

Supporting Information

The use of optical contrast to estimate the degree of reduction of graphene oxide.

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Optical contrast calculation on different substrate

Table 1: Normalized total color contrast calculated for different substrates in the case of single layer GO, reduced GO and graphene. 72 nm Al_2O_3 and 300 nm SiO_2 (bold columns) are the experimentally investigated substrates.

	Al_2O_3 80 nm	Al_2O_3 72 nm	Al_2O_3 50 nm	SiO_2 300 nm	SiO_2 285 nm	SiO_2 100 nm	SiO_2 90 nm
GO	0.38	0.41	0.66	0.41	0.30	0.26	0.26
rGO 200 °C	0.67	0.74	0.97	0.71	0.78	0.68	0.73
Graphene	1	1	1	1	1	1	1

Tab. 1 reports the calculated total color contrast (CC) of GO and reduced GO annealed in vacuum at 200 °C on different substrates normalized to the graphene one. The contrast of GO, reduced GO, and graphene on different substrates has been estimated using Fresnel's equations within standard thin films optics framework.¹ GO and reduced GO refractive index and thickness used for the calculation were the ones measured by Jung et al.²(data in Ref. 2 are reported only for pristine GO and GO annealed in vacuum at 200 °C), while graphene refractive index and thickness used were respectively $n_G = 2.6 - 1.3i$ and $d = 0.34$ nm.³ Al_2O_3 , SiO_2 and Si refractive index can be found in Ref. 3.

X-ray photoemission spectroscopy (XPS)

Fig. 1 reports the O 1s (left) and C 1s (right) X-ray photoemissioncore level spectra measured on GO/Au(100) as a function of the UHV annealing temperature. For helping the reader to direct visualize the reduction of the GO, the O 1s and C 1s spectral intensities reported in Fig. 1 were renormalized to the corresponding C 1s and O 1s atomic sensitivity factors.⁴ The resulting quantitative estimate of the C/O ratio is reported in the inset of Fig. 2 (full circles). This value monotonically raises from 2.0 (pristine GO) to 8.0 (GO annealed at 670 °C). This is a clear indication of GO reduction under UHV thermal treatment. Similar investigation of the C/O ratio in GO as function of UHV thermal annealing are reported by Mattevi et al.⁵ and Yang et al.⁶ respectively in the temperature ranges of 25-1100 °C and 25-900 °C (C/O ratios ranging from 1.5

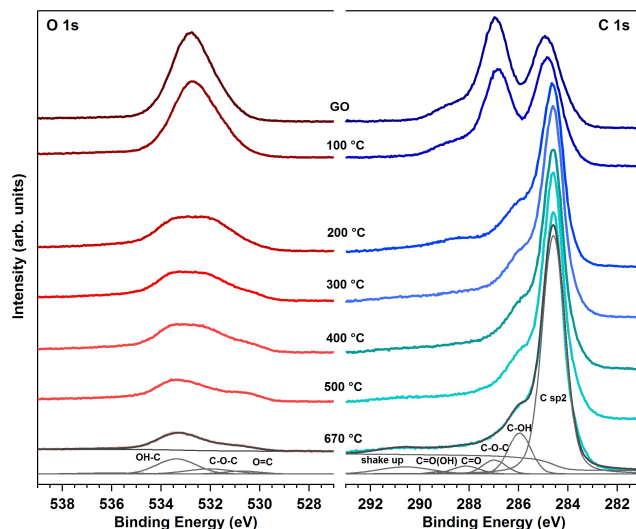


Figure 1: Core level O 1s (left) and C 1s (right) XPS spectra of GO/Au(100) as a function of the UHV annealing temperature. The spectral intensities are all normalized to the respective atomic O 1s and C 1s sensitivity factors.⁴ O 1s spectra are fitted by the sum of three components: $\underline{\text{O}}\text{H-C}$ (533.4 eV), $\text{C-}\underline{\text{O}}\text{-C}$ (532 eV) and $\underline{\text{O}}\text{=C}$ (530.4 eV). C 1s spectra are fitted by the sum of five components: $\underline{\text{C}}\text{=C/C-C}$ (C-H) (284.6-284.9 eV), $\underline{\text{C}}\text{-OH}$ (285.9 eV), $\underline{\text{C}}\text{-O-C}$ (286.9 eV), $\underline{\text{C}}\text{=O}$ (288.2 eV), $\underline{\text{C}}\text{=O(OH)}$ (289.3 eV), and the $\pi - \pi^*$ shake-up component (290.6 eV).

to 12.5, and 2.8 to 14.1 respectively in the two cases). In particular our trend of C/O ratio is in quantitative agreement with the one reported by Mattevi et al.⁵ A detailed analysis of the C 1s core level spectra brings a great deal of information. The C 1s spectra are all nicely fitted by the sum of five components assigned (in line with Refs. 7–9) to C atoms belonging to: aromatic rings and hydrogenated carbon ($\underline{\text{C}}\text{=C/C-C}$, $\underline{\text{C}}\text{-H}$, 284.6-284.9 eV), hydroxyl groups ($\underline{\text{C}}\text{-OH}$, 285.9 eV), epoxy groups ($\underline{\text{C}}\text{-O-C}$, 286.9 eV), carbonyl groups ($\underline{\text{C}}\text{=O}$, 288.2 eV), and carboxyl groups ($\underline{\text{C}}\text{=O(OH)}$, 289.3 eV) (the hump at 290.6 eV is assigned to a $\pi - \pi^*$ shake-up satellite¹⁰). Differently from other XPS investigations of GO,⁶ and in line with Refs. 7–9 we constrained to fixed values (within 0.1 eV) the binding energies of the four components related to oxygen linked carbon atoms. On the other hand the binding energy of the component related to the aromatic carbon, which is actually accounting for simplicity to both C-C and C-H bonding assigned at 284.6-285.1 eV, is evidently shifting towards lower binding energies (0.3 eV) due to the hydrogen desorption (weakening of the C-H component) from the GO basal plane.^{6,8} The relative abundances of each component of

the C 1s spectra are summarized in the graph of Fig. 2 as a function of the annealing temperature. The abundance curves show that, as a consequence of thermal annealing, all the groups containing oxygen tend to disappear, unlike those containing carbon only (aromatic groups), indicating a loss of oxygen in favor of sp^2 carbon domains formation (the sp^2 carbon content of $\sim 46\%$ in pristine GO increases up to $\sim 78\%$ at 670°C annealing temperature). The data are in excellent agreement with those reported in Ref. 5. In particular the sp^2 carbon content approaches 80% at about 700°C . This is a saturation temperature limit, as the sp^2 fraction negligibly increases ($\leq 2\%$) with further UHV annealing GO at 1100°C .⁵

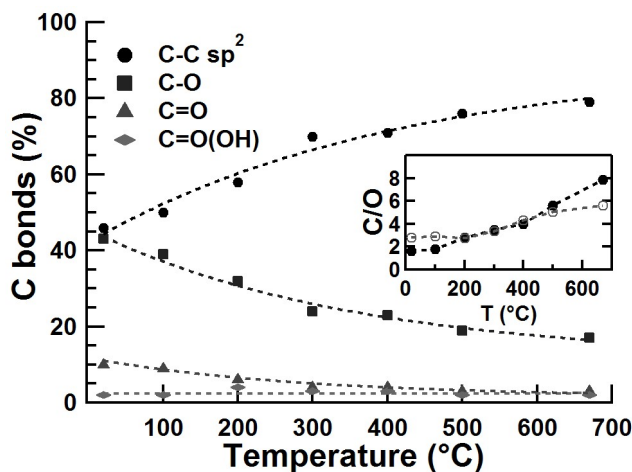


Figure 2: Relative weights of the C 1s spectral components as a function of the annealing temperature. (Inset) C/O ratio between the overall carbon and oxygen content, obtained respectively from the integrated intensity of C 1s and O 1s spectra (full circles) and from the stoichiometric analysis of the C 1s components (open circles).

The above assignment of the different C components was checked on a quantitative basis. Once the areas of the various components are corrected by the corresponding stoichiometric ratios (namely the areas of the components related respectively to $\underline{\text{C}}\text{-OH}$, $\underline{\text{C}}\text{-O-C}$, $\underline{\text{C}}=\text{O}$ and $\underline{\text{C}}=\text{O}(\text{OH})$ are respectively multiplied by a factor 1, 1/2, 1, 2), the C 1s spectra themselves can be used to estimate the C/O ratio. The result of such analysis is summarized in the inset of Fig. 2 (open circles). Apart from a slight discrepancy at room temperature and at 100°C , likely due to excess oxygen from water physi-sorbed on GO, such graph substantially superimposes to the conventional estimate of the C/O ratio (full circles). Thus the assignment of the C 1s components withstands a quantitative

check.

As far as the O 1s analysis is concerned, apart from the spectra taken at room temperature and 100 °C, with entangled contribution from water related O 1s,¹¹ the same visual inspection of the O 1s spectra lead to the identification of three components at 533.4 eV, 532 eV and 530.4 eV. The rationale to assign such components is guided by the following arguments. First, we observed that there are three local oxygen coordination: in hydroxyl groups OH-C , in epoxy groups C-O-C and in carbonyl O=C and carboxyl O=C-OH groups. Second, electron screening effect lead us to assign the lower binding energy component to the oxygen species double bonded to carbon (O=C and O=C-OH). Third, an unambiguous assignment of the other two components proceeds from a direct comparison of the evolution with temperature of the C 1s and O 1s spectra: as the component related to the carbon in epoxy groups at 286.9 eV and the O 1s component at 532 eV both show the same dramatic decrease with annealing temperature, therefore the assignment of such latter component to oxygen in epoxy group is straightforward.

Finally XPS was use to check the effect of air-exposure to UHV annealed GO. Fig. 3 reports the comparison of C 1s spectra of 200 °C UHV annealed GO acquired respectively before and after 1 hour of air exposure. The differences between the two spectra are negligible. Longer air exposure (up to 64 hours) were also investigated showing similar results.

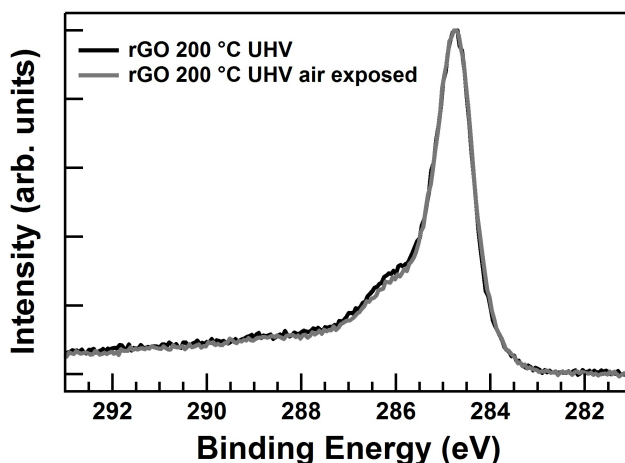


Figure 3: Core level C 1s XPS spectra of GO/Au(100) annealed at 200 °C in UHV acquired before and after 1 hour of air exposure.

Micro-Raman spectroscopy

Micro-Raman spectroscopy (μ RS) has been performed on the same set of samples that have been characterized by optical microscopy (samples with Al_2O_3 substrate). Fig. 4 reports all the spectra acquired for one, two, and three layer GO after UHV thermal annealing at the different temperatures under consideration. All the spectra have the characteristic shape of graphene-based materials. The two peaks (at $\sim 1330 \text{ cm}^{-1}$ and $\sim 1600 \text{ cm}^{-1}$) are assigned to respectively the D band, commonly related to defects (edges included), and the G band, characteristic of graphene.¹² Spectra in Fig. 4 are normalized to the G peak intensity. The information related to the D and G band peak energy positions and FWHM values of the spectra of Fig. 4 is summarized for clarity in Fig. 5 as a function of the annealing temperature. The variation of the GO Raman spectra was investigated with a systematic approach as a function of the annealing temperature and of the layer number. In the discussion we take full advantage of the results obtained in the previous section, where we have studied in detail the GO chemical evolution with the annealing temperature. Thus the variations of the Raman spectrum can be related and traced back to the variations of the GO chemical composition.

As can be directly observed in Fig. 4 and quantitatively reported in Fig. 5 (a), the energy position of the G band at $1601 \pm 2 \text{ cm}^{-1}$ which is inherently related to the patches of pure graphene in GO, is not dependent on the number of layers investigated, and remains unchanged (within an experimental indetermination of $\pm 2 \text{ cm}^{-1}$) as a function of the GO annealing temperature. This observation strengthens the validity to normalize all the spectra to the G peak intensity. For what concerns the values of the D band energy position and of the D and G bands FWHM an accurate observation of Fig. 4 and Fig. 5 indicate consistent trends for temperatures below 200°C , in the range $200\text{-}500^\circ\text{C}$, and above this latter value. Up to 200°C , a fully reliable data analysis and interpretation is complicated by the presence of water trapped between GO and the substrate or between GO layers as directly evidenced in our XPS analysis of the O1s core level and also evidenced in AFM and Fourier transform infrared spectroscopy experiments.^{2,13} Above 200°C , as shown in Fig. 5 (b), the width (FWHM) of the G peak monotonically decreases (in average for

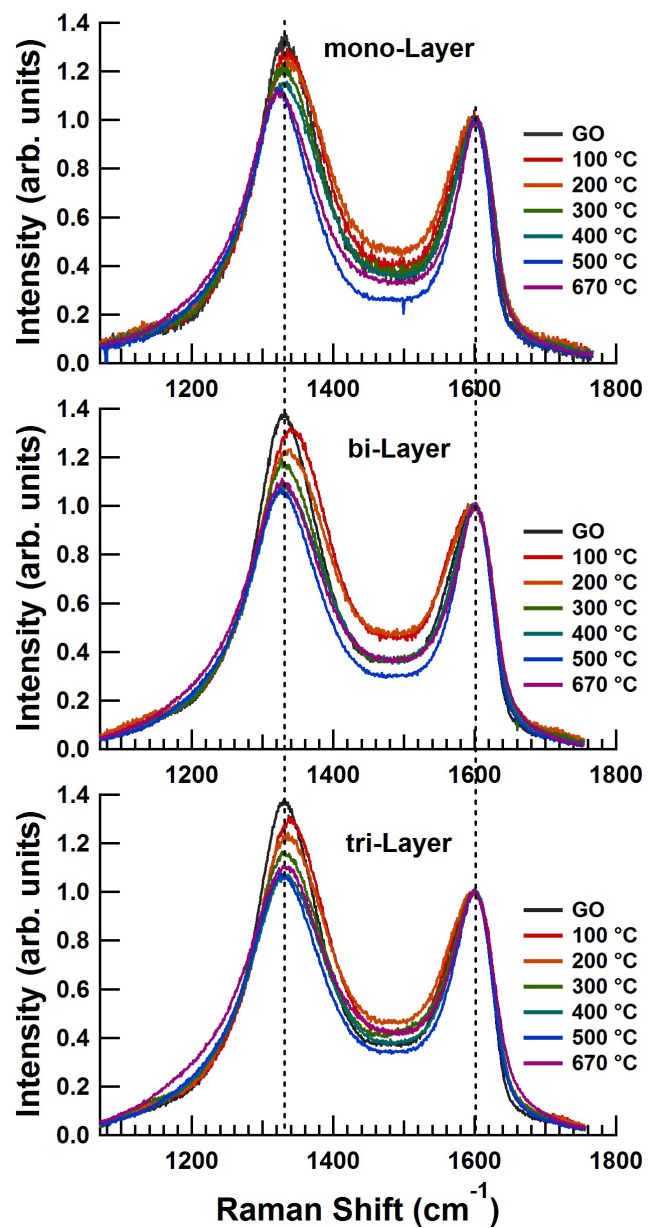


Figure 4: Raman spectra of GO single-, bi, and tri- layer reduced at different annealing temperatures; all the spectra are normalized to the G peak intensity.

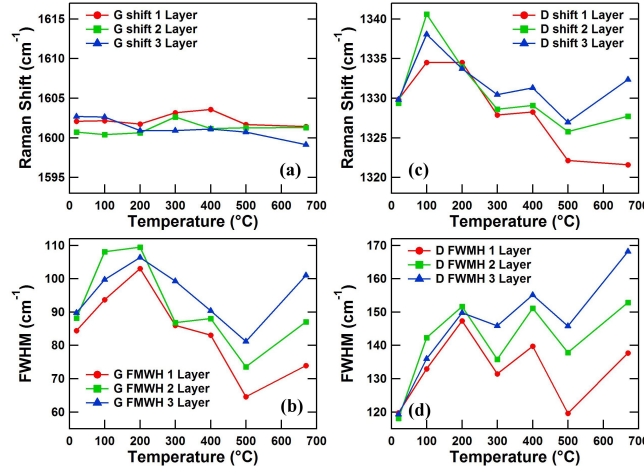


Figure 5: Temperature dependence of G (D) peak Raman shift and FWHMs of single, bi- and tri-layer spectra in left (right) top and bottom panel respectively.

the one, two and three layer case) from $105 \pm 5 \text{ cm}^{-1}$ at 200°C to a minimum value of $75 \pm 5 \text{ cm}^{-1}$ at 500°C . This points to an increase of the crystalline order of the pure graphene patches in the GO flakes. Above 500°C , the G FWHM increases again of about $10 \pm 5 \text{ cm}^{-1}$. We assign this occurrence to the increase of the relative weight of the D' peak (at around 1640 cm^{-1}) which is reported at 40 cm^{-1} higher frequency with respect to the G peak in graphene.¹⁴ More in detail, we assign this broadening to the appearance, with robust annealing temperatures, of topological defects, namely Stone-Wales defects and C vacancies, that exhibit specific spectral Raman features at 1640 and 1680 cm^{-1} as theoretically demonstrated in Ref. 15. The analysis of the D peak position and FWHM values is also particularly interesting. Above 100°C UHV annealing we observe an overall red shift of the D peak of about 12 cm^{-1} . This observation is related to the evolution of the C 1s line-shape in our XPS data. There (Fig. 1) we observe, as a function of the annealing temperature, a dramatic decrease of the C 1s component at 286.9 eV related to epoxy carbon, while the C-OH related peak at 285.9 eV survives the thermal annealing. Accordingly, in line with the theoretical calculations reported in Ref. 15 the increase of the relative weight of the hydroxyl groups in the defect related D band of GO has to be observed as an increase of the D Raman spectral weight at around $1380 \pm 10 \text{ cm}^{-1}$. This is in line with our red shift observation. The D peak width values, though quite scattered, exhibit an overall trend, in average, to an increase

of 10 cm^{-1} of the line-width. This, in consistence with the G peak width broadening above 500°C , can be ultimately related to the introduction, upon oxygen desorption with thermal annealing, of new type of defects in the GO texture: namely Stone Wales defects, and C vacancies. Little, but meaningful, can be told about the layer dependence of our Raman results. In particular, one can observe that (Fig. 5 (b) and (d)) both in the G and D peak case, $W(3) > W(2) > W(1)$ (where, with obvious notation, $W(n)$ is the line-width of n stacked GO layers). This can be assigned in general to layer-to-layer interactions as firstly proposed in Ref. 16.

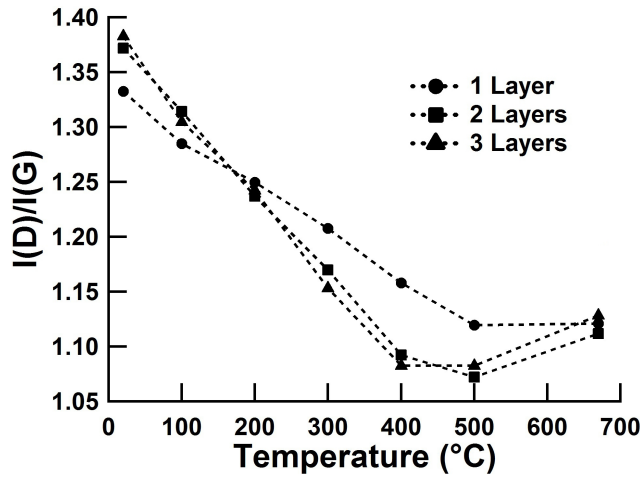


Figure 6: I_D/I_G ratio between D and G peak intensities for single-, bi-, and tri-layers as a function of the annealing temperature. (Inset) Corresponding values of L_a deduced from the Tuinstra-Koenig relation (plotted on the right side of the inset along with the analogous relation valid for $L_a < 2\text{nm}$).

Finally, after normalization to the G peak intensity, Fig. 4 clearly shows that the D peak exhibits a systematic decrease of its intensity as the annealing temperature increases. Fig. 6 reports the values of I_D/I_G as a function of the annealing temperature for one, two, and three layer GO. The overall trend is a regular decrease of I_D/I_G as the temperature is increased. This trend, that is common to all the three investigated systems, turns around above 500°C .

All such evidences point to the same conclusion that a thermal annealing above 500°C is not effective in improving the crystalline quality of the graphene patches in GO. Above such critical temperature the oxygen desorption is evidently accompanied by the introduction of topological

defects. It is worth noting that all C atoms in such defects exhibit a local sp^2 hybridization and, accordingly, the XPS analysis exhibits a monotonic increase of the sp^2 content as a function of the thermal annealing (see Fig. 2). Thus, while in XPS the topological defects formation is hindered and the quality improvement of GO seems to be a monotonic function of the UHV thermal annealing, on the other hand, a corresponding Raman spectroscopy analysis evidences that above 500 °C, the GO reduction substantially occurs via the formation of defects. In summary the GO thermal reduction is efficient up to moderate temperatures (~ 500 °C) but beyond these temperatures the process starts to backfire.

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