

## Graphene to Fluorographene: A Reactive Molecular Dynamics Study

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We have investigated, using fully reactive molecular dynamics methodology, the structural and dynamical aspects of the fluorination of graphene membranes leading to fluorographene formation. The strong and fast chemical reactivity processes involving fluorine produce distinct aspects of the observed in the case of the hydrogenation of graphene (the so called graphane formation). Fluorination tends to produce significant defective areas on the graphene membrane with alteration on the typical carbon-carbon distances, sometimes with the presence of large holes due to carbon losses. This may explain the broad distribution of values of lattice parameter experimentally observed.

### I. INTRODUCTION

Graphene is a two dimensional array of hexagonal units of  $sp^2$  bonded C atoms with very unusual and interesting electronic and mechanical properties [1]. Because of its electronic properties, graphene is considered one of the most promising materials for future electronics [2]. However, in its pristine state it is a gapless semiconductor, so a graphene-based transistor electronics can be seriously limited [3].

One way to open a gap is by chemical modifications of graphene membranes through oxidation [1, 4–8], hydrogenation [9–12] and/or fluorination [14]. The structures resulting from these processes are graphene oxide (GO) [13], graphane [9] and fluorographene (FG) [14].

GO has been produced by exposing graphite to liquid oxidizing agents and it is basically a graphene sheet randomly and inhomogeneously decorated with hydroxyl and epoxy groups. Graphane [9] was theoretically predicted and consists of a single-layer structure with fully saturated ( $sp^3$  hybridization) carbon atoms with C-H bonds in an alternating pattern (up and down with relation to the plane defined by the carbon atoms). Hydrogenation of monolayer graphene has already been reported [15–18]. More recently, Elias et al. [11] demonstrated the existence of graphane formation from graphene membranes through its fully hydrogenation and showed that graphene membranes with both surfaces exposed to atomic H exhibited a decreased crystal lattice parameters with relation to graphene [12]. Despite these promising results, the hydrogenation of graphene was observed to be an easily reversible process even at moderate temperatures, which compromises the use of graphane in applications where such stability is required.

Graphene covered with fluorine atoms could be a good alternative because it is a 2D analogue of the well-known ma-

terials; Teflon, which is composed of fluorinated 1D carbon chain, and graphite fluoride (GrF), a multi-layer graphene fluoride. However, obtaining FG from mechanical cleavage of graphite fluoride has proved to be a very difficult task.

Recently, important steps forward to the synthesis of FG were achieved [14, 19, 20]. One of the most successfully processes has been one in which graphene is exposed to atomic F generated from the decomposition of xenon difluoride ( $XeF_2$ ). It was shown that the resulting FG exhibits a strong insulating behavior at room temperature and high stability up to 400°C. Some Raman measurements also indicate that, even when the process is done during a long time, the resulting sample presents some regions with carbon atoms that are not bonded to fluorine atoms and the coverage saturation can vary depending on the method adopted for fluorination [14]. However, in spite of the importance of these materials, no detailed study of the fluorographene formation has been carried out up to now.

In this work we have investigated, using fully reactive molecular dynamics methods, the structural and dynamical aspects of the fluorination mechanism, leading to FG formation from graphene structures.

### II. METHODOLOGY

The fluorine incorporation process on graphene was studied with molecular dynamics (MD) techniques using reactive force fields (ReaxFF [21–23]) as implemented in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code [24]. ReaxFF is a reactive force field developed by van Duin, Goddard III and co-workers for use in MD calculations, allowing the simulation of many types of chemical reactions. ReaxFF has some characteristics which are similar to those found in standard non-reactive force fields, like MM3 [25]. In this kind of force field, the system energy is divided into partial energy contributions associated with, amongst others, valence angle bending and bond stretching, as well as, non-bonded van der Waals and Coulomb interac-

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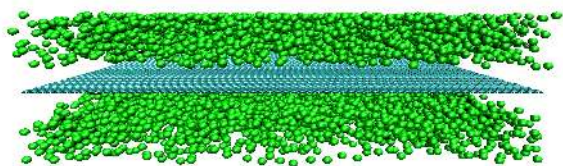


Figure 1: Initial configuration for the simulation of fluorination processes. Graphene membrane (cyan) embedded in fluorine atmosphere (green atoms)

tions [21–23]. However, in the case of ReaxFF, one main difference is that it can handle bond formation and dissociation as a function of bond order values.

The used structural model is composed of a large graphene membrane (initially with dimensions  $\sim 160 \times 160 \text{ \AA}$ ) embedded into a pure ( $F$ ) atmosphere (see Figure 1). The number of atoms in the gas was up to twice the number of carbon ones (about 9700 carbon atoms), and they were randomly distributed over both sides of the membrane. The typical time for a complete simulation was 0.5 ns, considering time steps of 1.0 fs using a Langevin thermostat.

### III. RESULTS AND DISCUSSION

Our results show that at 500K, and remarkably at 650K, the graphene membrane suffers significant damages. This observation is in good agreement with experimental works regarding fluorination/hydrogenation through ion bombardment [11, 14]. Since the observed damages were extensive at these temperatures, our analysis will focus on MD results from 300K.

The processes of the fluorine incorporation on the graphene membranes can be illustrated by the representative snapshots

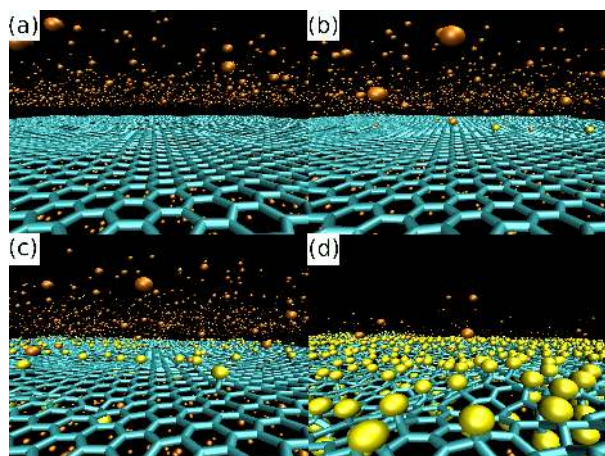


Figure 2: Representative snapshots from MD simulations of the fluorination process for stages (a) 10, (b) 60, (c) 210 and (d) 490ps. Graphene membrane is represented in cyan, fluorine atoms in orange when non-bonded (atmosphere) and yellow when bonded to carbon atoms.

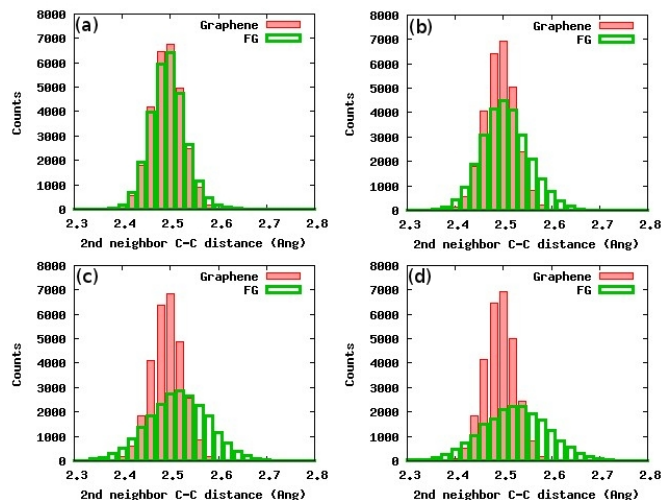


Figure 3: Histograms obtained for a graphene membrane (red) and fluorographene membrane (FG) (green) for four subsequent stages of fluorination process: (a) 10, (b) 60, (c) 210 and (d) 490ps.

of a 0.5ns simulation run at 300K, displayed in Figure 2. Initially, we have a planar graphene membrane (Figure 2 (a)), immersed into a fluorine atmosphere. In about 60ps after the beginning of the simulation, we can see some fluorine atoms randomly attached to the membrane (Figure 2(b)). This process continues (intermediate state in Figure 2(c)) and in about 490ps the fluorination reached its critical point (Figure 2(d)) with 12% of carbon atoms bonded to fluorine atoms. These results highlight the difference between the dynamics of  $F$  incorporation and prediction for the graphane (hydrogenated graphene) formation [12]. It is also possible to note that in the early stages of fluorination, trans geometry is the most common C-F configuration for adjacent fluorine atoms. This favours the formation of chair domains, as can be seen in fluorination advanced stages.

During the fluorination process, the carbon atoms which are bonded to fluorine ones have their  $sp^2$  hybridization changed to  $sp^3$ -like one. This transformation from a planar to a more tridimensional structure brings several new characteristics. For that reason, it is important to understand the geometry changes of the fluorinated system in comparison to pure graphene membranes. We show in Figure 3 histograms of *second-neighbor* distances (related to the unit cell of the lattice) of four stages of a fluorination simulation. It is possible to clearly see a broadening of the distribution of values for *second-neighbor* distances during the fluorination process. The final stages, Figure (3-c and 3-d), show a broad distribution of distances in the case of fluorographene. The FG obtained from fluorination of graphene membrane has a cell size  $\sim 1.3\%$  larger than that of graphene in vacuum. These results are in very good agreement with the experimental lattice parameters observed. The mean values of these distributions are also in good agreement with experimental results reported by Geim and co-workers [14]. In our simulations, typically, F-C bonding distances are about 1.4 Å, which agrees with theoret-

tical *ab initio* [26] and experimental [27] results.

#### IV. CONCLUSIONS

We have used a fully reactive molecular dynamics approach in order to study the structural and dynamical effects of the incorporation of F on graphene membranes through pure fluorine atmospheres. Our results showed that the fluorination process occurred without correlated domains formation and resulted in a fluorographene which has a unit cell 1.3% larger

than that found for graphene with a large-spread of second-neighbor distances. At high temperatures, it is notable the hole formation on graphene membrane due to carbon losses.

#### V. ACKNOWLEDGMENTS

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