Electronic Supplementary Information

Atomic Simulation of the Growth of Defect-free Carbon Nanotubes

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Fig. S1 Scheme of basin-hopping (BH) defects-healing strategy in the atomistic simulation.
Fig. S2 Selected SWCNTs simulated by liquid catalyst particles. (a) Ni_{19}, (b) Ni_{32} and (c) Ni_{55}.
Development of the force field for the carbon-metal interactions

The potential energy of the whole catalytic CNT growth system can be divided into three categories, i.e.,

$$E_{tot} = E^{cc} + E^{mc} + E^{mm}$$  \hspace{1cm} (S-1)

in which $E^{cc}$, $E^{mc}$, and $E^{mm}$ are the carbon-carbon (C-C), metal-carbon (M-C), and metal-metal (M-M) interaction energies, respectively. Here, the metal atoms represent the catalyst particle. These three potential energy terms can be further written as,

$$E^{cc} = \sum_{i} \sum_{j (j > i)} (E_{ij}^{cc})$$  \hspace{1cm} (S-2)

$$E^{mc} = \sum_{i} \sum_{j} (E_{ij}^{mc})$$  \hspace{1cm} (S-3)

$$E^{mm} = \sum_{i} \sum_{j (j > i)} (E_{ij}^{mm})$$  \hspace{1cm} (S-4)

in which $E_{ij}^{cc}$, $E_{ij}^{mc}$, and $E_{ij}^{mm}$ indicate the interaction energies of the C-C, M-C, and M-M atoms $i$ and $j$, respectively.

Like the former development of the reactive empirical bond order (REBO) potential,$^1$ we consider the following cases for the C-C interaction: (1) a C-C bond far away from the metal particle; (2) a C-C bond on the surface of the metal particle; (3) a C-C bond under the subsurface of the metal particle; and (4) a C-C bond inside the metal particle. For the M-C interaction, in addition to the bond order from the surrounding metals, we also consider the bond order from the surrounding carbons, which determine the types of carbon atoms in the selected M-C bonds (e.g., the carbon monomer, carbon dimer, carbon chain, carbon wall, AC edge or ZZ edge, etc.).

The important improvements of this newly developed REBO potential are mainly manifested in the M-C interaction, including the addition of (1) a parameter of local coordination to tune the M-C interaction while simplifying the form of the
original M-C potential; and (2) an angle dependent term to reflect the fact that a σ bond of the C-M interaction at the edge of the carbon wall tends to be perpendicular to the metal surface. It should be noted that the parameter fittings with this M-C potential are based on the density function theory (DFT) calculations of the carbon-nickel system. The details of the three interaction categories are introduced below.

**S1 Carbon-Carbon interaction**

The C-C interaction is mainly described by the modified REBO2 potential, including the repulsive interaction term $V^R(r_{ij})$ and attractive interaction term $V^A(r_{ij})$ as functions of the distance $r_{ij}$ between two paired atoms. A parameter $\alpha_{ij}^{cc}$ is added to reflect the screening effect of metal atoms on the C-C bond, which weakens the C-C interaction. As such, the C-C interaction is written as

$$E_{ij}^{cc} = \alpha_{ij}^{cc}[V^R(r_{ij}) - V^A(r_{ij})]$$  \hspace{1cm} (S-5)

$$V^R(r_{ij}) = f^{cc}(r_{ij}) \cdot (1 + Q / r_{ij}) \cdot A e^{-\alpha r_{ij}}$$  \hspace{1cm} (S-6)

$$V^A(r_{ij}) = b_{ij} f^{cc}(r_{ij}) \sum_{n=1,3} (B_n e^{-\beta_n r_{ij}})$$  \hspace{1cm} (S-7)

in which the parameters $Q, A, \alpha, \beta_n$, and $B_n$ are the parameters are described in the original REBO2 potential. In Eq. (S-7), $b_{ij}$ is the bond order function, depending on the local coordination and the bond angle of carbon atoms $i$ and $j$. The details of this term can also be found in the original REBO2 potential. $f^{cc}(r_{ij})$ in Eq. (S6) is the switching function of the C-C repulsive interaction, i.e.,

$$f^{cc}(r_{ij}) = \begin{cases} 
1, & r_{ij} < R_{cc1} \\
1 + \cos \left( \pi \cdot \frac{r_{ij} - R_{cc1}}{R_{cc2} - R_{cc1}} \right) / 2, & R_{cc1} < r_{ij} < R_{cc2} \\
0, & r_{ij} > R_{cc2}
\end{cases}$$  \hspace{1cm} (S-8)

in which $R_{cc1}$ and $R_{cc2}$ are two cutoff distances, as listed in table S1. In Eq. (S-5), $\alpha_{ij}^{cc}$ is given by
\[
\alpha_{ij}^{cc} = \begin{cases} 
1 & , N_{ij}^M < N_{1}^M \\
1 + \cos \left( \pi \cdot \frac{N_{ij}^M - N_{1}^M}{N_{2}^M - N_{1}^M} \right) / 2, & N_{1}^M < N_{ij}^M < N_{2}^M \\
0 & , N_{ij}^M > N_{2}^M 
\end{cases} 
\]  
(S-9)

\[N_{ij}^M = (N_i^M + N_j^M) / 2 \]  
(S-10)

in which \( N_{ij}^M \) is the averaged metal coordinates of atoms \( i \) and \( j \), and thus reflects the metal environment around a C-C bond. In Eq. (S-10), \( N_i^M \) and \( N_j^M \) represent the metal coordinates of atoms \( i \) and \( j \), respectively, as defined by equations (S-11) and (S-12) below. \( N_1^M \) and \( N_2^M \) are the cutoff numbers (see table S1). Similar to \( f_{cc}(r_{ij}) \) defined in equation (S-8), \( f_{cm}(r_{ik}) \) and \( f_{cm}(r_{jk}) \) in Eqs. (S-11) and (S-12) are the cutoff functions of the C-M interaction, which is defined in equation (S-13), i.e.,

\[N_i^M = \sum_{k}^{\text{metal}} f_{cm}(r_{ik}) \]  
(S-11)

\[N_j^M = \sum_{k}^{\text{metal}} f_{cm}(r_{jk}) \]  
(S-12)

\[f_{cm}(r_{ik}) = \begin{cases} 
1 & , r_{ik} < R_{cm1} \\
1 + \cos \left( \pi \cdot \frac{r_{ik} - R_{cm1}}{R_{cm2} - R_{cm1}} \right) / 2, & R_{cm1} < r_{ik} < R_{cm2} \\
0 & , r_{ik} > R_{cm2} 
\end{cases} 
\]  
(S-13)

in which \( R_{cm1} \) and \( R_{cm2} \) are the cutoff distances (see table S1). When \( N_{ij}^M \) exceeds \( N_2^M \), the C-C interaction is obviously reduced to 0, which corresponds to the cases of carbon atoms dissolved into the metal particle.

**Table S1** Parameters for equations (S-8), (S-9), and (S-13) with nickel as the metal catalyst.

| \( R_{cc1} \)       | \( R_{cc2} \)       |
|---------------------|---------------------|
| 1.7 Å               | 2.0 Å               |
S2 Metal-Carbon interaction

The M-C interaction is written as Eq. (S-14) nominally, including the distance dependence term $E_{ij}^{mc}(r_{ij})$ and the angle dependence term $E_{ijk}^{mc}(r_{jk}, r_{jl}, \theta_{ijl})$, i.e.,

$$E_{ij}^{mc}(r_{ij}) = E_{ij}^{mc}(r_{ij}) + E_{ijk}^{mc}(r_{jk}, r_{jl}, \theta_{ijl})$$  \hspace{1cm} (S-14)

Details of Eq. (S-14) are discussed below.

a) Distance dependence term $E_{ij}^{mc}(r_{ij})$

As shown in equation (S-15), the distance dependence term also includes Morse type repulsive $V^R(r_{ij})$ and attractive $V^A(r_{ij})$ terms, in Eqs. (S-16) and (S-17), respectively.\(^4\)

$$E_{ij}^{mc}(r_{ij}) = \alpha_{ij}^{mc} \cdot \left( V^R(r_{ij}) - V^A(r_{ij}) \right)$$  \hspace{1cm} (S-15)

$$V^R(r_{ij}) = f_{ij}^{mc}(r_{ij}) \frac{D_e}{S - 1} \exp \left\{ - \beta \sqrt{2S} (r_{ij} - R_e) \right\}$$  \hspace{1cm} (S-16)

$$V^A(r_{ij}) = f_{ij}^{mc}(r_{ij}) \frac{D_e S}{S - 1} \exp \left\{ - \beta \frac{2}{\sqrt{S}} (r_{ij} - R_e) \right\}$$  \hspace{1cm} (S-17)

$$R_e = R_{e1} - R_{e2} \cdot \exp \left( - C_R N_{ij} \right)$$  \hspace{1cm} (S-18)

in which $D_e$ is the equilibrium binding energy, and the parameters $D_e$, $S$, $\beta$, $R_{e1}$, $R_{e2}$ and $C_R$ are listed in table S2. In Eq. (S-18), $R_e$ is the equilibrium distance between metal atom $i$ and carbon atom $j$ that depends on the coordination number $N_{ij}$, which indicates the environmental influence from both the surrounding metals and carbons, i.e.,

$$N_{ij} = N_{ij}^M + \lambda N_{ij}^C$$  \hspace{1cm} (S-19)
\[ N^M_j = \sum_{\text{metal } k \neq i} f(r_{jk}) \]  

(S-20)

\[ N^C_i = \sum_{\text{carbon } l \neq j} f(r_{il}) \]  

(S-21)

**Table S2** Parameters for the equations (S-16), (S-17) and (S-18) with the nickel as metal catalyst.

| Parameter | Value |
|-----------|-------|
| \( D_e \) | 2.6 Å |
| \( \beta \) | 1.8 Å\(^{-1} \) |
| \( R_{e1} \) | 1.9 Å |
| \( S \) | 1.3 Å |
| \( R_{e2} \) | 0.2 Å |
| \( C_R \) | 0.5 |

In Eq. (S-19), \( \lambda = 0.08 \) is the weighing parameter for the metal and carbon coordinate contributions around atoms \( i \) and \( j \). \( \alpha^\text{mc}_D \) in Eq. (S-15) is given by

\[ \alpha^\text{mc}_D = \alpha^\text{mc}_D (N^C_j, N^C_j, N^M_j) \]  

(S-22)

\[ N^C_1_j = \sum_{k \neq j} f_{jk}(r_{jk}) \]  

(S-23)

\[ N^C_2_j = \sum_{l \neq j, k} f_{jl}(r_{jl}) \]  

(S-24)

\[ N^M_j = \sum_{m} f_{jm}(r_{jm}) \]  

(S-25)

One of the most important contributions of this newly developed M-C potential is the design of parameter \( \alpha^\text{mc}_D \), which acts as a function of \( (N^C_1_j, N^C_2_j, N^M_j) \), and thus can incorporate the influence of the local chemical environment surrounding the M-C bond. \( N^C_1_j \) is the number of nearest carbon neighbors of carbon atom \( j \), \( N^C_2_j \) is the number of next nearest carbon neighbors of carbon atom \( j \), and \( N^M_j \) is the number of metal coordinates around carbon atom \( j \). Different compositions of \( (N^C_1_j, N^C_2_j, N^M_j) \) indicate different local chemical environment cases (table S3). It should be noted that
$N_{j}^{C_{1}}, N_{j}^{C_{2}}, N_{j}^{M}$ are not always integers according to their definitions in equations (S-23), (S-24), and (S-25), respectively. Therefore, by fixing some of the knots of $\alpha_{D}^{mc}$, the other $\alpha_{D}^{mc}$ values can be interpolated using the tricubic-spline interpolation. To make our potential approach as reasonable as possible, we tune these crucial knots based on the energies of some typical structures calculated by the DFT. Fig. S3 and Table S3 show the typical structures and their formation energies for the tuning of the parameter knots, respectively. Via the parameter $\alpha_{D}^{mc}$, the effects of the local chemical environments on the M-C interaction can be taken into account. Furthermore, by tuning $\alpha_{D}^{mc}$, we can conveniently modulate the potential for carbon-metal interactions.

Fig. S3 Structures for adjusting the knots of $\alpha_{D}^{mc}$. a, Carbon monomer on Ni\textsubscript{55} surface. b, Carbon monomer in Ni\textsubscript{55}. c, Carbon dimmer on Ni\textsubscript{55} surface. d, Carbon dimmer in Ni\textsubscript{55}. e, Carbon ring on Ni substrate. f, Carbon wall on Ni substrate. g, (5, 5) carbon tube on Ni\textsubscript{55}. h, (10, 0) carbon tube on Ni\textsubscript{55}. i, Carbon chain with two open ends on Ni substrate.

Table S3 Formation energies $E_{f}$ for different carbon-nickel systems.
\[ E_f = E(C_{N+Ni}) - E(Ni) - N \varepsilon, \]

where \( N \) is the number of carbon atoms and \( \varepsilon \) is the energy per carbon atom in the graphene. However, for \( e \) and \( f \) (C on AC and ZZ edge), the \( E_f = E_{FE} - E_b \), in which \( E_{FE} \) and \( E_b \) are the formation energy of the free SWCNT end and the SWCNT-metal binding energy, respectively, and \( E_b = E_{NT} + E_{Ni} - E_{NT@Ni} \), in which \( E_{NT@Ni} \) is the energy of SWCNT attached on Ni. \( E_{NT} \) and \( E_{Ni} \) are energies of the isolated SWCNT and Ni, respectively. 

\[ E_{FE} = 0.5(2E_{NT2} - E_{NT1}), \]

in which \( E_{NT1} \) is the energy of a longer SWCNT and \( E_{NT2} \) is the energy of a shorter SWCNT, which is obtained by cutting the longer SWCNT into two equal segments. The factor 0.5 refers the fact that two open ends are formed when a SWCNT is cut into two SWCNTs.

\[ F^{mc}_{\theta} (r_{jk}, r_{jl}, \theta_{kjl}) \]

### Table: carbon atoms

| Carbon Atoms | \( N_j^C \) | \( N_j^M \) | \( E_f \) (eV) |
|--------------|--------------|--------------|--------------|
| #a: C monomer | 0            | 1            | 3.7          |
| #a: C monomer | 0            | 2            | 2.7          |
| #a: C monomer | 0            | 3            | 1.2          |
| #a: C monomer | 0            | 4            | 0.7          |
| #a: C monomer | 0            | 5-8          | 0.5          |
| #b: a C in a dimer | 1            | 1            | 3.0          |
| #b: a C in a dimer | 1            | 2            | 2.0          |
| #b: a C in a dimer | 1            | 3            | 1.0          |
| #b: a C in a dimer | 1            | 4            | 0.6          |
| #b: a C in a dimer | 1            | 5-8          | 0.2          |
| #c: a C in a chain | 2, 12        | 1, 2, 3, 8   | 0.81         |
| #d: a C on a Chain end | 1            | 1-8          | 0.20         |
| #e: a C on AC edge | 2            | 1            | 0.30 (1.41 ev/nm) |
| #e: a C on AC edge | 2            | 2            | 0.28 (1.31 ev/nm) |
| #e: a C on AC edge | 2            | 3            | 0.268 (1.26 ev/nm) |
| #f: a C on a ZZ edge | 2            | 4            | 0.20 (0.81 ev/nm) |
| #f: a C on a ZZ edge | 2            | 4            | 0.18 (0.73 ev/nm) |
| #f: a C on a ZZ edge | 2            | 3-10         | 0.164 (0.67 ev/nm) |
| #g: a C in a tube wall | 3            | 0-6          | 1-8          |

* \( E_f = E(C_{N+Ni}) - E(Ni) - N \varepsilon \), where \( N \) is the number of carbon atoms and \( \varepsilon \) is the energy per carbon atom in the graphene. However, for \( e \) and \( f \) (C on AC and ZZ edge), the \( E_f = E_{FE} - E_b \), in which \( E_{FE} \) and \( E_b \) are the formation energy of the free SWCNT end and the SWCNT-metal binding energy, respectively, and \( E_b = E_{NT} + E_{Ni} - E_{NT@Ni} \), in which \( E_{NT@Ni} \) is the energy of SWCNT attached on Ni. \( E_{NT} \) and \( E_{Ni} \) are energies of the isolated SWCNT and Ni, respectively. 

- \( E_{FE} = 0.5(2E_{NT2} - E_{NT1}) \), in which \( E_{NT1} \) is the energy of a longer SWCNT and \( E_{NT2} \) is the energy of a shorter SWCNT, which is obtained by cutting the longer SWCNT into two equal segments. The factor 0.5 refers the fact that two open ends are formed when a SWCNT is cut into two SWCNTs.

**b) Angle dependence term** \( F^{mc}_{\theta} (r_{jk}, r_{jl}, \theta_{kjl}) \)
The addition of the angle dependence term is another important improvement of this new potential. It was found recently that the C-M bond has a remarkable angle dependence for the carbon atoms at the edges of a graphene nanoribbon (GNR), which means the σ bond tends to be perpendicular to the metal surface. To include this bond orientation preference, we add an angle dependence term in our new potential, i.e.,

$$E_{\theta}^{mc}(r_{jk}, r_{jl}, \theta_{ljk}) = \sum_j [\alpha_{ljk}(N_{C1}^j, N_{C2}^j) \cdot (\vec{V}_{cj} \cdot \vec{V}_{mj})]$$  \hspace{1cm} (S-26)

$$\vec{V}_{cj} = \sum_{l \neq j}^{\text{carbon}} f^{cc}(r_{jl}) \cdot (\vec{r}_{l} - \vec{r}_{j})$$  \hspace{1cm} (S-27)

$$\vec{V}_{mj} = \sum_{k}^{\text{metal}} f^{cm}(r_{jk}) \cdot (\vec{r}_{k} - \vec{r}_{j})$$  \hspace{1cm} (S-28)

$$\vec{V}_{cj} \cdot \vec{V}_{mj} = \sum_{ljk}^{\text{carbon}} f^{cc}(r_{jl}) f^{cm}(r_{jk}) r_{jl} r_{jk} \cos(\theta_{ljk})$$  \hspace{1cm} (S-29)

in which $\theta_{ljk}$ is the angle between the carbon $j$-carbon $l$ bond and the carbon $j$-metal $k$ bond (C-C-M) (see Fig. S4). When $\theta_{ljk} = \pi$ (or $\cos \pi = -1$), the inner term of the right part of equation (S-29) obviously achieves minima. Similar to $\alpha_{D}^{mc}$, $\alpha_{ljk}$ is a function of $(N_{C1}^j, N_{C2}^j)$, which reflects the carbon coordinates around carbon $j$ and determines the angle dependence magnitude for different types of carbon atoms. Just like $\alpha_{D}^{mc}$, we fix some typical knots first and then obtain all of the $\alpha_{ljk}$ values by bicubic spline interpolation. The structures used to tune the $\alpha_{ljk}$ knots are shown in Fig. S4 and the fixed knots are listed in table S4. By taking this angle dependence term into account, the binding energy for graphene standing on a nickel substrate where $\theta_{ljk} = 90^\circ$ is lowered by 0.358 (eV/atom) compared with that where $\theta_{ljk} = 30^\circ$. 
Fig. S4 Angle dependence of the C-C-M bond. A GNR on an Ni substrate at angles of (a) 30°, (b) 60° and (c) 90°, respectively. The energy of (c) is 0.358 eV/atom lower than the one of (a).

Table S4 $\alpha_{ijkl}$ knots with nickel as the metal catalyst.

| Carbon Atoms         | $N^C_{j1}$ | $N^C_{j2}$ | $\alpha_{ijkl}$ |
|----------------------|------------|------------|------------------|
| C monomer            | 0          | 0          | 1.0              |
| C in dimer           | 1          | 0          | 1.0              |
| C in chain           | 2          | 1,2        | 0.01             |
| C on a chain end     | 1          | 1,2        | 1.0              |
| C on an AC edge      | 2          | 3          | 1.0              |
| C on a ZZ edge       | 2          | 4          | 1.0              |
| C in a tube wall     | 3,4,5      | 0-8        | 0.01             |

S3 Metal-Metal interaction

The M-M interactions of the nickel particle are described by the Sutton-Chen potential.\textsuperscript{5}
\[ E^{MM} = \sum_{i} \varepsilon [ \frac{1}{2} \sum_{j \neq i} (\frac{a}{r_{ij}})^m - c\sqrt{\rho_i}] \]  
\[ \rho_i = \sum_{j \neq i} (\frac{a}{r_{ij}})^n \]

where \( c \) is a dimensionless parameter, \( \varepsilon \) is a parameter with dimensions of energy and \( a \) is the lattice constant. \( m \) and \( n \) are positive integers, with \( n > m \). The nickel particle parameters are listed in table S5.

Table S5 Parameters of Sutton-Chen potential for nickel particle.

| Parameter | Value |
|-----------|-------|
| \( c \) | 39.755 |
| \( \varepsilon \) | 0.015731 eV |
| \( a \) | 3.52 Å |
| \( m \) | 6.0 |
| \( n \) | 9.0 |

S4 Validation of the potential

Three typical carbon caps (\( C_{20} \) with a pentagon in the center and five hexagons around, \( C_{21} \) with one hexagon in the center, three pentagons and three hexagons around, \( C_{24} \) with seven pentagons in the core-shelled formation) on a Ni(111) slab surface were selected to test the accuracy of new force field (NewFF) based on the new PES. The structural characteristics, formation energies obtained by three different force fields, including the DFT, reactive force field (ReaxFF),\(^6,7\) Texas A&M \(^1\) (Here, we thanks to Prof. Balbuena et al. in Texas A&M university for sharing their original code with us. For simplicity, the classical potential developed by them is named as ‘Texas A&M’ in our table and figures) and the newly developed force field in this study (NewFF) are shown in tables S6-S9 and Figs. S7-S8.

ReaxFF and Texas A&M are known as the best classical energy potentials that could be used to deal with chemical reactions at metal-carbon interface. Thus, we use them as the benchmarks and compare with our NewFF, which is specifically calibrated for the M-C interactions. From the following comparison, we can clearly see that:

(1) The formation energies of the three graphitic caps calculated by NewFF are
better than those calculated by ReaxFF and Texas A&M. The energetic order by Texas A&M is not consistent with the results of DFT. Although the energetic order obtained by ReaxFF is same as that calculated by DFT method, the ReaxFF underestimates formation energy by more than 60%. In comparison, NewFF not only gives same formation energy order, but in very good agreement with those calculated by DFT calculations with the largest error of ~ 20%, which is smaller than ReaxFF and Texas A&M.

(2) The optimized structures of the three caps by NewFF are similar with those optimized by ReaxFF and Texas A&M, but the results obtained by NewFF agree well with those obtained by the DFT method better than the former two.

Thus, from above discussion, we can conclude that the quality of NewFF is very high for M-C interactions, and thus the results obtained by the MD based on the newly developed potential energy surface should be more realistic.
Table S6 Comparison of formation energies* for Cap$_{20}$, Cap$_{21}$ and Cap$_{24}$ obtained by DFT calculations, ReaxFF, Texas A&M and NewFF.

| Method      | $E_f$ (eV) | Cap$_{20}$ (eV) | Cap$_{21}$ (eV) | Cap$_{24}$ (eV) |
|-------------|------------|----------------|----------------|----------------|
| DFT         | 11.42      | 10.5           | 15.15          |
| ReaxFF      | 4.34       | 4.03           | 5.75           |
| Texas A&M   | 14.52      | 22.20          | 13.27          |
| NewFF       | 11.50      | 7.79           | 14.56          |

* $E_f = E(C_N+Ni)-E(Ni) - N*\epsilon_G$. Where, N is the number of carbon atoms and $\epsilon_G$ is the energy per carbon atom in the graphene.

Fig. S5 The illustration of the structural characteristics, $d_T$ and $d_E$, of the optimized C$_{20}$, C$_{21}$ and C$_{24}$ clusters on the Ni slab. $d_T/d_E$ is the distances from the highest atom/edge atom to the first metal layer of the Ni(111) substrate.
**Table S7** Comparison of \( d_T \), \( d_E \) and \((d_T-d_E)\) of Cap24.

| Force fields     | \( d_T \) | \( d_E \) | \((d_T-d_E)\)* |
|------------------|------------|------------|-----------------|
| DFT              | 2.5        | 1.64       | 1.52439         |
| ReaxFF           | 2.40       | 1.78       | 1.348315        |
| Texas A&M        | 2.17       | 1.64       | 1.323171        |
| NewFF            | 2.41       | 1.47       | 1.639456        |

* \((d_T-d_E)\) is defined to compare the bending degree of the Cap24.

**Fig. S6** Optimized configurations of \( C_{24} \) on Ni(111) slab by different force fields.
**Table S8** Comparison of $d_T$ and $d_E$ of Cap20.

| Force fields         | $d_T$ | $d_E$ |
|----------------------|-------|-------|
| DFT                  | 2.77  | 1.55  |
| ReaxFF               | 2.53  | 1.46  |
| Texas A&M            | 2.41  | 1.57  |
| New PES              | 2.73  | 1.40  |

**Fig. S7** The optimized configurations of $C_{20}$ on Ni(111) surface by different force fields.
Table S9 Comparison of $d_T$ and $d_E$ of Cap21.

| Force fields  | $d_T$ | $d_E$ |
|---------------|-------|-------|
| DFT           | 2.93  | 1.55  |
| ReaxFF        | 2.68  | 1.34  |
| Texas A&M     | 2.66  | 1.36  |
| New PES       | 2.88  | 1.34  |

**Fig. S8** Optimized configurations of C$_{21}$ on Ni(111) surface by different force fields.
Details of density functional theory (DFT) calculation

Most of the DFT data sets used for the fitting are obtained from the previous works\textsuperscript{8, 9} and their relative supporting information. DFT calculations are performed with the Vienna Ab-initio Simulation Package (VASP)\textsuperscript{10, 11}. The generalized gradient approximation (GGA) is adopted for the exchange correlation by using Perdew-Burke-Ernzerhof (PBE) functional, with the spin polarization taken into account.\textsuperscript{12} The plan wave cutoff energy is set to be 400 eV and the projector-augmented wave (PAW) is used as the pseudopotential.\textsuperscript{13} The convergence criterion for energy and force is set to be $10^{-4}$ eV and 0.02 eV/Å, respectively.

Defect healing during the pure MD

**Fig. S9** (a-c) The defect of pentagon is healed to be hexagon via bond breakage and reconnection of the dangling carbon atom attached to the pentagon. (d-f) The defect of pentagon is healed to be hexagon via direct insertion of the diffused carbon atom. The catalyst is removed for sake of clear display.
Fig. S10 (a-c) The defect of heptagon is healed by reconstruction and connection of the attached carbon atom and chains.

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