Contents lists available at ScienceDirect

## Materials Letters

journal homepage: www.elsevier.com/locate/matlet

## Versatile and scalable synthesis of graphene nanoribbons

Mohammad Choucair<sup>a,\*</sup>, Bin Gong<sup>b</sup>, John Arron Stride<sup>c,d</sup>

<sup>a</sup> School of Chemistry, University of Sydney, Sydney 2006, Australia

<sup>b</sup> Mark Wainwright Analytical Centre, University of New South Wales, Sydney 2052, Australia

<sup>c</sup> School of Chemistry, University of New South Wales, Sydney 2052, Australia

<sup>d</sup> Bragg Institute, Australian Nuclear Science and Technology Organisation, PMB 1, Menai 2234, Australia

#### ARTICLE INFO

Article history: Received 12 August 2013 Accepted 20 December 2013 Available online 31 December 2013

Keywords: Carbon materials Nanocrystalline materials Graphene

#### ABSTRACT

The inability to readily upscale nanofabrication of carbon nanomaterials often restricts their application, despite outstanding performances reported in both the research laboratory and prototype stages. Here we report the direct chemical synthesis of graphene nanoribbons by a bottom-up approach based on the common laboratory reagents sodium and propanol; these are solvothermally reacted to give an intermediate precursor that is then rapidly pyrolized yielding single- and few-layer graphene nanoribbons. Our results show that confinement of the lateral dimensions of graphene can be achieved simply by varying the alcohol feedstock. The ability to produce bulk quantities of graphene nanoribbons by a low cost and scalable approach is anticipated to enable a wider range of affordable real-world graphene applications.

© 2014 Elsevier B.V. All rights reserved.

#### 1. Introduction

A graphene nanoribbon (GNR) is a thin elongated strip of singlelayer carbon. There have been recent attempts to achieve fine control of the lateral dimensions of graphene to form nanoribbons, as the electronic properties have been found to depend upon both the width and edge type [1–3]. Graphene nanoribbons have been obtained in small amounts by top-down and bottom up approaches [1,4,5]. When considering the methods available to synthesize GNRs, the factors governing the growth and formation can be inter-linked and are common between different synthetic avenues [3,6] e.g., temperature, nucleation sites and pressure. Ultimately, fine-tuning of these parameters will allow for the identification of potential chemical mechanisms which may occur to preferentially favor growth of one carbon nanostructure over another.

Recently reports of very strenuous organic syntheses have demonstrated bottom-up approaches to graphene-type molecules of different sizes [7,8] and successful attempts have been made to grow GNRs using chemical vapor deposition techniques [9,10]. In addition, elegant top-down approaches have been applied to induce morphological transformations in carbon nanostructures (nanotubes, graphene) to GNRs [11,12]. While there are limitations based on yields and the processes may be slow or complicated, the approaches mentioned so far capture a pivotal idea: graphene can be lengthened.

In our recent work we found porous 3-D extended graphene structures can be produced based on solvothermal syntheses and sonication [13,14]. However, the active role of the carbon

precursor on the size and morphology of the carbon nanostructure obtained after pyrolysis of the solvothermal product had not been characterized. In addressing this challenge, we found a relatively easy-to-perform chemical pathway to GNRs that may be extended for large scale processing.

### 2. Experimental

Sample preparation: The detailed experimental procedure is described elsewhere [13] with a 1:1 molar equivalent of propanol (5.0 ml) and sodium metal ( $\sim$  1.5 g) used. The reaction yielding the carbon material can be summarized as the rapid pyrolysis in air of the solvothermal product of propanol and sodium. The amount of carbon obtained was typically  $\sim$  0.15 g.

*Characterization*: Scanning electron microscopy (SEM) images were obtained using a Hitachi S900.

High resolution TEM images were taken on a JEOL 3000F Field Emission Gun in TEM mode at 300 kV.

Powder X-ray diffraction (PXRD) data was collected over the 5–60° 2 $\theta$  range with a 0.01° step size and 0.06°/min scan rate on a PANalytical X'Pert Pro diffractometer fitted with a solid-state PIXcel detector (40 kV, 30 mA, 1° divergence and anti-scatter slits, and 0.3 mm receiver and detector slits) using Cu-K<sub> $\alpha$ </sub> ( $\lambda$ =1.5406 Å) radiation.

#### 3. Results and discussion

From the SEM images we observe that the GNRs are long, reaching  $10 \,\mu m$  and form bundles, possibly due to van der Waal's







<sup>\*</sup> Corresponding author. Tel: +61 293517392.

E-mail address: mohammad.choucair@sydney.edu.au (M. Choucair).



Fig. 1. SEM images of a typical region in the GNR containing material. (a) The GNRs appear in discrete bundles and (b) magnified region in (a) highlighted by the box showing bundled GNRs. Scale bars indicate 1.66  $\mu$ m.



**Fig. 2.** A region of GNR material imaged under the TEM with an inset showing a magnified region of the lattice. An extended hexagonally arranged lattice can be observed; six polygons surround a central polygon, and so forth. The GNRs crimple and overlap. Scale bar indicates 5 nm and excludes image in the magnified inset.

interactions, akin to carbon nanotube bundling [4], Fig. 1. Large salt impurities remaining from the solvothermal procedure or the purification were not evident, see Supplementary material S1. There was no considerable damage caused by the purification procedure. The GNRs compare well morphologically with other synthesized GNRs [15,16].

The regular in-plane structure of the GNRs was evidenced by high resolution TEM, Fig. 2: the material produced is clearly not amorphous. The hexagonal array of carbon atoms was directly observed and was found to be extensive over the entire width and length of the GNRs. Crimpling, overlapping, and ripples in the GNRs were also apparent, indicated by regions of relative opacity; ripples and corrugation of GNRs has been suggested to be related to tensile edge stress effects [17]. TEM images taken of different regions demonstrating the bundling and extensive crystalline nature of the GNRs can be found in Supplementary material S3.

Evidence of layering was further highlighted under TEM with images of GNR bundles, Fig. 3. We can visibly count the number of layers from the contrasting fringes in the TEM images and were found to reach 15; from this we calculate that the inter-planar



**Fig. 3.** TEM image of GNR bundles viewed side-on to the layer formation. Up to 15 layers of GNRs can be counted by observing the contrasting darker regions indicative of individual layer sheets. The arrows guide the eye to single, double, and triple layer GNRs which have peeled away from the bundle. Scale bar indicates 5 nm.

spacing to be ca. 0.35 nm which is close to that of graphite (0.335 nm). We also observe the GNR layers peel away from the bulk bundle to give single, double, triple and multiple layers. The layers of GNRs also tend to curl, an observation which agrees with reports of energetic sacrifices during edge state reconstructions in graphene materials [18].

Due to the layering of the GNRs and apparent graphitic tendency, the crystallinity and structure of the GNRs was further investigated using SAED in order to determine the extent of graphitisation, see Supplementary material S4. The SAED spots were indicative of polycrystalline GNRs and there was evidence of GNRs being layered on top of one another with a small angular offset in some regions, which is supported by the Raman spectra, see Supplementary material S7. The polycrystalline patterns can be representative of layers, crimpling and folds, in-plane grain boundaries, or a combination of these; the pattern agrees with what we directly image.

Along with the (hk0) reflections evidenced by SAED, there is also a (112) graphitic reflection, whilst other primary graphitic features are *absent*. This illustrates that there may be a transitional, rather than a discrete degree of graphitisation; the material is not entirely graphitic. This may arise due to the GNRs displaying slight Download English Version:

# https://daneshyari.com/en/article/1644617

Download Persian Version:

https://daneshyari.com/article/1644617

Daneshyari.com