Multicolor, Fluorescent Supercapacitor Fiber

Meng Liao, Hao Sun, Jing Zhang, Jingxia Wu, Songlin Xie, Xuemei Fu, Xuemei Sun, Bingjie Wang,* and Huisheng Peng*

Fiber-shaped supercapacitors have attracted broad attentions from both academic and industrial communities due to the demonstrated potentials as next-generation power modules. However, it is important while remains challenging to develop dark-environment identifiable supercapacitor fibers for enhancement on operation convenience and security in nighttime applications. Herein, a novel family of colorful fluorescent supercapacitor fibers has been produced from aligned multi-walled carbon nanotube sheets. Fluorescent dye particles are introduced and stably anchored on the surfaces of aligned multi-walled carbon nanotubes to prepare hybrid fiber electrodes with a broad range of colors from red to purple. The fluorescent component in the dye introduces fluorescent indication capability to the fiber, which is particularly promising for flexible and wearable devices applied in dark environment. In addition, the colorful fluorescent supercapacitor fibers also maintain high electrochemical performance under cyclic bending and charge-discharge processes.

The ever-growing interests for flexible electronic devices have driven the revolution on matching energy storage systems that are highly flexible and wearable. In recent years, fiber-shaped supercapacitors have emerged as promising candidates attributed to the demonstrated high power density, cyclic stability, and flexibility. The potential to be woven into breathable and wearable power textiles via the well-developed textile technologies further makes them attractive for next-generation power systems, as well as in many other fields such as wearable electronics. Particularly, intelligent supercapacitor fibers with self-healing, electrochromic, and shape-memory capabilities have been developed aiming at a better adaptability for complex and harsh environment. However, it is important while remains challenging to produce dark-environment identifiable supercapacitor fibers, which show promise in improving the operation convenience and wearing security for nighttime users. To the best of our knowledge, few efforts have been made to realize the above goal, mainly attributed to the challenge of stable and uniform incorporation of luminous components into fiber electrodes with well-maintained energy storage performances.

Herein, a novel family of multicolor fluorescent fiber electrodes and supercapacitors has been produced to overcome the above challenge. Fluorescent dye particles are introduced and stably anchored onto the surfaces of aligned multiwalled carbon nanotubes (MWCNTs) to prepare hybrid fiber electrodes with a broad range of colors from red to purple. The fluorescent component in the dye introduces fluorescent indication capability to the fiber, which is particularly promising for flexible and wearable devices applied in dark environment. They also demonstrate a stable capacitance and color intensity after 10 000 charge–discharge cycles. The multicolor supercapacitor fibers also offer a general tactic toward aesthetic and customized designs for the development of other wearable energy harvesting and storage devices.

The preparation processes of the fluorescent fiber electrodes and supercapacitors are schematically demonstrated in Figure 1a and Figure S1 (Supporting Information). Briefly, aligned MWCNT sheets were continuously drawn from a spinable MWCNT array synthesized via chemical vapor deposition. Fluorescent dye particles were incorporated into MWCNT sheets via a copinning process. The fluorescent dyes were grounded to realize a uniform diameter distribution from 1 to 5 µm and then made into aqueous dispersions. The dispersions were further dipped onto aligned MWCNT sheets with dye particles embedded among MWCNTs skeletons, followed by a scrolling process to transform sheets into fibers. Based on a continuous preparation process, long fluorescent fiber, e.g., with a length of ≈2 m, can be produced (Figure 1b). The incorporation of high-content dye particles offered the fluorescent capability that can be clearly observed under the ultraviolet illumination in the dark (Figure 1c). Two fluorescent fiber electrodes were then coated with a layer of aqueous gel electrolyte, and twisted together to produce a fluorescent supercapacitor fiber with a diameter of ≈500 µm (Figure 1d,e). It demonstrated distinct fluorescence under ultraviolet illumination.

Fiber electrodes play a crucial part in the fluorescent performance and energy storage capability of the obtained supercapacitor. It is worth noting that the copinning process...
was verified highly important for the stability of the resulting hybrid fiber electrodes in comparison of conventional dip-coating method (Figure 2). For instance, the color intensity of a cospinning hybrid fiber was well maintained by 90.0% after 1000 bending cycles at 180°, compared with only 65.3% of the dip-coating hybrid fiber (Figure 2a,b). This phenomenon can be explained by the different configurations of the hybrid fibers derived from different preparation methods. For the scrolling method, the dye particles were stably anchored to the surface of the hybrid fiber (Figure 2c,e) due to the wrapping structure formed by aligned MWCNT bundles (Figure 2g). As a comparison, few dye particles can be found on the fiber surface for the dip-coating method (Figure 2d,f) in absence of the aforementioned wrapping structure (Figure 2h). As a result, the cospinning method was mainly adopted for production of hybrid fiber electrodes in this work. The inner distribution of the dye particles was further verified by the cross-sectional morphology of the hybrid fiber (Figure S2a,b, Supporting Information). With aligned MWCNT bundles effectively serving as supporting skeleton for dye particles, the color intensity of a scrolled fluorescent fiber electrode could even maintain by 86.3% after 5000 cycles at a bending angle of 180° (Figure S3a,b, Supporting Information). The slight decrease on specific volumetric capacitance may be attributed to the diameter increase after the introduction of dye particles. To enable a better fluorescent performance, a green supercapacitor fiber with maximal intensity was mainly investigated without specified otherwise. Galvanostatic charge–discharge curves displayed symmetric triangles at increasing current densities from 5 to 100 mA cm⁻³ (Figure 3c), indicating a highly reversible charge–discharge process at a wide range of current densities. For the cyclic voltammograms, typical rectangular shapes are well maintained at increasing scan rates from 100 to 1000 mV s⁻¹, suggesting a low internal resistance of the supercapacitor (Figure 3d). The energy storage performance can be further enhanced by introducing active materials with pseudocapacitances into the current system. For instance, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate can be introduced before the dying process to efficiently raise the specific volumetric capacitance to 11.98 F cm⁻³ at a current density of 10 mA cm⁻³ (Figure S6, Supporting Information) without obvious decrease on the color.

Figure 1. a) Schematic of the preparation procedures of the fluorescent fiber electrode. b,c) Photographs of continuously prepared fluorescent fiber with a length of 2 m under natural light and ultraviolet, respectively. d,e) SEM (scanning electron microscope) and optical microscope images of a fluorescent supercapacitor fiber, respectively.
intensity of the supercapacitors (Figure S7, Supporting Information).\[26–28\] Besides, tunable connection can be designed to realize higher output voltage and energy with good flexibility maintained. For instance, four fluorescent supercapacitor fibers were integrated in parallel or series for demonstration. The resulted power capacities and galvanostatic voltage window were accordingly quadrupled, accounting for its potential to satisfy various practical applications (Figure S8, Supporting Information).

Inherited from the fiber electrodes, the resulting fluorescent supercapacitor fiber was also flexible. The color intensity was maintained by 91.3%, 91.0%, and 90.4% at bending angles of 60°, 120°, and 180°, respectively (Figure 3e; Figure S9, Supporting Information), accompanied by stable specific capacitance with little variation (Figure S10, Supporting Information). The dependence of charge–discharge cycles had then been investigated. Impressively, both the capacitance and the color intensity of the fluorescent supercapacitor fiber demonstrated high stability during cyclic charge–discharge test. For instance, the capacitance and the intensity could maintain by 98.4% and 95.6% after 10 000 charge–discharge cycles, respectively (Figure 3f). The high stabilities on energy storage and

**Figure 2.** Fluorescent fiber electrodes prepared via cospinning and dip-coating method processes. a,b) Corresponding spectrum variation over 1000 bending cycles with a bending angle of 180° for fluorescent fiber electrodes prepared via cospinning process and directly dipping method, respectively. c,d) SEM images of fluorescent fiber electrodes prepared via cospinning process and directly dipping MWCNT fiber into dye dispersion, respectively (after 1000 bending cycles). e,f) Higher magnification of the region marked with a red rectangle in (a) and a blue rectangle in (b). g,h) Schematic illustration to the composite structures of dye particles-MWCNT fiber prepared through cospinning method and directly dipping, respectively.
optical performance were derived from the chemically and structurally stable components, e.g., aligned MWCNT and dye in this work.

The fluorescent supercapacitor fibers can be readily woven into flexible and wearable power textiles. For instance, 20 supercapacitor fibers (red, green, orange, and yellow) were divided into four groups and woven into a black textile (Figure 4a). The fluorescent emission can be clearly observed under illumination of ultraviolet light (Figure 4b). As an application demonstration, 16 fluorescent supercapacitor fibers divided into 4 groups were integrated into a glove to light up 4 red light-emitting diodes (LEDs) in parallel (Figure 4c). The high flexibility of the fluorescent supercapacitor fibers enabled normal charge and discharge processes under bending state without obvious decrease on brightness of the LEDs (Figure 4d). In another case, 18 fluorescent supercapacitor fibers were further woven into the band of a commercial Heart-Rate Monitoring Strap (Figure 4e). Apart from serving as a spare power source, the integrated fluorescent module also enhances the visibility, which can be clearly observed when illuminated in dark environment. It may prevent its user, for instance, a night runner from suffering a traffic accident by the obvious fluorescent emission under illumination. In addition, the fluorescent supercapacitor fibers also hold great potentials in supporting and protecting nighttime staffs including but not limited to security guards, construction workers, traffic policemen, and soldiers, which demonstrate specific requirements for both power supply and safety indication. This strategy may be also extended to fabrics as a general and promising method.[29,30]

Figure 3. a,b) Optical micrograph and spectrum of red, orange, yellow, green, blue, and violet fiber electrodes, respectively. c) Galvanostatic charge-discharge curves of a fluorescent supercapacitor fiber based on bare MWCNTs at increasing current densities from 10 to 100 mA cm$^{-2}$. d) Cyclic voltammograms with increasing scan rates from 100 to 1000 mV s$^{-1}$. e) Spectrum of a green fluorescent supercapacitor under different bending angles from 0 to 180°. f) Capacitance variation of a fluorescent supercapacitor fiber during 10 000 galvanostatic charge-discharge cycles at a current density of 10 mA cm$^{-2}$. $C_0$ and $C$ represent the specific capacitances before and after charge-discharge for different cycles, respectively. The inserted image in (f) indicated the spectrum before and after 10 000 charge-discharge cycles.
produced supercapacitor fibers, which largely extends their usage scenarios. For instance, the integration of fluorescence into supercapacitors extends their applications for labeling, signing, or warning in dark for smart electronics.\textsuperscript{[31,32]} Besides, a broad range of colors, e.g., from red to purple, has been realized with stable color intensity and high electrochemical performance under cyclic bending and charge–discharge processes, attributed to the stable interface between the fluorescent particles and MWCNT bundles. This work also provides a new platform for more aesthetic and customized designs of other wearable energy harvesting and storage devices aiming at real-world applications.

**Experimental Section**

**Preparation of Fluorescent Fiber Electrodes:** Aligned MWCNT sheets were directly drawn out of a spinnable MWCNT array which was synthesized by chemical vapor deposition and described in the Supporting Information. The fluorescent dyes (DayGlo LAX Series, Green: LAX-18, Orange: LAX-15, Yellow: LAX-17, Red: LAX-13, Blue: LAX-19, and Violet: LAX-20) were grounded for 2 h to realize uniform diameters ranging from 1 to 5 \( \mu \text{m} \). The resulted fluorescent dyes were dispersed in deionized water at a concentration of 60 mg mL\(^{-1} \) and then dropped onto stacked aligned MWCNT sheets. The dyes and MWCNT sheets were scrolled into hybrid fibers at a rotary rate of 1000 revolutions per minute, followed by evaporation of water to obtain the hybrid fiber electrodes. For the control experiment, the MWCNT sheet was first

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**Figure 4.** a,b) Photographs of twenty fluorescent supercapacitor fibers with four colors woven into a black textile under natural light and ultraviolet, respectively. c,d) Sixteen fluorescent supercapacitor fibers divided into four groups and woven into a glove to power four red light-emitting diodes. e) Eighteen fluorescent supercapacitor fibers integrated into a commercial Heart-Rate Monitoring Strap to extend its running time (inset: photograph of the integrated system under ultraviolet illumination).
scrolled into the MWCNT fiber, and the dye solutions were then directly coated onto the bare MWCNT fiber in preparation of a hybrid fiber.

**Fabrication of Fluorescent Supercapacitor Fibers and Textiles:** Two fluorescent fiber electrodes were uniformly coated and percolated with PVA (polyvinyl alcohol)∕H₃PO₄ gel electrolyte (mass ratio of 1∕1) and dried in vacuum. The above two fiber electrodes were then twisted, followed by coating another layer of gel electrolyte to avoid the short circuit of the supercapacitor fiber. The resulting supercapacitor fiber was further sealed into a heat-shrinkable tube (diameter of ≈100 μm) prior to weaving them into textiles. To prepare the fabrics, the encapsulated supercapacitor fiber was alternately woven over and under each curving wire at 90° based on a commercial textile. A colorful supercapacitor textile that was all composed of fluorescent supercapacitors can also be achieved by a plain weaving method.

**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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