

Supporting Information

High Pressure Chemistry of Graphite Oxide in Presence of Ar, N₂ and NH₃

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GO/Ar

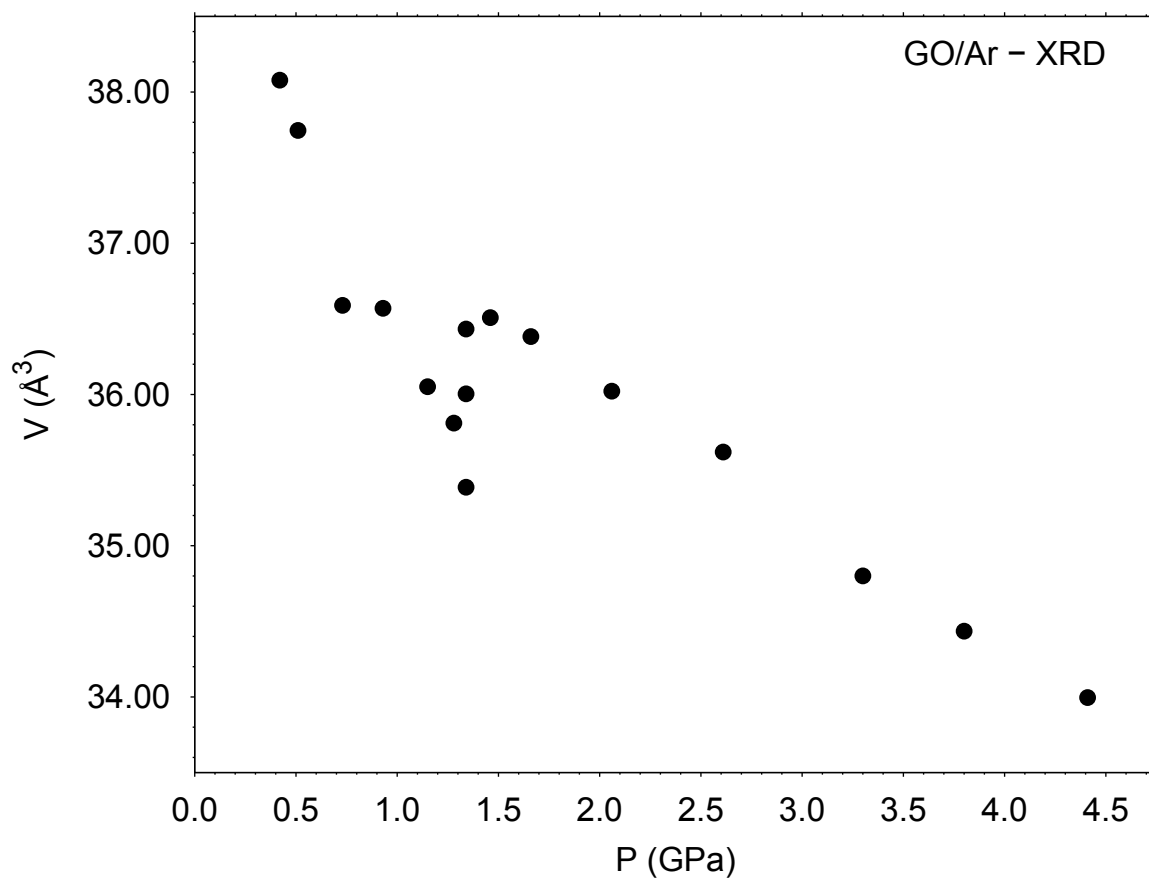


Figure S1: Pressure evolutions of the GO/Ar unit cell volume during the room temperature compression, showing the volume expansion at the solidification of Ar (1.3 GPa).

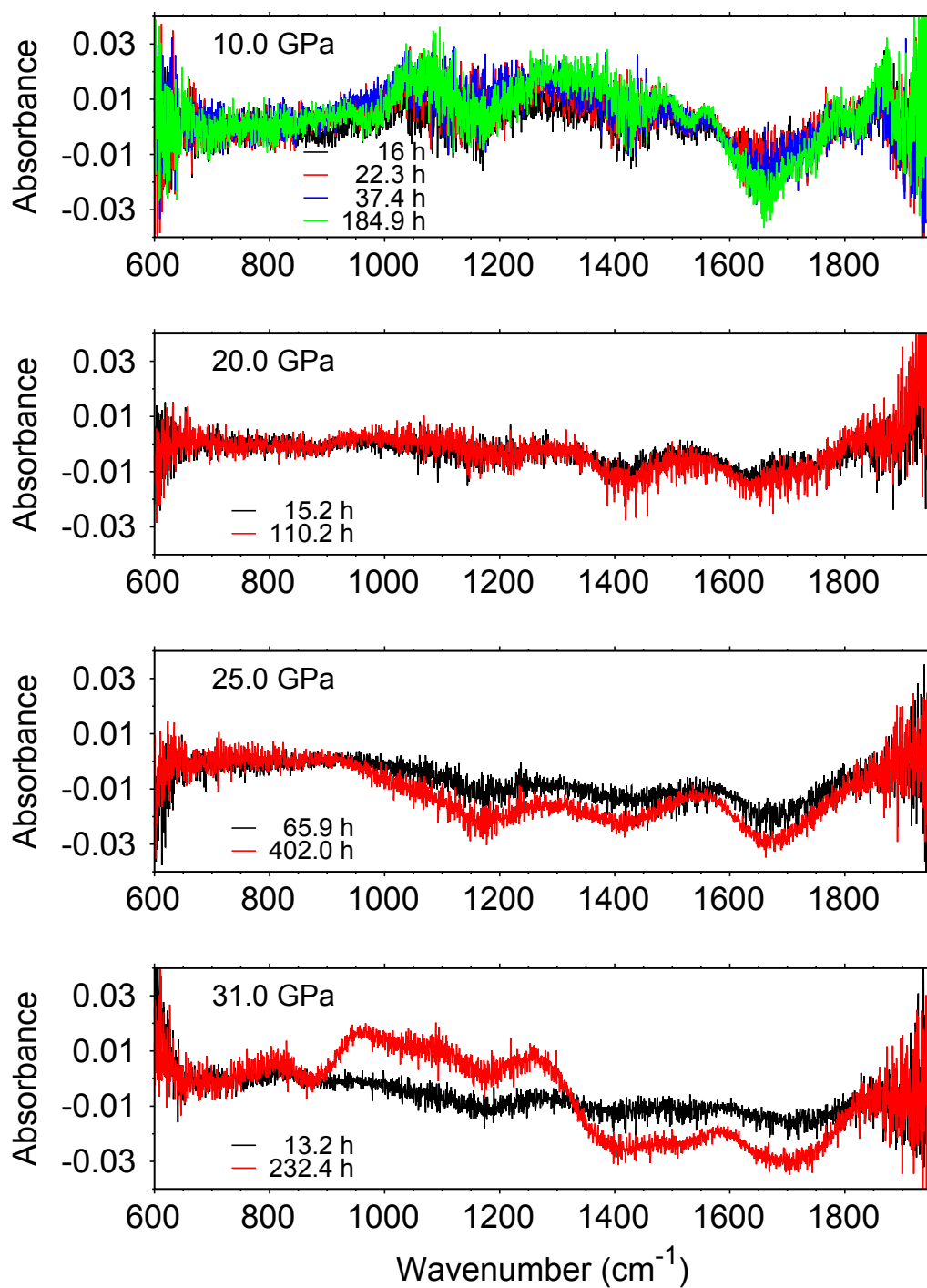


Figure S2: FTIR difference absorption spectra of the GO/Ar sample at several constant pressure values (10.0, 20.0, 25.0 and 31.0 GPa) between the spectrum acquired after the time interval indicated in the label and the spectrum acquired immediately after reaching the corresponding pressure.

GO/N₂ - irradiation

The drop cast samples have one side of the GO film ($\sim 10\text{ }\mu\text{m}$ thick) in direct contact with the bottom anvil of the DAC, whereas the remaining volume towards the upper anvil is occupied by bulk N₂. This sample geometry is such that the Raman spectra acquired in the N₂ stretching spectral range on the bottom side of the DAC mainly probe a very thin layer of N₂ molecules in direct contact with GO, whereas the spectra acquired on the top side of the sample contain contributions both from N₂ in contact with GO and from bulk N₂. The Raman spectra acquired in the N₂ stretching region on both sides of the sample show the presence of two components: a broad low frequency (2331.1 cm^{-1}) one and a narrow high frequency one (2331.5 cm^{-1}) (inset in Figure S3). However, whereas on the bottom side, only the low frequency one is observed, on the top side both components can be appreciated. The assignment of the high frequency component to liquid N₂, whose frequency position is in agreement with the literature data, is confirmed by focusing the Raman laser in the bulk N₂, rather than on the GO surface and observing the disappearance of the low frequency component. This observation and the presence of the low frequency component in the spectra acquired on the bottom side of the sample, suggest the assignment of the 2331.1 cm^{-1} band to N₂ molecules interacting with the GO and likely hosted within the first few layers of this materials, penetrated by the Raman laser wavelength.

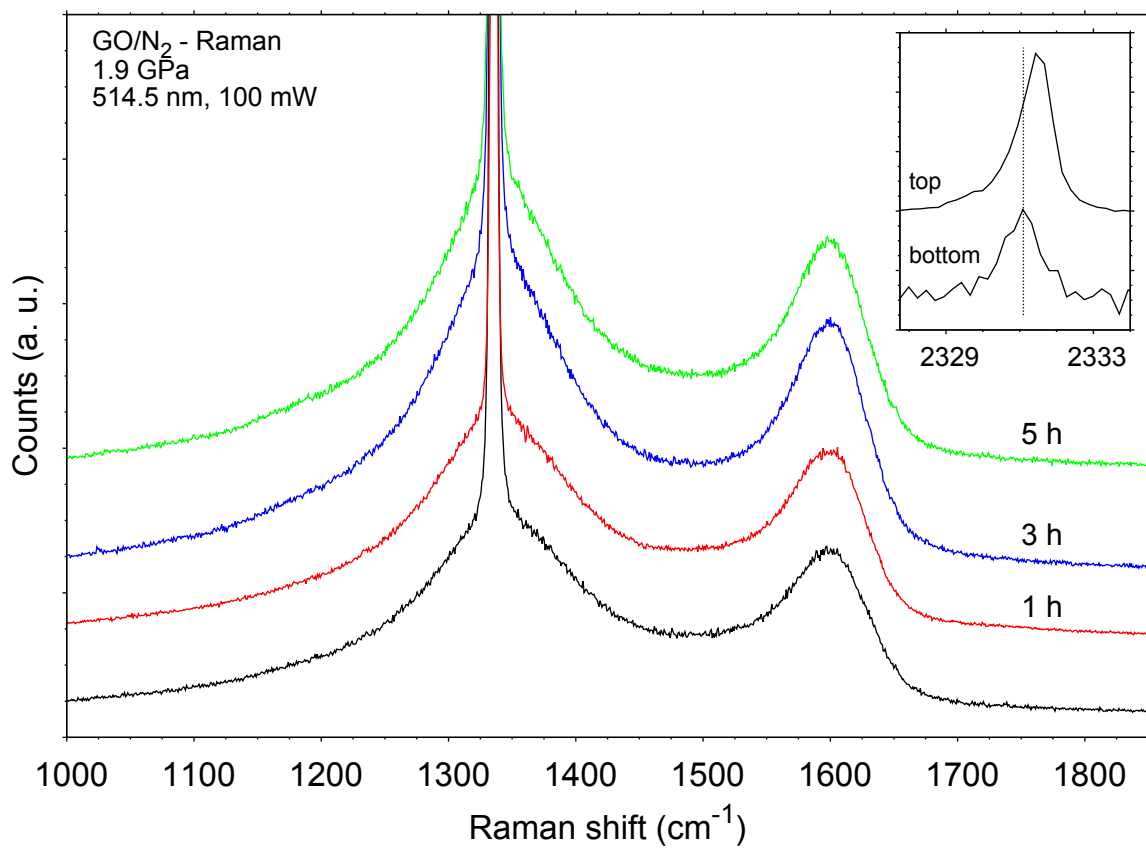


Figure S3: Spectra of the GO/N₂ sample at 1.9 GPa acquired before irradiation (bottom trace) and after three successive irradiations (514.5 nm) of the same power (100 mW) and increasing duration (1^o 1 h, 2^o 3 h, 3^o 5 h). In the insight the Raman spectra acquired in the N₂ stretching region on the top and bottom sides of the sample are shown.

GO/N₂ - heating

The infrared spectra indicate that a strong decrease of the transmission signal occurred upon increasing the temperature and an infrared spectrum of the sample could be acquired only after the first heating at 100 °C. An increase of the absorption intensity is observed in the spectral region between 800-1800 cm⁻¹, where the absorption profile after heating closely reminds that observed in the irradiated sample, as better appreciated in the difference absorption spectra (Figure S4). The characteristic bands assigned to the bending (663.5 cm⁻¹) and antisymmetric-stretching modes of CO₂ appear after heating, with the stretching mode showing two components at 2342.4 and 2351.4 cm⁻¹ as in the case of the irradiated sample.

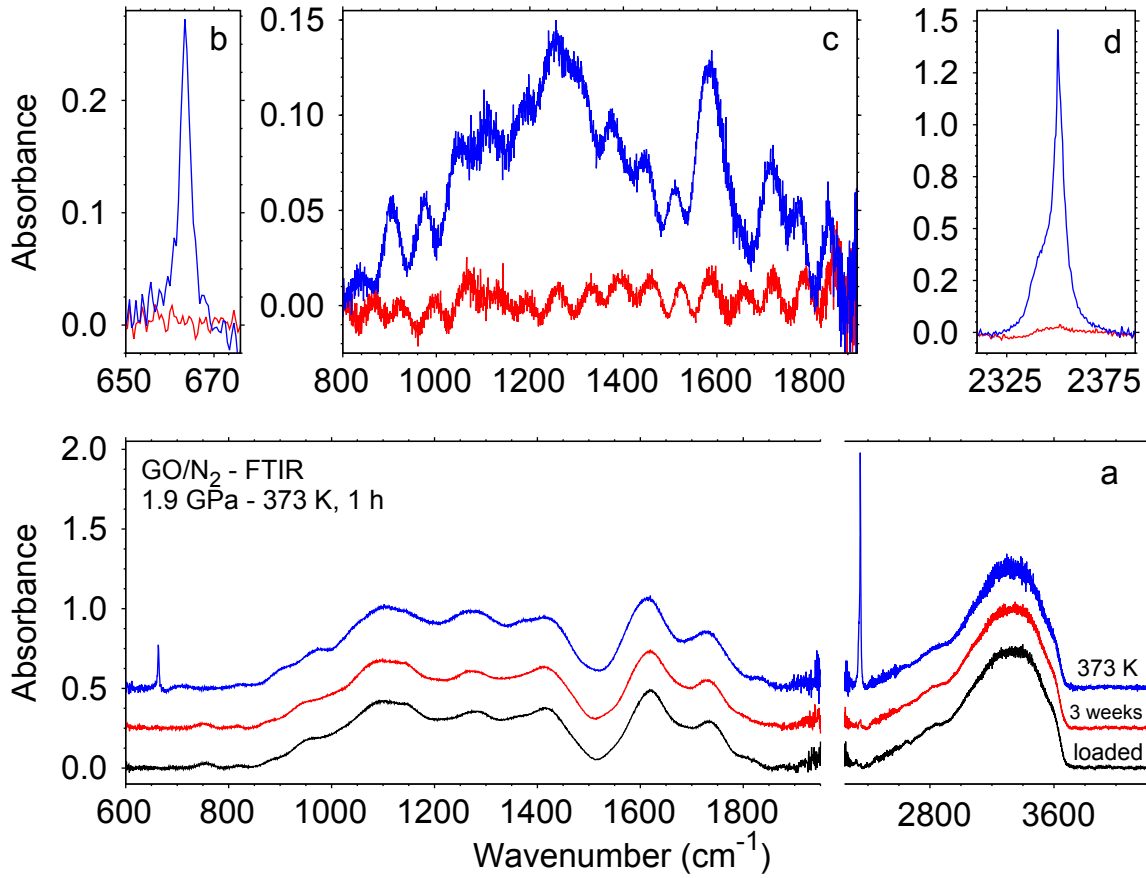


Figure S4: a) evolution of the FTIR spectra of GO/N₂ at 1.9 GPa before heating, after 3 weeks and after the 1^o heating (373 K, 1 h). The break on the Wavenumber axis corresponds to the saturating absorption of the diamond anvils. Upper panels: difference absorption spectra of the spectra reported in the lower panel with respect to the first one (black trace), in the characteristic absorption region of GO between 800-1800 cm⁻¹ (c) and in the bending (b) and anti-symmetric stretching (d) regions of CO₂.

The Raman spectra acquired before and after the first (373 K, 1 h) and second heating treatment (473 K, 1 h) are reported in Figure S5, whereas a comparison between the Raman spectra of the starting GO and of the recovered GO/N₂ samples after the irradiation and after the heating are reported in Figure S6, together with a mathematical fit of the Raman spectra of GO in the region between 1100-1800 cm⁻¹, indicating a slight decrease of the I_D/I_G value after irradiation and heating (see Figure S6 and Discussion in the manuscript). Finally, we report the FTIR difference absorption spectra for both irradiated and heated

samples in respect to the initial conditions (Figure S7).

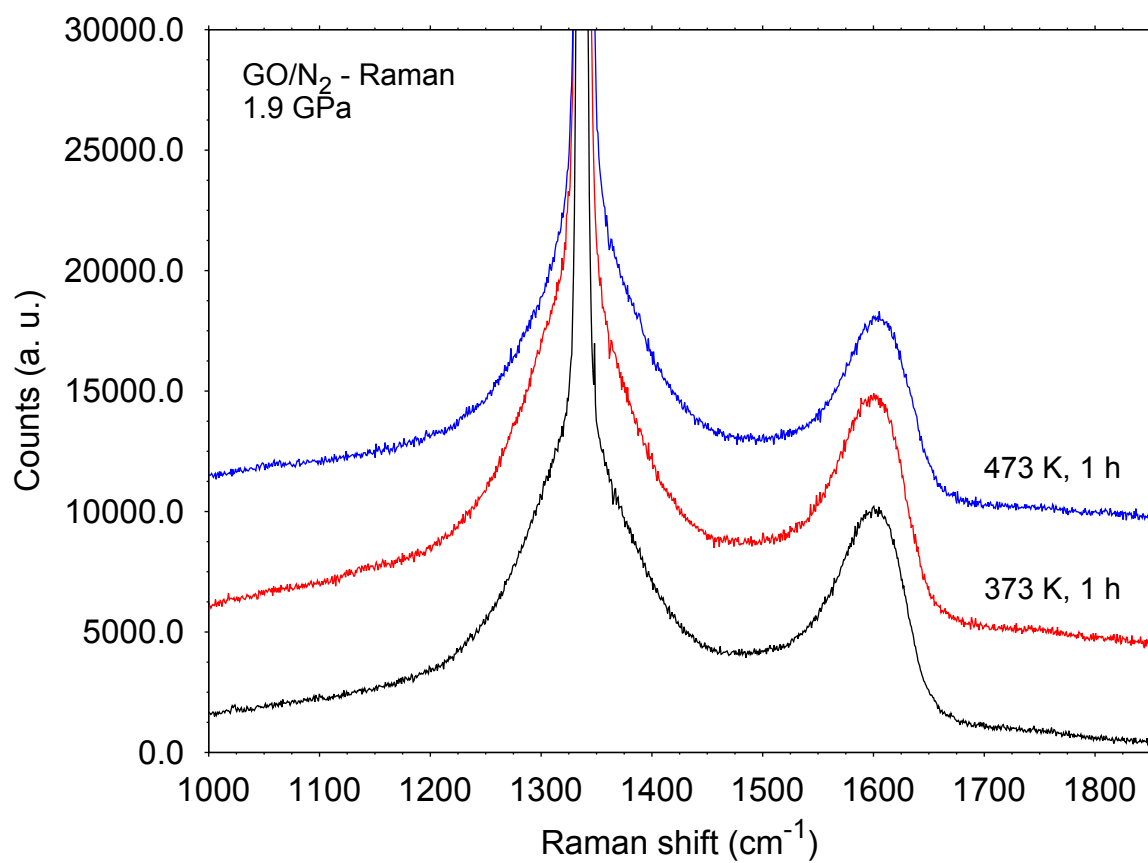


Figure S5: Raman spectra of the GO/N₂ sample at 1.9 GPa before heating and after two successive heatings (1 h) at 373 K and 473 K.

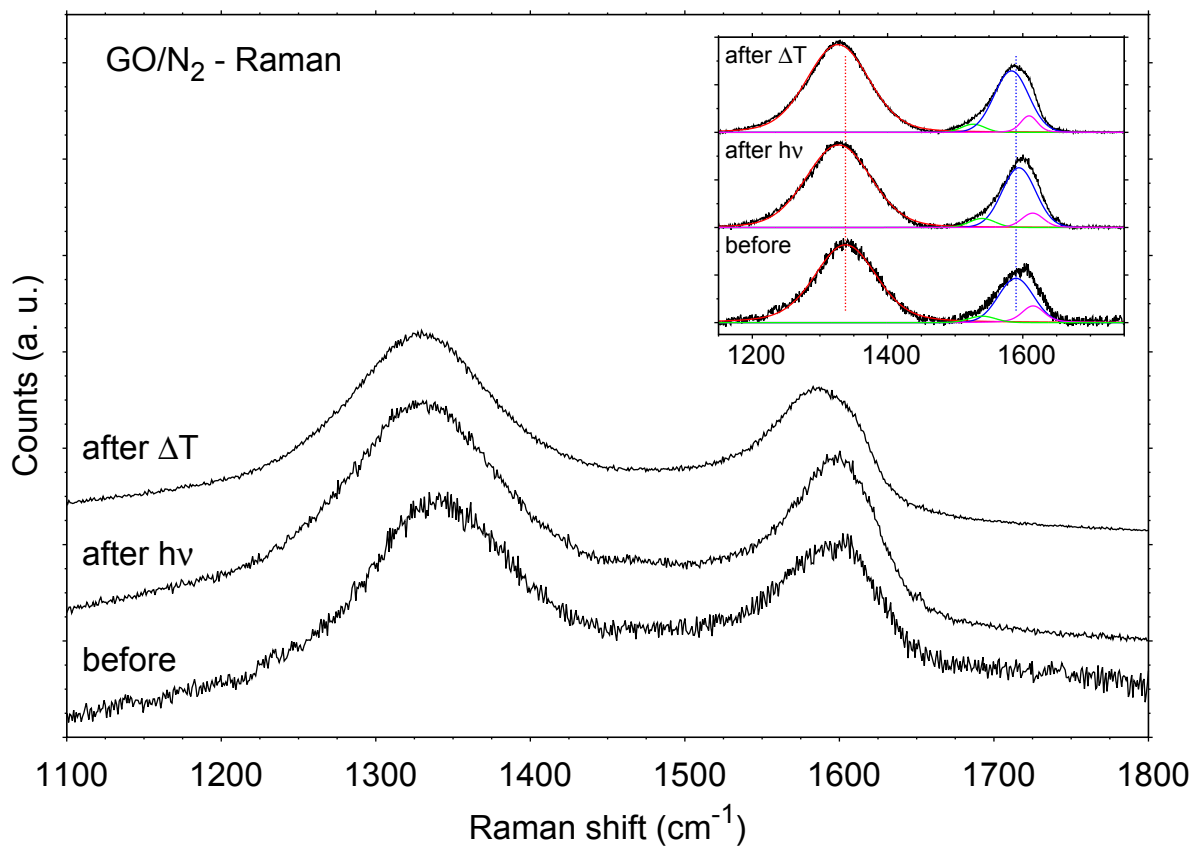


Figure S6: Raman spectra of the starting GO before any treatment (bottom trace) and of the recovered GO/N₂ systems after irradiation (middle trace) and after the heating (upper trace). In the inset a fit for the three spectra after background subtraction is reported. The unassigned 1540 cm⁻¹ band is an auxiliary fit component introduced according to other literature Raman data^{1,2} to take into account the asymmetry of the spectral profile. In order of increasing frequency the other three components correspond to the D, G and D' bands, according to the Raman analysis of graphite-like systems.

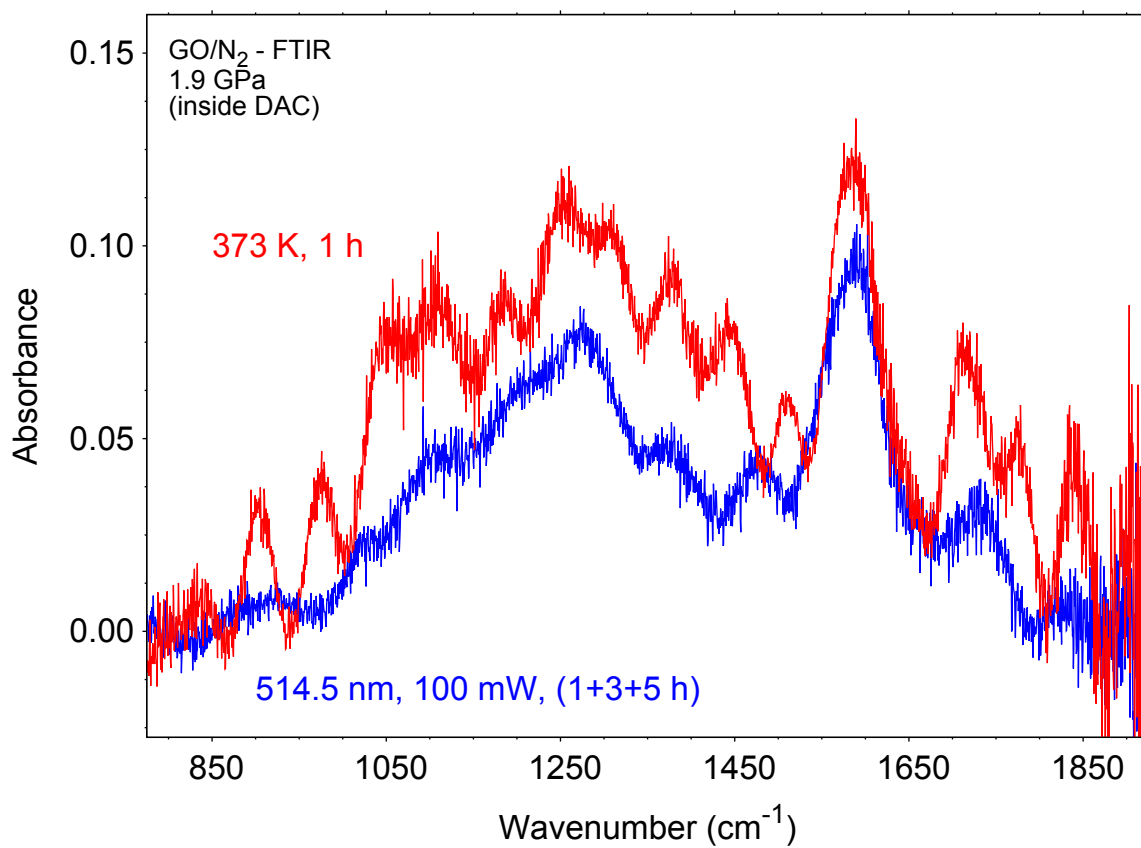


Figure S7: FTIR difference absorption spectra in the 800-1800 cm⁻¹ frequency region between the irradiated (blue) and heated (red) samples with respect the spectra acquired before irradiation and heating, respectively, at the same pressure (1.9 GPa).

GO/NH₃ - High pressure photo-excitation in solid NH₃ (514.5 nm)

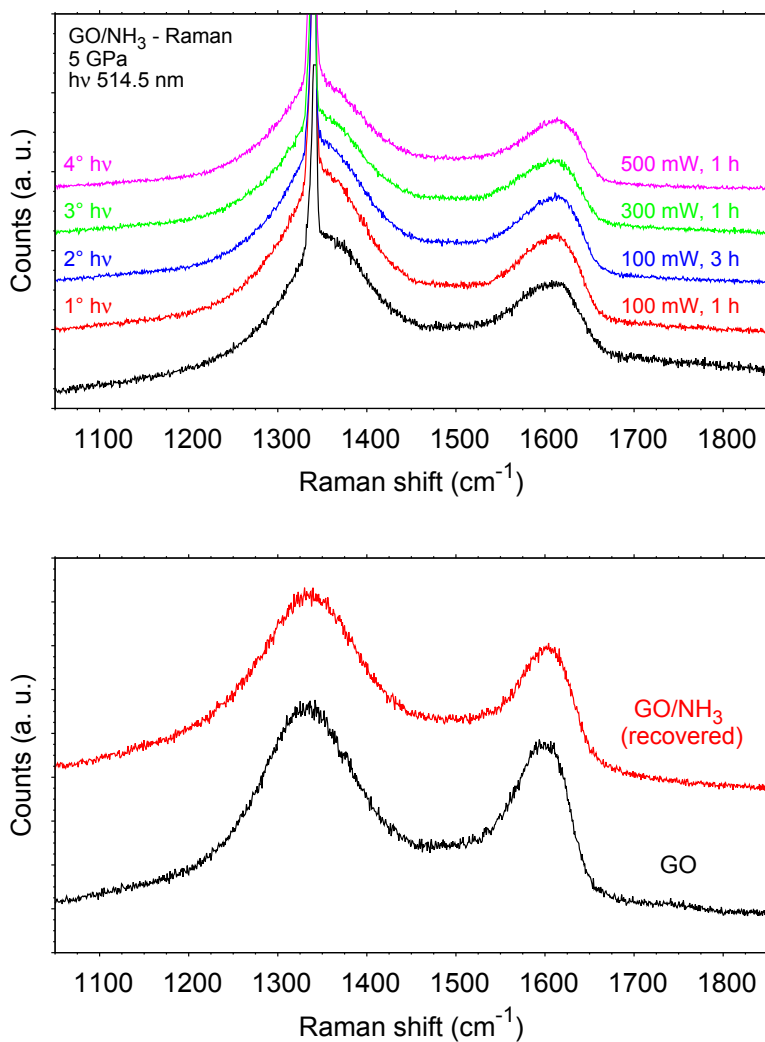


Figure S8. Upper panel: Raman spectra of the GO/NH₃ sample acquired before (lower trace) and after each irradiation at 5 GPa with the 514.5 nm wavelength. The sharp band at 1330 cm⁻¹ is due to the Raman signal of the diamond anvil. Lower panel: Raman spectra of the starting GO sample before loading NH₃ and of the recovered GO/NH₃ sample acquired at ambient conditions outside the DAC after the irradiations.

GO/NH₃ - High pressure photo-excitation in liquid NH₃ (UVML 350 nm)

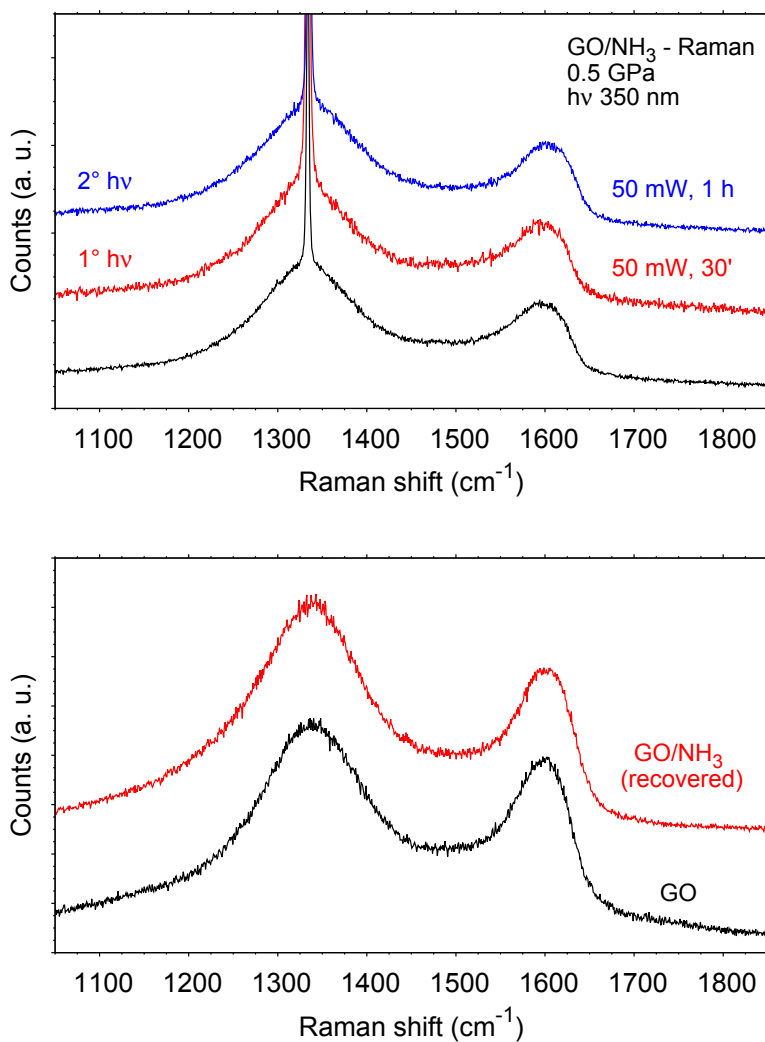


Figure S9: Raman spectra of the GO/NH₃ sample before and after two successive irradiations at 0.5 GPa of the same power (50 mW) and different duration (30' red trace and 1 h blu trace). Lower panel: Raman spectra acquired on the starting GO and on the GO/NH₃ recovered sample after the irradiations.

References

- (1) Xu, L.; Cheng, L. Graphite Oxide under High Pressure: A Raman Spectroscopic Study. *J. Nanomater.* **2013**, *731875*, 1 – 6
- (2) Kaniyoor A, Ramaprabhu S. A Raman Spectroscopic Investigation of Graphite Oxide Derived Graphene. *AIP Adv.* **2012**, *2*, 032183-1 – 032183-13.