequently the quality of the produced GO^{8b} . Overall, the amounts used and conditions employed were also in order with those commonly described in the literature^{12 8b 14 13 9b}. The final rGO products are correlated with the parent graphite powder as schematised in Figure 1.

Figure 1. Sample tree diagram of the graphite-derived materials studied. Acronyms are explained in the Materials and Methods Section.

Structural Analysis

The morphologies of aggregates and individual flakes derived from the parent graphite and its oxidized counterparts are shown in Figure 2. One noticeable difference in the aggregates is the tendency of graphite to show compact stacks with well-defined jagged edges. Contrastingly, the oxidized materials show wrinkled agglomerates where the layered arrangement is more visible due to the expansion of the basal plane stacks. Specifically for the IGO product, charging was often observed during SEM imaging which points to an electrically insulating character. While the initial graphite aggregates were in average $<50\ \mu\text{m}$ (as per commercial vendors), after the oxidation step these were broken into smaller particles. At the discrete flake level, the corrugated morphology of both HGO and IGO products is confirmed. In addition, it is relatively easy to find large areas with high TEM transparency.

Figure 2. (a) Representative SEM image of the initial material, graphite flakes; (b) TEM micrograph of a graphite flake; (c) Representative SEM image of the oxidised graphite using the classical Hummer's method; (d) TEM image of individual flakes from the material in (c); (e) Representative SEM image of the oxidised graphite using the Improved Hummer's method; (f) TEM micrograph of flakes from the material in (e).

Upon reduction, all products exhibit similar morphology, both at the aggregate and individual flake levels (Figures 3 and 4). The layered arrangement is retained and clearly visible in the SEM for the HGO- and IGO-derived sets of reduced graphene. Aggregates were generally of smaller dimensions ($<10\ \mu\text{m}$) than their oxidised counterparts. Further to this, the individual flakes were invariably transparent to the electron beam in medium resolution TEM. This suggests that the dispersed rGO flakes were significantly thinner than those of the initial and the oxidised graphite. Overall, the oxidation-reduction methodology used influences little in how the final rGO flakes and aggregates look like under the electron microscope (EM) at low/medium magnification. Still, given the profuse use of this technique by the community, it is important to document these results.

Figure 3. (a) Representative SEM image of the thermally reduced HGO (in N₂ atmosphere); (b) TEM micrograph of an individual flake from the material in (a); (c) Representative SEM image of the chemically reduced HGO (in hydrazine); (d) TEM micrograph of an individual flake from the material in (c); (e) Representative SEM image of the hydrothermally reduced HGO; (f) TEM micrograph of an individual flake from the material in (e).

Figure 4. (a) Representative SEM image of the thermally reduced IGO (in N₂ atmosphere); (b) TEM micrograph of an individual flake from the material in (a); (c) Representative SEM image of the chemically reduced IGO (in hydrazine); (d) TEM micrograph of an individual flake of the

product in (c); (e) Representative SEM image of the hydrothermally reduced IGO; (f) TEM micrograph of an individual flake from the material in (e).

XRD is a popular characterisation technique to quickly identify the structural arrangement, oxidation degree and phase purity of graphite and GO/rGO materials¹⁵. In contrast to the above EM analysis, the set of spectra shown in Figure 5 illustrates well how the final products are structurally different from the initial graphite material. The interlayer spacing (d) of the graphite basal planes was calculated from the (002) reflection of graphite, or equivalent in the case of the GOs and rGOs products (Table 1). The initial graphite powder shows the characteristic (002) reflection at $2\theta = 26.7^\circ$, which equates to 3.3 Å. In the case of HGO, the intensity of the equivalent peak was drastically reduced with the dominant reflection located now at $2\theta = 11.5^\circ$. As per previous studies^{3a, 16}, this is identified as the expanded GO basal planes. Similarly, the spectrum of the IGO product contains this peak but shifted to an even lower angle ($2\theta = 10.2^\circ$), logically implying a larger interlayer spacing than the HGO analogue. This observation is corroborated by previous studies^{10, 17} as the IGO products are expected to contain a higher proportion of intercalated water molecules between the oxidised basal planes. Of note is the entire absence of the reflection at $2\theta = 26.7^\circ$ which points to the complete oxidation of the initial graphite.

Figure 5. Powder XRD patterns for the graphite and graphite-derived materials studied. The broken lines are guides for the eyes and relate to the (002) peaks for the initial graphite (26.7°), HGO (11.5°) and IGO (10.2°). All intensities were normalised with reference to the graphite (002), or equivalent, peak.

As expected, and subsequent to the reduction step, all rGO products exhibited XRD spectra nearer to the one of the initial graphite. Whilst the peak at lower angles invariably disappeared, reverting back to 2θ values close to 26° , the shape of the dominant reflection is a matter deserving closer attention. Accordingly, the (002) peak of each rGO is considerably broader than that of the initial graphite. In fact, the full width at half maximum (FWHM) of this peak is claimed to reflect out-of-plane structural disorder¹⁸. Taken together, the (002) peak FWHM for rIGOs products is generally larger than for the analogous rHGOs. Further to this, in some cases the presence of a second reflection is visible, either as a shoulder (e.g. rHGO/hydrazine) or a peak (e.g. rHGO/hydrothermal). The larger FWHM can be assigned to a smaller grain size and/or higher density of defects together with increased lattice strain. On the other hand, the second peak is commonly related to incomplete reduction processes of GOs and remainders of

oxygen-containing functional groups and intercalated H₂O molecules¹⁹. These observations suggest that the rIGO products have smaller grains with a higher density of structural defects when compared to the rHGO analogues.

Table 1. Peak position and basal plane interlayer spacing for graphite, the two GOs and the sets of rGOs products.

Sample	Peak position (degree)	Interlayer spacing (Å)
G	26.7	3.3
HGO	11.5	7.7
rHGO/Hydrothermal	26.2	3.9
rHGO/Hydrazine	26.7	3.3
rHGO/N ₂	26.7	3.3
IGO	10.2	8.6
rIGO/Hydrothermal	25.6	3.4
rIGO/Hydrazine	25.1	3.5
rIGO/N ₂	26.1	3.4

To confirm structural differences in the various oxidised and reduced products, Raman spectroscopy was used. It is known that Raman spectroscopy can provide important insight into the specific type and relation of C-C bonds, being therefore a critical analytical tool for Nanocarbons such as graphene. As shown in Figure 6, the initial graphite exhibits two characteristic peaks at 1567 cm⁻¹ (G band) and 2693 cm⁻¹ (2D band). These are common in Nanocarbons and are assigned, respectively, to the E_{2g}-vibration mode of sp² carbon domains and the second order of the D band²⁰. Another characteristic peak, not visible in the initial graphite, is located at ~1355 cm⁻¹ (D band) and relates to the structural defects and partially disordered structures of the sp² domains²¹. For the present work, structural defects are, in a first stage, introduced by the attachment of functional groups such as hydroxyl, epoxy on the carbon skeleton²² and, later on, by the presence of vacancies, interlayer bonds or lattice corrugations containing a large number of sp³ carbon. Table 2 summarizes the peak positions, peak intensity (I) ratios and calculated crystallite size (L_a) for all the materials studied. In regards to the HGO and IGO products, both the D and G bands were present. The HGO spectrum also included the 2D band. With the graphite oxidation, the G band shifts to higher frequencies as seen for the

HGO and IGO Raman spectra. The blue shift of the G band occurs as a result of the activation and merging of the Raman-inactive D' band with the G band, caused by the defects²³. The intensity ratio of the D to the G peaks (I_D/I_G) is smaller for HGO than for IGO. For GOs, the I_D/I_G values can work as a proxy to infer their degree of oxidation²⁴. Remarkably, the 2D band is visible in HGO but not for IGO which further adds to the argument of more extensive oxidation taking place during the IGO synthesis method. Put together, the Raman results for the GOs matches the information extracted from the XRD characterisation.

Figure 6. Raman spectra for all the materials studied. The broken lines are guides for the eyes and refer to the graphite G and 2D bands along with the HGO D band (1351 cm^{-1}). All intensities were normalised with reference to the D or G bands, whichever was more prominent.

Table 2. Raman spectra peak positions, I_D/I_G (intensity ratio of D and G peaks) and L_a values of the G, GOs and rGOs materials.

Sample	D peak position	G peak position	2D peak position	I_D/I_G	L_a (nm)
G	-	1567	2713	0.41	32.4
HGO	1351	1572	2706	0.89	15.1
rHGO/Hydrothermal	1349	1572	2694	0.97	13.9
rHGO/Hydrazine	1355	1581	2704	0.97	13.9
rHGO/N ₂	1349	1574	2692	1.0	13.5
IGO	1359	1589	-	0.97	13.9
rIGO/Hydrothermal	1355	1595	-	0.98	13.8
rIGO/Hydrazine	1359	1581	-	1.0	13.5
rIGO/N ₂	1353	1585	-	1.0	13.3

After reduction, the position of the peaks for the sets of rHGO and rIGO products is mostly retained, with the rIGOs consistently showing comparatively higher wavenumbers for the D and G bands. The 2D band is observed exclusively in the set of rHGO products. This is a logical outcome from its presence in the parent HGO and indicates a higher degree of graphitisation, particularly in the rHGO/N₂ case^{22, 25}. In both sets, the slight increase in the I_D/I_G ratios could be attributed to the persistency of structural defects despite the removal of oxygen-containing functional groups. These results confirm the view that, irrespective of the reduction method used, it is not possible to entirely rearrange the carbon lattice. Still, the rHGO/N₂ approach appears to be the most effective way of doing this. Finally, we estimated the crystallite size for the different materials studied. The L_a is defined as the average size of the graphitic crystallite. It can vary between 0.2 and 1×10^4 nm²⁶ and can be calculated using the I_D/I_G ratio and the following relation²⁷:

$$L_a \text{ (nm)} = (2.4 \times 10^{-10}) \lambda_{\text{laser}}^4 (I_D/I_G)^{-1} \quad (1)$$

Where λ_{laser} is the wavelength of the laser source (i.e. 488 nm). Together, the L_a trend is (rGO/N₂) < (rGO/ hydrothermal) ~ (rGO/hydrazine) ~ IGO < HGO < graphite. This corroborates that the IGO method leads to more extensive oxidation and the thermal reduction in inert atmosphere is the most effective to eliminate functional groups and rearrange the carbon lattice.

The thermal stability of the initial graphite, HGO and IGO materials was measured in inert atmosphere (Figure 7a). As expected, there was no detectable mass loss for the graphite, in the range of 25-900 °C. By contrast, significant mass losses of 12% and 18% were observed up to 100 °C for HGO and IGO, respectively. Knowing the hydrophilic nature of GO, the elimination of adsorbed water molecules explains this result. A more dramatic mass loss was observed in the range of 100–300 °C, with the losses measured at 240 °C being 16% and 29% for HGO and IGO, respectively. These are commonly associated with the thermally-induced decomposition of oxygen-containing functional groups²⁸ and subsequent release of steam and gases such as CO and CO₂. To confirm this assumption, TGA-MS was carried out for the HGO sample. As shown in Figure S2, the mass loss step between 180 °C and 280 °C is related to the molecular mass peaks of 18, 28 and 44. Hence, CO and CO₂ are the main decomposition products (originating, for example, from carboxyl and epoxy functional groups, respectively)²⁹ together a minor release of H₂O. Overall, these mid temperature range results indicate that the IGO sample has a higher concentration of oxygen-containing functional groups than HGO³⁰. In the high temperature region (>300 °C), the mass losses in both GOs were continuous, reaching up to 66% for the IGO at 900 °C. This behaviour is expected as the materials undergo further carbonization and more stable groups such as phenols and carbonyls are eliminated²⁹. In particular, the higher rate of decomposition for the HGO from 500 °C onwards could be due to the catalytic activity of NaNO₃ remainders (not present in IGO). In regards to the rGOs, the TGA profiles generally showed smaller mass losses at 900 °C, with the maximum identified for the rIGO/hydrazine. Interestingly, the stability of the HGO and IGO derived products depended clearly on the reduction method employed following the trend hydrazine<hydrothermal<N₂. Moreover, the rIGOs were comparatively less stable than their rHGOs counterparts.

Figure 7. (a) TGA curves (under N₂ flow) for the initial graphite (black), HGO (blue) and IGO (red) materials; (b) TGA curves (under N₂ flow) for the entire set of rGOs. The thermal stability of the materials in (b) is clearly higher than the GOs in (a), being most noticeable for the thermally (N₂) reduced products.

The above structural analysis compared the outcomes of different oxidation-reduction methodologies and identified significant differences in the final products obtained. In particular, the oxidation degree of the GOs and the subsequent effectiveness in reconstructing the graphitic lattice displayed noticeable variations. Although the oxidation reactions are different, one point that may help explaining the larger oxidation degree of IGO and, subsequently, its more defect prone reduced counterparts, is the total time of graphite exposure to the oxidiser. Overall, the IGO method required 12 hours for the oxidising step while the equivalent in the HGO procedure was achieved in little more than 4 hours. As for the reduction step, in both sets, the thermal treatment in inert atmosphere is more effective in rearranging the carbon lattice not least due to the temperatures involved which are typical of carbonization processes.

Chemical Analysis

To further understand the sets of materials studied, in particular the types of functional groups present in the GOs and rGOs, FTIR spectra were acquired for all samples in the range of 500–

4000 cm^{-1} (Figure 8). Expectedly, the initial graphite spectrum did not show the fingerprint of relevant bands. This contrasts greatly with the oxidised products as both the spectra for HGO and IGO exhibit several strong characteristic peaks. The first to consider is the broad peak between 3200 cm^{-1} and 3700 cm^{-1} which is regularly attributed to the presence of hydroxyl groups. The predominance of this peak is massive in the IGO spectrum strengthening the view of a higher content of intercalated water and more extensive oxidation. At 1723 cm^{-1} and 1690 cm^{-1} the peaks can be assigned to the stretching vibration of C=O, included either in carboxyl or carbonyl moieties. More peaks can be identified in the region of 1400-1000 cm^{-1} , including O-H deformations in C-OH groups (at 1387 cm^{-1}), C-OH stretching vibration (at 1224 cm^{-1}) and C-O stretching vibrations in C-O-C epoxides (at 1062 cm^{-1})³¹. Here, the IGO peaks are less defined possibly due to the higher density of defects and associated larger number of different groups attached. After the reduction step, all the characteristic absorption bands of oxygen-containing groups (e.g. O-H, C=O and C-O) are substantially weakened and, in the case of the thermally treated samples, almost eliminated. Of note, we did not detect C-N related bands subsequent to the hydrazine reduction step. Likewise, the hydrothermal treatment seems to result in similar spectra below 2000 cm^{-1} with broad peaks at 1569 cm^{-1} and 1224 cm^{-1} . Taken together, the FTIR identified similar functional groups present in the different GOs and rGOs. With this it is confirmed that the chemical identity of the bulk materials appears to be identical. To assert that the surface chemistry follows this same trend - and how this may affect, for instance, the electrochemical behaviour of the materials - it is necessary to perform a more localised study with X-ray photoelectron spectroscopy (this will be the topic of a follow-up study³²).

Figure 8. FTIR spectra for all the materials studied. The broken lines are guides for the eyes and refer to the main bands observed in the graphite, GOs and rGOs. The initial graphite did not show relevant bands.

Conclusions

In this comparative study, GOs with different degree of oxidation were synthesized, followed by their reduction using a selection of methods. The effectiveness of the oxidation step ultimately limits the extension of lattice reconstruction, irrespective of the reduction approach used. For this reason, the rIGO materials are less structurally ordered than the rHGO ones. Within each set of rGOs, the thermal reduction under inert atmosphere leads to a more graphitised material. It remains to be investigated whether this is a beneficial outcome when optimising applications dependent on graphene-based materials. As for the chemical fingerprint of the GO and rGO bulk

materials, while differences are observed at the oxidised stage, these are generally smoothed out upon reduction. As demonstrated, it is important to approach the synthesis of rGO flakes in a rational way, and through this, appreciate their diversity. In particular, the structure of rGOs is highly dependent on the oxidation-reduction strategy selected which could influence (if not dominate) their performance for some of the applications proposed in the literature (e.g. supercapacitors).

Acknowledgements

We acknowledge KAUST for funding support (BAS/1/1346-01-01 & 02) and are thankful to the KAUST Core Labs for technical assistance.

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The comparative study of various reduced graphene oxide products, and respective precursors, shows that the final structure of these materials is dependent not just on the reduction step but also on the initial graphite oxidation procedure.