

Graphyne Hydrogenation: A Fully Atomistic Molecular Dynamics Investigation

Pedro Alves da Silva Autreto^{1,2} and D. S. Galvão¹

¹Instituto de Física “Gleb Wataghin”, Universidade Estadual de Campinas, 13083-970, Campinas-SP, Brazil

² Department of Mechanical Engineering and Material Science, Rice University, Houston-TX, U.S.A.

autretos@ifi.unicamp.br

Carbon-based materials of reduced dimensionality have shown to exhibit some extraordinary structural, thermal and electronic properties. One example of this is graphene, a single-planar layer of sp^2 -hybridized carbons that has become one of the hottest topics in materials science today. Due to its unique properties, graphene is considered as the basis for a new nanoelectronics. However, in its pristine form graphene is a zero bandgap semiconductor, which limits its use in transistor applications.

Diverse physical and chemical approaches have been tried to solve this problem. Ideally, the gap opening should not compromise other desirable electronic properties, such as, the linear dependence of the energy of the conduction and valence electrons with their momentum, i. e., the main Dirac cone properties.

In part due to it, there is a renewed the interest in other possible carbon-based 2D materials, as for example, the graphyne structures [1,2]. Proposed by Baughman and co-workers in 1987 [2], graphyne is a generic name for a carbon allotrope family of 2D structures, where benzenoid rings are connected by acetylenic groups, with the coexistence of sp and sp^2 hybridized carbon atoms. These structures share some of graphene unique properties [1], with the advantage of some of them are non-zero electronic bandgap systems [3]. Similar to graphene, that can be the structural basis to create carbon nanotubes, graphyne nanotubes are also possible [4,5,6]. Also, similarly to graphene, graphyne hydrogenation can be used to smartly tune its electronic band gap.

In this work we have investigated, through fully atomistic reactive molecular dynamics simulations, the dynamics and structural changes of the hydrogenation of single-layer graphyne membranes. The extensive MD study was carried out using reactive force fields (ReaxFF [7]), as implemented in the Large-scale atomic/Molecular Massively Parallel Simulator (LAMMPS) code [8]. We have used a NVT ensemble and the temperature was controlled using a Nosé-Hoover thermostat. The simulations were carried out at room temperature (300 K), and the typical time for a complete simulation run was of 2 ns, with time-steps of 0.1 fs. This approach has been successfully applied to the study of hydrogenated graphene [9]. The process of simulating the hydrogenation of the graphyne membranes were carried out considering an isolated single-layer graphyne sheet immersed into an atmosphere of atomic hydrogen. In this work, we restricted ourselves to investigate the α , β , and γ graphyne forms (Figure 1), although other structures are possible.

Our results showed that the existence of different sites for hydrogen bonding, related to single and triple bonds, makes the process of incorporating hydrogen atoms into graphyne membranes much more complex than the graphene ones (Figure 2). Our results show that hydrogenation reactions are strongly site dependent and that the sp -hybridized carbon atoms are the preferential sites to chemical attacks. In our cases, the effectiveness of the hydrogenation (estimated from the number of hydrogen atoms covalently bonded to carbon atoms) follows the α , β , γ -graphyne structure ordering. Another important result is that, in contrast with was reported to the case of graphene hydrogenation [9], we did not observe the formation of correlated domains (islands of hydrogenated carbons). This can be a consequence of the porous graphyne structure, which allows larger out-of-plane deformations (in comparison to graphene) and, consequently, an increase in the curvature with an increased local chemical reactivity. Consistently, in the case of graphene fluorination (fluorine is more reactive than hydrogen atoms) the formation of these domains are also suppressed [10].

References

- [1] D. Malko, C. Neiss, F. Vines, and A. Gorling, *Phys. Rev. Lett.* **108** (2012) 086804.
- [2] R. Baughman, H. Eckhardt, M. Kertesz, *J. Chem. Phys.* **87** (1987) 6687.
- [3] Q. Peng, W. Ji, and S. De, *Phys. Chem. Chem. Phys.* **14** (2012) 13385.
- [4] V. R. Coluci, S. F. Braga, S. B. Legoas, D. S. Galvao, and R. H. Baughman, *Phys. Rev. B* **68** (2003) 035430.
- [5] V. R. Coluci, S. F. Braga, S. B. Legoas, D. S. Galvao, and R. H. Baughman, *Nanotechnology* **15** (2004) S142.
- [6] G. Li et al., *Chem. Commun.* **46** (2010) 3256.

- [7] A. C. T. van Duin, S. Dasgupta, F. Lorant, and W. A. Goddard III, *J. Phys. Chem. A* **105** (2001) 9396.
 [8] S. Plimpton, *J. Comp. Phys.* **117** (1995) 1. <http://lammps.sandia.gov/>.
 [9] M. Z. S. Flores, P. A. S. Autreto, S. B. Legoas, and D. S. Galvao, *Nanotechnology* **20** (2009) 465704.
 [10] R. Paupitz, P. A. S. Autreto, S. B. Legoas, S. G. Srinivasan, A. C. T. van Duin, and D. S. Galvao, *Nanotechnology* **24** (2013) 035706.

Figures

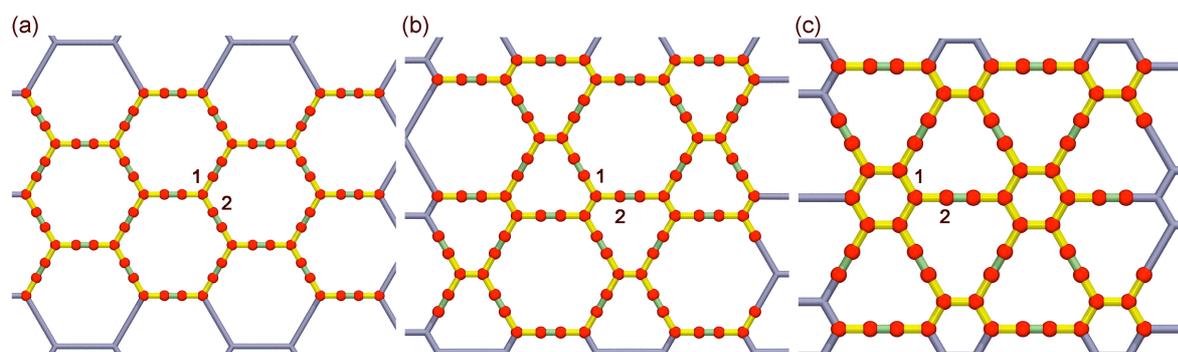


Figure 1: Structure of (a) α -graphyne (A), (b) β -graphyne (B) and; (c) γ -graphyne (G). The labeling 1 and 2 refer to non-acetylenic (1) and acetylenic (triple bonds) groups, respectively.

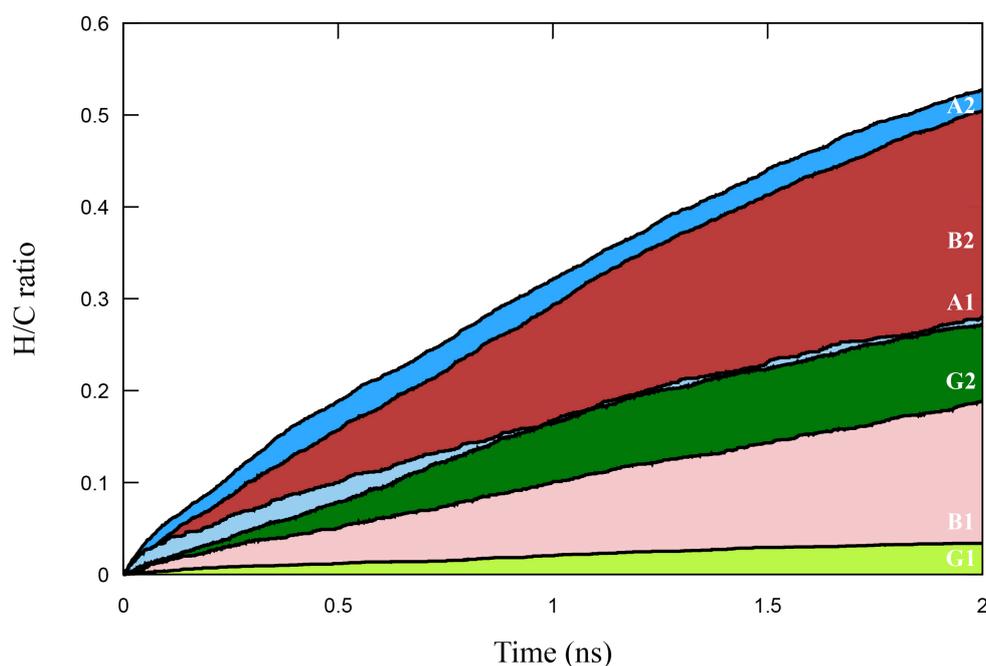


Figure 2: Incorporation of H atoms in time, for the sites indicated in Figure 1. Results for a simulation carried out at 300 K.