Electron-assisted growth of secondary carbon nanotunbes from endohedrally-confined Ni clusters — An atomistic multiscale approach

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Abstract

Although it is believed that the future provision of sustainable materials may depend upon the catalysis of chemical reactions by nanosized clusters of transition metals, their atomistic behaviour is still largely unknown. In the context of electron-assisted growth of endohedral carbon structures such as endohedral metallofullerenes, the present work aims at presenting a theoretical multiscale approach to simulate electron-induced metal–nanotube interactions, specifically highlighting the results obtained for an endohedrally-confined nickel nanoparticle (here 55 atoms) in a single-walled carbon nanotube. After modelling the electron irradiation for these systems, we developed a system-specific in-house code, which allowed us to overcome the computational time issues arising from the long timescales simulating such experiments would require, *i.e.* in the order of tenths to hundreds of seconds. This approach was then used to study a system where a Ni cluster is embedded in a single-walled nanotube. Our results show that the nickel cluster lowers the barrier for the displacement of carbon atoms, allowing for their displacement upon their interaction with the colliding electrons. In particular, the carbon atoms displaced get dissolved in the nickel cluster, allowing, once a certain carbon concentration is reached, for the nucleation of a sp^2 -hybridized structure on the surface of the endohedrally confined particle, followed by the growth of a new carbon nanotube inside the system.

1 Introduction

Carbon nanostructures exist in a multitude of shapes, and many of them such as fullerenes [1], carbon nanotubes (CNT) [2], or functionalized graphene flakes [3], hold promises in technological applications. However, currently, the most valuable synthetic approaches to produce such precious materials, involve harsh environmental conditions, e.g. chemical vapour deposition (CVD) [4], arc discharge reactor or laser evaporation [5]. Recent developments in aberration-corrected high-resolution transmission electron spectroscopy (AC-HRTEM) enabled reaching even atomic resolution, allowing for the development of a new imaging technique named *ChemTEM* [6], where the electron irradiation is applied both as tunable source of energy and as sub-Angström imaging probe. This technique holds promises also as an alternative synthesis method for carbon nanostructures. Indeed, Sinitsa et al. [7] proposed a method in which endohedral metallofullerene (EMF) formation was initiated by electron irradiation during a AC-HRTEM study of a metal cluster surrounded by amorphous carbon inside a carbon nanotube serving as a nano-reactor. The use of AC-HRTEM makes it possible not only to synthesize new, previously unattainable nano-objects, but also to study in situ the mechanisms of structural transformations [7]. Indeed, arc discharge reactor or laser evaporation [5] both require high temperatures, which lead to a loss of metal atoms by vaporisation or sintering [7]. This does not occur during a *ChemTEM* experiment, because the energy required to overcome the barriers is given to a single atom, meanwhile the rest of the structure is kept at room temperature (despite an obvious heat dissipation) [6]. Moreover, by varying the acceleration voltage different chemical processes can be triggered [8], whilst tuning the electron dose rate might control the rate of reactions [9]. For all these reasons, the *ChemTEM* methodology is well-suited for a targeted and controlled modification of nanostructures.

Using a CNT as a nano-reactor has been made possible only since recent years, thanks to the development of techniques to confine foreign species within the CNT's channels [10]. However, carbon nanostructures are quite sensitive to electron irradiation in the typical TEM's operating voltage regimes [11] and therefore the confined carbon nanotube might inevitably undergo structural changes during irradiation, possibly interacting also with the confined species. Thus, it cannot be considered solely as an inert nano-reactor. This was experimentally confirmed by Cao et al. [12], where irradiating nanometer-sized metal clusters being endoherallyconfined in SWNTs with a 80 keV beam showed an interaction of the metal cluster with the nanotube [12], [13], [7]. This induced a sputtering of carbon atoms and a rearrangement of the confining nanotube shell. Particularly interesting are the cases of Ni, Re, Os, W and Co clusters, where it was observed [12] that under *ChemTEM* conditions these metals might catalyze the formation of a secondary carbon structure or even a carbon nanotube, growing from the surface of the entrapped cluster inside the external NT section (e.q. see Fig. 1).



Figure 1: Time-series of AC-HRTEM images illustrating a Ni nanocluster, abstracting carbon atoms from a point of contact with the host NT and promoting/catalyzing the formation of a new carbon structure. Image taken from [12].

Up to our knowledge, no atomistic description of such process is available in literature yet. The lack of this knowledge, also caused by the technological limitations of stop-frame filming by means of AC-HRTEM, which is still unable to reveal mechanisms at this level of detail, hinders the possibility of manipulating these processes. Obtaining a detailed understanding of electron-induced metalcatalyzed carbon restructuring could provide further insights into the atomistic mechanisms of nucleation of sp^2 hybridized carbons at the metal surface. As these sites are considered to be the starting points for the growth of carbon nanostructures, important implications in the structure–properties relationships of such materials can be deduced. [14],[15].

This present work focuses in the development of a multiscale theoretical approach to simulate electronassisted metal-nanotube interactions: targeting in particular on the simulation of the initial processes of CNT growth onto an endohedrally-confined nickel nano-cluster (Ni@SWNT). Among the transition metals showing this interesting effect, nickel has been chosen because of its importance in catalysizing the growth of carbon nanostructures, such as carbon nanotubes [16]. In order to assess the behaviour of such systems, the present work is divided as follows: the next section illustrates the general computational details. The third section is devoted to the theoretical modelling of a *ChemTEM* experiment and to the practical implementation of our multiscale approach. The fourth section illustrates the geometry of the test system used for all our calculations that are presented and discussed in the fifth section.

2 Computational details

All molecular dynamics simulations were performed within the Amsterdam Modeling Suite 2018 (2018.106) [21], where we used the reactive forcefield (ReaxFF) [17][18] for Ni/C/H developed by Mueller *et al.* [19]. This forcefield was chosen as it had already been used for the successful simulation of the growth of defect-free carbon nanotubes [20]. All reactive molecular dynamics (MD) simulations were performed with iteration steps of 0.25 fs, while the temperature was controlled through the Nosé–Hoover chain thermostat with a damping constant of 100 fs. The simulation box was a cube with a side length of 300 Å. All force-biased Monte Carlo (fbMC) simulations were performed with a maximum atomic displacement of $\Delta = 0.12$ Åand a temperature of 1200 K. More details about the hybrid MD-fbMC procedure can be found in section 3.0.3 and the Supplementary Information. Imaging of the results was performed with the "Ovito" software version Version 2.9.0 [22]. Codes to handle SCM data were written in *Python* [23]. To analyze the results and to plot graphs Matlab (R2017b) was used [24].

3 Modelling a chemTEM experiment

The work of Cao *et al.* [12] has shown that the growth of carbon structures during the e^{-} -irradiation of a specimen happens over a time span of many seconds (see Fig. 1). The reason lies in the frequency of displacement events that are induced by an electron collision. Indeed, considering, for instance, that the calculated area of a primitive cell of graphene (containing 2 atoms) is 0.051 nm^2 [25], then with the reported [12] strength of the e^{-} -beam of $\sim 1.1 \times 10^6 \ e^{-} \mathrm{nm}^{-2} \mathrm{s}^{-1}$, only ca. 28 electrons are impinging every millisecond, *i.e.* 1 electron every $35 \,\mu s$. However, not all the collisions lead to the displacement of an atom, in particular only those events for which the energy transferred to the target atom is sufficiently high. Indeed, considering that the threshold energy of the electron beam for the generation of defects in a perfect SWNT is ~ 86 keV [12], and that in the experiments of Kecheng *Cao et al.* [12] the beam's energy was 80 keV, even assuming that the nickel lowers the displacement energy threshold, just a small fraction of electrons colliding will generate a remarkable effect. Therefore, electron irradiation of a Ni@SWNT specimen, can be envisioned as a sequence of fast events, the dynamics of the system right after a collision, and very slow events of relaxation, taking part in the time window between two electron induced displacements. Indeed, during the collision the bonds are rearranged very fast, atoms are displaced and the system thermalizes fast to a local minimum in the potential energy surface. After this, then there is a long time in which no irradiation induced-modification happens, and the system is allowed to thermalize to more stable minima by means of competing effects. Thus, the atomistic simulation of the evolution of a system under these conditions, naturally needs to endow different timescales. Following this idea Skowron S. T., Lebedeva I. V., Popov A. M. and Bichoutskaia E. developed an algorithm named CompuTEM [27], [28], [26] which proved the possibility of realistically model chemical reactions induced by an electron beam. Thanks to the accurate modelling of the electron-sample interaction, several mechanisms have been already elucidated: the work of Alexander S. Sinitsa et al. [7] described theoretically the formation of the endohedral nickel metallo-fullerenes and Irina V. Lebedeva et al. [29] explained the process of electron-assisted nanotube cutting, catalyzed by a nickel cluster adsorbed on the outer shell of the NT. Nevertheless, up to now, no atomistic explanation can be found for the most intriguing process an endohedral nickel cluster shows: the catalyzed growth of an endohedral secondary nanotube. This might be caused by the fact that CompuTEM approach, simulates the relaxation of the system between two different electronic collisions, that lead to a modification in the geometry, by employing high temperature NVT molecular dynamics. It was proven in past works, that such approach wouldn't be sufficient to explain the processes of growth of a defect-free carbon nanotube, being unable to fully consider relaxation effects and leading to highly defected structures [20]. There has been a great effort in explaining the atomistic processes of carbon nanotubes growth and the most promising results have been obtained by employing methods which allow to fast overcome the barriers for the carbon-carbon bond rotation at the nanotube-catalyst interface, like in the case of force biased Monte Carlo (fbMC) [20] or the basin-hoppin procedure [30]. Therefore, even if the CompuTEM approach works in simulating the exchange of energy between the beam and the system, it is most likely unable to properly describe the long timescale relaxations at the catalystnanotube interface, between two collisional events. This work therefore aims to fill this gap. In order to simulate the electronic collisions, a similar approach to the one used by Skowron S. T., Lebedeva I. V., Popov A. M. and Bichoutskaia E.[28] is employed and accurately described in the next section, whereas in order to get the complete picture regarding the slow process of formation of defect free sp^2 hybridized C islands, we employed an hybrid MDfbMC approach, for which details can be found in Sec. 3.0.3. The final simulation tool we developed follows the algorithm depicted in Fig. 3 and described in Sec. 3.1.

3.0.1 Theory and simulation of the electronic collisions

It is reported [11] that under high accelerating voltage electron irradiation, the main source of induced modification of carbon nanostructures is the displacement of carbon atoms due to electron collisions, a process called knock-on. This is related to the elastic Coulomb scattering of the colliding relativistic electron with a nucleus, for which the theoretical differential cross section has been derived by Mott [31],[32] as a solution of the Dirac equation. The angular dependence on the scattering angle Ω of the energy T transferred to the nucleus is given by [33]:

$$T(\Omega) = T_{max} \cos^2(\Omega) \tag{3.1}$$

Where Ω is the emission angle i.e. the angle between the initial direction of the colliding electron and the direction of displacement of the displaced atom (Fig. 2) and T_{max} is the maximum transferred energy by an head-on collision, i.e. $\Omega = 0$ and the electron is scattered backwards. Momentum conservation gives T_{max} according to [33]:

$$T_{max} = \frac{2ME(E+2mc^2)}{(M+m)^2c^2 + 2ME}$$
(3.2)

We will call threshold energy E_d , the minimum energy which is transferred to an atom in order to generate a vacancy-interstitial pair that doesn't spontaneously recombine. McKinley and Feshbach found an approximate formula [34] for the Mott's differential scattering cross section, accurate up to middle Z elements, which rewritten as function of the transferred energy T, defined before, it reads [33]:

$$\sigma(T) = \left(\frac{Ze^2}{4\pi\epsilon_0 2m_0c^2} \frac{T_{max}}{T}\right)^2 \frac{1-\beta^2}{\beta^4} \\ \left[1-\beta^2 \frac{T}{T_{max}} + \pi \frac{Ze^2}{\hbar c} \beta \left(\sqrt{\frac{T}{T_{max}}} - \frac{T}{T_{max}}\right)\right] \quad (3.3)$$

Where $\beta = v/c$, Z is the atomic number of the nucleus and m_0 is the electron rest mass. In Fig. 2 b), adapted from [33], the scattering geometry during the irradiation process is represented. The target atom sits in the center of the referential, \vec{e} is the incidence direction of the electron, α is the angle between \vec{e} and the normal to the XY plane, \vec{v} is the direction of emission of the atom, and γ and δ are the polar and azimuth angles respectively (in polar coordinates on XY). Electron irradiation of nanotubes by means of TEM experiments is usually performed in nontilted case, where the tube axis lies perpendicular to the direction of the electron beam [33]. Thus if the nanotube axis lies on the XY plane, then $\alpha = 0$ (Fig.2 b)), so that $\Omega = \gamma$ and the knock-on model will depend only upon the two characteristic γ and δ , emission and azimuth angles respectively. In our approach we make use of this geometry and more details can be found in Supplementary Information. Making use of ReaxFF, we have no description of electrons. Therefore, in our approach, the collision is simulated by exploiting the transfer of energy between a fictitious electron and a target nucleus. This is done by adding kinetic energy to the nucleus according to the following steps:

- 1. Target atom selection;
- 2. Generation of the characteristic angles (γ, δ) ;
- 3. Generation of the excess (x,y,z) velocities for the target atom.

First of all, a list of all the carbon atoms that are within a sphere of 11 Å from the center of mass of the nickel cluster is created. Indeed, although the beam's energy is not sufficient to displace atoms in the perfect lattice of the NT, we expect the cluster to lower the barriers for reactions, therefore allowing just in its neighborhood such displacement events. Moreover, the higher mass of the nickel atoms causes a decrease in the maximum transferrable energy T_{max} from the 80 keV beam, which is 15.8 eV for C and 3.23 eV for Ni. Being this energy very low for the nickel, we assumed that only collisions with carbon might lead to a permanent modification in the structure. Thus, after this, a random carbon atom is chosen from this list as target atom for the collision. At this point, random angles γ^* and δ^* are chosen uniformly within $0 \leq \gamma^* \leq \gamma_{max}$ and $0 \leq \delta^* \leq 360$. Here γ_{max} is the maximum angle for which the emission condition is met, i.e. $T(\gamma_{max}) = E_d$, with E_d the emission energy threshold. However the threshold energy is a quantity which is not well defined for our system due to the multitude of different configurations for the atoms. For this reason, we assumed for simplicity that the minimum energy that we wanted to consider was 10 eV lower than the $T_{max} = 15.8 \text{ eV}$ of the experiment. In such a way according to equation 3.1, $\gamma_{max} \sim 45^{\circ}$ and we assumed this to be a reasonable first approximation of the true maximum emission angle i.e. the maximum angle for which a knock-on is observed.

In order to add kinetic energy in a physical manner, a random probability p is then sampled from a uniform distribution and the emission angle γ^* is accepted if and only if:

$$p \le \frac{\sigma(T(\gamma^*))}{\sigma(T(\gamma_{max}))} \tag{3.4}$$

Angle δ^* has always unitary acceptance. If the condition of eq. 3.4 is not met, a new pair of $(\gamma^{**}, \delta^{**})$ is generated and the acceptance for the emission angle is tested again. This is repeated until the criterion is met. Condition 3.4 ensures a choice of angles that better mimic the process of Coulomb scattering for which larger emission angles have an higher differential cross section $\sigma(T)$. Once the angles (γ, δ) are determined, they are used to generate the excess velocities in a set of three orthonormal axes, for which vector \tilde{Z} is parallel to the direction of the $e^$ beam, thus being orthogonal to the tube axis. These excess velocities are generated simply by projection:

$$\begin{cases} V_{\tilde{Z}} = V_{max} cos(\gamma) \\ V_{\tilde{X}} = V_{max} sin(\gamma) cos(\delta) \\ V_{\tilde{Y}} = V_{max} sin(\gamma) sin(\delta) \end{cases}$$
(3.5)

Where from momentum transfer $V_{max} = \sqrt{\frac{2T(\gamma)}{M}}$. These velocities are added to the list of initial velocities of the target atom. Therefore, the system's dynamics after the collision can be simulated by means of a Molecular Dynamics (MD) routine, making use of this modified list of velocities. Although with some differences, this implementation followed the ideas promoted by the work of Skowron S. T., Lebedeva I. V., Popov A. M. and Bichoutskaia E.[28].



Figure 2: Schematic 2D **a**) and 3D **b**) representations of the angles involved in the process of direct knock-on. The electron incidence direction is \vec{e} whereas \vec{v} is the atom emission direction. Image **b**) adapted from [33].

3.0.2 Determination of the equivalent maximum transferred energy T_{max}

If the kinetic energy of the colliding electron is known, equation 3.2 gives the maximum transferred energy for a head-on collision. In the case of an 80 keV beam, $T_{max} = 15.8 \text{ eV} [12]$ which is $\approx 6 \text{ eV}$ lower than the estimated [35] displacement threshold energy $E_d \approx 22 \text{ eV}$ for an (11,11) carbon nanotube. As stated above, E_d is related to the minimum amount of energy required to displace an atom, thus it depends upon the strength of the interactions. In theoretical calculations this will depend upon the way interactions are parameterized, i.e. in our case upon the force field. For this reason, employing a T_{max} of 15.8 eV, might not be the best choice to represent the 80 keV beam's effects with our ReaxFF representation. In order to apply our method to simulate real experiments, we therefore need to estimate the equivalent T_{max}^{Reax} for our force field. In order to obtain this quantity, we first calculated the displacement energy threshold E_d^{Reax} for our force field, and then secondly we subtracted 5 eV from its value, obtaining an approximation of T_{max}^{Reax} for an 80 keV beam. To find E_d^{Reax} , calculations at different transferred energies have been carried out. The system we studied was an (11,11) capped carbon nanotube made up by 1800 C atoms and placed in the middle of a 300 Å squared simulation box. The nanotube was built with the "Atomic Simulation Environment" [36],[37] (version 3.17.0) using the package "NanoCap" [38] (version 1.0b15). Once the system has been built, a 300 K molecular dynamic simulation has been carried out in order to equilibrate the system over 250 ps. The excess velocities were then added to a single atom, keeping the emission angle null i.e. $\gamma = 0$, i.e. orthogonal to the surface of the nanotube. Calculations led to estimate the equivalent emission energy threshold $E_d^{Reax} \approx 26$ eV which is higher of the reported values of $\approx 22 \text{ eV} [35], \approx 17 \text{ eV} [12]$ and $\approx 20.5 \text{ eV} [33]$. From E_d^{Reax} we assumed T_{max}^{Reax} to be 21 eV. This value will be used in all calculations as the maximum kinetic energy, which can be transferred to a target C atom, when the electron is scattered backwards, i.e. when the emission angle $\gamma = 0$.

3.0.3 Hybrid MD-fbMC details

The time window between two electron-induced displacement events might be large enough for the system to thermalize to more stable minima. Thus, in order to ensure the proper relaxation of the carbon structure between two collisions, we decided not to use an high temperature MD, but rather we employed an hybrid MD-force biased Monte Carlo algorithm. The choice of this algorithm comes from the encouraging results which were obtained to simulate the growth of carbon nanotubes e.g. [?],[39], [40]. The heart of this algorithm relies in an iterative displacement of each atom along a random direction, and the acceptance of this new position is tested against the forces acting on the particle during that specific displacement [41]. Thus the evolution of the system's dynamics is based on a simple probabilistic description. The system simulated by fbMC is mainly located in an equilibrium state which once in a how is left to evolve toward another equilibrium configuration [42]. Thus many iterations are able to bring the system around a local minimum of the PES. However, fbMC doesn't allow us to have a proper description of time [40] and therefore the dynamics of the system has to be viewed as a pseudo-dynamics i.e. each Monte Carlo (MC) step has not to be considered as a true MD step. The trajectories of the particles moving along the PES are nonetheless of physical relevance if the displacement Δ is small enough [40],[42] and the principle of detailed balance is satisfied. Promising results [20], [39] regarding the growth of a defect free CNT form a Ni catalysts have been obtained using an hybrid MD-fbMC approach. For these reasons, we decided to use this approach with the following setup:

- 1. MC displacement $\Delta = 0.12$ Å;
- 2. MC temperature T = 1200 K;
- 3. Three subroutines of 150000 MC steps separated by 6.25 ps of NVT MD at 1200 K (3×150000 MC);
- 4. Two equilibrating MD routines of 6.25 ps at 1200 K, one before the application of the 3×150000 MC and one after.

A detailed justification for these parameters can be found in Supplementary Information.

3.1 Simulation algorithm

As stated above, electron irradiation of a specimen can be envisioned as a sequence of fast events, the dynamics of the system right after a collision, and very slow events of relaxation, taking part in the time window between

two electron induced displacements. Thus, the simulation of the evolution of a system under these conditions, naturally needs to endow different timescales. In order to achieve this, our algorithm follows the scheme graphically depicted in figure 3. First the system is equilibrated with an MD simulation over 6.25 ps. Then the energy is transferred to the target nucleus according to the algorithm described in section 3.0.1. After this another MD simulation of 500 fs is performed to simulate the fast dynamics of bond rearrangement after the collison. This amount of simulated time was chosen since the excess kinetic energy was already well redistributed (See supplementary information) and the atom could experience a well defined local minimum in the PES. At the end of this, if a substantial topological modification is detected (see Sec. 3.1.1), another equilibrating MD simulation is performed over 10 ps. Eventually the hybrid fbMC-MD routine is started with the setup presented in the previous section. After this, the simulation is restarted from the first MD simulation, using as input the final atoms' positions and velocities coming from the fbMC block. Each iteration of this algorithm should, therefore, hypothetically simulate one event of collision and the subsequent time window before the next one. The algorithm has been implemented on Python [23].

3.1.1 Identification of the topological changes: event detection algorithm EDA

The method developed in Sec. 3.0.1 to simulate the electron-carbon collisions, considers just the Coulomb scattering differential cross section $\sigma(T)$, disregarding the probability that this event would effectively lead to a knock-on defect. Moreover, the acceptance criterion for the emission angle γ (equation 3.4) will select more likely larger angles, thus lower transferred energies according to eq. 3.1. Therefore, once the target atom and the set of angles (γ, δ) are selected, we are still not ensured that this will lead to the generation of a knock-on defect. Blindly passing this result to the MD-fbMC routine might cost a lot of time without giving us any information. To overcome this problem we implemented a classification procedure based on the definition of *effective* collisions, i.e. those collisions which lead the system from initial state Ato final state B with $A \neq B$ after the application of the force biased algorithm. Once an *effective* collision is detected, the simulation can proceed to the MD-fbMC part, otherwise a new collisional event is simulated. Due to the always changing geometry of the specimen under irradiation and the very complex nature of it (i.e. a mixed system of a large amount of carbon and nickel atoms) it is extremely difficult to define a unique environment for each carbon atom. Thus, it is difficult to determine general conditions for which an atom endures an *effective* collision. Forced by this reason, we decided to introduce a simplification: each event of collision will be classified according to the *effective* collisions occurring in the pristine state of the system, i.e. when the nanotube has no defects yet.



Figure 3: Complete scheme of the algorithm to simulate irradiation induced effects for endohedral metal particles.



Figure 4: Snapshots of the three most probable collisioninduced events: Image **a**) shows the ejection of a carbon atom and image **b**) shows the zoom on the area where the atom has been ejected. Image **c**) shows the dissolution of a carbon in the cluster. Image **d**) shows the pre-dissolution of a carbon.

The pristine reference system (described accurately in Sec. 4) is an (11,11) CNT, endowed with a vacancy defect for a total of 1799 carbon atoms, and a nickel cluster endohedrally confined of 55 atoms. An accurate study (see supplementary information) allowed us to identify four *effective* collisions mechanisms:

- 1. *Ejection* event Fig.4 a), i.e. the target atom is ejected from the side of the nanotube. After the application of the fbMC algorithm the single vacancy defect is stabilized by a nickel atom Fig.4 b);
- 2. Dissolution event Fig.4 c), i.e. the target atom is detached from the nanotube and is dissolved in the nickel cluster. The carbon is never adsorbed onto the surface of the cluster but rather it is dissolved in the volume of the cluster mostly occupying subsurface sites, where it can maximize the interaction with nickel atoms. This behaviour is consistent with previous results [43], [44]. During the application of the fbMC algorithm, the carbon atom simply diffuses inside the nickel cluster, moving from one site to a neighbouring one. The single vacancy defect in the nanotube wall is stabilized by a nickel atom;
- 3. *Pre-dissolution* event see figure 4 d) i.e. the target atom is displaced inside the nanotube section, placed below the plane identified by the former neighbouring C atoms, being still connected only to one of them. The vacancy defect in the side of the nanotube is stabilized by a nickel atom, which

moreover hinders the displaced C atom from regaining its previous position in the lattice. This event might evolve either towards the dissolution of this atom inside the cluster or in the restoration of the initial unperturbed state;

4. Two atoms pre-dissolution event, which was observed just once and no image is reported. This process is similar to the pre-dissolution, but in this case two neighbouring atoms are displaced towards the inside of the tube. They remain connected between each other and one of the two is still connected to one of its carbon neighbours.

Among these four, the two atoms pre-dissolution was not considered due to its very low probability of happening. Each of the three other processes could be identified by means of geometrical and atom's connectivity information (see Supplementary Information). Thus, every time a collision needs to be simulated, our algorithm does the following: first a target atoms is selected, then the collisioninduced excess kinetic energy is given to the target nucleus following the algorithm in Sec. 3.0.1. After this a 500 fs MD is performed and at the end of it, our event detection algorithm (EDA) is launched. If EDA detects that the system experienced one of the three *effective* collisions defined above, the simulation continues with a 10 ps MD and then with the MD-fbMC; otherwise the procedure is restarted, selecting a new target atom, generating the excess velocities and so on. Concluding this section, it is better to remark that the EDA we implemented, is purely artificial and has no physical parallelism: the true dynamics of the system could be simulated by considering every single event of collision, even if that would not lead to any modification of the system. The criteria to classify an *effective* collision, have to be chosen with extreme care, since they could bias the dynamics of the system leading to a complete artificial behaviour. The three processes we decided to use to distinguish an *effec*tive collision, would represent the most probable knock-on mechanisms strictly for an unperturbed system, thus we expect that our model will work mainly in describing the initial stages for the evolution of the system. Nevertheless, this procedure is needed in order to have the chance to simulate even these first stages in a reasonable amount of computational time.

4 Test system details

The method developed so far has been used to simulate the dynamics of a nickel cluster endohedrally confined in a SWNT. The reference system we used for all the simulated *ChemTEM* calculations is the following: an (11,11)capped CNT, endowed with a vacancy defect for a total of 1799 carbon atoms, and a nickel cluster endohedrally confined of 55 atoms, placed in contact with the nanotube walls in the proximity of the vacancy defect. The nanotube was built with the "Atomic Simulation Environment" [36],[37] (version 3.17.0) using the package "NanoCap" [38] (version 1.0b15). The vacancy is induced in the side of the nanotube in order to let the cluster adsorb on such defect. This is consistent with most experimentally observed processes in which the nickel clusters are often observed to be already adsorbed on pre-existing defects in the nanotube sidewall (vacancy type defects are very common in SWNTs as defect-free nanotubes are virtually non-existent) [29]. Each calculation on this system was performed in a cubic box with the side of 300 Å. Once the system has been built, a 300 K molecular dynamic simulation has been carried out in order to equilibrate the system over 250 ps. This relaxed geometry was then used as input for all the calculations during simulated *ChemTEM* experiments.



Figure 5: Reference system we used for all the simulated *ChemTEM* calculations. In blue the direction of the electron beam is showed. In the red circle the initial vacancy defect is highlighted.

5 Results

Due to the intrinsic bidimensional nature of TEM images, the position of the cluster within the nanotube is not fully recoverable. Nevertheless, the experimental results, highly depend on the relative position of the NT wall in contact with the cluster and the directionality of the electron beam. Indeed, while electrons providing kinetic energy inwards with respect to the tube, promote events of dissolution, electrons colliding in the opposite direction would promote sputtering of the carbon atoms from the surface, thus leading to a different evolution of the system [45] (see Supplementary Information). In this work, we focus our attention to the processes triggered when the electron beam's direction is such that it would promote displacement of the carbon atoms towards the nickel cluster, i.e. along the blue arrow visible in Fig. 5. Several simulations have been performed following our algorithm (Fig. 3) using as initial state the system in Fig. 5. The temperature in the MD simulations was set to 1200 K by means of a Nosé-Hoover thermostat with a damping constant of 100 fs and an MD step of 0.25 fs. Such high temperature has been chosen because, electron collisions where simulated only for C atoms (see Sec. 3.0.1), thus the irradiation-induced heating of the Ni cluster was not taken into account. However in the supplementary information of the work of *Kecheng Cao et al.* [12], it is reported that temperatures in the range of 870 - 1370 K are needed for activating transition metal catalysts for the transformation and growth of carbon structures. Therefore a parallelism can be drawn between the processes triggered and promoted by the 80 keV e^{-} beam in nanotubes and analogous processes initiated thermally at 870 - 1370 K in bulk, even though technically the temperature of the materials in the AC-HRTEM experiments were essentially ambient, e.g. 290 - 300 K [12]. In order to properly take into account the effect of the electron collisions onto the metal cluster, we raised the MD temperature of the simulations up to 1200 K. Due to computational limitations, we could analyze just the first stages of the interaction between the nanotube and the nickel cluster *i.e.* $\sim 50 - 70$ iterations.

In particular we analyzed:

- 1. The total number of carbon atoms dissolved in the Ni cluster, making a distinction between carbon *monomers* and *dimers*;
- 2. The number of carbon atoms with more than one carbon nearest neighbour, in the following discussion called *structured* carbons;
- 3. The *total charge evolution* of the nickel cluster and of the carbon monomers and dimers;
- 4. The *average charge evolution* of the nickel cluster and of the carbon monomers and dimers.

A close examination of the evolution of all these quantities and of the geometry of the system, allowed us to recognize three distinct stages in the initial interaction between the nickel and the carbon nanotube under irradiation, namely:

- 1. Formation of a carbide (*Alloying stage*);
- 2. Aggregation of monomers into carbon dimers (*High Supersaturation stage*);
- 3. Dimers aggregate into pentagons or hexagons forming graphitic island (*Supersaturation stage*).

In the following, we will analyze each stage separately.

5.1 First stage: Carbon monomers formation and rearrangement

The initial behaviour of the system is similar among all simulations. In these first $\sim 15 - 20$ iterations the collisions allow the atoms which are in contact with the nickel,

to dissolve inside the cluster. This is clearly visible analyzing the evolution of the carbon monomers and of the structured carbon percentage in time, examples of these quantities are reported in Fig. 6 and Fig. 7 respectively. Indeed, the growth of the number of carbon monomers tracks the decrease in the percentage of structured carbons in the system, pointing out that these carbons come from the shell of the nanotube. Moreover, these C atoms are never adsorbed onto the surface of the cluster, being rather dissolved in the volume of the metal particle, mostly occupying subsurface sites where they maximize the interaction with nickel atoms. This behaviour is consistent with previous results [43], [44]. Therefore, due to the higher electronegativity of the carbons with respect to the nickel, the monomers will be partially negatively charged wheres the nickel atoms will have on average a positive charge, see Fig. 8. Increasing the number of monomers, leads to an increase in the total charge of the nickel cluster. This is in agreement with previous results [44]. Moreover, the average charge of the monomers Fig. 8 stays almost constant throughout this period, pointing out that even increasing the number of dissolved atoms, their environment doesn't vary much. These two observations suggest that the dissolved monomers, partially negatively charged, repel each other, occupying all the available sub-surface sites within the cluster. These intuitions are confirmed by the analysis of the geometry of the system within this time window Fig. 9, where both the formation of defects in the side of the nanotube, and the dissolution of carbon monomers, are visible. Moreover, the defects in the side of the tube are occupied by nickel atoms that stabilize them and often pop out from the nanotube wall, resembling the behaviour of nickel atoms adsorbed onto graphene vacancies defects [46], [51]. Although the system is utterly different from the free standing nickel particle, usually considered to study the growth of carbon nanotubes [16], [30], [20], [39], this initial behaviour is analogous for the two systems, resembling the so called *alloying stage* [39] believed to be the first step for the nucleation of a nanotube [43], [44].



Figure 6: Example of the evolution during the first 18 iterations of the C monomers and dimers content in the Ni cluster as function of time.



Figure 7: Example of the evolution during the first 18 iterations of the percentage of structured and the total number of dissolved C atoms.



Figure 8: Example of the evolution during the first 20 iterations of the average charges



Figure 9: Snapshots of an example system geometry during the *Alloying stage*. Carbon monomers dissolved in the nickel cluster are visible. Some nickel atoms pop out from the defects in the NT wall, this is supported by experimental data [26].

5.2 Aggregation of monomers into dimers

When the content of carbon monomers in the cluster reaches 20% - 25%, some monomers tend to aggregate into dimers. The first appearance of stable dimers is after ca. 20 iterations. Often, dimers might appear for fewer iterations. Nevertheless, their life is very short i.e. they quickly disappear during the fbMC routine in favour of monomers. The nucleation of stable carbon dimers, is characterized by a sudden drop of the content of monomers (e.g. Fig. 10 around iteration 25) with very little changes in the percentage of *structured* carbons in the system (e.g. Fig. 11 around iteration 25). Thus, the formation of this species is mostly due to the aggregation of monomers in the carbide. Also this stage finds its analogous for a free standing nickel particle, in the so called *supersaturation stage* [48], [49]. Moreover, the analysis of the average charge of a dimer Fig. 12 shows, first of all, that a dimer carries less negative charge than a monomer and secondly that this is more variable compared to the same quantity for the monomers. This suggests that the environment for the dimers might change significantly during the simulations. Indeed, dimers segregate mainly (but not just) at the surface of nickel Fig. 13 a) on which they can migrate from site to site. Nevertheless, due to the small size of the cluster (Gibbs Thomson effect [50]) and the strong interaction with the carbon shell, the nickel atoms are highly mobile. Moreover, in agreement with previous results for a free standing nickel cluster, C dimers were observed both in subsuperficial and in superficial states [39]. For all these reasons, the environment for each dimer might change substantially during its motion, leading to a more variable mean charge with respect to the subsurface dissolved monomers. It is also interesting to note that, at this point, a substantial amount of carbon atoms has been withdrawn from the outer carbon nanotube ca. 20 - 25 atoms. The nickel particle tends to bind very strongly to this defected area, protruding outside the nanotube wall and resulting in a partial escape of the cluster from its initial endohedral confinement Fig. 13 b). A previous work of Gao et al. [51] proved the very high strength of NI-C σ -bonds, higher than Ni-Ni bonds or Ni-C π bonds and showed how nickel clusters would tend to grow symmetrically with respect to a large defect on a graphene sheet, suggesting that this would rationalize the experimental findings that Ni nanoparticles are very stable on the CNT supports [52]. Our results, showing the strong interaction between the nickel and the defected sp^2 C lattice, and highlighting the cluster's preference for symmetrical disposition with respect to large vacancy defects in the nanotube wall, are rationalized by the work Gao et al. [51]. For sake of completeness, carbon dimers were observed to segregate both in the outer protruding side of the cluster and in the endohedrally confined half Fig. 13 c).



Figure 11: Example of the evolution during the supersaturation stage of the total carbon atoms dissolved in the cluster and the percentage of *structured* carbon. The moment in which monomers condense into dimers (\sim Iteration 25) is related to a small decrease of the total carbon content and an increase of structured carbons. This might be due to the reattachment of some monomers to the nanotube lattice.



Figure 10: Example of the evolution during the supersaturation stage of Carbon monomers and dimers as function of time. Around Iteration 25 the segregation of dimers is visible.



Figure 12: Example of the evolution during the supersaturation stage of the average charge per species as function of time. The charge per dimer is visibly more changing than the charge per monomer.



Figure 13: Snapshots of different simulations around the 30^{th} iteration. In snapshot **a**) three dimers are visible (red arrows) of which two segregated on the surface whereas the third one is in a subsuperficial site.

In snapshot **b**) the partial escape of the nickel cluster from the endohedrally confined position is visible. The cluster is placed almost symmetrically with respect to the nanotube wall.

In snapshot **c**) highlighted by the red arrow is visible a dimer formed on the outer surface of the cluster. The partial protrusion of the nickel particle might cause the lift and modification of part of the host carbon nanotube shell (black arrow).

5.3 Growth of a graphitic island

After the formation of a large defect in the nanotube wall, some systems exhibited the formation of graphitic islands. Indeed, when the concentration of total dissolved carbon atoms in the nickel cluster reaches ca. 37%, then the carbon dimers start to form longer chains and rings. This is characterized by a simultaneous drop of the total amount of dissolved carbons and an increase in the percentage of structured carbons Fig.14. Analysis of the number of monomers and dimers dissolved in the cluster, shows how the carbon dimers content decreases, whereas the carbon monomers don't show such evident modification, see Fig. 15. Thus we can conclude that the formation of structured carbons comes mainly from the aggregation of dimers. Figures 16 a) and b) show the snapshots of the system's geometry at the beginning and end of such a transformation, these moments are marked on the graphs (Fig. 14 and Fig. 15) with two vertical lines. In this specific example, we observe the formation of a first graphitic island composed by a pentagon, a hexagon, and a heptagon Fig. 16 b). At this point, if the electron beam continues to dissolve carbons inside the cluster, the graphitic island expands evolving towards a carbon cap Fig. 17 a) and b). The speed of formation of the graphitic island depends on the number of dissolution events happened during the simulations. Indeed, if a large amount of collisions lead to ejection events, then the amount of carbons fed into

the system is less, and the formation of dimers or long chains is delayed. Although the structure of the system and the way of providing carbons is completely different, the stages that our system follows are extremely similar to those, which a free standing nickel particle, that catalyzes the growth of a nanotube from carbons in gas phase, undergoes [16], [20], [49], [39]. This shows once more the potentiality of the *ChemTEM* [6] approach for a controlled modification of the specimen. For sake of completeness: in case the cluster wouldn't maintain it's endohedral position after stage 2, we couldn't observe the formation of such graphitic islands. It cannot be excluded that such effect is an artifact caused by the EDA procedure. Indeed, with respect to the initial geometry, an highly protruding (HP) cluster is much more different than a particle which remains mostly confined (EH endohedral), even if the confining NT shell is highly defected. For this reason, it might be possible that the classification of the collisional events, is no more valid. It has nevertheless to be pointed out that, the EH situation might have intrinsically more advantages in the formation of a graphitic island with respect to the HP. Indeed, the endohedral position of the nickel atoms, keeps favouring the dissolution of carbon atoms from the outer shell. In the case of HP, on the contrary, we can have the sputtering of atoms in the nanotube section from the interface region between the nickel and the NT. Moreover, EH has a larger cluster area which is far away from the interface with the nanotube. This, in turn, might lead to the aggregation of dimers away from this boundary, avoiding the chance of reincorporating carbon atoms into the NT wall. However, in order to make more reliable predictions, a more general approach for the classification of the collisional events is surely needed.



Figure 14: Example of the evolution of the percentage of *structured* carbons and of the total number of dissolved carbon atoms, during the formation of a graphititc island. The two lines identify the points at which snapshots a) and b) of figure 16 formation are taken.



Figure 15: Example of the evolution of the carbon monomers and dimers number, during the formation of a graphitic island. The two lines identify the points at which snapshots a) and b) of figure 16 are taken.



Figure 16: Snapshots of the geometry of the system described by the graphs in Fig.15 and Fig. 14 at iteration 39 and 45 i.e. at the beginning and end of the graphitic island nucleation process. In snapshot **a**) the presence of a high number of surface segregated dimers is visible. In snapshot **b**) it is visible the formation of a graphitic island composed by a pentagon, a hexagon and a heptagon. The upper section of the nanotube has been cut in order to have a better view of the effects taking place at the surface of the endohedrally confined cluster.



Figure 17: Snapshots of the geometry of the system shown in figure 16 after 50 and 60 iterations **a**) and **b**) respectively. In snapshot **a**) a large graphitic island of three pentagons and two hexagons is visible. In snapshot **b**) the graphitic island has rearranged forming a carbon cap of three hexagons and two pentagons. The upper section of the nanotube has been cut in order to have a better view of the effects taking place at the surface of the endohedrally confined cluster.

6 Conclusions

The use of AC-HRTEM irradiation onto a nickel cluster, endohedrally confined in a SWNT (Ni@SWNT), was proven experimentally [12], to catalyze in a controlled manner the formation of a secondary carbon nanotube. In this work, we obtained an atomistic description of the initial processes occurring for such secondary carbon structures to grow. In order to do so, firstly, we modeled the electron irradiation as a sequence of direct electron-atom collisions and relaxation events. The collisions are treated by giving a certain kinetic energy to a target atom, according to the differential cross section for Coulomb scattering, and the subsequent fast dynamics of bonds rearrangement is obtained employing Molecular Dynamics. Thanks to such modelling of the energy transfer between an atom and a colliding electron, we were able to identify the fundamental knock-on mechanisms for a Ni@SWNT. The relaxation is treated employing an hybrid MD-force biased Monte Carlo method, in order to drive quickly the system towards stable minima in the PES. Jointing together these two parts, according to scheme 3, we developed a multiscale simulation tool. Applying our in-house code to study the dynamics of the system after many collisional events, we were able to identify three stages of the initial interaction between the nanotube and the cluster, namely: Alloying or Unsaturated stage, High supersaturation stage and Supersaturation stage. The results of our model are in agreement with experimental results [12], [7]. In particular, we are able to say that, the nickel cluster lowers the barrier for C atoms displacement. Thus, the colliding electrons kick carbon atoms into the nickel clus-

ter where they get dissolved, finding a stabilizing environment. The nickel cluster, moreover, stabilizes the defect in the NT wall by binding very strongly to it. Once a certain C monomers concentration is reached, they start aggregating into carbon dimers. Increasing even more the number of dissolved carbon atoms, allows the segregation of dimers into trimers and then into small graphitic islands. If the electron beam keeps dissolving carbon atoms, the graphitic islands expand. These results are synthetized in Fig. 20 and compared with those of a free standing Fe cluster (from the work of Ding and Bolton [54]) in Fig. 19. Despite the simplicity of our model, our results seem reasonable and show very good agreement both with experimental [12], [7] (see Fig. 18) and theoretical works [20], [49], [39], [51], [44] (see Fig. 19 and Fig. 20), making us confident regarding the validity of this approach for the first stages of interaction of the nickel with the nanotube, under electron irradiation. However, in order to asses the formation of extensive carbon structures such as nanotubes, a further modelling and a more general EDA needs to be developed. Moreover, we suppose that, if the directionality of the electron beam would have been inverted with respect to the reference used in our study (see Fig. 5), the nickel would promote mostly sputtering events, leading to the rupture of the nanotube.



Figure 18: Example of the results obtained with our model (top), compared with the experimental TEM images obtained by *Alexander S. Sinitsa et al.* [7] (bottom). The blue arrow highlights the sp^2 hybridized secondary carbon shell. Color and size of the carbon atoms of the confining SWNT are changed for better visualisation.



Figure 19: Typical SWNT nucleation and growth as revealed by MD simulations. The iron cluster contained 50 atoms (diameter 1 nm) and the temperature is 1000 K. The graph shows the change in the number of dissolved carbon atoms (CD) during nucleation and growth. Results and images taken from the work of *Feng Ding and Kim Bolton* [54]



Figure 20: Initial stages of growth of a parasitic graphitic island, from a SWNT endohedral nickel cluster of 55 atoms, catalyzed by the irradiation of the electron beam of a HRTEM. We changed the color coding to better match the results of *Ding and Bolton* [54]. In purple are reported the nickel atoms, whereas in grey and green the carbon atoms. In green are reported those C atoms which are dissolved in the Ni cluster, whereas in grey those C atoms being still part of the confining SWNT. It has to be noticed that the results of *Ding and Bolton* [54] on the X-axis report time in ns, whereas in our case, we report the number of iterations. Due to the intrinsic absence of a timescale in fbMC, thus, our results are plotted against a pseudo-time, which shall not be compared directly with an absolute time reference.

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