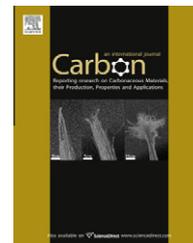


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# Tailoring the microstructure and mechanical properties of arrays of aligned multiwall carbon nanotubes by utilizing different hydrogen concentrations during synthesis

Jordan R. Raney<sup>a</sup>, Abha Misra<sup>b</sup>, Chiara Daraio<sup>a,\*</sup>

<sup>a</sup> Division of Engineering and Applied Science, California Institute of Technology, 1200 E. California Blvd., MC 105-50, Pasadena, CA 91125, USA

<sup>b</sup> Department of Instrumentation and Applied Physics, Indian Institute of Science, Bangalore, Karnataka 560012, India

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## ABSTRACT

We synthesize vertically aligned arrays of carbon nanotubes (CNTs) in a chemical vapor deposition system with floating catalyst, using different concentrations of hydrogen in the gas feedstock. We report the effect of different hydrogen concentrations on the microstructure and mechanical properties of the resulting material. We show that a lower hydrogen concentration during synthesis results in the growth of stiffer CNT arrays with higher average bulk density. A lower hydrogen concentration also leads to the synthesis of CNT arrays that can reach higher peak stress at maximum compressive strain, and dissipate a larger amount of energy during compression. The individual CNTs in the arrays synthesized with a lower hydrogen concentration have, on average, larger outer diameters (associated with the growth of CNTs with a larger number of walls), but present a less uniform diameter distribution. The overall heights of the arrays and their strain recovery after compression have been found to be independent of the hydrogen concentration during growth.

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## 1. Introduction

While the potential applications of carbon nanotubes (CNTs) have garnered much attention [1], the full realization of macroscale benefits from these nanoscale objects remains an active area of research. Chemical vapor deposition (CVD) is one of several approaches used to synthesize CNTs, commonly chosen for its high growth yield [2–4]. The vertically-aligned CNTs (VACNTs) resulting from this process have been proposed for use in a number of applications due to their unique structure, including field-emission electron sources [5], brushes for electrical motors [6], as well as fatigue-resistant foams [7]. In the CVD growth process, the catalyst, usually iron, can be deposited onto an oxidized silicon substrate prior to the CVD process [3]. Alternatively, an appropriate catalyst

precursor, such as ferrocene, can be floated into the system along with a carbon source [4]. This latter approach results in an increased quantity of catalyst particles throughout the resulting material. The continuous deposition of catalyst, however, allows for easier synthesis of tall VACNT arrays, suitable as bulk materials, when compared to the predeposited approach, which requires more elaborate synthesis procedures to obtain tall growth (compare Refs [3,4,8,9]).

The mechanical properties also differ between CNTs grown with pre deposited catalyst and those grown with floating catalyst [10]. For example, the floating catalyst approach has been shown to produce VACNTs that exhibit a foam-like hysteresis during compressive deformation followed by recovery to nearly their original height even after large strains [9]. Such recovery is not typically observed for

\* Corresponding author.

E-mail address: [daraio@caltech.edu](mailto:daraio@caltech.edu) (C. Daraio).

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VACNTs grown with predeposited catalyst (neither as a bulk material nor in the form of micro pillars) [8,10,11], with a recent study concluding that this is a result of differences in CNT surface roughness [12]. The foam-like response of VACNTs synthesized by the floating catalyst approach has already been exploited in the development of electrically conductive VACNT-based composites that absorb more than two orders of magnitude the amount of energy absorbed by typical polymeric foams of comparable bulk density [13].

Despite these promising characteristics, controlling the VACNT properties during synthesis remains a challenge. There have been a large number of studies regarding the optimization of predeposited catalyst CVD synthesis of VACNTs. Progress has been made in understanding how such factors as temperature [3], catalyst layer thickness [14], spacing of catalyst particles [15], various pretreatments of the substrate surface [16], and gas composition [17] can be altered to control certain microstructural properties of the resulting VACNTs. It has also been shown for this type of process that hydrogen can serve an important role in controlling the diameter of the resulting CNTs, as a result of breaking up the deposited catalyst layer into smaller particles [16], and that it can also help prevent the formation of amorphous carbon impurities [18,19].

In the floating catalyst case, there have been several studies about how gas composition affects the quality of synthesis [20–22]. The effect of hydrogen on the properties of individual CNTs has received some attention, but no systematic analysis has been performed to address its impact on bulk mechanical properties. One study of a xylene-based floating catalyst system, for example, concluded that depending on the precise hydrogen concentration present during growth the ensuing product could be soot, carbon fibers, carbon nanotubes, or nothing at all, over a relatively narrow range of hydrogen amounts [23]. However, the extreme hydrogen sensitivity observed in [23] might be set-up dependent, or intrinsic to xylene-based systems.

In the present study the effect of hydrogen concentration on the growth of VACNTs is investigated for a toluene-based floating catalyst system. It is found that multi wall VACNTs of consistent quality are obtained regardless of the hydrogen concentration (examined from 0% to 50% of the total gas feedstock); however the microstructure and mechanical properties change substantially. The purpose of this study is therefore twofold: (i) to explore how the microstructure of arrays of VACNTs depends on hydrogen concentration during synthesis, and (ii) how this changing microstructure affects the bulk mechanical properties of the VACNT arrays. The ability to tune the mechanical properties by altering the hydrogen concentration to be used during synthesis raises the possibility of constructing composite materials with desired strength and deformation properties. For example, this approach could be used to create multilayer materials similar to those reported elsewhere [13,24] but in which the localization of deformation under compressive loading can be predetermined and controlled [25].

## 2. Experimental

Vertically aligned arrays of multiwall CNTs were synthesized by floating catalyst thermal chemical vapor deposition at

atmospheric pressure. The system utilized a long quartz furnace tube with a 4.1 cm internal diameter and a 15 cm heating zone. The temperature of the heating zone was 825 °C. A thermally oxidized Si wafer was used as the substrate for CNT growth. A solution of ferrocene (the Fe catalyst precursor) and toluene (the carbon source) were mixed at a ratio of 0.02 g ml<sup>-1</sup>. A total of 50 ml of this solution was injected into the furnace at ~1 ml min<sup>-1</sup>. Synthesis cycles were performed with different quantities of hydrogen, varying from 0 to 400 sccm in 80 sccm increments (corresponding to concentrations from 0% to 50% of the total gas flow), with argon flow adjusted correspondingly from 800 to 400 sccm to maintain a total combined gas flow rate of 800 sccm. The amount of hydrogen used was fixed during each synthesis cycle. The result of this process was arrays of VACNTs with total thickness (i.e. height along the CNT axis) of ~1 mm. These thick VACNT arrays were resilient against handling and could be physically manipulated. Prior to any mechanical testing, VACNTs on their growth substrate were sectioned into square areas of ~16 mm<sup>2</sup>. The VACNTs were subsequently removed from the growth substrate, to which they were only weakly bonded, with a razor blade. The mass of each sample was measured with a microbalance. The sample height (along the long CNT axis) was determined using a commercial materials tester (Instron E3000). A small preload of about 0.2 N (~0.12 MPa for our samples) was used on all samples to ensure uniform contact. The apparatus measures displacement in 1 μm increments, resulting in an uncertainty of ~0.1% for our samples (~1 mm thick). The volume of each sample was obtained by multiplying the sample height by the corresponding cross-sectional area. Bulk density was then calculated by dividing the mass by the corresponding volume of each sample. The average bulk density of samples grown with no hydrogen in the feedstock was 0.229 g cm<sup>-3</sup>. However the bulk density was observed to vary with the sample's spatial position in the growth substrate. Higher densities were observed for CNTs grown on substrate areas closer to the entrance of the flowing gases, as reported elsewhere [26].

Quasistatic cyclic axial compression was performed with the same apparatus (Instron E3000), along the axis of the VACNTs. The stress–strain response was measured up to a set maximum compressive strain of 0.8 (chosen to avoid exceeding the force capacity of the apparatus), with a constant strain rate of 0.01 s<sup>-1</sup> for both loading and unloading.

Scanning electron microscopy (SEM) was conducted with a FEI Sirion at 15 kV on as-grown samples that had been removed from the growth substrate. Transmission electron microscopy (TEM) was performed using a FEI TF30UT at 300 kV. Samples were prepared for TEM by placing a small amount of the VACNTs into isopropyl alcohol and sonicating until the CNTs were dispersed. A small drop of this solution was placed on a TEM grid and the isopropyl alcohol was evaporated. Raman spectroscopy was performed with a Renishaw M1000 Micro Raman Spectrometer System using an Ar ion laser of wavelength 514.5 nm on samples removed from the substrate.

## 3. Results and discussion

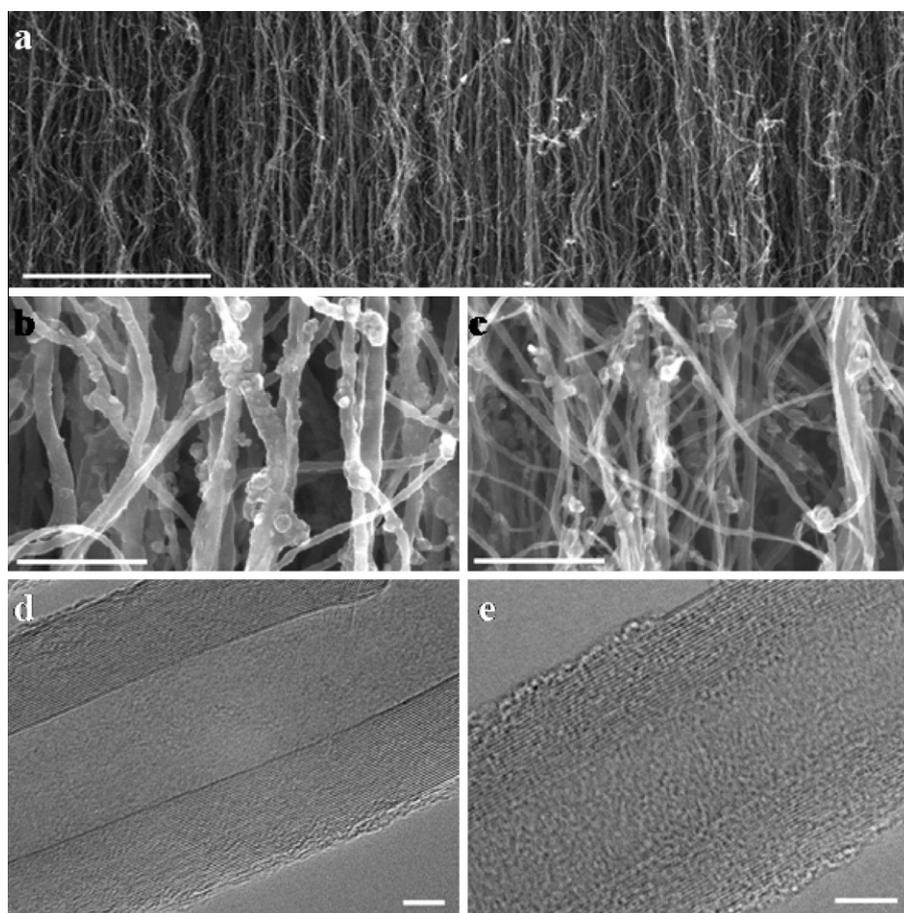
After completing synthesis of VACNTs using six different hydrogen concentrations (0–50% in 10% increments) the

resulting samples were characterized by SEM and TEM, as shown in Fig. 1. The SEM image in Fig. 1a shows the aligned nature of the CNTs as synthesized. SEM images at higher magnification for samples synthesized with no hydrogen (Fig. 1b) and maximum hydrogen (Fig. 1c) reveal a clear decline in the average diameter as the hydrogen concentration is increased. Likewise, TEM images in Fig. 1d and Fig. 1e display representative features of CNTs synthesized with no hydrogen and maximum hydrogen, respectively. Note the reduced number of walls present in CNTs produced with more hydrogen.

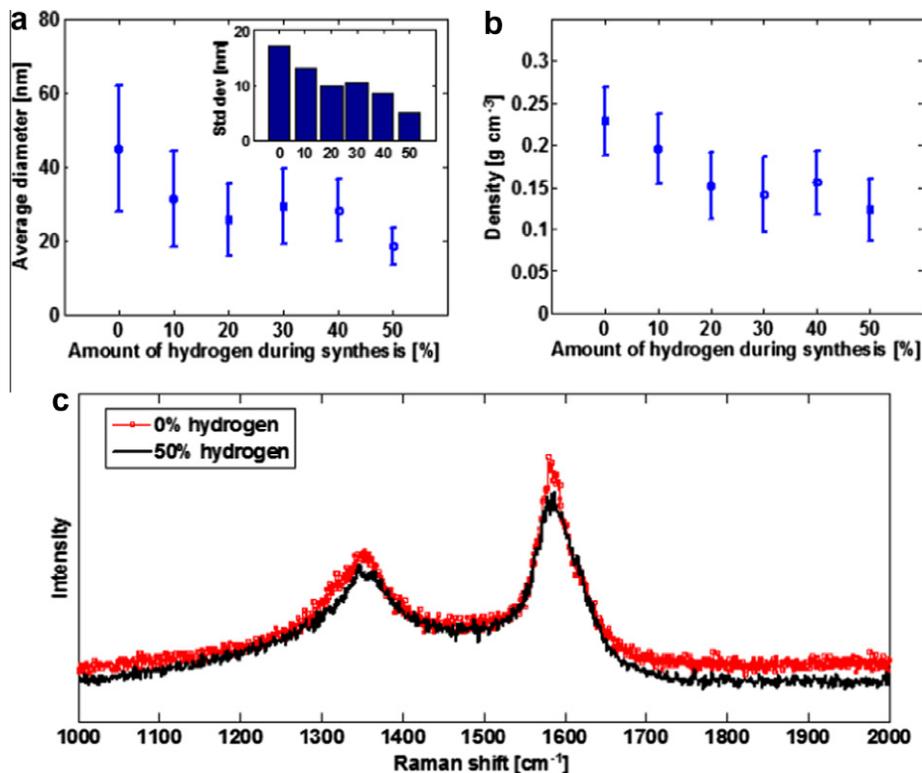
We relied on high resolution SEM to statistically quantify variations in the CNT diameters. For consistency, we acquired images of the CNTs at the vertical midpoint of the growth area, to measure the CNT diameters from the same location in every sample. Results are shown in Fig. 2a. The standard deviation of the diameter distribution corresponding to a particular hydrogen concentration also drops significantly with increasing hydrogen concentration (inset of Fig. 2a). That is, a higher concentration of hydrogen during synthesis results in CNTs with a lower average diameter and an increased uniformity of diameters. This effect is in agreement with observations made in the case of floating catalyst synthesis of single-wall CNTs [27].

At the macroscale, the average height of the VACNTs does not change significantly with variations in the hydrogen concentration. However, their bulk density presents visible changes when the amount of hydrogen is varied in the feed-stock (Fig. 2b). The average sample density for each hydrogen concentration was determined by taking the average bulk density over all samples grown on a substrate (about 20 samples for each hydrogen concentration). Variations in the mean sample densities are shown in Fig. 2b. It is evident that the decline in average CNT diameter that is observed for increased amounts of hydrogen in the synthesis process is reflected by a decrease of the average bulk density of the samples. Error bars in Fig. 2b are related to the variation in density that arises during growth in different areas of the substrate (see Section 2).

We used SEM images to characterize the areal density of the CNTs (number of CNTs grown per unit area). The areal density increases with the use of a higher concentration of hydrogen during synthesis, verifying that the reduction of bulk densities is not simply a result of a decline in the number of CNTs. High-resolution transmission electron microscopy (HRTEM) analysis of the individual multi-wall tubes revealed that the core diameter (the diameter of the innermost wall), does not statistically change with hydrogen concentration.



**Fig. 1** – (a) SEM image of a typical sample showing the mostly-aligned nature of VACNTs as synthesized; scale bar is 5  $\mu\text{m}$ . (b and c) High resolution SEM images of CNTs grown with no hydrogen and those grown with 400 sccm (50%) hydrogen, respectively; scale bars are 500 nm. (d and e) TEM images of characteristic CNTs synthesized with no hydrogen and with 400 sccm (50%) hydrogen, respectively; scale bars are 5 nm.



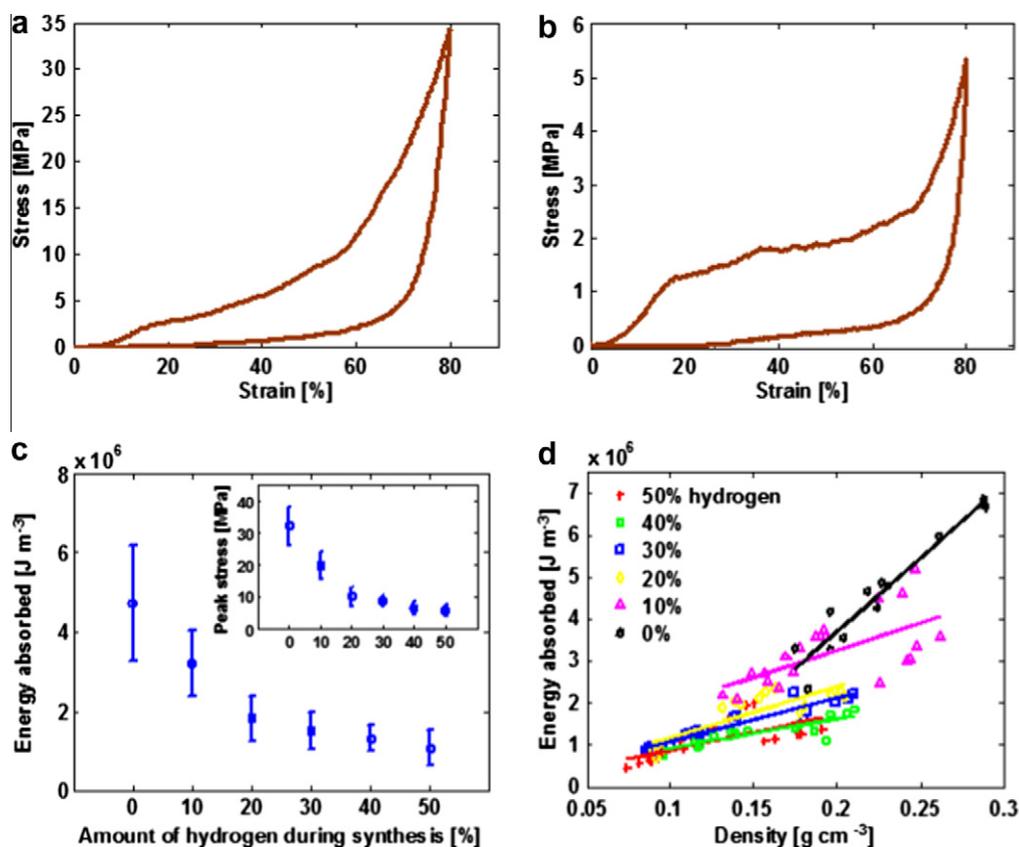
**Fig. 2 – (a) Average CNT diameter for each hydrogen concentration tested, as measured with high resolution SEM; the standard deviations of the respective diameter distributions are shown in the inset to emphasize the narrowing of the diameter distributions for increasing amounts of hydrogen. (b) Average bulk density of the CNT samples as a function of the hydrogen concentration. (c) Representative Raman spectra for samples grown with 0% (top curve) and 50% hydrogen (bottom curve). The D peak (left) is defect-induced, and the G peak (right) corresponds to in-plane displacement of graphitic carbon.**

A similar effect was observed in studies of floating catalyst systems with other additives instead of hydrogen [21], and also in studies of the effects of hydrogen in plasma-enhanced CVD systems [28]. The decline in the CNTs' outer diameters, from an average of  $\sim 46$  nm for 0% hydrogen to  $\sim 19$  nm for 50% hydrogen, corresponds to a change in the number of walls from  $\sim 56$  for 0% hydrogen to  $\sim 18$  for 50% hydrogen. The observed trend in the decline of CNTs' diameters is in agreement with earlier reports for CNTs grown in a CVD system with a predeposited catalyst [16,18,19]. It has been shown that introducing hydrogen into thermal CVD systems narrows Fe catalyst particles [16] and that this results in CNTs of smaller diameters [16,22,29,30]. We expect that this effect is the primary reason why our CNTs become narrower with increasing hydrogen concentration in the furnace. In order to rule out the possibility of hydrogen-induced etching as the cause of the observed smaller diameters, we placed already-synthesized CNTs back in the presence of hydrogen in synthesis conditions: we did not observe any perceptible etching or narrowing of the CNTs. Thus, the hydrogen alters the CNT diameters only when it is present during synthesis, affecting the catalyst.

It was a concern that increasing hydrogen concentrations could cause defects in the CNT walls [31]. Raman spectroscopy measurements were performed to provide more quantitative information on the possible formation of defects induced by hydrogen (e.g., Fig. 2c). Results showed the pres-

ence of the typical peaks associated with Raman spectra of multi-wall CNTs. The D peak (the left peak in Fig. 2c) is associated with lattice defects and particle-size effects [32]. The G peak (the right peak in Fig. 2c) is associated with in-plane displacement of graphitic carbon (e.g., Fig. 2c) [32]. The ratio of the intensity of these peaks is often used as an indicator of the quality of CNTs (e.g., [33]). It was found, however, that changing the hydrogen concentration resulted in no significant changes in this ratio. It is likely that the many walls (15–70) of our CNTs make them resilient against the marginal etching effects of hydrogen [28].

We performed quasistatic cyclic compression tests (see Section 2) to characterize variations in the mechanical properties of the VACNTs induced by the presence of hydrogen during the synthesis process (and by the related microstructural changes). All samples tested were of similar size and geometry, though it should be noted that VACNTs appear to exhibit compressive behavior that is independent of the geometry of the array [10]. Typical results for a loading and unloading cycle obtained from a sample grown with 0% hydrogen are shown in Fig. 3a and for a sample grown with 50% hydrogen in Fig. 3b. The stress-strain relationship for floating catalyst VACNTs under compression has been previously observed to exhibit a characteristic three-regime deformation behavior with hysteretic recovery [9], quite similar to classical foams [34]. This dissipative, hysteretic behavior is thought to be a result of friction that arises as the CNTs slide



**Fig. 3** – (a and b) Characteristic stress–strain curves obtained for the first cycle during quasistatic compression for the case of no hydrogen and that of 50% hydrogen, respectively. (c) Average energy absorbed per unit volume calculated for the first compressive cycle for each hydrogen concentration. The inset shows the variation of the peak stress values obtained at maximum (0.8) strain as a function of the hydrogen concentration used during growth. (d) Energy absorbed in the first compressive cycle plotted as a function of density for all concentrations of hydrogen.

past one another [7,9]. The three deformation regimes correspond to: (i) an initial linear elastic region for small strains, (ii) a plateau region associated with buckling for intermediate strains, and (iii) a final “densification” stage for high strains [7]. The representative results reported in Fig. 3a and b for our samples show that an increased hydrogen concentration during synthesis results in a stress–strain relationship that more closely conforms to that expected for an ideal foam, with three distinct regions with different behaviors [34], and a more distinct plateau region with lower peak stresses.

We relate this phenomenon to the observed changes in the microstructure of the VACNTs, and particularly to the different diameter distribution associated with each hydrogen concentration. As shown in Fig. 2a and the inset therein, an increased amount of hydrogen during synthesis leads to the growth of VACNTs presenting a much narrower diameter distribution, and therefore a more uniform microstructure. If the CNTs are approximated as Euler columns, as they can be when their length greatly exceeds their radius [35], their critical buckling stress is expected to be proportional to the square of the radius. An array of Euler columns of different diameters will not buckle at a single stress value. As a consequence, CNTs that are synthesized with a large amount of hydrogen (i.e., with small diameter variations within the array, e.g., a diameter distribution with a standard deviation

of less than 5 nm for the 50% hydrogen case) should buckle more uniformly compared to those synthesized without hydrogen (i.e., with a much wider diameter distribution, with a standard deviation of 17 nm). This analysis is in qualitative agreement with the results displayed in Fig. 3a, where the stress–strain curve for the VACNTs grown with no hydrogen shows a progressive buckling behavior (i.e., an approximate plateau regime with a gradual increase of stress) over a broad stress range between 2 and 10 MPa. In contrast, VACNTs synthesized with 50% hydrogen (Fig. 3b) display a more uniform buckling behavior (i.e., a distinct plateau regime) over a much narrower stress range, between 1.3 and 2.5 MPa. It was observed that VACNTs synthesized at all hydrogen concentrations recover approximately the same amount of strain (about 0.1 residual strain after the first compressive cycle to a maximum strain of 0.8) for all samples, regardless of hydrogen concentration.

The energy absorbed per unit volume by the VACNTs during a particular compressive cycle was calculated by integrating the area within the hysteresis loop in the stress–strain curve, and was compared among samples grown with different amounts of hydrogen. An increased amount of hydrogen during growth correlates not only with CNTs of narrower diameters but also with reduced energy absorption during compression (Fig. 3c). The decline in energy absorbed appears

to reach a plateau level when the amount of hydrogen used during synthesis increases to 40–50%. The peak stress obtained at maximum strain, 0.8, follows the same trend (see Table 1 and the inset of Fig. 3c). We attribute this decline in energy absorption and peak stress to the observed variation in the microstructural properties (i.e., the variation in the bulk density of the VACNT arrays and in the individual CNT diameters/number of walls). This decrease in peak stress and energy dissipation that occurs for the VACNTs synthesized with larger amounts of hydrogen matches the decreased diameters of the CNTs themselves (and hence a decrease in the force they can bear) rather than a decline in CNT quality, as noted in the Raman analysis.

As described earlier, the density of the VACNT arrays taken from a given substrate varies with position (higher densities are measured for samples taken from areas of the growth substrate closer to the entrance of the gases in the furnace). For any given hydrogen concentration, the energy absorption of each VACNT array depends nearly linearly on this density variation (see Fig. 3d). A similar relationship has been observed for VACNTs in the variation of peak stress with density [26]. However, it is interesting to note that two VACNT samples with the same bulk density, but synthesized with different concentrations of hydrogen, will typically absorb slightly different amounts of energy in compression, revealing that bulk density alone is not a sufficient predictor of mechanical properties. That is, a separate linear relationship between bulk density and energy absorption exists for each hydrogen concentration utilized (Fig. 3d).

It was shown in the past that VACNTs exhibit a preconditioning effect under compression [7,9,13] such that the first one or two cycles differ somewhat in their mechanical prop-

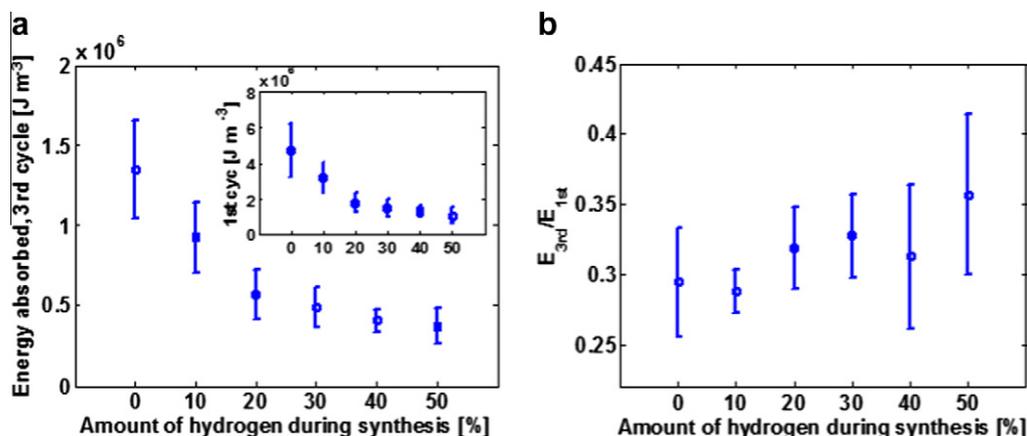
erties from later cycles. For example, earlier studies [7] showed a decline in energy dissipation (i.e., the area of the stress–strain hysteresis) from the first to subsequent cycles, although these later cycles rapidly reached a steady-state response, showing resilience against fatigue. In addition to looking at the mechanical properties of the first compressive cycle, we performed cyclic compressive tests to characterize the response of the CNT arrays at steady state. In our samples, the material response in compression reached steady-state by the third cycle. We compared the samples' behavior at the third cycle with that of the first cycle (in which preconditioning effects are substantial). The steady-state energy absorption and peak stress values showed roughly the same decline with increased hydrogen concentration as observed for the first cycle (e.g. compare the plot in Fig. 4a for the third cycle with the inset in the same figure). As expected, each VACNT sample displayed a softening and a drop in energy absorption from the first to the third cycle due to preconditioning effects. However, there is a slight decline in the size of this drop for samples synthesized with increasing hydrogen concentration (Fig. 4b). That is, the drop in energy dissipation from the first to later cycles associated with preconditioning becomes slightly smaller with increasing hydrogen concentration during synthesis. This is consistent with the observed constitutive response of the materials (compare Fig. 3a and b).

#### 4. Summary

We report that controlling the amount of hydrogen during floating catalyst chemical vapor deposition of vertically aligned arrays of carbon nanotubes has important structural

**Table 1 – Effect of H<sub>2</sub> concentration on peak stress and energy dissipation.**

H <sub>2</sub> conc. (%)	0	10	20	30	40	50
Avg. stress at 0.8 strain (MPa)	32.3 ± 5.9	19.8 ± 4.4	9.9 ± 3.3	8.6 ± 1.8	6.5 ± 1.8	5.9 ± 1.8
Avg. energy dissipation per unit volume (MJ/m <sup>3</sup> )	4.73 ± 1.45	3.21 ± 0.83	1.82 ± 0.57	1.51 ± 0.48	1.31 ± 0.31	1.08 ± 0.44



**Fig. 4 – (a) Average energy absorbed during the third cycle plotted as a function of the amount of hydrogen during synthesis. The inset shows the average energy absorbed during the first cycle as a comparison. (b) Ratio of average energy absorbed during the third cycle to that absorbed during the first cycle as a function of the amount of hydrogen during synthesis.**

and mechanical effects. Using a lower hydrogen concentration in the furnace feedstock leads to the growth of stiffer CNT arrays with higher average bulk density, a less uniform diameter distribution, and larger average CNT diameters (i.e., due to the growth of individual CNTs with a larger number of walls). A lower hydrogen concentration also leads to the synthesis of CNT arrays that can reach significantly higher peak stresses at maximum strain, and that can absorb increased amounts of energy during compression. Both the overall height of the arrays and their strain recovery after compression have been found to be independent of hydrogen concentration during growth.

We also found that the stress–strain curves for samples synthesized without hydrogen do not present the clear three-regime deformation behavior characteristic of CNT foams, likely a result of the non-uniformity of the associated CNTs. In contrast, samples synthesized with higher amounts of hydrogen better conform to the stress–strain behavior exhibited by ideal foams. This study shows that using different concentrations of hydrogen during synthesis allows for the tuning of microstructural properties of VACNTs, including the ability to control the distribution of CNT diameters and the number of CNT walls, and consequently their mechanical response. This contributes to an understanding of the tunability of CNT-based materials, at microstructural and bulk levels, and it is expected to facilitate the design of new materials with tunable mechanical properties for many potential applications, such as protective foams and novel laminar structural composites.

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