Journal of Materials Chemistry A

COMMUNICATION

Cite this: *J. Mater. Chem. A*, 2015, **3**, 19304

Received 12th August 2015
Accepted 27th August 2015

DOI: 10.1039/c5ta06317e

www.rsc.org/MaterialsA

Designing one-dimensional supercapacitors in a strip shape for high performance energy storage fabrics†

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With the advancement of miniaturized portable and wearable electronic devices, fiber-shaped energy-storage systems have attracted intensive attention due to their merits of flexibility, integratability and weavability. However, the inferior energy storage performance and relatively low stability derived from the curved fiber interface under severe deformations have largely limited their development. Here, we report a one-dimensional supercapacitor in a strip shape by mimicking bamboo strips of Chinese bed-mats. The strip-shaped supercapacitor is flexible with decent electrochemical performances. It delivers both a high energy density of 9.56 mW h cm^{-3} and a high power density of 2.91 W cm^{-3} that are sustainable to various deformations and outperforms other fiber-shaped counterparts. Such strip-shaped supercapacitors are further woven into a fabric that demonstrates both high structural and electrochemical stability under various deformations such as bending and twisting. The capability for high energy storage and feasibility for large-scale production provide an efficient platform in powering micro-electronic devices.

Introduction

Recently, wearable and smart textiles have been vigorously developed and show promising applications in portable electronic devices.[1] To this end, suitable power systems with high performance and flexibility are urgently needed. However, conventional power systems such as lithium-ion batteries and supercapacitors are made into a planar configuration which is geometrically limited in flexibility and weavability. Consequently, one-dimensional fiber-shaped energy storage systems including lithium-ion batteries[2,3] and supercapacitors[4–9] are created for flexible energy fabrics. However, compared with conventional planar counterparts, fiber-shaped energy storage devices are typically made by twisting two fibrous electrodes that have relatively low storage capability;[10,11] the twisted structure is apt to break apart under severe bending or twisting deformation; the woven fiber-shaped devices in a textile may slip off because the point-to-point contact among curved fibers can hardly afford a strong cohesion, making the fabric prone to disassemble under severe deformations. It is highly required to design new architectures that can combine the high energy storage capability of planar devices and weavability of fibrous devices.[4b,5,6,12,13]

Herein, a novel one-dimensional device with a strip configuration by mimicking bamboo strips of Chinese bed-mats has been developed as a general strategy to surmount the deficiencies of fiber-shaped devices. As a demonstration, the strip-shaped supercapacitor and the resultant energy storage fabric have been fabricated. For the strip-shaped supercapacitor, a high energy density of 9.56 mW h cm^{-3} and a high power density of 2.91 W cm^{-3} have been achieved. Moreover, it exhibits a high resistance to deformations, which enables the supercapacitor to be assembled into a fabric that is flexible and applicable in wearable electronic devices. The capability for high energy storage and feasibility for weavability provide an efficient platform in powering micro-electronics.

Experimental section

Preparation of strip-shaped CNT/PANI supercapacitors

The aligned CNT strip with a width of 2 mm and a thickness of 20 nm was made from a spinnable CNT array synthesized by chemical vapor deposition.[14] CNT strips were further stacked and densified by a solvent treatment prior to use. PANI was then deposited onto the aligned CNTs through an electro-polymerization of aniline at a potential of 0.75 V in an aqueous

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ta06317e

solution of aniline (0.1 M) and H_2SO_4 (1 M) using KCl-saturated Ag/AgCl and platinum as the reference and counter electrodes, respectively.[15] The resulting composite strip electrode was coated with a polyvinyl alcohol (PVA)/H_3PO_4 gel electrolyte and treated in a vacuum for 5 min. To prepare the gel electrolyte, PVA (1 g) was swelled in water (10 mL) for 5 h at room temperature, followed by heating for 1.5 h at 95 °C. The treated PVA was cooled down to room temperature and then H_3PO_4 solution (85 wt%, 1 g) was added, followed by stirring for 30 min. Two electrolyte-incorporated CNT/PANI composite electrodes were stacked together to produce a strip-shaped supercapacitor.

Characterization

The structures were characterized by scanning electron microscopy (SEM, Hitachi FE-SEM S-4800 operated at 1 kV). The electrical resistance was measured by using an Agilent 34401A digital multimeter. The thicknesses were obtained using a surface profiler (Veeco, Dektak 150). The cyclic voltammograms, galvanostatic charge–discharge curves and electrochemical impedance spectra were recorded by using a CHI 660a electrochemical workstation. The electrochemical impedance measurement was conducted from 10 mHz to 1 MHz with a voltage amplitude of 5 mV. The mechanical stability was measured on an HY0350 Table-top Universal Testing Instrument. The photographs were taken by using a digital camera (Nikon, J1). The optical micrographs were taken using an optical microscope (OLYMPUS-BX51).

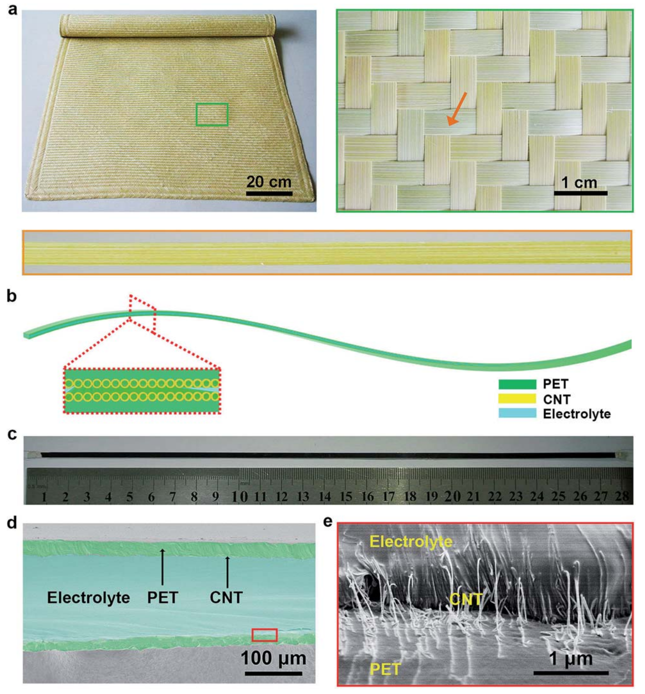

Fig. 1 (a) Photograph of the Chinese bed-mat woven from bamboo strips. (b) Schematic illustration of the strip-shaped supercapacitor. (c) Photograph of a strip-shaped supercapacitor with a length of 250 mm and a width of 2 mm. (d) Cross-sectional SEM image of a strip-shaped supercapacitor. The PET film and gel electrolyte are coloured with green and blue, respectively. The CNT layer is indiscernible given its thickness (less than 1 μm). (e) Magnified SEM image of the red rectangular zone in (d). It clearly demonstrates the CNT layer was paved on the PET film and infiltrated with the gel electrolyte.

Results and discussion

The construction of strip-shaped supercapacitors was inspired by the traditional Chinese bed-mats. Fig. 1a displays the structure of a Chinese bed-mat woven from bamboo strips. The flexibility and structural stability of the bed-mat are derived from the unique flattened bamboo strips. The face-to-face contact between the bamboo strips provides the fabric with a strong coherence, preventing the units from slipping off under severe deformations. Inspired by this unique configuration, we propose a general and effective method to develop flexible and wearable powering systems with high performances by making them into a striped structure. As shown in Fig. 1b, a strip-shaped supercapacitor has been studied as a demonstration. The strip-shaped supercapacitor is comprised of two strip electrodes. Here we differentiate the strip shape from fiber shape that the cross-section of a strip is a flattened rectangle. In this case, the strip shape exhibits both high flexibility that is derived from its large aspect ratio as well as a localized planar configuration which contributes to the high performance of devices.

It has been widely shown that the formation of an aligned structure can effectively extend the remarkable properties of carbon nanotubes (CNTs) to the macroscopic scale.[3,14,15] For instance, aligned CNT strips displayed both high flexibility and electrical conductivity with a large specific surface area.[3,14,15] Therefore, they can serve as a family of effective electrodes for flexible energy storage devices. Aligned CNT strips were typically prepared from a spinnable CNT array that had been synthesized by chemical vapor deposition,[3,14] and the aligned CNT strip was then paved on a poly(ethylene terephthalate) (PET) substrate as the electrode in the fabrication of the strip-shaped supercapacitor (Fig. S1†). As a critical property, the conductivity of the strip electrode closely relies on the layer number of CNT sheets. The electrical resistances greatly decreased with the increasing layer number of CNT strips and reached a platform at forty layers (Fig. S2†). Given that the charge transportation in CNT sheets follows a hopping mechanism, more CNTs benefit the formation of densified conducting networks, which gives rise to the decrease in resistance. Therefore, forty layers of CNT strips with a thickness of ~792 nm were used unless specified otherwise (Fig. S3†). The strip-shaped supercapacitors were prepared by stacking two CNT strip electrodes together. Different from the fiber-shaped supercapacitors with a twisted structure, the strip-shaped supercapacitor exhibited a layered configuration with a gel electrolyte being sandwiched between the two CNT strips (Fig. 1d and e).

We first examined the electrochemical performances of 1 cm strip-shaped supercapacitors through cyclic voltammograms (CVs) and galvanostatic charge–discharge measurements (Fig. S4†). The well-defined rectangular shape in *CV* curves and symmetrical triangular voltage profiles indicate a typical electrochemical double layer behavior. A volumetric capacitance of 24.6 F cm^{-3} was obtained according to the discharge process which slightly decayed at higher current densities and remained stable within 10 000 charge–discharge cycles. Noticeably, the specific capacitance of strip-shaped supercapacitors is slightly affected by their lengths (Fig. 2a). For example, a 25 cm supercapacitor delivered a capacitance of 21.2 F cm^{-3}, indicating that the properties of electrodes were well retained. In stark contrast, the specific capacitances of fiber-shaped supercapacitors made with the same weight of CNT fibers deteriorated dramatically with increasing length. For instance, their specific capacitances decreased from 16 to 2.6 F cm^{-3} when the fibrous device was extended from 1 to 25 cm (Fig. S5†). The difference arose from the low utilization of active materials in fiber-shaped supercapacitors as it was difficult for the electrolyte to effectively infiltrate into the fiber electrode. Also, the lower internal resistances of strip-shaped supercapacitors can better maintain the electrochemical properties with the increasing length, which was verified by the electrochemical impedance spectrum (EIS) (Fig. S6†). The maintained high electrochemical performance is critical for the use of the one-dimensional energy storage device. The strip-shaped supercapacitor with a length of 25 cm had been also carefully investigated. The *CV* curves maintained the rectangular shape at increasing scan rates from 10 to 100 mV s^{-1} (Fig. S7†), and the charge–discharge curves also remained as a symmetrical triangle at increasing current densities (Fig. S8†). No obvious decay in the specific capacitance was observed in the cycling measurement (Fig. 2b).

The high flexibility of the strip-shaped supercapacitor was first demonstrated by wrapping it on cylinders with decreasing diameters (Fig. 2c). The galvanostatic charge–discharge curves were well overlapped with the increasing curvatures. In addition, the specific capacitances remained almost unchanged even after bending for 1000 cycles (Fig. 2d). The identical EIS curves before and after bending manifest that the internal resistance of the strip device remained unchanged (Fig. S9†), revealing the high structural stability originating from the strip configuration. Importantly, the strip-shaped supercapacitor can stably work under and after bending in water, *e.g.*, the discharge capacitance was maintained at appropriately 81% after immersion in water for 48 h (Fig. 2e). This high stability is a key for many practical applications. The operation of supercapacitors in water could be attributed to the hydrophobic properties of the CNT strip electrode and the incorporated gel electrolyte was protected from dissolution by the stacked electrodes.

Recently, conducting polymers have been widely used as promising electrode materials for flexible supercapacitors because of their high flexibility, high specific capacitance, high conductivity, and ease of fabrication.[16] Polyaniline (PANI), one of them, is appreciated as an ideal candidate because of its high pseudocapacitance from redox reactions as well as easy incorporation by electrochemical polymerization.[15,16] PANI has been widely used as a pseudocapacitive material in wearable devices because of its excellent electrochemical properties.[17–19] The PET substrate can be employed to prevent the direct contact between

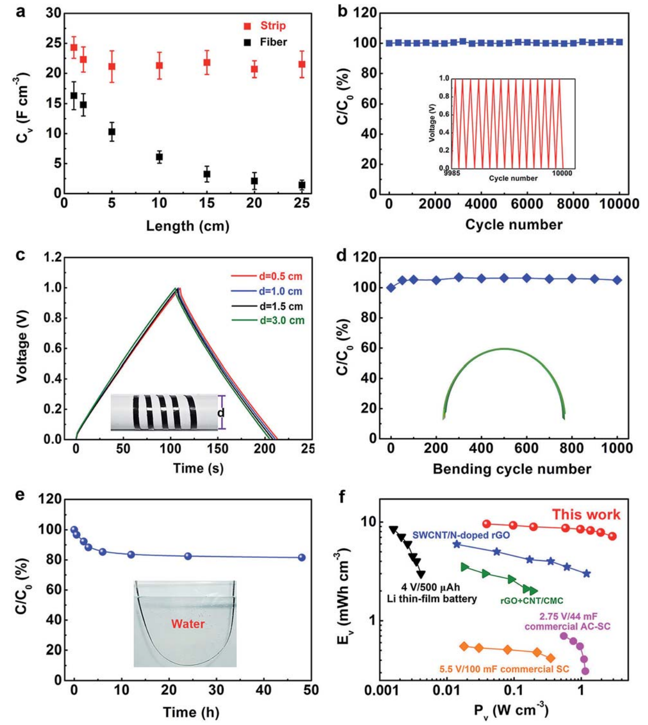

Fig. 2 Electrochemical performances of the strip-shaped supercapacitor. (a) Dependence of specific capacitance on the length of strip- and fiber-shaped supercapacitors. The weight of CNTs, the active material, in strip- and fiber-shaped supercapacitors is the same. Each point was collected from five parallel samples. (b) Cyclic performance of a strip-shaped supercapacitor. The inset graph displays the galvanostatic charge and discharge curves in the last 15 cycles. (c) Galvanostatic charge–discharge curves of a strip-shaped supercapacitor wrapped on cylinders with different diameters. (d) Dependence of specific capacitance on the bending cycle number. The supercapacitor was bent to 180° at a bending radius of 5 cm. Here C and C_0 correspond to the specific capacitances before and after bending for different times, respectively. (e) The capacitance retention with time in water. Here C and C_0 correspond to the specific capacitance before and after immersion in water, respectively. The length of the supercapacitor was 25 cm and the measurements were recorded at 0.1 A cm^{-3} at (b–e). (f) Comparison of volumetric energy and power densities with reported fiber-shaped supercapacitors and commercially available energy storage systems. Here the strip-shaped supercapacitor was made from the aligned CNT/PANI (70 wt%) composite electrode.

the human body and PANI, so it is safe for practical applications. In this case, the energy storage capability of strip-shaped supercapacitors was further enhanced by introducing pseudocapacitive PANI into CNT strips through electrochemical polymerization. As expected, the specific capacitances increased with the increase in PANI weight percentage below 70 wt% (Fig. S12†). They slightly decreased with the further increase in the PANI weight percentage as PANI aggregated on the surface of the CNT strip (Fig. S10 and S11†). Therefore, a weight percentage of 70% was mainly investigated below unless specified otherwise. The pseudo-capacitive behavior of the CNT/PANI composite was evidently manifested in the *CV* curves and galvanostatic charge–discharge curves (Fig. S13a and b†). Calculated from the galvanostatic charge–discharge curves, the

CNT/PANI composite electrode showed a high C_v of 421.7 F cm^{-3} (343.6 F g^{-1} for C_M and 47.8 F cm^{-2} for C_A) at a current density of 0.5 A cm^{-3}, which was sustained at even high current rates. Meanwhile, the C_M of the whole device (including the active material, electrolyte and PET substrate) was achieved to be 3.9 F g^{-1}. A high cyclic stability had been observed for over 3000 charge–discharge cycles, and the specific capacitances slightly declined with increasing lengths (Fig. S13c and d†).

We compared the specific capacitances based on the CNT/PANI composite electrode with previously reported fiber-shaped supercapacitors made from various materials including the CNT/PANI composite. Please note that the PANI proportion in strip- and fiber-shaped supercapacitors is the same so that we can make a fair comparison in which the configuration is the only variable. Hence, the configurational advantage in capacitance improvement was highlighted and the leading superiority looms large at high current densities (Fig. S14†).[5a,6b,7,20–23] The high capacitance promises a high energy density, and the sustainability to high currents provides the device a high power output (Fig. 2f).[5a,7,24–26] For example, the strip-shaped supercapacitor delivered a volumetric energy density of 9.56 mW h cm^{-3}, which is higher than the volumetric energy densities of fiber-shaped supercapacitors derived from reduced graphene oxide (rGO) + CNT/sodium carboxymethyl cellulose (CMC) and single-walled carbon nanotube (SWCNT)/N-doped reduced graphene oxide (N-doped rGO) composites[5a,6] and even comparable to that of a thin-film lithium battery.[24,25] The maximal volumetric power density reached 2.91 W cm^{-3}, which is on par with those of the commercial 2.75 V/44 mV activated carbon supercapacitor (AC-SC) and 5.5 V/100 mV commercial SC.[5a,26] In addition, the energy density of a strip-shaped supercapacitor was nearly insusceptible to the several-magnitude enlarged power density, which represents solid progress beyond fiber-shaped counterparts.

The flexible strip-shaped supercapacitors can be further integrated for high energy and power capabilities by connecting in series and parallel. For instance, the galvanostatic voltages linearly increased with the increasing number of supercapacitors being connected in series (Fig. 3a). The specific capacitance can be enhanced by connecting them in parallel. As shown in Fig. 3b and c, both the discharge time and output current increased by three times when three supercapacitors were assembled in parallel. The voltage profiles retained their shapes perfectly, suggesting that the connected devices stably performed without degradation. Furthermore, the capacitances linearly increased with the increasing number of supercapacitors (Fig. 3d). The predictable capacitance after integration is critical to the practical application as it is available to design and integrate appropriate strip-shaped supercapacitors according to the specific requirement in use.

The weavability of strip-shaped supercapacitors comes from their flexibility and compliance to deformations. The strip configuration can endure bending deformation because of its microscopic structure. The structure can be well maintained under a high bending speed of fifty times per minute due to the sandwiched architecture with a high contact area (Fig. S15a†). In strong contrast, for a typical fiber-shaped supercapacitor

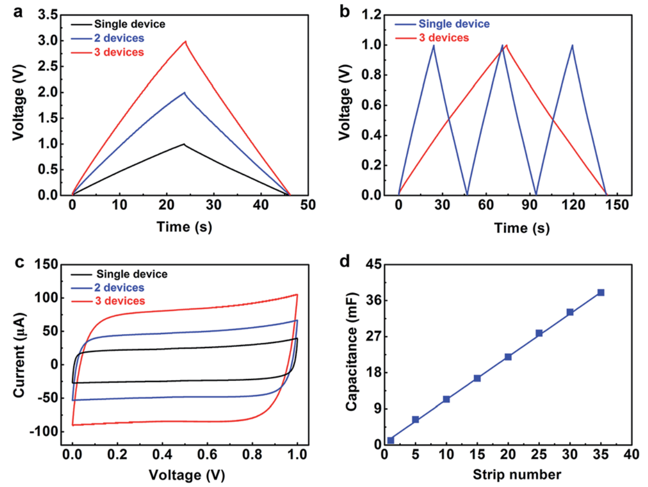

Fig. 3 Strip-shaped supercapacitors connected in series and parallel. (a) and (b) Galvanostatic charge–discharge curves of three strip-shaped supercapacitors connected in series and parallel. (c) *CV* curves of single, two and three strip-shaped supercapacitors connected in parallel. The scanning rate was 25 mV s^{-1}. (d) Relationship between the capacitance and number of connected strip-shaped supercapacitors.

twisted from two fiber electrodes, the fiber electrodes tended to separate from and crossed with each other under the same bending speed (Fig. S15b†), which drained the preserved charges rapidly. The two different shapes of supercapacitors were also studied for the self-discharge test (Fig. S16†). When strip- and fiber-shaped supercapacitors with the same length and CNT content were charged to 1 V and then rested for 1 h, the voltages of the fiber-shaped supercapacitors declined more rapidly, indicating a more severe self-draining.

The one-dimensional configuration, flexible structure and predictable capacitance enable the strip-shaped supercapacitors to be further woven into an energy storage fabric. Fig. 4a shows a typical energy storage fabric woven from 25 cm strip-shaped supercapacitors. The fabric can preserve its structure under various deformations such as bending and curling (Fig. 4b and S17†). The flexible and stable structure of the energy storage fabric from the strip-shaped supercapacitors was also verified through a quantitative study by tracing the galvanostatic charge–discharge curves under bending into different formats (Fig. 4c and S18†) when the supercapacitor units were connected in parallel as shown in Fig. S19.† Obviously, the curves were well overlapped at different deformations, indicating a high flexibility. To explore the contributions of the strip configuration to the structural stability of fabrics, we traced the stretching behavior of energy storage fabrics woven from strip- and fiber-shaped supercapacitors (Fig. 4d–g). When two fabrics (8 cm × 8 cm) were stretched from the diagonal direction under the same force of 3 N, the fabric made from strip units remained stable in the structure (Fig. 4d), while the fiber-woven fabric was obviously distorted (Fig. 4e). The mechanism for the above difference in stability is schematically illustrated in Fig. 4f and g. The strip-like supercapacitors were closely contacted through the flat surface with a higher contact area that offered a stronger cohesion compared with the point-to-point contact among the

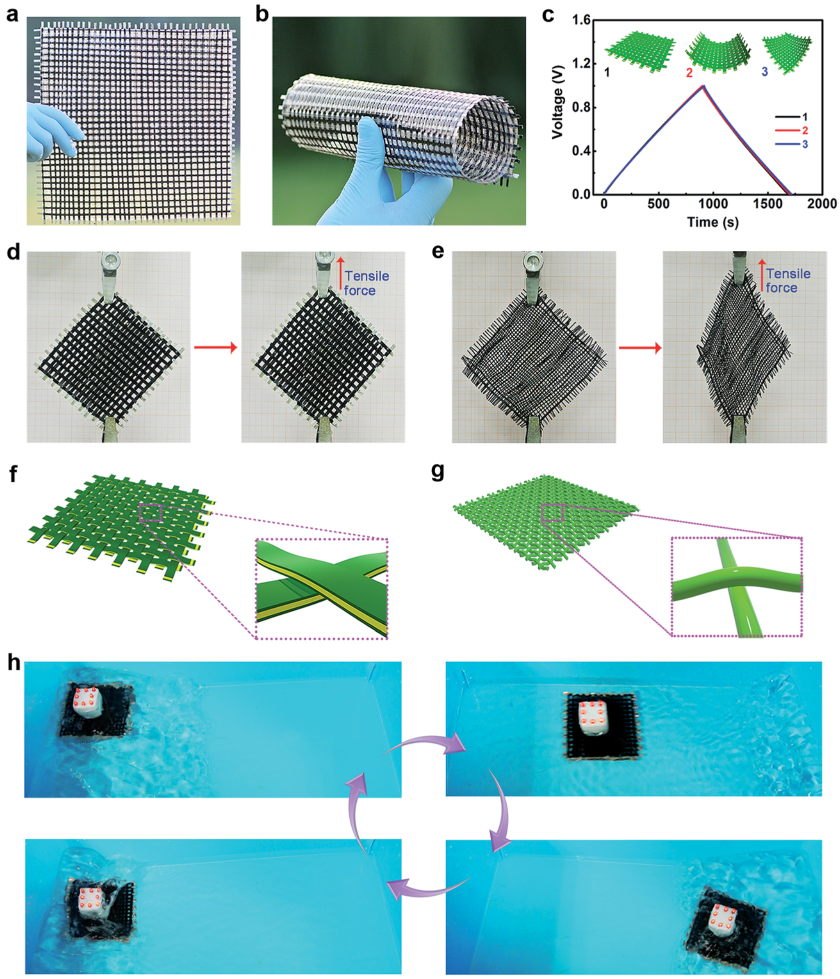

Fig. 4 (a) Photograph of an energy storage fabric woven from strip-shaped supercapacitors with a length of 25 cm. (b) Photograph of the curled energy storage fabric. (c) Galvanostatic charge–discharge curves of a fabric before and after bending in different directions. The supercapacitor units in the fabric were connected in parallel and the measurements were recorded at 0.5 A cm^{-3}. (d) and (e) Photographs of natural and deformed fabrics woven from strip- and fiber-shaped supercapacitors, respectively. They were diagonally stretched at a tensile force of 3 N. (f) Schematic illustration of the face-to-face contact between two strip-shaped supercapacitors in the fabric. (g) Schematic illustration of the point-to-point contact between two fiber-shaped supercapacitors in the fabric. (h) A supercapacitor fabric floated to power eight light-emitting diodes in a swift water current. The length of the used strip-shaped supercapacitor was 8 cm.

fiber-shaped supercapacitors. Therefore, the fabric woven from strips had been well maintained, while the fabric woven from fibers was seriously distorted due to their slipping under stretching. As a demonstration, the energy storage fabric from the strip-shaped supercapacitor had been used to light up eight light-emitting diodes (LEDs) mimicking floating beacons in sea provided that the contact electrodes were encapsulated with polydimethylsiloxane (PDMS) (Fig. 4h). The brightness of the LED remained almost unchanged although the water current around was swift.

Conclusion

In summary, we have developed a new family of high-performance supercapacitors by designing a new strip configuration. It has effectively combined the advantages of a planar shape (high energy storage capability and stability) and fiber shape (flexibility and weavability). Novel energy storage fabrics are further woven from these strip-shaped supercapacitors with remarkable electrochemical performances, and they can stably power various electronic devices even under harsh conditions such as floating in a swift water flow. A wide variety of other energy and electronic devices may be developed aiming at high performances based on a similar strategy by designing the strip configuration.

Acknowledgements

This work was supported by the NSFC (21225417) and the Program for Outstanding Young Scholars from the Organization Department of the CPC Central Committee. This work is supported in part by the Samsung Advanced Institute of Technology (SAIT)'s Global Research Outreach (GRO) Program (IO140919-02248-01).

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