

# In-plane mechanical properties of carbon nanotube films fabricated by floating catalyst chemical vapor decomposition

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**Abstract** Large-scale carbon nanotube (CNT) films fabricated by floating catalyst chemical vapor deposition (FCCVD) are promising reinforcement materials for high performance composites. However, little research has been reported on the four independent in-plane engineering constants of FCCVD CNT films, which are essential for understanding and prediction of mechanical behavior of FCCVD CNT film-based structures. The tensile strength in CNT-oriented direction is 127 MPa and the tensile modulus in oriented and transverse directions are 3.0 and 0.3 GPa, respectively. These mechanical properties are mainly attributed to the as-grown CNT-to-CNT contacts in the films. The Poisson's ratio in the oriented direction at

5 % strain is 0.75. A negative Poisson's ratio of  $-0.99$  is observed at 0.1 % strain in CNT-oriented direction. The in-plane shear modulus is 0.57 GPa, which is derived from the coordinate transformation between the on-axis and 45° off-axis compliance matrices. The in-situ scanning electron microscopy is adopted to observe the microstructure at different tensile strains. During the tensile testing, the reorientation of CNT bundles in CNT film is evaluated by numerical image processing and Raman spectroscopy.

## Introduction

Since the first well-recognized report of carbon nanotube (CNT) in 1991 [1], it has generated huge popularity in various areas due to their outstanding properties [2, 3]. CNT-reinforced composites can be used in various fields such as strain sensor, electrode in battery, gas detection, and so on [4–6]. The CNT composites exhibit excellent mechanical strength and other functional properties, such as high electrical conductivity, electrostatic shielding, and thermal stability [7]. However, the size of individual CNT is too small to be applied in industrial fields. Only CNT films should be the ideal candidate material for large-scale structures. Many methods can produce large-scale CNT film. For example, suspension-based vacuum filtration method [8–11], directly drawing method [12–14], floating catalyst chemical vapor deposition (FCCVD) method [15], and other methods including hydroentangling [16] and electrochemical chemical deposition [17]. However, the vacuum filtration method could not produce strong films [18]. Directly drawing method produces CNT films at high costs. Among these methods, the FCCVD is the most efficient way to produce large-scale CNT films with high quality at an acceptable cost [19]. FCCVD CNT film is one

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of the most promising reinforcement materials for high performance composites.

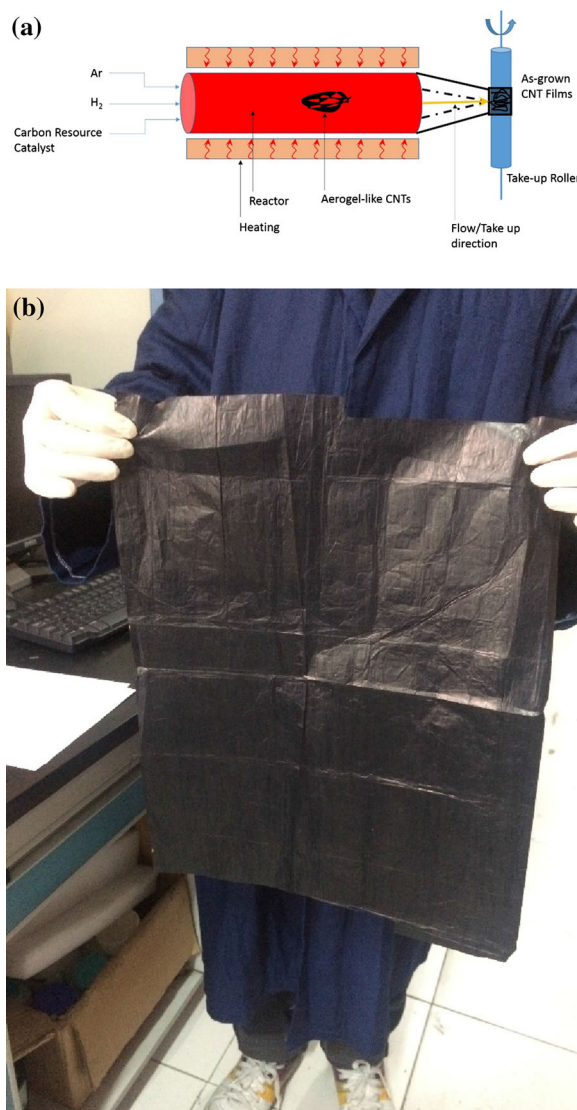
Therefore, the in-plane mechanical properties and engineering constants of FCCVD CNT films are critical for the understanding of CNT film-based structures. In addition, the engineering constants are also important to the numerical simulation of CNT films [20]. The in-plane stress state of the two-dimensional CNT film can be analyzed via its compliance matrix ( $[S]$ ) according to  $[\varepsilon] = [S][\sigma]$  [21]. In the compliance matrix, four independent engineering constants, longitudinal Young's modulus ( $E_1$ ), transverse Young's modulus ( $E_2$ ), major Poisson's ratio ( $\nu_{12}$ ), and in-plane shear modulus ( $E_s$ ), govern the mechanical behavior of CNT films. Once these engineering constants are known, the mechanical behavior of CNT films would be determined. Although many works have been done to research the mechanical properties of CNT films. For example, Ma and coworkers reported the fabrication of FCCVD CNT films and analyzed its mechanical strength via Weibull theory [15]. Coleman and Blighe investigated the factors controlling the strength and modulus of CNT films [22]. Ting and Chang studied the influence of CNT conjunctions on the failure process of CNT films [23]. Recently, Pourhabib and Ding used finite element analysis to predict the modulus of buckypaper [24]. However, little paper researched the in-plane engineering constants of FCCVD CNT films.

In this study, we investigated the four independent in-plane engineering constants of FCCVD CNT films. The uniaxial tensile testing measured the longitudinal Young's modulus, transverse Young's modulus, Poisson's ratio, and in-plane shear modulus. The in-situ scanning electron microscopy (SEM) was conducted to observe the microstructures of CNT films during tensile test. Transmission electron microscopy (TEM) was adopted to observe the structure of individual CNT in the films. The reorientation of CNT bundles was analyzed via numerical image processing and Raman spectroscopy.

## Experimental

### FCCVD CNT films

The CNT films were received from the Suzhou Institute of Nano-Tech and Nano-Bionics (Suzhou, China). It was fabricated by FCCVD methods as shown in Fig. 1a. The ethanol, ferrocene, and thiophene were injected into the heated reactor (1300 °C) at a feeding rate of 0.15 ml min<sup>-1</sup>. The Ar–H<sub>2</sub> mixture (volume ratio 1:1) was injected into the reactor at a rate of 4000 sccm. The aerogel-like carbon nanotubes grew spontaneously in the

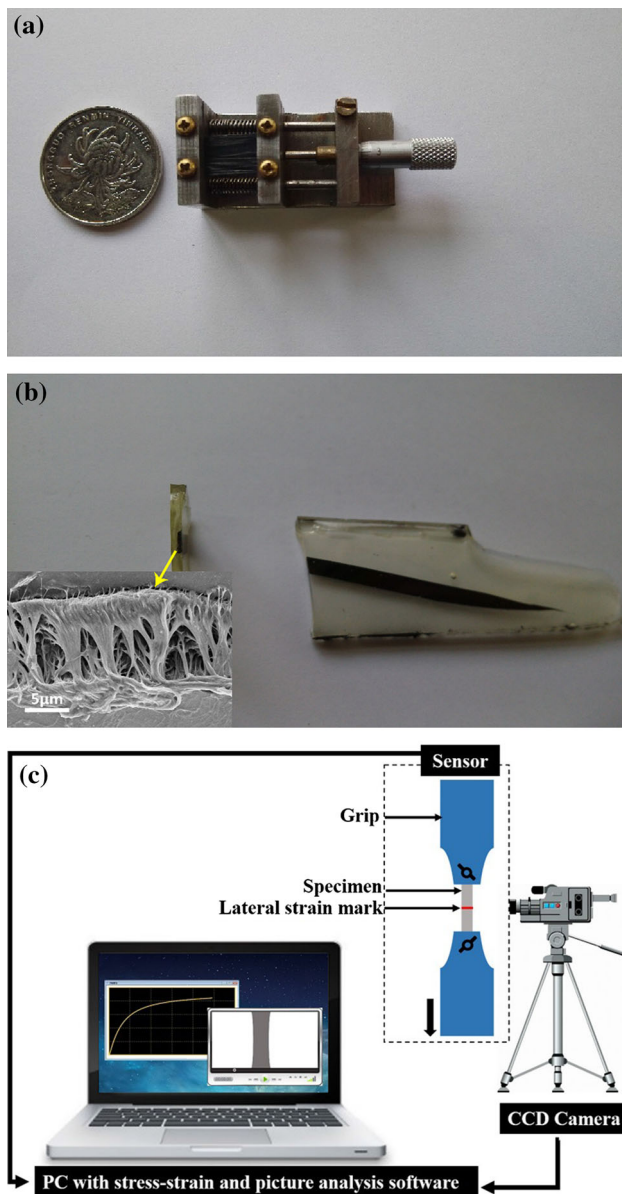


**Fig. 1** a FCCVD fabrication process, b large-scale CNT films

reactor, which can be blown out with the gas flow. The CNTs were wound onto the roller. During this process, the CNT bundles preferentially aligned to the take up direction. Thereafter, the porous CNT assemblies were densified by the ethanol. The as-prepared large-scale CNT films are shown in Fig. 1b.

### Characterizations of CNT films

The purification of CNT film was determined via thermal gravity analyzer (TGA). The microstructures of CNT films were observed by the field emission SEM (FESEM, HITACHI S-4800). A specially designed SEM stage (Fig. 2a) was mounted in SEM chamber to observe the in-situ CNT deformation during tensile test. The thickness of CNT film was measured from the cross section (Fig. 2b)



**Fig. 2** **a** In-situ SEM testing stage, **b** brittle fracture surface, **c** schematic of uniaxial tensile and Poisson's ratio testing apparatus

under SEM. In addition, the nano-pore analyzer (Quantachrome Porometer 3 G-zh) was used to measure the pore distribution in the film. TEM (JEOL JEM-2100) was employed to observe the structure of individual CNT in the films. The numerical imaging processing method and Raman spectroscopy were adopted to analyze the reorientation of CNT bundles [25].

During the tensile testing, the tensile loads were applied onto specimen in three directions: (1) preferential/longitudinal direction, in which most of the CNT bundles aligned parallel to each other. This preferential alignment was caused by the material flow during fabrication as shown in Fig. 1a. The preferential direction was further

defined as on-axis direction in the flowing, (2) transverse direction, which was perpendicular to the preferential direction, and (3) 45° off-axis direction. In addition, the gage length for tensile testing was 10 mm. The specimen width was 5 mm. All samples were tested on tensile tester (XS (08) XG, Fig. 2c). The extension rate was 0.3 mm min<sup>-1</sup>. A camera was used to record the lateral strain simultaneously. At least 20 specimens were tested successfully for statistical analysis.

## Results and discussions

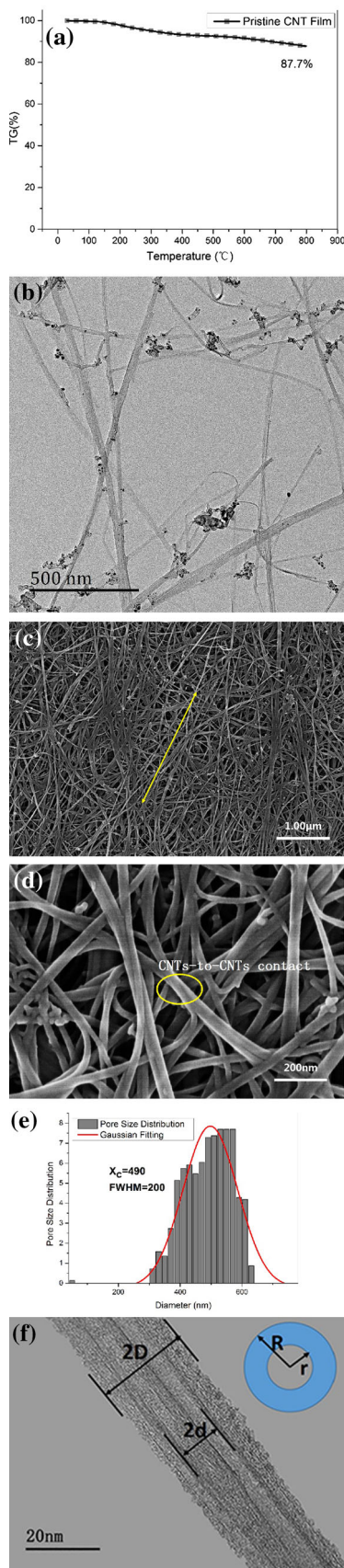
### Microstructures of CNT film

The TGA results in Fig. 3a demonstrated that the purification of CNT film was 87.7 %. The weight loss was the decomposition of catalyst and impurities in the film. As observed from TEM images (Fig. 3b), the CNT aggregated into bundles. The bundles entangled with each other and formed numerous contacts in CNT network as shown in Fig. 3c. The preferential alignment of CNT in the films is observed in Fig. 3c. Figure 3d shows the contact points between CNT bundles. It can be observed that two CNT bundles jointed into a big conjunction and formed Y-shape contact point. The length of the as-grown CNT-to-CNT contact was up to 250 nm, which was measured from the SEM images in Fig. 3d. This Y-shape conjunction spread out in the network and formed the freestanding CNT films via numerous contacts. This is quite different from that of vacuum filtration made buckypapers (BPs), in which the CNT bundles lay on each other and are held together by weak van der Waals forces only [22].

The thickness of the film was 10 ± 0.4 μm, which was measured from fracture surface as shown in Fig. 2b. The CNTs produced by FCCVD were MWCNT as shown in Fig. 3f. To determine the density of individual CNT ( $\rho_{\text{CNT}}$ ), the weight was calculated by assuming the MWCNT to be a hollow cylinder with an 11 nm outer diameter, a 5 nm inner diameter, and a wall density of 2.1 g cm<sup>-3</sup>, which equals to the density of graphite [26]. The inset picture in Fig. 3f illustrated this assumption. Therefore, the density of individual CNT can be calculated in Eq. (1) [27].

$$\rho_{\text{CNT}} = \frac{m}{V} = \frac{2.1 \times \pi(11^2 - 5^2)}{\pi \times 11^2} = 1.67 \quad (1)$$

In addition, Fig. 3e shows the pore distribution in CNT films. The Gaussian fitting demonstrated that the diameters of more than half of the pores ranging from 390 to 590 nm. Compared to the pore size in vacuum filtration made BPs, 10 μm [28], the FCCVD films had much smaller pore sizes, indicating more compact structure compared to BP. The



**Fig. 3** a TGA cure, b TEM image of CNTs, c FESEM image of CNT film under (arrow shows the preferential direction), d SEM images of the as-grown CNT-to-CNT contacts, e pore size and distribution, f TEM images of MWNTs

packing density ( $\mu$ ) was introduced to quantify the porosity of the films according to Eq. (2).

$$\mu = \frac{V_{\text{CNT}}}{V_{\text{total}}} = 1 - \frac{V_{\text{pore}}}{V_{\text{total}}} = \frac{\rho_{\text{film}}}{\rho_{\text{CNT}}}, \tag{2}$$

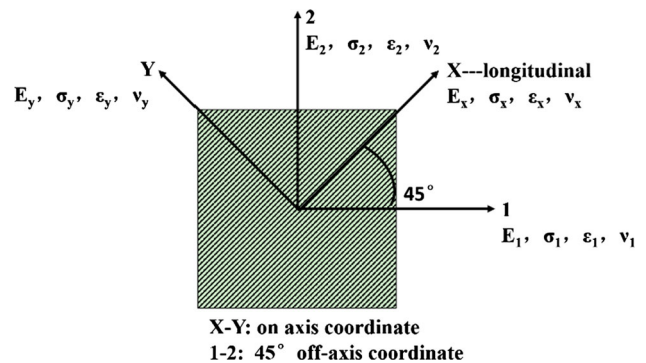
where  $V_{\text{CNT}}$ ,  $V_{\text{pore}}$ , and  $V_{\text{total}}$  were the volumes occupied by CNTs, air, and the film, respectively. The density of CNT film ( $\rho_{\text{film}}$ ) was measured to be  $0.189 \text{ g cm}^{-3}$ . Thus, packing density of CNT film was calculated to be 0.113, indicating the high porous structure of FCCVD films. This porous structure can provide enough space for resin filtration during composite fabrication.

**Engineering constants of CNT films**

Since a CNT film can be regarded as a 2D unidirectional material, the in-plane stress–strain relationship in longitudinal/on-axis direction can be determined by its compliance matrix in Eq. (3) [21].

$$\begin{bmatrix} \varepsilon_x \\ \varepsilon_y \\ \varepsilon_s \end{bmatrix} = \begin{bmatrix} \frac{1}{E_x} & -\frac{\nu_y}{E_y} & 0 \\ -\frac{\nu_x}{E_x} & \frac{1}{E_y} & 0 \\ 0 & 0 & \frac{1}{E_s} \end{bmatrix} \begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_s \end{bmatrix} \tag{3}$$

The components with subscript in letter were engineering constants expressed under on-axis coordinate system as shown in Fig. 4. The on-axis direction represents the preferential direction in the films. Once the longitudinal Young’s modulus ( $E_x$ ), transverse Young’s modulus ( $E_y$ ), Poisson’s ratio in longitudinal direction ( $\nu_x$ ), transverse direction ( $\nu_y$ ), and in-plane shear modulus ( $E_s$ ) are known, the relationship between stress–strain can be determined.



**Fig. 4** Coordinates system

Among them,  $E_x$ ,  $E_y$ ,  $\nu_x$ , and  $\nu_y$  can be determined by uniaxial tensile testing. However, it is difficult to carry out the pure in-plane shear testing in the ultrathin CNT films. Therefore,  $E_s$  was calculated from the transformation relationship between the compliance under different coordinates system as illustrated in Fig. 4. The compliance of CNT films in 45° off-axis can be determined according to Eq. (4) [21].

$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_6 \end{bmatrix} = \begin{bmatrix} \frac{1}{E_1} & -\frac{\nu_{12}}{E_2} & \frac{\nu_{16}}{E_6} \\ \frac{\nu_{21}}{E_1} & \frac{1}{E_2} & \frac{\nu_{26}}{E_6} \\ -\frac{\nu_{61}}{E_1} & \frac{\nu_{62}}{E_2} & \frac{1}{E_6} \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_6 \end{bmatrix} \quad (4)$$

where components with subscripts in mathematica form correspond to the engineering constants under the 45° off-axis coordinate system as shown in Fig. 4. These parameters can be determined from the uniaxial tensile testing along the 45° off-axis direction. The transformation relationship between the compliance matrices under on-axis and 45° off-axis coordinate can be expressed as Eq. (5) [29].

$$\begin{bmatrix} \frac{1}{E_1} \\ \frac{1}{E_2} \\ -\frac{\nu_{12}}{E_2} \\ \frac{1}{E_6} \\ \frac{\nu_{16}}{E_6} \\ \frac{\nu_{26}}{E_6} \end{bmatrix} = \begin{bmatrix} \cos^4 \theta & \sin^4 \theta & 2 \cos^2 \theta \cdot \sin^2 \theta & \cos^2 \theta \cdot \sin^2 \theta \\ \sin^4 \theta & \cos^4 \theta & 2 \cos^2 \theta \cdot \sin^2 \theta & \cos^2 \theta \cdot \sin^2 \theta \\ \cos^2 \theta \cdot \sin^2 \theta & \cos^2 \theta \cdot \sin^2 \theta & \cos^4 \theta + \sin^4 \theta & -\cos^2 \theta \cdot \sin^2 \theta \\ 4 \cos^2 \theta \cdot \sin^2 \theta & 4 \cos^2 \theta \cdot \sin^2 \theta & -8 \cos^2 \theta \cdot \sin^2 \theta & (\cos^2 \theta - \sin^2 \theta)^2 \\ 2 \cos^3 \theta \cdot \sin \theta & -2 \cos \theta \cdot \sin^3 \theta & 2(\cos \theta \cdot \sin^3 \theta - \cos^3 \theta \cdot \sin \theta) & \cos \theta \cdot \sin^3 \theta - \cos^3 \theta \cdot \sin \theta \\ 2 \cos \theta \cdot \sin^3 \theta & -2 \cos^3 \theta \cdot \sin \theta & 2(\cos^3 \theta \cdot \sin \theta - \cos \theta \cdot \sin^3 \theta) & \cos^3 \theta \cdot \sin \theta - \cos \theta \cdot \sin^3 \theta \end{bmatrix} \begin{bmatrix} \frac{1}{E_x} \\ \frac{1}{E_y} \\ -\frac{\nu_y}{E_y} \\ \frac{1}{E_6} \end{bmatrix} \quad (5)$$

Substituting  $\theta = 45^\circ$  into Eq. (5), the in-plane shear modulus ( $E_s$ ) can be calculated as Eq. (6).

$$\frac{1}{E_s} = \frac{4}{E_1} - \frac{1}{E_x} - \frac{1}{E_y} + \frac{\nu_y}{2E_y} \quad (6)$$

where  $E_1$ ,  $E_x$ , and  $E_y$  were the modulus in 45° off-axis, preferential and transverse direction.  $\nu_y$  was Poisson's ratio in transverse direction. The uniaxial tensile tests were carried out in preferential/on-axis and 45° off-axis directions to determine these constants.

### Modulus and tensile behavior

Figure 5 shows that the Young's modulus in longitudinal and transverse directions were 3 and 0.3 GPa, respectively. The highest tensile strength, 127 MPa, appeared in longitudinal direction. The strengths in transverse and 45-degree direction were 13 and 22 MPa, respectively. The poor CNT alignment in transverse direction led to the weakest strength. In 45-degree direction, the typical shear fracture surface (Fig. 6) indicated that the CNT bundles suffered from considerable shear force, which resulted in the poor tensile strength. In addition, the failure strain in longitudinal, 45-degree, and transverse direction were 26, 18, and 15 %, respectively. During the tensile process, more displacement was required to straighten the misaligned CNT bundles in transverse direction and 45-degree direction, rendering the larger tensile strains. This anisotropic mechanical property came from the preferential orientation of CNT bundles in the film as discussed previously.

Figure 7 [12, 16, 17, 22, 30–34] compares the mechanical properties of CNT films or BPs made by several different methods. It was obvious that FCCVD CNT films exhibited higher tensile strength and failure strain

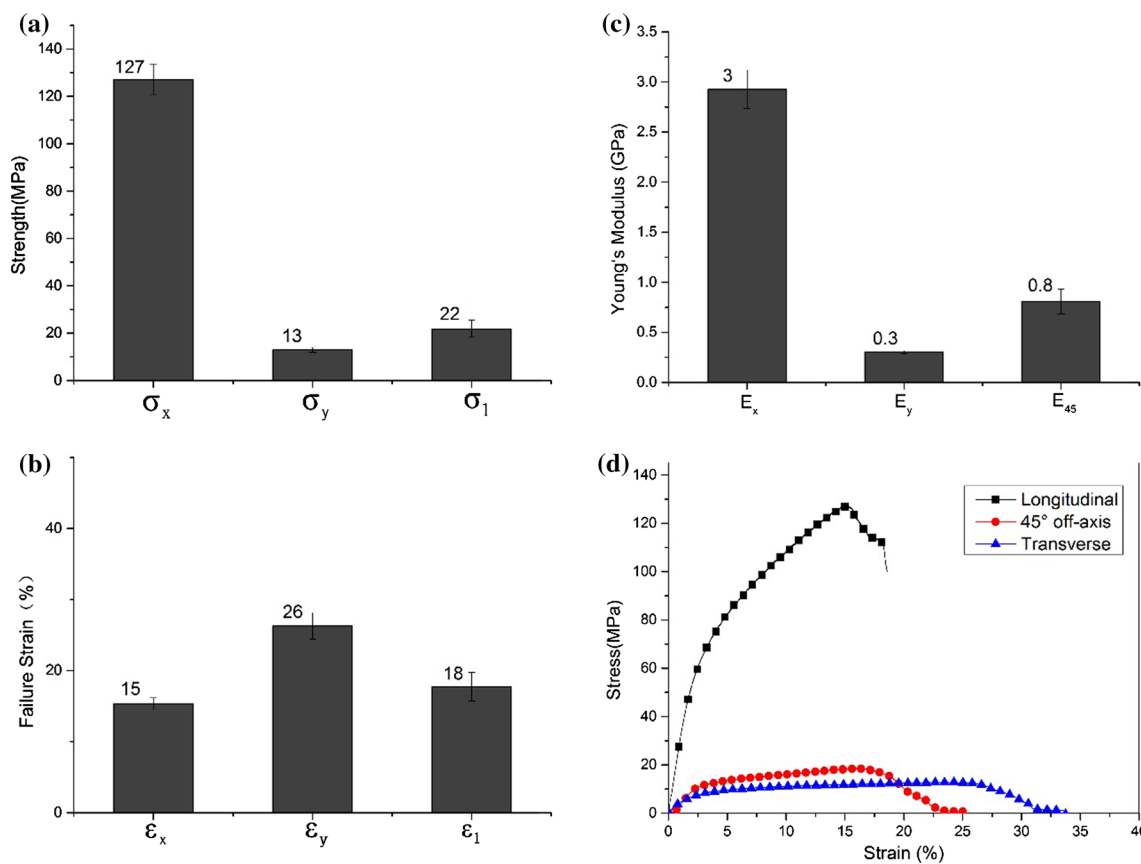


Fig. 5 a Tensile strength, b failure strain, c modulus, d typical stress–strain curves of CNT films in different directions

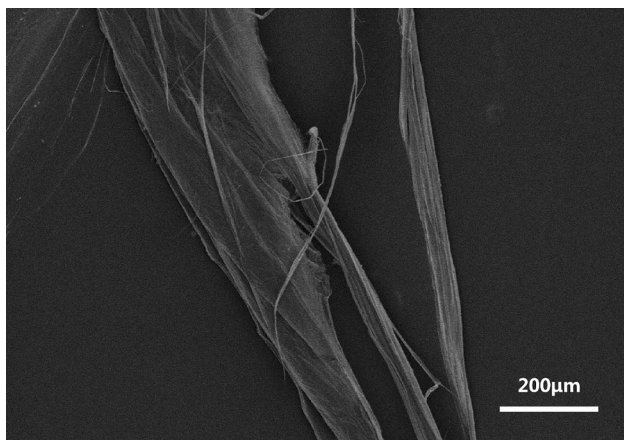


Fig. 6 SEM image of typical shear fracture surface in 45° direction

fabrication process. Therefore, the FCCVD CNT films obtained higher adhesion force at CNT conjunctions, resulting in better mechanical property.

In addition, the CNT films showed similar viscoelastic tensile behavior as polymer did as shown in Fig. 5d. The Hookean elasticity phenomenon appeared at small strain and followed by the viscoelasticity behavior after the yield

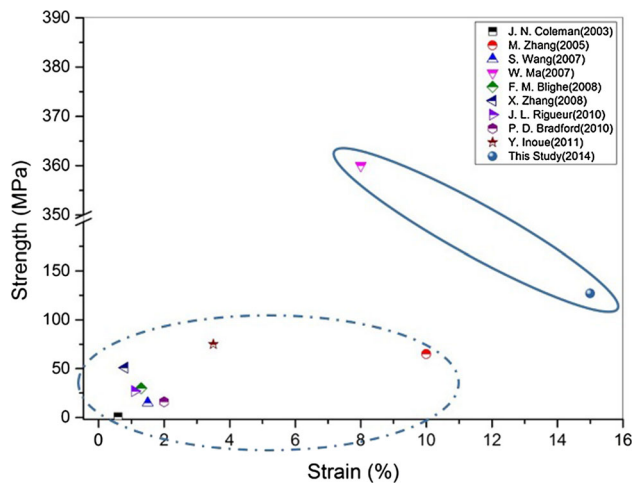
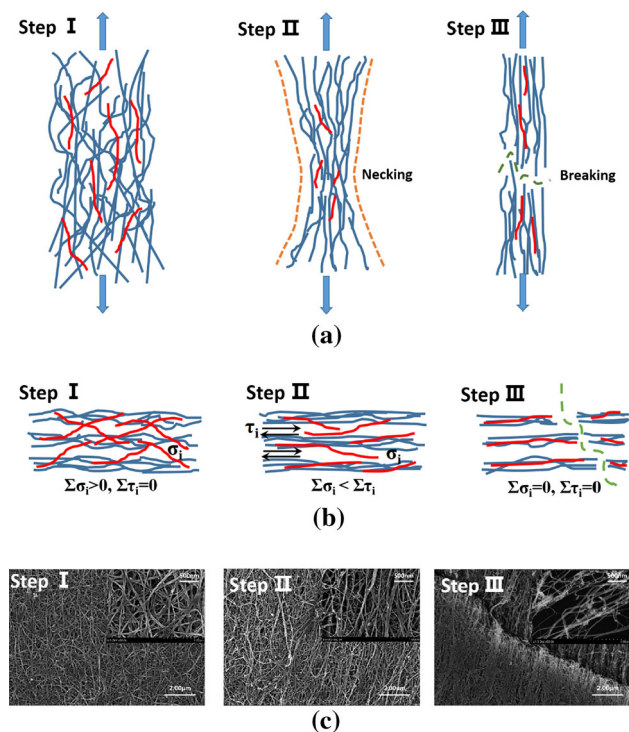
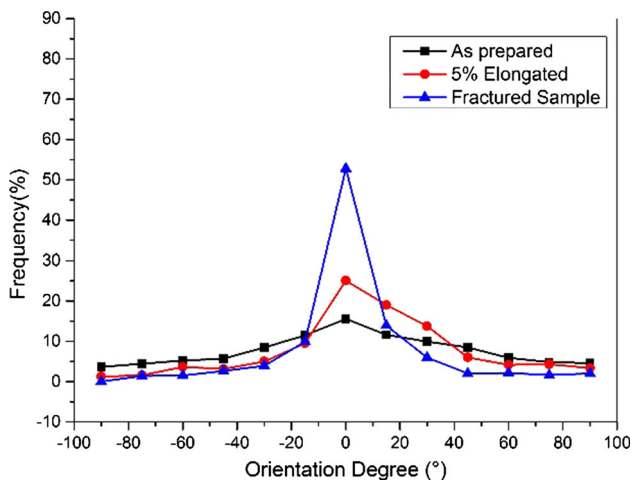


Fig. 7 Mechanical properties of FCCVD CNT films (solid line region) and buckypapers (dash line region)

point [35]. Specifically, all the elastic engineering constants must be calculated under linear tensile behavior. The stress–strain curves of CNT films showed the linear tensile behavior before yield point. All parameters for determining the elastic engineering constants were measured from this linear region.

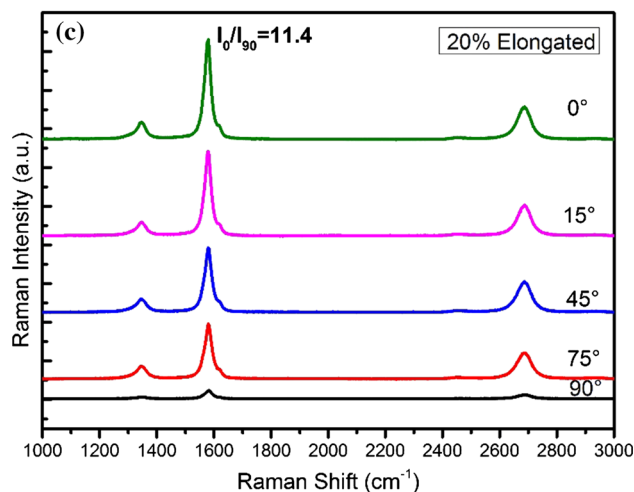
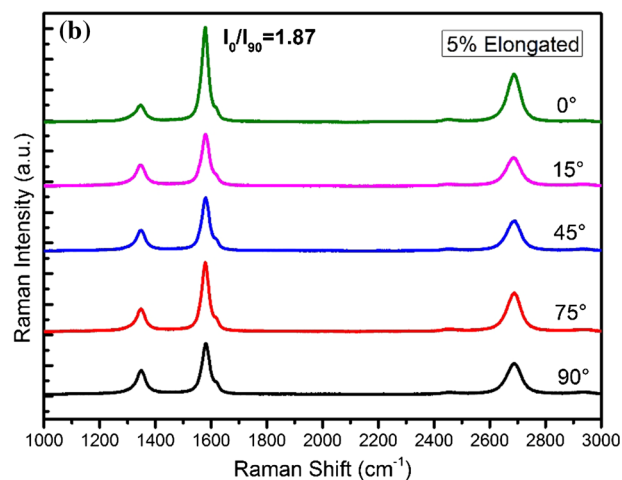
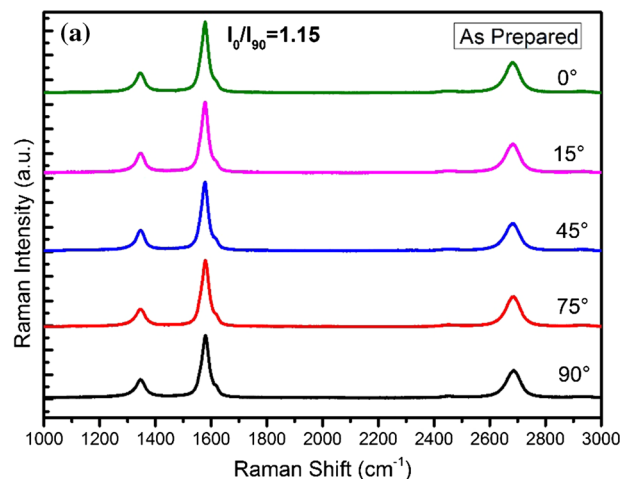


**Fig. 8** Failure steps of CNT films **a** top view, **b** side view, **c** in-situ tensile observations



**Fig. 9** Reorientation of CNT bundles simulated via numerical imaging process

The tensile behavior of CNT film was observed under in-situ SEM. At the first stage, the elongation of the curved and crimped CNT bundles led to the instant elastic behavior in CNT film as illustrated in step I in Fig. 8a. At the second stage, as shown in step two in Fig. 8a, the deformation of CNT bundles increased and the CNT-to-CNT contacts were to break. Consequently, the CNT bundles slipped from each other. The dissipation of friction energy in this process explained the plastic deformation of



**Fig. 10** Polarized Raman spectra of CNT film at 0 % strain (**a**), 5 % strain (**b**), and 20 % strain (**c**)

CNT film. Finally, inner CNT bundles pulled out from the network, resulting in the delamination in CNT films as shown in Fig. 8b. The CNT film broke up when the considerable CNT bundles had pulled out from the network.

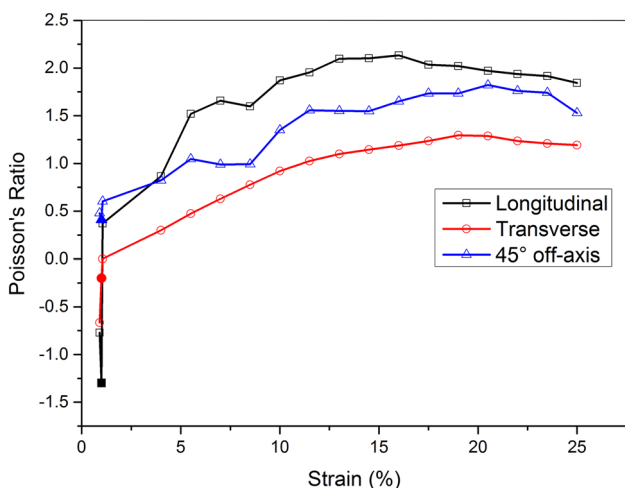
Figure 8c shows the reorientation phenomenon of CNT bundles during tensile testing. Figure 9 concludes the orientation of CNT bundles at different tensile stages based on the numerical image analysis. It showed that only 15.6 % of CNT bundles preferentially aligned to the longitudinal direction at initial stage. When the sample was elongated by 5 %, more than 25 % CNT bundles aligned along this direction. This value increased to 52.8 % before the CNT films broke up. The redistribution of CNT bundles was consistent with the failure mechanism as discussed previously. In addition, the polarized Raman results as shown in Fig. 10 also supported the reorientation of CNT bundles. In polarized Raman spectroscopy, the G-band intensity of CNTs shows the maximum when the polarization is parallel to the stretched axis ( $\psi = 0^\circ$ ) and shows minimum at the perpendicular direction ( $\psi = 90^\circ$ ) [25], where  $\psi$  is the angle between polarization vector and stretched axis. Thus, the higher ratio of  $I_0/I_{90}$  would indicate better CNT alignment in stretched axis. The  $I_0/I_{90}$  were 1.15, 1.87, and 11.4, respectively, at 0, 5, and 20 % (near to fracture) strain, which demonstrated that more CNT bundles aligned to the stretched axis during tensile process.

*Poisson’s ratio*

Poisson’s ratios (PRs) in preferential direction and transverse direction were two essential parameters in Eq. (3). The testing results are shown in Table 1 and Fig. 11.

**Table 1** PRs in different directions

Directions	Preferential direction ( $v_x$ )	Transverse direction ( $v_y$ )	45° off-axis direction ( $v_z$ )
PR at break	1.75	1.01	1.49
PR at 5 % strain	0.75	0.25	0.76



**Fig. 11** Typical PR curves in different directions

**Table 2** Parameters in compliance tensor for FCCVD CNT films

Parameters	$E_x$	$E_y$	$v_x$	$v_y$	$E_s$
Value	3 GPa	0.3 GPa	0.75	0.25	0.57 GPa

Figure 11 shows that all PRs increased gradually before 10 % strain and then leveled off until break. The increasing of PRs correlated to the reorientation of misaligned CNT bundles during tensile testing according to Fig. 8c. In addition, negative PRs were observed at 0.1 % strain in preferential direction and transverse direction, measured to be  $-0.99$  and  $-0.55$ , respectively. Baughman, Fan, and Ma also observed the negative PR in CNT films [36–38]. The meandering CNTs in the films were pliable. The initial tensile load would elongate the wavy CNTs. Thus, the meandering CNTs would spread out under the in-plane load and expanded laterally, rendering the negative in-plane Poisson’s ratio.

*Shear modulus*

Substituting  $E_1$ ,  $E_x$ ,  $E_y$ , and  $v_y$  into Eq. (6), the in-plane shear modulus was calculated to be 0.57 GPa. Due to the out of plane torsion force, it is difficult to carry out the pure in-plane shear testing for thin film in practice. We provided a more convenient way to calculate the in-shear modulus theoretically. By so far, all independent engineering constants in the compliance matrix of FCCVD CNT films are determined and shown in Table 2.

**Conclusions**

In this study, the in-plane mechanical properties and four engineering constants in compliance matrix of FCCVD CNT films were investigated. The Young’s modulus and the Poisson’s ratio in the compliance matrix were determined by the uniaxial tensile testing. The in-plane shear modulus was calculated to be 0.57 GPa based on the transformation between the compliance matrices of CNT films under different tensile loads. The tensile response of CNT bundles in the films was observed under in-situ SEM testing. The reorientation of CNT bundles was analyzed quantitatively via digital image processing method and Raman spectroscopy. The failure of CNT films was attributed to the slippage and pull out of CNT bundles.

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