Supplementary Information

Atomistic mechanism of carbon nanotube cutting catalyzed by nickel under the electron beam

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S1. EDX spectra for bundles of filled nanotubes

EDX spectra were recorded for small bundles of SWNTs (3-10 nanotubes) filled with each metal on a JEOL 2100F TEM equipped with an Oxford Instruments X-rays detector at 100 kV.

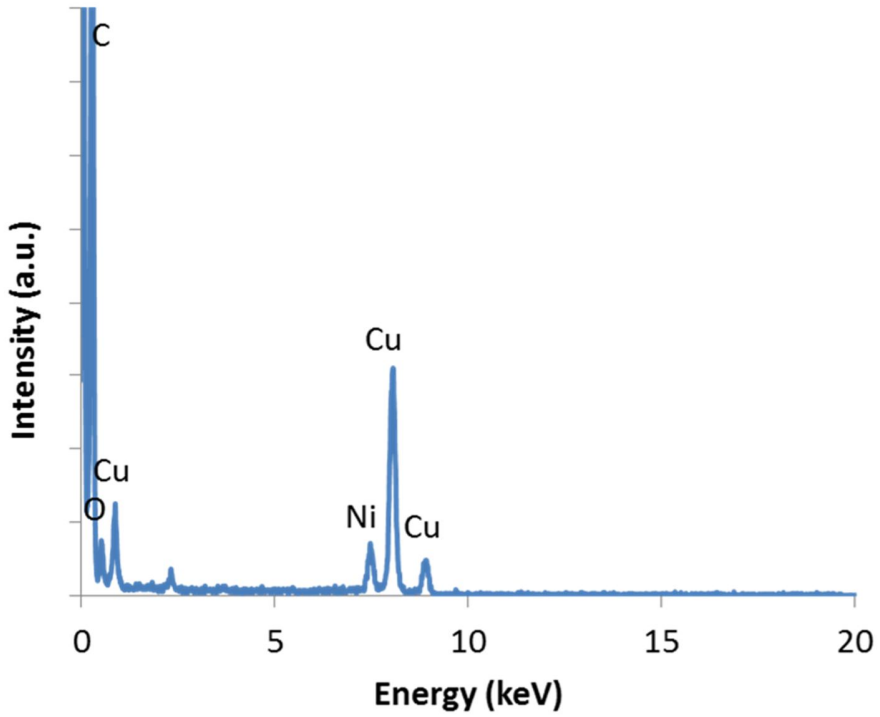

Figure 1S. The EDX spectrum of Ni-NPs@SWNT bundle (containing approximately 80 nanotubes) confirming the presence of nickel within the nanotubes. The Cu EDX peaks are due to the copper TEM specimen grid.

S2. Modeling of e-beam irradiation of pristine nanotubes and thermal treatment of carbon nanotubes with nickel clusters

To verify that the combination of both the metal cluster and electron irradiation is necessary to initiate nanotube cutting we performed supplementary simulations in the absence of each of these factors individually. Simulations for the pristine nanotube of 28 Å length with the same initial hole in the nanotube wall but without an absorbed metal cluster (Figure 3a) showed that carbon atom ejection is much rarer. The average time interval between ejection events is 1600 ± 400 s in 5 simulations using the same parameters as in series A and exceeds 1100 s in 5 simulations with the same parameters as in series B. This ejection rate is more than twice as slow as the rate observed in the simulations of irradiation-induced graphene-fullerene transformation[S1] and is an order of magnitude smaller than the ejection rate in the presence of the nickel cluster. A total of 16 carbon atoms were emitted in all simulations of the pristine nanotube in a duration of 2000 – 5000 s. Analysis shows that 7 of the emitted atoms were two-coordinate atoms in non-chain structures, 4 were one-coordinate atoms, while the rest consisted of a mixture of three-coordinate atoms in non-hexagonal rings, three-coordinate atoms neighbouring with two and one-coordinate atoms or non-hexagonal rings, and two-coordinate atoms in chains. The evolution of the structure of the pristine nanotube under electron irradiation is shown in Figure 3.

The following changes are induced in the pristine nanotube upon electron irradiation. First formation of non-hexagonal rings around the hole takes place (Figure 3b, Figure 3g). This can lead to curing of the hole in the nanotube wall (Figure 3c) that is accompanied by local deformation of the nanotube and manifests itself as a decrease in the total number of one and two-coordinate carbon atoms (Figure 3g). However, such states are not very stable and within the order of 100 s the nanotube is reconstructed (Figure 3d-f). The number of non-hexagonal rings increases again and these rings spread along the nanotube axis away from the hole (Figure 3d-g). The number of one and two-coordinate carbon atoms also increases and exhibits significant fluctuations (Figure 3g), demonstrating opening and closing of holes in the nanotube wall (see a hole on the reverse side of the nanotube in Figure 3f). In addition to non-hexagonal rings, bridges between opposite sides of the nanotube are formed by individual or chains of two-coordinate carbon atoms (Figure 3e and f). Therefore, simulations of the irradiation of pristine nanotube demonstrate that in the absence of the nickel cluster structural reconstruction induced by the e-beam proceeds via alternative pathways. In particular, the ejection rate of carbon atoms decreases drastically in the absence of the nickel cluster.

Simulations of the same initial structure with a nickel cluster adsorbed on the hole in the nanotube wall at temperature 2000 K but without electron irradiation did not reveal any structural rearrangements within tens of nanoseconds. In particular, no atom ejection is observed in such simulations. The duration of these simulations corresponds to the combined high-temperature relaxation steps of simulations with electron irradiation after 300 – 1000 "successful" electron collisions. Therefore, it is clear that the introduction of the high-temperature steps in order to allow relaxation of the structure between successive structure changing electron collisions does not directly affect the ejection rate. In addition, these simulations along with the simulations of electron irradiation of the pristine nanotube demonstrate that a combination of both electron irradiation and a metal cluster, are required to initiate nanotube cutting using low kinetic energy electrons (80 keV).

S3. Simulation results for relaxation temperature 1500 K

To investigate the effect of relaxation temperature T_{rel} we have performed series of simulations A2 and B2 with the parameters t_{rel} and $E_{\text{min}}^{(2)}$ similar to those of series A and B but with the temperature of the relaxation step of $T_{\text{rel}} = 1500$ K (Table 1S). Series A2 and B2 contain 5 simulation runs each. These simulations are interrupted before the nanotube cutting. Nevertheless, their duration is sufficient to make comparison with the results presented above for temperature $T_{\text{rel}} = 2000$ K.

In these simulations, the system is shown to pass through the same intermediate stages and the mechanism of nanotube cutting is qualitatively the same as in series A and B. The average times between irradiation-induced events and ejection events do not significantly alter as a product of changing the temperature (Table 1S). However, the relative abundance of two-coordinate carbon atoms in chains and one-coordinate carbon atoms is increased drastically compared to the results at temperature $T_{\text{rel}} = 2000$ K, especially in the simulation runs with short relaxation times, $t_{\text{rel}} = 10$ s. Therefore using a lower temperature during the relaxation MD stage of $T_{\text{rel}} = 1500$ K does not adequately describe irradiation events caused by electrons with the kinetic energy of 80 keV with the flux of 10^6-10^7 $e^-/nm^2/s$ at room temperature. In addition to testing the simulation parameters, these results qualitatively describe experiments with either increased electron flux or higher

temperature, revealing that electron flux and sample temperature can potentially be used to the level of imperfections with structures.

Table 1S. Calculated average time between different irradiation-induced events, their relative frequencies for impacted carbon atoms of different types and the number of atoms of different type averaged over total time for the simulation of nickel catalyzed electron beam assisted nanotube cutting with a MD relaxation step temperature of $T_{\text{rel}} = 1500$ K.

Irradiation-induced events	All		Ejection		Number of atoms[a]	
Simulation series	A2	B2	A2	B2	A2	B2
Minimal transferred energy E_{min} (eV)	13	10	13	10	13	10
Relaxation time t_{rel} (ps)	30	10	30	10	30	10
Total number of irradiation-induced events	12248	11792	336	150		
Average time between ejection events τ (s)	2.59 ± 0.05	0.99 ± 0.03	94 ± 7	74 ± 9		
Atom types	Not bonded to the cluster					
One-coordinate atoms	0.0032	0.0014	0.0387	0.0200	0.07	0.07
Two-coordinate atoms except atoms in chains	0.0262	0.0304	0.0387	0.0267	4.98	7.98
Two-coordinate atoms in chains[b]	0.0163	0.0174	0.0238	0.0067	3.12	4.05
Three-coordinate atoms in non-hexagonal rings	0.5296	0.557	0.0268	0.0067	82.85	91.36
Three-coordinate carbon atoms in hexagons	0.1538	0.1771	0.0030	0.0067	170.37	172.49
Total for atoms not bonded to the cluster	0.7291	0.7830	0.1310	0.0667	261.39	275.96
	Bonded to the cluster					
One-coordinate atoms	0.0287	0.0355	0.1994	0.2600	1.04	1.59

Two-coordinate atoms except atoms in chains	0.0501	0.0381	0.0417	0.0400	4.52	4.40
Two-coordinate atoms in chains[b]	0.0492	0.0923	0.1369	0.2133	5.99	9.00
Three-coordinate atoms in non-hexagonal rings	0.0079	0.0119	0.0030	0	0.55	0.64
Three-coordinate carbon atoms in hexagons	0.0026	0.0044	0	0	0.17	0.32
Adatoms	0.0682	0.0325	0.4673	0.4133	1.14	1.12
Ad-dimers	0.0038	0.0024	0.0208	0.0067	0.05	0.08
Total for atoms bonded to the cluster	0.2105	0.2170	0.8690	0.9333	13.46	17.15

[a] Fixed atoms at the nanotube edges are not counted.

[b] Two-coordinate carbon atoms which have at least one bond with two-coordinate or one-coordinate carbon atoms.

S4. Sensitivity of results to simulation parameters

In the following we address the choice of parameters for description of structure relaxation between successive irradiation-induced events. Since it is not possible to perform direct atomistic simulations of structure evolution between irradiation-induced events that take seconds under real conditions, a common approach is to accelerate its kinetics by increasing temperature. However, care should be taken in selecting adequate parameters for this simulation step. First of all, to separate the effects of electron irradiation and high temperature the temperature T_{rel} and duration t_{rel} of this high-temperature stage should be chosen so that thermally induced transformations of the pristine structure are virtually excluded, i.e. the following condition should be fulfilled

$$N_{\text{ev}} t_{\text{rel}} \ll t_{\text{th}},$$

where N_{ev} is the number of irradiation-induced events during the simulation of the irradiation-induced process and t_{th} is the characteristic simulation time required for the thermally induced process analogous to the considered irradiation-induced process to take place at the elevated

temperature T_{rel}. The simulations at high temperature without electron irradiation have shown no indication of nanotube cutting and even atom ejection. Therefore, this condition is clearly fulfilled for the considered process and the simulation parameters $E_{min} = 10-13$ eV, $t_{rel}=10-30$ ps and $T_{rel} = 1500 - 2000$ K.

The restriction on t_{rel} and T_{rel} from the other side is that they should be sufficiently large to describe recovery of bonds broken in the result of electron collisions. The results obtained at relaxation temperature $T_{rel} = 1500$ K show that this temperature is insufficient to describe structure relaxation between successive irradiation-induced events even at duration of the relaxation step of $t_{rel} = 30$ s. The relative abundance of two-coordinate carbon atoms in chains and one-coordinate carbon atoms is increased drastically as compared to the results at relaxation temperature $T_{rel}=2000$ K, especially in series B2 with the short relaxation time $t_{rel}=10$ s (both for the carbon atoms in the contact with the nickel cluster and not, Table 1S). Consequently, the contribution of these types of atoms to the irradiation-induced events increases (see Table 1S).

The choice of higher relaxation temperature $T_{rel}=2000$ K does not eliminate all restrictions on t_{rel} . In particular, the reactions reverse to the formation of carbon chains at the edge of the carbon network (similar to the process shown in Figure 4a and b), though they have a very low barrier, also have a large characteristic time in the pre-exponential factor that can be on the order of 10 ps.[S2,S3] Therefore, $t_{rel}\geq 10$ ps should be chosen to prevent unphysical generation of carbon chains. In addition to increasing the relaxation time t_{rel}, the excessive generation of chains can be suppressed by increasing the minimal transferred energy E_{min} for the corresponding types of atoms. Thus, it can be expected that structure relaxation between irradiation-induced events is somewhat better treated in series A of simulations. Indeed the total number of two-coordinate carbon atoms in chains averaged over time is greater by 20% in series B than in series A.

Nevertheless, the results are qualitatively similar in series of simulations A and B and are even quantitatively close in these two series. The relative frequencies of all irradiation-induced events and atom ejection events for different types of atoms are almost the same in the both series of

simulations (Table 1). The number of carbon atoms in chains and, correspondingly, the number of carbon adatoms averaged over time are greater in series B than in series A only by 30%. The time between atom ejection events is, correspondingly, 30% greater for series A than for series B. The time of complete cutting of the nanotubes in the finished simulations is one a half times greater in series B. This discrepancy in quantitative results of series A and B is acceptable and demonstrates that the simulation parameters approach the full description of the effect of electron irradiation.

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