Highly Compressible and All-Solid-State Supercapacitors Based on Nanostructured Composite Sponge

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Elastic electronics, which have the ability to endure large levels of strain without remarkable loss in their electronic performance and reliability,^[1-4] have attracted more attention due to wide applications.^[5–13] In order to power such electronics and build a self-powered strain-tolerant system, energy-storage devices that can accommodate large strain while maintaining the performance should be considered.^[14–17] Among different energy-storage devices, supercapacitors are important because of their higher power density, long cycle life, and high charge/ discharge rates as against that of batteries.^[18–35] Therefore, strain-tolerant supercapacitors should be fabricated to match the requirement of elastic electronics.

Stretchable supercapacitors based on graphene and singlewalled carbon nanotubes (SWCNTs) have been designed.[36-44] However, as a reverse case, the design and assembly of compressible supercapacitors have received less attention. The successful fabrication of a highly compressible supercapacitor depends mainly on the innovation of compression-tolerant electrode materials as well as the design of suitable configuration. While recent demonstrations have shown that graphene, SWCNTs, and their composite foams can serve as compressible supercapacitor electrodes,^[45–48] the supercapacitor devices based on these electrodes are coin cells or specific setups with a complicated configuration. In such supercapacitor devices, incompressible package materials were used. As a result, these devices cannot be compressed as one unit and the two electrodes have to move relative to the shell under strain. Furthermore, the liquid electrolytes are employed in these supercapacitors.^[45-48] The liquid-electrolyte-based configuration would suffer from the possible leakage of harmful electrolytes and undesired dislocation of electrode position because liquid electrolyte flows out or into the electrodes during

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compressing-releasing process. Unlike liquid electrolytes, gel electrolytes possess desirable electrochemical properties and excellent mechanical integrity.^[49–51] All-solid-state supercapacitors based on gel electrolytes are favored over their liquid counterparts, since they often avoid the possible leakage of harmful electrolytes and usage of package materials.^[51–57] Therefore, they exhibit excellent mechanical integrity as well as simplified configuration. If a gel electrolyte is utilized and the configuration is simplified in compressible supercapacitors, the supercapacitor devices could be highly compression-tolerant and compressed as one unit arbitrarily during the compression strain that they can endure.

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Here, we report highly compressible all-solid-state supercapacitors with integrated configuration based on nanostructured polyaniline (PANI)-SWCNTs-sponge electrodes. The PANI-SWCNTs-sponge electrodes were achieved by a "dipping and drying" strategy to coat SWCNT layer onto the skeleton of sponge and a subsequent chemical oxidation polymerization process to prepare PANI on the surface of SWCNTs. The compression tolerance of the sponge and the fault tolerance of SWCNT films are fully utilized in PANI-SWCNTs-sponge electrodes, leading to their high compression-tolerant ability. Based on PANI-SWCNTs-sponge electrodes, highly compressible all-solid-state supercapacitors were prepared using poly(vinyl alcohol) (PVA)/H₂SO₄ gel as electrolyte. Such all-solid-state supercapacitors possess an integrated configuration and can be compressed arbitrarily as an integrated unit under 60% strain, which is quite different from the case of previous reported compressible supercapacitors. Furthermore, the performance of as-prepared supercapacitors remains nearly unchanged when compressed under 60% strain. More importantly, owing to the all-solid-state and integrated configuration, several supercapacitors can be integrated and interconnected together in series or parallel on one chip to improve the output potential and/or current. It enlightens a broad area of compressible energy-storage devices to be compatible with highly compression-tolerant electronics.

Figure 1a schematically shows the experimental preparation of PANI–SWCNTs–sponge composite electrodes. In a typical experiment, the sponge was cut into a certain size to match the demand of the designed supercapacitor electrodes (Figure 1b). After that, the sponge was coated with SWCNTs by a repeated "dipping and drying" strategy based on SWCNT aqueous suspension (step I of Figure 1a). The amount of SWCNTs on the skeleton of sponge can be controlled by the "dipping and drying" time and the concentration of SWCNT aqueous suspension. In our case, three "dipping and drying" times were employed when the concentration of SWCNT aqueous suspension was about 3.0 mg mL⁻¹. The mass loading of SWCNTs on the skeleton of sponge was 2.2 mg cm⁻². The SWCNTs–sponge

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Figure 1. a) Schematic diagram of preparing PANI–SWCNTs–sponge composite electrodes. Optical images of b) sponge, c) SWCNs–sponge, and d) PANI–SWCNTs–sponge. SEM images of e) sponge, f) SWCNTs–sponge, and g) PANI–SWCNTs–sponge.

was then rinsed several times using deionized water to remove the surfactant on the surface of SWCNTs. Subsequently, a chemical polymerization process (step II of Figure 1a) was used to deposit PANI on the SWCNT surface to obtain a PANI– SWCNTs–sponge electrode (Figure 1d). The mass loading of PANI was 4.1 mg cm⁻². Therefore, the total mass loading of active materials on the skeleton of sponge was 6.3 mg cm⁻².

Scanning electron microscopy (SEM) clearly shows that sponge possess a continuous network (Figure 1e), indicating that sponge is a good scaffold for functional materials to achieve nanostructured supercapacitor electrodes.^[58] After coating SWCNTs by the "dipping and drying" process, SWCNTs-sponge (Figure 1c) remains the open porous architecture of original sponge (Figure 1f) and SWCNTs are tightly coated onto the skeleton of sponge by van der Waals interaction between SWCNTs and the skeleton of sponge (inset of Figure 1f). Raman spectroscopy was also used to characterize the SWCNTs-sponge, as shown in Figure 2a. The radial breathing modes, D and G bands of SWCNTs, are observed at 100-400 cm⁻¹, 1328 cm⁻¹, and 1597 cm⁻¹, respectively, indicating the existence of SWCNTs on the skeleton of sponge.^[59] Since the skeleton of the sponge is interconnected and free of junctions to cross, the SWCNT layer, like "skin," on the skeleton of the sponge is continuous, forming a continuous "skeleton/ skin" structure. Continuous "skeleton/skin" structure ensures that the electrons are readily transported throughout the SWCNT network in the SWCNTs–sponge. Thus the sheet resistance of the SWCNTs–sponge obtained by three "dipping and drying" times is low (about 33 Ω sq⁻¹).

Porous hierarchical architecture of SWCNTs-sponge with high electron-transport ability makes it an ideal substrate to further deposit other functional materials for various applications. PANI is one of the most promising pseudo-capacitive electrode materials due to its relatively higher conductivity and lower cost than many other conducting polymers.^[60] Therefore, PANI was deposited on the surface of SWCNTs in the SWCNTs-sponge (Figure 1g) by chemical oxidation polymerization to enhance the performance of composite electrodes through the synergistic effects from SWCNTs and PANI. During the process of depositing PANI, the porous hierarchical architecture in SWCNTs-sponge enables aniline molecules to infiltrate into the inner of SWCNTs-sponge easily and efficiently. Furthermore, SWCNTs-sponge remains its integrity during the deposition process because of its excellent mechanical strength as well as toughness. Raman spectroscopy also proves the formation of PANI in the SWCNTs-sponge. In Figure 2a, the peaks ascribed to PANI are observed at about 423/524 cm⁻¹ (C-C out-of-plane deformation), 829 cm⁻¹ (out ofplane C-H motion), and 1170 cm⁻¹ (C-H bending).^[61]

The results of stress-strain measurements with maximum strain of 60% for sponge, SWCNTs-sponge,



Figure 2. a) Raman spectra of sponge, SWCNs–sponge, and PANI–SWCNTs–sponge. b) Compressible stress–strain curves with a maximum strain of 60% for sponge, SWCNTs–sponge, PANI–SWCNTs–sponge, and all-sold-state supercapacitor. c) Electrical resistance changes of PANI–SWCNTs–sponge electrodes at different compressing-releasing cycles when they are as-prepared, in $1 \text{ M } \text{H}_2\text{SO}_4$ and coated by PVA/H₂SO₄. d) The variation of electrical resistance of PANI–SWCNTs–sponge coated by PVA/H₂SO₄ in the first 200 compressing–releasing cycles.

and PANI-SWCNTs-sponge are shown in Figure 2b. The compressible stress-strain curves of SWCNTs-sponge and PANI-SWCNTs-sponge are similar with that of sponge, showing the characteristic behavior of porous foam-like materials with three regions.^[3,62] For instance, when PANI-SWCNTs-sponge is compressed ($\varepsilon < 10\%$), it deforms linearly with respect to pressure, showing a Hooke's region (Region I). Region I represents the deformation of the intact PANI-SWCNTs-sponge. This linear elastic region lasts until the skeleton in PANI-SWCNTs-sponge start to buckle. With further compressive force, the skeleton with PANI and SWCNTs is buckled and collapsed. As a result, the stress-strain curve exhibits a plateau from 10% to 45% strain (Region II). This region is followed by the rapidly increasing slope of the stress-strain curve (Region III). At Region III, the skeleton with SWCNTs and PANI is crushed together, and the PANI-SWCNTs-sponge behaves like bulk materials, while in the releasing process, retreating stress is accompanied by timely recovery of the PANI-SWCNTs-sponge and the releasing curve almost returns to the origin, indicating that the morphology of PANI-SWCNTs-sponge can be totally restored without plastic deformation when the stress is fully removed. Thus, PANI-SWCNTs-sponge allows a large deformation without fracture or collapse. Furthermore, this property is also reflected from the full recovery of porous structure after large strain.

For PANI–SWCNTs–sponge, the neighboring PANI–SWCNT layer on the skeleton of sponge will contact each other at large compressible strain (Figure S1, Supporting Information), leading to the rapidly decreasing of their resistance, as shown in Figure 2c. Therefore, the PANI-SWCNTs-sponges can act as a compressible electrical conductor (Figure S2, Supporting Information). However, as compressible supercapacitor electrodes, it is of great significance to remain the resistance of PANI-SWCNTs-sponges unchanged in the supercapacitor devices under different strain levels. Unlike as-prepared PANI-SWCNTs-sponge, in the supercapacitor devices, the electrodes are usually immersed in the liquid or solid electrolyte. Therefore, the resistances of PANI-SWCNT-sponge electrodes in liquid or coated by solid electrolyte were measured, respectively. In the liquid electrolyte (1 M H₂SO₄), the neighboring skeleton of PANI-SWCNT-sponge still easily contact each other, exhibiting a similar behavior to the case of as-prepared PANI-SWCNT-sponge electrodes (Figure 2c). By contrast, after coating a layer of solid electrolyte (PVA/H2SO4) on the surface of electrode materials, the solid electrolyte layer will avoid the contact between neighboring conductive electrode materials on the skeleton of PANI-SWCNT-sponge at a large compressible strain, resulting in the negligible change of their resistance, as shown in Figure 2c. Furthermore, the resistance of PANI-SWCNT-sponge coated by solid electrolyte is nearly not altered in spite of repeated compressing-releasing process (Figure 2d). Therefore, the PANI-SWCNT-sponge would be excellent candidate of highly compressible solid-state supercapacitor electrodes, in which neither an insulating binder nor a low capacitance conducting additive is used.

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Figure 3. a) Schematic diagram of an all-solid-state integrated supercapacitor based on PANI–SWCNTs–sponge. b–d) Real-time optical images of a supercapacitor showing the compressing and recovering process. e) CV curves, f) galvanostatic charge/discharge curves, and g) specific capacitances of a representative compressible supercapacitor at different strains. Scan rate: 10 mV s⁻¹, charge/discharge current: 0.64 A g⁻¹. h) The Nyquist impedance plot of the compressible supercapacitor at different strains with frequency ranging from 10 kHz to 0.1 Hz.

Based on PANI-SWCNT-sponge, we fabricated the all-solidstate compressible supercapacitors with an integrated configuration, as depicted in Figure 3a. Au films on poly(ethylene terephthalate) (PET) substrates were used as current collectors. Filter paper served as a separator and the electrolyte was PVA/H₂SO₄. In all-solid-state compressible supercapacitors, the solid electrolyte-coated PANI-SWCNT-sponge electrodes remain the porous structure (Figure S3, Supporting Information). Figure 2b shows the stress-strain curve with maximum strain of 60% for an all-solid-state supercapacitor based on PANI-SWCNT-sponge electrodes. After a stress-strain cycle, releasing curve almost returns to the origin, suggesting that the volume of supercapacitors can be totally recovered without plastic deformations, as illustrated in Figure 3b-d. Furthermore, the supercapacitors can restore most of thickness after repeated compression.

In the CV curves of all-solid-state supercapacitors based on PANI–SWCNT–sponge electrodes (Figure 3e and Figure S4a, Supporting Information), two pairs of redox peaks are observed and they are attributed to the redox of PANI, corresponding to the structural conversions of leucoemeraldine/emeraldine and emeraldine/pernigraniline, respectively.^[63] When different compressible strains are applied to the supercapacitor, only very slight deviation is observed in the CV curves (Figure 3e), indicating the excellent electrochemical stability of all-solidstate supercapacitor under different compressible strains. It is also testified by their charge/discharge curves subjected to different compressible strains (Figure 3f), in which only a very slight difference is observed even under 60% compressible strain. The specific capacitance of PANI-SWCNT-sponge electrodes in all-solid-state supercapacitor is about 216 F g⁻¹, which is corresponding to a specific volumetric capacitance of 3.4 F cm⁻³. The Coulombic efficiency of all-solid-state supercapacitor is about 99%, which is higher or comparable than the case of previously reported carbon-based supercapacitor electrodes.^[63,64] When 60% strain is applied to all-solid-state supercapacitor, there is only about 3% loss in its specific capacitance (Figure 3g). Furthermore, the performance of all-solid-state supercapacitor is nearly not altered ever up to 100 compressingreleasing cycles (Figure S5, Supporting Information). Distinct from the liquid-electrolyte-based supercapacitor configuration, the resistance of solid electrolyte-coated PANI-SWCNTsponge electrodes is nearly not altered during the compressingreleasing process (Figure 2c,d), since the solid electrolyte layer avoids the contact between neighboring conductive electrode materials on the skeleton of PANI-SWCNT-sponge at a large compressible strain. Furthermore, all-solid-state integrated supercapacitor can be compressed as one unit arbitrarily and no electrolyte flows out or into the porous electrodes during compressing-releasing process.^[45] Therefore, all-solid-state supercapacitor shows stable electrochemical performances under less than 60% strain. However, when 70% strain is applied to the all-solid-state supercapacitor, there is nearly 13% drop in its capacitance, as shown in Figure S6 (Supporting Information). According to the galvanostatic charge/discharge curves at different current densities (Figure S4b, Supporting Information),





Figure 4. a) Au film patterns on PET substrates for assembling four supercapacitors into one unit in series. b–d) Real-time optical images of the resultant four supercapacitor group showing the compressing and recovering process. The galvanostatic charge/discharge curves of the four supercapacitor group and a single supercapacitor at 0.4 A g^{-1} . e) The CV curves of the four supercapacitor group and a single supercapacitor at the scan rate of 5 mV s⁻¹.

Ragone plots of all-solid-state supercapacitor are calculated, as show in Figure S4c (Supporting Information). A power density of 1.5 kW kg⁻¹ is achieved with an energy density of 8 W h kg⁻¹. In addition, obvious voltage drop (IR drop) originated from the internal resistance of supercapacitor is observed in Figure 3f and Figure S4b (Supporting Information). It indicates that the all-solid-state supercapacitors have high internal resistance, which is ascribed to the utilization of solid-state electrolyte and thick thickness of SWCNT/PANI-based composite sponge electrodes.^[56,65]

The all-solid-state compressible supercapacitor was examined by galvanostatic charge–discharge measurements for 1000 cycles (Figure S4d, Supporting Information). Its specific capacitance lost about 8% of the maximum capacity after 200 cycles and then remained nearly unchanged. Furthermore, all-solid-state compressible supercapacitor shows a similar behavior under 60%, but there is a 13% loss of the maximum capacity after 200 cycles. In addition, the practical application of supercapacitors is generally in the temperature range of –30 to 60 °C. ^[66] The all-solid-state compressible supercapacitor based on PVA/ $\rm H_2SO_4$ electrolyte can work well at 60 °C, as shown in Figure S7 (Supporting Information). Therefore, all-solid-state compressible supercapacitors can meet its practical application.

Impedance spectra that displayed as Nyquist plots were also employed to understand the performance of resultant allsolid-state supercapacitor at different compressive strains, as shown in Figure 3h. At different frequency portions, Nyquist plots show almost the same behavior under different compressible strains. The same behavior at high frequency domain indicates that the interior contact resistance of supercapacitor is unchanged under different strains. The knee frequency is often employed to evaluate the frequency dependence of a supercapacitor.^[67] Below knee frequency, supercapacitor begins to exhibit capacitive behavior. The knee frequency of Nyquist plots in Figure 3h is about 25 Hz, suggesting that most of supercapacitor's stored energy is accessible at frequency below 25 Hz. It is noticeable that, at low frequencies, the Nyquist plots are an almost vertical line, in which the imaginary part of impedance rapidly increases. It is the characteristic of capacitive behavior and represents the ion diffusion in the porous PANI–SWCNT– sponge electrodes.^[64]

In general, the total energy stored in a single supercapacitor is too low to meet the practical applications. As a result, several supercapacitors have to be connected together either in series, in parallel, or in combinations of the two to obtain a specific voltage and current. Therefore, for compressible supercapacitor devices, assembling several supercapacitors into one integrated unit that can be compression-tolerant should be considered. Although the thickness of all-solid-state compressible supercapacitor devices is thick, several compressible supercapacitors can be integrated and interconnected together in series or parallel on one chip to power the electronic devices. As a proof of concept, we integrated four all-solid-state supercapacitors into one unit in series by designing the Au film patterns on PET, as depicted in Figure 4a. This design reduces the complexity of the supercapacitor unit by removing intricate interconnects between supercapacitors and potentially increases the density of supercapacitor devices on one chip. The resultant integrated



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supercapacitor unit was powerful enough to light up a redlight-emitting diode (LED) when fully charged (Figure 4b). Furthermore, this integrated supercapacitor unit worked well when it was compressed and subsequently recovered, as shown in Figure 4c,d, indicating that four supercapacitors can be compressed as an integrated unit and display a good compressiontolerant ability. The CV curve of such a four in-series supercapacitor group (Figure 4e) exhibits an enhanced potential range of 0–3.2 V, which is four times that of a single supercapacitor. It is also reflected by the charge/discharge curve (Figure 4f), where the charge potential can be up to 3.2 V.

In summary, we fabricated compressible PANI-SWCNTssponge electrodes by combining a "dipping and drying" strategy with chemical oxidation polymerization. The nanostructured PANI-SWCNTs-sponge remains the porous hierarchical architecture and forms continuous "skeleton/skin" structure. More importantly, the structure of PANI-SWCNTs-sponge can be totally recovered when the stress is fully removed without plastic deformations. Based on PVA/H₂SO₄ gel electrolyte, highly compressible all-solid-state supercapacitors with integrated configuration were prepared by using PANI-SWCNTs-sponge as electrodes. The unique configuration enabled the resultant supercapacitors to be compressed as an integrated unit, leading to exhibit excellent performance stability under different compressible strains. The specific capacitance of such compressible supercapacitors lost only about 3% of maximum capacity under 60% compressible strain. Furthermore, several supercapacitors can be integrated onto one chip and are connected in series or parallel to improve the overall output potential and/or current. The highly compressible all-solid-state supercapacitors with integrated configuration will pave the way for advanced applications of supercapacitors in the area of compressible energy-storage devices to be compatible with compression-tolerant electronics.

Experimental Section

Preparation of PANI-SWCNTs-sponge Electrodes: Single-walled carbon nanotubes (P3-SWNT from Carbon Solutions Inc.) and sodium dodecylbenzenesulfonate with a weight ratio of 100:1 were dispersed in distilled water at a SWCNT concentration of 3 mg mL⁻¹. After 10 min bath sonication, the dispersion was ultrasonicated for 4 h using a probe sonicator (Sonics Inc.) to obtain the aqueous SWCNT dispersion. The sponge with about 4 mm thickness was first cleaned by water and acetone several times. After drying, the sponge was cut into desired shape. The aqueous SWCNT dispersion was subsequently dropped onto the surface of sponge until the sponge was saturated. Followed drying, SWCNTs were coated onto the skeleton surface of sponge. Repeating this dipping-drying process three times, the resultant SWCNTs-sponge was rinsed several times using deionized water to remove the surfactant on the surface of SWCNTs.

Subsequently, aniline monomers (Fluka) were polymerized on the surface of SWCNT layers in SWCNTs-sponge by a chemical oxidation polymerization method. The SWCNTs-sponge was first immersed in 0.2 \mbox{M} aniline solution (solvent: 1 \mbox{M} HCl) in a vacuum vessel for several minutes. After that, an equal volume of precooled 0.2 \mbox{M} ammonium persulfate (Sigma) solution was added into above aniline solution dropwise. The mixture was then kept at 0–5 °C for 30 min. The as-prepared PANI–SWCNTs–sponge was washed with deionized water several times and dried at room temperature.

The Fabrication of All-Solid-State Compressible Supercapacitors: First, the PVA/H_2SO_4 gel electrolyte was prepared, as previously reported. $^{\rm [68]}$

Following that, two pieces of PANI–SWCNTs–sponges were placed onto two PET substrates with Au film (150 nm), respectively, and the PVA/ H_2SO_4 gel electrolyte was dropped onto their surface until the PANI– SWCNTs–sponge was saturated. Then, one piece of filter paper with saturated electrolyte was put onto one of above PANI–SWCNTs–sponges on PET substrates with Au film. Subsequently, both of PANI–SWCNTs– sponge electrodes were left at room temperature for several hours. After that, two electrodes were pressed together and left at room temperature for several hours again. Finally, all-solid-state integrated supercapacitor was obtained. Based on two PET substrates with desired Au film shapes (Figure 4a), four supercapacitors can be assembled into one unit in series by a similar process.

Characterization: The morphologies and microstructures of sponge, SWCNTs-sponge, and PANI-SWCNTs-sponge were characterized by field-emission scanning electron microscopy (FE-SEM) (JSM-7600F). CV of the resultant supercapacitors was performed using a CHI 660D instrument (CHI Instruments). The galvanostatic charge-discharge of the supercapacitors was carried out on a supercapacitor test system (Solartron, 1470E). The Raman spectra were recorded with a spectrophotometer (WITec alpha 300 R) with operating wavelength of 532 nm. The stress-strain measurements of the samples were carried out using an Instron Universal Testing Machine (model 5567).

Supporting Information

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

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