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### Highly Stretchable Supercapacitors via Crumpled Vertically Aligned Carbon Nanotube Forests

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Stretchable supercapacitors have received increasing attention due to their broad applications in developing self-powered stretchable electronics for wearable electronics, epidermal and implantable electronics, and biomedical devices that are capable of sustaining large deformations and conforming to complicated surfaces. In this work, a new type of highly stretchable and reliable supercapacitor is developed based on crumpled vertically aligned carbon nanotube (CNT) forests transferred onto an elastomer substrate with the assistance of a thermal annealing process in atmosphere environment. The crumpled CNT-forest electrodes demonstrated good electrochemical performance and stability under either uniaxial (300%) or biaxial strains (300%  $\times$ 300%) for thousands of stretching-relaxing cycles. The resulting supercapacitors can sustain a stretchability of 800% and possess a specific capacitance of 5 mF cm<sup>-2</sup> at the scan rate of 50 mV s<sup>-1</sup>. Furthermore, the crumpled CNT-forest electrodes can be easily decorated with impregnated metal oxide nanoparticles to improve the specific capacitance and energy density of the supercapacitors. The approach developed in this work offers an alternative strategy for developing novel stretchable energy devices with vertically aligned nanotubes or nanowires for advanced applications in stretchable, flexible, and wearable electronic systems.

Stretchable electronics have received increasing attention due to their broad applications in the emerging wearable devices, biomedical devices, epidermal electronics, and biointegrated electronics that must sustain large deformations and conform to surfaces with complicated geometries while maintaining their normal functions and reliability.<sup>[1–6]</sup> Examples include interconnects,<sup>[7]</sup> loudspeakers,<sup>[5,8]</sup> pressure and strain sensors,<sup>[3,9]</sup>

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diodes,<sup>[11]</sup> radio frequency devices,<sup>[12]</sup> field effect transistors,<sup>[13]</sup> epidermal electronics,<sup>[2]</sup> and integrated circuits.<sup>[4]</sup> To integrate these stretchable electronics into a power-independent stretchable system in an elegant way, stretchable energy conversion/storage devices become of paramount importance.<sup>[14-17]</sup> Although over the decades, stretchable energy conversion devices like organic solar cells,<sup>[6]</sup> triboelectric nanogenerators,<sup>[18]</sup> and various piezoelectric devices<sup>[19]</sup> have been of great interest, energy storage devices such as electrochemical supercapacitors (SCs) have also been intensively explored for various applications. Their unique features of fast chargedischarge rate, high power density, long operation life, and modest energy excellently complement batteries.<sup>[17,20]</sup> However, most of the existing stretchable supercapacitors can only be stretched in one direction, whereas retaining functionality during multidirectional stretching is essential for many applications. Moreover, many of the

temperature sensors,<sup>[10]</sup> light emitting

stretchable SCs are affected by the applied strains, and are easily damaged if unexpected stretching happens to be larger than the predefined stretchability of the device in fabrication.<sup>[21]</sup>

Among the available materials, carbon-based nanomaterials have been extensively utilized for stretchable SC electrodes due to their high specific surface area, structural integrity, and low cost.<sup>[14,17,22]</sup> For example, Yu et al. presented stretchable

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SCs based on two periodically sinusoidal single-walled carbon nanotube (SWCNT) macrofilm electrodes, a polymeric separator, and an organic electrolyte.<sup>[16]</sup> The electrochemical performance of their stretchable SCs remained unchanged even under 30% applied tensile strain. Chen et al. reported a stretchable carbon nanotube (CNT)-wrapped fiber-shaped SC with high performance.<sup>[23]</sup> In another demonstration, Zang et al. utilized graphene paper origami to fabricate highly stretchable all-solid-state supercapacitors capable of areal stretchability of 800%.<sup>[14]</sup> In regard to fabrication, a few different strategies have been proposed for designing highly stretchable SCs, including the wavy-shape design, wire-shape design, textile-shape design, kirigami-shape design, origami-shape design, and serpentine bridge-island design.<sup>[16,21,24]</sup> In the wavy-shape design by harnessing mechanical instabilities, electrically conducting thin films or ribbons are first created or bonded on a prestrained substrate, followed by subsequent release of tensile strains in the substrate, resulting in self-assembled wavy-shaped or buckled structures. The instability induced patterns/structures enable the inherently nonstretchable materials to be employed as electrodes and interconnects that can withstand stretching without appreciable degradation in electrical performance.[14-16,25]

Here, we report a new type of highly stretchable and reliable supercapacitor based on crumpled vertically aligned CNT forests transferred to an elastomer substrate. The stretchable SCs consist of two crumpled CNT forest electrodes and one solid-state electrolyte layer of poly (vinyl) alcohol (PVA)-KCl, which also serves as a separator for the SC. The CNT forests are first transferred onto the prestrained elastomer substrate with the assistance of a thermal annealing process. Then, a thin layer of PVA-KCl gel is cast onto the CNT forest electrodes as the electrolyte and separator. After that, the two stretchable electrodes from crumpled CNT-forests covered with the gel electrolyte are assembled together to form a stretchable SC device. The crumpled CNT-forest electrodes have two major advantages: 1) CNT forests are very stable and can be easily patterned by annealing-assisted contact transfer, and 2) the vertical CNT forests have a larger surface area compared to a conventional thin flat film, and can be easily modified to be hybrid SCs, particularly in the crumpled states. Additionally, the 3D interconnected CNT forest on the top layer maintains the electrical conductivity under stretching deformations even larger than the prestrains defined in the fabrication. This simple method makes it possible to fabricate mechanically reliable, robust, wavy stretchable electrodes with improved performance. Electrochemical measurements demonstrate that the resultant stretchable crumpled CNT forest electrodes and SCs possess good energy and power densities, comparable with previous CNT-based supercapacitors in literature,<sup>[26,27]</sup> and the electrochemical performances of the stretchable SCs show little variation even under applied tensile strains of 300%.

**Figure 1**a illustrates the fabrication process for preparing a stretchable CNT-forest electrode bonded on an elastomer



**Figure 1.** Fabrication of crumpled-CNT forest electrodes. a) Schematic fabrication process flow for stretchable supercapacitor electrodes from PECVD grown multiwall CNT forest, including I) growth of CNT forest on silicon wafer covered with 5 nm Fe catalyst, II) pretreatment of the samples under 490 °C in air for 3 min, and then stamping the CNTs topside down onto a uniaxially or biaxially prestretched elastomer substrate, III) peeling off the wafer from the target substrate, IV) relaxation of the prestrain in the substrate along the first direction, and V) relaxation of the prestrain in its second orthogonal direction. b) SEM image of CNT-forest grown on a silicon wafer by PECVD for 5 min. The average height of the CNTs is around 20  $\mu$ m. c) SEM image of the parallel ridge pattern formed by the CNT-forest on an elastomer substrate after relaxation in one direction. d) SEM image of the control of the prestrate elastomer substrate (300% × 300%). The scale bar in (b) is 10  $\mu$ m and that in (c) and (d) is 100  $\mu$ m.



substrate. The multiwall CNT-forest is grown by plasmaenhanced chemical vapor deposition (PECVD) with a thin seeding layer of Fe catalyst (~5 nm) on the silicon wafer. The as-grown CNT-forest sample (Figure 1b) is then annealed on top of a hotplate at a temperature of 490 °C for 3 min. Due to the localized oxidation at the bottom of the CNT-forest, most CNTs are broken at the interface of the tube with the catalysts (Figure S1, Supporting Information). This leads to easy detachment of the CNT forest from the Si wafer, which greatly facilitates the dry transfer process (Figure S2, Supporting Information). Examinations by X-ray photoelectron spectroscopy (XPS) and Raman show that the annealing process does not change the properties of the CNT-forest. From the XPS spectrum, it is observed that the oxygen concentration after annealing is slightly increased from 0.71% to 3.71% (Figure S1b, Supporting Information), attributed to the keto, carboxyl, and hydroxyl groups on the CNT surface introduced by oxygen annealing. It should be noted that these surface groups are pseudocapacitive and will benefit the total capacitance of the electrodes.<sup>[28]</sup> In addition, as shown in Figure S1c (Supporting Information), the Raman spectroscopy reveals that the three peaks, 1324 cm<sup>-1</sup> (D band), 1571 cm<sup>-1</sup> (G band), and 1604 cm<sup>-1</sup> (D' band) before and after the oxygen treatment are similar (before  $I_D/I_C \approx 1.487$ and after  $I_{\rm D}/I_{\rm G} \approx 1.494$ ), indicating the treatment does not significantly change the defect density of the CNT forest.

After annealing, the pretreated sample is then stamped onto the prestretched elastomer film, VHB 4910 (acrylic, 1 mm thick, 3M Inc., US). In this stamping step, the elastomer and the wafer are pressed together manually to obtain a better bonding strength between the CNT forest and the elastomer. The prestrain applied on the elastomer film can be either uniaxial or biaxial to fabricate uniaxially or biaxially (two orthogonal in-plane directions) stretchable electrodes (Figure S2, Supporting Information). For easy illustration, we define the prestrains as  $\varepsilon_{pre1} = \Delta L_1/L_1$  and  $\varepsilon_{pre2} = \Delta L_2/L_2$ , where  $L_1$  and  $L_2$ are the orthogonal side lengths of the undeformed elastomer, and  $\Delta L_1$  and  $\Delta L_2$  are the corresponding changes in lengths in the deformed elastomer. The large prestrains can be applied according to the stretchability requirement of the final devices in the range of 0% to 300%. After peeling the wafer off, the prestrains stored in the elastomer substrates are relaxed along one direction or two directions sequentially to crumple the vertically aligned CNT-forest film (Figures S1c,d, Supporting Information). Self-assembled patterns are formed due to the mismatched strains and different material properties of the CNT-forest film and the elastomer substrate. The wavelength and amplitude of the patterns can be reversibly tuned by relaxing and stretching the substrates.<sup>[29]</sup> While similar hierarchical patterns have been fabricated with nanofilms resting on highly compressed elastomers,<sup>[29,30]</sup> this is the first demonstration of crumpling vertically aligned CNT-forests on substrates, resulting in a completely different type of structure. For the uniaxial relaxation of the sample, periodic sinusoidal wrinkles/ ridges are formed due to the buckling of the vertically aligned CNT-forest layer (Figure 1c). It can be seen that the CNT forest remains vertically aligned and protruded out of the substrate forming a hierarchical micro/nanostructural surface, like a unique "CNT carpet."[31] On the other hand, if the prestrains in the biaxially stretched substrates are sequentially released, a randomly wrinkled hierarchical structure across three different length scales is formed, as shown in Figure 1d. It is noted that the wavelength of the wrinkled CNT-forest can be tuned by changing the height of the CNT forest (Figure 1b). When the relaxed elastomer film is uniaxially or biaxially stretched again, the crumpled CNT-forest will be unfolded, resulting in the decreased amplitude and increased wavelength of the ridge patterns. Owing to the flexibility and intertwined networks formed in the crumpled CNT-forests (Figure S3, Supporting Information), the CNT-forest film can maintain good electrical conductivity (Figure S4, Supporting Information) over the cyclic crumpling/unfolding processes, enabling the creation of extremely stretchable and robust electrodes for supercapacitors.

The as-prepared crumpled CNT-forest films (both uniaxially and biaxially) are then tested as electrodes for supercapacitors. Figure 2a shows cyclic voltammetry (CV) curves of a representative crumpled CNT-forest electrode, measured in 1.0 M KCl solution at the scan rates of 20, 50, 100, and 200 mV s<sup>-1</sup>, respectively. The tested electrode is formed by a uniaxial prestrain of 300%. The CV curves remain rectangular at all scan rates, indicating the outstanding rate capability stemming from the easily accessible porous structures of the aligned CNT forest. Additionally, the entangled CNT network at the bottom of the CNT forest significantly reduces the series resistance of the CNT forest electrode and contributes to the good rate capability. The galvanostatic charge/discharge measurements are performed on the uniaxially crumpled CNT forest electrode at different current densities from 0.5 to 5 mA cm<sup>-2</sup> (Figure 2b). The triangular shape of the charge/discharge curves together with the rectangular shape of CV curves confirm the electric double layer (EDL) charge storage mechanism of the stretchable CNT-forest electrodes.

As shown in Figure 2c, little variation in the CV curves of the crumpled CNT forest electrodes is observed when they are subjected to different applied strains from 0% to 300%, indicating the robust electrochemical performance of the stretchable electrodes under large mechanical deformations. Such excellent performance is further confirmed by the similar charge/discharge times of the electrode under different strains (Figure 2d). The electrochemical impedance spectroscopy (EIS) measurements are also performed at open circuit voltage (OCV) under different strains to study the charge transfer properties of the uniaxially crumpled CNT electrodes (Figure 2e). It is observed that slight differences in capacitance for different strains appeared at the high or middle frequency range due to the microstructural changes in the CNT forest induced by different strains. However, at low frequencies where maximum capacitance is achieved, the CNT forest electrode shows very similar electrochemical capacitance under different strains. The specific capacitance of the uniaxially crumpled CNTforest electrode at different charge/discharge current densities under the stretch strains of 0%, 100%, 200%, and 300% is presented in Figure 2f. It was found that at lower current density (e.g., 0.1 mA cm<sup>-2</sup>), a high specific capacitance of 5 mF cm<sup>-2</sup> ( $\approx 2.5$  F cm<sup>-3</sup>) can be achieved and the specific capacitances of the electrodes are nearly the same when subjected to different strains up to 300%. When the current density increases to 5 mA cm<sup>-2</sup>, the specific capacitance decreases to 2.0  $\pm$ 0.5 mF cm^-2 (1  $\pm$  0.25  $\bar{F}$  cm^-3) and is more significantly affected



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**Figure 2.** Electrochemical performance of the crumpled-CNT-forest electrodes under large uniaxial deformations. a) CV curves of a representative crumpled CNT-forest electrode measured at scan rates of 20, 50, 100, and 200 mV s<sup>-1</sup>, respectively. The electrodes were formed by a uniaxial prestrain of 300%. The electrode was tested under 0% strain. b) The galvanostatic charge/discharge curves measured at a current density of 0.5, 1, 2, 5 mA cm<sup>-2</sup>. c) CV curves of the crumpled CNT-forest electrodes subjected to uniaxial strains of 0%, 100%, 200%, and 300%, and measured at a scan rate of 50 mV s<sup>-1</sup>. d) The galvanostatic charge/discharge curves of the same electrode subjected to uniaxial strains of 0%, 100%, 200%, and 300%, measured at 0.5 mA cm<sup>-2</sup>. e) The Nyquist impedance plots of the same stretchable electrode under different strains from 0% to 300%. f) Variation of the specific capacitance measured at different charge/discharge current densities ( $I_s = 0.1, 0.5, 1.0, 2.0, and 5 mA cm^{-2}$ ) when subjected to different uniaxial strains. The tests were carried out in 1.0 m KCl.

by the applied strains. This phenomenon is attributed to the stretching-induced resistance change in the CNT-forest network. Although the entangled CNT network provides the intertwined electric integrity after the transfer process (Figure S3, Supporting Information), the relaxation process reduces the distance between individual CNTs, leading to a better electric contact within the CNT network and thus reducing the film resistance significantly. Gravimetric capacitance of a uniaxially crumpled CNT-forest electrode was also calculated to be  $\approx 7.31~{\rm F~g^{-1}}$  at 0.1 mA cm<sup>-2</sup> ( $\approx 0.056~{\rm A~g^{-1}}$ ) and  $\approx 4.48~{\rm F~g^{-1}}$  at 5 mA cm<sup>-2</sup> ( $\approx 2.8~{\rm A~g^{-1}}$ ) under the stretch strain of 0%.

Figure 3 describes the electrochemical performance of the crumpled CNT-forest electrodes under biaxial strains. It can be observed from the CV and galvanostatic charge/discharge curves that the crumpled CNT forest electrode exhibited typical EDL charge storage behavior at different scan rates under  $0\% \times 0\%$  strain (Figure 3a,b). Moreover, compared with the uniaxially crumpled CNT forest electrodes, the biaxially crumpled samples demonstrate smaller film resistance because of their tighter contacts among CNT networks at the crumpled state. Nevertheless, compared with the uniaxial cases, the electrochemical performance of the biaxially crumpled CNT-forest electrodes shows slightly larger changes when they are subjected to different applied strains (Figure 3c). The CV curves of the biaxially

crumpled electrode measured at a scan rate of 100 mV s<sup>-1</sup> exhibit rectangular shapes under different strains but have different corner shapes due to the increased forest resistance at larger strain states. This indicates that the change of the CNT-forest resistance with applied strains in biaxially crumpled electrodes is larger than that of the uniaxially crumpled electrodes. The difference is also confirmed from the galvanostatic charge/discharge curves (Figure 3d). The charge/discharge time of one cycle scanned at 0.5 mA cm<sup>-2</sup> for the biaxially crumpled CNT forest electrode is 42.3 s in the relaxed state (0% × 0%), while the cycle time reduces to 39.6 s for the same electrode when subjected to a biaxial strain of 300% × 300%.

Figure 3e illustrates the EIS of a biaxially crumpled CNT electrode at OCV. Compared with uniaxially crumpled electrodes, the biaxial cases show relatively larger differences in the middle frequency range due to the larger resistance variation of the crumpled CNT-forest in different stretched states. The impedance change can be analyzed by an equivalent circuit in Figure S5a (Supporting Information), which consists of three major parts: 1) the series resistance for the high frequency response; 2) the constant phase element in parallel with a diffusion impedance and the CNT-forest film resistance for the middle frequency response; 3) the full capacitance (represented by a constant phase element) for the low frequency response.

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**Figure 3.** Electrochemical performance of the crumpled-CNT-forest electrodes under large biaxial deformations. a) CV curves of a representative crumpled CNT-forest electrode measured at scan rates of 20, 50, 100, and 200 mVs<sup>-1</sup>. The electrodes were formed by a prestrain of ( $300\% \times 300\%$ ). b) The charge/discharge curves measured at 0.5, 1, 2, 5 mA cm<sup>-2</sup>. c) CV curves of the crumpled CNT-forest electrodes subjected to biaxial strains of  $0\% \times 0\%$ , 150% × 150%, and 300% × 300%, measured at a scan rate of 100 mV s<sup>-1</sup>. d) Charge/discharge curves of the same electrode subjected to biaxial strains of  $0\% \times 0\%$ , 150% × 150%, and 300% × 300% and measured at 0.5 mA cm<sup>-2</sup>. e) The Nyquist impedance plot of the same stretchable electrode under different biaxial strains. f) Variation of the specific capacitance measured at different charge/discharge current densities ( $I_s$ = 0.2, 0.5, 1.0, 2.0, and 5 mA cm<sup>-2</sup>) when subjected to different biaxial strains. The tests were carried out in 1.0 m KCl.

Specifically, the CNT-forest under the strain states of 0%  $\times$ 0% and 300%  $\times$  300% is investigated across a wide potential range (0-0.8 V vs Ag/AgCl) to make the comparison and avoid instrument errors. As shown in Figure S6 (Supporting Information), the equivalent circuit in Figure S5 (Supporting Information) can be utilized to fit the experimental data very well. The series resistance of the biaxially crumpled CNT-forest electrode in the relaxed state (i.e.,  $0\% \times 0\%$ ) and highly stretched state (i.e.,  $300\% \times 300\%$ ) was 1.2 and 1.4  $\Omega$ , respectively, across the entire potential range, indicating the electrolyte resistance is small and good contact forms between the CNT-forest film and current collector (Pt wires). The full capacitances of the biaxially crumpled CNT-forest electrodes are nearly the same under different strains considering the near one  $\alpha$  value obtain in the fitting (Figure S5b, Supporting Information). This result indicates consistent capacitance behavior of the crumpled CNT supercapacitors at different strain states and is in good agreement with the capacitance obtained from the CV curves. Significant differences are observed for the film resistance R1 versus potential curve (Figure S5c, Supporting Information). The film resistance R1 of crumpled CNT-forest films under the strain of  $300\% \times 300\%$  is approximately three times larger than that without strain. Although the entangled CNT network at the bottom of the crumpled forest provided electrical integrity (Figure S3, Supporting Information), the conductivity of the crumpled CNT electrode is still affected by the applied strains due to the possible breakage of the network junctions under large mechanical deformations. The conductivity variation may cause significant difference in the capacitance of different strain states during high current density discharge of the capacitor (Figure 3f). While the capacitance between different strain states remains similar at a charge/discharge current density of 0.2 mA cm<sup>-2</sup>, the capacitances of the crumpled CNT electrode measured at 5 mA cm<sup>-2</sup> showed an obvious difference, reduced from 10.7 mF cm<sup>-2</sup> ( $\approx$ 5.35 F cm<sup>-3</sup>) at the strain of 0% × 0% to 6 mF cm<sup>-2</sup> ( $\approx$ 3 F cm<sup>-3</sup>) at the strain of 300% × 300%.

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**Figure 4** shows the electrochemical and mechanical stability of the crumpled CNT-forest electrodes under cyclic electrochemical and mechanical loadings, respectively. The specific capacitance of the electrode is calculated by  $C = I/A \times (dt/dV)$ , where *I* is the current applied to the electrode, *A* is the nominal area of the electrode, dt/dV is the reciprocal of the slope of the potential-time discharge curve obtained during the galvanostatic measurement. The electrochemical stability is tested by applying 10 000 constant current charge/discharge cycles at 1 mA cm<sup>-2</sup> to the crumpled CNT electrode at unstrained state. As presented in Figure 4a, the specific capacitance drops to ≈90% of its initial value after the first 500 cycles, but then remains almost constant for another 9500 testing cycles, indicating its excellent electrochemical stability. To further clarify

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the reason for capacitance decreasing in the electrochemical stability test, we perform XPS measurements for characterizing the surface composition of the crumpled CNT-forest electrodes before and after the cyclic electrochemical measurement. As

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shown in Figure S7 (Supporting Information), a slight increase of oxygen concentration on the surface happens after the stability test. The C 1s region scans in Figure S7b (Supporting Information) can be deconvoluted into three peaks: C=C (red), C-C (blue), and C-O (green). There is no new peak observed after the stability test. The increase of oxygen concentration may be due to the OH bond absorption on the crumpled CNT-forest surface or the oxidation of CNT-forest during the test. On the other hand, the initial drop in specific capacitance may be attributed to the possible detachment of certain CNTs that are loosely bonded to the substrate.

In the mechanical stability testing, the crumpled CNT electrode is stretched to a strain of 300% for 1200 uniaxial stretch/relaxation cycles. The CV curves are recorded every 200 mechanical cycles and the capacitance is calculated based on the discharge segment of CV curves. As shown in Figure 4b, the capacitance nearly retains its initial value after 1200 mechanical cycles, exhibiting the robust performance of the stretchable electrodes under multiple cyclic mechanical loadings. Additionally, Figure 4c shows the EIS curves measured after certain mechanical cycles. No significant difference is observed from these EIS curves. The extracted film resistance has little change during the mechanical cycles, demonstrating that the connections of the CNT network are well preserved under large cyclic mechanical loadings.

As a demonstration of complete device performance, a uniaxially stretchable supercapacitor (300% prestrain) is assembled for testing by stacking two uniaxially crumpled CNT-forest electrodes with a PVA/KCl gel electrolyte layer sandwiched between them. Figure 5 presents the performance of the crumpled CNTforest supercapacitor under different conditions. As illustrated in Figure 5a,b, the stretchable supercapacitor shows a typical EDL behavior, with a square shape for the CV curves and a triangular shape for the galvanostatic charge/discharge curves. When subjected to different strains, the electrochemical performance is maintained (Figure 5c) and similar charge/discharge curves can be obtained (Figure 5d). The impedance curves of the supercapacitor measured at different strain states are shown in Figure 5e. It can be seen that the impedance behaviors of the device at different strain states are similar over the entire frequency range, further confirming the robust mechanical properties of the crumpled CNT-forest supercapacitor under large strains. In addition, it can be observed that the specific capacitance ranges from 2 to 1 mF cm<sup>-2</sup> at different charge/discharge states subjected to different strains (Figure 5f), which is in good agreement with the specific capacitance of a single electrode.

For a supercapacitor device, it is important to evaluate the energy storage time by examining the leakage current and self-discharge time. Figure 5g shows the leakage currents of

**Figure 4.** Electrochemical performance of the stretchable crumpled CNTforest electrodes under cyclic electrochemical and mechanical loadings. a) The normalized capacitance of the crumpled-CNT-forest electrode subjected to a uniaxial strain of 0%, measured by 10 000 charge/discharge cycles at 1 mA cm<sup>-2</sup>. b) The normalized capacitance of the biaxially crumpled-CNT-forest electrode as a function of number of stretch/relaxation cycles up to 1200 cycles with uniaxial strain up to 300% for each cycle. c) Nyquist plots of the electrode for cyclic stretching (0, 200, 600, and 1200). The inset shows the corresponding film resistances extracted from (c).







**Figure 5.** Performance of a uniaxially stretchable all-solid-state supercapacitor with crumpled-CNT-forest as electrodes and polymer gel as electrolyte and separator. a) CV curves of the supercapacitor measured at different scan rates without strain. b) Charge/discharge curves at different current densities without strain. c) CV curves of the supercapacitors measured at a scan rate 50 mV s<sup>-1</sup> under the different applied strains. d) Charge/discharge curves at a current density of 0.2 mA cm<sup>-2</sup> under uniaxial strains from 0% to 300%. e) Nyquist impedance plot of the stretchable supercapacitor at different strains from 0% to 300%. f) Specific capacitance of the supercapacitors measured at different current density and under different strains. g) Leakage current measurement of a representative supercapacitor with and without 100% strain. A DC voltage 0.8 V was applied across the capacitor; the current required to retain that voltage was measured over a period of 12 h. h) Self-discharge curves of the same representative supercapacitor with and without 100% strain, obtained immediately after precharging to the maximum voltage of 0.8 V. The open-circuit voltages across the supercapacitor are recorded over 50% the operation voltage of 0.8 V versus time. i) The normalized capacitance retention measured by charge/discharge of the supercapacitor for 10 000 cycles at 1 mA cm<sup>-2</sup>. The solid-state electrolyte is PVA/KCl.

the crumpled CNT-forest supercapacitor with/without strains, which are in the range of 0.1–1  $\mu$ A cm<sup>-2</sup>. The long self-discharge time (3–4 h for 50% voltage retainment) is shown in Figure 5h. The electrochemical stability of the crumpled CNT-forest supercapacitor is examined by carrying out 10 000 galvanostatic charge/discharge cycles at 1 mA cm<sup>-2</sup> subjected to a strain of 100%. The specific capacitance drops to about 92% after the 10 000 measurements. The degradation is mainly attributed to the detachment of the CNT forest from the substrate and the electrolyte drying effect without encapsulation during the long-term tests. A biaxially crumpled CNT forest supercapacitor is also fabricated and tested in the same way as

the uniaxially crumpled CNT forest supercapacitor. The electrochemical performances of the all-solid-state biaxially stretchable supercapacitors with crumpled CNT-forest electrodes are presented in Figure S8 (Supporting Information). Similar to the uniaxially stretchable SCs, the CV curves, charge–discharge curves, and the Nyquist impedance of the biaxially stretchable device show little variation when they are stretched to different strain states of 100% × 100% and 200% × 200%, indicating the excellent performance of the SCs under large mechanical deformations (Figure S5, Supporting Information). The biaxially stretchable SCs also demonstrate good electrochemical stability, as shown in Figure S8h (Supporting Information). A retention



of 85% is observed after 10 000 galvanostatic charge–discharge cycles at 1 mA  $\rm cm^{-2}.$ 

For wearable and stretchable electronics, the crumpled CNTforest supercapacitor should maintain its electrochemical performance in constant motion. To demonstrate this point, CV curves at 50 mV s<sup>-1</sup> are measured under dynamic motions and are compared with the curves in static states. It can be seen from Figure S9 (Supporting Information) that the CV curves under different strains in a dynamic condition are nearly the same, indicating that the dynamic motion in application will not affect the charge/discharge behaviors of the crumpled CNTforest supercapacitor. The output voltage and capacitance can be changed on demand in practical applications by connecting two crumpled CNT stretchable supercapacitors in series or in parallel. To demonstrate the possibility of using the crumpled stretchable CNT-forest based supercapacitor in more complex configurations, we test two uniaxially crumpled CNT supercapacitors in either series or parallel connection case. As shown in Figure S10 (Supporting Information), the stretchable supercapacitor array made of crumpled CNT-forest also demonstrates a similar electrochemical performance when the connected supercapacitors are in different strain states.

We also show that the crumpled CNT-forest electrodes can be easily decorated with metal oxide nanoparticles impregnated for a hybrid supercapacitor with enhanced electrochemical performance. In this work, NiO nanoparticles (Aldrich-Sigma Inc.) are spray-coated onto the CNT-forest electrodes using an airbrush. The NiO nanoparticles are dispersed in methanol to form a solution of 1 mg mL<sup>-1</sup> concentration. After ultrasonication for about 1 h, the solution is sprayed onto the partially relaxed (100%) sample, as shown in Figure S11a (Supporting Information). The spray-coated samples are then stretched and relaxed for a few cycles to allow the nanoparticles to integrate into the CNT-forest (Figures S11b and S12, Supporting Information). The electrochemical performance of the crumpled CNT forest electrode impregnated with NiO nanoparticles is shown in Figure S11c-f (Supporting Information). Although the CV curves under different scan rates become slightly inclined compared to the CNT forest only electrode (Figure S11c, Supporting Information) indicating increased series resistance, the specific capacitance of the crumpled were CNT-forest electrode increases significantly from  $\approx 5$  to  $\approx 45$  mF cm<sup>-2</sup> at a charging/discharging current density of 0.1 mA  $\rm cm^{-2}$ (Figure S11f, Supporting Information). Additionally, it is found that the electrochemical capacitance and charge/discharge times remain almost the same under different strains (Figure S11d,f, Supporting Information). The crumpled CNT forest may serve as a better scaffold than the flat CNT-forest for impregnation by NiO nanoparticles to achieve excellent enhancement in capacitance ( $\approx$ 9×) and robust electrochemical performance under extreme mechanical loadings (Figure S11, Supporting Information). As shown in Figure S13 (Supporting Information), ≈92% capacitance of the electrodes can be retained after 10 000 charge/discharge cycles at 1 mA cm<sup>-2</sup>.

As shown in the Ragone plot in Figure S14a (Supporting Information), the volumetric energy densities and power densities of the crumpled CNT-forest SCs reach around 0.1 mWh cm<sup>-3</sup> and 100 mW cm<sup>-3</sup>, respectively, comparable to most other flexible/stretchable CNT supercapacitors.<sup>[26,27,32–34]</sup> Although these

values are slightly lower than those of the commercial activatedcarbon supercapacitor (AC-SC), they can be further enhanced by impregnating metal oxide nanoparticles to compete with the AC-SC operated in the same voltage range. Moreover, the outstanding stretchability of the crumpled CNT-forest supercapacitor makes it very promising for wearable electronic applications. In Figure S14b (Supporting Information), areal energy densities and power densities of the crumpled-CNT-forest SCs are also calculated and compared with the state-of-the-art CNT based flexible/stretchable SCs. Thanks to the crumpling process, the areal energy and power densities of the new stretchable CNTforest-based SCs are relatively high compared to other reported CNT-based flexible/stretchable supercapacitors in literature.

Figure 6 shows the comparison of the performance of the stretchable, all-solid-state, crumpled CNT-forest based supercapacitors with other energy-storage devices reported in the literature. The capacitances of this work are measured from CV curves at a rate of 50 mV s<sup>-1</sup>. The data from literature includes the CNT fiber-shaped stretchable SCs,[33] buckled SWCNT SC,<sup>[17]</sup> selective-wetting induced multiwall CNT SC,<sup>[27]</sup> CNT/ ion-gel SC,<sup>[35]</sup> vertically aligned CNT on polydimethylsiloxane (PDMS),<sup>[36]</sup> and aligned CNT forest on PDMS,<sup>[37]</sup> which are all categorized into four different types as indicated by the colored ellipses for easier comparison. It can be seen that either the uniaxial or biaxially stretchable SCs with crumpled CNT-forest electrodes showed similar specific areal capacitance compared to the sate-of-the-art CNT supercapacitors. Moreover, the crumpled CNT-forest supercapacitors exhibit large area strain (800% for biaxially, and 300% for uniaxially crumpled CNT supercapacitors) while maintaining high specific capacitance.



**Figure 6.** Performance comparison of the stretchable, all-solid-state, crumpled-CNT-forest supercapacitors with other CNT supercapacitors reported in literature. The capacitances of this work are measured by charge–discharge at a rate of 50 mV s<sup>-1</sup>. The other data from literature are the stretchable CNT-fiber wire-shaped supercapacitor,<sup>[33]</sup> buckled SWNT supercapacitor,<sup>[17]</sup> selective-wetting induced multiwall carbon nanotube supercapacitor,<sup>[27]</sup> CNT/ion-gel supercapacitor,<sup>[35]</sup> vertically aligned CNT stretchable supercapacitor on PDMS,<sup>[36]</sup> and aligned CNT-forest stretchable supercapacitor on PDMS,<sup>[37]</sup> which are categorized into four different types as indicated by the colored ellipses for easier comparison.

In summary, we have developed highly stretchable supercapacitors based on crumpled CNT-forests that are transferred onto prestrained elastomer substrates with the assistance of thermal annealing. The crumpled CNT-forest electrodes, formed by the mechanical instability of the CNT-forest and the underlying substrate, have demonstrated superior electrochemical performance under large uniaxial or biaxial strains. Little variation in CV, charge-discharge, and specific capacitance is observed even when the electrodes are stretched to a uniaxial strain of 300% or biaxial strain of 300%  $\times$  300%. Moreover, the electrode performance can be maintained over thousands of stretching-relaxing cycles. The stretchable SCs that are assembled by stacking two crumpled CNT-forest electrodes and separated by a thin layer of PVA-KCl gel as the electrolyte and separator are able to sustain a stretchability of 800% and possess a specific capacitance of 5 mF cm<sup>-2</sup> ( $\approx 1.25$  F cm<sup>-3</sup>) at the scan rate of 50 mV s<sup>-1</sup>. These stretchable supercapacitors can also be feasibly modified to hybrid SCs with crumpled CNT forests impregnated by metal oxide nanoparticles for a much larger specific capacitance and energy density. The presented approach paves the avenue for developing novel stretchable energy devices with vertically aligned nanotubes, nanowires, or nanofibers for advanced applications in the areas of stretchable, flexible, and wearable electronic systems.

#### **Experimental Section**

Synthesis of CNT Forest: CNT forests were grown by PECVD. An n-type silicon substrate (100) wafer was first coated with a 5 nm layer of iron catalyst using an electron beam evaporation system (CHA Industries, Inc.). The substrate was then placed on a quartz plate inside the 915 MHz PECVD reactor and pumped down to  $\approx$ 33 mTorr for CNT growth. The growth of a CNT forest was divided into three stages: heat up, pretreatment, and growth. During the heat up stage, the substrate was heated to 850  $^\circ\text{C}$  under 100 sccm  $\text{NH}_3$  gas flow for 120 s. Before pretreatment, the plasma was cured in the reaction chamber by the low magnetron power microwaves. Then, the chamber pressure and input magnetron power were simultaneously increased to 21.5 Torr and 2.1 kW. In the pretreatment stage, substrates were exposed to NH<sub>3</sub> plasma at constant temperature (850 °C) and pressure (21.5 Torr) for 180 s. In the heat up and pretreatment processes, the iron film dewetted and formed nanoislands on the substrate which functioned as the catalyst for CNT growth. In the growth stage, the flow rate of NH<sub>3</sub> was decreased to 50 sccm and mixed with 150 sccm of methane gas  $(CH_4/NH_3 = 3:1)$  to grow the vertically aligned CNT forest. The height of the CNT forest was simply tuned by the growth time. In testing, 300 s was used to grow vertically aligned CNT forests of 20-30 µm high.

Thermal Annealing of the CNT Forest Sample: To facilitate the transfer of the CNT forest from wafer to target substrates, the as-grown CNT forest was annealed on a hotplate at 490 °C for 3 min in ambient atmosphere. The catalyst particles which remained at the root of CNTs facilitated the etching of active carbon atoms in a slight oxidation environment when they were exposed to thermal annealing, leading to the easier transferring or peeling off of the CNT-forest from the wafer (Figure S1a, Supporting Information). The oxygen treatment in this procedure can purify the CNT forest (removing carbonaceous impurities) and introduce hydrophilic oxygenated functional groups which will benefit the SC capacitance.<sup>[38]</sup>

Transfer of CNT Forest to Elastomer Substrate: After annealing, the CNT forest on the Si wafer was able to be easily transferred onto prestretched elastomer substrates (VHB 4910, 3M Inc.). First, the elastomer substrate was either uniaxially or biaxially prestretched to a specific strain and fixed on the stretcher for stabilization. The side of the silicon

wafer with the CNT forest was then pressed onto the prestretched VHB film for 30 s, then slowly peeled off the wafer to transfer the CNT forest onto the prestretched substrate (Figure S2, Supporting Information). After the transfer, the prestretched elastomer was released in one or two orthogonal directions sequentially to form the uniaxially or biaxially crumpled CNT-forest electrodes. Note that the CNTs making up the CNT forest are intertwined with one another at the top ends and thus form an entangled network there (Figure S3, Supporting Information), which actually enhances the electric conductivity of the forest electrode after the transfer.

Fabrication of All-Solid-State Stretchable CNT-Forest Supercapacitors: 2.5 g PVA ( $M_w$  146 000–186 000, Sigma-Aldrich Inc.) was dissolved into 25 mL deionized water. The solution was heated up to 90 °C for 1 h with stirring until it became clear. Then, 3 g KCl was added into the solution and stirred for another 10 min. The prepared PVA–KCl solution was then degassed in a vacuum desiccator overnight to remove the bubbles. The PVA–KCl gel was finally casted onto the stretched CNT-forest electrodes. A small margin area was left uncovered for placing the Pt wire for electrochemical measurement. After 30 min of drying in air, the two prestretched CNT-forest electrodes were laminated together. The PVA–KCl gel serves as both electrolyte and separator. The assembled device was then tested by a standard two-electrode setup.

*Electrochemical Measurements and Calculation*: The crumpled CNT forest electrode was tested in a three-electrode setup at room temperature using a Bio-logic SP-300 potential station. Ag/AgCl in saturated KCl solution was used as the reference electrode, and Pt mesh was used as the counter electrode. 1  $\,$  M KCl solution was used as the electrolyte. Cyclic voltammetry was performed to characterize the electrochemical performance of the crumpled CNT forest electrode. The scan rate was varied from 20 to 200 mV s<sup>-1</sup>. ElS was used to achieve impedance spectra. The frequency range was from 200 kHz to 0.1 Hz and the sinusoidal potential amplitude was 10 mV. The ElS spectrum was recorded at open circuit voltage for the crumpled CNT electrodes. The specific areal capacitance of the crumpled CNT electrodes. The current density was tested from 0.1 to 5 mA cm<sup>-2</sup>. The voltage range was scanned from 0 to 0.8 V versus Ag/AgCl. The capacitance was calculated as

$$C = \frac{I}{\mathrm{d}V/\mathrm{d}t} \tag{1}$$

where  ${\it I}$  is the current density,  ${\rm d}{\it V}/{\rm d}{\it t}$  is the slope of the voltage-time curve.

For measuring the crumpled CNT-forest based supercapacitor, a two-electrode setup was used. The CV, EIS, and galvanostatic charge/ discharge were measured to evaluate the electrochemical performance of the SCs. The CV scan rate was varied from 20 to 200 mV s<sup>-1</sup>. The EIS spectrum was tested at 0 V (fixed for 2 min before the measurements) with the same setting of the single electrode measurements. The galvanostatic charge/discharge was measured from 0 to 0.8 V at the current density from 0.1 to 5 mA cm<sup>-2</sup>. Chronoamperometry was applied to test the leakage current of the crumpled CNT-forest supercapacitors. The supercapacitor was charged to 0.8 V and kept at 0.8 V for 12 h. The leakage current was recorded versus time. The self-discharge property of the crumpled CNT-forest supercapacitor was recorded by the OCV drop immediately after the leakage current test. The OCV was recorded versus time until it dropped to more than 50% of the original value. All the capacitance and current values were normalized to the nominal surface area under the relaxed state (0% strain) using ImageJ software. The volumetric and area capacitance are more accurate than the gravimetric values and can reflect the true performance of a supercapacitor.<sup>[39]</sup> For comparison, the gravimetric capacitance was also calculated based on the weight of CNT forest that was measured by an analytical balance (OHAUS, PA84C). In this work, thickness of the CNT-forest was measured from the SEM images. The volumetric energy density and power density of the crumpled CNT-forest supercapacitors were calculated based on the galvanostatic charge/discharge curves for the devices without strains.

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#### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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#### **Conflict of Interest**

The authors declare no conflict of interest.

#### Keywords

carbon nanotube forests (CNT-forests), crumpled CNT-forests, energy storage devices, flexible supercapacitors, stretchable supercapacitors

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