Supporting Information for
“Sub-Surface Nucleation of Graphene Precursors near a Ni(111) Step Edge”

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Movie S2: Computed QM/MD trajectory T1 for Ni(111) step-edge healing process. The total length of the movie is 40 ps; each frame is separated by 0.2 ps. Yellow/red spheres represent non-step-edge/step-edge Ni atoms, respectively; cyan spheres represent C atoms.

Figure S1. Ni(111) model surface, including step-edge defect, used for QM/MD simulation of graphene nucleation. Yellow/red spheres represent non-step-edge/step-edge Ni atoms, respectively.

Figure S2. Structures of trajectories T1-T10 following 64.5 ps QM/MD simulation. Annealing of the structures leads to the precipitation of the graphene precursor to the Ni(111) surface, along with the healing of the deformed Ni(111) surface structure. Yellow/red spheres represent
non-step-edge/step-edge Ni atoms, respectively; cyan spheres represent C atoms.

**Figure S3.** Structures of trajectories T1-T10 following 25 ps QM/MD simulation, after the addition of 50 carbon atoms. Yellow/red spheres represent non-step-edge/step-edge Ni atoms, respectively; cyan spheres represent C atoms.

**Figure S4:** Evolution of carbon cluster sizes in trajectory T1 as a function of simulation time.

**Figure S5:** Polygonal carbon ring populations for trajectories T1-T10.

**Figure S6:** Populations of $sp^2$-hybridized carbon atoms for trajectories T1-T10.
1. Details of QM/MD Simulations and Model Ni(111) Surface

Our QM/MD approach involves the integration of the classical equations of motion, in conjunction with a QM potential. The latter in this case was the self consistent charge density functional tight-binding (DFTB) method, as implemented in the DFTB+ program, and was computed ‘on-the-fly’ at each MD iteration. A finite electronic temperature of 3,000 K was enforced, and so orbital occupations for molecular orbitals near the Fermi level were described by a Fermi-Dirac distribution function. This approach alleviates DFTB convergence issues that arise from the presence of many near-degenerate Ni d orbitals and unterminated carbon dangling bonds, and has been used and validated by us in the previous investigations of transition-metal catalyzed single-walled CNT (SWCNT) nucleation and growth. It is noted here that $T_e = 3,000$ K is the highest temperature at which the pristine, crystalline Ni(111) surface structure could be maintained.

The equations of motion of nuclei were integrated using the Velocity-Verlet algorithm, with the NVT ensemble being maintained via a Nosé-Hoover chain thermostat (chain-length 3) connected to the degrees of freedom of the system. The nuclear temperature was maintained at 1,180 K throughout all simulations.

The Ni(111) step-edge model structure, consisting of 135 Ni atoms, is shown in Fig. S1. Periodic boundary conditions (PBC) were enforced on this model system throughout all simulations using $1 \times 1 \times 1$ k-point sampling using a standard Monckhorst-Pack scheme. Adjacent Ni(111) surfaces were separated by a vacuum region of ca. 1.2 and 4 nm in the y and z axes, respectively, and the outermost layers in the Ni(111) structure (marked by L1, L2 and L3) remained frozen during MD simulation. An alternative model for nucleation would be one that uses a 2-dimensional Ni(111) surface (i.e. one with no vacuum in the y-axis). However, for the step-edge to remain stable in such a model system would require a prohibitively large model system, one that is beyond our current computational means. However, the 1-dimensional constrained model employed here is not anticipated to adversely affect the natural dynamics of graphene precursor formation. Initially, the geometry of the Ni(111) model structure was relaxed at 0 K, before being equilibrated at 1,180 K for 10 ps. Presumably, the Ni(111) the region immediate to the Ni(111) step-edge is anticipated to have a higher carbon concentration, due to its higher chemical reactivity. We therefore assume a priori the existence of sub-surface carbon atoms in the Ni(111) model system near a Ni(111) step-edge defect. To this end, we supplied carbon atoms directly to randomly chosen interstitial sites in the Ni(111) structure at regular intervals of 0.5 ps for the first 25 ps of simulation, in the manner of Bolten et al. Ultimately this yielded a Ni:C ratio of 1:0.37. The initial velocity of each supplied carbon atom was defined according to a Maxwell-Boltzmann distribution at 1,180 K.
statistically independent trajectories were computed, denoted as $T_n$ ($n = 1, 2, \ldots, 10$). Following this period of carbon addition, the system was annealed at 1,180 K for a further 40 ps. While we assume a priori dissolved carbon atoms in the Ni(111) sub-surface region, simulations of the stages in the CVD process prior to this point, viz. the decomposition and dissolution of carbon species into the metal bulk, are ongoing within our group.

**Figure S1.** Ni(111) model surface, including step-edge defect, used for QM/MD simulation of graphene nucleation. Yellow/red spheres represent non-step-edge/step-edge Ni atoms, respectively.

2. **Extended Discussion of Graphene Nucleation Mechanism (Trajectory T1)**

The mechanism of graphene nucleation observed in trajectory T1 is depicted in Fig. 1 (main text) and movies S1 and S2. This trajectory typifies the nucleation mechanism observed in all computed trajectories. At low sub-surface carbon concentration, precipitation of carbon to the Ni(111) surface was generally the predominant phenomenon observed, as shown by the structure at 5.0 ps. At this point in the simulations, five of ten sub-surface carbon atoms had diffused onto the surface, four of which were trapped at Ni step-edge or other surface defect sites. Sub-surface carbon atoms easily coalesced to form polyyne chains; within the first 5 ps of simulation, a single C$_2$ chain was already observed. Two factors are assumedly at play in the formation of such sub-surface carbon chains, viz. the relatively low barrier preventing interstitial diffusion of sub-surface carbon, and the relative strengths of the Ni-C and C-C interactions. Carbon chain formations, such as that observed at 5.0 ps, ultimately drive the formation of larger sub-surface C$_n$ structures. For instance, a further 4.5 ps yields a ‘Y’-junction structure, such as those observed in previous simulations of graphene and SWCNT nucleation$^4$. After only another 2.5 ps, the size of this structure increased rapidly to 11 carbon atoms. It is at this point that similarities between the mechanism of this sub-surface $sp^2$ network nucleation and those observed on catalyst surfaces$^4$ and in vacuum$^9$ are lost. Due to the confinement of the surrounding Ni atoms, these branched chains easily interact with each other. Such interaction directly resulted in the formation of $sp^2$- and $sp^3$-hybridized C$_n$ structures
(for example, at 14.5 and 17.0 ps, respectively). Remarkably, the former of these structures features a hexagon located entirely in the Ni(111) sub-surface. Prior to this hexagon formation, a single pentagon was also fleetingly observed for ca. 1.5 ps, before being destroyed by a newly supplied carbon atom. The time scale over which this ring formation takes place suggests that the confinement effect of the Ni(111) surface affects not only the atomistic mechanism of nucleation, but also the kinetics of nucleation. For instance, here we demonstrate that $sp^2$-hybridized ring structures are formed in the Ni(111) sub-surface within 10-15 ps. On the other hand, at comparable carbon concentrations we have previously shown$^{5,10}$ that SWCNT nucleation on Fe and Ni catalyst surfaces takes between ca. 50 and several hundreds of picoseconds. In effect, Ni atoms here constrain the natural movement of the polyyne chains and carbon atoms in the sub-surface region. Thus, it is concluded that a high, local carbon concentration is necessary in order for graphene to form in this manner. Thus, as is the case with fullerene and CNT formation, graphene nucleation requires a momentarily high, localized carbon density. Further proof of this conclusion is found in trajectory T8, in which a single Y-junction branched polyyne structure was formed on the Ni(111) surface after ca. 16 ps, and remained until the end of the simulation, some 40 ps later. We concede at this point that the present simulations do not address any potential role(s) of surface/sub-surface hydrogen atoms on either the carbon solubility of the Ni catalyst, or the graphene nucleation mechanism itself. Simulations to this end are currently being performed within our group.

Figs. 1 and S2 show that $sp^3$-hybridized carbon was commonly observed in the sub-surface $C_n$ clusters. This is in direct contrast with fullerene and SWCNT nucleation, in which such $sp^3$-hybridized carbon was seldom observed, if at all. Nevertheless, the $sp^3$-hybridized carbon structures observed here were confined entirely within the Ni(111) sub-surface. With increasing $C_n$ cluster size, parts of the growing $C_n$ cluster naturally approached the Ni surface (Fig. S3). The formation of C-Ni bonds in the uppermost layers of the Ni(111) surface destroyed the pristine crystalline structure of the Ni(111) surface, immediately giving rise to new surface defect sites. This was most acute at near the original step-edge defect itself, presumably due to the increased reactivity of these Ni atoms. Upon precipitation, the amorphous $sp^2$/$sp^3$-hybridized structure transformed into planar network structure composed predominantly of $sp^2$-hybridized carbon atoms, as shown between 21 and 25 ps in Fig. 1. In the case of trajectory T1, almost the entire carbon structure precipitated in one concreted motion. This presumably need not be the case in general. Deeper embedding of the amorphous carbon structure in the Ni(111) surface makes no difference to the mechanism of precipitation, however, it does increase the amount of time before precipitation is observed (for example, trajectories T2, T3, and T5, Fig. S3). Precipitation itself results in a
decreasing number of C-Ni σ bonds (in the sub-surface), and an increasing number of C-Ni π bonds (on the surface), presumably due to the overwhelming C-C bond strength. Upon precipitation to the surface, the only C-Ni σ bonds observed existed between the edge of the new $sp^2$-hybridized carbon network and either the Ni(111) step-edge defect, or some other, newly formed surface defect site. The structure ultimately obtained (at 25.0 and 64.5 ps, Fig. 1) may be regarded as a graphene precursor, similar to those observed experimentally. However, the structure of the Ni(111) surface depends on the dynamics of the precipitating graphene precursor, and is by no means static. On the contrary, Figs. 1, S2, and S3 illustrate that in all cases, the original step-edge defect (red spheres) is largely or completely destroyed by the presence of the precipitating carbon cluster. This observation bears resemblance to the recently report of Gomez-Gualdron et al.\textsuperscript{11} concerning SWCNT nucleation, in which a dynamic relationship between the nanocatalyst and SWCNT structures was observed.

3. References

**Figure S2.** Structures of trajectories T1-T10 following 64.5 ps QM/MD simulation. Annealing of the structures leads to the precipitation of the graphene island precursor to the Ni(111) surface, along with the healing of the deformed Ni(111) surface structure. Yellow/red spheres represent non-step-edge/step-edge Ni atoms, respectively; cyan spheres represent C atoms.
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