Graphite oxide (GO) is known since the middle of the XIX century. In the latest years it has attracted a renewed interest as a precursor for a cheap large-scale production of graphene. Indeed, GO conserves graphite layered structure with an expanded interlayer distance that facilitates exfoliation. A subsequent reduction yields a material whose properties are very similar to those of graphene but strongly depend on the local structure and stoichiometry. However, many questions remain still open about GO and reduced GO (RGO) chemical homogeneity and the functional groups effectively present.

In previous spectroscopy studies the oxygen content in GO ranges from 22% to 32%. However, TEM images revealed that GO is very inhomogeneous at the nanometer scale. Still, no spatially resolved spectroscopic studies have yet been reported and only average evaluations are provided in literature. EELS in a STEM could give access to the suitable scale but GO and RGO are highly sensitive to irradiation.

In this study we overcame this limitation by adopting an experimental set up combining a liquid nitrogen cooling system at the sample stage, a low accelerated electrons beam (60 keV) and a liquid nitrogen cooled CCD camera with a low read-out noise of three counts r.m.s. and a negligible dark count noise. Hyperspectral core EELS images have been acquired in a low dose mode (order of $10^5$ e$^{-}$ nm$^{-2}$) at a 10 nm spatial resolution.

Chemical maps for GO and RGO (see figure) show regions within individual flakes with different oxidation levels. Whereas oxygen rates averaged over the whole area are in agreement with literature, we observe that the oxygen content can locally rise up to 60%.

Lower oxidized GO regions present a fine structure at the carbon K-edge similar to amorphous carbon, while highly oxidized regions show specific core EELS signatures. RGO samples display the well-known fine structure profile of graphite, proving an excellent restoration of the carbon network. Nevertheless regions characterized by residual oxygen exhibit an additional sharp peak.

These results have been combined with complementary DFT analysis of formation and binding energies for different oxygen functional groups and concentrations and EELS spectra simulations. This allowed us to provide a new structural model compatible with our experimental findings. We suggest a full functionalization with hydroxyl groups in the strongly oxidized regions, while in lower oxidized regions also epoxide groups are expected.

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Fig. 1: EELS hyperspectral analysis of Graphene Oxide and Reduced Graphene Oxide: oxygen concentration maps, associated histograms and carbon K-shell EELS edges extracted from the selected regions.