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One-step Production of Continuous Supercapacitor Fibers for a Flexible Power Textile

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Electronic Supplementary Information

Abstract Given that conventional bulky electrochemical energy storage devices are too rigid and heavy to be considered wearable, developing fully integrated power systems is expected to accelerate the successful commercialization of smart electronic textiles. Although great achievements have been made for fiber-shaped energy storage devices, there remain key challenges pertaining to their fabrication efficiency, scalability, and stability. Herein, a general and highly efficient method is developed to continuously fabricate supercapacitor fibers with lengths of kilometers at high production rate up to 118 m/h through a simple one-step wet spinning method. Beneficial from the designed unique two-circle-in-one-circle architecture, the resulting supercapacitor fibers demonstrated high electrochemical stability even after being bended for 1×10^5 cycles. As a demonstration, these continuous supercapacitor fibers were further woven into a flexible power scarf for large-scale applications in wearable electronics. This simple and scalable fabrication process combined with the unique structure provides a general and effective paradigm to design other fiber-shaped devices like sensors, batteries, and solar cells.

Keywords Continuous production; Wet-spinning; Fiber-shaped supercapacitors; Energy storage fabric

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INTRODUCTION

The booming development of smart textile has attracted great interests from both academy and industry as it not only functions like conventional fabric but also has some built-in special functionalities of information communication and storage, data processing, bio-signal monitors, and so on.[1–4] The progress of successful commercialization of smart textile is still impeded due to the absence of fully integrated energy storage devices as power systems. Conventional bulky power systems based on the electrochemical energy storage devices are generally not suitable for integration in e-textile because of their rigidity, heavy weight, and large volume. To this end, thin-film[5,6] and fiber-shaped energy storage devices[7–9] were created for flexible power systems. The thin-film energy storage devices typically suffer from the drawbacks of poor breathability, low wet permeability, low integration capability, and inferior resistance to complex deformations such as twisting. On the contrary, fiber-shaped energy storage devices possess some unique advantages of lighter weight, higher flexibility, and better integration, and they can be easily scaled up to satisfy the above application through the well-established textile manufacturing technologies.[10–12]

However, the current production processes for fiber-shaped energy storage devices are batch-wise which is time-consuming and inefficient. For example, the production of fiber-shaped supercapacitors often includes loading active materials, preparing fiber electrodes, coating gel electrolytes, assembling functional parts, and sealing the whole device.[13] In addition, they are mainly limited to short lengths in centimeters, which makes them difficult for large-scale applications by weaving technologies.[14] Although several attempts were recently made to extrude continuous functional fiber electrodes for constructing fiber-shaped supercapacitors,[12,15,16] post gel-electrolyte coating and twisting processes are required to make an intact fiber device. For instance, producing graphene oxide based fiber-shaped supercapacitors needs time-consuming reduction processes for higher electrical conductivities and meanwhile leads to poor mechanical strengths.[17–19] Moreover, the current two main configurations of the fiber-shaped energy storage devices, *i.e.*, twisting[20,21] and coaxial,[8,22–24] have inherent disadvantages. For a twisting structure typically with two fiber electrodes, they may separate from each other under severe bending or twisting deformation; for a coaxial structure, it is

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difficult to match the mass of active materials in inner and outer layers.

To solve these problems, we designed a general multichannel spinning method to continuously fabricate fiber-shaped supercapacitors with a unique two-circle-in-one-circle architecture and lengths of kilometers in one step. The as-spun supercapacitor fibers simultaneously exhibited high flexibility, structure stability, and electrochemical stability, and had been further woven into high-performance power textiles for promising wearable applications.

A customer-designed multichannel spinneret was built with two inner parallel nozzles for electrode inks and one outer larger nozzle carrying gel electrolyte (Fig. S1 in electronic supplementary information, ESI). When the electrode inks and gel electrolytes were simultaneously extruded into the coagulation bath, the gel electrolyte was quickly solidified to stabilize the two fiber electrodes and meanwhile functioned as a separator (Fig. 1a). A highly viscous electrode ink by blending conducting polymer like poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and highly conductive carbon nanotube (CNT) was prepared for two fiber electrodes, in which PEDOT:PSS acted as host materials because of its combined high spinnability, electrical conductivity, and pseudocapacitance. Chitosan/poly(vinyl alcohol) (PVA) blend was chosen as the gel electrolyte by taking advantages of the easy solidification of chitosan and the relatively high mechanical strength of PVA.

EXPERIMENTAL

Preparation of Electrode Ink

To prepare the electrode ink, 0.52 g of PEDOT:PSS pellets

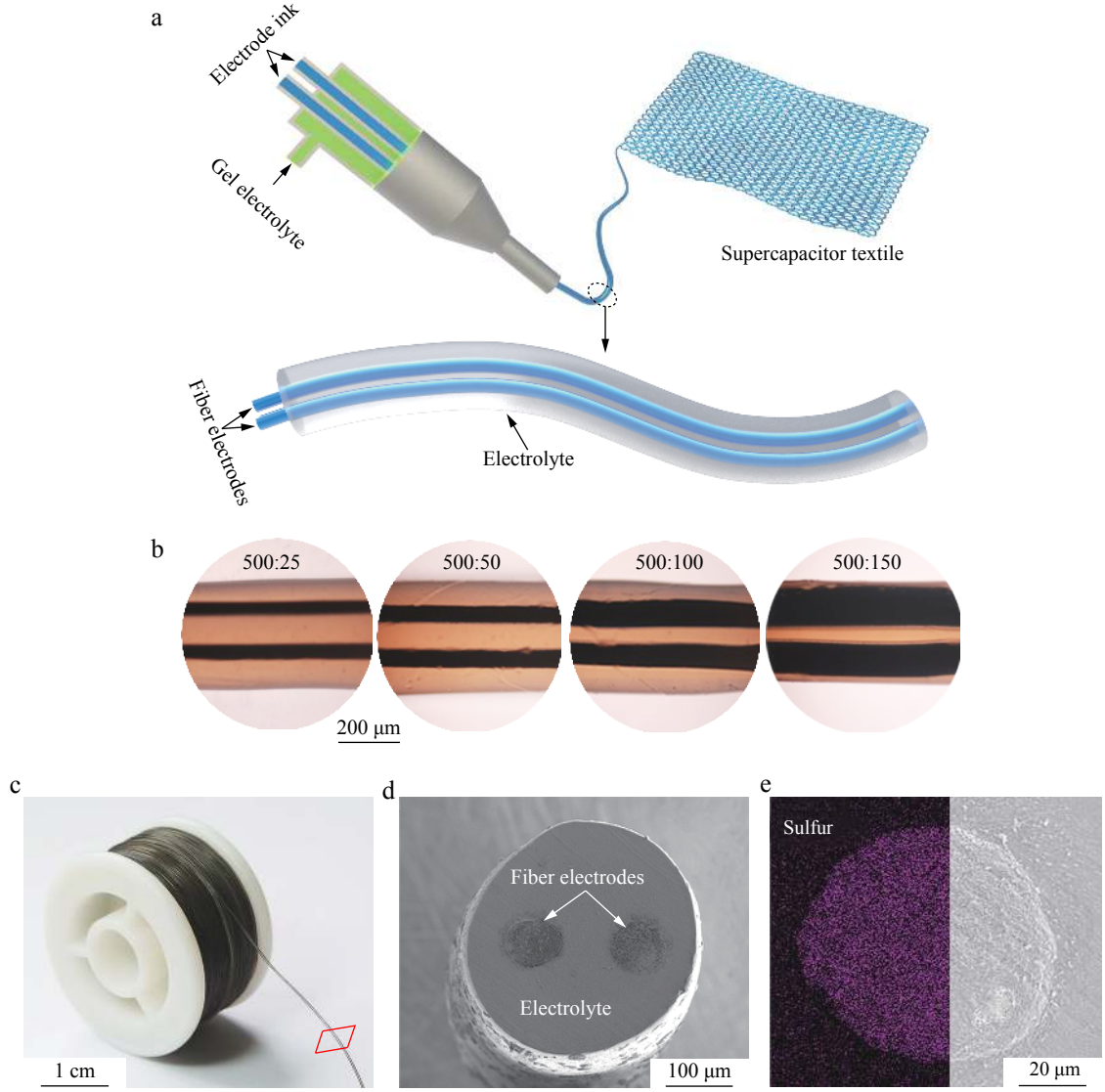

Fig. 1 Multichannel spinning process and the structure of continuous supercapacitor fibers: (a) schematic illustration of the continuous fabrication of supercapacitor fibers toward energy storage textiles; (b) optical micrographs of the supercapacitor fibers produced under increasing flow rates of gel electrolyte and electrode ink; (c) photograph of a continuous supercapacitor fiber collected on a Teflon winder; (d) a cross-sectional SEM image of a supercapacitor fiber; (e) energy X-ray dispersive mapping of sulfur element in a fiber electrode (The sulfur comes from the PEDOT:PSS in the electrode ink.)

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(Sigma-Aldrich), 4 g of CNT aqueous dispersion (10 wt%, Chengdu Organic Chemicals Co., Ltd.), and 13.73 g of deionized water were blended together by mechanical stirring at 800 r/min for 1 h to obtain a homogeneous black suspension, followed by 1 h bath sonication before being allowed to rest overnight. The viscosity of the PEDOT:PSS/CNT ink reached *ca.* 17600 mPa·s. In the electrode ink, the concentrations of PEDOT:PSS and CNT were 30 and 23 mg/mL, respectively. The corresponding solid weight percentages of PEDOT:PSS and CNT in the ink were 56.5% and 43.5%, respectively. To further increase the electrical conductivity of the electrode ink, 6.4 mL of Ag nanowire (NW) aqueous dispersion (10 mg/mL, Suzhou Goldstones Technology Co., Ltd. China) was added to the above mixture dispersion, and its solid content was maintained to be no more than 6.5 wt%. α-MnO_2 nanoparticles were synthesized by a chemical bath deposition method.[25] Typically, 0.316 g of $KMnO_4$ and 0.1152 g of citric acid were dissolving in 100 mL of deionized water and then kept at 75 °C for 6 h, followed by washing repeatedly in deionized water. Subsequently, the as-synthesized MnO_2 (0.306 g) was added to the PEDOT:PSS/CNT mixture with a solid weight percentage of 25 wt%.

Preparation of Gel Electrolyte

The gel electrolyte was composed of chitosan/PVA as polymeric matrix and $LiClO_4$ as the electrolyte salt. Chitosan solution (4 wt%) was blended with PVA solution (10 wt%) in a volume ratio of 2.5/1, followed by adding 0.5 mol/L $LiClO_4$ under vigorous stirring at 1000 r/min for 1 h. Afterwards, the gel electrolyte was subjected to sonication and filtration by vacuum for several times. The viscosity of the gel electrolyte was *ca*. 28700 mPa·s. To obtain chitosan solution, 4 g of chitosan powder (Aladdin) was completely dissolved in 100 mL of 2 wt% acetic acid solution under vigorous stirring at room temperature. 10 g of PVA particles (Aladdin, 1799) were swelled in 100 mL of deionized water at room temperature for 3 h and then heated to 90 °C for 1.5 h to obtain a 10 wt% PVA solution.

Fabrication of Supercapacitor Fiber

A supercapacitor fiber was continuously produced by a one-step process using a specially designed multichannel spinneret (Fig. S1 in ESI). During the preparation process, the electrode ink was injected into two parallel channels while the gel electrolyte was injected into the outer channel of spinneret. They were then simultaneously extruded out of the outlet by applying air pressure to each reservoir. Typically, the flow rates of the gel electrolyte and electrode ink were 500 and 50−100 μL/min, respectively. The nozzle was immersed into a coagulation bath that was prepared by dissolving 5 g of NaOH and 8 g of $LiClO_4$ in 100 mL ethanol/water mixture solution (volume ratio of 1/1). The gel electrolyte was quickly solidified by NaOH to stabilize the two fiber electrodes and meanwhile functioned as the separator, and then the as-spun supercapacitor fiber was drawn by rollers in a ratio of 2/3 and collected on a winding spool. The supercapacitor fiber was washed for several times by deionized water containing 0.5 mol/L $LiClO_4$ to prevent the diffusion of lithium salt from the gel electrolyte and dried in air at room temperature. The same concentrations of $LiClO_4$ in the gel electrolyte, coagulation, and washing water can avoid the diffusion of $LiClO_4$.

RESULTS AND DISCUSSION

Wet-spinning Supercapacitor Fibers

The spinning process of the continuous supercapacitor fibers is demonstrated in Video S1 (in ESI). Two fiber electrodes in the gel electrolyte were maintained to be continuous and separated. No obvious miscibility between them was observed. After soaking in a coagulation bath for seconds, the supercapacitor fiber could be completely formed with sufficient mechanical strength to be taken out of the solution. An as-fabricated supercapacitor fiber is shown in Figs. S2 and S3 (in ESI), from which two continuous fiber electrodes were arranged in parallel and encapsulated by the gel electrolyte. A clear boundary between two fiber electrodes was well maintained to preclude possible short circuit risks. The multichannel spinning method enabled a controllable fabrication in tuning the diameters of two fiber electrodes in supercapacitor fiber by regulating the flow rates of gel electrolyte and electrode ink (Fig. 1b). For our supercapacitors, it is easy to match the mass of active materials by fixing the flow rate of electrode ink across the two inner parallel nozzles in this method. Given that a higher flow rate of electrode ink may produce a short circuit under deformations because of the smaller space between two fiber electrodes, a flow rate ratio of gel electrolyte to electrode ink at 500/50 to 500/100 would be mainly studied in the following discussion. A continuous supercapacitor fiber was collected on a Teflon winder (Fig. 1c), and it could reach over kilometers in length. A cross-sectional scanning electron microscopy (SEM) image of a supercapacitor fiber (Fig. 1d) showed that two continuous fiber electrodes were tightly wrapped by the electrolyte without any gaps or voids, which was beneficial to the structure stability during deformations and the transport of both electrons and ions at electrolyte/electrode interfaces. In each fiber electrode, the host material of PEDOT:PSS was revealed by the energy-dispersive X-ray spectrometry mapping (Fig. 1e), in which CNT was distributed uniformly as conducting networks (Fig. S4 in ESI).

Electrochemical Performances

The electrochemical performances of our supercapacitor fibers were examined by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements. For the supercapacitor fiber made from PEDOT:PSS/CNT, it exhibited well-defined rectangular shape in CV curves with increasing scanning rates from 25 mV/s to 250 mV/s (Fig. S5a in ESI) and symmetrical triangular shape of GCD curves at increasing current densities (Fig. S5b in ESI), revealing a good rate capability. Cyclic voltammograms of the supercapacitor fiber fabricated by electrode ink with different ratios of PEDOT:PSS/CNT at scanning rate of 10 mV/s (Fig. S24 in ESI) showed that a small amount of CNT made a great difference to the CV curves of PEDOT. Because of the high volume percentages of CNT in supercapacitor fiber, the redox pairs of PEDOT:PSS were too weak to be found on CV curves. A volumetric capacitance (C_V) of 16.3 F/cm^3 was

delivered at a current density of 0.11 A/cm^3 according to the discharge curves, which slightly decayed to 14.8 F/cm^3 at 1.1 A/cm^3 and remained about 96% of the initial value after 5000 cycles (Fig. S6 in ESI). The storage capability of the as-spun supercapacitor fibers was also closely related to the flow rate ratio between the gel electrolyte and electrode ink because of the varying volume percentages of active materials (Figs. S7 and S1b in ESI). By incorporation of pseudocapacitive α-MnO_2 nanoparticles (Figs. S8 and S9 in ESI) into the PEDOT:PSS/CNT blends, the specific capacitance of the supercapacitor fiber was further improved to 63.5 F/cm^3 (Fig. S10 in ESI) and the volumetric energy density was increased accordingly by 387% (Fig. S11 in ESI). The volumetric energy and power densities reached 5.5 mWh/cm^3 and 0.48 W/cm^3, respectively, which were on par with commercially available energy storage devices (Fig. S12 in ESI).[11,26]

The Multichannel Spinning Method

The multichannel spinning method demonstrated several main advantages. Firstly, it exhibited high production rates typically such as 118 m/h with a simple one-step process (Fig. 2a). The specific capacitances of the as-spun supercapacitor fibers were well maintained with the increasing production rates from 4 m/h to 118 m/h by regulating the

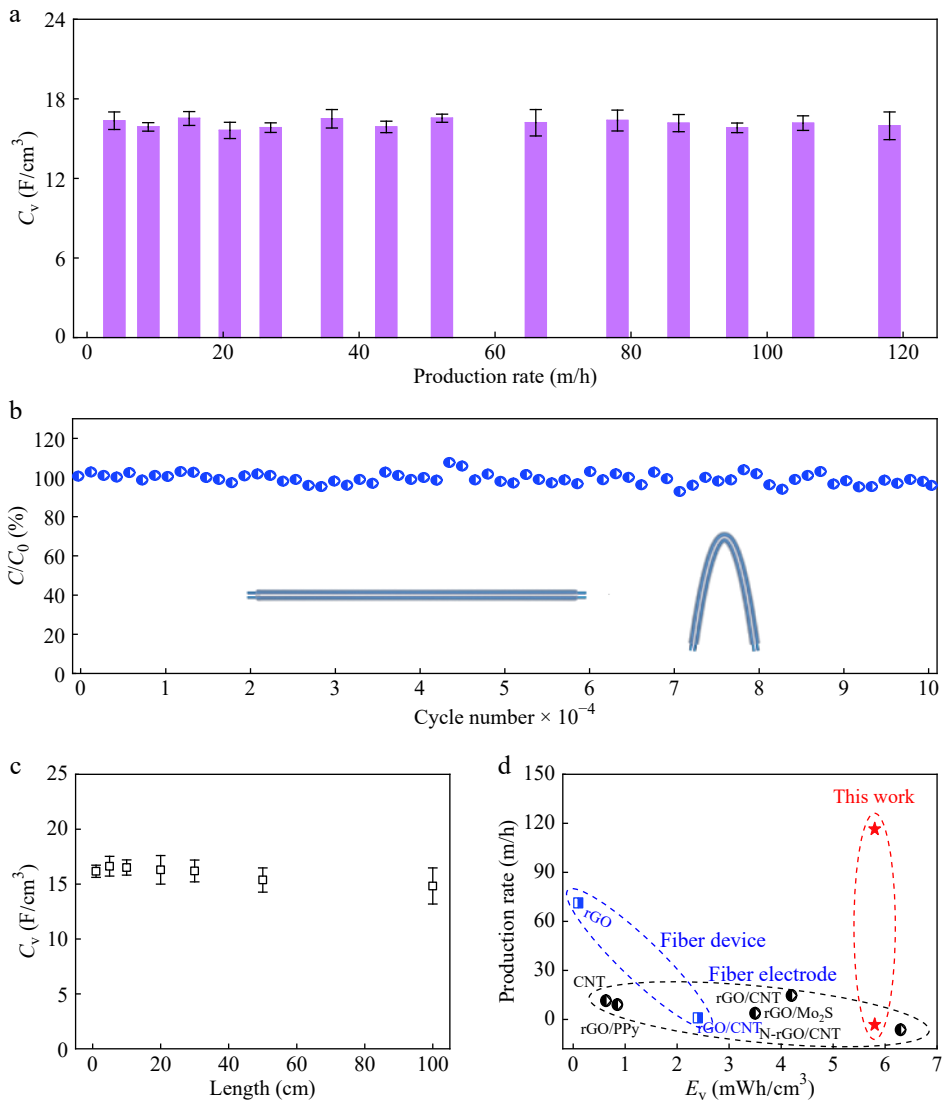

Fig. 2 The production processes and performances of the as-spun supercapacitor fibers: (a) dependence of the specific capacitance variation of supercapacitor fibers on the production rate (Here C_0 and C correspond to the specific capacitances of the supercapacitor fiber produced at a low production rate of 4 m/h and the other production rates, respectively. The production rate means the device lengths per hour under different flow rate ratios between gel electrolyte and electrode ink.); (b) dependence of specific capacitance on the bending cycle number (Inset is the bending status. Here C_0 and C correspond to the specific capacitances before and after bending, respectively.); (c) dependence of specific capacitance on the length of supercapacitor fibers (For each supercapacitor, 10 samples were tested.); (d) volumetric energy densities and production rates of the supercapacitor fibers compared with those of other supercapacitor fiber (Here rGO, PPy, and N-rGO represent reduced graphene oxide, polypyrrole, and nitrogen-doped reduced graphene oxide, respectively.)

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speed of winding spool, which was favorable for large-scale productions and practical applications. Compared with the other device configurations such as planar, coaxial, and twisting architectures, to the best of our knowledge, this two-circle-in-one-circle architecture showed the highest repeatability and stability at the individual variations during production (Figs. S13 and S14 in ESI). Secondly, the supercapacitor fiber with the two-circle-in-one-circle architecture was highly flexible. After bending for 1×10^5 cycles, the specific capacitances remained almost unchanged (Fig. 2b). The high flexibility was also confirmed by tying it into a knot (Fig. S15 in ESI). Thirdly, the device length of the as-spun supercapacitor fibers can be increased by two orders (Fig. 2c and Fig. S16 in ESI) with well-maintained specific capacitance by introducing highly conductive Ag NW into the electrode ink, which also contributed to the good rate performance of the fiber-shaped supercapacitors with different lengths (Fig. S23 in ESI). The electrical conductivities of electrode inks were greatly enhanced from 15 S/cm for bare PEDOT:PSS to 637 S/cm for the PEDOT:PSS/CNT/Ag NW composite (Fig. S17 in ESI). The enhanced electrical conductivity of the supercapacitor fiber was verified by the electrochemical impedance spectrum (Fig. S18 in ESI) and perfect rectangular CV curves even at a high scanning rate of 2000 mV/s (Fig. S19 in ESI). Fourthly, the as-spun supercapacitor fibers exhibited both high energy density and high production rate in comparison with those presented in the previous studies (Fig. 2d),[14,17,19,27–33] which are highly desired for their potential applications in wearable electronics.

Supercapacitor Fabric

The high flexibility, production rate, and electrochemical stability of the as-spun supercapacitor fibers enabled them to be further woven into flexible power textiles. The mechanical properties of the supercapacitor fibers fabricated under increasing flow rates between gel electrolyte and electrode ink were studied by stress-strain curves (Fig. S20 in ESI), and we chose the supercapacitor fiber with the highest tensile strength of 118.2 MPa for weaving machines. They were then woven into fabrics with cotton yarns by braiding machine (Video S2 in ESI). The cotton yarns fixed on the braiding machine were used as wrap thread to be interwoven with the weft thread composed of the resulting supercapacitor fibers and cotton yarns in a twill weave model (Figs. 3a–3c and Fig. S21 in ESI). A flexible supercapacitor

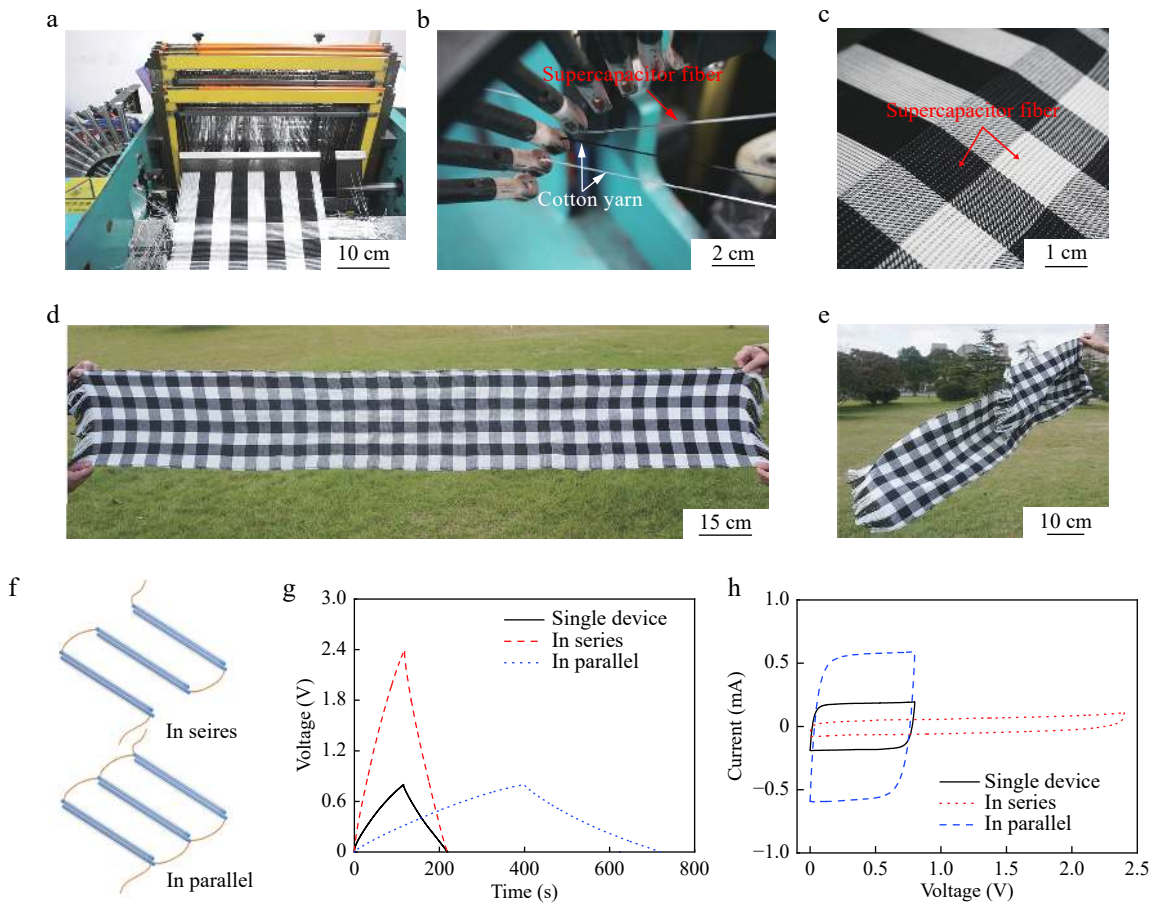

Fig. 3 The weaving process of the long supercapacitor fiber into a flexible power scarf for large-scale applications: (a, b) photographs showing the weaving process to form textiles by braiding machine; (c) photograph of the supercapacitor scarf at a high magnification; (d) a supercapacitor scarf with the size of 180 cm × 30 cm by weaving the supercapacitor fibers with cotton yarns; (e) the supercapacitor scarf demonstrated to be flexible; (f) illustrations of three supercapacitor fibers connected in series and parallel, respectively; (g) GCD curves for three supercapacitor fibers connected in series and in parallel measured at a constant current of 0.13 mA; (h) CV curves of three supercapacitor fibers connected in series and in parallel recorded at a constant scanning rate of 25 mV/s

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scarf with the size of 180 cm × 30 cm was successfully produced (Fig. 3d). It wore comfortable (Fig. 3e and Fig. S22 in ESI) and might effectively provide power for the external electronic device. The capacitance and energy of the supercapacitor scarf were appropriately 1.34×10^6 F and 116 Wh, respectively. Multiple supercapacitor units in the textile can be easily assembled in series, in parallel, or in both to meet high voltage or current or both needs, respectively (Fig. 3f). For example, the operating voltage was tripled from 0.8 V to 2.4 V for three connected supercapacitor fibers in series, while both the discharge time and output current increased by three times when three were assembled in parallel (Figs. 3g and 3h).

CONCLUSIONS

In conclusion, a general and effective multichannel spinning approach was developed for continuously producing supercapacitor fibers with lengths of kilometers at high production rates up to 118 m/h at a simple one step. Based on the designed two-circle-in-one-circle configuration, they showed high volumetric energy and power densities as well as high flexibility and stability, *e.g.*, the high electrochemical properties had been well maintained even after bending for 1×10^5 cycles. The long supercapacitor fiber was woven into a flexible scarf as a demonstration for large-scale applications. This fabrication strategy and structure design may be also extended to other fiber-shaped devices like sensors, batteries and solar cells.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-019-2301-5.

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