Precautions for the evaluation of thickness in chemically modified graphene sheets by scanning probe microscopy

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Exfoliation and reduction of graphite oxide is one of the most promising ways to obtain processable graphene sheets at large scale in the near future. In order to characterize the properties of the obtained sheets, scanning probe microscopies (SPM) are widely employed. An accurate determination of the thickness is of crucial importance for graphene, due to the fact that its properties are heavily dependent on the number of layers. The common procedure to achieve this is measuring the height of the sheet relative to the employed substrate (sheet-to-substrate). Nonetheless, this method provides some contradictory results, for example in thickness measurements carried out before (GO) and after (rGO) the reduction, which do not show the expected thickness decrease following the reduction [1] due to the removal of oxygen functionalities. In order to clarify the validity of the obtained measures, we have evaluated in this work the effect of both, the nature of the substrate (HOPG, Si/SiO2, mica and borosilicate glass slide) and the specific SPM technique employed (STM, contact AFM and both attractive and repulsive Tapping AFM) in the measured thickness of both GO and rGO individual sheets. The results can be summarized in two general observations [2]:

1. Sheet-to-substrate apparent heights are dependant both on the employed substrate and the specific SPM technique (some examples can be seen in Figure 1).

2. On the other hand, results of sheet-to-sheet measurements (i.e., measuring the thickness of folded sheets, or the thickness in regions where different sheets overlap) provide constant apparent heights regardless of the substrate or the SPM mode (examples of this presented in Figure 1).

In view of these results, it becomes clear that the sheet-to-sheet approach leads to more realistic measurements, while the sheet-to-substrate measurements do not reflect the actual width of the sheets. Thus, measuring thickness over overlapped or bend sheets, provides height values of ~0.9-1.1 nm and ~0.5-0.7 nm for GO and rGO respectively. This decrease in the thickness is the expected behavior, as the reduction involves the removal of a large fraction of the oxygen functional groups that distort the graphitic skeleton. Even so, the thickness is not restored to the value expected for fresh graphene (0.34 nm), as a clear indication for the fact that a considerable proportion of oxygen remains in the sheets after reduction (as complementary XPS and Raman analyses confirm).

Sheet-to-substrate measurements are in general conditioned by differences in the interaction between the SPM tip and the different materials involved (sheet and substrate in the present case). Due to the inherent nature of data acquisition in SPM, those differences are translated into artificial height values. Although the induced error is quite small (a few to several tenths of nm [2]) to present a problem in other conditions, it proves to be crucial for atomically thin sheets, being of the same order as the measured magnitude. Thus, the actual width of the sheets becomes completely masked, providing inconsistent values. With this in mind, a sheet-to-sheet approach would be the convenient choice

whenever possible, thus eliminating the possible artifacts arising from material inhomogeneities and providing more accurate values.

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References

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[2] Solís-Fernández P., Paredes J.I., Villar-Rodil S., Martínez-Alonso A., Tascón J.M.D., Carbon **48** (2010) 2657.

Figures

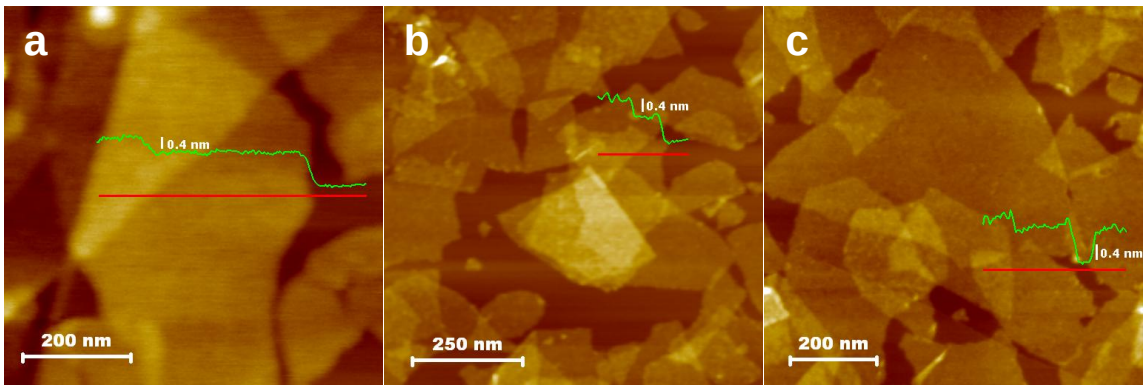

Figure 1. *Contact AFM (a), repulsive (b) and attractive tapping (c) images of rGO deposited onto HOPG. Included line profiles show the apparent sheet-to-sheet and sheet-to-substrate heights.*