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Spanning the “Parameter Space” of Chemical Vapor Deposition Graphene Growth with Quantum Chemical Simulations

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Abstract

Graphene is a 2-dimensional allotrope of carbon with remarkable physicochemical properties. Currently, the most promising route for commercial synthesis of graphene for technological application is chemical vapor deposition (CVD). The optimization of this chemical process will potentially enable control over crucial properties, such as graphene quality and domain size. Such optimization requires a detailed atomistic understanding of how graphene nucleation and growth takeing place during CVD. This mechanism depends on a multitude of synthetic parameters: temperature, CVD pressure, catalyst type, facet and phase, feedstock type, and the presence of chemical etchants, to name only a few. In this feature article, we highlight recent quantum chemical simulations of chemical vapor deposition (CVD) graphene nucleation and growth. These simulations aim to systematically span this complex CVD "parameter space", towards providing the necessary understanding of graphene nucleation to assist the optimization of CVD graphene growth.

1. Introduction

Graphene is a 2-dimensional allotrope of carbon that consists of a 1-atom-thick hexagonal carbon lattice. It exhibits remarkable properties, including high specific surface area,¹ transparency,²⁻³ thermal conductivity,⁴ mechanical strength,⁵ carrier mobilities,⁶⁻¹⁰ and a room-temperature half-integer quantum Hall effect for both electrons and holes.⁶⁻⁹ Graphene also enables single molecule detection¹¹ and superlubricity.¹² These properties of graphene have driven intense research efforts towards establishing new technologies in fields as diverse as electrochemistry,¹³ fuel-cells¹⁴ and enhanced catalysis,¹⁵ gas sensing,¹⁶ spintronics,¹⁷ electronics,¹⁸ ultrafast DNA sequencing,¹⁹ and a number of green chemistry applications including water remediation and CO₂ capture,²⁰ and enhanced catalytic applications.

1.1. CVD Graphene Synthesis

Today the most promising and reliable method for producing single layer graphene on a commercial scale is chemical vapor deposition (CVD). Mechanical exfoliation of graphite, particularly highly-oriented pyrolytic graphite (HOPG) can also be used to synthesize multi- and single-layer graphene with relatively high quality.^{10, 21} However, domain size, layer-control, and scalability are some of the issues that arise immediately via this synthetic route, limiting its practicality.

CVD addresses each of these problems, and this has led to a wealth of scientific studies aimed at optimizing the CVD synthesis of graphene. CVD consists of the decomposition of a carbonaceous feedstock gas (traditionally acetylene, methane or ethanol in the case of carbon nanotubes and graphene) at high temperature over a late-transition metal foil.²¹⁻²⁶ Recent reports demonstrate that a wide range of transition metals can be used for CVD graphene synthesis:

Co,²⁷ Ru,²⁸ Rh,²⁹ Pd,³⁰⁻³¹ Fe,³² Re,³³ Ir,³⁴⁻³⁵ Pt,³⁶⁻³⁷ Au,³⁸⁻³⁹ and Ag.⁴⁰ There is also evidence of metalloids (Ge⁴¹) being used for CVD graphene synthesis. Ni⁴²⁻⁴⁹ and Cu^{32, 50-59} foils are perhaps the most promising catalysts for routine, controllable synthesis of graphene, since both lead to high structural quality and large domain sizes, while not sacrificing catalytic efficiency. However, controlling the number of graphene layers formed during CVD on Ni catalysts, due to the high carbon solubility of this metal, remains an issue. Despite having a far lower carbon solubility,⁶⁰ Cu catalysts have been shown to have the same problem.⁶¹⁻⁶² The tendency towards formation of multi-layer graphene can be mitigated by using thinner catalyst foils.²³ However, a recent study using Ni_xCu_{1-x} alloy films represents an alternative approach towards overcoming this problem.⁶³

1.2. The “Parameter Space” of CVD Graphene Synthesis

CVD graphene synthesis is governed by a multitude of physical parameters, such as temperature, feedstock pressure and composition, catalyst composition and facet, catalyst phase and morphology/topography, catalyst carbon solubility, the presence of templates/precursors and the presence of chemical etchants (e.g. H₂). Ultimately, CVD graphene growth is governed by how each of these elements in the CVD "parameter space" influences the CVD mechanism at the atomic scale. Optimizing the efficiency and product of CVD graphene synthesis therefore requires a detailed understanding of the role played by each element during graphene nucleation and growth. Understanding the inter-relationships of different elements in the CVD parameter space is also critical in this respect.

A number of theoretical investigations have characterized isolated aspects of the parameter space of CVD growth. For instance, Gao et al.^{45, 64} used density functional theory (DFT) to

characterize fragment structure and adsorption on terraced and defective Ni(111) catalysts. On a pristine Ni(111) terrace, they observed that sp polyyne chains dominate fragments smaller than C₁₂, whereas C₁₂ itself and larger fragments are composed of sp² hybridized carbon. In the presence of a step edge on Ni(111), Gao et al. showed that this sp/sp² transition instead occurs at C₁₀; this result highlights the importance of the catalyst topography for graphene nucleation. DFT investigations conducted by van Wesep et al.,⁶⁵ using Cu(111) catalysts, demonstrated that small fragments are dominated by sp chains until C₁₀, before sp² hybridization starts to dominate. Combined with results from Gao et al.,^{45, 64} these results show that the type of catalyst fundamentally controls the graphene nucleation mechanism. In a similar vein, Shu et al.⁶⁶ investigated the mechanism of methane decomposition on Cu(111), Ni(111), Ir(111) and Rh(111) utilizing DFT, specifically focusing on surface versus sub-surface mediated processes. The nature of adsorption was shown to be fundamentally dependent on the type of catalyst; for Cu(111) (and low H₂ pressures), subsurface carbon atoms are dominant, while at higher H₂ pressures (>1000 Pa) surface-adsorbed CH species are dominant. Conversely, on Ni(111) sub-surface carbon atoms are observed, while for Ir(111) and Rh(111) surface carbon atoms are observed. Zhang et al.⁶⁷ also considered the role of the catalyst facet on the methane decomposition mechanism. Specifically, they investigated the Cu(111) and Cu(100) surfaces using DFT calculations, finding that surface-adsorbed CH_x dominate nucleation and growth on both facets. The role of graphene precursor fragments was investigated by Yuan et al.⁶⁸, who used DFT to show that C₂₁ (corannulene) and C₂₄ (coronene) exhibit remarkable stability on Ni(111), Cu(111), Ru(0001) and Rh(111) surfaces, thus concluding that they are likely stable graphene precursors.

Despite the wealth of simulations concerned with graphene nucleation and growth, a single unified approach aimed at spanning these parameters had not been utilized. This was our initial motivation - our research over recent years has aimed to systematically "span" the parameter space of graphene nucleation and growth using quantum chemical simulations. Towards this aim, we have progressively established how pertinent environmental factors including catalyst type,⁶⁹ catalyst phase⁷⁰ and catalyst topography⁷¹⁻⁷² (including the presence of step-edge defects) influence the graphene nucleation/growth mechanisms. Similarly, we have investigated how the presence of graphene templates⁷³⁻⁷⁴ and chemical etchants⁷⁵ (hydrogen) alter the nucleation pathway. More recently we have considered the role of subsurface carbon species⁷¹ and carbide phases^{72, 76} during graphene nucleation and growth.

In this feature article, we detail our recent advancements in this field and summarize the main conclusions we have developed regarding graphene nucleation and growth mechanisms during the CVD process.

2. Simulating Graphene Nucleation and Growth

A number of computer simulations of graphene nucleation and growth have been reported over the last decade.⁷⁷ The methodologies primarily used for studying graphene nucleation and growth are static DFT calculations, dynamic Monte Carlo or molecular dynamics (MD) simulations based on tight binding potentials.⁷⁸⁻⁸⁵

Our research in this area combines full density functional theory calculations, which provide an accurate equilibrium structures, with the semi-empirical density functional tight binding (DFTB) approach. DFTB is a two-center approximation to the generalized gradient approximation (GGA) density functional theory (DFT). DFTB is comparable in accuracy to

GGA-DFT, but is $\sim 100 - 1000$ times faster, due to its tight-binding formalism. This enables us to build a detailed understanding of the atomistic graphene nucleation mechanism, by combining DFTB with classical molecular dynamics (MD) (i.e. by propagating the classical equations of motion using a quantum chemical potential calculated using DFTB). For simulating graphene nucleation and growth on transition metal catalysts, we have employed the “trans3d” DFTB parameter set⁸⁶ for describing the two-center interactions between C, H, Fe and Ni. In the case of copper catalysts, we employ DFTB parameter sets developed independently.⁷⁰ All simulations discussed here were performed using the DFTB+ software.⁸⁷

3. Spanning the Parameter Space of CVD Graphene Synthesis

3.1. Graphene Precursors and Templates

Despite the abundance of literature concerning CVD graphene growth, questions remain regarding the roles of precursors and templates in the growth process. There is agreement that graphene growth ultimately proceeds via Smoluchowski ripening (the process in which larger carbon fragments form via direct coalescence of smaller fragments) on a range of metal substrates.^{57, 73-74, 88-90} STM imaging has found that C_{24} and C_{21} fragments are common during CVD on a number of catalysts, and computational simulations indicate that similar homocyclic structures represent common stable or meta-stable fragments.^{45, 64, 68, 90} However, the mechanisms of precursor formation and precursor aggregation remain largely beyond the reach of experimental imaging techniques, and this is particularly the case for carbon precursors smaller than C_{24} . To address this issue, we have performed a number of DFTB/MD studies of graphene nucleation on Ni(111)⁷⁴ aimed at identifying how graphene island precursors influence the early stages of graphene growth.

The presence of a template, such as coronene, dramatically influences carbon coalescence and graphene nucleation on Ni(111). In the absence of such a template, a high-density ensemble of C₂ moieties (~83% of a graphene monolayer) adsorbed on a 3-layer model Ni(111) surface at 1,180 K gives rise to a 2D carbon structure closely resembling pentaheptite, which is a Haeckelite-like material consisting predominantly of pentagon and heptagon rings.^{59, 91-94} As shown in Figure 1 (a,b,c), these C₂ units quickly oligomerize, forming longer polyyne chains. Subsequent cross-linking⁹⁵ between these chains leads to a high density of pentagon and heptagon defect rings, in a near one-to-one ratio (Figure 1(d)). These defects remain "kinetically trapped" in the structure over the timescale of the simulation, and this is due to the high carbon density present on the surface. The initial ring formed in this process is a pentagon, and so this mechanism bears some resemblance to the "pentagon-first" mechanism observed in previous simulations of carbon nanotube cap⁹⁶⁻⁹⁸ and fullerene formation.⁹⁹

The formation of a 2D Haeckelite structure here is somewhat unexpected, as Ni(111) may be expected to template the formation of a hexagonal carbon lattice, even without a template. This is because the graphene and Ni(111) unit cells are nearly commensurate with each other, leading to near-epitaxy between single-layer graphene and Ni(111).¹⁰⁰ In this sense, the formation of the Haeckelite structure is reminiscent of "reverse-templating" effects observed during carbon nanotube nucleation, in which the nucleating solid-phase carbon nanotube structure deforms the surface layers of the underlying catalyst.¹⁰¹ This Haeckelite monolayer is ~ 0.1 eV/C higher in energy compared to graphene, indicating that it is only a metastable state during graphene formation.⁷⁴

The effect of a coronene template on this mechanism is depicted in Figure 1(e,f,g); here the surface-adsorbed carbon ensemble includes C₂ units and a C₂₄ template, adsorbed on a model 3-

layer Ni(111) catalyst surface held at 1,180 K. The overall carbon density remains the same as that employed above, however. Extension of the template structure occurs rapidly, due to the high reactivity of C_2 , and ring formation occurs as it did in the absence of the template, i.e. via polyynes formation and cross-linking. From Figure 1(h), however, the effect of template addition is immediate; hexagon formation is now the dominant feature of C_2 aggregation, whereas the formation of pentagons, and particularly heptagons, is more limited. Ultimately the structure formed (Figure 1 (g)) resembles a near-perfect graphene sheet extended over the simulated supercell. This is not only a result of the presence of the C_{24} template, but also due to more active defect healing mechanisms. Despite the overall carbon density being the same as that used for Haeckelite formation (Figure 1(a,b,c)), the removal and diffusion of pentagon defects through the extended sp^2 carbon structure is also more noticeable. For instance, after 50 ps of simulation, all pentagon defects formed in the structure have migrated to its edge. We note here that these results do not preclude graphene nucleation and growth in the *absence* of a template (as we discuss in detail below). Rather, these results show that the presence of graphene precursors lead to a clearly evident templating effect that will influence the nucleation mechanism under conditions of high carbon densities.

Jiao et al.⁷³ have also investigated the role of smaller C_{13} fragments during the initial stages of graphene nucleation and growth. In these simulations C_{13} templates were combined with a high surface carbon density (~129% of monolayer graphene) on model 3-layer Ni(111) surfaces at 1,180 K. Atomic carbon was deposited in the Ni(111) subsurface, consistent with X-ray data indicating that the immediate Ni(111) subsurface is largely carbon free, even in the case of bulk Ni carbide catalysts.¹⁰² Our previous computational studies have revealed similar phenomena

regarding sub-surface nickel carbides; we return to a more detailed discussion of the role of sub-surface carbon and the carbide phase in Section 3.4 below.

Figure 1. Evolution of monolayer carbon structures on Ni(111), using high carbon density. Non-templated structure formed after (a) 0 ps (b) 2.5 ps and (c) 50 ps. Ultimately this structure resembles Haeckelite. (d) Populations of pentagons, hexagons and heptagons formed in (a, b, c) as a function of time. Templated structure formed after (e) 0 ps (f) 2.5 ps and (g) 50 ps shows hexagon formation is now dominant, whereas defect formation is more limited. (h) Populations of pentagons, hexagons and heptagons formed in (e, f, g) as a function of time. Reproduced from Ref 74. Copyright 2011 American Chemical Society.

In the earliest stages of Jiao et al.'s⁷³ simulations, coalescence of individual C₁₃ fragments was observed, indicating a Smoluchowski-like ripening mechanism. The high density of carbon surrounding these fragments, however, quickly suppressed this mechanism, resulting in polyyne chain elongation and oligomerization. The mechanism observed in these simulations is thus comparable to those reported previously;⁷³ carbon aggregates to form sp hybridized chain networks⁷³⁻⁷⁴ when not close to a template. Once long enough, these chains isomerize forming sp² hybridized carbon rings, generally via an initial pentagon. We note that these DFTB/MD simulations are consistent with DFT calculations indicating that, for Ni(111) catalysts, linear chains are more thermodynamically stable for fragments smaller than ~C₁₀, whereas sp² ring structures dominate larger fragments.^{45, 64}

3.2. The Role of Catalyst Metal

The type of catalyst metal used during CVD is a key parameter controlling graphene growth.^{69-70, 103-104} Varying the type of metal catalyst opens up a wide range of different catalyst unit cell structures and symmetries, surface facets and topographies, carbon-catalyst interaction strengths, carbon solubility and melting points etc., all of which are factors known to influence growth.⁷⁷ We address the role of catalyst topography separately in Section 3.4.

To this end we have investigated the mechanism of graphene growth on Cu(111), Ni(111) and Fe(111) surfaces using DFTB/MD simulations and DFT calculations.^{69-72, 74, 76} Despite these three catalyst facets having similar structure, there is a wide range of metal-carbon interaction strengths between Fe (which interacts most strongly with carbon), Ni and Cu (which interacts most weakly). This enables the influence of carbon-metal interaction strength on graphene growth to be probed directly. Further, while Fe(111) and Ni(111) remain solid at typical CVD

temperatures, Cu(111) is liquid, or at least surface-molten.¹⁰⁵ This enables us to elucidate the influence of catalyst phase on the graphene nucleation and growth mechanisms.

Figure 2. (a) Graphene formation on Cu(111) surface as a function of time. Red atoms are copper atoms originally in the surface layer, and quickly diffuse into the sub-surface, owing to the molten state of the catalyst at this temperature (1,180 K). (b) Population of carbon rings as a function of time. Hexagon rings are formed quickly due to extensive defect healing events. Reproduced from Ref 70. Copyright 2014 Royal Society of Chemistry.

At high carbon densities graphene growth on Cu(111), like growth on Ni(111), follows a pathway of initial polyene chain formation, followed by Y junction isomerization to form pentagons and subsequently heptagons, consistent with Haeckelite growth.⁷⁰ Unlike growth on Ni(111) however, growth on Cu(111) does not result in extensive Haeckelite coverage due to rapid defect healing to graphene as seen in Figure 2. We note here that these simulations use

identical parameters to those detailed in Section 3.1, aside from the type of catalyst used. This defect healing is driven by the highly mobile copper atoms in the catalyst surface, which is a result of copper's lower melting point. As can be observed in Figure 2, the crystalline (111) structure in this catalyst surface disappears almost instantaneously at 1,180 K, leaving an essentially amorphous, highly mobile catalyst surface. The greater extent of defect healing observed here is consistent with CVD experiments achieving higher quality graphene sheets.^{22, 67, 106-107} The fact that the simulated Cu(111) catalyst is surface-molten is also consistent with experimental reports showing that graphene quality is independent of the copper catalyst facet.^{51, 107-108}

Figure 3. Formation of $C_x\text{-Fe-C}_x$ bridging structures on Fe(111), observed in DFTB/MD simulations at 1,800 K. Reproduced from Ref 69. Copyright 2013 American Chemical Society.

Graphene growth on Fe(111), like on Ni(111), initially takes place via polyynes chain formation, which then isomerizes into a pentagon via a Y-junction precursor structure. For both catalysts, these relatively thermodynamically unstable precursors and chains are stabilized by σ -bonding between terminal carbon atoms and the catalyst surface. However this stabilization is larger in the case of Fe(111), since strong π interactions also take place between iron catalysts and surface-adsorbed carbon. Combined, these stronger σ and π interactions on Fe(111) result in a mechanism that is closely mediated by the catalyst surface, to the point that polyynes extension and oligomerization is impeded. Instead, we observe $C_x\text{-Fe-C}_x$ structures (Figure 3), which

degrade the Fe(111) catalyst surface by inducing persistent vacancy defects. The strong Fe-C affinity leads to carbon occupying these surface vacancies, which suggests that an iron carbide may form over far longer timescales than those simulated. While similar C_x -M- C_x bridging structures are observed on Ni(111), the carbon chains are generally longer, and these structures are more transient compared to those formed on Fe(111). This is attributed to the stronger interaction between surface-adsorbed carbon and the catalyst for Fe(111).

3.3. The Role of Catalyst Topography

The micro- and nano-scale topography of the metal catalyst, which is comprised of flat terraces, step-edges, corners, and screw dislocations, plays a crucial role in determining the quality of CVD-grown graphene. The role of the catalyst step-edge defect in graphene nucleation and growth has been investigated on a number of occasions.^{104, 109-110} Experimental observations indicate that graphene nucleation near the metal step-edge occurs at lower surface C monomer concentrations, compared to that on a terrace¹¹⁰. The interaction between graphene and the metal step-edge defect has also been the subject of theoretical investigation.^{109, 111-112} DFT calculations suggest that the graphene nucleation near a step-edge has a significantly lower barrier than that on a terrace.¹¹² Theoretical investigations typically have assumed that the metal surface to remain largely static during the process of graphene nucleation. However our recent DFTB/MD simulations indicate that the catalyst surface topography during graphene nucleation is less static than originally thought. In this section, we discuss these simulations, which illustrate the role and dynamics of the catalyst topography during graphene nucleation and growth.⁷¹⁻⁷² Three models were applied to address this issue: (1) step-edge Ni surface with high subsurface carbon

concentration; (2) Ni terrace structure with high subsurface carbon density; (3) Ni terrace structure with low subsurface carbon density.

3.3.1. Nucleation at a Ni(111) Step-Edge Defect

We first employed a 5-layer periodic step-edge model Ni(111) structure to investigate graphene nucleation, by supplying the subsurface carbon atoms at intervals of 0.5 ps. In contrast to previous theoretical works, which rely on static surface structures, we provided evidence indicating that the Ni(111) step-edge defect at 1,180 K is in fact highly malleable. This is immediate from Figure 4, which depicts the almost complete destruction of the original step-edge defect in the process of graphene nucleation. This destruction was due to the diffusion of subsurface carbon atoms to the Ni(111) surface. It is evident from Figure 4 (5–12 ps) that both the diffusion of subsurface carbon and the increase of subsurface carbon concentration led to the enlargement of the original step-edge, *via* the migration of subsurface Ni atoms to the surface. The diffusion of subsurface carbon atoms simultaneously brought about the migration of surface Ni atoms into the subsurface region. One example is that one Ni atom originally in the step-edge defect finally resides at the bottom of the model Ni(111) surface (after 25 ps). Both migration of Ni atoms and the diffusion of subsurface carbons made it difficult to clearly define the step-edge itself, especially as the subsurface carbon cluster approached the surface region (Figure 4, 21.0 ps and 23.0 ps). Such deformation of the Ni(111) step-edge represents a state far from thermodynamic equilibrium during graphene nucleation and growth. After carbon cluster migrates onto the deformed surface (25.0 ps), annealing this system over long periods of time results in the ‘healing’ of these defective Ni(111) surface features.

Figure 4. Evolution of trajectory T1 with step-edge defects on Ni(111) surface under high subsurface carbon concentration. Reproduced from Ref 71. Copyright 2012 Royal Society of Chemistry.

Interestingly, the healed Ni(111) step-edge structure at 64.5 ps is nearly identical to the initial structure, even though the Ni atoms present in the final step-edge are not those in the original step-edge, with $\sim$ half of the atoms in the final step-edge defect originally residing in the bulk. In

stark contrast, during this healing process, the structure of the graphene island precursor changed little with the exception that the number of anchoring C-Ni bonds increased. Thus, our simulations demonstrated that the carbon species can destroy step-edge sites, present on Ni(111) during the nucleation process. As we discuss below, new step-edge defects can be formed on Ni(111) during graphene nucleation.

3.3.2. Step-Edge Self Assembly with High Carbon Densities

The conventional assumption in graphene growth models was that catalyst step-edges are active sites that remain static throughout the graphene growth process.^{49, 64} However, our simulations⁷¹ show that the step-edge is highly malleable, and the deformed step-edge can subsequently “heal” itself back. As discussed in the previous section, an existing step-edge can actively anchor and stabilize the nascent carbon island⁷¹ as it nucleates. However, the formation mechanism of the step-edge itself, during graphene nucleation, was not well established.

To address this issue, we performed simulations detailing the mechanism of catalyst step-edge defect self-assembly on Ni(111) terraces, which takes place naturally during the graphene nucleation process.⁷² We note that, in contrast to the catalyst model detailed in the previous section, these simulations employed a pristine Ni(111) terrace structure, and induced graphene nucleation by introducing interstitial sub-surface carbon. An example of catalyst step-edged self-assembly, using high sub-surface carbon densities (~37 atom%, 50 atom% and 66 atom%) is shown in Figure 5. From this figure it is evident that the lower layers of the Ni(111) surface exhibited relatively crystalline features, whereas the sub-surface layers are significantly disrupted and expanded by the presence of intercalated carbon atoms/clusters. A direct consequence of this catalyst mobility is the almost instantaneous formation of step-edge defects

from the originally crystalline Ni(111) structure, following the precipitation of the graphene precursor structures. This step-edge self-assembly is driven by the formation of thermodynamically favorable Ni-C σ -bonds at the graphene edge, following carbon precipitation. This is consistent with the apparent positive curvature of graphene precursors observed experimentally.⁸⁸ Figure 5 also shows that, when the precursor precipitated to the catalyst surface, the precursor-catalyst interface is dynamic. A conclusion that can be drawn from this observation is that nickel catalyst interfaces cannot be "engineered" towards controlling the structural quality of graphene, because this will ultimately be controlled and determined by the structure of the nucleating graphene precursor, or graphene edge in larger graphene sheets.

Figure 5. Step-edge self-assembly observed during single-layer graphene nucleation on Ni(111). The step-edge defect is circled in blue. Reproduced from Ref 72. Copyright 2014 American Chemical Society.

3.3.3. Nucleation on Ni(111) Terraces with Low Carbon Densities

The simulations detailed in Section 3.3.2 demonstrate that step-edge defect sites can be formed on Ni(111) catalyst facets, provided the carbon density is sufficiently high. The carbon densities used in these simulations far exceed those typically observed in CVD experiments (e.g. ~ 0.15 atom%⁴⁹). The latter density reflects the average density, which is not necessarily an accurate indication of local carbon densities within the catalyst subsurface. The simulations detailed in

Section 3.3.2 therefore establish a mechanism of graphene nucleation in the presence of high subsurface carbon density, but do not reflect low carbon density conditions.

To address the latter situation, we have recently performed DFTB/MD simulations with a low subsurface carbon concentration (~ 0.7 atom%), which are illustrated in Figure 6. The model catalyst used in these simulations, and all other simulation conditions, are identical to those detailed in Section 3.3.2; the single difference is the sub-surface carbon concentration. The first 5 snapshots in Figure 6 represent the basic steps for the graphene nucleation: (1) precipitation of subsurface carbon atoms onto the surface; (2) polyynes chain formation on the surface; (3) “Y-junction” polyyne chain formation; (4) initial ring formation; (5) ring condensation. These are also the elementary processes for the growth of carbon nanotubes⁹⁷ and fullerenes⁹⁹. Whereas high subsurface carbon densities lead to this process taking place partially in the catalyst subsurface,⁷¹⁻⁷² low carbon densities lead to an entirely catalyst-mediated process. The first 3 processes (i.e. polyyne chain formation) are the rate determining steps of graphene nucleation and growth for the case of low subsurface carbon density, according to these results. At low subsurface carbon concentration, the structure of the Ni(111) terrace remains largely intact, since surface-adsorbed carbon atoms are relatively isolated from each other (owing to the lower carbon density). An exception here is the observation of local “point defects” in the nucleating sp^2 carbon structure, which consist of single Ni atoms intercalating into the graphene sheet, stabilized by two or more carbon atoms/chains. After the graphene precursor forms more completely, these Ni atoms typically diffuse back into metal surface (Figure 6 (b,c) and 480 ps). Lower carbon density leads to a significantly higher-quality graphene structure, compared to the high carbon density simulations discussed in the previous section. This is attributed to the higher prevalence of defect healing events at the edge of the growing sheet, and the prevention of defect

rings in the first place, both of which are maximized with lower carbon density. In the former case, the edge carbon atoms of graphene precursors are σ -bonded to the step-edge of Ni surface, the defect rings in the middle region of graphene islands remain due to their weak π -interactions with the underlying Ni surface.

Figure 6. Graphene nucleation on Ni(111) at 1,180 K using a subsurface carbon density of ~ 0.7 atom%, viewed from (a) above (b) side-on and (c) above, showing only the graphene layer.

3.4. The Role of Sub-Surface Carbon and the Carbide Phases

3.4.1. Carbon Density and Multi-Layer Graphene Formation

Ni catalysts have a significant carbon solubility, and therefore a tendency towards forming multi-layer graphene (MLG), as opposed to single layer graphene (SLG). Controlling the subsurface carbon density¹¹³⁻¹¹⁴ *via* altering the feed rate of carbon source and temperature (i.e. cooling rate) is a common strategy to avoid MLG formation.

To establish the role of subsurface carbon density in determining SLG versus MLG growth, we have investigated the nucleation mechanism as a function of subsurface carbon density using DFTB/MD simulations. Using subsurface carbon densities of ~ 37 , 50 and 66 atom%, which correspond to 74, 100, and 133% of the carbon required to form continuous SLG on a 4-layer Ni(111) model catalyst. Figure 7 illustrates the mechanism observed at 1,180 K, and the key differences obtained as a function of subsurface carbon density. At 37 atom%, SLG is obtained via the mechanism discussed in Section 3.3.2. For subsurface carbon densities of 50% and higher, MLG is instead obtained. Structural confinement is a key factor during the nucleation of both the first (top) and second (bottom) nucleating sp^2 networks; it inhibits the precipitation of the first layer and promotes the formation of second layer underneath it. In this respect, these simulations point to a "concerted" nucleation mechanism, in which both layers form at the same time. For both layers, the atomistic formation mechanism is essentially consistent with that of SLG formation at lower subsurface carbon density. Increasing the subsurface carbon density further (66 atom%) leads to the formation of curved, fullerene-like structures on the catalyst surface (Figure 7). These simulations indicate that controlling subsurface carbon density can enable preferential formation of SLG over MLG.

3.4.2 Crystalline vs. Amorphous Carbide Phases

The carbon solubility of Ni (~ 0.9 atom %)⁵⁵ means that stable carbide phases can potentially form under typical CVD conditions. Whether or not this is in fact the case has been a matter of some contention.^{49, 100, 102, 115-116} Recently, Ni_3C was observed during the graphene growth process on nickel catalysts, indicating that it may play a role as an intermediate catalyst phase in graphene nucleation.¹¹⁷⁻¹¹⁸

Figure 7. Higher subsurface carbon densities leads to the formation of double- and multi-layer graphene on Ni(111). Trajectories B₃ (left) and C₃ (right) employ carbon densities of 50 and 66 atom %, respectively. The formation of each individual graphene layer takes place in the Ni(111) surface, via the same chemical mechanism. Individual graphene layers are highlighted with different colors for clarity. Adapted from reference 72. Copyright 2013 Royal Society of Chemistry.

To elucidate this possibility further, DFTB/MD simulations of graphene nucleation from both amorphous and crystalline model Ni₃C phases were performed.^{72, 76} We note that, in contrast to other simulations discussed here, no additional carbon was supplied in these simulations, i.e. all graphitic carbon originated from the carbide structure itself. These simulations demonstrate that precipitation and aggregation of carbon atom layers within the carbide subsurface significantly disrupted the catalyst surface structure, for both amorphous and crystalline Ni₃C. This is observed via an analysis of the Lindemann index, δ ,¹¹⁹⁻¹²⁰ shown in Figure 8. The rapid increase of δ for both systems indicates that the Ni₃C surface region undergoes a solid-liquid phase transition upon annealing at 1,180 K, irrespective of whether it is amorphous or crystalline. All

atoms were highly mobile, enabling the rapid precipitation of inner layer carbon atom, facilitating the coalescence of surface-adsorbed polyyne chains and further stabilizing the formed graphene precursor. The growth mechanism from amorphous and crystalline Ni_3C catalysts is similar to that described above for $\text{Ni}(111)$ catalysts. The eventual decrease in δ for both amorphous and crystalline Ni_3C illustrates that the systems ultimately re-solidify due to the formation of C-C bonds and the subsequent sp^2 -hybridized carbon network. Nonetheless, the crystalline Ni_3C exhibited a more solid-like character, as indicated by the smaller δ in Figure 8. This is attributed to the greater structural coherency in the crystalline Ni_3C lattice, which impedes carbon diffusion and precipitation. In contrast, carbon precipitation in amorphous Ni_3C took place quickly, as indicated by the more drastic initial increase of δ . In light of the rapid disruption of both the amorphous and crystalline Ni_3C phase, it is deduced from that these simulations that nickel carbide phases are likely to be meta-stable intermediate phases observed during the graphene growth process at CVD-relevant temperatures.

However, these simulations also show how nickel carbides can serve as both catalyst and carbon feedstock, potentially enabling facile graphene synthesis via carbon precipitation. Taking crystalline Ni_3C as an example, a schematic of graphene nucleation process is depicted in Figure 9. Carbon atoms in the immediate subsurface layers precipitate quickly to form a graphene precursor, forming a carbon free nickel layer. This "carbon vacancy" leads to a concentration gradient that drives subsequent subsurface carbon diffusion towards the surface.

Figure 8. Lindemann index values δ during thermal annealing of crystalline and amorphous Ni_3C at 1180 K.

Figure 9. Evolution of DFTB/MD simulations of graphene nucleation at 1180 K from crystalline Ni_3C system, in two independent trajectories (a) and (b). The location of the periodic boundary is indicated by the red line. A surface nickel atom in (a) is highlighted by a yellow arrow. The polyyn chain, which exhibited sinusoidal-like vibration in (b), is highlighted in yellow line. The mutual bonding carbon atoms in (b) are highlighted in purple and green circle, respectively.

Figure 10. Evolution of SCC-DFTB/MD simulations of graphene nucleation at 1180 K from Ni_xC precursors. (a) Ni_3C , (b) Ni_2C and (c) NiC . The red circles highlight the Y-junction and rings formation.

Our simulations have also probed the graphene nucleation mechanism from amorphous Ni_2C , and NiC carbides,⁷² thus elucidating the role of subsurface carbon density for carbide catalysts. These simulations show that the atomistic mechanism of nucleation is independent of the carbide

carbon concentration, see Figure 10. In each case, subsurface carbon atoms precipitate rapidly to the surface, resulting in a segregated nickel–carbon interface, and the ensuing nucleation mechanism is similar to that described above. However, the kinetics of graphene nucleation displays a positive correlation with subsurface carbon density. For low carbon densities, i.e., Ni_3C and Ni_2C , many competing, dispersive, smaller fragments form, which fail to coalesce effectively over the nickel surface due to the strong terminating Ni–C σ -bonds. The formation of graphene precursor was only observed in the presence of high carbon densities that were relatively localized (Figure 10). There is therefore no difference between graphene nucleation on Ni(111) and Ni_xC catalysts in this respect.

3.5. Healing During Growth: The Role of Hydrogen

A crucial parameter in CVD graphene synthesis is the presence of non-carbonaceous species in the CVD feedstock "mix". Most notably, the presence of H_2 can lead to improvement in the quality of as-grown graphene.^{112, 121-124} Vlassioug and co-workers¹²⁴ found that hydrogen plays a dual role in graphene growth; it is both a co-catalyst (driving the formation of active surface carbon species necessary for SLG growth), and an etching reagent (controlling the size and morphology of graphene sheet). Theoretically, Zhang and co-workers¹¹² performed DFT calculations and illustrated that low hydrogen concentration favors SLG growth, whereas higher concentrations favor the growth of bilayer or few-layer graphene. Despite these efforts, many details of how hydrogen provides this dual action during graphene growth remained unclear. To address these issues, we performed DFTB/MD simulations to reveal the influence of hydrogen on the growth of free standing graphene flakes.⁷⁵

(a) $H/C=0.6$

(b) $H/C=0.4$

(c) $H/C=0.2$

Figure 11. The evolution of the largest fragment in representative PAH formation trajectories at H/C ratios of (a) 0.6, (b) 0.4, and (c) 0.2. Reproduced from Ref 75. Copyright 2013 American Chemical Society.

The single parameter used in these simulations was the H/C ratio, which ranged from hydrogen-rich conditions ($H/C = 0.8$), through to hydrogen-poor conditions ($H/C = 0.2$). Our simulations show that higher hydrogen density leads to the inhibition of graphene growth, but improves the quality of graphene sheets due to more extensive defect healing during nucleation. For a hydrogen-rich environment, the formation of polygonal carbon rings is limited, even over relatively long annealing periods. Decreasing hydrogen density is favorable for graphene growth, in particular, for size control (Figure 11). It is immediate from Figure 11 that higher hydrogen concentration ($H/C=0.6$) gives rise to the smaller graphene precursor with higher quality, all polygonal rings consisting of hexagons, compared with the cases of $H/C=0.4$ and 0.2 . Hydrogen atoms diffuse freely over the basal plane of the nucleating graphene precursor, presumably with a very low barrier. As a consequence, the diffusion of hydrogen atoms induced facile formation and cleavage of C-C bonds, leading to more frequent transformation from pentagons/heptagons to hexagons, i.e. defect healing processes (Figure 11, 275.5 – 275.9 ps). With decreasing hydrogen concentration ($H/C=0.4$), the quality of graphene sheet is similar with that at $H/C=0.6$. The distinct difference is that the size of graphene structure is larger at the higher H/C ratio than at the lower ratio.

For H/C ratios of 0.4 and 0.6, the role of hydrogen in defect healing is the same; hydrogen atoms result in the local reorganization of defect carbon rings. It is evident from Figure 11(a,b) that some edge carbon atoms were doubly or triply hydrogenated, giving rise to the formation of single C-C bonds. This indicates that the graphene sheet edge is easily reconstructed, due to its increased chemical reactivity. However, it is interesting to note that most defect rings finally reside at the edge of graphene structure for both $H/C=0.6$ and 0.4 cases. There is therefore a high possibility of them being converted into hexagons with the assistance of terminating hydrogen.

The number of defect pentagon and heptagon carbon rings increases significantly at $H/C=0.2$. From Figure 11(c) it is observed that the graphene sheet consists of two regions with an obvious difference. The region on the left is dominated by hexagons, while that on the right side is dominated by pentagon-heptagon defects, structurally similar to Haeckelite/pentaheptite.⁹⁴ We note that hydrogen-poor conditions ($H/C=0.2$) can also induce carbon "cap" formation, akin to fullerenes, due to the presence of many pentagon defects that induce the positive curvature. In this case Figure 11(c) shows that the majority of hydrogen atoms terminate the cap edge. This fact, combined with the low hydrogen concentration, leads to less frequent defect healing events.

4. Conclusions and Outlook

In this feature article, we have presented an overview of our quantum chemical graphene nucleation and growth simulations, and highlighted how these simulations systematically provide a detailed picture of this process at the atomic level. Our main objective is to simulate CVD graphene growth as systematically as possible, varying individual parameters in order to understand how they influence the chemical pathways of nucleation. However, since it is not trivial to observe many of the phenomena revealed in these simulations experimentally, our simulations additionally highlight how CVD graphene growth can be potentially tuned and controlled experimentally. For instance, we have established the influence of: (1) catalyst type, for Ni, Fe and Cu; (2) catalyst phase, for Ni and Cu catalysts; (3) catalyst facets and surface structure for Ni catalysts; (4) carbide phases, both amorphous and crystalline, for Ni; (5) hydrogen, which provides a dual role in graphene growth and defect healing; and (6) graphene precursors, which provide clear templating effects during graphene nucleation and form the

rationale for the success of experimentally observed “seeded” growth of high-quality graphene.¹²⁵

However, many dynamic aspects of CVD graphene growth remain unexplained. For example, while CVD graphene growth has been demonstrated on the majority of transition metals, detailed mechanisms have only been developed in a few cases (e.g. Ni, Cu, Fe, Co). A number of experiments^{63, 126-129} highlight the potential importance of bimetallic alloy catalysts for graphene (and carbon nanotube) synthesis. However, no mechanistic insights have yet been proposed for these catalysts, or alloy catalysts in general. The addition of chemical etchants (e.g. NH₃,¹³⁰ thiophene,¹³¹ H₂O¹³² etc.) into the CVD mix also shows a dramatic influence over the CVD process. However, a detailed understanding as to the origins of this influence has only been developed in the case of hydrogen.¹³³⁻¹³⁶ The question as to whether or not carbide phases play an active role during graphene formation remains an open question, even for popular catalyst such as Ni. These unexplained aspects of CVD graphene growth must be addressed if we are to routinely and reliably produce high-quality graphene on a commercial scale using this technique.

In part, this arises from current molecular dynamics and Monte Carlo algorithms, which limit simulations of graphene nucleation and growth to ~ nanosecond timescales. A number of MD and MC methods have been proposed to overcome this well-known timescale problem, such as force biased MC methods,¹³⁷⁻¹³⁸ parallel replica dynamics,¹³⁹ umbrella sampling,¹⁴⁰⁻¹⁴³ hyperdynamics¹⁴⁴ and temperature-accelerated dynamics, and bond-boosting methods.¹⁴⁵ However, the efficacies of these methods have not yet been demonstrated in the context of emergent phenomena such as graphene nucleation and growth. Investigation towards this aim is ongoing in our research groups. Current quantum chemical algorithms (i.e. DFT and DFTB) also limit the size of model systems that can be investigated practicably. While empirical tight

binding⁸¹ and ReaxFF¹⁴⁶⁻¹⁴⁸ force fields provide a faster alternative, both must be parameterised appropriately to ensure sufficient accuracy. Despite these challenges, it is clear that quantum chemical and molecular simulations will remain an invaluable tool in this field in the years to come.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Izaak Mitchell studied chemistry at The University of Newcastle, Australia, receiving a BSc (Hons I) and the Dean's medal in 2014. He is currently undertaking a PhD in quantum chemistry under the supervision of Dr Alister Page at The University of Newcastle, Australia. The focus of his PhD research is development of accelerated molecular simulation algorithms, and their application to nanoscale self-assembly processes.

Hai-Bei Li studied chemistry at University of Science and Technology of China (USTC), and she received her Ph.D. degree in chemistry in 2010 under the supervision of Prof. Jinlong Yang and Prof. Shanxi Tian at USTC. From 2010 to 2013 she worked as a postdoctoral fellow in the group of Prof. Morokuma at the FIFC, Kyoto University, focusing on the growth mechanism of nanocarbon materials. Currently, she works at school of Ocean in Shandong University, Weihai. Her research focuses on the reaction mechanism of organo- and organometallic-catalyzed reactions.

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Stephan Irle received a Diploma in Chemistry (1992) from the University of Siegen in Germany and a Ph.D. (1997) in Chemistry from the University of Vienna. In 1998, he became Associate Scientist at the Cherry L. Emerson Center for Scientific Computation at Emory University in Atlanta, GA, U.S.A. In 2006, he moved to Japan and became Associate Professor at Nagoya University. He was granted tenure in 2011 and became a full Professor of Chemistry

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Keiji Morokuma finished PhD at Kyoto University in 1963 under Prof. Kenichi Fukui and did postdoc with Prof. Martin Karplus; he is proud to have two Nobel Laureates as supervisors. After being Professor at University of Rochester, Institute for Molecular Science and Emory University, since 2006 he has been at the FIFC, Kyoto University. He has worked on method developments and applications to many chemical problems.

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