Probing the Thermal Deoxygenation of Graphene Oxide Using High-Resolution In Situ X-ray-Based Spectroscopies

Abhijit Ganguly,† Surbhi Sharma,† Pagona Papakonstantinou,* and Jeremy Hamilton

Nanotechnology and Advanced Materials Research Institute, NAMRI, University of Ulster, Jordanstown campus, BT37 0QB, United Kingdom

ABSTRACT: Despite the recent developments in graphene oxide due to its importance as a host precursor of graphene, the detailed electronic structure and its evolution during the thermal reduction remain largely unknown, hindering its potential applications. We show that a combination of high-resolution in situ X-ray photoemission and X-ray absorption spectroscopies offer a powerful approach to monitor the deoxygenation process and comprehensively evaluate the electronic structure of graphene oxide thin films at different stages of the thermal reduction process. It is established that the edge plane carboxyl groups are highly unstable, whereas carbonyl groups are more difficult to remove. The results consistently support the formation of phenol groups through reaction of basal plane epoxide groups with adjacent hydroxyl groups at moderate degrees of thermal activation (~400 °C). The phenol groups are predominant over carbonyl groups and survive even at a temperature of 1000 °C. For the first time, a drastic increase in the density of states (DOS) near the Fermi level at 600 °C is observed, suggesting a progressive restoration of aromatic structure in the thermally reduced graphene oxide.

INTRODUCTION

Since the discovery of graphene,1−3 immense efforts have been focused on graphene oxide (GO),4−5 because it is the most promising precursor for obtaining large quantities of this unique material and because GO is a useful material on its own right. Graphene oxide can be visualized as individual sheets of graphene decorated with oxygen functional groups on both basal planes and edges, which has been prepared by oxidative exfoliation of graphite. The presence of oxygen makes GO amenable to chemical functionalization, nevertheless it disrupts the extended sp2 network of the graphene hexagonal lattice. To convert GO back to graphene, the chemical/thermal reduction of GO is so far the most attractive procedure because of its simplicity, reliability, high yield, and low cost.6−14 Chemical treatment, especially exposure to hydrazine, is the most widely used route to reduce GO in solution.7,9−12 However, the chemically reduced GO (CRGO) suffers from a relatively low C/O atomic content,12 with a considerable amount of residual O-moieties.7,12 Also, hydrazine treatment leads to the formation of nitrogen-functional groups,7,12 along with the inherent toxicity of hydrazine. Improvements have been accomplished by either postheating at low temperatures (200−500 °C),8,10,11 or by replacing hydrazine by alternative less toxic reducing agents, for example sodium borohydride or alkaline solutions.13,15 The use of nontoxic and biocompatible reducing agents such as vitamin C (L-ascorbic acid),16 green tea,17 melatonin,18 saccharides such as glucose, fructose, and sucrose19 or the use of environmentally friendly processes such as hydrothermal dehadration20 have also been reported. In another approach,21−23 the reduction of GO was achieved by a TiO2 assisted photocatalytic method, in which the electrons photogenerated by UV-irradiated TiO2 were injected into GO reducing the oxygen-containing functional groups. Such low-temperature deoxygenating processes, although not completely effective in reducing GO, are amenable to electronic applications of graphene patterned onto glass or plastic substrates as well as to the synthesis of a wide range of functional hybrids with use in polymer composites, biosensors, energy storage, and conversion technologies.24 In comparison, thermal reduction at high temperatures (900−1000 °C), particularly in ultra-high vacuum (UHV), is found to be highly efficient in producing graphenelike films with a significantly high C/O ratio,12 with no introduction of any contaminants. However, such high-temperature processing is unlikely to be compatible with fabrication techniques used for most electronic applications. Practically the majority of the studies report the presence of various amounts of residual oxygen in reduced graphene oxide, with the electrical conductivity reaching values several orders of magnitude lower than that of mechanically exfoliated graphene.

To make further progress on optimizing and designing reduction processes, which is key to numerous applications, GO needs to be well characterized and its thermal deoxygenation needs to be well understood. Thermal reduction of GO has been shown to involve the removal of oxygen groups by formation of carboneous species (CO2, CO) thus creating defects in the form...
The specific objectives of the present work were i) to elucidate the evolution of oxygen groups and probe their survival rate upon heat treatment; ii) to determine the nature of the residual oxygen containing functional groups that remain after reduction; iii) to clarify how the heat treatment affects the electronic structure of GO. To do that, we carried out high-resolution in situ C 1s and O 1s core level and Valence band X-ray photoemission as well as X-ray absorption temperature dependent spectroscopic studies on GO. The analysis of these studies helped to develop a comprehensive view into the temperature evolution of electronic structure and surface chemistry of GO nanosheets. We found a predominance of phenol groups, which originate from the reaction of basal plane epoxide groups with adjacent hydroxyl groups, at moderate temperatures. It was established that these phenol groups survive even at temperatures of 1000 °C.

**EXPERIMENTAL SECTION**

**Synthesis.** Highly oxidized graphene oxide (GO) was produced using a modified Hummers’ process. The starting material graphite powder (product: 78391) with particle size ≤20 μm was purchased from Fluka and is denoted here as pristine graphite. All other chemical and reagents were purchased from Aldrich.

A mixture of 2.5 g of graphite and 1.9 g of NaNO3 was placed in a flask cooled in an ice bath; 85 mL of H2SO4 was added to the mixture and stirred until homogenized. Solution of 11.25 g of KMnO4 in distilled water was gradually added to the solution while stirring. After 2 h, the solution was removed from the ice bath, and further stirred for 3 days. Finally, brown-colored viscous slurry was obtained. The slurry was added to 500 mL aqueous solution of 5 wt % H2SO4 over 1 h while being continuously stirred. The mixture was stirred for a further 2 h. Subsequently, 10 mL of H2O2 (30 wt % aqueous solution) was then added to the mixture and stirred for further 2 h. This mixture was then left to settle overnight. The mixture was filtered and further purified by dispersing in 500 mL aqueous solution of 3 wt % H2SO4 and 0.5 wt % H2O2. After two days of precipitation, the supernatant solution was removed. This process was repeated five times. The solid product obtained after the rigorous cleaning process was rinsed using copious amounts of distilled water and dried in an oven, as reported in literature. The resulting solid was dispersed in water by ultrasonication for 2 h to produce a GO aqueous dispersion. After one-day sedimentation, the thick flakes were removed and the supernatant was collected for further measurements.

**Characterization Techniques.** High-resolution transmission electron microscopy (HRTEM) analysis were carried out using JEOL 2100F, which has a point resolution of 0.19 nm. TEM samples were prepared on Holey carbon-coated Cu 300 mesh grids.

High-resolution X-ray photoelectron spectroscopy (XPS) analysis was carried out using SCIENTA ECSA 300 equipped with monochromatic Al Kα (hν = 1486.6 eV) X-ray source at 17010.
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highly oxidized GO sheets are expected to be thicker, 6,7,28 due to intercalated water molecules trapped between adjacent graphene oxide sheets, 29 with the Δss values been reported to vary from ~0.6 nm for dry GO to ~1.2 nm for hydrated samples. The difference on the interlayer distance estimated by TEM is able to provide information on crystalline size, the degree of hybridization, crystal disorder, the extent of chemical modification, which plays an important role for characterizing graphitic materials because it determines the number of layers in the thermally reduced GO (TRGO) sample prepared by vacuum-heat treatment at 1000 °C, compared with that of pristine graphite (PG). The right panel of part c of Figure 1 shows the 2D band region, magnified. The spectra were shifted in y scale for clarity.

X-ray Diffraction (XRD). As evidenced from the XRD spectra (part b of Figure 1), the starting pristine graphite, PG, exhibits atomically flat pristine graphene sheets with a well-known van der Waals thickness of ~0.337 nm, 7,9,27 estimated by using Bragg’s equation for the (002) peak located at ~26.4°. The (002) diffraction peak is found to be shifted for GO to ~11.3° indicating higher interlayer spacing (Δss = 0.782 nm). The highly oxidized GO sheets are expected to be thicker, 6,7,28 due to intercalated water molecules trapped between adjacent graphene oxide sheets, 29 with the Δss values been reported to vary from ~0.6 nm for dry GO to ~1.2 nm for hydrated samples. The difference on the interlayer distance estimated by TEM (0.48 Å) and XRD (0.78 Å) techniques can be explained bearing in mind the sample preparation and the environment in which the measurements were carried out. XRD measurements were performed on the samples comprised of thin films of GO in air, whereas TEM measurements were carried out in vacuum, on samples produced from dilute dispersion of GO on a TEM grid. The (002) XRD peak for GO shows considerably larger full width half-maximum (fwhm), compared to PG. Upon thermal reduction (at 1000 °C in vacuum), the TRGO sample (originated from the GO) exhibits a structure closer to pristine graphite PG as revealed by the shifting of (002) peak back to 26.4° (Δss = 0.337 nm), even though its fwhm still remained larger than that of PG (part b of Figure 1), implicating the presence of strains/defects.

Raman Spectroscopy. Raman spectroscopy has played an important role for characterizing graphitic materials because it is able to provide information on crystalline size, the degree of hybridization, crystal disorder, the extent of chemical modification, and distinguish single layer graphene or nanotubes from multilayer ones. 30–38 The micro-Raman spectra (part c of Figure 1) of all of the samples exhibited three main characteristic peaks: the G mode, a doubly degenerate (TO and LO) phonon mode (E_{2g} symmetry) at the Brillouin zone center observed at ~1575 cm$^{-1}$, originating from in-plane vibration of sp$^2$ carbon atoms; the D mode arising from the doubly resonant disorder-induced mode (~1350 cm$^{-1}$) and the symmetry-allowed 2D overtone mode (~2700 cm$^{-1}$). 31–34 The GO sample shows a prominent D peak with intensity comparable to G peak, in sharp contrast to the smaller D peak of PG, indicative of significant structural disorder due to the O-incorporation. The D band, attributed to in-plane A_{1g} (LA) zone-edge mode, is innately Raman-active at the graphitic edges. 31–33,35 Consequently, for small graphene sheets with limited sizes, like the GO nanosheets synthesized by the harsh Hummers’ method, the D band is expected to develop dramatically. Additionally, the sharp increase in $I_D/I_G$ ratio (from ~0.26 for PG to 0.93 for GO) indicates a decrease in the in-plane crystal or domain size from ~17 nm (PG) to ~4.7 nm (GO). The G peak of GO is shifted to higher wavenumbers (~15 cm$^{-1}$) and broadens significantly with respect to that of graphite. Similar upward shifting of the G band has been observed in heavily oxidized carbon nanotubes 33 and was related to the emergence of a new Raman active band (D’ mode, ~1620 cm$^{-1}$) overlapped with the G band. 30 The D’ band, usually inactive, becomes Raman-active due to phonon confinement caused by defects. 30–32 Besides the influence of D’ band, Kudin et al. 35 have considered the contributions from the isolated double bonds as been responsible for yielding Raman bands at little higher frequencies, for heavily oxidized GO. The vacuum-heat treatment (at 1000 °C) tends to shift back the Raman peaks (~12 cm$^{-1}$ red-shift of G peak with respect to GO), closer to the positions recorded for PG, indicative of the tendency to recover the hexagonal carbon network. The 2D band at ~2700 cm$^{-1}$, which originates from a two phonon double resonance Raman process and is indicative of crystalline graphitic materials, exhibited the most interesting changes. Generally, the position and shape of the 2D peak are highly sensitive to the number of graphene layers, and has been utilized to distinguish the single-layer from few-layer graphene. 31–34 For the graphene samples prepared by micromechanical exfoliation of graphite 31,33,35 or by chemical vapor deposition 36 on thin metal (e.g., nickel) films, the single sharp 2D peak of monolayer graphene has been observed to become wider and asymmetric with an upshift in peak position, with increasing the layer number. However, in our study it is not possible to determine the number of layers in the thermally reduced GO...
because the GO nanosheets were drop dried on a Si substrate to prepare a thin film. Hence, the Raman spectrum is the resultant signal of several stacked nanosheets, each one consisting of a few layers (2–4, as observed from TEM). The steep decrease in intensity and broadening of the 2D peak for GO compared with those of PG are mainly attributed to the steric effects of oxygen moieties on the stacked layers as well as to the partial amorphization and reduction in sp$^2$ domains.$^{31,38}$ Interestingly, the TRGO exhibits two distinguishable peaks close to 2700 and 2950 cm$^{-1}$ corresponding to the 2D band and to a (D + G) combination mode induced by disorder.$^{32}$ Such remarkable features, namely the simultaneous emergence of a sharp 2D band and of a lower intensity distinguishable D + G peak, vividly support the presence of smaller disorder in TRGO, when compared with GO.

Interestingly, after annealing a slight increase in the D peak intensity is observed, with the $I_D/I_G$ ratio increased to $\sim 1.1$, indicating a decrease in the size of sp$^2$ domains upon thermal reduction ($\sim 4$ nm). Naturally, a decrease in this ratio would be expected upon annealing because the disorder associated with the oxygen defects diminishes. Our experimental observations suggest that for the TRGO sample (heated at $\sim 1000$ °C), even though the sp$^2$ sites are partially restored, the forced removal of oxygen at such high temperature leads to the creation of strains and/or topological defects on the C structure,$^{5,27}$ and hence to the isolation of the sp$^2$ clusters forming smaller and dispersed sp$^2$ domains. Similar behavior that is a slight increment or no change in $I_D/I_G$ ratio has been observed in a number of studies$^{36,41}$ involving post heating hydrazine reduction. Recent studies$^{36,41}$ have shown that the intensity ratio $I_{2D}/I_{D+G}$ may be a powerful indicator for the aromatic C-structural order of the graphitic materials, because the 2D band is sensitive to the aromatic C-structure, whereas the combination mode of (D + G) is lattice disorder induced band for crystalline graphitic materials.$^{37}$ Well-resolved 2D and (D + G) bands in TRGO sample and its higher $I_{2D}/I_{D+G}$ ratio (1.3 times higher than GO) indicate the restoration of aromatic C-structure upon thermal reduction of GO.$^{36,37}$

**Figure 2.** High-resolution C1s XPS spectra: deconvoluted peaks with increasing reduction temperature ($T_r$). Insert of part c of Figure 2: C/O ratio as a function of $T_r$. (Error bars represent the standard deviation estimated from six sets of data). Insert of part f of Figure 2: C1s spectra for starting/precursor graphite (PG).
The starting graphite (PG) shows 2 main peaks, namely sp² (284.47 eV) and C—OH (285.53 eV) (insert of part f of Figure 2). The presence of a weak C—O peak (∼285.5 eV) in graphite, associated with atmospheric oxidation, has previously been observed by Hontoria-Lucas et al. 43 Furthermore, Barinov et al. 44 assigned the same peak at ∼285.6 eV to C—O single bond, calculating its close chemical shift of ∼1.5 eV to higher BE relative to sp² peak.

Here, we have judiciously assigned the peak at ∼285.5 eV to hydroxyl/phenolic group, and its neighboring peak at ∼286.5 eV to epoxy group, because it should have a larger BE compared to hydroxyl groups. 12,27,45 The C=O double-bond emission occurs at even higher BE range and arises from >C=O (∼287.5 eV) followed by COOH (∼289 eV). 12,45

Contribution of Oxygen Moieties on GO structure. In pristine GO, the C/O atomic ratio, calculated by dividing the area under C1s peak with that of O1s peak-area and multiplied by the ratio of photoionization cross sections, was found to be only 2.08 (insert of part c of Figure 2), with a C contribution of ∼67.5% (Table S1 of the Supporting Information). Another important parameter that can be used to characterize the degree of oxidation in GO is the sp² carbon fraction, which was estimated by dividing the area under sp² peak with that of C1s peak area. We found, the sp² fraction of GO is only 40% (part a of Figure 3). Carbon atoms connected with hydroxyl and epoxy groups are sp³ hybridized. In the basal plane, carbon atoms bonded with C—O—C (epoxides) prevail over (1.5 times higher) the hydroxyl C—OH groups (Figure 3), in agreement with molecular dynamic simulations, according to which the ratio of epoxides to hydroxyls increases with increasing the oxidation. 10,12,28 The contribution of >C=O and COOH is found to be more substantial compared to C—OH and C—O—C ([>C=O + COOH]/[C—OH + C—O—C] = 1.4). This can be understood bearing in mind that at harsh oxidation conditions, such as those encountered in Hummers’ process, the oxidation of C—O single bonded groups to C=O double bonded species is energetically favorable, 12,27,46

Interestingly, maximum contribution is found from >C=O groups. Their profusion in GO supports their definite existence on GO as predicted by the Dekany model, 46 which identified >C=O contributions in the form of ketones/quinines, updating the Scholz-Boehm 48 and Hontoria-Lucas 43 models. More recently, Ajayan et al. 15 suggested the possible generation of ester carbonyls through the reaction of tertiary alcohols with nearby carboxylic acids, at high degrees of oxidation.

Thermal Evolution of GO. Restoration of Aromatic C-Structure. Upon heating under UHV, the C1s spectrum exhibits a transformation from a double peak at room temperature to a single sharp peak (∼284.5 eV) at 1000 °C, resembling the C1s peak of PG and been indicative of a trend to restore the sp² bonding graphene character (part b of Figure S2 of the Supporting Information). A clear shift of peak-maxima back to lower BE with increasing temperature signifies the transformation of electrically insulated GO to the conducting nature of graphite. The evolution of the C/O atomic ratio (insert of part c of Figure 2 and Table S1 of the Supporting Information) reveals an increase in C-content as reduction temperature (T_r) increases, and an associated decrease of the O groups. A maximum C-content of ∼97% can be achieved upon heating at 1000 °C, with only ∼3% of remnant O contribution (C/O ratio ∼33.02), alike PG (Table S1 of the Supporting Information). The (π—π*) shakeup satellite peak, observed for PG (insert of part f of Figure 2) around ∼290.5 eV, appears upon heating at high temperatures ≥400 °C (parts c—f of Figure 2). This indicates that the delocalized π conjugation, a characteristic of aromatic C structure, is to some extent restored in TRGO samples. 10,11,15

Thermal Stability of Hydroxyl Groups. Parts a and b of Figure 3 present (i) the relative contribution of the carbon bonds

![Figure 3](dx.doi.org/10.1021/jp203741y.j.physchem.c.2011.115.17009–17019)
in GO and (ii) the normalized intensity of O-related peaks (relative to sp$^2$ peak-intensity) as a function of annealing temperature in UHV respectively. These figures serve as useful guides for monitoring the evolution of the functional groups and provide insight into the mechanism of thermal reduction process.

At room temperature the determination of separate >C=O and COOH contributions was possible, however, for temperatures higher than 200 °C, we denote their combined involvement as C=O (oxygen doubly bonded to carbon), since the deconvolution into two separate peaks was not feasible. The C—O component (singly bonded oxygen, C—OH, and C—O—C) remains almost unchanged (region I of part b of Figure 3) up to 200 °C, most possibly due to insufficient temperature and/or partial contribution from the transformation of C=O to C—O. Above 200 °C, C=O continues to be reduced and, around 800 °C, it almost saturates with a minimal contribution.

Useful information can be obtained from the dispersion of the peak positions as a function of temperature. It is worth pointing out that at 200 °C, the C=O peak is centered at $\sim 288.3$ eV, between the >C=O ($\sim 287.5$ eV) and COOH (288.9 eV) components (part a of Figure 2 and part a of Figure 4). However, at high temperatures it shifts to BE representative of >C=O. Therefore, it is reasonable to postulate that at low reduction temperatures ($T_r < 400$ °C) the doubly bonded C=O component has contributions from both >C=O and COOH groups, however at higher temperatures ($T_r > 600$ °C) is dominated by >C=O groups.

In part b of Figure 2 one can note that at $T_r > 200$ °C the C—O—C is reduced fast, and at $T_r \geq 400$ °C, it is hard to be identified (parts d–f of Figure 2). Interestingly, over the temperature range 200—400 °C the C—OH increases rapidly (region II of part b of Figure 3), followed by a reduction at $T_r > 400$ °C (region III of part b of Figure 3). C—OH persists even at 1000 °C, at a level similar to that observed in the original graphite material PG (blue dotted line, part b of Figure 3). Our observations are consistent with other reports, where the C—OH contribution survives in TRGO showing that annealing at 1000 °C is not adequate to completely remove the oxygen,$^{10,12,14}$ even though possessing higher C/O ratio ($\sim 33.02$). Complete thermal pyrolysis of C—OH is thermodynamically difficult,$^{28}$ mainly due to its intercalating position into the interlayer galleries between intact conjugated domains.$^{46}$

**Thermo-Gravimetric Analysis (TGA) Studies.** Interestingly, the anomalous trend of C—OH (part b of Figure 3) clearly implicates a double transition zone on the reduction path of GO. The phenomenon is vividly illustrated in TGA results (part b of Figure 4). The GO starts to lose mass upon heating even below 100 °C, which is associated with elimination of loosely bound or adsorbed water and gas molecules. First, major mass loss can be observed along with an exothermic signal of mass loss rate ($\text{d}W/\text{d}T$, I, part b of Figure 4) around 200 °C, yielding CO, CO$_2$, and steam as byproduct of the reduction process. Second, the largest mass loss, and corresponding exothermic $\text{d}W/\text{d}T$ signal, starts at $T_r > 300$ °C and continues until 600 °C. (II, part b of Figure 4).

The higher curvature in TGA curve and the asymmetric nature of $\text{d}W/\text{d}T$ signal, at 300–500 °C, implies the presence of two antagonistic activities: either (i) release of byproduct and subsequent trapping and/or (ii) loss of doubly bonded C=O component and simultaneous feeding of C—OH. In the same phase, C—O also shows an increase (region II of part b of Figure 3), whereas C=O species decreases. Above 500 °C, higher slope in TGA & sharp-rise in $\text{d}W/\text{d}T$ signal indicate a rapid decomposition of O-species, as observed in part b of Figure 3 (region III).

### Anomalous Trend of Hydroxyl Groups and Formation of Phenol

Such anomalous trend of temperature evolution of C—OH has never been reported before, though Lerf et al.$^{29}$ have already predicted the formation of phenol (or aromatic diol) groups during deoxygenation, even at 100 °C, because of the close proximity of C—O—C and C—OH on the basal plane. Presence of enolic OH species is also considered by Dekány et al.$^{46}$ in order to interpret the planar acidity of GO. Hence, it can be envisaged that initial rise of C—OH is mainly contributed by newly formed phenolic groups in expense of C—O—C, which show huge loss at $T_r \geq 400$ °C. In addition, though C—O—C and C—OH become inseparable at $T_r \geq 600$ °C, part a of Figure 4 clearly shows that singly bonded C—O group retains its peak-position at that of C—OH, indicating the complete loss/conversion of C—O—C.

Formation of phenolic groups is clearly evidenced from the high-resolution O1s peaks (Figure 5). Deconvolution of O1s spectra (part a of Figure 5) produces 3 main peaks around 531.08, 532.03, and 533.43 eV assigned to C=O (oxygen doubly bonded to aromatic carbon denoted as II),$^{10,13,14,44}$ C=O (oxygen singly bonded to aliphatic carbon denoted as I),$^{6,45}$ and phenolic (oxygen singly bonded to aromatic carbon denoted as I3)$^{6,45}$ groups respectively. The pristine GO shows an additional peak at higher BE (14—534.7 eV), corresponding to the chemisorbed/intercalated adsorbed water molecules.$^{14}$ Thermal treatment of GO clearly causes a shift of O1s spectra to the higher
energy side and a simultaneous transformation of O1s spectra from a single peak to a double feature with the development of a prominent phenolic I3 peak (Figure 5). Although all the O-species decrease in integrated intensity with increasing $T_r$ (part a of Figure 6), the relative intensity of phenol group (peak I3) shows a sharp rise around 400 °C, as observed in C1s spectra (Figure 3), followed by a progressive increase relative to other species (part b of Figure 6). In addition, the relative intensity of peak I2, O singly bound to aliphatic C, exhibits an initial increase at 200 °C and a subsequent reduction. The initial increase is most possibly due to the internal conversion of $C=O$ to $O=C$ at low $T_r$, as described earlier. Undoubtedly, the evolution of O1s spectra provides further corroborating evidence on the existence of double transition zone during thermal reduction of GO.

The XPS analysis reveals the OH-moieties on basal plane are the most thermally stable species, in contrast to observations made on chemical reduction of GO. Further corroborative evidence on the evolution of the basal and edge plane O groups, upon thermal reduction, is provided by NEXAFS studies.

**Figure 5.** High-resolution O1s XPS spectra deconvoluted peaks with increasing $T_r$.

**Figure 6.** Temperature-dependence of (a) the integrated intensity of O1s peak components (I1–I4), and (b) the corresponding relative contribution estimated by dividing the area under each component by whole O1s peak-area. I1 denotes $C=O$ (oxygen doubly bonded to aromatic carbon); I2 denotes $C—O$ (oxygen singly bonded to aliphatic carbon), I3 denotes phenolic (oxygen singly bonded to aromatic carbon), and I4 denotes chemisorbed/intercalated adsorbed water molecules groups. Error bars represent the standard deviation estimated from six sets of data. The lines shown are guides to the eye only.

**High-Resolution In Situ Synchrotron Near-Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy.** Soft X-ray absorption spectroscopy probes unoccupied electronic states and is another powerful tool for characterizing graphitic materials, by providing information on the degree of bond hybridization in mixed $sp^2/sp^3$ bonded carbon, the specific bonding configurations of foreigner functional atoms and the degree of alignment of graphitic crystal structures. Fingerprints of the species surviving at each step of the thermal treatment were provided by NEXAFS. Here, NEXAFS was deliberately performed at 90° incidence of the linearly polarized X-rays. At normal incidence of the polarized X-ray beam, the electric-field vector $E$ lies within the graphene plane and thus transitions to states of $\sigma^*$ symmetry are more prominent than those to $\pi$ symmetry.

The high-resolution C K-edge NEXAFS spectrum (part a of Figure 7), of pristine GO, provides a clear presence of both unoccupied $\pi^*$ (1s–$\pi^*$) and $\sigma^*$ (1s–$\sigma^*$) states around 285.2 and 293.03 eV respectively, revealing that GO nanosheets, even though highly oxidized, still maintain the aromaticity of the original pristine material, PG. Although GO produces a plethora
of O-related resonances, unfortunately, NEXAFS database in literature is not rich enough to deconvolute and assign all the peaks. Upon judicious review of the available literature we have assigned the peak-positions,9,47,49 as shown in part a of Figure 7.

Upon thermal treatment, a number of important changes can be identified in the spectra of TRGO. The \( \pi^* \) resonance (I\(_2\)) clearly shifts to higher energies, moving toward the position of I\(_2\), whereas its fwhm becomes broader due to presence of mainly C–OH moieties. The two resonances between the \( \pi^* \) and \( \sigma^* \) discernible at \( \sim 287 \) eV (I\(_2\)) and \( \sim 288.7 \) eV (I\(_4\)) disappear at 400 °C. The assignment of these intermediate peaks in the absorption spectra of graphene related structures is highly debatable. In particular, the presence of peak around 288 eV was originally observed in the NEXAFS spectra of HOPG55 and few-layer graphene56 and was attributed to the free electron like set of bands corresponding to electronic excitations lying between graphite layers (interlayer states). Others have provided evidence that this feature (\( \sim 289 \) eV) originates from \(-\text{COOH} \) moieties present in single-wall carbon nanotubes,53 carbon fibers,49 and GO.9,47 Here, given the prominence of I\(_4\) peak in heavily oxidized graphene films and its complete disappearance upon thermal annealing, we have assigned its origin to COOH consistent with XPS, where the presence of a sufficient density of carboxylic moieties in GO has been confirmed. The broad asymmetric peak I\(_3\) originates mainly from \( \pi^*(C–O–C) \) contributions and partly by \( \pi^*(C–\text{OH}) \).9,47

The \( \sigma^* \) region, which is strongly enhanced due to normal incidence of the polarized beam is dominated by doubly bonded C=O moieties (peaks I\(_2\) to I\(_6\)).53,54 Its temperature evolution reveals a huge loss of C=O groups, which agrees well with our earlier XPS discussion on thermal instability of C=O groups. At 400 °C, there is a curious splitting of the \( \sigma^* \) peak (1s–\( \sigma^* \)) into 2 peaks, with the simultaneous emergence of the \( \sigma^* \) exciton peak (I\(_5\)).49 The appearance of the distinct peak I\(_5\) supports the progressive restoration of graphitic structure in GO, however its reduced/subexpressed structure, compared to \( \pi^* \) peak, indicates the existence of small graphene planes/domains,49 as predicted in XRD and Raman studies.

Remarkably, after thermal reduction, transitions to states of \( \sigma \) symmetry are seen to decrease dramatically compared to transitions to states of \( \pi \) symmetry. This is visualized in Figure S3 of the Supporting Information, which depicts the intensity ratio of \( \pi^*/\sigma^* \) peaks at the C K-edge, as a function of annealing temperature. This ratio is used to provide an estimate of the relative concentration of sp\(^2\) domain configurations in a sp\(^3\) matrix consisting of carbon atoms connected to oxygen groups.53 High values of \( \pi^*/\sigma^* \) ratio around the temperature zone of 400–600 °C due to the substantial reduction of edge plane doubly bonded C=O moieties are consistent with the appearance of aromatic characteristic (\( \pi^* \)) plasmon peak at the same \( T_r \) range. At higher temperatures \( T_r > 400 \) °C, the change in \( \pi^*/\sigma^* \) is less dramatic due to slow reduction in both edge and basal plane O-moieties.

Further evidence on the significant loss of oxygenated functional groups upon thermal treatment at 400 °C is provided by the O K-edge NEXAFS spectra presented in part b of Figure 7, where the main peaks are assigned according to literature.9,47,50–52 Two distinctive peaks I\(_1\) and I\(_2\) appearing at the low energy tail of O K-edge attributed to the \( \pi^* \) state of COOH groups located at the GO edge sites,9,47 disappear at 400 °C.

**High-Resolution In Situ Valence Band (VB) Spectroscopy.**

Valence band spectroscopy is another powerful tool\(^{13,57,58}\) to evaluate how the \( \pi \) conjugated system has been progressively restored after thermal treatment. Part a of Figure 8 shows the high-resolution VB spectra recorded at different temperatures. On the basis of photoemission spectroscopic data and theoretical band structure calculations for graphite, the region from 2 to 12 eV above Fermi level (\( E_F \)) represents characteristics of C2p electrons, the section 12–22 eV corresponds to C2s valence electrons, followed by the O2s region at higher BE.44,59–62

A number of interesting features can be identified from the VB spectra. As prepared GO is dominated by O2s with a band centered at 26.3 eV\(^{56}\) and its Fermi edge shifted to higher energies revealing the insulating nature of the material. The shoulder located at \( \sim 8 \) eV is associated with strong \( \sigma \) bonding states (C2p-\( \sigma \)) in graphitic-like carbon, indicating the presence of a substantial sp\(^2\) ordering.44,59,60 Thermal reduction improves the contribution from C2p states and simultaneously reduces the O2s confirming the deoxygenation of O-moieties. In particular thermal treatment at 600 °C, induces the growth of a new sharp double feature with peaks at 2.3 and 3.25 eV associated with conjugated \( \pi \) bonds (C2p-\( \pi \) bands) of graphene.44,59,60 An enrichment of the \( \pi \)-peak intensity in the valence band

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**Image Descriptions**

**Figure 7.** High-resolution (a) C K-edge and (b) O K-edge synchrotron NEXAFS spectra, recorded at different reduction temperatures. The spectra were shifted in y-scale for clarity.

**Figure 8.** (a) High-resolution valence band (VB) spectra, recorded at different \( T_r \). The spectra were shifted in y-scale for clarity. (b) Enlarged view of VB spectra at the vicinity of Fermi level (\( E_F \)). (c) Intensity ratios of C2p-\( \pi \) to C2p-\( \sigma \) (\( \pi \) to \( \sigma \)) and the separation between O2s and C2s peak-maxima, as a function of \( T_r \). The lines shown in (c) are guides to the eye only.
photoemission data implies the formation of sizable graphene domains with 3-fold coordination.\(^\text{60}\) VB spectra at 1000 °C resemble those of the starting graphite. Interestingly, the \(\pi\)-derived density of states (DOS) at the vicinity of \(E_F\) in the range of 0–2.0 eV (part b of Figure 8) rises with increasing temperature, with the steepest rise occurring at 600 °C. This rise in VB provides a strong indication for the existence of metallic character in the reduced graphene.\(^\text{34,62}\) The simultaneous rise of DOS at \(E_F\) and the enrichment of \(\pi\)-peak intensity in C2p region definitely reflect the progressive restoration of \(\pi\) conjugated aromatic C-structure by deoxidation via thermal treatment. Curiously, further increase in temperature (>600 °C) caused a reduction in the \(\pi\)-derived DOS indicating the presence of a high level of defects. The observation is consistent with Raman and XRD results, which confirmed that thermal treatment at 1000 °C is not adequate for the complete restoration of aromatic C-structure. Presumably, the enforced removal of basal O-species produces strains in C=C bonds and topological wrinkles or hole-like defects on the atomic C structure.\(^\text{6,27}\) Consistent with the XPS results the \(\pi/\sigma\) ratio obtained from C2p-\(\pi\)/C2p-\(\sigma\) bands shows an initial drastic increase followed by a slower increase (part c of Figure 8).

Another important observation is the progressive decrease in the O2s–C2s peak separation with thermal treatment illustrated in part c of Figure 8. The augmentation of O2s–C2s separation has been associated with the presence of intermediates between the \(\mathrm{C=O}\) double bond groups and the \(\mathrm{C=O}\) single bonded O to C, in progressively oxidized graphitic materials, following the order: \(\mathrm{C–O–C} > \mathrm{C=O} > \mathrm{C–OH}\).\(^\text{61}\) Thus, the smallest separation, observed in highly reduced GO (~800 °C), would be attributed to the prevalence of phenolic/hydroxyls over other O-species.\(^\text{61}\) The larger separation at low temperatures would indicate contribution from \(\mathrm{C–O–C}\) and \(\mathrm{C=O}\) moieties.\(^\text{61}\)

**CONCLUSIONS**

Employing a combination of high-resolution in situ temperature-dependent spectroscopic techniques including XPS, VB, and NEXAFS, we have clarified a number of important issues concerning the evolution of the electronic structure of GO upon the heat treatment. (i) First it is established that, upon progressive thermal treatment, the edge-plane COOH groups become highly unstable, whereas \(\mathrm{C=O}\) are more difficult to be removed. (ii) The \(\mathrm{C–OH}\) group in the phenolic form is the most thermally stable of all the oxygen species (part c of Figure 9). (iii) The thermal evolution of \(\mathrm{C–OH}\) groups exhibits a well-defined transition temperature around 400 °C. At lower temperatures, there is an upward trend due to the formation of phenol groups, whereas at \(T_r > 400\) °C there is decreasing trend due to their decomposition (parts b–c of Figure 9). (iv) Valence band spectra reveal a drastic increase in the DOS near \(E_F\) at 600 °C, whereas further increase in temperature reduces the DOS to levels similar to those of graphite. The ability to achieve higher DOS at considerably lower temperatures compared to 1000 °C normally considered for partially restoring the aromaticity of thermally reduced graphene oxide holds significant advantages for nanoelectronics application.

**ASSOCIATED CONTENT**

Supporting Information. Table of XPS analyses, figure of TEM images, figure of XPS spectra, and a figure of intensity
ratio of $\mathcal{R}^*$ contribution. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

**Corresponding Author**
*E-mail: p.papakonstantinou@ulster.ac.uk.*

**Author Contributions**
These authors contributed equally.

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**REFERENCES**