Tuning Graphene Oxide electronic properties through low-temperature thermal annealing

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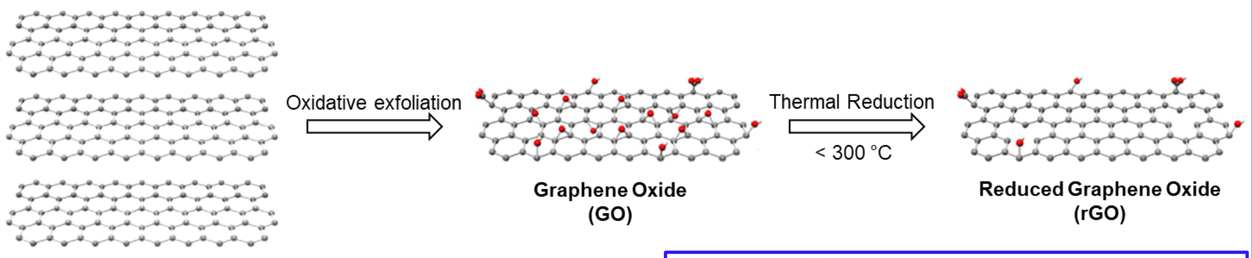
Abstract

Graphene Oxide (GO) is a single-atom layer of carbon with both the sides and area of the flake functionalized with groups containing oxygen such as, epoxide hydroxyls, ketones and carboxyl acids.[1–4] The presence of these functional groups makes the flakes well dispersible in water making them easy to be processed. However, GO is not suitable for application electronics due to insulator behavior for the presence of oxygenated functional groups. To restore the conjugation into the carbon framework, removal of oxygen atoms from the flake surfaces is needed and several methods have been investigated in these years.[5,6] Among the vastness of protocols studied, GO thermal reduction is one of the most promising route due to the absence of chemical reagents involved in the process that does not require any further purification steps.[5,7,8] We investigated the thermal reduction of GO in a range of temperature < 300 °C in air and inert atmosphere, characterizing the chemical modification on the flakes surface via XPS and solid-state NMR spectroscopy. The change of oxidation degree in GO by varying the reduction temperature and the atmosphere leads to chemically different materials with different electronic behaviors. Those differences have been highlighted by measuring the electrical resistivity on thin films and using the different thermally reduced GOs as electrodes in supercapacitors..

Introduction

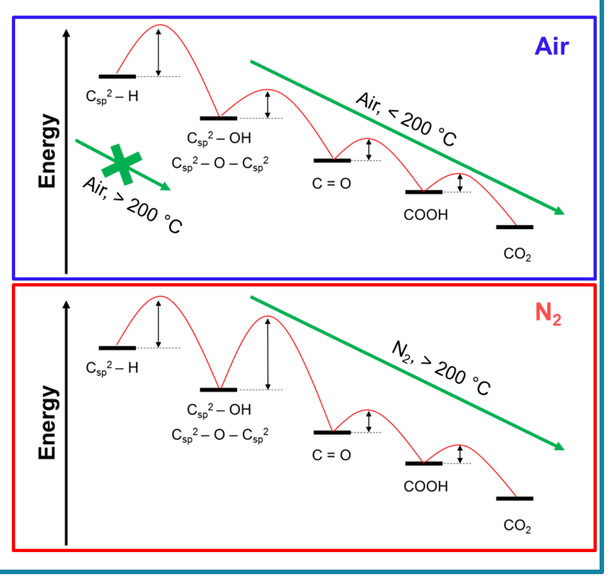
Graphene Oxide (GO) is one-atom layer of carbon atoms with oxygen containing functional groups attached to both sides of the plane and, they make GO a good electrical insulating material interrupting the conjugation between Csp^2 atoms.[1–4] It can be produced through Hummer's method in high scale from graphite.[9] To restore the Csp^2 conjugation and therefore restoring the conductivity properties, the reduction to reduced GO is needed. Among the vastness of the reduction processes, the thermal reduction is one of the cleanest method. To make this method suitable with different substrates, where GO can be deposited, relatively low reduction temperature are wanted.



Graphite

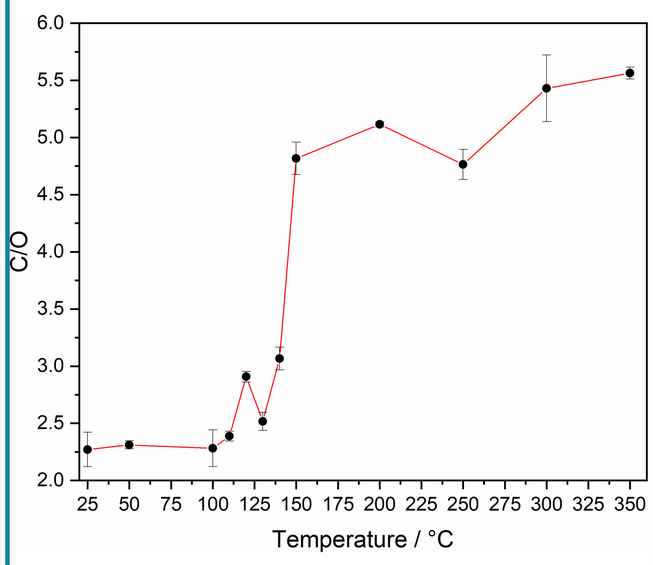
$$GO \xrightarrow[\Delta]{\text{Air or } N_2} rGO + CO_2 + CO$$

In this work we investigated temperatures of annealing lower than 300 °C performing the thermal reduction in inert atmosphere (Ar or N_2) or Air. The experiments highlights that a good degree of reduction of GO can be achieved with temperature between 150 and 200 °C in Air. This result can be reasonably explained taking in consideration the step-wise CO_2 releasing process. The oxidation of Csp^2-OH and Csp^2-O-Csp^2 moieties is favored at 200 °C in Air with respect to the oxidation of Csp^2-H. Therefore, it is possible to achieve the elimination of oxygenated carbon without promoting the ignition of the material. The reduction in inert atmosphere can be achieved with minimum temperature >200 °C, which is the temperature to promote the oxygen reorganization on the GO surface to promote CO_2 release.



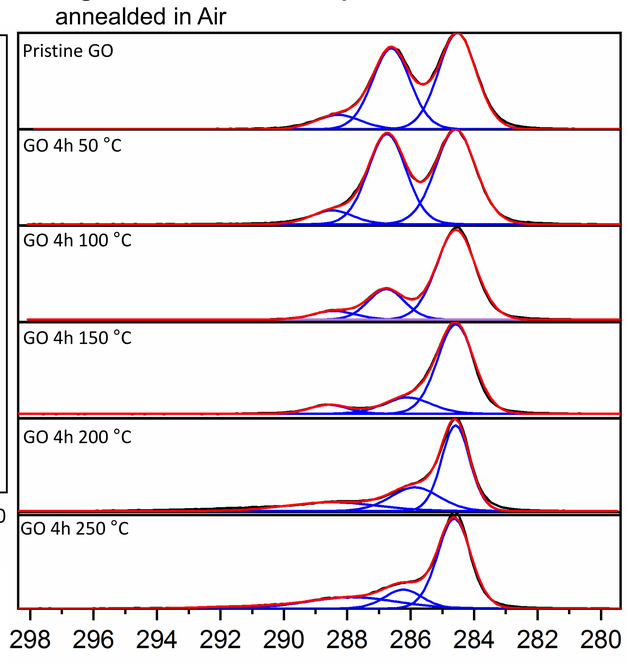
Structural Characterizations

C/O ratio from **XPS** of GO thermal annealed in Air

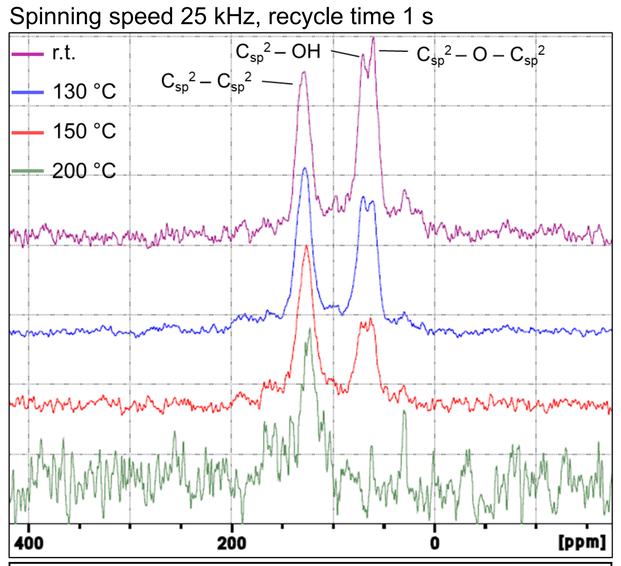


XPS C/O ratio of GO annealed in Air in a range of temperature between 25 and 350 °C shows a sigmoidal trend. It is constant from 25 to 130 °C and then it starts to increase dramatically from 150 to 200 °C. In the last segment from 250 to 350 °C it is almost constant again. Temperatures above 350 °C were not explored because the ignition temperature of GO is 347 °C.[10] The High Resolution XPS of C1s shows a clear decreasing of C-O peak (287 eV) from 150 °C. These results are confirmed by ^{13}C Solid-State NMR that shows a constant decrease of hydroxyl and epoxyl peak (75 ppm), reaching the flattening of the peak at 200 °C. X-Ray Powder Diffraction of GO thermal annealed from 100 to 150 °C in Ar shows a slightly shift of GO peak from 10° to 12° and GO annealed at 200 °C shows mainly the peak referred to graphene at 23°. GO annealed in Air shows almost the same shift for the peak at 10°, but the peak at 23° starts to be the most relevant already at 150 °C, confirming that the partial reduction of GO can be obtained starting from 150 °C in Air.

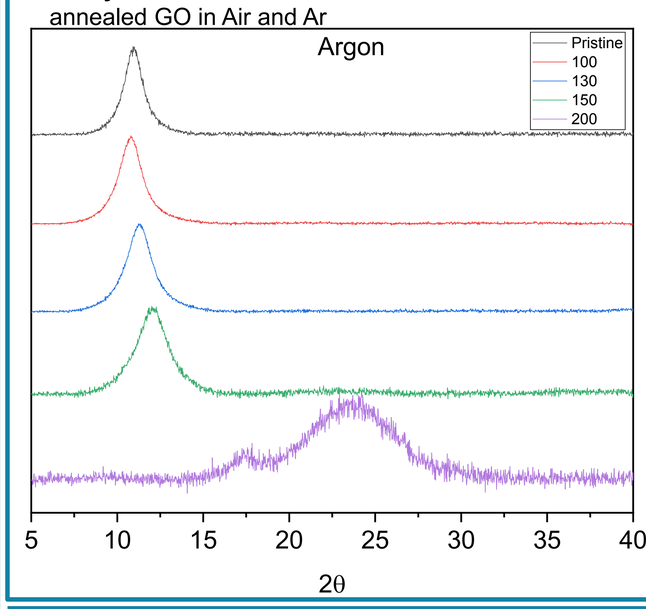
High resolution XPS C1s peaks of GO thermal annealded in Air

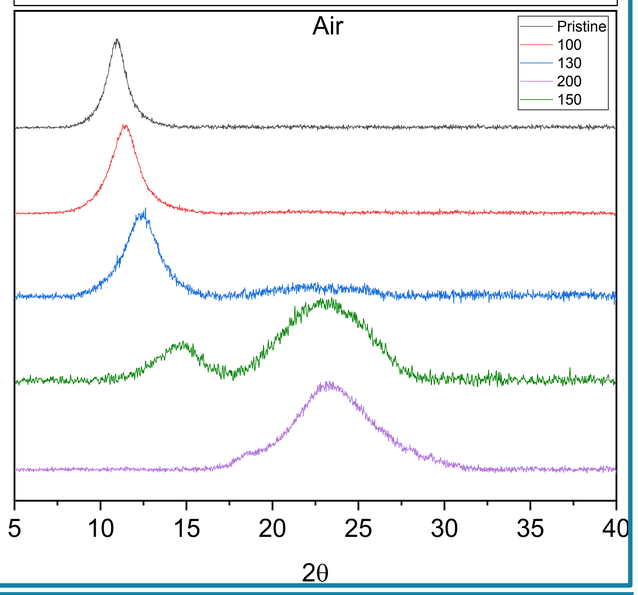


500 MHz, DP-MAS, ^{13}C
Spinning speed 25 kHz, recycle time 1 s



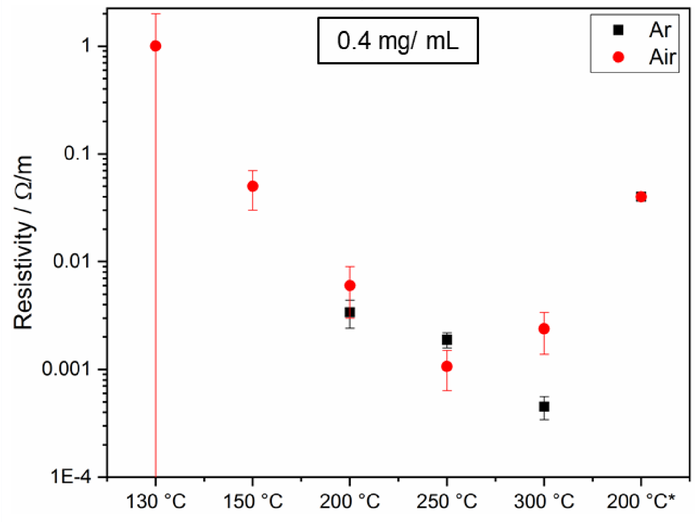
X-Ray Powder Diffraction of thermal annealed GO in Air and Ar



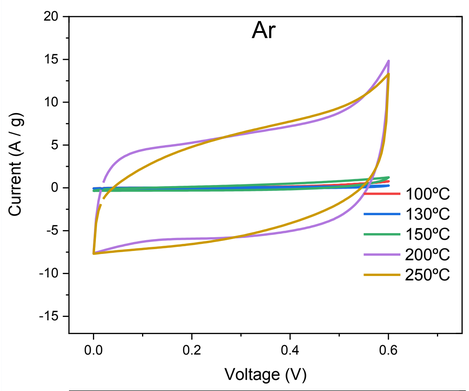


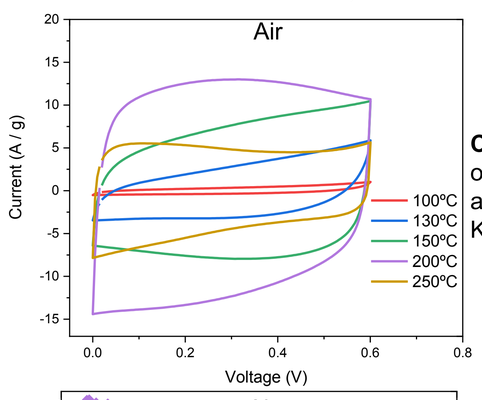
Electrical Characterizations

Four Point Probe resistivity measurement of thermal annealed GO drop casted on glass slides.

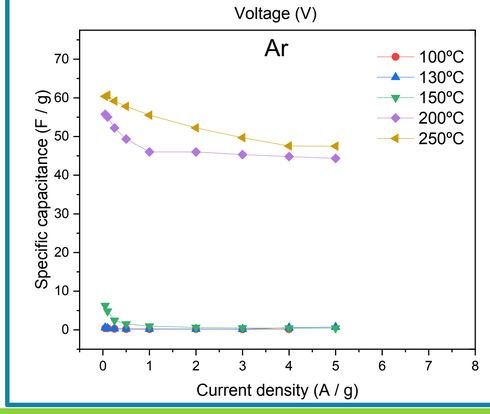


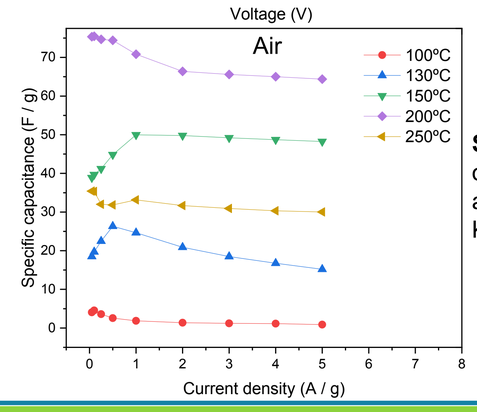
The resistivity measured of thermal annealed GO in inert atmosphere (Ar) is higher than the detection limit of the instrument for temperature lower than 150 °C. From 200 °C to 300 °C, the resistivity decreases constantly from $3*10^{-3}$ to $4*10^{-4}$ Ω/m. On the contrary, the thermal reduction of GO in air shows a constant decreasing of the resistivity until 10^{-3}, by increasing the annealing temperature until 250 °C. At 300 °C, the resistivity starts to increase due to the partial combustion of the GO layers.[10]
No specific capacitance (SP) was measured for GO annealed in Ar for temperature until 150 °C and a SP of about 50 F/g was measured for annealed GO at 200 and 250 °C. The GO materials annealed in Air shows a linear enhancement of SP improving the temperature from 100 °C to 200 °C with a maximum of 65 F/g. At 250 °C in Air, the SP decreases to 30 F/g





Ciclyc Voltammetry of annealed GO in Ar and Air with electrolyte KCl 10^{-4}





Specific Capacitance of annealed GO in Ar and Air with electrolyte KCl 10^{-4}

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Acknowledgements

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