HIGH CRYSTALINE GRAPHENE NANORIBBONS FROM HELICAL-RIBBON CARBON NANOFIBERS

Helena Varela-Rizo[1], Iluminada Rodriguez-Pastor[1], César Merino[2], Ignacio Martin-Gullon[1]*

[1]Chemical Eng. Dept, University of Alicante, Spain
[2]Grupo Antolín, Burgos, Spain
*Corresponding Author: Email Adress: gullon@ua.es,

Introduction

Graphene has emerged as a promising material for nanoscale applications due to its high crystallinity and exceptional properties. Graphene nanoribbons (GNR), which consists of a few elongated strips of graphene that possesses straight edges [1], also represent an interesting variety of this material. Some processing methods have been reported, i.e. chemical, sonochemical, lithographic or chemical vapor deposition, however high scale and cheap production methods are still a challenge. Common chemical or sonochemical methods, use natural graphite flakes as starting material, which is highly oxidized (yielding graphite oxide) and exfoliated, by temperature or mechanically, to produce graphene oxide or oxidised graphene nanoribbons (GONR). This process starting with natural graphite gives low yields of single layer graphene structures, remaining still a considerable amount of non-exfoliated carbon. Recently, oxidative methods, combined with sonication, have been used to obtain GNRs [2], with high yields, by unzipping carbon nanotubes (CNTs). In the same way, helical-ribbon or stacked-cup CNFs can also be an attractive starting material for GNR production. Due to this singular CNF us composed by catalytically grown ribbon of 5-6 stacked graphene layers rolled up along the fiber axis forming a continuous spiral [3]. These structures present some advantages respect to the MWCNTs, providing also a lower cost process: they are cheaper, the dimensions can be much bigger, and from the production point of view, the process starts from a material that is already a rolled ribbon of only few layers. In this work we report a sonochemical oxidative method (Hummers method) to produce GNRs by cutting and unravelling helical ribbon carbon nanofibers. MWCNTs and graphite were also used for comparison purposes.

Experimental

Commercial CNFs, GANF grade Debulked and Stripped (Grupo Antolin Ingenieria, Burgos, Spain) were used as received. MWCNT, produced at the facilities of the University of Kentucky-Center for Applied Energy Research (KY, USA)24 and also used as received. Natural graphite from Timcal was also used. H2SO4, ethanol and ether were purchased from VWR and KMnO4 from Sigma-Aldrich.

The CNFs were suspended from 2-12 h in concentrated H_2SO_4. Then they were treated with different $KMnO_4$ vs. GANF ratios (100, 200, 200, 400 wt-%). The reaction was stirred 1 h at room temperature and then heated to 55-70 °C during 1 h, as reported by Kosynkin et al. When the $KMnO_4$ was consumed, the reaction was quenched by pouring over ice containing H_2O_2. The solution was filtered and the solid was repeatedly washed with acidic water and ethanol/ether. Same procedure was followed with the MWCNTs and the graphite. MWCNTs was oxidized just with 500 wt-% KMnO4 and graphite with 400 wt-% $KMnO_4$. For graphite, reaction temperature was increased to 98ºC.

Results

XRD, Raman, IR-ATR and XPS show extensive oxidation of the CNFs when adding 400 and 500 wt-% $KMnO_4$. Same results are obtained with the MWCNTs and the graphite.

Fig. 1 shows the TEM micrographs of the oxidized CNFs (A-D), oxidized MWCNTs (E) and oxidized graphite (F). Unravelling of CNFs increases with $KMnO_4$ content. Some GONRs are found, but intact CNFs can also be observed at 100 and 200 wt-% $KMnO_4$. On the other hand, 400 and 500 wt-% $KMnO_4$ produced yields almost completely unravelled CNFs, with nice nano platelets. In addition, all carbon product forms a homogeneous and stable suspension, with no settling. The average yield of this oxidized graphene ribbons is at around 45% at the 400 wt-% $KMnO_4$ process. In the oxidized CNTs samples still some CNTs can be observed, although it also forms an stable suspension. Graphite, since has bigger dimensions, provides larger GONRs, but some of the oxidized product settled, indicative of a aggregation state (non-exfoliation). Fig. 2 corresponds to the scattering area diffraction electron (SAED) pattern of a GONR. Good quality of crystals can be noticed.

Conclusions

Crystalline GONRs were successfully obtained from commercial carbon nanofibers. Oxidation ratio produces different grades of unraveling, but not substantial differences are noticed over 400 wt-% KMnO4. The size of the nanoribbons is smaller than these obtained from graphite, but process conditions are softer and quality of crystals can be competitive.

References

[1] Campos-Delgado J, Romo-Herrera JM, Jia J, Cullen DA, Muramatsu Y, Kim YA, Hayashi T, Ren Z, Smith DJ, Okuno Y, Ohba T, Kanoh H, Kaneko K, Endo M, Terrones H, DresselhausMS, Terrones M. Nano Lett 2008, 8, 1912-1915.
[2] Kosynkin DV, Higginbotham, AL, Siniskii A, Lomeda JR, Dimiev, A, Price, BK, Tour, JM. Nature 2009, 458, 872-877
[3] Vera-Agullo J, Varela-Rizo H, Conesa JA, Almansa C, Merino C, Martin-Gullon I. - Carbon 2007, 45, 2751-2758

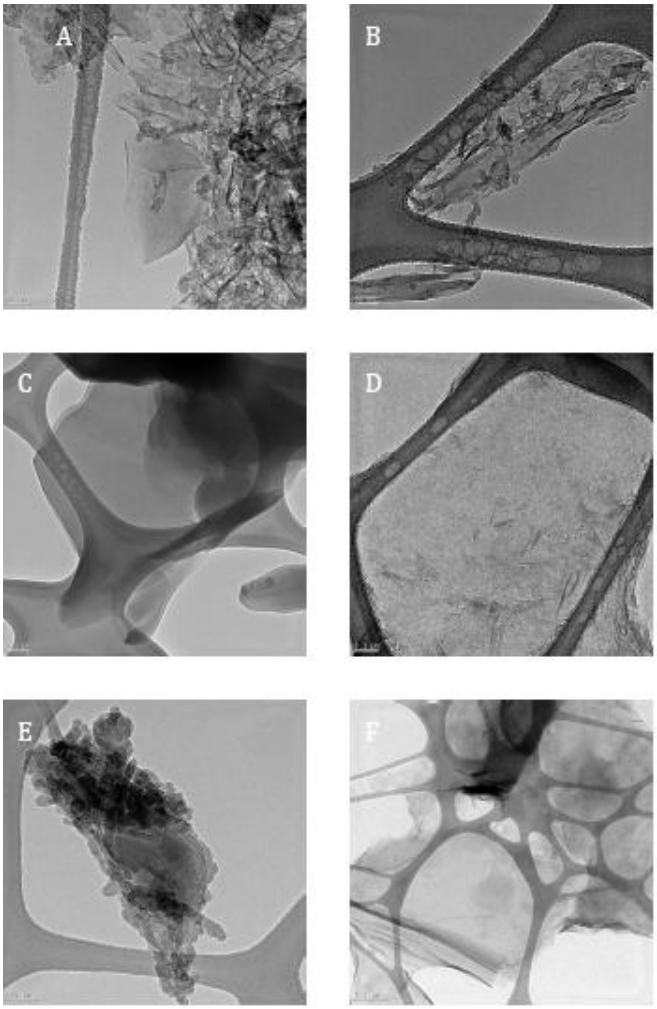

Fig. 1. TEM micrographs of GANF 100 wt-% oxidized (A), GANF 200 wt-% oxidized (B), GANF 400 wt-% oxidized (C), GANF 500 wt-% oxidized (D), CNT 500 wt-% oxidized (E) and graphite 400 wt-% oxidized

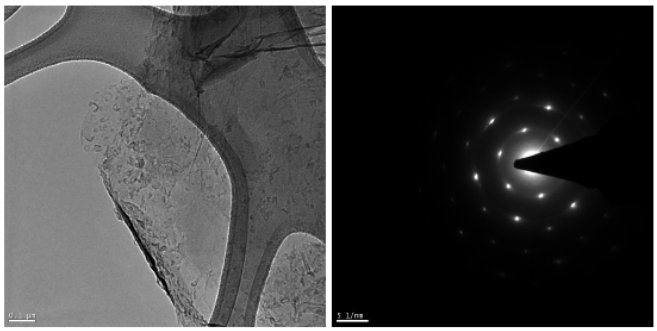

Fig. 2. TEM micrograph of a GNR and SAED pattern