NOVA

University of Newcastle Research Online

nova.newcastle.edu.au

Eveleens, Clothilde A.; Hijikata, Yuh; Irle, Stephan; Page, Alister J. 'Chiral-selective carbon nanotube etching with ammonia: a quantum chemical investigation'.
Published in the *Journal of Physical Chemistry C* Vol. 120, Issue 35, p. 19862-19870
(2016)

Available from: <http://dx.doi.org/10.1021/acs.jpcc.6b06997>

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Energy & Fuels*, copyright ©2016 American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <http://dx.doi.org/10.1021/acs.jpcc.6b06997>

Accessed from: <http://hdl.handle.net/1959.13/1344753>

Chirality-Selective Carbon Nanotube Etching with Ammonia: A Quantum Chemical Investigation

Clothilde A. Eveleens,¹ Yuh Hijikata,² Stephan Irle,² Alister J. Page^{1}*

¹Newcastle Institute for Energy and Resources, The University of Newcastle, Callaghan 2308,
Australia

²Institute of Transformative Bio-Molecules (WPI-ITbM) and Department of Chemistry, Graduate
School of Science, Nagoya University, Nagoya 464-8601, Japan

Abstract

Density functional theory is employed to demonstrate how ammonia-derived etchant radicals (H, NH, and NH₂) can be used to promote particular (n,m) chirality single-walled carbon nanotube (SWCNT) caps during chemical vapour deposition (CVD) growth. We reveal that the chemical reactivity of these etchant radical species with SWCNTs depends on the SWCNT chirality. This reactivity is determined by the extent of disruption to the π -conjugation of the cap structure caused by reaction with the etchant species. H and NH₂ attack single carbon atoms and preferentially react with near-zigzag SWCNT caps, whereas NH prefers to attack across C-C bonds and selectively etches near-armchair SWCNT caps. We derive a model for predicting abundances of (n,m) SWCNTs in the presence of ammonia-derived radicals, which is consistent with (n,m) distributions observed in recent CVD experiments using ferrocene and ammonia. This model also demonstrates that chiral-selective etching of SWCNTs during CVD growth can be potentially exploited for achieving chirality-control using standard CVD synthesis.

1. Introduction

A single-walled carbon nanotube (SWCNT) consists of a single graphene sheet rolled into a cylinder. The angle between the axis of the tube and the graphitic lattice vectors defines the chiral angle θ , and chiral indices (n,m) .¹ Chirality is the fundamental physical property of any SWCNT, because a SWCNT's electrical, optical and mechanical properties depend on chirality. Prospective SWCNT applications, such as chemical sensors,² field effect transistors³ and transparent metal electrodes,⁴⁻⁵ ideally require the selective synthesis of particular (n,m) SWCNTs. Despite intense efforts, a technique capable of such “chirality-controlled” growth, capable of producing arbitrary (n,m) SWCNTs on a commercial/industrial scale, remains elusive.

Much of the progress made in gaining chirality controlled SWCNT growth has been made with traditional chemical vapour deposition (CVD). CVD sample distributions can be biased by changing the carbon source, temperature, catalyst support and most successfully, the type of catalyst. Notably, FeCoMo catalysts in alcohol CVD produce predominantly (6,5) and (7,5) SWCNTs.⁶ Most recently a solid-phase WCo catalyst was used to produce 92% (12,6) SWCNTs.⁷ Such solid-phase catalysts exploit epitaxy between the graphitic and crystalline catalyst facet and in order to selectively produce particular (n,m) SWCNTs. This is consistent with reports using “traditional” transition metal catalysts that demonstrated lower temperatures yielded narrower (n,m) distributions. Typically, low temperature CVD experiments produce near-armchair SWCNTs in high abundance,⁸⁻⁹ which can be conveniently be explained in terms of screw-dislocation growth models.¹⁰⁻¹¹

A number of alternative strategies for SWCNT chirality-control have also been reported. Liu *et al.*¹² successfully synthesized semiconducting (7,6), (6,5), and metallic (7,7) nanotubes from chirality-pure SWCNTs seeds using catalyst-free vapor phase epitaxy (VPE).¹² VPE has since been

used to grow (9,1), (8,3), (10,2), and (6,6) SWCNTs.¹³ However, yields are restricted, as are the range of chirality-pure seeds available for this technique. Significant effort has also gone into synthesizing SWCNTs from the bottom-up using precursor templates such as ‘nanorings’ that correspond to the desired SWCNT chiral structure,¹⁴ or hemispherical polyarenes that are comparable to SWCNT caps.¹⁵ The rationale behind these methods is that many SWCNTs with different diameters and sidewall structures could be accessed by using different templates. Elongating and growing structures from templates remains an ongoing challenge.

In contrast, the addition of etchant gases, such as H₂, O₂, and CO₂, to the CVD feedstock has largely been overlooked as a tool for influencing chirality distributions of CVD-grown SWCNTs. Indeed, this is not their intended function; the reason for their addition is so that amorphous carbon is removed (or etched) from the catalyst surface, improving catalyst lifetime and thus CVD efficiency. However, the presence of etchants has been shown to influence the distribution of (n,m) SWCNTs produced during CVD. For example, using small amounts of NH₃ Zhu *et al.*¹⁶ were able to shift the chiral angle distribution such that 90% of SWCNTs exhibited a chiral angle between 20-30°. The addition of thiophene to the CVD feedstock gas has also been shown to favour the growth of (9,8) chirality SWCNTs, although it is unclear if this is achieved via an etching mechanism, or thiophene blocking active sites on the catalyst surface.¹⁷ Zhou *et al.*¹⁸ produced 97% semiconducting SWCNTs by adding H₂O to their CVD growth, and this preference was attributed to the difference in reactivity and ionization potential between metallic and semiconducting tubes.

To our knowledge, no mechanism explaining this phenomenon has yet been proposed. It is likely that etchants such as ammonia influence a number of mechanistic aspects of SWCNT growth, the net result of which is a change in the (n, m) chirality distribution. These aspects could include

feedstock adsorption and decomposition pathways, the alteration of catalyst size distributions, catalyst activation/deactivation through the formation of stable nitride phases, and the direct etching of nucleated SWCNT caps. A previous study has demonstrated that nucleated (n, m) SWCNT caps exhibit chirality-dependent chemical reactivity on Ni nanoparticles.¹⁹ On this basis, we hypothesise that chirality-dependent reactivity of SWCNT caps is a key component of chirality-selective etching, *i.e.* the selective destruction of particular (n, m) SWCNTs by chemical etchants during growth, leading to chirality-selective growth.

To verify this hypothesis, and following the experiments of Zhu *et al.*,¹⁶ we use density functional theory (DFT) to investigate the chemical reactivity of different (n,m) SWCNTs with NH_3 based radical species (NH_2 , NH and H). We demonstrate that particular (n,m) SWCNT chiralities are intrinsically more reactive than others (*i.e.* in the absence of a catalyst nanoparticle), and reveal why this is the case. We also derive a model to predict abundances of (n,m) SWCNTs during CVD growth, as a function of the etchant composition, and demonstrate that (n, m) -dependent SWCNT cap reactivity is an important component of the chirality-selective etching process.

2. Computational Details

2.1. Model Systems

Our hypothesis regarding chiral selective etching is that particular (n,m) SWCNTs are intrinsically more reactive with chemical etchants such as NH_3 and NH_3 -based radical species (NH_2 , NH and H). We note that considering atomic hydrogen in this context also enables us to comment on the role of atomic hydrogen produced during catalytic CVD of hydrocarbon feedstock,²⁰⁻²⁴ and the role of H_2 as an additive, used extensively in SWCNT growth.²⁵⁻²⁷ We test

this hypothesis using model SWCNT caps; caps are chosen here, as opposed to extended SWCNT structures, since they are more reactive due to their higher structural curvature.²⁸⁻²⁹ Hence, the most likely stage during growth for a SWCNT to be etched and destroyed is immediately after, or during, nucleation. A number of previous theoretical investigations have considered the reactivity of SWCNT cap edges, both with^{19, 30-31} and without³²⁻³⁴ catalyst nanoparticles. However, we know of no study concerning the reactivity between a SWCNT cap and nitrogenous radicals. We consider caps with $0^\circ \leq \theta \leq 30^\circ$ (*viz.* (5,5), (6,5), (7,4), (8,3), (9,2), (10,1) and (11,0) caps), shown in Figure 1. The diameters of these caps are $\sim 0.7 - 0.8$ nm, which is at the low end of SWCNT diameters obtained in transition-metal CVD growth experiments.^{9, 35-36} However, a previous work³⁷ has demonstrated that trends in reactivity are largely invariant to tube diameter, which enables us to employ smaller model systems without sacrificing accuracy. While there is a slight variation in diameters here, this variation is as small as possible for (n,m) SWCNTs for which $n + m$ is constant. Thus, potential diameter effects are negated here as much as possible. We do not include a catalyst interface in our model system. This simplification follows a number of recent investigations, which show that reactivity of SWCNT edges is an intrinsic property of the SWCNT structure, and not necessarily the SWCNT-catalyst interface³⁸⁻⁴¹ (the influence of the SWCNT-catalyst interface on etching processes is the subject of ongoing investigation in our research groups and will be reported elsewhere). We note that our series of caps includes the (6,5) SWCNT, which has been produced in high abundance in CVD experiments,^{6, 8, 42} as have near arm-chair $(n, n-1)$ SWCNTs.⁴³ All SWCNT cap structures were generated using the NanoCap software package⁴⁴ and obey the isolated pentagon rule, with each cap including six pentagons.

Figure 1. B3LYP/6-31G(d)-optimized (5,5), (6,5), (7,4), (8,3), (9,2), (10,1) and (11,0) SWCNT cap structures. All caps are hydrogen terminated. Diameters (nm) are shown in italics.

2.2. Quantum Chemical Methods

DFT geometry optimizations were performed using the B3LYP⁴⁵⁻⁴⁷ exchange correlation functional with a 6-31G(d) basis set. Adsorption energies between the cap and the etchant species (X = NH₂, NH and H) were calculated using,

$$\Delta E = E_{cap-X} - (E_{cap} + E_X) \quad (1)$$

which is defined as the energy difference between an optimized cap-X structure (E_{cap-X}) and the sum of the individual cap (E_{cap}) and etchant (E_X) energies. H and NH₂ groups were added directly to individual carbon atoms, while NH groups were added across C-C bonds (since direct addition to individual carbon atoms does not yield a local minimum in this case). All cap and cap-X structures were optimised in the lowest spin state. Gibbs free energies of reaction was calculated based on the harmonic approximation between 600 - 1500 K using B3LYP/6-31G(d), as CVD SWCNT growth is typically conducted within this temperature range. All geometry optimizations and frequency calculations were performed using the Gaussian09 package.⁴⁸

3. Results and Discussion

3.1. Chemical Reactivity of (n, m) SWCNT Caps

We begin our discussion by considering H adsorption on (n, m) SWCNT caps. H adsorption energies at each adsorption site, for all (n, m) caps, are shown in Figures 1 and 2. As anticipated, all calculated adsorption energies (ΔE) were exothermic, and thus thermodynamically favourable.

Adsorption energies values ranged from -349 kJmol^{-1} (for the $(9,2)$ cap) to -21 kJmol^{-1} (for the $(10,1)$ cap). The $(10,1)$ cap had the largest variation between the least- and most-reactive sites, for those caps considered here. This variation in reactivity systematically decreased from near-zigzag to near-armchair caps (Figure 2), indicating a decrease in reactive selectivity from zigzag ($\theta = 0^\circ$) through to armchair ($\theta = 30^\circ$) SWCNTs. The single exception to this trend is the $(11,0)$ cap. However, the variation in reactivity for the $(11,0)$ cap is only $\sim 10 \text{ kJmol}^{-1}$ smaller than the $(10,1)$, which is considered not to be significant here.

Figure 2. (a) B3LYP/6-31G(d) adsorption energies (kJmol^{-1}) of H, on $(5,5)$, $(6,5)$, $(7,4)$, $(8,3)$, $(9,2)$, $(10,1)$ and $(11,0)$ SWCNT cap structures as a function of reaction position on the cap structure. (b) Adsorption energies at all reaction positions on each (n, m) SWCNT cap, average reactivity is marked in black ($\times$), and the maximum reactivity is marked in red ($\times$). Chiral angles for each (n, m) SWCNT are also given.

Comparing the largest adsorption energies of each cap, (9,2) was the most reactive and (5,5) was the least (Figure 2). The maximum cap - H adsorption energies increased as the chiral angle decreased from 30°, peaking at (9,2) after which it moderately decreased again towards 0°. The average adsorption energy (Figure 2) was generally comparable across the range of chiral angles considered here and between -197-159 kJmol⁻¹. The most reactive carbon atoms were located at the edge of the cap structure in all cases, except for the (5,5) armchair cap; here the most reactive sites were the carbon atoms that form the sole pentagon at the cap apex. More generally, for all (*n*, *m*) cap structures, pentagon carbon atoms were more reactive than hexagon carbon atoms. We will discuss the origins of this reactivity at greater length below.

To simulate the potential influence of SWCNT growth on these adsorption energetics, we have also considered adsorption using extended cap structures shown in Figure S1 (i.e. those caps shown in Figure S1, with an added layer of hexagons at the cap edge). As shown in Figure S1 the magnitude of the average H reactivity decreased to values between -182 and -140 kJmol⁻¹. For the (11,0) zigzag cap, a small number of reactions were slightly endothermic, by 0.5 kJ mol⁻¹. Most importantly, the location of the most and least reactive sites remained the same, for all (*n*,*m*) chiralities.

In general, NH₂ reactivity on these (*n*, *m*) cap structures is analogous H reactivity. Adsorption energies for radical NH₂ on (5,5), (6,5), (7,4), (8,3), (9,2), (10,1) and (11,0) cap structures are presented in Figure 3. As expected, overall, NH₂ is a weaker etchant (i.e. NH₂ reactivities are less exothermic) than H with average adsorption energies ranging between -107-90 kJmol⁻¹. Adsorption energies ranged between -264 kJmol⁻¹ (for the (9,2)) and 11 kJmol⁻¹ (for the (10,1)). As for H, the most and least reactive sites for NH₂ were found along the cap edge, except for the (5,5) cap for which the cap apex proved most reactive. This trend correlates with the π-orbital axis

vector (POAV) in this region of the cap structure. Similarly, the variation of NH_2 reactivities decreased from near-zigzag to near-armchair caps, with (10,1) exhibiting the greatest variation in reactivity, and (5,5) the smallest.

Figure 3. (a) B3LYP/6-31G(d) adsorption energies (kJmol^{-1}) of NH_2 on (5,5), (6,5), (7,4), (8,3), (9,2), (10,1) and (11,0) SWCNT cap structures as a function of reaction position on the cap structure. (b) Adsorption energies at all reaction positions on each (n,m) SWCNT cap, average reactivity is marked in black ($\times$), and the maximum reactivity is marked in red ($\times$). Chiral angles for each (n, m) SWCNT are also given.

Figure 4. (a) B3LYP/6-31G(d) adsorption energies (kJmol^{-1}) of NH on (5,5), (6,5), (7,4), (8,3), (9,2), (10,1) and (11,0) SWCNT cap structures as a function of reaction position on the cap structure. (b) Adsorption energies at all reaction positions on each (n,m) SWCNT cap, average reactivity is marked in black ($\times$), and the maximum reactivity is marked in red ($\times$). Chiral angles for each (n, m) SWCNT are also given.

Based on the maximum cap - etchant adsorption energies, these results suggest that (9,2) cap structures would be etched preferentially with both H and NH₂ species on a thermodynamic basis. We elucidate further the ramification of this result regarding SWCNT populations observed during growth below.

Reactivities between NH and SWCNT cap structures are illustrated in Figure 4. This figure shows that, of the three reactive etchant species considered, NH is the most reactive (as anticipated, as it forms two bonds with the SWCNT cap). NH reactivities span -626 kJmol⁻¹ (for (5,5)) to -297 kJmol⁻¹ (for (11,0)). NH reactivity generally decreases from armchair (most reactive) to zigzag (least reactive). However, while variations in reactivities for H and NH₂ consistently decreased between near-zigzag and armchair caps, no clear trend in the variation in NH reactivity is observed. As shown in Figure 4 the smallest variation is observed for the (5,5) cap, whereas the largest variation is observed for (7,4). In contrast to H and NH₂, these results indicate that NH would preferentially etch away armchair and near-armchair SWCNTs, over near-zigzag and chiral SWCNTs, during the growth process.

The nature of the cap - NH interaction is fundamentally different to the cap - H and cap - NH₂ interactions. As NH is isoelectronic with atomic oxygen, its interaction with extended sp² carbon structures, such as SWCNTs and graphene flakes is based on the C-C bond, rather than individual carbon atoms.⁴⁹⁻⁵⁰ NH chemisorbs across C-C bonds in the cap, either breaking the bond in the process (akin to an ether in the case of atomic oxygen), or forming an aziridine-like structure (akin to an epoxide structure in the case of atomic oxygen). The former C-C bond cleavage reaction is the most exothermic (-361 to -626 kJmol⁻¹), and is observed exclusively around the cap edge at armchair sites. On the other hand aziridine-like structures are formed away from the edge and are generally less exothermic (-297 to -497 kJmol⁻¹). This is consistent with previous reports,⁴⁹⁻⁵⁰ and

is explained via two factors. Firstly, the armchair-site C-C bonds have greater freedom to be deformed and broken, releasing more strain energy in the process. Secondly, the cleavage of these C-C bonds leads to a C-N-C structural unit that retains sp^2 character, stabilising it energetically.

3.2. Factors Determining SWCNT Cap Reactivity

The reactivity of sp^2 -hybridized carbon structures such as SWCNTs and graphene is commonly explained in terms of aromaticity and π -conjugation, which can be quantified by an energy decomposition analysis (EDA).⁴⁹⁻⁵¹ For this analysis ΔE can be decomposed as follows;

$$\Delta E = E_{\text{def}} + E_{\text{int}} \quad (2)$$

where E_{def} (deformation energy) is the energy of the etchant and the cap at the optimized geometry of the complex separated by an infinite distance, relative to the energy of the cap and etchant at their respective optimized geometries (i.e. the energy required to deform the cap structure to the etchant-adsorbed cap structure), and E_{int} (interaction energy) is the interaction energy between the deformed cap and etchant (i.e. $E_{\text{int}} = \Delta E - E_{\text{def}}$).

For H and NH_2 , and all (n,m) caps considered here, the adsorption energy is directly proportional to E_{int} whereas there is little to no correlation with E_{def} . This is shown for the (6,5) cap in Figure 5(a) and (b). The relationship between ΔE , E_{def} and E_{int} for all other caps is shown in Figure S4.

Reactivity here (ΔE) correlates directly with E_{int} , rather than E_{def} , and this is consistent with previous reports of other, sp^2 hybridized carbon structures.⁴⁹⁻⁵¹ This dependence on E_{int} arises from the disruption to the π -conjugated molecular orbital structure of the SWCNT cap by the etchant.

In turn this leads to a loss of aromaticity, destabilizing the electronic structure, and an increasing reactivity. The only exceptions to the correlated trend between ΔE and E_{int} are observed for a handful of structures observed for the (9,2), (10,1) and (11,0) caps with NH_2 , in which reaction between the cap edge and NH_2 led to the zigzag edge locally deforming into a structure including a C_3 trigonal ring (Figure S5). This structural motif has a high degree of ring strain, and therefore an unusually high energy.

Figure 5. Correlation between ΔE , E_{def} (x) and E_{int} (♦) (equation (2)) for reaction for the (6,5) SWCNT cap with (a) H, (b) NH_2 and (c) NH etchants. In (c), reaction between NH and the SWCNT cap leads to two distinct data series corresponding to C-C cleaved and aziridine-like structures.

Two distinct groups of E_{int} and E_{def} values are observed for NH (Figure 5(c)). Both series show a clear linear correlation between ΔE and E_{int} . In contrast to H and NH_2 , there is also a weak linear correlation between ΔE and E_{def} for NH. This reflects the fundamentally different nature of the interaction between NH and the SWCNT cap, compared to both H and NH_2 (i.e. H/ NH_2 adsorb directly to individual carbon atoms in the SWCNT cap, whereas NH adds across C-C bonds). The two distinct data series arise from the two different types of functionalized product structures obtained with NH, i.e. C-C cleaved or aziridine-like structures. The C-C cleaved structures correspond to E_{int} values between ~ -970 to -550 kJmol^{-1} and E_{def} values between $\sim +100$ to $+430 \text{ kJmol}^{-1}$. The aziridine-like structures correspond to E_{int} values between ~ -440 to -600 kJmol^{-1} and E_{def} values between $\sim +70$ to $+120 \text{ kJmol}^{-1}$. The lower E_{def} for the aziridine like structure is consistent with the smaller deformation to the SWCNT cap in this case, since the C-C bond remains intact.

On a number of previous occasions,^{28, 52-54} reactivity of planar and curved sp^2 carbon structures, such as SWCNTs, has been rationalized on the basis of the π -orbital axis vector (POAV) pyramidalization angle, θ_{p} .^{28, 55} For a sp^2 hybridized carbon atom, the POAV is defined as the vector which makes equal angles to the atom's three σ -bonds. θ_{p} is the difference between the POAV and 90° , meaning that sp^2 hybridized carbons (preferring to be planar) have $\theta_{\text{p}} = 0^\circ$ whereas sp^3 hybridized carbons have $\theta_{\text{p}} = 19.5^\circ$. For any sp^2 hybridized carbon, addition of curvature leads to a loss of spatial overlap of the p-orbitals and a shift in hybridization from sp^2 to an intermediate between sp^2 and sp^3 .^{28, 52} This re-hybridization places strain on the carbon frame and affects the π -orbital alignment.⁵⁶ Thus, the POAV provides a numerical measure of this alignment. SWCNTs

are preferentially reactive at their caps and defect sites, rather than pristine sidewalls, and this has been ascribed to the higher curvature and larger θ_P values in these regions of the SWCNT structure.^{28, 52}

For the (n,m) cap structures considered here, no obvious correlation is observed between the POAV and the reactivities with H, NH or NH₂. This is evident from Figure S6, which depicts ΔE as a function of POAV for each individual cap / etchant. While this is contradictory to previous reports,^{28, 52} we note that POAV is simply a measure of geometrical distortion, and does not describe explicitly the electronic phenomena responsible for reactivity (in this case π conjugation in the cap structure). Thus, while there can be a correlation between POAV and chemical reactivity, this correlation is not guaranteed in principle. With regards to (n,m) SWCNT caps, at least with the chemical specie considered here, the key factor determining reactivity is E_{int} , and not geometrical strain (as measured by POAV).

Previous studies have also correlated reactivity of SWCNTs and SWCNT caps with the molecular orbital structure of the tube, and the local density of states (DOS).^{30, 57} For instance, the higher reactivity of metallic SWCNTs (compared to semiconducting SWCNTs) has been attributed to their larger DOS in the conduction band near the Fermi level.^{54, 58-59} It follows that SWCNT cap structures with smaller HOMO-LUMO gaps should be more reactive. However, this is not necessarily the case. For example, the HOMO-LUMO gap (provided in square brackets in units of kJ mol⁻¹) increases in the order (11,0) [81.3] < (6,5) [100.7] < (9,2) [106.9] < (10,1) [109.6] < (7,4) [114.1] < (8,3) [114.4] < (5,5) [286.9]. According to this sequence, the (11,0) cap (i.e. that with the smallest HOMO-LUMO gap) should be the most reactive, yet this is not observed. Instead, the (9,2) cap is the most reactive for H and NH₂, whereas the (5,5) cap is most reactive for NH. *In*

all cases, the most reactive site is found at the cap edge. A previous study also found that SWCNT cap edges exhibit a greater local DOS, leading to enhanced reactivity in this region of the cap.³⁰ Thus, for SWCNT caps (as opposed to extended tube structures, or planar graphene sheets), while the HOMO-LUMO gap is a contributing factor to determining reactivity, it is evidently overpowered in most cases by the energy associated with the deformation of the SWCNT cap edge. We note though that this trend confirms that, in general, SWCNTs with higher chiral angles are more stable than small chiral angles.⁵⁸

Thus, to summarise, the reactivity between H, NH and NH₂ with SWCNT cap structures is not determined exclusively by single factor. Rather, a combination of factors influences this reactivity, however our energy decomposition analysis indicates that E_{int} is the dominant influence.

3.3. Chirality-Dependent SWCNT Etching with Ammonia

Previous experiments have shown that NH₃ decomposes both pyrolytically and catalytically (on iron, nickel and tungsten), producing NH₂, NH and H.⁶⁰⁻⁶⁵ It is reasonable then to presume that these radical intermediates will be present during CVD growth with NH₃, albeit with a limited lifetime. Given the reactive selectivity of NH₂, NH and H for certain (n,m) SWCNTs established above, we now investigate whether the concentrations of NH₂, NH and H present in the CVD feedstock can alter the abundance of individual (n, m) SWCNTs *via* selective etching.

We begin by considering how the populations of individual (n, m) SWCNTs are influenced by the H:NH, H:NH₂ and NH:NH₂ radical ratios. We do not consider non-radical NH₃ itself here as a chemical etchant, due to its relatively low reactivity. At an arbitrary temperature, the abundance ($P_{(n,m)}$) of an (n,m) SWCNT is defined as,

$$P_{(n,m)} = x_{E1}P_{E1} + x_{E2}P_{E2} \quad (3)$$

where x_{E1} and x_{E2} are the mole fractions of etchants E1 and E2 (i.e. $x_{E1} + x_{E2}=1$), and P_{E1} and P_{E2} are the relative abundances of the (n,m) SWCNT when $x_{E1} = 1$, and $x_{E2} = 1$, respectively. The abundances are calculated here *via* an inverse Boltzmann distribution at temperature T ,

$$P_{Ei} = \frac{\exp\left(\frac{\Delta_{\text{rxn}}G}{kT}\right)}{\sum \exp\left(\frac{\Delta_{\text{rxn}}G}{kT}\right)} \quad (4)$$

where $\Delta_{\text{rxn}}G$ is the Gibbs free energy of reaction [$\Delta_{\text{rxn}}G = \sum(\Delta G)_{\text{products}} - \sum(\Delta G)_{\text{reactants}}$]. ΔG here are calculated for individual products (etchant-adsorbed cap structures) and the reactants (constituent caps and etchant) with free energy corrections calculated within the harmonic approximation. For all (n, m) SWCNTs, P_{Ei} values are calculated in the thermodynamic limit, i.e. by considering only the most reactive cap sites, discussed above. This assumption is made to simplify analysis. However, it is validated by the sensitivity of Boltzmann populations P_{Ei} , which vary significantly even for very small differences in ΔG (e.g. 1-10 kJ mol⁻¹). Considering that the differences between $\Delta_{\text{rxn}}G$ for the most reactive cap sites, and other cap sites, are much larger by comparison (e.g. > 20 kJ mol⁻¹), the probability of these reactions are such that they would yield a negligible difference to the results presented below. Established models for growth based on CNT-catalyst edge energetics propose there is a kinetic preference for chiral SWCNTs, especially at lower temperatures.¹¹ We therefore exclude the achiral (5,5) and (11,0) SWCNTs from our abundance model, considering the significant thermodynamic and kinetic barriers that impede their growth.^{6, 9}

Calculated abundances for the (6,5), (7,4), (8,3), (9,2), (10,1) SWCNTs, based on cap reactivity with NH₂, NH and H, are presented in Figure 6. We consider here only a single reaction

temperature of 1000 K, because trends in calculated abundances are largely invariant to the temperature applied (see Figure S8). Figure 6(a) and (b) show that similar (n, m) abundances are obtained with variable $\text{NH}:\text{NH}_2$ and $\text{H}:\text{NH}$ ratios at 1,000 K. This reflects the fact that the mechanism of interaction between the cap and H/NH_2 are both similar, and different from the $\text{cap}-\text{NH}$ interaction, as discussed above. When NH is the only active etching species, $\sim 88\%$ of SWCNTs produced are $(10,1)$. Conversely, when NH_2 and H are the lone etchants, $(6,5)$ SWCNTs dominate, with abundances of $\sim 55\%$ and $\sim 70\%$, respectively. Pure NH_2 and H also yield broader (n, m) abundance distributions as well, with $(7,4)$ and $(8,3)$ SWCNTs also having appreciable abundances. This analysis indicates that, of NH_2 , NH and H , NH is by far the most selective reactive etchant species. As both $\text{NH}:\text{NH}_2$ and $\text{H}:\text{NH}$ ratios vary, the $(9,2)$ SWCNT abundance remains at $\sim 0\%$, and decreases with increasing NH_2/H mole fraction. We note here however that at higher temperatures (Figure S9) $(9, 2)$ abundances increase slightly, but remain below 10% at 1,500 K. The low abundance of the $(9, 2)$ SWCNT here is because it exhibited the greatest reactivity with H and NH_2 , discussed above, meaning that it is the most likely to be etched away during nucleation and growth.

The effect of a variable $\text{H}:\text{NH}_2$ ratio on (n, m) SWCNT abundances is detailed in Figure 6(c). It is immediate from Figure 6(c) that $(6,5)$ SWCNTs are the most abundant, and this is largely independent of the $\text{H}:\text{NH}_2$ ratio. Similarly, $(10,1)$ SWCNTs exhibit abundances $< 10\%$, and this is also independent of the $\text{H}:\text{NH}_2$ ratio. For the $(8,3)$ and $(7,4)$ SWCNTs, abundances are relatively low ($\sim 10 - 20\%$) and comparable across the range of $\text{H}:\text{NH}_2$ ratios. However, as a lone etchant, H is more selective in promoting $(7,4)$ and $(6,5)$ SWCNT growth, compared to NH_2 . Conversely, NH_2 is more selective for producing $(8, 3)$ SWCNTs, compared to H . When the $\text{H}:\text{NH}_2$ mole fractions are both $\sim 50\%$, Figure 6(c) shows that the abundances of $(8,3)$ and $(7,4)$ SWCNTs is

likely to be approximately the same. As observed in Figure 6(a) and (b), the abundances of the (9,2) SWCNT remains $\sim 0\%$ in all cases here. H and NH_2 have a similar effect on the (n,m) abundances in the presence of NH, while H has a stronger effect than NH_2 in the mixture of H and NH_2 .

Figure 6. Abundances of chiral (6,5), (7,4), (8,3), (9,2), (10,1) SWCNTs as a function of variable (a) NH:NH₂ (b) NH:H and (c) H:NH₂ ratios at 1,000 K.

Previous experiments¹⁶ demonstrated that the addition of NH₃ to the feedstock gas during CVD growth on iron catalysts lead to the promotion of near arm-chair SWCNT chiralities, and greater chiral angle selectivity. For instance, by adding NH₃ the distribution in chiral angles was reduced such that 50% of SWCNTs exhibited a chiral angle between 27-29°. This was consistent with a marked increase in abundances for (12,11) and (13,12) SWCNTs in particular, and a decrease in the abundances of chiral SWCNTs (e.g. $\sim(n, n/2)$ and $\sim(n, n/3)$ SWCNTs) and near-zigzag SWCNTs. According to the results presented here, the change in chiral angle distribution is consistent with an NH₂/H-rich CVD atmosphere. However, our results do not preclude other potentially important phenomena (e.g. the alteration of CVD chemical pathways and size-dependent catalyst activation/deactivation by nitrogenous species) playing a role. Such an NH₂/H-rich atmosphere could be reasonably expected, considering that decomposition of NH₃ ($\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$) is more likely than decomposition of NH₂ ($\text{NH}_2 \rightarrow \text{NH} + \text{H}$). Our results presented here demonstrate that NH₂ and H etchant species can selectively remove $(n, n/2)$ and $(n, n/3)$ SWCNTs (i.e. (8,3), (7,4)) and near-zigzag SWCNTs (i.e. (10,1)), while simultaneously promoting the abundance of near-armchair SWCNTs (i.e. (6,5)). This would not be the case if NH were the predominant etchant species present. In this case, near zigzag SWCNTs would be produced in greatest abundance (Figure 6(a), (b)). Our results therefore suggest that chirality-selective etching is a potentially viable, but as yet largely unexplored, route towards chirality-controlled SWCNT growth. Our results also show that the direct etching of nucleated SWCNT caps by etchant species, at least in the case of ammonia-derived radicals, is a key component of this process.

Conclusions

We have presented the first DFT calculations showing the trends in and origins of chemical reactivity for (n, m) SWCNT caps with ammonia-based radicals. (6,5), (7,4), (8,3), (9,2), (10,1) and (11,0) SWCNT caps are most reactive towards H, NH and NH₂ at their end-edge, and (5,5) at its tip. Reactivity is primarily determined by disruption to the π -conjugation of the cap by the etchant. Predictive (n, m) distributions calculated using the most reactive cap sites as a basis show that NH₂ and H both selectively etch near-zigzag chiral SWCNTs. This similarity is reflected in the way they interact with single C atoms of the cap structures. Conversely, NH adds across the C-C bonds of the cap structure, and preferentially etches near-armchair SWCNTs.

It has previously been shown that the addition of ammonia during CVD changes the (n, m) SWCNT distributions towards larger diameters and higher chiral angles. According to our results, this is consistent with having a high concentration of NH₂ and H in the CVD atmosphere. However, our results do not discount other potentially important phenomena (e.g. alteration of CVD chemical pathways by nitrogenous radicals, and catalyst activation/deactivation by nitrogenous species). The influence of these phenomena on chirality-selective etching remains unknown, and is currently being investigated within our research groups. Nevertheless, the results presented here demonstrate that fine-tuning the etchant composition during SWCNT growth is an important aspect of achieving chiral-selectivity via etchant addition.

Acknowledgement

AJP and SI acknowledge support from the Australian Research Council (ARC DP140102894) and the Japan Society for the Promotion of Science (Open Partnership 13039901-000174). This work was in part supported by two CREST (Core Research for Evolutional Science and

Technology) grants to SI from JST. SI and AJP acknowledge support by the JSPS Sakura program for bilateral researcher exchange. The authors are grateful for generous supercomputing grants from The National Computational Infrastructure (NCI) National Facility and INTERSECT, Australia.

Supporting Information

Full details of references 7, 42, 48; B3LYP/6-31G(d) adsorption energies of NH₂, NH and H on all (*n,m*) cap structures; EDA analysis for all functionalised (*n,m*) cap structures; POAV analysis of all functionalised (*n,m*) cap structures; spin density analysis of all functionalised (*n,m*) cap structures; calculated abundances of all (*n,m*) SWCNTs with variable NH:NH₂, NH:H and H:NH₂ ratios at temperatures between 600 - 1,500 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Corresponding Author

*alister.page@newcastle.edu.au

References

1. Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C., *Science of Fullerenes and Carbon Nanotubes*. Academic Press, Inc.: 1996.
2. Kong, J.; Franklin, N. R.; Zhou, C. W.; Chapline, M. G.; Peng, S.; Cho, K. J.; Dai, H. J., Nanotube Molecular Wires as Chemical Sensors. *Science* **2000**, 287, 622-625.
3. Artukovic, E.; Kaempgen, M.; Hecht, D. S.; Roth, S.; Gruner, G., Transparent and Flexible Carbon Nanotube Transistors. *Nano Lett.* **2005**, 5, 757-760.

4. Zhang, M.; Fang, S. L.; Zakhidov, A. A.; Lee, S. B.; Aliev, A. E.; Williams, C. D.; Atkinson, K. R.; Baughman, R. H., Strong, Transparent, Multifunctional, Carbon Nanotube Sheets. *Science* **2005**, *309*, 1215-1219.
5. Zhang, D. H.; Ryu, K.; Liu, X. L.; Polikarpov, E.; Ly, J.; Tompson, M. E.; Zhou, C. W., Transparent, Conductive, and Flexible Carbon Nanotube Films and Their Application in Organic Light-Emitting Diodes. *Nano Lett.* **2006**, *6*, 1880-1886.
6. Miyauchi, Y. H.; Chiashi, S. H.; Murakami, Y.; Hayashida, Y.; Maruyama, S., Fluorescence Spectroscopy of Single-Walled Carbon Nanotubes Synthesized from Alcohol. *Chem. Phys. Lett.* **2004**, *387*, 198-203.
7. Yang, F.; Wang, X.; Zhang, D.; Yang, J.; Luo, D.; Xu, Z.; Wei, J.; Wang, J. Q.; Xu, Z.; Peng, F. et al., Chirality-Specific Growth of Single-Walled Carbon Nanotubes on Solid Alloy Catalysts. *Nature* **2014**, *510*, 522-4.
8. Lolli, G.; Zhang, L. A.; Balzano, L.; Sakulchaicharoen, N.; Tan, Y. Q.; Resasco, D. E., Tailoring (n,m) Structure of Single-Walled Carbon Nanotubes by Modifying Reaction Conditions and the Nature of the Support of Como Catalysts. *J. Phys. Chem. B* **2006**, *110*, 2108-2115.
9. Bachilo, S. M.; Balzano, L.; Herrera, J. E.; Pompeo, F.; Resasco, D. E.; Weisman, R. B., Narrow (n,m)-Distribution of Single-Walled Carbon Nanotubes Grown Using a Solid Supported Catalyst. *J. Am. Chem. Soc.* **2003**, *125*, 11186-11187.
10. Ding, F.; Harutyunyan, A. R.; Yakobson, B. I., Dislocation Theory of Chirality-Controlled Nanotube Growth. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 2506-2509.
11. Artyukhov, V. I.; Penev, E. S.; Yakobson, B. I., Why Nanotubes Grow Chiral. *Nature Commun.* **2014**, *5*.
12. Liu, J.; Wang, C.; Tu, X. M.; Liu, B. L.; Chen, L.; Zheng, M.; Zhou, C. W., Chirality-Controlled Synthesis of Single-Wall Carbon Nanotubes Using Vapour-Phase Epitaxy. *Nature Commun.* **2012**, *3*.
13. Liu, B. L.; Liu, J.; Tu, X. M.; Zhang, J. L.; Zheng, M.; Zhou, C. W., Chirality-Dependent Vapor-Phase Epitaxial Growth and Termination of Single-Wall Carbon Nanotubes. *Nano Lett.* **2013**, *13*, 4416-4421.
14. Omachi, H.; Segawa, Y.; Itami, K., Synthesis of Cycloparaphenylenes and Related Carbon Nanorings: A Step toward the Controlled Synthesis of Carbon Nanotubes. *Acc. Chem. Res.* **2012**, *45*, 1378-1389.
15. Scott, L. T.; Jackson, E. A.; Zhang, Q.; Steinberg, B. D.; Bancu, M.; Li, B., A Short, Rigid, Structurally Pure Carbon Nanotube by Stepwise Chemical Synthesis. *J. Am. Chem. Soc.* **2012**, *134*, 107-10.
16. Zhu, Z.; Jiang, H.; Susi, T.; Nasibulin, A. G.; Kauppinen, E. I., The Use of NH₃ to Promote the Production of Large-Diameter Single-Walled Carbon Nanotubes with a Narrow (n,m) Distribution. *J. Am. Chem. Soc.* **2011**, *133*, 1224-7.
17. Yuan, Y.; Wei, L.; Jiang, W. C.; Goh, K.; Jiang, R. R.; Lau, R.; Chen, Y., Sulfur-Induced Chirality Changes in Single-Walled Carbon Nanotube Synthesis by Ethanol Chemical Vapor Deposition on a Co/SiO₂ Catalyst. *J. Mater. Chem. A* **2015**, *3*, 3310-3319.
18. Zhou, W.; Zhan, S.; Ding, L.; Liu, J., General Rules for Selective Growth of Enriched Semiconducting Single Walled Carbon Nanotubes with Water Vapor as in Situ Etchant. *J. Am. Chem. Soc.* **2012**, *134*, 14019-26.

19. Wang, Q.; Wang, H.; Wei, L.; Yang, S. W.; Chen, Y., Reactive Sites for Chiral Selective Growth of Single-Walled Carbon Nanotubes: A DFT Study of Ni₅₅CN Complexes. *J. Phys. Chem. A* **2012**, *116*, 11709-11717.
20. Wang, X. K.; Lin, X. W.; Mesleh, M.; Jarrold, M. F.; Dravid, V. P.; Ketterson, J. B.; Chang, R. P. H., The Effect of Hydrogen on the Formation of Carbon Nanotubes and Fullerenes. *J. Mater. Res.* **1995**, *10*, 1977-1983.
21. Wang, Y.; Gao, X.; Qian, H.-J.; Ohta, Y.; Wu, X.; Eres, G.; Morokuma, K.; Irle, S., Quantum Chemical Simulations Reveal Acetylene-Based Growth Mechanisms in the Chemical Vapor Deposition Synthesis of Carbon Nanotubes. *Carbon* **2014**, *72*, 22-37.
22. Oguri, T.; Shimamura, K.; Shibuta, Y.; Shimojo, F.; Yamaguchi, S., Bond Dissociation Mechanism of Ethanol During Carbon Nanotube Synthesis Via Alcohol Catalytic CVD Technique: Ab Initio Molecular Dynamics Simulation. *Chem. Phys. Lett.* **2014**, *595–596*, 185-191.
23. Page, A. J.; Saha, S.; Li, H.-B.; Irle, S.; Morokuma, K., Quantum Chemical Simulation of Carbon Nanotube Nucleation on Al₂O₃ Catalysts via CH₄ Chemical Vapor Deposition. *J. Am. Chem. Soc.* **2015**, *137*, 9281-9288.
24. Eres, G.; Rouleau, C. M.; Yoon, M.; Puretzky, A. A.; Jackson, J. J.; Geohegan, D. B., Model for Self-Assembly of Carbon Nanotubes from Acetylene Based on Real-Time Studies of Vertically Aligned Growth Kinetics. *J. Phys. Chem. C* **2009**, *113*, 15484-15491.
25. Zhang, G.; Qi, P.; Wang, X.; Lu, Y.; Mann, D.; Li, X.; Dai, H., Hydrogenation and Hydrocarbonation and Etching of Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* **2006**, *128*, 6026-7.
26. Hou, P. X.; Li, W. S.; Zhao, S. Y.; Li, G. X.; Shi, C.; Liu, C.; Cheng, H. M., Preparation of Metallic Single-Wall Carbon Nanotubes by Selective Etching. *ACS Nano* **2014**, *8*, 7156-62.
27. Li, W. S.; Hou, P. X.; Liu, C.; Sun, D. M.; Yuan, J.; Zhao, S. Y.; Yin, L. C.; Cong, H.; Cheng, H. M., High-Quality, Highly Concentrated Semiconducting Single-Wall Carbon Nanotubes for Use in Field Effect Transistors and Biosensors. *ACS Nano* **2013**, *7*, 6831-9.
28. Srivastava, D.; Brenner, D. W.; Schall, J. D.; Ausman, K. D.; Yu, M. F.; Ruoff, R. S., Predictions of Enhanced Chemical Reactivity at Regions of Local Conformational Strain on Carbon Nanotubes: Kinky Chemistry. *J. Phys. Chem. B* **1999**, *103*, 4330-4337.
29. Zheng, G. S.; Wang, Z.; Irle, S.; Morokuma, K., Origin of the Linear Relationship between CH₂/NH/O-SWNT Reaction Energies and Sidewall Curvature: Armchair Nanotubes. *J. Am. Chem. Soc.* **2006**, *128*, 15117-15126.
30. Gómez-Gualdrón, D. A.; Balbuena, P. B., Effect of Metal Cluster-Cap Interactions on the Catalyzed Growth of Single-Wall Carbon Nanotubes. *J. Phys. Chem. C* **2009**, *113*, 698-709.
31. Borjesson, A.; Zhu, W. M.; Amara, H.; Bichara, C.; Bolton, K., Computational Studies of Metal-Carbon Nanotube Interfaces for Regrowth and Electronic Transport. *Nano Lett.* **2009**, *9*, 1117-1120.
32. Zhao, J.; Balbuena, P. B., Structural and Reactivity Properties of Finite Length Cap-Ended Single-Wall Carbon Nanotubes. *J. Phys. Chem. A* **2006**, *110*, 2771-2775.
33. Zhao, J.; Balbuena, P. B., Effect of Nanotube Cap on the Aromaticity of Single-Wall Carbon Nanotubes. *J. Phys. Chem. C* **2008**, *112*, 13175-13180.
34. Liu, Y. Y.; Dobrinsky, A.; Yakobson, B. I., Graphene Edge from Armchair to Zigzag: The Origins of Nanotube Chirality? *Phys. Rev. Lett.* **2010**, *105*.
35. Lolli, G.; Zhang, L.; Balzano, L.; Sakulchaicharoen, N.; Tan, Y.; Resasco, D. E., Tailoring (n,m) Structure of Single-Walled Carbon Nanotubes by Modifying Reaction

Conditions and the Nature of the Support of Como Catalysts. *J. Phys. Chem. B* **2006**, *110*, 2108-2115.

36. Wang, B.; Poa, C. H. P.; Wei, L.; Li, L.-J.; Yang, Y.; Chen, Y., (n,m) Selectivity of Single-Walled Carbon Nanotubes by Different Carbon Precursors on Co Catalysts. *J. Am. Chem. Soc.* **2007**, *129*, 9014-9019.

37. Li, H. B.; Page, A. J.; Irle, S.; Morokuma, K., Single-Walled Carbon Nanotube Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates. *J. Am. Chem. Soc.* **2012**, *134*, 15887-15896.

38. Li, H.-B.; Page, A. J.; Irle, S.; Morokuma, K., Theoretical Insights into Chirality-Controlled SWCNT Growth from a Cycloparaphenylene Template. *ChemPhysChem* **2012**, *13*, 1479-1485.

39. Li, H.-B.; Page, A. J.; Irle, S.; Morokuma, K., Single-Walled Carbon Nanotube Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates. *J. Am. Chem. Soc.* **2012**, *134*, 15887-15896.

40. Artyukhov, V. I.; Liu, Y.; Yakobson, B. I., Equilibrium at the Edge and Atomistic Mechanisms of Graphene Growth. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 15136-15140.

41. Liu, Y.; Dobrinsky, A.; Yakobson, B. I., Graphene Edge from Armchair to Zigzag: The Origins of Nanotube Chirality? *Phys. Rev. Lett.* **2010**, *105*, 235502/1-4.

42. He, M.; Jiang, H.; Liu, B.; Fedotov, P. V.; Chernov, A. I.; Obratsova, E. D.; Cavalca, F.; Wagner, J. B.; Hansen, T. W.; Anoshkin, I. V. et al., Chiral-Selective Growth of Single-Walled Carbon Nanotubes on Lattice-Mismatched Epitaxial Cobalt Nanoparticles. *Sci Rep* **2013**, *3*, 1460.

43. Page, A. J.; Ding, F.; Irle, S.; Morokuma, K., Insights into Carbon Nanotube and Graphene Formation Mechanisms from Molecular Simulations: A Review. *Rep. Prog. Phys.* **2015**, *78*.

44. Robinson, M.; Marks, N. A., Nanocap: A Framework for Generating Capped Carbon Nanotubes and Fullerenes. *Comput. Phys. Commun.* **2014**, *185*, 2519-2526.

45. Becke, A. D., Density-Functional Thermochemistry .3. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

46. Lee, C. T.; Yang, W. T.; Parr, R. G., Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron-Density. *Phys. Rev. B* **1988**, *37*, 785-789.

47. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623-11627.

48. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A. et al. *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009.

49. Page, A. J.; Chou, C. P.; Pham, B. Q.; Witek, H. A.; Irle, S.; Morokuma, K., Quantum Chemical Investigation of Epoxide and Ether Groups in Graphene Oxide and Their Vibrational Spectra. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3725-35.

50. Zheng, G.; Wang, Z.; Irle, S.; Morokuma, K., Origin of the Linear Relationship between CH₂/NH/O-SWNT Reaction Energies and Sidewall Curvature: Armchair Nanotubes. *J. Am. Chem. Soc.* **2006**, *128*, 15117-26.

51. Hopffgarten, M.; Frenking, G., Energy Decomposition Analysis. *WIREs Comp. Mol. Sci.* **2012**, *2*, 43-62.

52. Lin, T.; Zhang, W. D.; Huang, J.; He, C., A DFT Study of the Amination of Fullerenes and Carbon Nanotubes: Reactivity and Curvature. *J. Phys. Chem. B* **2005**, *109*, 13755-60.
53. Chen, Z.; Thiel, W.; Hirsch, A., Reactivity of the Convex and Concave Surfaces of Single-Walled Carbon Nanotubes (SWCNTs) Towards Addition Reactions: Dependence on the Carbon-Atom Pyramidalization. *ChemPhysChem* **2003**, *4*, 93-7.
54. Seo, K.; Park, K. A.; Kim, C.; Han, S.; Kim, B.; Lee, Y. H., Chirality- and Diameter-Dependent Reactivity of NO₂ on Carbon Nanotube Walls. *J. Am. Chem. Soc.* **2005**, *127*, 15724-9.
55. O'Connell, M. J., *Carbon Nanotubes: Properties and Applications*. CRC Press: 2006.
56. Haddon, R. C.; Scott, L. T., Pi-Orbital Conjugation and Rehybridization in Bridged Annulenes and Deformed Molecules in General - Pi-Orbital Axis Vector Analysis. *Pure Appl. Chem.* **1986**, *58*, 137-142.
57. Joselevich, E., Electronic Structure and Chemical Reactivity of Carbon Nanotubes: A Chemist's View. *ChemPhysChem* **2004**, *5*, 619-24.
58. Liu, B.; Jiang, H.; Krashenninnikov, A. V.; Nasibulin, A. G.; Ren, W.; Liu, C.; Kauppinen, E. I.; Cheng, H. M., Chirality-Dependent Reactivity of Individual Single-Walled Carbon Nanotubes. *Small* **2013**, *9*, 1379-86.
59. Yang C-M.; An, K. H. P., J. S. ; Park, K. A.; Lim, S. C.; Cho, S-H; Lee, Y. S.; Park, W.; Park, C. Y.; Lee, Y. H., Preferential Etching of Metallic Single-Walled Carbon Nanotubes with Small Diameter by Fluorine Gas. *Phys. Rev. B* **2006**, *73*, 075419.
60. Grunze, M.; Brundle, C. R.; Tománek, D., Adsorption and Decomposition of Ammonia on a W(110) Surface: Photoemission Fingerprinting and Interpretation of the Core Level Binding Energies Using the Equivalent Core Approximation. *Surf. Sci.* **1982**, *119*, 133-149.
61. Grunze, M.; Golze, M.; Driscoll, R. K.; Dowben, P. A., Ammonia Adsorption and Decomposition on a Ni(110) Surface *J. Vac. Sci. Tech.* **1981**, *18*, 611-615.
62. Dirtu, D.; Odochian, L.; Pui, A.; Humelnicu, I., Thermal Decomposition of Ammonia. N₂H₄ - an Intermediate Reaction Product. *Cent. Eur. J. Chem.* **2006**, *4*, 666-673.
63. Drechsler, M.; Hoinkes, H.; Kaarmann, H.; Wilsch, H.; Ertl, G.; Weiss, M., Interaction of Nh₃ with Fe(110): Identification of Surface Species by Means of Secondary Ion Mass Spectroscopy (Sims). *Appl. Surf. Sci.* **1979**, *3*, 217-228.
64. Bassignana, I. C.; Wagemann, K.; Küppers, J.; Ertl, G., Adsorption and Thermal Decomposition of Ammonia on a Ni(110) Surface: Isolation and Identification of Adsorbed Nh₂ and Nh. *Surf. Sci.* **1986**, *175*, 22-44.
65. Hüttinger, M.; Küppers, J., Intermediate Product Identification for Ammonia Decomposition at Ni (110). *Surf. Sci.* **1983**, *130*, L277-L282.

ToC Graphic