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**Oxygen-functionalized alkyne precursors in carbon nanotube growth**

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Functionalization of carbon nanotubes (CNTs) with heteroatoms enables covalent attachment, opening up a world of potential material structures. However, common functionalization techniques are hazardous and lack precision. Here, we evaluate an *in situ* functionalization technique using oxygen-containing alkyne precursors. CNTs were successfully derived from propargyl alcohol and propiolic acid, at  $67 \pm 7$  and  $19 \pm 3$   $\mu\text{m min}^{-1}$ , respectively. While there was no substantial increase in the oxygen content of resultant CNT structures (all less than 1% O), Fourier transform infrared spectroscopy revealed subtle incorporations of carboxyl and hydroxyl functionality. An analysis of reactor effluent showed that both oxygen-containing species shed oxygen groups, where propargyl alcohol yielded a reactive atmosphere high in methylacetylene, and propiolic acid thermally degraded to acetylene and  $\text{CO}_2$ , potentially explaining the enhanced catalyst lifetimes (approximately 75 min). These results support the universality of alkyne-promoting chemistries and delineate the limits of stable, oxygen-bearing alkynes to support point-directed functionalization schemes.

Evidence that carbon nanotubes (CNTs) can form from intact C<sub>2</sub>-C<sub>4</sub> subunits, primarily as alkynes, in a polymerization-like growth mechanism opened the doors for functionalized alkynes to direct the placement of heteroatoms in CNT lattice structures. If possible, this would alleviate the need for *ex situ* functionalization, the costs and environmental burdens associated with high concentration acid processing, and eliminate the random nature currently limiting CNT functionalization. Here, we demonstrate that oxygen-functionalized alkynes dominantly shed their oxygen-containing groups prior to or simultaneously with incorporation in the CNT, resulting in limited incorporation of oxygen groups into the CNT structure. As a whole, the work sheds light on fundamental reaction processes that give rise to carbonaceous nanostructures through polymerization and defines the limits of current *in situ* functionalization strategies.

chemical vapor deposition (CVD) (chemical reaction), nanostructure, environmental impact, sustainability, nucleation & growth

## Introduction

Carbon nanotubes (CNTs) can be enhanced through the covalent addition of heteroatoms (e.g., O, N, or S), allowing them to disperse in a particular solvent or matrix or bind with other species of interest. These advantages make functionalized CNTs preferable to pristine CNTs in a range of applications (e.g., sensors). Covalent attachments to CNTs often commence with carboxylic acid chemical routes, largely due to their chemical versatility; common derivatization reactions can be employed to convert carboxyl groups to a range of other functionalities (e.g., amine,<sup>1</sup> amide, ester,<sup>2,3</sup> or acid halide<sup>4</sup>).<sup>5</sup> To impart these carboxylic acid groups, processes generally consist of refluxing CNTs in a strong, oxidizing acid (e.g., nitric acid, sometimes with the addition of sulfuric acid), for durations as long as 24 hours. Though this method successfully produces carboxyl-functionalized CNTs (with around 10% surface oxygen<sup>6</sup>), it has substantial disadvantages. First, strong oxidizers can damage CNTs, reducing their lengths and disrupting their *sp*<sup>2</sup> networks, even destroying single-walled CNTs (SWCNTs) completely.<sup>7</sup> Second, there is no spatial control over functionalization, where the process is thought to be semi-random and/or act on defect sites within the CNT, making it implicitly difficult to produce tailored materials. Third, the process is time-consuming and dangerous, especially at scale. Finally, the approach carries a large environmental footprint, due to both the energy required and the

manufacture of the oxidizing acid.<sup>8</sup> Several Principles of Green Chemistry discourage the use of solvent-based secondary treatments because of their high environmental impacts.<sup>9</sup> To improve upon the current state of functionalization practices, there is need for a new strategy that can enable spatially selective direction of desired concentrations of heteroatoms, while minimizing damage, process time, and environmental impact. Furthermore, it would be ideal if such an implementation could be exploited *during* CNT growth, rather than require an additional *ex situ* wet chemical treatment.

To realize an *in situ* CNT functionalization scheme, the proposed mechanisms governing CNT growth may yield valuable insight. The widely held vapor-liquid-solid (VLS) or vapor-solid-solid (VSS) model theorizes that carbon-containing precursors in the vapor phase dissolve into a liquid or solid catalyst particle as C atoms, and the resulting supersaturated catalyst particle precipitates as a solid (CNT).<sup>10,11</sup> While valuable for explaining several observations, VLS alone implies CNT formation is the product of a physical crystallization rather than a chemical reaction. Accordingly, all carbonaceous precursors would dissociate into C<sub>1</sub> subunits and would yield similar structures, which is not universally observed.<sup>12–15</sup> Another mechanism, which is not mutually exclusive to all the tenants of VLS or VSS, involves a polymerization-style reaction of alkynes at the catalyst surface. Supporting evidence for this mechanism has shown that CNT growth rates from alkynes are significantly faster than those from alkenes or alkanes,<sup>16</sup> and alkyl groups attached to alkynes (e.g., vinyl and methylacetylene) can persist into growing CNT structures.<sup>15</sup> This interesting finding presents the opportunity for structural control via precursor selection: As the direct incorporation of the alkyne bond into the CNT lattice could result in the persistence of small alkyl substituents, then perhaps heteroatom-containing alkynes could act as carriers to facilitate the directed placement of those heteroatoms.

Exploring the limits of this alkyne-incorporation hypothesis, we note that oxygen-bearing functional groups (e.g., alcohol or carboxyl) might be introduced into the CNT lattice via alkynes bearing the substituents of interest. Structurally, the ideal candidate for alcohol-functionalized CNT growth would be ethynol, a C<sub>2</sub> alkyne with a hydroxyl substitution. However, ethynol can potentially undergo tautomerization to ethenone. Further, extreme conditions are required to produce ethynol (i.e., under pulsed UV laser at 12 K),<sup>17</sup> limiting commercial availability. The next logical alcohol candidate that is sufficiently small to undergo polymerization but contains the important functional moieties is propargyl alcohol, a C<sub>3</sub> alkyne with hydroxyl group attached

to an  $sp^3$  carbon (i.e.,  $\text{HC}\equiv\text{C}-\text{CH}_2-\text{OH}$ ). The carboxylic acid analog is propiolic acid (i.e.,  $\text{HC}\equiv\text{C}-\text{COOH}$ ). Both are liquids at standard conditions, with low vapor pressures (15.6 and 3.52 mm Hg, respectively, at 25°C; see **Table S1**). Though the reactivity and small size of these two alkynes can present health hazards,<sup>18–20</sup> their usage in synthesis could produce a net benefit by eliminating the need for *ex situ* CNT functionalization via acid reflux, potentially reducing material and energy consumption. Finally, we note that while acetylene and propargyl alcohol are both bulk commodity chemicals (priced at \$6.21 per mol (Airgas) and \$4.22 per mol (Sigma-Aldrich), respectively; non-bulk pricing) that can be readily deployed for use in CNT fabrication, propiolic acid is quite expensive (\$157.50 per mol, Sigma-Aldrich), and thus might be limited in its commercial potential.

Oxygen additives serve myriad other functions in CNT formation; primarily, oxygen's presence seems to enhance the lifetime of the growth catalyst. In particular, early studies showed that ethanol could be used as both a carbon source as well as a growth promoter,<sup>21</sup> generating long CNTs.<sup>22,23</sup> This effect was extended to other alcohol additives. Subsequent work by Magrez et al.<sup>24,25</sup> went on to illustrate that  $\text{CO}_2$ , delivered in conjunction with or 'equimolar' to acetylene, could promote CNT formation via a dehydrogenation reaction, and Shi et al.<sup>26</sup> went on to illustrate conclusively that only the acetylene was acting to form CNTs, whereas the  $\text{CO}_2$  was dehydrogenating the reactive C species to promote CNT growth. Further, Shi et al.<sup>27</sup> explored the role of water and  $\text{O}_2$  on CNT formation, illustrating a critical role with regard to catalyst ripening, but not necessarily with respect to the suite of reactive gas-phase products available to the catalyst for reaction or via promotion of any other reactions at the catalysts. Understanding of the multiple roles of oxygen atoms in the reactive atmosphere of heterogeneous catalysis is critical during exploration of oxygen-bearing alkyne additives to the CNT growth environment when an oxygen moiety added to contribute to structural C–O bonds in the CNT might go on to serve many auxiliary roles. Here, we evaluate a strategy to direct the placement of oxygen-functional groups in a growing CNT structure *in situ* by adding oxygen-containing alkynes (propargyl alcohol and propiolic acid) and describe the fate of those oxygen moieties (see **Figure S1**).

## Results and discussion

This study used an ambient-pressure cold-wall reactor<sup>28</sup> to minimize thermal transformations of the precursor gases prior to impinging on the substrate-supported-catalyst. Then, CNTs were grown via three experimental modes: (1) using individual precursors (i.e., acetylene, propargyl alcohol, or propiolic acid) as the only carbon source over a range of partial pressures, (2) adding varied amounts of propargyl alcohol to a fixed partial pressure of acetylene (0.01 atm) to evaluate competitive processes, and (3) using maximum alkyne partial pressures for effluent analysis (**Table S2**; note that maximum partial pressures of liquid precursors were limited by their vapor pressures).

Investigating the effects of individual gases, propargyl alcohol and propiolic acid successfully generated vertically aligned CNTs (VACNTs; **Figure 1**). This is the first time that oxygen-bearing alkynes have generated CNTs, where several prior studies have confirmed the role of small, aliphatic C<sub>2</sub>-C<sub>4</sub> alkynes (and particularly acetylene) in CNT formation.<sup>15,16</sup> Structurally, the alignment of the forest is comparable to other VACNT forests grown from complex, thermally derived gas mixtures,<sup>27,29</sup> but less aligned than an acetylene-derived forest generated in the same cold-wall reactor. Hermans Orientation Factors (HOFs) can be used to evaluate alignment,<sup>30,31</sup> where HOF values range from -0.5 (perpendicular to the axis of interest) to 0 (random orientation) to 1 (perfectly aligned). Acetylene-, propargyl-, and propiolic-acid-derived CNTs exhibited HOFs of  $0.31 \pm 0.04$ ,  $0.17 \pm 0.02$ , and  $0.16 \pm 0.02$ , respectively. This suggests that CNTs derived from propargyl alcohol or propiolic acid, both of which contain an additional carbon after the alkyne moiety (i.e., 3 carbons total), may have more defect sites than those produced with acetylene only, perhaps suggesting incorporation of a C<sub>3</sub> structure into the lattice. Such C<sub>3</sub> incorporation has been observed previously,<sup>15</sup> but it remains to be shown if heteroatom cargoes also transfer into the growing CNT structure.

One may speculate that the higher defect density in the propargyl alcohol- and propiolic acid-fed forests would manifest as two interesting phenomena: (1) reduced control of the chiral angle during growth and (2) a potential for intra-tube coupling reactions to occur between side groups that project from the tube structure. First, failure of the tube lattice to close in order to accommodate the oxygen-containing functional group would give rise to a more defective structure, or the functional group could frustrate ring closure reactions directly and yield more defective structures. This is consistent with the observations (**Figure 1**). Such defects would necessarily disrupt any continuity in the chiral angle or crystallinity,<sup>32,33</sup> and one might extend

this logic to conclude that chiral control would be diminished in structures grown from alkynes containing heteroatoms (which are not chiral-directing themselves). Here, we note that quantitative evaluation of the chiral distribution in these forests is not possible because the tubes are multi-walled (i.e., contain mixed chiral angles that prohibit the use of fluorescence excitation-emission spectral mapping and lack the radial breathing mode in Raman spectroscopy). Second, if any chemical crosslinking could occur in the CNT forest, it would exist either between tube walls (i.e., “intra-tube coupling”) in the multi-walled system, or between two tube structures (i.e., those supported by different catalysts; “inter-tube coupling”). While inter-tube coupling should not occur due to the spacing between individual multi-walled tube structures (approximately 8 nm),<sup>27,34</sup> there is evidence of reactive species present on the tube walls that could give rise to both of these types of coupling (results presented below). Such intra-tube coupling would be difficult to demonstrate, but not impossible. Strategies would include attempts to illustrate differences in intra-tube connection strength (e.g., sword-in-sheath style removal<sup>35–37</sup> or variations in dispersibility via sonication). Finally, the effects might manifest as electronic or mechanical differences in the structures, and these should be explored as part of future study.

To evaluate whether the oxygen group accompanied its alkyne host into the CNT structure, we employed x-ray photoelectron spectroscopy (XPS). Interrogating the middle of the forests, a comparison of the O (1s) peak from samples grown from acetylene, propargyl alcohol, and propiolic acid displayed minimal differences in oxygen content (0.14%, 0.08%, and 0.10%, respectively), close to the expected detection limit of 0.1% (**Figure 2a**). This suggests that if some oxygen from the alcohol or acid is present within the structure, it is insignificant compared to ambient oxygen that is natively present in the structure. (Note that samples were well-dried prior to analysis, and adsorbed water would not have interfered with the measurement.) Similarly, no significant shift in C (1s) peak occurred (**Figure 2b**); a shift to higher binding energies is thought to occur with increased oxidation, but it has not been observed even in highly oxidized CNTs.<sup>6</sup> To contextualize this low oxygen content, Wepasnick et al. observed concentrations between 4.3 and 9.5% O (by XPS) with 1 hr sonication in 20–70% nitric acid.<sup>6</sup> Pasquini et al.<sup>38</sup> observed a range of O contents (1.3 to 3.2%) through systematic oxidation (2 hr reflux in 70% nitric acid) and subsequent annealing (from 400 to 900°C) in H<sub>2</sub>. Assuming these values are intercomparable, then the incorporation of O observed here was substantially lower.



We hypothesized that the low oxygen contents may have resulted from carbon-starved forest growth, where CNTs might not form until sufficient acetylene was generated from thermal or catalytic decomposition of the oxygen-bearing alkyne. To test this hypothesis and determine if co-polymerization of an oxygen-containing alkyne and acetylene was possible, we augmented CNT formation rates with direct delivery of acetylene (0.03 atm) and then doped with 0.0021 atm or 0.0035 atm propargyl alcohol (limited by the vapor pressure of the liquid starting material). CNT forests grown via this co-delivery method of acetylene and propargyl alcohol contained less surface oxygen than acetylene alone, at 0.29% versus 0.90% (Figure 2c). Subtle differences in peak shape may be attributed to variations in water-bound oxygen and alcohol-bound oxygen (see discussion and analysis in the Supplementary Information, **Figure S2, Table S3**). Notably, there were no discernable peaks at the lower binding energies anticipated for carbonyl-bound oxygen of carboxyl groups (531.1–531.8 eV).<sup>39</sup> For water- (535.5–536.1 eV) and alcohol-bound oxygen (532.3–533.3 eV), the relative peak positions might inform minor differences in oxygen binding; the addition of propargyl alcohol to acetylene growths (Figure 2c) resulted in trivial shifts in the O (1s) peak to lower binding energies (centered at 532.8, 532.4, and 532.6 eV for acetylene alone, and doped with 0.21% and 0.35% propargyl alcohol, respectively), perhaps suggesting the presence of progressively weaker-bound oxygen. However, we caution against overinterpretation of these relatively minor differences (see Supplementary Information).<sup>40</sup> Further, there was no significant shift in C (1s) binding energy, indicating no substantial differences in species covalently bound to carbon were present (Figure 2d). Thus, even when the VACNTs were given ample C<sub>2</sub>-carbon (i.e., acetylene) to accelerate growth and co-incorporate oxygen-bearing alkynes, the end-result of oxygen tethered to or incorporated in the CNT structure was not observed. Efforts to detect oxygen on the surface of the CNTs via other methods (e.g., elemental analysis [EA] and thermogravimetric analysis with mass spectrometry [TGA-MS]) also yielded no significant differences in oxygen-relevant regions (see **Figure S3, Table S4**). Fourier transform infrared spectroscopy (FTIR) results indicated only minor differences on triplicate acetylene-derived forests as compared to propargyl alcohol- and propiolic acid-grown counterparts (**Figure 3**). In particular, propiolic acid-fed forests exhibited differences (i.e., non-zero difference spectra when compared to acetylene and considering errors throughout) in the O-H region, and red-shifted from the C-OH, C=O, and mono-substituted alkyne regions.<sup>41,42</sup> The red shift could result from the unique electric field or microenvironment

effects,<sup>43</sup> but seems to indicate some incorporation of oxygen groups that escape detection by other methods (XPS and EA, with a detection limit of 2% O, in particular). Overall, in other spectral regions, the standard error is distributed widely about the mean and indicates the triplicates are heterogeneous. Considering the small molecular differences as measured by a variety of techniques, we infer that in both cases, oxygen-containing functional groups separate from the alkyne moiety, which can subsequently or coincidentally incorporate into the CNT structure. If such oxygen atoms are liberated from the alkyne during CNT growth, then the well-established effect of oxygen-containing gases on the catalyst lifetime<sup>22–24,44–46</sup> should be observable via *in situ* growth kinetics.

The optically transparent, cold-walled reactor allows for real-time VACNT forest growth diagnostics via height measurement with a laser displacement sensor reflected off a silicon nitride cap. A comparison of growth rates for each precursor can inform a mechanistic understanding of precursor incorporation in CNT growth: when delivered directly in the cold-wall reactor, faster growth rates could suggest the direct incorporation of a molecule into the CNT lattice, whereas lower growth rates may imply a lack of direct incorporation (e.g., steric hindrance or poor catalyst binding) and/or the need for a thermal or catalytic transformation to a more favorable CNT formation structure. As expected<sup>16</sup> and as a positive growth control, we observed rapid CNT formation from acetylene. In contrast, propargyl alcohol (**Figure 4a**) exhibited slower growth rates ( $67 \pm 7 \mu\text{m min}^{-1}$  at 0.0035 atm propargyl alcohol), compared to  $85 \pm 2 \mu\text{m min}^{-1}$  for acetylene-only (0.0028 atm) CNT formation. At low partial pressures of carbonaceous gasses ( $\leq 0.0008$  atm), growth rates were similarly low and increased steadily with higher concentrations of precursor, indicating a potential mass limitation. Interestingly, acetylene growth rates increased faster with partial pressure than growth rates for propargyl alcohol and propiolic acid. This is consistent with a mechanism wherein oxygen-bearing alkynes lose their oxygen-containing functional groups prior to or during incorporation into the CNT lattice at the catalyst. If so, then the evolved gases should reveal the presence of oxygen-containing species, and catalyst lifetime should be enhanced. Reserving discussion of the gas products for later, we note that the latter effect was observed: CNTs catalyst lifetimes from oxygen-bearing alkynes were systematically longer (e.g., from  $22 \pm 4$  to  $80 \pm 10$  min) relative to their acetylene counterparts (e.g., from  $7 \pm 3$  to  $160 \pm 20$  min) across a range of partial pressures (**Figure 4b**). This corroborates the general principle that low levels of oxygen-containing gases tend to enhance the

growth lifetime of CNTs. This effect has been observed with low concentrations of oxidants, irrespective of their delivery as a precursor (e.g., ethanol<sup>23</sup>) or as an additive (e.g., air<sup>47</sup> or CO<sub>2</sub><sup>48</sup>). Magrez et al.<sup>25</sup> proposed and Shi et al.<sup>26</sup> illustrated this effect was through a dehydrogenation reaction at the catalyst. Others have postulated that oxygen (e.g., in the form of water vapor or diatomic O<sub>2</sub>) functionally “polishes” the catalyst to remove carbonaceous overcoating in a combustion-like process,<sup>44</sup> and while certainly plausible, there is little experimental evidence to support this theory. Similarly, oxygen groups in the gas phase may promote favorable gas chemistries, thereby prolonging the formation of the target nanostructures. However, the net effect of molecular oxygen is highly dependent on the reactive environment, where oxygen can be used to both promote soot forming pathways or reduce soot and soot precursor formation.<sup>49–51</sup> Finally, we note that redox-driven enhancement of catalyst activity would not be enabled by oxygen in principle: The catalyst must be reduced initially to become active<sup>52</sup> and can exhibit two-electron switching during the nanotube formation process.<sup>53</sup> Thus, oxidative species such as molecular oxygen or water acting at the catalyst would reduce the catalyst lifetime, and that effect has not been observed. Taken together, the results shown here illustrate that even very low levels of oxygen in the reactor can lead to measurable enhancements in catalyst lifetime and prolonged nanotube growth, offering a mechanism for improved, precision control of nanostructure at molecular length scales.

To evaluate the potential for competition between acetylene and the oxygen-functionalized acetylenes reacting at active sites on the catalyst, we delivered both the acetylene and the oxygen-bearing alkyne simultaneously. Briefly, varying proportions of acetylene were delivered with a fixed partial pressure of propargyl alcohol (either 0.07 or 0.35%, limited by the room-temperature vapor pressure of propargyl alcohol liquid and the bubbler flow rate). There was no substantial evidence for competitive binding or enhancement of propargyl alcohol, as the growth rate did not significantly increase or decrease (**Figure 5a**). However, the lifetime of the catalyst increased with sufficient delivery of propargyl alcohol (0.35%), consistent with the expectation for oxygen-bearing gases to increase growth lifetime (Figure 5b). These growth kinetic profiles cumulatively suggest that propargylic species lose attached functional groups prior to incorporation into the growing CNT structure.

To investigate the reactive transformations occurring in the reactor, effluent gas was diverted through a stainless-steel canister and subsequently analyzed by gas chromatography

(GC). Alkanes (methane, ethane, propane, butane, pentane), alkenes (ethylene, propylene, butene, pentene), alkynes (acetylene, methylacetylene, vinylacetylene), alcohols (methanol, ethanol), and CO and CO<sub>2</sub> (following a methanizer) were quantified robustly by flame ionization detection with authentic.<sup>26,54</sup> Cold-wall reactors are intended to minimize gas-phase transformations of precursor species and decouple the thermal treatment of the catalyst and the starting material feedstock gases. Nevertheless, the resistively heated substrate necessary to heat the catalyst warms the bulk reactive zone, allowing for both thermal and catalytic transformations<sup>28,54</sup> and resulting in a wide range of species (**Figure 6**). Several interesting features emerge. First, acetylene and methylacetylene were present in all active cases, consistent with their role as important CNT-forming molecules.<sup>15,16</sup> Next, CO and CO<sub>2</sub> were abundant in the propargyl alcohol- and propiolic acid-fed reactions. Magrez et al.<sup>24,25</sup> and others<sup>26,55</sup> have shown the enhancing effect of CO<sub>2</sub> to promote nanotube growth, especially in combination with acetylene. Shi et al.<sup>26</sup> demonstrated conclusively using isotope tracers that the CO<sub>2</sub> does not supply an active carbon source to support CNT formation, but instead is a dehydrogenation enhancer (as proposed by Magrez et al.<sup>25</sup>). Thus, the extended lifetimes observed in the propiolic acid- and propargyl alcohol-fed growths can be attributed to the presence of these highly oxidized species. Further, their presence is evidence that the oxygen moieties are separating from their alkyne carrier. In the case of propiolic acid, this results in a source of both CO<sub>2</sub> and acetylene. In the case of propargyl alcohol, the dominant fragmentation products are CO and methylacetylene, as well as methanol and acetylene. In either breakdown pathway, both an active growth precursor and a “growth enhancer” (e.g., a species that extends the reaction lifetime, CO and methanol) are formed. Growth rates observed in propargyl alcohol-derived growths with thermally generated acetylene are faster than anticipated for a growth from a comparable amount of acetylene delivered directly or “cold.” Thus, there is a rate-enhancement effect at play, potentially from a combination of species or propargyl alcohol itself. Finally, in all cases, ethylene, ethane, and methane were formed, where higher levels of methane were observed in the propargylic-sourced growths. This is somewhat unsurprising: while acetylene can and does rearrange to form propargyl radicals that can ultimately liberate methyl species,<sup>56</sup> the propargylic, oxygenated species (with three C atoms) have a higher yield of methyl group formation via formation of acetylene and loss of oxygen moieties in this study. Ethylene and ethane were detected in quantities proportional to acetylene, suggesting these gaseous byproducts

were formed from successive reductive hydrogenation of the alkyne, which can occur on catalytic surfaces<sup>57</sup> or the gas phase alone.<sup>54</sup>

Together, these reactive byproducts present a few challenges: (1) They create a heterogeneous gas mixture that can lead to structural defects in the forests, (2) they are a necessary consequence of thermal processing and may be unavoidable in such heated, heterogeneous catalysis, and (3) they represent a source of unwanted greenhouse gases (i.e., methane) and smog-forming volatile organic compounds (VOCs). The abundance of the emitted, measured gases in these cases are  $60 \pm 10$  and  $131 \pm 9$  kg total VOCs per kg CNTs for propargyl alcohol and propiolic acid, respectively, versus  $323 \pm 1$  kg/kg for acetylene (**Table S5**, Figure 6). Note that in the case of acetylene, the feedstock gas itself is quantified as part of the VOC load, whereas in the case of the oxygenated precursors, the feedstock is not explicitly quantified in the emitted species. Perhaps a better indication of carbon utilization is given by carbon conversion efficiencies, which are on par with other experimental cold-wall reactors (e.g., 5.4 to 7.4 mg CNTs per g precursor carbon for acetylene fed growth (**Figure S4**) versus 4.2 to 14 mg CNTs per g precursor carbon, as reported previously<sup>15,58</sup>). Note that the best C conversion efficiency observed was for acetylene (5.4 to 7.4 mg CNTs per g precursor carbon), whereas the propargylic, oxygenated species exhibited poorer conversion efficiencies (0.7 to 3.6 mg CNTs per g precursor carbon). Even with the prolonged catalyst lifetime conferred by the growth-enhancing oxygen functional groups, the net conversion to CNT structure is reduced relative to the acetylene-only fueled CNTs. This is in contrast to the increase in efficiency observed when CO<sub>2</sub> is added to an acetylene growth (1.6% versus 0.42%),<sup>26</sup> which is a more cost-competitive strategy.

## Conclusions

We endeavored to provide an *in situ* route to produce oxygen-functionalized carbon nanotubes without the need for caustic, environmentally and economically expensive solvents at temperature and with improved direction of the functional group loci. While the current methods are undesirable from many perspectives, they are a necessary first step toward covalent attachment of CNTs to anything else, and overcoming the random nature of this process is critical to enable a world of potential new CNT-based structures, hierarchical materials, and devices. Ultimately, we were able to produce CNTs from propargyl alcohol and propiolic acid

for the first time. However, we illustrated that they bring only a trivial amount of oxygen functionality with them. Instead, the dominant route is for the oxygen groups to shed from their alkyne carrier, serving to extend the growth lifetime, but not the total carbon yield, of the CNTs.

Several interesting questions remain: (1) Is the oxygen being lost thermally prior to or simultaneously with incorporation into the growing CNT structure? (2) If prior to, would other conditions be more conducive to direct incorporation of functional alkynes with their heteroatom “cargo”? (3) Would substituted ethynyl groups perform better? (e.g., if propargyl, a C<sub>3</sub> moiety, plus oxygen is too large to incorporate, would ethynyl, a C<sub>2</sub> moiety, plus oxygen be able to do so? Ethynyl groups tend to be unstable, tautomerize, and would likely need to be generated and used *in situ*). (4) If successful, could the technique be extended to other types of functional groups? Finally, alternative methods to direct the covalent linkages in CNTs may need to be explored.<sup>59</sup> These could include trying to engineer defects in particular locations<sup>60</sup> to encourage carboxyl addition via wet chemical techniques at precise defect locations. Here, we note that this strategy might also help experimentally to confirm the role of defects in functional group placement, which has only been hypothesized to date. Alternatively, since methylacetylene has been shown to direct the delivery of methyl moieties on a CNT surface,<sup>15</sup> strategies to substitute methyl functional groups—a non-trivial chemistry<sup>61</sup>—may be most promising for controlled covalent modification of the CNT surface. Such molecular-level control of the target structure would unlock the potential for novel, hybridized CNTs that leverage and extend their remarkable properties.

## Methods

### *CNT synthesis*

CNTs were fabricated in an atmospheric pressure, cold-wall reactor (SabreTube, Absolute Nano), which relies on a strip of silicon wafer (46×11 mm) to resistively heat the catalyst, minimizing thermal transformations of gas-phase precursors.<sup>62,63</sup> An approximately 5×5 mm piece of catalyst wafer (1 nm Fe + 10 nm Al<sub>2</sub>O<sub>3</sub> diffusion barrier on 0.5 mm thick Si wafer) was placed on top of the heating element in each experiment. To enable real-time CNT forest height measurements using a Keyence LK-H157 laser displacement system, a “cap” wafer (Si<sub>3</sub>N<sub>4</sub>-coated Si) was placed on top of the catalyst to reflect the incident laser. From the laser displacement versus time data, three key parameters were extracted: terminal height (height of



CNT forest at end of growth), catalyst lifetime (time between 1–99% of the terminal height), and growth rate (linear fit of the data from 25–75% of the terminal height).<sup>63</sup> The growth rate curves exhibit a sigmoidal shape, where there is a lag or “induction period” (i.e., slowly increasing growth rate initially), followed by relatively linear growth, then decreases as the CNT forest approaches its terminal height prior to an “abrupt termination” event.<sup>63–65</sup>

Each experiment began by flushing the reactor with 500 sccm helium (ultra-high purity (UHP), 99.999%, Airgas) for 10 min. Then, an annealing mixture of equal parts hydrogen (UHP, 99.99%, Airgas) and helium at 600 sccm was introduced for 2 minutes, before annealing at 700°C for two minutes. After annealing, the growth mixture was delivered to the 700°C reactor: approximately 600 sccm with 50% hydrogen, a variable amount of alkyne precursor, and balance helium. The alkyne precursors were tested in two modes: an alkyne alone or some combination of alkynes. Specifically, when delivered as the sole carbon source, acetylene (9.997% in helium, Airgas) was delivered at 0.00030–0.0068 atm, propargyl alcohol (99%, Sigma Aldrich) at 0.00015–0.0035 atm, or 0.00015–0.00078 atm propiolic acid (98+%, Alfa Aesar). When delivered simultaneously, acetylene was introduced over a range of partial pressures (0–0.03 atm), with fixed levels of propargyl alcohol partial pressures (either 0, 0.00070, or 0.0035 atm). For the XPS co-delivery experiments, 0.03 atm acetylene was delivered with 0.0021 or 0.0035 atm propargyl alcohol. At end of growth, determined by the laser displacement data, the heating element was turned off, and the reactor was flushed with 500 sccm of helium for 10 minutes.

In experiments using propargyl alcohol or propiolic acid, a custom-made, small-volume bubbler was filled with 1.25 mL of the liquid precursor and submerged in a water bath to maintain a 25 °C liquid temperature (see **Figure S6**). Helium was bubbled into the liquid to promote partitioning into the gas phase, and the vapor traveled to the reactor through a line wrapped with heated tape to prevent condensation. Delivery rates of each liquid precursor were limited by the vapor pressure of each precursor at 25°C (see Table S1). In the experiments where acetylene was the only precursor, it flowed through an empty, pre-combusted bubbler with enough helium to mimic the gas flow of an equivalent propargyl alcohol experiment, so that the gas flow path was identical for each precursor. The full experimental setup is detailed in the Supporting Information.

### ***Materials characterization***

VACNT forest topography was characterized with a Zeiss Merlin Gemini field emission scanning electron microscope, with 5 kV accelerating voltage and 184 pA probe current. Images were captured of the sides of the forests, focused on the region representing the middle of growth. This same region was studied for surface elemental composition via XPS, performed with a Physical Electronics PHI VersaProbe II scanning XPS microprobe, using an Al K $\alpha$  source. The 0–1100 eV range was surveyed to determine all surface elements present, followed by more detailed scans of the O (1s) and C (1s) regions of the spectrum. Additional characterization techniques (Elemental Analysis, Thermogravimetric Analysis with Mass Spectrometry) were employed and are reported in the Supporting Information (Figures S3, Table S4).

#### ***Fourier Transform Infrared Spectroscopy***

Detection of functional groups via FTIR was performed with an Agilent Cary 660 FTIR spectrometer, equipped with a Pike Technologies GladiATR Single Reflection Attenuated Total Reflection (ATR) accessory. CNTs were scraped from their substrates, deposited on the diamond ATR cell, and pressed with an anvil to ensure contact. Spectra were recorded in the 4000–400 cm<sup>-1</sup> range with 256 scans each and 2 cm<sup>-1</sup> resolution, and analyzed for oxygen bonding with available spectral libraries.<sup>41,42</sup>

#### ***Effluent analysis***

Gas samples of reactor effluent were collected during approximately the middle of CNT growth by flushing 150-mL canisters with at least three volumes of effluent. The samples were analyzed using an SRI Instruments 8160C gas chromatograph (GC) with a flame ionization detector (FID). Using a standard loop and 6-port valve, 1 mL of gas was concentrated onto a cryo-focusing trap, consisting of ResSil-C 80/100 mesh silica beads, submerged in liquid nitrogen. The sample was introduced to a HayeSep-N column (80/100 mesh, 6'  $\times$  1/8" OD  $\times$  0.085" ID) by submerging the trap in boiling water. Compound identities were confirmed with authentic standards, which were also used to calibrate the instrument daily.

#### ***Hermans Orientation Factor calculation***



The HOF was calculated for a sample of each precursor (acetylene, propargyl alcohol, propiolic acid) using the micrographs shown in Figure 1 following the procedure outlined by Xu et al.<sup>30</sup> The HOF was determined for length scales of 50–100 nm in 10-nm increments, and the reported value was averaged over this range.

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## Declaration of Conflicts, Other Disclosures

The authors declare no conflict of interest or other disclosures.

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### Figure captions

**Figure 1.** Scanning electron microscope micrographs illustrate successful carbon nanotube formation from (a) acetylene (0.0008 atm), (b) propargyl alcohol (0.0006 atm), and (c) propiolic acid (0.0006 atm). Structures of each precursor appear in the inset. Herman's Orientation Factors corresponding to these images are  $0.31 \pm 0.04$ ,  $0.17 \pm 0.02$ , and  $0.16 \pm 0.02$ , respectively, signifying that the acetylene forest is better aligned than the propargyl alcohol and propiolic acid forests.

**Figure 2.** X-ray photoelectron spectroscopy (XPS) spectra of carbon nanotubes (CNTs) normalized to C (1s) intensity. (a,b) CNTs derived from acetylene, propargyl alcohol, and propiolic acid show similar oxygen concentrations via (a) the O (1s) peak, with nearly identical location of (b) the C (1s) peak, which indicates lack of difference in C–O bonding. (c,d) When varying amounts of propargyl alcohol were added to 0.03 atm acetylene growths, (c) the presence of propargyl alcohol did not increase O concentration, and (d) the C (1s) peak location did not change substantially. The two groups (a,b; c,d) of CNTs were grown and analyzed at different times (i.e., the data within each pairing is self-consistent).

**Figure 3.** Fourier transform infrared spectroscopy spectra of (a) carbon nanotubes grown from acetylene, propargyl alcohol, and propiolic acid (Ac, PgOH, and PyOOH, top to bottom, respectively), normalized to the  $2700 \text{ cm}^{-1}$  peak. The solid line is the mean of 3 spectra, whereas the shading indicates 1 standard deviation about the mean. (b) Where a solid black line indicates the zero point, different spectra highlight non-zero differences, where the Ac signal is subtracted

from the PgOH and PyOOH signals. Shaded regions indicate library reference locations of important oxygen-containing functional groups.<sup>41,42</sup>

**Figure 4.** Carbon nanotube (a) growth rate and (b) catalyst lifetime as a function of precursor partial pressure for experiments with single precursors. Propargyl alcohol and propiolic acid yield similar growth rates, both consistently lower than acetylene over the range of partial pressures tested. Forests grown from propargyl alcohol or propiolic acid exhibit longer catalyst lifetimes than growths from acetylene. Error bars represent standard deviation on triplicate samples.

**Figure 5.** (a) The addition of propargyl alcohol (labeled as PgOH) to variable amounts of acetylene has no significant impact on growth rate, though (b) catalyst lifetime increases when enough propargyl alcohol is present.

**Figure 6.** Gas-phase composition of effluent from an acetylene- (0.01 atm), propargyl alcohol- (0.0035 atm), and propiolic acid- (0.0008 atm) derived forest (labeled as Ac, PgOH, and PyOOH, respectively). Panel (a) shows the absolute concentrations detected, while (b) normalizes to the precursor partial pressure delivered in each sample, in order to compare the relative species abundance between precursors.