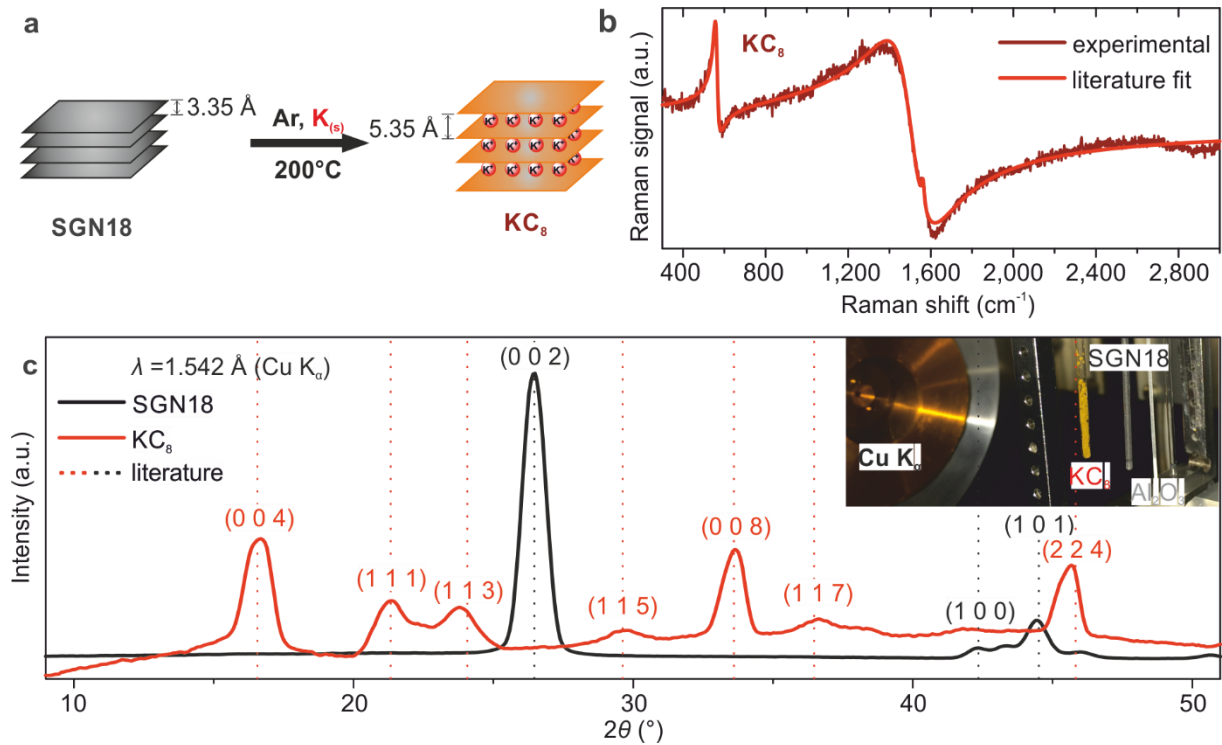
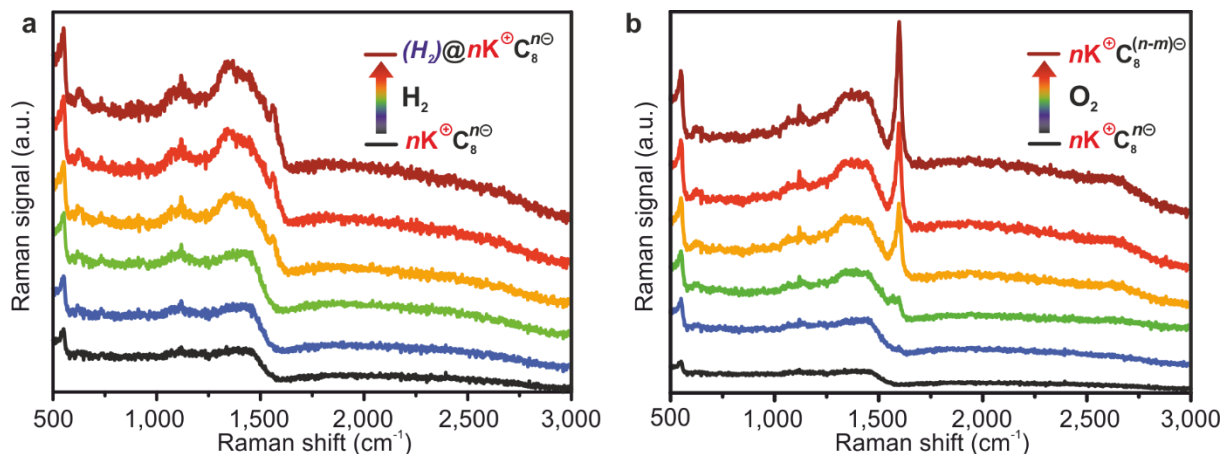


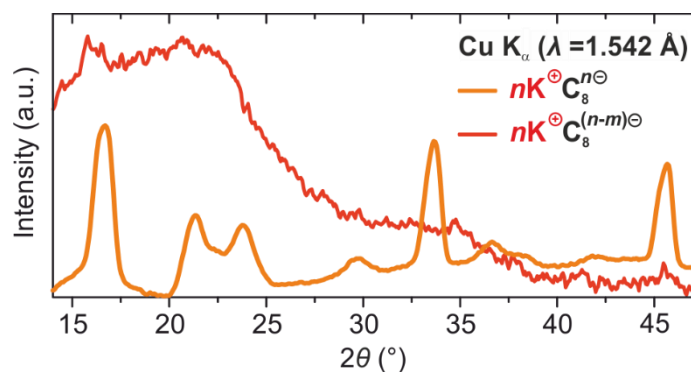
Supplementary Information



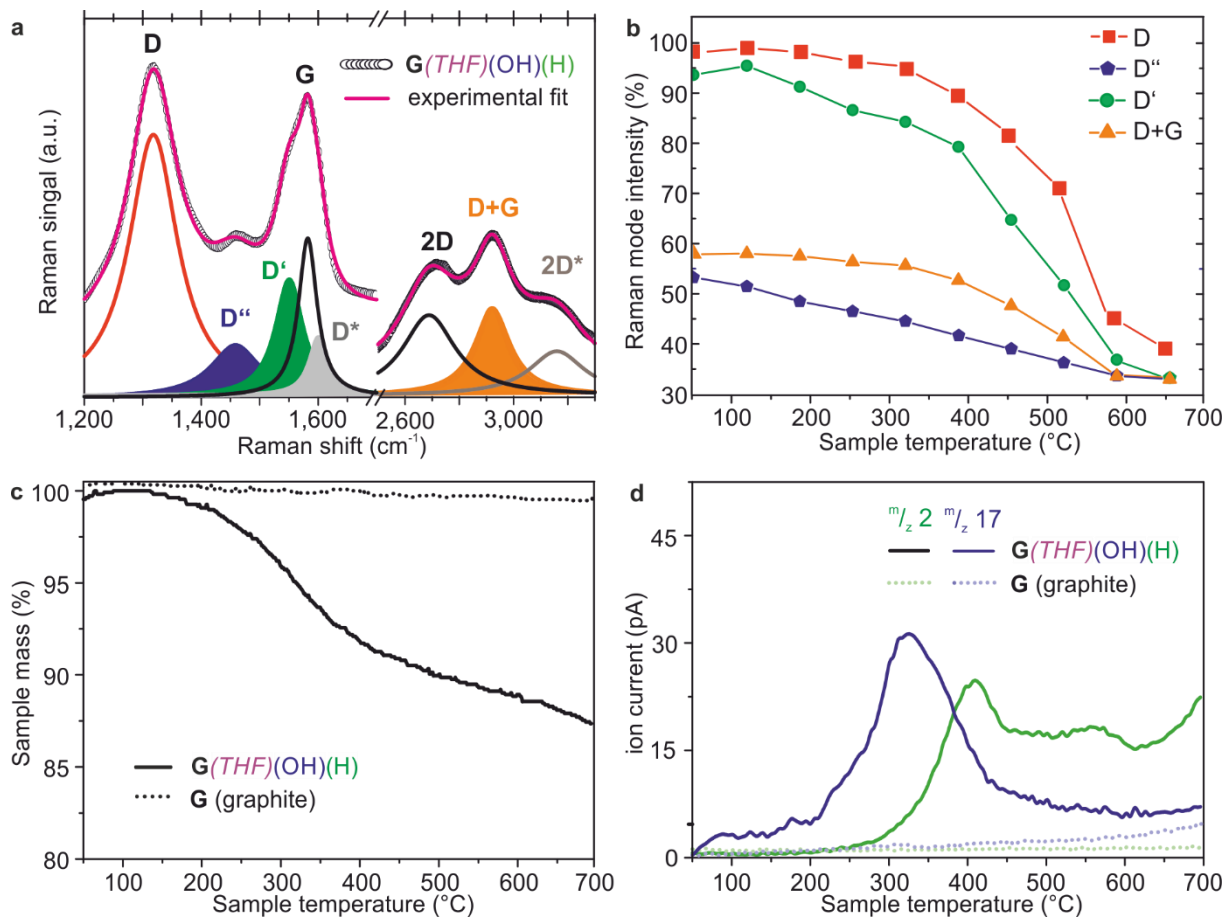
Supplementary Figure 1: X-ray diffraction analysis of the potassium intercalated graphite starting material. a) Synthesis of the stage I GIC by potassium intercalation into the SGN18 graphite. b) *In situ* Raman spectrum of KC₈ indicating saturation doping. c) XRD pattern of pristine graphite (black) and KC₈. The interlayer distance between the sheets was determined to increase from 3.35 Å (graphite) to 5.35 Å in KC₈. The black dashed lines are literature values for the position of reflections of graphite,¹ the orange dashed lines for KC₈ (full orthorhombic model)².



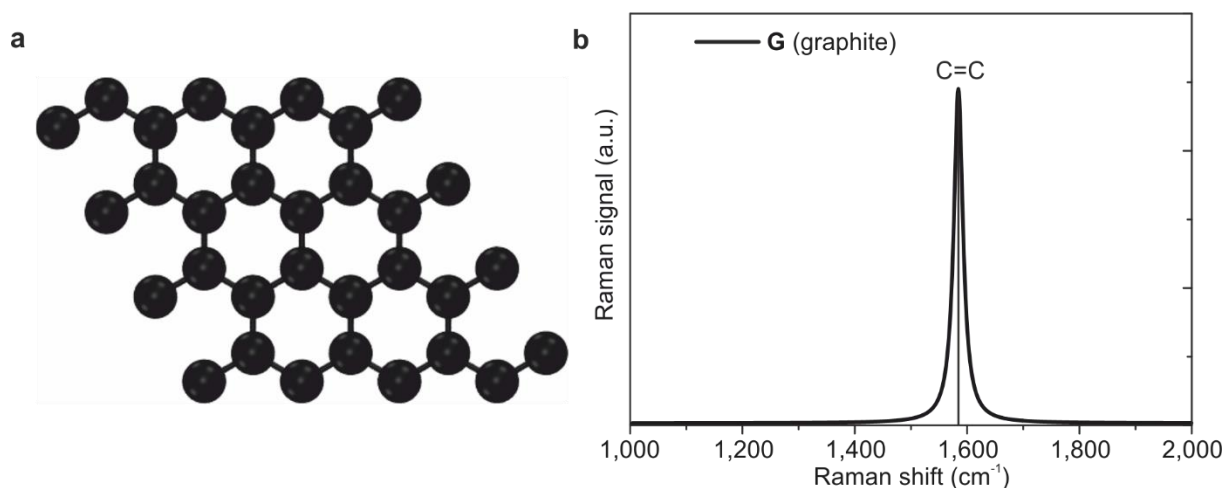
Supplementary Figure 2: Hydrogen and oxygen addition to GICs. *In situ* Raman spectroscopy of KC_8 exclusively exposed to a) molecular hydrogen H_2 and b) molecular oxygen O_2 . The Raman spectra indicate a) intercalation of molecular hydrogen without covalent addend binding and b) oxidation of the GIC in the case of its exposure towards oxygen, respectively.



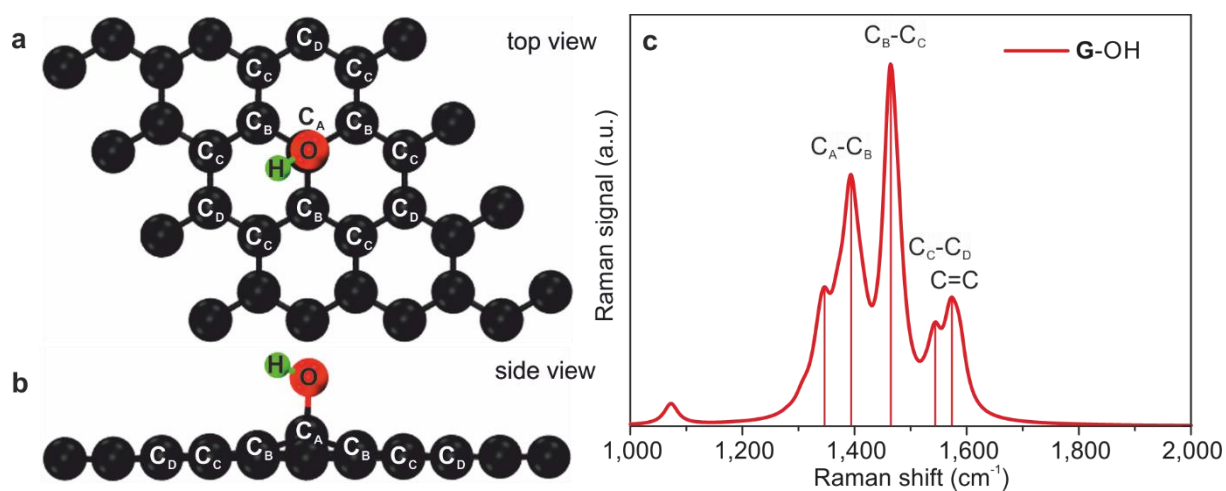
Supplementary Figure 3: XRD of oxygen treated GIC. The characteristic XRD pattern of stage I GIC KC_8 under inert conditions (orange) is compared with the pattern of the material obtained after exposure to oxygen (c.f. **Figure 2a-b**). In the latter case, no crystallinity is detected. The X-ray pattern predominantly shows amorphous carbon, with some tiny reflections indicating relicts of intercalated potassium with approximately 5.6 Å lattice distance. It has to be noted, that a small unreacted fraction of KC_8 in the bulk sample can be identified by the small reflections on top of the broad reflection in the short range of 2θ .



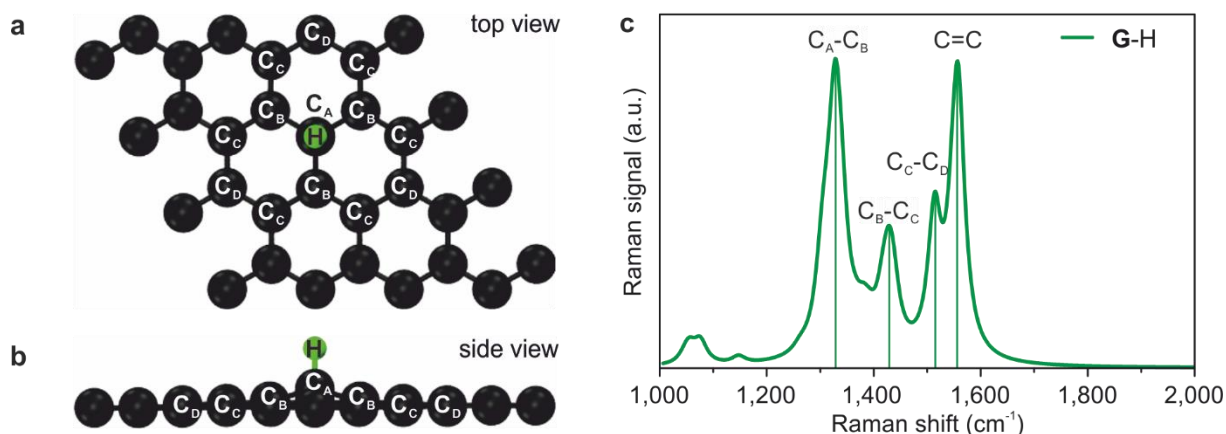
Supplementary Figure 4: TG-MS and TDRS analysis of the sample in Fig. 3. a) Raman spectrum of $G(THF)(OH)(H)$ with respective fitted modes. b) Evolution of main Raman modes upon TDRS analysis. c) Weight loss curve of pristine SGN18 (-0.1 %) and $G(THF)(OH)(H)$ (-15 %) by annealing under inert gas atmosphere (He) to 700 °C. d) Correlating MS traces for m/z 2 (H_2) and m/z 17 (OH). The TG-MS coupling proves the detachment of hydroxyl (200-400 °C) and hydrogen (350-600 °C) moieties from the sample upon heating.



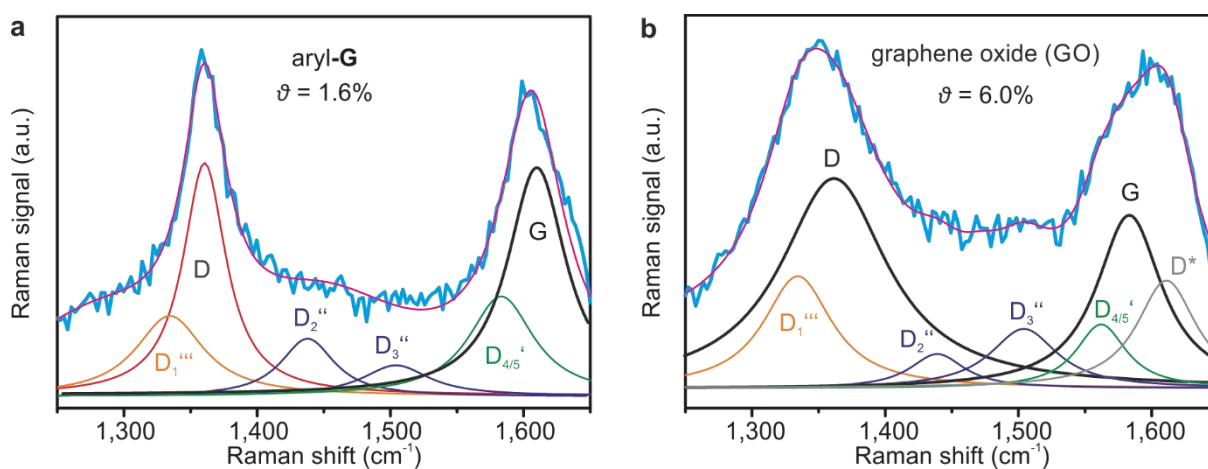
Supplementary Figure 5: Calculated reference spectrum of graphene. a) Reference pristine graphene (**G**) unit cell. b) Respective calculated Raman spectrum for pristine graphene **G** without defects.



Supplementary Figure 6: Identification and assignment of new Raman bands in G-OH. Unit cell for the simulation of hydroxylated graphene (**G-OH**). The picture shows the optimized geometric structure. a) top view indicating the basal C atom assignment surrounding the sp^3 carbon atom functionalized by -OH. b) Side view indicating the shift in z-direction due to the sp^3 hybridization. c) Calculated Raman spectrum indicating the typical fingerprint originating from the lattice carbon atoms influenced by the sp^3 functionalization with hydroxyl groups. For the detailed information on vibrational frequencies and a visualization of the modes see Supplementary Tables 1 and 2.



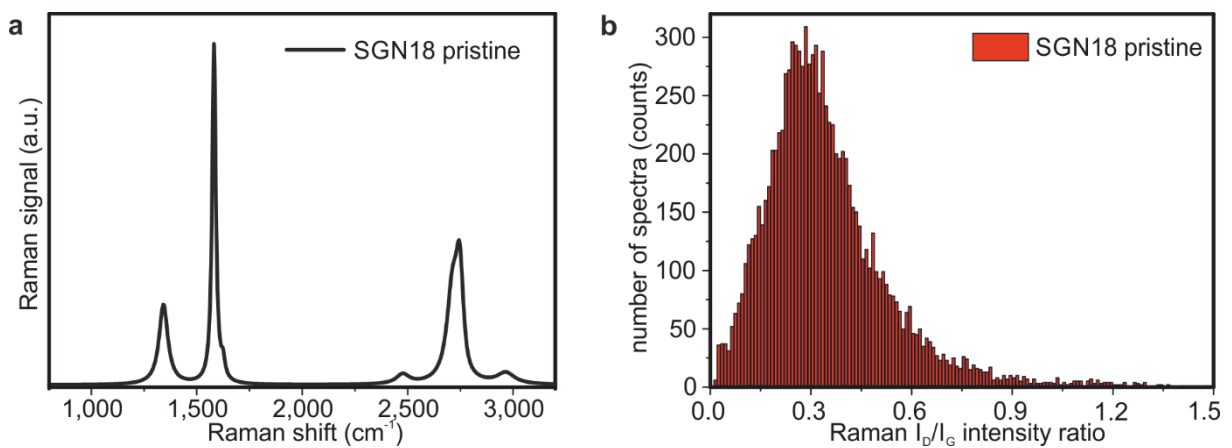
Supplementary Figure 7: Identification and assignment of new Raman bands in G-H. Unit cell for the simulation of G-H. The picture shows the geometrical optimized structure from a) top view indicating the basal C atom assignment surrounding the sp^3 carbon atom functionalized by -H. b) Side view indicating the shift in z-direction due to the sp^3 hybridization. c) Calculated Raman spectrum indicating the typical fingerprint originating from the lattice carbon atoms influenced by the sp^3 functionalization with hydrogen atoms. For the detailed information on vibrational frequencies and a visualization of the modes see Supplementary Tables 1 and 2.



Supplementary Figure 8: Bulk Raman spectra of functionalised graphene derivatives. Fitted Raman spectra for single layers of a) arylated graphene and b) graphene oxide.⁶ The fitting was carried out similar to Figure 4 in the manuscript. The identified components of the spectrum perfectly match the obtained Raman modes and can therefore be correlated. Note that for aryl-G and GO, the second D'' mode can be identified.



Supplementary Figure 9: SEM image of pristine material. SGN18 graphite under 2,500x magnification.



Supplementary Figure 10: SRS analysis of the pristine graphite material. SGN18 serving as reference. 10,000 spectra were recorded leading to a) the mean Raman signature and b) an I_D/I_G intensity distribution given in the histogram right.

Supplementary Table 1: Overview of experimental and calculated data.

a) Calculated data

graphene derivative	γ ($C_B C_A C_B$)	Δz / Å	C=C [cm ⁻¹]	C _C -C _D [cm ⁻¹]	C _B -C _C [cm ⁻¹]	C _A -C _B [cm ⁻¹]	C-X [cm ⁻¹]
G	120°	/	1,572	/	/	/	/
G-H	114.5°	0.46	1,574	1,427	1,348	1,324	2,641
G-OH	113.7°	0.60	1,576	1,464	1,393	1,346	3,614

b) Experimental Data

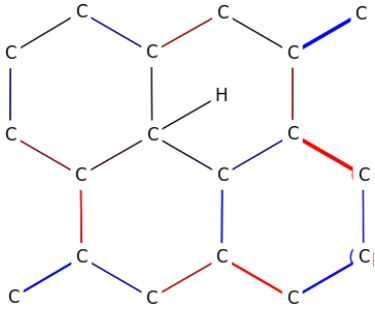
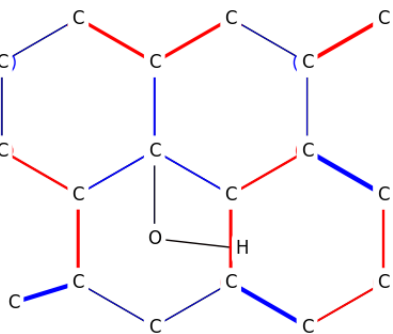
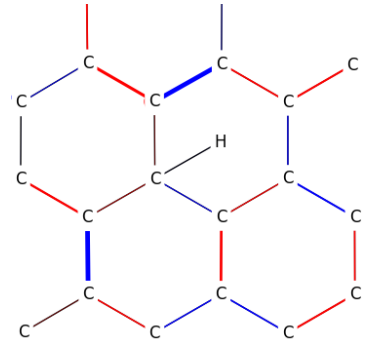
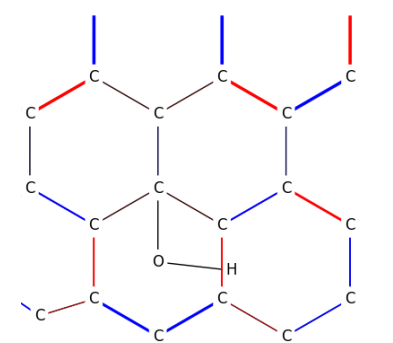
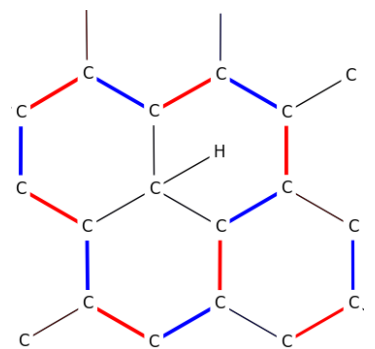
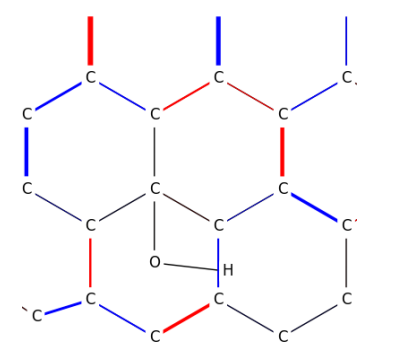
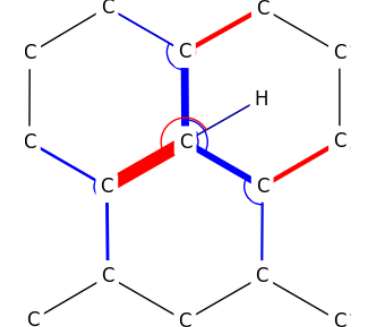
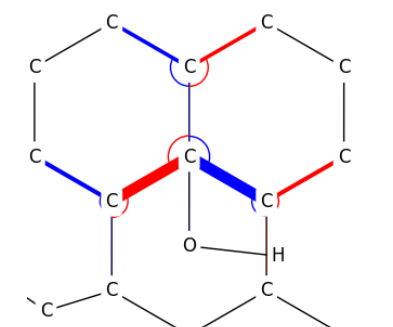
<i>in situ</i>			G-mode [cm ⁻¹]	D ₅ / D ₄ [cm ⁻¹]	D ₃ / D ₂ [cm ⁻¹]	D ₁ [cm ⁻¹]	
			1,575	1,559/1,518	1,442/1,483	1,325	
workup			G-mode [cm ⁻¹]	D' [cm ⁻¹]	D'' [cm ⁻¹]	D''' [cm ⁻¹]	
			1,576	1,550	1,458	1,325	

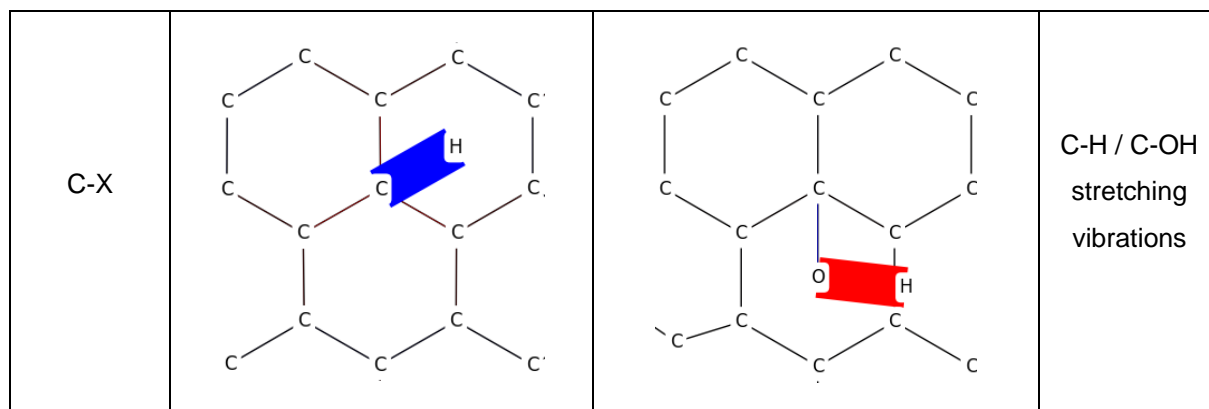
c) Overview Raman Mode Labeling

<i>calculation</i>			C=C	C _C -C _D	C _B -C _C	C _A -C _B	
<i>in situ</i>			G-mode	D ₅ / D ₄	D ₃ / D ₂	D ₁	
workup			G-mode	D'	D''	D'''	

a) Calculated data for pristine graphene **G**, hydrogenated **G-H** and hydroxylated **G-OH** functionalized derivatives (methods see ESI). The values indicate the change in dihedral angle γ , the shift of the functionalized sp^3 carbon atom out of the basal plane Δz as well as the calculated phonon frequencies for the lattice carbon atoms influenced by the introduced addend. b) Experimental data of *in situ* functionalized KC₈ (see Figure 1) and of the functionalized graphene obtained after workup (see Figure 3). c) Correlation of the Raman mode labelling used for the *in situ* functionalized material (D₁-D₅), calculated phonon frequencies (C_A-C_B, C_B-C_C, and C_C-C_D), and of the material obtained after workup (D', D'', and D''').

Supplementary Table 2: Calculated vibrational modes.

Graphene derivative	G-H	G-OH	Description of the mode
C=C			symmetric framework stretching
C _C -C _D			symmetric framework stretching
C _B -C _C			asymmetric / symmetric C ₂ mode
C _A -C _B			asymmetric stretching mode



Simplified visualization of calculated vibrational modes using QVibplot³. The thickness of the lines representing the individual modes is proportional to the stretching amplitude of the respective mode. The phase of the displacement is reflected by different colors.

References

1. Vecera, P., *et al.* Degree of functionalisation dependence of individual Raman intensities in covalent graphene derivatives. *Sci. Rep.* (2016), <http://dx.doi.org/10.1038/srep45165>.
2. Ralph W.G. Wyckoff. *Crystal Structures Vol.1*, Second edition, Interscience Publishers, New York, 7-83 (1963).
3. Laurin, M. QVibeplot: A program to visualize molecular vibrations in two dimensions, *J. Chem. Educ.* **90**, 944–946 (2013).