

# A Review on Thermal Exfoliation of Graphene Oxide

Muge Acik<sup>1</sup> & Yves J. Chabal<sup>1</sup>

<sup>1</sup> Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, TX, USA

Correspondence: Yves J. Chabal, Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, TX 75080, USA . E-mail: [chabal@utdallas.edu](mailto:chabal@utdallas.edu)

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## Abstract

Exfoliation, i.e. individual separation of carbon sheets, is of great interest to produce single-layered graphene nanosheets. Chemical or thermal treatments are popular approaches to exfoliate graphite chunks. In general, these conventional methods are assisted with intercalation via covalent or non-covalent functionalization, expansion, and swelling, adsorption of organic molecules in gas phase, solid nanoparticle insertion or direct molecular exfoliation. However, direct covalent modification of graphene is challenging and the zero-band gap of graphene limits its use in field-effect transistors in nanoelectronics. Therefore, the use of a band-gap tunable p-type semiconducting reduced graphene oxide (rGO) is an alternative route. There are several approaches to tune its band gap, including tailoring the chemistry. Critical parameters include the control of oxygen amount determined by the degree and time of oxidation and reduction conditions (e. g. temperature), often leading to nonstoichiometry. This short review therefore highlights the production of rGO focusing primarily on the effect of thermal treatment on the nature and the role of oxygen during thermal exfoliation of GO. The impact of oxygen functionalization on the modulation of the band gap is also reviewed for chemically and thermally reduced GO, as well as chemically treated rGO followed by a thermal exfoliation.

**Keywords:** band gap, reduced graphene oxide, thermal reduction, exfoliation

## 1. Introduction

### 1.1 Background and Outline

Separation of thin layers of graphene (a 2D material) from a 3D layered bulk graphite results in an increase of its electrical conductivity. To understand the different physical and chemical characteristics of exfoliated graphene for a large area production of graphene sheets, it is important to explore the various types of exfoliation processes. To our knowledge, few common preparation routes for graphene (mechanical exfoliation, CVD-growth on metals or SiC) have been explored for a large area thin film production, driven by the need for an alternative material to silicon for transistors with its low power capability. Apart from the very well-known graphene growth methods, there are several other chemical or thermal processes to exfoliate the chunks of graphite into the layers of graphene. Exfoliation of wet chemically derived graphite layers is one route for separation of individual graphene sheets, particularly attractive for a large area sheet manufacturing with a large volume production. Though, the most common drawback of wet techniques is the production of by-products, which contaminate the graphite layers. It is also hard to eliminate the defects on the basal plane due to the harsh nature of the reducing agents and agglomeration issues in organic solvents. In general, GO reduction in solution result in irreversible particle aggregation in solvents. This is attributed to the interlayer  $\pi$ - $\pi$  conjugate interaction between the graphene sheets. Chen et al. could solve this problem by preventing the agglomeration issue with a subsequent treatment of intercalation, grafting and then exfoliation of GO with  $\gamma$ -ray irradiation in styrene. As a result, a one step procedure could yield in high percent, low-cost, efficient large-scale monolayer production (Chen et al, 2010). Several organic solvents have been studied to exfoliate GO assisted by a thermal reduction. One of these popular solvents is propylene carbonate (PC). Thermal treatment of GO sheets in PC helped further reduction of GO providing an excellent dispersion. This technique could lead to large-scale production with an easy one-step procedure. The capability of PC for exfoliation is attributed to high dipole moment of PC (5.0 D), which could play a crucial role to disperse GO platelets at pH~3 involving the contribution of other solubility parameters of PC (Zhu et al., 2010). Improvements have been demonstrated for the reduction in PC. For instance, increase of ultrasonication time for a large number of particle distribution in the solvents has been shown to increase the exfoliation level of GO as colloidal particles. This could be explained well with the strong

electrostatic repulsion as a result of partial ionization of the GO functional groups in a solvent media (Zhang et al., 2011). Unfortunately, wet chemical processes provide a solution dispersion of GO but liquid suspension of GO followed by a chemical reduction usually has disadvantages, such as defect introduction into the graphene basal plane preventing the  $sp^2$ -C restoration. Improvements have been also shown in this field. For instance, a liquid phase exfoliation could be demonstrated as a technique to produce high quality, oxide-free and defect-free graphene sheets upon treatment with N-methyl-2-pyrrolidone (NMP) and a subsequent thermal treatment at  $\sim 800^\circ\text{C}$  (Oh et al., 2012). Therefore, thermal treatments are heavily used as next steps following wet-processing techniques for thin film preparation. In principle, thermal annealing processes are necessary to produce clean patches of multilayers of graphene sheets in large quantities, which need to be understood well, if a wet ambient is a concern for materials properties.

For these reasons, the main focus of this brief review is to examine the production of high quality sheet exfoliation mainly by thermal treatment via oxygen removal from GO (i.e. thermal reduction or chemically treated rGO followed by a subsequent thermal reduction). Treating graphene oxide (GO) with thermal treatments or a combination of chemical and thermal processes therefore tunes the band gap of the resultant material (rGO) with varying degree of reduction (i.e. depending on the amount of oxygen removed). Although there are several other methods for tuning up the band gap such as oxygen insertion into graphene, our main focus is to review the oxygen behavior in thermal reduction of GO. Parameters affecting the oxygen functionalization; such as heat, moisture, defects or intercalants in reduced GO (rGO) are also within focus of this review article, which tailor the materials optical, electrical, mechanical, and physical properties. Oxygen incorporation and removal plays a key role in this process since bandgap of graphene is opened with functionalization. For this purpose, we discuss and evaluate the nature and the role of oxygen during GO synthesis and GO thermal reduction, in particular the factors that affect intra-sheet interactions and result in sheet-to-sheet variations and therefore bulk-scale production of exfoliated graphene for a low-cost manufacturing. We use the term “reduced graphenes” or rGO for thermally treated GO, and do not address other reduction pathways with details. There are four different subsections to be reviewed next: 1) nature of oxygen for a band gap, 2) selected techniques for rGO production and exfoliation processes, 3) factors affecting oxygen removal and 4) effect of lowering reduction temperature and heat- or chemical-free approaches on GO exfoliation.

### 1.2 Nature of Oxygen for a Band Gap

Oxygen functionalization is known to tune the bandgap of graphene. A gradual reduction of oxygen concentration of GO also tailors the bandgap of the material as a different route. Therefore, the nature of oxygen is significant to tune a bandgap, which is necessary to understand in specific cases given in this section. For nonstoichiometric and hygroscopic compounds like GO, a linear correlation between the bandgap and the molar oxygen concentration has been established (Jung et al., 2009) and theoretical studies have predicted a linear increase of the bandgap with an increase of the oxygen to carbon ratio (Boukhvalov & Katsnelson, 2008). Huang et al. also showed that bandgap of the material increases with the increase of oxygen coverage density (Huang et al., 2012). In particular, density functional theory (DFT) with Vienna *Ab initio* simulations indicated that local minima at a O/C ratio of 11.1% and 25% open a bandgap of 0.780 and 0.354 eV, simultaneously, as shown in Figure 1.

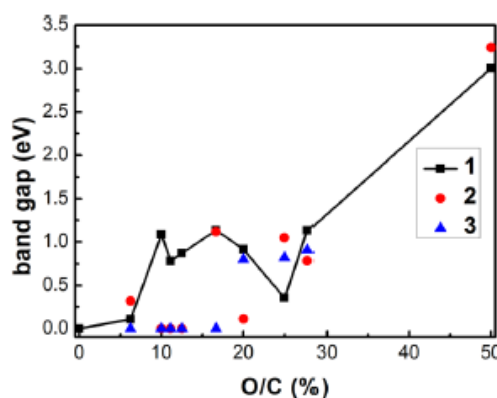


Figure 1. The bandgap of reduced graphene oxide vs. the O/C ratio. The squares correspond to the most stable configurations, and the circles, triangles correspond to the second most and the third most stable configurations, respectively. Reprinted with permission from (Huang et al., 2012). Copyright, the Journal of Applied Physics, American Institute of Physics

A combination of hydrazine and ammonia treatment for GO in water was another approach to tune the bandgap of rGO (Figure 2). Few layered reduced GO (FRGO) was obtained and a gradual functional group removal upon treatment was shown for  $sp^3$  to  $sp^2$  transitions from GO to FRGO decreasing from 2.8 eV to 0.02 eV (Shen et al., 2011).

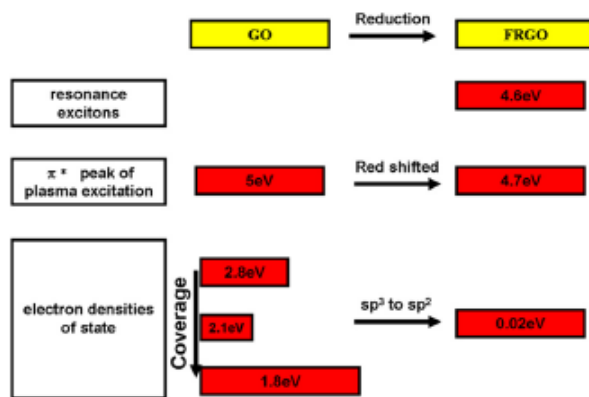


Figure 2. Schematic diagram of the transitions of band-gap through the reducing process from GO to FRGO. Reprinted with permission from (Shen et al., 2011). Copyright, Applied Physics Letters, American Institute of Physics

However, such conventional reduction methods provide a reduction nature with extremely fast kinetics, which makes the control difficult over the chemical organic moiety during reduction. Slower reduction kinetics is necessary to eliminate the aggressive mild chemical behavior of hydrazine. Gas-based hydrazine reduction of GO was achieved rather than following a wet chemistry protocol with a good control of moiety and the order of reduction (Figure 3). A stepwise hydrazine treatment in a controllable and progressive manner results in tuning of the optical bandgap from 3.5 eV to 1.0 eV (Mathkar et al., 2012).

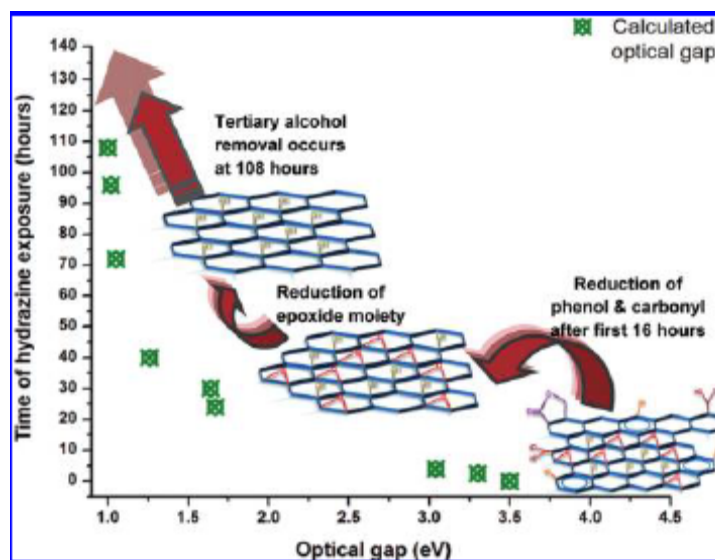


Figure 3. Gradual decrease in optical bandgap upon exposure to hydrazine vapors. The optical bandgap, as calculated by Tauc's analysis shows a progression from 3.5 eV down to 1 eV. Reprinted with permission from (Mathkar et al., 2012). Copyright, the Journal of Physical Chemistry Letters, American Chemical Society

Although, chemical approaches give an idea for tuning the band gap, the amount of oxygen present in oxidized sheets is not easy to determine. The presence of out-of-plane oxygen not only swells the interlayer but also

contributes to expansion and exfoliation. One disadvantage is the non-uniformity of the sheet dispersion and uncontrollable sheet size and shape, hindering process optimization and reproducibility. Each individually modified material is different in terms of the physical and electronic characteristics. Therefore, it is critical to derive a fundamental understanding of both surface modification and interlayer chemistry for many layers of reduced graphene oxide. In the following sections, we will first discuss the use of GO in several different chemical and physical approaches and in only thermal treatments. Then, we will focus on the factors affecting oxygen removal and therefore the bandgaps calculated upon gradual thermal treatments. Lowering thermal treatment temperatures decrease the defect formation and vary the oxygen concentration in the sheets during reduction, which will also be discussed next. Lastly, few new techniques are also provided for exfoliation of GO without the need of heat or chemical treatments.

### 1.3 Selected Techniques for rGO Production and Exfoliation Processes

There are several approaches to produce and modify rGO. Table 1 summarizes a few selected methods. These are: 1) modification of thin films by intercalating organic or inorganic molecules in between many layers of oxidized graphene in solution. Initial functionalization can occur through covalent or non-covalent (weak) binding to open up the interlayer spacing, followed by either chemical or thermal processing or a combination of both to cleave the bonds and to remove the molecules for sheet expansion; 2) thermal treatment of GO to obtain “rGO” followed by functionalization for modifying the edges. GO is likely to go into spontaneous reduction in the presence of other chemicals to form composites; 3) chemical reduction in combination with thermal annealing to eliminate the chemical residuals and clear the patches of rGO; and 4) direct surface coating of GO for composites followed by a thermal or hydrothermal treatment through simultaneous reactions.

Among these different approaches, direct thermal treatment is an effective means of modulating the band gap of the exfoliated sheets by oxygen removal. Therefore, control on the degree of reduction is a key factor. The increase of the Raman intensity of the red-shifted G peak as a function of temperature indicates that rGO is a band-gap tunable compound (Cuong et al., 2010).

Table 1. Selected approaches for exfoliation processes

Precursor	Treatment	Process	Specifications	Resulting Material	Ref.
GO	thermal	intercalation, exfoliation	aggregates by tetrabutyl-ammonium	high-throughput, large-sized sheets	Ang et al., 2009
GO	chemical, thermal	treated by hydrazine monohydrate	200°C, 500°C, 800°C, 1000°C in Ar, ultra high vacuum or H <sub>2</sub>	rGO	Yanga et al., 2009
GO	hydrazine treatment in a SiO <sub>2</sub> medium	followed by thermal treatment	500°C in N <sub>2</sub>	rGO-SiO <sub>2</sub> composite	Zhu et al., 2011
rGO	Langmuir–Blodgett assembly	followed by thermal treatment	500°C for an hour in a forming gas	rGO as a transparent electrode	Wöbkenberg et al., 2011
rGO	tetrasulfonate salt of copper phthalocyanine	hydrazine exposure followed by a thermal treatment	120°C for an hour in vacuum ambient	rGO with photocatalytic activity	Chunder et al., 2010
GO	coated with TiO <sub>2</sub> nanoparticles	hydrothermal treatment	400°C in Ar	rGO-TiO <sub>2</sub> nanocarbon composites	Wang et al., 2011

rGO	Coated with ZnO	thermal treatment	200°C for an hour in air	specific capacitance (135 F g <sup>-1</sup> )	Chen et al., 2011
GO	hydrazine vapor for 12 hours	thermal treatment, aligned ZnO nanorods or tubes	400°C in Ar for 1 hour	rGO-ZnO-poly(3-hexylthiophene) composite	Figure 2 Yang et al., 2011
rGO	chemical	covalent functionalization, intercalation, exfoliation	ferrocene	rGO-ferrocene composite	Avinash et al., 2010
GO	solar radiation	simultaneous reduction and exfoliation	metal/metal oxide (CuO, NiO and Fe <sub>2</sub> O <sub>3</sub> ) dispersion at 150-200°C	rGO-metal oxide composites	Sasikaladevi et al., 2011
GO	chemical	molecular intercalation, direct exfoliation	in-situ polymerization of aniline	rGO-polyaniline hybrid composites	Chen et al., 2011
GO	chemical	intercalation, exfoliation	glucose	rGO-glucose composites	Shen et al., 2012

Eda et al. also showed that a slight reduction of GO sheets results in an increased fluorescence intensity of the blue fluorescence (Eda et al., 2009). A 25-nm-thick GO film heated by a tip at 1000°C results in only a few layers of GO on SiC interface to be left underneath the hot AFM tip. This enables modulating the band gap as demonstrated in its current-voltage (I-V) characteristics (Wei et al., 2010). Ekiz et al.'s study also emphasizes the importance of tuning the degree of both oxidation and reduction between gradual decrease and increase of the amount of oxygen in rGO (Ekiz et al., 2011).

The band gap modulation mechanism is still not clear for most of the rGO community. Defects have been shown to play a critical role for tuning a band gap. Based on the modeling studies, Xiao et al. explains that opening a band gap with the oxygen plasma induced disorder enhances the thermopower of modified graphenes (Xiao et al., 2010). Decomposition of rGO after annealing at 300°C is accompanied by a carbon loss indicated by desorption components of H<sub>2</sub>O, CO<sub>2</sub>, CO and O<sub>2</sub>. This phenomenon was shown spectroscopically by Acik et al. who correlated the carbon loss with defect formation leading to CO<sub>2</sub>/CO production (i.e. structural decomposition) (Acik et al., 2010). Increase of epoxy coverage increased the defect concentration and the release of CO/CO<sub>2</sub> species, whereas a low coverage prevents any distortion. Surface density of the epoxy species was therefore found to be the key factor to control the lattice damage on the basal plane of graphene. This leads to a new direction for thermal annealing of GO, which could be adjusted with a controllable epoxy coverage to prevent damage of the sheets with heat. Interlayer reactions are also likely to occur between trapped molecules such as H<sub>2</sub>O and defective graphene patches, leading to additional oxidation through carbonyl formation (Figure 4) (Acik et al., 2010).

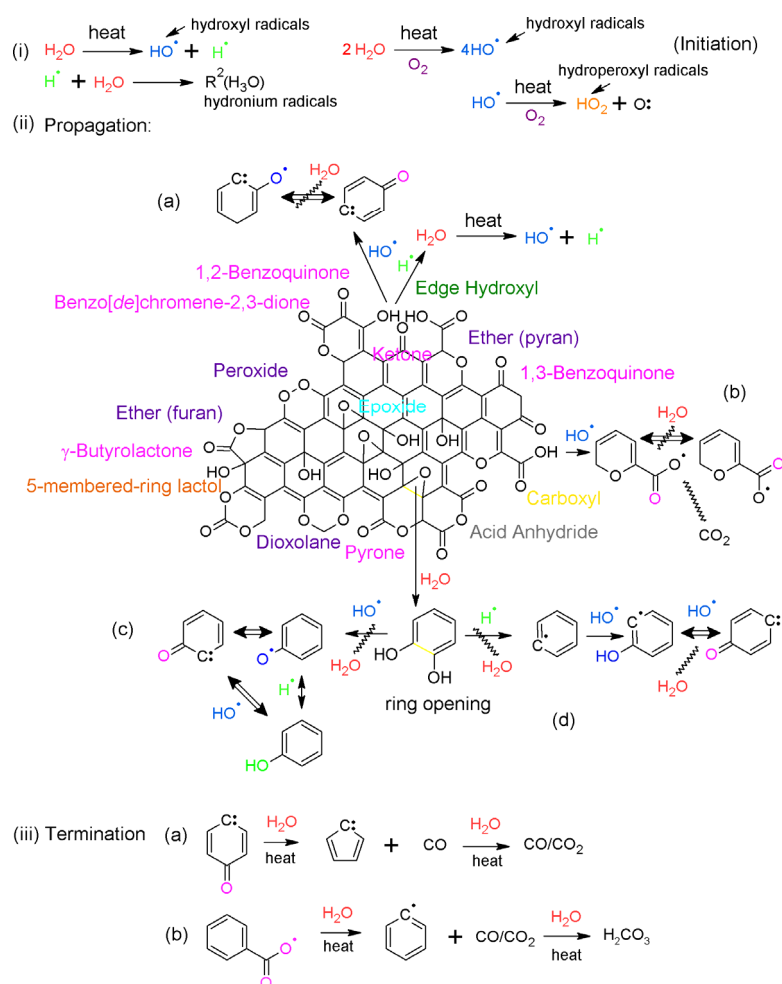


Figure 4. Schematic illustration of thermal reduction mechanisms for GO: i) radical formation, ii) intermediate radical reactions and iii) termination. Reprinted with permission from (Acik et al., 2011). Copyright, the Journal of Physical Chemistry C, ACS Publishing Group

A recent study showed graphene monoxide production having a band gap of  $\sim 0.9$  eV with a thermal reduction ( $\sim 500$ - $700^\circ\text{C}$ ) of GO in vacuum. Intercalated water in GO demonstrated an unobserved atomic structure and morphology, which is a phase segregation resulting in graphitic regions with little or no oxidation after annealing (Mattson et al., 2011). It was also found that water molecules from the ambient or at the  $\text{SiO}_2$ /graphene interface can split into  $\text{H}^+$  and  $\text{OH}^-$  with further attaching to graphene and generating a band gap (Echtermeyer et al., 2008). Fast water transport as a function of temperature and the close-to-zero intrinsic thermal expansion are found to be the key factors for pseudonegative thermal expansion of GO and vary based on the humidity levels. Therefore, removal and insertion of interstitial water induces a highly negative thermal expansion coefficient (Zhu et al., 2012). Replacement of intercalated water with methanol or ethanol was shown to prevent defect enlargement during annealing. In particular, when ethanol is decomposed during its integration into the etch holes of reduced graphene oxide (rGO), a new hexagonal carbon ring was formed leading to improved graphitization of rGO (Gong et al., 2012). Ethanol was shown as atypical reductant, which reduces the oxygen concentration of GO and further has the capability of restoring the  $\text{sp}^2$ -conjugation. This study demonstrated the individual intercalation of methanol, ethanol and water into GO interlayers and a further thermal treatment at a stepwise temperature range of  $60$ - $300^\circ\text{C}$  could be investigated. These modification reactions are therefore critical for the performance of graphene field effect devices that uses exfoliated graphene as top gate electrodes. The next section will focus on the factors affecting oxygen removal and its impact to produce rGO in a manufacturable scale.

#### 1.4 Factors Affecting Oxygen Removal

The materials physical and electronic properties are greatly affected by the oxidation conditions. Even for the

same synthesis procedure, variation in time of oxidation, temperature, and the initial concentration and type of oxidant determine the amount of oxygen, oxygen components and their thermal stability for each individual platelet of exfoliated graphene layers. This section therefore reviews all these common factors, which determine the bandgap of the material. In regards to GO exfoliation, it is important to know the level of sheet attraction to each other with a certain interlayer distance and how strong the reaction between GO layers and the solvent media. This layer interaction is also significantly influenced by the oxygen functional groups, i.e. the degree of oxidation. Modified Hummers' method with shorter time synthesis and a lower oxidation temperature were shown to play crucial roles in exhibiting larger sheets and higher thermal stability (Shao et al., 2012). Jeong et al.'s study confirms that different oxidation times can trigger the band gap of GO from 1.7 to 2.4 eV modifying the oxygen-to-carbon ratio (Jeong et al., 2009, Figure 5). Regarding oxidation levels, density functional theory (DFT) calculations predict that a fully oxidized graphene has an indirect 2.14 eV band gap with a very low conduction band minimum (for an epoxy pair along the zigzag direction), whereas a mixture of a normal, an unzipped epoxy and an epoxy pair has a slightly lower energy in its ground-state phase and a much larger band gap (Xiang et al., 2010).

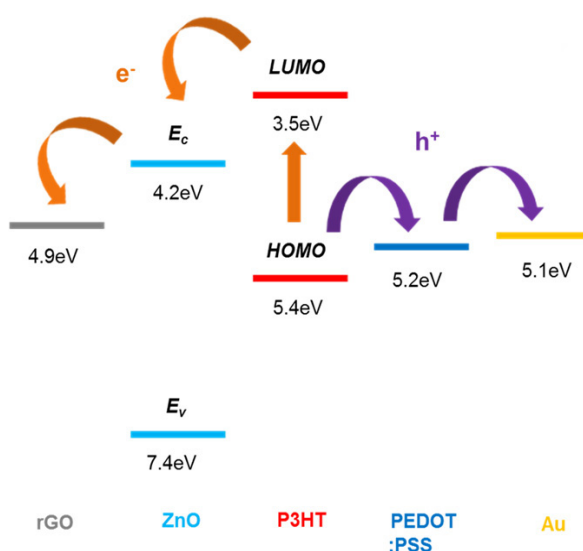


Figure 5. The energy level diagram with respect to the vacuum level for a typical rGO/ZnO/P3HT/PEDOT:PSS/Au device. Reprinted with permission from (Jeong et al., 2009). Copyright, Journal of Physics D: Applied Physics, iop publishing

A similar challenge is faced during annealing steps of thermal processing. Indeed, the degree of reduction is important for the applications of rGO. For example, there is a decrease of the barrier height for an epitaxial graphene/GO junction showing a Schottky barrier after thermally reducing GO at 180°C for 16 hours with pretreated at 100°C for 30 minutes for physisorbed water removal (Wu et al., 2008). Oxygen removal during reduction of GO also depends on the reduction ambient (vacuum, Ar, N<sub>2</sub> or H<sub>2</sub>), temperature control, and kinetics as discussed in (Acik et al., 2011). Based on the spectroscopic measurements, the reduction of two different batches of GO having relatively the same thickness leads to similar amount of oxygen remaining even after high temperature anneals (~850°C). Even for large initial oxygen concentrations, the resulting amount of oxygen remains large after high temperature anneals (~850°C) because the amount of initial trapped water molecules is high (independent of the number of stacked layers). This is attributed to the large amount of additional carbonyls that are formed at intermediate temperature anneals, when trapped water molecules react with the defective sites in the interlayer. Since carbonyls are highly stable compounds, subsequent reduction is hindered. Ganguly et al.'s study with a combination of X-Ray photoemission and X-Ray absorption spectroscopies confirmed the fact that edge plane carboxyl groups of GO are highly unstable and could be only removed by a thermal treatment at ~400°C, whereas the edge plane carbonyls remained even at ~1000°C. A drastic increase of density of states near the Fermi level was also observed after annealing at ~600°C, which indicated the sp<sup>2</sup> restoration in the thermally reduced GO (Ganguly et al., 2011).

The reduction time is another factor that modifies the degree of oxidation in rGO. For instance, few layer GO reduced at 150°C in air (for 0 to 260 min) modulates the band gap of GO (intrinsically ~2.2 eV): 1.4 eV, 0.8 eV,



and 0.5 eV for 20 min., 90 min., and 260 min. reduction, respectively (Chang et al., 2010), going through insulator-semiconductor-semi-metal transitions with reduction (Eda et al., 2009). In this study, a much faster reduction at 300°C anneal is also shown to generate a much less controllable band gap than a 150°C anneal. Acik et al. also showed that kinetics affect thermal reduction as well. For instance, the overall carbonyl concentration is much reduced after 1 h anneal, compared to 5 min anneal at the same temperatures. This is ascribed with the fact that the oxygen groups are efficiently removed even though additional carbonyls are initially formed; they decompose in the absence of water but oxygen is not fully removed. Short annealing times at 850°C also result in oxygen aggregation at the sheet edges in rGO (Figure 3) (Acik et al., 2010, Figure 6). Therefore, both factors prevent a complete oxygen removal with a thermal treatment.

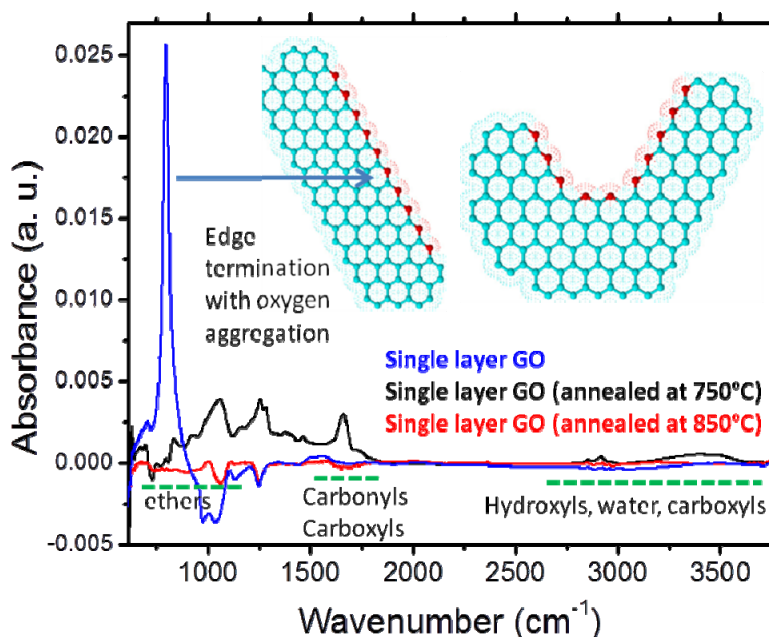


Figure 6. Absorbance spectra of initial (black), annealed at 750°C (red) and 850°C (blue) of single layer GO illustrating oxygen aggregation at the edges. Reprinted with permission from (Acik et al., 2010). Copyright, Nature Materials, Nature Publishing Group

### 1.5 Effect of Lowering Reduction Temperature and Heat- or Chemical-free Approaches on GO Exfoliation

In the previous discussions, reducing GO at elevated temperatures was shown to reduce the oxygen concentration, but introduces defects in rGO. For this reason, recent developments have been found to lower the reduction temperatures for defect-free graphene sheet production. This section therefore highlights the necessity of lower thermal temperatures with selected reduction examples and cases of heat- and chemical-free ambient as different techniques. One approach to lower the thermal reduction temperature was microwave-assisted rapid thermal reduction (~165°C) of GO in a mixed solution of N,N-dimethylacetamide and water. Microwave brings an advantage of heating GO in a very short time resulting in a pre-exfoliation process for a rapid production. The results indicated that microwave-assisted reduced GO conductivity is  $\sim 10^4$  times larger than GO (Chen et al., 2010). Interaction of nanoparticles with graphene sheets is advantageous to prevent collapsing exfoliated graphene sheets by improving physical and colloidal properties, such as surface area, accessibility, storage and electronic conductivity. A facile nanoparticle decoration of GO with platinum acetylacetonate was shown without the need of high temperatures or surfactants (Figure 7). Surface functionalization through a low temperature treatment (~500°C in nitrogen gas for 2 hours) resulted in exfoliation of reduced graphene sheets (Mayavan et al., 2012).



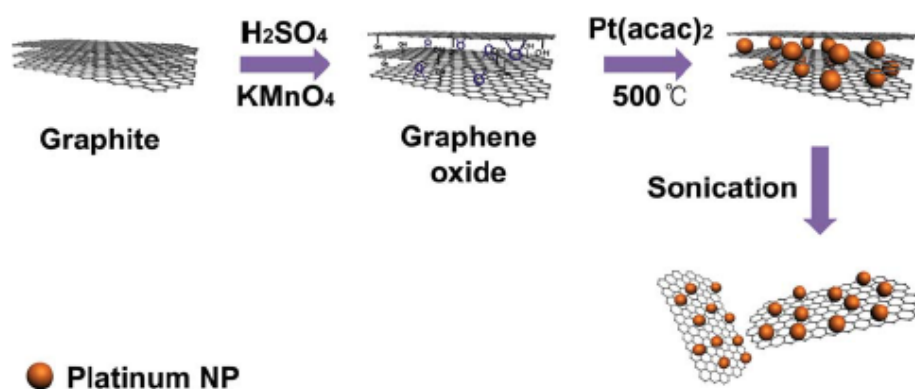


Figure 7. Schematic for the synthesis of Pt-Graphene. Reprinted with permission from (Mayavan et al., 2012). Copyright, Journal of Materials Chemistry, RSC Publishing

In addition, rapid synthesis of few-layered graphene sheets were obtained by hydrogen induced reduction-exfoliation of GO at low temperatures ( $\sim 200^\circ\text{C}$ ) (Kaniyoor et al., 2010). For an efficient way of capturing  $\text{CO}_2$  gas, thermally exfoliated graphene nanoplates were also prepared using a novel high efficiency sorbent. Exfoliation was followed with a GO expansion by a low-heat treatment at  $150\text{--}400^\circ\text{C}$  (Meng et al., 2012). In addition, in-situ reduction of GO with thermal exfoliation ( $\sim 135^\circ\text{C}$ ) via a vacuum-assisted method could be obtained for large quantity graphene production with improved high surface area of  $758\text{ m}^2/\text{g}$  under vacuum (Zhang et al., 2011).

Several new plasma-assisted techniques have been recently demonstrated for exfoliating GO in large quantities without using heat treatments. Ar assisted radiofrequency plasma exposure at high pressure was used to thin down the multilayer GO platelets in a controllable and reproducible fashion. This micromechanical cleavage technique helped reduction and exfoliation to few-layered graphene sheets without using heat treatments of wet chemical processes (Cardinali et al., 2011). Another approach was a chemical-free method for high quality large-area graphene sheet production. Therefore, solar electromagnetic radiation is one way. In principle, when radiation is absorbed, the photoacoustic effect occurs with a further optical radiation conversion to heat. Therefore, a thermal expansion develops in time. Eswaraiah et al. also demonstrated GO exfoliation with a solar exfoliation technique that increases the temperature to  $150\text{--}200^\circ\text{C}$  and therefore overcome the van der Waals forces between the graphene sheets (Eswaraiah et al., 2011). We brought only few examples to your attention for development of new scientific areas for one-step facile and high throughput GO exfoliation. Since this topic is out of our topic, we only introduced the importance of various approaches for exfoliating GO. All of the above bring new insights to explore new highly efficient exfoliation techniques for a large-scale production of highly conductive rGO with a reasonable bandgaps.

## 2. Conclusion and Outlook

Graphene has attracted the attention of the scientific community and is becoming an important part of the electronics world. Large area production and modulation of the band gap of graphene sheets are both critical properties for a variety of applications. This review has focused on the mechanistic understanding of gradual oxygen removal during the reduction of GO, particularly by thermal treatments. Factors that affect the nature of the oxygen, and therefore the bandgaps of rGO were discussed. In this respect, the control of the oxygen in the exfoliated rGO is critical because it affects the materials properties. Understanding the mechanisms and surface modification reactions through intercalation and functionalization is necessary for bandgap modulation of reduced graphenes for organic nano-electronics in world wide applications. Although several approaches have been developed and demonstrated for the exfoliation of rGO difficulties, such as defect formation or intercalated species like water molecules make the complete control of exfoliation impossible. This also tailors the bandgaps in an uncontrollable fashion. To conclude, future studies are yet necessary to figure out the new techniques for faster, one-step, high throughput of large area sheet production with defect-free patches and a controllable mechanistic understanding to tune the bandgaps.

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