



# Tuning the grade of graphene: Gamma ray irradiation of free-standing graphene oxide films in gaseous phase



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## ARTICLE INFO

### Article history:

Received 28 July 2014

Received in revised form

24 September 2014

Accepted 14 October 2014

Available online 24 October 2014

### Keywords:

Radiation chemistry

Gamma irradiation

Solution-free chemistry

Graphene oxide reduction and graphene

bucky-papers

## ABSTRACT

A direct approach to functionalize and reduce pre-shaped graphene oxide 3D architectures is demonstrated by gamma ray irradiation in gaseous phase under analytical grade air, N<sub>2</sub> or H<sub>2</sub>. The formation of radicals upon gamma ray irradiation is shown to lead to surface functionalization of the graphene oxide sheets. The reduction degree of graphene oxide, which can be controlled through varying the  $\gamma$ -ray total dose irradiation, leads to the synthesis of highly crystalline and near defect-free graphene based materials. The crystalline structure of the graphene oxide and  $\gamma$ -ray reduced graphene oxide was investigated by x-ray diffraction and Raman spectroscopy. The results reveal no noticeable changes in the size of sp<sup>2</sup> graphitic structures for the range of tested gases and total exposure doses suggesting that the irradiation in gaseous phase does not damage the graphene crystalline domains. As confirmed by X-ray photoemission spectroscopy, the C/O ratio of  $\gamma$ -ray reduced graphene oxide is increasing from 2.37 for graphene oxide to 6.25 upon irradiation in hydrogen gas. The removal of oxygen atoms with this reduction process in hydrogen results in a sharp 400 times increase of the electrical conductivity of  $\gamma$ -ray reduced graphene oxide from 0.05 S cm<sup>-1</sup> to as high as 23 S cm<sup>-1</sup>. A significant increase of the contact angle of the  $\gamma$ -ray reduced graphene oxide bucky-papers and weakened oxygen rich groups characteristic peaks across the Fourier transform infrared spectra further illustrate the efficacy of the  $\gamma$ -ray reduction process. A mechanism correlating the interaction between hydrogen radicals formed upon  $\gamma$ -ray irradiation of hydrogen gas and the oxygen rich groups on the surface of the graphene oxide bucky-papers is proposed, in order to contribute to the synthesis of reduced graphene materials through solution-free chemistry routes.

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## 1. Introduction

Potential applications of graphene have dramatically increased over the past 10 years and are nowadays covering most of the research fields in materials science [1–4]. The range of graphene chemistries, morphologies and grade which can be processed is virtually boundless due to the diversity of growth and surface modification mechanisms which have been developed on sp<sup>2</sup> carbon based materials [5,6]. Epitaxial growth, chemical vapour deposition (CVD) and mechanical cleavage of graphite for instance lead to the formation of very high grade of graphene materials with very low sp<sup>3</sup> carbon contents [7,8]. The dimension, ranging from nano-scale

to micron sized and the number of layers superimposed across the graphene sheets may be finely tuned to produce materials with very versatile and specific bulk and surface properties [8]. The development of 3D dense or porous architectures is therefore critical to fully benefit from the natural properties of graphene [9,10]. A limitation of the current graphene growth and synthesis technologies, however, still resides in the inter-connectivity between graphene sheets and grains, intrinsic to their fabrication growth processes, which is still hindering the true potential of assemblies made of graphene materials [11,12]. Although advances have been made recently in this regards, current frontiers in graphene science therefore head towards the design of fully interconnected 3D architectures made purely of graphene [6,13]. The major limitation hindering large scale graphene based materials development therefore resides in production up-scaling and the ability to adapt the grade of graphene materials quality to specific industrial requirements. The synthesis and reduction of graphene oxide (GO) therefore appears as the most promising solution towards low cost and mass

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production of in fine graphene materials [14]. The reduction of GO fabricated from graphite by the Hummers' method [15] is a cheap and fast technique to produce low grade graphene materials and is currently industrially up-scaled as a route to produce efficiently graphene structures and composites [16,17]. 3D GO architectures, typically referred to as bucky-papers (BP), can be fabricated by vacuum filtration of suspended GO in solution, to form thin films, fibres or complex 3D frameworks [13,18–20]. The higher sp<sup>3</sup> carbon and defect contents across GO sheets, which primarily consist of the residual oxygen groups on the surface of the GO sheets and of new vacancies generated upon exfoliation and oxidation, must be alleviated to recover the electrical and thermo-mechanical properties of pristine graphene [21–23]. Current GO chemical reduction routes are typically performed in aqueous solution due to the facile dispersion of GO sheets in water by surface solvation [24]. The formation of graphene fibres and aerogels was also recently reported and show to lead to highly porous graphene materials with superior properties for solvent adsorption and tensile strength [25,26]. Alternative non-invasive functionalization routes, such as hard X-ray lithography, were previously shown to lead to effective and specific functionalization of thick arrays of carbon nanotubes by interfering with the surface electronic density of the graphitic walls in air, which lead to the formation of highly crystalline, but yet hydrophilic nanotubes [27]. Recently, radiation chemistry by gamma ray irradiation, a simple and efficient strategy to uniformly induce chemical reactions in solutions via production of reactive radicals [27,28] has been used to reduce GO suspended either in aqueous solution or organic solvents [29–35]. Radicals, such as ethoxy or hydronium [36,37] generated across the solvent act as reducing agents against oxygen functional groups present on the GO surface. However, a limitation of any solution based reduction processes resides in subsequent aggregation and partial restacking of functionalized or reduced GO into macro-clusters due to strong hydrophobic interactions between sp<sup>2</sup> carbons across the graphene planes, making any further reprocessing or chemical modifications in solution challenging and largely inefficient [38]. Novel routes to specifically functionalize or reduce GO from pre-formed 3D architectures to form highly interconnected networks of graphene materials are therefore desperately required.

Here, a novel method to simultaneously tune the grade and form 3D architectures of virtually any shape solely composed graphene is demonstrated. The simple and efficient approach leading to variable grade and crystallinity graphene materials consists in reducing pre-assembled GO 3D architectures by irradiation with a <sup>60</sup>Co  $\gamma$ -ray source in gaseous phase. Gas molecules may be split at low energy into free radicals and are able to specifically oxidize or reduce reactive functional groups present on the surface GO sheets, such as hydroxyl and carbonyl. This straightforward functionalization process of GO sheets leads to enhanced sp<sup>2</sup> carbon ratio and thus has the potential to either lead to novel functionalities or restore properties of pristine graphene sheets. The small kinetic diameter of gases such as H<sub>2</sub>, O<sub>2</sub> or N<sub>2</sub> should allow for an even and near unimpeded diffusion between the packed GO sheets. The presence of oxidative or reductive radicalized gases combined to the high penetrability of  $\gamma$ -ray across carbon materials may lead to a highly tuneable functionalization and reduction process by solely adjusting the total irradiation dose. Here, the impact of the total irradiation dose on both the surface properties of the GO sheets and on the morphology of the initial 3D assembly are here studied and critically discussed and chemical mechanism pathways are proposed based on the evidence of chemical changes across the materials. This highly novel and efficient route offers promising perspectives for breakthrough in mass production of graphene materials across a range of applications including sensing, nano-scale thermal conductors, molecular separation and nano-electronics [18].

## 2. Experimental

### 2.1. Materials

Natural flake graphite, with particle size distribution comprised between 25 and 45  $\mu\text{m}$ , were purchased from Sigma Aldrich (USA). Sulfuric acid (98%) (H<sub>2</sub>SO<sub>4</sub>), sodium nitrate (NaNO<sub>3</sub>), potassium permanganate (KMnO<sub>4</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub> at 30 wt%) and hydrazine hydrate (35 wt%) were ordered from ChemSupply (Australia). The high purity gases, H<sub>2</sub>, air, and N<sub>2</sub> (>99.9%), and all aforementioned chemicals, were of analytical grade and used as such without modification.

### 2.2. Preparation of GO suspensions

GO suspensions were prepared from natural flake graphite following a modified Hummers method previously described. In a typical process, a 30 wt% graphite, 15 wt% NaNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> solution was vigorously stirred at 10 °C for 1 h to initiate exfoliation. Then an excess amount of KMnO<sub>4</sub>, in an approximate 30 wt% of the initial sample batch, was added gradually and the temperature of the mixture and stirring maintained for 2 h at 10 °C to allow for full salts dissolution. The mixture was then heated to 38 °C at 10 °C min<sup>-1</sup> and stirred for up to 4 h until formation of a viscous brownish paste corresponding to the full exfoliation process. At this point, the paste was mixed with an equal volume of deionized water and temperature increased to 95 °C in a *bain-marie* under stirring for 15 min. An additional 50 mL of deionized water was added to the solution to quench the reaction, followed by approximately 5 vol% of a 30 wt% H<sub>2</sub>O<sub>2</sub> solution until the colour of diluted solution became bright yellow to finalize the oxidation of the graphite sheets in GO sheets. The GO suspension was then filtered on a porous anodized alumina membrane with a nominal average pore size of 0.1  $\mu\text{m}$  from Millipore under vacuum and thoroughly backwashed 5 times with excess 10 vol% HCl solution prior to rinsing with an excess amount of deionized water. The solid was subsequently redispersed in deionized water and ultra-sonicated for 30 min with a FS300b Decon ultrasonic bath at 60 W. Potentially remaining un-exfoliated graphite particles were then removed from the GO suspension by centrifugation at a 2000 rpm for 30 min, on an Eppendorf Centrifuges 5430R, to collect the GO rich supernatant. Naturally present hydrophilic functional groups such as hydroxyl, carboxyl and epoxy groups were introduced onto the surface of the GO sheets during exfoliation–oxidation process which favoured the stability of the suspension of the sheets in water (Fig. S1a). The GO suspensions were found to be very stable even 2 days after the sonication, while graphite dispersions would typically settled at the bottom of their containers within hours (Fig. S1b). The concentration of the GO suspension was obtained by thermo-gravimetric analysis and found to lie at 0.5 g mL<sup>-1</sup> ( $\pm 2.5\%$ ).

### 2.3. Fabrication of freestanding GO films and gamma ray irradiation

GO thin films were processed by first sonicating a 50 mL volume of the processed GO suspension in the same conditions previously described in order to de-stack potentially agglomerated GO sheets in a fashion similar to that previously reported [39]. The GO films were formed by vacuum filtration with a house-line vacuum on alumina membranes prior to vacuum drying at room temperature for at least 6 h. The GO films were then gently peeled from their filter membranes to form free-standing GO films made of tightly stacked GO sheets [9]. The thickness of the GO films was measured with a Micrometre (Mitutoyo 293-240 with a 0.05  $\mu\text{m}$  accuracy) and found to lie consistently around 25  $\mu\text{m}$  ( $\pm 1 \mu\text{m}$ ). The freestanding GO BPs were placed into 40 mL tan glass vials with irradiation

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