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Shear stress mediated scrolling of graphene oxide

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ABSTRACT

Graphene oxide scrolls (GOS) are fabricated in high yield from a colloidal suspension of graphene oxide (GO) sheets under shear stress in a vortex fluidic device (VFD) while irradiated with a pulsed laser operating at 1064 nm and 250 mJ. This is in the absence of any other reagents with the structure of the GOS established using powder X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry, X-ray photoelectron spectroscopy, Raman spectroscopy, transmission electron microscopy, atomic force microscopy and scanning electron microscopy.

1. Introduction

In recent years, graphene scrolls have attracted attention as a novel one dimensional (1D) tubular topology materials derived from rolling up a 2D sheet of ubiquitous graphene. Graphene and graphene oxide (GO) scrolls have properties akin to other carbon nano-materials, including high thermal and electrical conductivities and excellent mechanical properties [1,2], with potential in a number of applications. These include hydrogen storage [3,4], supercapacitors [5–7], batteries [8,9], sensors [10] and electronic devices [11,12]. However, gaining access to graphene scrolls has proved challenging, not only for graphene, but also for graphene oxide and reduced graphene oxide.

Graphene scrolls are accessible directly from graphite using a spinning disc processor (SDP) [13], via sonication of graphite intercalation compounds [14] and from preformed graphene sheets in isopropyl alcohol [15]. Graphene oxide scrolls (GOS) have been prepared from graphene oxide using Lyophilization methods [16], microwave irradiation of graphene oxide [17] and a Langmuir–Blodgett approach, also from preformed graphite oxide [18]. Fabricating such scroll structures from graphene or graphene oxide usually suffers from limitations, including low yield, and using harsh chemicals and energy intensive high temperature and sonication processing, with long processing times. In the present research, we have developed a facile method for the synthesis of GOS from GO sheets in aqueous solution, under high shear stress in a vortex fluidic device (VFD) [19]. This dynamic thin film microfluidic platform has an angled tube rapidly rotating, with the angular dependence important in a number of applications. Within the thin film, typically below ca 500 μm thick, shear stress develops along with pressure waves which can mediate a number of biochemical, chemical and materials transformations [19]. The VFD can be operated in the so called confined mode which is suited for small scale processing, and under continuous flow mode. The latter is an attractive feature of the device for addressing scalability of any processing at the inception of the science. Here jet feeds deliver reagents into the inclined rapidly rotating tube, which is typically a 20 mm OD borosilicate glass or quartz tube.

The VFD is a versatile microfluidic platform with a number of applications, including slicing of single, double and multi-walled carbon nanotubes [20], protein folding [21], enhancing enzymatic reactions [22], protein immobilization [23], fabricating C_{60} tubules using water as an anti-solvent against toluene [24], exfoliation of graphite and boron nitride [25], growth of palladium and platinum nano-particles on carbon nano-onions [26], probing the structure of self-organized systems, and controlling chemical reactivity and selectivity [27].

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In an earlier study we developed the use of a SPD, which by necessity operates under continuous flow, for preparing graphene scrolls directly from graphite, albeit in only 1% yield [13]. The mechanism of this simultaneous exfoliation and scroll formation is understood on a theoretical basis, with a graphene sheet lifting up and bending back under shear, then contacting the upper surface of this graphene sheet, as a stable transition state [13]. Further bending back then leads to spontaneous scroll formation [13]. We hypothesised that GO dispersed in solution has the potential to form scrolls under shear as a shape with the least resistance to shear stress. However, these scrolls will not be packed at the van der Waals limit between carbon atoms between successive turns of the scroll because of the high levels of defects and oxygenation. In contrast, graphene scrolls generated from graphite using a SDP have successive layers of carbon atoms at the van der Waals limit, at distances similar to the distances between layers in graphite itself. We also hypothesised that irradiation of GO under high shear using a pulsed NIR laser may facilitate scroll formation. This is based on the expected increased flexibility of the GO sheets with high induced vibrational energy. There is also potential for a reduction in site defects of the GO on absorption of laser light at 1064 nm, as has been established during slicing of carbon nanotubes in the VFD at the same wavelength [20].

In the present study, we systematically explored the different processing parameter space of the VFD for generating scrolls of GO dispersed in water, along with varying the laser power and the choice of solvent, including isopropyl alcohol (IPA) as a solvent that has been used in forming graphene scrolls [15], and which is environmentally friendly. Further optimization involved recycling the collected solution, but there was little change to the nature of the product (Fig. S6. Supplementary Information).

2. Experimental

2.1. Chemicals and materials

Graphene oxide sheets (GO) (average sheet size: ~ 5 μm in cross section) were synthesized by a modified Hummer's method and purchased from Sigma Aldrich and Carbon Solution, with both product giving similar results.

2.2. Preparation of GOS

The as-received GO was dispersed in water at a number of different concentrations with each solution sonicated for 30 min to afford a black stable dispersion, noting that no scrolls were observed after sonication (Fig. 2a-c), prior to processing in the VFD under the described conditions, under a continuous flow rate of 0.45 mL/min in a rotating quartz glass tube 20 mm OD diameter and 18.5 cm long inclined at 45°. Optimal parameters for GOS formation were 4k rpm rotational speed, laser power 250 mJ and 0.2 mg/mL concentration of GO in water. The processing involved delivering a suspension of GO to the hemispherical base of the tube in the VFD with the resulting thin film irradiated by a 5 nanosecond pulsed Q-switch Nd: YAG laser operating at 1064 nm, with an 8 mm diameter laser beam and a repetition rate of 10 Hz.

2.3. Characterization

The GOS were characterized by scanning electron microscopy (SEM) performed using a FEI Quanta 450 High Resolution Field Emission SEM, with a voltage of 10 kV, and working distance of 10 mm, Atomic force microscopy (AFM) – (Nanoscope 8.10 tapping mode), Transmission electron microscopy (TEM) was conducted on a TECNAI 20 microscope operated at 120 and 200 kV. Raman measurements were recorded at an excitation wavelength of 532 nm (≤5mW) at room temperature. X-ray powder diffraction (XRD) data were collected using a Bruker Advanced D8 diffractometer (capillary stage) using Cu Kα radiation ($\lambda = 1.5418$ Å, 50 kW/40 mA, $2\theta = 5-80^{\circ}$). Samples for SEM and Raman analysis were prepared on clean silicon wafers. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were recorded on a Perkin Elmerat operating at a heating rate of 3 C^{o}/min under a nitrogen gas flow. X-ray photoelectron spectroscopy (XPS) data was acquired using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyser. The incident radiation was monochromatic Al Kα X-rays (1486.6 eV) at 150 W (15 kV, 15 ma). Survey (wide) scans were taken at an analyser pass energy of 160 eV and multiplex (narrow) high resolution scans at 20eV. Scanned area is about 0.8 mm × 0.3 mm and the depth is less than 10 nm (volume is approx. 2400 μm^3). Survey scans were carried out over 1200-0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 ev steps and 250 ms dwell time. Base pressure in the analysis chamber was 1.0×10^{-9} torr and during sample analysis 1.0×10^{-8} torr.

3. Results and discussion

3.1. Optimisation of fabrication of GOS

Details of the processing for transforming 2D GO sheets into 1D tubular like GOS under shear stress within a VFD are summarised in Fig. 1. As received GO was readily dispersed in water as a stable uniform colloidal solution, which is made possible by the hydrophilic groups on the surface of the 2D sheets [6,18]. Fig. 1a schematically shows flat sheets of GO, before processing in the VFD, with Fig. 1b showing the salient features of the VFD which houses a 20 mm OD diameter quartz tube, 18.5 cm in length, inclined at 45°, which is rapidly rotated with the solution irradiated with a pulsed laser operating at 1064 nm (see below discussions on optimisation studies). Fig. 1c schematically shows partially and fully scrolled GO after processing in the VFD, in accordance with the TEM images (see below).

Establishing the optimum conditions for forming GOS involved systematically exploring the parameter space of the VFD operating under continuous flow. This involved varying the rotational speed from 2k rpm to 8k rpm, followed by using different laser power, 250 mJ, 400 mJ and 600 mJ, at different flow rates of 0.1, 0.45, 1.0 and 1.5 mg/mL, and varying the concentration of GO, 0.1, 0.3 and 0.5 mg/mL. In addition, isopropyl alcohol (IPA), as an alternative solvent which is readily removed in vacuo post processing, was also tested for GOS formation, with GO at 0.2 mg/mL, for different rotational speeds (See Supplementary Information for details). A flow rate of 0.45 mL/min has been established as a good starting point for a number of applications of the VFD with the tube fixed at 45° tilt angle which is the optimal angle for all processing using the VFD [19]. The optimised parameters for the highest conversion to GOS were 4k rpm with the pulsed laser operating at 250 mJ, for an aqueous suspension of GO at 0.2 mg/mL. Under these conditions there is no evidence for residual 2D GO sheets and thus the conversion to GOS or partial GOS is essentially quantitative. Varying these parameters resulted in samples with significantly less GOS and partial GOS, as judged using a number of characterisation techniques (see below).

3.2. Characterisation of the GOS

The structure of GOS was initially examined using transmission electron microscopy (TEM), atomic force microscopy (AFM) and