

Electronic Supplementary Information

Classical molecular dynamics simulations of carbon nanofiber nucleation: effect of carbon concentration in Ni carbide

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1. Movies

Movie S1:

Descriptive title: Simulated atomistic process of carbon nanofiber nucleation at high carbon concentration.

Video legend: Molecular dynamics trajectory of the carbon precipitation process during carbon nanofiber nucleation, with the initial Ni carbide at 1.5 ML of carbon atoms in the first and second Ni subsurfaces.

Keywords: Molecular dynamics, carbon naonfiber, carbon concentration, Ni-carbide, nucleation, precipitation, graphene

Movie S2:

Descriptive title: Simulated atomistic process of carbon nanofiber nucleation at medium carbon concentration.

Video legend: Molecular dynamics trajectory of the carbon precipitation process during carbon nanofiber nucleation, with the initial Ni carbide at 1.0 ML of carbon atoms in the first and second Ni subsurfaces.

Keywords: Molecular dynamics, carbon naonfiber, carbon concentration, Ni-carbide, nucleation, precipitation, graphene

Movie S3:

Descriptive title: Simulated atomistic process of carbon nanofiber nucleation at low carbon concentration.

Video legend: Molecular dynamics trajectory of the carbon precipitation process during carbon nanofiber nucleation, with the initial Ni carbide at 0.5 ML of carbon atoms in the first and second Ni subsurfaces.

Keywords: Molecular dynamics, carbon nanofiber, carbon concentration, Ni-carbide, nucleation, precipitation, graphene

2. Validation of Method

The parameterization of the Morse potential was validated by calculating the heat of solution (ΔH), the energy difference between O- and T-site (E_d), the adhesion energy (E_a), and the binding energy (E_b) of carbon atoms in Ni-C systems, using classical many-body Tersoff potential, modified embedded atom method potential, and pair Morse potential for C-C, Ni-Ni, and Ni-C interactions, respectively. To have a comparison with previous results, the initial atomic structures (shown in Fig. S1) are the same as used in previous works for calculating a similar energy, and all the energies are calculated at 0 K after structural relaxation.

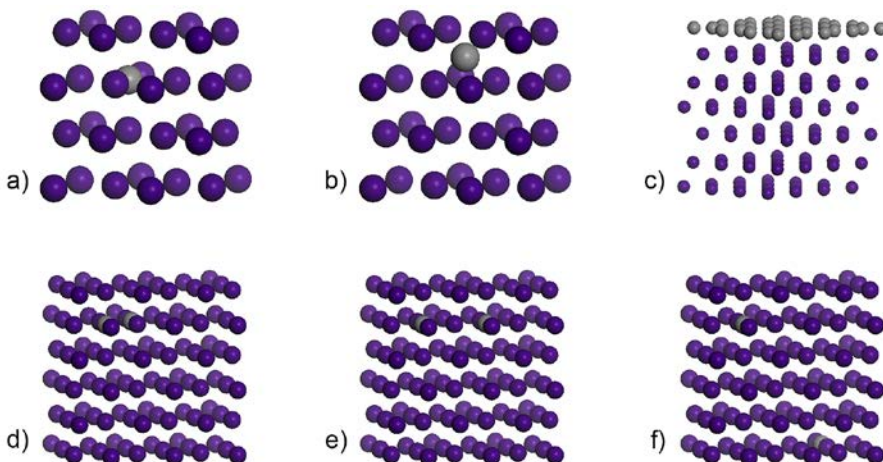


Fig. S1 Ni-C systems used for calculating different energies of carbon atoms (Ni in purple, C in gray). C atom occupies (a) O- or (b) T-site of $2 \times 2 \times 2$ Ni supercell. (c) Graphene with the carbon atoms located at the bridge-top sites of $2 \times 2 \times 2$ Ni (111) six-layer slab surface. Two carbon atoms occupy (d) nearest-neighbour, (e) next-nearest-neighbour, or (f) isolated O-sites of $3 \times 3 \times 3$ Ni supercell.

The system for ΔH calculation consists of a carbon atom occupying the O-site of the $2 \times 2 \times 2$ Ni supercell (Fig. S1a). ΔH of the C atom is given by the following expression:

$$\Delta H = E_{Ni-C} - E_{Ni} - E_c, \quad (1)$$

where E_{Ni-C} is the energy of the $2 \times 2 \times 2$ Ni supercell + O-site C atom system, E_{Ni} is the energy of the $2 \times 2 \times 2$ Ni supercell, and E_c is the energy per carbon atom in graphite.

E_d of a C atom in Ni crystal is obtained from the difference between energies of the $2 \times 2 \times 2$ Ni supercell + O-site C atom system (Fig. S1a) and the $2 \times 2 \times 2$ Ni supercell + T-site C atom system (Fig. S1b). E_d is compared with the energy barrier for the C atom diffusing from the O-site to the T-site.

Graphene with 32 carbon atoms located at the bridge-top sites of the surface of the $2 \times 2 \times 2$ Ni (111) six-layer slab is considered for calculating E_a . The graphene was 2 Å above the first layer of the Ni slab. E_a per C atom in the graphene is given by the formula

$$E_a = \frac{1}{32} (E_{slab/graphene} - E_{slab} - E_{graphene}), \quad (2)$$

where $E_{slab/graphene}$, E_{slab} , and $E_{graphene}$ are the energies of the $2 \times 2 \times 2$ Ni (111) six-layer slab + graphene system, the $2 \times 2 \times 2$ Ni (111) six-layer slab, and the graphene plane, respectively.

The $3 \times 3 \times 3$ Ni supercell + interstitial carbon atoms structures are employed for calculating E_b s. The C-C pair is located at the nearest-neighbour (Fig. S1d) or the next-nearest-neighbour (Fig. S1e) O-sites. E_b s of the C-C pairs at the two configurations are estimated with respect to the energy of the isolated configuration (Fig. S1f), in which the two C atoms are located at the O-sites at large distance in the Ni crystal lattice:

$$E_b = E_{nearest} - E_{isolated}, \quad (3)$$

or

$$E_b = E_{next-nearest} - E_{isolated}, \quad (4)$$

where $E_{nearest}$, $E_{next-nearest}$, and $E_{isolated}$ are the energies of the $3 \times 3 \times 3$ Ni supercell + interstitial carbon atoms structures having the nearest-neighbour C-C pair, the next-nearest-neighbour C-C pair, and the isolated C atoms, respectively.

The calculated values of ΔH , E_d , E_a , and E_b are shown in Table S1, which are in good agreement with the results based on DFT and experiments in the same Ni-C systems.

Table S1. Comparison of present values of ΔH , E_d , E_a , and E_b (in eV) based on classical theory with previous DFT and experimental values.

	Present	Previous
ΔH	0.724	0.18–0.75 ^a
E_d	1.617	1.62 ^a 1.641, 1.678 ^b
E_a	–0.224	–0.205 ^c
E_b (nearest)	0.112	–0.07–0.1 ^a
E_b (next-nearest)	0.362	–0.01–0.1 ^a

^aReference 1 and references therein.

^bReference 2.

^cReference 3.

Using our parameterized Morse potential we have also successfully simulated the clock reconstruction for C atoms adsorbed on a Ni (100) surface, as shown in Fig. S2. At a C coverage of 0.5 ML in the 4×4 Ni (100) surface, the C adsorbates induce clockwise-counter-clockwise rotation of the Ni atoms after structural relaxation, leading to the Ni (100)-(2 \times 2) $p4gC$ structures. The lateral displacements of the Ni atoms are 0.45 ± 0.1 Å, in good agreement with previous experimental and theoretical results.^{4–7}

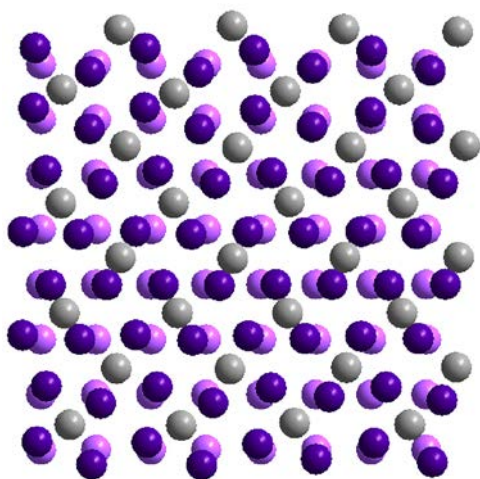


Fig. S2 Carbon-induced clock reconstruction of Ni atoms in 4×4 (100) plane. Light (deep) purple balls denote Ni atoms before (after) reconstruction. Gray balls denote C atoms located at the fourfold hollow sites of the Ni (100) surface.

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3. Supplementary Figures

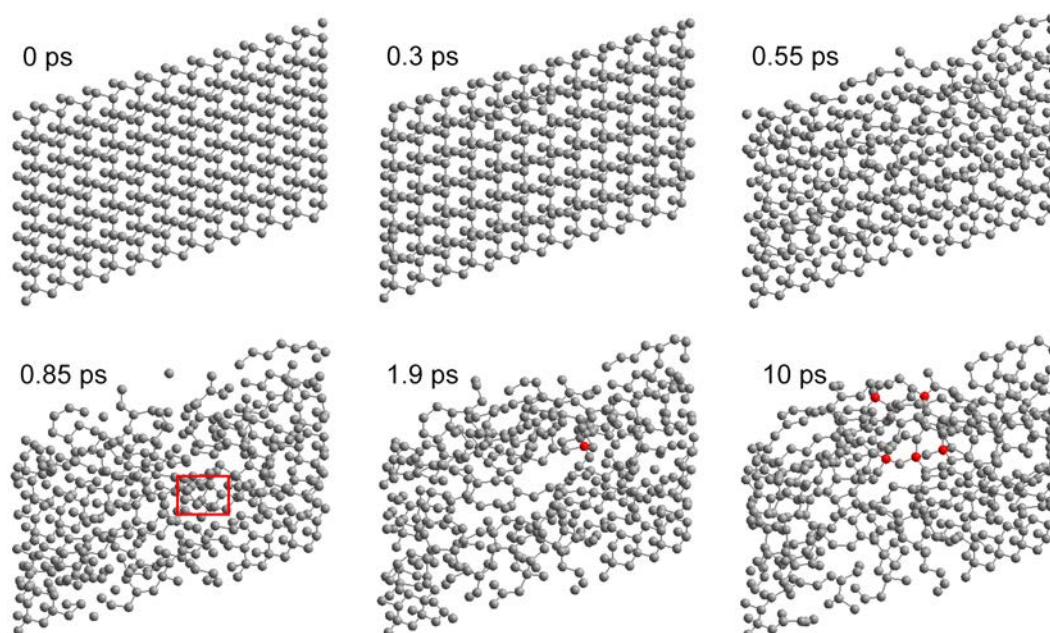


Fig. S3 Evolution of the configuration of C atoms shown in Fig. 3. Ni atoms are not shown.

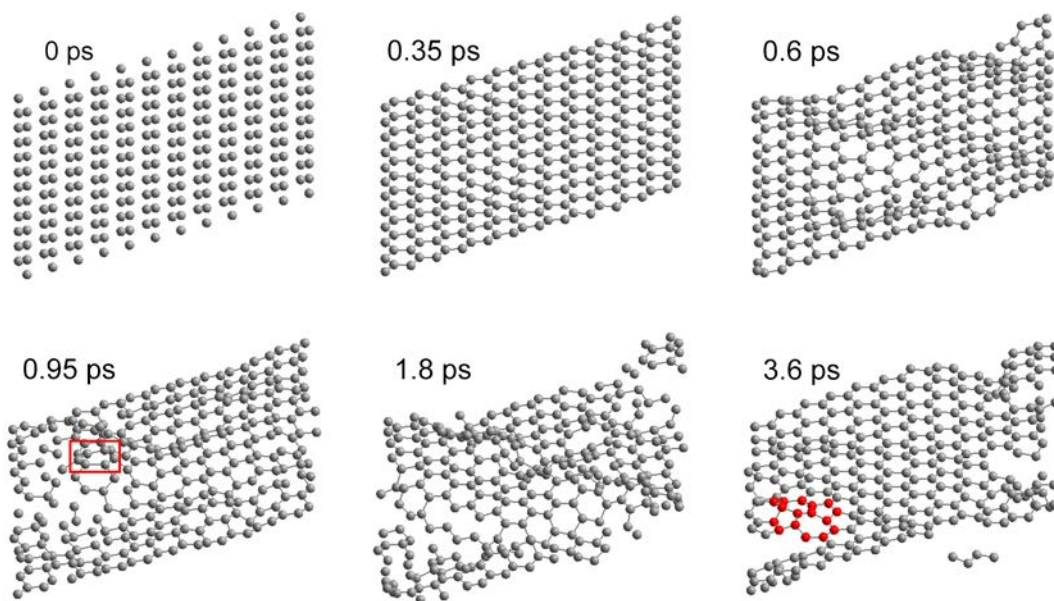


Fig. S4 Evolution of the configuration of C atoms shown in Fig. 4. Ni atoms are not shown.

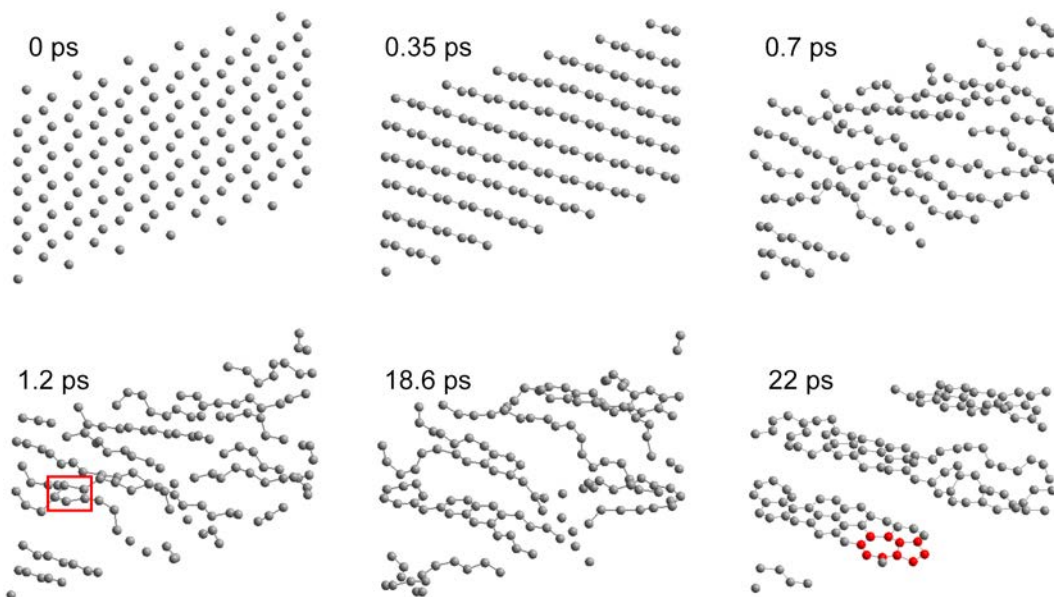


Fig. S5 Evolution of the configuration of C atoms shown in Fig. 5. Ni atoms are not shown.

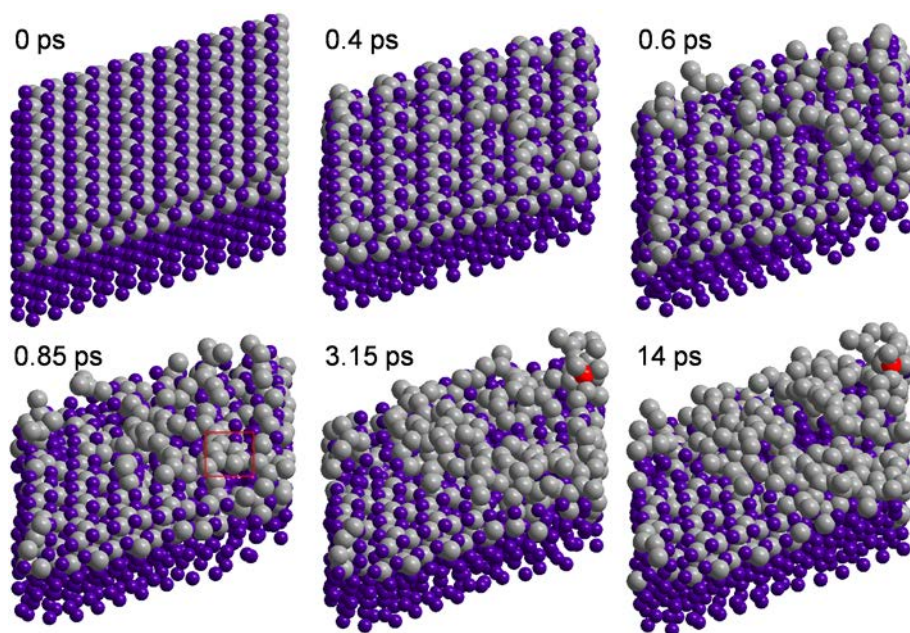


Fig. S6 Snapshots of the MD trajectory of carbon precipitation process during CNF nucleation, with the initial Ni carbide at 1.25 ML of carbon atoms in the first and second Ni subsurfaces. Purple (gray) balls denote Ni (C) atoms. Red balls represent the typical sp^3 -hybridized carbon atoms. The rectangle denotes the polygonal carbon atom ring initially formed in the Ni surface.

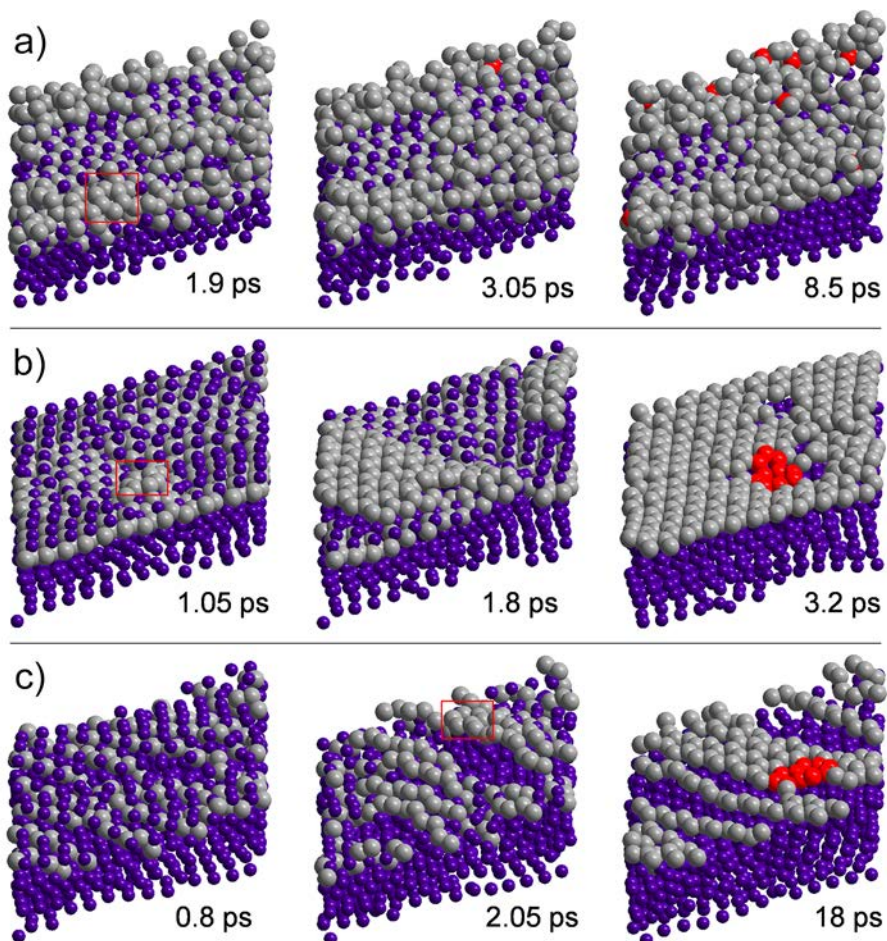


Fig. S7 Precipitation evolutions of carbon during CNF nucleation at 873 K. Other simulation conditions are the same as in (a) Fig. 3, (b) Fig. 4, and (c) Fig. 5 as depicted in the Models and Methods of the manuscript. Rectangles denote the polygonal carbon atom ring initially formed in the Ni surface, and red balls the significant graphite disorders.

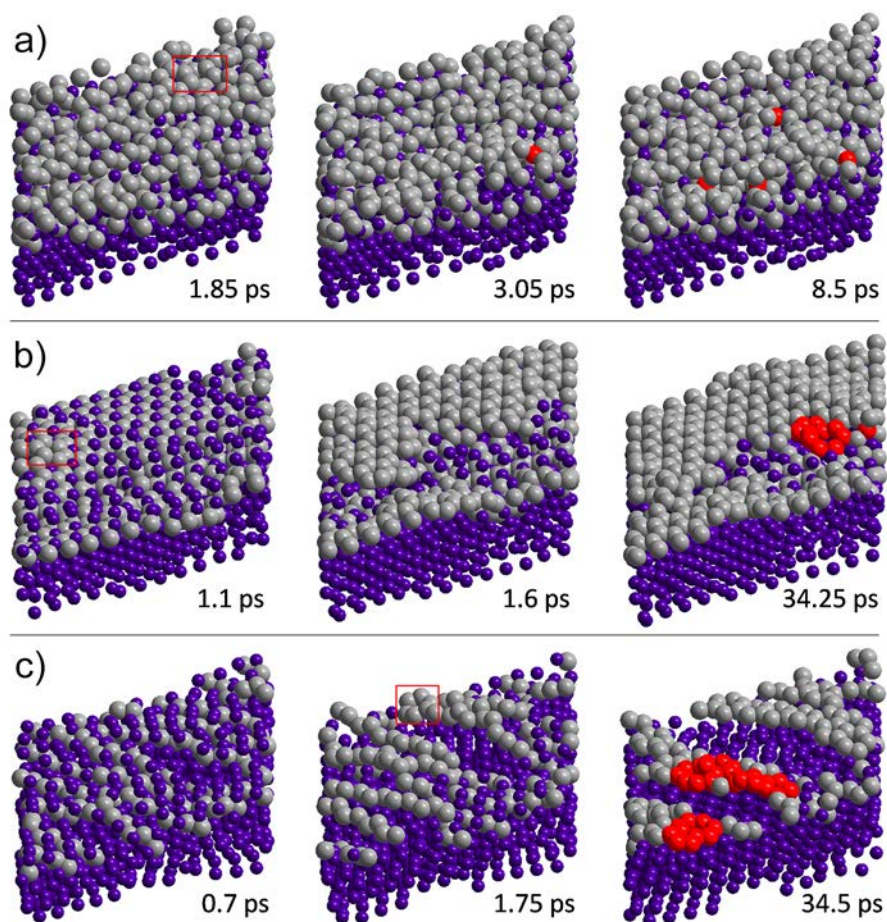


Fig. S8 Precipitation evolutions of carbon during CNF nucleation at 1073 K. Other simulation conditions are the same as in (a) Fig. 3, (b) Fig. 4, and (c) Fig. 5 as depicted in the Models and Methods of the manuscript. Rectangles represent the polygonal C rings initially formed in Ni surface, and red balls the significant graphite disorders.