Gradually Crosslinking Carbon Nanotube Array in Mimicking the Beak of Giant Squid for Compression-Sensing Supercapacitor

Yang Zhao, Jingyu Cao, Ye Zhang, and Huisheng Peng

Portable and wearable electronics are undergoing rapid development, but these flexible devices may break and fail to work under high compressive strains. Here, presented is a new free-standing compressible carbon nanotube array (CCNA) with a unique gradually crosslinking structure, which mimics the gradient structure of the beak of the giant squid. The CCNAs can tolerate various compressive strains and demonstrate high reversible compressibility up to 1 000 000 cycles with high electrical conductivities. On the basis of the CCNA, a novel all-solid-state compression-sensing supercapacitor (CSS) that can store energy and tolerate and sense the external strain change is produced. It demonstrates a high capacitance of 93.2 mF cm$^{-2}$ and can be maintained by 94% even after 3000 continuous compressing cycles at a strain of 60%. In addition, it also shows superior strain sensing capability and stability up to 1900 compressive cycles. These flexible CSSs promise a wide range of applications including electronic skins and advanced bioelectronic devices.

1. Introduction

Portable and wearable electronics will be an independent part of our daily life in the near future.\cite{1-6} These wearable bioelectronic devices suffer from different levels of stresses during their practical applications.\cite{6-10} However, under high compressive strains, conventional electronic devices may break mechanically and fail to work, which might even cause serious safety hazards such as the leakage of toxic components.\cite{11-14} To overcome these challenges, flexible electronic devices that can tolerate various compressions and effectively work under strains without remarkable performance loss are greatly needed.\cite{15,16} Further, the energy-storing and sensing functions of portable and wearable bioelectronics are generally realized by combining two kinds of devices.\cite{17-20} Thus, the seamless integration of two functions into one device without increasing the size and compromising the flexibility is highly desired and remains challenging. Therefore, the resulting integrated device should not only retain energy storage capability, but also be endowed with the ability to sustain and feel different strains. A possible solution to the above problem lies in designing and fabrication of elastomeric electrodes into a single device that can realize both energy storage and compression sensing capabilities.

Aligned carbon nanotube (CNT) arrays that exhibit high electrical conductivities along the axial direction have been widely studied as electrode material for a variety of electronic devices.\cite{21-23} However, they are usually unable to reversibly sustain compressions and strains.\cite{21} Nature offers many interesting examples with gradually changing structures which possess unique and superior properties.\cite{24-30} For example, the beak of giant squid exhibits a mechanical and pigmentation gradient owing to the gradually crosslinking of the inner macromolecules (Figure 1a).\cite{31,32} From the translucent to black parts, the mechanical strength of the squid beak gradually changes from soft to hard, which has been evolved and optimized over millions of years to help the squids survive nature.

Herein, we report the compressible carbon nanotube array (CCNA) with unique gradually crosslinking structure, in mimicking the gradient structure of the beak of giant squid (Figure 1). From top to bottom, the CNTs of the CCNA turned from well aligned to highly crosslinking structure. The CCNAs can tolerate various compressive strains and demonstrate high reversible compressibility up to 1 000 000 cycles, superior compressive strength up to 409 KPa, and high electrical conductivities on the level of 10$^5$ S m$^{-1}$. The CNTs at the top of the CCNAs show a highly aligned porous structure with high surface area, which is beneficial for the permeation of electrolyte with low ion-transport resistance. A novel all-solid-state compression-sensing supercapacitor (CSS) based on CCNA as elastic electrodes was fabricated and it can store energy and sense the external strain change with high performances. It demonstrates high capacitance of 93.2 mF cm$^{-2}$, which can be maintained by 94% even after 3000 continuous compressing cycles at a strain of 60%, and it has superior sensing capability and stability up to 1900 compressive cycles. The above powering and sensing functions can be efficiently tuned by varying the internal design to satisfy the application demands of a variety of wearable and integrated electronics.
2. Results and Discussion

2.1. Fabrication and Characteristics of the CCNA

As shown in Figure 1b and Figure S1 in the Supporting Information, the CCNA had a unique gradually crosslinking organization, which shared the similar gradient structure with the beak of giant squid in strategy. The CCNA was synthesized via a chemical vapor deposition process, and the growth time was found to affect the crosslinking structure. Therefore, the influence of CCNA growth time on the structure and compressive performance of the CCNA were first carefully investigated. As shown in Figure 2a–e and Figures S2–S5 in the Supporting Information, with the increasing growth time from 60 to 80 and to 100 min, the structure of the aligned CNTs became more crosslinked and the diameter and wall numbers of the CNTs were also increased. The compressive stress–strain curves showed that although the mechanical strength of the CCNA was expected to be increased with the growth time, however, the sample grown for 80 min showed the best reversibly compressive performance (Figures S6–S8, Supporting Information) and was thus used in the following studies unless otherwise specified.

The resulting CCNA showed a height of 1.2 mm, and the building CNTs were highly aligned (Figure 2a). For the current catalyst, the Fe particles were found to induce the growth of CNTs from the bottom. In other words, the bottom part of the CCNA was first formed. Interestingly, the CNTs were linear at the beginning and then became more crosslinked with the increasing growth time (Figure 2b–d and Figure S9, Supporting Information). The aligned CNTs were multiwalled with typically eight to nine walls, as shown in Figure 2e. The Raman and Brunauer–Emmette–Teller characterization of the CCNAs were given in Figures S10 and S11 in the Supporting Information, which demonstrated a specific surface area of 261.5 m² g⁻¹. Compressive stress–strain curves of the CCNAs were compared by increasing the strains from 10% to 60% (Figure 2f), and the CCNAs were well recovered after compressing for all cases. A high compressive strength of 409 KPa that far exceeded the reported sponge electrodes[13,15,13] and was close to natural skins has been achieved at the compressive strain of 60%. The changes in electrical resistance of the CCNA were also traced under increasing compressive strains (Figure 2g), and they obviously decreased from 5.77 to 0.97 Ω with the increasing strain from 0% to 60%.

The high compressive stability was further validated by repeated compressive tests at a compressive strain of 40% (Figure 2h). The stress–strain curves were well overlapped for the 1st, 1000th, and 3000th cycle. In fact, the height of the CCNA was maintained by 95.7% after compressing for 3000 cycles (Figure S12, Supporting Information), and the unique gradually crosslinking structure has been further maintained (Figure S13, Supporting Information). Moreover, the CCNA showed only a slight decrease in stress response over 1 00 000 compressive cycles at a strain of 20% (Figure 2i), demonstrating remarkable reversible compressibility. The combined high mechanical strength, low electrical resistance, and superior compressive performance of the CCNA make it promising...
for compressible electrodes. In addition, the formed channels among aligned CNTs typically with diameters of tens to hundreds of nanometers make the CCNA efficient to incorporate active materials and transport electrolytes.

2.2. Fabrication and Energy-Storing Performance of the CSS

The CCNA was then coated with poly(vinyl alcohol) (PVA)/H$_3$PO$_4$ gel electrolyte (Figure S14, Supporting Information), and the resulting two CCNAs were assembled with a cellulose separator sandwiched between them to construct the CSS (Figure S15, Supporting Information). The energy-storing performance of the CSS was first investigated under increasing strains and compressing cycles. Figure 3a shows galvanostatic charge/discharge curves of the CSS with increasing strains from 0% to 60% at the current density of 1 mA cm$^{-2}$. Without compression, the CSS demonstrated a high areal specific capacitance of 93.2 mF cm$^{-2}$ (30.5 F g$^{-1}$ and 1165 mF cm$^{-3}$ for gravimetric and volumetric capacitances, respectively). The areal capacitance of the CSS did not show obvious changes with the increasing thickness of the electrode (Figure S16, Supporting Information), which might be due to the similar permeation states of gel electrolyte. The charge–discharge curves were well maintained under compressing, and the charge–discharge time increased with the increasing strain. The electrochemical stability was also verified by the almost unchanged rectangular shape of the cyclic voltammograms under various strains (Figure 3b). Interestingly, the areal specific capacitance of the CSS was increased from 93.2 to 116.0 mF cm$^{-2}$.
with the increasing compressive strain from 0% to 60%, which obviously differed from the previous compressible supercapacitors (Figure 3c and Figure S17, Supporting Information). The increasing capacitances may be a result of the increasing contact area between the electrode and electrolyte, as well as the decreasing electrode resistance under compressing.

The rate capability and cyclic voltammogram of the CSS at the strain of 60% demonstrated superior rate performance (Figure 3d and Figure S18, Supporting Information). The compressive stress–strain curves of the CSS with increasing strains from 10% to 60% showed high compressive strengths of >300 KPa (Figure 3e). Note that the stresses always remained above zero in the releasing process, indicating that the volume of the CSS could be completely recovered without mechanical failure. The cyclic stress–strain curves at a strain of 60% demonstrated excellent compressibility and resilience of the CSS (Figure S19, Supporting Information). Furthermore, the capacitance of the CSS can be maintained by 94% even after 3000 continuous compressing cycles at a strain of 60% (Figure 3f). The capacitance retention increase after 1000 cycles may be caused by the accidental compressed state of the CSS during the electrochemical testing process to ensure the good electrical contact between the CSS and conductor. The above high stability was also verified by Nyquist plots before and after compressing, as shown in Figure S20 in the Supporting Information.

2.3. Strain Sensing Performance of the CSS

Interestingly, this CSS can also function as a strain sensor with high sensing performance (Figure 4). Here, the sandwiched PVA/H₃PO₄ gel electrolyte acted as a dielectric layer
for capacitive strain sensing and as an elastomeric substrate to prevent short circuit and irreversible structure change during compressing. As shown in Figure 5a–f, the CSS showed stable and reliable relative capacitance changes under various compressive strains with high repeatability. With the increasing strain from 0% to 60%, the relative capacitance changes of the

![Figure 4. Schematic diagram of the CSS function as a strain sensor before and after compressing.](image)

![Figure 5. The strain-sensing performance of the CSS. a–f) Relative capacitance response curves of the CSS under increasing strains of 10%, 20%, 30%, 40%, 50%, and 60%. g) Relative capacitance changes with increasing compressive strains. h) Relative capacitance responses of the CSS during continuously changing compressive strains between 30% and 50%. i) Relative capacitance responses during period holdings (5 s) with the compressive strains increased from 20% to 60% and then decreased back to 20%.](image)
CSS showed a monotonic increase (Figure 5g). The CSSs demonstrated stable relative capacitance changes with the increase of electrode thickness (Figure S21, Supporting Information). The CSS indicated a rapid and repeating response with constantly changing compressing strains (Figure 5h).

The CSS was held at certain strains for a period of time (e.g., 5 s), and the relative capacitance changes were recorded to evaluate its sensing reliability. With the increasing strains from 20% to 60% and then back to 20%, the relative capacitances remained unchanged without distinct drifts during each period (Figure 5i), demonstrating a reliable and stable response with the symmetry capacitance signals. The CSS was also compressed with increasing tested frequencies at a compressive strain of 40% (Figure 6a–d). The change of relative capacitances was almost independent upon the applied frequency from 0.01 to 0.1 Hz. Furthermore, during 1900 continues compressing–releasing cycles, the CSS worked well without obvious fatigues (Figure 6e).

Therefore, an individual CSS can function as both supercapacitor and strain sensor, and it was thus promising to design and produce flexible smart systems. As an application demonstration, five CSSs were integrated onto a circuit to make a multifunctional device (Figure 7a–c and Figure S22, Supporting Information). Here, four CSSs were connected in series as the energy-storing units to supply power and the central CSS functioned as the sensing unit to detect the external pressure. As shown in Figure 7d–f, when a small pressure of 30 KPa was applied on the flexible integrated circuit, the green light-emitting diode (LED) was lightened. The blue or red LED was lightened up when medium pressure of 55 KPa or high pressure of 80 KPa was applied, respectively. The relative capacitance changes of the central CSS demonstrated a good strain response during the whole compressing–releasing process (Figure 7g). Furthermore, by using these multifunctional CSSs, it was easy to realize the function conversions between energy storage and sensing in the same device, which greatly simplified...
the integration and modification processes of wearable and integrated electronic systems simplified and easy to realize. For example, the internal design and function of the wearable integrated system could be easily transformed into another type to endow the system with better sensing sensitivity or higher energy storage capacity (Figure S23, Supporting Information). Therefore, using these unique CSSs, the compatibility and adaptability of the wearable integrated electronic system may be greatly improved to better accommodate the application demands in the future.

3. Conclusion

In summary, we have developed a free-standing CCNA with unique gradually crosslinking structure with high reversible compressibility and electrical conductivity. Based on the CCNAs as the electrodes, we further fabricated the novel CSS that can store energy, sense the strain change, and effectively work under various strains with high performances. In addition, the remarkable powering and sensing properties can be efficiently tuned by varying the internal design to satisfy a variety of wearable and integrated electronic devices. By employing these intelligent and multifunctional CSSs, the fabrication, integration, modification, and function conversion processes of wearable and integrated electronic systems can be greatly simplified. These flexible CSSs are promising candidates for a variety of applications ranging from electronic skins to integrated smart systems. Our work represents a stepping stone toward the design of next-generation wearable bioelectronic devices.

4. Experimental Section

Preparation of CCNAs: CCNAs were synthesized through a chemical vapor deposition on a silicon wafer predeposited with Fe (1.2 nm)/Al₂O₃ (5 nm) as catalysts. A mixture of argon (flowing rate of 400 sccm) and hydrogen (flowing rate of 30 sccm) served as the carrier gas, and ethylene (flowing rate of 90 sccm) as carbon source. The growth of CCNAs was conducted in a tube furnace at 750 °C for 80 min.

Fabrication of CSSs: PVA/H₃PO₄ gel electrolyte was used for the CSSs. The electrolyte was prepared by dissolving 1 g PVA into 9 g deionized water (at 90 °C), followed by adding 1 mL H₃PO₄. Two CCNA electrodes were coated with PVA/H₃PO₄ gel electrolyte and assembled together to form the CSS. A separator (TF4030, NKK) was sandwiched between them to prevent short circuit. The size and weight of a typical CSS were...
5.0 × 5.0 × 1.6 mm and 7.92 mg, respectively. The weights of one CCNA electrode, separator, and gel electrolyte were 0.785, 0.34, and 6.05 mg, respectively.

Characterization and Calculation: The structures and morphologies of the electrodes were characterized by scanning electron microscopy (SEM, Hitachi FE-SEM S-4800), transmission electron microscopy (TEM, JEOL JEM-2100F), Raman spectrometer (Dilor LabRam-1B, He-Ne laser of 4 mW), and automatic specific surface area and porosity analyzer (Quadsorb evo). The electrical conductivities were measured by Keithley Model 2400 Source Meter. The thicknesses were obtained using a surface profiler (Veeco, Dektak 150). The compressive stress–strain curves were tested with a HY0350 Table-top Universal Testing Instrument. The electrical conductivities of the electrode were measured with a Keithley Model 2400 Source Meter by keeping good electrical contact between the CCNA and conductor. The galvanostatic charge–discharge, cyclic voltammograms, and rate capability of the CSSs were measured by an electrochemical workstation (CHI 660E). The capacitance response of the CSS as strain sensor was characterized with YD2817B capacitance testing apparatus (Yangzi Electronic Co. Ltd.). The photographs were taken by a digital camera (Nikon, J1). The capacitance (C) was calculated from the equation \( C_A = \frac{(I \times \Delta t)}{\Delta V} \), where I, \( \Delta t \), and \( \Delta V \) represent the discharge current, discharge time, and voltage window, respectively. The areal (\( C_{A} \)), mass (\( C_{M} \)), and volumetric (\( C_{V} \)) specific capacitances were calculated by dividing the capacitance (C) by the area, mass, and volume of the electrode, respectively.

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.

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