COMMUNICATION

Reactive Events at the Graphene Oxide-Water Interface

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Graphene oxide exhibits interesting reactive events at its interface with water, with water as an active participant. The reactive events are influenced by the level of oxidation of the graphene oxide sheet. The fully oxidized sheet tends to make the interfacial water media acidic leaving the sheet negatively charged, whereas the reduced sheet can form comparatively long lived carbocations as well as split water forming two alcohol groups on the sheet.

Graphene oxide (GO),[1,2] ranging from a single sheet to a few layers of graphite oxide, has multiple applications spanning water treatment to energy storage,[3–9] thus sparking significant interest in the scientific community. An interesting aspect of GO is the presence of both hydrophilic oxygen-bearing groups and hydrophobic carbon graphene-like structure. This in turn provides a handle to tune the properties of the material by, for example, changing the oxidation level of the sheet. Whereas graphene-oxide reactivity in aqueous media with additional species (solute, ions) has been reported in the literature: adsorption,[4,10–13] aggregation,[14,15] nanopores,[16–20] etc.., very few findings have been reported regarding its intrinsic reactivity with neat water. Recently, a paper by Mouhat *et al.*[21] showed the reactive nature of graphene-oxide in aqueous media: proton transfer, epoxide opening, and even dehydration events. In this communication,[21] it is confirmed that the graphene oxide sheet is more reactive than previously thought and, furthermore the oxidation level of the graphene oxide sheet plays an important role in the reactivity of the GO-neat water interface.

In this article, to explore the reactivity of the graphene oxide sheet, two different oxidation levels of graphene (ratio C/O equal to 2 and 4, respectively) were studied by Born-Oppenheimer Molecular Dynamics (BOMD), at the DFT level of theory, with a thin layer of water (20 Å) deposited on one side. These models were previously used to investigate the origin of the signatures of the interfacial water in vibrational sum frequency (a surface sensitive spectroscopic experiment) spectra of these systems.[22] Five different starting points for each level of oxidation were used to start five BOMD simulations in the canonical ensemble (NVT) ensemble for 5 ps of equilibration and then 25 ps of production each (see ESI for details). These sheets were built with a mix of alcohol and epoxide oxygen groups with a thin water film in contact with the sheet. The water layer is exposed to air (vacuum) on the other side (see Figure S1 for a schematic of the simulated systems). After equilibration followed by the production run, several new species were seen to have formed: alcohol and epoxide, are of course still present but there are also alkoxide, ether, and ketone groups on the sheet, and in the bulk hydronium species form as well. For $GO_{2/1}$, starting from an initial ratio of 50.0 epoxides and 40.0 alcohols, at the end of the five simulations there are, on average, 45.4 epoxides, 2.2 ethers, 41.0 alcohols, 0.6 alkoxides and 1.4 ketones. For $GO_{4/1}$, starting from 24.0 epoxides and 20.0 alcohols, the sheets evolve to, on

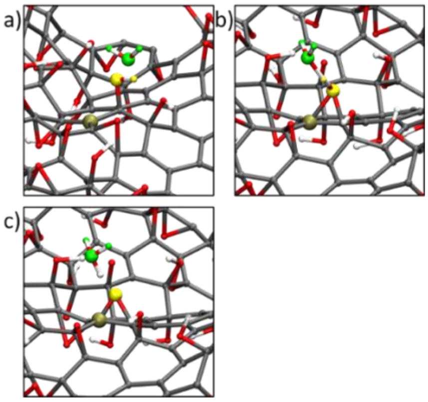

Figure 1. Protonation of a water molecule by an alcohol in the $GO_{2/1}$ case a) Water and Alcohol. b) intermediate structure c) Hydronium and epoxide. Atoms of the reactive species are arranged by colours (yellow, green, tan) and colours are kept throughout to highlight proton jumps.

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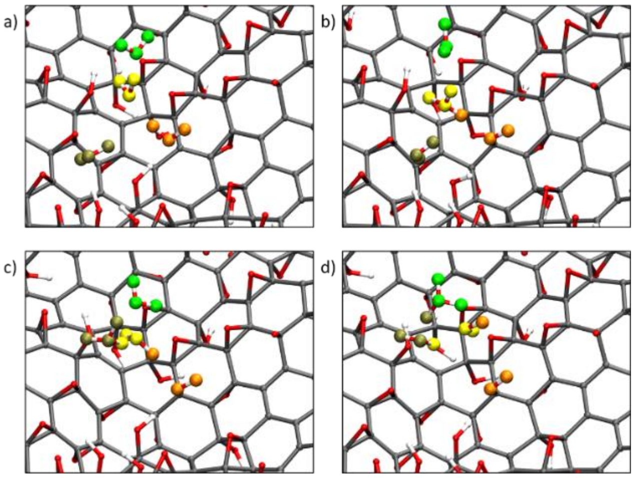

Figure 2. Water addition on the $GO_{2/1}$ sheet. a) Initial step; b) Water addition forming an alcohol on the GO sheet and hydronium, c) and d) multiple proton jumps away for the sheet. Atoms of the reactive species are coloured (orange, yellow, green, tan) throughout to highlight the proton jumps.

average, 19.2 epoxides, 2.0 ethers, 20.0 alcohols, 3.0 alkoxides and 0.0 ketones. This communication will assert the formation of these species and the formation of long-lived hydronium ions in the case of $GO_{2/1}$.

At both oxidation levels, the initial type of event that is seen is the epoxide opening event (and the reverse reaction, epoxide closing) responsible for the formation of alkoxide. As previously reported,[21] this event is believed to be due to the release of the strain of the GO sheet. On average, three open epoxides (alkoxides) were observed at the end of the simulations in the $GO_{4/1}$ case, and less than one for $GO_{2/1}$ This illustrates that the opening of epoxide events on the $GO_{4/1}$ sheet tend to be permanent, whereas for the $GO_{2/1}$ sheet, one can see the opening of epoxide, forming an alkoxide but the alkoxide is more of a transient species in this case. Specifically, in $GO_{2/1}$, the alkoxide reacts with another carbon of an epoxide leading to a new epoxide opening event, forming a new alkoxide. This new alkoxide can either be protonated (by a hydronium or by another alcohol nearby) to form an alcohol, evolve into a ketone, or form an epoxide by reacting with a carbocation. The sheet re-equilibrates to reduce initial stress akin to an "epoxide diffusion process".[23] This feature means that the initial configuration of the oxygen-bearing group might not be as decisive as previously thought, since, with enough equilibration time, the sheet will reorganize itself. Given the timescales that are accessible by BOMD, the use of several different starting points is hence essential for adequate sampling. A key point, highlighting the difference of reactivity between $GO_{2/1}$ and $GO_{4/1}$, is the fact that the sheet can stabilize the carbocation formed along with the alkoxide in epoxide opening events, notably, by its graphene-like (island of carbon sp^2 without any oxygen-bearing groups) region, which are more numerous in the $GO_{4/1}$ sheet (as the ratio C/O is higher). Hence the number of alkoxides (and thus carbocations) is very low (less than one on average) in the $GO_{2/1}$ sheet and higher in $GO_{4/1}$ (three on average), despite the former having nearly twice as many epoxides as the latter. This key reactivity (rearrangement) of the sheet will, only in the case of $GO_{2/1}$, permit the water protonation where a water molecule will get protonated by an alcohol group (similar to previous findings) and then the alkoxide will close to form an epoxide (Figure 1) (or a ketone). This resulting epoxide formation can lead to another epoxide opening nearby (forming an alkoxide) or if another carbocation from an already epoxide opening event is nearby, it will react with it. In both cases, the charged pair alkoxide/carbocation will become an alkoxide and a hydronium pair, with a separation of the order of a few Angstroms, resulting in a non-immediate protonation of the alkoxide formed (due to the distance as well as due to the better stabilisation of this alkoxide via hydrogen bonding). The total charge on the GO sheet will be then slightly negative. Epoxides can also give rise to a breaking of the C-C bonds, forming an ether as already confirmed both experimentaly[24] and by simulations.[25] Hydroniums, in the $GO_{2/1}$ sheet, can also come from the water addition on the GO sheet (Figure 2). The steps and final products of the addition of water are different than the $GO_{4/1}$ sheet, as in the latter both charges were on the GO sheet (alkoxide-carbocation pair).[22] The first step, in the $GO_{2/1}$ case, starts when a water molecule approaches a carbocation site (formed by epoxide opening): this water reacts by attacking the carbocation, forming a transient protonated alcohol. This protonated alcohol gives its proton to a water molecule, forming a stabilized hydronium. This reaction has two outcomes: this positive charge is now in the aqueous media (like the water protonation by an alcohol shown in Figure 1) but this time the GO sheet has also become more oxidized. This reactivity also increases the level of oxidation of the GO sheet.

Another reaction that is observed, with a transient hydronium this time, is the dehydration of the sheet (seen mainly in $GO_{2/1}$). Starting from an arrangement of three alcohols and a water molecule (Figure 3a), an alcohol protonates a water molecule to form a hydronium and, in this case, a ketone (Figure 3b) (but alkoxide can also form) with the rupture of the carbon-carbon bond. The proton then subsequently hops to another alcohol

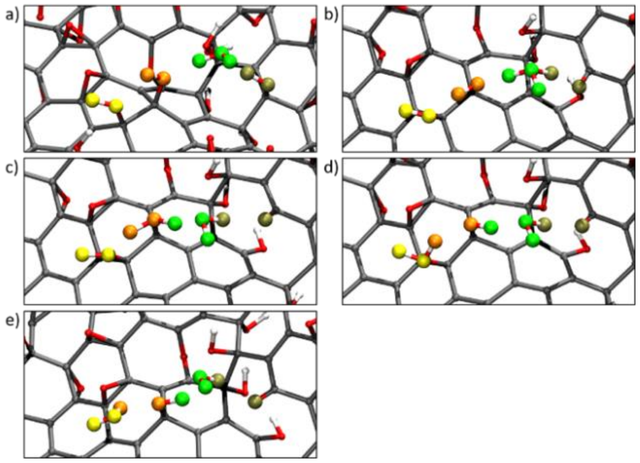

Figure 3. Dehydration of the $GO_{2/1}$ sheet: a) initial structure b) formation of a hydronium and a ketone, c) first proton jump to a nearby alcohol forming a protonated alcohol and a water molecule d) second proton jump to another alcohol e) dehydration of the protonated alcohol forming a water molecule. Atoms of the reactive species are arranged by colours (orange, yellow, green, tan) to highlight the proton jumps.

(Figure 3c) and in turn, another proton hops to a new alcohol, forming a protonated alcohol (Figure 3d) which then leaves the GO sheet forming a water molecule (Figure 3e). This effectively reduces the oxidation level of the GO sheet. On the other hand, dehydration reactivity in $GO_{4/1}$ (resulting in epoxide formation) is similar to the one found in the study by Mouhat *et al*[21] where three alcohols are a very specific arrangement (only in one of their sheets), three carbon apart. However, in this communication it is shown that for the more oxidized $GO_{2/1}$, the water serves as a relay between the alcohols and moreover the breaking of a carbon-carbon bond is also observed. This point indicates that the reactivity in $GO_{2/1}$ does not depend on the arrangement but rather on the environment of the two endpoints of the reactive chain and does not exclude the possibility of a longer reactive hopping chain. In the $GO_{2/1}$ case, the hydronium comes from two reactions: alcohol deprotonation forming an epoxide and the hydronium or water addition forming an alcohol and the hydronium. These two events result in the transfer of the positive charge defect from the sheet (in both cases, a carbocation from a previous epoxide opening event) to the aqueous media (a hydronium), and the second event also increases, albeit slightly, the oxidation level of the graphene sheet. The proton can, during its lifetime (several picoseconds, as proton formed for less than 1 ps are not counted) shuttle across multiple water molecules by hopping as shown in Figure 4 demonstrating that is not a transient species. The combination of a lower pKa of graphene oxide alcohol,[26,27] the stress on the material and the limit of the number of positive charge defects it can have on its very few graphene-like regions, facilitates the formation of long-lived hydroniums in $GO_{2/1}$.

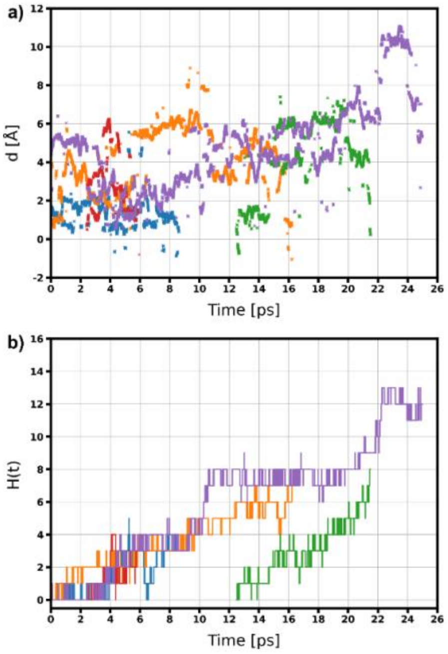

Figure 4. a) Distance between the oxygen of the hydronium and the instantaneous water interface in the $GO_{2/1}$ case. b) Corresponding hydronium hopping function H(t). Each colour corresponds to a different hydronium from different simulations. The different colours indicate the five different simulations carried out.

In Figure 4a the distance (d) between the oxygen of the hydronium and the Willard-Chandler instantaneous water interface[28] is reported while Figure 4b shows the hydronium hopping function H(t) as a function of time (t). This function quantifies the forward hopping of the proton between waters (see ESI for details). One can see that the hydrated proton (hydronium) can stay either in the vicinity of the instantaneous water interface (where $d < 3$ Å) or jump further away ($d > 5$ Å) but doesn't move to the air-water interface (despite the slight propensity for this interface in simulations and experiments of the air-water interface).[29–32] This behaviour is easily explained by the fact that the GO sheet is negatively charged[21] and hence, hydronium is attracted to the sheet.[33] The proton moves by either hopping parallel to the interface (variation in H(t) but not in the distance d) or perpendicularly (variation in both). The proton can react by protonating back an alkoxide forming an alcohol (which is the reverse of the first reaction). It can also protonate an alcohol (reverse of the second reaction) on the GO sheet, reducing the GO sheet. It can also, as shown in Figure 4, purple simulation, stay in the aqueous media for the whole simulation. One can also observe that the proton can hop to a "trapped" water molecule, very close to the GO sheet (where d is less than 0 Å). In most of the cases, this is when the hydronium is either formed (Figure 4, green curve) or annihilated (Figure 4, green, orange, blue curves). In some case, the hydronium is also present at the beginning of the production part of the runs, since it formed during the "discarded" equilibration. The fact that the formation can also be seen in the production run after a short (Figure 4,red curve) or longer (Figure 4, green curve) time shows that it is not an artefact. In the case of the $GO_{4/1}$ sheet, two $GO_{2/1}$ type of events are absent (non transient water protonation and ketone formation): this seems consistent with the hypotheses that the positive defect formed in $GO_{4/1}$ is stabilised by the presence of larger graphene-like regions, thus delocalizing the carbocation. As stated before, both sheets need to relieve their strains by opening epoxide to an alkoxide-carbocation pair. In $GO_{2/1}$, it can form an epoxide again by having the alkoxide react with another carbon to relieve stress (which in turn opens another epoxide). Contrary to the case of $GO_{2/1}$ where the positive charge defect cannot be stabilized by the carbon sheet and thus delocalizing the positive charge into the aqueous media is favoured, the carbocations in the $GO_{4/1}$ are non-transient. $GO_{4/1}$ can also have a water addition type reactivity, thereby oxidizing the sheet (but without forming a hydronium). Here, two charged species, the alkoxide and the carbocation, are neutralized by splitting a water molecule and react with a proton and the hydroxide respectively, forming two alcohols.[22]

In conclusion, different reactive events (see Table 1) with water are observed depending on the level of oxidation of the GO sheet. The more oxidized one ($GO_{2/1}$) will react with water forming new species like hydronium and can also rearrange itself forming different oxygen groups like ketone or ether. The most important feature is the long-lived hydronium-alkoxide pair produced. $GO_{4/1}$ (less oxidized) also reacts with water albeit differently, not forming long-lived hydroniums and less likely to rearrange to form new oxygen groups (only ether). For the most

Table 1 Comparison of the reactivity of $GO_{2/1}$/water and $GO_{4/1}$/water interfaces

$GO_{2/1}$ (more oxidized)	$GO_{4/1}$ (less oxidized)
Epoxide opening forming a transient carbocation	Epoxide opening forming a long-lived carbocation
Long-lived hydronium (with Grotthuss transport)[32]	Transient hydronium (< 1ps)
A water reacts with another water and carbocation forming an alcohol and a hydronium	A water reacts with an alkoxide and carbocation forming two alcohols
Protonation of water by an alcohol forming hydronium and an alkoxide (which can react with a carbocation forming an epoxide or a ketone)	Protonation of water by an alcohol forming a transient hydronium / alkoxide pair (and the transient hydronium protonates the same (or different) alkoxide forming back a water/alcohol pair)
Dehydration (two alcohols into a ketone/alkoxide and water)	Dehydration (two alcohols into an epoxide and a water)
Epoxide into ether (breaking of the C-C bond)	

part, it forms a non-transient carbocation-alkoxide pair which, although rarely, can “split water” forming two new alcohol groups. These reactive events can play an important role in the catalytic activity of graphene oxide, either by providing an acidic interface (as in $GO_{2/1}$), or a long-lived carbocation formed on graphene-like islands (as in $GO_{4/1}$). For both oxidation cases, water plays an active role and the resulting active sites are not solely the oxygen-bearing groups – the acidic interface and the carbocations formed can also be major players.

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There are no conflicts to declare.

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