Two Dimensional Polymerization of Graphene and its Oxide: Bottom-up Approach

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Abstract

We demonstrate a bottom-up synthesis of graphene oxide via a two dimensional polymerization. Experimental evidence is conveyed as well as a general framework of the two dimensional polymerization within which an improved bottom-up procedure for the synthesis of graphene and its oxide can emerge.

The synergy between unmatched electrical, optical and mechanical properties of graphene has resulted in vigorous research into methods for its large-scale production. All of the established procedures are physical in nature (exfoliation, CVD and thermal decomposition of SiC). An alternative method is chemical in nature and rests upon the reduction of graphene oxide which is produced by chemical exfoliation of graphite to form a dispersion of graphene oxide platelets.

Sheets of graphene oxide (GO) with atomic thickness have established themselves as a new carbon-based nanoscale material that also paves the route to an alternative production of graphene.

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The solubility of GO in water and other solvents allows it to be uniformly spray or spin coated on substrates to form thin films which makes it useful for macroelectronics. Graphene oxide has an optical band gap of 1.7 eV to 2.1 eV. Controlled oxidation provides tunability of its electronic and mechanical properties up to the point of its turning into the semi-metallic graphene upon complete removal of the C-O bonds. Therefore, we assume the synthesis of GO via a two dimensional polymerization a successful attempt at bottom-up synthesis of graphene.

In general, chemical oxidation methods such as Brodie’s, Staudenmaier’s, Hummers or a variation of these, produce GO by introducing functional groups such as carbonyl, hydroxyl and epoxy in between the layers forming graphite. These functional groups weaken the Van der Waals bond between layers (approx. 300 nN per 1 µm²) which cause them to peel off. This approach is scalable and amenable to improvement as already proved. The detailed chemistry of oxidation and subsequent reduction, as well as the chemical tuning of graphene platelets is an active area of research. However, it represents a top-down approach.

In this paper we suggest an alternative approach towards graphene and GO synthesis. It is bottom-up in a sense that it starts from simple monomer and through a carefully tailored two dimensional polymerization arrives at graphene or GO platelets. A key component of this approach is the understanding what monomer and polymerization rule can yield hexagonally spanned networks representing graphene or GO. This understanding is physical in nature and summons up in the following statement: the bonds formed between the monomer units help span the intermediate hexagons in the lattice of graphene or GO. With this in mind we proceed with the explanation of the general framework behind the two dimensional polymerization of graphene and its oxide.

Polymerization occurs in a variety of reaction processes that involve different functional groups present in reacting molecules. A dictionary definition of polymerization states that it is a process of reacting monomer molecules together in a chemical reaction to form polymer chains or three dimensional networks (branching). Interestingly, the resulting molecule, that is the polymer, comprises of multiple repetition of units of low molecular mass. This repetition occurs in one dimension!
Figure 1: (a.) Monomer unit; (b.) Polymerization rule; (c.) Upon polymerization the bonds formed between the benzene rings span a graphene plane. As a result a chemical synthesis of graphene is proved to be possible.

Graphene and its oxide are two dimensional sheet organic macromolecules that have a crystal lattice, that is they are comprised of repeating in two dimensions monomer units. What are these units? How does a two dimensional polymerization work? These are the questions we address here.

A straightforward response to the inquiry of what monomer units one needs to introduce to initiate two dimensional polymerization, is a monomer that has four functional groups reacting in pairs. However, there exists a more elegant solution. It is applicable in the two dimensional polymerization of graphene and its oxide. Consider the monomer unit in Fig 1a.

This unit contains alternating functional groups A and B attached to a benzene (for graphene) or cyclohexane (for GO) carbon ring. Imposing a polymerization rule that depends on the chemical reaction between A and B we can produce the step depicted in Fig 1b.
The newly formed bond (depicted in color) appears in an arbitrary position in the ring with equal probability for all positions. The letters in the ring denote the positions functional groups had prior to the reaction. Given this rule, one is tempted to assume that the A and B functional groups above and below the bond would also react. However, they are attached with covalent bonds to an sp\(^n\) hybridized carbon atom and these bonds are rigid. Such a reaction would require their bending and this is energy prohibitive. More probable is the reaction with an additional monomer unit. When this occurs we arrive at the lattice represented in Fig [Fig1].

The hexagonal symmetry is present in this newly formed structure. The bonds formed during the polymerization are depicted in color. The key to the understanding of the formation of this lattice is the observation that the intermediate (to the monomer rings) hexagons are spanned by three newly formed bonds. The letters in the monomer hexagons stand as a reminder of where the functional groups were. If one traces the central monomer hexagon and the surrounding it six monomer hexagons, one is convinced that this is the only possible configuration the original monomer units undergone two dimensional polymerization in Fig [Fig1] can arrange in space.

In the general framework discussed here the reacting groups A and B are not specified. We do not see any restriction at this stage and these groups could be any compliant with the rule in Fig [Fig1].

The particulars behind the experimental test of the general framework discussed in the previous section are dependent on the choice of the functional groups A and B reacting to form the lattice pattern of graphene or its oxide. One possible choice for the monomer in a proof-of-concept experiment is 1,3,5 - trihydroxybenzene given in Fig [Fig2] and the chemical reactions behind the polymerization (more appropriately in this case is the term polycondensation) are nucleophilic additions to carbonyl groups.

It exists in equilibrium with its second form the tautomer 1,2,5 - cyclohexanetriole (phloroglucin) where the A functional group is an oxygen atom and B functional group the hydrogen attached to the cyclohexane ring. This is our reacting substance and represents the monomer having very low solubility in water < 1%. Upon its introduction in minute quantities (≈ 0.1%) in a water so-
olution of a base (5 % KOH) the monomer is deprotonated as depicted in Fig. 2b with the possibility of the CH - acidic carbon atom to exist in three different positions and undergo two dimensional polymerization according to the polymerization rule (see Fig. 2c) to arrive at the hexagonal lattice formations Fig. 2d. Given enough time (in our case 4 weeks at room temperature and at dark) large platelets of graphene oxide form Fig. 2e via the attachment of hydrogen cations at the deprotonated sites as well as rearrangement of the bonds.

The successful synthesis of graphene oxide flakes is confirmed in a series of Raman spectroscopic studies, SEM and TEM imagery as well as SAED electron diffraction studies. Experimental evidence is conveyed in Fig. 3 and Fig. 4.

In summary, we have proposed a two dimensional polymerization for the synthesis of graphene and its oxide. A proof-of-concept experiment was conducted and the experimental evidence for the feasibility of this two dimensional polymerization conveyed. This bottom-up approach towards graphene and graphene oxide production could be refined within the general framework presented here.

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Supporting Information Available

For the preparation of the solution containing the reacting monomer we used potassium hydroxide bought from Valerus Ltd. ([http://www.valerus-bg.com](http://www.valerus-bg.com)), with 85% KOH; The monomer is Phloroglucinol, that is 1,3,5 – (OH)₃ C₆H₃.2H₂O purchased from Carlo Erba ([http://www.carloerbareagents.com](http://www.carloerbareagents.com)) and used as received.

The used mixture is 4.25 wt. % KOH: a measure of 0.8 g KOH in 13 mL of H₂O (DI 18 MΩ.cm) with added 3 mL solution of phloroglucinol;

The solution of phloroglucinol is prepared in an ultrasonic bath: a measure of 0.127 g of the substance dissolved in 20 mL of H₂O

Thus a concentration of 0.1 wt. % of phloroglucinol is achieved; the initial solution has a bluish purple tint
The mixture was left for 4 weeks in a closed with parafilm glass eprouvette in a semi-darkened room.

The color of the mixture has changed to yellowish tint and a white semi translucent sediment appeared at the bottom of the vessel.

The sediment was separated in a centrifuge (10 000 rmp) in a series of 10 fomentations with DI. The procedure was a consecutive fomentation, centrifuge and removal of the water column above the sediment. This removed the water soluble salts.

An aliquota was taken on a silicon wafer as well as on a TEM grid

Micro Raman spectrum; SEM and TEM imagery as well as SAED diffractoscopy analysis were conducted.

The scanning electron images were taken using a LYRA I XMU scanning electron microscope (Tescan). The TEM observations and selected area electron diffraction (SAED) analyses were performed on a JEM2100 high resolution transmission electron microscope (HRTEM JEOL) operated at 200 kV. The Raman measurements were carried out using micro-Raman spectrometer LabRAM HR800 Visible with He-Ne (633 nm) laser. At room temperature an objective ×100 was used both to focus the incident laser beam and to collect the scattered light.

This material is available free of charge via the Internet at [http://pubs.acs.org/](http://pubs.acs.org/).
Figure 2: Proposed synthesis of GO (a.) 1,3,5-trihydroxybenzene a phenol-like substance exists in two forms with its tautomer 1,2,5-cyclohexanetriole (phloroglucin) and represents our monomer; (b.) activated in a water solution of a base via deprotonation; (c.) The activated phloroglucins start reacting arranging themselves in a hexagonal lattice. This represents the two-dimensional polymerization; (d.) platelets form; (e.) the deprotonated sites acquire hydrogen cations from the solution to turn the platelets into graphene oxide.
Figure 3: SEM images on a TEM grid of large GO platelets produced in the two dimensional polymerization of phloroglucin (a) & (b); Scalebars are 20 µm in (a) and 5 µm in (b); (c) The expected Raman spectra signatures measured at laser excitation $\lambda = 632.8$ nm that are the D, G, 2D and D + D' peaks.\textsuperscript{13} In our spectra G peak shows hardening and reaches the highest position of 1600 cm$^{-1}$ and D peak appears at 1370 cm$^{-1}$. The second order of the D peak, 2D (or G’) peak position is usually observed in the range 2640- 2700 cm$^{-1}$ depending on the number of layers and the D + D’ peak at 2940 cm$^{-1}$ is due to the defect activated combination of phonons. The wide spreading 2D band and the shoulder at higher wavenumbers indicate formation of multi-layer GO sheets. Additionally, a peak centered at 1450cm$^{-1}$ is modulating the spectrum. Its origin is attributed to a C-OH mode (phenol -OH group) and the characteristic medium band of the carbon ring.\textsuperscript{13} Insert represents a picture of the formations where Raman spectrum was recorded.
Figure 4: TEM images of GO flakes. The scale bar in (a.) and (b.) is 50 nm; Scale bar in (c.) is 5 nm; (d.) The electron diffraction image of the flakes confirm the carbon hexagonal lattice of GO. The periods are $d_{10}=(2.50 \pm 0.27)$ and $d_{11}=(1.47 \pm 0.13)$. The theoretical ratio $\Delta = \frac{d_{10}}{d_{11}} = \sqrt{3}$ for this lattice is confirmed by the experiment $\Delta_{exp} = 1.70$