ENABLING LARGE STRETCHABILITY IN ASSEMBLIES OF NANOCARBONS THROUGH PRESTRESSING

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Abstract
In this paper, carbon nanotube (CNT) based continuous fibers, thin graphene laminates, and films with CNTs in random orientation are used to form buckled structures through prestressing of rubber substrates. The resulting nanocarbon assembly/rubber substrate composites exhibit excellent flexibility and stretchability and showed stable electrical and electrochemical performances during repeated stretching cycles.

1. Introduction

Just as in the development of structural composites with enhanced ductility, research in highly deformable functional composites is rapidly evolving. Nanocarbon assemblies addressed here include carbon nanotube (CNT) based continuous fibers, thin graphene (GR) laminates, and films with CNTs in random orientation. In spite of their superb mechanical and physical properties, CNTs and GRs are inherently more brittle comparing to traditional structural metals and ceramics. Large deformability of CNT and GR based assemblies are highly desirable for their applications in multifunctional composites and energy storage devices.

The large stretchability in these nanocarbon assemblies are accomplished using a stretching-then-releasing process of a substrate on which the nanocarbon fiber or film is attached. First, in the case of continuous CNT fibers, the study of their stretchability was motivated by the observation of formation of hinge-like kink bands along the fiber length when it was subjected to dynamic compressive loading. The large stretchability of CNT fibers was attributed to the highly densely distributed buckles. Next, in the case of GR, 4-layer laminates were fabricated using a layer-by-layer stacking technique. The high quality of resulting film was verified by Raman spectroscopy and unidirectional buckling was accomplished by stretching-then-releasing of the PDMS substrate on which the GR film was attached. Third, we have demonstrated that omnidirectional stretchability can be accomplished in CNT films with remarkable uniformity in buckled structures, and deformation up to 200% tensile strain was achieved.

2. Results and Discussion

2.1 CNT fiber based stretchable composites

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Two kinds of CNT fibers were adoped in this study. One was spun from a vertically aligned array consisting of mainly multiwalled CNTs, denoted as dry spun CNT fiber [1]. Another was spun directly from a gas phase suspension of CNTs, known as aerogel spun CNT fiber [2].

The potential of the CNT asemmblies to form buckled structure was first noticed in our study of the compressive behavior of dry spun CNT fiber using single-fiber tensile recoil test[3]. The failure morphologies of the CNT fiber are identified in the scanning electron microscopic (SEM) images shown in Fig. 1.

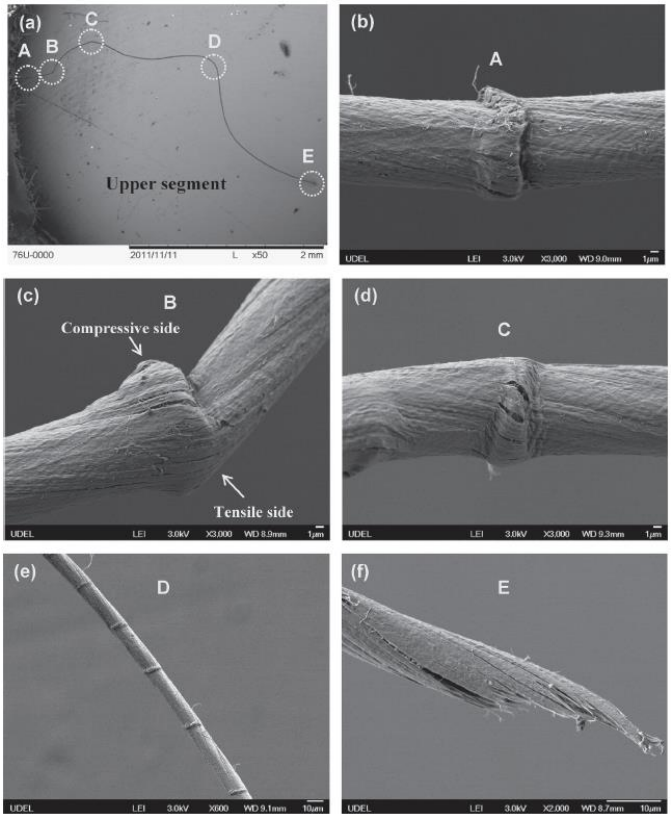

Figure 1. Surface morphology of pure CNT fiber after recoil test at tensile failure stress of 1.48 GPa. (a) Overall view of the upper specimen segment, (b-e) compressive damages at locations (A-D) away from the clamped end and (f) fiber fracture end.[3]

As can be seen from Fig. 1a-e, massive kinking and severe buckling of the fiber were observed when the fiber was broken under axial tensile loading without cutting. The tensile fracture end of the fiber is shown in Figure 1f. As a result of the compressive damage generated during tensile recoil process, fully developed kink band and cracking can be found on the compressive side of the buckled fiber, while on the tensile side, there is no obvious tensile damage. On the basis of these microscopic observations, it can be concluded that recoil failure of pure CNT fiber occurred in the kinking mode[3].

Taking advantage of the ‘‘hinge-like’’ structure developed in compressive failure, we developed a stretchable conductor based on buckled CNT fibers (Fig.2a-e), which showed very little variation in electric resistance under stretching-then-releasing cycles with a maximum strain of 40% (Fig. 2f)[4].

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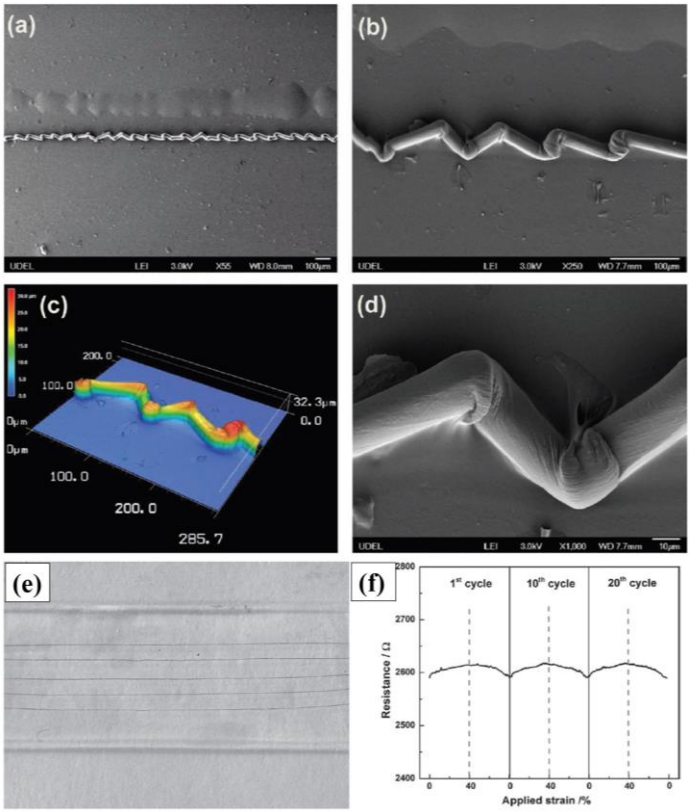

Figure 2. a,b) Low-magnification SEM images of one kinked CNT fiber. c) Color 3D image of kinked CNT fiber taken by a laser microscope. d) An enlarged SEM view of two kinks in the CNT fiber. e) Photograph of a stretchable conductor with five kinked CNT fibers. f) Electrical resistance variation of a CNT fiber/PDMS composite film with cyclic stretching to the prestrain level of 40%. Only data of the 1st, 10th, and 20th cycles are shown for comparison.[4]

Then, the durability of two types of buckled CNT fibers, dry spun and aerogel spun, have been studied during 10,000 mechanical enlongation cycles. It turned out that both types of fibers showed excellent stability. The electric resistance of dry spun CNT fiber showed an increment of 1.3% after 10,000 cycles(Fig. 3c) [5]. The aerogel spun CNT fiber conductor was un-twisted by the compressive force generated in releasing the prestrained substrate and its electric resistance increased by about 6.5% after 10,000 cycles (Fig. 3f)[5].

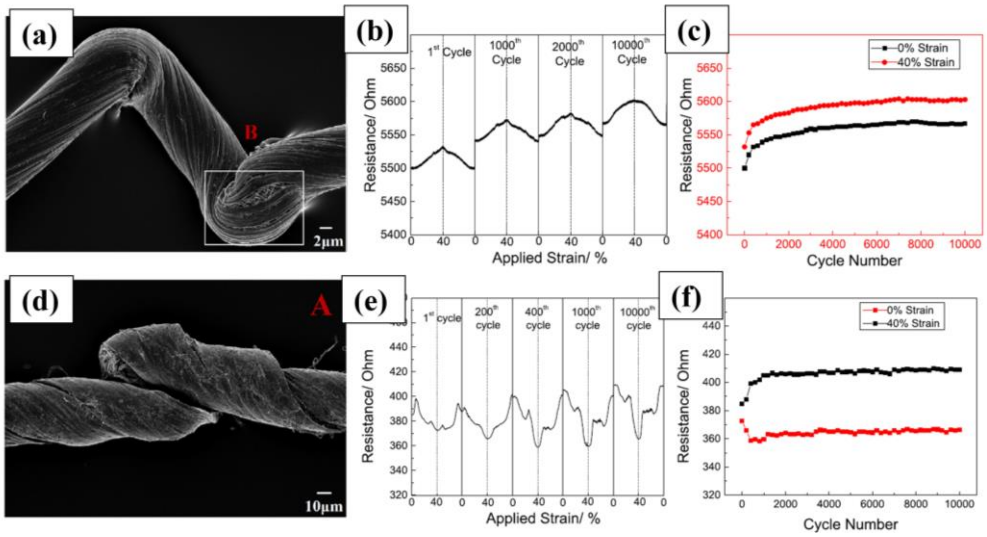

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Figure 3. a) SEM image of a buckled dry spun CNT fiber after 10,000 stretching-releasing cycles. Resistance variation of the buckled dry spun CNT fiber (b) during cyclic stretching to the prestrain level of 40% and (c) at 0% and 40% strain levels during 10,000 stretching-releasing deformation cycles. d) SEM image of a buckled aerogel spun CNT fibers after 10,000 stretching-releasing cycles. Resistance variation of the buckled aerogel spun CNT fiber (e) during cyclic stretching to the prestrain level of 40% and (f) at 0% and 40% strain levels during 10,000 stretchingreleasing deformation cycles.[5]

Inspired by the excellent stretchability and performance stability of the CNT fiber based buckled structure, a facile approach was adopted to fabricate stretchable wire-shaped supercapacitor (WSS) with a stretchability of 100% using spandex fiber as the substrate and H_2SO_4 -poly (vinyl alcohol) (PVA) gel as the solid electrolyte (Fig. 4a and 4b)[6].

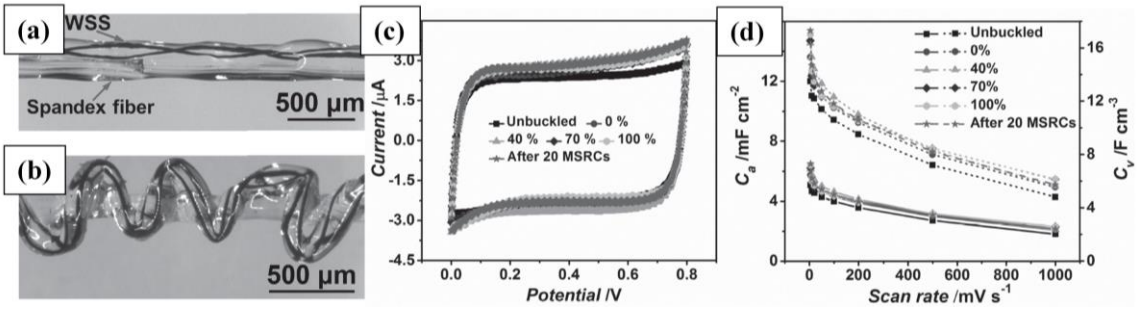

Figure 4. a) Straight WSS combined with prestrained spandex fiber and b) buckled WSS with relaxed spandex fiber. c) CV curves of stretchable WSS at different applied strains and after 20 mechanical stretching-releasing cycles (MSRCs). d) Specific areal capacitance C_a (solid lines) and specific volumetric capacitance C_V (dash lines) as functions of scan rate.[6]

As shown in Figure 4c, apart from the slightly enlarged areas enclosed by CV curves in the stretched states, the nearly identical CV curves confirmed their similar performance and excellent electrochemical stability of the supercapacitor which was stretched to large strains of up to 100% and after 20 MSRCs. The specific capacitances surpassed those of the initial unbuckled supercapacitors throughout the entire scan rate range (Fig. 4d).

2.2 GR laminate based stretchable composites

GR films fabricated by chemical vapor deposition are promising electrode materials for stretchable energy storage devices. The four-layer GR laminate was fabricated by laminating as-received single layer GR films, following the procedures adopted in our previous work to form buckled structure with a stretchability of 40% strain[7].

The buckled GR laminate on a polydimethylsiloxane (PDMS) film substrate subject to various applied tensile strains has been characterized by atomic force microscopy and micro-Raman mapping. The four-layer GR laminate was deformed into an irregular wavy structure upon relaxing the prestrain of the PDMS film (Fig. 5a-b)[7]. As the applied tensile strain varied from 0% to 40% (Fig. 5c-e), the maximum amplitude of the ripples in the wavy GR laminate decreased from 146.8 nm at 0% to 124.5 nm at 20% and 120 nm at 40%[8]. It was apparent in Fig. 5f that the increase in applied tensile strain led to the flatter film morphology.

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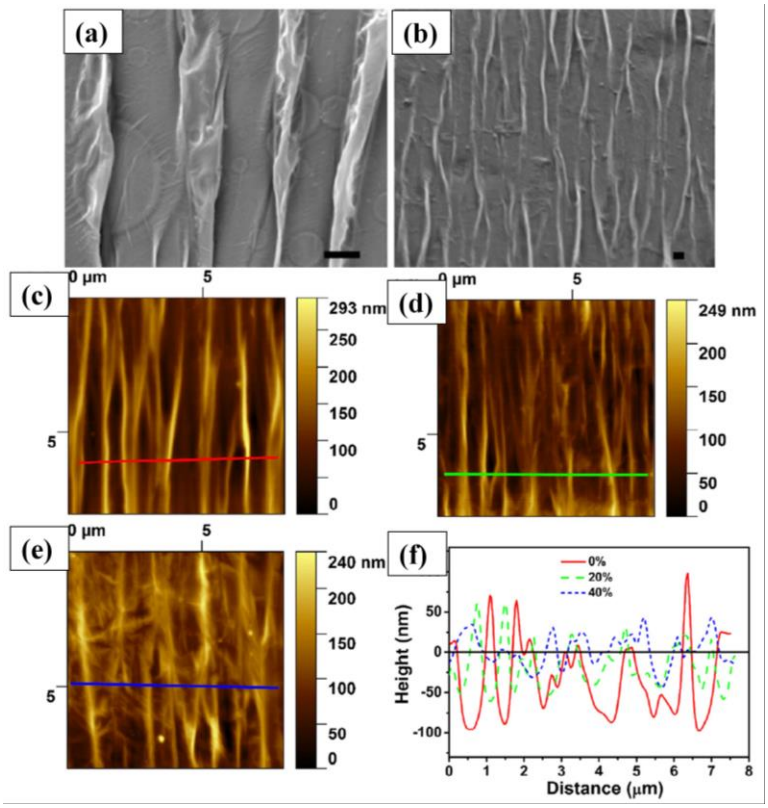

Figure 5. a, b) SEM images of the buckled 4 layer GR laminate[7]. The scale bars are 1 µm in a and 20 nm in b. AFM images of GR laminate at applied tensile strains of (c) 0%, (d) 20% and (e) 40%[8]. (f) Profiles of the ripple heights along the lines marked in (c), (d) and (e)[8].

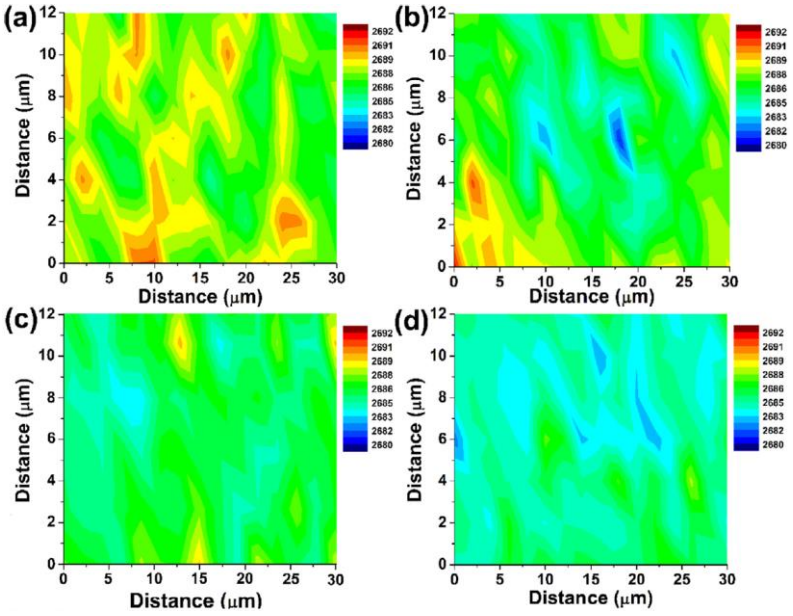

Figure 6. 2D band micro-Raman maps of (a) unbuckled GR laminate and buckled GR laminate at tensile strain of (b) 0%, (c) 20% and (d) 40%.[8]

Fig. 6 exhibits the 2D band spatial variation of a four layer unbuckled GR laminate and buckled GR laminate at different tensile strains. As shown in Fig. 6b-d, when the applied tensile strain increased

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from 0% to 40%, the area with yellow and red color which represented the 2D band position in the range of 2687–2692 cm^{-1} decreased, while blue color area corresponding to the position of 2684–2680 cm^{-1} increased spatially[8], implying that the compressive strain induced in the buckling process was relieved gradually when the applied tensile strain increased[9,10,11].
The small redshift of 2D band and the indiscernible D band demonstrated that the applied tensile strains of up to 40% only caused a strain variation of less than 0.2% in the GR films without observable damage, confirming that the GR film in the buckled state is suitable for its application as a stretchable electrode[8].

2.3 CNT film based omnidirectionally stretchable composite

Freestanding and highly conductive films with randomly oriented CNTs were fabricated first using the floating catalyst chemical vapor deposition method (FCCVD)[12]. The isotropic buckled structure was realized by releasing omnidirectionally prestretched silicon rebber substrate on which CNT film was attached. The resulting composite film showed a continuous and isotropic buckled architecture (Fig. 7a and b) and exhibited an omnidirectional stretchability of 200% strain.

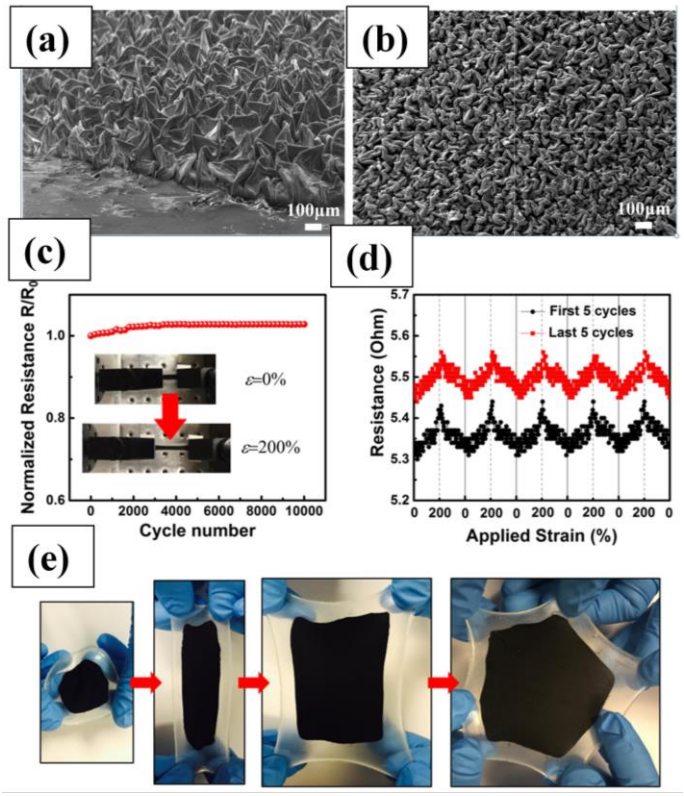

Figure 7. SEM images of isotropic buckled CNT film a) side view and b) top view. c) Normalized electrical resistance as a function of 10,000 uniaxial stretching-releasing cycles at a strain of 200%; the inset shows the buckled CNT film being stretched from 0% to 200% strain. d) Electrical resistance variation of the buckled CNT film during 10,000 uniaxial stretching-releasing cycles at a strain of 200%. e) Photos of buckled CNT film at various stretching states. [13]

The mechanical durability of the stretchable composite film was confirmed by monitoring the resistance variation of the film during 10,000 stretching and releasing cycles. The resistance showed a small increment of less than 3% for the buckled film subjected to uniaxial stretching to 200% strain (Fig. 7d). More importantly, this stretchability and resistance variation were reversible within the prestrain range and even after 10,000 uniaxially stretching and releasing cycles (Fig. 7d). The overall

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resistance increase during 10,000 deformation cycles was less than 3% (Fig. 7c), demonstrating a good mechanical durability of the stretchable CNT film. To make a direct observation of the excllent flexibility and stretchability of the CNT film, photos showing the film stretched to different shaps are given in Fig. 7e.

3. Conclusions

This research has demonstrated the feasibility of enabling large stretchibility in assemblies of nano carbons through prestressing a polymer substrate and then buckling of the nano carbons. Nanocarbon assemblies, including CNT fibers, GR laminates, and ramdomly oriented CNT film, have been adopted for fabricating multifounctional composites and energy storage devices. Excellent electro-mechanical durability has been demonstrated.

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