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Research Article

Experiment Research on Deformation Mechanism of CNT Film Material

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Nanometer composite usually has multilevel structure, and deformation mechanism of its multilevel structure is the hot spot at present. The paper studies deformation mechanism of multilevel structure of CNT film material under tension loading and its influence on film mechanical properties by jointing multiscale experiment methods such as tensile test, digital image correlation, SEM observation, and in situ micro-Raman spectroscopy. The result shows that, during film loading process, the deformation of CNTs inside the film endures elastic elongation and glide successively, with very small axial elongation, which is about 7% of film deformation; the deformation of CNT bundle network structure endures deformation mechanism such as CNT bundle extension, rotation, and glide, and this structure deformation occupies about 93% of film deformation that large structure deformation makes CNT film have good toughness; during film loading process, the formation of CNT bundle long chain and glide mechanism in the chains help to improve film strength and toughness.

1. Introduction

With rapid development of micro/nanotechnology, various new types of nanometer composite continuously appear, and their common characteristic is multilevel structure on different scales. Film material constituted of CNT is the representative type that the multilevel structure includes CNT element of micro- and nanoscale and CNT bundle network of mesoscale, and this material is characterized by good strength and flexibility with large deformation, which has wide application prospect in new technology field such as energy, biology, and environment [1]. It is scientifically important for the development and application of new materials to deeply understand deformation characteristics and mechanical properties of multilevel structure of nanometer composite.

At present, some research progress has been made in deformation measurement technology of different scale structures of materials, for example, the effective application of micro-Raman spectroscopy [2, 3] in microscale experimental mechanics research field: Deng et al. studied multiscale deformation and interface mechanical behavior of CNT fiber, suggesting that bundle interface glide of microscale is the reason for material structure failure [4]; Trakakisa et al. assessed stress transfer of high volume fraction CNT complex substance made by buckypaper method from polymer to the individual or fasciculation CNTs [5]; Kao et al. researched deformation action and heating influence of SWNT/epoxy resin composite and loading transfer inside double wall CNTs [6, 7]; Wagner research institute [8] and Qiu et al. [9] measured strain distribution around fiber and microhole inside the composite with CNT as sensing medium; Ma et al. researched macroperformance and microstructure deformation of single wall CNT fiber and film under displacement loading [10, 11]. In another experiment technique aspect, Li et al. developed multiprobe mechanical test system and applied this system into grasp, loading, and measure of Si nanowire and other one-dimensional nanostructures [12]; Wang et al. used SR X-ray to research inner structure deformation of compressed foamed aluminum combined with X-ray fault technique (SR-CT) and digital image analysis method and calculated porosity, intersecting surface, and other important parameters based on the reconstructed images [13]. Generally speaking, one experiment method aims at one particular measurement scale; therefore, comprehensive measurement of composite material multilevel structure deformation is still a difficult problem, and it needs new experiment method to solve the problem.

This paper comprehensively takes advantage of multiscale experimental methods, such as macro tensile experiment and transverse shrinkage deformation measurement, SEM observation, and in situ micro-Raman spectroscopy to measure deformation of multistructure of film. On the basis of synthesizing several pieces of experimental information, this paper analyzes the deformation evolution mechanism of film multistructure under loading and discusses the influence of bearing deformation of multistructure to strength and toughness performance of film.

2. CNT Film Material and Mechanical Performance Experiment

Aiming at multistructure of CNT film material, this paper uses tensile stress-strain curve and transverse shrinkage deformation measurement to obtain macro deformation characteristics of film, observes deformation of CNT bundle net structure through SEM observation, and monitors axial elongation of CNT elements through in situ micro-Raman spectroscopy.

2.1. Multistructure of CNT Film Material. CNT film material is prepared by chemical vapor deposition process [14]. CNT film has multiscale structures, which is shown in Figure 1. The thickness of macro film is about 20 μm. From the mesoscale, film is a kind of loose net structure composed of 0.01–0.05 μm diameter CNT bundles (Figure 1(b)). From the microscale, carbon nanotube bundle consists of double wall CNT collapse stacking (Figure 1(c)). In order to determine the dominant direction of CNT bundles in film material, it exercises polarized Raman spectra intensity measurement experiment along different directions. Just as Figure 1(d) shows, the intensity of polarized Raman spectra is greatly changed with the intersection angle between incident/scattered light polarization direction and film longitudinal direction (pulling direction during film preparation) and the peak intensity in the longitudinal direction is about 1.5 times the vertical direction, which shows that longitudinal distribution of CNT bundles in the film is dominant [15].

2.2. Tensile Experiment of Film Material in the Macroscale. Two rectangular specimens, whose long sides are paralleled with the longitudinal direction of the film and the direction of a 45° angle with the longitudinal direction (Figure 2(a)), are used for tensile experiment. The width of sample is 2 mm, and the test gauge is 10 mm. The average strain loading rate is 1.5% strain per minute.

Typical tension nominal stress-nominal strain curve and an example of tensile true stress-true strain curve of longitudinal film specimen are shown in Figure 2(b). In order to avoid the influence of a cross-sectional area calculation on the comparative analysis, the mechanical properties of film materials are discussed based on nominal stress-strain curve. The figure shows that film stress presents the characteristics of the three stages with strain variation: the elastic stage I (the stress rapidly increases with strain), the plastic stage II (the stress slowly increases with strain), and the damage-fracture stage III (the stress decreases gradually). The judgment on elastic and plastic stages in this paper is from the measurement results of the film unloading in stage I and stage II, respectively, as shown in Figures 2(c) and 2(d). The film deformation in stage I is recoverable, and the film deformation in stage II is unrecoverable. The average elastic modulus of the film in longitudinal direction and the 45° direction is estimated as 220 MPa and 115 MPa, respectively, the average tensile strengths are estimated as 64 MPa and 24 MPa, and the average elongations are approximately 25% and 19%. Here, the cross-sectional area is calculated with the method where width of the sample is multiplied by the thickness observed. The great different between mechanical properties of longitudinal direction and 45° direction of the film can be seen, and the film has good toughness in both directions.

Film produces significant lateral shrinkage in the tension process, just as shown in Figures 3(a)–3(d) shot in the digital image correlation experiment (FOV size of 15 × 15 mm^2). Taking into account the accuracy of image processing, it provides the transverse deformation data under the lower strain (less than 20%), as shown in Figure 3(e). The transverse contraction deformation of the initial film stretching is small; afterwards, it increases almost linearly with increasing tensile strain. Generally speaking, the transverse shrinkage deformation along the longitudinal stretching is greater than that in the 45° direction. In addition, there is a long range of strain (5%) in the initial part of the 45° direction tension that the transverse shrinkage deformation is scarcely observed.

2.3. Raman Experiment for Deformation Measurement of CNTs in Film. During the film tension process, it exercises the measurement of in situ micro-Raman spectral information. The instrument of Raman measurement is Renishaw InVia Reflex Raman spectrograph, and 632.8 nm He-Ne laser light source, 50x objective, and line focusing are selected. Raman information under different loading condition is collected from the same position of the specimen.

G' band shape under typical loading conditions obtained from the experiment is shown in Figure 4(a), and under strain the G' band shift to lower wave number indicates that CNTs within the film are loaded. Specific changes in G' band Raman shift with strain reflect axial deformation of CNTs inside the film. Just as Figure 4(b) shows, from the initial loading to the large strain (longitudinal direction is 18%, 45° direction is 15%) scale of film, G' band Raman shift decreases linearly, indicating that CNTs are elastically deformed in this process. Afterwards, G' band Raman shift with strain decreased slowly, indicating that slippage among CNT bundles happens within the film [4]. The change of full width at half-maximum (FWHM) of G' band provides

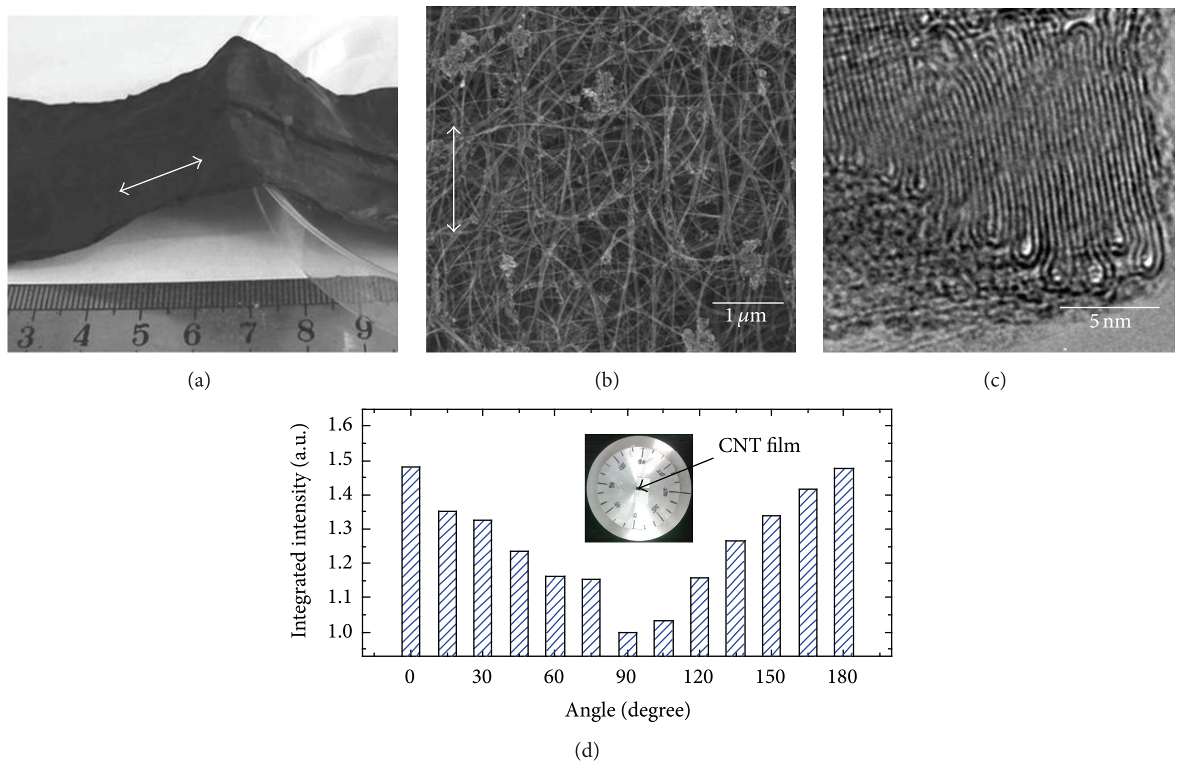

Figure 1: Multistructure of CNT film material. (a) Macro picture of film; (b) SEM image of film, and two-way arrow indicates the longitudinal direction of film; (c) TEM image of the end of a CNT bundle; (d) the integrated intensity change of Raman G′ band with the intersection angle between incident/scattered light polarization direction and film longitudinal direction of CNT film (the inset shows that film test-piece during the experiment is fixed on the central location of rotation platform and the longitudinal direction is paralleled with 0–180° groove of the platform).

much information about the stress distribution in the CNT film. As shown in Figure 4(c), in elastic stage, the FWHM of G′ band has almost no change. This illustrates uniform bearing of CNTs in film. After entering plastic stage, the FWHM of G′ band increases gradually. This illustrates that some CNTs have begun to bear more loads than others. When slippage occurs, the uneven distribution of stress is no longer increasing. In addition, under strain G′ band intensity is increased (Figure 4(a)), indicating the aligning of CNTs towards the loading direction within the film [17].

2.4. SEM Experiment of Mesoscale CNT Bundle Net Deformation in Film. In order to know the structure deformation method of CNT bundle network, micro morphology of the damaged film in the longitudinal direction and 45° direction is observed by SEM, and it is compared with the unloading images, just as Figure 5 shows.

After the tension loading, significant changes occurred in the geometry shapes of CNT bundle network inside the film. After longitudinal tension, CNT bundle long chain along the loading direction is formed inside the film (Figure 5(b)), indicating that curved CNT bundles have stretched and rotated towards the loading direction inside the film; the fracture end showed drawing shape (Figure 5(c)), and CNT bundles along the fracture are substantially straightened and arranged along the loading direction (Figure 5(d)), showing that slippage failure occurs in the film.

After tensile loading along the 45° direction, CNT bundles within the film are mainly characterized by two forms (Figure 5(e)): one is the mutually spaced CNT bundle long chain, and there is about a 20° angle between long-chain orientation and loading direction; the other one is cross-shaped arrangement between the long chains. The direction of fracture of the distal edge is consistent with the direction of CNT bundle long chain and relatively flat (Figures 5(f) and 5(g)), showing that slippage damage along CNT bundle long chain occurs in the film.

3. Multistructure Deformation Mechanism Analysis of CNT Film

3.1. Deformation Evolution of CNT Bundle Network Structure. According to microscopic morphology of CNT film (Figure 1(b)), the CNT bundle network can be viewed as the composition of numerous CNT bundle micro units. The structure of micro unit is shown in upper left area of Figure 6. In the micro unit, the intermediate sections of two CNT bundles contact each other to form overlap region by relying on Van der Waals and other interactions, and the end portions are separated at an acute angle.

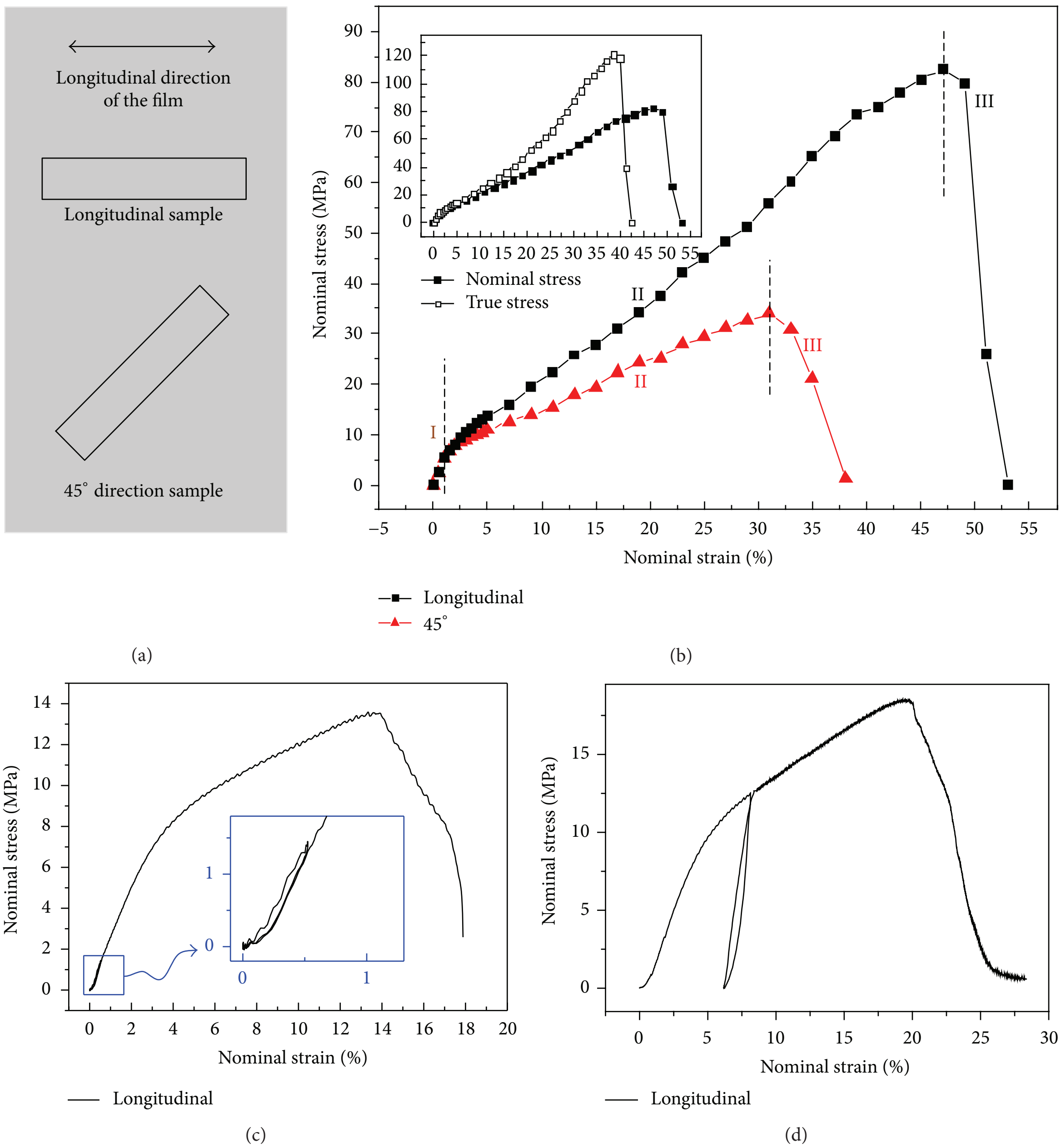

Figure 2: (a) Figure of uniaxial tensile sample preparation method of CNT film in longitudinal direction and 45° direction; (b) typical tensile nominal stress-nominal strain curve of CNT film, and the inset shows the comparison between nominal stress and true stress in the longitudinal tension [16]; (c) film tensile nominal stress-nominal strain curve in stage I (1.45 MPa) with unloading and reloading process; (d) film tensile nominal stress-nominal strain curve in stage II (12.5 MPa) with unloading and reloading process.

Based on multiscale experimental results, this paper presents the deformation evolution mechanism of CNT bundle micro unit under the film tensile loading, which defines the structural deformation evolution of the entire CNT bundle network (Figure 6). When load is applied to the film initially, the curved CNT bundles inside micro units are straightened gradually. If the applied load is removed at this time, micro units will return to original shape. As the applied load increases, the CNT bundles inside micro units begin to rotate, and "CNT bundles long chain" along the direction of the overlapping area is formed. The load has begun to mainly bear by "long chains." The rotation of CNTs makes the transverse shrink deformation of film become significant. In this case, even if the applied load is removed, micro units cannot return to original shape. When the network with a number of "long chains" continues to be loaded, due to low shear strength, slippage among bundles will appear in the "long chain" [4, 18] and spread among the "long chain,"

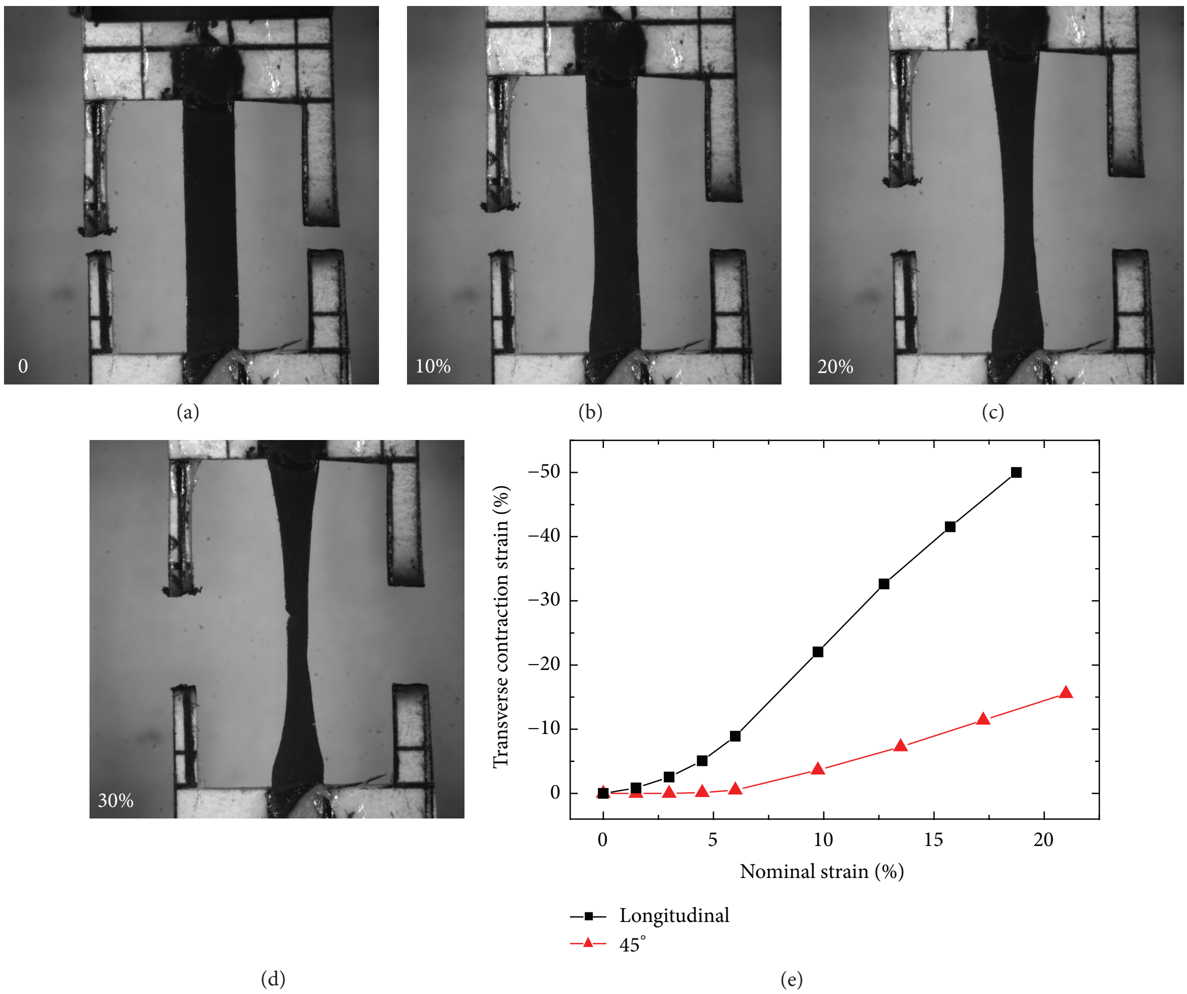

FIGURE 3: Transverse contraction deformation during the stretching process of CNT film along the longitudinal direction and 45° direction. (a–d) Images of typical strain condition during longitudinal tension process; (e) change of transverse shrinkage strain in the tension process.

and the accumulation of slippage damage will lead to shear failures of the long chain and entire failure of CNT bundle network eventually.

When the film is stretched along the 45° direction, there are two stress components paralleled and perpendicular to the direction of the CNT bundle micro unit overlapping area, so the micro unit generates two variants: the first is the deformation which has the same process as the longitudinal tension, accompanied with integral rotary of micro unit to loading direction; the second is the bending degree of CNT bundles in micro unit that increases gradually, so that the acute angle between bundles gradually becomes an obtuse angle, and then two rotating bundles present crossing shape while the whole micro unit rotates towards the loading direction.

It should be noted that, before the occurrence of slippage, the increases of axial elongation of CNTs with the film strain are constant. However, during this process, the deformation of film is changed from elastic to plastic. This phenomenon may be related to changes of the Van der Waals interaction; that is, the rotation of CNT bundles results in increased contact area among CNT bundles and decreased Van der Waals interaction [19].

3.2. Correlation of Multilevel Structure Deformation Evolution and Film Mechanical Property. Deformation evolution of multilevel structure of the CNT film determines the mechanical properties of the film, such as toughness and strength. Macroscopic deformation of the film material comes from two parts of the axial elongation of microscopic CNTs and the structure deformation of mesoscale CNT bundle network, and the latter is the main source of film elongation, and this assertion comes from the in-depth analysis of the Raman experimental data. Within a certain range of film strain (the longitudinal direction is 18%, and 45° direction is 15%), the decline rate of Raman G′ band Raman shift with strain reflects the contribution of axial elongation of CNTs to macroscopic deformation of film. The decreasing rate of G′ band frequency in longitudinal strain is about 0.16 cm^{-1}/1% (Figure 4(b)), and the initial decreasing rate of the CNT fiber under tension is 2.2 cm^{-1}/1% [17] with the same preparation method. If it is the same as the description

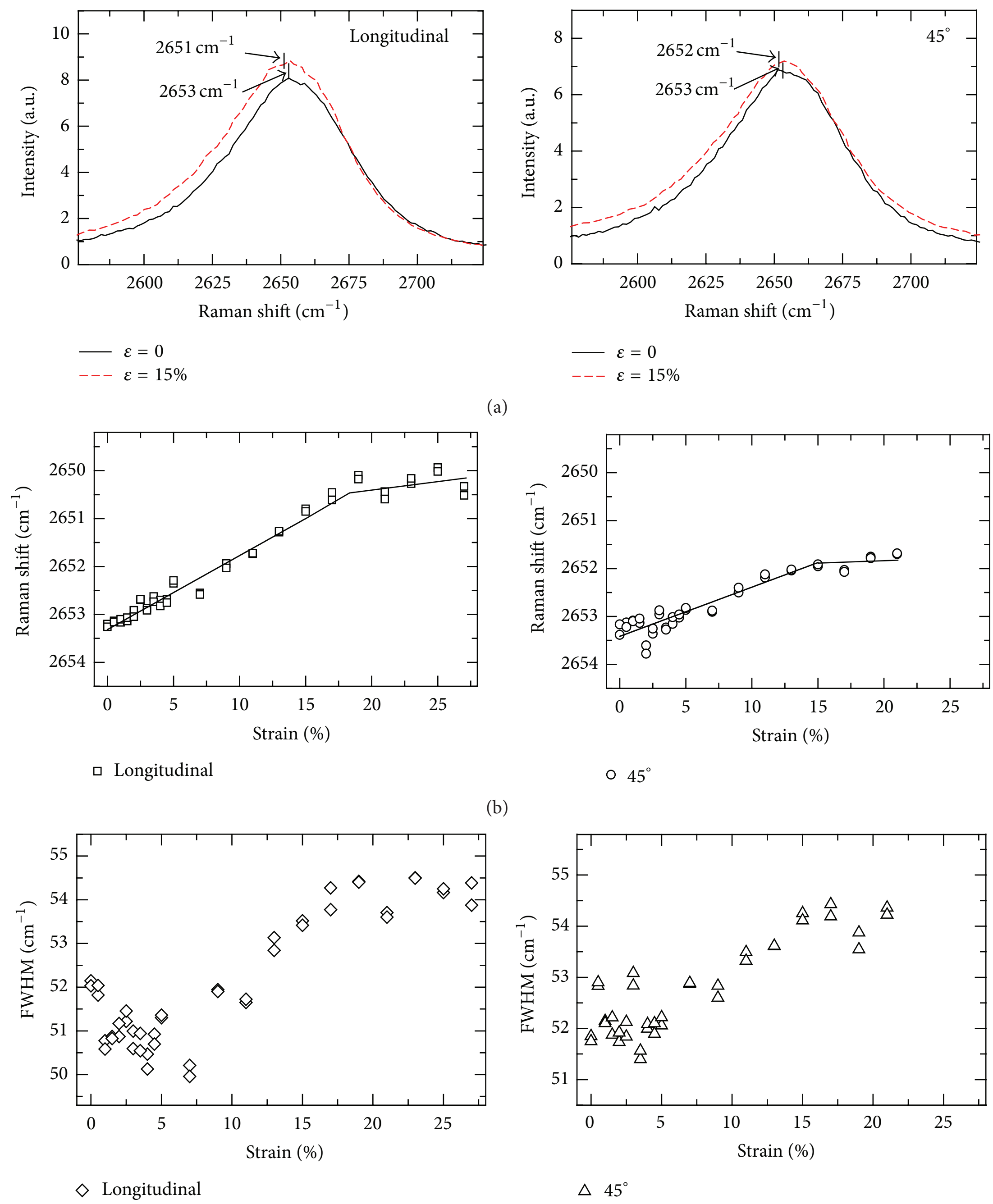

FIGURE 4: Change of G′ band information during CNT film tension. (a) G′ band shape under typical loading condition; (b) change of G′ band Raman shift with strain, and the full line is used for guiding sight line; (c) change of the full width at half-maximum (FWHM) of the G′ band with strain.

in the literature [17], the fiber deformation of this stage comes from the axial elongation of CNTs, and it can be estimated that the axial elongation of the CNTs in film contributes to only about 7% of the macroscopic deformation of the film. It can be seen that the majority part of the macro deformation comes from the structural deformation of CNT bundle network. CNT bundle network experiences structure evolution process, which includes unbending, rotation of CNT bundles, and slip among CNT bundles, which can make the film produce a large number of geometrical elongations, so that the film has a higher toughness. When it strains along the 45° direction, inclined arrangement of CNT bundles undergoing above deformation processes makes the CNT bundle network less elongated along the loading direction, so that ductility of the film along the 45° direction is less than ductility along the longitudinal direction.

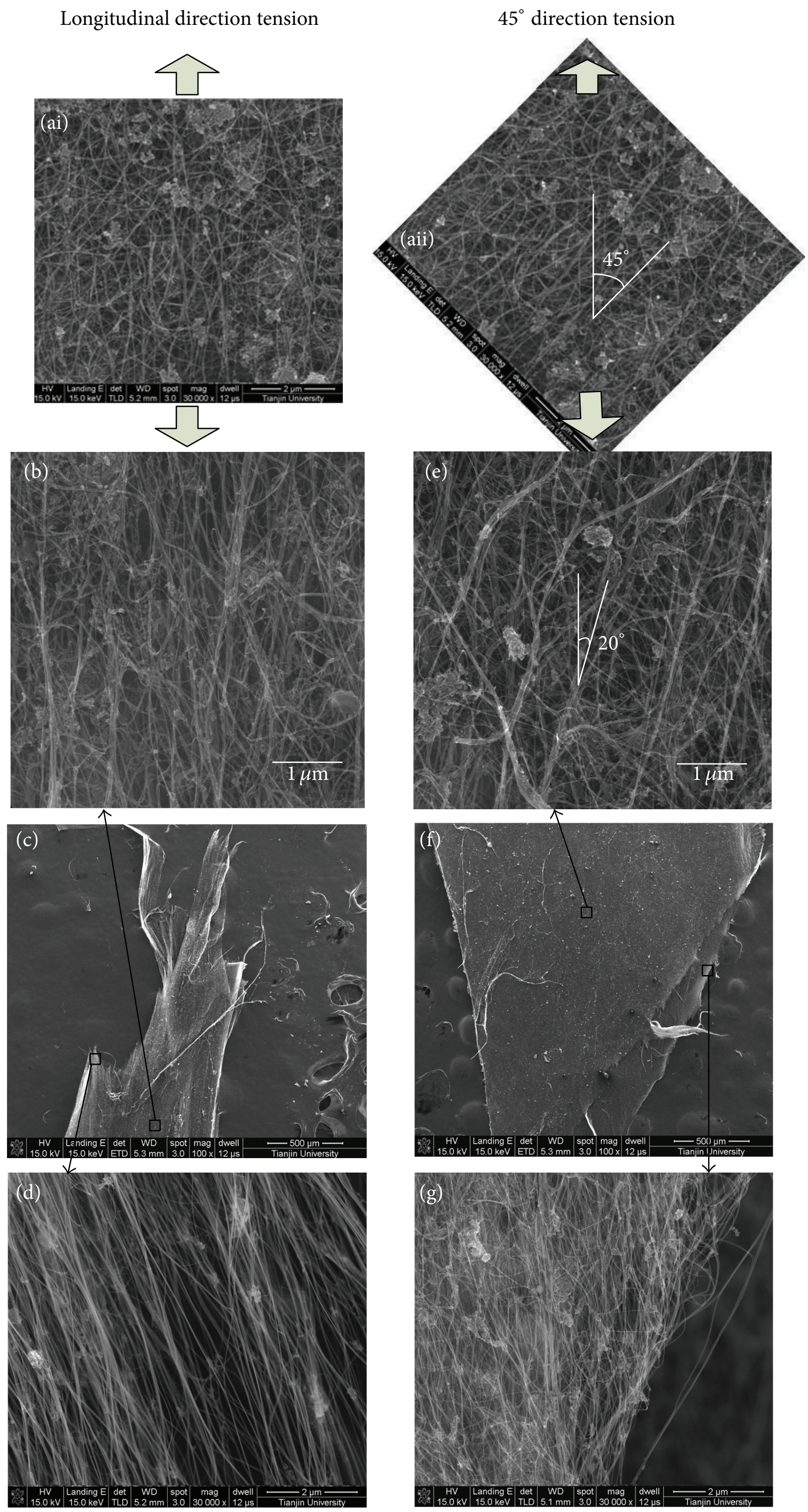

Figure 5: SEM images of CNT bundle network when CNT film is not loaded (ai-aii) and stretched to the damage along the longitudinal direction (b–d) and 45° direction (e–g).

During the film loading process, the formation of CNT bundle long chain and inner chain slippage mechanism is good to improve film strength and toughness. From the beginning when film is loaded, the axial stress of CNTs linearly increases; and slippage among bundles will happen if the stress surpasses the interface shearing limit among bundles inner long chain. The slide will result in reallocation of stress and the majority of stress will be transferred to

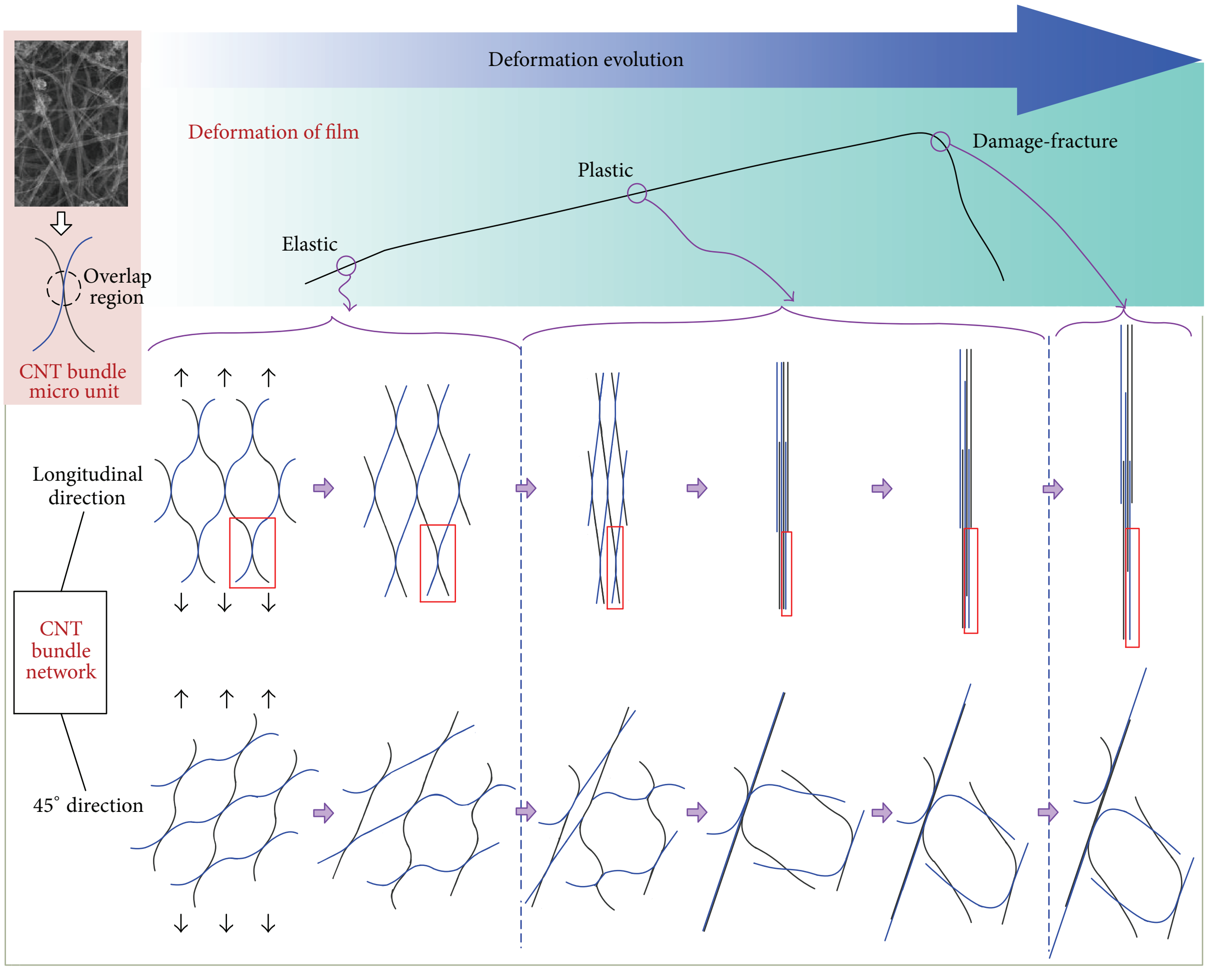

FIGURE 6: Diagrammatic sketch of deformation evolution process of CNT film multilevel structure. The square frame in the picture indicates micro unit of CNT bundles.

surrounding long chains of slipped CNT bundles. When slippage occurs in these long chains, the stress will be transferred to other long chains. The constant turnover of major bearing CNT bundles postpones the occurrence of stress concentration which is helpful to improve the strength and toughness of the film.

4. Conclusions

This paper puts forward an experimental method aiming at multilevel structure deformation measurement. Combining with tensile test, digital image correlation, SEM observation, and in situ micro-Raman spectroscopy and other multiscale experiment methods, the measurement and analysis of multilevel structural deformation action of CNT film material are realized effectively.

The experiment shows that, during film loading process, the deformation of CNTs in film endures elastic elongation and glide successively, with very small axial elongation, which is about 7% of film deformation; structure deformation of CNT bundle network is the main source of film elongation, which occupies about 93% of film deformation. Based on the experiment results, the structure deformation evolution mechanism of CNT bundle network is put forward, which indicates the reason for producing great number of geometry elongations. The influence of deformation evolution of multilevel structure on strength and toughness properties of film is also further analyzed. Some huge structural deformations which are originated from unbending, rotation of CNT bundles, and slippage among CNT bundles make CNT film have good toughness, and these deformation mechanisms of CNT bundle network can be applied in developing flexible big deformation materials. During the film loading process, the formation of CNT bundle long chain and slippage mechanism inside the chain are good for improving the strength and toughness of the film.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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