



## Regular Article

## Graphene nanosheets: Mechanisms for large-area thin films production



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## ABSTRACT

Large scale manufacture of graphene nanosheets (GNS) is one of the greatest challenges. The longitudinal unzipping of carbon nanotubes has created the possibility of large scale production with well-controlled widths. However, this mechanism can only produce ribbons of graphene (GNR). In this work, we have explored new mechanisms and approach for efficiently producing large-area GNS thin films. We show that the GNR/GNS can be functionalized by anion/cation initiators. The resulting negatively and positively charged functionalized GNR/GNS can form large-area thin films through side-by-side and layer-by-layer electrostatic attractions. These findings provide a solid theoretical basis for producing large-area thin films.

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## 1. Introduction

The excellent mechanical, electrical, thermal and optical properties of graphene and the existing capability of influencing these properties through functionalization, has stimulated extensive research on the production of graphene and its applications. In general, when selecting a method of manufacturing graphene nanosheets (GNS), it is important to consider the cost, quantity, size, and quality of sheets, as well as the compatibility of GNS with potential commercial application processes. One of the major challenges, however, has been the lack of a scalable production method for synthesizing high quality GNS thin films with a controllable layer thickness. Production of GNS by micromechanical cleavage or “scotch-tape” peeling of graphite [1,2] appeared to be simple as it does not require large investments or complicated equipment; but there is no controllability of the size and thickness of graphene, and can only be used for small-scale laboratory tests. Later, various methods of synthesis, such as epitaxial growth [3–5], chemical vapor deposition (CVD) [6,7] and substrate-free gas phase synthesis [8,9], have also been developed. However, all of these methods are not suitable for large scale manufacture, as they require an accurate control of cooling rates. In addition, the use of high temperatures complicates the incorporation of graphene into practical device systems. Longitudinal unzipping of carbon nanotubes [10,11] offers the possibility of the large scale production of graphene nanoribbons (GNR) with a well-controlled width.

GNRs are promising candidates for applications in field-effect transistors, transparent conductive films and opto-electronic devices. In making semiconductor devices, for instance, functionalization of GNR has been tried with anionic (p-sulfobenzene-diazonium) and cationic (p-aminobenzene-diazonium) moieties to make GNR thin film transistors [12]. The negatively/positively charged functionalized GNR was assembled on silicon oxide/silicon surfaces using a layer-by-layer technique to achieve thickness control in the nanometer range.

In this work, anionic- and cationic-functionalizations of GNR/GNS are examined using commonly used anionic and cationic initiators, namely iso-butyl lithium and proton (strong protic acid having a weak nucleophilic counterion) respectively. Both basal plane and edge functionalizations of GNR/GNS are considered and the large area thin film formation is investigated.

## 2. Methodology

A section of a 2D-graphene nanosheet containing 36 carbon atoms with hydrogen atoms added to the dangling perimeter carbon,  $C_{36}H_{16}$ , was used to study the fabrication of graphene thin films. The graphene nanosheet,  $C_{36}H_{16}$ , was functionalized with (i) an isobutyl anion ( $C_4H_9^-$ ) and (ii) a proton. Both the edge and basal plane functionalizations were considered. The resultant anionic functionalized GNS [af-GNS]<sup>-</sup>, and cationic functionalized GNS [cf-GNS]<sup>+</sup> were brought to interact with each other and the interactions between them were examined for possible thin film formation.

In every step, the geometry of the reactants and products were fully optimized using density functional theory (DFT) with a hybrid functional B3LYP [13–16] and a 6-31G\*\* basis set [17]. The atomic charges were analyzed by the Mullikan method. For reactants and products having an odd number of electrons, the unrestricted formalism, DFT (UB3LYP)/6-

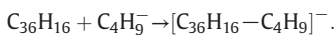
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31G\*\*, was used. All computations were carried out using the ab initio quantum chemistry package, Gaussian 09 [18]. The charge density diagrams were generated using Gauss View.

### 3. Ionic functionalization

We had used first principle calculations to reveal mechanisms of various chemical reactions [19–22]. In this work, to examine the anionic functionalization of GNS, we have studied the reaction between isobutyl lithium and a portion of the GNS with hydrogen atoms added to dangling perimeter carbon atoms ( $C_{36}H_{16}$ ). The anionic moieties can attach to the edge as well as to the basal plane carbon atoms of the GNS:

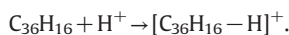


The DFT(B3LYP)/6-31G\*\* optimized geometries of the edge and basal plane anionic functionalized GNS [af-GNS]<sup>−</sup> are presented in Fig. 1(a) and (b) respectively. The C atom of the GNS with which the anion reacted and formed a new –C–C– bond is highlighted. In this reaction, when the anion reacts with a C atom of the GNS, the pi-bond at that C atom breaks and the negative charge moves to other C atoms through the conjugated pi-bonds of GNS. One such pathway is shown by the series of green arrows. The partial atomic charges calculated from Mulliken population analysis showed that the negative charge is now distributed on several edge C atoms of the GNS as shown in Fig. 1(c) and (d).

When the isobutyl anion reacts with GNS, the hybridization of the GNS carbon atom (at which the reaction occurs) changes from  $sp^2$  to  $sp^3$ . This hybridization change and the breakage of the pi-bond consume energy, whereas the formation of a new bond releases energy. Depending

on the amount of energy consumption and release, the functionalization reaction can be exothermic or endothermic. The difference in energy between the product [ $C_{36}H_{16} - C_4H_9$ ]<sup>−</sup> and the reactants [ $C_{36}H_{16} + C_4H_9^-$ ] shows that both the edge and basal plane functionalization reactions are exothermic with  $\Delta H = 136.42$  kcal/mol and  $-97.09$  kcal/mol respectively, i.e., the edge functionalization is preferable. This is because carbon atoms at the edge are more flexible – hence edge functionalization consumes less energy during hybridization change.

To examine the cationic functionalization of GNS, we have studied the reaction between  $H^+$  and  $C_{36}H_{16}$ :



The DFT(B3LYP)/6-31G\*\* optimized geometries of the edge and basal plane cationic functionalized GNS [ $C_{36}H_{16} - H$ ]<sup>+</sup> are presented in Fig. 2(a) and (b) respectively. The C atom of the GNS with which the cation reacted, and formed a –C–H bond, is highlighted.

As the cationic initiator  $H^+$  approaches the GNS carbon atom, the pi-bond with that carbon atom breaks and gives the electrons to that C atom. As a result, the C atom next to it becomes positively charged and it is carried away to the other carbon atoms through the conjugated pi-bonds. One such pathway is shown by the series of green arrows in Fig. 2(a) and (b). A Mulliken partial charge analysis showed that the positive charge is distributed over several carbon atoms of the GNS as shown in Fig. 2(c) and (d). When the proton forms a –C–H bond with GNS, some energy is released and the hybridization of the C atom of the GNS changes to  $sp^3$ . This hybridization change and the breakage of pi-bond consume energy. Hence the reaction can be exothermic or endothermic depending on the amount of energy consumed and released. The difference in

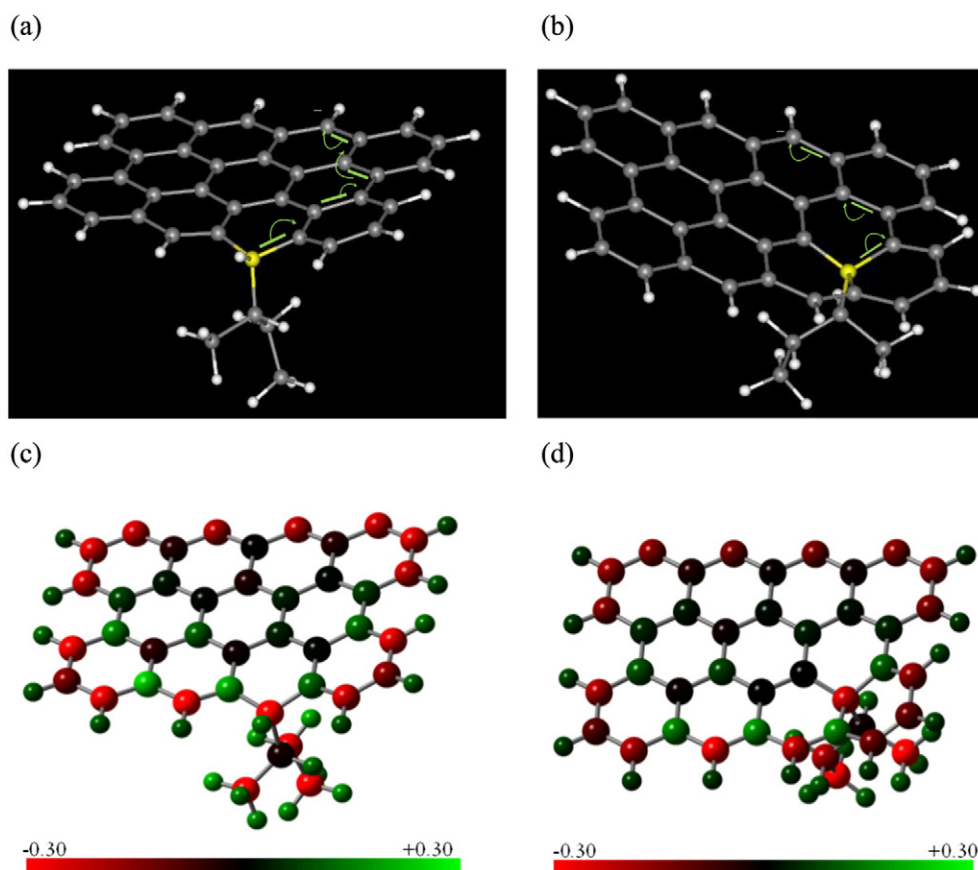


Fig. 1. DFT(B3LYP)/6-31G\*\* optimized geometry of (a) edge [af-GNS]<sup>−</sup>, (b) basal plane [af-GNS]<sup>−</sup>, and charge distribution of (c) edge [af-GNS]<sup>−</sup>, (d) basal plane [af-GNS]<sup>−</sup> (atoms are colored according to charge – negative charge (red color), is distributed over several carbon atoms).

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