Microwave reduction of graphene oxide rationalized by reactive molecular dynamics

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Obtaining graphene (GRA) in industrial quantities is among the most urgent goals in today’s nanotechnology. Elegant methods involve the oxidation of graphite with its subsequent solvent-assisted exfoliation. The reduction of graphene oxide (GO) is challenging leading to a highly-disordered oxygen-rich material. A particularly successful microwave-induced reduction of GO was reported recently (Science, 2016, 353, 1413–1416). We mimic the experiment by reactive molecular dynamics and establish the molecular mechanisms of reduction and their time scales as functions of temperature. We show that the rapid removal of oxygen groups achieved by microwave heating leaves GRA sheets intact. The epoxy groups are most stable within GO. They can rearrange into the carbonyl groups upon quick heating. It is important to avoid creating holes upon graphite oxidation. They cannot be healed easily and undermine GRA thermal stability and electronic properties. The edge oxygen groups cannot be removed by irradiation, but their effect is marginal on the properties of μm GRA sheets. We demonstrate that different oxygen groups are removed from GO at drastically different temperatures. Therefore, it is possible to obtain separate fractions, e.g. carbonyl-, hydroxyl- and carboxyl-free partially reduced GO. Our results guide the improvement of the GO reduction methods and can be tested directly by experiment.

1. Introduction

The solvent-assisted exfoliation of graphite is a promising experimental technique for the production of graphene (GRA) in high (industrial) quantities. However, only low yields of single-layer GRA, with generally broad thickness distributions of multi-layer GRA, have been observed through exfoliation thus far. Exfoliation is thermodynamically unfavorable and, therefore, requires external investments of energy (sonication, centrifugation, electrochemical exfoliation, etc.). The intercalation of electrolytes has been found useful to enhance exfoliation. Surfactants (amphiphilic molecules) are able to change favorably the thermodynamics of exfoliation. The restacking of GRA after exfoliation is possible and should be efficiently prevented. A thoughtful selection of the exfoliation solvent is very important. The treatment of graphite with strong oxidizers (Hummer’s method) produces graphite oxide, also frequently referred to as graphitic oxide and graphitic acid (GA). GA is composed of carbon, oxygen, and hydrogen in variable ratios depending on the oxidation conditions. The usually reported carbon to oxygen ratios in GA range from 2.1 to 2.9. Efforts to prepare GA with a tailored percentage of oxygen (oxidation degree) are known to match certain application needs. High fractions of oxygen result in a lower-density, ~1000 kg m⁻³, material with large and irregular inter-layer spacing. GA is interesting for a variety of applications. GA readily undergoes exfoliation in water and aqueous solutions producing graphene oxide (GO) with yields of up to 100%. However, GO lacks several favorable properties of GRA. Removal of the oxygen functional groups is challenging, leading to a highly disordered material with drastically inferior properties. It has not been possible yet to obtain good-quality GRA from GO. Therefore, the product of GO reduction is called reduced GO (rGO) to underline its difference from pristine GRA. While GO and rGO can be useful in catalysis, energy storage and other applications, their utility in electronics is much less feasible. Sustainable methods enabling the efficient chemical modification of GO and rGO into GRA would be of high importance.

Recently, Voiry and co-workers reported an interesting GO reduction method by using 1- to 2-second long microwave pulses. Upon irradiation, large arcing was observed around GO typically lasting 50–100 ms. The authors correlate arcing with a vigorous GO reduction. An estimated short-time growth of the GO temperature is a few thousand degrees celsius. Prior to microwaving, a mild annealing was performed at 300 °C for 1 hour under an argon atmosphere. The authors compared microwaving with and without annealing at 300 °C, and con-
cluded that the preliminary annealing was of crucial importance. The Raman spectrum of the reported rGO is reminiscent of the pristine GRA spectrum synthesized by chemical vapor deposition. Furthermore, X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy reveal a highly-ordered structure with a negligible content of oxygen functional groups. The reported rGO exhibits very good charge mobilities of over 1000 cm² V⁻¹ s⁻¹ in field-effect transistors and unexpectedly low Tafel slopes of ~38 mV per decade for the rGO catalyst support in the oxygen evolution reaction. The success of Voiry and co-workers⁶⁰ demonstrates the fundamental possibility to produce high-quality GRA from GO, employing what one would call a brute-force approach. Avoiding additional reactants allows one to limit the number of undesirable by-products. Microwaves were also successfully applied by Matsumoto and co-workers,¹⁶ who employed molecularly engineered oligomeric ionic liquids. The concentration of high-quality GRA of ~100 g L⁻¹ was reported.

In this paper, we report a detailed theoretical analysis of the chemical transformations occurring in GO upon microwave irradiation. We demonstrate that the fast temperature increase, achievable by microwaves, leads to a rapid removal of most oxygen containing groups, while at the same time, the stability of the GRA sheet is not undermined. We show that carbonyl, hydroxyl, carboxyl and epoxide groups leave GO at very different temperatures, allowing one to obtain different fractions of reduced GO. The carbonyl group can be removed by mild annealing. By raising the temperature one can eliminate hydroxyl, then carboxyl, and then epoxide groups. The epoxide groups cannot be removed from GRA edges without destroying the sheet itself. Holes in the GRA sheet cannot be healed easily. Therefore, it is important to avoid hole formation during the preliminary steps of graphite oxidation and exfoliation. By identifying the mechanisms of the microwave-driven GRA reduction reactions and describing the corresponding conditions and time scales, we provide a detailed interpretation of the experimental findings,⁶⁰ investigate the possibilities of reduction to high-quality GRA, and outline directions of future method improvements.

### 2. Methodology

Reactive molecular dynamics (RMD) was used to simulate the effect of microwave irradiation on GO. RMD allows one to simulate chemical reactions in real-time. RMD employs all algorithms of classical MD in conjunction with sophisticated interaction potentials. The potential functions are designed to reproduce potential energy surface (PES) in the simulated system, including possible electronic polarization, solvation effects, covalent reactions, and the existence of radicals. The parametrization coefficients (force field) are derived by scanning PES by ab initio methods. The current work relies on the force field developed by van Duin and co-workers⁶¹ for hydrogen, carbon, and oxygen atoms.

The simulations were conducted in the constant temperature constant volume ensemble. Constant temperature was maintained by using the Berendsen thermostat with a relaxation time of 50 fs.⁶² The equations-of-motion were propagated with a time-step of 0.1 fs. The interactions were computed explicitly between all atoms in the box, neglecting information about the existing molecules. The total potential introduces a relationship between the bond order and the bond energy. The bond order evolves during RMD as a function of interatomic distances, allowing for covalent bond breakage and formation. The bond order is present in all valence interaction terms, i.e. it accounts for thermally induced fluctuations of valence angle and torsion angle energies. The energies and forces associated with these terms approach zero upon molecule dissociation. Unlike in classical MD, bonded atoms also interact via non-bonding terms.

Computer simulations provide atomistic control and allow us to focus on individual oxygen functional groups. While a realistic GO can contain a mixture of different functional groups over a broad range of combinations, we separate GO into four systems: hydroxylated GO, carboxylated GO, epoxylated GO and carbonylated GO. Such a representation allows us to compare systematically different degrees of GO oxidation, and to study their reduction mechanisms and possible introduction of defects. First, the RMD systems (Table 1) were annealed at 600 and 800 K for 1 ns. Microwaving of GO results

<table>
<thead>
<tr>
<th>#</th>
<th>Name</th>
<th>Composition</th>
<th>x (O), w/w%</th>
<th># Independent simulations</th>
<th># Time-steps, ×10⁶</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Moderately hydroxylated</td>
<td>C₂₁₈H₅₇O₂₉</td>
<td>15</td>
<td>12</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>Moderately carboxylated</td>
<td>C₂₄₇H₅₇O₂₈</td>
<td>24</td>
<td>12</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>Moderately epoxylated</td>
<td>C₂₁₈H₂₈O₂₃</td>
<td>12</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>Moderately carbonylated</td>
<td>C₂₄₈H₁₄O₂₉</td>
<td>13</td>
<td>8</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>Weakly hydroxylated</td>
<td>C₂₁₈H₁₆O₁₆</td>
<td>9</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>Weakly carboxylated</td>
<td>C₂₃₄H₄₄O₁₂</td>
<td>15</td>
<td>12</td>
<td>70</td>
</tr>
<tr>
<td>7</td>
<td>Weakly epoxylated</td>
<td>C₂₁₈H₁₆O₁₈</td>
<td>10</td>
<td>14</td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td>Weakly carbonylated</td>
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<td>10</td>
<td>8</td>
<td>18</td>
</tr>
<tr>
<td>9</td>
<td>Hole defect</td>
<td>C₂₀₅H₁₆O₁</td>
<td>—</td>
<td>10</td>
<td>60</td>
</tr>
</tbody>
</table>
in vigorous heating of the material, up to several thousand degrees celsius. To simulate this effect, we subjected the RMD systems to quick heating from 600 K with a continuous temperature increase of $1 \times 10^{-3}$ K fs$^{-1}$ or $1 \times 10^{-4}$ K per time-step. This pace of heating is enough to achieve a nearly uniform temperature increase over an entire simulated sheet, due to the high thermal conductivity of GRA and GO. In this way, the conditions of the relevant reactions were identified. Finally, equilibrium RMD simulations were conducted at the determined temperatures to characterize the reaction kinetics. Since the carbonyl groups were unstable at 600 K, we additionally simulated the carbonylated GRA at 300, 400, and 500 K for 100 ps to obtain the temperature of their removal. The size of the simulation cell with periodic boundary conditions was set to $8 \times 8 \times 8$ nm$^3$. The cell was sufficiently large to mimic the experimental conditions, in which there was no buildup of elevated pressure due to the formation of gaseous products.

We investigated preliminarily the effect of the GRA sheet flexibility by reducing the carboxylated, hydroxylated, and epoxylated coronene molecules, whose carbon backbone is quite rigid. No differences were observed compared with the reduction of the larger and, therefore, more flexible GRA sheets used in the main simulations (Table 1).

Avogadro (version 1.1.1) was used to construct and optimize initial geometries of GO and defective GO. RMD simulations were conducted by the LAMMPS module. The evolution of Cartesian coordinates was visualized and the molecular images were prepared in VMD (version 1.9.2). In-home tools were used for all other procedures.

3. Results and discussion

Considering carboxyl, hydroxyl, carbonyl, and epoxy groups, we prepared weakly and moderately oxidized GO monolayers (Table 1) to identify possible differences in their reductions. Moderately oxidized GO was equipped with oxygen groups from both sides (Fig. 1). The groups were grafted at random positions with a single restraint: no new group should be placed in the ortho-position to an existing group. We constructed separate RMD systems for each oxygen group. These systems can be interpreted as different regions of GO, in which a particular functional group prevails. Furthermore, such an approach allows us to characterize the conditions necessary for the removal of every group.

The GO samples were annealed at 600 K for 1.0 ns to mimic the experimental methodology. Only the in-plane carbonyl groups from the GRA surface were removed during this stage, whereas all other oxygen groups remained intact. The in-plane C=O groups exhibit low stability, since they have the same structure as carbon monoxide, and since the additional C–C covalent bonds on the surface of GRA are quite strained. Consequently, the removal of C=O is straightforward and thermodynamically favorable when the temperature is moderately elevated. Note that only in-plane C=O groups can be removed during mild annealing. In turn, the edge C=O groups are extremely stable and none of them was separated. The separation of an edge group would transform GO into a non-singlet state with a radical character. Apart from C=O, mild annealing is helpful to eliminate amorphous carbon, which can be formed during oxidation, and small organic admixtures, which should evaporate at 600 K. The annealing stage is likely important, because admixtures deteriorate the thermal conductivity of GO and may lead to unexpected reactivity at high temperatures induced by microwaves. We also repeated mild annealing at 800 K and got quantitatively the same results.

Microwave irradiation leads to a very quick heating of the samples, as demonstrated experimentally, and the RMD simulations were designed to mimic this situation (see section 2). Each simulation was stopped when all in-plane oxygen groups were removed, and a new simulation was started from a different distribution of momenta and a slightly shifted geometry. RMD simulations of every system were repeated 3–7 times to derive statistically meaningful averages and to estimate error bars.

Fig. 2 summarizes which oxygen groups leave GO at which time (temperature) during the quick heating. The first hydroxyl groups start to leave at 1300 K, the first carboxyl groups at

Fig. 1 Graphene oxide model: (a) face view; (b) back view; (c) side view.

Fig. 2 Diagram of GO reduction under nanosecond heating in a vacuum.
2200 K, and the first epoxy groups at 2800 K. Further heating leads to drastic sheet deformations (at \(\sim 3000\) K) and eventually the destruction of the overall GRA structure (at \(\sim 3500\) K). It is important to note that the reported temperatures (1) correspond to defect-free starting geometries; (2) were obtained by heating in a vacuum; (3) heating lasted for about a nanosecond. The simulation conditions are roughly similar to those expected in the experiment of Voiry and co-workers\(^6\) although the latter were not accurately determined. The success of the microwave-based method relies on a very quick annealing process, during which the C–C bonds of GO are not broken. If annealing had been performed over macroscopic times, this would have led to the transformation of the entire species into amorphous carbon and subsequent oxidation.

The final reduction reaction products are water vapor and carbon dioxide, which are formed when the oxygen containing groups meet one another and oxygen in the vapor phase. The formation of the final products occurs later than their separation from GO, and therefore, these steps are chemically decoupled from the GO reduction.

Fig. 3–6 depict representative conformations of the GO samples during heating. The snapshots present immediate configurations and are not statistical averages. They are meant to represent visually the changes in the structure and degree of chemical reduction of the GO samples with increasing temperature. Quantitative information regarding the progress of the reduction reactions over time at a particular temperature is presented in subsequent figures. The temperatures reported in Fig. 3–6 are approximate, \(\pm 100\) K.

At 600 K, an ideal GO sheet exhibits nearly perfect geometry, which cannot be visually distinguished from the absolute-zero conformation. Different in-plane oxygen groups leave the surface at very different temperatures: 500 K (carbonyl), 1300 K (hydroxyl), 2200 K (carboxyl), and 2800 K (epoxy). The epoxy group\(^6\) is most stable, because it is bound to the sheet by two polar covalent bonds simultaneously. At the same time, the separation of the epoxy group can be achieved faster than critical non-reversible deformations of the GRA sheet. Since different oxygen groups exhibit very different stabilities, it is possible to obtain separate fractions, e.g. carbonyl-, hydroxyl- and carboxyl-free partially reduced GO.

The first significant structural perturbations of the GRA backbone were observed at \(\sim 1500\) K, irrespective of the oxygen groups grafted. At this temperature, a number of oxygen groups still reside on the GRA surface. In a few cases, we observed the migration of the oxygen groups over the GRA surface. After a covalent bond with a certain carbon atom was broken, another covalent bond was formed with an adjacent carbon atom within a few ps. While the in-plane oxygen groups were gradually removed, most of the edge oxygen groups were not. Cleansing the edges leads to the formation of radicals. Radical scavenging requires additional reactants, which are not available in our RMD simulations. The supply of molecular hydrogen at elevated pressures can likely be useful to reduce the edges as well. Fig. 3–5 show that almost all in-plane oxygen groups can be removed by the end of heating.

The oxidation of GRA typically leads to the emergence of holes\(^6\) which subsequently act as additional edges of GO. One such hole is depicted in Fig. 6. We demonstrated that the oxygen groups occupying the hole cannot be removed by heating. Even at 3500 K, they are still not removed, despite large-scale geometric perturbations. These oxygen groups

![Fig. 3](image-url) Structural deformations of GO decorated with epoxy groups upon nanosecond heating.
should be removed by other, probably chemical, methods. The survival of the oxygenated holes indicates that it is important to design oxidation procedures, e.g. Hummer's method of graphite oxidation and subsequent GO exfoliation, to minimize damage of the initial graphite structure.

Fig. 4  Structural deformations of GO decorated with carboxyl groups upon nanosecond heating.

Fig. 5  Structural deformations of GO decorated with hydroxyl groups upon nanosecond heating.

Fig. 7 characterizes the structure generated by the epoxy group. The epoxy group is bound to two adjacent carbon atoms of GRA via polar covalent bonds, and therefore, its removal requires significant amounts of thermal energy. The structure of the in-plane epoxy group is different from that of
hydrocarbon oxides, e.g. ethylene oxide. Due to geometric restraints, the C–C bond length is ∼1.7 Å, while the C–C bond length is 1.41 Å in pristine GRA. Thermal fluctuations at high temperatures range from 1.5 to 2.3 Å. While 2.3 Å corresponds to non-bonded carbon atoms, they are kept together by other carbon atoms in the lattice. After the oxygen atom is removed, at ∼20 ps (Fig. 7), the involved carbon atoms restore their initial covalent bond, whose length returns to 1.4 Å. The subsequent bond length fluctuations are significantly smaller compared to the fluctuations of the same bond when it was part of the epoxy group. Our RMD analysis indicates that the epoxy group represents a major hazard to the GRA stability upon fast heating.

The GO reduction of different oxygen groups at fixed temperature is analyzed in Fig. 8. Up to five independent RMD simulations per system were performed and their results were statistically averaged. Note that the RMD simulations were conducted at different temperatures selected by the previous quick-heating RMD simulations, depending on the functional group. Fast reductions at the reported temperatures indicate that somewhat smaller temperatures can be used to remove the oxygen groups over longer periods of time, μs or ms.

The most frequently observed defects created upon the GO reduction are visualized in Fig. 9. Breakage of C–C bonds is the most common defect; however, it does not destroy the sheet. If a reactant is supplied, these defects will constitute most probable reaction sites. At high temperatures, some epoxy groups isomerize into edge carbonyl groups. During this process, the C–C bond breaks apart, giving rise to a new small hole (Fig. 6). As we exemplify above, the removal of oxygen from such holes is not possible by the microwave induced heating without destructing a large part of the GRA sheet. Above 2000 K, the GRA/GO sheets bend significantly with a simultaneous partial breakage of C–C bonds. The bending can lead to tubular structures, as reported experimentally.68

Does the density of oxygen groups influence the reduction pace? High degrees of oxidation may undermine the stability of the sheet and, therefore, oxygen removal could occur faster. Fig. 10 depicts the detachment of the oxygen groups in the weakly oxidized GO systems (Table 1). Both moderately and
weakly oxidized GO are reduced substantially (∼90%) at the respective temperatures for 100 ps. Reduction of the moderately oxidized GO occurs faster during the first ps (Fig. 8), but slows down at the end of the RMD simulations. Thus, we confirm that high densities of oxygen in GO promote a faster initial reduction. It should be possible to convert highly oxidized GO into weakly oxidized GO very quickly and, possibly, at modest temperatures, whereas a complete reduction requires several thousand degrees celsius.

4. Conclusions

The ultrafast microwave induced reduction of GO was studied by RMD simulations. We confirmed and rationalize the experi-

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**Fig. 8** (a) Removal of the oxygen groups from the GRA surface (GO reduction) versus time. Note temperature differences. (b) Removal of the hydroxyl groups at 1500 K in the course of a few independent RMD simulations. The symbol sizes are commensurate with the standard errors associated with the computed property.

**Fig. 9** Most frequent structural defects observed upon microwave irradiation of GO: (a) carbon–carbon bond breakage; (b) carbonyl group formation; (c) bending of the sheet. Typical examples are highlighted by the red-contour transparent squares. The visualized defects were observed upon continuous heating of the reduced GO above 2000 K. The carbon–carbon bond length threshold was set to 0.18 nm, which is about 30% larger than the conventional bond length in pristine GRA.

**Fig. 10** Removal of the oxygen groups from the weakly oxidized (Table 1) GRA surface versus time.
mentally observed removal of a substantial fraction, over 90%, of oxygen groups by microwave irradiation without destroying the GRA sheet and, for the first time, report the atomistic details of the transformations that occur during the GO reduction. Microwave heating leads to a fast temperature increase, facilitating the rapid removal of oxygen containing groups on timescales that are too short to undermine GRA sheet stability. We showed that in-plane oxygen groups exhibit very different stabilities. The carbonyl group can be removed by mild annealing at temperatures below 600 K. Elimination of the hydroxyl group on a nanosecond time scale requires rapid heating to 1500 K, whereas elimination of the carboxyl group requires 2200 K. The epoxide group is most stable. Its rapid removal requires temperatures on the order of 2800 K.

The edge oxygen groups are systematically more stable than the in-plane groups. They cannot be removed by microwaving, since the required temperature initiates the prompt decomposition of GRA. Fortunately, the fraction of the edge oxygen groups is negligible in sufficiently large GRA sheets (μm × μm), and therefore, the edge groups do not deteriorate the valuable electronic properties of GRA. If still necessary, the edge groups can be removed by hydrogen catalytically. According to RMD, microwaving leads to the formation of 1–2% of edge C==O groups starting, most frequently, from the epoxide groups. Because of the double bond, the C==O groups remain stable only at the edges of the sheet and in the holes. The formation of stable C==O groups leads to the emergence of additional holes within the GRA sheet. The edge C==O groups cannot be removed by annealing and, therefore, contribute to the amount of the residuary oxygen groups reported in the experiment.69

The reported reduction temperatures were identified with an assumption of very prompt reactions (100 ps). If GO reduction is to occur on the microsecond to millisecond time scale, the reaction characteristic times will probably be reduced by a few hundred degrees celsius. However, an ultrafast reduction flow is very important to prevent the simultaneous destruction of the GRA sheet itself. Unlike the simulated ideal geometries, real GRA contains structural defects, which substantially decrease its thermal stability. For instance, Nan and co-workers69 reported that GRA species synthesized by chemical vapor deposition and mechanical cleavage start to contain sp³-type defects at 500–600 °C in air. In turn, a perfect structure in low vacuum was observed up to 900 °C.70 The primary reactions, which lead to a partial decomposition of real GRA at 800–1000 °C, occur with metal catalyst particles and involve the re-arrangement of sheets into tubular structures upon annealing.68 These reactions are not fast and can be avoided if annealing lasts less than a second.

To recapitulate, microwave irradiation provides a promising solution for increasing the quality of GRA obtained from GO by exfoliation and subsequent reduction. Most of the in-plane oxygen groups can be removed, whereas the GRA backbone can be preserved intact, provided that the microwave pulses are short. Further method development efforts should be directed to a more precise temperature control and analysis of the effect of contaminants in the GO sample upon microwaving.

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Notes and references