

Oxygen transfer in graphene interactions with O-containing fluids: simulation vs. experiments

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All the stages of emerging commercial applications of graphene – preparation, functionalization and utilization – are profoundly affected by interaction with oxygen-containing gases or liquids. Thus, for example, exfoliation of graphite relies on the formation of oxygen surface functionalities at graphene edges as well as its basal planes [1]. Similarly, surface oxygen functionalization is ubiquitous in Fermi-level and band-gap engineering of graphene [2, 3]. And fuel-cell applicability of both pristine and heteroatom-doped graphene (in ORR) is critically dependent on its surface (electro)chemical properties and the efficiency of oxygen transfer [4-6]. Nevertheless, the essential details of oxygen transfer are both controversial and unclear. Here we present results that highlight the critical issues and, especially, the assumptions typically made in the increasingly voluminous quantum chemical simulations of such interactions. In particular, we discuss (i) if and when graphene-O₂ interactions occur at edge or basal-plane sites, and (ii) the relative roles of substitutional N and B in oxygen transfer.

The abundant experimental and theoretical literature on oxygen transfer in pristine and doped graphene-based materials (e.g., graphite, activated carbons, carbon blacks) is too often neglected in simulations of the behaviour of graphene itself. Figures 1 and 2 highlight some of the resulting inconsistencies, as well as some unresolved issues. Free carbon edge sites, with or without electron density alterations due to the presence of

adjacent B (or N), have a very high affinity for O₂ and graphene planarity is preserved upon its chemisorption. The distortion of planarity observed upon B-assisted O₂ chemisorption [5] on the basal plane does decrease as graphene size increases, but the affinity for O₂ decreases even further; it is thus much more likely that, in the absence of gas-phase atomic oxygen, the epoxy (or ether) groups form by edge-to-basal-plane spillover.

References

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Figure 1: Optimized geometry of C₅₃H₁₇B upon interaction with O₂ at the adjacent C edge site.

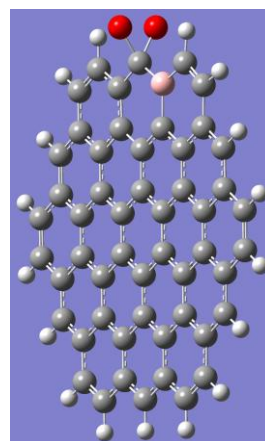


Figure 2: Optimized geometry of C₅₃H₁₇B upon interaction with O₂ in the basal plane.

