SYSTEMATIC COMPARATIVE STUDY OF THERMALLY REDUCED GRAPHENE OXIDE

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Graphene oxide (GO) used as graphene precursor represents the easiest and cheapest way to produce large thin films of graphene. GO can be reduced via thermal or chemical methods to partially recover graphene properties. Reduced graphene oxide (rGO) has attracted big attention due to its mechanical, optical and chemical properties which make it suitable for applications like gas sensors and transparent conductors [1,2]. These potential industrial applications of rGO motivate the efforts of characterizing this material in all its aspects. In particular, many aspects of the reduction mechanism need yet to be understood.
In this work we present a systematic and detailed study of the GO thermal reduction process in ultra-high vacuum (UHV) based on the comparison of optical contrast, X-ray Photoemission Spectroscopy (XPS), and Raman analysis. The properties of rGO extracted from the three different investigation techniques are summarized all in a single parameter, the annealing temperature. In this way, the simple optical contrast (calibrated with quantitative information from the corresponding XPS and Raman analysis) becomes an important and easy-to-use parameter providing information not only on the thickness and optical behavior of the rGO layers but also, indirectly, on their electronic and vibrational properties.
Optical contrast analysis (performed on rGO deposited on 72 nm Al_2O_3/Si(100) for best optical contrast) is reported in Fig. 1a and shows the complete recovery of graphene contrast at a reduction temperature of 670°C, despite the presence of residual oxygen. Optical microscopy images of single layer rGO and graphene sheets are reported in Fig. 1a for comparison.
XPS analysis shows a gradual increase of the sp^2 hybridized carbon content, up to 80% at a reduction temperature of 670°C (Fig. 1c). The residual oxygen content, shown in Fig. 1b, suggests the presence of trapped water between overlapping GO sheets, confirming the exceptional impermeability of graphene [3].
Structural properties of rGO were monitored by Raman spectroscopy. The Tuinstra-Koenig relation allowed to estimate the size variation of sp^2 carbon patches within the GO sheets [4]. The fraction of rGO sp^2 carbon areas is reported in Fig. 1c for different reduction temperatures. The evolution of optical, chemical, and structural properties, summarized in Fig. 1c, shows similar trends but different asymptotic values. While graphene optical contrast seems to be restored, chemical and structural properties of rGO do not converge to the graphene ones. The difference between XPS and Raman curves (respectively C_{sp2}/C_{tot} and S_a

reported in Fig. 1c) indicates that part of graphene-like patches are made of amorphous carbon instead of crystalline sp^2 carbon (characteristic of graphene).
GO is prepared using a modified Hummers method starting from graphite flakes of 500 μm maximum particle diameter. XPS (PHI 1257 spectroscometer, monochromatic Al Kα source, hν = 1486.6 eV) analysis was performed on samples prepared by Drop-Casting of 80 μL GO solution on Au(100) substrate and reduced at different temperatures in the same spectrometer UHV chamber. Raman (LABRAM spectrometer Horiba-Jobin Yvon, $\lambda = 633$ nm, 1 μm spatial resolution and spectral resolution of 2 cm^{-1}) and optical contrast (confocal optical microscope, 20× MPLAN objective) analyses were performed on samples prepared by Drop-Casting of 80 μL GO solution on 72 nm thick Al_2O_3/Si(100) and reduced at different temperatures in the UHV chamber of the XPS setup.

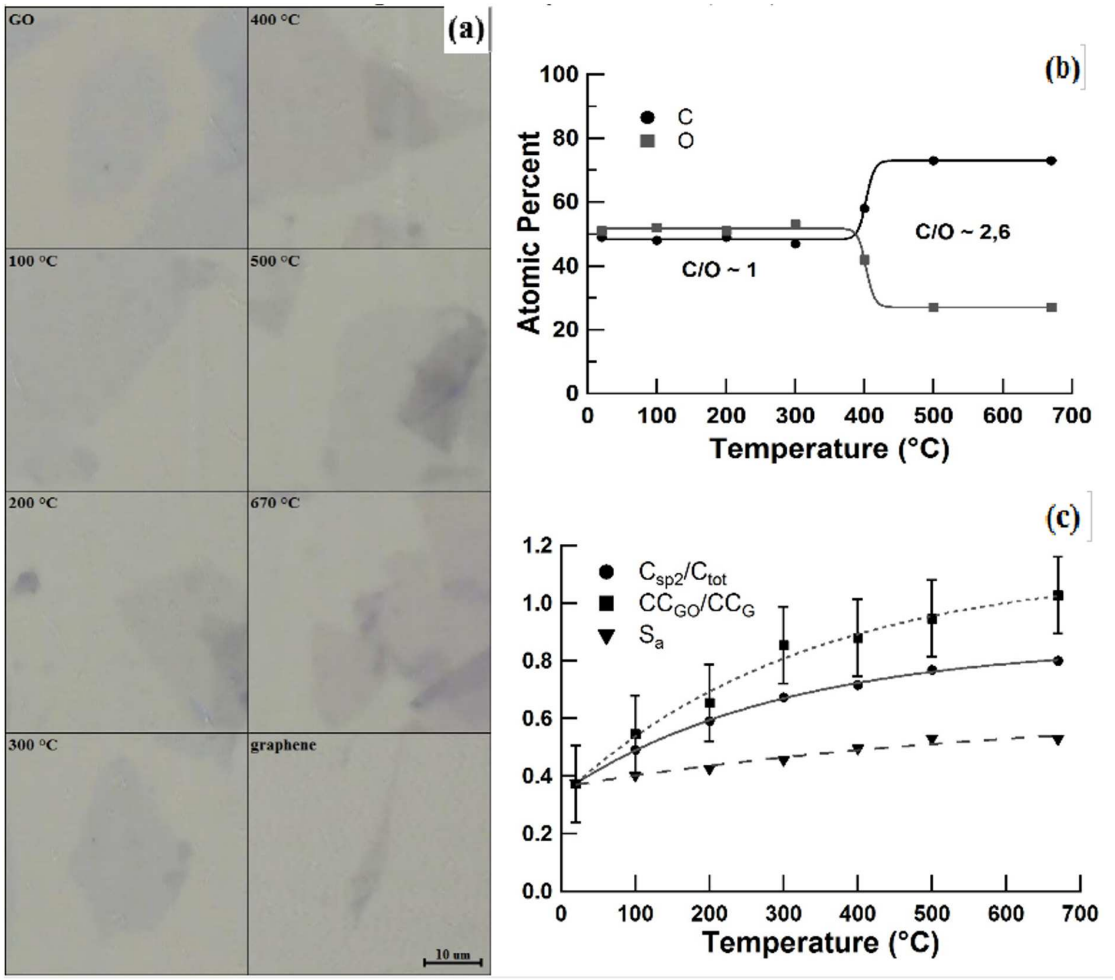

Figure 1: (a) Optical microscopy images of single layer rGO and graphene sheets. Reduction temperatures are reported for each image. Contrast increases with the annealing temperature. (b) Atomic percentages of carbon and oxygen obtained from XPS analysis. The values of C/O ratio indicate the presence of water. (c) Optical (squares), chemical (dots) and structural (triangles) properties evolution as a function of temperature: respectively, normalized rGO contrast(CC_{GO}/CC_G), sp^2 carbon abundance (C_{sp2}/C_{tot}), and honeycomb lattice fraction area (S_a).

References

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