

## How hydrogenation changes Biphenylene Carbon (Graphenylene) topology

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### Abstract

Biphenylene Carbon (BPC), also known as graphenylene, is a porous graphene-like structure, which has been seen as a good candidate for filtration systems. Many theoretical studies have been carried out to understand which compounds this 2D membrane could selectively separate. However, these studies did not explicitly consider BPC chemical reactions. Such approaches will fail in the presence of many reactive compounds, such as ions in the solution. In this way, the understanding of how such structures can interact with ions is of the vital importance for BPC use as filtration membranes. Here we report the first detailed study for hydrogen ion BPC interactions. The hydrogenation process was investigated using fully atomistic reactive molecular dynamics (FARMMD) simulations, which can mimic many of experimental approaches, as well as, have been successfully applied for other carbon nanostructures. Our results show that during hydrogenation, BPC structure undergoes significant structural changes evolving to a new form, which resemble the structures known as graphynes. These unexpected results have important implications for using BPC as filtration membranes and also suggest a new approach to synthesize graphynes, which are 2D carbon allotrope forms.

### Key words:

Nanotechnology, molecular dynamics, graphene.

### Introduction

With the advent of graphene, there is a renewed interest in carbon-based structures. Graphene and several of its derivatives present a great number of interesting physical properties, which can be exploited in many applications, such as filtration membranes. Graphene can work as impermeable membranes to standard gases, such as argon and helium<sup>1</sup>. However, for effective selectivity a higher level of porosity than the presented by graphene is needed. Therefore, there is a great interest in discovering new graphene-like porous membranes. Biphenylene carbon (BPC), sometimes called graphenylene, is one of these structures. BPC is a porous two-dimensional (planar) allotrope carbon form and presents a very interesting topology, with its pores resembling typical sieve cavities and/or some kind of zeolites<sup>2,3</sup>. With the presence of some gases BPC can be instable, so in this work we study the change in BPC topology during hydrogenation.

### Results and Discussion

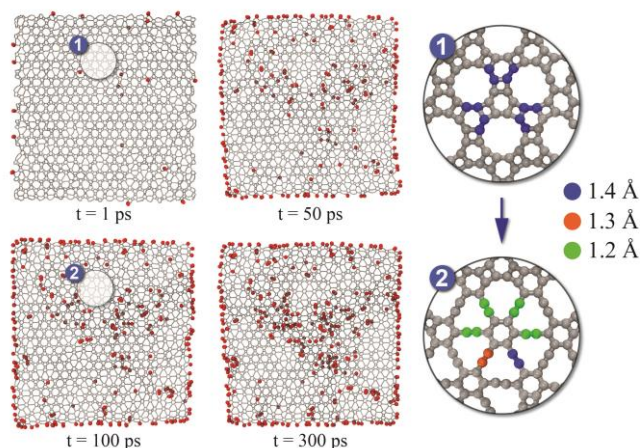
We have carried out an extensive study through fully atomistic reactive molecular dynamics (FARMMD) simulations with the reactive force field ReaxFF<sup>4</sup>, as implemented in the well-known Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code<sup>5</sup>. The system considered in our simulations is composed of BPC membranes embedded into a pure H atmosphere, using a constant box volume (NVT ensemble).

Our results show that hydrogenation induces significant topological BPC changes. Such changes depend directly on the amount of hydrogen incorporated into the BPC structure, what is sensitive to temperature values. Our results also show that an extensive hydrogenation can produce significant structural damages. In Figure 1, we present representative snapshots from FARMMD simulations, which show the changes in the BPC topology during the hydrogenation. Some parts of this new structure resembles the material known as graphynes, which are also graphene-like porous membranes and have been considered to be used in nanoelectronics due to their interesting electronic properties.

When one hydrogen atom is incorporated into the structure, the carbon hybridization changes from  $sp^2$  to  $sp$ . It causes a chain

reaction in neighboring carbons, which change the double bonds to triple ones.

Our results also show that when one hydrogen is incorporated into the structure, another hydrogen becomes more likely to be incorporate around that region.



**Figure 1.** Representative snapshots from MD simulations showing the BPC structural changes during hydrogenation.

### Conclusions

Our results show that, under hydrogenation, BPC structure undergoes significant structural changes, its topology evolving to new forms, which resemble the structures known as graphynes. An extensive hydrogenation can produce significant structural damages, with the formation of large defective area and structural holes.

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