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Effect of electro-mechanical coupling on actuation behavior of a carbon nanotube cellular structure

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ABSTRACT

We demonstrate the effect of mechanical strain on the electrostrictive behavior of catalytically grown cellular structure of carbon nanotube (CNT). In the small strain regime, where the stress–strain behavior of the material is linear, application of an electric-field along the mechanical loading direction induces an instantaneous increase in the stress and causes an increase in the apparent Young's modulus. The instantaneous increase in the stress shows a cubic-polynomial dependence on the electric-field, which is attributed to the non-linear coupling of the mechanical strain and the electric-field induced polarization of the CNT. The electrostriction induced actuation becomes >100 times larger if the CNT sample is pre-deformed to a small strain. However, in the non-linear stress–strain regime, although a sharp increase in the apparent Young's modulus is observed upon application of an electric-field, no instantaneous increase in the stress occurs. This characteristic suggests that the softening due to the buckling of individual CNT compensates for any instantaneous rise in the electrostriction induced stress at the higher strains. We also present an analytical model to elucidate the experimental observations.

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1. Introduction

Catalytically grown cellular structure of carbon nanotube (CNT), akin to foam like materials, has gained significant importance for their excellent mechanical, sensing and electro-mechanical properties [1–6]. Moreover, owing to the extreme ease of their mass production in any pattern [7,8], these CNT based structures have high potential to become an important engineering material in the near future.

Fig. 1 shows a pictograph of a cellular structured CNT sample (shown in the inset) along with its microstructural details at higher magnification. As shown in Fig. 1, the microstructure of a cellular CNT sample consists of free-standing and nominally vertically aligned bundles of CNT, which are often constricting or entangling. Due to this anisotropic configuration of these cellular CNT samples, their physical properties, such as mechanical strength, electrostriction induced actuation, etc., in the axial (i.e., parallel to the nominal length of a CNT) and the transverse directions are inherently different; notably, the properties along the axial direction is often of major importance for their many-fold superiority over the properties in the transverse direction.[1] These cellular structures have shown super-compressibility along the axial direction where the samples not only show significantly large stress–strain hysteresis, but also almost fully recover their original dimensions even after several hundreds of loading–unloading cycles to 80% of compressive strain [5]. Thus, these ultra-low density samples have been proposed as preferable materials for shock absorption and damping applications [5,9,10]. In addition, these cellular structures of CNT also show electrostriction

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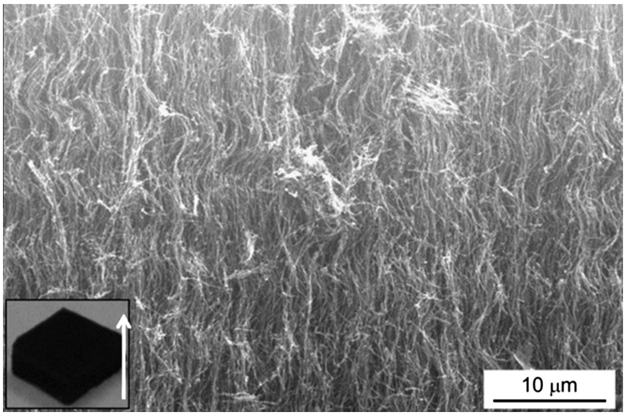

Fig. 1 – A representative micrograph of the cellular structured CNT sample showing the configuration of the CNT along the axial direction (shown by the vertical solid arrow). These CNT are multiwalled. The inset at the lower left corner shows a digital pictograph of a sample.

induced ultra-high actuation [1,2,11,12]; for example, macroscopic sheets of single walled CNT (SWCNT) showed axial strains of up to >1% under physiological conditions [1]. The extraordinary compressibility and large electrostrictive actuation, when combined with their high thermo-mechanical stability at >400 °C in the air [13], readily make them suitable for myriad real-life sensor–actuator applications.

Based on a quantum-molecular dynamics based theoretical analysis, it has been proposed that the tensile-load bearing capacity of a SWCNT significantly reduces if an electric-field is applied in the direction of loading [14]. Furthermore, it was also proposed through similar theoretical analysis that the electric-field induced polarization (or, equivalently, the charge density distribution) is significantly enhanced at very large electric-field if the SWCNT is pre-deformed [15]. However, an experimental evidence of such an electro-mechanical coupling in a CNT structure is not available. Furthermore, it is also not known how the electrostriction induced actuation behavior of cellular structure of CNT, where several thousands of CNT are placed next to each other in close proximity, would change due to such an electro-mechanical coupling. Such an effect is of major technical importance as invariably a sensor or an actuator has to sustain mechanical straining due to its casing or over a period of continuous use. To study the aforementioned effects, we examined the effect of electric-field on the mechanical behavior of the cellular structure of the CNT under compression, and corroborate the experimental findings with an analytical model.

2. Experimental

Large sheets of cellular structure of multi-walled CNT (MWCNT) were grown on silicon dioxide substrate using the catalytic thermal chemical vapor deposition process; the details of the processing technique are available in Ref. [8]. Fig. 1 shows a representative scanning electron micrograph of the CNT sample showing the cross-sectional view along the axial direction. CNT samples of ~2.0 mm length and ~2.0 mm width were cut from a large sheet using a sharp

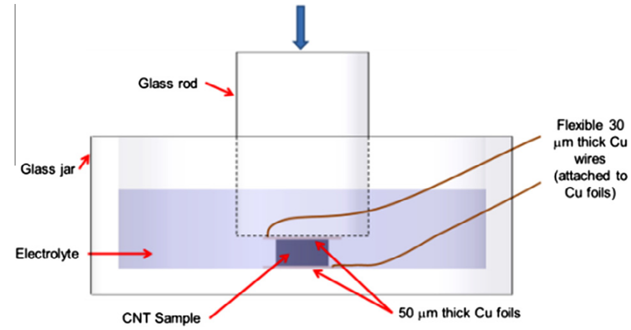

Fig. 2 – The experimental set-up employed to apply an electric field in presence of a mechanical stress (or strain). Both, the stress (and, strain) and the electric field, were applied in the axial direction. All tests were conducted at room temperature.

X-Acto knife. The height of a typical sample was ~1.1–1.2 mm. The typical bulk density of these samples was measured to be ~0.28 g/cm^3, indicating these cellular structures were only ~20% dense (the density of CNT is ~1.4 g/cm^3 [16]).

Fig. 2 shows a schematic of the test-set up. The sample was placed between two Cu foils. An electric potential difference was applied between the two Cu foils using a dual-source-meter (Keithley 2602A); thus, the generated electric-field was parallel to the axial direction. Using a source-meter enabled us to also measure the current–voltage (I–V) characteristic of the samples. The sample was immersed in a 20% concentrated H_2SO_4 solution for the generation of double charge layers, as discussed in Ref. [1]. A mechanical tester (Instron 5967), equipped with a 100 N load cell and a glass loading-rod, was used to apply compressive loads on the sample. Samples were loaded to various strains ranging from 10% to 30% at a constant engineering strain-rate of 10^{-3} s^{-1}. Following loading, the samples were completely unloaded at the same strain-rate of 10^{-3} s^{-1}. The stress–strain data was digitally recorded for each loading–unloading cycle. To isolate the effects of the strain on the electrostriction behavior of the CNT samples, the actuation behavior of the samples was also measured under no-load (or, no pre-deformation) condition. To do so, a laser-interferometry based extensometer, instead of the linear variable displacement transducer (LVDT) attached to the mechanical tester, was used to measure the displacement while the rest of the experimental set-up remained the same. The sample, the electrolyte, the flexible Cu wires and the Cu foils were replaced after each test.

3. Results

Fig. 3a shows the effect of the electric-field, applied along the axial direction on the electrostriction induced axial strain of the cellular structured CNT sample. The sample was immersed in a 20% H_2SO_4 solution and compressive load was not applied. Fig. 3a readily shows that the uniaxial strain, ε monotonically increased with the applied electric-field, E_f and the following gives the relationship between these two quantities:

$$\varepsilon = CE_f^2 \quad (1)$$

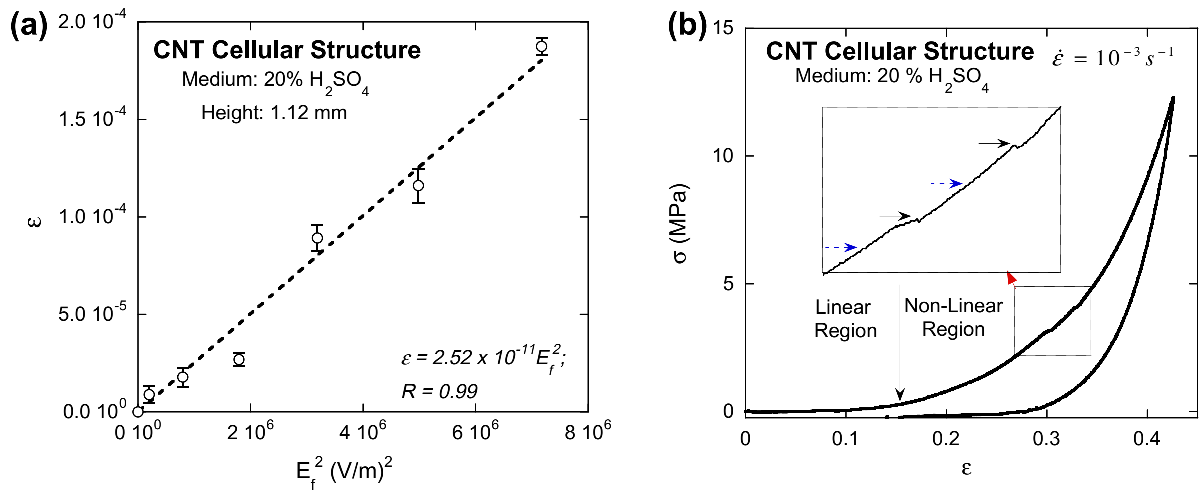

Fig. 3 – (a) Variation in the electrostriction induced axial strain of the cellular structure of CNT with the applied electric-field. The dotted line shows the linear best-fit curve of type y = Cx; this imposes the "$\varepsilon = 0$ at $E_f = 0$" condition. (b) The stress–strain response of a CNT sample in the absence of electric-field over the first loading–unloading cycle. The downward arrow shows the strain across which the stress–strain behavior of the sample transitions to the non-linear regime from the linear regime. The graph in the inset (enclosed by broken lined rectangle) shows a magnified view of the area enclosed by the broken lined rectangle on the full plot. The solid and broken horizontal arrows show some of the large- and small- stress plateaus, respectively, formed due to the buckling of the CNT. Considerable softening, shown by a dip in the stress value, is noted near the solid horizontal arrows.

where C is the equivalent uniaxial electrostriction coefficient of the cellular structure of the CNT. C was equal to 2.52×10^{-11} m^2/V^2 for the sample tested in this study. Irrespective of the direction of the applied electric field, the induced strain in the samples was always tensile; therefore, the parabolic form of Eq. (1) is appropriate. Furthermore, the parabolic dependence of the electrostrictive strain on the applied electric-field is consistent with the theoretically reported dependence of the surface charge density (or, polarization) of SWCNT on the applied electric field [14,15]. This observation suggests that the polarization of individual CNT and also, thereby the repulsive Columbic forces generated between neighboring CNT predominantly govern the electrostriction behavior in these cellular CNT samples submerged in an electrolyte.

Fig. 3b shows a representative stress–strain behavior of a cellular structure of the CNT sample tested under compression at a quasi-static strain rate of 10^{-3} s^{-1}. The following salient features of the mechanical behavior of these samples are readily apparent: (a) the stress–strain behavior appears to be linear at low strains (i.e., on the left side of the downward arrow in Fig. 3b), and (b) the stress non-linearly increased with the applied strain at high strains. In the linear region, the behavior is dominated by the commutative elastic outward bending of individual CNT [5,17], where the bending of a CNT is resisted by the neighboring columns of the CNT. The bending controlled compressive strain may fully recover upon the release of the stress. However, due to the slide or breaking of the constrictions (or, entanglement) (Fig. 1), which are formed due to the crossing of two or more CNT, some of the strain energy was dissipated resulting in a finite stress–strain hysteresis. These samples manifested stress–strain hysteresis even if they were loaded–unloaded in this linear region only. Since the CNT sample did not instantaneously recover its original length following the removal of the compressive load, we call this region as "linear" and refrain from using the term "elastic". Strengthening due to the densification of the cellular structure and the buckling of CNT dominated the stress–strain behavior in the non-linear region [5,13,18–21]. Buckling of the CNT may often lead to softening of structure [5,21], or formation of a stress plateau on the stress–strain plots [19]; a few of these locations in Fig. 3b, which is a representative stress–strain plot, are indicated by horizontal arrows. It appears that the instances of small scale buckling were manifested as serrations in the stress–strain plots (broken arrows in Fig. 3b, inset) whereas large scale buckling, perhaps involving complete folding of CNT [5], often led to a decrease in stress with strain (i.e., softening, as indicted by solid arrows in Fig. 3b, inset).

Fig. 4 shows the effect of electro-mechanical coupling on the electrostriction induced actuation behavior of the cellular structure of CNT in the linear and non-linear regimes of the stress–strain behavior. In both regimes, application of an electric-field induced a significant deviation from the usual stress–strain behavior. In the linear region, there was an instantaneous increase in the stress value and a small increase in the apparent Young's modulus, E of the sample, whereas no such instantaneous increase in the stress value was recorded in the non-linear region, but increase in the Young's modulus remained significant. Interestingly, a short burst of stress jump followed by a significant dip in the stress was observed following the application of an electric-field in the non-linear region; this suggests occurrence of a large scale buckling due to the "attempted" rapid rise in the stress in response to the electrostriction induced actuation or expansion. The suggestion of the occurrence of the aforementioned buckling is also supported by the instantaneous decrease in the stress upon re-

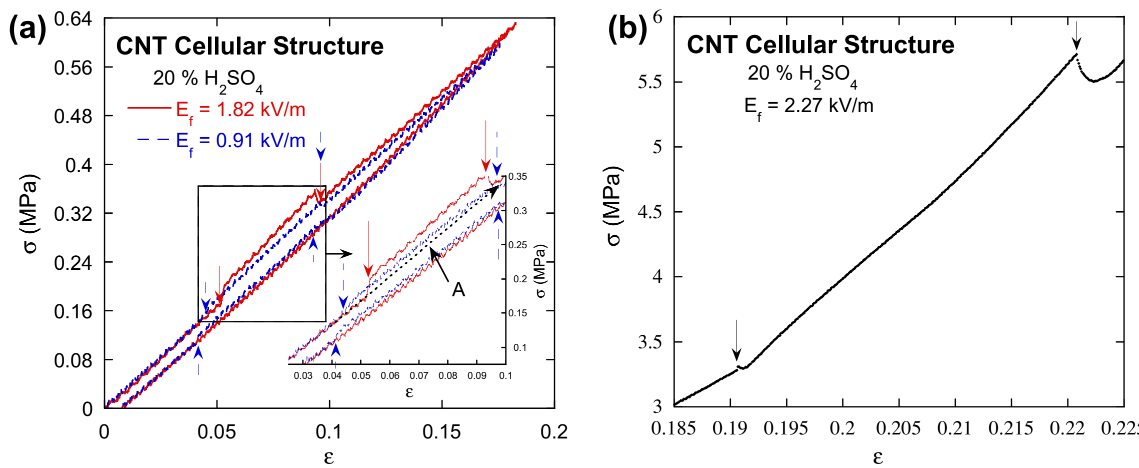

Fig. 4 – The effects of electro-mechanical coupling on the stress–strain behavior of cellular structure of CNT samples in the (a) linear and (b) non-linear regimes. The vertical arrows show the instant of the application of an electric-field, and the corresponding pair of the arrow shows the instant at which the electric-field was switched-off. The inset in (a) is a magnified view of the enclosure formed by the broken-line-rectangle. The broken line, as indicated by an arrow with "A" in the inset, is the expected stress–strain path if the electric-field would have not been applied. Preliminary study, where experiments were conducted on slightly longer and less dense CNT samples, did not show any noticeable effect of the size and the density of CNT sample on the basic nature of the aforementioned electro-mechanical coupling.

moval of the electric-field (shown by the rightmost downward arrow in Fig. 4b). Fig. 4a also reveals that the electric-field induced changes in the stress–strain behavior were although dependent on the applied electric-field, the CNT structure did not seem to have any long-term memory of the deformation incurred under the electric-field, and as soon as the electric field was switched off, its stress–strain behavior became identical to that of the sample which was not exposed to any electrical excursion. This is further corroborated with the observations that upon switching-off the electric-field in both regimes, the stress instantaneously dropped to the level that would be expected if the electric field was not applied at all; the same was also observed for the values of the Young's modulus. This property of absorption of extra strain energy upon application of electric-field and reverting back to its shape as if no electric-field has been applied can easily be employed to further improve the shock absorption and damping capacity of the CNT based dampers. Furthermore, as shown in Fig. 4a (broken blue[2] line), similar changes in the stress–strain behavior were also observed if an electric-field was applied while unloading.

Fig. 5a and b systematically summarize the effect of the electric-field on the stress–strain behavior of the cellular structured CNT samples: (i) the instantaneous rise in the stress as well as the Young's modulus monotonically increased with the applied electric-field and (ii) the increase in the Young's modulus was more rapid in the non-linear region as compared to the linear region. The choice of the axes in Fig. 5b and the related physics will be discussed below.

4. Discussions

Since the following parameters predominately affect the Young's modulus of a cellular structure of the CNT: (i) the inherent stiffness of the CNT bundles, and (ii) the Columbic repulsion between the neighboring CNT, application of an electric-field should enhance the Young's modulus of these samples as both of the above strongly depend on the extent of the polarization of CNT. The columbic repulsion between neighboring CNT is primarily generated due to the electric-field induced polarization of individual CNT and thereafter formation of double charge layer at the CNT/electrolyte interface; the same mechanism also causes the capacitive interaction between CNT bundles [1,6]. Furthermore, since the distance between the adjacent CNT rapidly reduce with the compression-induced densification of the cellular structure, the Columbic repulsion between the CNT will increase at high strains. Therefore, the Young's modulus of the sample would increase much faster upon application of an electric field in the non-linear regime as compared to the linear regime; this readily explains the trends observed in Fig. 5a.

The theoretical study on SWCNT by Tang et al. [15] proposes that the electric field polarization increases linearly with the applied electric field if the applied strain is zero; however, the electric-field induced polarization increases non-linearly with the electric field once the sample incurs a finite mechanical strain. The addition of the non-linear component derives its physical significance from the effect of the mechanical strain driven non-linear electro-mechanical coupling on the electric-field induced polarization of a CNT. This increase in the polarization due to the imposed strain is consistent with the several reports proposing a change in the surface charge density and the band-gap energy of CNT following its deformation [14,15,22,23]. Since the force (and hence the stress, as well as the strain for the extremely stiff CNT) is proportional to the product of the polarization (or, dipole moment) (refer to Supplemental material 1 for the equation

[2] For interpretation of color in Fig. 4, the reader is referred to the web version of this article.

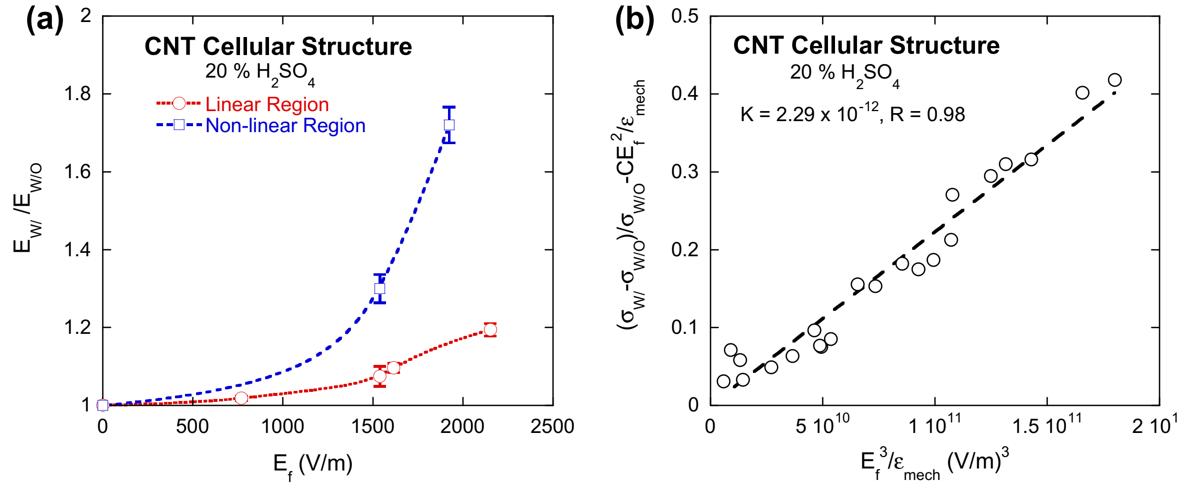

Fig. 5 – Variation in the (a) Young's modulus (*E*), and (b) instantaneous increase in the uniaxial stress (*σ*) upon the application of electric-field. The subscript "W/" and "W/O" denote the corresponding values after (i.e., with) and before (i.e., without) the application of an electric-field, respectively. The value of C in (b) is taken from Fig. 3a.

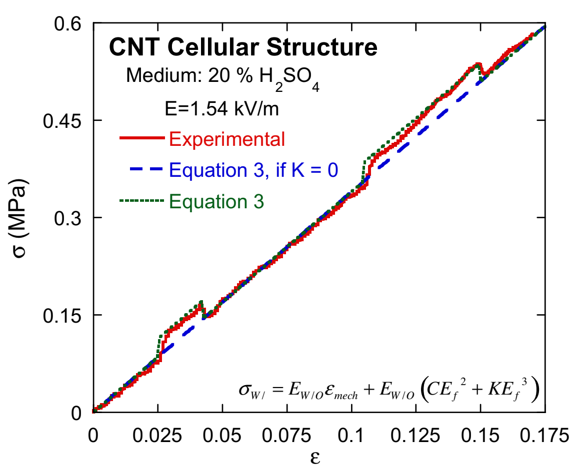

Fig. 6 – Comparison between the experimentally determined stress–strain behavior in the linear regime and the prediction using Eq. (3). The dashed line shows the prediction by Eq. (3) if the effect of the electro-mechanical coupling on the electric-field induced polarization is neglected (i.e., *K* = 0).

relating the dipole moment and the electric-field in the presence and the absence of deformation) and the applied electric field, the following gives, in the simplest form, the electrostriction induced strain if the CNT sample is pre-deformed:

$$\varepsilon = CE_f^2 + KE_f^3 \tag{2}$$

where *K* is a constant representing the effect of the electro-mechanical coupling of CNT.

When an electric field is applied across the cellular structure of CNT, individual CNT inherently tries to expand by a strain as predicted by Eq. (2); however, they are not allowed to axially expand due to the fixed distance between the two loading rods of the mechanical testing machine (which is operating in the constant displacement rate mode). Therefore, an additional stress has to be applied on the CNT sample to constrain its aforementioned upward movement. Since the stress–strain curve at small strains is linear, the total stress can be given by the following:

$$\sigma_{W/} = E_{W/O}\varepsilon_{mech} + E_{W/}\varepsilon = E_{W/O}\varepsilon_{mech} + E_{W/}(CE_f^2 + KE_f^3) \tag{3}$$

where ε_{mech} is the mechanically imposed compressive strain and ε is the electrostriction induced strain, as given by Eq. (2).

Since the increase in the Young's modulus is very small in the linear region (<20%, as shown in Fig. 5a) and $E_{W/O}\ \varepsilon_{mech} = \sigma_{W/O}$ at the instant when the electric-field is applied, dividing Eq. (3) by $\sigma_{W/O}$ gives the following:

$$\frac{\sigma_{W/} - \sigma_{W/O}}{\sigma_{W/O}} - \frac{CE_f^2}{\varepsilon_{mech}} = K\frac{E_f^3}{\varepsilon_{mech}} \tag{4}$$

The left hand side and the right hand side of Eq. (4) are the ordinate and the abscissa in Fig. 5b, respectively, and the achievement of an excellent linear-curve fitting parameter (R~1) clearly validates the proposed understanding behind Eq. (4). Furthermore, Fig. 5b also gives a value of *K* (=2.29×10^{-12} m^3/V^3) for the tested CNT samples, facilitating the use of Eq. (3) to predict the stress–strain behavior of the CNT samples at small strains in the presence (and also, in the absence) of an electric-field.

Fig. 6 compares the experimental stress–strain behavior of a representative CNT sample and the prediction using Eq. (3). It clearly shows that Eq. (3), which captures the effect of the electro-mechanical coupling on the electric-field induced polarization of CNT, can predict the effect of electric field on the mechanical behavior of the cellular structure of CNT (refer to Supplemental material 2 for a few more such comparisons). If the effect of the mechanical strain on the electric-field induced polarization of CNT is not considered (i.e., *K* = 0), the electrostriction induced actuation remains very small (shown by blue[3] dash line); therefore, several folds higher (>100 times) actuation is possible in these cellular structures of CNT samples if they are pre-deformed to a small strain. Interestingly, the observed non-linear effect of

[3] For interpretation of color in Fig. 6, the reader is referred to the web version of this article.

mechanical strain on the electrostriction induced actuation in these CNT samples occurred at much smaller electric-fields as compared to the theoretical predictions for individual SWCNT [14,15]; this might be attributed to the fact that the employed CNT were multi-walled, and also that the Columbic interactions and mechanical constraining effects from the neighboring CNT might generally enhance the electrostriction induced actuation. This, indeed, provides an extraordinary additional tool for designing CNT based actuators. It should be noted that such actuation is not possible in the non-linear regime due to the dominant role of buckling in the deformation of the CNT.

5. Conclusions

(i) The cellular structure of CNT, which is immersed in a dilute acidic electrolyte, showed high electrostriction induced actuation even in the absence of a mechanical load. The electrostriction induced strain was directly proportional to the square of the applied electric field.
(ii) There was a strong effect of the electric-field on the mechanical behavior of the cellular structure of CNT. Application of an electric-field induced an instantaneous increase in the stress at small strains ($\varepsilon < 15\%$); however, the Young's modulus of the sample increased upon application of an electric field at all strains.
(iii) If the cellular structure of CNT samples are excited after pre-straining to small strains, the electrostriction induced strain increases many folds, even by two orders of magnitude.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.04.010.

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