Journal of Materials Chemistry A



View Article Online

View Journal | View Issue

COMMUNICATION



Cite this: J. Mater. Chem. A, 2016, 4, 10124

Received 5th May 2016 Accepted 6th June 2016

DOI: 10.1039/c6ta03762c

www.rsc.org/MaterialsA

Stretchable supercapacitor based on a cellular structure[†]

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Stretchable supercapacitors are critical for a variety of portable and wearable electronic devices, and they have been typically realized by the use of non-active elastic substrates that do not contribute to the energy storage capability. Here a new family of stretchable supercapacitors is fabricated from cellular carbon nanotube film-based electrodes with high electrochemical performances. They display high specific capacitances that can be maintained by 98.3% after stretching by 140% for 3000 cycles. In addition, their voltage and current windows are tuned by varying the configuration of the film electrode.

Introduction

Flexible and stretchable electronics have been rapidly developed with a wide range of promising applications, such as smart sensors, flexible displays and artificial skins.¹⁻⁶ Supercapacitors, one of the important energy storage devices in powering portable and lightweight electronic devices, are desired to be designed to be stretchable.^{7,8} However, traditional supercapacitors are rigid and heavy. In recent years, stretchable supercapacitors have attracted much attention and have been successfully fabricated.9-13 They are generally fabricated by depositing active materials onto elastic substrates to realize stretchability. However, there remain some challenges for this method, e.g., there exists a mechanical mismatch between the electrode material and the substrate during stretching; the substrate adds extra weight and volume to the device, while it does not contribute to the electrochemical storage capability; it is applicable to limited

materials that should be flexible enough to form the required wave-like structure.

In nature, a variety of biological materials provides inspiring paradigms in the development of advanced materials, particularly by designing different structures for different functionalities.^{14,15} A cellular structure represents one of the most common biological structures with open and closed pores in a two-dimensional film or three-dimensional foam.¹⁶ This unique structure can resist a broad spectrum of deformations such as bending and stretching. For instance, the antler of the North American elk has a cellular bone structure that accommodates large deformations under attacking;¹⁷ bird bones and feathers are composed of cellular structures to withstand bending, stretching or other deformations during flying.¹⁸

Inspired by nature, here we demonstrate a general and effective strategy to fabricate a highly stretchable supercapacitor by designing electrodes such as carbon nanotube (CNT) films into a cellular structure. The specific capacitance of the supercapacitor can be maintained by 98.3% for 3000 cycles under 140% strain. In addition, its voltage and current windows are tunable by simply varying the configuration of the cellular CNT film electrodes, which avoids the complex connection with a large number of electrically conducting wires in its conventional counterparts.

Experimental section

Two cellular CNT films were sandwiched with a 10 wt% $H_3PO_4/$ polyvinyl alcohol (PVA) gel electrolyte to produce a stretchable supercapacitor.¹⁹ Polyaniline (PANI) was electrodeposited onto the cellular CNT film through electropolymerization of aniline.^{20,21} It was conducted in an aqueous solution of aniline (0.1 M) and H_2SO_4 (1 M) at a potential of 0.75 V with a three-electrode system where a platinum wire functioned as the counter electrode, while potassium chloride-saturated Ag/AgCl served as the reference electrode. The calculations on the specific capacitance of the device are described in the ESI.[†]

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ta03762c

Results and discussion

To obtain the cellular CNT film, CNT arrays were firstly synthesized by chemical vapor deposition on silica wafers with a cellular patterned catalyst, followed by pressing and peeling off from the silica wafers.²² The patterned silica wafer was obtained by using a paper mask with the desired cellular pattern to be exposed to the coating source, so the catalyst was only deposited on the exposed part in the silica wafer. Fig. 1a shows a typical cellular CNT film. The resulting cellular CNT film was flexible and freestanding with a uniform thickness (Fig. 1b and S1[†]). The CNT film was composed of multi-walled CNTs with few defects (Fig. S2 and S3[†]). The cellular structure endowed the CNT film with stretchability. The cellular CNT film could be stretched by $\sim 150\%$ with an ultimate tensile strength of 230 MPa (Fig. 1c). The elongation at breaking was much larger than that of the pristine CNT film, which stretched by $\sim 2\%$ (Fig. S4[†]). In addition, the maximal strain, which represents the degree of deformation, is tunable by varying the cellular structure (length a_0 and width b_0). We carefully investigated the structure with a primitive unit (Fig. S5†). The maximal strain increased almost linearly with increasing a_0/b_0 ratio at a fixed line width (w of 1 mm). The film with a_0 of 10 mm and b_0 of 2 mm was selected to be discussed below for simplicity. The cellular CNT film exhibited a highly stable electrical property under stretching. We also tracked the electrical resistance during the stretching process. Importantly, the resistance varied by less than 1% even at 140% strain (Fig. 1d). It also showed high stability after stretching over 10 000 times (Fig. 1e).

To fabricate the supercapacitor, the H_3PO_4/PVA gel electrolyte was sandwiched between two cellular CNT film-based electrodes. The gel electrolyte also acted as the separator of the supercapacitor to avoid a short circuit. We firstly investigated the electrochemical performance of supercapacitors fabricated from CNT film electrodes with increasing thicknesses. At a current density of 0.5 mA cm⁻², the specific capacitance firstly increased from 24.9 to 42.4 F g⁻¹ with increasing the thickness from 27.1 to 38.3 μ m and then decreased to 26.7 F g⁻¹ with further increasing the thickness to 54.4 μ m (Fig. 2a). The



Fig. 1 Stretchable cellular CNT film. (a) Photographs of the stretchable CNT film under increasing strain from 0%, 20%, 60% and 100% to 140%. (b) Cross-sectional scanning electron microscope (SEM) image of the CNT film. (c) Stress–strain curve of the cellular CNT film. (d) Dependence of electrical resistance on strain. (e) Dependence of electrical resistance on stretching cycle at a strain of 140%. For both (d) and (e), R_0 and R_{ε} correspond to the electrical resistances before and after stretching, respectively. ΔR represents the difference in electrical resistance after and before stretching.

responding Nyquist plots of the supercapacitors with increasing thickness of the film are shown in Fig. S6.† The equivalent series resistance, obtained by the intercept with the axis of the plot, gradually decreased with increasing thickness of the film. This phenomenon may be explained by the gradually decreasing electrical resistance (Fig. S7[†]). However, the weight of the CNT film increased with the increasing thickness (Fig. S8[†]), so the specific capacitance decreased. Therefore, the film with 38.3 µm thickness was mainly studied below. Galvanostatic charge-discharge curves between 0 and 1 V shared a symmetric triangular shape at increasing current densities from 0.2 to 5 mA cm⁻² (Fig. 2b), suggesting a high reversibility and Coulombic efficiency over a wide range of current densities.23 The specific capacitance dropped from 72.9 to 60.4 mF $\rm cm^{-2}$ when the current increased from 0.5 to 1 mA $\rm cm^{-2}$ and then remained almost unchanged with the further increase in current density, which was consistent with the property of a double-layer capacitor (Fig. S9[†]). The specific capacitances calculated based on the charge-discharge curves reached

a gravimetric capacitance of 42.4 F g⁻¹ ($C_{\rm M}$) (or 72.9 mF cm⁻² for the areal capacitance ($C_{\rm A}$) and 19.0 F cm⁻³ for volumetric capacitance ($C_{\rm V}$)) at a current density of 0.5 mA cm⁻² or 0.29 A g⁻¹. The energy and power densities of the supercapacitor reached 0.701 mW h cm⁻³ and 337.0 mW cm⁻³ at current densities of 0.2 and 5 mA cm⁻², respectively. A typical rectangular shape was observed for the cyclic voltammograms of the supercapacitor and was well retained at increasing scan rates from 20 to 500 mV s⁻¹, indicating low internal resistance (Fig. S10†). In addition, the supercapacitor exhibited high stability over 50 000 charge–discharge cycles (Fig. S11†).

Note that the cellular structure also contributed to the permeation of the electrolyte into the CNT film electrode. As a comparison, the electrochemical performance of a supercapacitor with a cellular-free CNT film electrode was studied under the same conditions. No obvious voltage drop in the galvanostatic charge–discharge curve was observed for the cellular structure; in contrast, a sharp voltage drop appeared



Fig. 2 Electrochemical performance of the stretchable supercapacitor. (a) Dependence of specific capacitance on the thickness of the CNT film. (b) Galvanostatic charge–discharge curves at increasing current densities from 0.2 to 5 mA cm⁻². (c) Galvanostatic charge–discharge curves with increasing bending angles from 0 to 180°. (d) Cyclic voltammograms with increasing strains from 0 to 140%. (e) Dependence of capacitance ratio on stretching cycle under a 140% strain. Here C_0 and C correspond to the capacitance before and after stretching for different cycles, respectively. (f) Cyclic performance of a 140% stretched supercapacitor.



Fig. 3 Schematic illustrations of the configurations and corresponding galvanostatic charge–discharge curves of the stretchable supercapacitor. (a and b) Increased voltages by connection in parallel. (c and d) Increased currents by connection in series. (e and f) Simultaneously increased voltage and current. The current densities at (b), (d) and (f) were 1, 0.5 and 1 mA cm⁻², respectively.

without the cellular structure. Therefore, the internal resistance in the cellular supercapacitor was much lower (Fig. S12[†]).

The electrochemical performance of the cellular supercapacitor was carefully investigated under multiple deformations, including bending and stretching. With increasing the bending angle from 0 to 180° or increasing the strain from 0 to 140%, the charge–discharge curves and the cyclic voltammogram curves remained almost unchanged (Fig. 2c, d, S13 and S14†). The energy and power densities varied by less than 6% under stress with the strain ranging from 0 to 140% (Fig. S15†). Even under the repeated stretching, the specific capacitance was well maintained by 98.3% for 3000 cycles at 140% strain (Fig. 2e). Even under a stretched state, the specific capacitance of the supercapacitor remained almost unchanged even after 45 000 cycles (Fig. 2f).

Compared with other stretchable supercapacitors based on elastomeric polymer substrates (20–200%),^{11–13,24–28} this cellular supercapacitor displayed a large and tunable strain. Moreover, the specific capacitance of the cellular supercapacitor could be further improved by introducing pseudocapacitive PANI into the cellular CNT film (Fig. S16 and S17†). By introducing 5 wt% PANI, the specific capacitance reached 204.0 F g⁻¹ (or 340.2 mF cm⁻² and 87.8 F cm⁻³) at a current density of 2.0 mA cm⁻² or 1.1 A g⁻¹ (Fig. S18†). The specific capacitance was higher than

those of the reported supercapacitors based on elastomeric polymer substrates (7.6–201.1 F g⁻¹).^{11–13,24–28} In addition, the specific capacitance of the cellular supercapacitor was almost one to two orders of magnitude higher than the other stretchable supercapacitors when the weight of the elastic substrate was included.

Another advantage of the cellular supercapacitor lay in the tunable voltage and current after interconnection in parallel and/or series through its intrinsic configuration. As a proof of this concept, we interconnected six primitive supercapacitors in parallel by increasing the units of the repeated primitive cellular CNT film (Fig. 3a). The discharge time increased under the same current (Fig. 3b). We also integrated six primitive supercapacitors in series via easily tailoring the cellular CNT film electrodes. Based on the configuration in Fig. 3c, the output voltage was enlarged by a factor of six (Fig. 3d). Here, one individual CNT film had three roles with the half parts covered with electrolyte acting as the positive and negative electrode and the uncovered part acting as the external collector. Furthermore, the output current and voltage could be simultaneously enhanced by further programming the covering area of the electrolyte (Fig. 3e and f). The intrinsic structure obviously reduced the complexity in integration compared with the conventional methods. It avoided the additional resistance and



Fig. 4 Powering a commercial electronic watch using the stretchable supercapacitor. (a and b) Schematic illustration and photograph of the structure of the electronic watch with a stretchable supercapacitor as a "watch strap". (c) Galvanostatic charge–discharge curve of the "watch strap" at a current of 0.57 mA. (d and e) Photographs of the "watch strap" at the wrist, the middle arm and the upper arm to power the watch.

unnecessary volume introduced by the external circuits which contained excess and heavy metal conductors.

The stretchable cellular supercapacitors were further demonstrated to effectively power various wearable and portable devices. For instance, Fig. 4a shows a cellular supercapacitor in a combination of series and parallel connections. It served as a "watch strap" for a commercial electronic watch (Fig. 4b). After charging to 4 V, the "watch strap" had successfully driven the electronic watch for about ten seconds (Fig. 4c). Due to the stretchability of the "watch strap", it was applicable to different people with different sizes of wrists (Fig. 4d). In addition, the "watch strap" could be further stretched to the arm (Fig. 4e). The electronic watch was able to function during the stretching process. Based on the cellular structure that offered the supercapacitor the function of ventilation, it is particularly promising for wearable electronic devices and electronic skin.

In summary, we have demonstrated a new family of stretchable supercapacitors by designing a cellular structure mimicking nature. They display remarkable electrochemical performances with both large, tunable strain under stretching and almost one to two orders higher specific capacitances compared with conventional stretchable counterparts through the use of elastic substrates. In addition, the specific capacitance of the cellular supercapacitor can be maintained by 98.3% after stretching by 140% for 3000 cycles. The cellular structure also makes the supercapacitor permeable to air and water, which is important for a variety of application fields such as wearable and medical electronics.

Acknowledgements

This work was supported by NSFC (21225417, 51573027, 51403038), STCSM (15XD1500400, 15JC1490200) and the Program for Outstanding Young Scholars from Organization Department of the CPC Central Committee. Part of the sample fabrication was performed at the Fudan Nano-fabrication Laboratory.

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