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# Density Functional Theory Study of 1,2-, 1,3- and 1,4-Dinitrogen Doping in Graphene

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## Extended Abstract

The prompt development of carbon-based nanostructured materials has received a wide-spread interest due to their novel physico-chemical properties and applications [1]. Modification of 2D graphene with heteroatom substitution is one of the efficient approaches to tuning its electronic and chemical properties. Nitrogen-doped graphene has stimulated lots of interest in manipulating the properties of graphene for applications in diverse research areas [2]. Experimental and theoretical studies revealed that doping configuration of nitrogen dopants in graphene can significantly influence the material properties [3], [4], [5], [6]. In this study, the finite-sized graphene model, $C_{186}H_{36}$, was considered to investigate double nitrogen doping within six-membered rings of graphene. Graphitic nitrogen atoms were employed due to their efficiency in fine-tuning the performance of oxygen reduction reaction (ORR) activity and opening of band gap. Three possibilities of dinitrogen doping are 1,2-, 1,3- and 1,4-substitutions, which may consider correspondingly as ortho-, meta-, and para-like substitutions. This comprehensive computational study presents the results of positional preference of double nitrogen doping in multiple non-equivalent six-membered rings. Our aim is to investigate the positional preference of the above-mentioned three different doping possibilities and to reveal any selectivity for doping of two nitrogen atoms within the rings. All structures were fully optimized using density functional theory (DFT) at B3LYP/6-31G(d) level. The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) values for all the positional isomers were calculated at TPSSh/6-31G(d) level using B3LYP/6-31G(d) optimized geometries. Relative stabilities of these isomers generally follow the trend: 1,4- > 1,3- > 1,2-substitution. Interestingly, the location of the ring plays a role in determining the relative stabilities of double nitrogen dopants. Our computational study predicts that the most stable isomers have two nitrogen atoms doped close to the zigzag edge. However, the nitrogen doping at the armchair edge provides the structures with high relative energy. The effect of nitrogen dopants in graphene on HOMO and LUMO energies and HOMO-LUMO energy gaps was analyzed. Our study indicates that the band gap can be opened by controlled nitrogen doping in the graphene model.

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