

Proposal Code CH- 4116

Proposal Title High-pressure synthesis of novel nanocomposite materials based on nitrogen doping of graphene oxide

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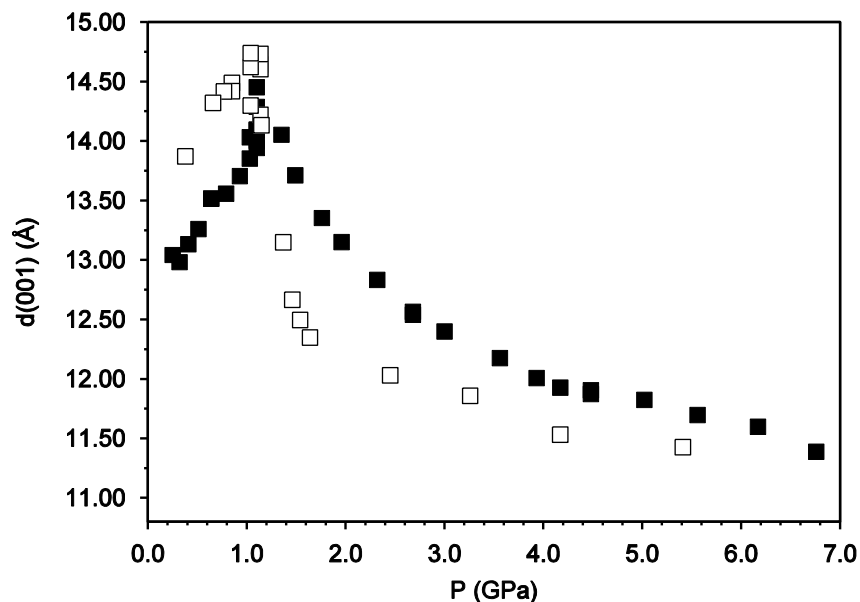
In this proposal we have studied the pressure induced insertion of argon, nitrogen and ammonia between the planes of graphene oxide (GO) by XRD experiments performed at ID09A. GO is characterized by an enhanced interlayer spacing with respect to graphite due to the presence of several functional groups. As a consequence, the insertion of molecular systems between the planes is facilitated especially when a high external pressure is applied. Once the molecules are properly inserted, their spontaneous reactivity, or eventually driven by photochemical or thermal mechanisms, with the GO functional groups represents an interesting approach for obtaining a variety of innovative carbon based materials potentially recoverable to ambient conditions. However, the knowledge of the filling mechanism and of the structural changes determined by the filling is preliminary to the chemistry.

Membrane DAC loaded with pure GO, GO and Ar, GO and N₂, GO and NH₃ were prepared in Florence where we had already performed FTIR and Raman experiments directed to the characterization of the same samples as a function of pressure. As expected the signatures of the filling were not evident in these experiments and could be extracted only indirectly by the comparison of the spectral features measured in GO before and after the compression. As a matter of fact, X-ray diffraction was mandatory to probe how the spacing between the layers is affected by pressure and the use of synchrotron radiation is dictated by the sample characteristics: few thin layers of low Z atoms in a DAC. The employment of the four different samples is due to the need to compare which is the effect of compression when the interlayer spacing is and is not filled by guest molecules. In addition, the run with Ar is necessary to have a medium that should not be reactive to be compared with N₂ and NH₃. The latter two molecules are indeed of interest because the incorporation of nitrogen in graphene oxide layers is a key issue for a twofold reason: enhancing the catalytic activity and introducing chemical functionalities containing N atoms, the first step to activate further selective functionalizations.

X-ray powder diffraction patterns were acquired on the four different samples during room temperature compression and decompression cycles, the corresponding EOSs were determined. Pure GO was compressed up to 13 GPa, GO/Ar up to 4.4 GPa, GO/N₂ up to 5.6 GPa and GO/NH₃ up to 6.8 GPa. The comparison of the data collected in the GO/Ar and GO/N₂ samples, and those acquired on pure GO unambiguously revealed the successful insertion of these atoms/molecules between the planes. In fact, after the decompression the interlayer spacing in pure GO was found to decrease by 10% with respect to the starting material, whereas both in GO/Ar and GO/N₂ samples the initial d spacing was entirely recovered attesting the presence of interlayer soft matter to prevent the collapse of the layered structure. As expected, much more important are the data collected in the GO/NH₃ sample which also represents the most attractive system from chemical point of view.

In contrast to what observed in pure GO, GO/Ar and GO/N₂ the XRD patterns of GO/NH₃ provide evidence for a particular behavior of the 001 diffraction peak, related to the separation between the planes, which exhibits a shift to low angles on compression up to 1.1 GPa, pressure where a shift inversion towards high angle values occurs up to the highest investigated pressure (see figure). This behavior is characteristic of auxetic materials and corresponds to an increase of the interlayer spacing due to the insertion of liquid ammonia. This effect is remarkable as it corresponds to a 10.8% increase in the d-spacing from 0.2 to 1.1 GPa. Above 1.1 GPa, where solidification of NH₃ takes place, the spectra show an inversion in the pressure evolution of the 001 peak position to high 2θ values, indicating a continuous decrease of the interlayer spacing up to the maximum investigated pressure. Correspondingly, the pressure evolution of the unit cell volume closely follows that of the interlayer spacing, exhibiting a negative compressibility in the pressure range between 0.2 and 1.1 GPa with a 10.5% increase. A reversible behavior affected by some hysteresis is observed during decompression. Complementary spectroscopic studies performed at LENS have shown that once NH₃ is unloaded after the decompression, a chemical modification of both the functional groups and of the basal plane of the pristine material is evident. These chemical modifications occur both in purely compression experiments as well as the sample is treated by laser light at high pressure. These results appear extremely interesting opening new perspectives for high pressure chemical doping and functionalization of GO and for the synthesis of new advanced carbon based nanostructured materials.

A manuscript discussing the GO/NH₃ data is ready to be submitted whereas another manuscript containing the GO, GO/Ar and GO/N₂ data is in the preparation stage.



Pressure evolution of the interplane distance during compression (full symbols) and decompression (empty symbols).