Supporting Information


Hydrogel Cryo-Microtomy Continuously Making Soft Electronic Devices

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Calculation

Maximum Deflection under Solvent Pressure: For a single carbon nanotube (CNT) from CNT array, a beam sway model was used to calculate its maximum deflection under pressure. An individual CNT pillar on the silicon wafer was treated as a beam supported at one end as shown in Figure 2a. Under the solvent pressure, the large deformation of a single CNT is possible because of the extraordinary flexibility of CNT and its resistance to fracture. In this case, the relation between the Young’s modulus and the maximum deflection was expressed by Equation (1).\[^1\]

$$\delta = \frac{WL^3}{6EI} = \frac{8PL^4}{\pi ED^3} \quad (1)$$

where W (equal to PDL) is the total external force, P is the pressure, D is the diameter, L is the length, E is the Young’s modulus of CNT, and I (equal to $\pi D^4/64$) is a cross-sectional second moment.

Next the deflection for CNT under pressure was estimated. Assuming that the Young’s modulus of an individual CNT is 1 TPa\[^1\] the calculation results show that a pressure of only 0.1 Pa will cause a maximum deflection of 0.25 mm for a CNT with 10 nm in diameter and 1,000 μm in length. Assuming that the value of Young’s modulus remains relatively constant, a pressure of only 200 Pa would be sufficient to cause a maximum deflection of 0.5 mm for each CNT in an array consisting of 1,000 CNTs. Therefore, the stability of ultra-high CNT is so low that it cannot resist the external force and deform easily.

However, when the diameter of CNT increases by 2 or 4 times to 20 or 40 nm, the deflection will decrease to 32 μm and 3.8 μm, respectively. Therefore, with the assumption that the nitrogen-doping regrowth only changes the diameter of CNT but not affects the modulus, the ability of a single CNT to resist external pressure improves significantly after 10 min of nitrogen doping. It can maintain an upright state without severe bending deformation under the same pressure. Furthermore, the macroscopic CNT array can keep upright without severe deformation under external force. However, when the CNTs are too large (e.g., 40 nm), the spacing among CNTs will be significantly reduced, which is not conducive to electrolyte penetration into the array, so 10 min was chosen as the optimized regrowth time.
It is seen from the above simple calculation that capillary forces are large enough to cause the bending of CNT and the increase of the diameter of CNT can improve its resistance to external forces. Furthermore, the capillary forces generated by water also have a significant effect on the morphology of macroscopic CNT array. Many studies have reported that the introduction of water could induce a self-assembly of CNTs to form various interesting morphologies or cause a densification of CNT forests.\textsuperscript{[2,3]} The above phenomenon mainly results from the remarkable mechanical and structural properties of the CNTs, such as vertical alignment, narrow spacing, high surface area, flexibility, and mechanical strength.

Similarly, for the ultra-high aligned CNT arrays in this experiment, the introduction of PVA electrolyte will also lead to the flexural deformation of CNTs. For the patterned arrays, the patterns are even destroyed due to the deflection of CNTs. Therefore, nitrogen-doping regrowth will ultimately improve the overall stability of aligned CNT array by increasing the diameter of individual CNTs. As a result, the introduction of PVA electrolyte into the array will not cause the destruction of array patterns.

**Calculation of Specific Capacitance and Energy and Power Densities of Supercapacitors:** The capacitance (C) in two-electrode system was calculated from Equation (2).\textsuperscript{[4]}

\[
C = \frac{(I \times \Delta t)}{\Delta V} \quad (2)
\]

where I, \( \Delta t \), and \( \Delta V \) correspond to the discharge current, discharge time, and voltage window, respectively. The device areal (\( C_A \)) and volumetric (\( C_V \)) capacitances were calculated by dividing the capacitance by the area and volume of device including fingers of two electrodes and the interspace between fingers, respectively. The volumetric energy (\( E_V \)) and power (\( P_V \)) densities, and areal energy (\( E_A \)) and power (\( P_A \)) densities were obtained according to Equations (3-6).

\[
E_V = \frac{C_V \times \Delta V^2}{(2 \times 3600)} \quad (3)
\]

\[
P_V = \frac{E_V \times 3600}{\Delta t} \quad (4)
\]

\[
E_A = \frac{C_A \times \Delta V^2}{(2 \times 3600)} \quad (5)
\]

\[
P_A = \frac{E_A \times 3600}{\Delta t} \quad (6)
\]

**Calculation of the Sensitivity of Sensors:** The linear working window of a sensor was determined by the sensing range that the electrical resistance varied linearly with the
measurand (coefficient of determination ($R^2 \geq 0.95$)).[5]

The strain sensitivity was defined as the slope of resistance profile in the linear working window and quantified by gauge factor (GF), as shown by Equation (7).[6]

$$GF = \frac{S_2 - S_1}{\varepsilon_2 - \varepsilon_1}; S = \frac{(R - R_0)}{R_0} \tag{7}$$

where $\varepsilon_1$ and $\varepsilon_2$ denote the starting and ending strains of the linear working window, respectively, $S_1$ and $S_2$ denote the starting and ending relative resistance changes of the linear working window, respectively, while $R_0$ and $R$ represent the resistances at the initial state and under strains, respectively.

The sensitivity ($S$) of a pressure sensor was used to evaluate the pressure-sensing performance, defined as in Equation (8).[7]

$$S = \partial \left[ \frac{R - R_0}{R_0} \right] / \partial P \tag{8}$$

Where $P$ refers to the applied pressure while $R_0$ and $R$ represent the resistances at the initial state and under pressure, respectively.

The temperature coefficient of resistance (TCR) is adopted to assess the sensitivity of a temperature sensor, defined as in Equation (9).[8]

$$TCR = \left[ \frac{(R_T - R_0)}{R_0} \right] / \partial T \tag{9}$$

Where $T$ refers to the measured temperature, $R_T$ is resistance under measured temperature and $R_0$ is original resistance.
Figure S1. Typical scanning electron microscopy image of the interface between N-MWCNT electrode and PVA electrolyte of the obtained soft supercapacitor slices.
Figure S2. Young’s modulus of our soft electronic device slice based on nanoindentation test.
Figure S3. Transmission electron microscopy images of a) pristine MWCNT and b) N-MWCNT-10 min and c) N-MWCNT-20 min. Scanning electron microscopy images of d, g) pristine MWCNT array, e, h) N-MWCNT-10 min array and f, i) N-MWCNT-20 min array.
Figure S4. Raman spectra of pristine MWCNT and N-MWCNT with different regrowth periods. The intensity ratio of D to G bands (I_D/I_G) increased from 0.425 for pristine MWCNT to 0.749 for N-MWCNT-10 min and 0.877 for N-MWCNT-20 min.
Figure S5. Water contact angle of a) pristine MWCNT and b) N-MWCNT-20 min.
Figure S6. X-ray photoelectron spectra of a) pristine MWCNT and N-MWCNT-10 min and b) the deconvoluted N 1s spectra of N-MWCNT-10 min. The weight percent of nitrogen in the N-MWCNT-10 min was approximately 3.4 wt%.
Figure S7. Photographs of a) N-MWCNT-10 min array and b) N-MWCNT-20 min array. To ensure the structure stability, N-MWCNT array with regrowth period of 10 min was used later if not specified.
Figure S8. Optical microscopic images of a drop of 10-μL aqueous PVA electrolyte with different PVA concentrations penetrating into the aligned N-MWCNT array electrodes. Here, 1.0 M H₃PO₄ was used for all PVA electrolyte. The initial contact angle difference was likely due to the top roughness difference of different N-MWCNT arrays.
Figure S9. a) Viscosities of sol-state PVA electrolytes with different PVA concentrations. b) Conductivities of pristine sol electrolytes and freeze-thawed gel electrolytes with different PVA concentrations and 1.0 M H₃PO₄. The pristine sol electrolyte was frozen at -30 °C for 1 h and thawed at ambient temperature to obtain the freeze-thawed gel electrolyte.
Figure S10. X-ray diffraction spectra of pristine plastic PVA, PVA-H₃PO₄ sol and freeze-thawed PVA-H₃PO₄ gel.
Figure S11. Differential scanning calorimetry curves of 1.0 M H$_3$PO$_4$ solution, 0.09 g·mL$^{-1}$ PVA sol and deionized water.
**Figure S12.** a) Differential scanning calorimetry curves of aqueous PVA electrolytes with different concentrations of $\text{H}_3\text{PO}_4$. b) Conductivities of pristine sol electrolytes and freeze-thawed gel electrolytes with different concentrations of $\text{H}_3\text{PO}_4$. Here PVA concentration was 0.09 g·mL$^{-1}$. The pristine sol electrolyte was frozen at -30 °C for 1 h and thawed at ambient temperature to obtain the freeze-thawed gel electrolyte.
Figure S13. Customized masks with a) four and b) two kinds of array patterns on a 4-inch stainless steel for the fabrication of patterned aligned N-MWCNT arrays.
Figure S14. a) Designing patterns and b) size parameters of the three kinds of interdigital electrodes. The red dotted boxes in a indicate the scope used to calculate the areas of devices. c-e) Galvanostatic charge-discharge curves at a current of 18.75 μA, Nyquist plot and Ragone plot of the soft supercapacitors with size parameters shown in a, b with a shared thickness of 50 μm, respectively.
Figure S15. Cyclic voltammogram of the soft supercapacitors with increasing thicknesses at a scanning rate of 50 mV·s⁻¹.
Figure S16. Typical galvanostatic charge-discharge curves for the soft supercapacitor with thickness of 50 μm at different current densities.
Figure S17. a, b) Image and working parameters of a larger-scale slicing equipment, respectively. The above equipment allows a larger sample size and can operate at a higher speed than the lab-scale microtome we used. Here, a potentially improved production efficiency is estimated. Firstly, the significantly increased sample cell size can allow the increased number of samples processed simultaneously. For example, it is possible to section 25 samples with a cross-sectional size of 1 cm × 1 cm fixed in 1 row simultaneously. Besides, a sectioning stroke can be completed within 1 s at the rate of 125 mm·s⁻¹. Therefore, we may perform 300 sectioning strokes of 25 samples in 5 min, namely producing 7500 slices. Noticeably, the above estimate shows that cryo-microtomy is promising to realize high-efficiency standard preparation of soft thin electronic devices.
Figure S18. Coulombic efficiency of the soft supercapacitors during 10,000 charge-discharge cycles.
Figure S19. a) Scanning electron microscopy image of the surface of the soft supercapacitor using PVA-saline gel electrolyte, showing sodium chloride crystal after drying. b) Galvanostatic charge-discharge curves of the supercapacitors based on PVA-PBS and PVA-saline gel electrolyte at a current density of 0.6 mA·cm$^{-2}$. 
Figure S20. a) Schematic of soft supercapacitors with PVA-H₃PO₄-KI-VOSO₄ gel electrolyte. b) Galvanostatic charge-discharge curves for the soft supercapacitors based on PVA-H₃PO₄-VOSO₄, PVA-H₃PO₄-KI and PVA-H₃PO₄-KI-VOSO₄ gel electrolytes at 0.6 mA·cm⁻². c) Comparison of cyclic voltammograms of supercapacitors based on PVA-H₃PO₄ and PVA-H₃PO₄-KI-VOSO₄ gel electrolytes at 200 mV·s⁻¹. d) Galvanostatic charge-discharge curves for the soft supercapacitor with PVA-H₃PO₄-KI-VOSO₄ gel electrolyte at incremental current density.
Figure S21. Schematic of the soft sensor that can detect strain, pressure and temperature.
Figure S22. a) Relative resistance changes and b) corresponding GF of strain sensors with different thicknesses under 20% strain.
Table S1. Young’s modulus values of our soft electronic device slices, skin and some commonly used materials in skin-mounted or implantable electronic devices.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Young’s modulus (Pa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our soft devices</td>
<td>$(2.23–2.92) \times 10^4$</td>
<td>This work</td>
</tr>
<tr>
<td>Skin</td>
<td>$(2.02–3.24) \times 10^4$</td>
<td>This work</td>
</tr>
<tr>
<td>Hydrogel skin</td>
<td>$(2.73\pm7.44) \times 10^4$</td>
<td>[9]</td>
</tr>
<tr>
<td>PDMS</td>
<td>$(0.42–2.04) \times 10^6$</td>
<td>[10]</td>
</tr>
<tr>
<td>Polyimide</td>
<td>$(3.53–6.84) \times 10^9$</td>
<td>[11]</td>
</tr>
<tr>
<td>Silicon</td>
<td>$(1.34–1.82) \times 10^{11}$</td>
<td>[12]</td>
</tr>
<tr>
<td>CNT film</td>
<td>$(1.70–10.80) \times 10^{11}$</td>
<td>[13]</td>
</tr>
<tr>
<td>Gold</td>
<td>$(30.4–89.0) \times 10^{11}$</td>
<td>[14]</td>
</tr>
</tbody>
</table>
**Table S2.** Comparison of areal capacitances of our soft supercapacitors fabricated by cryo-microtomy with those of supercapacitors obtained by other fabrication methods.

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Fabrication method</th>
<th>Device areal capacitance (mF·cm⁻²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-MWCNT</td>
<td>Cryo-microtomy</td>
<td>23.1</td>
<td>This work</td>
</tr>
<tr>
<td>Ti₂C₂Tₓ MXene</td>
<td>Extrusion printing</td>
<td>10.75</td>
<td>[15]</td>
</tr>
<tr>
<td>PG/WJM-graphene: SWCNTs</td>
<td>Screen printing</td>
<td>1.324</td>
<td>[16]</td>
</tr>
<tr>
<td>Ti₃C₂Tₓ MXene</td>
<td>Stamping</td>
<td>15.25</td>
<td>[17]</td>
</tr>
<tr>
<td>δ-MnO₂/PEDOT:PSS</td>
<td>Inkjet printing</td>
<td>0.26</td>
<td>[18]</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Capillarity-driven printing</td>
<td>7.53</td>
<td>[19]</td>
</tr>
<tr>
<td>Au/RuO₂</td>
<td>Laser-writing</td>
<td>27</td>
<td>[20]</td>
</tr>
<tr>
<td>Graphene</td>
<td>Screen printing</td>
<td>1.0</td>
<td>[21]</td>
</tr>
</tbody>
</table>
**Table S3.** Comparison of power and energy densities of our soft supercapacitors and those of other reported supercapacitors.

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Power density (μW·cm(^{-2}))</th>
<th>Energy density (μWh·cm(^{-2}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-MWCNT</td>
<td>240 480 1200 2400</td>
<td>8.20 6.27 4.33 4.00</td>
<td>This work</td>
</tr>
<tr>
<td>Ti(_3)C(_2)T(_x) MXene</td>
<td>11.4 22.5 44.1 75.1 115.4 157.7</td>
<td>0.3166 0.3120 0.3065 0.2086 0.1603 0.1094</td>
<td>[15]</td>
</tr>
<tr>
<td>PG/WJM-graphene: SWCNTs</td>
<td>11 22 54 110 220 600 1130 2100 5400 11600 20130</td>
<td>0.63 0.58 0.53 0.51 0.48 0.41 0.361 0.3 0.19 0.112 0.064</td>
<td>[16]</td>
</tr>
<tr>
<td>Ti(_3)C(_2)T(_x) MXene</td>
<td>6.02 12.5 30 64 123 330</td>
<td>0.76 0.73 0.715 0.703 0.67 0.63</td>
<td>[17]</td>
</tr>
<tr>
<td>NiCoP@NiOOH//ZIF-C</td>
<td>270.5 560 1260 1680</td>
<td>13.9 11.4 10 9</td>
<td>[22]</td>
</tr>
</tbody>
</table>
References for the Supplementary Information


