Production of Pyrrolidine – Functionalized Graphene in Solution

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Abstract

The formation of stable graphene solutions is a topic of great interest that has been the focus of recent investigations. The approaches proposed comprise the exfoliation of graphite in high boiling point solvents [1], the formation of graphene oxide (GO) followed by its reduction in solution (RGO), [2,3] or the formation of graphene nanoribbons (GNR) from carbon nanotubes (CNT) using an oxidation approach similar to that used for the formation of GO.
Recently, the formation of GNR was observed “in situ” by unzipping of carbon nanotubes under ultra-high vacuum scanning tunneling microscopy (UHV STM) [4]. The CNT under observation were functionalized by the 1,3-dipolar cycloaddition reaction [5], and the functionalization route seems to be responsible for the unzipping of the CNT under these conditions. The present work demonstrates the formation, in solution, of graphene nanoribbons by unzipping of functionalized carbon nanotubes and graphene sheets (GS) through exfoliation of functionalized graphite. CNT and graphite were functionalized by 1,3-dipolar cycloaddition reaction, binding pyrrolidine-type groups to their surface. The solutions containing the functionalized GNR and GS presented the characteristic UV-visible spectra of graphene solutions. The graphene ribbons or flakes deposited by solvent evaporation on a Si surface were characterized by Raman spectroscopy and observed by transmission electron microscopy (TEM). Image analysis demonstrated that the assembled graphene formed regular stacks with an interlayer spacing of approximately 0.50 nm. TEM evidence is presented in Figure 1. The X-ray diffraction analysis showed a graphene-to-graphene interlayer distance of approximately 0,56nm. Molecular modeling was used to study the crystalline stacking of pyrrolidine functionalized GNRs, yielding interlayer distances in the range of 0.50 to 0.51 nm, for functionalized graphene with 50-70 surface C atoms per functional group. These results are in agreement with TEM observation and X-ray diffraction analysis. The assembled graphene could re-dissolve in the solvent to form stable solutions.

References

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Acknowledgments
The authors are thankful to the Institute of Nanostructures, Nanomodelling and Nanofabrication for project Grafitran (PEst-C/CTM/LA0025/2011). M. Melle-Franco acknowledges support by the Portuguese “Fundação para a Ciência e a Tecnologia” through the program Ciência 2008 and the project SeARCH (Services and Advanced Research Computing with HTC/HPC clusters) funded under contract CONC-REEQ/443/2005, and **FCT** for PhD grant SFRH/BD/87214/2012.

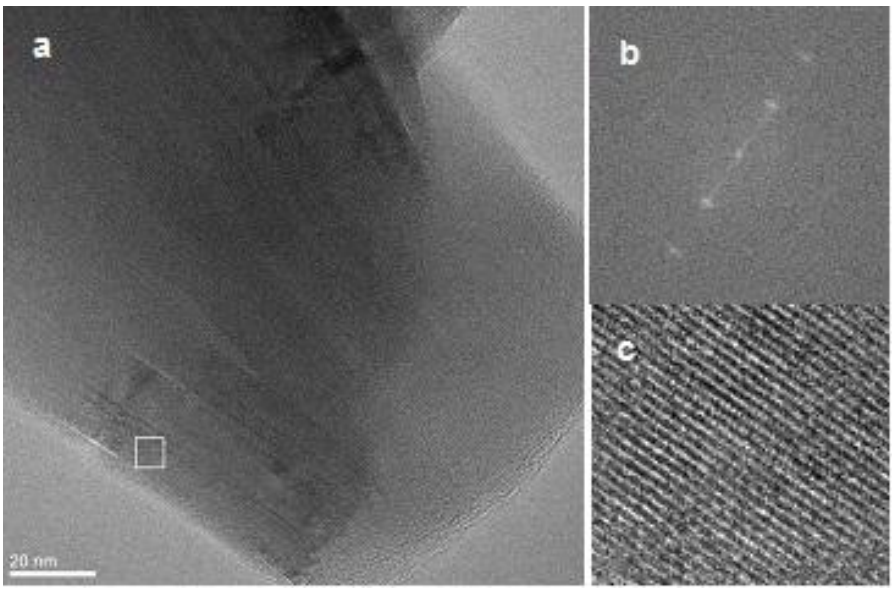

Figure 1. TEM micrograph of GNR formed in ethanol by unzipping of functionalized CNT, (a); FFT performed on the area within the square frame in micrograph a) (b); magnification of the image area in the square frame in micrograph a), showing the regular pattern (c).