Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supplementary information

Molecular evidence for feedstock-dependent nucleation mechanisms of CNTs

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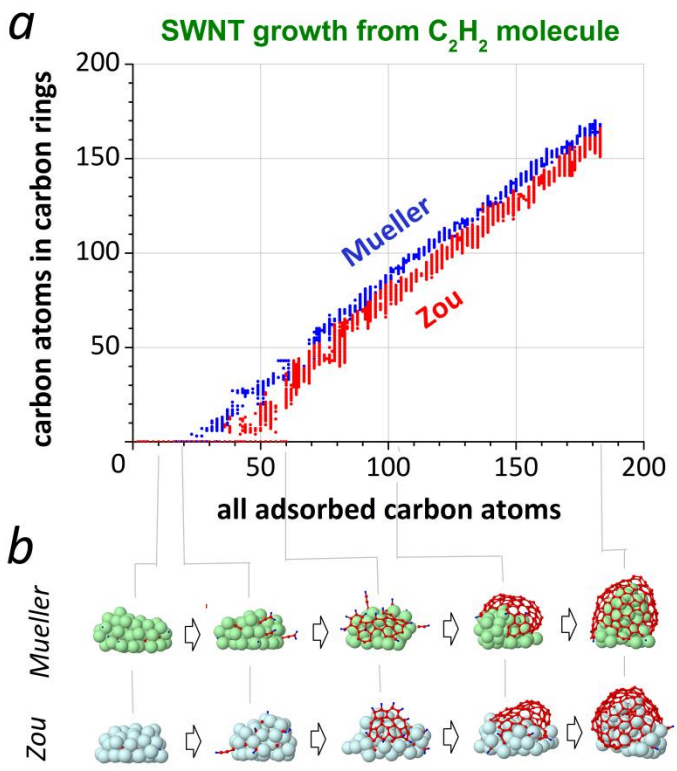
S1. SWNT growth from C_2H_2 feedstock: ReaxFF-Mueller vs ReaxFF-Zou

ReaxFF-Mueller has already shown its ability to simulate of SWNT nucleation and subsequent growth from C_x [8] and C_xH_y feedstocks [24]. However, C-O, Ni-O, H-O and O-O interactions are not considered in this force field, and hence the simulation of CNT nucleation/growth from $C_xH_yO_z$ feedstock is not accessible by the ReaxFF-Mueller. The ReaxFF-Zou, on the other hand, does include these interactions. Table 1 in the manuscript compares some results provided by ReaxFF-Zou and ReaxFF-Mueller, showing that there are small differences between both force fields. Such differences can in principle affect e.g., in the onset of the incubation stage. Namely, the difference in Ni cohesive energy (-4.45 eV in ReaxFF-Zou and -4.5 eV in ReaxFF-Mueller) leads to a change in the formation volume of Ni cluster (0.78 eV in ReaxFF-Zou and 0.68 eV in ReaxFF-Mueller) and allows for an increase in the number dissolved C atoms in the cluster (from about 18% to about 30%). Nevertheless, our test simulations indicate that SWNT growth rates and nucleation/growth steps are identical (see Supplementary Figure 1a and 1b, respectively), although the super-saturation point is slightly shifted in ReaxFF-Zou case due to a relatively high C capacity of Ni cluster.



Supplementary Figure 1. ReaxFF-Mueller vs ReaxFF-Zou: (*a*) Evolution number of the number of carbon atoms in the carbon network, cap or tube during SWNT nucleation/growth from C_2H_2 feedstock; (*b*) Nucleation/growth steps of SWNT. Here, Ni atoms are in light green or light blue colors in these simulation results used ReaxFF-Mueller or ReaxFF-Zou, respectively.

Figure 1*a* demonstrates that the SWNT growth rates are the same, although the fluctuations are a slightly higher in ReaxFF-Zou. Further, the sequence of the formation of carbon nanostructure, i.e., (free-standing) polyyne carbon chains, (vertical or horizontal) graphene-like patches and a carbon cap or tube surrounds/covers the nanoparticle (Figure 1*b*) [24], indicates that the growth mechanism does not change due to from one force field to the other.

S2. C-C association/dissociation reactions in the cap/tube-catalyst interface

The overall results indicate that the association (incorporation) to the carbon network and dissociation of network carbon atoms in the catalyst-tube interface depends on the three carbon contributors, *vis*. surface C species, dissolved C atoms and gas-phase (etched) C species. Although numerous C-C association and simultaneous C-C dissociation reactions occur in the interface, the amount of C atoms in the cap or tube gradually increases. We compare the number of these reactions in Table 1.

Supplementary Table 1. The C-C association/dissociation reactions in the tube (cap)-cluster interface during the SWNT nucleation/growth from $C_xH_yO_z$ feedstock. The calculations were continued until the system contained 96 adsorbed C atoms. The reaction numbers are recorded with a 1 picosecond interval.

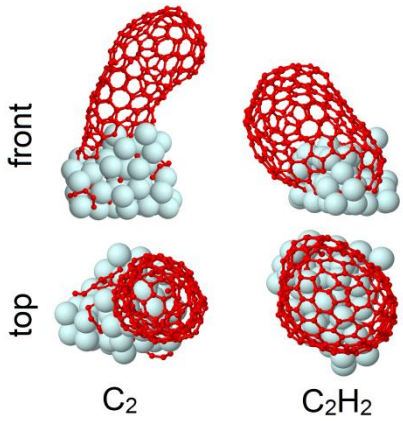
	number of C atoms, involved in C-C reactions in the tube (cap)-end									Gained or lost C atoms in the tube (or cap)		
	number of C atoms, transform from other C species to a ring C			number of C atoms, transform from a ring C to other C species			total number of C atoms, involved in transformations					
dissolved C	3338	6239	897	3345	6292	910	6683	12531	1807	-7	-53	-13
surface C	3770	11536	2770	3683	11405	2679	7453	22941	5449	87	131	91
gas-phase C	0	1	94	6	3	102	6	4	196	-6	-2	-8
Total	**7108**	**17776**	**3761**	**7034**	**17700**	**3691**	**14142**	**35476**	**7452**	**74**	**76**	**70**
feedstock type	CH_2O	C_2H_6O	$C_{13}H_{24}O_{11}$	CH_2O	C_2H_6O	$C_{13}H_{24}O_{11}$	CH_2O	C_2H_6O	$C_{13}H_{24}O_{11}$	CH_2O	C_2H_6O	$C_{13}H_{24}O_{11}$

In total, 14142, 35476 and 7452 C-C (association and dissociation) reactions occur in the tube (or cap) - cluster interface upon growth of an incipient SWNTs with 74, 76 and 70 carbon atoms until the system contains 96 carbon atoms in the cases of CH_2O, C_2H_6O and $C_{13}H_{24}O_{11}$

feedstocks, respectively. Overall, the fractions of the transformation of dissolved C atoms to ring-C are 47%, 35% and 24%, and the fractions of the transformation of surface-C to ring-C are 53%, 65% and 73% for CH_2O, C_2H_6O and $C_{13}H_{24}O_{11}$, respectively. This indicates that the contribution of dissolved C atoms to SWNT growth decreases and a contribution of surface-C to SWNT increases with increasing the amount of carbon atoms in the feedstocks. While the tube in the end gains 87, 131 and 91 C atoms due to transformation of surface-C for CH_2O, C_2H_6O and $C_{13}H_{24}O_{11}$, respectively, the tube also loses 7, 53 and 13 C atoms during the transformations of dissolved C atoms in these feedstock cases. Also, the tube (cap) eventually loses six, two and eight edge C-atoms upon the direct interaction with gas-phase carbon species, although the reaction probabilities are quite different, i.e., 0.04%, 0.01% and 2.6% for CH_2O, C_2H_6O and $C_{13}H_{24}O_{11}$, respectively. In total, the grown tube (cap) gains 74, 76 and 70 C atoms due to surface C species, while it loses some atoms because of dissolving into the Ni cluster or being etched from the cluster.

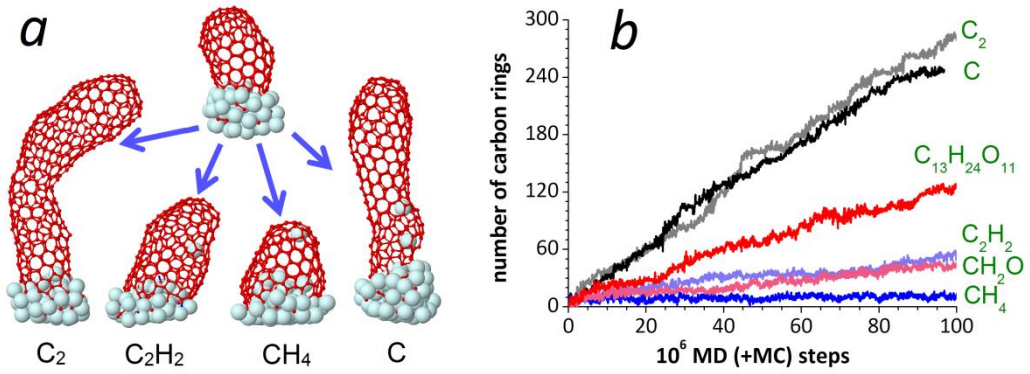
S3. Tube diameter vs feedstock: two supplementary evidences

We present two supplementary evidences to support our idea that the feedstock type affects the tube diameter.



Supplementary Figure 2. CNT growth from C_2 and C_2H_2 feedstocks.

First evidence. Figure 2 presents two grown tubes from C_2 and C_2H_2 feedstock on a Ni_{55} nanocluster. The tube-cluster systems contain 242 or 244 C atoms, respectively. The results indicate that the ratio of the C incorporation rates for C_2 and C_2H_2 cases ($C_{inc}(C_2)/C_{inc}(C_2H_2)$) is about 22:1. Although the number of C atoms in both tubes is nearly the same, the tube diameters are significantly different.



Supplementary Figure 3. (*a*) Continued CNT growth from C, C_2, C_2H_2 and CH_4 feedstocks. (*b*) Formation rate of carbon rings in a grown tube or tube growth rate as a function of a carbon feedstock.

Second evidence. Figure 3*a* demonstrates a continued growth of (an already grown) small tube from C_x, C_xH_y and $C_xH_yO_z$ feedstocks: the resulting tube diameter differs as function of the feedstock type. The formation rate of carbon rings or the C incorporation rate depends on the type of growth feedstock, as shown in Figure 3*b*. Both results indicate that the diameter of the original tube can change during the growth due to different C incorporation rate, which depends on the feedstock type: fast C incorporation (or fast CNT growth) leads to a decrease in the tube diameter.

These two observations, i.e., the growing a narrow (broader)-diameter tube due to a fast (slow) C incorporation, are an agreement with recent experimental evidences [55, 56].