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Molecular evidence for feedstock-dependent nucleation mechanisms of CNTs<sup>†</sup>

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Atomic scale simulations have been shown to be a powerful tool for elucidating the growth mechanisms of carbon nanotubes. The growth picture is however not entirely clear yet due to the gap between current simulations and real experiments. We here simulate for the first time the nucleation and subsequent growth of single-wall carbon nanotubes (SWNTs) from oxygen-containing hydrocarbon feedstocks using the hybrid Molecular Dynamics/ Monte Carlo technique. The underlying nucleation mechanisms of Ni-catalysed SWNT growth are discussed in detail. Specifically, we find that as a function of the feedstock, different carbon fractions may emerge as the main growth species, due to a competition between the feedstock decomposition, its rehydroxylation and its contribution to etching of the growing SWNT. This study provides a further understanding of the feedstock effects in SWNT growth in comparison with available experimental evidence as well as with ab initio and other simulation data, thereby reducing the simulationexperiment gap.

## Introduction

Carbon nanotubes (CNTs) have attracted the attention of many researchers for several decades, thanks to their geometrydependent electronic, mechanical and optical properties.<sup>1</sup> Among the various synthesis techniques, chemical vapour deposition (CVD) is an often preferred technique due to its simplicity, high degree of control and scalability.<sup>2</sup> In spite of tremendous efforts, the synthesis of nanotubes with controlled properties can be achieved in the CVD process only to some extent, at least in part due to our current incomplete understanding of the growth mechanism.<sup>2,3</sup>

Probably the most sought-after property is chirality-controlled growth. It is often believed that control over the nucleation stage

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### **Conceptual insights**

This work demonstrates the crucial role of carbon and non-carbon species in CNT growth from oxygen-containing hydrocarbons (CxHvOz) through atomistic simulations. Over the past two decades, many researchers have employed atomic scale simulations to study CNT growth. Nevertheless, there are no reports yet on simulated nucleation and growth from  $C_x H_y O_z$ . Despite the fact that a vast majority of experiments use these feedstocks, most simulations so far considered pure carbon as the feedstock, assuming that the non-carbon species play little or no role of importance in CNT growth. In contrast, this work demonstrates how non-growth species have a direct impact on the CNT nucleation and growth. We distinguish three classes of growth contributors, whose formation is found to depend on a competition between feedstock decomposition, its rehydroxylation and its contribution to etching of the growing CNT. Also, we demonstrate the dependence of the tube diameter on the C incorporation rate, in excellent agreement with the in situ TEM evidence. Finally, we explain the role of oxygen and hydrogen in broadening and necking of CNTs. In summary, these simulations are the first of their kind, provide new microscopic information on the CNT nucleation nature, and assist in reducing the gap between simulations and real experiments.

eventually also allows control of the CNT chirality.<sup>4</sup> To support this, some transmission electron microscopy (TEM) studies have shown time-resolved details of metal catalysed single-wall CNT (SWNT) nucleation and consequent growth at the atomic level.<sup>5,6</sup> However, the atomic scale dynamics of the CNT nucleation processes cannot be captured by current TEM resolution.<sup>3,6</sup> Consequently, a variety of computational techniques have been applied to gain complementary information on various effects, including the importance of the carbon chemical potential<sup>7</sup> or the metal-mediated defect healing,<sup>8</sup> the necessity of a carbide phase,<sup>9</sup> and the influence of the  $C_x$  growth feedstock,<sup>10,11</sup> and all these have contributed to unravelling and explaining experimental observations. In particular, the dislocation theory of chirality-controlled nanotube growth, proposed by Ding and co-workers,<sup>12</sup> successfully addresses the growth rate-chiral angle proportionality,<sup>13</sup> and the axial rotation of SWNTs.<sup>14</sup> In this kinetic approach, however, the main issue of debate is the neglect of the role of the catalyst nanoparticles, the substrate, the feedstock pressure, and temperature on the resulting (n,m) distribution of grown SWNTs.<sup>15–20</sup>

Besides these important factors in CVD-based CNT growth, the choice of the carbon feedstock is one of the main parameters for tuning the SWNT diameter<sup>15-17</sup> and chirality.<sup>18-20</sup> However, real growth species, including hydrocarbon and noncarbon species such as hydrogen, oxygen, and hydroxyl radicals are generally not taken into account in computer simulations. and it is still a major issue.<sup>2</sup> Only very recently, the first dynamic simulation study on SWNT nucleation using hydrocarbons as a carbon source has been reported, investigating the decomposition of the hydrocarbon molecule,<sup>21</sup> the appearance of carbon chains and networks<sup>22,23</sup> and the formation of a carbon cap<sup>24</sup> on the transition metal nanoparticle surface. These investigations revealed that the dual role of hydrogen and thus the competition between (re)hydrogenation and dehydrogenation processes during the incubation stage are critical for the dynamics of the SWNT nucleation process.<sup>24</sup> Besides hydrocarbons, oxygen-containing hydrocarbon  $(C_r H_\nu O_z)$  feedstocks are also widely used in SWNT growth and thus understanding the role of oxygen is also very important.<sup>25-27</sup> To this end, Oguri and co-workers have very recently studied the decomposition of ethanol molecules on a Ni catalyst surface.<sup>28,29</sup> Although such investigations are quite interesting and give useful information on the onset of SWNT nucleation, understanding the whole picture of SWNT nucleation and growth from C<sub>r</sub>H<sub>v</sub>O<sub>z</sub> species, however, still remains unclear.

In this work, we report on carbon nanotube cap nucleation and consequent SWNT growth using different  $C_xH_yO_z$  feedstocks through combined reactive molecular dynamics and timestamped force-bias Monte Carlo (MD/tfMC) simulations,<sup>8,24</sup> for the first time. In particular, we found that the competition between catalytic dissociation of the  $C_xH_yO_z$  feedstock and its hydroxylation and subsequently its etching process is critical in determining the main carbon contributors for SWNT growth.

### Computational methodology

#### MD/tfMC simulation technique

Simulation of the Ni-catalysed SWNT growth from  $C_xH_yO_z$  species is performed using a combined reactive MD and tfMC technique.<sup>8,24</sup> In MD/tfMC, the impacts of the growth species on the nanocatalyst surface and the initial chemical reactions taking place during the first few picoseconds are accounted for by the MD module,<sup>24</sup> while the tfMC module subsequently takes care of the longer time relaxation of the system after each chemical reaction. While the exact system dynamics are not reproduced in tfMC calculations, it provides a realistic (albeit not exact) dynamical path, and reproduces end configurations in full agreement with (very long) MD simulations.<sup>8</sup>

#### ReaxFF

In order to properly describe the bond dissociation and formation processes, including the C–C bond dissociation,  $H_2$  or  $H_2O$  formation and other reactions during both the MD and the

 $\label{eq:table_$ 

	ReaxFF		Other simulation	
	Zou	Mueller	methods	Experiment
E <sub>coh</sub> (Ni), eV	-4.45	-4.50	$-4.42^{35}$	$-4.44^{36}$
$\Delta H$ (C), eV	$0.62^{a}$	$0.78^{a}$	$0.20 - 0.36^{37}$	$0.42 - 0.49^{37}$
	$0.29^{b}$	$0.68^{c}$	$0.40^{38}$	
$V^{\rm F}$ (Ni <sub>x</sub> C)/ $\Omega_0$	$0.78^{a}$	$0.68^{a}$	$0.64 - 0.97^{c  37}$	—
		0.71 <sup>c</sup>		
$E_{\text{des}}$ (H <sub>2</sub> ), eV	$1.22^{b}$	$1.66^{39}$	$0.42 - 1.19^d$	$1.2 - 1.3^{e  34}$
<sup><i>a</i></sup> For Ni <sub>864</sub> C. <sup><i>b</i></sup> Ni(111). <sup>33</sup> <sup><i>e</i></sup> For	For Ni <sub>55</sub> T > 500	C. <sup>c</sup> For Ni K. <sup>34</sup>	<sub>32</sub> C. <sup><i>d</i></sup> For Ni(100),	Ni(110) and

tfMC cycles, the ReaxFF potential<sup>30</sup> is applied with new forcefield parameters developed by Zou et al.<sup>31</sup> To validate the forcefield quality, we evaluated test simulations carried out using new parametrized ReaxFF (ReaxFF-Zou) against results obtained using parameterization by Mueller et al. (ReaxFF-Mueller),<sup>32</sup> and other simulations and experimental data,<sup>33-39</sup> which are shown in Table 1. In particular, ReaxFF-Zou reproduces the cohesive energy of nickel (-4.45 eV) in excellent agreement with experiments  $(-4.44 \text{ eV})^{35}$  as well as DFT calculations (-4.42 eV)<sup>36</sup> while the ReaxFF-Mueller result is somewhat off (-4.50 eV). While the heat of solution of the C atom in the Ni<sub>864</sub> bulk (0.62 eV) is slightly higher than the experimental value of about 0.42-0.49 eV,37 the value for the Ni55 nanocluster (0.29 eV) is in the range of both experimental and other simulation results (0.2–0.4 eV).<sup>37,38</sup> The formation volume  $V^{\rm F}$ quantifies the deformation of the Ni crystal upon incorporation of C in the lattice (Ni<sub>x</sub>C). It is defined as  $V^{\rm F} = V(\rm Ni_xC) - x\Omega_0(\rm Ni)$ , where  $V(Ni_xC)$  and  $\Omega_0(Ni)$  are the volume of the relaxed  $Ni_xC$ structure and the volume per atom of elemental Ni, respectively, where x is the number of Ni atoms in the system. We found that the  $V^{\rm F}/\Omega_0$  ratio (0.78) is in close agreement with the ab initio data of Siegel et al. (0.64–0.8),<sup>37</sup> although the value is slightly higher than the value calculated using the ReaxFF-Mueller parametrization (0.68 and 0.71 for Ni<sub>864</sub>C and Ni<sub>32</sub>C, respectively). Also, we calculated the energy barrier of  $H_2$ desorption from the Ni surface to be 1.22 eV, which is close to the range of DFT calculation results  $(0.42-1.19 \text{ eV})^{33}$  and in very close agreement with the experimental activation energy (1.2–1.3 eV),<sup>34</sup> while the ReaxFF-Mueller parametrization yields a slightly too high value (1.66 eV).<sup>39</sup> In spite of quantitative differences between ReaxFF-Mueller and ReaxFF-Zou results, our test simulations indicate that such small differences do not affect the overall growth mechanisms (see Fig. 1 in the ESI<sup>+</sup>). The overall results indicate that the new ReaxFF potential is sufficiently accurate to address catalysed CNT growth using MD/tfMC simulations.

#### Simulation details

For the simulation of SWNT growth, a Ni<sub>55</sub> nanocluster is initially equilibrated at 2000 K using the canonical Bussi thermostat.<sup>40</sup> The nanocatalyst is physisorbed on a virtual Al surface, employing a *z*-integrated Lennard-Jones potential.<sup>23</sup> In order to gain a generic understanding of the role of  $C_xH_yO_z$ 



Fig. 1 Ball-stick model of the three  $C_xH_yO_z$  feedstocks, *i.e.*, (a) formaldehyde, (b) ethanol and (c)  $\beta$ -methyl lactoside molecules. C, H and O atoms are shown in red, blue and green colours, respectively.

feedstocks, we use three different molecules, *viz.* formaldehyde (CH<sub>2</sub>O) and ethanol (C<sub>2</sub>H<sub>6</sub>O) molecules, which have double or single C–C bonds, respectively, and complex  $\beta$ -methyl lactoside (C<sub>13</sub>H<sub>24</sub>O<sub>11</sub>) molecule (Fig. 1).

The molecules are allowed to impinge on the cluster one by one, while keeping their number density in the simulation cell constant during the simulations. Due to lower pyrolysis temperature of the  $C_{13}H_{24}O_{11}$  (~445 K)<sup>41</sup> and  $C_2H_6O$  (1050–1275 K)<sup>42</sup> molecules, compared to CH<sub>2</sub>O (2200–2650 K),<sup>43</sup> different molecular fractions can already be found in the gas-phase before the molecule impinges on the catalyst surface at 2000 K. However, we found that the formation rate of the pyrolysis products is very low. When a gas-phase species adsorbs on the nanocluster, the resulting structure is allowed to relax by the application of tfMC.<sup>23,24</sup> During the relaxation, no new feedstock is allowed to enter the simulation cell.

#### **DFT calculations**

The VASP software<sup>44</sup> is used for DFT calculations of adsorbed/ dissociated/desorbed H<sub>2</sub> and H<sub>2</sub>O molecules on/from the Ni<sub>55</sub> nanocatalyst. Optimizations are done in the generalized gradient approximation (GGA), using the revised Perdew– Burke–Ernzerhof (RPBE) functional,<sup>45</sup> and the projector augmented wave (PAW) method.<sup>46</sup> Methfessel–Paxton smearing of the first order is used,<sup>47</sup> along with a  $\Gamma$ -centered (1 × 1 × 1) *k*-point mesh. Supercells with sizes of (20 × 20 × 20) Å are employed, except for the structures where H<sub>2</sub> and H<sub>2</sub>O are desorbed from the nanoparticle, in which case the size is (30 × 30 × 30) Å. Spin polarization with no symmetry constraints is employed. The energy cutoff is set to 500 eV, and the energy convergence to 1 × 10<sup>-6</sup> eV. A magnetic moment is applied to the Ni atoms.

### **Results and discussions**

From our results we infer that SWNT nucleation and its subsequent growth from  $C_x H_y O_z$  feedstocks can be distinguished into three stages, which are similar to SWNT growth from nonoxygen containing hydrocarbon species:<sup>24</sup> (i) incubation,



Fig. 2 Base-growth process of SWNTs from  $C_xH_yO_z$  species, divided into three stages. Ni, C, H and O atoms are shown in cyan, red, blue and green colours, respectively.

(ii) cap formation and (iii) continued (tube) growth, as illustrated in Fig. 2. We find that the SWNT nucleation from  $C_xH_yO_z$  feedstocks is clearly different from both pure carbon  $(C_x)^{7-10,48}$  and hydrocarbon  $(C_xH_y)$  species.<sup>22–24</sup> However, fast C dissolution after the feedstock dissociation at the onset of the incubation stage is identical for all types of growth species.

#### Feedstock-catalyst reactions

As representative for all  $C_x H_y O_z$  feedstocks, we here analyse the entire adsorption/dissolution process of the ethanol ( $C_2H_6O$ ) molecule on/in a Ni nanocatalyst. After impingement on the cluster, the molecule typically first binds to the surface with its O-atom (Fig. 3a and b). While the feedstock sticking probability depends on the nature of the Ni facets,<sup>33</sup> the Ni nanoparticle is amorphized at high temperature and therefore it does not contain any specific facets during the entire growth process. Consequently, all C-H, C-O and C-C bonds of the molecule are gradually broken (Fig. 3c-j). In particular, C-C bonds from the surface CH<sub>x</sub>CO fragment (*e.g.*, HCCO in Fig. 3f) are dissociated (Fig. 3g) during the simulation, which concurs with previous ab initio MD calculation results.<sup>29</sup> Yet, binding of another H-adatom to the remaining CO fragment leads to weakening and consequently breaking of the single C-O bond (Fig. 3i and j). In the CH<sub>2</sub>O case, however, such H binding is rather rare due to low concentration of H adatoms and consequently CO fragments remain longer on the cluster or desorb from the cluster. After C-O bond breaking, the single C atom quickly dissolves into clusters. During the feedstock dissociation, H adatoms eventually associate with a remaining OH fragment or another H adatom and desorb as a water or hydrogen molecule from the cluster surface, respectively (Fig. 3k and l).

#### Hydrogenation vs. oxidation

Employing nudged elastic band (NEB)<sup>49</sup> calculations (Fig. 3m), the energy barrier for the recombination of OH and H species on the Ni<sub>55</sub> cluster is found to be 1.53 eV (red open squares in Fig. 3m). This value is slightly higher than DFT values for different nickel facets, *i.e.*, 0.87 eV for Ni(111), 0.94 eV for Ni(110) and 1.39 eV for Ni(100) surfaces (red up triangles, red right triangles and red down triangles, respectively, in



**Fig. 3** (a–l) Adsorption and dissociation steps of ethanol molecules on Ni<sub>55</sub> clusters. The fractions or individual atoms of other adsorbed ethanol molecules are coloured in white, for the sake of clarity. (m) Association/ dissociation activation barriers in desorption/adsorption of H<sub>2</sub> (blue lines with open squares) and H<sub>2</sub>O molecules (red lines with open squares) on Ni<sub>55</sub> nanoclusters. DFT values for H<sub>2</sub>O on Ni(111), Ni(110) and Ni(100) surfaces<sup>33</sup> are indicated by red up, red down and red right triangles, respectively. DFT data for H<sub>2</sub>O on Ni<sub>55</sub> is indicated by red squares. Also, DFT data for H<sub>2</sub><sup>33</sup> are shown in blue. Furthermore, the blue star indicates the experimental activation energy barrier for H<sub>2</sub> desorption.<sup>34</sup>

Fig. 3m).<sup>33</sup> These species subsequently desorb as a H<sub>2</sub>O molecule from the Ni surface. The same water formation mechanism was also reported in *ab initio* MD studies.<sup>28</sup> In contrast to the recombination and desorption, H<sub>2</sub>O re-adsorption is found to be barrier-less. The adsorbed molecule preferably desorbs again from the surface rather than dissociatively chemisorbing on the catalyst surface: the desorption and splitting barriers are 0.91 eV (our DFT value is 0.71 eV, see red squares in Fig. 3m) and 1.25 eV, respectively. Thus, most adsorbed H<sub>2</sub>O molecules desorb again without proceeding to decompose to OH + H species, which is in agreement with both experimental<sup>50,51</sup> and DFT calculation results.<sup>52</sup> As mentioned above, H adatoms freely diffuse over the cluster surface (with a maximum diffusion barrier of 0.51 eV) compared to adsorbed OH, until they recombine with either an OH species (1.53 eV) or another H adatom (1.22 eV) in order to desorb as H<sub>2</sub>O or H<sub>2</sub> molecules, respectively. Our results show that the OH diffusion barrier is rather high, about 2 times higher than the H diffusion barrier due to its high adsorption (binding) energy, which is in agreement with DFT calculation results.<sup>33</sup> Also, the value for the H<sub>2</sub> desorption energy barrier (blue open squares in Fig. 3m) is in close agreement with the experimental activation energy in the range of 1.2–1.3 eV (blue star in Fig. 3m)<sup>34</sup> and first-principle results, ranging from 0.42 eV to 1.37 eV for different nickel surfaces (blue triangles in Fig. 3m).<sup>33</sup> While both recombination energy barriers differ somewhat from DFT values, overall DFT and MD/tfMC calculations indicate that the formation rate of OH&H pairs on the cluster surface (*i.e.*, HO\* + H\* + Ni  $\rightarrow$  H<sub>2</sub>O↑ + Ni) is relatively slow compared to the H&H formation rate (i.e.,  $H^* + H^* + Ni \rightarrow H_2 \uparrow + Ni$ ). Furthermore, the positive reaction energies of 0.66 eV for H<sub>2</sub> and 1.18 eV for H<sub>2</sub>O are close to firstprinciple values in the range of 0.36-0.90 eV for H<sub>2</sub> (blue triangles and squares) and 0.20-0.94 eV for H<sub>2</sub>O (red triangles and squares),<sup>33</sup> indicating the endergonic nature of both H<sub>2</sub> and H<sub>2</sub>O desorption reactions. Therefore, both desorbed molecules preferably re-adsorb again on the catalyst surface. While the  $H_2$  adsorption barrier is non-zero (0.24 eV) unlike  $H_2O$ adsorption, the chemical dissociation barrier of the H<sub>2</sub> molecule (0.56 eV) is much lower than the dissociation barrier of the H<sub>2</sub>O molecule (1.25 eV). Comparing dissociative adsorption and associative desorption probabilities of H<sub>2</sub> and H<sub>2</sub>O molecules, the results point out that the probability for hydrogenation is higher than for oxidation during the CNT growth from  $C_x H_y O_z$  species. In addition, the high non-dissociative adsorption rate of H<sub>2</sub>O due to its zero-barrier can assist in the growth of defect-less SWNTs.25

#### Super-saturation point

When a  $C_xH_yO_z$  molecule completely dissociates, all C atoms are found as dissolved species in Ni<sub>55</sub> nanoclusters, which is similar to simulation studies of SWNT nucleation from  $C_x^{7^{-10,48}}$ and  $C_xH_y$  species<sup>22–24</sup> at the onset of SWNT nucleation. This scenario of " $C_xH_yO_z$  adsorption/dissociation, C dissolution, as well as H<sub>2</sub> and H<sub>2</sub>O desorption" continues until the nanocluster is saturated, *i.e.*, no space is available in the catalyst. At this supersaturation point (indicated by the dashed line in Fig. 4a),<sup>48</sup> the number of dissolved C atoms can gradually increase up to about 30% of the amount of Ni atoms (Fig. 4a, dissolved C). After supersaturation, the amount of dissolved C atoms reduces through the formation of different carbon species and subsequent incipient carbon nanostructures on the catalyst surface.

#### Surface carbon species

The appearance of surface C species can be explained by decreasing the catalyst activity after its saturation. As a result, feedstock fractions preferably remain at and diffuse over the catalyst surface rather than splitting and diffusing into the catalyst.<sup>10</sup> The results indicate that a surface carbon species is the product of the competition between the feedstock dissociation due to the saturated catalyst and its re-hydroxylation/ etching caused by non-carbon surface species such as H, O and OH. Because of this competition, the number of remaining  $C_kH_nO_m$  species increases on decreasing their carbon content, as shown in Fig. 4b. Consequently,  $C_2H_nO_m$  species, including carbon dimers, are the predominant species found among all surface species in all feedstock cases, which is in agreement with the theoretical suggestions.<sup>11,53</sup> Recent first-principles calculation results led to the conclusion that chiral selective



**Fig. 4** (a) Distribution of adsorbed C atoms as a function of its total number during SWNT growth from CH<sub>2</sub>O molecules: number of dissolved C atoms, surface C atoms and ring-related C atoms. (b) Relative fractions of surface C species ( $C_kH_nO_m$ ) during the SWNT nucleation/growth from CH<sub>2</sub>O,  $C_2H_6O$  and  $C_{13}H_{24}O_{11}$  molecules. (c) Evolution of the number of pentagons, hexagons and heptagons as a function of the number of C adatoms during the growth from CH<sub>2</sub>O,  $C_2H_6O$  and  $C_{13}H_{24}O_{11}$  molecules.

CNTs can elongate through the addition of C<sub>2</sub>-fragments instead of adding C atoms one-by-one and the incorporation of C<sub>2</sub> species into the SWNT rim continues the growth without changing its chirality.<sup>11,53</sup> Furthermore, C<sub>6</sub>H<sub>n</sub>O<sub>m</sub> species, including C<sub>6</sub> polypne chains, increase when the growth feedstock contains more carbon atoms. The appearance of such six-atom chains eventually leads to hexagon formation on the catalyst surface, hence the fast network elongation. When incipient carbon rings, *e.g.*, pentagons or hexagons, appear on the surface, the number of surface C species considerably decreases (Fig. 4a). While their amount fluctuates around a constant number in stage II, it gradually lowers in the final growth stage due to the blocking of most of the available area on the catalyst surface by the growing tube (Fig. 4c).

#### Desorption vs. etching

While the supply probability of surface C species to the growing carbon network is obviously very high after the supersaturation point, the contribution of desorbed or etched gas-phase species to the growth process is not negligible. In Fig. 5, desorbed and etched species, *i.e.*, gas-phase non-C and C species are analysed. In particular, the number of desorbed  $H_mO_n$  species, including water and hydrogen molecules, is relatively high, *i.e.*, it corresponds to about 70% of all desorbed species for all three cases (Fig. 5b).

We find that desorption of  $H_2O$  and  $H_2$  is favourable for all cases (Fig. 5a). From the NEB calculations presented in the previous sections, we find that adsorbed  $H_2$  molecules easily split to H adatoms due to the low dissociation energy barrier, whereas adsorbed  $H_2O$  molecules prefer to desorb again rather than dissociate to OH and H surface species.<sup>50–52</sup> Consequently, the concentration of desorbed  $H_2O$  molecules increases in comparison to the concentration of desorbed  $H_2$ molecules. H adatoms originating from splitting  $H_2$  molecules may lead to etching of a growing cap/tube,<sup>54,55</sup> in addition to their contributions to the etching process of surface carbon species. Also,  $H_2O$  dissociative adsorption may contribute to removal of amorphous carbon from the cluster, improving



**Fig. 5** (a) Fractions of most common desorbed and etched species as well as (b) fractions of desorbed non-carbon (*i.e.*,  $H_mO_n$ ) and etched carbon species (*i.e.*,  $CH_mO_n$ ,  $C_2H_mO_n$  and  $C_{3+}H_mO_n$ ) during SWNT growth from  $C_xH_yO_z$  molecules.

defect-less tube growth.<sup>25,26</sup> However, we do not observe SWNT oxidation and subsequent SWNT damage caused by adsorbing  $H_2O$ , which is again in agreement with earlier experimental evidence.<sup>25</sup>

Besides non-carbon species, re-adsorption of etched carbon species (about 30% of all gas-phase species in Fig. 5b) can be responsible for two effects, *i.e.*, (1) enhancing the tube growth or (2) increasing topological defects or additional structures on the grown tube.<sup>56,57</sup> Fig. 4a shows that desorption of carbon monoxide occurs in all the feedstock cases, whereas desorption of ethylene molecules is only found in the ethanol-assisted SWNT growth. Here, the high desorption rate of CO and C<sub>2</sub>H<sub>4</sub> molecules in the CH<sub>2</sub>O and C<sub>2</sub>H<sub>6</sub>O cases, respectively, can be explained by the existence of the strong carbonyl (C=O) group in formaldehyde and the much weaker C-O linkage in ethanol molecules, respectively. The results show that the total amount of other etched species is also not minor, although their partial concentration is negligible: the ratio of  $CH_mO_n/C_2H_mO_n/$  $C_{3+}H_mO_n$  desorbed species is about 27/1/0, 8/27/0 and 16/3/5 (in %) for the CH<sub>2</sub>O, C<sub>2</sub>H<sub>6</sub>O and C<sub>13</sub>H<sub>24</sub>O<sub>11</sub> cases, respectively (Fig. 5b). Thus, the analysis of all carbon-containing species clarifies which etched carbon species have a high probability to contribute to SWNT nucleation and growth from  $C_x H_y O_z$ feedstocks.

#### **Carbon contributors**

We find three types of species contributing to the growing tube, *i.e.*, surface carbon species, dissolved carbon atoms and gasphase (previously etched) carbon species, as shown in Fig. 6a.

These contributors can directly transform to ring-related carbon atoms through their incorporation into the tube rim. Also, ring-C atoms can transform to these contributors again. Overall, these four carbon species can transform to other species during the growth process. In particular, surface C species subsequently convert or transform to all other carbon species, *i.e.*, dissolved, ring- and gas-phase C species, as a function of the feedstock type (Fig. 6b). The conversion to the dissolved and gas-phase species depends on the carbon index in the feedstock. In particular, the transformation to dissolved



Fig. 6 (a) Three types of carbon contributors during SWNT growth. Transformation of (b) surface carbon species, (c) dissolved carbon atoms, (d) gasphase (etched) carbon species and (e) ring-related carbon atoms to other carbon species. Each bar is an average of two (short and long relaxation after each reaction) simulation runs for the same feedstock.

C atoms increases with decreasing amount of C in the feedstock and this phenomenon can be explained by the dissociation/ etching rate of the feedstock or/and its fraction(s). In contrast, the conversion to gas-phase C species increases with increasing carbon amount in the feedstock. This phenomenon can be explained by the high re-hydroxylation and etching rates of the precursor(s). Obviously, both conversion/transformation rates indicate that there is a competition between hydroxylation/ etching of the remaining fraction(s) due to hydrogen/oxygen adatoms and dissociation/dissolution of the fraction(s) due to the catalyst. Also, the incorporation of both surface (Fig. 6b) and dissolved C species (Fig. 6c) to the carbon network or to the tube-end is related to the feedstock type, while these contributors mainly transform to each other. However, nearly all gasphase (etched) carbon species transform to surface C species for all feedstock cases (Fig. 6d). Also, the transformation of ring-C to surface C species is significant, although its contribution to dissolved C is also not negligible (Fig. 6e). Both transformations strongly depend on the amount of carbon atoms in the feedstock. Obviously, the surface C species are overall the main contributors to the CNT growth for all three C<sub>r</sub>H<sub>v</sub>O<sub>z</sub> feedstocks (see Table 1 in the ESI<sup>†</sup>). Regarding DFT calculation results,<sup>11</sup> we also suggest that dissolved carbon atoms (C1) favour change in the SWNT chirality, while surface C species  $(C_n)$  result in both chirality change and growth.

Despite the huge number of C–C association and dissociation reactions at the tube–catalyst interface, the amount of C atoms in the grown network linearly rises during the SWNT nucleation/growth (Fig. 4a, ring C). In the carbon network, the number of hexagons continuously increases, while the formation of pentagons and heptagons initially speeds up and subsequently their number remains constant during the growth (Fig. 4c). While the ring formation rates per adsorbed C atom for all feedstock cases are identical, the formation rate depends on the C sticking/incorporation rate (see the ESI,† Fig. 3b). Consequently, a high rate of hexagon formation due to carefully chosen feedstocks assures the growth of a less-defective tube with a certain diameter.<sup>58</sup>

#### Tube diameter vs. feedstock

We compare the effect of small (CH<sub>2</sub>O) and large (C<sub>13</sub>H<sub>24</sub>O<sub>11</sub>) feedstock molecules, which contain a similar C/H/O ratio (~1/2/1), resulting in two growth modes: "tangential", when the tube and nanoparticle diameters are identical ( $d_{\text{CNT}}/d_{\text{NP}} \approx 1$ ) (Fig. 7b), and "perpendicular", when the tube diameter is smaller than the nanoparticle diameter ( $d_{\text{CNT}}/d_{\text{NP}} < 0.8$ ) (Fig. 7c and d), respectively.

This feedstock effect was already reported by He and co-workers.<sup>16</sup> In their study, Fe-catalysed-SWNTs with narrow diameter were produced by using CO as the carbon source, while large-diameter SWNTs were produced by using CH<sub>4</sub>. They explained that CO based growth leads to a high amount of dissolved carbon, resulting in a tube that is narrower than the nanoparticle diameter, while CH4 yields less dissolved C in the nanoparticle and a large diameter tube.<sup>59</sup> In our results, the tube-nanoparticle ratio, however, seems not to significantly depend on the concentration of dissolved C in the liquefied nanoparticle, as shown in Fig. 7a. Instead, the figure clearly indicates that the C incorporation and the tube elongation (growth) rates are significantly changed when the  $d_{\text{CNT}}/d_{\text{NP}}$  ratio alters. While both feedstocks have the same C/H/O ratio, the carbon supply of the large feedstock allows a high C incorporation and thus results in fast tube growth with a narrow-diameter. In contrast, under low C incorporation, the wide-diameter tube grows slowly. Such growth behaviour is in agreement with recent in situ TEM observations. Zhang et al. observed a change of SWNT diameter as a function of the ratio between carbon supply  $(C_{supply})$  and carbon incorporation  $(C_{inc})$  rates and they found that necking and broadening of SWNTs occurs when  $C_{supply}/C_{inc} < 1$  and  $C_{supply}/C_{inc} > 1$ , respectively.<sup>60</sup> In particular,



**Fig. 7** (a) Dependence of the alloying of the Ni nanoparticles with dissolved C atoms (black lines with squares), the incorporation rate of C contributors to SWNT rims (red lines with circles) and the growth rate of SWNTs (blue lines with triangles) on the diameter ratio between the nanoparticles (nanocatalysts) and tubes ( $d_{\rm NT}/d_{\rm NP}$ ), grown from (b) CH<sub>2</sub>O and (c and d) C<sub>13</sub>H<sub>24</sub>O<sub>11</sub> feedstocks. The values of incorporation and growth rate are normalized. The first (b) and second (c) tubes both contain about 120 C atoms. The third tube (d) is an extended version of the second tube, which consists of about 360 C atoms. The black line indicates the surface of the virtual Al substrate.

they proposed two reasons for necking and subsequent cessation of SWNTs, *i.e.*, insufficient active carbon species (or fast carbon incorporation) and a certain amount of stress exerted at the tube–catalyst interface. Overall, it indicates that fast (or slow) carbon incorporation leads to SWNT growth with a narrow (or wide) diameter. This explanation completely corroborates our results in Fig. 7a: the carbon incorporation rate inversely depends on the  $d_{\rm NT}/d_{\rm NP}$  ratio. Besides, in the  $C_xH_yO_z$ case, this phenomenon is also observed in both  $C_x$  and  $C_xH_y$ feedstock cases (see Fig. 2 and 3 in the ESI<sup>†</sup>).

We also find that the incorporation of hydrogen or oxygen adatoms into the grown tube leads to an increase or reduction of the tube diameter. In particular, reactive hydrogen atoms can quickly impinge on a carbon sheet or a cap-end and reduce the sheet/cap-catalyst adhesion. Consequently, the carbon cap expands over the surface by shrinking its rim diameter such that the carbon sheet can partially cover the catalyst surface. Our previous studies revealed that such carbon nanosheets can even transform to free-standing single or parallel carbon sheets at low growth temperatures due to high H and lower C concentrations.<sup>23,24</sup> The appearance of such parallel carbon nanowalls<sup>23</sup> may explain the nucleation onset of multi-walled CNTs (MWNTs),<sup>24</sup> as earlier proposed by Hofmann and co-workers.<sup>5</sup> On the other hand, such transformations are less frequent in  $C_xH_yO_z$  based SWNT growth due to the oxygen scavenging of reactive hydrogen atoms.<sup>27</sup> As a result, the nucleation probability of CNTs with a low-wall-number or a narrow-diameter increases during the C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>-based growth.<sup>20,27</sup> This suggestion is supported by an experimental observation of the Fe-catalysed SWNT and double-walled CNT (DWNT) growth from  $C_x H_y O_z$  and  $C_x H_y$ 

feedstocks.<sup>20</sup> In particular, they found SWNT/DWNT population yields (in %) of about 92/8, 89/11 and 25/75 for ethanol (C<sub>2</sub>H<sub>6</sub>O), toluene (C7H8) and methane (CH4)-based CNT growth, respectively. Such a yield sequence is also compatible with the sequence of pyrolysis temperatures of these molecules, which are  $\sim 1025$  K,  $\sim$ 1050 K and  $\sim$ 1470 K, respectively. Our calculation results also agree with this evidence: a large  $(C_{13}H_{24}O_{11})$  feedstock with a low pyrolysis temperature ( $\sim 445$  K) yields narrow-diameter tubes (perpendicular mode) and a small (CH<sub>2</sub>O) feedstock with high pyrolysis temperature (2200-2650 K) results in large-diameter tubes (tangential mode). This indicates that the fast decomposition increases the carbon concentration and thus its incorporation rate. On the other hand, Wang and co-workers grew narrow- and widediameter tubes using CO and C<sub>2</sub>H<sub>2</sub> feedstocks, respectively, while the decomposition rate of C<sub>2</sub>H<sub>2</sub> is much higher than that of CO.<sup>15</sup> They thus concluded that the feedstock pressure is a key factor for chirality (diameter) control. Also, Lu et al. found that the diameters of SWNTs were closely related to the carbon feeding rate by selective activation of nanoparticles.19

In general, from our calculation results and available theoretical and experimental evidence,<sup>11,15–20,27,59,60</sup> we conclude that the tube diameter can be controlled by the incorporation rate of the aforementioned three carbon contributors. Besides the choice of catalyst, temperature and pressure, the choice of feedstock and associated growth precursors allows tuning of the formation of desirable carbon contributors due to competition between alloying catalysts and non-carbon etchant species, which can eventually steer the diameter and possibly chirality of SWNTs.

### Conclusion

The nucleation of incipient SWNTs from oxygen-containing hydrocarbon feedstocks is computationally studied for the first time. All simulation results are obtained using a combined MD/tfMC simulation technique. The overall results indicate that if we can control the formation of the three main carbon contributors, *i.e.*, dissolved C atoms, surface C species and gasphase (etched) C species, we can control the carbon incorporation into the rim of the growing cap/tube. Our results show that the appearance of these contributors is due to catalyst and etchant species, which result either completely or partially from the dissociation of the carbon feedstock. Therefore, the choice of the growth feedstock determines the competition between these processes, and allows preferable carbon species to be selectively incorporated into a growing tube, contributing to controlled SWNT quality (defect density) and radius.

## Conflicts of interest

There are no conflicts to declare.

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