

# Boosting Graphene Reactivity with Oxygen by Boron Doping: DFT Modeling of the Reaction Path.

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## Abstract

Graphene (G) reactivity toward oxygen is very poor, which limits its use as electrode for the oxygen reduction reaction (ORR). Contrarily, boron-doped graphene (BG) was found to be an excellent catalyst for the ORR[2,3,4,5]. Through a density functional study, comparing molecular (circumcoronene) and periodic approaches (in a 4x4 or 8x8 cell) and different functionals (B3LYP vs PBE), we show how substitutional boron in the carbon sheet can boost the reactivity with oxygen leading to the formation of bulk borates covalently bound to graphene ( $\text{BO}_3\text{-G}$ , see Fig. 1) in oxygen-rich conditions. These species are highly interesting intermediates for the  $\text{O}=\text{O}$  breaking step in the reduction process of  $\text{O}_2$  to form  $\text{H}_2\text{O}$  as they are energetically stable.

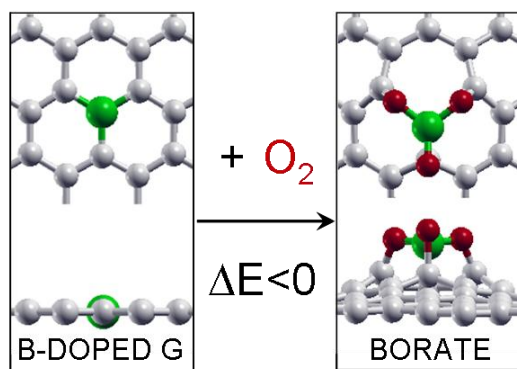
In this talk we show the reaction energies for molecular oxygen dissociation on BG are negative (exothermic processes, see Fig.2), in net contrast with pure G where reaction energies are highly positive (endothermic processes). The stability of oxygenated BG species is enhanced when the boron atom is directly bound to oxygen. We highlight the reaction products of  $\text{O}_2$  with both G and BG, finding the same conclusions with all methods used, which definitely consolidates our results.

We show that BG sheets can be much more easily oxidized than G ones and depending on the oxygen conditions the extent of oxidation of the boron-doped species can be different, but, at common oxygen pressures, borates are the most stable. The existence of oxygenated B species was proved before by XPS measurements; [2,3] however, their role in the chemistry of B-doped graphene has been totally overlooked and underestimated. We believe that our results are not only relevant in the context of ORR but could be more generally useful for the interpretation of nonmetal doped graphene based catalysis.

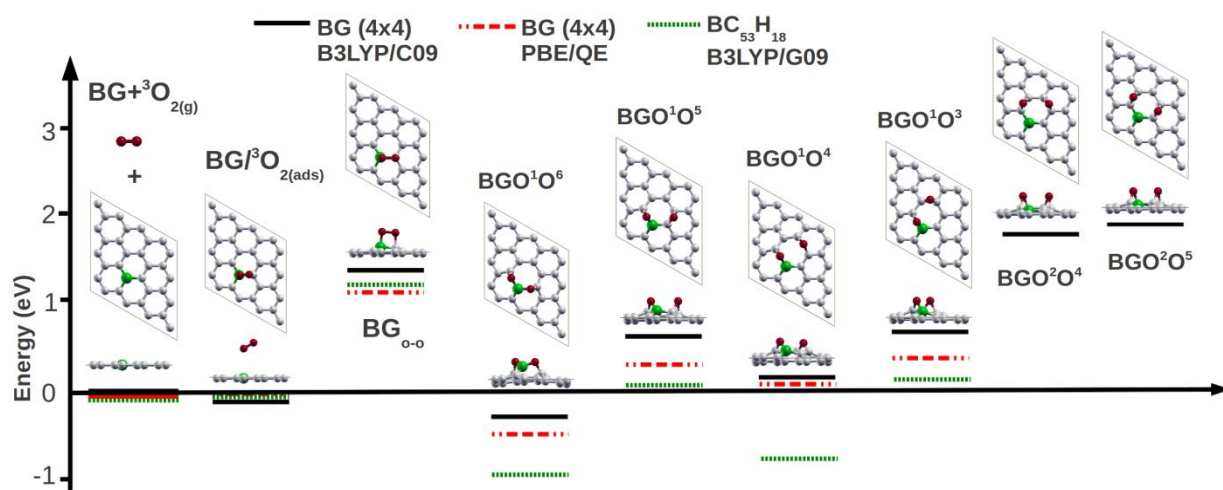
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## Figures



**Fig.1** Formation of stable bulk borates, from boron doped graphene and oxygen.



**Fig.2** Energy profile for molecular oxygen physi-/chemisorption on BG. Top and side views of the balls and sticks 4 × 4 models.