

Activation of graphenic carbon due to substitutional doping:

Mechanistic understanding from first-principles

Joydeep Bhattacharjee

School of Physical Sciences
National Institute of Science Education and Research
Int. of Phys. Campus, Sachivalay Marg
Bhubaneswar, India, 751005
jbhattacharjee@niser.ac.in

Abstract

Nitrogen and boron doped graphene and carbon nanotubes are popularly in focus as metal-free electro-catalysts for oxygen reduction reactions (ORR) central to fuel-cells. N doped CNTs have also been reported to chemisorb mutually, promising a route to their pre-determined robust assembly into devices and mechanical reinforcements. We propose from first-principles a common mechanistic understanding of these two aspects pointing to a more generic chemical activation of carbon atoms due to substitution by boron(B) or nitrogen(N) in experimentally observed configurations. Wannier-function based orbital resolved study of mechanisms suggest that increase in order of C-N bonds in attempt to retain π -conjugation among carbon atoms causes mechanical stresses and loss of charge neutrality of nitrogen as well as carbon atoms, which remedially facilitate chemical activation of N coordinated C atoms, enhancing sharply with increasing coordination to N and proximity to zigzag edges. Activated C atoms facilitate covalent adsorption of radicals in general, diradicals like O_2 relevant to ORR, and also other similarly activated C atoms leading to self-assembly of graphenic nano-structures, while remaining advantageously inert to ordinary graphenic C atoms. Similar activation of C atoms and ORR facilitation is also observed upon substitution of N by C in hexagonal boron nitride sheet.

References

[1] Joydeep Bhattacharjee, J Phys. Chem. Lett., **6** (2015) 1653-1660.