Putting the 'Chemistry' back into CVD Nanomaterial Growth - Insight from Quantum Simulations

(*Discipline of Chemistry, School of Environmental & Life Sciences, University of Newcastle, Australia*) ○Alister J. Page
Keywords: Carbon nanotube; graphene; boron nitride; density functional tight binding; molecular dynamics

Over the last few decades, catalytic chemical vapor deposition (CVD) has matured as a synthetic technique for producing many low-dimensional inorganic nanomaterials, such as carbon nanotubes (CNTs), graphene, boron nitrides and transition metal dichalcogenides. The general mechanism of graphene and CNT formation during CVD is now well established [1]. However, by and large this picture of nucleation has been developed by considering the chemistry of carbon by itself, when, in reality, there are many other chemical species present in a CVD reaction chamber. In this lecture I will discuss our recent quantum chemical simulations that show the influence of such species on the nucleation and growth mechanisms of carbon nanomaterials during CVD (e.g. H_2 [2,3], H_2O [4], NH_3 [5], etc.).

In contrast to carbon nanomaterials, little is known regarding the catalytic pathways underpinning CVD synthesis of boron nitride nanomaterials [1]. I will present the first mechanism explaining the nucleation of boron nitride nanotubes (BNNTs) via CVD of boron oxide and ammonia borane, based on reactive molecular dynamics simulations [6]. Strikingly, BNNTs nucleate via a 'network fusion' mechanism, by which distinct BN fragments first form before 'clicking' together on the nanoparticle surface (Figure 1). We also reveal key roles played by H_2O and H_2 partial pressures and the presence of solid-phase catalytic nanoparticles on this mechanism.

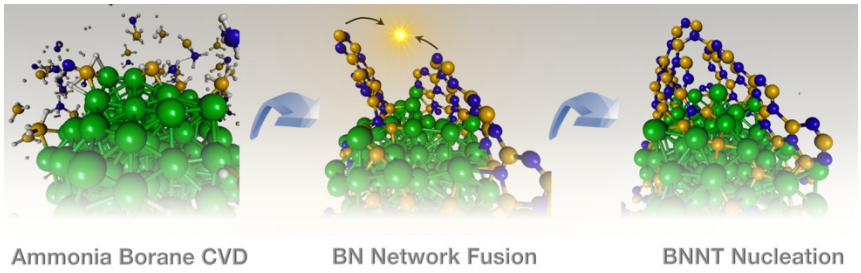

Figure 1. Network fusion nucleation of BNNTs during Ni-catalysed ammonia borane CVD.

[1] B. McLean et al., *Phys. Chem. Chem. Phys.* **19**, 26466-26494 (2017). [2] I. Mitchell et al., *Carbon* 128, 215 (2018). [3] A. Saeed et al., *Adv. Func. Mater.*, **30**, 2005016 (2020). [4] Hussein, A. et al., *Nanoscale*. **12**, 12263-12267 (2020). [5] C. A. Eveleens et al., *Nanoscale* **9**, 1727 (2017). [6] B. McLean, G. Webber, A. J. Page. *J. Am. Chem. Soc.* **141**, 13385-13393 (2019).