

# The role of intercalated water in multilayered graphene oxide

## SUPPLEMENTARY INFORMATION

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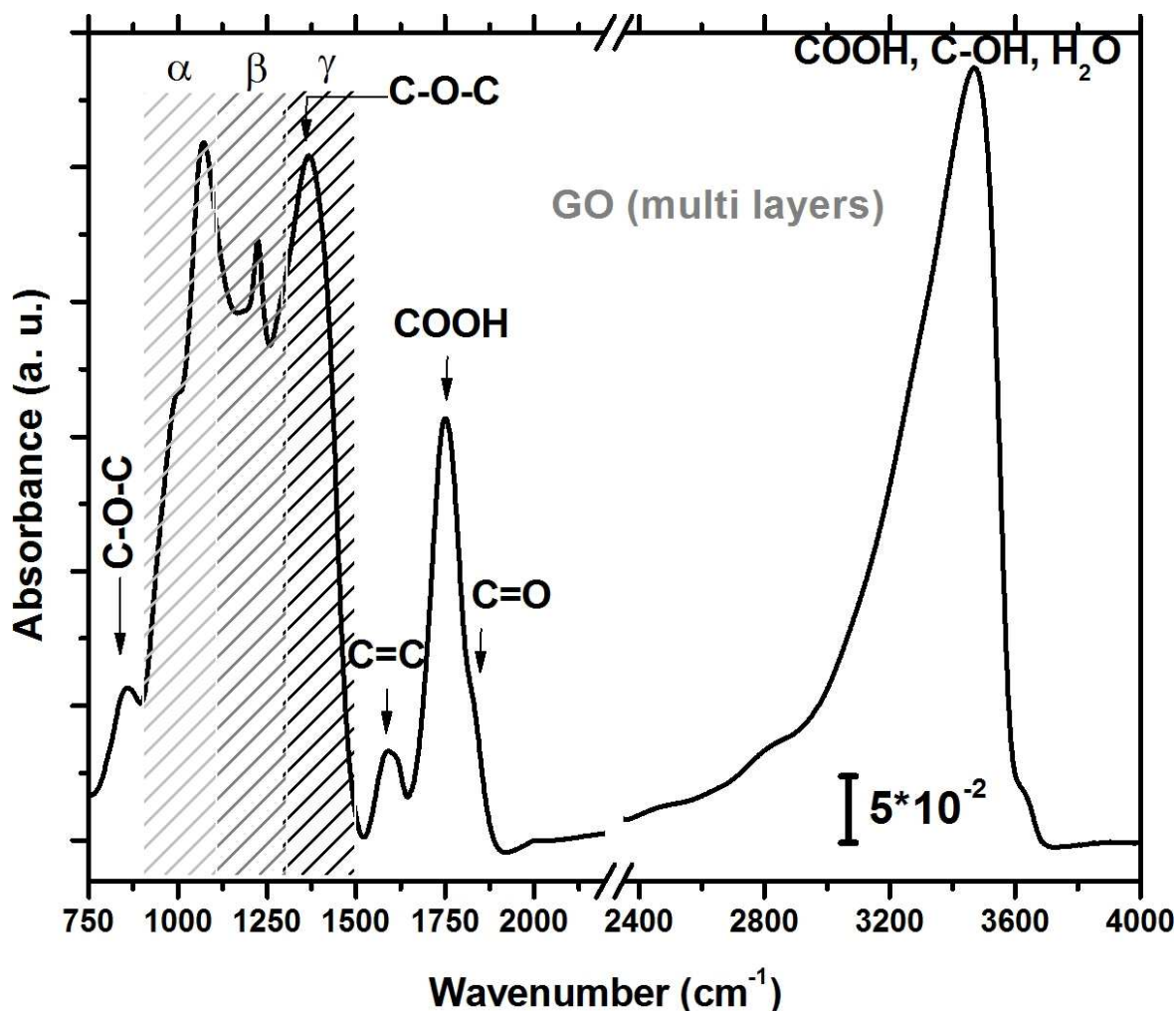
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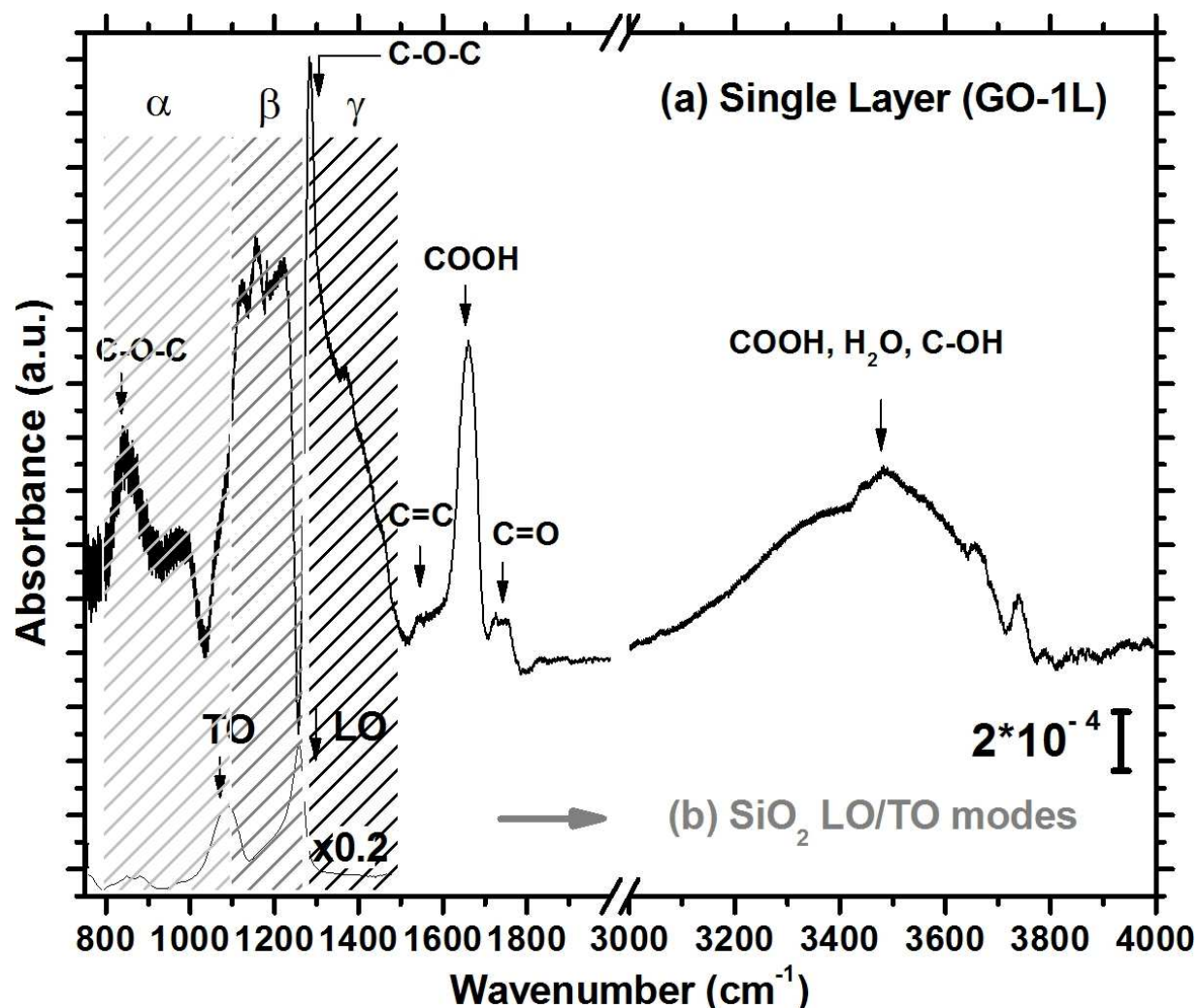
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**Figure S1 Infrared absorbance spectrum of multilayered GO at room temperature.**

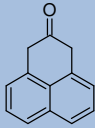
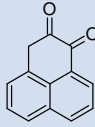
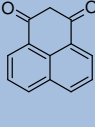
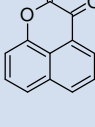
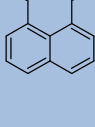
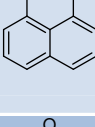
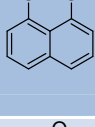
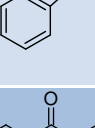

Vibrational modes are hydroxyls (possible COOH and H<sub>2</sub>O) (C-OH, 3000-3750 cm<sup>-1</sup>), carbonyls and/or carboxyls (C=O, COOH ~1500-1900 cm<sup>-1</sup>), sp<sup>2</sup>-hybridized C=C (in-plane stretching, ~1500-1600 cm<sup>-1</sup>), epoxides (C-O-C, 1280-1320 cm<sup>-1</sup> and ~850 cm<sup>-1</sup>) and some overlapped regions such as α-region (lactols, peroxides, dioxolanes, hydroxyls, 1,3-dioxan-2-ones, anhydrides, carboxyls, epoxides, 900-1100 cm<sup>-1</sup>), β-region (oxolan-2-ones, peroxides, ethers, ketones, pyran-2,3-diones, lactols, anhydrides, epoxides, *o*-benzoquinones, *p*-benzoquinones, 1100-1280 cm<sup>-1</sup>), and γ-region (ethers, epoxides, peroxides, ketones, *m*-benzoquinones, *p*-benzoquinones, 1280-1500 cm<sup>-1</sup>).



**Figure S2 Infrared absorbance spectrum of GO (single layer) at room temperature.** (a) The vibrational modes are shown for hydroxyls (possible COOH and H<sub>2</sub>O) (C-OH, 3000-3800 cm<sup>-1</sup>), ketones (C=O, 1720-1800 cm<sup>-1</sup>), carboxyls (COOH) and/or H<sub>2</sub>O (1600-1720 cm<sup>-1</sup>), sp<sup>2</sup>-hybridized C=C (in-plane stretching, 1500-1600 cm<sup>-1</sup>), epoxides (C-O-C, 1280-1320 cm<sup>-1</sup> and 800-900 cm<sup>-1</sup>) and some overlapped regions such as  $\alpha$ -region (lactols, peroxides, dioxolanes, hydroxyls, 1,3-dioxan-2-ones, anhydrides, carboxyls, epoxides, 900-1100 cm<sup>-1</sup>),  $\beta$ -region (oxolan-2-ones, peroxides, ethers, ketones, pyran-2,3-diones, lactols, anhydrides, epoxides, *o*-benzoquinones, *p*-benzoquinones, 1100-1280 cm<sup>-1</sup>), and  $\gamma$ -region (ethers, epoxides, peroxides,

ketones, *m*-benzoquinones, *p*-benzoquinones, 1280-1500  $\text{cm}^{-1}$ ). (b) Vibrational modes of  $\text{SiO}_2$  (TO and LO) appear at  $\sim 1078 \text{ cm}^{-1}$  and  $1240 \text{ cm}^{-1}$ , respectively. They are shown to explain the sharp losses at these frequencies in spectrum (a) that are due to the surface modification as a result of pretreatment of  $\text{SiO}_2$  surface using methyl alcohol and/or acetone during preparation of samples on the substrates.

**Table S1. Models of carbonyl compounds in overlapped regions and their simulated IR frequencies**

Carbonyl compounds	Structures	Simulated IR frequencies (cm <sup>-1</sup> )	Corrected IR frequencies (cm <sup>-1</sup> )	Regions
ketones		864, 1290, 1503, 1536	814, 1240, 1453, 1486	$\beta, \gamma$
<i>o</i> -benzoquinones		852, 1273, 1705, 1734	802, 1223, 1655, 1684	$\beta$
<i>m</i> -benzoquinones		845, 1526, 1573	795, 1476, 1523	$\gamma$
pyran-2,3-diones		763, 1209, 1699	713, 1159, 1649	$\beta$
anhydrides		1046, 1182, 1767, 1802	996, 1132, 1717, 1752	$\alpha, \beta$
pyran-2-ones		1180, 1380, 1709	1130, 1330, 1659	$\beta, \gamma$
1,3-dioxan-2-ones		1123, 1863	1073, 1813	$\alpha$
oxolan-2-ones		1247, 1854	1197, 1804	$\beta$
<i>p</i> -benzoquinones		864, 1060, 1294, 1671	814, 1010, 1244, 1621	$\beta$

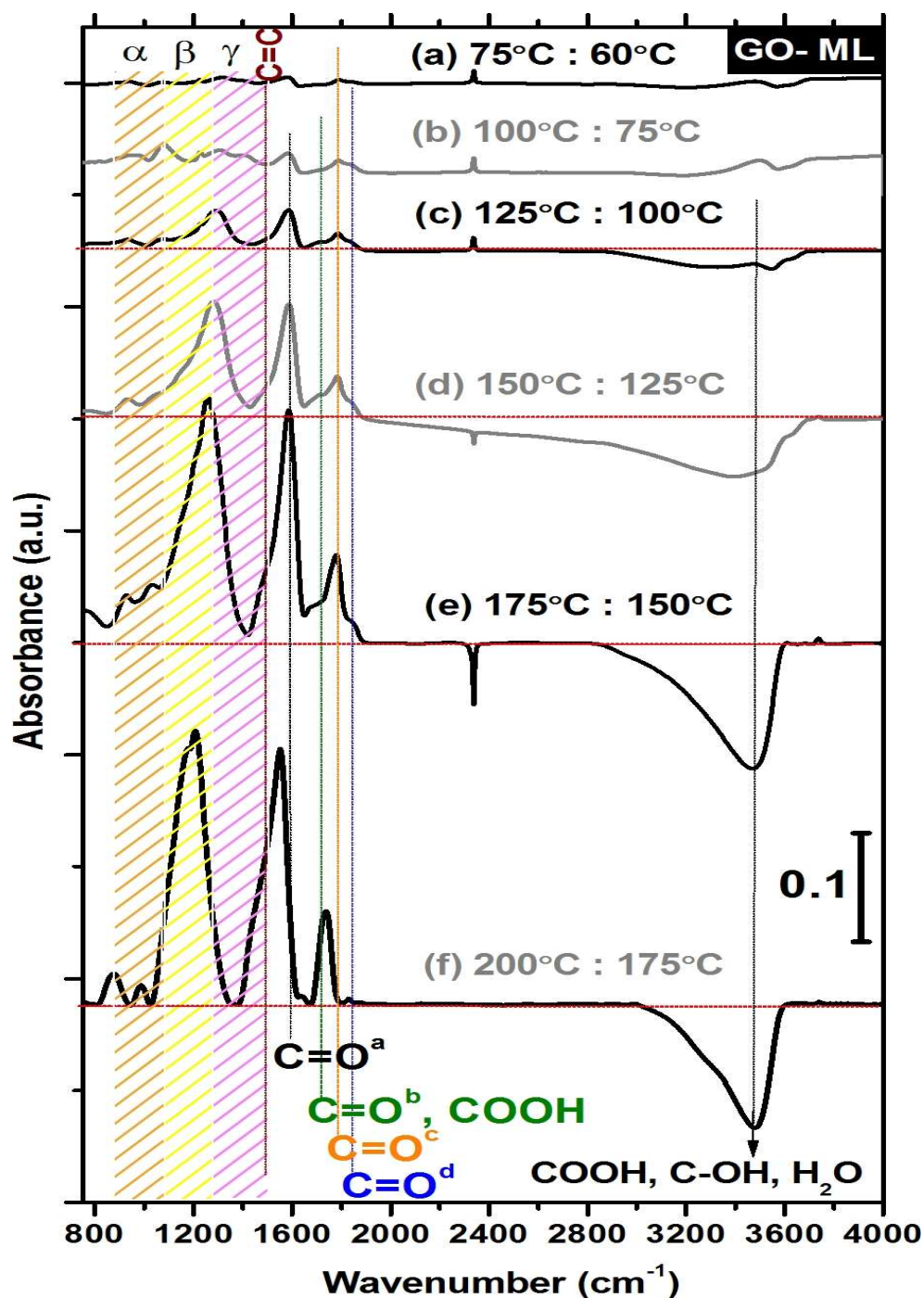
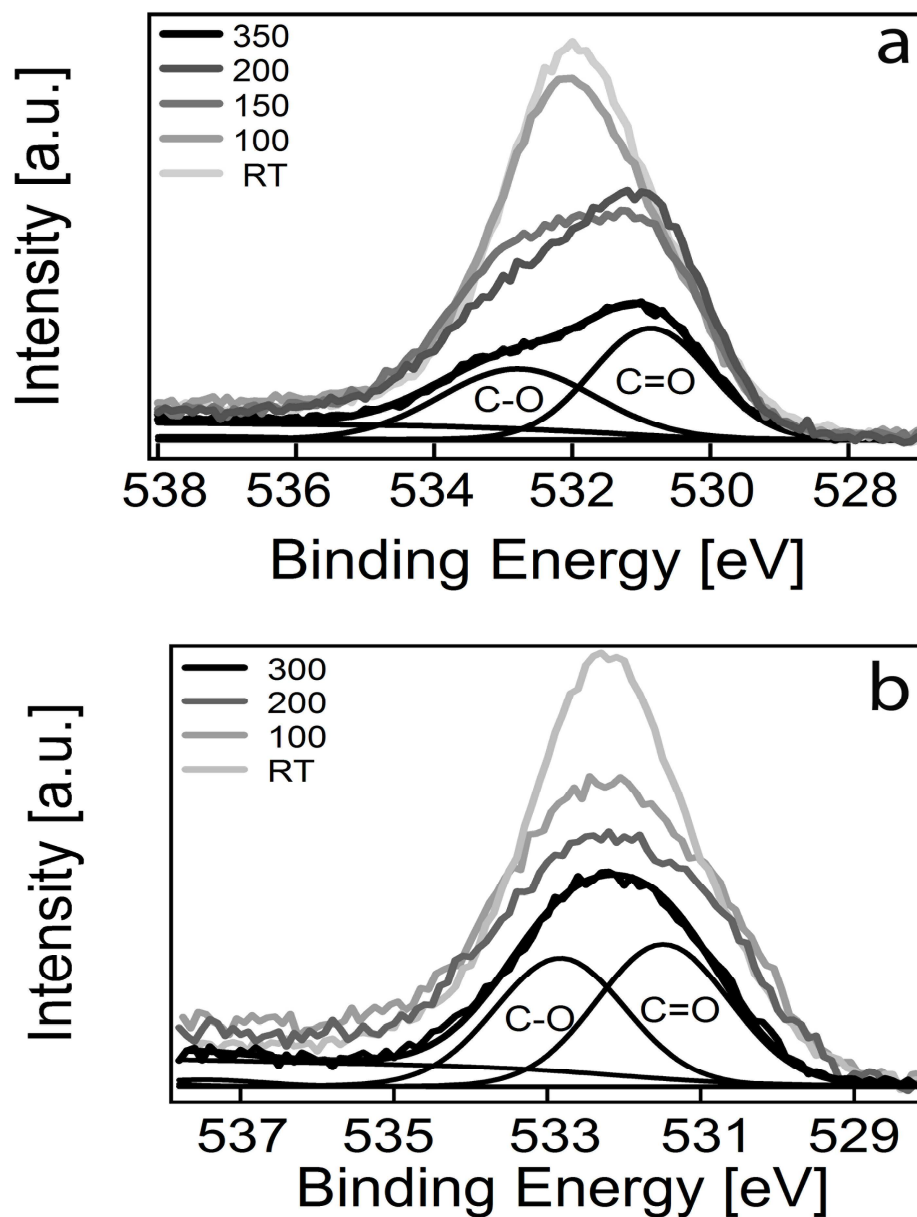


Figure S3 Differential infrared absorption spectra of multilayered GO in transmission, i.e. referenced to the spectrum collected at the temperature indicated after the colon. Change in functional groups is shown at specific temperatures of (a) 60-75°C, (b) 75-100°C, (c) 100-125°C,

(d) 125-150°C, (e) 150-175°C, (f) 175-200°C. Four different peaks are apparently observed at 60-175°C represented as (C=O<sup>a</sup>, ~1400-1650 cm<sup>-1</sup>), (C=O<sup>b</sup>, ~1650-1750 cm<sup>-1</sup>), (C=O<sup>c</sup>, ~1750-1800 cm<sup>-1</sup>), and (C=O<sup>d</sup>, ~1800-1900 cm<sup>-1</sup>). The possible groups for C=O<sup>a</sup> are ketones, pyran-2,3-diones, pyran-2-ones, *m*-benzoquinones and *p*-benzoquinones. The C=O<sup>a</sup> peak overlaps with sp<sup>2</sup> hybridized C=C in-plane stretching mode (~1580 cm<sup>-1</sup>). The C=O<sup>b</sup> peak (~1650-1750 cm<sup>-1</sup>) is ascribed to anhydrides, pyran-2-ones, *p*-benzoquinones and *o*-benzoquinones. The C=O<sup>c</sup> peak (~1750-1800 cm<sup>-1</sup>) is possible for pyran-2-ones and C=O<sup>d</sup> peak (~1800-1900 cm<sup>-1</sup>) for 1,3-dioxan-2-ones and oxolan-2-ones.

The presence of carbonyl species, characterized by relatively strong dipole moments [R1], further enhances the infrared absorbance of sp<sup>2</sup>-hybridized C=C vibrations (1500-1600 cm<sup>-1</sup>) that overlap with the absorption region of carbonyls, as noted in Figs S2. Therefore, contribution of C=C vibrations needs to be taken into account when examining the spectra of Figs 2i-ii, e.g. adding to the carbonyl contribution at ~1550 cm<sup>-1</sup>.

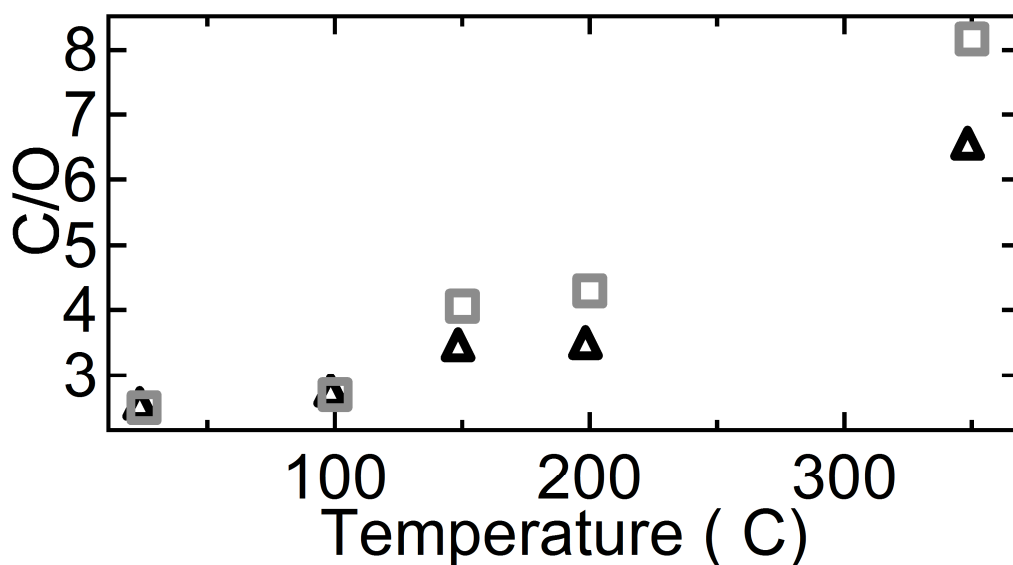
[R1] D. R. Lide, *CRC handbook of chemistry and physics*. (84<sup>th</sup> Ed., CRC Press LLC, Florida, 2003).



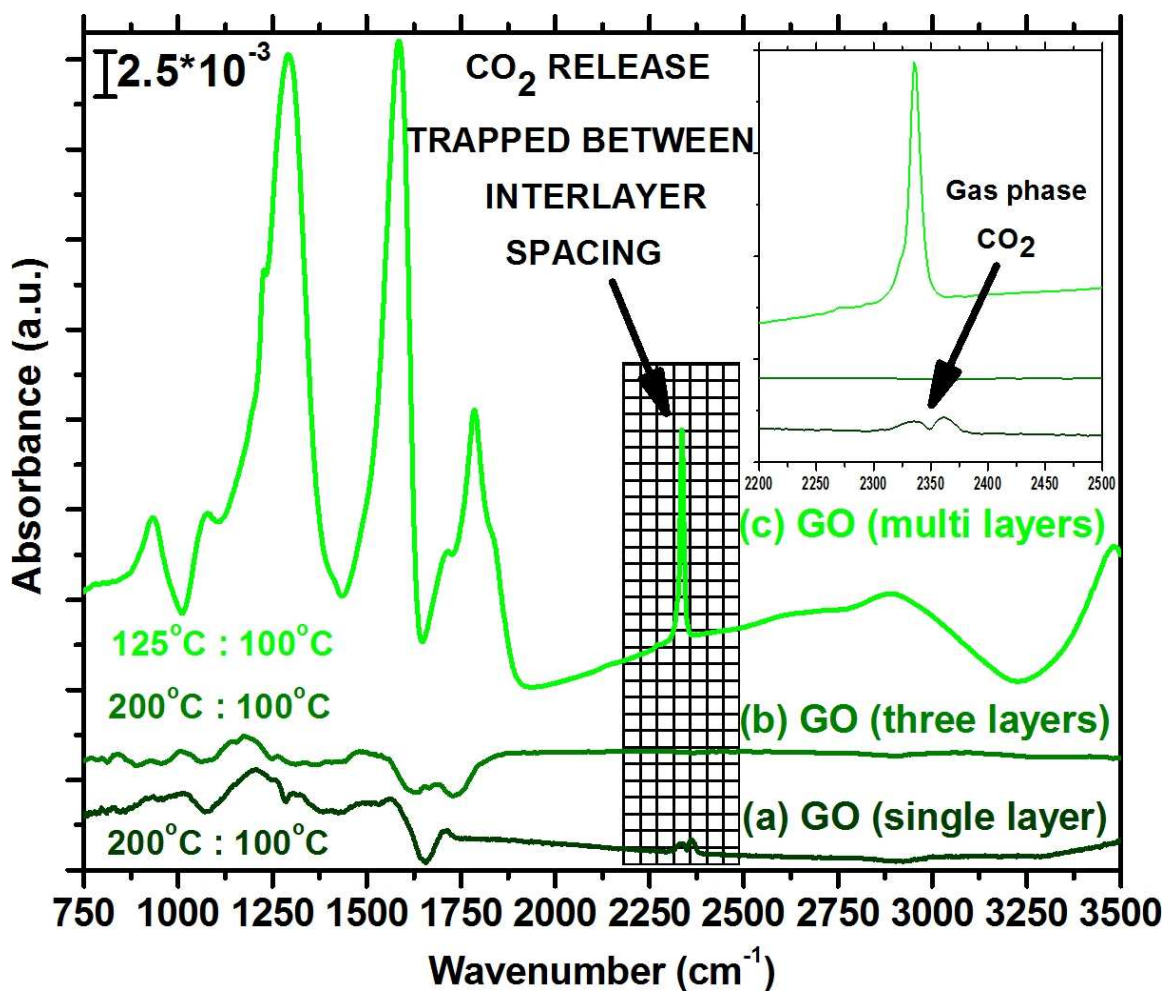
**Figure S4 XPS analysis summarizing C=O and C-O formation due to interactions upon thermal annealing.** The O1s XPS spectra ( $h\nu=1253.6$  eV) collected on multilayered GO (a) and one layered GO (b) thin film (a) deposited on Au (10 nm)/SiO<sub>2</sub> (300nm)/Si and annealed in UHV at the indicated temperatures for 15 min. By deconvolving, the O 1s peaks (via fit by Doniach-



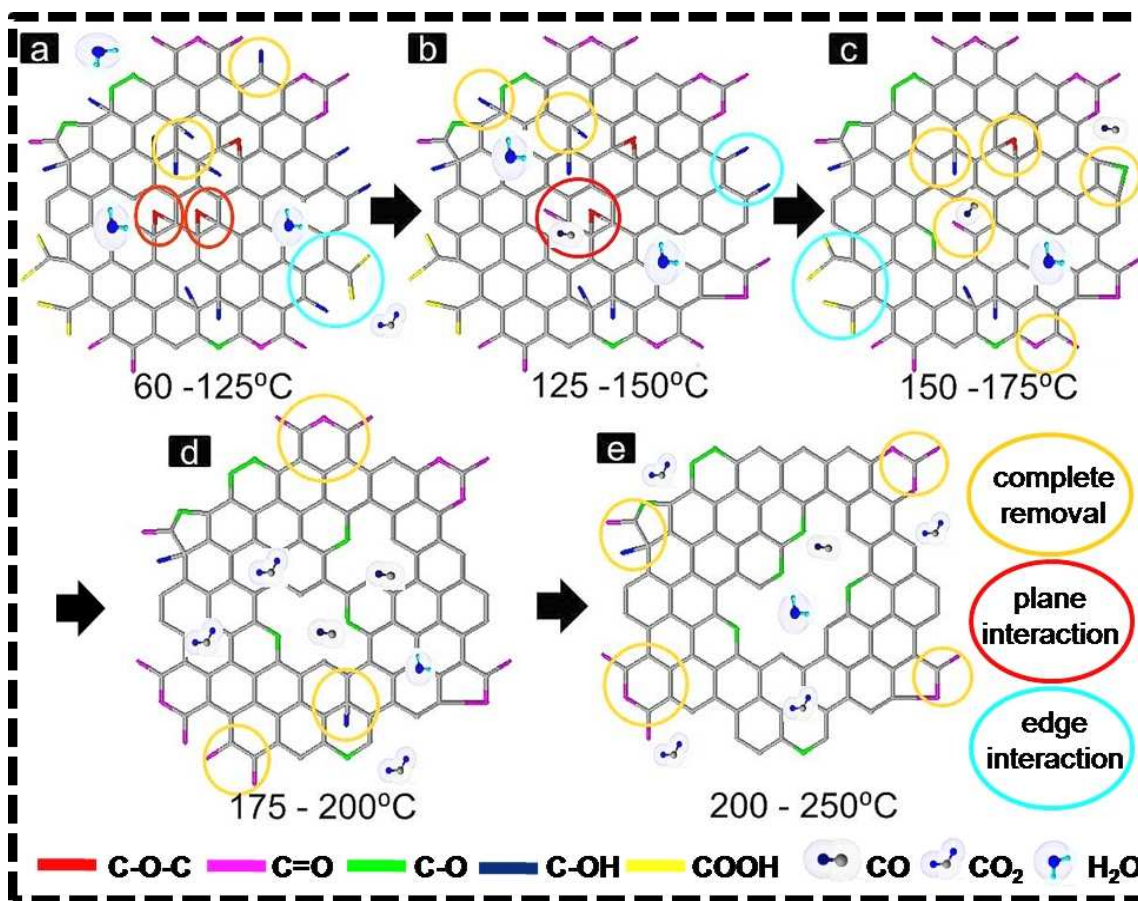
Sunjjic function after subtracting a Shirley background) two component have been identified as C-O bonds (533 eV) and C=O (531.2 eV) bonds. It has been found an increase of C=O component along with a loss of C-O passing from the annealing temperature of 150 up to 200 °C on multilayered GO thin film. Whereas one layered GO film shows a consistent decrement of both the components up to 300 °C.



**Figure S5** The atomic ratios (C/O) identified by XPS as a function of annealing temperature. The black triangles (a) are calculated considering the entire area underneath O1s peak, while the grey squares (b) are calculated counting only the 66% of the area underneath the C=O component of the O1s peak collected after annealing at 25-350 °C. The latter estimation of C/O atomic ratio would minimize the contribution of the C=O bonds in the total account of the oxygen concentration.



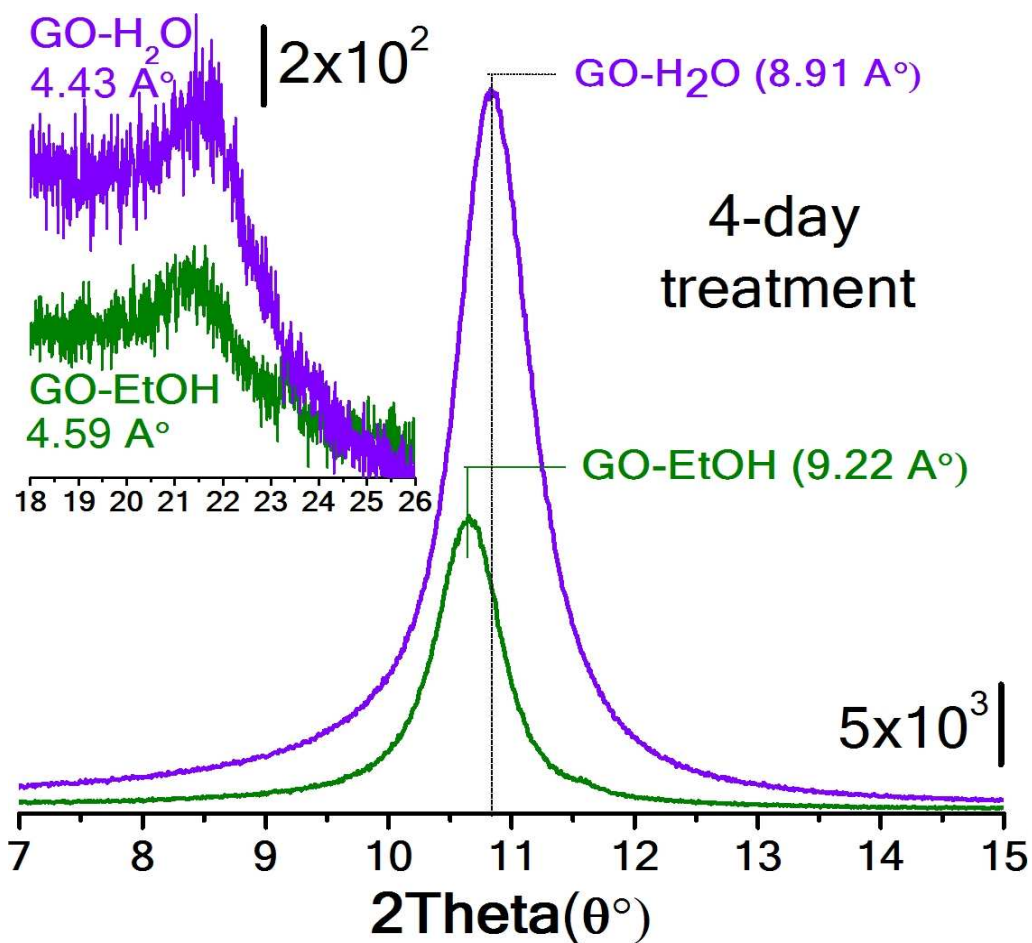
**Figure S6 Infrared differential spectra showing the formation  $\text{CO}_2$ .** (a) GO (single layer) at 100-200°C (b) GO (three layers) at 100-200°C and (c) GO (multi layers) at 100-125°C showing the presence of trapped  $\text{CO}_2$  (single peak at  $\sim 2250\text{-}2400 \text{ cm}^{-1}$ ) in between the interlayer spacing of GO. This spectrum is distinct from the doublets observed for free  $\text{CO}_2$  gas (see the magnified region in the inset), confirming that the  $\text{CO}_2$  gas is trapped (i.e. interacting) within the GO layers.



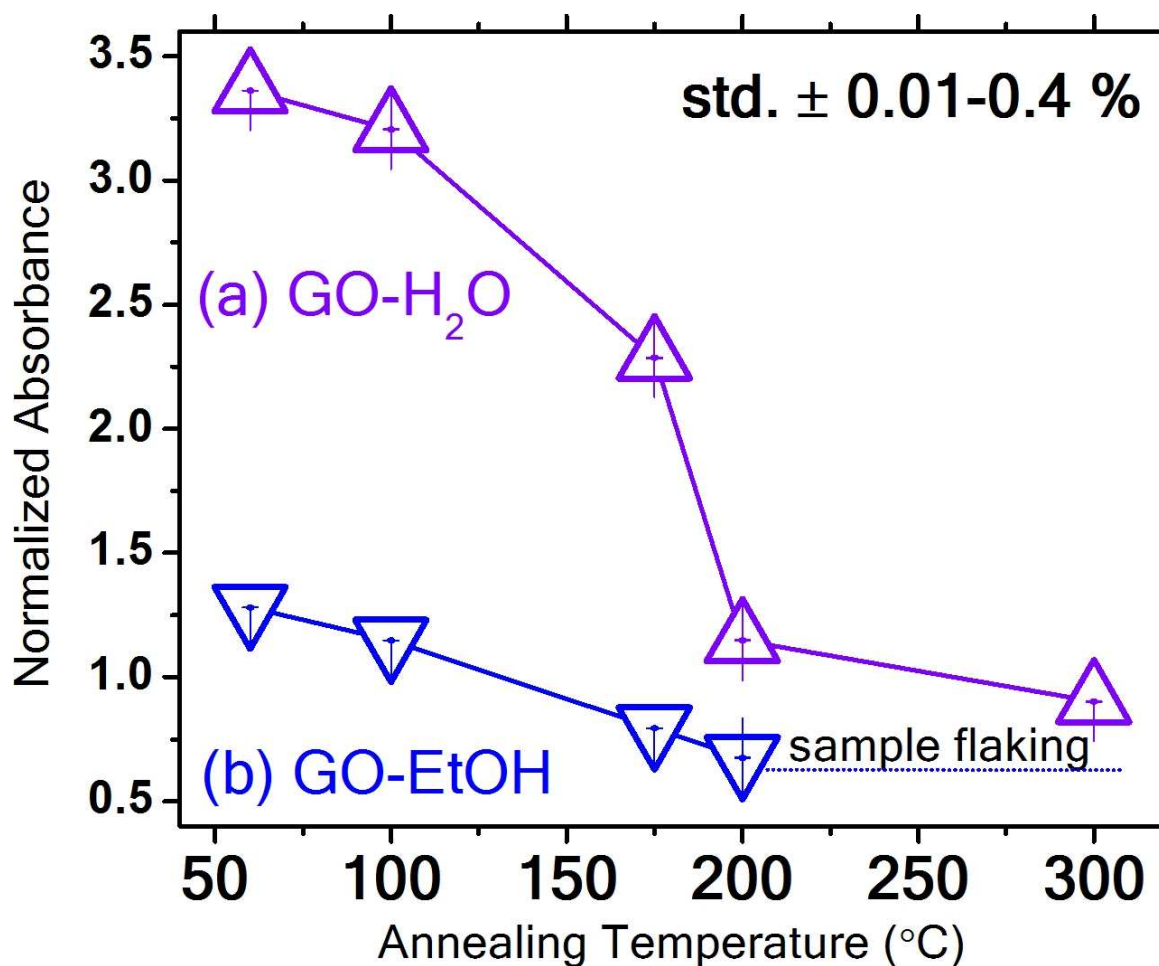
**Figure S7 Intrashheet interactions [R2] shown within only one layer of multilayered GO with a schematic representation of the removal of species from the basal plane.** (a) Initiation of removal of hydroxyls and epoxides and a possible neighboring interaction between a hydroxyl and a carboxyl at the edge are summarized at 60-125°C. (b) Intermediate carbonyl formation within a defect, formation of a lactone at the edge as well as continuous removal of hydroxyls and epoxides and a possible interaction between two nearby hydroxyls are presented at 125-150°C. (c) Initiation of removal of ketones both from the edges and defects and a possible interaction between two carboxyls are shown at 150-175°C. (d-e) Continuous disappearance of ketones and hydroxyls is presented at 175-250°C resulting in vacancy formation and release of CO and CO<sub>2</sub>. Each species is

identified with certain colors: C-O (green), C=O (pink), COOH (yellow), OH (blue), epoxide (red), carbon (gray), H for H<sub>2</sub>O (aqua), O for H<sub>2</sub>O, CO and CO<sub>2</sub> (blue). Removal of species is indicated in orange circles, formation of intermediate species during plane interactions in red circles and interacting edge species in aqua circles.

[R2] H. P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon* **1994**, 32, 759-769.



**Figure S8 XRD analysis of 4-day intercalation of ethyl alcohol (GO-EtOH, green) in comparison with GO-H<sub>2</sub>O (purple).** The interlayer spacing of GO increases upon alcohol intercalation from 8.91 Å in GO-H<sub>2</sub>O to 9.22 Å in alcohol-intercalated GO. A small contribution of graphite peak is observed at 4.59 Å in alcohol-intercalated GO, compared to 4.43 Å of GO-H<sub>2</sub>O.



**Figure S9 Comparison of normalized integrated absorbance of OH contribution for GO-H<sub>2</sub>O and GO-EtOH as a function of temperature.** The total hydrogen bonding contribution involving C-OH, COOH and H<sub>2</sub>O integrated over a range of 3000-3700 cm<sup>-1</sup> (std.  $\pm 0.01-0.4\%$ ) are shown for intercalation of (a) water in multilayered GO (GO-H<sub>2</sub>O, purple) and (b) a following ethyl alcohol introduction (GO-EtOH, blue) for 4 days. Each open triangle shows the mean values of two different measurements, which was normalized to the initial amount of oxygen (800-1850 cm<sup>-1</sup>) at room temperature. The blue dotted line shows missing data points of 300°C measurement for GO-EtOH due to the initiation of sample flaking.