Graphene nanoribbons and nanoflakes from functionalized carbon precursors

Maria C. Paiva,[1*] Eunice Cunha,[1] Helena Rocha,[1] M. Fernanda Proença,[2] Natália Alves,[3,4] João F. Mano,[3,4] Manuel Melle-Franco,[5] Francis Leonard Deepak,[6] Mariam Debs,[6] Paulo E. Lopes[7]

[1] Institute for Polymers and Composites/I3N, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal
[2] Department of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[3] 3B's Research Group – Biomaterials, Biodegradables and Biomimetics, University of Minho, Headquarters of the European Institute of Excellence on Tissue Engineering and Regenerative Medicine. AvePark, 4806-909, Caldas das Taipas, Guimarães, Portugal.
[4] ICVS/3B´s PT Government Associate Laboratory, Braga/Guimarães, Portugal
[5] Computer Science and Technology Center, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[6] International Iberian Nanotechnology Laboratory (INL), Av. Mestre José Veiga, 4715-330 Braga, Portugal
[7] Pole for Innovation in Polymer Engineering (PIEP), University of Minho, Campus of Azurém, 4800-058 Guimarães, Portugal
*mcpaiva@dep.uminho.pt

INTRODUCTION

The process of formation of graphene by exfoliation of carbon nanotubes (CNT) or graphite originates graphene nanoribbons (GNR) and graphene nanoflakes (GNF), respectively. These nanoparticles are expected to present interesting electronic properties, depending on their shape, size, and on their edge shape. Several methods for the unzipping of nanotubes were described in the literature [1]. The major limitations to the application of these methods are related to low yield, or to the formation of highly oxidized GNRs. The present work was motivated by the observation of the unzipping of functionalized CNT under ultra-high vacuum scanning tunneling microscopy (UHV STM) [2]. The CNTs under observation were functionalized by the 1,3-dipolar cycloaddition reaction [3], a potential route for the production of GNRs without oxidation. The formation of graphene flakes was observed when functionalized graphite was exfoliated under similar conditions as the CNT. The graphite was functionalized by the same procedure as the CNT.

MATERIALS AND METHODS

The carbon nanotubes were NC7000 produced by Nanocyl® (Nanocyl SA, Belgium), and the exfoliated graphite was XGnP, supplied by XG Sciences Inc., USA. CNT and XGnP were chemically functionalized by the 1,3-dipolar cycloaddition reaction of azomethine ylides, using *N*-benzyloxy-carbonylglycine and paraformaldehyde. The functionalization was carried out at 250 ºC for 3 hours using a procedure described elsewhere [3]. The GNR and GNF were produced in ethanol using an Ultrasonic Processor. The solutions were characterized by UV-visible spectroscopy, and the nanoparticles deposited by evaporation on Si wafers were analyzed by Raman spectroscopy and by X-rays diffraction. TEM observations illustrated the formation of graphene domains and their tendency to form regular stacks.

The production of composite films was tested using the layer-by-layer technique, and was followed in situ by a quartz crystal microbalance. The solutions were characterized by point of zero charge (PZC) measurements and the formed films were analyzed by

electron microscopy.

RESULTS AND DISCUSSION

The carbon precursors were functionalized by the 1,3-dipolar cycloaddition reaction, bonding pyrrolidine groups at the CNT and graphite surface. It was observed that the functionalized graphite flakes suffered a similar process of graphene formation under the same exfoliation conditions as the CNT. The GNR and GNF solutions were prepared in ethanol. After solvent evaporation the GNR and GNF were characterized by Raman spectroscopy, showing the formation of few layer graphene stacking. The formation of these nanoribbon bundles was observed by high resolution transmission electron spectroscopy (HRTEM). Image analysis demonstrated that the nanoribbons formed regular stacks, with an interlayer spacing of approximately 0.50 nm. Molecular modeling illustrated the crystalline stacking of pyrrolidine functionalized GNR, yielding interlayer distances of 0.51 nm, in agreement with TEM observation. X-ray diffraction results supported these conclusions.

Fig. 1 compares the Raman spectra of the functionalized CNTs and the GNRs formed after unzipping of their outer wall in solution. The GNRs tend to stack upon solvent evaporation, and the stacking could be characterized by TEM (**Fig. 2**), showing an interlayer spacing of approximately 0.49 nm.
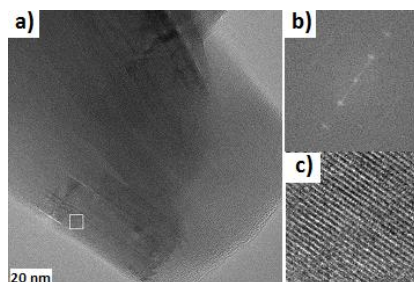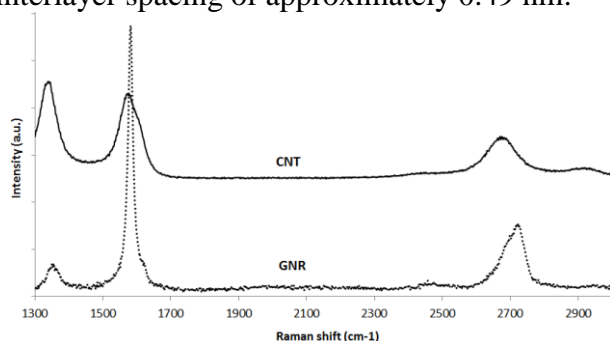

Fig. 1. *Raman spectra of the functionalized CNTs and the GNRs deposited on Si*

Fig. 2. *TEM micrographs of a) GNR stack; b) FFT and c) magnification of the square frame on a)*

The stacked GNR and GNF deposited by solvent evaporation remain soluble, that is, addition of ethanol to the deposited nanoparticles leads to their complete dissolution. PZC measurements indicated a positive value for the ethanol solutions of functionalized GNR. The deposition of a GNR layer on hyaluronic acid was achieved, as measured on a quartz balance.

CONCLUSIONS

A process for GNR and GNF formation in solution was described and the products were characterized by UV-visible and Raman spectroscopies, by HRTEM and X-rays diffraction. Molecular models were used to study the packing/stacking effects in these functionalized graphene nanoparticles. Layer-by-layer deposition was achieved using an aqueous solution of hyaluronic acid and ethanol GNR solution.

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