

## Unusual infrared-absorption mechanism in thermally reduced graphene oxide

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The version of this Supplementary Information originally published had an incorrect title. This has now been amended as above.

## Unusual infrared-absorption mechanism in thermally reduced graphene oxide

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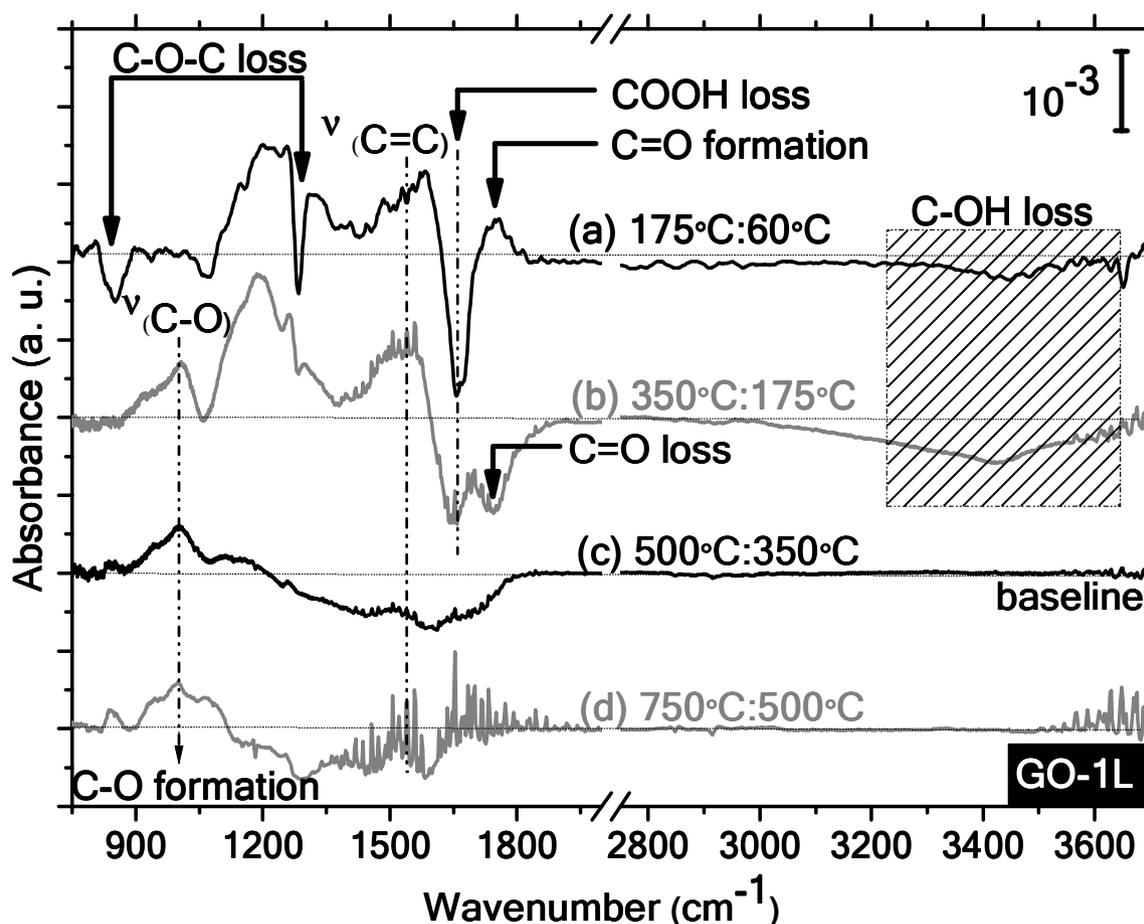
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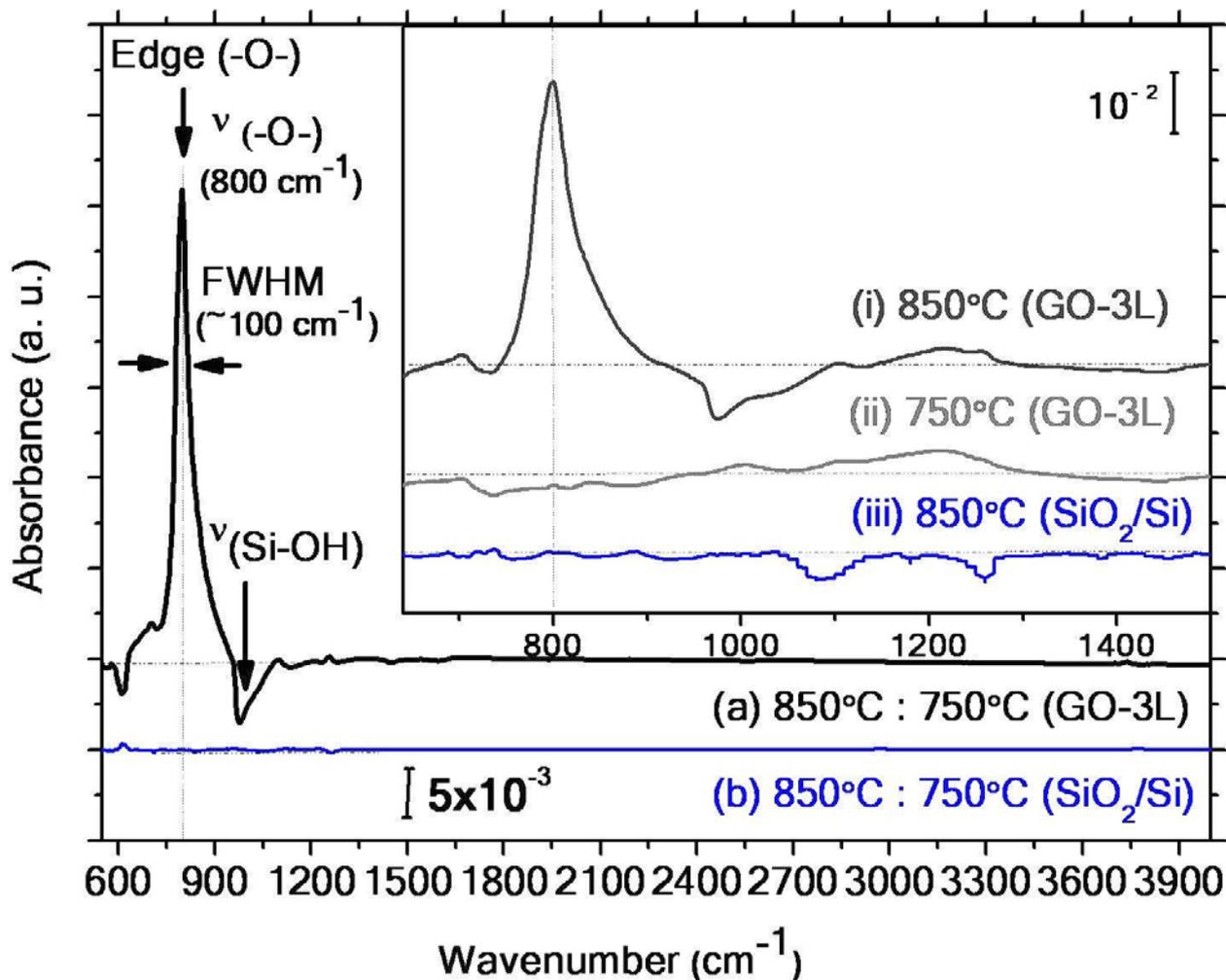
**Supplementary Figure S1 Transmission infrared differential spectra of reduced GO (single layer).** Variations upon thermal annealing at (a) 175°C:60°C (b) 350°C:175°C (c) 500°C:350°C (d) 750°C:500°C are represented in the following oxygen species: hydroxyl desorption (namely phenol, C-OH) (3050-3800  $\text{cm}^{-1}$  and ~1070  $\text{cm}^{-1}$ ) including all C-OH vibrations from COOH and H<sub>2</sub>O, formation of ketonic groups (1600-1650  $\text{cm}^{-1}$ , 1750-1850  $\text{cm}^{-1}$ ) in (a) and their loss in (b), loss of carboxyl (COOH) (1650-1750  $\text{cm}^{-1}$  including C-OH vibrations at 3530  $\text{cm}^{-1}$  and 1080  $\text{cm}^{-1}$ ), loss of epoxide (C-O-C) (1230-1320  $\text{cm}^{-1}$  of asymmetric stretching and ~850  $\text{cm}^{-1}$  of bending motion), formation of etheric groups (900-1100  $\text{cm}^{-1}$ ), all other C-O and C=O contribution in  $\beta$ -region (1100-1280  $\text{cm}^{-1}$ ) and  $\text{sp}^2$ -hybridized C=C (1500-1600  $\text{cm}^{-1}$ , in-plane vibrations).

## Section 1.

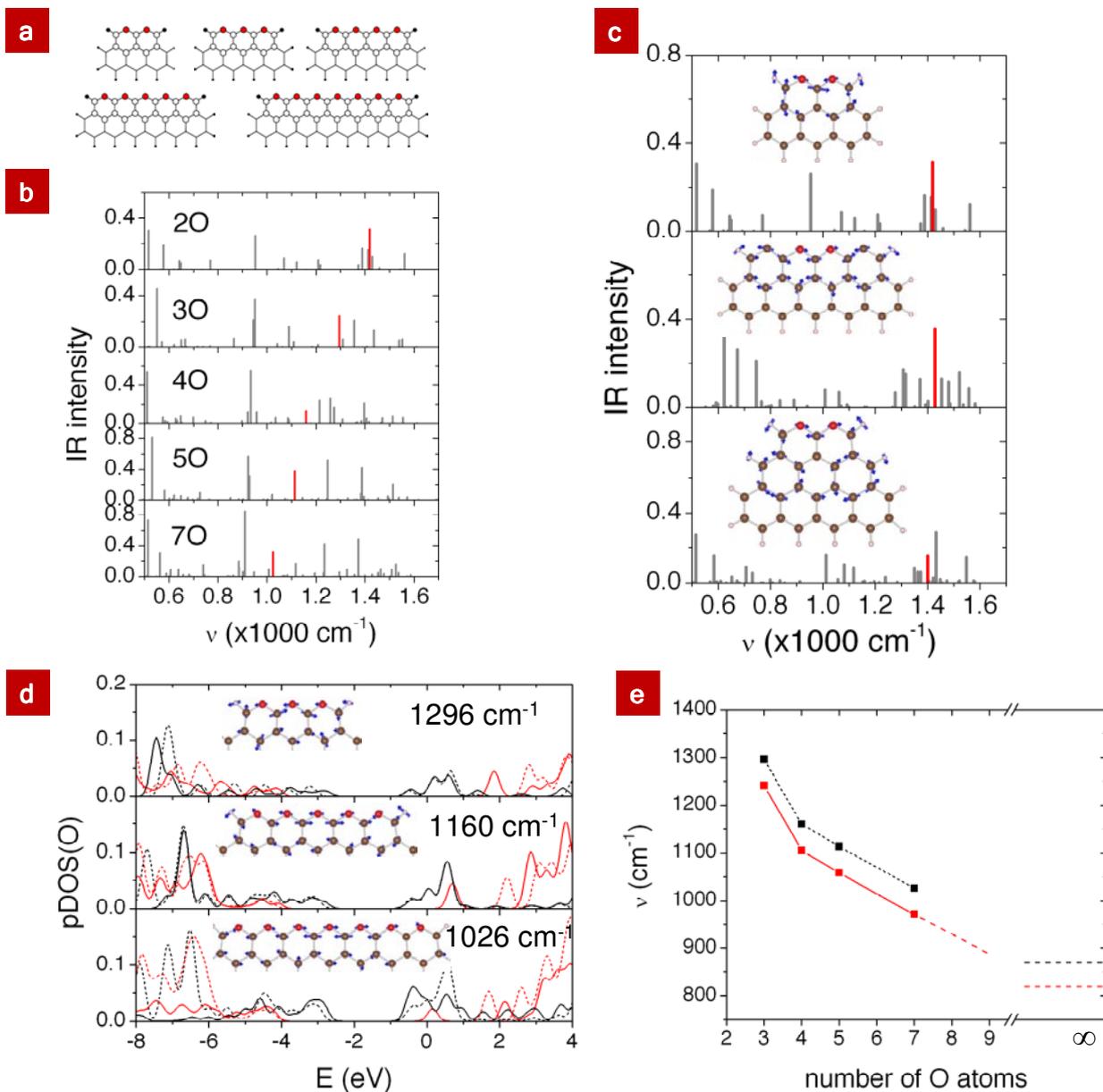
### Brief description of the structural evolution of single layer GO after annealing at 175-750°C (Fig. S1).

Between 60 and 175°C, epoxide species decompose completely, most of the hydroxyl and carboxyl species are removed while some C=O containing ketonic species are formed (Supplementary Fig. S1a). Hydroxyl, carboxyl and ketonic species continuously disappear between 175 and 350°C while some C-O containing etheric groups are formed (Supplementary Fig. S1b). No hydroxyl groups can be observed after 350°C (Supplementary Figs S1c-d) probably because they can easily decompose due to strong interaction with neighboring hydroxyl and carboxyl groups, leading to formation of intermediate ketones [S1]. Interestingly, the in-plane vibration ( $1580\text{ cm}^{-1}$ ) of the C=C bonds is observable only below 350°C (Supplementary Figs S1a-b) for two reasons: 1) the amount of  $sp^2$  hybridization increases when out-of-plane oxygen species, such as hydroxyl (C-OH), carboxyl (COOH) and epoxide (C-O-C) groups are removed and 2) usually weak C=C phonon absorption is enhanced when the symmetry is perturbed by neighboring oxygen.

[S1] Bagri, A. et al. Structural evolution during the reduction of chemically derived graphene oxide. *Nat. Chem.* **2**, 581-587 (2010).



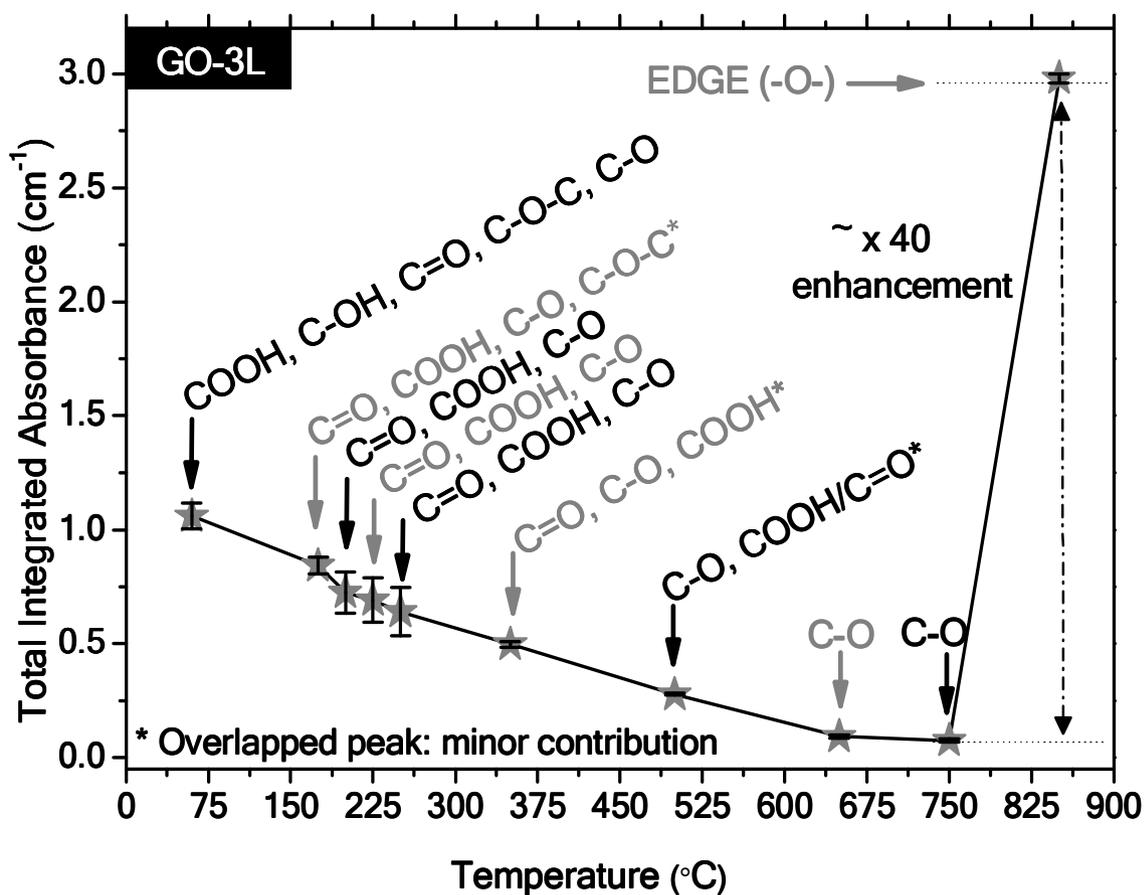
Supplementary Figure S2 Transmission infrared differential (a) and absorbance (i-ii) spectra of GO (three layers: 3L) at high temperatures (850-750°C). A new peak appears at 800 cm<sup>-1</sup> with fwhm of ~100 cm<sup>-1</sup>. A loss corresponding to Si-OH was observed at ~980 cm<sup>-1</sup>. The inset shows the absorbance spectra at 750°C (i) and 850°C (ii) anneals for single layer GO and (iii) bare clean SiO<sub>2</sub>/Si surface at 850°C referenced to the room temperature clean SiO<sub>2</sub>/Si surface. Absorbance unit is abbreviated as 'a. u.'.



**Supplementary Figure S3 Cluster simulation results for finite number of edge ether.** (a) Cluster models for agglomerated edge ethers increasing from two to seven, (b) their simulated IR intensities where the asymmetric C-O-C stretch mode is indicated by the red line. (c) Examination of the asymmetric C-O-C stretch mode frequency as indicated by the red line with increasing carbon rings along (middle:  $\nu=1428\text{ cm}^{-1}$ ) or away (bottom:  $\nu=1400\text{ cm}^{-1}$ ) from the

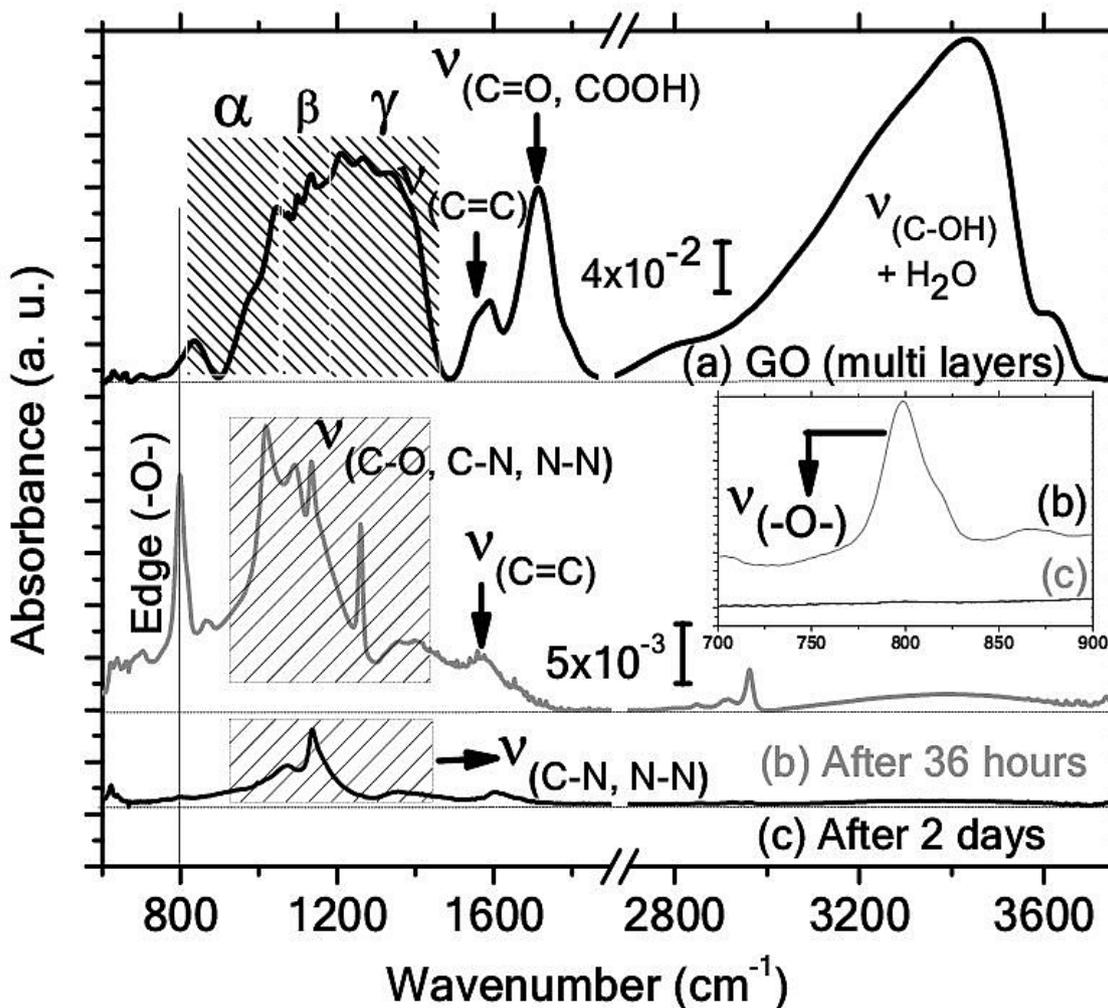
edge in comparison with the original model of two ethers (top:  $\nu=1419\text{ cm}^{-1}$ ). The corresponding vibration shape is given for each case. (d) Effect of asymmetric C-O-C stretch mode on electronic density of states (DOS) for 3, 5 and 7 edge O atoms, together with their vibration frequencies. For each case, DOS projected onto O- $\pi$  (black) and O- $\sigma$  (red) orbitals are shown when the system is in its ground states (dashed) or after atomic displacements (solid). (e) Asymmetric C-O-C stretch mode frequency versus the number edge O atoms. The infinite number corresponds to edge oxidized GNR for which our calculated frequency is  $870\text{ cm}^{-1}$ . Block symbols are our calculated values, whereas red ones are the corrected values by  $-55\text{ cm}^{-1}$ .

The asymmetric C-O-C stretch mode frequency is quite different from  $800\text{ cm}^{-1}$  when only several ether groups appear next to each other. Fig. S3 displays our simulated data with increasing the number of edge ethers from two to seven (Fig. S3a). The C-O-C asymmetric mode is as high as about  $1400\text{ cm}^{-1}$  for two edge ethers, and decreases down to  $1026\text{ cm}^{-1}$  for seven (Fig. S3b). We have confirmed that including more carbon rings in the model does not change the frequency (Fig. S3c). We also checked change of the electronic states with the C-O-C asymmetric mode vibration (Fig. S3d). The significant lowering of O- $\sigma^*$  states (the red solid line) can be seen clearly. At seven ethers, electrons under such vibration are found to exchange their occupation between O- $\sigma^*$  and O- $\pi$  orbitals. The C-O-C asymmetric mode frequency variation with increasing the size of ether chain is plotted in Figure S3e, where tens of edge ethers are required to reach the observed  $800\text{ cm}^{-1}$  value.



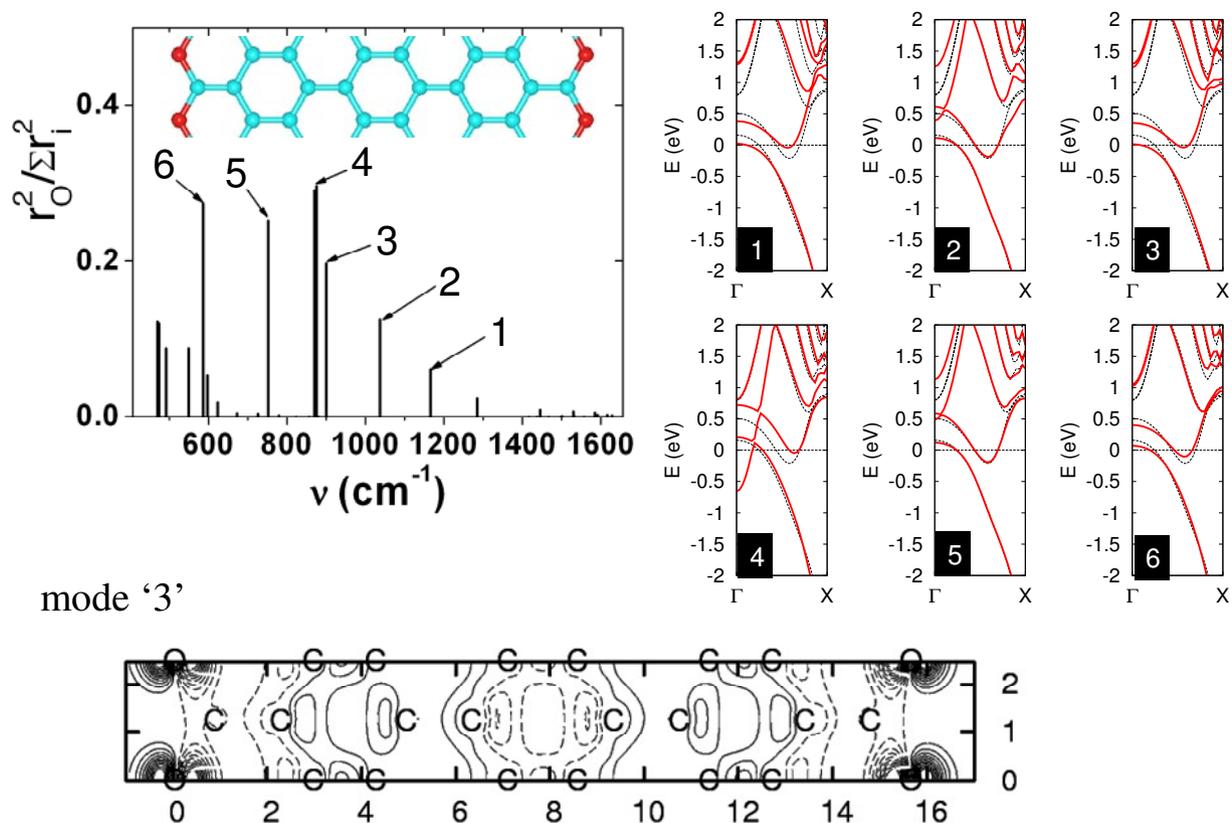
**Supplementary Figure S4 Integrated absorbance vs. annealing temperature measured at 60°C (GO with three layers).** Each temperature is shown with a different color (60-850°C from red to brown in sequence). The existing functional groups at each specific temperature are also ordered in terms of the area size. Almost all of the functional groups disappear at 500°C and only C-O containing edge ether contribution remains thereafter. The peak at 800  $\text{cm}^{-1}$  indicates a maximum variation in dipole moment at 850°C with a 40 times more enhancement compared to 750°C. The standard deviations (s.d. 0.1-3%) shown with error bars are obtained from the mean values of fluctuations in the values of total integrated areas. (\*) Overlapped peak area with minor contribution from both COOH and C=O containing species.

Supplementary Fig. S4 summarizes the TOTAL intensity of all oxide modes of GO (three layers) as a function of thermal annealing. The initial integrated intensity decreases from  $\sim 1.0 \text{ cm}^{-1}$  to  $\sim 0.08 \text{ cm}^{-1}$  after a  $750^\circ\text{C}$  anneal, when only  $\sim 8\text{-}10\%$  of oxygen remains in three layers of GO. Upon annealing to  $850^\circ\text{C}$ , the integrated area of the edge ether (mode centered at  $800 \text{ cm}^{-1}$ ) increases to a value of  $\sim 3.0 \text{ cm}^{-1}$ , namely by a factor of  $\sim 40$ .



**Supplementary Figure S5 Time-dependent study of wet chemical reduction of GO (multi layers) in aqueous media.** Transmission infrared absorbance spectra of (a) GO (multi layers)

showing vibrational modes of hydroxyl (possible COOH and H<sub>2</sub>O) (C-OH, 3000-3750 cm<sup>-1</sup>), ketone and/or carboxyl (C=O, COOH ~1700-1900 cm<sup>-1</sup>), sp<sup>2</sup>-hybridized C=C (in-plane stretching, ~1550-1650 cm<sup>-1</sup>), epoxide (C-O-C, ~1350 cm<sup>-1</sup> and 800-900 cm<sup>-1</sup>) and some overlapped regions such as α-region (lactol, peroxide, dioxolane, hydroxyl, C=O contribution, carboxyl and epoxide, 900-1100 cm<sup>-1</sup>), β-region (C=O contribution, peroxide, ether, lactol, anhydride and epoxide, 1100-1280 cm<sup>-1</sup>), and γ-region (ether, epoxide and C=O contribution, 1280-1500 cm<sup>-1</sup>). Variations upon exposure to hydrazine monohydrate under reflux at 100°C are indicated after (b) 36-hour treatment and (b) 2-day treatment. A new peak appears at 800 cm<sup>-1</sup> after 36-hour treatment disappearing after 2-day treatment. Vibrational modes of C-N (1000-1400 cm<sup>-1</sup>) and N-N (~1040 cm<sup>-1</sup>) become visible.



**Supplementary Figure S6 Electronic band structure change with vibrations of six normal modes for edge oxidized GNR.** The change of electronic band structure is shown under vibration of six normal modes involving significant O displacements. In the band structures (right), the red lines are for excited system, and the ground state band structure is shown in the black dashed line. In the bottom, two dimensional electron density increase (solid) or decrease (dashed) is given for the mode '3' displacement. Note the contour levels are 0.1, 0.2,...  $e/\text{\AA}^2$  for the solid lines and -0.1,-0.2,... for the dashed lines.

In case of edge oxidized GNR, all six vibration modes with significant O displacements are examined to check their effects on the electronic band structure (Fig. S6). Except for the mode

'4', all other modes modulate occupation of the  $\pi$  bands only near the Fermi level. Their electron fluctuations in real space are similar to the one shown in the contour plot. Therefore, only the mode '4' is unique to give enhanced IR absorption.

## Section 2.

### Ruling out the other possibilities for a contribution at $800\text{ cm}^{-1}$ :

**1. Issues related to nitridation during wet chemical reduction:** Although the mechanism of chemical reduction is not well understood, and some of the IR peaks ( $1000\text{--}1400\text{ cm}^{-1}$ ) cannot be unambiguously assigned (Supplementary Fig. S6c), they are believed to be associated with N-containing species. Indeed, first principle calculations showed that C-N, N-H, N-N, etc. are likely to be formed upon hydrazine reduction [S2]. In any case, this uncertainty does not affect the assignment of aggregated cyclic edge ether at  $800\text{ cm}^{-1}$ .

[S2] Kim, M. C., Hwang, G. S., Ruoff, R. S. Epoxide reduction with hydrazine on graphene: a first principles study. *J. Chem. Phys.* **131**, 064704-5 (2009).

**2. Issues related to silicon carbide formation:** The unlikely possibility of forming SiC upon thermal annealing is also ruled out based on the work of Blau *et al.* [S3] who showed that SiC formation could only be achieved on SiO<sub>2</sub> substrates in the presence of a metal catalyst such as iron nanoparticles.

[S3] Muñoz, E. et al. Synthesis of SiC nanorods from sheets of single-walled carbon nanotubes. *Chem. Phys. Lett.* **359**, 397–402 (2002).

### Section 3.

#### Supplementary Method (silicon substrate cleaning):

The surface of all Si(100) substrates (FZ-grown, double-side polished, with the dimensions of  $3.8 \times 1.5 \text{ cm}^2$ ), with a 7 nm-thick thermal oxide, are cleaned by washing with ethyl acetate, methanol and distilled water several times, and then dried with nitrogen gas. All organic and metallic contaminants are removed by immersing in a piranha solution ( $\text{H}_2\text{SO}_4$ :  $\text{H}_2\text{O}_2$  = 2:1, v:v) at  $90^\circ\text{C}$  for 15 minutes and rinsed well with distilled water. After this treatment, the thermal oxide is clean and hydroxyl-terminated. This is the surface used as reference for all thermal and chemical treated GO samples.

### Section 4.

#### Fittings for total integrated area calculations.

*Integrated ranges for single layer GO:* 3000-3800  $\text{cm}^{-1}$  (hydroxyl: C-OH), 1500-1820  $\text{cm}^{-1}$  (ketones and carboxyl: C=O by subtracting C=C contribution from deconvoluted peaks), 1230-1310  $\text{cm}^{-1}$  (epoxide: (C-O-C) including additional contribution from other groups), 850-1195  $\text{cm}^{-1}$  (total contribution from C-O and C=O containing chemical species) and 650-1200  $\text{cm}^{-1}$  (aggregated edge ether: (-O-) at 800  $\text{cm}^{-1}$ ).

*Integrated ranges for three layers of GO:* 3000-3800  $\text{cm}^{-1}$  (hydroxyl: C-OH), 1500-1820  $\text{cm}^{-1}$  (ketone and carboxyl: C=O by subtracting C=C contribution from deconvoluted peaks), 1230-1310  $\text{cm}^{-1}$  (epoxide: (C-O-C) by subtracting LO mode of  $\text{SiO}_2$ ), 800-1195  $\text{cm}^{-1}$  (all contributions from C-O containing chemical species by subtracting TO mode of  $\text{SiO}_2$ ) and 650-1200  $\text{cm}^{-1}$  (edge ether: (-O-)). (\*) The small peak observable at 1280  $\text{cm}^{-1}$  as a part of C-O containing chemical species is attributed to wagging modes of epoxides (C-O-C), which appear in the

region of (1230-1330  $\text{cm}^{-1}$ ). Therefore, this small contribution cannot be observed at temperatures higher than 175°C and not counted as epoxide contribution.

**Standard deviations for single layer GO:** 0.1% for 60°C, 0.2% for 500°C, 1% for 175°C, 225-350°C and 650-750°C, 2% for 200°C and 850°C. **Standard deviations for GO-3L:** 0.1% for 500-750°C, 0.2% for 350°C and 850°C, 1% for 175°C, 2% for 60°C and 3% for 200-250°C.