

# Electron Beam Induced Chemical Reactions Involving Nanocarbon: Theoretical Perspective

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The recent progress in high-resolution transmission electron microscopy (HRTEM) has given rise to the possibility of *in situ* observations of nanostructure transformations and chemical reactions induced by electron irradiation. In this talk, we discuss atomistic modelling of irradiation-induced processes in HRTEM, as well as mechanisms of such processes recognised due to modelling. Accurate molecular dynamics (MD) techniques based on first principles are employed in the analysis of single irradiation-induced events, and classical MD simulations are combined with a kinetic Monte Carlo algorithm to simulate continuous irradiation of nanomaterials [1,2].

Structural characterisation of individual molecules by HRTEM is fundamentally limited by the element and electron energy-specific interactions of the material with the high-energy electron beam (e-beam). We examine the key mechanisms controlling the interactions between the e-beam and C–H bonds present in all organic molecules. We identify the low atomic weight of hydrogen as the principal cause of instability of organic molecules resulting in facile displacement of atomic hydrogen by the e-beam. It is demonstrated theoretically and proven experimentally [3] that exchanging all hydrogen atoms within molecules with the deuterium isotope, and therefore doubling the atomic weight of the lightest atoms in the structure, leads to a more than two-fold increase in the stability of organic molecules in the e-beam. Substitution of H for D significantly reduces the amount of kinetic energy transferred from the e-beam to the atom (main factor contributing to stability) and also increases the barrier for bond dissociation, primarily due to the changes in the zero-point energy of the C–D vibration (minor factor).

Since the imaging e-beam obliterates the C-H bond and destroys individual small polyaromatic molecules over time, we replace all hydrogen atoms for much heavier atoms (chlorines) to achieve greater durability of the molecule against electron irradiation. We deposit perchlorocoronene, C<sub>24</sub>Cl<sub>12</sub>, molecules on graphene and observe in HRTEM structural transformations induced by the e-beam in real time with near-atomic resolution. We find that perchlorocoronene radicals are preferably aligned along the armchair direction in graphene, which is entirely consistent with our theoretical predictions. Theoretically predicted behavior of polyaromatic radicals anchored to graphene and experimentally observed behaviour of stable halogenated radicals in HRTEM reveals common transformations of small radicals on graphene and enables capturing the atomistic mechanisms of the chemical bond formation [4].

Functionalization of pristine graphene sheets with organic functional groups has been developed for several purposes, mainly to improve dispersibility of graphene in common organic solvents, which is a crucial move toward the formation of nanocomposite materials with graphene. Organic functional groups also offer new properties that could be combined with the properties of graphene such as conductivity. When organic molecules are covalently attached to the graphene surface, its extended aromatic character is perturbed, enabling the control of its electronic properties. The development of a band gap through chemical doping is a powerful method for the use of graphene in nanoelectronic devices.

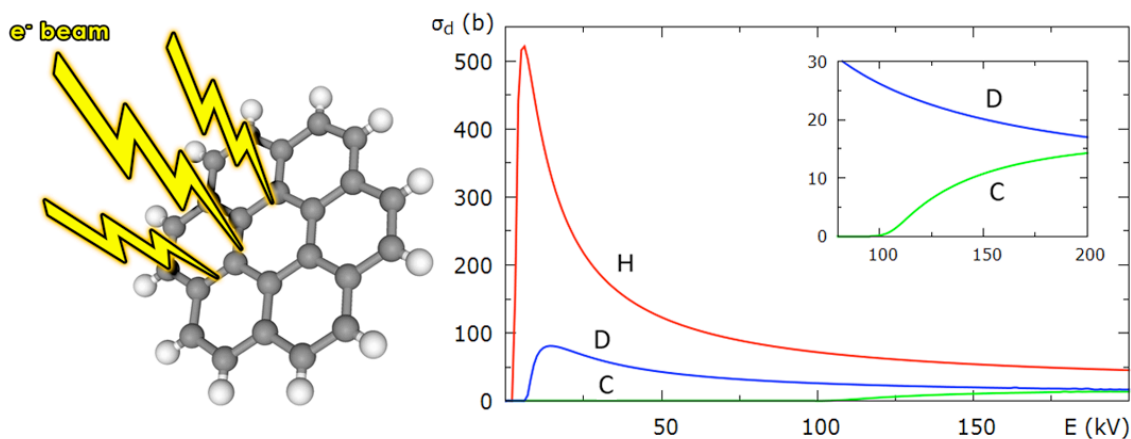


Figure 1: Ejection cross-sections as a function of electron beam kinetic energy (transferred in the direction of the bond extension) for protium (red), deuterium (blue) and carbon (green) of the C–H and C–D bonds in coronene and deuterated coronene. Inset shows the cross-sections of C and D at commonly used TEM e-beam energies of 80-200 keV.

## References

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- [4] This research was supported by an ERC Consolidator grant to EB.